



DURBAN UNIVERSITY OF TECHNOLOGY
INYUVESI YASETHEKWINI YEZOBUCHWEPHESHE

VALORISATION OF SEWAGE SLUDGE FOR SUSTAINABLE BIOENERGY AND BIORESOURCES RECOVERY THROUGH HYDROTHERMAL TREATMENT

by

Boldwin Mutsvene (21649785)

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Supervisor _ _ _ _ _ Date: _ _ _ 19 May 2025 _ _ _ _ _

Prof. M. Chetty

Co-Supervisor _ _ _ _ _ Date: _ _ 20/05/2025 _ _ _ _ _

Prof. S.K.K. Pillai

Co-Supervisor _ _ _ _ _ Date: _ _ 20/05/2025 _ _ _ _ _

Prof. F. Bux

DECLARATION

I, **Boldwin Mutsvene** (21649785), declare that:

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ABSTRACT

Amid rising global concerns over water and energy security, wastewater treatment plants (WWTPs) face a critical challenge in transforming sludge from an environmental burden into a valuable resource. The intricate composition of sludge, rich in organic matter and nutrients yet complex to harness, demands innovative solutions. This study developed an integrated hydrothermal treatment (HT)–based system to enhance energy recovery and nutrient valorisation from waste-activated sludge (WAS), thereby promoting sustainable wastewater management.

Hydrothermal treatment promoted this transformation by breaking down complex organic matrices under high temperature and pressure, thereby making nutrients more bioavailable. At the optimised HT condition (220 °C, 20 min), soluble chemical oxygen demand (SCOD) increased more than tenfold (from 284 ± 15 mg/L to 3161 ± 45 mg/L), while phosphate and ammonium rose from 64.04 ± 12 mg/L and 10.3 ± 5.2 mg/L to 172.8 ± 21 mg/L and 151.6 ± 17 mg/L, respectively.

However, this solubilisation also released inhibitory compounds, including phenolics (from 59.8 ± 1.2 to 119.4 ± 1.4 mg/L) and heavy metals, potentially constraining downstream recovery. Magnetic biochar (MBC) synthesised from sugarcane bagasse (550 °C) was applied for post-HT detoxification. Under the optimised RSM-CCD conditions (pH 6.54, 5 g/ L, 35 min), removal efficiencies reached 37.9 % for phenolics, 60.4 % for As, and over 75 % for Cu, Ni, and Pb. Despite effective contaminant removal, nutrient co-adsorption resulted in 50.3 ± 1.0 % phosphate and 47.2 ± 1.5 % ammonium loss.

To mitigate these trade-offs, struvite precipitation was optimised (pH 9.24, $\text{MgCl}_2 \cdot \text{H}_2\text{O}$ 10-25 mL/L sludge), yielding 79.5% phosphate and 32% ammonium recovery with 69.02% purity. Phosphorus fractionation revealed a 70% increase in water-soluble phosphorus, confirming enhanced bioavailability. Concurrently, HCl-extractable phosphorus (HCl-P) declined by 23% as HT effectively disrupts mineral-bound phosphorus complexes, facilitating the release of otherwise immobilised phosphorus.

Four AD scenarios consisting of untreated (S1), hydrothermally treated (S2), adsorbed (S3), and struvite-precipitated (S4) sludges were subsequently evaluated for biomethane potential. HT-treated sludge achieved an over 270% increase in methane yield, with methane production escalating from 2.3 mL CH₄/g VS to 72.7 mL CH₄/g VS and reduced the lag phase from 3.5 to 1.2 days.

Scenario 4 (HT + AD + adsorption + struvite) was the most economically efficient option, with a profitability improvement of over 200%, an ROI of 45.04 %, and an NPV of approximately US\$2.5 billion over a 30-year lifespan, as determined by the techno-economic evaluation. Sensitivity analysis has revealed that energy recovery efficiency, market value of struvite, and taxation are the most significant economic variables. A break-even point in a full-scale operation was estimated to be within five years.

The life cycle assessment (LCA) reported decreases in global warming potential (GWP) of 21.3 % (S2), 37.4 % (S3), and 8.53 % (S4) compared to conventional sludge disposal (S1). These positive gains affirm the co-benefits to the environment and economy that accompany the integration of these processes.

Despite the limitations of bench-scale HT-integrated sludge valorisation, including heat losses and the scarcity of LCA datasets, the study provides a validated framework for upscaling HT-integrated sludge valorisation systems. The results advance circular economy efforts as WWTPs are converted into bioresource recovery hubs that mitigate eutrophication, increase renewable energy production, and contribute to meeting SDGs 6 (Clean Water) and 13 (Climate Action). This work helps fill the gap between waste and resource recovery, ensuring the sustainability of next-generation wastewater treatment and representing a sustainable, energy-efficient, and economical future for sludge management.

Keywords: Nutrient recovery, biogas production, struvite precipitation, toxin removal, sustainable wastewater management, technoeconomic analysis, life cycle assessment, integrated approach, valorisation of wastewater.

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“I can do all things through Christ who strengthens me.” Philippians 4:13 (NKJV)

This verse has been a guiding light for me, reminding me that with faith and perseverance, all challenges can be overcome.

DEDICATION

I dedicate this research work to my son, Kylan Anozivaishe Mutsvene, and my daughter, Consuelo Ruvarashe Mutsvene.

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ACRONYMS AND NOMENCLATURE

1,4-DCB	1,4-dichlorobenzene
AACE	Association for the Advancement of Cost Estimating International
AD	Anaerobic Digestion
AP	Acidification potential
AP	Apatite phosphorus
BOD	Biochemical oxygen demand
BP	Break-even point
CCD	Central composite design
CEPCI	Chemical engineering plant cost index
CHP	Combined Heat and Power
COD	Chemical oxygen demand
DOE	Design of Experiments
EP	Eutrophication potential
FCI	Fixed capital investment
GC-TCD	Gas chromatography-thermal conductivity detector
GWP	Global warming potential
HPLC	High-performance liquid chromatography
HRT	Hydraulic retention time
HT	Hydrothermal treatment
HX	Heat exchanger
IAP	Ion Activity product

ICP-AES	Inductively coupled plasma atomic emission spectroscopy
ICP-OES	Inductively coupled plasma optical emission spectroscopy
FTIR	Fourier transform infrared spectroscopy
IP	Inorganic phosphorus
IRR	Internal rate of return
LCA	Life cycle assessment
LCI	Life cycle inventory
LCIA	Life cycle impact assessment
LCOE	Levelised cost of electricity
MBC	Magnetic biochar
MgCl ₂	Magnesium chloride
NAIP	Non-apatite inorganic phosphorus
NPV	Net present value
ODP	Ozone depletion potential
OFMSW	Organic fraction of municipal solid waste
OLR	Organic loading rate
OP	Organic phosphorus
PCs	Phenolic compounds
PO ₄ ³⁻	Phosphate ion
PODP	Photochemical ozone depletion potential
ROI	Return on Investment
RSM	Response surface methodology

SEM-EDS	Scanning electron microscopy with Energy-dispersive spectroscopy
SI	Supersaturation index
TAN	Total ammoniacal nitrogen
TFM	Tetrafluoromethane-based vessels
TIC	Total investment cost
TMP	Theoretical methane production
TOC	Total organic carbon
TS	Total solids
VFA	Volatile fatty acids
VIF	Variance inflation factors
VS	Volatile solids
WWTP	Wastewater treatment plant
XRD	X-ray diffraction
ZVI	Zero-valent iron

PREFACE

Technical papers

1. **Mutsvene, B.**, Chetty, M., Bux, F., & Kumari, S., 2025. Waste to wealth transformation: Maximising resource and energy recovery through hydrothermal treatment of sewage sludge - A technoeconomic evaluation. *Case Studies in Chemical and Environmental Engineering*, 11, 101182. <https://doi.org/10.1016/j.cscee.2025.101182>
2. **Mutsvene, B.**, Chetty, M., Bux, F., and Kumari, S. Valorisation of sewage sludge for sustainable bioresources and bioenergy recovery through hydrothermal treatment. *Journal of Chemical Engineering Research and Design*. **[Under review]**.
3. **Mutsvene, B.**, Chetty, M., Bux, F., and Kumari, S. A life cycle assessment of hydrothermal treatment for nutrient recovery and biogas production. *Scientific African*. **[Under review]**.

Review papers

1. **Mutsvene, B.**, Chetty, M., Kumari, S., Bux, F. and Diaz, I., 2024. Effects of Hydrothermal Pretreatment of Organic Waste to Enhance Biogas Production and Recovery of Nutrients: A Review. *Available at SSRN 4843510*. [preprint]. Available at SSRN: <http://dx.doi.org/10.2139/ssrn.4843510>

Conferences

1. **Mutsvene, B.**, Chetty, M., Bux, F. and Kumari, S., 2024. Nutrient Recovery and Biogas Production: Advancing Sustainable Wastewater Management with Hydrothermal Treatment—A Life Cycle Assessment. Conference Proceedings. 41st CAPE TOWN Int'l Conference on "Chemical, Biological and Environmental Engineering" (CCBEE-24) Nov. 21-22, 2024 Cape Town (South Africa). <https://www.iicbe.org/upload/2971C1124131.pdf>
2. **Mutsvene, B.**, Chetty, M., Bux, F., and Kumari, S., 2024 Valorisation of sewage sludge for sustainable bioenergy recovery through hydrothermal treatment: A preliminary techno-economic evaluation approach. WISA 2024 Biennial Conference & Exhibition. 12 to 14 June 2024. Durban ICC. (South Africa). Validation Number: WISA 2023-0079-003101

Book chapters

1. Armah, E.K., Chetty, M., Adedeji, J.A., Estrice, D.E., **Mutsvene, B.**, Singh, N. and Tshemese, Z., 2022. Biochar: production, application and the future. In Biochar-Productive Technologies, Properties and Applications. IntechOpen.
2. Armah, E.K., Chetty, M., Adedeji, J.A., Kukwa, D.T., **Mutsvene, B.**, Shabangu, K.P. and Bakare, B.F., 2021. Emerging trends in wastewater treatment technologies: the current perspective. Promis Tech Wastewater Treat Water Qual Assess, 1, p.71.

CHAPTER 1: INTRODUCTION TO THE STUDY

1.1 Background and context of the study

The challenges that the wastewater treatment industry is currently experiencing can be attributed to the increasing amount of waste-activated sludge (WAS) and the necessity to manage the resources in a sustainable manner. Waste activated sludge, created throughout the treatment of the wastewater, contains a significant amount of phosphorus, nitrogen and carbon and offers opportunities for the recovery of resources and energy. Its management is, however, limited by the environmental issues, operation costs and strict operational regulations. The blistering development of cities and industrialisation has only intensified the generation of sludge, and the scarcity of important materials like phosphorus provokes the need to find innovative recovery solutions.

The median nitrogen and phosphorus levels of the sludge in the South African sewage sludge are 28.9 g/kg and 13.5 g/kg, respectively, and in the province of KwaZulu-Natal, the phosphorus amount is slightly higher (Korentajer 1991). Traditionally, sewage sludge is an effective source of nutrients in agriculture due to cost efficiency and has been used to supplement phosphorus in areas that have limited access to inorganic fertilisers. The UK recycles 60 to 80% of sewage sludge (around 3.6 million tons per year), which is then applied to agricultural lands (Lofty *et al.* 2022; Koumoulidis *et al.* 2024). A small portion, 11% of sludge, is used as compost in wastewater treatment plants in South Africa for agriculture or irrigation (Western Cape Government 2021).

Nevertheless, the traditional ways of disposal, namely land application, landfilling and incineration, are becoming less sustainable owing to the concerns of heavy metal contamination, greenhouse gas emissions and the regulatory constraints. This has changed focus to innovative technologies that treat waste-driven sludge and reclaim valuable resources. The concept of hydrothermal treatment (HT) has emerged as a revolutionary process that is carried out at high temperatures and pressure to decompose the complex organic matter into bioavailable forms.

One of the prospective applications is Struvite recovery, which is a slow-release phosphorus fertiliser which helps to reduce dependence on phosphate rock resources and prevents the risks of eutrophication (Talboys *et al.* 2016). Besides, wastewater represents an important latent energy source which can be utilised in the process of treatment, which implies that anaerobic digestion is a feasible choice to recover energy (Cengiz *et al.* 2024). Potential of HT has been underutilised, and the nature of scalability is a challenge due to the problems with operational parameters optimisation, product inhibition and its integration into a traditional treatment system.

Because of the increasing insufficiency of the conventional methods of wastewater treatment, HT has a great prospect of converting wastewater treatment plants to resource recovery hubs. Important environmental challenges can be solved with this integration, like in the case of phosphorus depletion in water pollution, concurrently ensuring renewable energy and sustainability.

1.2 Importance of hydrothermal treatment in bioresources and bioenergy recovery

Nevertheless, the ways through which sludge can be disposed of, such as landfilling and ocean dumping, which have become common over the years, are gradually being limited because of secondary pollution and strict policies. It is suggested that HT will be effective to convert sewage sludge into useful products as it can be employed to hydrolyse, depolymerise and mineralise complex feedstocks to produce bioenergy, biofuels and nutrient-rich by-products. Among the advantages of using HT is that it enhances the recovery of phosphorus, usually in the form of struvite, which is a sustainable and environmentally friendly fertiliser because it releases complex phosphorus-containing compounds into a bioavailable form. HT decreases the sludge volume and recovers phosphorus, nitrogen, and carbon, and transforms them into useful products like biogas, hydrochar, and struvite, which are in line with the concepts of the circular economy. Research shows that HT recovers as much as eleven times more than the amount of energy recovered through landfill (Chen *et al.* 2020b).

1.3 Problem statement

This study considers a local wastewater treatment plant (WWTP) in one of the fast-growing cities which receives domestic and industrial wastewater, and represents the predicament in wastewater treatment facilities in developing countries face. The plant was originally constructed to handle nearly a million people, but due to increased population and anthropogenic activities, it has synchronously increased its daily capacity from 65 ML to 100 ML. Hence, there is overproduction of WAS, which exceeds the current sludge management capacity. Agricultural application has become saturated and poses a threat to the environment and plant operations (du Preez and van Huyssteen 2020; Grobelak *et al.* 2024). The heavy metals and pathogens are washed into local water bodies, and this results in eutrophication and contamination. Also, treated effluent is released into a local river, which is a vital water source in the region, contributing to the issue of the water quality and well-being of the ecosystem in the long term.

Sludge contains phosphorus (P), which is an important agricultural ingredient, but it is not fully exploited. Phosphorus recovery is emphasised due to the depletion of naturally occurring phosphate rock deposits, as it is estimated that these deposits would be exhausted within a century (Amar *et al.* 2022). On the other hand, excessive release of these nutrients exacerbates eutrophication, which then threatens the aquatic life. Slow-release fertiliser produced from wastewater, in the form of struvite, is a sustainable solution; however, there is a dire need to overcome technical challenges, including the need to optimise crystallisation and overcome the challenges of contaminated feed.

The technology of HT has potential in WAS management, increasing nutrient solubilisation and decreasing the sludge volume (Kang *et al.* 2021). Nonetheless, there are serious operational problems involved in combining HT with other downstream operations, including adsorption to eliminate toxins, precipitation of struvite and anaerobic digestion (AD) to generate biogas. Critical HT parameters (temperature and residence time) influence nutrient recovery, biogas yields, as well as economic viability but remain poorly understood. The variability in sludge composition, greater hydrodynamic complexities at a larger scale, and high energy requirements make its widespread adoption difficult.

Sustainably, HT-based phosphorus recovery can help to mitigate eutrophication and limit the use of synthetic fertilisers, which is in line with a circular economy model. Nevertheless, the investigated WWTP focuses more on disposal rather than the recovery of resources, limiting its potential benefits. The purpose of this research is to optimise the integrated technologies and trace the behaviour of phosphorus, and also to examine scalable solutions to come up with a model that will be used to manage wastewater sustainably. This way, it can promote waste management and resource reuse and comply with SDG 6 (clean water) and SDG 13 (climate action).

1.4 Research gap and novelty statement

1.4.1 Research gap

Despite growing interest, phosphorus recovery and wastewater valorisation remain underdeveloped, with key gaps limiting industrial adoption (Carrillo *et al.* 2024; Nyambiya *et al.* 2025; Raniro *et al.* 2025). Inasmuch as the conversion of struvite and biogas is well researched and well known, the conversion of phosphorus along the wastewater treatment continuum is not well understood. Specifically, its behaviour during hydrothermal treatment (HT) under various conditions, such as temperature and residence time, has not been characterised in detail, limiting optimisation for downstream recovery.

Adsorption of toxins is essential to improve the purity of downstream products; however, it makes the process complex because biochar-based adsorbents need to be balanced between inhibitor removal and nutrient availability for struvite crystallisation. Moreover, ammonium and other by-products of HT may suppress AD and, thus, reduce nutrient and bioenergy recovery (Zhang *et al.* 2024). These issues are complicated by the fact that there are no scalable solutions that consider the hydrodynamic and economic limitations of real-world WWTPs, especially in resource-limited areas such as Sub-Saharan Africa. The research fills these gaps by tracking phosphorus transformations systematically throughout HT, adsorption, nutrient recovery and AD, making it possible to have an optimised resource recovery strategy.

1.4.2 Novelty and contributions

The research particularly covers the limited understanding of transforming phosphorus during the hydrothermal processing through elucidating the behaviour of phosphorus under different temperature and residence time conditions. It also bridges the disparity in integrated sludge valorisation by developing a scalable process that combines hydrothermal treatment, magnetic biochar adsorption, struvite precipitation, and anaerobic digestion. The research shows an improved nutrient recovery and biomethane yield through optimum toxin removal and preservation of nutrient availability, validated by techno-economic and life cycle analyses. These contributions present a viable, sustainable structure of circular wastewater management in resource-constrained areas.

1.5 Aim and objectives

1.5.1 Aim of the study

This study aims to optimise an integrated process for valorising WAS from a local WWTP. It focuses on phosphorus recovery and renewable energy generation through anaerobic digestion. Hydrothermal treatment enhances resource recovery by solubilising nutrients and breaking down the sludge structure. The process includes toxin removal, phosphorus recovery through struvite precipitation, and AD for biogas production.

1.5.2 Objectives

1. To characterise the waste-activated sludge from the selected WWTP in terms of physicochemical, elemental, and macromolecular composition to determine its resource and energy potential.
2. To optimise hydrothermal treatment parameters (temperature; residence time) to enhance solubilisation and bioavailability of organic matter.
3. To evaluate the adsorption efficiency of magnetic biochar (MBC) synthesised from sugarcane bagasse in removing inhibitory compounds (phenolics and heavy metals) from HT effluents under optimised pH, dosage, and contact time.

4. To recover phosphorus as struvite from pre-treated sludge liquor and perform a complete phosphorus fractionation and mass balance to quantify transformation pathways.
5. To assess the influence of HT and intermediate valorisation steps on anaerobic digestion performance, measuring biogas yield, methane content, and kinetic parameters.
6. To conduct a preliminary techno-economic analysis that quantifies capital, operating, and energy costs, and determines economic indicators such as net present value (NPV), internal rate of return (IRR), and payback period for the integrated system.
7. To perform a life-cycle assessment (LCA) to evaluate the environmental impacts of integrating HT, adsorption, nutrient recovery, and AD compared to conventional sludge management.

1.6 Scope

This study is within the boundaries of the seven research objectives as above. It involves the process of characterising waste-activated sludge in order to define its potential as a nutrient and energy source and optimising the hydrothermal treatment in order to promote solubilisation and organic matter degradation. Sugarcane bagasse is studied as a raw material for magnetic biochar production to eliminate the inhibitory compounds produced during hydrothermal treatment, and recover phosphorus using the precipitation with struvite is studied using the fractional analysis and mass balance. The performance of the anaerobic digestion is evaluated by the biogas yield and potential of methane based on the effect of hydrothermal pretreatment and intermediate. Techno-economic analysis assesses system feasibility based on NPV, IRR and payback period, and an LCA determines the level of environmental impact against conventional sludge management.

1.7 Significance of the study

The study is important because it is able to create a holistic model on how waste-activated sludge can be converted into useful bioresources using a combined hydrothermal-adsorption-nutrient recovery-anaerobic digestion system. The systematic linkage between process optimisation, toxin reduction, phosphorus reuse, and bioenergy production further develops the scientific knowledge about the sludge valorisation and demonstrates a scalable pathway for circular wastewater management. The incorporation of techno-economic and life cycle analysis also proves the environmental and financial feasibility of the proposed approach, providing realistic insights into the sustainable implementation in resource-limited areas.

1.8 Dissertation structure

Chapter 1: Introduction - Establishes the foundation of the study, including its aims, objectives, problem statement, novelty, and limitations, while situating the research within the context of wastewater management and resource recovery.

Chapter 2: Literature Review - Critically reviews sludge management, HT, nutrient recovery, and biogas production. It highlights current challenges, advances, and research gaps in integrated sludge valorisation.

Chapter 3: Hydrothermal Treatment - Examines HT as a pretreatment technology, optimising temperature and retention time for improved nutrient solubilisation, organic matter decomposition, and enhanced AD efficiency.

Chapter 4: Adsorption - Investigates the use of magnetic biochar for toxin removal, evaluating its impact on improving resource quality and sustainable sludge valorisation.

Chapter 5: Precipitation - Explores phosphorus recovery as struvite, optimises process conditions, and assesses its scalability as a slow-release fertiliser in circular economy applications.

Chapter 6: Biogas Production - Analyses the effects of HT on AD performance, comparing biomethane potential from hydrothermally treated and untreated WAS, as well as from adsorption and precipitation effluent streams.

Chapter 7: Technoeconomic Evaluation - Evaluate the feasibility of scaling up the integrated system by assessing economic metrics, including NPV, IRR, and sensitivity factors that influence wastewater management decision-making.

Chapter 8: Life Cycle Assessment - Assesses environmental impacts using the LCA framework, quantifying emissions, energy consumption, and resource recovery, demonstrating alignment with circular economy principles.

Chapter 9: Conclusion and Recommendations - Summarises key findings, highlights achievements and limitations, and provides recommendations for optimising HT, resource recovery, and biogas production, alongside directions for future research .

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

The activated sludge process is a widely used and cost-effective wastewater treatment technique that effectively removes organic pollutants from wastewater. However, it generates significant amounts of sewage sludge, which increases annually (Khanh Nguyen *et al.* 2021). Due to the presence of pathogens and heavy metals, sewage sludge is often considered hazardous biowaste. Traditional disposal methods, such as incineration, ocean dumping, and landfilling, are discouraged due to environmental pollution and stringent regulations (He *et al.* 2014).

Various valorisation technologies have been explored in response to the rising sludge volumes from WWTPs. Among these, biogas production is prominent but hindered by the complex nature of the sludge, resulting in low yields. HT has been developed as a promising pretreatment method to increase biogas productivity. Furthermore, WWTPs serve as nutrient reservoirs, and currently, there is interest in recovery methods for nutrients such as phosphorus, whose depletion has sparked significant attention. Adsorbents, such as biochar (produced through pyrolysis) and hydrochar (obtained through subcritical water treatment), have been explored for nutrient reclamation (Takaya *et al.* 2016).

Bio-electrochemical systems (BES), such as microbial fuel cells (MFCs) and microbial electrolysis cells (MECs), represent innovative technologies for on-site energy production and nutrient recovery. BES has seen extensive research on its use for removing nitrogen; however, there has been limited research on its potential for phosphorus recovery (Almatouq *et al.* 2020). The potential for phosphorus recovery as struvite, a slow-release, eco-friendly fertiliser, has emerged to address rock phosphate shortages if it is scaled up in WWTPs.

Although relatively limited in terms of full-scale applications, HT of sludge has been extensively studied at laboratory and small pilot scales under different conditions for reactor operation. HT for AD operates at lower temperatures and pressures, focusing on nutrient recovery rather than substantial carbon reduction. As a thermal treatment tailored

for wet biowaste, HT offers advantages in pathogen destruction, sludge volume reduction, and resource recovery, despite the challenges posed by its high water content (>95%) (Park *et al.* 2019b).

Globally, over 907 million kg of phosphorus is consumed annually as fertiliser, with nitrogen fertiliser usage being three times higher (Randive, Raut and Jawadand 2021). HT's ability to recover such nutrients and its versatility in sludge management underscore its growing relevance in sustainable wastewater treatment (Hii *et al.* 2014; Kim, Lee and Park 2015; Wu and Vaneeckhaute 2022).

2.1.1 Introduction to sewage sludge valorisation

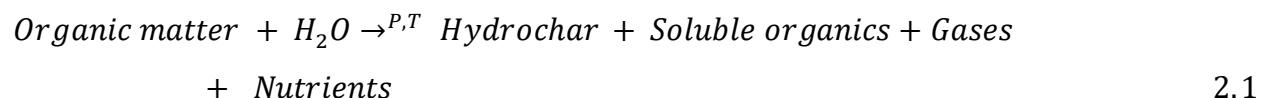
Around 98 % of phosphorus consumed in the human diet is lost through sewage, along with additional contributions from industrial wastes and detergents (Omidire 2021). Wastewaters rich in phosphorus and nitrogen originate from various sources, including municipal and industrial effluents, agriculture, and livestock farming. One method for removing these nutrients is the precipitation of phosphate (PO_4^{3-}) and ammonium (NH_4^+) as struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), which has been successfully recovered from diverse wastewater streams, including industrial and sewage effluents. In domestic wastewater, urine accounts for 50-80% of phosphorus and 75% of nitrogen, primarily excreted as urea (Arredondo *et al.* 2015).

Phosphorus, a critical nutrient for plant growth, often limits agricultural productivity. However, using wastewater sludge in agriculture requires careful management to mitigate risks from pathogens, heavy metals, and other contaminants (Pettersson and Johansson 2022). Proper treatment and testing ensure its safe and practical application.

Excess NH_4^+ in water bodies exacerbates eutrophication, impairing self-purification and inhibiting photosynthesis in algae through alterations in chlorophyll fluorescence and electron transport (Li *et al.* 2019). This fosters the suppression of phytoplankton, harm to aquatic life, and algal blooms (Yi 2022). NH_4^+ in effluent also impacts chlorination, producing harmful disinfection by-products. Furthermore, $\text{NH}_3\text{-N}$ generated during equilibrium poses risks to aquatic organisms by suppressing protein metabolism (Su *et al.* 2023). These adverse effects necessitate robust strategies for nutrient removal.

2.1.2 Importance of hydrothermal treatment in resource recovery and bioenergy production

HT involves heating at high temperatures (< 374 °C) and pressures below those of subcritical water, specifically 22.1 MPa (Scrinzi *et al.* 2022). While HT produces valuable outputs, some by-products can be detrimental and require careful handling. The fundamental reaction can be summarised in Equation 2.1.



Hydrothermal conversion of biomass under subcritical water conditions efficiently generates value-added compounds. Subcritical water offers rapid reaction rates, low mass transfer resistance, and gas-like diffusivity, making it a highly effective medium (Khandelwal *et al.* 2024).

2.2 Sources of phosphorus

2.2.1 P sources in wastewater

Figure 2.1 shows the breakdown of the sources of phosphorus in wastewater. The distribution focuses on the dominant roles that certain sectors and activities play in disposing of phosphorus, resulting in pollution, and provides invaluable insights, specifically in controlling phosphorus-overloaded wastewater and in the recovery of resources strategies (Yesigat *et al.* 2022).

It is observed that the contribution from livestock activities and sewage is the highest, accounting for 34% of the phosphorus loading. Livestock operations can produce phosphorus through excreta and related waste streams that enter water bodies. Likewise, sewage containing all human-generated waste, such as faeces and urine, also considerably affects phosphorus content, contributing 24%. These two sources emphasise the importance of improving agricultural and urban waste management practices to reduce phosphorus pollution.

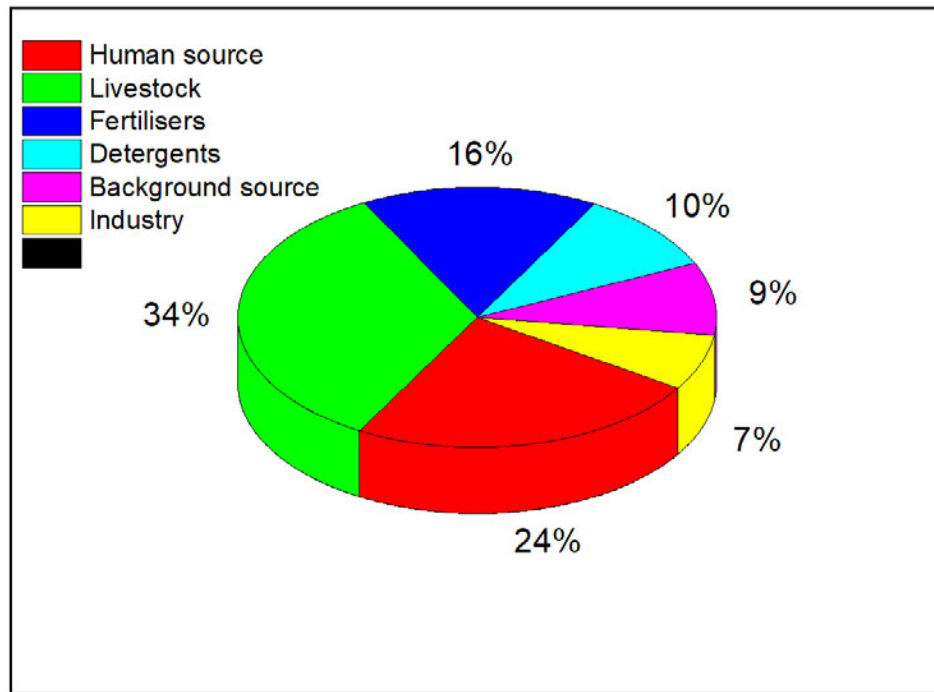


Figure 2.1 Distribution of phosphorus sources in wastewater

Source: (Yesigat *et al.* 2022)

Detergents account for 10% of the phosphorus due to phosphate-containing cleaning products. This illustrates why phosphate control or simple changes, such as reducing the use of phosphate-containing detergents, may reduce phosphorus discharges. Fertilisers account for 16% of the phosphorus runoff from farmland that uses phosphorus-based fertilisers. To curb such contributions, precision farming methods and nutrient management strategies must be employed.

Approximately 7% of the discharges can be attributed to industries associated with food processing and the chemical industry, among others. The remaining 9% comprises background sources, including basic natural erosion and minimal human influence. These figures confirm the multiplicity of phosphorus sources, which can only be overcome by cross-cutting strategies and measures that include policy, technological innovation, and stakeholder engagement.

2.2.2 Naturally occurring P sources

The finite nature of phosphorus, predicted to be depleted within 50-100 years (Amar *et al.* 2022), has prompted researchers to investigate its recovery from municipal wastewater systems.

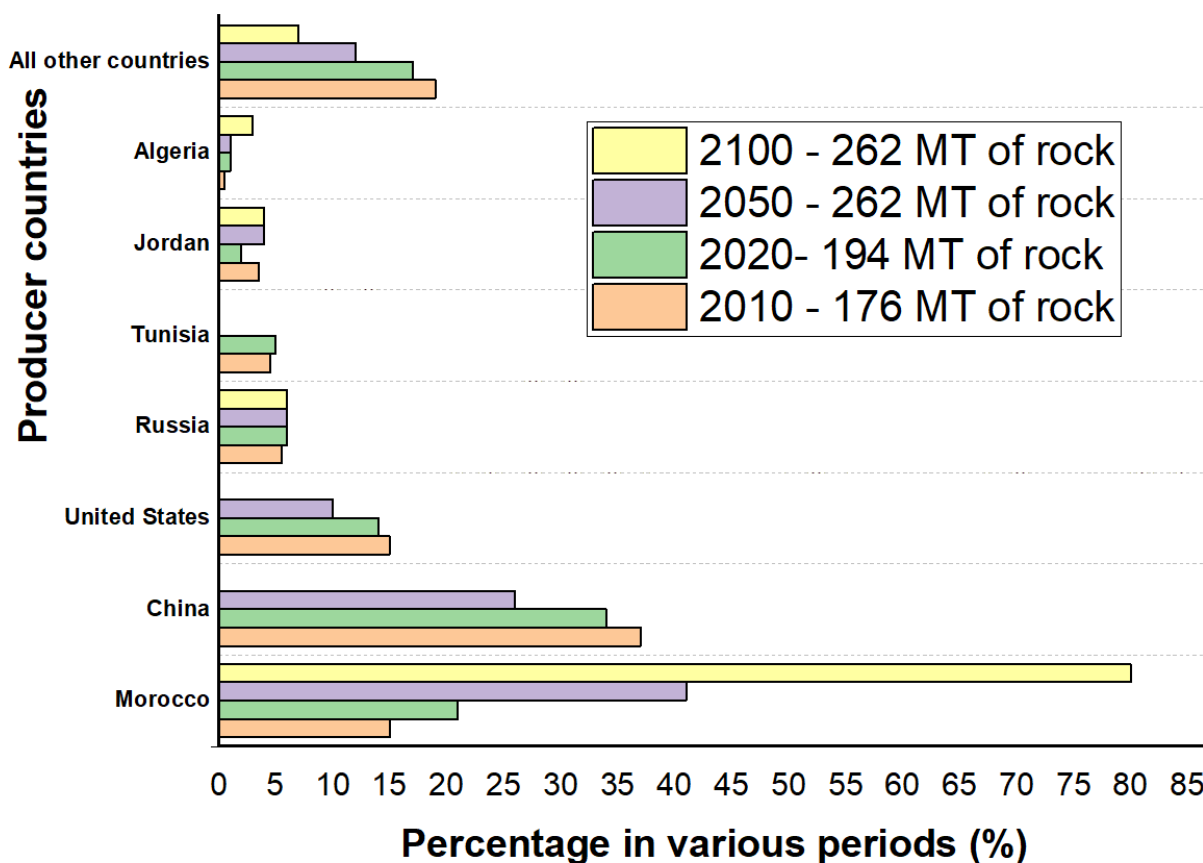


Figure 2.2 Phosphate rock reserves distribution and future predictions in the world

Source: (Jasinski 2014)

Phosphorus, an essential element, is primarily found in sedimentary rocks, with relatively scarce sources in igneous rocks. Economically viable high-quality deposits are unevenly distributed globally due to the interplay of physical, chemical, and geological factors in coastal upwelling zones and fluctuating sea levels. These unique conditions result in the limited global distribution of phosphate deposits (Daneshgar *et al.* 2018; Illakwahhi, Vegi

and Srivastava 2024). Few new phosphate rock discoveries have been made in the past century (Filippelli 2011), as illustrated in Figure 2.2.

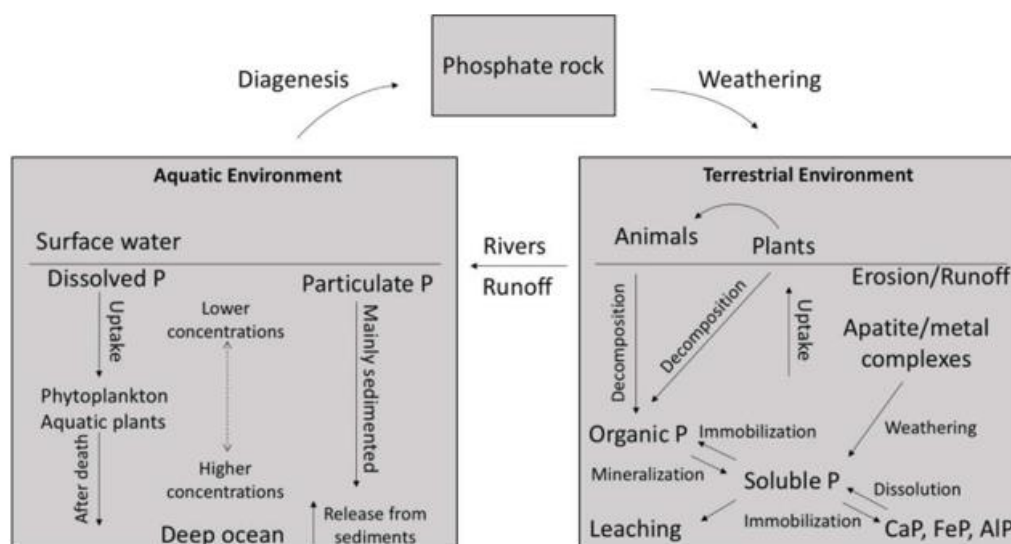


Figure 2.3 Natural phosphorus cycle in aquatic and terrestrial environments

Source: (Ahlström and Cornell 2018)

The debate over the future of phosphate rock production and its eventual depletion is highly contentious. With a growing global population, the demand for phosphorus is set to rise, driven by the need for increased food production. However, many reserves remain untapped due to the lack of economically viable extraction techniques (Amar *et al.* 2022).

Phosphate minerals have two main applications in agricultural and non-agricultural activities. Approximately 95% of global phosphorus production is used in agriculture, primarily as fertilisers and animal feed additives (Daneshgar *et al.* 2018). Non-agricultural uses, accounting for less than 5% of global phosphorus consumption, include applications in the food industry (e.g., polyphosphate additives), corrosion control in public water systems, boiler scaling prevention, and detergent production (Alewell *et al.* 2020). Figure 2.3 illustrates a simplified natural phosphorus cycle showing the movement between the terrestrial and aquatic environments. The rocks weather and release phosphate that plants uptake and enter the food chain. Organic phosphorus is returned to the soil through decomposition, whereas leaching and runoff transport it to aquatic systems. Phosphorus

is cycled between dissolved and particulate forms in water and affects biological productivity and sedimentation.

2.3 Characterisation of the WWTP WAS to determine its resource and energy potential.

Evaluation of the resource and energy potential of the waste-activated sludge (WAS) stream is dependent on its extensive characterisation. Recovery and treatment methods are determined based on the WAS's physical, chemical, and biological properties through a study of its properties. The composition of the WAS needs to be understood to determine the suitability of treatment technology for energy production and resource recovery (Chen *et al.* 2024). Accounting for organic matter and calorific value enables decision-making on energy recovery methods by providing a platform to regulate the amount of energy that is extractable from WAS (Oladejo *et al.* 2019).

Characterisation is one of the significant strengths, considering that contaminants such as heavy metals and pathogens must be identified to ensure that the resource recovery processes meet the environmental regulations and standards (Lucia *et al.* 2022). In sustainable wastewater management and the circular economy, WAS is gaining traction as a valuable bioresource. As a resource-efficient and waste-reduction approach, its rich organic matter and nutrient content make it suitable for conversion into bioenergy and bioresources. However, the way WAS is characterised and used determines whether wastewater treatment plants become waste disposal facilities or resource recovery hubs, which embrace sustainability goals, and the availability of WAS to be used effectively to recover resources and energy helps to realise the transition to a circular economy (Luo *et al.* 2024).

2.3.1 Physicochemical properties of WAS

Characterisation of wastewater is crucial to delivering basic data for reliable modelling and design of biological treatment processes. In particular, the solid fractions in WAS and its derivatives must be understood, especially when applied to AD, which is one of the cornerstone processes in wastewater treatment.

2.3.1.1 Solids content

The presence of solids in wastewater significantly influences the effectiveness of biological treatment processes. Proper sludge characterisation is, therefore, fundamental to optimising treatment system performance. The solid matrix of waste-activated sludge (WAS) is a key indicator of operational and design parameters across various waste management processes.

TS represents the combined organic and inorganic matter in sludge, encompassing suspended and dissolved fractions (Adjovu *et al.* 2023). In wastewater treatment, TS content is particularly critical for designing and operating AD systems. It determines the biomass feed concentration within a reactor, directly impacting process efficiency (Armah *et al.* 2017). Based on solids concentration, sludge is classified as low (<10%), medium (10-20%), or high solids (20-40%). High TS content is advantageous for reactor design and process economics, as it reduces reactor volume requirements and minimises water usage, thus lowering operational costs (Neshat *et al.* 2017).

Sources of TS include industrial discharges, municipal wastewater, agricultural fertilisers, road runoff, and soil erosion. TS concentration is a critical parameter in regions with intensive industrial and irrigation activities, often expressed in milligrams per litre (mg/L) (Bhardwaj, Boora and HAU 2023). TS levels tend to be higher in arid areas due to increased evaporation, rendering these ecosystems particularly vulnerable to human activities. Elevated TS concentrations degrade water quality and influence wastewater treatment plant performance and sludge management strategies (Brix, 2020).

A key fraction of TS is the organic component, which volatilises upon combustion at 550°C, known as VS or total volatile solids (TVS). The biodegradability of organic matter and its potential for bioenergy production are strongly correlated with VS content (Zhang and Chen 2018; Xu *et al.* 2020; Babu *et al.* 2023). Higher VS levels indicate a greater proportion of biodegradable material, making sludge a more viable feedstock for biogas generation. Consequently, VS is a reliable predictor of energy yield and methane production, which are central objectives of AD.

Total dissolved solids (TDS) refer to solid constituents that pass through a 2.0 μm membrane, primarily consisting of salts, minerals, and small organic molecules. Elevated TDS levels indicate increased mineral content, which affects effluent discharge, reuse, and recycling processes (Peng *et al.* 2020; Velmurugan and Pandian 2024). Conversely, total suspended solids (TSS) include particulate matter retained on the filter during TDS analysis.

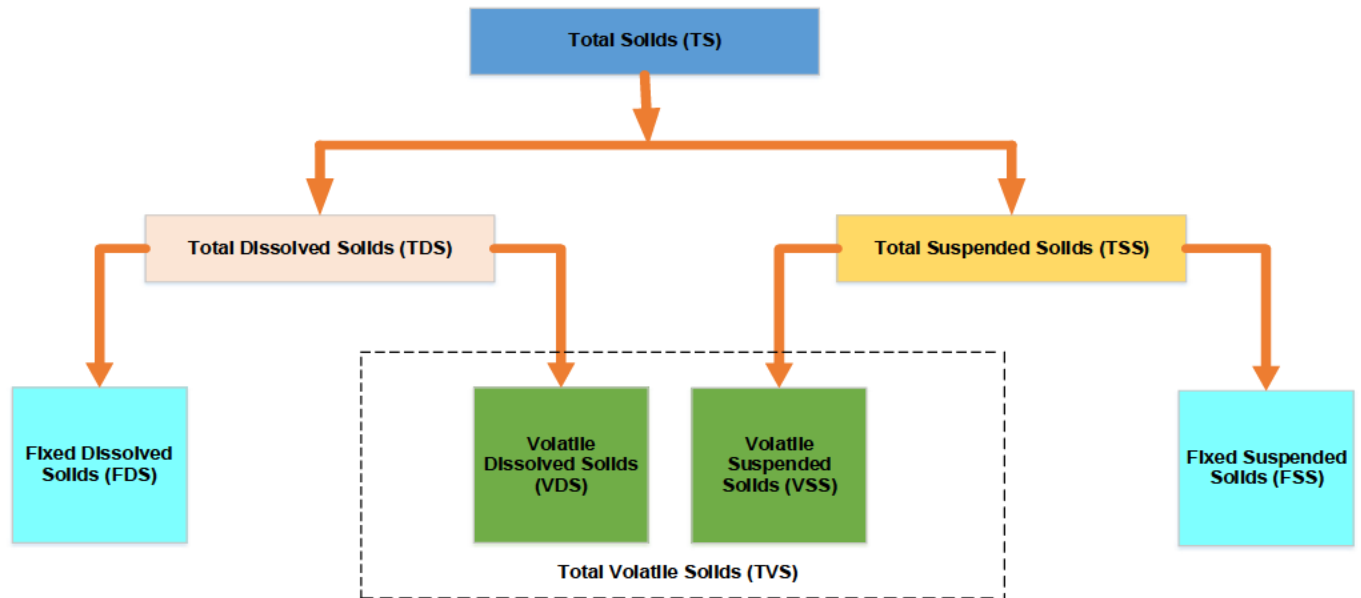


Figure 2.4 Hierarchical relationship between total solids (TS), total suspended solids (TSS), total dissolved solids (TDS), and their volatile and fixed fractions in wastewater sludge.

Figure 2.4 illustrates the interrelationships among TS, VS, TDS, and TSS, providing a comprehensive assessment of sludge composition and treatability. Understanding these parameters is essential for optimising treatment processes, enhancing energy recovery, and designing sustainable sludge management strategies.

2.3.1.2 Moisture and ash content, and bulk density

Moisture content dictates the handling and processing requirements of waste-activated sludge. Dewatered sludge typically comprises 8-12% solids, corresponding to a moisture content of approximately 88-92% (Liu *et al.* 2021b). High moisture levels present significant challenges, particularly in transportation and pumping, where increased weight directly escalates costs and negatively impacts logistics. Moreover, the elevated water

content diminishes the efficiency of thermal processes such as incineration, pyrolysis, or gasification, as additional energy is required to evaporate the surplus moisture before treatment (Quan *et al.* 2022). Consequently, effective dewatering and drying processes are essential to reduce moisture content to levels that facilitate subsequent sludge management and resource recovery operations.

Biomass decomposition, whether through thermochemical or biochemical pathways, invariably produces a solid residue (Kang *et al.* 2021). It is an important parameter for characterising solid and liquid biomasses. Ash is the inorganic incombustible residue at 575°C by dry oxidation, according to the definition by Jacob-Lopes, Zepka and Dias (2024). This parameter characterises one part of the complete compositional analysis of biomass, as high ash content indicates the mineral content and inorganic substances within the biomass, which may be beneficial for recovering valuable elements such as phosphorus. Sewage sludge ash (SSA) is another promising resource concerning phosphorus recovery because phosphorus contents in this ash may amount to 9% of weight or more (Jacob-Lopes, Zepka and Dias 2024). On the other hand, a high ash content indicates a low organic fraction and, consequently, a low calorific value, thereby reducing energy through processes such as combustion, pyrolysis, or even thermal hydrolysis. Therefore, the optimisation of ash content is an important parameter in mineral recovery processes and energy production strategies when considering sludge management.

The fixed solids content is equally important in assessing material stability and nutrient content, representing the inorganic, non-volatile fraction of sludge. The measurement of fixed solids thus constitutes a fundamental basis for establishing the most appropriate and effective treatment and resource recovery strategy for sludge.

Another important parameter of sludge management is bulk density, which determines the methods of storage, transportation, and treatment. Bulk density is defined as the mass of the sludge per unit volume, considering both the liquid and solid components, and it is of critical importance in determining the capacity of the processing unit. A higher bulk density means a higher mass per unit volume, which may lead to increased energy and time consumption during dewatering and drying. The bulk density of sludge is a

prerequisite to optimising handling procedures, improving management practices, and reducing overall sludge management costs (Ezemagu *et al.* 2021).

It is essential to identify salinity, as it affects the rate of HT, the nutrient recovery process, and the quality of the recovered bioresources. High salinity may negatively impact microbial growth, subsequent biogas production, resource recovery, and the transition phases. Moreover, knowledge of salinity levels enables the determination of risks associated with corrosion of equipment parts and the suitability of water reclamation for reuse, making the process sustainable and environmentally friendly (Velmurugan and Pandian 2024).

2.3.2 Elemental composition

The ultimate analysis of WAS indicates the percentage of the elemental composition, such as carbon (C), hydrogen (H), nitrogen (N), sulphur (S), and oxygen (O), in the material. From a commercial point of view, it is also an essential tool for determining the suitability of the material for energy recovery processes. These elemental concentrations are altered significantly by hydrothermal treatment.

The decomposition of organic matter and the removal of the elements oxygen and hydrogen in the form of gaseous by-products typically increases the carbon content in the solid residue during HT (Reza *et al.* 2014). The energy density of the treated sludge from this enrichment is increased. At the same time, nitrogen and sulphur are volatilised into gaseous forms, which lowers the risk of the subsequent thermal process producing harmful emissions.

Accordingly, C/H, C/N, and C/S are key elemental ratios that help determine energy potential and associated environmental considerations in the treated WAS (Singh *et al.* 2023a). Due to the high energy-bearing potential of carbon-rich material, high values of C/H have resulted in higher values of energy density (Seah *et al.* 2024). Especially important for AD, the optimum balance of the C/N ratio improves biogas production while imbalances accumulate NH_3 and inhibit microbial activity (Yellezuome *et al.* 2022). The C/S ratio has a similar impact on the sulphur emission during thermal processing, so the presence of a low C/S ratio may result in higher sulphur dioxide emissions, and thus,

more gas scrubbing technologies are needed to meet environmental standards (Barani *et al.* 2018).

2.3.3 Organic composition

2.3.3.1 Total organic carbon (TOC)

Treating wastewater is among the most important applications, and TOC is a crucial parameter since it reflects the amount of organic matter in the wastewater and, therefore, controls its energy recovery potential. The determination of TOC allows the quantification of the breakdown of organic matter, directly influencing the efficiency of treatments such as AD. Generally, TOC levels are proportional to biodegradable organic substrates available for conversion into biogas, increasing the energy yield of sludge (Zhou *et al.* 2024).

Breaking down complex organic polymers in WAS into simpler soluble compounds by the HT has increased the soluble organic carbon fraction of the original waste. Increased biodegradability of the substrate makes a downstream AD process more efficient. The process water generated during hydrothermal treatment has been found to contain dissolved organic matter concentration from 2 to 20 g/L as a function of feedstock characteristics and operating conditions (Herklotz and Mumme 2013).

The soluble organic compounds from this process water are anaerobically digested, i.e. converted to biogas, yielding energy potential. Despite the inhibitory by-products generated during hydrothermal treatment, such as ammonia, phenolics, and furans, microbial activity during digestion may be inhibited (Zhou *et al.* 2024). The energy recovery potential of WAS and its hydrothermal treatment increases TOC solubilisation. However, the formation of these inhibitory compounds must be monitored and managed to maximise the efficiency of any integrated treatment process. Accurate TOC measurements will determine how well hydrothermal treatment, the pretreatment process, breaks down complex organic materials into simpler, more digestible forms. This is crucial for optimising the treatment process to ensure maximum energy recovery from waste-activated sludge.

2.3.3.2 Proteins and carbohydrates (macromolecules)

WAS is important in the biodegradability of proteins and carbohydrates and has the potential for energy recovery. Proteins are composed of amino acids, of which there are many different types, and represent the primary nitrogen source for these microbial communities, on which complex organic matter is broken down during AD. However, the energy production associated with this degradation also produces volatile fatty acids and biogas (Dumitraşcu, Borda and Aprodu 2023; Zhou *et al.* 2024). Like the above, microorganisms also metabolise carbohydrates, composed of sugar monomers, easily generating VFAs, which helps improve biogas yield (Qiu *et al.* 2023). Efficient microbial digestion of WAS and its derivatives is required to optimise energy recovery from these macromolecules.

Several methods, including the Kjeldahl-N, Lowry, and Bradford methods, have been used to measure proteins (Ekka *et al.* 2022). At the same time, the anthrone method and phenol-sulphuric acid method have been used to determine total carbohydrates (Zhang *et al.* 2020c; Chen *et al.* 2023). However, methodologies for the rapid and sensitive quantitative analysis of proteins and carbohydrates are still highly desired. Due to the complex composition of effluents and the low concentrations of proteins and carbohydrates in these effluents, the methods have limitations, including low sensitivity, complex pretreatments, and low selectivity. This restricts their application to the measurement of proteins and carbohydrates at modest concentrations in bioreactor effluents. In addition, the Lowry method is susceptible to interference from numerous substances and requires complex preparation procedures (Yan *et al.* 2023).

The phenol-sulfuric and anthrone methods require heating samples in strong sulfuric acid and complex preparation techniques, which are expensive and unstable in sulfuric acid reagents (Boshagh 2021). The analysis of low concentrations of proteins and carbohydrates in bioreactor effluents may not be compatible with them.

The documented relationship between COD and proteins ranges from 1.50 to 1.53 gCOD/g protein (Sophonsiri and Morgenroth 2004; Ahnert *et al.* 2021). This relationship is important as it helps to ascertain the accuracy of the characterisation process. HT of WAS enhances the concentration of readily biodegradable substrates so that subsequent

AD and biogas production may be enhanced (Zhang and Chen 2018; Xu *et al.* 2020; Babu *et al.* 2023). In practice, however, conditions such as temperature, pressure and retention time influence the extent of solubilisation. Optimising these parameters to maximise the breakdown of macromolecules and minimise the formation of inhibitory by-products is essential.

2.3.4 Nutrient composition

Wastewater sludge nutrient content depends on the source and treatment process (Kominko, Gorazda and Wzorek 2019). Reza *et al.* (2019) also report high levels of nitrogen, phosphorus, and potassium, all important macronutrients essential for plant growth. Concentrations of phosphorus in wastewater sludge can be high, particularly between 2 and 4 w%, depending on the source and the treatment process (Chen *et al.* 2020a).

2.3.4.1 Nitrogen transformations

Wastewater treatment processes (WTPs) transform organic nitrogen in waste-activated sludge through various pathways, often resulting in the production of ammonium (NH_4^+), nitrate (NO_3^-), and nitrite (NO_2^-). The microbial breakdown of organic nitrogen compounds, which releases ammonium ions, is called ammonification. The nitrogen cycle in the wastewater treatment system involves nitrification, i.e., a two-step process where ammonium is oxidised to nitrite by ammonium-oxidising bacteria (AOB), and nitrite is oxidised to nitrate by nitrite-oxidising bacteria (NOB) (Marin-Batista *et al.* 2019; Li *et al.* 2021). HT may alter the chemical composition and bioavailability of nitrogenous compounds, and may also significantly transform organic nitrogen into less labile nitrifiers, thereby decreasing the short-term availability of ammonium for nitrification.

Biofertilisers rich in nitrogen, obtained from treated sewage sludge, are applied per the principles of a circular economy, thereby increasing soil fertility and reducing chemical fertiliser use. However, safety standards must still be strict to avoid environmental contamination and minimise health risks. Therefore, a complete characterisation of the forms and concentrations of nitrogen within WAS and its derivatives is required. This

characterisation is pivotal for optimising treatment processes and advancing nitrogen recovery strategies toward embodied biofertilisers.

2.3.4.2 Phosphorus fractionation

Waste-activated sludge phosphorus exists in different fractions, each with distinct responses to treatment processes. This includes the main fractions of orthophosphate (inorganic phosphorus, IP), non-apatite inorganic phosphorus (NAIP), apatite phosphorus (AP), and organic phosphorus (OP). In soluble forms, orthophosphate is highly bioavailable and can be readily assimilated by microbes. NAIP, associated with Al, Fe and Mn oxides, is bioavailable under specific conditions, while AP, bound to calcium minerals, is more stable and primarily accessible in acidic environments. Incorporated into organic matter, OP requires mineralisation to be bioavailable (Ewens 2022).

Results indicate that phosphorus solubility fractions are correlated with their chemical forms (Guo *et al.* 2024). The water-soluble and NaHCO_3 -soluble fractions are dominated by orthophosphate, indicating immediate availability for biological uptake or reaction, such as struvite crystallisation. The primary NAIP association is with glycation between NaOH -soluble fractions due to its binding to amorphous iron and aluminium oxide, which forms a slowly available form. AP accounts for a stable, long-term phosphorus source in HCl -soluble fractions and is prevalent. OP is present in NaHCO_3 soluble (loosely bound) and NaOH -soluble (localised to humic substances) forms and must undergo mineralisation for its release as orthophosphate. Residual-P includes stable refractory phosphorus forms, which are resistant to extraction and largely inaccessible.

The distribution of phosphorus fractions is critical to nutrient recovery and treatment. For instance, high orthophosphate levels indicate higher water-soluble or NaHCO_3 -soluble phosphorus (solubility fraction), suggesting immediate availability. Conversely, a high apatite phosphorus content indicates HCl -soluble fractions, which are suitable as long-term nutrient sources. These categories complement one another in assessing phosphorus transformations across systems.

The efficiency of phosphorus recovery methods hinges on the fraction distribution within WAS. Studies report variations in phosphorus content, with activated sludge containing

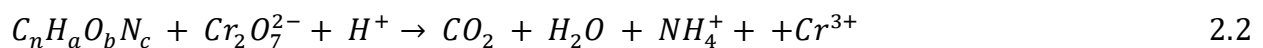
approximately 1.4 wt% phosphorus (Cordell *et al.* 2011), predominantly as orthophosphate (Pokhrel *et al.* 2018). NAIP typically accounts for most inorganic phosphorus, constituting 68-73% of total solid phosphorus in WAS (Guo *et al.* 2024).

Organic phosphorus (OP) displays complexity due to its diverse roles in microbial communities. A substantial portion exists as polyphosphates, stored intracellularly by phosphorus-accumulating microorganisms, which are readily converted to orthophosphate upon cell lysis. Under aerobic and anoxic conditions, microorganisms assimilate phosphorus as polyphosphates, while anaerobic conditions trigger phosphorus release for energy generation (Sun *et al.* 2020b).

2.3.5 Oxygen demand parameters

COD and biochemical oxygen demand (BOD) are key parameters used to assess the biodegradability of wastewater and the effectiveness of treatment processes. COD is the quantity of oxygen needed to chemically oxidise all the organic matter (biodegradable and non-biodegradable) in the wastewater using potent oxidising agents under acidic conditions, as shown in Equation 2.2. However, BOD measures the amount of oxygen microorganisms consume for a specific period, usually 5 days (BOD₅), to decompose organic substances under aerobic conditions. The BOD:COD ratio is an indicator of the proportion of the organic matter that is readily biodegradable, and the higher the BOD:COD, the higher the proportion of biodegradable organic matter that has to be treated biologically (Rudaru, Lucaciu and Fulgheci 2022). A good understanding of how HT impacts SCOD and BOD levels is crucial when designing solid treatment and sludge management strategies to recover resources and energy.

The COD test determines the oxygen demand for the oxidation of soluble and particulate organic matter. COD can be continuously monitored with a COD analyser, which helps to control the process more effectively and increase plant efficiency. This parameter is a key indicator of sewage and waste organic pollutant levels in municipal and industrial wastewater.



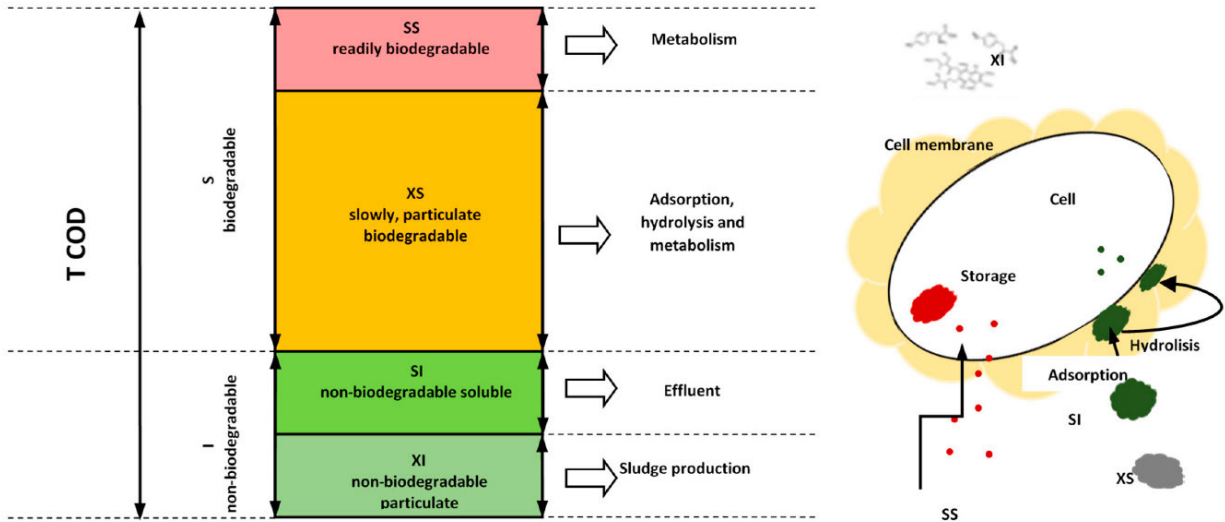


Figure 2.5 Schematic diagram of the COD fractions and their fates in a biological wastewater treatment plant

Source: (Choi *et al.* 2017)

COD and BOD variations cannot indicate the degradability of the contaminants in WWTPs (Płuciennik-Koropczuk and Myszograj 2019). The COD fractionation and balancing can be determined via different techniques with different degrees of precision. The favourable characteristics of wastewater are achieved by categorising COD according to ATV-A 131 (a method that improves the accuracy and precision of determining the COD fraction). This approach is generally effective when the wastewater characteristics align well with the method's assumptions.

Partitioning organic contaminants into biodegradable and non-biodegradable fractions is crucial in developing biological nutrient removal technologies. This knowledge significantly equips plant operators with the skills to manage the activated sludge process, including understanding oxygen requirements, maintaining sludge age, and recognising the kinetic parameters that govern the biological reactor's performance. Additional fractions, such as substrates involved in metabolic steps, contribute mainly to the overall biomass quantity. Within the substrates, a clear differentiation can be made between those that exhibit easy biodegradability and those that undergo gradual hydrolysis. The residual organic material exhibits inertness and lacks biodegradability. Figure 2.5 illustrates the fractionation of COD present in municipal wastewater.

The effluent's total COD ($\text{g O}_2/\text{m}^3$), partitioned into constituent fractions, may be computed utilising Equation 2.3 (Can-Güven 2021).

$$COD_t = S_s + S_I + X_s + X_I \quad 2.3$$

S_s is COD of soluble, readily biodegradable substrates; S_I is COD of inert, soluble organic substrates; X_s is COD of particulate, slowly biodegradable substrates; X_I is COD of inert, particulate organic substrates, and in detail, as shown in Equation 2.4.

$$COD_t = S_{VFA} + S_F + S_I + X_s + C_X + X_H + X_I \quad 2.4$$

Where: S_{VFA} is COD of volatile fatty acids; S_F is COD of fermentable organic substrates; C_X is COD of slowly biodegradable colloidal substrates; X_H is COD of heterotrophic biomass fraction. COD values established as total COD (TCOD) and soluble COD (SCOD) are the basic metrics in characterising the sludge containing organic matter. Whereas particulate COD (PCOD) accounts for the amounts of SCOD that can be eliminated by sedimentation, filtration, and flotation, TCOD is calculated as a sum of SCOD and PCOD. SCOD is further categorised into readily biodegradable COD (rbCOD), slowly biodegradable COD (sbCOD), and inert COD (Pola *et al.* 2022).

2.3.6 Volatile fatty acids (VFAs) and alkalinity

VFAs and alkalinity are key to the stability and efficiency of the AD process of wastewater. Acetic, propionic, and butyric acids are intermediate products of the acidogenesis phase during AD. VFAs are then accumulated by methanogenic archaea to utilise as a substrate and converted into methane and carbon dioxide, the significant components of biogas (Al-Sulaimi *et al.* 2022). Notwithstanding, excessive VFA accumulation can lead to acidification, inhibiting methanogenesis and potentially causing digester failure. Total alkalinity (TA) (mostly as bicarbonates) buffers the system, stabilising pH by neutralising acids for conducive microbial activity. Optimal AD performance requires a balanced VFA concentration and sufficient alkalinity, as the breakdown of organic matter releases reactive limiting ions (Santinello *et al.* 2024).

2.3.7 Toxicity and heavy metals

2.3.7.1 Heavy metals

Heavy metals, in environmental science and toxicology, are defined as metals and metalloids that possess toxicity; these include lead, mercury, cadmium, arsenic and chromium. These elements are of particular concern because they are persistent in the environment and have the potential for bioaccumulation.

As for the heavy metals, they are autotrophic or incorporated into the particle surface of sludge or microbial cells in waste-activated sludge. The adsorption mechanisms include electrostatic attraction, ligand exchange, surface complexation, and precipitation. Therefore, when excess sludge is disposed of, heavy metals are also precipitated from the wastewater (Liu *et al.* 2023).

Many studies report no fixed minimum density for a metal to be classified as heavy; definitions vary. Some sources consider heavy metals as a material with a density greater than 5 g/cm³, while others indicate that the division can be done based on the density between 3.5 g/cm³ and 7 g/cm³ (Vidican *et al.* 2020). This irregularity suggests that density alone cannot be used as a reliable criterion for distinguishing between heavy metals.

Due to the vagueness and potential for misunderstanding of the broad term 'heavy metals', it is advisable to specify particular metals of interest. This approach enhances clarity, particularly in cases involving environmental impact and assessment, or where a regulatory context is present. The presence of heavy metals significantly complicates the management of sewage sludge, having a negative impact on both the environment and human health. Cadmium, lead, mercury, and arsenic, among other heavy metals, are persistent in the environment and can accumulate in the food chain, posing a risk to the ecosystem and human health. Sewage sludge is limited in its use, especially in agriculture, due to the potential for soil contamination that the subsequent crop can absorb. Nevertheless, the heavy metal concentration needs to be reduced to a level that is safe for use or disposal (Singh *et al.* 2023b).

Regulating the levels of heavy metals in sewage sludge to be disposed of through land application plays a crucial regulatory role in managing the use of heavy metals. Heavy metals, such as cadmium, copper, nickel, lead, zinc, mercury and chromium, are limited in their concentration by the European Union's Sewage Sludge Directive (86/278/EEC) applicable to both sludge and soil. These regulations are designed to prevent the accumulation of dangerous substances in agricultural soils to such an extent that they pose a hazard to human health and the environment. Regulations are crucial for allowing the safe use of sewage sludge in agriculture and for reducing the risk of environmental hazards (EPA 2024).

2.3.7.2 *Phenolic compounds*

Phenolic compounds (PCs) are a class of organic pollutants of wastewater with one or more hydroxyl groups attached to an aromatic benzene ring. These compounds are found in effluents from petrochemical, pharmaceutical, and paper manufacturing industries. Since PCs are toxic, persistent, and can bioaccumulate, they present enormous environmental and health risks (Rabinovich and Rouff 2021). They can also impact human and wildlife health, as well as disrupt ecosystems. For this reason, environmental protection efforts prioritise the eradication of PCs from wastewater.

HT has been shown to cause chemical changes to sewage sludge, and the concentrations of toxicity markers (phenolic compounds) can be modified. Phenolic compounds are both toxic and persistent in the environment. Several studies have found that HT can reduce overall sewage sludge toxicity by reducing the concentration of these compounds in sewage sludge (Rabinovich and Rouff 2021). Nevertheless, HT's efficiency in removing phenolic compounds depends on various factors such as temperature, pressure, and duration of treatment (Mu'azu *et al.* 2017).

On the other hand, PCs exhibit a broad spectrum of applications in biochemistry and industrial synthesis, thereby serving as highly advantageous materials that add value to various processes. These compounds find utility as antiseptics, dyes, antioxidants, synthetic resins, biocides, paints, and varnishes, among other significant applications (Minatel *et al.* 2017). Hence, if the efficient separation and recovery of these components from the aqueous phase can be achieved, it would yield substantial economic

advantages, simultaneously mitigating the environmental impact of the HT process and reducing the overall cost associated with biofuel production (Chen *et al.* 2015).

2.3.8 Precision, accuracy and analytical equipment

Analytical equipment is indispensable for the comprehensive characterisation of WAS, providing information on its physicochemical properties, elemental composition, and organic content. The resource and energy potential of WAS, particularly when derivatives are being considered from downstream processes such as hydrothermal processing, adsorption, struvite precipitation and AD, depends on an accurate characterisation. Quantification and identification of organic and inorganic constituents are possible based on several advanced analytical techniques, including gas chromatography (Mass Spectrometry (GC-MS); thermal conductivity detector (GC-TCD)), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Fourier Transform Infrared Spectroscopy (FTIR), among others. The energy potential in the sludge is further determined by calorimetric analysis.

Consequently, these measurements depend heavily on rigorous calibration protocols and the maintenance of high-quality equipment (Sun *et al.* 2020a). Spectral calibrations typically manage repeatability and reproducibility; spectra are sometimes compared to certified reference materials to ascertain accuracy. Regular servicing is essential to prevent systemic errors and maintain data integrity. Procedural errors and contamination should be detected and corrected with quality assurance measures, such as analysing blanks, standards, and control samples. Duplicates or triplicates can be performed to get statistical validation.

Errors resulting from operator inconsistencies and sample heterogeneity should also be identified and quantified, as well as systematic errors, such as instrument drift. To refine confidence further, additional advanced methodologies were developed to analyse the precision and accuracy of the measured data through uncertainty propagation analysis (Zhang 2024). WAS's composition is variable, so representative analyses must be obtained by strictly adhering to any sample preparation protocols used (e.g., homogenisation and drying).

Not only do these analytical practices enhance the reliability of WAS characterisation, but they also improve the predictive accuracy of downstream processes. An example of an application of this work is modelling the biodegradability and nutrient recovery potential of sludge based on data analysis from TOC and High-Performance Liquid Chromatography (HPLC). The elemental balance, including phosphorus, nitrogen, and trace metals, must be developed to assess suitability for struvite precipitation and potential inhibitory effects on hydrothermal treatment.

2.4 Effect of operating conditions on the HT of sewage sludge

HT effectively enhances sludge biodegradability by breaking down complex organic polymers into simpler substances, improving microbial metabolism during subsequent processes such as AD, as shown in Figure 2.6. The efficiency of this transformation is influenced by key operating conditions, notably temperature and reaction time, which require optimisation to maximise nutrient recovery and biogas production.

Struvite precipitation, a notable outcome of HT, is influenced by parameters such as pH, molar ratios of magnesium to phosphorus, and the presence of competing ions like calcium, which can form alternative precipitates with phosphorus (Enyemadze *et al.* 2021). These factors are optimised effectively to enhance phosphorus recovery and the quality of the recovered products.

At elevated hydrothermal conditions, chemical reactions such as decarboxylation become prominent, facilitating the release of volatile organic acids and gases, including carbon dioxide (Ischia and Fiori 2021). They are essential reactions for the decomposition of organic matter and the solubilisation of nutrients.

Additionally, product composition depends on HT operational parameters, which necessitate fine control to achieve the desired outcomes. For instance, HT enhances the solubilisation of organic matter, but proteins in sludge show little decomposition under specific conditions (Xu *et al.* 2018a). Process efficiency is influenced by other variables, such as feedstock composition, solid content, and catalyst, which also play key roles (Zhang and Chen 2018).

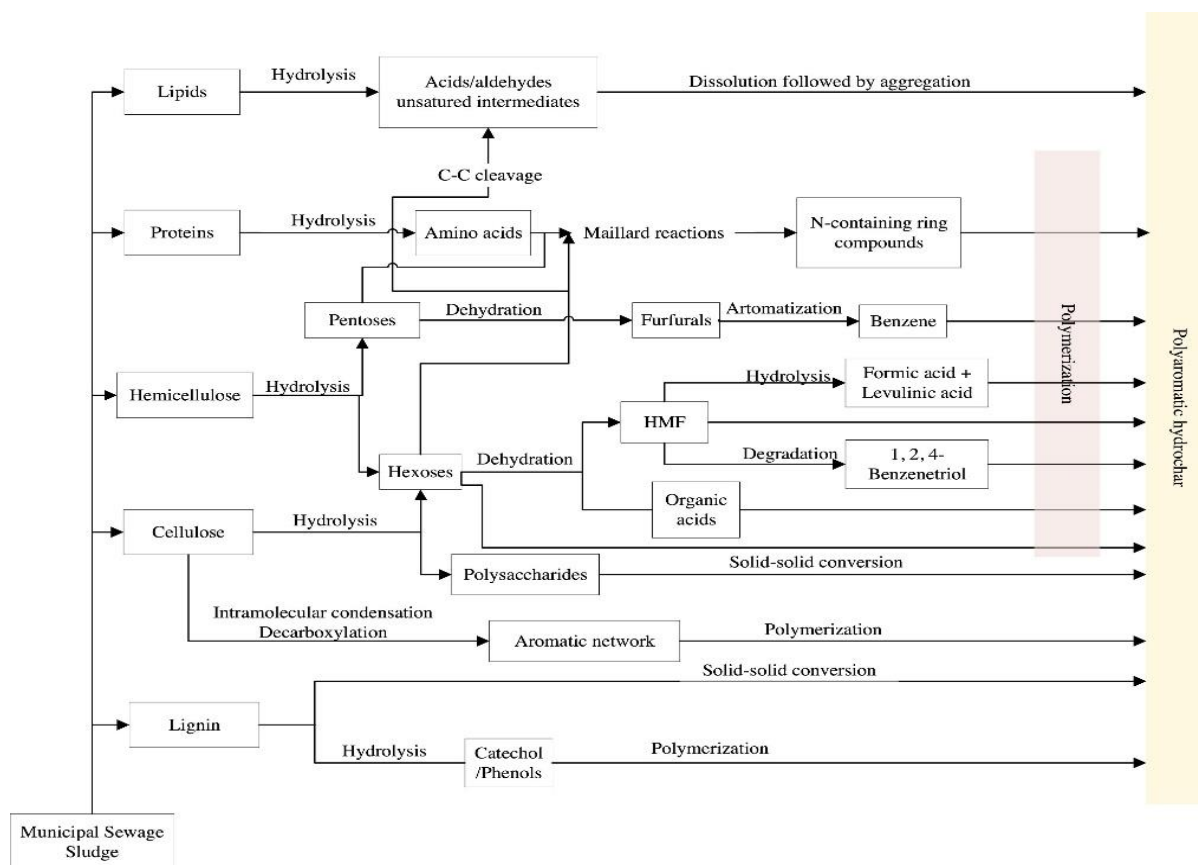


Figure 2.6 Overview of reaction mechanisms of the HT of sewage sludge

Source: (Gómez *et al.* 2020)

2.4.1 Importance of various operating conditions

The efficiency of the HT process is especially affected by operating conditions, especially in terms of enhancing the solubility of organic matter in WAS. HT processes help to dissociate complex organic compounds into simpler, soluble molecules. This degradation significantly increases SCOD and BOD levels, and a higher BOD/COD ratio is particularly interesting, as it indicates improved biodegradability. By enhancing organic matter solubilisation, biogas production could be improved from readily biodegradable substrates (Wu and Vaneckhaute 2022).

Identifying key parameters such as temperature, pressure, and reaction time to optimise the best conversion of complex organics into biodegradable forms and minimise the formation of refractory compounds that can limit treatment efficiency (Zaccariello *et al.* 2022). Additionally, optimal HT conditions also enhance the release of volatile organic

acids and other compounds crucial for energy recovery. Furthermore, these operating conditions interactively influence the efficiency of nutrient recovery (Xu *et al.* 2018b).

In another study, Dou *et al.* (2024) investigated the application of deep eutectic solvents (DES) in enhancing phosphorus recovery from sewage sludge during hydrothermal carbonisation. Their findings demonstrated that the DES effectively disrupted the sludge floc structure, promoting the conversion of polyphosphate (Poly-P) to pyrophosphate (Pyro-P) and orthophosphate (Ortho-P). The addition of DES increased the proportion of Ortho-P/Pyro-P from 12.9% to 19%, indicating improved phosphorus release. Moreover, the total organic content increased slightly to 10,653 mg/L at 180°C with the addition of DES, suggesting that the lactic acid used in the DES formulation reacted with organic matter during HTC, thereby altering the physicochemical characteristics of the resulting hydrochars. This study highlights a promising and sustainable strategy for enhancing phosphorus solubilisation and valorisation from sewage sludge.

2.4.1.1 Temperature

The impact of temperature is of great importance in HT, as it is a critical variable due to its effect on reaction kinetics, product selectivity, and process efficiency (Devnath *et al.* 2024). Indeed, elevated temperatures increase reaction rates, solubilise compounds, and make desirable transformations. However, optimal temperature ranges are essential to maximise beneficial reactions while minimising undesirable by-products (Kakar, Tadesse and Elbeshbishy 2022).

Results from another study suggest that temperature has a greater impact on the degree of disintegration of sewage sludge (DD) than reaction time. As shown in Figure 2.7, Park *et al.* (2019a) exhibited that DD increased function with temperature and reaction time, reaching 32.3% of maximum DD at 300°C and 1 h. Kim, Lee and Park (2015) showed that exposure to temperatures between 150° and 270 °C elevated DD by over 30%. Both deoxygenation and dehydration processes are driven by temperature, resulting in an increase in carbon content and a decrease in hydrogen and oxygen levels (Zhang *et al.* 2015a; Zhang *et al.* 2019a; Śliz and Wilk 2020).

Biomass decomposition at high temperatures produces free radicals and volatile compounds, which lowers hydrochar yield. In a study by Cuevas, Martínez Cartas and Sánchez (2019), it was observed that short-time HT of olive endocarps at high temperatures decreased hydrochar yield and promoted carbonyl group loss and formation of CO₂ and formic acid and facilitated desirable transformations. Similarly, Keiller *et al.* (2019) observed significant decomposition of cellulose, hemicellulose, and lignin in saltbush at temperatures up to 260°C, enhancing the breakdown of carbohydrate-rich feedstocks.

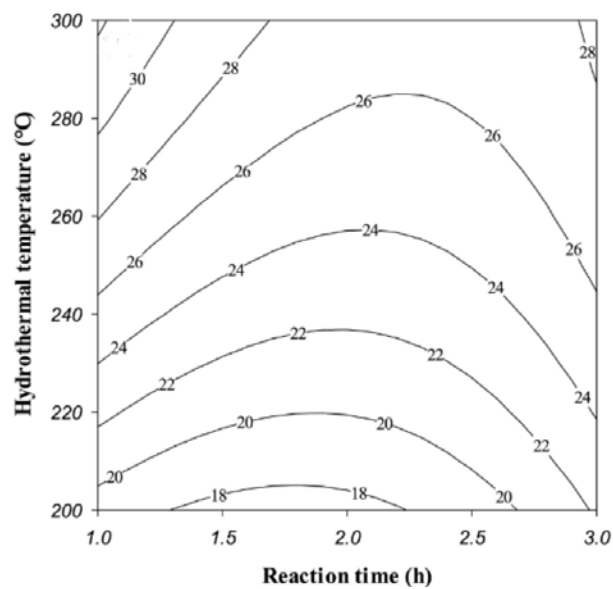


Figure 2.7 Response surface plots for disintegration degree (DD)

Source: (Park *et al.* 2019a)

In the context of phosphorus recovery, HT promotes the solubilisation of organic phosphorus (OP) into inorganic forms, thereby improving phosphorus bioavailability and facilitating the transformation from non-apatite inorganic phosphorus (NAIP) to stable apatite phosphorus (AP). However, the increased stability of AP may limit its immediate bioavailability, necessitating further treatment for effective recovery (Tangredi *et al.* 2023).

2.4.1.2 pH

pH is a critical parameter influencing the efficiency and outcomes of HT of sewage sludge. It impacts the solubilisation of organic matter, nutrient release, and pathogen destruction, while also affecting the removal of heavy metals (Kossńska *et al.* 2023). An optimised

pH range facilitates hydrolysis and acidogenesis, enhancing dewaterability and reducing sludge volume. However, extreme pH values can inhibit microbial activity, thereby reducing the degradation efficiency of organic matter (Gong *et al.* 2021).

Studies reveal that feedstock properties, operating conditions, and degradation mechanisms influence pH variations during HT. Villamil *et al.* (2018) observed an acidic pH (5.1 ± 0.1) in the HT liquid fractions, whereas for alkaline and neutral conditions, the pH decreased after pretreatment, and the drop in pH was greater for alkaline conditions (from 10.1 to 8.7) compared to neutral conditions (from 7.6 to 7.1). During alkali treatment, the biomass itself consumes some of the alkali (Nazari *et al.* 2018), which results in pH reduction. It could also be due to the formation of acidic compounds by the degradation of macromolecules. Conversely, a slightly elevated pH in acidic treatments is associated with protein desorption or loss of volatile acidic compounds.

The pH changes dynamically during HT due to the breakdown of sewage sludge into VFAs, ammonium nitrogen, and amino acids (Aragón-Briceño, Ross and Camargo-Valero 2017b). Temperatures above 220°C often increase pH levels due to protein degradation, leading to the formation of ammonium (Devnath *et al.* 2024). Catalysts, acids, or bases can modulate pH, enhancing ionic strength and promoting reactions that improve solubilisation and decomposition of recalcitrant compounds. Lowering pH, such as with H₂SO₄ addition, mimics higher temperatures by promoting hydrolysis and depolymerisation, facilitating the release of bioavailable substrates, as also observed by Wang *et al.* (2018d); Huezo, Vasco-Correa and Shah (2021). However, prolonged low pH conditions may encourage polymerisation, forming secondary chars with improved energy density (Volpe *et al.* 2023). In contrast, catalysts that increase pH can accelerate hydrolysis, favouring biocrude production over hydrochar yields (Nizamuddin *et al.* 2017).

Nutrient and heavy metal solubility is also regulated by pH. In the phytochemical reaction of heavy metals, they tend to precipitate at high pH as hydroxides or sulphides, while at lower pH, heavy metals are released and removed (Lin *et al.* 2023). This is a key element for effective nutrient recovery, heavy metal management, and process efficiency, as it balances pH, making it a cornerstone of optimising HT for sewage sludge valorisation.

2.4.1.3 Pressure

HT of sewage sludge is a pressure-critical operation, as process efficiency and product quality depend heavily on operating pressure. Optimisation of this parameter leads to increased organic matter solubilisation, faster reaction kinetics, and improved overall conversion rates (Munir *et al.* 2018). Sludge decomposition and volume reduction are facilitated by better organic decomposition when water molecules become more soluble and mobile due to elevated pressure (Pola *et al.* 2021b).

Until now, most studies of HT have been conducted under autogenous pressure, correlating its effects with temperature changes associated with rising pressure and rising temperature (Khandelwal *et al.* 2024). Zhu *et al.* (2011) found that increasing pressure from 20.5 to 23.5 MPa at 400°C altered phosphorus (P) speciation during hydrothermal gasification, reducing the organic phosphorus (OP) content in the solid product but increasing soluble P in the liquid phase. These results suggest that higher pressure benefits the solubility of important metal phosphate species.

Thermodynamic equilibrium is also influenced by pressure, which increases the density of the reaction medium, promotes the infiltration of organic solids, and decreases the decomposition rate. Hii *et al.* (2014) showed that higher pressure results in higher solubility of oxidising agents such as oxygen. Nevertheless, excessive pressure can lead to increased energy consumption and accelerated equipment corrosion and erosion (Nizamuddin *et al.* 2017). However, balancing the advantages of the increased pressure with its drawbacks is essential to sustain safe and high-pressure operations.

To optimise HT for both nutrient recovery and biogas production as well as system reliability, careful integration of pressure with other parameters (temperature, residence time and pH) is required. Future research should focus on the interplay between pressure and other variables to improve process efficiency and scalability.

2.4.1.4 Reaction time

Reaction time is a critical factor influencing product yields, quality, and nutrient migration during HT. Prolonged reaction times enable chemical and physical processes to reach equilibrium, facilitating the extensive decomposition of organic matter (Tangredi *et al.*

2023). However, temperature and reaction time interact significantly, necessitating their optimisation to facilitate hydrolysis and polymerisation reactions effectively (Wang *et al.* 2018d).

A solid recovery yield is more complex to predict based on reaction time than on temperature (Funke and Ziegler 2010). Many researchers utilise the severity factor $f(T, t)$, derived from the Ruyter coalification model, to quantify the combined effects of time and temperature, as shown in Equation 2.5. The severity function integrates the time-temperature equivalence principle, positing that comparable product characteristics can result from shorter durations at higher temperatures or longer durations at lower temperatures (Yahav Spitzer, Mau and Gross 2018; Wang, Chang and Liu 2019; Liu *et al.* 2021a).

$$f(T, t) = 50t^{0.2}e^{-\frac{3500}{T}} \quad 2.5$$

Where t is the reaction time (s) and T is the temperature (K).

Studies indicate dehydration occurs at approximately 140°C for 240 min, whereas decarboxylation processes become prominent between 160°C and 200°C over the same duration, leading to hydrochar with reduced O/C and H/C ratios (Danso-Boateng *et al.* 2015b). Extended reaction times enhance hydrochar porosity, hydrophobicity, and energy densification through processes such as HMF deposition in the pores from sludge-derived sugars (He, Giannis and Wang 2013). However, excessively long durations may increase ash content and reduce hydrochar's calorific value, making it less suitable for combustion (Peng *et al.* 2016).

Reaction time also affects hydrochar surface functionality and volatile matter content. Short durations produce rapid yields but may compromise material properties. Longer times foster the development of polyaromatic structures, enhancing stability but potentially increasing ash content (Khan, Saeed and Khan 2019). Consequently, reaction time should align with treatment goals, striking a balance between product quality, energy efficiency, and operational costs.

Although extended durations improve organic matter solubilisation and sludge volume reduction, they incur higher energy costs and operational challenges, including fouling risks (Fan, Hornung and Dahmen 2022). Careful selection of reaction time, alongside other parameters, ensures effective HT outcomes tailored to the intended applications (Czerwińska *et al.* 2024; Hidalgo *et al.* 2024).

2.4.1.5 Sludge concentration

Sludge concentration has a significant impact on the efficiency and performance of HT. While higher concentrations can improve process efficiency, they demand greater energy and more robust equipment investments. The feedstock composition, including the proportions of cellulose, hemicellulose, and lignin, also plays a crucial role in hydrothermal processing. These structural components hydrolyse at different temperatures: cellulose above 200 °C, hemicellulose at 180 °C, and lignin around 210 °C, leading to diverse decomposition behaviours (Okolie *et al.* 2020).

Oils are primarily yielded from cellulose and hemicellulose, whereas char is produced from lignin, and this indicates the structural influence in the HT's products (Chen *et al.* 2020b; Li *et al.* 2023). This motivates optimising HT-sludge concentration and understanding these compositional characteristics to improve HT efficiency and output for specific resource recovery goals.

2.4.1.6 Catalysts

A catalyst is an indispensable feature in the process and effectiveness of HT processes, as it accelerates reaction kinetics and decreases the activation energy. These are both homogeneous and heterogeneous catalysts, which are typically metals or metal oxides, ultimately enhancing the overall process (Djandja *et al.* 2021). Indeed, the HT process is autocatalytic, and other organic acids such as levulinic, lactic, acetic, and formic acids can act as promoters to generate hydrochar while lowering the pH value.

While under HT, the reactivity of the sludge components differs. For instance, lignin reacts more readily in high-pH conditions than cellulose and hemicellulose do during the delignification process. With optimised reaction time and temperature, salts or acids as catalysts improve the formation of hydrochar (Wang *et al.* 2018c). For instance, sodium

salts have been determined to enhance the HT process greatly by cutting the time required for the formation of carbon colloids to 1.4 h from 2.5 h (Ming *et al.* 2013). However, the type or choice of catalyst used in the reaction should be carefully selected to prevent reactor corrosion.

Research shows that promoters include alumina, silica, and zeolite to enhance the sewage sludge HT. Among these, alumina is particularly efficient in decomposing organic matter and boosting biogas yields (Wang *et al.* 2018e). The proper selection and application of catalysts can thus optimise HT, making it a more sustainable and effective method for sludge treatment.

2.4.2 Various operating conditions and associated products

Hydrothermal processes offer a novel approach to converting the organic carbon in sludge into valuable combustion products, albeit their adoption is relatively recent. While some full-scale hydrothermal carbonisation (HTC) facilities based on HTCycle and TerraNova® technologies exist, HTP applications for complete sludge valorisation remain scarce. In contrast, incineration and HT for AD have been widely adopted since the mid-1990s (Reißmann, Thrän and Bezama 2018).

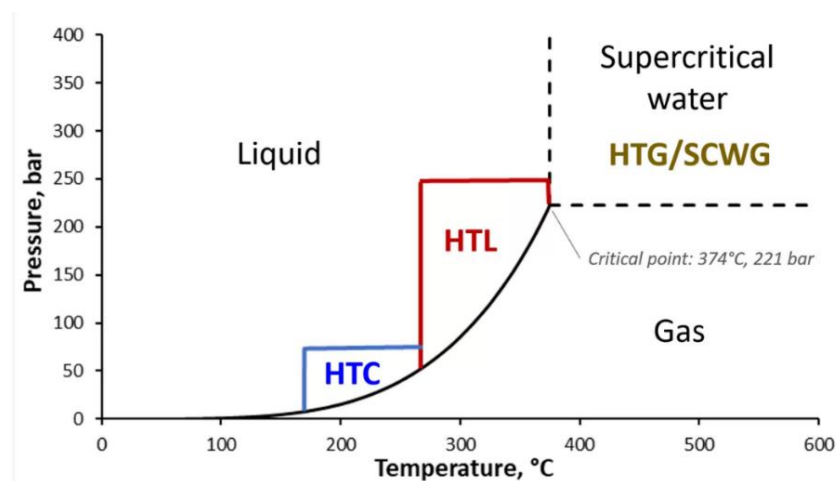


Figure 2.8 Pressure–temperature phase diagram of water illustrating operational regimes of hydrothermal processes.

Source: (Reißmann, Thrän and Bezama 2018)

HT processes are classified based on their operating parameters into three categories: HTC (Shi *et al.*, 2019), hydrothermal liquefaction (HTL) (Zhang and Chen, 2018), and hydrothermal gasification (HTG) (Hu *et al.* 2020b). HTC predominantly produces solids, HTL generates liquid products, and HTG favours gaseous outputs, as illustrated in Figure 2.8. Each method exploits specific temperature, pressure, and reaction durations tailored to optimise desired outputs. This diversity underscores the necessity for operational optimisation, balancing energy recovery, product purity, and environmental impact. By understanding and refining these parameters, HTPs can enhance the sustainability and economic feasibility of wastewater management systems.

HTC transforms sludge into carbon-rich hydrochar, operating at temperatures of 180-300°C and pressures of 10-88 bar to maintain water in the liquid phase (Becker *et al.* 2019). Reaction times range from 0.1 to 4 h, and the severity factor, as shown in Equation 2.2, is used to optimise conditions. Higher severity favours increased hydrochar carbon content and structural changes. HTC also facilitates phosphorus recovery by acid-induced migration to the aqueous phase, enabling precipitation. Technologies like Glatt's PHOS4green convert hydrochar into phosphate fertilisers, while HTC liquor contains carbon, nutrients, and organic acids (Villamil *et al.* 2018).

HTL operates at 200-400°C and >40 bar to produce bio-oil, a potential diesel additive. Fast reactions, including hydrolysis, dehydration, and decarboxylation of organic compounds, underpin its chemistry. HTL has been extensively studied for microalgae due to its potential as a cleaner biomass feedstock (Xue *et al.* 2015; Fan, Hornung and Dahmen 2022).

HTG occurs at >400°C, producing syngas (H_2 , CO). Catalysts enhance reactions but may cause scaling or corrosion. High temperatures and residence time significantly influence gas yields (Shahbeik *et al.* 2022). Overall, hydrothermal processes improve VS breakdown, reduce sludge mass, and enhance biomolecule bioavailability

2.4.3 Various operating conditions facilitate other reactions.

2.4.3.1 Maillard reactions

The Maillard reaction, occurring under high-temperature and high-pressure conditions (e.g., 180-200 °C), produces chemical compounds such as furans, pyrazines, pyrroles, aldehydes, and pyridines. These compounds negatively affect methane production during AD by inhibiting microbial activity (Danso-Boateng *et al.* 2015b). Severe Maillard reactions between carbohydrates and proteins generate these inhibitory intermediates, thereby reducing methane yield (Dumitraşcu, Borda and Aprodu 2023; Zhou *et al.* 2024).

2.4.3.2 Formation of toxic compounds

HT produces phenolic and aromatic compounds, particularly in the liquid phase, which are toxic to anaerobic bacteria. These phenolic compounds inhibit microbial activity, reducing methane yield and overall AD efficiency (Usman *et al.* 2023; Zhou *et al.* 2024). Effective mitigation strategies, such as optimised reaction parameters, are essential to minimise the formation of these toxic intermediates.

2.4.3.3 Colour changes in sludge post-HT

As illustrated in Figure 2.9, the sludge darkens progressively with increased pretreatment temperatures and prolonged reaction times, indicating more severe thermal conditions. For instance, after 5 min of processing at 145 °C, the colour of the sludge was minimal. However, the colour intensity, measured in PtCo units, rose from 1710±14 at 145 °C to 2525±7, 4235±21, and 5795±7 at 160, 175, and 190 °C, respectively.

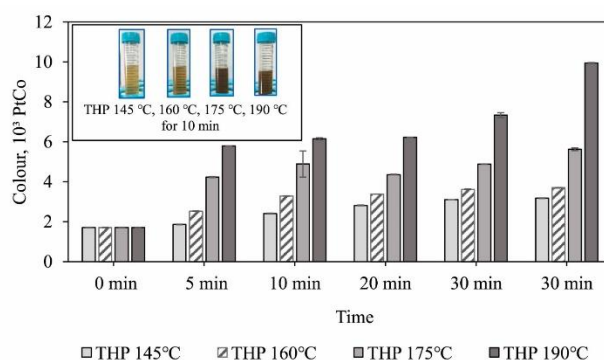


Figure 2.9 Changes in sewage sludge colour after HT

Source: (Ngo *et al.* 2023)

A significant darkening was observed when the treatment was extended to 30 min at 190 °C, with colour intensity reaching 9945 ± 21 PtCo. This phenomenon aligns with findings by Langone and Basso (2020), who reported a threefold increase in sludge colour intensity when the treatment temperature was raised from 145 to 160 °C.

The darkening is attributed to Maillard reactions, which commence above 150 °C (Dumitraşcu, Borda and Aprodu 2023; Zhou *et al.* 2024). These reactions produce melanoidins, which are complex, recalcitrant compounds responsible for the browning effect. While melanoidins enhance sludge solubilisation, as seen at 190 °C ($45 \pm 0.8\%$ solubilisation degree), they adversely affect AD efficiency, yielding only 315 ± 11 mL biogas/g VS_{added}, compared to 387 ± 9 mL and 389 ± 6 mL biogas/g VS_{added} at 145 °C for 20 and 30 min, respectively.

2.5 Adsorption of toxins using biochar

Biochar, derived from the pyrolysis of biomass such as sugarcane bagasse (SCB), has emerged as a low-cost and effective adsorbent for removing heavy metals, including zinc (Zn) and copper (Cu), from contaminated water and soil (Ambaye *et al.* 2021). In KwaZulu-Natal, where sugarcane is produced on a massive scale, sugarcane bagasse, often treated as waste (Mkhwanazi, Isa and Vallabh 2023), can be repurposed for adsorption applications, leveraging its abundant cellulose, pentosan, and lignin content. These components provide functional groups, such as carboxylic, carbonyl, amine, and hydroxyl groups, enabling SCB to bind and remove metal ions from aqueous solutions effectively (Świechowski *et al.* 2022).

Various pyrolytic conditions affect the efficiency of biochar for adsorption purposes in various ways. When biochar is subjected to pyrolysis at a temperature range of between 350-650 °C, the enhanced stability and surface properties enable interaction with species of interest, leading to improved adsorption. Analysis using ATR-FTIR tools and SEM images reveals that the micropore surface area and the presence of carboxylic or lactonic functional groups are directly associated with adsorption performance. For instance,

phenol adsorption is enhanced with larger functional group densities, validating biochar's potential for removing organic and inorganic pollutants (Tan *et al.* 2018).

Compared to other adsorbents, activated carbon (AC) has a superior adsorption capacity due to its large available surface area and richness in functional groups, such as hydroxyl and carboxylic acid groups. However, due to its high production cost, interest in biochar has increased. Scholars presented data on how SCB can complement AC in the adsorption of HM, particularly in terms of adsorption capacity, while being more cost-effective (Wu *et al.* 2020).

Besides the toxin removal capability, both the biochar and hydrochar improve the AD processes. Fagbohunge *et al.* (2017) discovered that some effects of biochar include minimising inhibitors such as ammonium, enhancing buffering capacity and nutrient retention, and increasing biogas production. Hydrochar, however, requires caution due to its high content of sulphur and heavy metals, and should therefore only be used in large-scale power plants equipped with reliable fume extraction systems (Gerner *et al.* 2021).

2.5.1 Hydrothermal processing for metal removal from organic waste

Heavy metals in organic waste pose significant risks to the environment, as well as to human and animal health, when disposed of untreated. Hydrothermal processing provides an effective solution by concentrating heavy metals into a small volume of solid residue, simplifying their subsequent treatment compared to their dispersed state in raw waste. Recent advancements in applying hydrothermal processing for heavy metal removal demonstrate its potential, as summarised in Table 2.1.

Table 2.1 Hydrothermal treatment of sewage sludge in various cases

Process type	Treated material	Processing condition			Metals	Reference
		Temperature (°C)	Pressure (MPa)	Time (min)		
HT	Activated sludge	170	0.7	30	Cd and Cu	(Laurent <i>et al.</i> 2011)
	Sewage sludge	110 - 130	7 - 9	30	Cr, Cu, Ni, Pb and Zn	(Yabalak and Gizir 2013)
	Excess sludge	210	-	30	Cu and Zn	(Wu <i>et al.</i> 2016)

WO	Sewage sludge	200 - 240	4 - 4.1	60	Al, Cu, Fe, and Zn	(Zhang <i>et al.</i> 2017b)
HTC	Biomass	260	1 - 5	30	Heavy metals	(Reza <i>et al.</i> 2013)
	Activated sludge	170 - 280	-	60	Cd, Cr, Cu, Ni, and Zn	(Shi <i>et al.</i> 2013)
HTL	Biomass	300	10	20	Pb	(Liu and Zhang 2009)
	Sedum	370	22	10	Cu, Pb, Zn	(Yang 2010)
	Sewage sludge	280 - 360	10	20	Pb, Zn, Cu and Ni	(Leng <i>et al.</i> 2014)

*Where HT represents hydrothermal treatment, WO is wet oxidation, HTC is hydrothermal carbonisation, and HTL is hydrothermal liquefaction.

It is noteworthy that limited knowledge exists regarding the behaviour of metals during hydrothermal processing, particularly in the WO process. Literature provides scarce insights into the effects of HT on heavy metals. However, studies such as those conducted by Wu *et al.* (2016) have observed reductions in heavy metal concentrations following hydrothermal processing. These findings underscore the need for further research to elucidate the mechanisms governing metal transformations under these conditions.

2.5.2 Nature of toxins

2.5.2.1 Phenolics

Phenolic compounds (PC), comprising an aromatic ring attached to hydroxyl groups, are prevalent in plants and microorganisms and are synthesised industrially for applications in drugs, polymers, and dyes (Friend 2016). Phenol, the simplest structure, serves as the foundation for all PCs, with classifications ranging from simple monomers to complex polymers such as lignans, tannins, and flavanols (Figure 2.10).

These compounds are significant pollutants in industrial wastewater due to their high toxicity and persistence. Regulatory frameworks require their effective use to safeguard the environment and people's health (Thang *et al.* 2019).

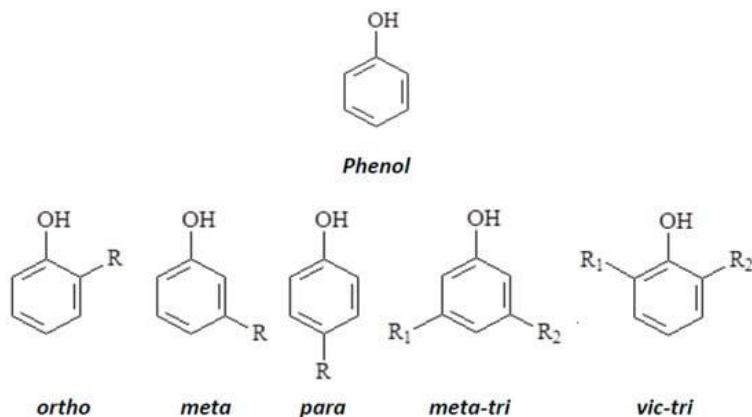


Figure 2.10 Structure and nomenclature for phenol and substitution patterns of phenolic compounds

Source: (Mu'azu *et al.* 2017).

Phenolic compounds react with soil nitrates and chlorine, producing other toxicants, including chlorophenols and nitrophenols, that have odour and toxicity even at low concentrations. To mitigate these effects, many states and nations have established a maximum phenol concentration in wastewater of 1 ppm or less (Zdarta *et al.* 2022). Phenol at high concentrations has toxic effects; it may cause injuries in the liver, kidney, and nervous system (Mehrez *et al.* 2024).

Several techniques have been employed in the treatment of phenolics in wastewater, including adsorption, reverse osmosis, electro-Fenton, and coagulation-flotation. Of these, adsorption offers the most benefits due to its simplicity and operational convenience (Khelfaoui and Chaouch 2023). The adsorption of phenolic compounds using agricultural waste and sewage sludge-based activated carbon (SBAC) is a cost-effective and environmentally friendly method. From this perspective, recent studies have presented chemically activated SBAC as more effective, and they call for continued enhancements to the formulation to improve functional characteristics and feasibility for large-scale production (Mu'azu *et al.* 2017).

The nature of the interaction of PCs with SBAC depends on the molecular structure and substituents of the adsorbate. Substituents like nitro- and chloro-groups produce stronger interactions with SBAC surfaces and, therefore, improve the adsorption efficiency. The sequence of adsorption capacity follows the trend: 4-nitrophenol > 2-chlorophenol >

phenol, based on molecular size and substituent properties (Kong *et al.* 2014). Additionally, the equilibrium time depends on the molecular weight of the adsorbate and, therefore, requires adsorption enhancement approaches (Masomi *et al.* 2014).

However, when considering humic acid in wastewater, the ability to recover phosphorus is reduced because humic acid forms complexes with magnesium and ammonium ions, thereby disrupting struvite crystallisation and altering crystal morphology. These interactions illustrate the complexities of managing multi-pollutant wastewater systems, a reality that has been described by Zhang *et al.* (2015c).

Despite their toxic nature, PCs also present opportunities for recovery. Advances in HT enhance the solubilisation of PCs, facilitating their removal and valorisation. The treatment process reduces sludge volume and extracts bioavailable compounds, contributing to sustainable wastewater management. The integration of adsorption and HT processes supports the dual goals of pollutant mitigation and resource recovery, aligning with circular economy principles (Minatel *et al.* 2017).

2.5.2.2 Heavy metals

WAS contains heavy metals such as Cd, Pb, As and Hg. Due to their toxicity, persistence, and bioaccumulative nature, their presence poses significant environmental and health risks to humans. In comparison, unlike organic pollutants, heavy metals cannot be biodegraded, resulting in contamination of soil, water, and air if they are not correctly handled (Li *et al.* 2020a). The recovery and treatment of heavy metals from sludges are therefore important to sustainable waste management.

The sources of heavy metals in wastewater include industrial discharges, agricultural runoff, and household waste. The heavy metals present in municipal wastewater originate from industries such as the mining, electroplating, and manufacturing sectors (Peng *et al.* 2018a). If WAS is used on heavily polluted agricultural land, these heavy metals may leach into groundwater or crops, which then enter the food chain and pose risks to human and animal health. For example, cadmium exposure is known to cause kidney damage and bone demineralisation, which leads to neurological development in children (He *et al.* 2014).

Treatment of heavy metals in WAS through HT is a promising environmental approach. HT operates under subcritical water conditions and may modify the chemical speciation and mobility of heavy metals. It has been studied that the bioavailability of heavy metals can be significantly reduced by HT at an optimum temperature through the formation of stable forms, such as insoluble sulphide and oxide (Park *et al.* 2019b). Nevertheless, the efficiency of immobilisation is determined by the chemical composition of the sludge, the process parameters and the type of metal of interest. For example, arsenic and chromium may volatilize under certain conditions, and gas-cleaning technology will be used to capture and neutralise the volatilized elements (Zhou *et al.* 2024).

Heavy metal adsorption using biochar derived from HT or pyrolysis is an effective post-treatment strategy. The positive attraction to heavy metals and the ability to remove them from wastewater sludge indicate that biochar has a high surface area and functional groups that are present (Wu *et al.* 2021). Magnetic biochar modified with iron oxide exhibits high adsorption performance for lead and cadmium metal ions (Takaya *et al.* 2016). Specifically, a high level of adsorption efficiencies can be realised by optimising the biochar production conditions, such as pyrolysis temperature and feedstock type.

2.5.3 Adsorbents

Biochar is known to have extensive use in removing contaminants from wastewater and soil due to its large specific surface area and compatible surface chemistry, which exhibit a strong affinity for metal ions and various contaminants (Zhang *et al.* 2018). The adsorption capacity has a positive relationship with specific surface area and aromaticity; moreover, biochar used in another study exhibits better performance at higher pyrolysis temperatures of more than 450 °C (Tan *et al.* 2015).

The adsorption process involves both electrostatic interactions and ion exchange, as well as surface complexation and precipitation with specific functional groups, such as oxygen-containing groups like carboxylic acid (-COOH) and hydroxyl (-OH) groups (Ambaye *et al.* 2021). For instance, sludge-derived biochar demonstrated a strong ability for lead (Pb) adsorption through interactions, including surface adsorption and inner-

sphere complexation. Similar mechanisms have also been reported for the adsorption of mercury (Hg) and cadmium (Cd) (Sun *et al.* 2014).

2.5.4 Biochar production techniques and mechanisms

Biochar can be described as a carbon-rich solid material obtained from biomass (e.g., wood, manure, leaves) through pyrolysis at temperatures below 900°C in an environment with limited oxygen (Godlewska *et al.* 2017). Some conventional processes include pyrolysis, gasification and HTC (Ng *et al.* 2017). Feedstock, temperature and residence time affect the yield and composition of bio-oil, biochar and syngas, as illustrated in Table 2.2.

Table 2.2 Thermochemical process conditions and product yields

Process	Temperature (°C)	Residence time	Biochar yield (%)	Bio-oil yield (%)	Syngas yield (%)
Fast Pyrolysis	500 - 1000	< 2 s	12	75	13
Gasification	750 - 900	10–20s	10	5	85
Torrefaction	~290	10–60 min	80	0	20
Hydrothermal Carbonisation	180 - 300	1–16 h	50-80	5-20	2 -5
Slow Pyrolysis	300 - 700	Hours-Days	35	30	35

Source: (Takaya *et al.* 2016; Armah *et al.* 2022)

2.5.5 Physical and chemical activation of biochar

Research to improve the ability of biochar to adsorb has been intensified. Nevertheless, some limitations are still observed, especially in the physical separation and re-utilisation of small particle-sized biochar with low bulk density after pollutant adsorption. By synthesising magnetic biochar with magnetic mediums like Fe, Fe₂O₃ or Fe₃O₄, or through pyrolysis activation or chemical co-precipitation, this problem can be solved effectively. It is a promising material for wastewater treatment applications, possessing high pollutant adsorption performance and the additional advantage that external magnets can be used to separate the present material (Sharma *et al.* 2022).

Most chemical reactions involved in the preparation of magnetic biochar tend to involve co-precipitation mechanisms, as depicted in Equations 2.6-2-9, and the formation of Fe_3O_4 and Fe_2O_3 improves the functionality of the resultant product.



When metal-containing solutions come into contact with biochar materials, enhanced adsorption characteristics are achieved in the composites. For instance, hydrophilic biochar, combined with zero-valent iron nanoparticles, has been shown to exhibit a synergistic action that effectively removes organic and inorganic contaminants in environmental remediation processes (Shaheen *et al.* 2022).

2.5.6 Magnetic biochar

Magnetic biochar has garnered considerable research interest due to its high adsorption capacity and can be easily magnetically separated, making it a promising candidate for various applications, including wastewater treatment and pollutant elimination. This material is prepared by embedding an iron compound into biochar, which exhibits specific characteristics, including a large surface area, albeit less extensive than that of the raw biochar, as well as magnetism and high adsorption capacity for pollutants. Different production techniques have also been employed, including the treatment of chestnut shell biochar with Fe ions subjected to microwave heating at a temperature of 450 °C, as well as the impregnation of biochar with iron salts such as Fe_2O_3 and $FeCl_3$ in controlled pyrolysis conditions (Son *et al.* 2018; Li *et al.* 2020b). Such methods produce magnetic biochar with unique morphological and functional properties that enhance the sorption of pollutants.

Magnetic biochar has higher adsorptive capacities for the target pollutants, including As (V), Pb^{2+} , Cu^{2+} , and Zn^{2+} , with the potential of adsorbing 3-4-fold the biochar-designed capacity. For instance, it has been demonstrated that this process can suitably and at a

low cost eliminate arsenic, which has been the subject of numerous experiments with detrimental effects on health and the environment (Son *et al.* 2018). The practical application of this adsorbent is attributed to the presence of oxygen-containing functional groups, -COOH and -OH, which serve as binding sites for metal ions.

However, a high level of iron loading may limit adsorption efficiency due to pore plugging in the biochar matrix. Fe doping is efficacious in improving magnetic features within the range of 0.025-0.05 mol/L, while adsorption is not affected by it (Son *et al.* 2018). Other applications include the selective adsorption of heavy metals, whereby a magnetic biochar derived from kelp and hijikia shows a high rate of copper removal while reducing the uptake of zinc and cadmium.

The concentration of raw materials to iron compounds during the synthesis of magnetic biochar is a critical determinant of adsorption efficiency and carbon yield. The research indicates that an impregnation ratio of 0.5 yields the maximum pollutant adsorption and biochar production levels (Zakaria, Jamalluddin and Abu Bakar 2021). Apart from this ratio, adsorption reduces for higher biochar concentrations due to interference with direct contact between iron and pollutants. Because the amount of biochar is inversely proportional to the removal efficiency of pentachlorophenol (PCP) in wastewater, the influence of the ratio of ZVI-to-biochar in ZVI-magnetic biochar composites (ZVI-MBC) was studied (Devi and Saroha 2014). Increasing the ZVI-to-biochar ratio from 1:0.5 to 1:2 increased the removal rate of the PCP from 90.1% to 97.45% due to improved ZVI dispersion on the biochar surface. Overloading, however, is known to deplete efficiency since it prevents ZVI particles from moving freely within the biochar matrix.

The studies by Liu *et al.* (2024) highlighted that the pyrolysis temperature is a significant factor that determines the texture and adsorption capacity of magnetic biochar. The adsorption increase influences the porosity and surface area in function of increased temperatures, as illustrated by Congo red dye at 800 °C. High temperatures nonetheless have adverse impacts on the structure and performance of materials. For instance, the removal of arsenic was achieved with better efficiency at 350 °C than at 450 °C, due to enhanced ash formation and electrostatic attraction effects at lower pyrolysis

temperatures. Temperature management is, therefore, crucial to achieving a balance between structural stability and adsorption efficiency.

2.5.7 Antagonistic behaviour of biochar

The adsorption of phosphate ($\text{PO}_4\text{-P}$) onto biochar varies significantly across different wastewaters, with concentrations ranging from less than 14 mg/L to over 15,000 mg/L (Takaya *et al.* 2016). In this study, the initial $\text{PO}_4\text{-P}$ concentration was approximately 400 mg/L. Results demonstrated coefficients of variation below 5% for most samples, except for greenhouse waste, which exhibited higher variability due to heterogeneity.

Interestingly, greenhouse waste, press cake hydrochar, and commercial oak biochar produced at 450°C exhibited $\text{PO}_4\text{-P}$ release. This phenomenon, also observed in biochar processed at low and high temperatures (Zeng *et al.* 2013), was independent of the char's phosphorus content. For example, water extraction tests showed that oak hydrochar and commercial biochar at 450 °C and 650 °C released 1.18 ± 0.04 , 0.554 ± 0.003 , and 1.19 ± 0.03 mg/g $\text{PO}_4\text{-P}$, respectively, while greenhouse waste biochar produced at 400°C and 600 °C released 2.1 ± 0.1 and 3.5 ± 0.2 mg/g $\text{PO}_4\text{-P}$. These findings align with observations that biochar phosphorus may not always be fully extractable by water or concentrated acids (Zhao *et al.* 2023).

Adsorption performance was further investigated by comparing oak and greenhouse waste biochar at varying initial $\text{PO}_4\text{-P}$ concentrations. Adsorption improved with higher initial concentrations, attributed to greater concentration gradients that enhance the filling of reactive sites (Takaya *et al.* 2016). However, as the $\text{PO}_4\text{-P}$ concentration increased, the adsorption efficiency declined, reflecting the limited availability of active sites (Phuong Tran *et al.* 2021). This study observed peak adsorption efficiency of over 70 mg/L $\text{PO}_4\text{-P}$ for most samples.

These findings highlight the complexity of biochar's interaction with $\text{PO}_4\text{-P}$, which is influenced by factors such as initial concentration, pyrolysis conditions, and the type of feedstock. A comprehensive understanding of these dynamics is critical for optimising biochar for phosphorus recovery in wastewater management.

2.5.8 Regeneration, recovery, and disposal of spent adsorbents

2.5.8.1 The significance of regeneration in sustainable adsorption

The key to the adsorption studies is regeneration, as this is the crucible of environmentally responsible stewardship and economic rationality. Recently, scholars have started to consider regeneration not as a technical afterthought but rather as a characteristic indicator of the sustainability profile of an adsorbent. Regeneration can increase the life-cycle of adsorbents by recovering sorbent capacity and reducing the amount of material wasted, as well as lowering the environmental impact of the production of the raw materials (Baskar *et al.* 2022). Also, it is simply the circular economy in action, as the so-called waste is turned into valuable resources. But, as attractive as this ideal is, there are obstacles in the way of effective regeneration. There is a slow, gradual structural degradation or pore collapse of many promising materials after being subjected to repeated cycles, revealing an indirect yet sensitive trade-off between recovery efficiency and material longevity.

2.5.8.2 Re-regeneration methods: evaluating routes and opportunities.

With time, there have been various regeneration approaches such as thermal, chemical, electrochemical and biological processes, each possessing its own advantages and disadvantages. Thermal regeneration is commonly used with activated carbons and biochars and is a technique that uses heating in the range of 300 and 700 °C to volatilise or oxidise contaminants being adsorbed onto the loaded adsorbent. It is fast but it needs a large amount of energy, and there is the risk of secondary pollutants, e.g. dioxins or PAHs (Zhang *et al.* 2019b). A more recent development, microwave heating, has similar desorption in a fraction of the time, but is too costly to be developed in developing regions.

Chemical regeneration, on the contrary, is more flexible. Dilute acids, alkalis, or chelating solutions, including EDTA, can be effective at removing heavy metals or adsorbing anions, and in many cases can regain over 90 % of the adsorption capacity in the first few cycles (Kołodziejńska, Krukowska and Thomas 2017). Nevertheless, the irony is understandable when the chemical treatment of a single waste stream may result in another waste stream in case the eluates are not neutralised or reused. By contrast, the process of electrochemical regeneration does not need any external solvents; a low-

voltage current is used to oxidise adsorbed species, which enables almost full regeneration without destruction of the adsorbent matrix (Shahadat and Isamil 2018). Nevertheless, the challenge of electrode fouling and scale-up is still feasible.

In situ oxidation of organics on contaminated carbon surfaces has been proven to be a promising method using emerging hybrid systems, including advanced oxidation processes (AOPs), which combine Fenton or persulphate reactions (Acevedo-García *et al.* 2020). In the meantime, biological regeneration, which involves the use of microbial consortia to biodegrade contaminants, speaks to the eco-friendly sentiments, but is progressive only in biodegradable organics. Table 2.3 provides a summary of the key methods.

Table 2.3 Comparative summary of key regeneration methods for spent adsorbents

Regeneration Technique	Typical Agents/Conditions	Advantages	Limitations	Key References
Thermal / Microwave	300-700 °C, air or N ₂	Rapid desorption, robust performance	High energy demand; potential pore collapsing	(Falciglia <i>et al.</i> 2018; Zhang <i>et al.</i> 2019b)
Chemical (acid/base/chelator)	0.1M HCl, NaOH, EDTA*	High selectivity, potential for metal recovery	Produces secondary effluents	(Kołodzyńska, Krukowska and Thomas 2017; Gupta <i>et al.</i> 2020)
Electrochemical	Low-voltage oxidation	Low chemical use, minimal adsorbent loss	Electrode degradation, cost	(Shahadat and Isamil 2018)
AOPs*	H ₂ O ₂ /Fe ²⁺ (Fenton), persulphate	Strong organic degradation	Limited for metals; reagent cost	(Acevedo-García <i>et al.</i> 2020)
Biological	Mixed microbial cultures	Sustainable, non-toxic	Slow kinetics, narrow applicability	(Abromaitis <i>et al.</i> 2016)

*EDTA - Ethylenediaminetetraacetic acid, AOPs- Advanced Oxidation Processes

2.5.8.3 *Recovery of adsorbed metals: from contaminant to commodity*

While regeneration focuses on the adsorbent, the recovery of the adsorbed metals offers a second dividend. In principle, every desorption cycle represents not only renewal but also potential resource recovery. Studies have shown that metals such as copper, lead, and zinc can be selectively leached from spent biosorbents using weak acids or chelating agents, and then precipitated or electrodeposited as usable metal salts (You *et al.* 2017; Rusmin *et al.* 2022). Moreover, combining recovery with regeneration can significantly reduce overall process costs while minimising the system's life-cycle impact.

2.5.8.4 *End-of-life disposal and stabilisation*

When regeneration becomes economically or technically unsustainable, safe disposal is the final act in the adsorbent's lifespan. Stabilisation and solidification (S/S) methods immobilise residual metals by embedding them in cementitious or phosphate matrices, thereby preventing leaching under landfill conditions (Ramrakhiani *et al.* 2017). Encapsulation, essentially sealing the sorbent in an inert shell, provides additional assurance against the release of contaminants. Nevertheless, disposal must not be done casually, and thermal incineration can produce energy, although there is a danger of volatilising heavy metals unless the emissions are tightly controlled. The simplest pathway is landfilling, but the standards of leaching, like the TCLP of the US EPA (< 5 mg/L Pb), must be met unconditionally (Baskar *et al.* 2022). Even biochar enriched with certain nutrients can be used again as a soil amendment, although the content of metals must not exceed agricultural safety levels (Meena *et al.* 2024), which proves that even “waste” can be used in a new role in the right setting.

2.5.8.5 *Economic and Environmental Dimensions*

Operationally, the costs of regeneration are mainly influenced by the consumption of energy and reagents. The thermal methods need about 4-8 kWh/kg adsorbent, where electrochemical and chemical methods need between 1-3 kWh/kg adsorbent, depending on the design efficiency (Vukelic *et al.* 2018). Economics, however, are not independent of environment metrics, and life-cycle assessments invariably indicate reduced global warming potential and toxicity indicators by 40 % of that of single-use disposal in regenerated systems (Baskar *et al.* 2022). Essentially, regeneration converts a linear

waste pathway into a circular pattern, reminiscing of industrial ecology as well as pragmatic sustainability. The second frontier, the academics believe, is hybrid schemes which combine regeneration and recovery and stabilisation, and this would not only provide cleaner effluents but also healthy resource cycles.

2.5.9 Effect of operating parameters on adsorption

Several factors have been identified that affect the adsorption efficiency of biochar in reducing toxins, as shown in Figure 2.11.

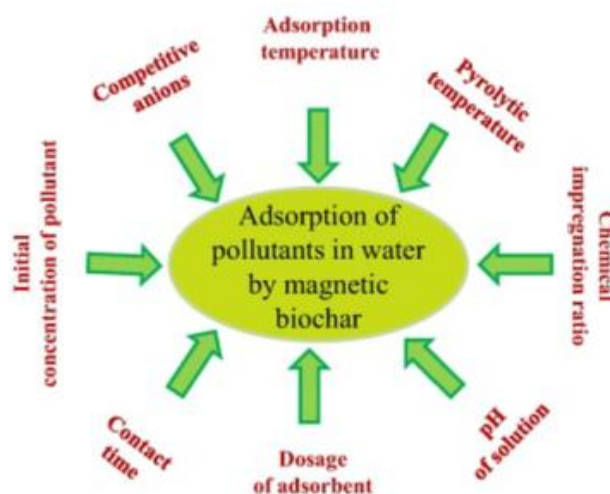


Figure 2.11 Factors affecting the effectiveness of magnetic biochar during the adsorption of toxins

Source: (Li *et al.* 2020b)

2.5.9.1 pH

pH plays a pivotal role in the adsorption process, as observed in a study by Khumalo, Bakare and Rathilal (2023), where the highest ciprofloxacin (CIP) removal occurred at a pH of 6. Deviation from this optimum pH impaired CIP adsorption on chitosan-CNT, regardless of contact time, adsorbent dose, or initial concentration. At $\text{pH} < 6.1$, positively charged CIP molecules interact strongly with the negatively charged chitosan-CNT surface, enhancing adsorption. However, under highly acidic conditions ($\text{pH} < 6$), the protonation of hydrophilic groups ($-\text{OH}$, $-\text{NH}_2$, and $-\text{COOH}$) on the adsorbent surface results in electrostatic repulsion, reducing adsorption efficiency. Increased chitosan

solubility under these conditions further diminishes its effectiveness as an adsorbent (Saheed, Oh and Suah 2021).

At pH values above the point of zero charge (pH_{pzc}), the adsorbent surface becomes deprotonated, causing electrostatic repulsion between the adsorbent and anions, such as phosphate. Conversely, at $\text{pH} < \text{pH}_{\text{pzc}}$, protonated surfaces enhance electrostatic attraction, facilitating higher adsorption capacity, as demonstrated for magnesium ferrite/biochar composites (Qu *et al.* 2022).

In another study, higher pH levels favour adsorption for pollutants like methylene blue (MB) and cadmium (Cd (II)). MB adsorption increased significantly from 1.31 to 16 mg/g as the pH rose from 2 to 8.8, attributed to reduced competition between hydrogen ions and MB (Mallampati, Tan and Valiyaveetil 2015). Similarly, for magnetic biochar, Cd(II) adsorption was most efficient between pH 2.6 and 6.5, as proton competition for binding sites decreased at higher pH levels, thereby enhancing adsorption efficiency (Mahanty and Mondal 2021).

The effect of pH on anion adsorption varies. For instance, phosphate adsorption using zirconia-iron oxide nanoparticles decreased from 99.75% to 41.06% as the pH increased from 1.5 to 10, attributed to the competition between phosphate and hydroxyl ions at higher pH levels (Zhang *et al.* 2017a). Similarly, arsenate (As(V)) adsorption on pine biochar declined as pH increased beyond 3-9 due to changes in the dominant anionic species and electrostatic interactions (Cho *et al.* 2017).

2.5.9.2 Temperature

Sun *et al.* (2015) further demonstrated that the adsorption capacity for crystal violet removal by Fe_3O_4 -coated biochar increased with temperature, reaching a peak at 40 °C. This informed the research that the adsorption process was endothermic. On the other hand, Mohan *et al.* (2014) noted that the use of magnetic and non-magnetic corn stalk biochar to remove fluoride decreased with the increase in temperature from 25 to 45 °C. Likewise, Essandoh *et al.* (2017) observed that metribuzin adsorption on magnetic switchgrass biochar increased slightly when the temperature was raised from 25 to 35 °C and then normalised up to 45 °C.

In these studies, the adsorption efficiency and temperature trends are not generalizable for all pollutants or biochars. Such variability can only be understood on a case-by-case basis to successfully assess adsorption processes and fine-tune operating conditions.

2.5.9.3 Contact time

Al-Senani and Al-Fawzan (2018) indicated that cadmium adsorption was rapid in the first 20 minutes and gradually decreased as equilibrium was approached, typically within 50-100 minutes. The adsorption rates of Cd(II) and Pb(II) from the synthetic mineral adsorbent showed similar trends, increasing rapidly in the first 20 minutes due to the availability of active sites. A gradual decrease in the adsorption rate occurred afterwards as the sites became saturated, achieving equilibrium at 30 minutes (Jung *et al.* 2017).

Further investigations into magnetic biochar revealed that insoluble silicates on the surface formed a barrier, thereby reducing the adsorption of the internal layer (Jung *et al.* 2017; Peng *et al.* 2018a). In the case of Mg-ferrite/biochar composites, 90 % phosphate was adsorbed in the first 2 h and reached the equilibrium at 10 h. These effects were attributed to the fact that the adsorption sites became fully occupied, repulsive forces between any adsorbed phosphate ions, and the reduction in the concentration gradient of phosphate between the solution and the adsorbent (Jung, Lee and Lee 2017).

2.5.9.4 Competitive anions

Competitive anions affect the efficiency of pollutant removal from water by vying for adsorption sites available on biochar. Acidic ions can either enhance or inhibit the adsorption of heavy metals and organic matter. For instance, phosphate (PO_4^{3-}), a common competitive ion, impacts arsenic adsorption more than silicate or sulphate, as observed with magnetic biochar derived from rice husks (Yan *et al.* 2022). Lin *et al.* (2017) demonstrated that for arsenite (As (III)) adsorption, the interference hierarchy was $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{NO}_3^-$. Similarly, Nadagouda *et al.* (2024) revealed in their work that phosphate exhibited a stronger binding affinity to As(III) compared to chloride (Cl^-) and bicarbonate (HCO_3^-).

Inorganic anions are also critical in the production of organic pollutants. Ahmadian *et al.* (2022) observed that the presence of CO_3^{2-} , HCO_3^- , and H_2PO_4^- inhibited the adsorption

of Acid Orange 7 (AO7) on biochar, with CO_3^{2-} exerting the most significant effect. However, at low concentrations (1.85 mM), halide ions such as Cl^- and Br^- promoted the oxidative degradation of AO7, although inhibition was noted at higher concentrations.

Regarding phosphate removal, Zhang *et al.* (2017a) reported that common anions such as Cl^- , SO_4^{2-} , and NO_3^- had a minimal impact when their concentrations were below 150 mg/L. However, HCO_3^- significantly hindered phosphate adsorption due to competition for active sites.

Salt and metal ions also influence the adsorption of pollutants. Zhang *et al.* (2015b) examined the effects of various electrolytes on Cr (VI) adsorption and found the sequence of effectiveness to be $\text{NaCl} > \text{Ca}(\text{NO}_3)_2 > \text{CaCl}_2 > \text{Na}_3\text{PO}_4 > \text{Na}_2\text{SO}_4$. Electrostatic interactions likely govern Cr(VI) adsorption, whereas the presence of Na^+ , Mg^{2+} , and Ca^{2+} differentially affected the removal of Cd^{2+} and Pb^{2+} . Chen *et al.* (2017) observed that Pb^{2+} adsorption was largely unaffected by these ions, but Cd^{2+} removal, particularly in the presence of Ca^{2+} , was significantly influenced.

2.5.9.5 Adsorbent dosage

The influence of adsorbent dosage on the adsorption of Cd(II) ions using iron-modified biochar (5, 7.5, and 10 g/L) was investigated, revealing a decrease in adsorption capacity with increasing biochar dosage (Kołodziejńska, Krukowska and Thomas 2017). Similarly, Pan, Jiang and Xu (2014) observed that the removal rate of Cr(VI) from solutions using $\text{Na}_2\text{SO}_3/\text{FeSO}_4$ -modified peanut straw biochar improved with higher biochar doses. At a concentration of 4 g/L and a solution pH of 7.1, a 100% removal rate was achieved for Cr(VI) (1.5 mM). Increasing magnetic biochar dosage for antibiotics decreased unit adsorption capacity but enhanced the removal rate from 23.4% to 99.1%.

The efficiency of adsorption is strongly influenced by adsorbent dosage. Typically, increasing the amount of magnetic biochar improves the pollutant removal rate, albeit with a decline in unit adsorption capacity. Hence, the balancing or dosing of biochar is a crucial parameter to consider, as it provides the optimal pollutant-removing capacity while being cost-effective with available resources.

2.5.9.6 Initial pollutant concentration

This shows that the initial pollutant concentration is a key determinant of the adsorption capacity of magnetic biochar. Essandoh *et al.* (2017) observed that, at a pH of 5, the biochar's adsorption capacity increased from 15.1 to 39.6 mg/g as the initial concentration of metribuzin in the aqueous solution increased from 40 to 100 mg/L. This increase was attributed to the fact that the driving force for adsorption increases with the initial concentration. Similarly, Jung *et al.* (2017) reported enhanced phosphate adsorption by magnesia ferrite/biochar with higher initial phosphate concentrations. This phenomenon likely results from increased interaction opportunities between the biochar's binding sites and the phosphate ions in the solution.

2.5.10 Adsorption isotherms and kinetics

Adsorption isotherms describe the relationship between the quantity adsorbed onto a surface and its concentration in the bulk phase at a constant temperature. These models are instrumental in understanding adsorption mechanisms and capacities. Standard isotherms include the Langmuir, Freundlich, Brunauer-Emmett-Teller (BET), Dubinin-Radushkevich (D-R), and Temkin models, as shown in Figure 2.12.

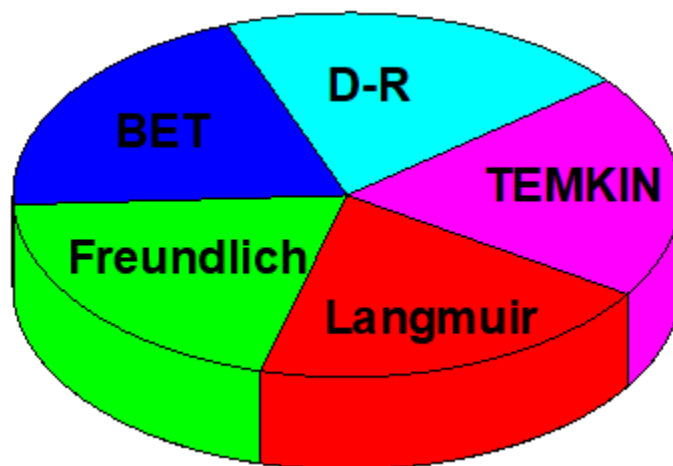


Figure 2.12 Common adsorption isotherm models describing solute–surface interaction mechanisms

The Langmuir Isotherm assumes monolayer adsorption on a homogeneous surface, free from intermolecular interactions, as expressed in Equation 2.10 (Elbidi *et al.* 2021).

$$Q_e = \frac{Q_{max}K_L C_e}{1 + K_L C_e} \quad 2.10$$

Where Q_e represents the equilibrium amount of adsorbate adsorbed per unit mass of adsorbent (mg/g or mol/g), Q_{max} is the maximum adsorption capacity, corresponding to monolayer coverage of the adsorbent surface, K_L is the Langmuir constant, related to the affinity between the adsorbate and the adsorbent (L/mg or L/mol) and C_e is the equilibrium concentration of the adsorbate in the bulk solution (e.g., mg/L or mol/L).

This model is particularly suited for cases where adsorption sites have uniform energy. The Freundlich isotherm, an empirical model, accounts for heterogeneous surface adsorption, as represented by Equation 2.11 (Elbidi *et al.* 2021).

$$Q_e = K_F C_e^{1/n} \quad 2.11$$

Where K_F and n represent system-specific constants. The model offers a more comprehensive explanation of multilayer adsorption systems; however, it becomes less accurate at high pressures.

BET Isotherm extends Langmuir's concept to multilayer adsorption, helpful in calculating specific surface areas using non-reactive probing gases as represented by Equation 2.12 (Zakaria, Jamalluddin and Abu Bakar 2021)

$$\frac{P/P_0}{Q(1 - P/P_0)} = \frac{1}{kQ_m} + \frac{(k - 1)P/P_0}{kQ_m} \quad 2.12$$

Where P and P_0 represent the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, Q (mol) is the quantity of the adsorbed substance per gram of adsorbent, Q_m is the monolayer adsorption capacity, which represents the amount of adsorbate required to form a single layer over the entire surface of the adsorbent and k is the BET constant, related to the energy of adsorption in the first layer compared to subsequent layers.

The Dubinin-Radushkevich (D-R) Isotherm is based on Polanyi potential theory, which distinguishes between physical and chemical adsorption (Chu *et al.* 2024). Its model, as shown in Equations 2.13, 2.14 and 2.15, incorporates the adsorption energy.

$$\ln Q_e = \ln Q_{max} - \beta(\epsilon)^2 \quad 2.13$$

Where Q_e signifies the amount of adsorbate per unit mass of adsorbent at equilibrium (mg/g or mol/g), Q_{max} is the theoretical maximum adsorption capacity (monolayer capacity), indicating the adsorbent's saturation limit, β is a constant related to the mean free energy of adsorption per molecule (mol^2/J^2), and ϵ is the Polanyi potential, defined as:

$$\epsilon = RT \cdot \ln \left(1 + \frac{1}{C_e} \right) \quad 2.14$$

Where R is the universal gas constant ($8.314 \text{ J/mol}\cdot\text{K}$), T is the absolute temperature (K), and C_e is the Equilibrium concentration of the adsorbate in the solution.

The D-R model is instrumental in distinguishing physical adsorption (low β) from chemical adsorption (high β) based on the magnitude of the adsorption energy.

The mean free energy (E) of adsorption can be computed using Equation 2.15.

$$E = \frac{1}{\sqrt{2\beta}} \quad 2.15$$

A value of $E < 8 \text{ kJ/mol}$ suggests physical adsorption, and a value of $E > 8 \text{ kJ/mol}$ shows a high likelihood of chemical adsorption.

Temkin Isotherm considers adsorbate-adsorbent interactions, either physisorption or chemisorption (Mabuza, Premilall and Daramola 2022), as shown in Equation 2.16

$$Q_e = B_T \cdot \ln K_T + B_T \cdot \ln C_e \quad 2.16$$

Where B_T is the Temkin constant related to adsorption energy, as given by Equation 2.17.

$$B_T = \frac{RT}{b_T} \quad 2.17$$

Where b_T is a constant associated with the variation of adsorption energy (J/mol).

Adsorption kinetics evaluate reaction rates, which are typically represented by pseudo-first-order, pseudo-second-order, or pseudo-nth-order models (Huang, Liu and Zhang

2021). The adsorption rate ceases at a particular time since it does not increase proportionately with time, as indicated in Equation 2.18; it is influenced by the reaction order (x) and the kinetic constant (k_x)

$$\frac{dQ}{dt} = k_x(Q_e - Q)^x \quad 2.18$$

When x is 1, the model indicates an adsorption system characterised by exponential decay, while if x is 2, the model implies a time-dependent inverse relationship. These models illustrate the intricacies of adsorption processes on biochar. The experimental data further validate these equations by adsorption curve fitting.

2.6 Precipitation techniques for extracting phosphorus from the pretreated WAS

2.6.1 Background of struvite

Struvite, or magnesium ammonium phosphate hexahydrate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), is a crystalline compound valued for its slow-release fertiliser properties due to its low solubility. It forms under alkaline conditions when magnesium, ammonium, and phosphate ions are present in equimolar concentrations, with a molecular weight of 245.43 g/mol. Solubility varies with pH as it dissolves in acidic environments; it is sparingly soluble in neutral conditions and remains insoluble in alkaline conditions.

Table 2.4 Physicochemical properties of struvite crystals

Characteristics	Nature of struvite
Chemical name	Magnesium Ammonium Phosphate Hexahydrate (MAP)
Chemical formula	$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$
Molecular weight	245.43 g mol ⁻¹
Particle Size	1.5-3mm
Composition	Mg: 10.73% P: 12.54% Hydrogen 1.64% (NH_4) ₂ O H: 4.93% (H_2O) N: 5.71% O: 65.20%
Name	Named after Heinrich Christoph Gottfried Struve (1772–1851)
Colour	White, yellowish-white, brownish-white.
Luster	Vitreous
Hardness	1½–2 (Mohs scale)
Structure	Orthorhombic (space group Pmn21) Presence of regular PO_4^{3-} octahedral, distorted Mg (H_2O) ₆ ²⁺ octahedral, and NH_4^+ groups

Aspect	White glowing crystal
Specific gravity/ density	1.705 g/cm ³
Tenacity	Brittle
Type of bond	Hydrogen bonds
Solubility constant	10 ^{-13.26}

Source: (Krishnamoorthya *et al.* 2021)

Recovered struvite typically contains 11-26 % total phosphorus, depending on the source and production method, of which only 0.02 % is water-soluble, and the remainder is acid-soluble (Negrea *et al.* 2010). This unique solubility makes it an ideal slow-release fertiliser, matching phosphorus availability with plant uptake and minimising seedling toxicity by releasing nutrients only when activated by organic acids from plant roots (Katanda *et al.* 2016). Compared to conventional phosphate fertilisers like triple superphosphate (TSP) and mono-ammonium phosphate, struvite offers better synchronisation with plant nutrient requirements. The summary of the physicochemical properties of struvite is shown in Table 2.4.

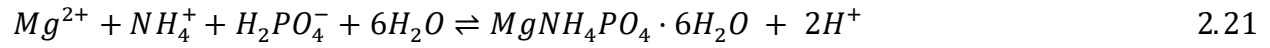
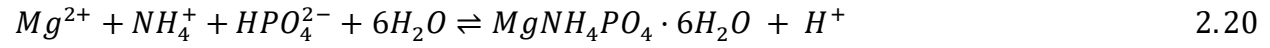
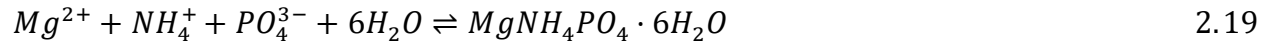
The precipitation of struvite depends on several factors, including solution thermodynamics, fluid hydrodynamics, mass transfer, and precipitation kinetics, which encompass nucleation, growth, aggregation, and crystal breakage (Rahaman *et al.* 2014).

2.6.2 The chemistry of struvite precipitation

The process of struvite crystallisation involves the reaction of magnesium ions (Mg^{2+}), ammonium ions (NH_4^+), and phosphate ions (PO_4^{3-}) in the presence of water to form magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4 \cdot 6H_2O$), commonly known as struvite.

The determination of the formation of struvite from the primary phosphate ion (PO_4^{3-}) is given by Equation 2.19. This reaction occurs under fully alkaline conditions, in which all three ions form a coordinate bond with six water molecules. Equation 2.20 shows that hydrogen phosphate HPO_4^{2-} is the partially protonated form of phosphate, which is H_3PO_4 . It is a weak reaction that eliminates one hydrogen ion (H^+), hence slightly decreasing the pH. In Equation 2.21, $H_2PO_4^-$ is involved, which is dihydrogen phosphate, the species most readily protonated from phosphate. It releases two hydrogen ions (H^+),

and thus, the pH is reduced even more (Rabinovich and Rouff 2021; Natividad-Marin, Burns and Schneider 2023).



Such reactions depend on pH, ionic concentrations, and molar ratios, and the system used must operate at an alkaline pH to ensure an equilibrium that favours the formation of struvite (González-Morales *et al.* 2021). The stoichiometry also shows how phosphate species within the solution affect the formation of struvite, influencing both reaction pathways and the pH balance. This is important in enhancing the quantitative yield of struvite in wastewater treatment systems.

Nucleation is one of the complex yet fundamental stages in crystallisation, which implies the generation of a crystalline nucleus from a supersaturated solution. Several mechanisms can drive this multifaceted phenomenon, which is influenced by various factors. Figure 2.13 illustrates the formation of struvite aggregates during an experiment conducted at a constant pH.

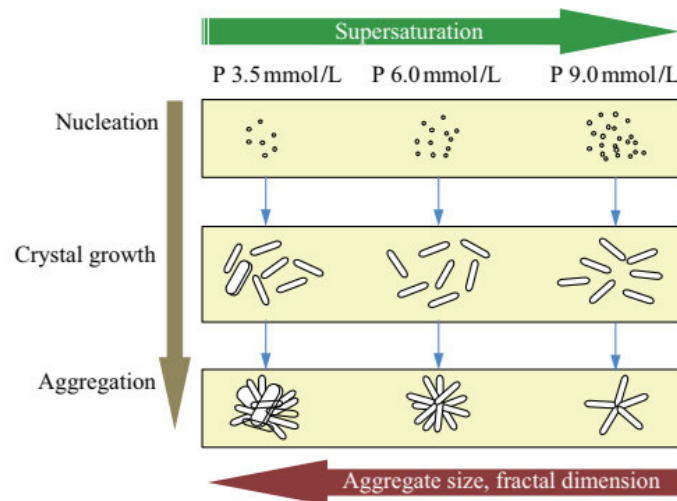


Figure 2.13 Schematic illustration of the formation of struvite aggregates at constant pH
Source: (Ye *et al.* 2014)

Nucleation can be classified into two primary types: primary nucleation, which occurs without pre-existing crystals, and secondary nucleation, which involves existing crystalline structures (Makoveeva 2021). The extent of supersaturation determines the nucleation behaviour, as it affects both crystal size and growth dynamics (Ye *et al.* 2014; El Kadi and Janajreh 2017). It begins homogeneously when no solid phase is present or heterogeneously in the presence of foreign particles that promote crystallisation.

Primary nucleation is the process by which several new crystals are formed in a supersaturated solution. The process, often referred to as homogeneous nucleation, occurs through molecular collisions and interactions that cause the formation of a nucleus, ultimately leading to the development of a lattice structure. These nuclei may or may not reach thermodynamically stable points as determined by supersaturation levels and the prevailing systems (Zhu *et al.* 2023).

Struvite crystal formation involves two key phases: (i) nucleation (crystal birth) and (ii) crystal growth. Forecasting these mechanisms is quite complex, as the chemical and physical processes are influenced by the properties of the initial crystalline phase, the equilibrium between the liquid and solid phases, mass transfer between the two phases, and reaction kinetics (Rahman *et al.* 2014)

2.6.3 Operating parameters for crystallisation

The processes of crystallising struvite are regulated by factors such as pH, molar ratio, degree of supersaturation, temperature and the addition of seeds (Yesigat *et al.* 2022). Precipitation is based on the solubility product constant (K_{sp}), where exceeding the solubility threshold in an aqueous solution leads to solid precipitation (Shih *et al.* 2017a).

2.6.3.1 pH

It is evident that the pH range of 7-11 is suitable for expressing struvite, and that the range of 9-11 is especially suitable for crystallisation (Tarragó *et al.* 2018; Le *et al.* 2020). In solution, different kinds of phosphorus species appeared at different pH conditions, where H_3PO_4 at the solution pH condition of 0-1 and $H_2PO_4^-$ at 4-6 are non-chemical reactivity, while HPO_4^{2-} at 9-11 and PO_4^{3-} at >12 are chemically active for struvite precipitation (Chen *et al.* 2021).

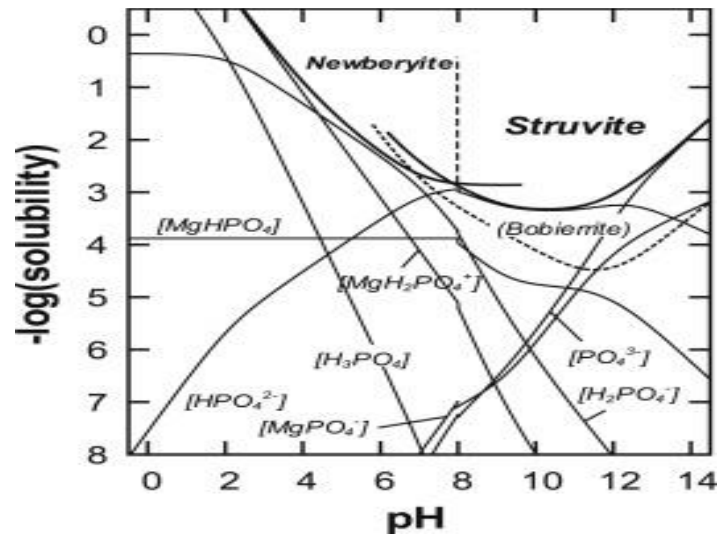


Figure 2.14 Conditional solubility curves of newberyite, bobierrite and struvite

Source: (Shih *et al.* 2017b)

Struvite primarily precipitates at a pH higher than 8, with ammonium ions (NH_4^+) serving as the pH buffer. However, Michałowski and Pietrzyk (2006) investigated the possibility that pure struvite may convert into $\text{Mg}_3(\text{PO}_4)_2$, which is less soluble and less reactive in the precipitation process than $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. Phosphorus removal is exclusively dependent on the degree of supersaturation, which in turn depends on pH and ion concentrations.

As demonstrated in Figure 2.14, conditional solubility curves highlight the interplay of newberyite (MgHPO_4), bobierrite ($\text{Mg}_3(\text{PO}_4)_2$), and struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) (Shih *et al.* 2017a); Guan *et al.* (2023). Bayuseno and Schmahl (2020) observed that hydrogen release during struvite formation lowers the pH, inhibiting further crystallisation at acidic levels.

MgCl_2 is often used to precipitate magnesium ammonium phosphate, with pH control achieved through aeration and crystallised phosphorus recovery. This process can involve ammonia stripping, where liquid digestate undergoes air stripping in a packed column, followed by crystallisation recovery using sulfuric acid to produce ammonium

sulphate fertiliser (Wu *et al.* 2021). Elevated temperatures and controlled pH significantly improve efficiency. The process of ammonia stripping is shown in Equation 2.22



The pH of a solution affects the ion concentration profiles of orthophosphate and ammonia, as well as the supersaturation ratios and growth rates of struvite crystals. Higher pH values render the zeta potential more negative, thereby accelerating growth rates (Prywer, Sadowski and Torzewska 2015). However, excessively high pH can result in a high positive zeta potential, thereby prolonging nucleation times (Fromberg, Pawlik and Mavinic 2019).

Increasing pH reduces the size and thickness of struvite crystals. For example, Wu *et al.* (2022) reported a fivefold decrease in average crystal size when pH increased from 8 to 10, with further reductions as pH rose to 11. Additionally, Mg^{2+} ions form $Mg(OH)_2$ at higher pH levels, which interferes with struvite crystallisation (Rayshouni and Wazne 2022). When pH exceeds 10.5, insoluble $Mg_3(PO_4)_2$ forms (Sarkar *et al.* 2024), as shown in the reactions represented by Equations 2.23 and 2.24.

When the pH exceeds 10.5, $Mg_3(PO_4)_2$ precipitation occurs (Sarkar *et al.*, 2024), as indicated by the reactions represented by Equations 2.23 and 2.24.



Therefore, knowledge of such parameters is crucial for improving the efficiency of struvite recovery and phosphorus removal.

2.6.3.2 Mg/PO_4 molar ratio

$Mg: PO_4$ ratio is a very sensitive parameter that directly determines the performance and purity of the precipitation process of NH_4 -struvite. Wastewater is generally characterised by an imbalance between Mg/PO_4 , with magnesium present in a smaller amount, hence acting as a limiting reactant (Guadie *et al.* 2020). For maximum recovery of struvite, it is recommended that the ratio of Mg to PO_4 be 1:1, implying that, in practice, different ratios may be required to control competing reactions and impurities.

By increasing the Mg/PO₄ molar ratio, Lothenbach, Xu and Winnefeld (2019) proved that the chemical equilibrium of the system is altered. At ratios between 0.5-1.0, higher concentration of available reactants, especially Mg and PO₄, decreases when the concentration of hydroxide ions (OH⁻) and pH increase. Ratios exceeding 1.0 reduce the concentrations of Mg, P and K, which are beneficial in stabilising K-struvite formation. The changed crystalline type depends on the Mg/PO₄ below 0.5, newberyite (MgHPO₄·3H₂O) is typical; at the 0.5-0.7, cattiiite (Mg₂KH(PO₄)₂·15H₂O) is favoured; and at the Mg/PO₄ more than 1.0, the K-struvite becomes dominant alongside smaller amounts of brucite and cattiiite.

Figure 2.15 illustrates that changes in the Mg/PO₄ ratio determine the crystal structure. The balance of this ratio enables desirable nutrient absorption and the reduction of unfavourable side products, such as Mg(OH)₂, which form at high pH values and limit magnesium availability for struvite crystallisation (Rahman *et al.* 2014; Wu *et al.* 2021).

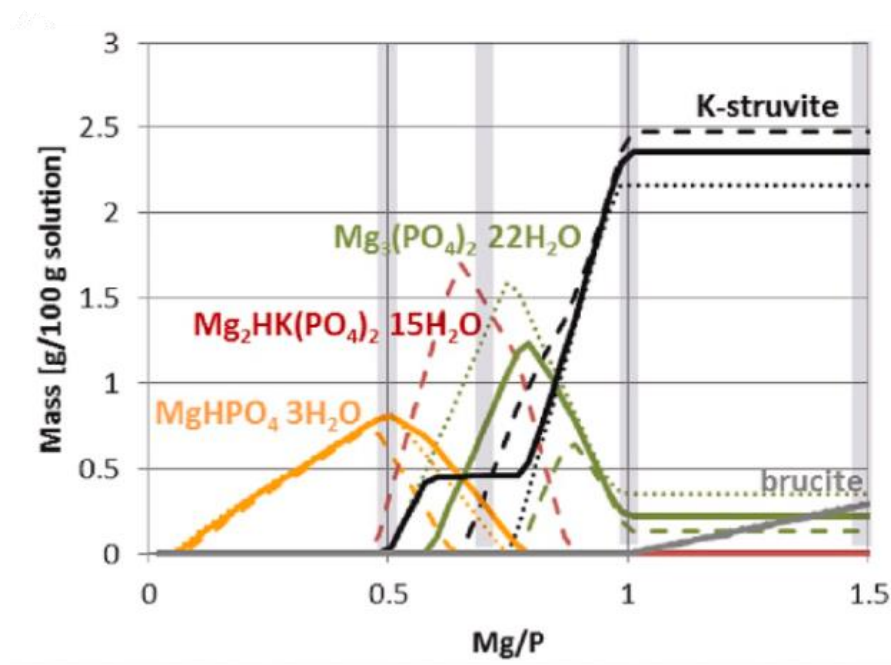


Figure 2.15 Effect of Mg/PO₄ ratio on K-struvite formation
Source: (Lothenbach, Xu and Winnefeld 2019).

These findings indicate that the ratios of Mg to PO₄ in wastewater treatment need sufficient accuracy and monitoring. While a 1:1 ratio is the theoretical minimum for struvite formation, process variations, including pH adjustments and the presence of competing ions, require tailored approaches to maximise recovery efficiency and product quality.

2.6.3.3 Temperature

Temperature plays a crucial role in the solubility of crystalline solids, as it affects the crystalline morphology, including struvite. Several research works have focused on the temperature-dependent solubility of struvite. For instance, solubility was found to decrease with temperature, with solubility values varying from 13.18 for the test solution at 25°C to 13.07 for the test solution at 35°C, with the least solubility at 30°C (Hanhoun *et al.* 2011). Lower solubility under these conditions enhances precipitation; however, elevated temperatures can distort crystal morphology and size (Le Corre *et al.* 2009).

Temperature affects nearly all aspects of crystal growth, including the mechanisms that govern them. Increased temperature tends to promote diffusion-controlled growth more than lower temperatures, which advances surface integration in crystal growth (González-Morales *et al.* 2021). These dynamics emphasise the need to optimise temperature to balance precipitation rates and crystal quality.

Experimental studies also reveal that elevated temperatures (20°C-80°C) impact the thermodynamic stability of K-struvite. Lothenbach, Xu and Winnefeld (2019) noted that as the temperature increased to 40°C and 80°C, the solubility of K-struvite shifted, resulting in secondary crystal formations such as bobierite and Mg₃(PO₄)₂·4H₂O, as shown in Figure 2.16. These changes were accompanied by a rise in phosphorus and potassium concentrations in the solution, while magnesium concentrations declined, further influencing precipitation dynamics.

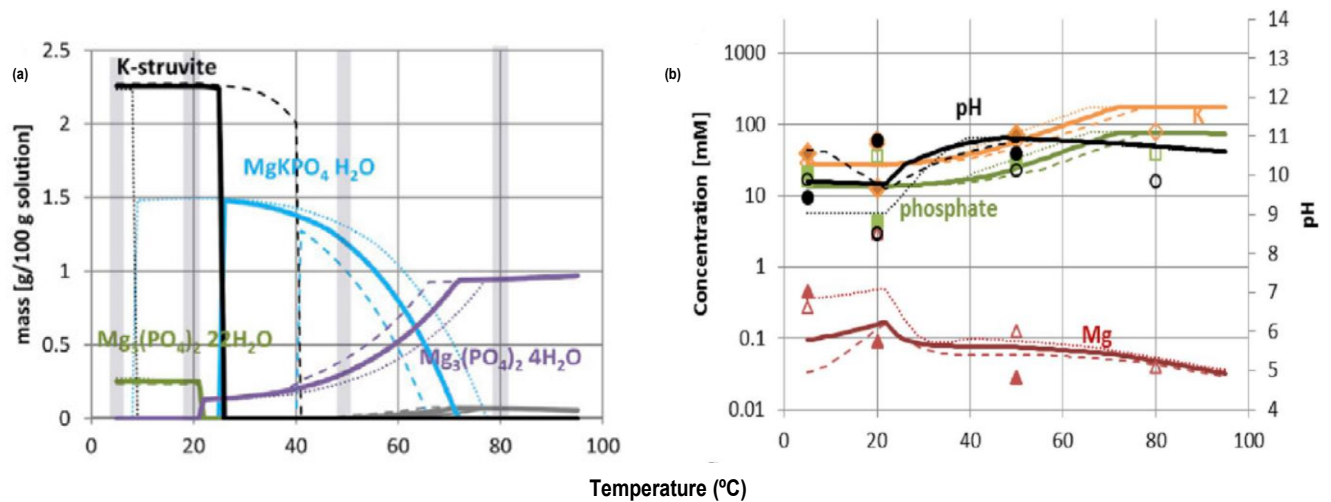


Figure 2.16 Effect of temperature on K-struvite formation

Source: (Lothenbach, Xu and Winnefeld 2019).

Beyond crystal solubility, temperature affects the release of phosphorus from waste-activated sludge (WAS). Pokhrel *et al.* (2018) demonstrated that at pH 4 (Figure 2.17), a temperature of 35°C solubilised approximately 40% of total phosphorus within 2 days, reaching 50% after 7 days. Higher temperatures accelerated the liberation of phosphorus from non-apatite inorganic phosphorus (NAIP) and apatite phosphorus (AP) fractions, while organic phosphorus (OP) remained stable.

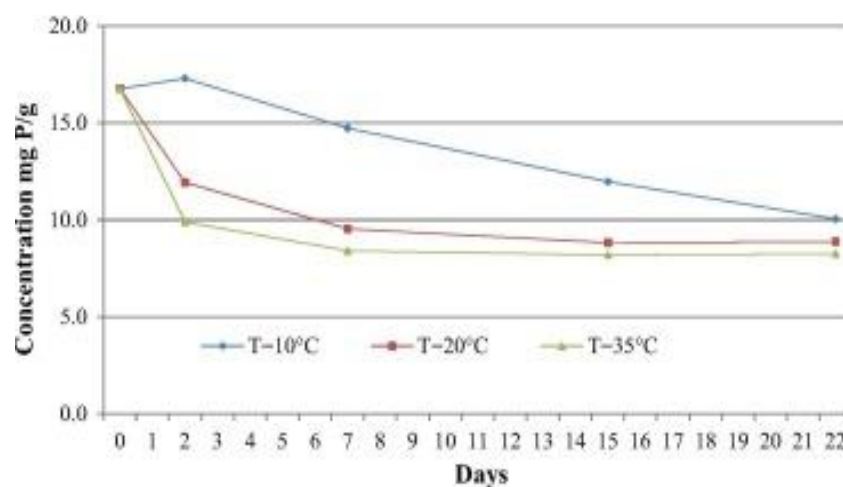


Figure 2.17 Total P in solid WAS under different temperatures at a pH of 4

Source: (Pokhrel *et al.* 2018)

Both temperature and solution pH have a significant influence on nutrient recovery and struvite precipitation efficiency. It is noteworthy to fine-tune these parameters to achieve a higher recovery of phosphorus, while also preserving the crystal structure and process efficiency.

2.6.3.4 Seeding

Hu *et al.* (2020a) proposed the idea of crystal seeding to improve the efficiency of struvite precipitation. Over the last four decades, researchers have explored a range of materials, including NH₄-struvite, sand, zeolite, lignite, and eggshell powder, for their potential to enhance struvite crystallisation (Gao *et al.* 2018; Volpin *et al.* 2018). Seeding helps small struvite particles adhere to seed surfaces, significantly boosting the surface area for nucleation and crystal growth (Guan *et al.* 2021). Ye *et al.* (2014) indicate that these seed centres lower the energy barrier for nucleation, which accelerates the crystallisation process.

According to Gao *et al.* (2018), struvite forms efficiently when magnesium, potassium, and phosphorus are present in a molar ratio of 1:1:1 at a pH level of 11. The use of these precipitates as seed material proved to be effective, leading to a notable enhancement in the removal efficiencies of potassium (K) and phosphorus (P). The application of preformed K-struvite increased K removal from 55.7% (without seeding) to 65% at a dosage of 30 g/L, with no additional enhancements noted at higher doses. Similarly, the efficiency of phosphorus removal rose from 86.5% to 97.1% with the exact dosage applied. This highlights the effectiveness of struvite seeding in promoting crystallisation (Figure 2.18 (a)).

Hu *et al.* (2020a) also evaluated NH₄-struvite as a seed material, as illustrated in Figure 2.18 (b). The experiments revealed that increasing the NH₄-struvite dosage from 0 to 1 g/L improved K recovery from 24.8% to 30.5% and NH₄ recovery from 85.9% to 91.9%, consistent with findings by Kim *et al.* (2007). The dual phases of struvite precipitation, that is, nucleation and crystal growth, are enhanced by introducing preformed struvite, which acts as a nucleating agent and provides a larger surface area for crystal growth (Burns, Sheehan and Schneider 2021). However, excessive seeding material can inhibit nucleation and limit recovery efficacies (Gao *et al.* 2018; Hu *et al.* 2020a).

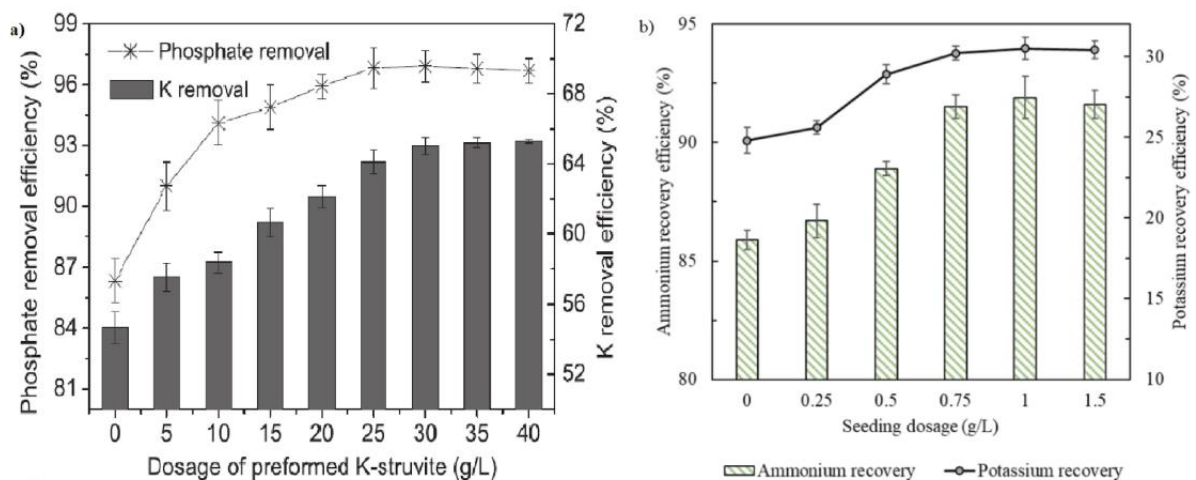


Figure 2.18 The variations in the P and K removal efficiencies with the dosage of (a) K-struvite as seed and (b) NH₄-struvite as seed
Source: (Gao *et al.* 2018; Hu *et al.* 2020a)

Huang *et al.* (2014) found that, when increased from 5 to 20 g/L, NH₄-struvite seed concentration brought an increased NH₄-N removal from 90.7% to 95.4%. as demonstrated by Kim *et al.* (2007) the NH₄-N removal efficiency improved from 86.4 to 96.8% by choosing optimum amount of NH₄-struvite dosages between 0 and 40 g/L and retrieving NH₄-struvite with alternative seeding materials, e.g. sand. It has also been demonstrated that, due to its large surface area, sand is promising for increasing precipitation rates (Li *et al.* 2022a). It is essential to note that the self-seeding mechanism of struvite crystallisation can be utilised to reduce the need for a high degree of multi-stage seeding (Adnan *et al.* 2004).

2.6.3.5 Influence of coexisting ions

Struvite crystallisation is influenced by pH, magnesium availability, and competing ions, such as calcium (Ca²⁺), which can reduce crystallisation efficiency or introduce impurities. Optimal conditions typically require a Mg: Ca molar ratio below 1 and a pH range of 7–11 to minimise interference (Sarkar *et al.* 2024).

The presence of sodium ions (Na⁺) has a significant impact on struvite formation, particularly during pH adjustment with sodium hydroxide (NaOH). High Na⁺

concentrations can lead to competitive interactions with NH_4^+ and K^+ for Mg^{2+} and phosphate ions, resulting in the formation of sodium-struvite, which hinders the recovery of K-struvite or NH_4 -struvite, as shown in Figure 2.19. Studies indicate that substituting NaOH with MgO for pH adjustment can mitigate this issue, as MgO serves both as an alkaline agent and a source of magnesium (Kutlar, Engin and Yilmazel 2024).

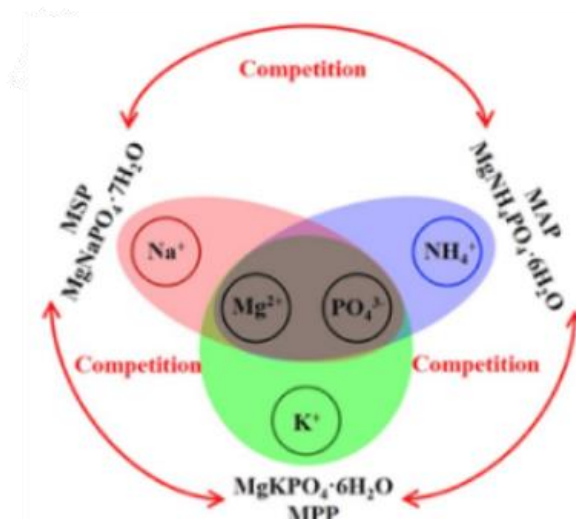


Figure 2.19 Effect of sodium and ammonium ions on K^+ during struvite recovery

Source: (Xu *et al.* 2015)

Foreign impurities, such as calcium ions (Ca^{2+}) and carbonate ions (CO_3^{2-}), significantly influence struvite crystallisation. Calcium ions, when adsorbed on the surface of a crystal, occupy ammonia-binding sites, thereby inhibiting the crystallisation of struvite (Hakimi, Jegatheesan and Navaratna, 2020). Additionally, calcium ions react with phosphate or carbonate ions to form insoluble compounds such as calcium phosphate (commonly hydroxyapatite) or calcium carbonate (typically calcite), as demonstrated in Equation 2.25.



These reactions alter the stability and composition of the struvite crystals formed by Peng *et al.* (2018b). This competition, particularly at Ca:Mg molar ratios $\geq 1:1$, reduces struvite purity and recovery efficiency. For instance, higher Ca concentrations increase

phosphorus removal (from 81% to 98%) but decrease the efficiency of ammonia removal (from 42% to 33%) due to competing precipitation reactions.

As research has shown, the crystallisation process is susceptible to calcium ion concentration. The presence of elevated calcium ions results in a significant reduction of struvite crystal nucleation and linear growth rates, as well as a lower purity of the crystals (Hutnik *et al.* 2020). Additionally, the ratio of $\text{Ca}^{2+}/\text{Mg}^{2+}$ is critical; ratios exceeding 0.2 have been shown to inhibit struvite formation and its purity. An increase of the $\text{Ca}^{2+}/\text{PO}_4^{3-}$ molar ratio from 0.5 to 1.0 additionally has a negative effect on both the formation and purity of struvite crystals (Tao, Fattah and Huchzermeier 2016).

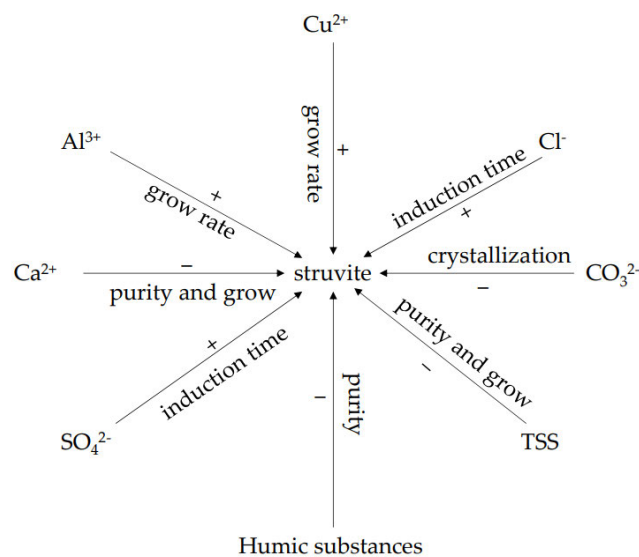


Figure 2.20 Summary of the effect of foreign particles on struvite crystallisation

Source: (Wu *et al.* 2022)

Vivianite can form instead of struvite in iron-rich conditions, compromising product purity. A comparative study on hydrochars found increased vivianite precipitation during AD due to microbial Fe(III) reduction. The findings indicate that the formation of struvite or vivianite in AD solids largely depends on the Mg/Fe molar ratio and the pH of the AD suspension (Wang *et al.* 2021a). Struvite crystallisation can also be interfered with by other foreign ions, by SO_4^{2-} , NO_3^- and F^- . The effect of Cu^{2+} and Al^{3+} ions on crystal growth is presented in Figure 2.20, although the ions may also influence the rates of nucleation.

Struvite crystal growth rate in the presence of K^+ has been shown to promote the growth rate of larger particles approximately 46 μm in size (Stanclik *et al.* 2019).

Competing ions are managed, and appropriate pH adjustment methods are selected to optimise struvite recovery. The measures improve product quality and reduce impurities, which promotes more efficient nutrient recovery for slow-release fertilisation applications.

2.6.4 Thermodynamic equilibrium model for struvite precipitation

Solution chemistry predominantly determines nutrient recovery through struvite crystallisation, but significantly impacts the formation of crystals and removal efficiency. The struvite ($MgNH_4PO_4 \cdot 6H_2O$) is formed from the combination of magnesium, ammonium and phosphate ions in the presence of water (Equation 2.19).

Solution supersaturation is a significant factor determined by the concentrations of reactive species, pH, and ionic strength. The Ion Activity Product (IAP) and Solubility Product are used to quantify supersaturation. Struvite precipitation is primarily driven by supersaturation, which is most strongly dictated by solution pH and the concentration of other reactive species. In the case of struvite, the contribution of multiple ions, however, complicates a direct determination of solute concentration. To address this, the IAP, as presented in Equation 2.26, is adopted to quantify supersaturation.

$$IAP = [Mg^{2+}][NH_4^+][P_4^{3-}] \quad 2.26$$

Equation 2.27 is derived to quantify the degree of supersaturation using the supersaturation index (SI) based on the IAP.

$$SI = \log\left(\frac{IAP}{K_{sp}}\right) \quad 2.27$$

The SI indicates the solution's state, in that if $SI < 0$, the solution is undersaturated (no precipitation occurs); if $SI = 0$, the solution is at equilibrium; and if $SI > 0$, the solution is supersaturated (precipitation occurs). The K_{sp} value for struvite has been well-documented, with a reported value of 13.26 (Krishnamoorthya *et al.* 2021).

The driving force for the crystallisation of struvite is defined in Equation 2.28.

$$F = -\frac{R_g}{\alpha} \ln \Omega \quad 2.28$$

Where R_g is the gas constant ($8.31 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$), α is 3, T is the absolute temperature, and Ω is the supersaturation ratio of the solution (SI), α is a constant parameter (value = 3 for struvite crystallisation), and $\ln(\Omega)$ is the natural logarithm of the supersaturation ratio (Ω). A negative driving force (J/mol) highlights the release of free energy necessary for struvite formation.

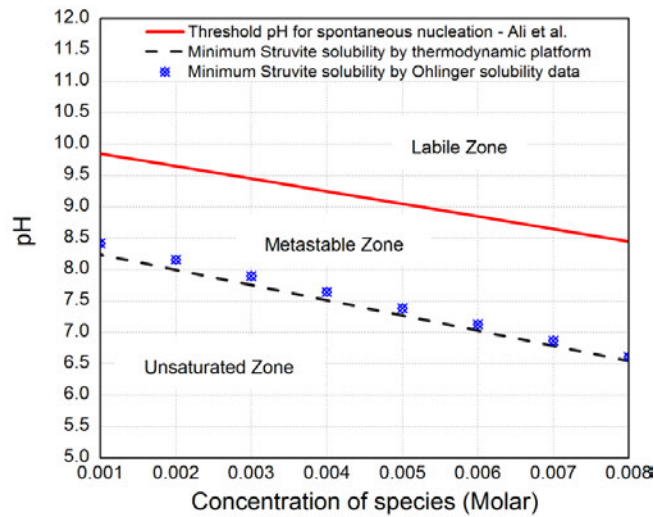


Figure 2.21 Zones in which struvite precipitation takes place

Source: (Mousavi, Choudhury and Rahaman 2019)

At a given temperature, the solubility of struvite is primarily influenced by the concentration of reactive ions and the solution pH. Consequently, struvite precipitation occurs in distinct zones defined by these factors. Figure 2.21 illustrates the zones where struvite is most likely to precipitate. In the unsaturated zone, any crystals formed dissolve back into the solution, and precipitation does not occur. In the metastable zone, also referred to as the saturated zone, the solution is saturated, and crystal growth may take place if seed material is introduced. However, the available Gibbs free energy is insufficient for significant crystal nucleation. Over time, nucleation may still occur if the conditions are maintained. In the labile zone, also known as the unstable zone, the solute

concentration exceeds the equilibrium value, leading to spontaneous nucleation. Crystal growth in this zone is extremely rapid (Mousavi, Choudhury and Rahaman 2018).

The equilibrium speciation model PHREEQC is commonly employed to simulate these processes. With modifications to include the solubility product of struvite (Soltani, Natividad-Marin and Schneider 2023), PHREEQC enables the accurate prediction of precipitation behaviour under varying conditions.

2.6.5 Sources of magnesium

Although phosphorus recovery from wastewater holds significant potential, the low magnesium concentration in wastewater poses a limitation for struvite formation (Rahman *et al.* 2014). When the molar ratio of phosphate to magnesium falls below 1.0, a spontaneous reaction can result in the formation of precipitate that differs from struvite (Guadie *et al.* 2020). Maintaining the Mg/PO₄ ratio at or above 1.0 is crucial for successful struvite crystallisation, often requiring the addition of external magnesium sources. However, the cost of these supplements represents a significant financial burden (Huang *et al.* 2014; Guadie *et al.* 2020).

Magnesium reagents can account for up to 75 % of total production costs. Recent studies suggest that using affordable magnesium sources can reduce costs by 18-81% (Freire *et al.* 2025). Low-cost options, such as magnesite or magnesite by-products, have been proven effective in removing ammonium and phosphate (Wang *et al.* 2018b; Aguilar-Pozo *et al.* 2023).

The feasibility of struvite synthesis is influenced by cost, availability, and environmental impact. Magnesium chloride and magnesium oxide require significant energy during production, contributing to their high costs and carbon footprint. Conversely, magnesium carbonate is a more economical and environmentally friendly option. In South Africa, the abundance of cryptocrystalline magnesite presents a sustainable option for magnesium (Mg) sourcing, which is essential for making struvite recovery commercially viable in developing regions (Mavhungu *et al.* 2018). However, solutions containing MgO and MgCO₃ often lack visible precipitates unless chelating agents, such as EDTA, are used

(Siciliano *et al.* 2020). Table 2.5 summarises the advantages and disadvantages of various magnesium sources.

Table 2.5 The advantages and disadvantages of magnesium sources

Magnesium Source	Advantages	Disadvantages	References
Magnesium Oxide (MgO)	Increases pH; Versatile	Requires preparation (8–16 h); energy-intensive	(Warmadewanthi and Liu 2009; Stolzenburg <i>et al.</i> 2015; Shokouhi 2017)
Magnesium Hydroxide (Mg(OH) ₂)	Cost-effective, high alkalinity, low heavy metal content, high solubility	Limited equilibrium solubility	(Shokouhi 2017; Mamakoa <i>et al.</i> 2019; Yesigat <i>et al.</i> 2022)
Magnesium Chloride (MgCl ₂)	Readily available, high phosphorus removal efficiency	Expensive; energy-intensive; high carbon footprint	(Shokouhi 2017; Kiani <i>et al.</i> 2019)
Cryptocrystalline Magnesite (MgCO ₃)	Low cost; reduced environmental impact; hybrid properties (Mg, Ca, Fe, Si); abundant in SA	Produces substantial sludge	(Masindi, Gitari and Pindihama 2016; Mavhungu <i>et al.</i> 2018)
Magnesium Sulphate (MgSO ₄ ·7H ₂ O)	Effective phosphorus removal, High Solubility, Ease of Handling	Cost Implications; Environmental Considerations (high carbon footprint)	(Mamakoa <i>et al.</i> 2019; Galamini 2022)

Comparative studies of commercial magnesium salts reveal MgCl₂ as the most efficient for phosphorus removal, followed by MgSO₄ and MgO. MgCO₃ demonstrated the least efficiency (Zeng, Mangan and Li 2006). Seawater, a natural source of magnesium, also presents a promising alternative for reducing chemical costs and environmental impacts, as it is reported to contain 1276-1300 mg/L of Mg²⁺ (Fattah *et al.* 2022; Fontana *et al.* 2023).

2.7 Effect of HT on the production of biogas through AD

2.7.1 Overview of metabolic and biochemical pathways of the AD process

Anaerobic digestion (AD) is a microbial-driven, oxygen-free process widely employed for the stabilisation of sewage sludge and recovery of bioenergy. It transforms complex organic matter into biogas, predominantly consisting of methane (CH₄) and carbon

dioxide (CO₂), as well as a nutrient-rich digestate, making it a cornerstone of sustainable wastewater management (Abdoli and Ghasemzadeh 2024). As shown in Figure 2.22, AD proceeds through four interdependent stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis, each facilitated by distinct microbial consortia (Rea 2014; Nayak and Dutta 2024).

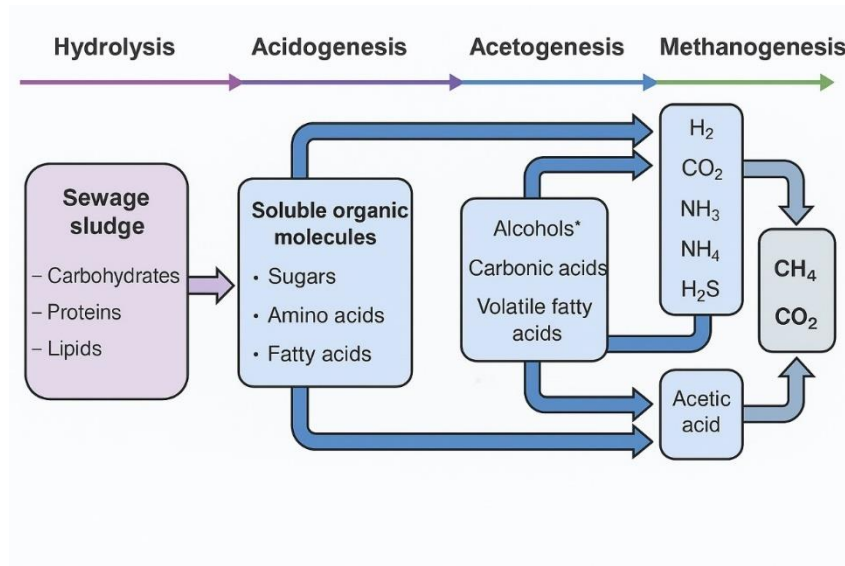


Figure 2.22 Schematic representation of the four-stage AD process for sewage sludge.
Source: (Nayak and Dutta 2024; Qian *et al.* 2025)

2.7.1.1 Hydrolysis

Hydrolysis, the first and often rate-limiting stage of anaerobic digestion, involves the enzymatic cleavage of complex organic biopolymers into simpler, soluble monomers that can be readily utilised by subsequent microbial communities (Nayak and Dutta 2024). During this step, proteins are broken down into amino acids, carbohydrates into monosaccharides, and lipids into fatty acids and glycerol. The general reaction for carbohydrate hydrolysis is represented by Equation 2.29.



This transformation is mediated by extracellular enzymes such as proteases, cellulases, and lipases, and is crucial for making particulate-bound organics accessible for further degradation.

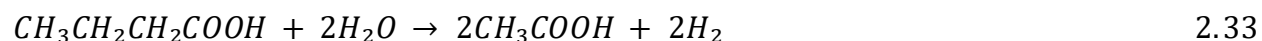
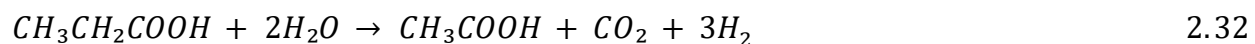
2.7.1.2 Acidogenesis

During acidogenesis, acidogenic bacteria convert the soluble products of hydrolysis into volatile fatty acids (VFAs), alcohols, hydrogen (H₂), carbon dioxide (CO₂), and ammonia (NH₃). This stage is crucial for producing intermediates required in later AD steps (Radetic 2024). Typical fermentation pathways include glucose conversion to ethanol and CO₂, and acetic acid, CO₂, and H₂ are presented in Equations 2.30 and 2.31



2.7.1.3 Acetogenesis

During the acetogenesis phase of anaerobic digestion, intermediate compounds, such as volatile fatty acids (VFAs) and alcohols, produced during acidogenesis, undergo further microbial transformation. This process is carried out by syntrophic acetogenic bacteria, which work in close association with hydrogen-consuming methanogens (Radetic 2024). The conversion is thermodynamically feasible only under conditions of low hydrogen partial pressure, which is maintained by methanogens that scavenge the hydrogen produced. These interactions are essential for maintaining process stability and ensuring efficient substrate turnover. Representative reactions during acetogenesis include the conversion of propionic acid into acetic acid, carbon dioxide, and hydrogen, as shown in Equation 2.32. Similarly, butyric acid is oxidised to acetic acid and hydrogen as shown in Equation 2.33.



2.7.1.4 Methanogenesis

Methanogenesis is the terminal stage of anaerobic digestion, where specialised methanogenic archaea convert intermediate products into methane (CH₄), the primary

component of biogas (Wang *et al.* 2023). This process plays a critical role in energy recovery and carbon stabilisation. Methanogens operate through three principal metabolic pathways, depending on the availability of substrates and environmental conditions. In the acetoclastic pathway (Equation 2.34), acetate is directly cleaved into methane and carbon dioxide. The hydrogenotrophic pathway (Equation 2.35) involves the reduction of carbon dioxide using hydrogen, typically under conditions of hydrogen limitation. A third, less common route is the methylotrophic pathway (Equation 2.36), where methanol and other methylated compounds are converted to methane (Li *et al.* 2024b).



Approximately 70% of methane is generated through acetoclastic pathways, while 30% derives from hydrogenotrophic routes (Nayono 2010; Khan *et al.* 2024). Process efficiency is influenced by parameters such as pH, temperature, and substrate composition. Hydrolysis often remains the bottleneck due to the recalcitrant nature of lignocellulosic and particulate matter (Scherzinger and Kaltschmitt 2021).

Understanding the synergy between microbial communities and their functional roles is pivotal in enhancing AD performance, particularly in the context of co-digestion and pre-treatment strategies such as hydrothermal treatment.

2.7.2 Organic loading in anaerobic digestion processes

Organic loading rate (OLR) represents a critical determinant of anaerobic digester performance, influencing microbial activity, process stability, and methane yield. Excessive loading can trigger acidification and the accumulation of volatile fatty acids (VFAs), while under-loading underutilises reactor capacity. Thus, optimising OLR is essential for balancing substrate availability with microbial conversion efficiency. Studies have shown that methane yield generally increases with moderate increments in OLR, up

to a threshold beyond which inhibition occurs due to substrate overaccumulation or ammonia toxicity (Zhang *et al.* 2022; Aili Hamzah *et al.* 2023; Alkhrissat 2024).

In mesophilic systems, where digesting animal manure or sewage sludge is involved, optimum methane generation has been reported between 2.5 and 4.0 g-VS/L.d, where hydrolysis and methanogenesis remain synchronised. For instance, Zhang *et al.* (2022) demonstrated a threefold enhancement in methanogenic activity and hydrolysis efficiency at an OLR of 3.5 g VS/L.d. However, at higher rates, an excessive organic influx can surpass the buffering capacity, leading to a pH decline and the inhibition of methanogens (Campbell *et al.* 2022).

From a broader perspective, variability in OLR also explains discrepancies between batch and continuous reactor studies, particularly in hydrothermally treated (HT) sludge. HT significantly alters substrate biodegradability and VFA concentrations, thereby shifting the optimal OLR window (Aragón-Briceño, Ross and Camargo-Valero 2021). In integrated HT-AD systems such as the present study, OLR optimisation is pivotal to achieving synergistic benefits, maximising methane recovery while maintaining process stability and avoiding inhibitory intermediates. Ultimately, defining the balance between substrate solubilisation and microbial tolerance underpins sustainable operation and scalability of HT-coupled AD technologies.

2.7.3 Effect of HT on anaerobic digestion

HT has been proven effective in enhancing AD by disrupting the EPS network, thereby improving solubilisation and biodegradability (Li *et al.* 2022b). Studies indicate a positive correlation between COD solubilisation and HT temperature. For instance, thermal pretreatments of municipal wastewater sludge at optimal conditions increased COD solubilisation by $18.3 \pm 7.5\%$ and volatile suspended solids (VSS) reduction by $27.7 \pm 12.3\%$ compared to untreated sludge. Although initial methane production rates increased significantly ($p = 0.0013$) in biochemical methane potential (BMP) tests, ultimate methane yields were not substantially affected (Nazari *et al.* 2017).

Thermal pretreatment improves AD by enhancing cell disintegration, reducing digestate viscosity, and releasing organic compounds for biodegradation (Pham *et al.* 2023).

Dewaterability, hindered by the gel-like structure and hydrophilic nature of EPS, is enhanced by HT. HT effectively disrupts sludge structure, releasing bound moisture and improving dewaterability (Chen *et al.* 2022). This process can be categorised into solubilisation (≤ 120 °C), hydrolysis (140-180 °C), and carbonisation stages (200-260 °C). However, temperatures above 200 °C are unfavourable, potentially leading to the degradation of nitrogenous organics and the formation of toxic compounds through polymerisation reactions (Dumitraşcu, Borda and Aprodu 2023; Zhou *et al.* 2024).

Combined treatments, such as HT with alkali or acid addition, have also shown promise in enhancing sludge biodegradability and methane production (Nahar *et al.* 2024). HT conditions significantly influence methane yield. For instance, hydrothermal treatment of WAS at 150-170 °C for 30 min resulted in a 24-59% increase in biogas production (Wilson *et al.* 2011). Similarly, treating sewage digestate at 220 °C or its liquid fraction improved the methane yield by 58% (Aragón-Briceño, Ross and Camargo-Valero 2017b).

The integration of hydrochar into AD processes further enhances biogas production. Hydrochar's porosity facilitates microbial metabolism, reduces the inhibitory effects of ammonia and fatty acids, and stabilises the AD process (Xu *et al.* 2018a; Li *et al.* 2021). However, excessive HT temperatures (≥ 170 °C) can reduce methane yields due to the formation of inhibitory Maillard reaction products (Choe *et al.* 2021). For instance, methane production decreased by 27.2% and 44.1% at 170 °C and 180 °C, respectively, compared to untreated sludge.

Direct Interspecies Electron Transfer (DIET) facilitates enhanced electron flow between microbial communities, improving the overall efficiency of AD. However, excessive hydrochar or biochar, commonly used to promote DIET, can inhibit the digestion process by altering microbial activity and substrate availability (Qi *et al.* 2021).

Valorisation opportunities are also possible with HT liquid fractions, and at high organic loads, these fractions can be managed by biological or chemical stabilisation. Energy recovery from AD of HT liquid fractions has been shown to be possible, with COD reductions of over 85% (González-Arias *et al.* 2022). Although more work is needed to

optimise methane production from these fractions, they represent a significant opportunity to move towards a zero net emission economy on an enormous scale.

2.7.3.1 The effect of VFAs and alkalinity due to HT in AD

The buffering capacity of AD systems is heavily influenced by the concentrations of VFA and alkalinity levels, which in turn affect their buffering capacity. HT also markedly stimulates the solubilisation of organic matter, increasing VFA formation, especially under alkaline conditions. For instance, thermal-alkali pretreatment has been shown to increase SCOD and VFA concentrations, thereby improving gas yields in subsequent digestion stages (Li *et al.* 2024a). However, this increase in VFA would require adequate buffering capacity to prevent a pH drop that could inhibit methanogenesis. Additionally, HT releases ammonia from organic nitrogenous compounds, promoting alkalinity and thereby increasing the system's buffering capacity.

VFAs have particular significance as direct precursors for methane production, supplying a continued substrate for methanogens. On the other hand, alkalinity is vital for neutralising the acids generated during digestion and for maintaining a pH range between 6.8 and 7.2, which supports methanogenic activity (Thompson, Young and Baroutian 2021; Qiu *et al.* 2023). The balance between VFA production and alkalinity defines their resilience and efficiency to organic loading fluctuations. The increases in biogas production resulting from HT-induced VFA increases are, however, limited by the potential for acidification and require careful monitoring of alkalinity (Sakaveli *et al.* 2024).

Stabilisation of the AD process under HT conditions can be achieved through operational strategies, including adjustments to HT conditions and the addition of alkaline agents, provided that the targeted buffering capacity can be maintained. Such an arrangement maintains efficiency and stability in bioenergy production at a sustained level. As with AD systems, the stability of digestion is indicated by VFA/TA ratios below 0.4; ratios between 0.4 and 0.8 require close monitoring; and ratios above 0.8 indicate process instability that requires action (Omine *et al.* 2021). On the other hand, VFA and alkalinity serve as complementary strategies to stabilise an AD system. Managing their interplay post-HT is critical to optimising AD for effective and sustainable bioenergy production.

The pH level is a critical parameter affecting microbial activity during AD. Extreme pH variations can inhibit essential microbial groups, particularly methanogens, disrupting the digestion process (Qiu *et al.* 2023). Maintaining an optimal pH range ensures the stability of the microbial community, enhancing biogas yield.

2.7.3.2 Pretreatment of HT sludge before use in AD

HT process water may contain inhibitory compounds such as phenols, alkoxyphenolics, furans, and ketones that hinder AD. These compounds are typically removed using organic solvents such as methylene chloride, tetrahydrofuran, toluene, ethyl acetate, acetone, ether, methanol, petroleum ether, and n-hexane. However, some of these solvents pose significant health risks (Singh *et al.* 2023b). Among the solvents tested, petroleum ether (PE) yielded the highest methane production, followed by cyclohexane (CH), dichloromethane (DM), and ethyl acetate (EA) (Chen *et al.* 2016).

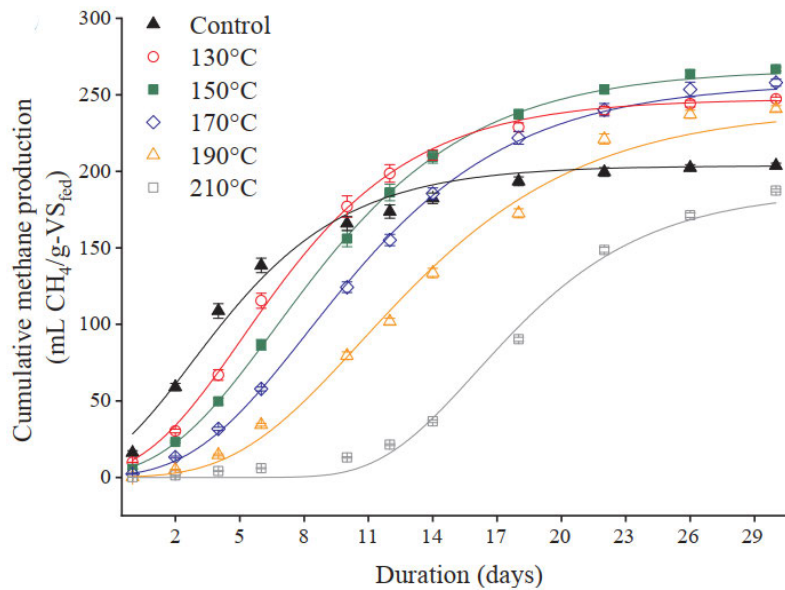


Figure 2.23 Cumulative methane production from hydrothermally (un)treated PS and the 1st AD digestate

Source: (Yuan *et al.* 2019)

Theoretical estimations of biogas production are imperative in determining the process performance of AD systems and are often derived using models like the Buswell equation (Yuen and Lau 2023) and Boyle's equation (Song *et al.* 2024). These models provide

insight into the potential methane yields from specific substrates, aiding in the optimisation of AD processes.

While AD can tolerate HT process water to a certain extent, its efficiency requires optimisation to maximise the extraction of organics (Zhou *et al.* 2024). Yuan *et al.* (2019) explored two hydrothermal treatment strategies for methane production with Strategy I (HT + AD System) having concentrated primary sludge (PS) hydrothermally pretreated at temperatures of 130, 150, 170, 190, or 210 °C for 30 min before anaerobic digestion and Strategy II (1st AD + HT + 2nd AD System) with PS being first subjected to anaerobic digestion, followed by hydrothermal treatment under the same conditions as Strategy I, with a second round of anaerobic digestion to extract additional methane.

Results indicated that all HT conditions, except 210 °C, enhanced methane yields compared to the control during the 30-day AD test (Figure 2.23). The 150 °C pretreatment produced the highest methane yield, a 31% increase over the control, followed by 170 °C (27%), 130 °C (21%), and 190 °C (18%). The 210 °C treatment exhibited a prolonged lag phase due to the dissolution or recombination of organics, which delayed methane production but showed potential for sustained biogas output.

2.7.4 Kinetic models application

Acquiring a valid kinetic model is a complex task, as the AD process is itself a complicated, multi-stage dynamic process that involves several bacterial groups. The highest level of complexity occurs when both the disintegration and hydrolysis steps are considered, which are the primary process pathways for the degradation of proteins, carbohydrates, and fats in the presence of various inhibitors. The simulation of anaerobic co-digestion of various wastes has been proposed for general compositions, simplifying the analysis. This has been demonstrated in a study where wastewater was assumed to be composed of carbohydrates, proteins, lipids, and other compounds (Xie SiHuang *et al.* 2016).

The Monod-type kinetic models have been widely used to describe the process kinetics of anaerobic digesters (Tunay *et al.* 2022). Although there has been some success in applying Monod-type kinetics to the anaerobic process, some research workers have

found it challenging to apply them to their systems. For instance, it is reported that the effluent substrate concentration, expressed as COD, was not independent of the substrate concentration entering the reactor when pure or heterogeneous cultures were used. In the model proposed by Contois, the specific growth rate was considered a function of the growth-limiting nutrient, as determined by both input and effluent substrate concentrations, using an empirical constant related to microbial concentration (Tunay *et al.* 2022). On this basis, Chen and Hashimoto developed kinetic models for substrate utilisation and methane production, suggesting that the Contois-type kinetic models would be more suitable than the Monod-type kinetic models for predicting digester performance (Zainol 2012). However, there is limited published information available on the process kinetics of AD treating ice cream wastewater using Contois-type kinetics. In view of all these, several kinetic models have been employed in the past decades for the AcoD process to present the overall biogas production. Some of these models include First-order (Lebona *et al.* 2019), Chen and Hashimoto (Lopes *et al.* 2021), dual-pool First-order and the Contois (Tunay *et al.* 2022), Monod (Tsapekos *et al.* 2018), second order and the modified Gompertz model (Lebona *et al.* 2019). However, the selection of different models to adopt in a particular study is crucial, as the relationships between these parameters and process or biological parameters are sometimes challenging to highlight. Mostly, it depends on the input variables needed. For instance, the modified Gompertz kinetic model equation is commonly used to model cumulative biogas production (Tsapekos *et al.* 2018). As crucial as they are, kinetic studies play a vital role in the design of industrial anaerobic reactors and in understanding anaerobic degradation, reactor design, and operation. The control and prediction of treatment plant operation, the optimisation of plant design and the results of scale-up pilot studies are defined within the framework of a generally accepted approach to defining specific parameters of system performance (Kovalovszki *et al.* 2017).

Elagroudy *et al.* (2020) studied methane production and hydrolysis kinetics in batch mode of non-biodegradable organic fraction from the substrate of green and air-dried corn stover to develop and determine the ultimate methane production and the hydrolysis kinetic constant. In this study, it was found that the conventional First-order hydrolysis

kinetic model failed to describe the entire hydrolysis of corn stover. This was due to the two first-order decay periods observed during the hydrolysis of corn stover used in this study. A model commonly used in the past decades to describe the AD system is the *First-order model*. In the model, it is assumed that the rate of substrate removal is proportional to its concentration (Nguyen *et al.* 2016). Some of the most widely used kinetic models are presented in Table 2.6, which outlines their advantages and disadvantages.

Table 2.6 Qualitative analysis of models

Model	Advantages	Disadvantages	References
First-order Kinetic Model	- Simple, easy to fit.	- May not account for lag phases or changing substrate pools.	(Maleki, Bokhary and Liao 2018)
Modified Gompertz Model	- Adequate for describing processes dominated by a single reaction rate. - Accounts for the lag phase, maximum production rate, and biogas potential. - Widely used in AD studies for cumulative biogas yields.	- Assumes symmetric growth, which may not align with all experimental conditions.	(Villamil <i>et al.</i> 2019; Elagroudy <i>et al.</i> 2020)
Chen & Hashimoto Model	- Explicitly designed for AD, incorporating microbial decay. - Often used for continuous systems or varying organic loading rates.	- Requires more parameters and potentially more complex fitting.	(Lopes <i>et al.</i> 2021)
Dual-pool First-order Model	- Models both rapidly degradable and slowly degradable substrate pools. - Provides a more accurate representation of heterogeneous substrates.	- Higher complexity and parameter requirements.	(Ali <i>et al.</i> 2024)

2.8 Technoeconomic evaluation for integrating bioenergy and bioresource recovery using HT.

Economic sustainability in the wastewater treatment sector is a critical factor influencing the implementation of struvite crystallisation processes. Minimising production costs is essential to enhance the competitiveness of the struvite fertiliser market. Recovering phosphorus as struvite not only reduces the chemical costs associated with conventional phosphorus removal but also mitigates expenses related to sludge disposal in landfills (Kumar and Pal 2013).

Nitrogen (N), phosphorus (P), and potassium (K) are of emphasis in the actions that certain EU member states are taking to promote nutrient recovery from waste streams. Revised regulatory frameworks, including updates in 2019, have positively impacted the economic feasibility of nutrient recovery on a larger scale (Muys *et al.* 2021). The market value of recovered struvite depends on its quality and demand, with prices ranging from \$40 to \$550/ton (Yetilmezsoy *et al.* 2017)

In another WWTP, recovering 20% of phosphorus as crystalline struvite from wastewater would generate significant annual financial savings of approximately \$640,000 (Gonzalez-Silva *et al.* 2022). As demonstrated by Le *et al.* (2020), human urine (850 mg/L phosphorus and 1830 mg/L potassium), which, when recovered, yields an economic profit of \$0.26/m³ if struvite recovery achieves 98.4% phosphorus removal and 70.5% potassium removal under optimal conditions (pH 10±0.2 and Mg/K molar ratio 1.25). Hu *et al.* (2020a) also estimated a similar amount of revenue benefit (\$4.92/m³) based on the struvite recovery at pH 9.5 from the produced water with a Mg/PO₄ molar ratio of 1:1.

Recovery of struvite is highly influenced by the cost of magnesium (Mg) sources. Commercial-grade Mg sources are costly, with prices ranging from \$1.17 to \$2.78/kg (Lahav *et al.* 2023), and can be in the form of MgCl₂•6H₂O and MgSO₄•7H₂O. A significant cost savings can be achieved by utilising alternative sources of Mg, such as seawater or locally available Mg-rich materials. For example, Rift Valley Lake's Mg sources were used to remove 97% or more phosphorus from synthetic and actual urine at less than 75% of the cost of commercial Mg sources (Guadie *et al.* 2020).

In another study, a net cash flow analysis was used to evaluate the annual and capital costs of each system, determining its profitability. Revenues, operating and maintenance (O&M) costs, and taxes were regarded as key factors. About 25-65% of a plant's total operating cost is associated with sewage sludge treatment and disposal at a wastewater treatment plant (Yesigat *et al.* 2022).

The break-even point (BP) and the IRR are critical metrics of project feasibility. The levelised cost of electricity (LCOE) assembles all annual costs into a standard unitary cost

(\$/kWh) for a more rounded overview of energy technology economics (Green and Southard 2019).

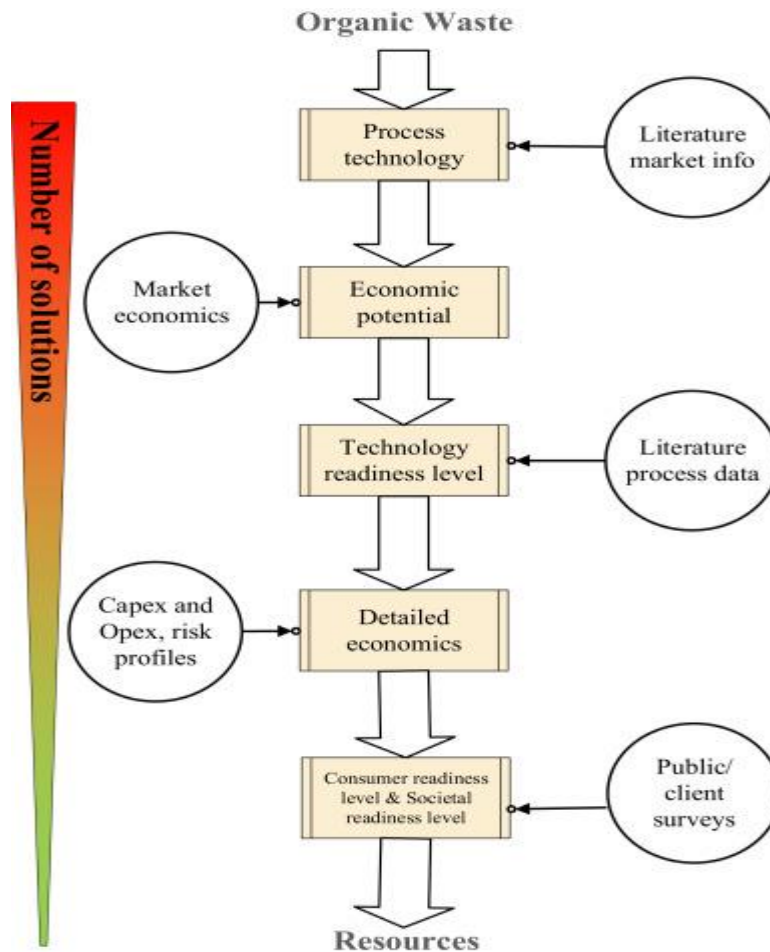


Figure 2.24 Technoeconomic guideline for assessment of resource recovery potential of hydrothermal processing.

Source: (Munir *et al.* 2018)

The analysis of sensitivity to variables such as discount rates, electricity prices, project lifetime, and tax credits on financial parameters, including NPV, BP, IRR, and LCOE, should be prioritised for decision-making purposes (Kassem *et al.* 2020). When one variable is changed, keeping others constant, its contribution to the overall financial outcome is noted.

Sewage sludge contains many recoverable resources, including nutrients (phosphorus, nitrogen, and potassium), organic substances, and inorganic materials that can offset

plant operating costs. A technoeconomic assessment framework for assessing resource recovery potential through hydrothermal processing, based on technoeconomic and mass balance calculations, is illustrated in Figure 2.24. Its path is from process technology and economic potential to technological instrumentality, detailed economics (including capital expenditure (CAPEX), operating expenditure (OPEX), and risk), and societal readiness levels.

Despite promising bench-scale and pilot results, scaling hydrothermal and nutrient recovery technologies to full-scale operation remains constrained by technological and economic challenges. Capital-intensive reactor designs, energy demands for high-temperature operations, and complex heat integration often increase CAPEX and OPEX, limiting adoption in resource-constrained utilities (Yesigat *et al.* 2022; Rojas *et al.* 2025). Additionally, chemical dependencies, particularly the reliance on commercial-grade magnesium salts, create supply chain and cost barriers that undermine profitability (Lahav *et al.* 2023). Process scalability is further limited by operational uncertainties, such as reactor hydrodynamics, fouling control, and sludge heterogeneity, which impact throughput and system stability.

Economic scalability also depends on market readiness for recovered products, such as struvite, where inconsistent purity, a lack of regulatory certification, and low farmer awareness hinder demand (Muys *et al.* 2021; Soo and Shon 2024). To overcome these barriers, studies recommend modular pilot systems integrated into existing WWTPs, recovery of waste heat from anaerobic digestion, and policy incentives or subsidies to offset capital costs and stimulate recovered nutrient markets (Kassem *et al.* 2020; Gonzalez-Silva *et al.* 2022). Broader adoption will therefore require combined process optimisation, industrial symbiosis, and supportive governance frameworks, ensuring scalability from laboratory innovation to commercial implementation.

2.9 The life cycle assessment of integrating HT, resource recovery and AD.

LCA is a full methodology that deals with the evaluation of the environmental impact of a product, process or activity during its entire life cycle (raw material extraction, end-of-life disposal) (Cremiato *et al.* 2018). LCA quantifies resource utilisation, emissions, and waste outputs, enabling the identification of environmental hotspots in waste management systems and informed decision-making.

The concept of LCA originated in the 1960s and 1970s, initially from energy studies, and has since evolved into a broader framework encompassing resource use, emissions, and waste implications. By the 1980s, the methodology had reached maturity and was used to analyse whole product life cycles, with applications in various industries, such as waste management, construction, and energy systems (Lucchetti *et al.* 2019).

HT, resource recovery, and AD can be advantageously integrated for sustainable wastewater management. Nutrient solubilisation and reduction in sludge complexity are improved via the hydrothermal treatment of sludge, enabling downstream nutrient recovery by struvite precipitation and energy production through AD. This approach also addresses the primary environmental issues, including eutrophication, resource depletion, and GWP (Ayodele, Ogunjuyigbe and Alao 2017; Cremiato *et al.* 2018; Kumar and Samadder 2022).

To match the requirements for a coherent classification of environmental impact categories, a robust framework for a life cycle impact assessment (LCIA) procedure should be developed, as shown in Figure 2.25. The categories proposed in this framework were identified by Khoshnevisan *et al.* (2020); Paes *et al.* (2020); Rebello *et al.* (2020). A proposed framework for a South African LCIA is outlined in Figure 2.25, in which life cycle inventory data are linked with classified environmental impact categories, sub-resource groups, and primary resource groups. This system is a structured method for evaluating the environmental effects of resource use and exhaustion.

The category of impacts is classified into five areas: water resources, air resources, land resources, mined resources, and energy reserves. For instance, for water resources, this includes both water use (surface and groundwater) and water quantity. For water quality,

this encompasses eutrophication potential and acidification potential. Regional and global air quality impacts are considered via photochemical ozone creation and GWP. Regional and global air quality impacts are considered via photochemical ozone creation and GWP.

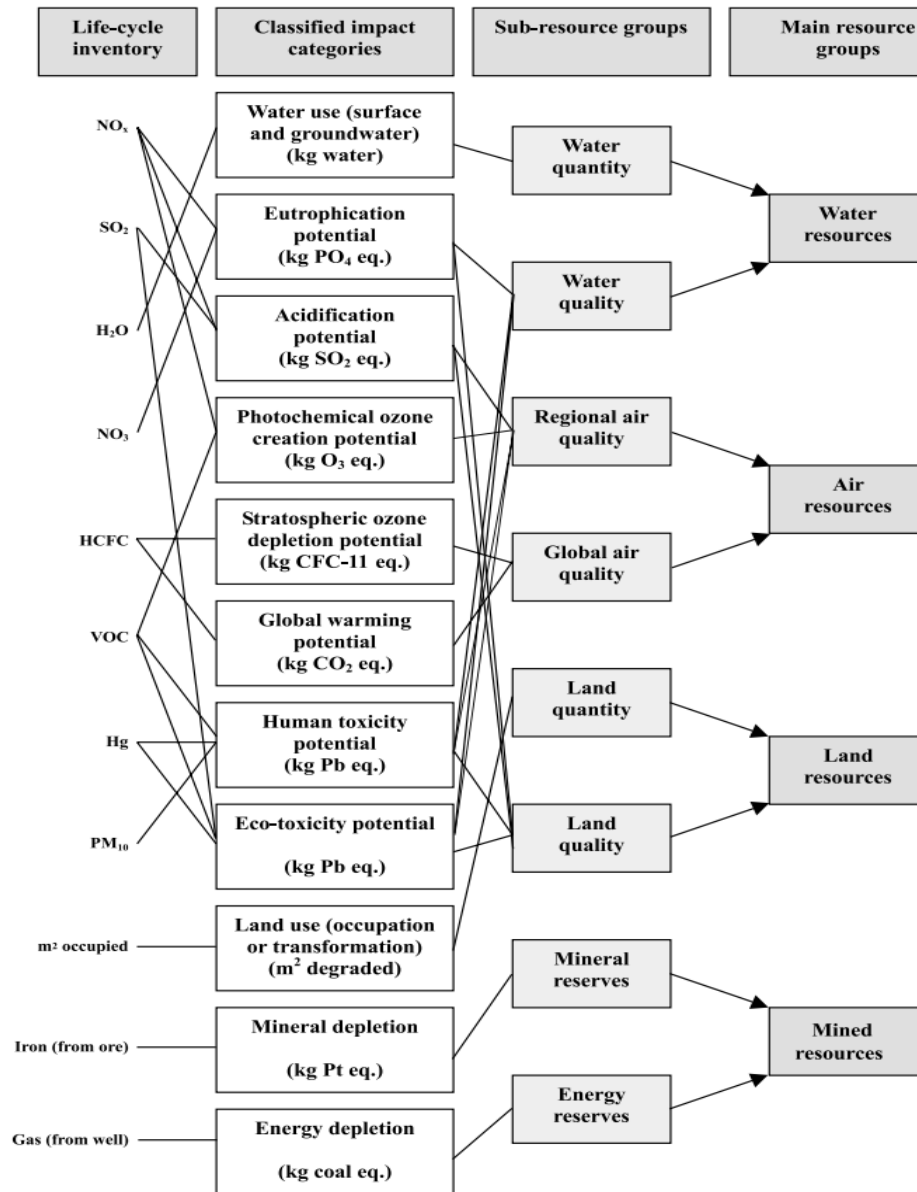


Figure 2.25 Proposed framework for a South African LCIA procedure

Source: (Brent 2003)

Land resources are divided into land quantity and quality, addressing aspects like land use and ecotoxicity potential. Resource depletion is represented by the depletion of

energy reserves, highlighting the environmental costs associated with the extraction of minerals and energy (Sheydaei, Nabi and Yazdian 2024).

This framework integrates environmental categories relevant to South African contexts, promoting a comprehensive evaluation of the life cycle impacts of various processes and products. It emphasises the interconnectedness of resource use and environmental degradation while supporting the development of regionally appropriate sustainability strategies.

2.10 Design of Experiments

The design of experiments (DOE) is a systematic methodology for exploring the relationships between input variables (factors) and output responses to optimise a process. Response Surface Methodology (RSM) has demonstrated its effectiveness in optimising WTPs (Tariq, Maqbool and Abbas 2021).

The number of experimental runs (N) required is calculated using Equation 2.37.

$$N = f^2 + f + q \quad 2.37$$

Where f is the number of input variables, and q is the replicate number of the central point. Independent variables, such as temperature and reaction time, were normalised to values of -1 (low), 0 (central), and +1 (high), as shown in Equation 2.38.

$$y_i = \frac{Max - Min}{2} + Y_i \frac{Max - Min}{2} \quad 2.38$$

Where Max is the uncoded high level, and Min is the uncoded low level of the variable. Y_i and y_i are the actual (uncoded) value of the variable being studied and the coded value of the variable after transformation, respectively.

A regression model (Equation 2.39) is crucial in the optimisation of HT processes and can be developed using experimental data, which can then validate the optimised results experimentally (Esfandiar, Nasernejad and Ebadi 2014).

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \quad 2.39$$

Where Y is the output response, β is the regression coefficient, X_i is the independent factors (1,2,3 are input variables), and the constant β_0 is the response of Y when all main effects are 0.

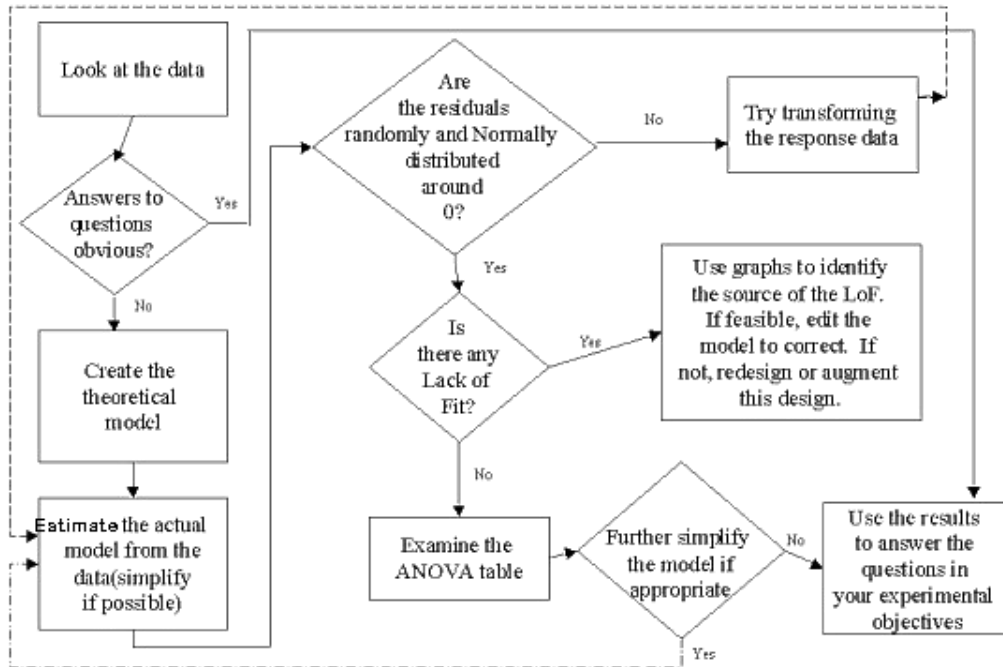


Figure 2.26 Flowchart of DOE analysis steps

Source: (NIST 2025)

The DOE has a systematic approach to arriving at the final optimisation solution, which must be followed step by step for favourable results. The DOE methodology follows a structured flowchart (Figure 2.26).

The key step in DOE analysis is Data Examination, which involves initial data analysis and includes identifying anomalies and generating response distribution graphs (e.g., histograms, box plots, scatter plots). Model Fitting is a critical step, as it helps develop theoretical frameworks and simplify models using stepwise regression or assessing parameter significance (p-values). Residual plots are used to validate model assumptions. Analysis of variance (ANOVA) is crucial because it identifies significant factors that contribute to the variation in the data. Adjustments or transformations are

made as needed. Finally, optimisation is conducted using the validated model to determine optimal conditions, addressing experimental objectives such as factor significance and response maximisation.

There is a host of RSM types, such as central composite design (CCD), Box-Behnken Design (BBD), Three-Level Factorial Design, Optimal Designs, Doehlert Design, Taguchi Method for RSM, Hybrid Designs and Plackett-Burman Designs for Screening (Montgomery 2017). However, the CCD and BBD are more prominent, especially in waste management systems, and these are discussed in Table 2.7 (Li, Lu and Gao 2021). Each design is more suitable for a specific type of experiment and depends on the goals, limitations, and number of factors involved.

Table 2.7 Comparison of the CCD and BBD

Design	Advantages	Disadvantages
Central Composite Design (CCD)	• Flexibility - Flexible in fitting both factorial and star points and applying for efficient estimation of linear, interaction and quadratic effects. • Rotatability - This can be designed to be made rotatable so that prediction variance has a uniform value at equal intervals from the middle point. • Sequential Experimentation - Allows the supplementation of the existing factorial plans with other points.	• Extended Factor Levels - This may require factor levels that exceed the range of values observed in the experiments, potentially leading to an impractical or hazardous situation. • Increased Runs - In the case of a high number of factors, the number of experimental runs may be relatively large. • Rigid Data Collection - With the need for a structured approach to collection points, they can be rigid and do not have to be feasible.
Box-Behnken Design (BBD)	• Efficiency - As a rule, it needs fewer experimental runs than CCD, at least at three and four factors. • No Extreme Combinations - It does not cover the confirmations where all factors are set at their highest or lowest levels, thus minimising the experiments to the worst conditions possible. • Rotatability - Almost commensurate with rotation; capable of yielding evenly matched prediction performance across the resolution of the design space.	• Limited Factor Levels - The design employs three levels for each factor, which can be limiting, particularly if the system under study exhibits more than simple nonlinearities. • Poor Corner Coverage - No experimental points placed at the vertex of the design space may exclude certain information regarding the interaction of factors at their 'extreme' settings. • Prediction Quality - Some regions have lower prediction accuracy than others.

Researchers must weigh the experiment's goals, the number of factors to be studied, and the practicality of the number of runs that can be carried out. CCD allows for adjunct

definitions of factor levels, providing greater flexibility when dealing with a wide range of factor levels in complex models, with the potential for an increased number of runs and extended factor levels. On the other hand, the performance of BBD is more efficient in terms of the number of runs and the intensity of experimental conditions; however, the levels of factors and no-cover elements restrict the degree of interaction among factors.

2.11 Chapter summary

The role of waste-activated sludge (WAS) in sustainable wastewater management and HT of WAS as a transformative resource recovery approach was critically examined in this literature review chapter. It investigated the physicochemical properties of WAS with an emphasis on bioenergy and nutrient recovery, especially phosphorus. An analysis was conducted to examine how key operating parameters of HT (temperature, pH, and pressure) affect biogas production, nutrient solubilisation, and heavy metal removal. The chapter also discussed the limitations established by inhibitory by-products, including phenolic compounds and melanoidins and optimisation strategies for enhancing process efficiency. In addition, the environmental implications of WAS management, including phosphorus recovery, toxicity, and heavy metal issues, were reviewed to demonstrate the importance of an integrative use of advanced technologies and regulatory frameworks. This provides a basis for understanding the opportunity for HT to support the realisation of circular economy goals through effective WAS valorisation.

CHAPTER 3: OPTIMISATION OF HYDROTHERMAL TREATMENT PARAMETERS FOR ENHANCED VALORISATION OF WASTE-ACTIVATED SLUDGE

3.1 Introduction

The purpose of this chapter is to provide a quantitative analysis of the data collected to optimise HT parameters for waste-activated sludge (WAS) from the local WWTP. The overall objective is to select operating conditions that maximise resource and energy recovery. In this chapter, a thorough analysis was conducted based on temperature, reaction time, pressure, and HT performance, which revealed a robust basis for further development in the valorisation of WAS to bioenergy and bioresources.

Valorisation of WAS based on HT processing is a pivotal method, as HT can enhance the solubilisation of nutrients and decompose complex organic matter (Park *et al.* 2019b; Pham *et al.* 2021). HT accelerates chemical reactions in a water-saturated environment, degrading the organic matrix into more bioavailable forms by subjecting WAS to elevated temperatures and pressures. The solubilisation allows nutrients, such as phosphorus and nitrogen, to be recovered and enhances the biodegradability of organic matter for subsequent processes such as AD. The treatment further reduces sludge volume, enabling the achievement of cost-effective and environmentally sustainable sludge treatment. Due to these attributes, HT has gained traction as an optimal choice for valorising the WAS in valuable bioenergy and bioresources.

The study focuses on the optimisation of the two critical operating conditions, temperature and reaction time, which define the efficiency of HT. However, changes in pH and pressure behaviour were also noted after each reaction cycle. The kinetics of organic matter decomposition and solubilisation of nutrients are influenced by temperature and the pressure (autogenous), which maintains water in a subcritical state for effective reaction pathways. The amount of solubilisation and stabilisation of the sludge components is also heavily dependent on the reaction time. The study seeks to systematically vary these parameters and identify conditions that maximise energy yields and nutrient recovery, keeping other inhibitory by-products to a minimum.

The benefits of HT are well aligned with the objectives of this research. The suitability of this technology results from its capacity to improve the bioavailability of nutrients such as phosphorus, reduce sludge volume, and improve biogas production in downstream AD processes. Furthermore, HT is characterised by the production of valuable by-products, in particular hydrochar and process water, that also offer further resource recovery potential. This is directly applicable to traditional sludge management problems, and these benefits directly address the challenges faced by the local WWTP under scrutiny.

Knowledge of calorific value, which enables quantification of the energy potential of WAS, forms a central component of the optimisation of HT. This value depends on the elemental composition, and to determine it, the focus will be on the carbon and hydrogen content.

3.2 Methodology for HT optimisation

HT experiments were performed using a 100 mL Teflon-lined stainless steel hydrothermal reactor (HTR) with an inner diameter of 6 cm and a height of 12 cm (Intelligent Magnetic Heating Stirrer, Shanghai, China), as depicted in Plate 3.1. The reactor's operational thresholds included a maximum pressure of 6 MPa and a maximum temperature of 240°C. The system comprised a reactor body, a heating mantle, and a steam condenser.



Plate 3.1 Hydrothermal reactor used for the pretreatment process.

Each experimental run involved charging 80 mL of waste-activated sludge (WAS) into the reactor. To remove residual oxygen, nitrogen gas was purged through the reactor for 3 min before sealing (Wang *et al.* 2021b). An intelligent agitator, rotating at 160 rpm, ensured uniform mixing of the reactor contents throughout the process.

The experiments were conducted in duplicate to ensure reproducibility, and relative errors of measured variables were recorded. At the end of each reaction, the process was halted by quenching the reactor in a water bath. Once cooled to room temperature, the treated sludge was subjected to physicochemical analyses.

Following treatment, each sludge sample was centrifuged in a 50 mL tube at 5000 rpm for 10 min to separate the liquid and solid phases. The supernatants, representing the liquid sludge phase, were collected. To obtain a soluble organic solution, the hydrothermally treated sludge mixture was filtered through a 0.45 µm nylon filter.

3.2.1 Design of Experiments

Optimisation was carried out using a central composite design (CCD) within the framework of RSM, facilitated by Design Expert software (Version 13, Stat-Ease, Inc., Minneapolis, MN, USA). The thermal pretreatment process was optimised through a full factorial design to evaluate the effects of two independent variables, temperature and residence time, on the solubilisation of COD from waste-activated sludge (WAS). Additional response variables analysed included changes in protein, carbohydrate, phosphate, and ammonium concentrations, as outlined in Table 3.1. Soluble COD (SCOD) was considered the primary response variable in accordance with Zhou, Meshref and Dhar (2021). The input factors were temperature, ranging from 150°C to 230°C (Park *et al.* 2019b; Chen, Dai and Dong 2022) and residence time, ranging from 20 to 70 min (Park *et al.* 2019b). The experiments were conducted in duplicate, resulting in a total of 27 runs, with the average results presented in Table 3.1.

This structured design enabled a systematic evaluation of the process variables, providing the basis for identifying optimal operating conditions for HT. Design Expert software was utilised for regression analysis, ANOVA, and optimisation, as well as for

advanced data visualisation. The software's features were instrumental in determining significant interactions and establishing the predictive model.

3.2.2 Sample analyses

Following each hydrothermal treatment run, samples were collected and analysed. The methods used ensured the consistency and reliability of evaluating the physicochemical properties of treated waste-activated sludge in accordance with Standard Methods (APHA 2017).

3.2.2.1 General characterisation

The valorisation of sewage sludge through HT for improved solubilisation was conducted using waste-activated sludge (WAS) samples collected from a local WWTP treating domestic and industrial wastewater. The plant employed primary sedimentation and a trickling filter as pretreatment for a fraction of the wastewater, followed by activated sludge aeration tanks with fine bubble diffusion. WAS was collected directly from the underflow of the secondary settling tank, which is responsible for dewatering. Samples were stored in air-tight 20 L containers, transported to the laboratory, and analysed for initial parameters within 3 h of collection. General characteristics, including pH, conductivity, and COD, were determined on the day of collection. To ensure consistency and sample freshness, WAS samples were collected monthly and stored at 4°C until experimentation.

The aqueous phase of the samples was analysed using standard methods (APHA 2017). Key characteristics assessed included TS, VS, COD, TOC, total organic nitrogen (TON), phenolic compounds, acetate, propionate, butyrate, sodium, ammonium, potassium, magnesium, calcium, and phosphate, among others. The pH of the sludge and solvents was measured using a calibrated pH meter (Lovibond SensoDirect 150, Germany). Adjustments were made as required using 1 N sodium hydroxide (NaOH) or 1 N hydrochloric acid (HCl). Chemicals and reagents were sourced from Sigma-Aldrich (St. Louis, MO, USA) unless otherwise specified. Conductivity, TDS, salinity, and dissolved oxygen were determined using a handheld multiparameter water quality monitoring instrument, the YSI 556 Multi-Probe System (YSI Inc., Yellow Springs, OH, USA). This

systematic approach ensured the accurate characterisation of the sludge and its aqueous phase for subsequent HT experiments.

3.2.2.2 Physicochemical properties

The physicochemical properties of the samples were analysed following the Standard Methods (APHA 2017). TS, VS, TSS, and VSS were determined using standard procedures. TOC content was measured with TOC TNTplus Vial Test, HR (30–300 mg/L C), 25 Tests (Hach Company, Loveland, CO, USA), and a calibrated DR 3900 Spectrophotometer (Hach Company, Loveland, CO, USA).

COD analysis was conducted on both the particulate and soluble fractions. Total COD (TCOD) was measured for the particulate fraction, while soluble COD (SCOD) was determined using filtrates passed through 0.45 µm nylon filters. High-range TNT822 COD TNTplus Vial Tests, HR (Hach Company, Loveland, CO, USA) were employed. Samples were digested at 150°C for 120 min using a DRB200 Digital Reactor Block, 2-Block Model (Hach Company, Loveland, CO, USA). Each sample was run against a blank prepared with distilled water (purity of 18.2 MΩ·cm) to ensure accuracy and consistency. Sample dilutions were performed as required to comply with the concentration limits of the kits and the spectrophotometer. Measurements were conducted at ambient temperature, and results were recorded systematically. Particulate COD was calculated as the difference between TCOD and SCOD.

Biochemical oxygen demand over five days (BOD₅) was measured using the OxiTop® Measuring System (WTW GmbH, Weilheim, Germany), which operates on pressure difference through piezoresistive electronic pressure sensors. Appropriate dilutions were made to prevent oversaturation and ensure accurate results. A blank sample was used as a reference during all measurements. Results were recorded for subsequent analysis.

3.2.2.3 Proximate and ultimate analysis

The sludge from the waste-activated sludge (WAS) stream and other streams was settled and filtered, and the residue was dried in an oven at 105°C overnight in preparation for elemental composition analysis (CHNS/O). Elemental analysis was conducted using a PerkinElmer 2400 Series II CHNS/O Elemental Analyser (PerkinElmer Inc., Waltham,

MA, USA), with cysteine as the calibration standard. Two milligrams of each sample were measured before analysis. The oxygen content was calculated by subtracting the sum of carbon, hydrogen, nitrogen, sulphur, and ash percentages from 100% (Rahman *et al.* 2021).

Ash content was determined separately using ceramic crucibles. The crucibles were pre-ignited in a muffle furnace at 600°C for 1 h, cooled in a desiccator for 1 h at room temperature, and weighed. Approximately 0.5 g of the dried sludge sample was placed in a crucible and heated in a muffle furnace at 600°C for 1 h, or until a whitish-grey ash was obtained. After cooling the furnace to 200-300°C, the crucibles were transferred to a desiccator to cool to room temperature, and then they were weighed again (APHA 2017). The ash content was calculated using Equation 3.1.

$$\% \text{ Ash} = \frac{m_{ash}}{m_{sample}} \times 100\% \quad 3.1$$

where m_{ash} = mass of the ashed sample (in grams); m_{sample} = mass of the sample only (in grams).

An analytical balance with a precision of four decimal places was utilised for all measurements to ensure accuracy. This methodology ensured precise determination of elemental composition and ash content, which is critical for subsequent analyses.

3.2.2.4 Nutrients determination

Ammonium, orthophosphates, total organic carbon (TON), nitrates and nitrites were determined using a Gallery Automated Photometric Analyser (Thermo Fisher Scientific, Waltham, MA, USA). The samples were first filtered to a pore size of less than 0.45 µm, and necessary dilutions were made and recorded.

3.2.2.5 Sequential phosphorus extraction

Sequential phosphorus extraction was performed to fractionate and quantify different forms of phosphorus (P) in sewage sludge, following a modified protocol (Hedley, Stewart and Chauhan 1982; Pokhrel *et al.* 2018). Approximately 1 g of dried sample was sequentially extracted with 20 mL of progressively stronger reagents in 50 mL polypropylene centrifuge tubes. The steps included: (1) deionised water for readily

soluble, bioavailable P ($\text{H}_2\text{O-P}$); (2) 0.5 M NaHCO_3 (pH 8.2) for weakly sorbed organic and inorganic bioavailable P ($\text{NaHCO}_3\text{-P}$); (3) 0.1 M NaOH for strongly sorbed, potentially bioavailable P (NaOH-P); (4) 1 M HCl for non-bioavailable apatite or calcium-bound P (HCl-P); and (5) the residual fraction representing non-bioavailable P (Residual-P). Each step involved shaking at 150 rpm for 16 hours at 25°C , followed by centrifugation at 5000 rpm for 10 minutes, and then filtering the supernatant through a $0.45\ \mu\text{m}$ or equivalent filter. All extractions were performed in duplicate.

Total phosphorus (TP) was determined by combining filtrates and digesting them with acid persulfate to convert all P forms to orthophosphate, followed by colour development using a molybdate-ascorbic acid reagent. Absorbance was measured at 880 nm using a spectrophotometer (APHA 2017; Phansi *et al.* 2022). Inorganic P (IP) was calculated as the sum of $\text{H}_2\text{O-P}$, $\text{NaHCO}_3\text{-P}$, NaOH-P , and HCl-P , while organic P (OP) was obtained by subtracting IP from TP. This method provided detailed P speciation, including bioavailable and non-bioavailable fractions, to characterise phosphorus dynamics in the sludge. Phosphatases are found on the surface of human skin; therefore, gloves must be worn every time to avoid sample contamination (Iammarino *et al.* 2020). Unless noted otherwise, phosphate units are reported by the instrument as PO_4^{3-} . To convert to phosphorus as P, the result is multiplied by 0.327

3.2.2.6 Macromolecules

Proteins

Various streams' samples were tested for protein concentration using the Biuret test, which employs the formation of a violet-coloured complex when Cu^{2+} reacts with peptide bonds in alkaline conditions. Bovine serum albumin (BSA) standard solutions (0.2, 0.4, 0.6, 0.8 and 1.0 mg/mL) were prepared by diluting stock BSA with distilled water, and an unknown sample was similarly dissolved. To each test tube in the series, 2 mL of standard or unknown solution and 2 mL of 1% CuSO_4 solution were added, and then the mixtures were gently mixed. Then, 2 mL of a 2% NaOH solution was added to all the tubes to create an alkaline environment, and the tubes were gently swirled to mix.

In the reaction mixtures, the violet-coloured complex was allowed to form by incubating at room temperature for 10-15 min. A blank solution (2 mL of distilled water, 2 mL of 1% CuSO₄, and 2 mL of 2% NaOH) was used in a spectrophotometer at 540 nm for calibration (Appendix B). All BSA standard solutions and the unknown sample were recorded for absorbance readings. The absorbance values of the BSA solutions were plotted against their known concentrations to form a standard curve. The absorbance of the unknown sample was compared to the standard curve by interpolation, and the protein concentration of the unknown sample was determined using the necessary multipliers.

Carbohydrates

Carbohydrate concentration was determined by the phenol-sulphuric acid method (Biswal *et al.* 2020). A tightly sealed container was used to store 5 g of phenol dissolved in 100 mL of distilled water (1.25 % w/v) as a phenol solution. The standard was sodium alginate (Merck, 9005-38-3), used for calibration purposes. Sodium alginate is an acidic polysaccharide that has a negative charge at a pH of 4.0 (Zhang, Sheng and Yu 2008). Carbohydrate-containing material was prepared by transferring 1 mL of well-mixed material into test tubes. For soluble carbohydrates (after filtration with a 0.45 µm filter), 0.5 mL of the sample was added, followed by 0.5 mL of the phenol solution. It was mixed and allowed to stand at room temperature for 5 min. In addition to the above, the test tubes were heated in a water bath at 90 °C for 10 min to determine total carbohydrates.

In this case, 2.5 mL of concentrated sulphuric acid was added carefully into each test tube. Mix gently and allow to cool to room temperature. Absorbance was measured at 490 nm with a blank (phenol-sulphuric acid reagent and distilled water) as the reference. Standard solutions with known carbohydrate concentrations were prepared and treated identically to the samples to create a calibration curve (Appendix B). A standard curve was formed by plotting the absorbance of these standards versus their concentrations. Interpolating their absorbance values against the calibration curve enabled the computation of sample concentrations of carbohydrates.

3.2.3 Solubilisation of sludge

The solubilisation of components was calculated to evaluate the efficiency of hydrothermal treatment. All analyses were performed in accordance with the Standard Methods for the Examination of Water and Wastewater (APHA 2017). Equations 3.2 to 3.4 were utilised to determine the solubilisation percentages for COD, VSS, and TSS, respectively. These parameters were critical for assessing the solubilisation effects induced by hydrothermal treatment.

$$COD \text{ Solubilisation (\%)} = \frac{SCOD_{HT} - SCOD_{WAS}}{TCOD_{WAS}} \times 100 \quad 3.2$$

$$VSS \text{ Solubilisation (\%)} = \frac{VSS_{WAS} - VSS_{HT}}{TSS_{WAS}} \times 100 \quad 3.3$$

$$TSS \text{ solubilisation (\%)} = \frac{TSS_{HT} - TSS_{WAS}}{TSS_{WAS}} \times 100 \quad 3.4$$

In these equations, the subscripts "HT" and "WAS" refer to hydrothermally treated samples and untreated waste-activated sludge (WAS), respectively. The calculations were fundamental in quantifying the extent to which hydrothermal treatment enhanced the solubilisation of organic and suspended matter.

3.2.4 Physical properties after HT

Filterability was assessed using a vacuum filtration set-up. A 50-mL sludge sample was placed in a filtration funnel lined with pre-weighed qualitative filter paper (pore size: 30–50 μ m). A vacuum pump was used to draw the liquid through the filter, and the time it took for 50 mL to pass through the paper was recorded using a stopwatch. The filtration rate was calculated using Equation 3.5.

$$Filtration \text{ rate (mL/min)} = \frac{\text{Volume of filtrate collected (mL)}}{\text{Time taken to collect the filtrate (min)}} \quad 3.5$$

The bulk density of the sludge was measured by determining its mass and volume. A known mass of sludge (m) was gently transferred into a pre-measured cylindrical container of known volume. The bulk density (ρ) was calculated using Equation 3.6.

$$\rho = \frac{m}{V} \quad 3.6$$

where m represents the dry mass of the sludge (kg) and V is the volume of the sludge (m³).

The container was weighed before and after filling to ensure accurate mass measurement. All measurements were performed at room temperature, and the sludge was handled to minimise moisture loss during the procedure.

The specific heat capacity (C_p) of sewage sludge was determined using a simple calorimetric set-up consisting of an expanded polystyrene cup outfitted with a digital temperature probe and a heater of known power consumption. The experiment was conducted under controlled conditions, with draft shields in place to minimise heat exchange with the external environment. A control experiment using water was performed first, leveraging its known specific heat capacity (4.18 J/g°C) at room temperature to validate the methodology (Qasem *et al.* 2023).

For the sludge sample, 100 mL (mass was determined from density measurements) of the liquid sewage sludge was placed in the polystyrene cup, and the heater was operated at a constant power (250 W) for 2 min. The change in temperature (ΔT) of the sludge was recorded using the digital temperature probe. The heat energy supplied (Q) during this period was calculated using Equation 3.7.

$$Q = P \times t \quad 3.7$$

where 't' is the heating time in seconds.

The specific heat capacity of the sludge ($C_{p, \text{sludge}}$) was then calculated using Equation 3.8.

$$C_{p, \text{sludge}} = \frac{Q}{m \cdot \Delta T} \quad 3.8$$

where Q represent heat energy supplied by the heater (J), m is the mass of the sludge sample (g), and ΔT is the temperature change of the sludge (°C).

The heat absorbed by the polystyrene cup itself was accounted for by subtracting the energy absorbed by the cup, which was determined using its specific heat capacity (C_p , polystyrene) and mass, from the total heat supplied. This adjustment ensured that the calculated C_p of the sludge reflected only the thermal properties of the sludge sample.

Scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM-EDS) (Zeiss Ultra Plus FEG SEM, Germany) was used to further investigate the adsorption mechanism and determine the surface morphology characteristics of the samples. Surface functional groups were detected using FTIR (ATR-FTIR: Agilent Cary 630, Santa Clara, CA, USA) with a wavenumber range of 400-4000 cm^{-1} and a resolution of 0.96 cm^{-1} . XRD analyses for crystalline phase determination were performed in a 2θ range from 3° to 90° , with a step width of 0.01° , a scan speed/duration time of 30.00 $^\circ/\text{min}$, and a time speed of 0.2 seconds per step, using PXRD (MiniFlex600, Rigaku, Tokyo, Japan). The XRD spectra in this research were also compared with those from the International Centre for Diffraction Data (ICDD).

3.2.5 Hydrochar yield

The sludge was filtered both before and after the hydrothermal treatment. The residue obtained from the filtration process was dried at 105°C for 24 h, and the mass yield was subsequently recorded. The yield of hydrochar was quantified as the mass of hydrochar (in grams) produced per litre of sludge (Aragón-Briceño, Ross and Camargo-Valero 2017a).

The higher heating value (HHV) of the fuel, based on its elemental composition (C, H, N, O, S), was calculated using the modified Dulong's formula, which is widely used for biomass and sludge analysis, as shown in Equation 3.9 (Seah *et al.* 2024).

$$HHV(\text{MJ/kg}) = 0.3491C + 1.1783H - 0.0151N + 0.1005S - 0.1034O - 0.0211 \text{ Ash} \quad 3.9$$

Where C, H, N, S, and O are the mass fractions (% w/w) of carbon, hydrogen, nitrogen, sulphur and oxygen, respectively, in the sample. The percentage composition (by weight) of ash in the dry sample was also taken into consideration. The coefficient for ash (-0.0211) accounts for its non-combustible nature, which reduces the overall energy

content of the fuel. XRD, FTIR and SEM-EDS analysis were performed as described in Section 3.2.4.

3.3 The effect of input factors on the output responses

3.3.1 Influence of temperature and reaction time on response factors

Temperature is a key parameter in HT operations, significantly affecting the solubilisation of organic matter, nutrient release, and the disintegration of complex organics. Table 3.1 illustrates an improvement in the SCOD, a critical indicator of the degradation of organic polymers into simpler, soluble compounds, resulting from an increase in temperature between 150 °C and 230 °C. Such a range of temperatures has been demonstrated to trigger an SCOD rise of up to 200 %, thus demonstrating a gradual degradation of the recalcitrant organic matter into forms more convenient for subsequent processes such as AD (Park *et al.* 2019b). Along with the SCOD increase, the release of nutrients, particularly phosphorus and nitrogen derivatives, as organic matrices containing these elements is broken down under hydrothermal conditions.

Hydrothermal conditions at high temperatures facilitate essential reactions that enhance the degradation of organic matter and promote the recovery of nutrients. At higher temperatures, decarboxylation reactions are predominant, indicating that the carboxyl groups from organic molecules are removed to form volatile organic acids and gases, such as carbon dioxide (Ischia and Fiori 2021).

Solubilisation of organic matter and nutrient fractions in WAS is strongly influenced by their retention time during HT. Extended retention times facilitate the breakdown of complex organic compounds while simultaneously enhancing the solubilisation of constituent proteins and carbohydrates. The levels of SCOD and VFAs are altered, which are essential intermediates in subsequent AD processes.

Studies have shown that increasing the retention time to a certain threshold confers higher SCOD and VFA concentrations. Kakar *et al.* (2020) found that at 170 °C, the solubilisation of COD increased with retention times up to 30 min, with a solubilisation

rate of 48%; beyond this, solubilisation saturated. Similarly, Kakar, Tadesse and Elbeshbishy (2022) observed a significant increase in solubilisation (3 to 31%) when HT was applied at temperatures between 150 and 270 °C, indicating the importance of temperature and residence time on solubilisation efficiency.

Table 3.1 Hydrothermal treatment experimental matrix with input factors and output responses

Run	Temp (°C)	Time (min)	Pressure (MPa)	pH in	pH out	SCOD	PO ₄ -P	NH ₃ -H	Proteins	Carbohydrates
1	185	45	1.15±0.07	6.95	5.50±0.01	5376±171	142.2±2.1	142.01±7.46	7266±292	2383±80
2	220	70	4.33±0.11	6.03	5.21±0.04	4737±108	111.6±1.8	244.68±1.71	6671±465	1964±132
3	231.063	45	4.80±0.14	6.95	6.06±0.03	5188±112	121.3±2.8	207.87±3.21	7787±220	2314±109
4	150	20	0.52±0.04	6.95	6.05±0.03	3520±136	100.8±1.8	42.12±2.78	4984±292	1703±107
5	138.937	45	0.40±0.02	6.95	6.27±0.03	3122±103	94.0±1.2	24.14±3.90	4562±285	1138±106
6	185	45	1.15±0.07	6.95	5.50±0.03	5309±123	142.9±2.1	140.15±3.17	6993±273	2345±94
7	220	70	4.28±0.04	6.03	5.76±0.08	4669±204	92.7±2.4	232.68±3.52	6547±357	1951±151
8	185	45	1.16±0.03	6.95	5.52±0.04	5337±131	144.7±1.6	145.88±2.95	6795±261	2371±79
9	150	20	0.50±0.04	6.95	6.11±0.03	3528±109	120.1±1.3	42.88±1.22	4835±250	1703±87
10	185	77.9	1.08±0.04	6.03	4.48±0.03	6509±834	155.0±3.4	152.17±2.61	8431±1106	2409±321
11	185	45	1.15±0.07	6.95	5.56±0.02	5292±128	143.2±1.3	148.38±4.47	6646±248	2352±89
12	220	70	4.37±0.09	6.03	5.51±0.17	4750±146	99.8±4.3	248.39±1.34	6323±329	1900±86
13	220	70	4.29±0.06	6.03	5.61±0.02	4832±124	92.3±2.0	246.68±2.55	6621±389	1977±104
14	220	20	3.73±0.18	6.03	6.02±0.01	7951±136	169.2±2.1	172.11±2.23	11383±476	3502±97
15	150	20	0.49±0.03	6.95	6.14±0.03	3544±122	115.3±4.0	45.25±1.88	4934±339	1710±53
16	220	20	3.63±0.04	6.03	6.01±0.01	7725±134	182.9±2.3	169.95±2.16	10986±417	3457±130
17	150	70	0.68±0.04	6.03	5.30±0.05	5762±194	130.7±1.8	41.54±1.32	7712±339	1977±75
18	150	70	0.67±0.02	6.03	5.26±0.04	5812±105	129.2±1.9	43.03±1.22	7638±338	1958±64
19	150	70	0.67±0.03	6.03	5.24±0.03	5755±162	132.8±2.6	45.91±1.64	6844±296	2040±87
20	185	45	1.16±0.06	6.95	5.52±0.04	5450±143	142.3±1.7	139.05±6.95	7043±328	2320±129
21	150	70	0.70±0.04	6.03	5.25±0.01	5589±305	127.6±2.4	44.01±2.98	7762±371	1913±115
22	185	45	1.13±0.04	6.95	5.55±0.02	5205±185	145.7±2.1	142.10±3.42	6943±273	2364±102
23	185	45	1.17±0.04	6.95	5.57±0.05	5280±211	144.1±1.2	150.16±4.05	7117±262	2358±55
24	185	12.1	1.02±0.03	6.95	5.61±0.02	7053±121	190.9±1.8	127.69±4.66	9448±451	3222±157
25	220	20	3.80±0.14	6.03	6.02±0.01	7788±114	169.9±3.3	179.10±1.84	10267±383	3241±112
26	150	20	0.45±0.07	6.95	6.08±0.03	3512±108	119.4±3.4	42.61±1.70	4835±250	1703±87
27	220	20	3.70±0.14	6.03	6.00±0.04	7807±122	167.9±6.5	178.88±2.61	11705±502	3400±151

Table 3.2 shows the spread and measure of the central tendency to summarise the distribution data about HT. The spread and measures of central tendency ensure that the data are scientifically robust, provide actionable insights, and communicate results clearly and effectively. The outliers (138.94°C and 231.06°C for temperature, and 12.10 min and 77.90 min for time) are the result of the set limit exploration through the RSM design strategy. This ensures a reliable estimation of higher-order effects in the studied region.

Table 3.2 Summary of the spread of the input and output parameters data in HT optimisation

Name	Units	Minimum	Maximum	Mean	Std. Dev.
Input variables					
Temperature	°C	138.94	231.06	185.00	30.28
Residence time	min	12.10	77.90	45.00	21.63
Output responses					
SCOD	mg/L	3122	7951	5422	1371
Ammonia H	mg/L	24.14	248.39	131.09	73.03
Phosphate	mg/L	92.29	190.90	134.39	27.18
Carbohydrates	mg/L	1137.85	3501.96	2284.37	603.38
Proteins	mg/L	4562.44	11705.10	7373.22	1952.72

The optimal conditions for HT, derived from the DOE framework, provide a balanced approach to maximising SCOD solubilisation, nutrient recovery, and hydrochar quality. The DOE analysis indicated that a temperature range of 150-230°C, combined with a reaction time of 20-70 min and moderate pressure levels, yields the highest SCOD levels, thereby enhancing the bioavailability of organic matter. The increased SCOD directly correlates with the enhanced potential for subsequent AD and biogas production. Simultaneously, these conditions promote the release of critical nutrients, such as phosphorus and nitrogen, into the aqueous phase, which can be efficiently recovered through processes like struvite precipitation.

3.3.2 SCOD in response to input variables

The impact of temperature on SCOD is significant, with higher temperatures leading to increased solubilisation of organic matter. At 150°C with a short residence time of 20 min, the SCOD value is approximately 3520 mg/L. In contrast, at 220 °C for the same

residence time, the SCOD value rises significantly to 7951 mg/L, as shown in Figure 3.1. This apparent trend highlights the role of elevated temperatures in facilitating the thermal degradation of recalcitrant organic compounds, breaking them down into simpler, soluble intermediates. Improved solubilisation bolsters the critical role that temperature plays in HT process optimisation.

Residence time has significantly affected SCOD, as more organic matter can be broken down through hydrothermal treatment. By increasing the residence time, complex organic compounds were also degraded to soluble intermediates, thereby increasing the SCOD value.

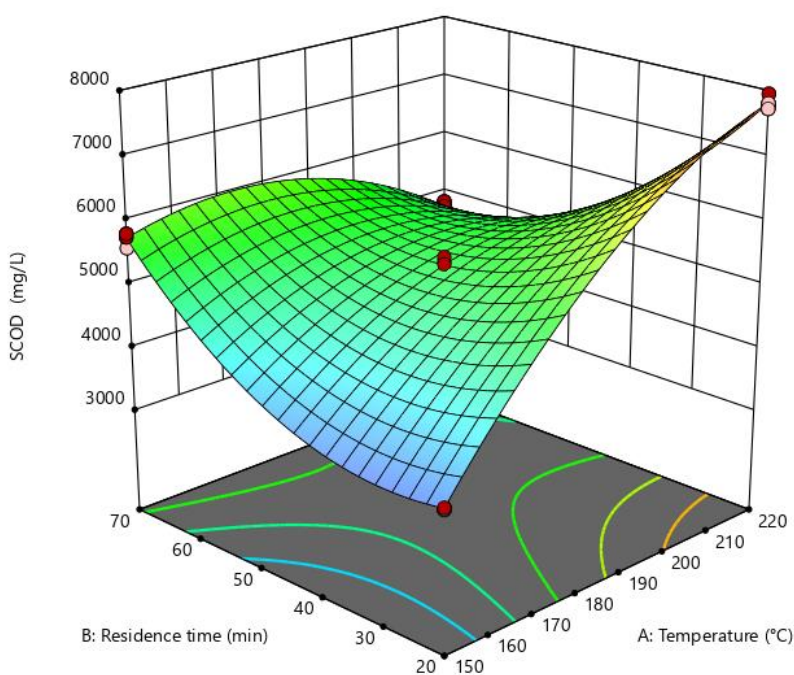


Figure 3.1 Surface plot for SCOD response to input parameters

3.3.2.1 Effect of temperature

Enhanced solubilisation of organic matter is indicated by the increase in SCOD with hydrothermal treatment at elevated temperatures. This trend aligns with the thermal degradation of recalcitrant organic compounds, resulting in the release of soluble intermediates, as observed by Devos, Haddad and Carrère (2021), at temperatures

above 160 °C. In another study by Pham *et al.* (2023), higher reaction temperatures for acid-catalysed hydrothermal sewage sludge treatment result in higher dissolved organic carbon and SCOD levels, indicating greater organic matter solubilisation. This reinforces the central importance of temperature in enabling enhanced solubilisation efficiency of hydrothermal processes.

3.3.2.2 *Effect of residence time*

Extending the residence time during HT of sewage sludge enhances the solubilisation of organic matter, as evidenced by increased levels. For instance, at 185°C, prolonging the residence time from 45 to 77 min elevated SCOD from approximately 5292 mg/L to 6509 mg/L. This trend suggests that prolonged exposure enables a more thorough breakdown of complex organic compounds into soluble forms. However, this effect is not permanent, especially for longer residence times that exceed certain limits. Additional increases in residence time could lead to low yields or, in some cases, even adverse effects, such as the creation of refractory compounds that cannot be further degraded.

This agrees with the literature findings, which establish optimal residence times, maximising solubilisation and minimising the accumulation of non-biodegradable substances. (Hidalgo *et al.* 2024). A study on the hydrothermal carbonisation of sewage sludge revealed improved dewaterability and hydrochar properties at an increased residence time; however, these improvements stabilised beyond a certain point, suggesting that an optimal residence time is necessary to achieve the desired outcomes (Czerwińska *et al.* 2024). Therefore, optimising residence time is vital to balance the effectiveness of solubilisation and process efficiency without generating recalcitrant by-products.

3.3.2.3 *Interaction effect of operating parameters in relation to SCOD*

As Figure 3.2 shows, SCOD concentrations are significantly influenced by the interplay of temperature and residence time during HT of sewage sludge. Increased levels of both parameters result in enhanced SCOD, suggesting a synergistic effect that breaks down complex organic compounds into soluble forms. This could be due to the intensification of hydrolytic reactions and the degradation of recalcitrant materials at higher

temperatures and longer exposure times (Canencio *et al.* 2025). Nevertheless, these conditions are to be optimised since the excessive severity of both variables results in the formation of refractory compounds, such as humic substances, furans, phenolics, and ammonia, which may adversely affect subsequent processes. It is essential to balance these factors to maximise bioenergy recovery and resource efficiency in sludge management.

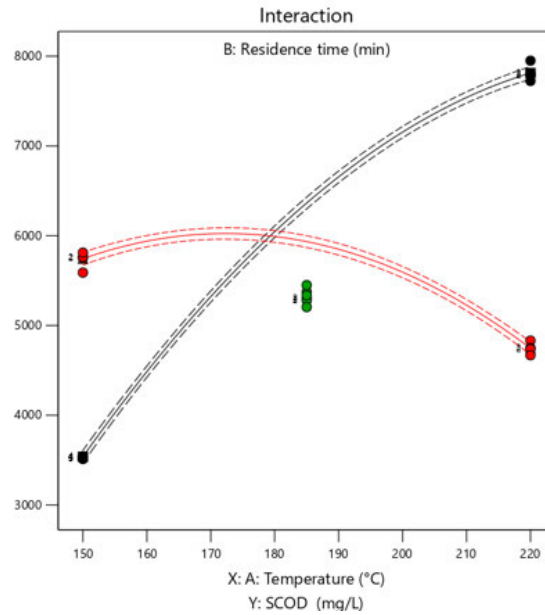


Figure 3.2 Interaction of variables in SCOD solubilisation.

Studies such as Pham *et al.* (2021) corroborate this analysis by observing that enhanced sludge solubilisation through the use of hydrothermal pretreatment at elevated temperatures and extended residence time positively affected subsequent biogas production during AD.

At low temperatures (150°C), even longer residence times resulted in relatively low SCOD values (3500 mg/L). This observation shows that temperature is a limiting factor in the solubilisation process. At high temperatures (220°C), shorter residence times still achieve relatively high SCOD values (7800 mg/L), suggesting that temperature becomes the dominant factor. A strong interaction effect is demonstrated as the maximum SCOD (7951 mg/L) is produced at a combination of high temperature (220°C) and short residence time

(20 min). Results indicate that both temperature and residence time act in synergy to improve SCOD. The interaction ensures that, at high temperatures, even shorter times are sufficient to solubilise organic matter effectively. Additionally, it is essential to understand that operating at high temperatures with modest residence times may be more economical than prolonging the process at lower temperatures.

3.3.2.4 The analysis of variance (ANOVA)

The ANOVA presented in Table 3.3 shows notable interaction effects between temperature and residence time on SCOD during HT.

Table 3.3 ANOVA for quadratic model – SCOD response

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	4,879E+07	5	9,757E+06	1800,20	< 0.0001	significant
A-Temperature	1,308E+07	1	1,308E+07	2412,90	< 0.0001	
B-Residence time	9,002E+05	1	9,002E+05	166,08	< 0.0001	
AB	2,782E+07	1	2,782E+07	5132,39	< 0.0001	
A ²	3,555E+06	1	3,555E+06	655,95	< 0.0001	
B ²	5,115E+06	1	5,115E+06	943,69	< 0.0001	
Residual	1,138E+05	21	5420,01			
Lack of Fit	8584,19	3	2861,40	0,4894	0,6940	not significant
Pure Error	1,052E+05	18	5846,44			
Cor Total	4,890E+07	26				

The ANOVA conducted reveals that temperature is the most influential factor affecting SCOD levels during hydrothermal treatment of sewage sludge, with a highly significant p-value (<0.0001). Thus, high temperatures significantly alter the SCOD, underscoring its importance in the solubilisation of organic matter. Similarly, a favourable p-value (<0.05) was observed between residence time and SCOD, indicating that both the duration of treatment and SCOD have a significant effect on the degradation of organic matter. Additionally, the statistical significance of these two parameters (temperature and residence time) indicates that their joint effect is needed to maximise SCOD levels. These results are consistent with studies elsewhere stressing the value of both temperature and residence time to hydrothermal process efficiency and demonstrating that increasing residence time during HT results in a decrease in the hydrochar yield and organic matter content, pointing to more extensive organic material decomposition (Czerwińska *et al.* 2024).

Therefore, the statistical analysis corroborates the critical influence of temperature and residence time on the solubilisation of organic matter during hydrothermal treatment, consistent with findings reported in the literature. The statistical analysis also confirms the key role of temperature and residence time in the hydrothermal solubilisation of organic matter, as reported in the literature (Czerwińska *et al.* 2024). To this end, a statistical predictive quadratic model has been proposed to predict SCOD response, as reported in Table 3.4 and Equation 3.10.

Table 3.4 Coefficients of the predictive model

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	5323.14	1	27.71	5265.52	5380.76	
A-Temperature	819.69	1	16.69	784.99	854.40	1.0000
B-Residence time	-215.05	1	16.69	-249.76	-180.35	1.0000
AB	-1318.56	1	18.41	-1356.84	-1280.28	1.0000
A ²	-689.32	1	26.91	-745.29	-633.35	1.06
B ²	826.80	1	26.91	770.83	882.77	1.06

$$SCOD = 5323.14 + 819.69A - 215.05B - 1318.56AB - 689.32A^2 + 826.80B^2 \quad 3.10$$

where A is the temperature, and B is the residence time.

For the quadratic regression model of SCOD through HT of sewage sludge, the ANOVA indicates a highly significant model fit, with an F-value of 1,800.20 and a p-value of < 0.0001. This indicates the model's robustness in relating the SCOD to the predictor variables, namely temperature (A) and residence time (B), as the likelihood of observing such an extreme F-value based on random variation is extremely low (0.01%).

The main effects of temperature (A), residence time (B), their interaction (AB), and the quadratic terms (A², B²) are all statistically significant (p < 0.05). This further underscores the importance of both linear and non-linear contributions of these variables and, in turn, their interplay in influencing SCOD levels. This fits the data reasonably well because a lack of fit should suggest model inadequacy if it were significant (F-value = 0.49, p-value = 0.6940).

The R² value for the model (0.9977) means that the model explains 99.77% of the variability in SCOD. Adjustments for the number of predictors (adj R² = 0.9971) maintain

a close relationship to the R^2 , implying that these terms included were justified and the model is not being overfit. The adjusted R^2 is within reasonable agreement with the predicted value of R^2 (0.9963) compared to an adjusted R^2 (0.99547) and a difference of 0.00085 (less than 0.2); it further validates the reliability of the model. A strong signal-to-noise ratio is exhibited by an adequate precision ratio of 137.257, exceeding the desired value (4) (Tariq, Maqbool and Abbas 2021), and that represents the design space navigation capability of this model.

Table 3.5 Fit statistics for SCOD

Std. Dev.	73.62	R²	0.9977
Mean	5422.25	Adjusted R²	0.9971
C.V. %	1.36	Predicted R²	0.9963
		Adeq Precision	137.2565

Overall, the statistical metrics indicate that the quadratic regression model effectively characterises the relationship between temperature, residence time, and SCOD of WAS through HT, and that the contributions to the main effects and the interaction are significant and highly predictive.

3.3.3 Phosphate and ammonium concentration in response to input variables

Phosphate and ammonium concentrations in the effluent from HT of waste-activated sludge (WAS) serve as key indicators of nutrient solubilisation and recovery efficiency. Phosphorus is released through the breakdown of organic matter and phosphate mineral complexes, while ammonium is generated primarily from the deamination of nitrogenous compounds.

The experimental results (Table 3.1) highlight the influence of temperature and residence time on phosphate concentrations, which range from approximately 92 mg/L to 190 mg/L (Figure 3.3 (a)). Similarly, ammonium concentrations exhibit significant variation in response to temperature and residence time, as shown in Figure 3.3(b).

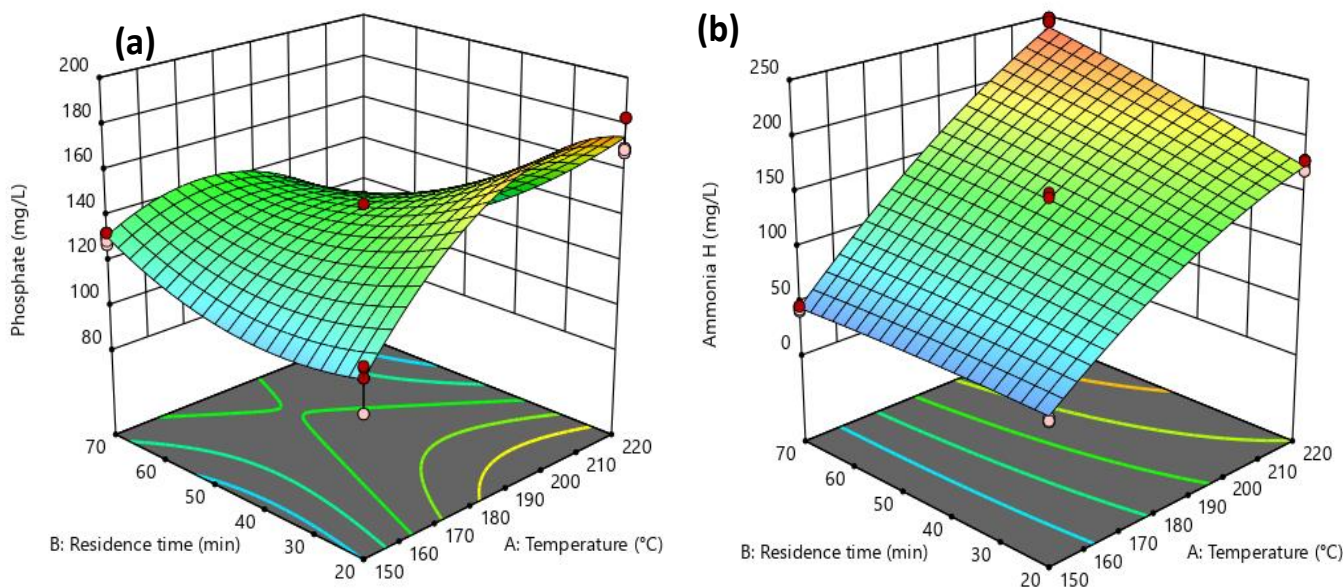


Figure 3.3 Surface plot for (a) phosphate and (b) ammonium concentration response to input parameters

3.3.3.1 Effect of temperature on phosphate and ammonium release

Temperature plays a pivotal role in phosphorus solubilisation during HT, with higher temperatures significantly enhancing orthophosphate concentrations. For instance, at a constant residence time of 20 minutes, phosphate concentrations increase from 115 mg/L at 150°C to 182.9 mg/L at 220°C. This trend aligns with the principles of thermal hydrolysis, as at high temperatures, organic matrices break down, releasing phosphorus that was previously bound in soluble orthophosphates. A subcritical water environment is an ideal medium for the hydrolysis of recalcitrant phosphorus compounds (Hii *et al.* 2014). Previous studies by Takaya *et al.* (2016) suggest that an increase in temperature enhances the recovery of bioavailable phosphorus; hence, HT is a viable option for sustainable fertiliser manufacturing.

For ammonium, the temperature has a direct relationship with the concentration, highlighting its role in nitrogen solubilisation. At high temperatures, organic nitrogen, primarily derived from proteins, is deaminated, leading to an increased release of ammonium. For instance, at 150°C and 20 min, the concentration of ammonium is 42.12 mg/L, but it increases to 248.39 mg/L at 220°C and 70 min. This rise emphasises the

progressive decomposition of complex nitrogenous compounds when subjected to high temperatures. Previous studies support these findings, illustrating that thermal processes accelerate protein degradation, enriching the aqueous phase with ammonium (Sun *et al.* 2020b). The cubic regression model ($p < 0.0001$) further validates temperature as a statistically significant factor in ammonium solubilisation, consistent with the literature, which identifies HT as a promising nitrogen recovery technique.

3.3.3.2 Effect of Residence Time on phosphate and ammonium release

Residence time during HT is another crucial factor affecting phosphate and ammonium concentrations. At 185°C, increasing the residence time from 20 to 77 min enhances the phosphate concentration from 144 mg/L to 190 mg/L, demonstrating that extended reaction times promote the further breakdown of phosphorus-containing matrices. However, Figure 3.3(a) suggests a plateau effect at prolonged durations, indicating kinetic limitations where solubilisation stabilises. Beyond an optimal residence time, extended durations do not yield substantial improvements and may result in energy inefficiencies or nutrient degradation (Takaya *et al.* 2016). This highlights the need to strike a balance between maximising phosphate recovery and process efficiency.

For ammonium, residence time influences concentration but is secondary to temperature. As shown in Figure 3.3(b), increasing residence time from 20 to 70 min at 185°C raises ammonium concentration from 127.69 mg/L to 152.17 mg/L. This steady increase reflects continuous nitrogen solubilisation. However, prolonged residence times can lead to substrate depletion, as nitrogen-rich materials become limiting factors. This phenomenon is supported by the work of Hii *et al.* (2014), who investigated the impact of hydrothermal pretreatment temperature on the conversion of organic and nitrogen compounds in sludge. Their results showed that the solubilisation of organic nitrogen compounds improved with an increase in temperature, resulting in the liberation of free ammonia in the aqueous phase. However, at higher temperatures (>200 °C), volatilisation and transformation of ammonia into nitrogen-containing gases resulted in a significant loss of aqueous ammonia. These findings, in the context of this study, reinforce the trend observed in the reduction of ammonia following hydrothermal treatment. These results

validate the fact that high temperatures favour the release of ammonia and its subsequent loss through volatilisation and transformation reactions.

3.3.3.3 Interaction of input variables in phosphate and ammonium concentration changes

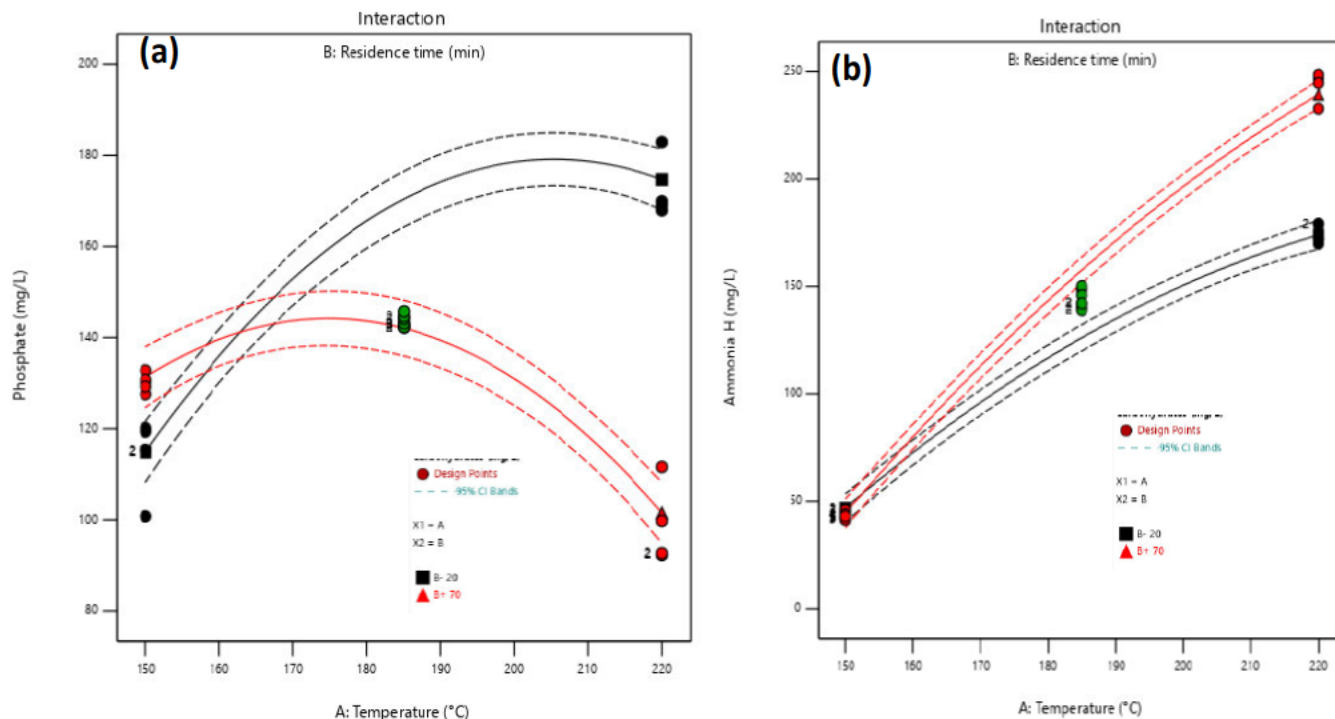


Figure 3.4 Interaction effects of input variables on (a) phosphate and (b) ammonium concentrations following hydrothermal treatment.

Statistical analyses (Figure 3.4) reveal that temperature and residence time interact significantly in influencing phosphate and ammonium concentrations. The quadratic model exhibits strong fit statistics, with an adjusted R^2 of 0.9359 for phosphate and 0.9966 for ammonium (Table 3.6), indicating high predictive accuracy.

Table 3.6 Fit Statistics for phosphate concentration and ammonium concentration

Phosphate Concentration			
Std. Dev.	6,88	R^2	0,9482
Mean	134,39	Adjusted R^2	0,9359
C.V. %	5,12	Predicted R^2	0,9014
		Adeq Precision	28,9195
Ammonium concentration			
Std. Dev.	4.25	R^2	0.9975
Mean	131.09	Adjusted R^2	0.9966
C.V. %	3.24	Predicted R^2	0.9958
		Adeq Precision	94.4691

Notably, temperature (F-value = 23.18) and residence time (F-value = 82.61) significantly influence phosphate concentration, while their interaction (F-value = 169.37) suggests synergistic effects (Table 3.7). For ammonium, the interaction between temperature and residence time is statistically significant ($p < 0.0001$), with combined effects driving nitrogen solubilisation (Table 3.7). At high temperatures (e.g., 220°C), moderate residence times yield optimal ammonium release, whereas excessively long durations result in diminishing returns. The nonlinearity observed in the model, with significant contributions from quadratic and interaction terms (A^2B , AB^2), further underscores the complexity of ammonium dynamics under HT conditions.

Table 3.7 ANOVA for quadratic model regarding phosphate concentration and ammonium concentration

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Phosphate concentration						
Model	18218,35	5	3643,67	76,90	< 0.0001	significant
A-Temperature	1098,35	1	1098,35	23,18	< 0.0001	
B-Residence time	3914,27	1	3914,27	82,61	< 0.0001	
AB	8025,02	1	8025,02	169,37	< 0.0001	
A ²	4920,28	1	4920,28	103,85	< 0.0001	
B ²	1086,70	1	1086,70	22,94	< 0.0001	
Residual	995,00	21	47,38			
Lack of Fit	335,20	3	111,73	3,05	0,0553	not significant
Pure Error	659,80	18	36,66			
Cor Total	19213,35	26				
Ammonium concentration						
Model	1,383E+05	7	19763,38	1096,52	< 0.0001	significant
A-Temperature	16877,90	1	16877,90	936,43	< 0.0001	
B-Residence time	299,64	1	299,64	16,62	0,0006	
AB	4581,94	1	4581,94	254,22	< 0.0001	
A ²	1869,23	1	1869,23	103,71	< 0.0001	
B ²	29,69	1	29,69	1,65	0,2148	
A ² B	174,41	1	174,41	9,68	0,0058	
AB ²	482,58	1	482,58	26,77	< 0.0001	
A ³	0,0000	0				
B ³	0,0000	0				
Residual	342,45	19	18,02			
Lack of Fit	1,39	1	1,39	0,0732	0,7897	not significant
Pure Error	341,06	18	18,95			
Cor Total	1,387E+05	26				

3.3.3.4 Regression model for prediction

The predictive models in Equations 3.11 and 3.12 define the contributions of temperature (A) and residence time (B) to the solubilisation of phosphate and ammonium.

Phosphate Concentration (coded)

$$= 144.19 + 7.51A - 14.18B - 22.40 AB - 25.64 A^2 + 12.05 B^2 \quad 3.11$$

Ammonium concentration (coded)

$$= 143.92 + 69.80A + 9.30B + 16.92AB - 15.81A^2 - 1.99B^2 + 7.83 A^2B + 13.02 AB^2 \quad 3.12$$

The coefficients indicate that temperature has the most decisive influence on both phosphate and ammonium solubilisation, while residence time introduces nonlinear effects. The interaction term (AB) implies that the simultaneous positive changes of both parameters may not produce optimal results, thus reinforcing the importance of careful optimisation.

Both temperature and residence time significantly influence phosphate and ammonium solubilisation during hydrothermal treatment (HT) of WAS. Increasing temperature enhances organic decomposition and the release of phosphate and ammonium, while optimal residence time maximises nutrient recovery with minimal energy input. The quadratic and cubic regression models developed in this study provided robust predictive frameworks for optimising these HT parameters. These findings relate to Takaya *et al.* (2016), who have shown that hydrochar prepared at 250 °C had high phosphate and ammonium sorption capacities (up to 30 mg P/g and approximately 146 mg N/g, respectively), which proves that the mobility of nutrients is highly dependent on the temperature-driven surface chemistry and mineral phases. Likewise, Sun, Mohammed and Liu (2020) documented phosphorus recovery efficiencies of more than 90 % of concentrated blackwater by precipitation of struvite at high temperature and under alkaline environment (pH of 8.6-9.0) with controlled Mg/P molar ratios (1.1-1.5), which showed that increased temperature and high pH conditions favour phosphorus availability and precipitation to crystalline forms. Together, these results support the idea that thermal-hydrolytic and precipitation reactions under optimised HT conditions can help improve nutrient recovery and scalable energy-integrated wastewater treatment approaches.

3.3.4 Macromolecule concentrations in response to input variables

The solubilisation of macromolecules, particularly proteins and carbohydrates, during HT is highly temperature- and time-dependent. Protein solubilisation has a separate thermal hydrolysis pathway, degrading complex proteinaceous matter into soluble peptides and amino acids. Carbohydrate solubilisation, however, is regulated by the depolymerisation and hydrolysis of polysaccharides into simpler sugars. These trends can be demonstrated using the experimental results (Table 3.1), where changes are shown for the concentration of macromolecules under different HT conditions (Figure 3.5(a) and (b)).

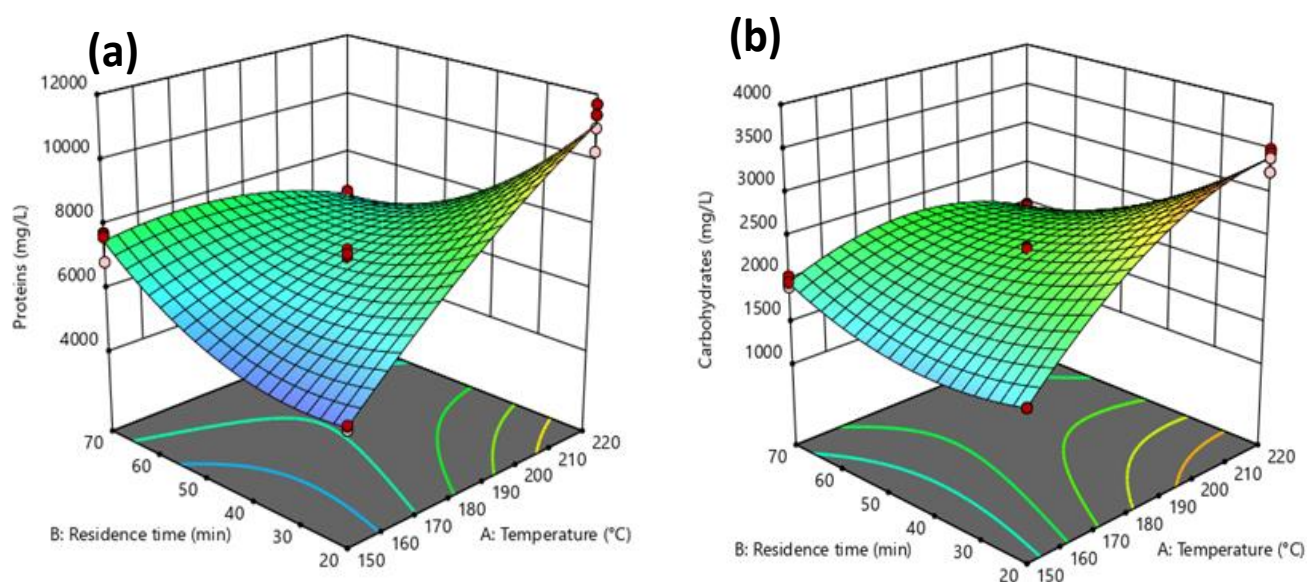


Figure 3.5 Surface plot for (a) protein and (b) carbohydrate concentration response to input parameters

Temperature plays a critical role in the breakdown of macromolecules. As shown in Figure 3.5(a), protein concentration in the aqueous phase increases from 4562 mg/L at 150°C to 11383 mg/L at 220°C over a residence time of 20 min. This trend aligns with the findings of Kim, Lee and Park (2015), who demonstrated that elevated temperatures denature proteins and enhance peptide bond cleavage, thereby increasing the solubilised protein fraction. However, at temperatures above 220°C, secondary reactions such as Maillard reactions can occur between amino acids and reducing sugars, leading to the formation

of recalcitrant compounds and reducing protein solubilisation efficiency (Dumitraşcu, Borda and Aprodu 2023; Zhou *et al.* 2024).

3.3.4.1 Effect of temperature on protein and carbohydrate solubilisation

Carbohydrate solubilisation follows a similar pattern, peaking at 3502 mg/L at 220°C, as shown in Table 4.1 and Figure 3.5(b). At lower temperatures (150°C), carbohydrate concentrations remain around 1703–1710 mg/L, indicating that the thermal energy is insufficient to disrupt polysaccharide bonds entirely. Studies by Steinbruch *et al.* (2020) confirm that optimal carbohydrate hydrolysis occurs between 180 and 220°C, with degradation occurring beyond this range due to the formation of inhibitory by-products. These findings highlight the necessity of optimising HT conditions to maximise macromolecular recovery while minimising degradation losses.

3.3.4.2 Effect of residence time on protein and carbohydrate solubilisation

Residence time significantly impacts macromolecule recovery, with prolonged durations enhancing solubilisation efficiency up to a saturation point. Protein solubilisation improves with increased residence time, rising from 6646 mg/L to 8431 mg/L at 185°C when the reaction is extended from 20 to 77 min (Figure 3.5(a)). This suggests that extended exposure to subcritical water conditions facilitates thorough protein hydrolysis. However, excessive residence time can lead to the formation of inhibitory by-products and protein re-polymerisation, as presented in the literature (Kim, Lee and Park 2015).

Similarly, carbohydrate solubilisation benefits from moderate residence times but declines at excessively long durations. At 150°C, carbohydrate concentration remains relatively low (1977 mg/L at 70 min), indicating that prolonged residence time alone cannot compensate for insufficient thermal energy. Conversely, at 220°C, the carbohydrate concentration peaks at 3457 mg/L at 20 min, then declines to 1900 mg/L at 70 min, suggesting the degradation of solubilised sugars into smaller, unmeasurable fragments or inhibitory compounds (Zhou *et al.* 2024). Figure 3.5(b) illustrates this trend, confirming the need to balance residence time to optimise carbohydrate recovery while avoiding degradation losses.

3.3.4.3 Interaction effects of temperature and residence time

The interaction of temperature and residence time significantly influences macromolecule solubilisation, as evidenced by ANOVA results ($p < 0.0001$) in Table 3.8.

Table 3.8 ANOVA for quadratic models for protein concentration and carbohydrates

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Protein concentration						
Model	9,699E+07	5	1,940E+07	188,91	< 0.0001	significant
A-Temperature	3,263E+07	1	3,263E+07	317,76	< 0.0001	
B-Residence time	4,302E+06	1	4,302E+06	41,90	< 0.0001	
AB	5,093E+07	1	5,093E+07	496,02	< 0.0001	
A ²	2,065E+06	1	2,065E+06	20,11	0,0002	
B ²	8,586E+06	1	8,586E+06	83,62	< 0.0001	
Residual	2,156E+06	21	1,027E+05			
Lack of Fit	1.027E+05	3	34219.60	0.2999	0.8250	not significant
Pure Error	2.054E+06	18	1.141E+05			
Cor Total	9.914E+07	26				
Source	Sum of Squares	df	Mean Square	F-value	p-value	
Carbohydrates concentration						
Model	9,410E+06	5	1,882E+06	707,06	< 0.0001	significant
A-Temperature	3,482E+06	1	3,482E+06	1308,30	< 0.0001	
B-Residence time	1,735E+06	1	1,735E+06	651,89	< 0.0001	
AB	2,955E+06	1	2,955E+06	1110,24	< 0.0001	
A ²	9,941E+05	1	9,941E+05	373,49	< 0.0001	
B ²	5,244E+05	1	5,244E+05	197,03	< 0.0001	
Residual	55896,41	21	2661,73			
Lack of Fit	2829,97	3	943,32	0,3200	0,8108	not significant
Pure Error	53066,44	18	2948,14			
Cor Total	9,466E+06	26				

Temperature drives the breakdown of proteinaceous material through thermal hydrolysis, while residence time enables further progression of hydrolysis. At 150°C and 20 minutes, the protein concentration is 4562 mg/L, whereas at 220°C under the same residence time, it increases to 11705 mg/L. Similarly, extending residence time from 20 to 77 min at 185°C increases protein concentration from 6646 mg/L to 8431 mg/L (Figure 3.6(a)). The interaction of variables showed a similar trend in carbohydrates (Figure 3.6(b)). These trends highlight the synergy between temperature and residence time in protein solubilisation.

For carbohydrates, the most potent effect is observed at 220°C, where depolymerisation reaches maximum efficiency at shorter residence times. Table 3.8 confirms the significance of temperature ($F = 1308.30$, $p < 0.0001$) and residence time ($F = 651.89$, p

< 0.0001), reinforcing their dominant role in carbohydrate hydrolysis. However, extended residence times at high temperatures can result in degradation, as indicated by the quadratic term B^2 ($F = 197.03$, $p < 0.0001$), highlighting the importance of optimising both factors simultaneously.

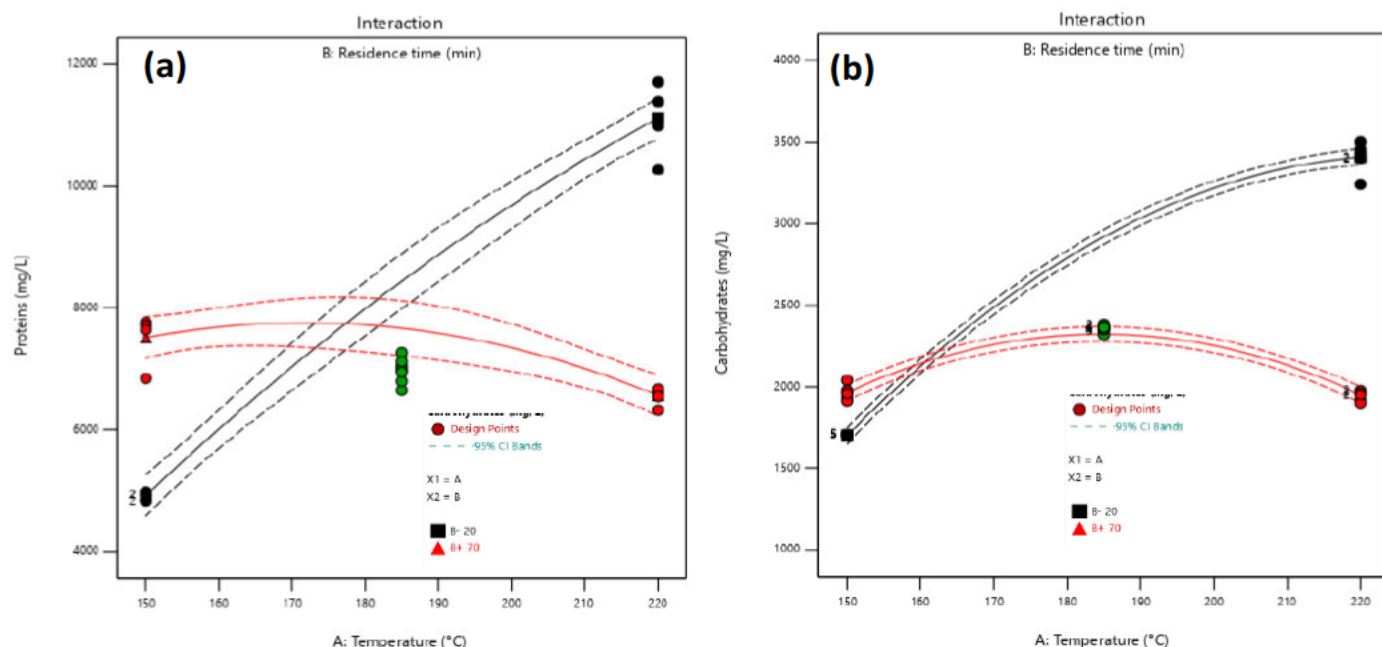


Figure 3.6 Interaction of variables (a) Proteins (b) Carbohydrates

3.3.4.4 Predictive models for protein and carbohydrate solubilisation

The quadratic regression models developed for protein and carbohydrate solubilisation (Equations 3.13 and 3.14) provide robust predictive frameworks for optimising HT conditions. The models demonstrate high predictive accuracy, with adjusted R^2 values of 0.9709 for protein and 0.9927 for carbohydrates, indicating that the models account for nearly all variability in macromolecule solubilisation (Table 3.9). The coefficients confirm that temperature exerts the most decisive influence, while residence time plays a secondary yet significant role.

Table 3.9 Fit Summary for macromolecule solubilisation

Proteins			
Std. Dev.	332.94	R^2	0.9788
Mean	7373.22	Adjusted R^2	0.9709
C.V. %	4.52	Predicted R^2	0.9548
		Adeq Precision	36.6945
Carbohydrates			
Std. Dev.	51,59	R^2	0,9941

Mean	2284,37	Adjusted R²	0,9927
C.V. %	2,26	Predicted R²	0,9902
		Adeq Precision	92,0852

Protein concentration

$$= 6979.70 + 1294.69A - 470.12B - 1784.12 AB - 525.33 A^2 + 1071.22 B^2 \quad 3.13$$

Carbohydrates concentration

$$= 2356.28 + 422.98A - 298.57B - 429.77AB - 364.51 A^2 + 264.75 B^2 \quad 3.14$$

Overall, the study confirms that temperature and residence time significantly affect the solubilisation of proteins and carbohydrates during HT. Increased temperatures improve protein and carbohydrate recovery rates with optimal residence times, achieving the best solubilisation, without leading to degradation. The quadratic regression models are a predictive instrument for optimising HT conditions, ensuring effective recovery of macromolecules. These results are consistent with previous studies, and the findings are of great value for the development of scalable wastewater treatment strategies aimed at nutrient recovery and the valorisation of bioresources (Steinbruch *et al.* 2020; Zhou *et al.* 2024).

3.4 Optimisation of the hydrothermal treatment process

Optimisation of the HT process is an essential aspect towards improving the efficiency in the recovery of nutrients and utilisation of resources from waste-activated sludges. As stated by the analysis and the values determined by Design Expert software (Figure 3.7), the optimal conditions for this process were identified as a temperature of 220°C and a residence time of 20 min.

These operating conditions were selected to maximise the output responses, SCOD, ammonia, phosphate, carbohydrates, and protein concentrations while ensuring process efficiency. Ideally, within the limits of experimental accuracy, the output responses should

have been 7951, 174.89, 174.69, 3407.84, and 11107.81 mg/L for SCOD, ammonia, phosphate, carbohydrates, and protein concentration, respectively, based on the prediction.

Such operating conditions were chosen to maximise the output results, SCOD, ammonia, phosphate, carbohydrates and protein concentrations without compromising the efficiency of the process. Optimally, based on the prediction and within the limits of experimental accuracy, the output responses should have been 7951, 174.89, 174.69, 3407.84, and 11107.8 mg/L for SCOD, ammonia, phosphate, carbohydrates, and protein concentration, respectively. Similarly, Wang, Li and Chang (2017); Zhang *et al.* (2020d) have indicated 220 °C as the optimal temperature to realise effective HT of sewage sludge with residence times of around 20 min, achieving a balance between process efficiency and operational costs.

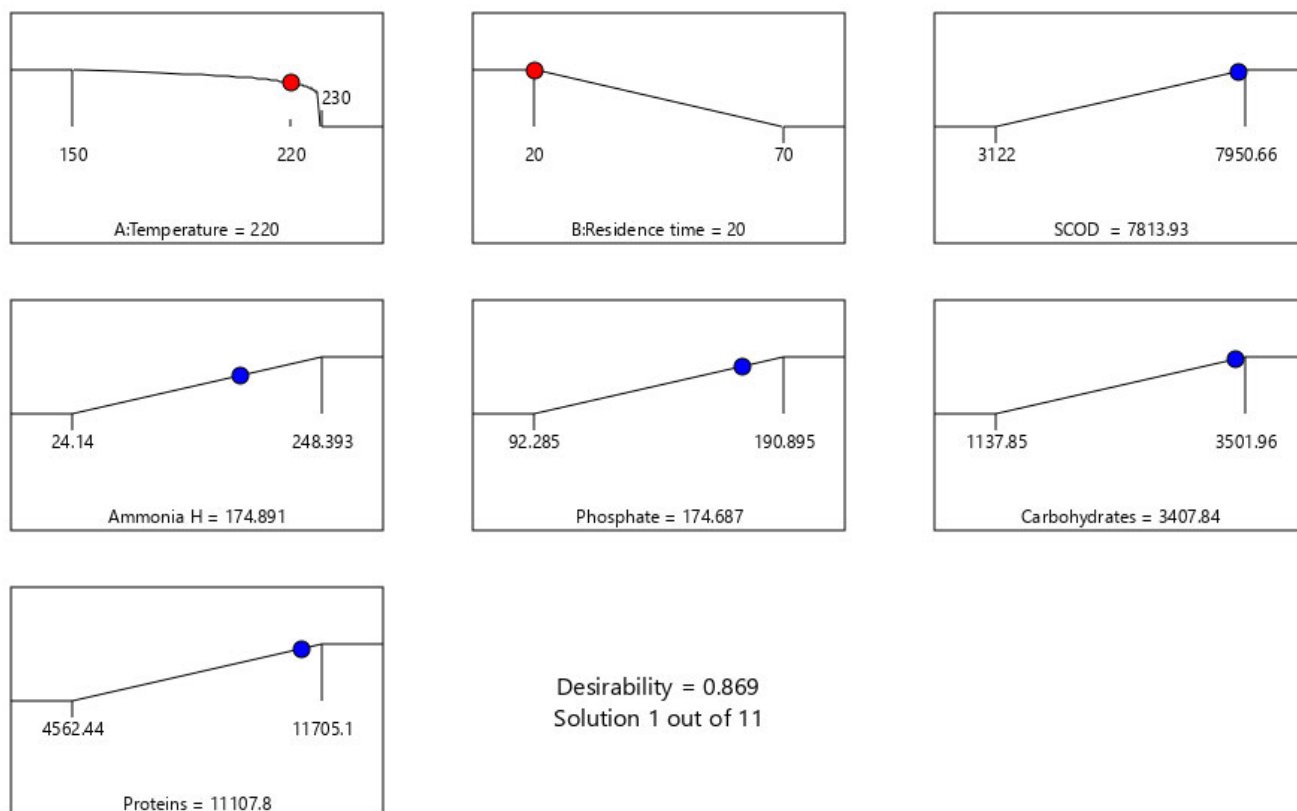


Figure 3.7 Ramp for the optimum results of the hydrothermal treatment process.

Wu and Vaneeckhaute (2022) demonstrated that nutrient recovery yields continued to decline as the temperature exceeded 220 °C, while an extended residence time of more than 20 min increased energy consumption without commensurate improvement in the quality of the final products. At 0.869, the predictive model's desirability index indicates good alignment between the optimisation and expected outcomes, meaning that the process parameters were chosen to produce reliable and reproducible results within the limits of the experiments. In practical applications, Luis Pérez (2021) has reported that a desirability factor greater than 0.8 is often acceptable, as it means that its response prediction is in a good balance of experimental reliability. This optimised combination of 220°C and 20 min is thus confirmed not only by the present study but also by various other works in the field, reinforcing its validity for high-efficiency HT processes.

3.5 Validation of the optimised process parameters

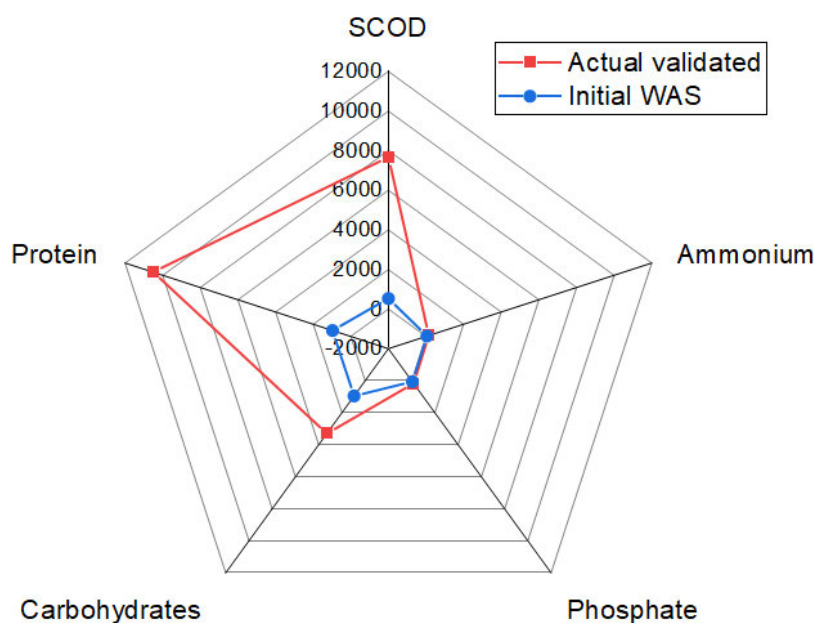
The validation of the optimised process parameters is a critical step in ensuring the reliability and accuracy of the predictive models generated during optimisation. To achieve this, duplicate experiments were conducted under the optimised conditions of 220°C and a 20-minute residence time. The initial concentrations of key components in the WAS were recorded as SCOD (536 mg/L), ammonium (51.90 mg/L), phosphate (64.04 mg/L), carbohydrates (951.86 mg/L), and protein (971.95 mg/L). These values served as a baseline for evaluating the process's efficacy.

Table 3.10 shows a strong correlation between predicted and experimentally validated values, with the deviations of most responses remaining low. SCOD, phosphate, carbohydrates, and protein showed deviations of 2%, 1%, 3%, and 5%, respectively, indicating the robustness of the model in predicting the performance of HT. Ammonium, however, demonstrated a more significant deviation of 13%; this difference is likely due to the volatilisation of nitrogenous compounds into ammonia or nitrogen oxides, a well-known phenomenon in high-temperature processes involving proteinaceous matter (Wu *et al.* 2021).

Table 3.10 Predicted and actual validation values of the HT process.

Response	Predicted value (mg/L)	Actual validated (mg/L)	Deviation	% Deviation
SCOD	7814	7670	101.77	2%
Ammonium	174.89	151.58	16.48	13%
Phosphate	174.69	172.79	1.34	1%
Carbohydrates	3407.84	3292	81.91	3%
Protein	11107.81	10515	419.17	5%

The radar plot in Figure 3.8 presents a visual representation of the solubilisation dynamics of different constituents before and after HT. Among the responses, SCOD, protein, and carbohydrates showed the highest increases, which suggested an increased breakdown of complex organic compounds into soluble intermediates. This points out the efficiency of the process in enhancing the biodegradability and nutrient recovery potential of WAS.

**Figure 3.8 Radar plot comparing the initial and post-HT concentration**

The near-perfect alignment of phosphate concentrations between predicted and actual values (1% deviation) suggests that the hydrothermal conditions favour the retention of bioavailable phosphorus in the aqueous phase, which is critical for subsequent nutrient recovery processes.

The excellent agreement between the actual and predicted concentrations of phosphate (1% deviation) suggests that the hydrothermal conditions support phosphorus bioavailability in the aqueous phase, which is essential for subsequent nutrient recovery. Similarly, the modest deviations in SCOD (2%) and carbohydrates (3%) further validate the model's ability to forecast the solubilisation of organic compounds accurately.

Overall, the validation results underscore the reliability of the predictive model, demonstrating its applicability in replicating experimental outcomes under the specified conditions. These findings also reinforce the significance of hydrothermal treatment as a robust pretreatment technology for resource recovery from WAS.

3.6 Other factors that affect the hydrothermal treatment process

Although pressure and pH were not controlled in the reactions, some notable changes have been observed, highlighting how these factors are influenced by temperature and pressure during HT, as shown in Table 3.1. These observations highlight the complex dynamics within the HT process, providing insights into how variations in these parameters affect the overall efficiency of organic matter solubilisation and nutrient recovery.

3.6.1 Pressure

Pressure plays a crucial role in HT, significantly influencing the physicochemical properties of water and the reaction pathways that occur within the reactor. Maintaining water in a subcritical state where it acts both as a reactant and a solvent requires elevated pressure conditions. In subcritical water, typically achieved under pressures exceeding the vapour pressure of water at the operating temperature, the dielectric constant decreases, and the solubility of organic and inorganic compounds is enhanced. These properties promote the dissolution of recalcitrant compounds, enhance the hydrolysis of complex organic molecules, and facilitate the solubilisation of nutrients, making HT a highly effective method for the pretreatment of WAS (Khandelwal *et al.* 2024).

Figure 3.9 visually depicts how pressure varies with temperature during the HT process. Although the pressure was not actively regulated in this study, it was autogenously

generated within the sealed reactor. The data presented in Table 4.1 reflect this relationship, with pressure values increasing as temperature rises. Specifically, at lower temperatures (approximately 150°C), pressures ranged from 0.45 to 0.70 MPa for residence times of 20 to 70 minutes, respectively. In contrast, at the optimum temperature of 220°C, pressures stabilised at approximately 3.70 MPa. This increase in pressure follows the intrinsic relationship between temperature and vapour pressure as described by the Clausius-Clapeyron equation.

The data in Table 3.1 further illustrate that pressure remains relatively constant at higher temperatures (above 200°C), indicating the system's equilibration. This trend agrees with the Clausius-Clapeyron relation (He *et al.* 2023), in which the vapour pressure stabilises at high temperatures to form a more stable reaction condition in the reactor.

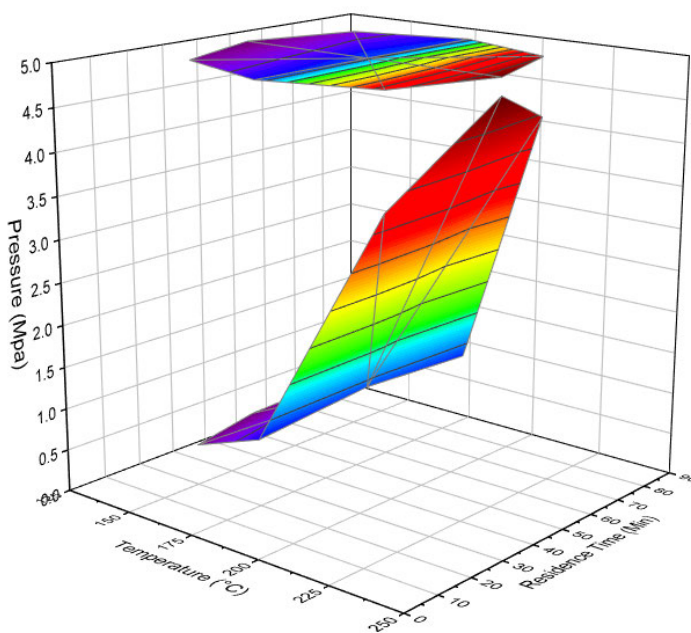


Figure 3.9 Pressure response to the controlled input parameters

Pressure is imposed in an autogenous fashion, making direct manipulation impossible, although observed pressure-temperature dynamics yield helpful information on the operating conditions that produce high efficiency. For example, the pressure-temperature profiles indicate that maintaining a higher pressure, in combination with the desirable

reaction temperature, is necessary for maximum solubilisation of organic matter and maximum nutrient release.

Understanding how pressure affects the kinetics of the reaction and nutrient recovery through HT requires a careful analysis of this data. This observed relationship between pressure, temperature, and residence time can help guide future reactor design optimisation and process scaling-up studies (Zaccariello *et al.* 2022). Furthermore, these factors must be understood in their interaction to take advantage of the solubilisation of organic matter, the release of nutrients and the ultimate valorisation of WAS to bioenergy and bioresources.

3.6.2 pH changes

The pH was not actively regulated during HT either; instead, it was measured before and after each experimental run to determine its natural behaviour under a range of operating conditions (Figure 3.10). This approach provided valuable insights into the chemical dynamics of the HT process.

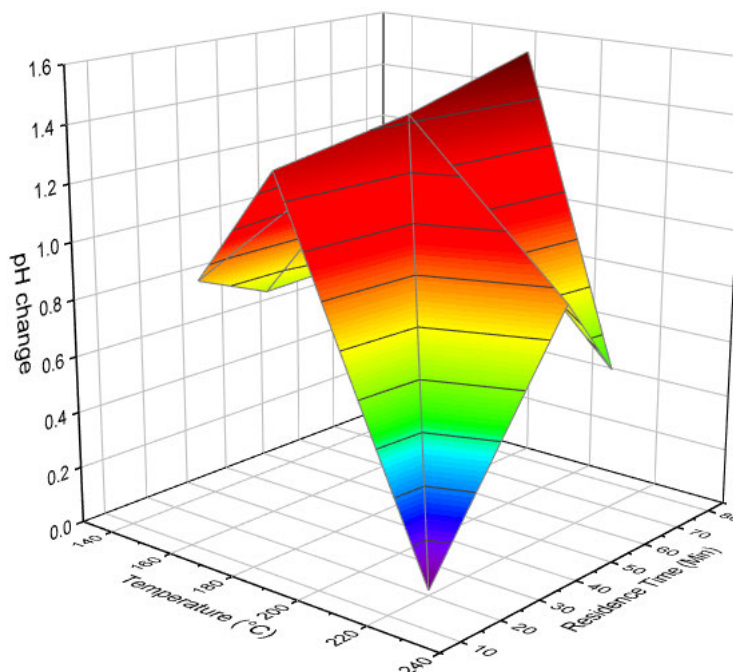


Figure 3.10 pH change response to the controlled input parameters

Data from Table 3.1 reveal that the pH of the sludge consistently decreased during the initial stages of HT. For instance, at 150°C and a 20-minute reaction time, the pH declined from an initial value of 6.95 to 6.05, reflecting the formation of acidic intermediates, such as VFAs and organic acids. This acidification corresponds to the decomposition of complex organic matter. However, at higher temperatures and longer reaction times, the pH displayed a slight upward trend. For example, at 220°C and 20 min, the pH stabilised at 6.02, likely due to the release of ammonia from protein hydrolysis or the dissolution of alkaline compounds in the sludge matrix (Aragón-Briceño, Ross and Camargo-Valero 2017a; Sun *et al.* 2020b).

The acidic conditions observed at lower pH favour the solubilisation of phosphorus, as evidenced by the increased phosphate concentrations in the aqueous phase. Runs conducted at 220°C achieved the highest phosphorus release (~169.9 mg/L) while maintaining a pH close to 6. This behaviour aligns with findings by Sun *et al.* (2020b), which suggest that acidic environments enhance phosphorus bioavailability by preventing its reprecipitation into less soluble forms.

However, SCOD and TOC are heavily influenced by the acidic microenvironment and an increase in the solubilisation of organic matter. For instance, Table 3.1 shows that the SCOD values reached as high as 7951 mg/L under these conditions. Such improved biodegradability is critical to efficient downstream processes, such as AD. Nevertheless, the acidic conditions may also allow the release of heavy metals and additional treatment of the aqueous phase may be required (Villamil *et al.* 2018).

Through further studies, HT could be performed with targeted pH adjustments to optimise nutrient recovery. This can include using acid or base catalysts to increase the solubilisation of compounds, such as phosphorus, while minimising the release of undesired contaminants (Wang *et al.* 2018a). Controlled experiments are crucial for providing a more comprehensive understanding of the interplay between pH, temperature, and reaction time, which could ultimately improve the valorisation potential of waste-activated sludge.

3.7 Comprehensive characterisation of the optimised hydrothermal stream

A comprehensive characterisation of the optimised HT stream is critical to inform the subsequent process, enabling the planning and design of the downstream process. A comparative analysis was made regarding the behaviour of WAS before and after the HT process. These properties include physical and chemical properties, as they are imperative in the choice of downstream processes. It is worth noting that this thorough characterisation was conducted under optimum conditions determined in this study, rather than for individual runs.

3.7.1 Physicochemical properties

The optimisation of HT significantly alters the solid and soluble fractions of WAS, reflecting enhanced solubilisation and resource availability. The reduction in TS and VS content post-HT, as depicted in Table 3.1 and Figure 3.11, correlates with a notable increase in SCOD and TOC. These trends highlight the solubilisation of organic and inorganic matter during HT, with SCOD and TOC serving as reliable indicators of the extent of solubilisation.

$$COD\ Solubilisation\ (\%) = \frac{SCOD_{HT} - SCOD_{WAS}}{TCOD_{WAS}} \times 100 = \frac{7670 - 536}{12465} \times 100 = 57.23225\%$$

The 57.2% COD solubilisation, calculated using Equation 3.2, aligns with findings from previous studies (*Zhang and Chen 2018*), although it is marginally lower than the 65% reported by Kim, Lee and Park (2015). This discrepancy may stem from differences in initial sludge composition or HT conditions, such as temperature and duration. Pretreatment strategies such as dewatering the sludge to concentrate particulates with high COD content could further enhance solubilisation efficiency (Kakar, Tadesse and Elbeshbishy 2022).

Such findings corroborate the role of HT in enhancing sludge biodegradability and nutrient recovery potential. However, optimising parameters such as sludge composition, HT temperature, and residence time remains essential for maximising COD solubilisation and minimising the formation of refractory by-products (Hii *et al.* 2014).

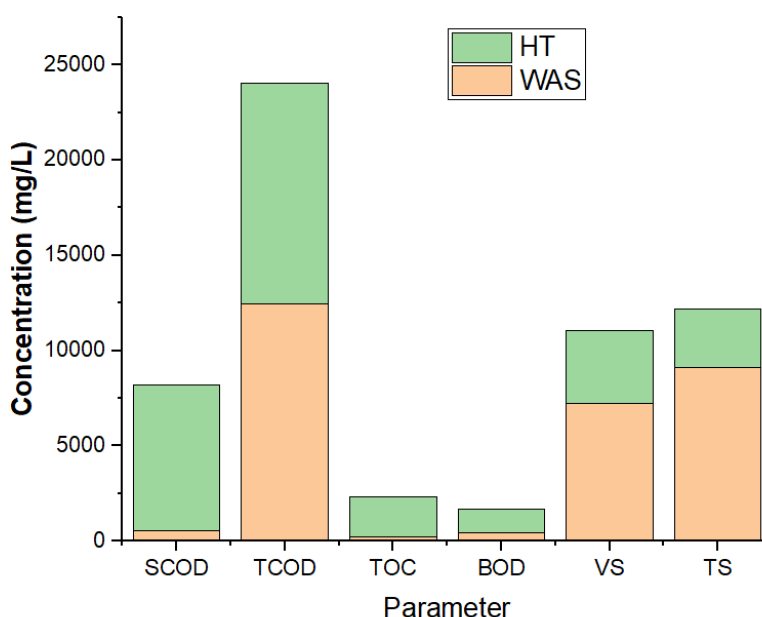


Figure 3.11 Variation of physicochemical properties in response to HT

The observed physicochemical transformations during HT, including increased SCOD and reduced TS, directly impact downstream applications such as AD. Elevated SCOD enhances substrate availability for microbial metabolism, potentially increasing biogas yield during AD. Meanwhile, the reduced solids content lowers viscosity, facilitating improved mixing and pumping efficiency in reactors (Edifor *et al.* 2021).

Moreover, the enrichment of TOC in the liquid phase highlights the potential for resource recovery, particularly in the extraction of organic acids and biofuels. However, the increased ammonia and phosphate concentrations post-HT necessitate careful monitoring to mitigate potential inhibitory effects during AD or nutrient recovery processes (Takaya *et al.* 2016; Rahman *et al.* 2021).

3.7.2 Nutrient and macromolecular analysis

The results of this study highlight the significant efficacy of HT in promoting nutrient solubilisation and macromolecular breakdown in WAS. As shown in Figure 3.12 and calculated using Equation 3.15, phosphate and ammonium solubilisation efficiencies reached 270% and 292%, respectively, reinforcing the transformative potential of HT in

nutrient recovery applications. These findings align with studies such as Takaya *et al.* (2016); Aragón-Briceño, Ross and Camargo-Valero (2017a), which report enhanced nutrient release under elevated hydrothermal conditions.

HT facilitates the thermal decomposition of organic nitrogen and phosphorus complexes into bioavailable forms, such as ammonium (NH_4^+) and orthophosphate (PO_4^{3-}). The increased nitrogen concentrations observed in this study, driven by protein hydrolysis, mirror the findings of Wilson and Novak (2009), who documented similar transformations under comparable conditions.

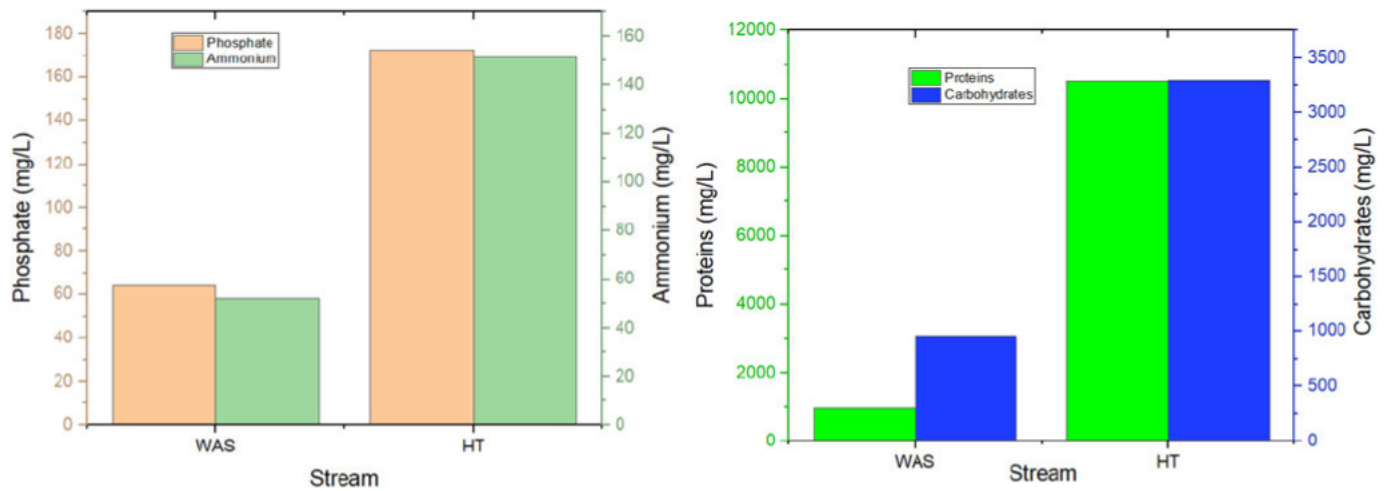


Figure 3.12 Nutrient and macromolecular analysis before and after HT

$$\text{Macromolecule Solubilisation Efficiency}(\%) = \frac{\text{Total nutrient}_{\text{HT}}}{\text{Total nutrient}_{\text{WAS}}} \times 100\% \quad 3.15$$

The significant increase in protein and carbohydrate solubilisation, computed at 1082% and 346%, respectively, demonstrates HT's ability to break down complex macromolecules into simpler, soluble compounds. These changes improve the bioavailability of organic matter, which is critical for subsequent biological processes such as AD and nutrient recovery, a finding consistent with research by Kim, Lee and Park (2015). However, in another study, the concentration of soluble protein increased

significantly for HT in the temperature range from 120 °C to 170 °C, while a gradual decrease was observed for HT between 200 °C and 250 °C (Zhong *et al.* 2022).

Figure 3.13 and Appendix B3 provide insight into the transformation of phosphorus fractions after high-temperature (HT) treatment. Enhanced bioavailability of phosphorus fractions, such as water-soluble and NaOH-soluble phosphorus, was observed. Conversely, the HCl-soluble fraction decreased, likely due to the prior release of encapsulated phosphorus into more accessible forms during HT. This observation aligns with Ekpo *et al.* (2016), who reported a similar redistribution of phosphorus fractions in thermally treated sludge.

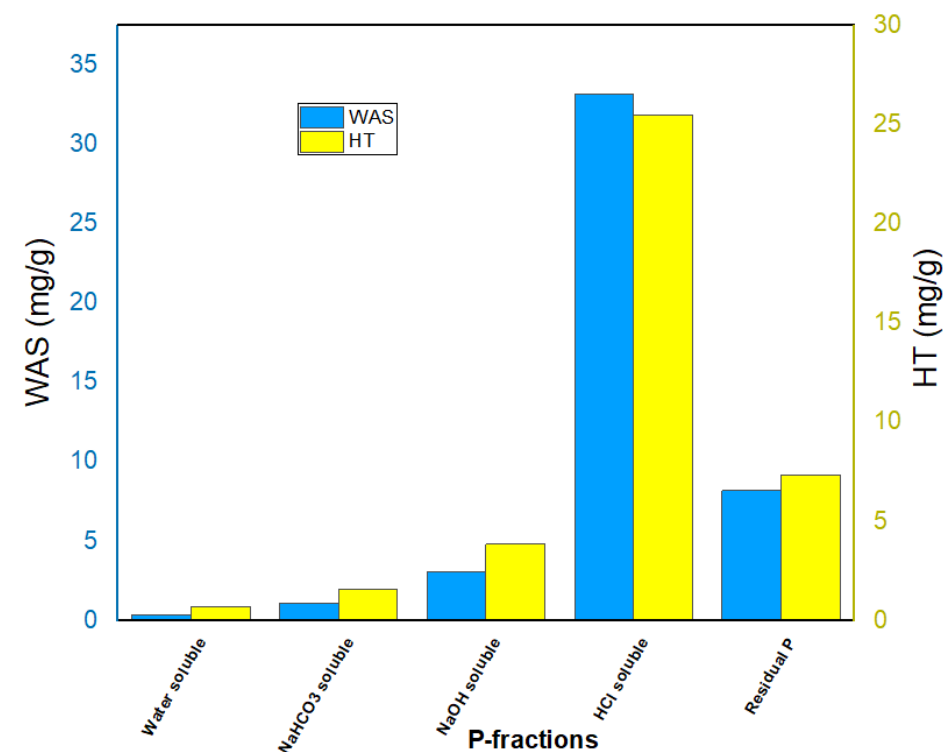


Figure 3.13 P-Fractionation before and after HT

The solubilised nutrients are suitable for direct recovery as fertilisers and enhance the efficiency of AD. Increased SCOD and reduced solids content enhance substrate availability, resulting in higher biogas yields. This finding is consistent with the study by Villamil *et al.* (2020), which clearly demonstrates the potential for HT-treated sludge to be superior to untreated sludge in AD processes. This is a temperature-sensitive process

whereby higher temperatures lead to organic disruption, involving the hydrolysis of macromolecules, while concurrently affecting the fate of phosphorus and nitrogen. Feedstock characteristics, such as the presence of metals, also affect the bioavailability of nutrients after high-temperature (HT) processing. Phosphorus recovery strategies can be influenced by the precipitation of inorganic phosphates with metals such as iron, aluminium, calcium and magnesium (Ekpo *et al.* 2016).

3.7.3 Elemental Analysis

Figure 3.14 and Appendix B2 represent the ultimate analysis of WAS before and after HT, showing the elemental distribution of carbon (C), hydrogen (H), nitrogen (N), sulphur (S), and oxygen (O). The HT-driven compositional changes offer critical insights into transformations and their implications for resource recovery and environmental performance.

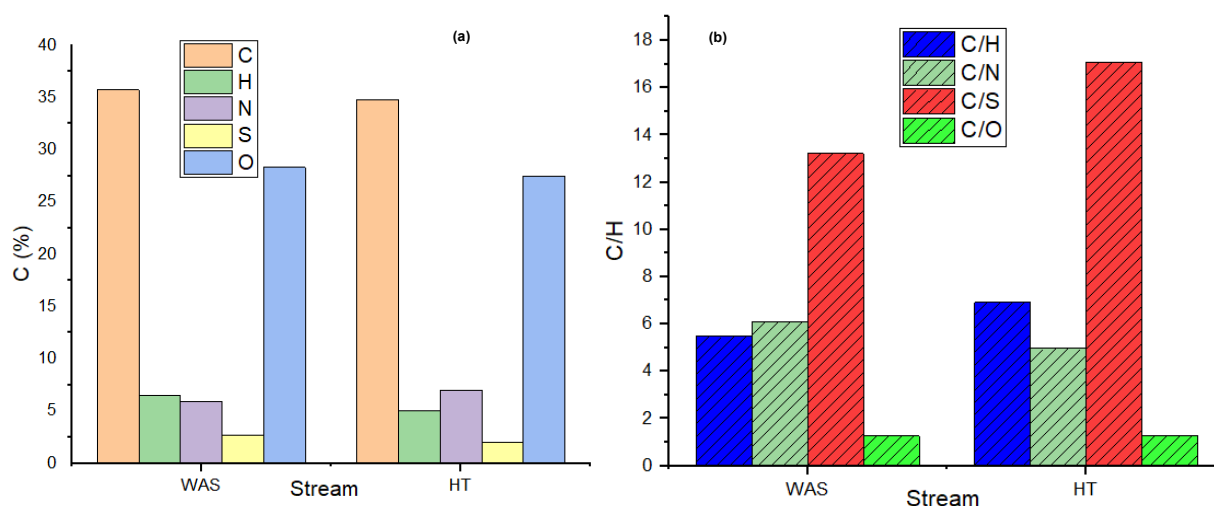


Figure 3.14 (a) Percentage distribution (b) carbon ratios against other elements before and after HT

The elemental composition showed some reduction in carbon, hydrogen, sulphur, and oxygen contents post-HT, but there was also a significant rise in nitrogen. These changes could be attributed to the volatilisation of hydrogen and oxygen as water, the release of sulphur compounds as gases, or the retention or transformation of nitrogen in soluble

forms, such as ammonium (NH_4^+). This aligns with findings from Barani *et al.* (2018), who observed similar trends in hydrothermally treated sludge.

The increase in the C/H ratio from 5.47 to 6.92 signifies improved energy density, making it more suitable for bioenergy applications such as combustion and gasification, as carbon-rich materials exhibit higher calorific values. The optimised elemental composition improves the HHV from 14.7 to 16.9 MJ/kg, as corroborated by Barani *et al.* (2018), who reported similar calorific enhancements in treated biomass.

This aligns with the expected dehydration and decarboxylation processes during HT, which enrich carbon in the solid phase while reducing hydrogen and oxygen (Reza *et al.* 2014). The reduction in the C/N ratio from 6.07 to 4.96 highlights enhanced nutrient recovery potential, particularly for nitrogen, which is vital for downstream processes such as fertiliser production and AD (Ma *et al.* 2018). In their co-digestion studies, Sawatdeenarunat *et al.* (2015) used a C/N ratio of about 20. However, over time, the ideal C/N ratio may vary depending on digestion temperatures and the type of waste being digested.

The significant rise of the C/S Ratio from 13.22 to 17.06 suggests reduced sulphur contamination, which is beneficial for minimising sulphur dioxide emissions during thermal treatment processes. The increase in the C/S ratio after HT results mainly from the volatilisation of sulphur (as hydrogen sulphide and other gases) and solubilisation, which decreases solid-phase sulphur. Moreover, the partial decomposition of organic matter leads to the formation of recalcitrant carbon, which contributes to the solid-phase carbon content. The rise in carbon is relative to sulphur and can further increase the C/S ratio; this finding supports the environmental benefits of HT (Li *et al.* 2018a).

The carbon content is maintained, as indicated by the unchanged C/O ratio, which is crucial for maintaining structural integrity during thermal processes. The stability in oxygen content relative to carbon enables reliable behaviour in energy recovery and material transformation.

3.7.4 Toxins and inhibitory compounds

In this study, toxins are categorised as phenolic compounds (PCs) and heavy metals due to their significant environmental and health implications. HT influences the release, degradation, and potential redistribution of these contaminants, necessitating detailed monitoring to mitigate downstream contamination risks.

The management of PCs in wastewater presents a significant challenge due to their toxicity and persistence. Following HT, phenolic concentrations increased from 59.8 ± 1.2 mg/L to 119.4 ± 1.4 mg/L (Figure 3.15), indicating a 100% rise. This increase aligns with the breakdown of lignin and other organic compounds, a well-documented phenomenon in HT processes. However, this dual effect of HT-enhancing nutrients and macromolecular solubilisation, while generating inhibitory and toxic substances, necessitates additional treatment measures to ensure safe downstream applications. The presence of PCs can inhibit microbial activity, particularly in AD, thereby reducing biogas production efficiency. Moreover, their persistence in wastewater presents environmental concerns, advocating for effective removal or neutralisation strategies. Mu'azu *et al.* (2017) suggest that optimising HT parameters, such as temperature and residence time, can mitigate the formation of these by-products.

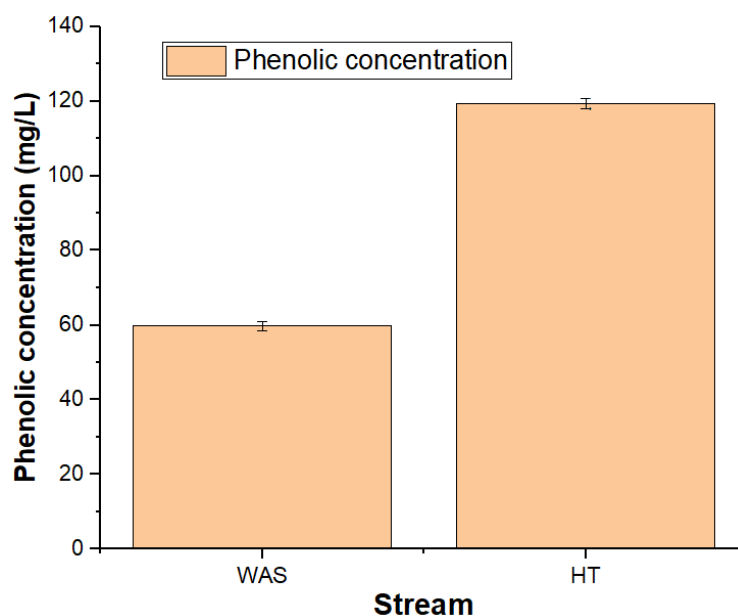


Figure 3.15 Phenolic compounds' behaviour after HT

HT also significantly impacts the distribution and behaviour of heavy metals such as As, Cu, Ni, Pb, and Zn. Appendix B4 illustrates notable shifts in metal concentrations in both untreated and HT-treated WAS. For instance, arsenic levels declined from 2.2×10^{-4} to 9.3×10^{-5} mg/kg, consistent with partial dissolution into the liquid phase during HT. Similarly, lead concentrations decreased slightly from 1.0×10^{-5} to 9.2×10^{-5} mg/kg (Appendix B4). These reductions suggest a partial redistribution of heavy metals, likely influenced by HT conditions, such as temperature, pressure, and reaction dynamics, leading to potential embedment into the hydrochar matrix.

The mobility and speciation of heavy metals under HT conditions are inherently complex. Redistribution patterns indicate that their behaviour under elevated temperature and pressure differs significantly from ambient conditions. Pola *et al.* (2021a) report that metals such as lead and cadmium exhibit an increased tendency to remain in the aqueous phase, forming soluble complexes that pose challenges for effluent management. Effective post-treatment strategies, including chemical precipitation, adsorption, or ion exchange, are essential to mitigate these environmental risks (Singh *et al.* 2023b).

3.8 Changes in the physical properties of WAS

3.8.1 Filterability and dewatering

HT significantly enhances the filterability of WAS, as evidenced by the filtration rate data in Figure 3.16. The filtration rate for HT broth was measured at 4.46 mL/min, a substantial improvement compared to 1.67 mL/min for untreated WAS broth. This indicates that HT disrupts the EPS matrix and hydrolyses complex organic matter, as also noted by Hii *et al.* (2014). Such a transformation decreases filtration resistance, which facilitates the recovery of water in dewatering processes. Filterability improvement is of paramount importance to diminish transportation costs and simplify downstream treatment.

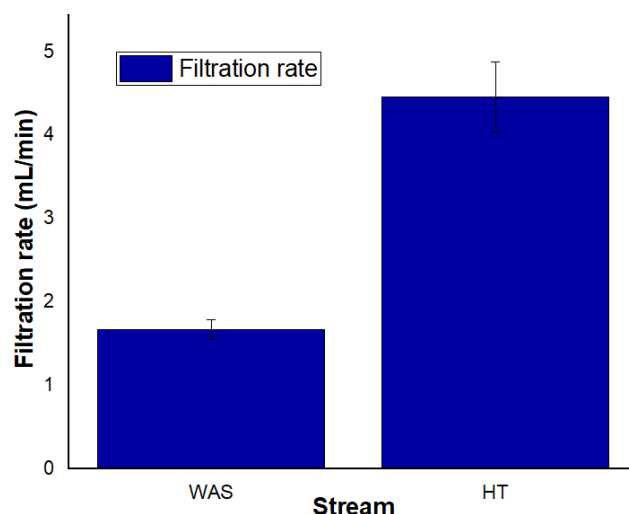


Figure 3.16 Filterability properties of sludge before and after HT

Studies, such as those by Chen *et al.* (2022), corroborate these findings, highlighting the potential of HT to enhance dewatering efficiency by disrupting floc structures. Not only does this improve solubilisation, but it also improves the filtration rate, making it easier to perform sludge management operations. Wang, Li and Chang (2017) demonstrated that the occurrence of HT conditions disrupts the EPS network such that bound water is released. Optimisation of sludge handling and minimisation of the operational costs of wastewater treatment plants depend on this. Improvements in resource recovery potential and operational efficiency are a double advantage resulting from physical transformations of HT in WAS. The energy and cost savings resulting from reduced dewatering come from significant improvements in filterability.

3.8.2 Bulk Density and volumetric properties

The reduction in the volume of WAS after HT, as shown in Figure 3.17, is another indicator of the changes that occur through HT. A decrease from 70 mL to 63 mL (11%) directly correlates to an increase in bulk density from 995 kg/m³ to 1044 kg/m³. This can be attributed to the reduced water-binding capacity of the sludge, a phenomenon consistent with the findings of Kang *et al.* (2021). While higher bulk density offers advantages for transportation, it may also lead to increased energy demands for pumping and agitation

(Ezemagu *et al.* 2021). Therefore, a cost-benefit analysis is essential to optimise operational parameters for balancing these trade-offs.

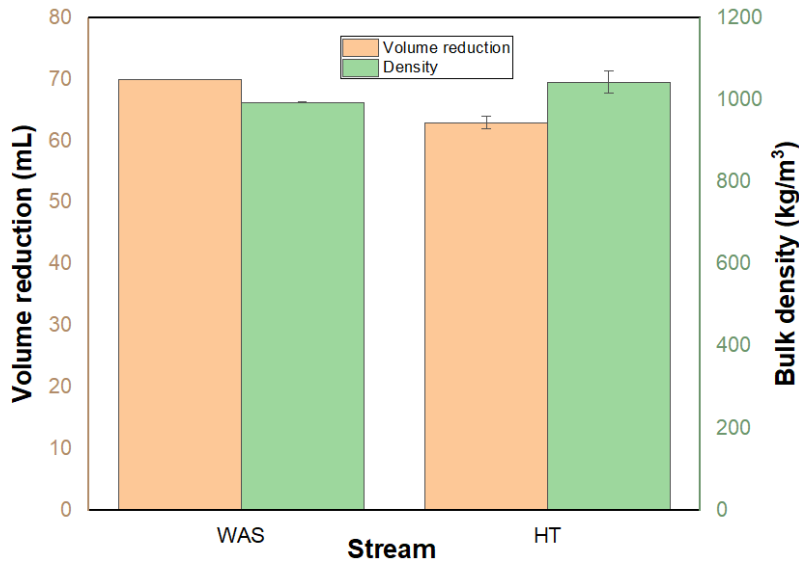


Figure 3.17 Changes in volumetric and bulk density properties of sludge

3.8.3 Specific heat capacity

As shown in Figure 3.18, the increase in specific heat capacity (C_p) from 3929 kJ/kg.°C for WAS to 3963 kJ/kg.°C for HT-treated sludge suggests enhanced thermal properties, which are beneficial for downstream processes such as AD. These values, however, remain below the C_p of water (4194 kJ/kg.°C), indicating that sludge retains favourable energy transfer characteristics after treatment. Similar observations by Danso-Boateng *et al.* (2015a); Wilk *et al.* (2022) reinforce the importance of C_p in assessing heating requirements for AD.

Kim, Lee and Park (2015) reported that a marginal increase in C_p can improve energy efficiency during thermal processes. This supports the argument for integrating HT as a pretreatment step for WAS.

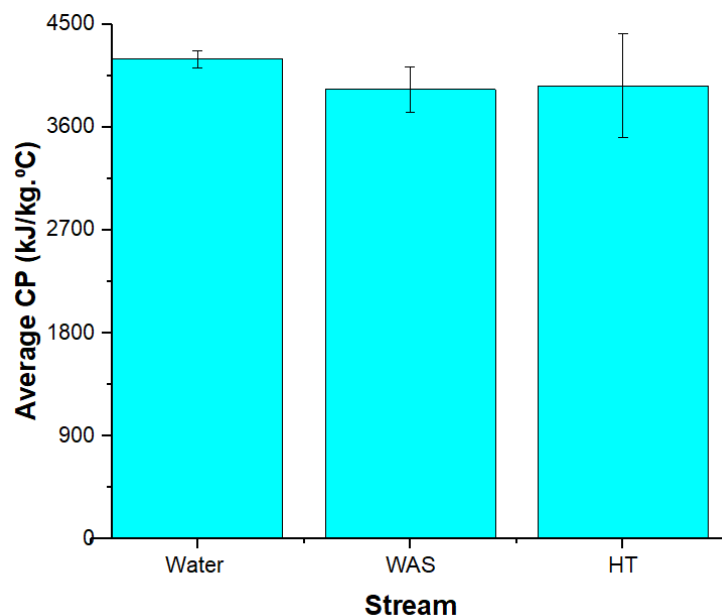


Figure 3.18 Specific heat properties before and after HT

3.9 Structural comparative characterisation

Morphology, crystallography, and functional groups of the WAS and the HT streams were determined using SEM, XRD, and FTIR, respectively.

3.9.1 Changes in morphological properties

Before HT, the sludge exhibited a carbon (C) content ranging from 40.67 wt% to 53.89 wt%, paired with oxygen (O) levels between 32.77 wt% and 33.63 wt%, indicating a high organic matter concentration typical of untreated WAS (Figure 3.19(a)). After HT, the carbon content increased to 47.46 wt% at site 1 (Figure 3.19(b)), reflecting enhanced carbonisation and potential for higher energy density in the resulting hydrochar. However, the carbon content decreased significantly to 17.73 wt% at Site 2, possibly due to variations in process conditions or the degree of organic matter solubilisation. Oxygen levels similarly showed contrasting behaviour, with a decrease to 27.72 wt% at Site 1 and an increase to 41.77 wt% at Site 2, suggesting site-specific differences in oxidative reactions during HT.

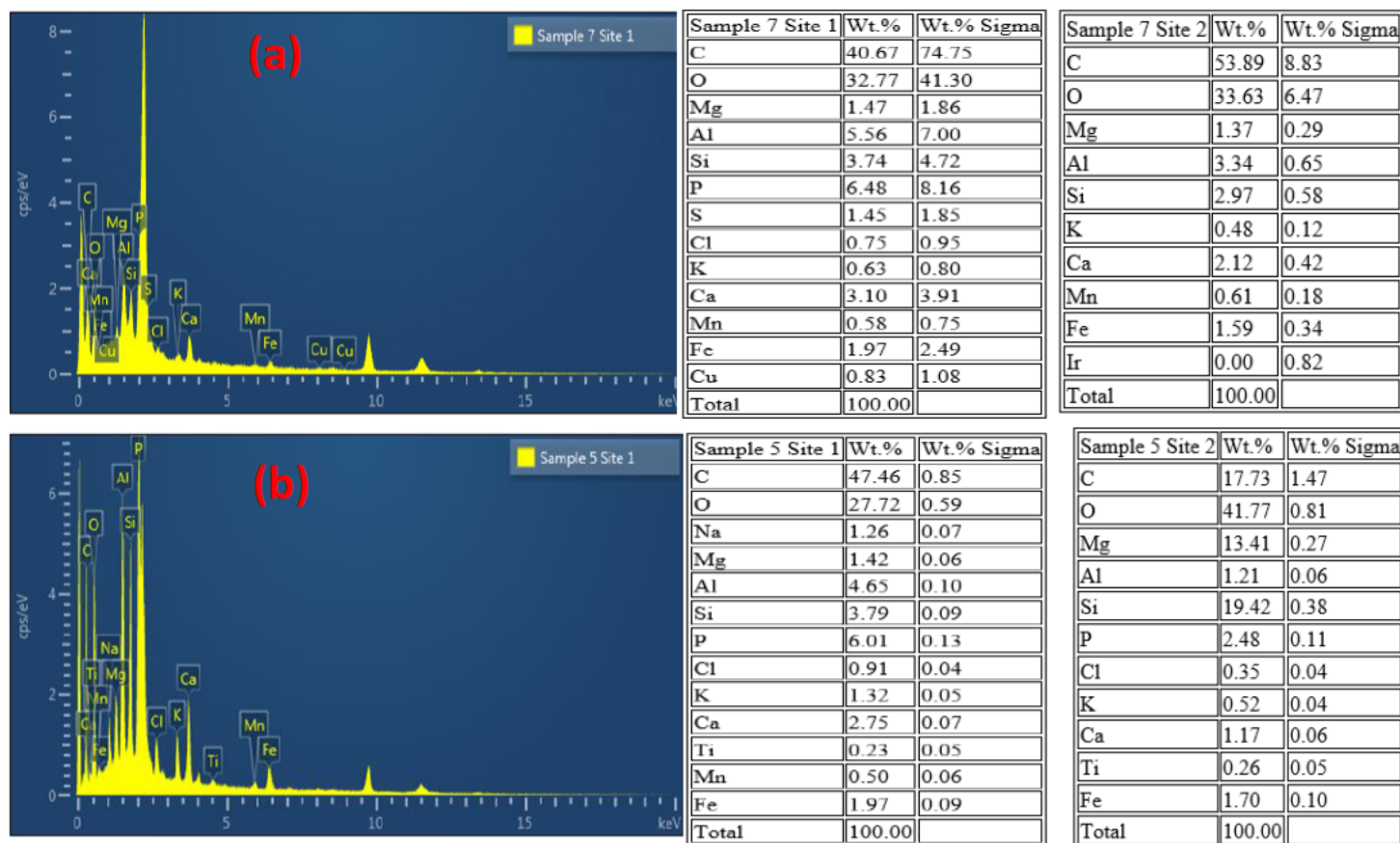


Figure 3.19 SEM-EDS elemental composition (a) WAS stream, (b) HT stream.

Phosphorus (P), an essential nutrient for recovery, showed slight reductions after HT, dropping from 6.48 wt% to 6.01 wt% at site 1 and from 2.48 wt% to 1.42 wt% at site 2. These changes may indicate partial solubilisation of phosphorus compounds into the aqueous phase, enhancing their potential bioavailability. Elements like aluminium and silicon remained relatively stable, indicating their resistance to solubilisation under HT conditions.

The SEM image of the HT in Figure 3.20(b) showcases a material with a rough, granular texture and irregularly shaped particles. The densely packed spherical or oval-like structures suggest aggregated formations, likely a result of the breakdown and restructuring of organic and inorganic components during HT. The presence of small voids or pores between these aggregates indicates increased porosity, a common

characteristic of hydrothermally treated materials, which enhances adsorption capacity and catalytic potential.

The particle size distribution appears non-uniform, ranging from smaller granules to larger clusters, reflecting partial solubilisation of organic matter and precipitation of inorganic minerals. This structural transformation aligns with the changes observed in the elemental composition, including carbon enrichment and the precipitation of elements such as magnesium and calcium. The smoothness of the granules further supports the idea of HT-induced solubilisation and reprecipitation, resulting in a more compact and stable material.

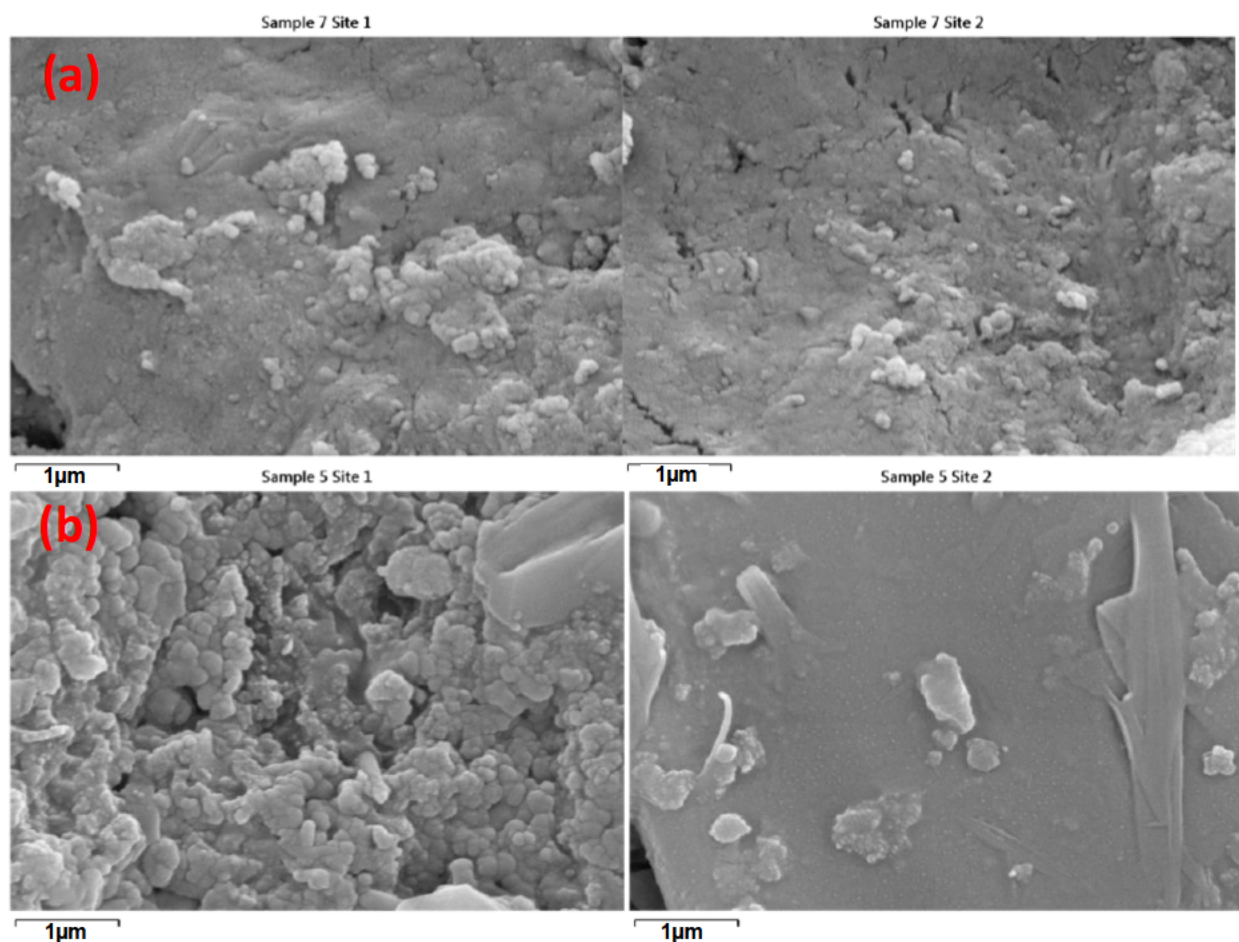


Figure 3.20 Scanning electron microscopy (SEM) micrographs showing morphological characteristics of (a) untreated waste-activated sludge (WAS) and (b) hydrothermally treated (HT) sludge.

The combined insights from elemental analysis and SEM morphology suggest that HT significantly modifies the physical and chemical properties of WAS. The increased carbon content and enhanced porosity in the HT solids improve their potential for energy recovery and adsorption applications.

3.9.2 Changes in crystallography

The XRD analysis presented in Figure 3.21 provides a comparative insight into the structural changes in WAS before and after HT. The key differences between the two states are reflected in the intensity and pattern of the diffraction peaks, signifying alterations in crystallinity and phase composition.

The XRD analysis presented in Figure 3.21 provides a comparative insight into the structural modifications of waste-activated sludge (WAS) before and after hydrothermal treatment (HT). Distinct differences are evident in the intensity and distribution of diffraction peaks, indicating variations in crystallinity and phase composition.

Before HT, the WAS exhibited sharper and more pronounced peaks, particularly within the 2θ range of 20° - 30° , which are characteristic of crystalline mineral phases such as quartz (SiO_2), calcite (CaCO_3), and other silicate-based compounds naturally embedded in the sludge matrix. The higher peak intensity observed in the pre-HT sample reflects a greater degree of structural order and mineral crystallinity, consistent with the predominance of these inorganic constituents.

Following HT, the diffraction pattern demonstrated a substantial reduction in peak intensity accompanied by peak broadening. This behaviour signifies a decline in crystallinity and the formation of amorphous phases, attributed to the decomposition, dehydration, and decarbonation reactions that occur under elevated temperatures and pressures. The emergence of a broad hump centred around $2\theta \approx 20^\circ$ indicates the presence of disordered carbonaceous structures and amorphous organic–mineral complexes resulting from thermal breakdown and reprecipitation processes.

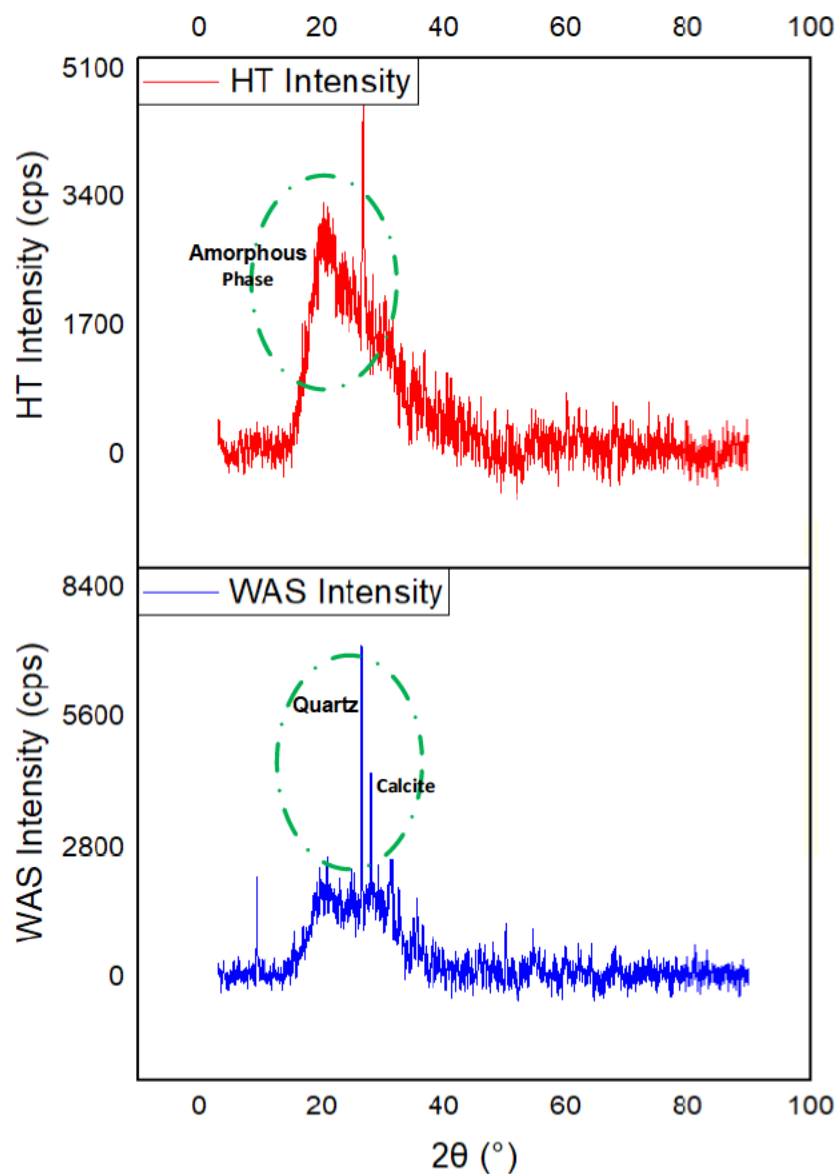


Figure 3.21 X-ray diffraction (XRD) spectra of waste-activated sludge before and after hydrothermal treatment

These transformations correlate with morphological changes observed in the SEM micrographs (Figure 3.20), which reveal increased surface roughness, granular disintegration, and enhanced porosity in the post-HT sample. The transition from crystalline minerals to amorphous carbonaceous phases consequently enhances surface reactivity, improves adsorption capacity, and facilitates nutrient recovery, aligning with the fundamental objectives of hydrothermal treatment in upgrading sludge functionality.

The conversion of crystalline quartz and calcite phases into amorphous carbon-rich structures represents a key physicochemical transformation that underpins the enhanced reactivity and bioresource recovery potential of hydrothermally treated sludge (Gopinath *et al.* 2021; Zhang *et al.* 2023a).

3.9.3 Changes in functional groups

The FTIR spectra in Figure 3.22 reveal significant molecular transformations in the WAS before and after HT. In the untreated WAS sample, the spectra exhibit low transmission intensities, indicating a limited presence or availability of functional groups.

In contrast, the HT-treated sample exhibits a notable enhancement in transmission intensity across key wavenumber ranges, indicating the breakdown of complex organic compounds and the release of functional groups under the high-temperature and high-pressure conditions of HT.

Key functional groups emerge post-HT, particularly in regions associated with hydroxyl (-OH) stretching ($3600\text{--}3200\text{ cm}^{-1}$), carbonyl (C=O) stretching ($\sim 1700\text{ cm}^{-1}$), and aliphatic C-H stretching ($2900\text{--}2800\text{ cm}^{-1}$). These peaks indicate the decomposition of polymeric substances, such as proteins and polysaccharides, into simpler molecules, as well as the potential formation of carboxylic acids and alcohols. For example, the heightened peak near 1640 cm^{-1} correlates with amide bonds from proteins, reflecting their hydrolysis during HT (He *et al.* 2016).

Furthermore, the intensity increases in the $1000\text{--}1200\text{ cm}^{-1}$ range, corresponding to phosphate and silicate groups, suggesting mineral transformations or the release of inorganic compounds. The observed molecular changes align with the solubilisation of organic matter and the precipitation of inorganic species during HT, enhancing the sludge's suitability for resource recovery applications.

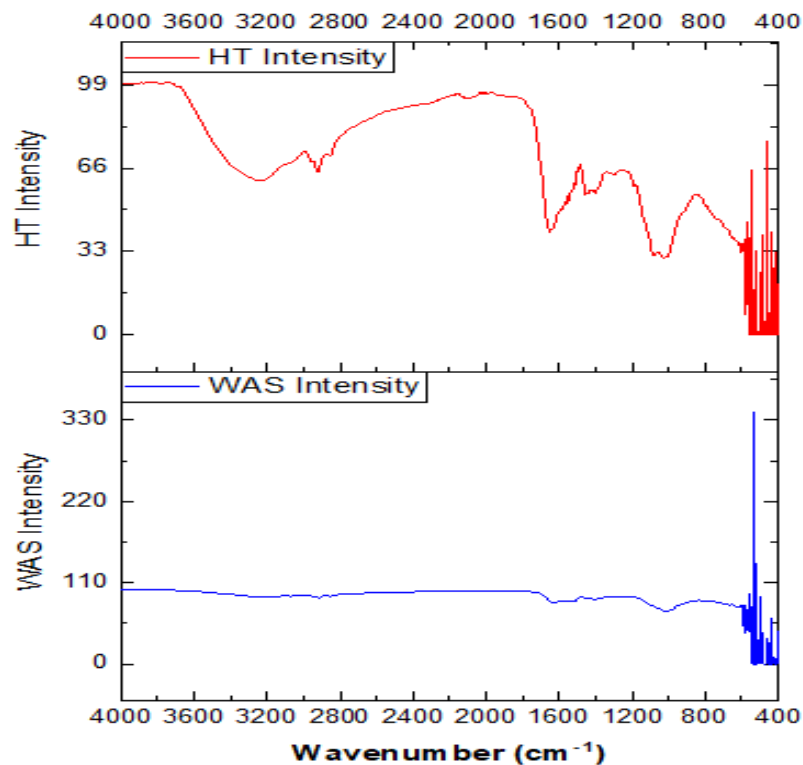


Figure 3.22 Fourier-transform infrared (FTIR) spectra of waste-activated sludge before and after hydrothermal treatment

The differences in the spectra suggest that HT can alter the molecular composition of WAS, thereby improving reactivity and opening up the prospect of nutrient recovery and bioenergy production. These results are consistent with those of Flemming *et al.* (2024), indicating that thermal treatment leads to a sequential breakdown of polymeric substrates, thereby increasing the availability of functional groups and enhancing material properties for downstream processes.

3.10 Hydrochar recovery, composition, and phosphorus retention

The HT process yields hydrochar, a valuable solid product with significant advantages over dried waste-activated sludge (WAS) in terms of higher energy density and resource recovery potential. Figure 3.23 illustrates that hydrochar and dried sludge recovery yields were 2.21 ± 0.05 g/L and 4.61 ± 0.09 g/L, respectively. Compared to conventional WAS

treatment methods, hydrochar presents economic and environmental benefits across sectors such as agriculture, energy production, and environmental remediation, particularly due to its high adsorption capacity.

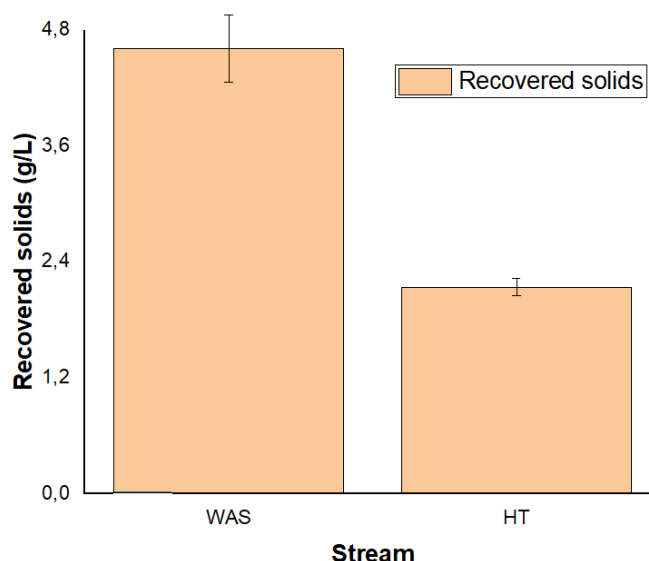


Figure 3.23 Comparison of recovered solid yields (hydrochar) from waste-activated sludge before and after hydrothermal treatment

The higher heating value (HHV) of hydrochar, calculated using Equation 3.9, is 16.9 MJ/kg, which is marginally greater than that of untreated WAS (14.7 MJ/kg). This suggests that hydrochar can serve as a viable energy source before further processing, as its superior calorific value enhances combustion efficiency. Hydrochar's elemental composition includes carbon (35.27%), hydrogen (5.38%), nitrogen (4.18%), sulphur (2.11%), and oxygen (17.32%), with an increased carbon fraction contributing to enhanced thermal stability and aromaticity. These properties, arising from hydrolysis, dehydration, and decarboxylation reactions, align with findings by Park *et al.* (2019b); Sharma, Sarmah and Dubey (2020), who reported an increased calorific value with elevated HT temperatures due to enhanced carbon retention and reduced hydrogen and oxygen content.

Although hydrochar's HHV remains lower than that of sub-bituminous coal (19-24 MJ/kg) (Danso-Boateng *et al.* 2015a; Villamil *et al.* 2019), it is still a viable biofuel alternative. Its

high carbon content supports its application in environmental remediation as a soil amendment and a cost-effective adsorbent (Mahmood Al-Nuaimy *et al.* 2024). Thus, hydrochar plays a crucial role in circular economy principles and sustainable resource recovery.

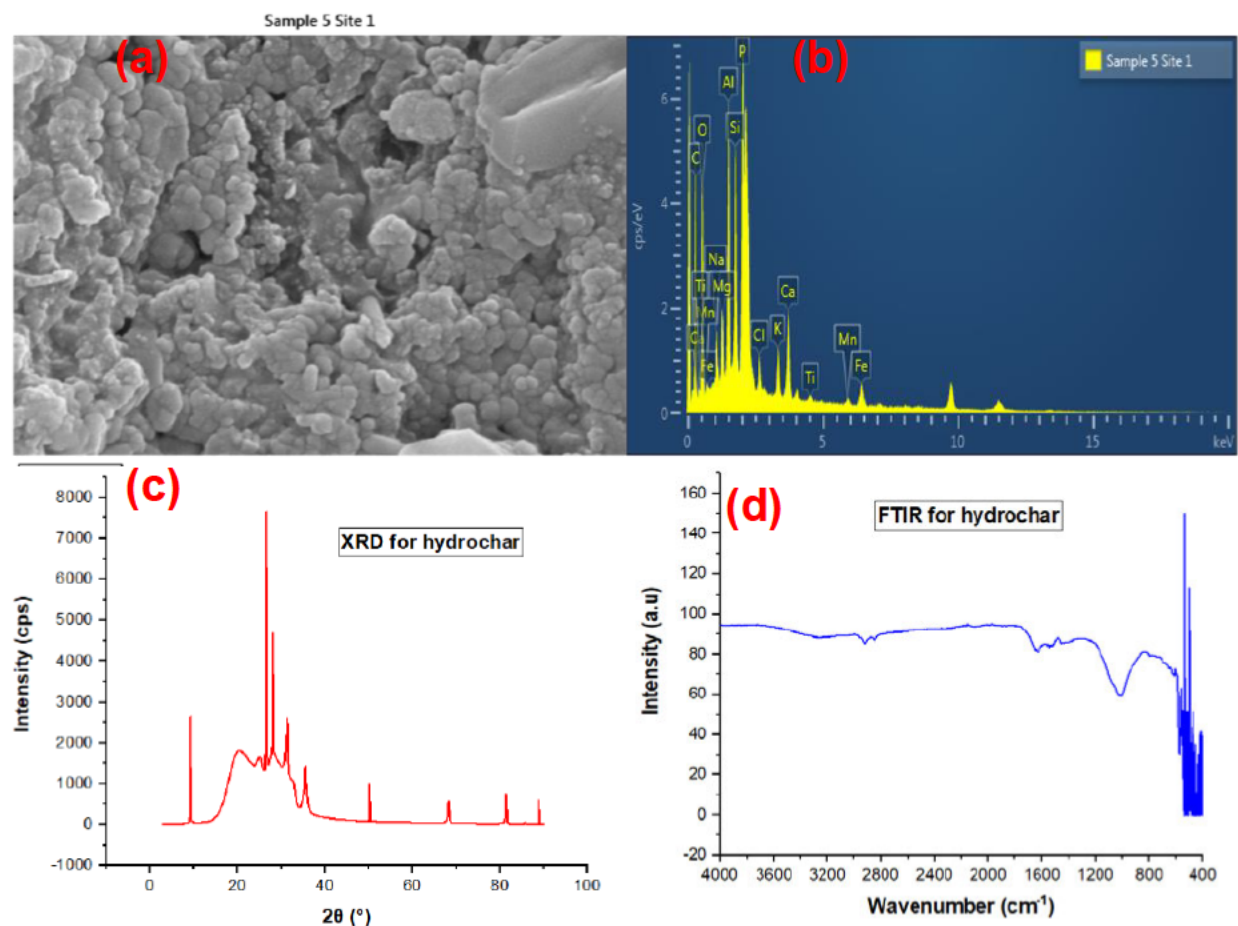


Figure 3.24 Properties of hydrochar (a) SEM image (b) EDS (c) XRD (d) FTIR spectra

Beyond energy applications, hydrochar exhibits considerable adsorption potential for nutrients and contaminants, as demonstrated by FTIR, SEM-EDS, and XRD analyses (Figure 3.24, Appendices B2 and B4). In this study, hydrochar yielded 2.21 ± 0.05 g/L with a phosphorus content of 6.01 wt%, indicating its ability to retain phosphorus and influence phosphorus recovery during struvite precipitation. Its elemental composition includes carbon (47.46 wt%), oxygen (27.72 wt%), and trace amounts of magnesium (1.42 wt%),

aluminium (4.65 wt%), and calcium (2.75 wt%) based on EDS analysis (Figure 3.24 (b)), which provide active adsorption sites for pollutants and nutrients.

The FTIR spectra of the hydrochar also indicate the presence of the relevant functional groups necessary for adsorption processes. Thus, vibrations in the region of 3420 cm^{-1} are associated with hydroxyl groups (-OH), and vibrations at 1620 cm^{-1} are indicative of carboxyl (-COOH) groups (Figure 3.24 (d)), which enhance hydrochar's adsorption capacity for phosphorus and organic contaminants through hydrogen bonding and electrostatic interactions. SEM imaging (Figure 3.24 (a)) depicts a highly porous surface morphology, indicative of significant adsorptive capacity, facilitating the retention of phosphorus ($16.6 \pm 1.6\text{ mg-P/g}$) XRD analysis (Figure 3.24 (c)) confirms the presence of crystalline hydroxyapatite (25.26° , 31.5° , 36.9° , and 42.3°) and quartz minerals (26.6° , 36.9° , 42.5° , and 50.4°), contributing to hydrochar stability and pollutant immobilisation (Phuong Tran *et al.* 2021). The coexistence of crystalline phases and the amorphous carbon matrix further supports hydrochar's function as a nutrient-adsorbing material.

In addition to its adsorption properties, hydrochar's HHV of 16.9 MJ/kg reinforces its potential as a bioenergy feedstock. However, over 62% of the total phosphorus remains trapped within the hydrochar matrix, posing challenges for the recovery of phosphorus downstream. Optimising phosphorus release before utilisation may require acid digestion or thermal reactivation (Gherghel, Teodosiu and De Gisi 2019). These findings align with those of Wu *et al.* (2021); Belluati *et al.* (2024), who identified similar adsorption mechanisms and valorisation pathways for hydrothermally derived carbon materials.

Hydrochar thus emerges as a multifunctional product with promising applications in bioenergy, environmental remediation, and nutrient recovery, reinforcing its role in advancing sustainable wastewater management.

3.11 Chapter summary

In this chapter, the optimum conditions for HT of WAS from a local WWTP were delineated. Critical parameters, such as temperature and residence time, were comprehensively studied, as well as their effect on key response factors, using a

systematic approach based on the design of experiments through RSM. HT proved its efficacy as a solubilisation enhancer and in the nutrient recovery process by successfully establishing predictive mathematical models and identifying optimum operating conditions (220°C and 20 min). Results from the analysis indicated substantial effects of HT upon the efficiency and performance of downstream processes such as AD and nutrient recovery via struvite precipitation. Improved energy yields and resource recovery were highlighted through key findings, including increases in SCOD, ammonium, phosphate, protein, and carbohydrate concentrations.

Moreover, HT also showed promise in generating value-added byproducts, such as hydrochar, as a sustainable approach to wastewater management. The synergistic effects of optimised HT conditions on energy recovery and nutrient availability underscore its transformative power in contemporary wastewater treatment techniques. These findings support the broader objectives of environmental sustainability and the principles of the circular economy, promoting resource conservation and waste reduction. The chapter provides a solid foundation for HT to serve as a crucial technology in the valorisation of sewage sludge, with scalable and efficient technologies for both the recovery of bioresources and their co-processing within the plant.

CHAPTER 4: EFFICIENCY OF USING BIOCHAR FOR TOXIN REMOVAL IN HYDROTHERMAL TREATMENT PROCESSES THROUGH ADSORPTION

4.1 Introduction

HT is increasingly recognised as a key technology for the valorisation of wastewater resources, notably waste-activated sludge (WAS). HT operates at a subcritical temperature of water at which complex organic and inorganic materials decompose to produce value-added biogas, hydrochar, and nutrient-enriched aqueous fraction. It results in a significant reduction in sludge volume, enhanced solubilisation of organic matter, and nutrient recovery that aligns with circular economy principles. However, HT also produces by-products consisting of toxins, such as heavy metals and phenolic compounds (PCs), which pose a significant risk to human health and could lead to considerable environmental contamination if not properly treated.

The presence of heavy metals in HT effluent, often originating from industrial sources, and phenolics from the degradation of lignin and other organic compounds exemplifies the dual challenge of resource recovery and environmental safety (Mehrez *et al.* 2024). The hydrochar and aqueous streams from HT can be contaminated with these toxins, which then could inhibit subsequent biological treatment processes. There is a need to address these concerns to exploit the full potential of HT as a sustainable wastewater valorisation method.

As an adsorbent for pollutant removal, biochar is a porous, carbon-rich material produced by the pyrolysis of biomass. It has a high specific surface area, functionalized surface chemistry, and stability, enabling it to adsorb a broad range of contaminants, including heavy metals and phenolics. Heavy metal ion exchange, electrostatic attraction and complexation by ions are all important interaction parameters, while phenolic compounds are removed by π - π interactions and hydrogen bonding (Ambaye *et al.* 2021). Biochar modification, most recently through magnetisation, also improves its adsorption capabilities and simplifies recovery after adsorption, offering practical advantages for wastewater treatment.

In the KwaZulu-Natal province of South Africa, there is an abundance of SCB, a by-product of sugarcane processing. The annual milling capacity of sugarcane in South Africa is estimated to be approximately 6 million tonnes, resulting in around 1.7 million tonnes of dry bagasse (Mkhwanazi, Isa and Vallabh 2023). Notably, one-third of this bagasse is surplus to factory requirements, equating to approximately 0.6 million tonnes of SCB underutilised per year.

Biochar production from this surplus SCB presents a sustainable utilisation opportunity for pollutant adsorption from HT effluents. Conversion of excess SCB to biochar not only solves waste disposal challenges but also supports environmental remediation. Consequently, in this context, it is possible to apply substantial amounts of surplus SCB in KwaZulu-Natal to design biochar production and mitigate waste and environmental pollution.

The primary objective of this chapter is to evaluate the heavy metal and phenolic compound adsorption efficiency of SCB-derived biochar from HT effluent. The study examines the optimal conditions for adsorption, focusing on critical parameters such as pH, temperature, and the dosage of biochar. It also studies the performance of biochar adsorption as influenced by changes in biochar modification, including magnetisation and operational feasibility. The results of this study aim to guide the integration of biochar-based HT for systems within wastewater valorisation, thus enhancing the sustainability of these technologies.

4.2 Methodology

4.2.1 Biochar production

The products from the hydrothermal pretreatment stage were directed to the detoxification unit, where biochar served as the adsorbent. The biochar was produced from locally sourced sugarcane bagasse obtained from the Sugar Milling Research Institute (SMRI-UKZN), as shown in Figure 4.1.

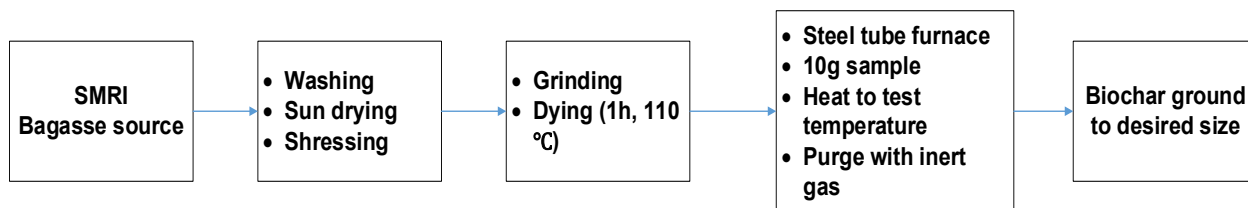


Figure 4.1 Flowsheet for biochar production

The bagasse feedstock was washed with distilled water to remove dust, air-dried at room temperature, and then oven-dried at 110 °C for 1 h. The dried bagasse was cut into small fragments and placed in ceramic crucibles for pyrolysis in a Steel Tube Furnace (Model A08A23HWB, Bogo Ticino, Italy). To maintain oxygen-free conditions, nitrogen gas was pumped at a rate of 100 mL/min for 45 min to purge the system. To select the best biochar for adsorption, the samples were pyrolysed at temperatures of 450, 500, 550, 600, and 650 °C for 4 h, with a heating rate of 15 °C/min. After pyrolysis, the biochar samples were ground, sieved through a 600 µm sieve, dried at 105 °C, and stored under vacuum at 4 °C for subsequent use (Kumar *et al.* 2021). The samples were labelled T450, T500, T550, T600, and T650 based on the pyrolysis temperature.

4.2.2 Preparation of magnetic biochar

The best biochar (determined by the treatment temperature) was used for the optimisation after magnetic activation, based on BET and elemental analysis, as the exclusion criteria. The magnetic biochar (MBC) was synthesised from sugarcane bagasse using the methods of Son *et al.* (2018) and Li *et al.* (2020b). Biochar (50 g) was suspended in 500 mL of distilled water. A ferric chloride solution was prepared by dissolving 18 g (110.97 mmol) of FeCl₃ in 1,300 mL of distilled water, stirring for 5 minutes at room temperature. Separately, 36.6 g (131.64 mmol) of FeSO₄·7H₂O was dissolved in 150 mL of distilled water and stirred for 5 minutes at room temperature. The FeSO₄·7H₂O solution was then added to the FeCl₃ solution and stirred vigorously at 60-70 °C for 5 min.

The combined Fe²⁺/Fe³⁺ solution (1450 mL) was slowly added to the biochar suspension at room temperature and stirred gently at 50 rpm for 30 min. A 10 M NaOH solution was then added dropwise (~1 h) to the mixture using a disposable pipette until the pH reached

10-11. During the addition of NaOH, the suspension turned dark brown at a pH of ~6 and black at a pH of ~10. The mixture was further stirred for 1 h and then aged at room temperature for 24 h to complete precipitation.

The Fe₃O₄-magnetised sugarcane bagasse was filtered and washed repeatedly with distilled water and ethanol. These washings, along with exposure to 10 M NaOH during Fe₃O₄ precipitation, removed residual carboxylic acids, phenolic compounds, and other acidic organic materials from the biochar. The MBC was vacuum-filtered and dried overnight at 50 °C in a hot air oven. It was stored in plastic containers until further use.

The adsorption capabilities of MBC were compared with those of commercially available activated carbon (AC). The AC was magnetised using the same procedure and labelled as magnetic activated carbon (MAC).

4.2.3 Biochar characterisation

Figure 4.2 shows a comprehensive characterisation of biochar in this study.

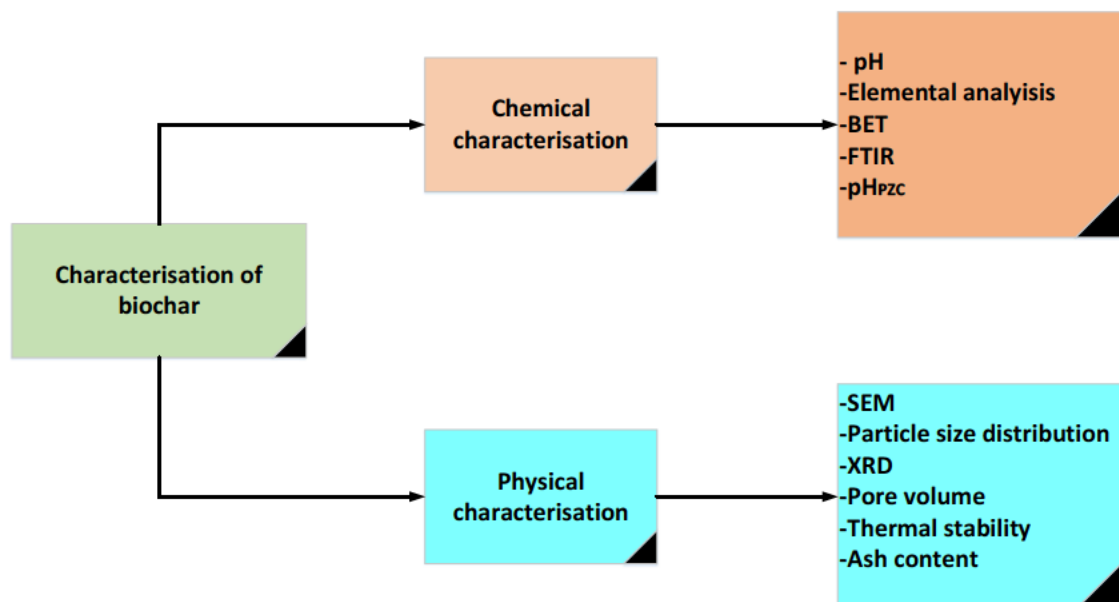


Figure 4.2 A Comprehensive characterisation of biochar

The pH of the different types of biochar was measured in a 5% (w/v) biochar/distilled water suspension after 24 h of stirring at 160 rpm. The pH was determined using a calibrated pH meter (Lovibond SensoDirect 150, Germany). The carbon, nitrogen,

oxygen, and hydrogen content of the samples was determined using an elemental analyser (CHNS/O analyser), and the ash content of the biochar samples was determined by combusting the dried samples to a constant weight in a muffle furnace, as outlined in previous chapters. The specific surface area and pore size distribution of the biochar samples were analysed using a Micromeritics TriStar II Plus 3.01 BET Surface Area and Porosity Analyser (Micromeritics Instrument Corporation, Norcross, GA, USA). This analysis employed N₂ sorption isotherms and the BET method at 77 K (-196°C), following the methodology of Brunauer, Emmett, and Teller (Brunauer, Emmett and Teller 1938; Sumaraj *et al.* 2020).

The salt addition method was used to determine the pH at the point of zero charge (pH_{pzc}) values of the biochar samples, following the procedure described by Hai *et al.* (2024). In this method, 0.1 g of biochar and modified biochar (MBC) samples were mixed with 50 mL of a 0.1 M KNO₃ solution. The pH of the suspensions was adjusted to initial values of 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 using either 0.1 M HNO₃ or 0.1 M NaOH solutions. The pH of each suspension was measured using a pH meter (Lovibond SensoDirect 150, Germany). Each flask was agitated in a shaker bath for 24 h at 200 rpm and 30 °C, after which the equilibrium pH of the solution was measured. The difference between the initial and equilibrium pH was plotted against the initial pH of the solution, and the point at which the graph crossed the x-axis was recorded as the pH_{pzc}, after which the equilibrium pH of the solution was measured. Crystallography, morphology and functional groups were determined using XRD, SEM-EDS and FTIR, as described in Section 3.2.4.

4.2.4 Design of experiments for adsorption

The adsorptivity of heavy metals and phenolic compounds (PC) (collectively referred to as toxins) was investigated by considering pH, adsorbent dosage, and contact time as the input variables. In contrast, the concentrations of heavy metals and PC were regarded as the output factors. A central composite design (CCD) under RSM was employed to design the experiments and generate the number of experimental runs required to determine the optimal operating conditions for the adsorption of PC and heavy metals.

The input parameters included pH (3-9) (Li *et al.* 2020b), adsorbent dosage (5-15 g/L) (Kołodęńska *et al.* 2017), and contact time (35–100 min) (Kılıç *et al.* 2013; Yap *et al.* 2017; Maneechakr and Mongkollertlop 2020), as detailed in Table 4.5. Design Expert software was utilised to design 20 experimental runs with 5 centre points, which were conducted in duplicate to ensure reliability.

4.2.5 Experimental setup for adsorption

250 mL conical flasks were used as reactors in batch mode, and 100 mL of hydrothermally treated waste-activated sludge was added to each flask. MBC was introduced into the reaction vessels according to the designed experimental matrix. The mass of the adsorbent was measured on a dry basis in a humidity-free environment, with a permissible accuracy of ± 0.1 g.

The experiments were conducted at room temperature and atmospheric pressure. The pH of the solution was measured using a calibrated pH meter (Lovibond SensoDirect 150, Germany), and the pH was adjusted as necessary using 2 M NaOH or 2 M HCl. The pH was monitored and maintained with an accuracy of ± 0.1 pH units. The conical flask was placed on the OrbiShake Platform Shakers, Model 261 (Labotec, Midrand, South Africa), at 160 rpm for the duration of the investigation for that particular run.

4.2.5.1 Phenolic compounds and heavy metals analyses

Total phenolic content was determined by the Folin-Ciocalteu (F-C) assay, which measures the reducing capacity of phenolic compounds as indicators of their concentration (Ainsworth and Gillespie 2007; Lamuela-Raventós 2018). A stock solution of gallic acid was diluted to prepare a series of standards (0.1 mg/L – 1.0 mg/L) for the standard calibration curve. Phenolic compounds were extracted using an appropriate solvent (methanol or ethanol), and then the particulates were removed by filtering the samples.

0.5 mL of each sample or standard solution and 0.5 mL of Folin-Ciocalteu reagent were mixed at room temperature in test tubes. The mixtures were vortexed and then incubated in the dark at room temperature (20 °C) for approximately 5-10 min to allow the reagent to react with the phenolic compounds. Then, 1.5 mL of a 20% sodium carbonate solution

was added to each tube, and the mixtures were thoroughly mixed. The tubes were then allowed to stand for 30 minutes at room temperature, after which the phenolic content could cause a blue colour development proportional to the concentration of the phenolics present.

Reaction mixtures were measured at 725 nm using a spectrophotometer with a blank solution containing all reagents except the sample as a reference, and the absorbance of each reaction mixture was observed. Absorbance values of the standard solutions were plotted against known concentrations, and a standard curve was drawn. The standard curve was used to calculate the phenolic content of each sample and report it as milligrams of gallic acid equivalents (mg GAE) / litre of sample. However, this method did not identify specific phenolic compounds, yet meaningful quantification of total phenolic content was achieved (Appendix B).

The heavy metal analysis was performed by first drying the adsorption effluent in an oven at 105°C. The dried samples were then subjected to microwave-assisted digestion using a Milestone Ethos Pro 24/16 high-throughput rotor (Milestone Srl, Sorisole, Italy), following a controlled temperature and pressure protocol. The digestion process involved adding 8 mL of concentrated nitric acid (65%) and 2 mL of hydrogen peroxide (30%) to the dried sample (up to 0.3 g) within closed Tetrafluoromethane-based vessels (TFM). The vessel was sealed, and the mixture was heated in the microwave digestion system, following a programmed temperature profile to ensure complete digestion. After cooling, the digested samples were diluted with distilled water to the required volume. The heavy metal concentrations were subsequently analysed using Atomic Absorption Spectrometry (4200 MP-AES, Agilent Technologies, USA).

The percentage of toxin removal, T_i , in the solution was determined as shown in Equation 4.1.

$$\% T_i = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad 4.1$$

C_0 and C_e are the initial and equilibrium concentrations, respectively, of any given heavy metal or phenolics in mg/L.

The characterisation of the impregnated biochar to determine surface morphology, crystallography, functional groups, pore occupation, voidage, and other properties was conducted using SEM-EDS, XRD, FTIR, and BET techniques, following the procedures previously outlined in Section 3.2.4.

The optimised conditions were replicated and compared with MAC, and a validation measure for the optimisation results was also conducted. The capacity of the adsorbent in relation to the adsorbed metals or phenolics was calculated according to Equation 4.2.

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad 4.2$$

Q_e represents the amount of adsorbate adsorbed at the equilibrium. (mg/g); V is the volume of the solution (L); and m is the weight of the adsorbent (g). All samples studied in this work were obtained from batch experiments.

4.2.6 Magnetic biochar recovery experiments

The initial mass of the magnetic biochar (m_0) was measured after equilibration experiments and separation using a permanent magnet. Then, the remaining biochar pulled by the magnet was dried for 24h at 35 °C and weighed (m_i); this is the difference between a loaded magnet and an unloaded magnet. The recovery efficiency (R_E) was measured using Equation 4.3.

$$R_E = \frac{m_0 - m_i}{m_0} \times 100\% \quad 4.3$$

4.3 Production of magnetic biochar for the adsorption process

4.3.1 Selection of the pyrolysis temperature to produce biochar

The optimal adsorption properties of biochar are critically determined by the selection of pyrolysis conditions, particularly temperature. The physicochemical properties (BET surface area, pore size distribution, and elemental composition) of the biochar determine its selectivity as an adsorbent for chemically distinct heavy metals and organic pollutants. The total surface available for pollutant capture directly correlates with BET surface area,

a standard measure of adsorption potential. Pyrolysis temperatures at elevated levels typically result in the development of a more porous structure and enhanced adsorption efficiency (Tan *et al.* 2018).

Table 4.1 BET screening for pyrolysis temperatures

Sample ID	Surface area (m ² /g)	BET surface area (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (Å)
T450	183.2540	62.3338 ± 6.9611	0.059574	30.742
T500	223.0466	75.8693 ± 8.4726	0.086257	36.427
T550	293.0009	99.6642 ± 14.1299	0.117967	43.376
T600	148.6975	50.5794 ± 5.6484	0.059874	25.230
T650	110.2840	37.5131 ± 4.1892	0.044407	15.076
Activated Carbon	530.0972	260.3236 ± 25.3897	0.223503	34.342

BET surface area and elemental composition analyses were conducted to identify the optimal pyrolysis temperature, and results are summarised in Tables 5.1 and 5.2. At 550 °C, it was found that biochar had the highest BET surface area (99.7 m²/g) and single-point surface area (293 m²/g). Elemental analysis confirmed these findings, reporting a maximum carbon content (62.44 %) at 550 °C. Biochar with a high carbon content exhibits higher aromaticity and stability, thereby demonstrating improved pollutant adsorption through π - π interactions and hydrophobic effects (Świechowski *et al.* 2022).

At temperatures greater than 550 °C, anomalies in surface area, pore volume, and pore size began to decrease. This is likely caused by pore coalescence and the sintering or melting of biomass ash components containing alkali and alkaline earth metals, which block the pore structure of biochar (Tan *et al.* 2018).

From an elemental analysis standpoint, it was found that pyrolysis temperatures cause immense variations across pyrolysis temperatures (Table 4.2). The optimal T550 biochar exhibited a carbon content comparable to that of commercial activated carbon, albeit with slightly reduced surface and pore properties. The ash content was lowest at 550 °C (21.42%), further confirming its suitability for adsorption applications.

Table 4.2 Elemental analysis and ash content

Material	C (%)	H (%)	N (%)	S (%)	O (%)	Ash (%)
T450	54.17	1.65	1.16	0.12	4.52	38.50 ± 0.18

T500	58.23	4.11	1.12	1.64	9.32	27.22 ± 1.03
T550	62.44	4.46	1.61	2.21	8.41	21.42 ± 4.11
T600	32.89	1.82	0.7	0.56	27.47	37.12 ± 1.03
T650	31.71	1.35	0.41	0.22	25.69	40.84 ± 0.98
Activated Carbon	80.42	1.74	0.71	0.52	16.09	1.04 ± 0.08

Fourier Transform Infrared (FTIR) spectroscopy offers critical insights into the surface chemistry and functional group composition of biochar produced at different pyrolysis temperatures. The analysis conducted compares biochar produced at 450 °C, 500 °C, 550 °C, 600 °C, and 650 °C with commercial activated carbon, focusing on the evolution of functional groups and their implications for adsorption properties as shown in Figure 4.3.

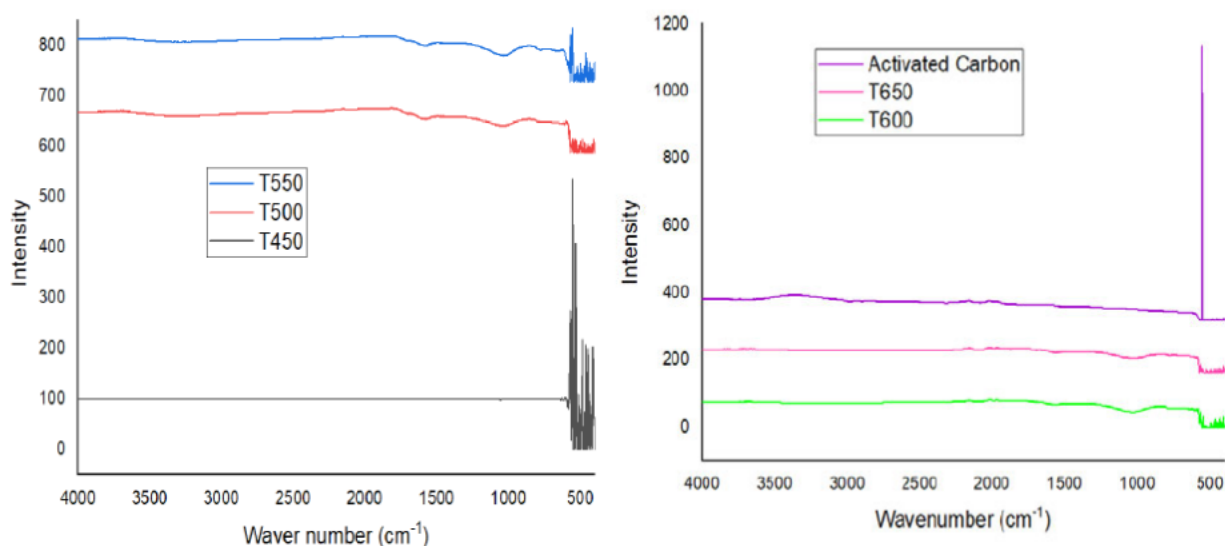


Figure 4.3 FTIR comparison of different pyrolysis temperatures

The FTIR spectra exhibit the presence and transformations of key functional groups as the pyrolysis temperature increases. Broad hydroxyl (-OH) stretching bands (3200-3600 cm⁻¹) were evident in biochar produced at 450 °C (T450) and 500 °C (T500), which displayed distinct hydroxyl peaks, indicating superior adsorptive properties. These peaks diminish at higher temperatures (T600 and T650), suggesting dehydration and loss of

volatile functional groups as the carbon matrix becomes more aromatic (Tan *et al.* 2018). C-H stretching vibrations ($2800-3000\text{ cm}^{-1}$) represent aliphatic $-\text{CH}_2$ and $-\text{CH}_3$ groups, which are prominent in T450 and T500 but decrease at T550 and beyond, reflecting the decomposition of aliphatic compounds and the formation of a more graphitic structure (Świechowski *et al.* 2022). Carbonyl ($\text{C}=\text{O}$) stretching vibrations ($1650-1750\text{ cm}^{-1}$) signifying the presence of carboxyl and ketone groups are observed for T450, T500, and T550, but weaken at T600 and T650, indicating thermal decarboxylation. Aromatic $\text{C}=\text{C}$ stretching vibrations ($1450-1600\text{ cm}^{-1}$) peaks become more pronounced at T550 and above, consistent with increased aromaticity and graphitisation of the biochar. C-O stretching vibrations ($1000-1300\text{ cm}^{-1}$) are associated with alcohols, ethers, or esters present in T450 and T500 but are significantly reduced at higher temperatures, further supporting the loss of labile functional groups.

Commercial activated carbon exhibits minimal hydroxyl and aliphatic functional groups compared to biochar samples, indicating a highly aromatic and stable surface chemistry. This aligns with its superior BET surface area ($260\text{ m}^2/\text{g}$), enabling it to serve as a benchmark for adsorption performance. Biochar at T550 most closely resembles activated carbon in terms of its spectral features and elemental composition (62.44% carbon, Table 4.2), highlighting its potential as a cost-effective alternative for adsorption processes. The FTIR analysis highlights the significant impact of pyrolysis temperature on the functional group composition and adsorption properties of biochar. T550 emerges as the most promising biochar for adsorption due to its balanced physicochemical characteristics.

Biochar produced at $550\text{ }^\circ\text{C}$ demonstrated superior adsorption properties, characterised by a high BET surface area, an optimised pore structure, and a favourable elemental composition. These findings underscore the importance of temperature control in biochar production, particularly for applications that involve adsorption. Future work should explore methods to enhance the performance of T550 biochar, potentially through chemical activation or surface modification, to match or exceed the capabilities of commercial activated carbon.

4.3.2 Magnetic biochar production

The production of magnetic biochar (MBC) builds upon the biochar described earlier, modifying it to improve separation capabilities from sludge after adsorption. The magnetisation process primarily aims to enhance the recovery of biochar post-treatment using an electromagnet, aligning to create a more efficient and economically viable adsorption material.

From Table 4.3, it is evident that magnetisation affected the physical and chemical properties of biochar. The single-point surface area decreases by approximately 20%, and the BET surface area experiences a marginal reduction of about 3%. These changes indicate that the magnetisation process introduces structural alterations, potentially caused by the infiltration of iron into the biochar matrix, which may affect the adsorption capacity of the biochar. This is further corroborated by the ash content analysis, which shows a substantial 70% increase in ash for MBC compared to untreated biochar.

Table 4.3 Comparison of magnetic biochar to magnetic activated carbon

Material	Surface area (m ² /g)	BET surface area (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (Å)	C (%)	H (%)	N (%)	S (%)	O (%)	Ash (%)
Biochar	242.4806	91.1198 ± 11.5623	0.108378	47.576	62.44	4.46	1.61	2.21	8.41	21.42±4.11
Magnetic Biochar (MBC)	195.5911	88.3000 ± 9.8491	0.092965	42.113	50.08	2.56	0.83	1.13	9.88	36.65±0.22
Activated carbon	530.0972	260.3236 ± 25.3897	0.223503	34.342	80.42	1.74	0.71	0.52	16.09	1.04±0.08
Magnetic Activated carbon (MAC)	335.8090	158.7323 ± 14.8336	0.139277	35.097	58.04	1.27	0.51	0.59	16.66	23.52±0.62

The elemental analysis highlights significant reductions in carbon content, dropping from 62.4% to 50.08% after magnetisation. Such reductions affect the adsorption efficiency of MBC, as carbon content correlates with aromaticity and the biochar's ability to interact with non-polar contaminants through mechanisms such as π - π interactions. Despite

these drawbacks, the trade-off is justified by the improved recovery efficiency and the operational complexity.

When comparing MBC with magnetic activated carbon (MAC), notable differences emerge. MAC maintains a significantly higher BET surface area ($158.7 \text{ m}^2/\text{g}$) and superior pore volume ($0.139 \text{ cm}^3/\text{g}$) compared to MBC ($88.3 \text{ m}^2/\text{g}$ and $0.093 \text{ cm}^3/\text{g}$, respectively). The enhanced surface properties of MAC are attributed to its chemical activation process, which optimises its porous structure for adsorption applications. However, MBC demonstrates competitive performance due to its higher pore size ($42.11 \text{ \AA}$), which can favour the adsorption of larger molecular toxins, such as phenolic compounds.

Plate 5.1 visually illustrates the distinction between magnetised and unmagnetised biochar. The ash from the magnetised biochar (MBC) is distinctly reddish compared to the original, greyish ash of the unmagnetised biochar. This colour change signifies the incorporation of iron into the biochar matrix during the magnetisation process. The iron particles infiltrate the crevices and interstices of the biochar, leading to noticeable structural and compositional changes.

The reddish hue in the magnetised ash is indicative of iron oxide formation, primarily in the form of magnetite (Fe_3O_4) or hematite (Fe_2O_3), which are commonly observed in magnetised materials (Chernavskiy *et al.* 2023). This incorporation of iron oxides is further supported by ash content analysis, which reveals a significant 70% increase in ash content for MBC compared to its unmagnetised counterpart. On the other hand, the ash content in activated carbon, the control, increased by over 2000 % post-magnetisation, indicating a much greater degree of iron doping. Moreover, these results align with the literature, which reports that excessive doping levels result in constraints on pore accessibility and functional group availability, thereby impeding magnetisation (Tan *et al.* 2018; Świechowski *et al.* 2022).

The infiltration of iron into the biochar matrix reduces the available surface area and pore volume, as the iron particles occupy previously accessible adsorption sites. This reduction compromises the adsorption efficiency of the biochar, particularly for smaller molecular toxins that rely on micropores for effective capture. However, the magnetisation process

offers a significant advantage in enabling efficient separation of the biochar from sludge post-adsorption, an essential consideration for industrial-scale applications.

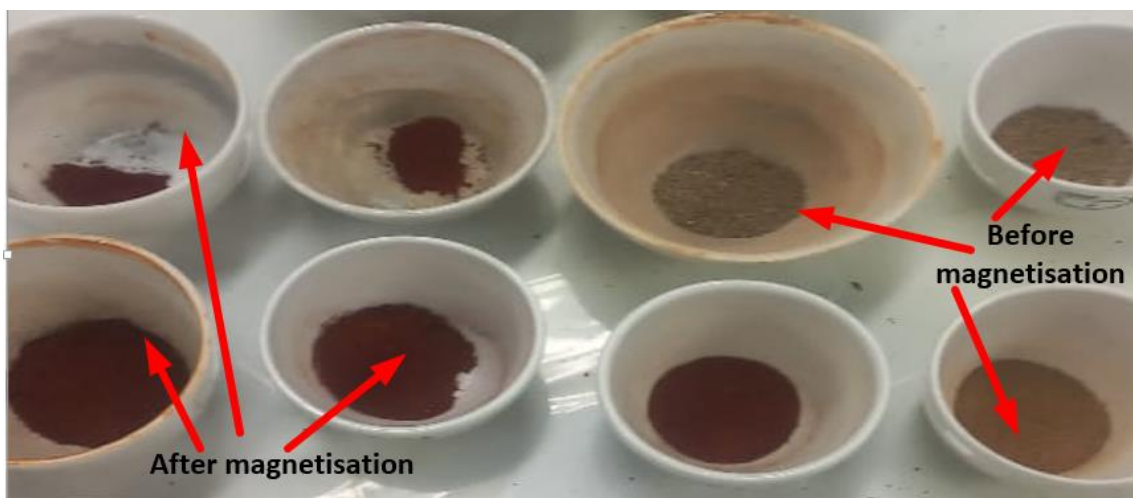


Plate 4.1 Ash composition before and after magnetisation

While magnetisation introduces structural and compositional trade-offs, its advantages in facilitating biochar recovery justify its application in specific scenarios. However, ongoing refinement and optimisation are essential to maximise the dual benefits of adsorption efficiency and recovery feasibility.

Magnetic biochar (MBC) can serve as a practical alternative to conventional biochar for wastewater treatment, where efficient recovery and reuse are both feasible and desirable. MBC achieves sufficient performance for practical applications, especially for larger molecular toxins, despite the reductions in surface area and adsorptive efficiency.

4.3.3 Magnetic biochar properties

4.3.3.1 FTIR analysis

This was demonstrated through functional group changes, as analysed by FTIR spectroscopy after magnetisation (Figure 4.4), indicating that iron was incorporated into the biochar structure. Strong new peaks were seen at $\text{ca } 613 \text{ cm}^{-1}$ and 880 cm^{-1} , indicative of Fe-O and Fe-OH vibrational modes, as well as the MBC spectrum. In turn, this is a clear indicator of the successful introduction of Fe into the biochar matrix (Tan *et al.* 2017). Figure 4.4 shows that these functional groups are absent in the unmagnetised biochar.

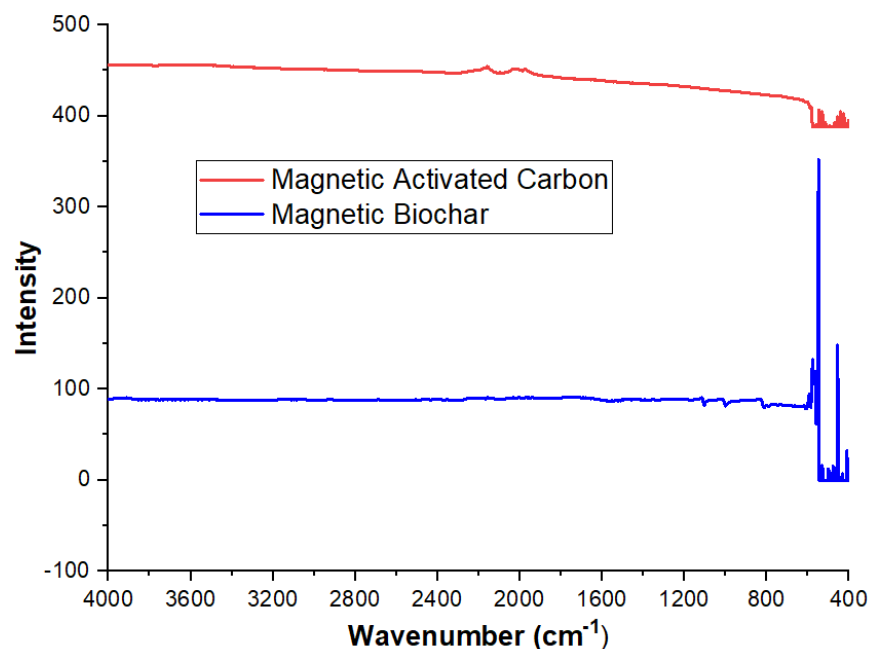


Figure 4.4 FTIR magnetic biochar and activated carbon

After magnetisation, peaks at 1122 cm^{-1} , attributed to C-O ether stretching vibrations, dwindled in intensity. This reveals that C-O groups were actively involved in the binding of Fe ions during magnetisation (Wu *et al.* 2020). Finally, in MBC, vibrational peaks near 1600 cm^{-1} , assigned to aromatic C=O and C=C stretching, became more pronounced. That can be explained by the catalytic effects of Fe, which catalyses the condensation and polymerisation of aromatic compounds (Rawal *et al.* 2016). Due to these structures, the redox activity of the material can be enhanced facilitating the coordination of phosphate and heavy metal adsorption (Zhang *et al.* 2018). The oxygen-containing functional groups in MAC were fewer and exhibited higher aromaticity than those in MBC. The lack of Fe-O-related peaks in MAC indicates its non-iron-modified structure, differentiating its adsorption specificity from that of MBC.

4.3.3.2 XRD analysis

XRD analysis provided further evidence of structural changes in MBC after magnetisation (Figure 4.5).

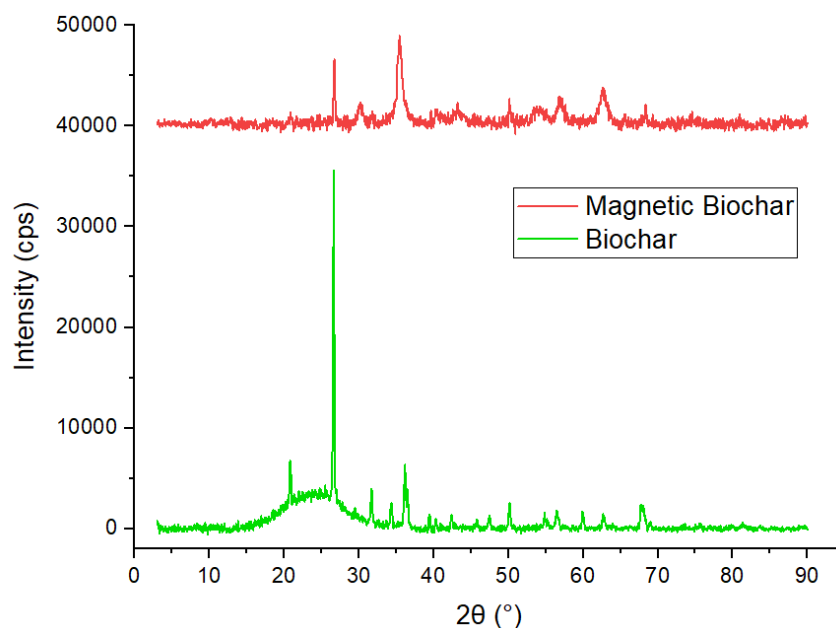


Figure 4.5 XRD for comparison between biochar and MBC

For MBC, prominent peaks were observed at 2θ values of 30.09° , 35.42° , 43.05° , 56.94° , and 62.51° , which correspond to the cubic crystal structure of magnetite (Fe_3O_4). These findings are consistent with the incorporation of Fe-based magnetic phases into the biochar matrix, confirming successful magnetisation. These peaks are in agreement with literature reports that identify these positions as characteristic of magnetite structures (Tan *et al.* 2017). The XRD spectrum of BC displayed fewer defined peaks, indicating its predominantly amorphous structure. Peaks related to crystalline impurities, such as KCl and NaCl, were also observed. These impurities arise from inorganic elements present in the raw biomass, which crystallise during pyrolysis (Mondal *et al.* 2024). Washing steps or acid treatment may also be able to reduce these residues after pyrolysis, thereby enhancing the adsorption efficiency.

MBC exhibited a greater degree of crystalline structure compared to BC, resulting in enhanced mechanical stability and magnetic properties. However, the incorporation of Fe compounds likely led to a decrease in porosity and surface area, a common drawback associated with the use of magnetisation (Zhang *et al.* 2018).

MAC appeared to have sharper and more intense peaks at nearly the same positions, suggesting that this material has a higher degree of crystallinity than MBC. This increased crystallinity makes it a more efficient adsorbent than its counterparts with lower crystallinity, albeit at a higher production cost. Nonetheless, MBC is more economical than MAC and still possesses functional magnetic properties.

The intense peaks for magnetite suggest that MBC could play a role in the recovery of both phosphates (essentially lost) and heavy metals through sorption (Luo *et al.* 2021). These magnetic properties simplify the recovery and recycling process, making it suitable for use in sustainable wastewater treatment systems.

The XRD data support the analysis of the successful magnetisation of biochar; the appearance of peaks of magnetite supports the integration of magnetic phases. Although MBC presented lower crystallinity and adsorption capacity compared to MAC, it can be asserted that MBC is more cost-effective, and its ease of recovery makes it a viable option for implementation on an industrial scale in nutrient and heavy metal removal processes. Further optimisation of the magnetisation process is recommended to enhance the trade-off between magnetic and adsorption properties.

4.3.3.3 SEM analysis

The SEM analysis of unmagnetised biochar and MBC provides critical insights into their surface morphology and elemental composition, complementing the findings from FTIR and XRD analyses.

For the unmagnetised biochar, SEM images in Figure 4.6 show a porous structure with well-defined micropores, indicative of a high surface area suitable for adsorption. This morphology aligns with the higher BET surface area and porosity observed in unmagnetised biochar. The surface contains distinct crevices and interstices, which provide active sites for pollutant adsorption (Jagnade and Panwar 2024). MBC exhibits a rougher and more irregular surface compared to BC. The porous structure appears partially filled, likely due to the deposition of Fe_3O_4 nanoparticles during the magnetisation process. The reduction in visible pore structures supports the findings from BET analysis, where MBC exhibited a lower surface area and pore volume compared to BC.

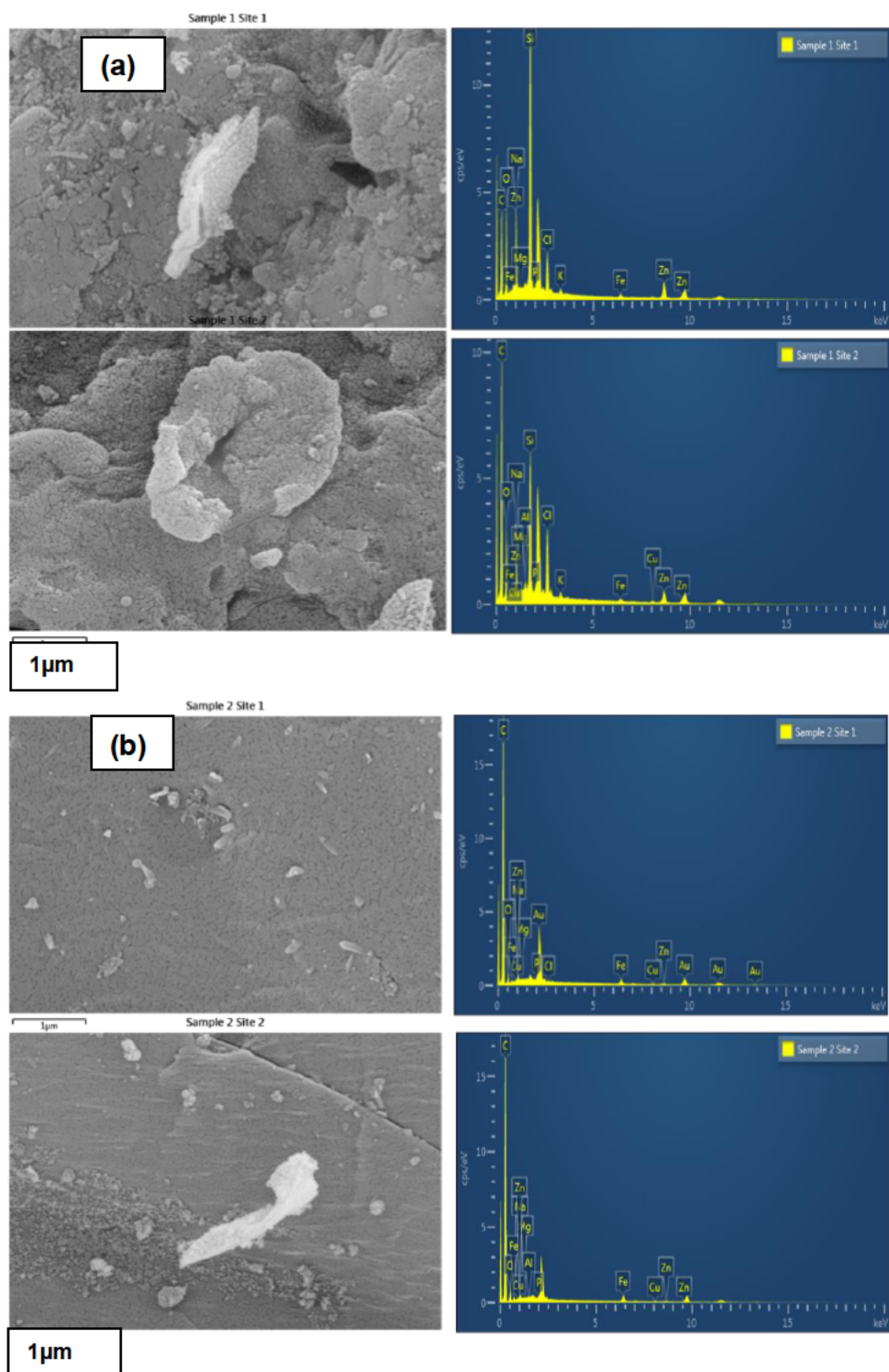


Figure 4.6 SEM-EDS analysis (a) biochar (b) magnetic biochar

The elemental composition, measured as weight percentage (wt%) at different sites, reveals significant differences between BC and MBC. BC contains a higher proportion of oxygen (27.46% and 19.08% at two sites), reflecting the presence of oxygenated functional groups that are critical for adsorption. MBC shows reduced oxygen content (9.48% and 11.27%), indicating a loss of oxygenated functional groups during magnetisation, consistent with FTIR results. In BC, the iron content was minimal (0.63% and 0.41%), representing residual inorganic matter. While in MBC, a substantial increase in iron content (2.38% and 2.79%) confirms the successful incorporation of Fe_3O_4 during magnetisation. This corroborates the Fe-O and Fe-OH peaks observed in FTIR and the magnetite diffraction patterns identified in XRD.

4.4 Adsorption studies

The selected magnetic biochar above (magnetised T550) was used in the adsorption studies. Table 4.4 presents the input factors, along with their respective operational ranges and outliers for each parameter. Table 4.5 displays the input and output response matrix for each of the 20 runs, as designed by RSM-CCD.

Table 4.4 Input variables for adsorption

Factor	Name	Units	Minimum	Maximum	Mean	Std. Dev.
A	pH		2.30	10.70	6.50	2.12
B	Adsorbent dosage	g/L	1.59	18.41	10.00	4.24
C	Contact time	min	12.84	122.16	67.50	27.55

4.4.1 Phenolics adsorptions

Key input factors strongly influence the efficiency of phenolic compound removal in adsorption processes, that is, adsorbent dosage, contact time, and pH. These variables govern the adsorption mechanism, which includes interactions such as electrostatic forces, π - π bonding, and electron-donor-acceptor (EDA) complexation.

Adsorbent dosage determines the availability of active sites for binding, with higher dosages typically enhancing removal efficiency until a saturation point is reached. Contact time affects the establishment of equilibrium between phenols and the adsorbent,

influencing the adsorption capacity. Meanwhile, pH critically impacts the ionisation state of phenolic compounds and the surface charge of the adsorbent, as acidic conditions favour molecular phenol forms for stronger interactions. Prior studies suggest that optimal removal efficiencies are achieved by carefully balancing these factors to maximise adsorption while avoiding issues such as site saturation or unfavourable electrostatic repulsions at high pH (Khelfaoui and Chaouch 2023). Understanding these parameters provides the foundation for designing effective wastewater treatment processes. The input parameters were analysed individually, as shown in Figure 4.7, and the variables that affect the responses are discussed.

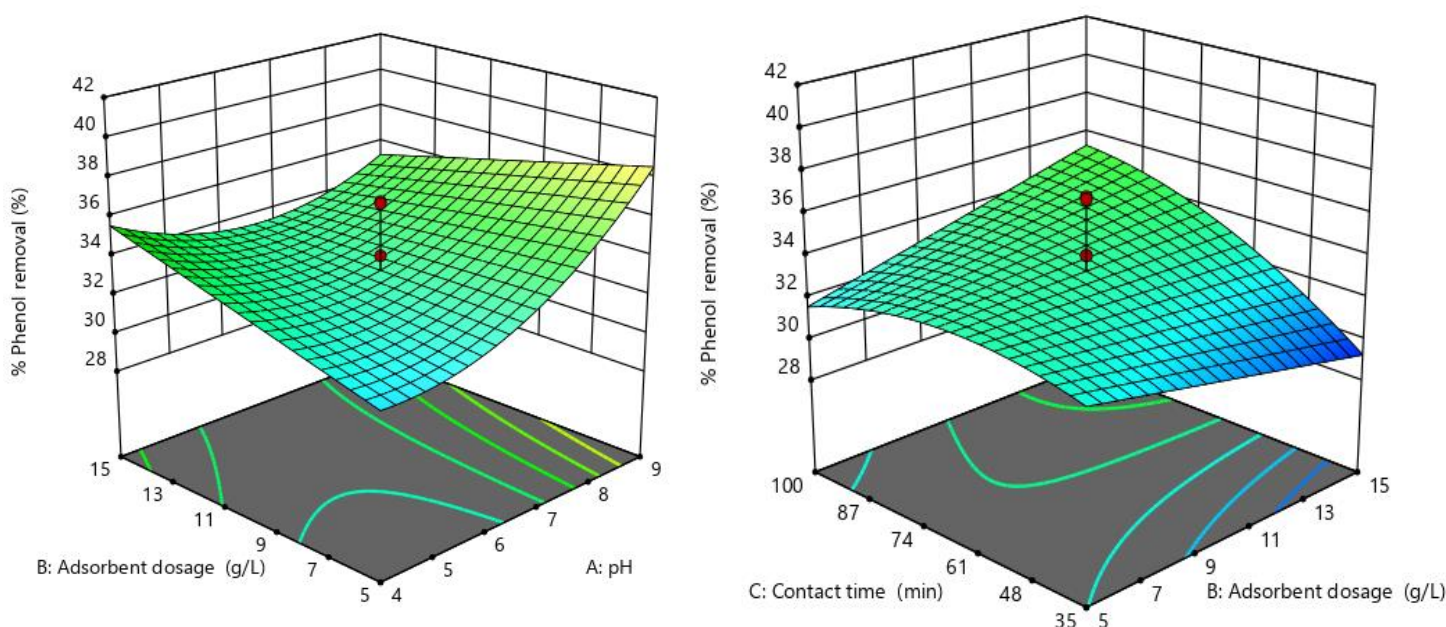


Figure 4.7 Effect of operating parameters on PC removal efficiency

Table 4.5 Input factors and output factors for the optimisation of the adsorption process

Run	Time (min)	pH	Dosage (g/L)	Phenol removal (%)	Phenol capacity (mg/g)	PO ₄ -P removal (%)	NH ₄ removal (%)	Arsenic (As)	Copper (Cu),	Nickel (Ni)	Lead (Pb)	Zinc (Zn)
1	100	4	15	41.5±0.2	5.52±0.02	49.6±0.4	49.8±2.3	67.7±2.7	16.4±0.6	71.3±7.2	61.5±3.1	75.5±1.5
2	67.5	6.5	10	31.2±0.3	6.22±0.06	52.2±0.9	55.6±1.1	67.3±5.5	38.0±1.1	67.2±5.9	62.4±2.8	80.3±1.2
3	67.5	6.5	10	29.3±0.2	5.85±0.03	55.8±0.9	53.2±0.1	67.0±5.6	37.4±4.6	69.7±6.6	62.8±2.9	80.0±1.7
4	67.5	2.3	10	28.7±0.6	5.74±0.13	38.4±1.1	58.9±1.1	54.4±7.7	38.6±1.1	76.5±4.7	66.5±2.3	74.6±1.5
5	100	9	15	28.5±0.0	3.79±0.00	63.7±0.5	60.7±0.5	63.5±6.2	28.2±2.1	60.5±8.6	56.1±3.7	75.2±1.5
6	100	4	5	36.8±0.2	14.71±0.06	48.5±0.6	54.1±0.5	64.5±6.0	61.6±1.1	60.0±8.3	62.3±3.3	74.6±1.5
7	35	9	5	31.7±0.5	12.67±0.19	59.7±0.5	63.2±0.9	60.0±6.8	67.2±1.0	70.1±7.0	64.9±2.8	77.7±1.3
8	67.5	6.5	10	29.7±0.2	5.94±0.03	55.5±0.9	53.4±0.9	68.1±5.4	40.2±1.5	64.1±8.2	60.7±3.1	78.2±1.6
9	67.5	6.5	18.409	36.6±0.2	3.97±0.02	55.7±0.5	56.6±1.1	67.7±5.5	29.7±0.8	59.0±8.9	62.7±3.1	78.8±1.3
10	35	4	15	34.1±0.9	4.53±0.13	50.5±0.9	51.8±1.1	52.6±8.0	51.5±1.7	81.1±4.1	68.4±2.5	79.9±1.2
11	35	4	5	36.7±0.3	14.66±0.13	45.1±0.6	51.3±0.8	54.0±7.8	57.0±0.7	88.6±2.6	68.9±2.5	77.1±1.9
12	35	9	15	38.7±0.6	5.15±0.08	61.0±1.1	62.2±0.9	57.9±7.1	59.5±0.7	50.3±10.3	62.2±3.3	77.2±1.4
13	67.5	6.5	10	30.1±1.6	6.01±0.32	51.5±0.2	54.4±0.6	67.5±5.5	38.3±3.0	73.4±5.7	66.5±2.8	79.5±1.2
14	122.158	6.5	10	30.8±0.5	6.16±0.09	55.4±1.0	57.8±1.3	65.2±5.9	55.8±0.8	54.8±9.8	58.1±3.4	69.0±1.8
15	67.5	6.5	1.59104	34.9±0.6	43.85±0.79	57.0±0.7	52.7±1.1	68.4±5.4	61.3±0.7	66.6±9.6	62.4±2.6	81.1±1.1
16	100	9	5	32.0±1.1	12.76±0.44	61.4±0.5	73.3±0.6	51.5±8.2	70.5±0.5	62.1±9.9	54.8±4.2	72.8±1.6
17	12.8417	6.5	10	36.8±0.2	7.35±0.03	54.5±1.6	57.9±0.3	53.7±7.9	65.0±2.0	70.0±4.0	66.5±2.5	73.3±1.6
18	67.5	6.5	10	31.2±1.2	6.24±0.23	51.7±0.6	52.5±0.4	69.5±5.8	39.9±2.5	65.7±9.9	62.1±3.1	80.3±2.2
19	67.5	10.7	10	28.8±0.2	5.76±0.03	67.7±0.3	78.5±1.2	52.6±8.0	59.5±0.7	49.4±12.2	59.1±4.5	81.6±1.1
20	67.5	6.5	10	33.2±0.2	6.64±0.05	53.5±0.6	53.0±1.0	65.7±5.8	39.2±3.7	61.9±5.1	59.7±4.5	79.3±1.2

4.4.1.1 Adsorbent dosage

The adsorption efficiency of phenolic compounds was evaluated over an adsorbent dosage range of 1.59-18.41 g/L (Table 4.4). Favourable removal was observed at lower dosages, particularly at 5 g/L, where run 6 achieved a PC removal efficiency of 36.8% with a notable adsorption capacity of 14.71 mg/g. The behaviour of run 15, with a dosage of 1.59 g/L, was strikingly similar, showing a removal efficiency of 34.9% and a very favourable adsorption capacity of 43.85 mg/g. These findings highlight the importance of selecting an appropriate adsorbent dosage to optimise removal efficiency while maintaining a high adsorption capacity.

Conversely, higher adsorbent dosages, as shown in run 9 (18.411 g/L), resulted in a lower removal efficiency (36.6%) and reduced adsorption capacity (3.97 mg/g). This decline is primarily attributed to adsorbent agglomeration, which diminishes the available surface area and active sites (Wang *et al.* 2019a). Although π - π interactions and electron-donor-acceptor mechanisms have been reported to facilitate the adsorption of aromatic and phenolic compounds onto carbonaceous materials (Zhao and Zhu 2020), these effects were not directly analysed in this study and are therefore discussed as potential rather than confirmed mechanisms.

In multiple studies, it has been demonstrated that maintaining an adsorbent dosage in the range of 4-10 g/L strikes a balance between adsorption efficiency and operational cost-effectiveness (Soliman and Moustafa 2020; Lawal *et al.* 2021). The dosages in this range avoid the pitfalls of site saturation and provide a maximum active site for adsorption with no excessive waste of adsorbent. These findings are crucial for scaling up the process in wastewater treatment applications, where economic and operational feasibility become key considerations.

4.4.1.2 Contact time

The efficiency of PC removal during adsorption is a highly sensitive parameter to contact time. It controls the relationship between the adsorbate and adsorbent at equilibrium and considers the kinetics of adsorption, as well as practical treatment times.

Based on the data in Table 4.5, run 6, with a contact time of 100 minutes, achieved the highest phenol removal efficiency of $41.5 \pm 0.2\%$ and a phenol adsorption capacity of 14.71 ± 0.06 mg/g. This result underscores the importance of sufficient interaction time to optimise adsorption, a phenomenon described by the Langmuir isotherm, which suggests a saturation point in adsorption capacity at equilibrium (Elbidi *et al.* 2021).

Shorter contact times, such as run 17 (12.8 min), resulted in a comparable phenol removal of $36.8 \pm 0.2\%$ with an adsorption capacity of 7.35 ± 0.03 mg/g, demonstrating that equilibrium can still be approached effectively within reduced durations. Conversely, extended durations, such as run 14 (122.16 min), yielded diminishing returns, with phenol removal stabilising at $30.8 \pm 0.5\%$ and a capacity of 6.16 ± 0.09 mg/g. These findings align with the phenomenon of the Freundlich isotherm, which predicts that as high-energy binding sites become saturated, the adsorption process becomes less favourable (Elbidi *et al.* 2021).

Excessive contact times may lead to secondary phenomena, such as desorption or competitive adsorption effects, reducing overall efficiency. Salim *et al.* (2021) observed a similar trend, where phenolic compound adsorption reached an equilibrium around 120 min, with negligible improvements beyond this point. Similarly, Lawal *et al.* (2021) reported that phenolic adsorption increased significantly in the first 60 min but plateaued with extended durations of up to 180 min, indicating practical limits to contact time optimisation.

These results suggest that operating within a practical contact time range, such as 30-100 min, achieves efficient phenolic compound removal while minimising energy and time costs. Optimising this parameter ensures a balance between adsorption performance and operational feasibility, which is critical for wastewater treatment applications.

4.4.1.3 pH

The removal efficiency of PCs during adsorption is significantly influenced by pH, as it determines the ionisation state of phenolics and the surface charge of the adsorbent. At pH values below the pKa of phenol (9.95), phenolics predominantly exist in their protonated form, favouring adsorption through π - π interactions and hydrogen bonding.

For instance, at pH 4 in run 1, the phenol removal was 41.5%, with an adsorption capacity of 5.52 mg/g. Comparatively, at a more acidic pH of 2.3 in run 4, the phenol removal efficiency was slightly lower at 28.7%, with an adsorption capacity of 5.74 mg/g. The results suggest that greater sorption occurs under acidic conditions, for which electrostatic repulsion is reduced, and the π - π interactions between the adsorbent surface and functional groups are stronger. This balance between operational cost and removal efficiency is achieved at a pH of 6.5. In run 2, the removal efficiency of phenolics was 31.2%, with an adsorption capacity of 6.22 mg/g at this pH. These results are in agreement with previous studies, which propose that the maximum adsorption of PCs occurs under near-neutral conditions, thereby balancing the maximum protonation of biocharfunctional groups without compromising the rate of adsorption (Lawal *et al.* 2021).

On the other hand, the efficiency of PC removal fell to as low as 28.8%, with an adsorption capacity of 5.76 mg/g at higher pH values, e.g., pH 10.7 (run 19). The reduction in adsorption is primarily due to the predominance of phenolate anions and the increased electrostatic repulsion between the adsorbent, which has a negative charge, and PCs. These results are consistent with previous studies, such as that of Wang *et al.* (2019b), which highlight decreased adsorption efficiency in alkaline conditions because of unfavourable electrostatic forces. Therefore, by operating within an operational pH of approximately 6.5, phenol is effectively removed without compromising cost efficiency.

4.4.1.4 Interaction of variables

The results of the ANOVA for the phenol removal efficiency, including interactions with pH and contact time, are presented in Table 4.6. The reduced quadratic model was found to be statistically significant, with an F-value of 4.01 ($p = 0.0264$), confirming the model's reliability. The influence of the quadratic term of contact time (C^2 , $p = 0.0126$) on phenol removal efficiency was statistically significant in the model's terms. On the contrary, pH (A, $p = 0.2236$) and contact time (C, $p = 0.1302$) as linear factors have no significant effects, indicating that these factors play a more pronounced role when considered in quadratic or interactive terms. The F-value of the Lack of Fit of 0.91 ($p = 0.5854$) indicates that the lack of fit is not significant as compared to the pure error, which is desired as it implies that the model adequately fits the experimental data.

Table 4.6 ANOVA for phenolic removal

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	42.57	3	14.19	4.01	0.0264	significant
A-pH	5.67	1	5.67	1.60	0.2236	
C-Contact time	9.01	1	9.01	2.55	0.1302	
C ²	27.89	1	27.89	7.88	0.0126	
Residual	56.61	16	3.54			
Lack of Fit	37.76	11	3.43	0.9110	0.5854	not significant
Pure Error	18.84	5	3.77			
Cor Total	99.17	19				

The synergy between low pH and high adsorbent dosage was evident in run 1, where a pH of 4 and a dosage of 15 g/L achieved a phenol removal efficiency of 41.5% with an adsorption capacity of 5.52 mg/g. Run 5, at a higher pH of 9, with the exact dosage, had a lower efficiency of 28.5% with an adsorption capacity of 3.79 mg/g. The observation of this disparity emphasises the importance of acidic conditions increasing adsorption because of π - π interactions, which prevail at lower pH values. This is consistent with the enhanced sorption of PCs at lower pH, as reported by Zhao and Zhu (2020), who attributed this to protonation mechanisms.

Contact time plays a significant role, as the adsorption process was significantly affected by the quadratic term of contact time (C²) (p-value = 0.0126). Unlike the linear effect of pH (A), contact time (C) was not statistically significant (p = 0.2236 and p = 0.1302, respectively), indicating that its influence is more pronounced when considered through quadratic interactions. For instance, in run 6, a dosage of 5 g/L and a contact time of 100 min yielded the highest removal efficiency of 36.8% and an adsorption capacity of 14.71 mg/g. This result highlights the importance of allowing sufficient contact time to achieve equilibrium between the adsorbate and the adsorbent, thereby enhancing adsorption efficiency. This is further indicative of the observations made by Lawal *et al.* (2021), which state that equilibrium time is crucial for optimal adsorption performance. The model is confirmed to be adequate and robust by the non-significant lack of fit (F-value = 0.91, p = 0.5854), meaning the model fits the experimental data very well without overfitting.

Further exploring the interactions between factors such as contact time and other parameters can reveal optimal operational conditions for removing phenolic compounds in wastewater treatment, ensuring both efficiency and economic viability.

4.4.1.5 Mathematical model development

The mathematical model for phenolic removal by adsorption was developed using a systematic methodology rooted in RSM and central composite design (CCD). Three key input variables were defined in the experimental design: pH, adsorbent dosage, and contact time, operating within predetermined boundaries (Table 4.5). The relationship between these inputs and the response variable (phenolic removal efficiency) was modelled by deriving a quadratic equation for phenol removal efficiency, as presented in Table 4.7.

Table 4.7 Model equation coefficients in terms of coded and actual factors

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	31.51	1	0.5379	30.37	32.65	
A-pH	-0.6445	1	0.5090	-1.72	0.4345	1.0000
C-Contact time	-0.8120	1	0.5090	-1.89	0.2669	1.0000
C ²	1.38	1	0.4910	0.3377	2.42	1.0000

The final model mathematical equation, in terms of coded and actual factors, is given by Equation 4.4.

$$\% \text{ Phenolic removal (coded)} = 31.51 - 0.6445A - 0.8120C - 1.38C^2 \quad 4.4$$

where A is pH, and C is contact time

Equation 4.4 predicts phenolic compound removal based on specific factor levels and provides a basis for optimisation. The coefficients were derived using regression analysis, and their significance was validated using ANOVA.

The model statistics indicate reasonable predictive capacity despite certain limitations, as shown in Table 4.8. The coefficient of determination (R^2) of 0.7334 suggests a moderate correlation between the observed and predicted values, with the adjusted R^2 (0.5778) reflecting the proportion of variance explained by the model after accounting for the

number of predictors. While the predicted R^2 (0.4930) is lower, its closeness to the adjusted R^2 (<0.2 difference) indicates consistency in model predictions (Frost 2019). The adequate precision ratio of 9.064, significantly above the threshold of 4, confirms a sufficient signal-to-noise ratio, validating the model's applicability for exploring the design space.

Table 4.8 Fit Statistics for adsorption of phenolic compounds

Std. Dev.	2.44	R²	0.7334
Mean	33.84	Adjusted R²	0.5778
C.V. %	7.20	Predicted R²	0.4930
		Adeq Precision	9.0635

Moderate predictive accuracy is not uncommon in complex systems, such as adsorption processes, where variability arises from nonlinear interactions and experimental uncertainties. The standard deviation of 2.44 and the coefficient of variation (C.V.) of 7.20% suggest acceptable precision given the inherent complexity of the system. The inclusion of significant terms, such as pH and contact time, ensures that the model captures critical trends.

4.4.2 Heavy metal adsorption

4.4.2.1 General trends in heavy metal adsorption

The adsorption of heavy metals onto magnetic biochar exhibits varying responses across different metals, which are significantly influenced by pH, adsorbent dosage, and contact time, as illustrated in Figure 4.8. While specific trends overlap with those observed in phenolic adsorption, unique behaviours reflect the distinct chemical interactions of heavy metals with biochar. The ANOVA and Fit summary tables for heavy metals are embedded in Appendix C.

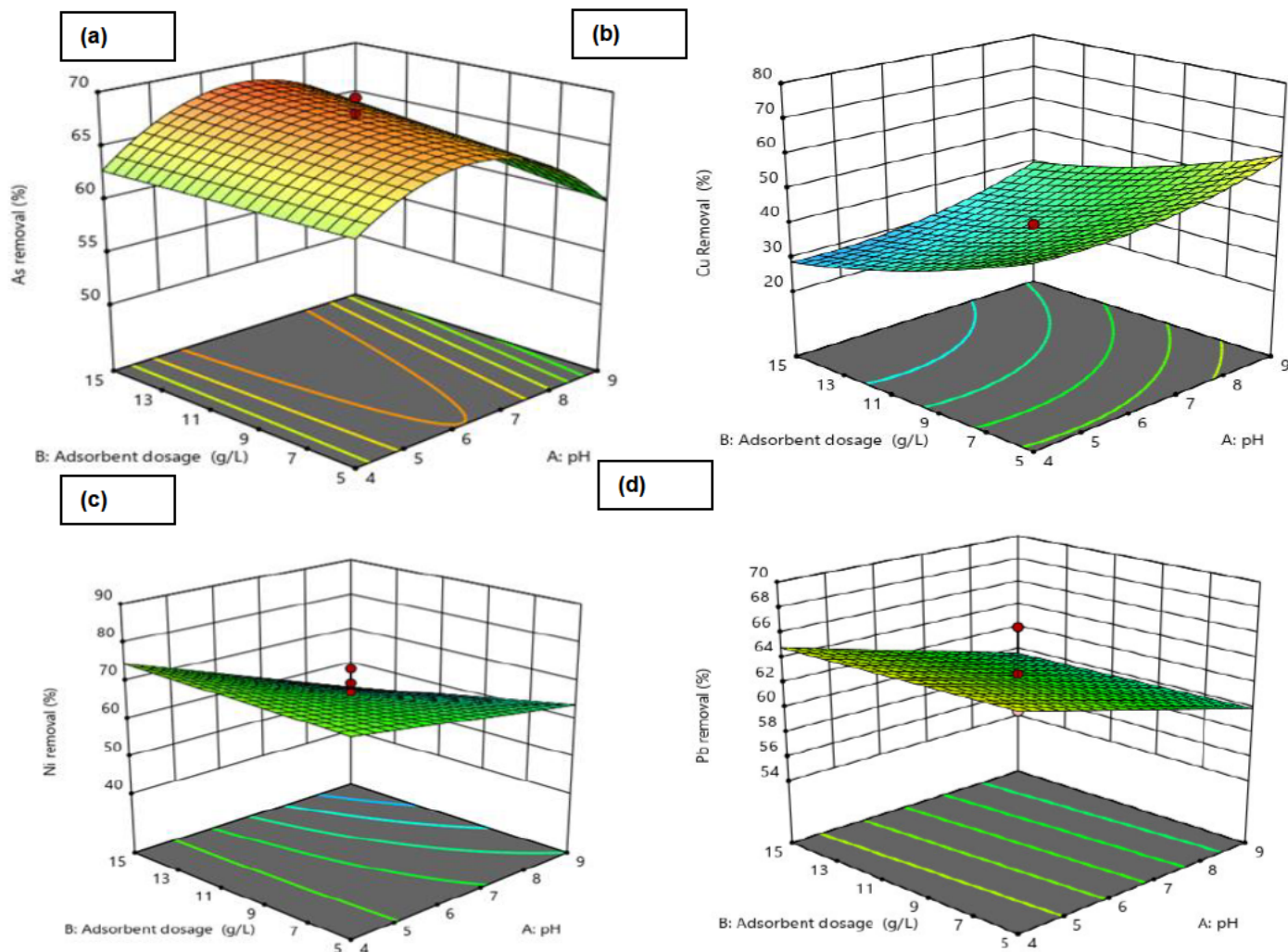


Figure 4.8 Heavy metals removal surface plots (a) As, (b) Cu, (c) Ni, and (d) Pb removal efficiencies.

Arsenic (As) adsorption

The adsorption of arsenic was strongly dependent on contact time, as demonstrated in run 10 (122.16 min), where 65.2% removal was achieved, indicating that equilibrium was established during prolonged contact. However, diminishing returns were observed beyond the intermediate contact time, consistent with equilibrium adsorption for phenolics. Interaction effects, particularly pH-contact time (AC, $p = 0.0002$), as shown in Appendix C1, were significant, suggesting a need to optimise conditions for effective arsenic removal.

Copper (Cu) adsorption

Copper adsorption exhibited sensitivity to adsorbent dosage and contact time. Runs 6 and 11, with dosages of 5 g/L, demonstrated efficient Cu removal of 61.6% and 57%, respectively. Higher dosages, such as in run 9 (18.41 g/L), resulted in reduced efficiency (29.7%), mirroring the agglomeration effects noted in phenolics. Quadratic terms (B^2 and C^2) were significant, highlighting the non-linear relationship between operational parameters and Cu removal.

Nickel (Ni) adsorption

Significant interactions, as illustrated by AB ($p = 0.0366$), emphasised the importance of multi-factor optimisation. Run 11, at pH 4 and a contact time of 35 min, achieved the highest Ni removal (88.6%), indicating acidic conditions and shorter durations favour rapid adsorption. These findings align with trends in phenolic adsorption under low-pH environments.

Lead (Pb) and zinc (Zn) adsorption

Lead removal was primarily driven by contact time (C , $p < 0.0001$), with Run 11 achieving 68.9% removal at 35 minutes. Zinc removal efficiency was high across runs, averaging 77.29%, but a predictive model could not be derived due to statistical inconsistencies.

4.4.2.2 ANOVA and Predictive mathematical models' development for heavy metals

The ANOVA tables (Appendix D) for heavy metal adsorption reveal significant statistical trends and behaviours across different metals, highlighting the influence of operational parameters such as pH, adsorbent dosage, and contact time.

Arsenic (As) adsorption

The quadratic model for arsenic removal (Equation 4.5) showed high significance ($F = 26.98$, $p < 0.0001$), with critical contributions from contact time (C , $F = 40.77$, $p < 0.0001$) and interaction terms, such as pH-contact time (AC , $F = 31.47$, $p = 0.0002$). The significance of C^2 ($F = 41.42$, $p < 0.0001$) indicates the non-linear effects of contact time, where intermediate contact times optimise removal efficiency. The high R^2 of 0.9604, adjusted R^2 of 0.9248, and adequate precision of 14.2266 validate the model's robustness

and predictive capability. However, the predicted R^2 of 0.7378 indicates some loss of predictive power, likely due to complex interaction effects, such as pH-contact time (AC, $p = 0.0002$).

As removal %

$$= 8.99239 + 12.60897A - 1.33642B + 0.625615C + 0.080361AB \\ - 0.043811AC + 0.014344BC - 0.824444A^2 - 0.000058B^2 \\ - 0.002881C^2 \quad 4.5$$

Copper (Cu) adsorption

Copper removal (Equation 4.6) displayed exceptional significance across several parameters. Adsorbent dosage (B, $F = 428.42$, $p < 0.0001$), contact time (C, $F = 117.19$, $p < 0.0001$), and their interaction (BC, $F = 182.60$, $p < 0.0001$) were identified as critical factors. The quadratic terms (B^2 , $F = 21.53$, $p = 0.0009$) highlighted diminishing returns with increasing dosage, consistent with agglomeration effects. The model achieved an exceptional R-squared value of 0.9909, a predicted R^2 value of 0.9412, and an adequate precision of 38.0600, exhibiting exceptional predictability.

Cu Removal %

$$= 92.03133 - 6.29192A - 0.459397B - 0.617521C + 0.038061AB \\ + 0.008676AC - 0.054951BC + 0.564978A^2 + 0.091376B^2 \\ + 0.006979B^2 \quad 4.6$$

Nickel (Ni) Adsorption

The 2FI model for nickel removal (Equation 4.7) was significant ($F=18.25$, $p<0.0001$), with all three main factors: pH (A, $F=54.21$, $p<0.0001$), dosage (B, $F=4.69$, $p=0.0495$), and contact time (C, $F=19.19$, $p=0.0007$), playing vital roles. Interaction terms (AB, $F = 5.43$, $p = 0.0366$) indicated synergistic effects between pH and dosage. The model, with an R^2 of 0.8939, although slightly lower than for other metals, remains robust, with adequate precision at 17.3216. However, a predicted R^2 of 0.7415 suggests some variability in adsorption performance under different operational conditions.

Ni removal %

$$= 130.01512 - 4.75223A - 0.729793B - 0.829801C - 0.251140AB \\ + 0.062620AC + 0.028377BC \quad 4.7$$

Lead (Pb) Adsorption

Lead adsorption followed a simpler linear model (Equation 4.8) with high statistical significance ($F = 32.04$, $p < 0.0001$). Contact time (C , $F=57.76$, $p<0.0001$) and pH (A , $F=38.21$, $p<0.0001$) were key contributors, while adsorbent dosage was not significant ($p=0.7058$). The lack of significant interaction terms simplifies optimisation but may limit flexibility compared to other metals. These fit statistics collectively support the development of robust predictive models for optimising heavy metal adsorption.

$$Pb\ removal\ \% = 76.19343 - 1.04324A - 0.032435B - 0.098666C \quad 4.8$$

4.4.3 Nutrient losses through adsorption

Nutrients such as phosphates and ammonium are critical for downstream processes and are not inherently toxic. However, during the adsorption process, these essential nutrients often exhibit a significant tendency to co-adsorb alongside toxins.

This unintended adsorption can lead to nutrient depletion, negatively affecting subsequent recovery and utilisation stages. Therefore, it becomes imperative to optimise the adsorption process to target toxins while minimising nutrient loss selectively. A well-balanced optimisation strategy not only preserves essential nutrients for reuse but also enhances the sustainability and efficiency of the overall treatment process. This dual objective underscores the necessity for precise control and a thorough understanding of the adsorption dynamics, particularly under varying operational conditions, such as pH, contact time, and adsorbent dosage. Figure 4.9 will be referenced in the forthcoming discussion.

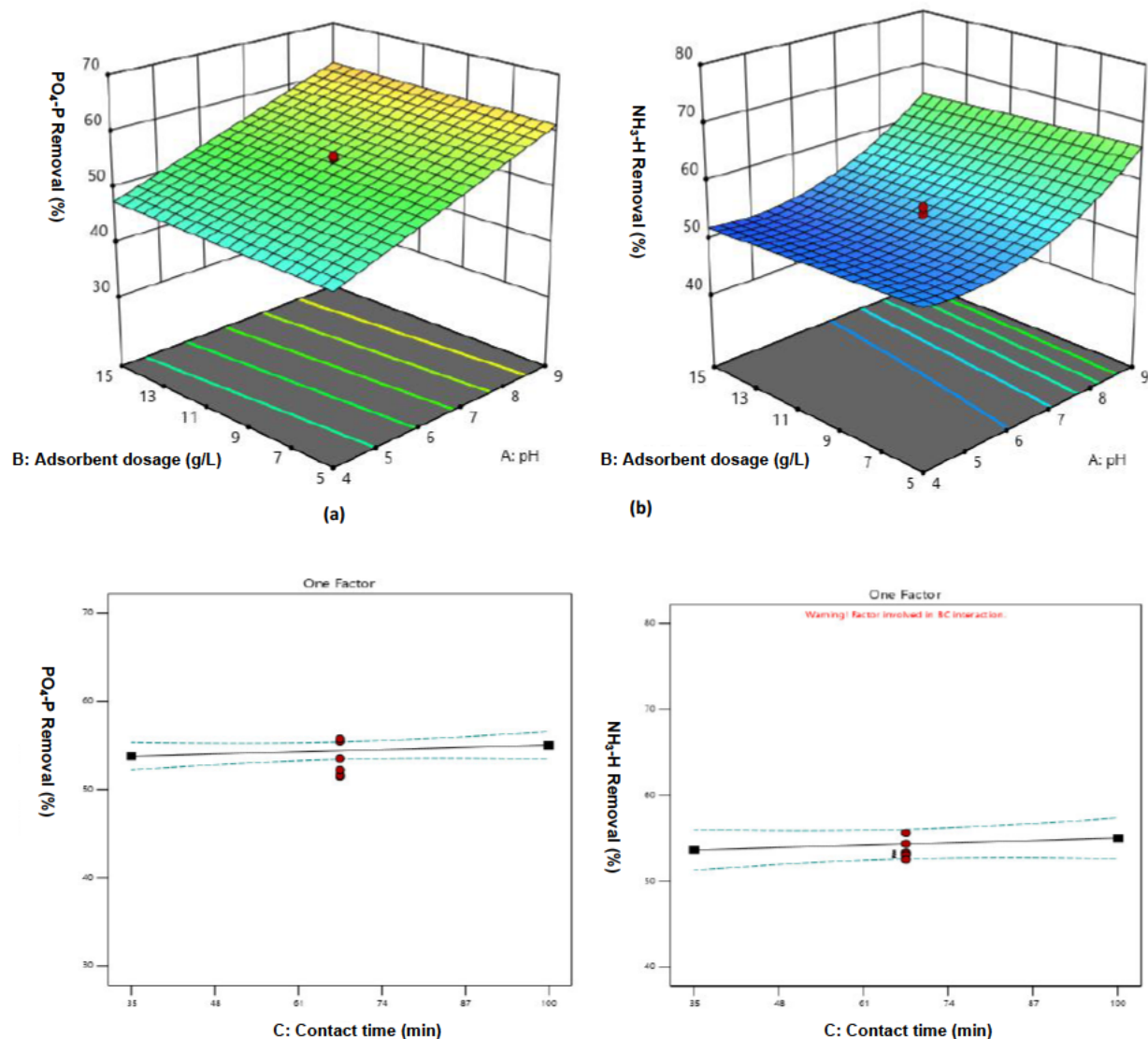


Figure 4.9 Effect of operating parameters on (a) phosphate loss and (b) ammonium loss

4.4.3.1 Adsorbent dosage

The adsorbent dosage is a critical factor influencing nutrient loss during adsorption, particularly for essential nutrients like phosphate (PO_4^{3-}) and ammonium (NH_4^+). Based on the experimental runs, the optimum dosage range of 5-10 g/L is most effective in balancing nutrient retention and toxin removal. Run 6, with a dosage of 5 g/L, demonstrated moderate nutrient losses, with PO_4^{3-} and NH_4^+ removals of 48.5% and 54.1%, respectively, supporting its potential as a baseline for optimisation.

As the dosage increases, the trends in nutrient loss become more variable. For instance, at 10 g/L (run 2), PO_4^{3-} removal was 52.2%, while NH_4^+ removal increased to 55.6%, indicating that higher dosages can enhance the adsorption of some nutrients due to increased surface area availability. However, excessive dosages, such as in run 9 (18.41 g/L), led to diminishing returns in nutrient retention, with phosphate removal stabilising at 55.7%. These findings align with the literature, which indicates that excessive adsorbent dosages can lead to agglomeration effects, thereby reducing adsorption efficiency (Wang *et al.* 2019a).

Maintaining the dosage within 5-10 g/L is operationally advantageous, as it mitigates the overuse of biochar and balances nutrient retention for downstream processes. This dosage range provides sufficient active sites for binding while also preventing excessive nutrient adsorption, as indicated by Lawal *et al.* (2021), who also found similar trends in optimising biochar for nutrient recovery.

An overall adsorbent dosage of 5 g/L is found to be the most promising to minimise nutrient loss while still ensuring effective removal of the toxins. There is a critical balance in this wastewater treatment process that emphasises resource recovery alongside pollutant removal and aligns with the tenets of the circular economy.

4.4.3.2 pH

The pH level has a significant influence on nutrient loss during the adsorption process, as it affects the ionisation state of nutrients and the surface charge of magnetic biochar. Table 4.5 shows that PO_4^{3-} and NH_4^+ removal change across the tested pH range, indicating their importance during adsorbate optimisation.

At acidic pH (run 1, pH 4), PO_4^{3-} and NH_4^+ losses were 49.6% and 49.8%, respectively. The lower removal efficiency suggests limited nutrient loss, which aligns with the reduced electrostatic attraction between the adsorbent and negatively charged phosphate ions under acidic conditions. Conversely, at a higher pH of 9 (run 7), phosphate and ammonium removal increased to 59.7% and 63.2%, respectively, due to enhanced interaction between the adsorbent and ionised nutrients, potentially leading to undesired nutrient loss.

The pH of 6.5 (run 2) offers a balance, achieving removal efficiencies of 52.2% for PO_4^{3-} and 55.6% for NH_4^+ , respectively. This pH minimises excessive nutrient adsorption while maintaining adequate toxin removal efficiency, supporting the dual goals of wastewater treatment to remove toxins while preserving nutrients for downstream applications.

In another study, the effect of the surface charge of biochar and the ionisation state of the adsorbate on the adsorption of Pb^{2+} ions by magnetic coconut biochar was explored, and results showed that the Pb^{2+} adsorption was optimal around a pH of 5, with maximum adsorption influenced by the proper biochar surface charge and Pb ionisation state (Xu *et al.* 2022). Literature supports the preference for a near-neutral pH for nutrient retention. Zhang *et al.* (2020a) found that optimising pH reduces nutrient adsorption, preserving phosphorus for recovery as struvite. Cai and Ye (2022) observed that the adsorption capacity for phosphate declined progressively as the initial pH exceeded 7. This phenomenon may be attributed to the reduction of positive charges on the biochar surface when the pH of the solution approaches the pH_{PZC} .

Therefore, maintaining a pH near a neutral point is pivotal for balancing toxin removal with nutrient retention. At this pH, the adsorption process is sustainable and conducive to resource recovery objectives, minimising phosphate and ammonium loss. This balance could be further optimised for operation, assisting in wastewater valorisation efforts.

4.4.3.3 Contact time

Contact time is essential in minimising nutrient loss in adsorption processes since it directly impacts the equilibrium state between adsorption efficiency and nutrient retention. Experimental results highlight that maintaining contact times within the range of 30-60 min is optimal for balancing the adsorption of phenolic compounds with reduced nutrient loss. Run 7 (contact time: 35 min) achieved 59.7% PO_4^{3-} removal and 63.2% NH_4^+ removal, while run 12, under similar conditions, achieved 61.0% PO_4^{3-} and 62.2% NH_4^+ removal. These results underscore the efficacy of intermediate contact times in promoting selective adsorption without excessive nutrient uptake.

In contrast, longer contact times demonstrated incommensurable benefits. Run 14 (contact time: 122.16 min) yielded relatively lower removal efficiencies of 55.4% PO_4^{3-}

and 57.8% NH_4^+ , indicating over-adsorption equilibrium. Similarly, shorter durations failed to optimise nutrient retention. Run 17 (contact time: 12.84 min) resulted in removal efficiencies of 54.5% for PO_4^{3-} and 57.9% for NH_4^+ , respectively.

Haddad *et al.* (2018) demonstrated that three biochars derived from magnesium-pretreated cypress sawdust removed up to 50% of phosphate within 15 min of contact time, achieving equilibrium at 180 min. This underscores the challenges faced in trying to reduce nutrient loss, as most of them have a higher affinity for adsorption from the liquid media to the active sites of biochar, even in shorter durations.

4.4.3.4 Interaction of variables

The interaction of variables in the adsorption process for nutrient recovery reveals significant trends, especially concerning pH, which emerges as the dominant factor for phosphate and ammonium removal. For phosphate removal, the ANOVA results indicate that pH contributes overwhelmingly, with an F-value of 170.18 ($p < 0.0001$), suggesting its significant influence compared to adsorbent dosage and contact time, whose p-values exceed 0.3 (Table 4.9). Runs 5 and 19 demonstrate that higher pH values (9-10.7) correlate with increased phosphate removal, reaching up to 67.7% in Run 19, which aligns with the strong statistical significance of pH.

Table 4.9 ANOVA for phosphate and ammonium removal

Source	Sum of Squares	df	Mean Square	F-value	p-value	
PO₄³⁻ removal						
Model	760.42	3	253.47	57.47	< 0.0001	significant
A-pH	750.64	1	750.64	170.18	< 0.0001	
B-Adsorbent dosage	4.67	1	4.67	1.06	0.3186	
C-Contact time	5.10	1	5.10	1.16	0.2981	
Residual	70.57	16	4.41			not significant
Lack of Fit	52.76	11	4.80	1.35	0.3924	
Pure Error	17.81	5	3.56			
Cor Total	831.00	19				
NH₄⁺ removal						
Model	906.42	5	181.28	23.11	< 0.0001	significant
A-pH	533.06	1	533.06	67.94	< 0.0001	
B-Adsorbent dosage	8.76	1	8.76	1.12	0.3086	
C-Contact time	6.21	1	6.21	0.7912	0.3888	
BC	33.64	1	33.64	4.29	0.0574	not significant
A ²	324.76	1	324.76	41.39	< 0.0001	
Residual	109.84	14	7.85			
Lack of Fit	103.45	9	11.49	8.99	0.0131	
Pure Error	6.39	5	1.28			significant
Cor Total	1016.26	19				

Similarly, for ammonium removal, pH and its quadratic effect (A^2) are critical, as evidenced by their significant F-values of 67.94 and 41.39, respectively ($p < 0.0001$). However, interactions such as BC (adsorbent dosage and contact time) exhibit borderline significance ($p = 0.0574$), underscoring complex dependencies. Notably, run 16, with a pH of 9 and a dosage of 5 g/L, achieves the highest ammonium removal of 73.3%, confirming the sensitivity of ammonium recovery to pH optimisation.

While the lack of fit and F-value for phosphate removal is non-significant ($p = 0.3924$), indicating model adequacy, the ammonium model's significant lack of fit ($p = 0.0131$) necessitates caution. Nonetheless, both models demonstrate sufficient predictive capabilities ($R^2 > 0.74$), supporting their utility in navigating the adsorption process design space effectively. These findings reinforce the necessity of optimising pH alongside adsorbent and contact time to achieve minimum nutrient loss.

4.4.3.5 Model development

The adsorption process for PO_4^{3-} and NH_4^+ using magnetic biochar can be optimised using mathematical models derived from RSM. The ANOVA results for phosphate removal (Table 5.9) highlight the dominance of pH as a critical factor, with a high F-value (170.18) and statistical significance ($p < 0.0001$). The model fit for phosphate removal demonstrates robust predictability, with an R^2 of 0.9151 and a predicted R^2 of 0.8654, suggesting that the model can reliably navigate the design space with a minimal difference of 0.0497 between the predicted and adjusted R^2 . Furthermore, the adequate precision of 26.550 indicates a strong signal-to-noise ratio, reinforcing the model's reliability.

For ammonium removal, the ANOVA data reveal that pH also plays a significant role ($F = 67.94$, $p < 0.0001$). Despite a slightly lower predicted R^2 of 0.7444, the adjusted R^2 (0.8533) and adequate precision (17.947) confirm the model's capability to guide process optimisation (Table 4.10). However, a significant lack of fit ($p = 0.0131$) suggests minor discrepancies in capturing variability, which can be addressed by refining the experimental ranges.

Table 4.10 Fit statistics for nutrient loss

Phosphate removal	Std. Dev.	2.10	R ²	0.9151	Ammonium removal	Std. Dev.	2.80	R ²	0.8919
	Mean	54.41	Adjusted R ²	0.8991		Mean	57.54	Adjusted R ²	0.8533
	C.V. %	3.86	Predicted R ²	0.8654		C.V. %	4.87	Predicted R ²	0.7444
			Adeq Precision	26.5502				Adeq Precision	17.9465

The final predictive equations for PO₄³⁻ and NH₄⁺ removal integrate key parameters, such as pH, adsorbent dosage, and contact time, as shown in Equations 4.9 and 4.10, and as indicated in Table 4.11.

Table 4.11 Coefficients in terms of coded factors for nutrient recovery

Factor	Coefficient Estimate (Coded)	df	Standard Error	95% CI Low	95% CI High	VIF
% Phosphate removal						
Intercept	54.41	1	0.4696	53.41	55.41	
A-pH	7.41	1	0.5683	6.21	8.62	1.0000
B-Adsorbent dosage	0.5850	1	0.5683	-0.6198	1.79	1.0000
C-Contact time	0.6113	1	0.5683	-0.5935	1.82	1.0000
% Ammonium removal						
Factor	Coefficient Estimate (Coded)	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	+54.33	1	0.8010	52.61	56.05	
A-pH	+6.25	1	0.7580	4.62	7.87	1.0000
B-Adsorbent dosage	-0.8008	1	0.7580	-2.43	0.8249	1.00
C-Contact time	+0.6742	1	0.7580	-0.9514	2.30	1.0000
B*C	-2.05	1	0.9903	-4.17	0.0735	1.0000
A ²	+4.70	1	0.7312	3.14	6.27	1.00

$$\% PO_4 - P \text{ Removal (Coded)} = 54.41 + 7.41A + 0.5850B + 0.6113C \quad 4.9$$

$$\begin{aligned} \% NH_3 - N \text{ Removal (Coded)} \\ = 54.33 + 6.25A - 0.8008B + 0.6742C - 2.05 \\ + 4.70A^2 \end{aligned} \quad 4.10$$

These models are valuable tools for predicting nutrient removal efficiency, provided the inherent limitations, such as variability and minor predictive errors, are acknowledged and managed. Future optimisation can integrate real-time monitoring and dynamically adjust operational parameters to achieve a balance between high removal efficiency and minimal nutrient loss, as evidenced by run 5 for phosphate ($63.7 \pm 0.5\%$) and run 16 for ammonium ($73.3 \pm 0.6\%$).

4.5 Optimisation of the adsorption conditions

The point of zero charge (pH_{PZC}) is a critical parameter in adsorption studies as it determines the pH at which the surface charge of an adsorbent becomes neutral. For biochar, the pH_{PZC} was 6.53, while for magnetic biochar (MBC), it increased to 7.14, as shown in Figure 4.10. This increase can be attributed to the deposition of iron oxides during magnetisation, which alters the surface functional groups and charge characteristics (Qu *et al.* 2022). The magnetisation of biochar introduces positive surface sites, which shift the pH_{PZC} to higher pH values. This modification enhances the biochar's affinity for negatively charged species at pH levels below the pH_{PZC} .

In another study, the BC derived from rice husk (RH) had pH_{PZC} of 7.22 and 7.64 for biochar produced at 550 °C and 700 °C, respectively, while softwood pellets with pH_{PZC} of 6.57 and 6.78 for biochar produced at 500 °C and 700 °C, respectively (Neusatz Guilhen *et al.* 2022). According to a study by Mahanty and Mondal (2021), the pH_{PZC} values were 2.65 and 6.5 for MBC and BC, respectively. These results showed that the MBC was acidic. This could have been facilitated by the presence of carboxyl and phenolic groups, as well as iron impregnation onto the adsorbent's surface.

The knowledge of pH_{PZC} facilitates the selection of an optimum adsorption pH according to the target adsorbed species. For instance, below the pH_{PZC} , the positively charged surface of MBC has a higher affinity to negatively charged ions, including PCs and orthophosphates. However, at pH values higher than the pH_{PZC} , the surface charge is negative, and hence, positively charged ions, such as heavy metal ions and ammonium, adsorb onto the surface. This dual behaviour allows for optimal pH tuning to maximise

adsorption efficiency while minimising nutrient loss, as nutrients like phosphates are also negatively charged and can undergo co-adsorption.

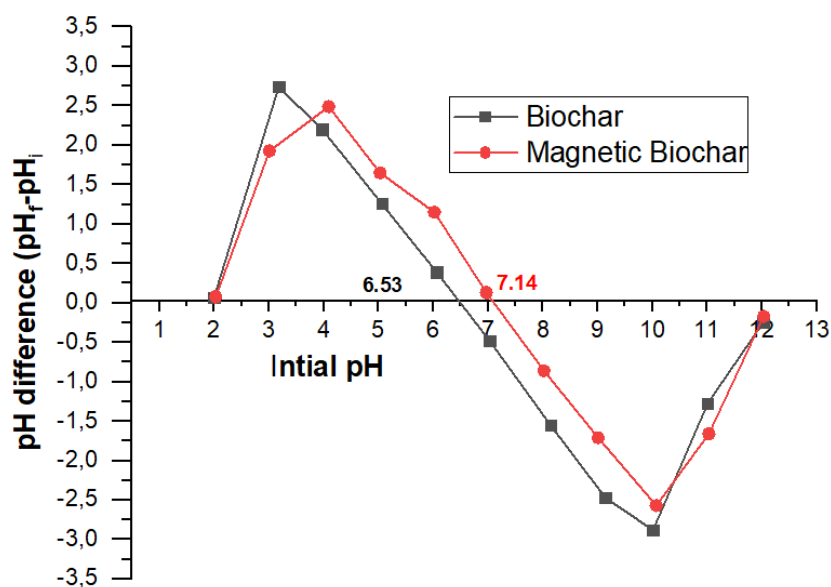


Figure 4.10 Point of zero charges for biochar and magnetic biochar.

pH is a dominant factor in electrostatic interactions, as well as in the ionisation states of adsorbates and the adsorbent surface charge. As seen by Hadi *et al.* (2015), the pH affects not only the charge of the adsorbent but also the dissociation pH of the PCs and heavy metals. The interaction between the MBC surface and PCs increases at low pH levels, resulting in enhanced adsorption efficiency and protonation of the MBC surface. Nevertheless, at pH greater than 8, the deprotonation of the biochar surface, as well as PC electrostatic repulsion, results in the loss of adsorption capacity.

The determination of pH_{PZC} is essential in practical applications for the selectivity of adsorbates in the optimum pH range. To ensure effective adsorption while minimising competitive adsorption of essential nutrients such as phosphates, pH should be maintained below the pH_{PZC} of 7.14 for PCs and heavy metals. The adsorption process is further optimised for wastewater treatment applications by combining the pH_{PZC} with other variables, such as contact time and adsorbent dosage, in a manner that balances pollutant removal with nutrient retention.

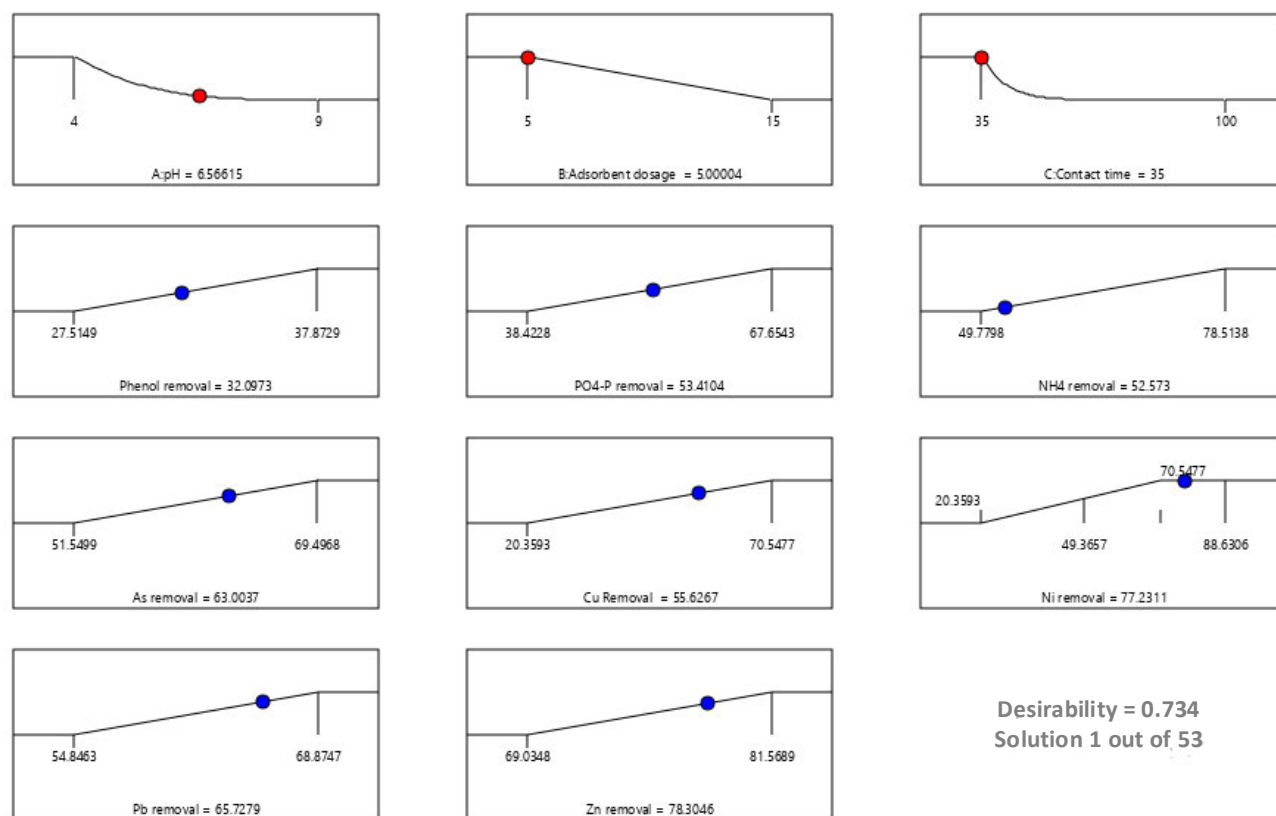


Figure 4.11 Ramp solutions for the optimisation of the adsorption process.

To identify the optimum operating conditions, specific goals were established using the criteria tab in the Design Expert software. The primary objectives were to maximise the removal of phenolic compounds and heavy metals while minimising nutrient loss through adsorption. Through systematic analysis and modelling, the optimal conditions were determined to be a pH of 6.57, an adsorbent dosage of 5 g/L, and a contact time of 35 min. These parameters achieved a balanced and efficient performance across all targets, as summarised in Figure 4.11.

Under these optimised conditions, the removal efficiencies were as follows: phenolic compounds (32.1%), PO₄-P (53.1%), NH₄⁺ (52.6%), arsenic (63.0%), copper (55.6%), nickel (77.2%), lead (65.7%), and zinc (78.3%). These results are expected to be well within the limits of experimental accuracy; however, in practical applications, this may not always be the case.

The determined conditions reflect a practical compromise between pollutant removal and nutrient retention, ensuring the system's practicality and sustainability. This optimisation provides a strong foundation for implementing MBC in wastewater treatment processes, striking a balance between environmental benefits and operational efficiency.

4.6 Validation of experimental results

To verify the predicted outcomes, a validation study was conducted under optimum conditions (35 min, pH 6.57, and 5 g/L adsorbent dosage). Run 21 utilised MBC, while run 22 served as the control using MAC. The results, summarised in Table 4.12, indicate the model's predictive accuracy and highlight differences in adsorption performance.

For run 21, MBC demonstrated a phenolic removal efficiency of $37.9 \pm 3.1\%$, which closely aligns with the predicted value of 32.1% ($\Delta\% = 18.07$). Similarly, arsenic removal showed minimal deviation ($\% \Delta = -0.95\%$), with $62.4 \pm 1.3\%$ observed compared to 63.0% predicted. The low standard deviations (e.g., $SD_{21} = 0.42\%$ for arsenic) and coefficients of variation ($CV_{21} = 0.7\%$) reinforce the high precision of these measurements. These values fall within the acceptable range for this study, as standard deviations below 5% and coefficients of variation below 15% are generally considered robust (Pathirana *et al.* 2020; Matheri *et al.* 2021).

Table 4.12 Validation of the adsorption process

Run	Phenol removal (%)	PO ₄ removal (%)	NH ₄ removal (%)	As (%)	Cu (%)	Ni (%)	Pb (%)	Zn (%)
Predicted	32.1	53.1	52.6	63.0	55.6	77.2	65.7	78.3
21 (MBC)	37.9 ± 3.1	50.3 ± 1.0	47.2 ± 1.5	62.4 ± 1.3	60.4 ± 0.6	76.8 ± 4.8	67.9 ± 4.1	78.6 ± 0.3
22 (AC)	41.9 ± 1.7	68.3 ± 1.9	46.9 ± 0.6	64.1 ± 1.4	65.7 ± 2.0	84.8 ± 5.5	76.1 ± 1.8	75.4 ± 2.1
SD ₂₁	4.10	1.98	3.82	0.42	3.39	0.28	1.56	0.21
SD ₂₂	4.90	7.60	2.85	0.55	5.05	3.80	5.20	1.45
%Δ 21	18.07	-5.27	-10.27	-0.95	8.63	-0.52	3.35	0.38
% Δ 22	30.53	28.63	-10.84	1.75	18.17	9.84	15.83	-3.70
CV ₂₁	11.7%	3.8%	7.7%	0.7%	5.9%	0.4%	2.3%	0.3%
CV ₂₂	13.2%	12.5%	5.7%	0.9%	8.3%	4.7%	7.3%	1.9%

MAC revealed higher removal efficiencies for most parameters compared to MBC, except for ammonium ($46.9 \pm 0.6\%$) and zinc ($75.4 \pm 2.1\%$). This suggests that while MAC may achieve better overall pollutant removal, MBC offers advantages for specific adsorbates, particularly in balancing nutrient retention and pollutant removal. It is also considered a cost-effective option, as it utilises waste biomass; however, significant efforts need to be made to improve MBC's adsorptive properties.

4.7 Characterisation of magnetic biochar before and after adsorption at optimum conditions

After completing the adsorption process, optimisation, and validation, it is essential to analyse the properties of the adsorbent to evaluate its performance. Table 4.13 illustrates significant reductions in the textural properties of magnetic biochar (MBC) post-adsorption. The BET surface area decreased by approximately 54%, while the single-point surface area showed a reduction of around 48%. Similar trends were observed for pore volume and pore size, with substantial declines in these parameters. These changes indicate successful adsorption, as the adsorbed material occupied the active sites of the biochar.

When compared to the control set-up, MAC exhibited a BET surface area reduction of over 65% and a decrease of approximately 40% in single-point surface area. These results highlight that the performance of MBC in this study is comparable to that of MAC, reinforcing its potential as a cost-effective alternative for adsorption applications.

Table 4.13 Comparison before and after adsorption against activated carbon

Material	Surface area (m ² /g)	BET surface area (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (Å)
MBC	195.5911	88.3000±9.8491	0.092965	42.113
Recovered MBC	100.4941	39.7808±6.7981	0.026337	10.558
MAC	335.8090	158.7323±14.8336	0.139277	35.097
Recovered MAC	204.2737	54.9579±8.9019	0.096975	70.582

The FTIR analysis of magnetic biochar (MBC) before and after adsorption, as shown in Figure 4.12(a), reveals significant changes in functional groups, underscoring the

adsorption mechanisms involved. Key differences are evident when comparing the FTIR spectra of MBC to those of recovered MBC after adsorption, as well as to MAC.

For MBC and recovered MBC, the peak at approximately 613 cm^{-1} , corresponding to Fe-O stretching vibrations, is present in MBC, indicating successful magnetisation. The recovered MBC peak is diminished, possibly due to interaction with adsorbates, such as heavy metals or organic toxins. Post-adsorption, the intensity of the 880 cm^{-1} peak (Fe-OH stretching) also decreases, indicating the involvement of hydroxyl groups in contaminant binding. The recovered MBC also exhibits enhanced intensity in vibrational bands near 1600 cm^{-1} (aromatic C=C and C=O stretching), indicating condensation and interaction with aromatic structures (Rawal *et al.* 2016).

The comparison with MAC reveals that MBC displays more oxygen-containing functional groups than MAC, as evidenced by peaks near 1122 cm^{-1} (C-O stretching), which diminish after adsorption. This indicates that these groups are also involved in the contaminant-binding process (Wu *et al.* 2020). In contrast, MAC has higher aromaticity and fewer Fe-O-related peaks, indicating the non-iron-modified structure favours adsorption through π - π interactions rather than electrostatic bonds. The results are in agreement with the literature, which highlights the importance of surface functional groups, particularly hydroxyl and carbonyl groups, in adsorption processes (Tan *et al.* 2017). The diminished peaks in recovered MBC highlight the interaction of these groups with pollutants during adsorption, indicating their involvement in contaminant removal.

In Figure 4.12 (b), the XRD analysis of MBC before and after adsorption (recovered MBC) demonstrates significant alterations in the crystalline structure, which indicates an effective adsorption process and material interaction.

A significant reduction in intensity was observed in the recovered MBC compared to MBC, which exhibits a strong diffraction peak at $2\theta \approx 40^\circ$. This means contaminants are being adsorbed, and they are highly likely to disrupt the crystalline structure of the magnetic component (Wu *et al.* 2021). Recovered MBC broadens peaks around $2\theta \approx 30^\circ$ and 50° , indicating the adsorption of adsorbates onto the biochar surface, which results in the modification of both magnetic and carbonaceous structures. During the process, peaks

corresponding to Fe_3O_4 , such as those near $2\theta \approx 35^\circ$, become less distinct due to the interaction of magnetic iron oxides with the adsorbates (Li *et al.* 2018b). These changes partially support past literature, which shows that magnetisation can increase adsorption capacity by enhancing the interaction between magnetic nanoparticles and pollutants, yielding observable structural changes (Zhang *et al.* 2020a). The reduced adsorbate-induced intensity and peak shifts confirm the effective adsorbate binding and the material transformation post-adsorption.

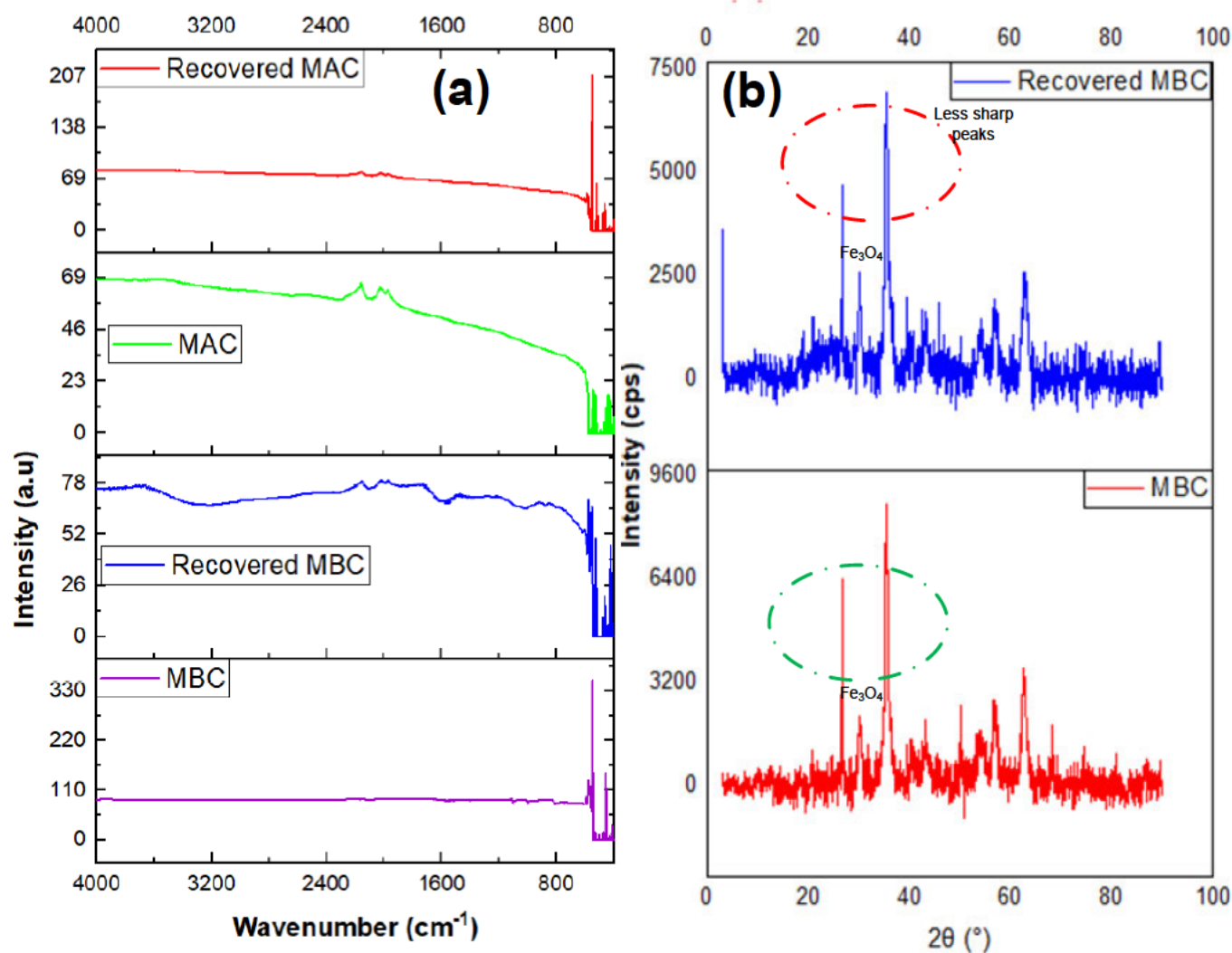


Figure 4.12 (a) FTIR analysis of MBC before and after adsorption (b) XRD analysis of MBC before and after adsorption

Figure 4.13 illustrates an SEM image of MBC and recovered MBC after adsorption, showing significant morphological and compositional changes resulting from the adsorption process.

The MBC micrograph (Figure 4.13(a)) shows a smooth and uniform surface with minimal visible pores or irregularities, typical of pristine biochar. This structure facilitates the initial adsorption of pollutants. Recovered MBC (Figure 4.13(b)) shows the surface that becomes rougher and more irregular after adsorption, with noticeable agglomeration and particle deposition. These changes suggest the binding of contaminants and a transformation of the surface texture.

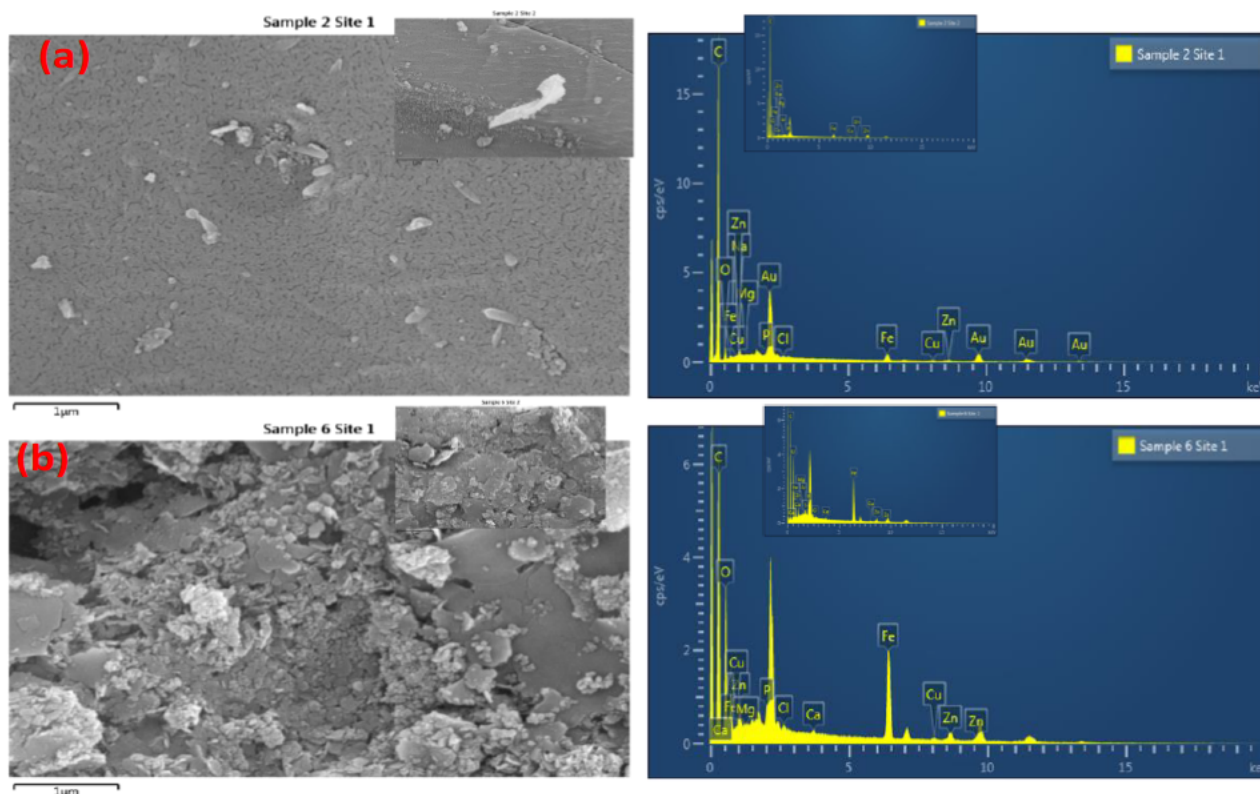


Figure 4.13 SEM-EDS analysis of MBC (a) before and (b) after adsorption

The carbon content decreases significantly, from 86% in MBC to 54.41% in recovered MBC, as adsorbed species replace carbonaceous active sites. Oxygen content increases substantially, from 9.48% to 27.88%, reflecting the incorporation of oxygenated contaminants or the formation of oxygen-rich functional groups on the surface. Iron

content rises from 2.38% to 13.15%, indicating the adsorption or retention of iron-rich particles during the process. Zinc and phosphorus concentrations also increased (Zn from 0.78% to 2.84%, P from 0.16% to 0.48%), suggesting these elements were part of the adsorbed pollutants.

These findings align with studies conducted elsewhere, demonstrating that adsorption processes lead to increased surface heterogeneity and the incorporation of pollutants into the biochar matrix (Zhao and Zhu 2020). The enhanced oxygen and metal content confirm the effective binding and transformation of pollutants in the material post-adsorption.

Critical insights into the adsorption process are gained from changes in the elemental content of the MBC before and after adsorption as determined by the CHNS analysis (Appendix B2). Surface interactions and adsorption of organic and inorganic pollutants resulted in a marked decrease in carbon content, from 50.08% to 47.59%. The support for the notion that pollutant adsorption occurs is further provided by corresponding increases in nitrogen content, from 0.83% to 1.12%, and oxygen content, from 9.88% to 16.60%. A slightly higher C/H ratio of 20-22 was observed after adsorption, typical of adsorption processes, indicating enhanced aromaticity and stability. The C/N ratio decreased from 60 to 42, indicating nitrogen-enriched adsorbed materials. Relative oxygen content on MBC was higher than on MAC, underscoring its efficient adsorption capabilities. These elemental shifts reveal the capacity of MBC to capture pollutants due to its unique adsorption properties. The results align with those of Tan *et al.* (2018); Świechowski *et al.* (2022), with elemental property changes in the adsorbents confirming the occurrence and degree of adsorption interactions.

4.8 Recovery of magnetic biochar

The primary motivation for magnetising biochar was to facilitate its efficient recovery after the adsorption process, reducing the likelihood of secondary pollution by enabling pollutant desorption and reuse (though desorption was outside the scope of this study). Over time, MBC may lose magnetic strength due to the leaching of the magnetic medium, highlighting the importance of periodically monitoring its magnetic properties (Zhao *et al.*

2021). Additionally, interactions with gelatinous and oily components in wastewater can result in unavoidable losses of biochar, compromising recovery rates.

This study analysed MBC recovery to quantify potential losses under optimised adsorption conditions. As shown in Table 4.14, five experimental runs were performed, yielding an average recovery rate of 98.1%, with approximately 2% of the MBC lost in each cycle. Without proper management, these losses could pose environmental risks through downstream processes.

In larger-scale applications, the recovery efficiency could be lower due to differences in hydrodynamics, such as increased flow rates and turbulence. This necessitates the use of appropriately designed electromagnets to maintain recovery rates and ensure operational feasibility (Rehman *et al.* 2024). Regular assessments are recommended to optimise the system for effective, cost-efficient, and environmentally sustainable operations.

However, at larger-scale operations, the recovery efficiency may be lower due to differences in hydrodynamics, including increased flow rates and turbulence. Consequently, sustaining the recovery rates and maintaining operational feasibility requires the use of appropriately designed electromagnets (Rehman *et al.* 2024). Optimal operation of the system is recommended for regular assessment to ensure cost efficiency and environmentally sustainable operations.

Table 4.14 Magnetic biochar recovery efficiency under optimised adsorption conditions

Case	MBC Loaded (g)	MBC Recovered (g)	% Recovery
1	1.0372	1.0150	97.9%
2	1.0164	0.9963	98.0%
3	1.0237	1.0098	98.6%
4	1.0311	1.0095	97.9%
5	1.0232	1.0031	98.0%
Average	1.0263	1.0067	98.1%
Standard Deviation (SD)	0.008	0.0072	0.3%

The results of this analysis demonstrate the feasibility of MBC recovery; however, scaling to real-world applications will require careful system design and monitoring to minimise losses effectively.

4.9 Chapter summary

In this chapter, magnetic biochar adsorption efficiency in removing toxins from hydrothermal treatment effluents is comprehensively investigated. It investigates the production of biochar from SCB and the subsequent magnetisation of biochar to facilitate its recovery and for improved adsorption properties. The study determined that 550°C is the optimal pyrolysis temperature for producing effective adsorbing biochar, while simultaneously balancing high surface areas, pore volumes, and an optimal elemental composition.

Key results show MBC's superior recovery (98.1 %), demonstrating a robust adsorption performance under MBC optimised conditions (pH 6.57, a dosage of 5 g/L, 35 min contact time) with moderately high removal of heavy metals (e.g. arsenic, copper) and low PCs removal efficiency with minimum possible nutrient loss (e.g. phosphate, ammonium). Comparisons with magnetic activated carbon (MAC) indicate that MBC is an effective alternative, offering comparable adsorption efficiency for larger molecular toxins.

Advanced characterisation techniques, including SEM, XRD, and FTIR, confirm structural and functional modifications in MBC pre- and post-adsorption, underscoring the mechanisms of pollutant capture. This study emphasises the potential of MBC as a sustainable and scalable solution for wastewater valorisation, aligning with circular economy principles.

CHAPTER 5: INTEGRATED APPROACHES TO PHOSPHORUS RECOVERY THROUGH STRUVITE PRECIPITATION IN WASTE-ACTIVATED SLUDGE TREATMENT

5.1 Introduction

Phosphorus recovery from waste-activated sludge (WAS) has emerged as a crucial solution to address both resource scarcity and environmental degradation. WAS is a by-product of wastewater treatment processes, containing significant quantities of nutrients, including phosphorus, nitrogen, and potassium, alongside organic and inorganic materials. Phosphorus in WAS exists in various forms, including orthophosphate, non-apatite inorganic phosphorus, apatite phosphorus, and organic phosphorus, which determine its bioavailability and recovery potential.

The recovery of phosphorus from WAS as struvite (magnesium ammonium phosphate, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) offers a dual benefit. It transforms waste into a value-added product while preventing or reducing phosphorus pollution from entering water bodies. Struvite, a slow-release fertiliser, is widely recognised for its high nutrient value and reduced environmental impact, making it a promising solution for achieving circular economy objectives.

HT has gained prominence as it enhances the bioavailability of nutrients, including phosphorus. The solubilisation of organic phosphorus into orthophosphate during HT is particularly beneficial for subsequent recovery processes, as orthophosphate is the primary form required for struvite crystallisation.

Struvite precipitation is the process through which magnesium, ammonium and orthophosphate ions are induced to crystallise under controlled conditions of pH and magnesium concentrations, among others. The primary controlling factors were chosen to be pH and magnesium concentration, as these directly determine the supersaturation, nucleation, and growth of struvite, as well as ammonium volatilisation and side reactions. Their interaction dictates the overall efficiency of precipitation, which makes them the most critical parameters to optimise in wastewater treatment systems.

This process not only helps to recover phosphorus but also minimises the total nutrient concentration in effluents, contributing to the prevention of eutrophication in receiving water bodies. However, the recovery of struvite as a fertiliser especially adheres to the principles of sustainable wastewater management, as it aims to reduce synthetic fertilisers and close nutrient loops.

However, during HT, some toxins are produced, necessitating their removal by adsorption, as explained earlier in the preceding chapter. It also helps maintain the high quality of the recovered struvite that is required for use in agricultural activities. The quality of the struvite is thus assessed to determine its effectiveness, purity and commercial viability as a fertiliser and to address regulatory and environmental concerns.

This integration of HT and struvite precipitation represents a revolutionary advancement in wastewater management, addressing challenges such as resource recovery, waste management, and environmental restoration (Figure 5.1). By leveraging these technologies, the WWTPs can transition from conventional waste disposal systems to multi-product recovery hubs (hydrochar for heating, struvite, biomethane) that support circular economy principles and sustainability objectives.

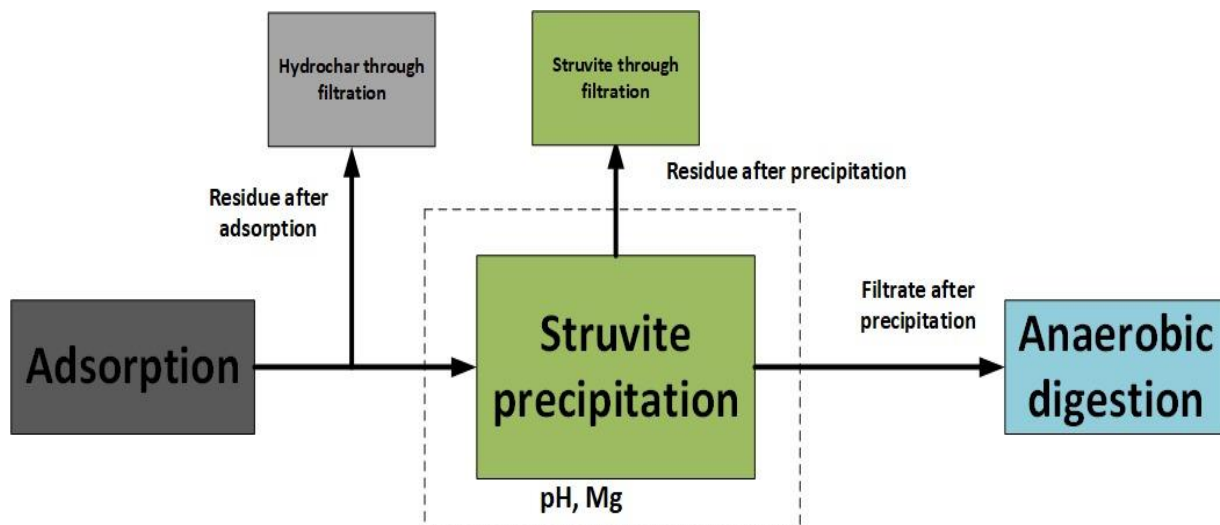


Figure 5.1 Process flows around the precipitation unit

Mass balances were conducted to track the flow and transformation of phosphorus throughout the integrated valorisation processes. This is crucial because it ensures process efficiency, enables optimising nutrient recovery and loss prevention, validates experimental results, supports technoeconomic and environmental evaluations, and provides information that helps in enhancing the scalability of the process.

Thus, this chapter endeavours to provide a comprehensive discussion of the methodologies, findings, and implications of the suggested technologies, namely, the efficiency of hydrothermal treatment on phosphorus solubilisation, assessment of struvite precipitation optimisation, and mass balance on phosphorus content in the treatment process.

5.2 Methodology for phosphorus recovery through struvite precipitation

After magnetic separation from detoxification effluent using the optimised conditions, precipitation experiments were conducted to harvest struvite from the sludge.

5.2.1 Operating parameters for effective precipitation of struvite.

To optimise the precipitation of struvite, the pH and the concentration of the magnesium source were systematically varied as the primary input variables. The output responses were the concentrations of phosphate (mg/L) and ammonium (mg/L) in the precipitate (residue), as well as the percentage recovery of each nutrient, which was also recorded. The experiments were designed based on the RSM framework and Design-Expert 13 software, utilising CCD due to its flexibility in fitting both factorial and star points, as well as applying efficient estimation of linear, interaction, and quadratic effects (Li, Lu and Gao 2021).

The experiments were conducted over a pH range of 7 to 11 (Perwitasari *et al.* 2018). The pH was adjusted by adding 3 mol/L NaOH or 2 mol/L HCl as required until the desired pH value was achieved. The magnesium source solution was prepared by dissolving 20 g of magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) in 1 L of deionised water. The amount of magnesium source added to the reaction vessel was determined by the stoichiometric

relationship of ammonium (NH_4^+) to phosphate (PO_4^{3-}) ion as proposed by Munir *et al.* (2017); Shih *et al.* (2017a), in this study, the volume of the prepared Mg source was varied between 1.00 and 2.50 mL, corresponding to concentrations ranging from 0.974 mM to 2.40 mM in the final volume. The selected volume was then added to 100 mL of the wastewater sample. Only analytical-grade reagents were used to ensure reliability and reproducibility, and solutions were stored at 4 °C to maintain stability.

The matrix of the experimental design is presented in Table 5.2, which shows the combinations of pH and volume of the magnesium source used in the experiment. Such results were subjected to statistical analysis using ANOVA to build predictive mathematical models. These models shed light on the effects of input parameters on the recovery of phosphate and ammonium, revealing optimal operating conditions for struvite precipitation. All runs were conducted in duplicate to ensure the reliability of the experimental data, and the predicted values were cross-validated against the models and experimental runs at the determined optimum conditions.

5.2.2 Experimental setup for the struvite precipitation process and analysis of the products

Before conducting the precipitation experiments, hydrochar was separated by vacuum filtration using Whatman No. 42 filter paper (25 μm). This step ensured that measurements of the struvite precipitate were free from interference by hydrochar and other solid particles. The recovered hydrochar was subsequently dried, and its mass was recorded and analysed for product properties, such as functional groups, morphology, and crystallography, using FTIR, SEM-EDS, and XRD analyses, as described in Section 3.2.4 and discussed in Section 3.10.

Precipitation experiments were conducted in 500 mL Erlenmeyer flasks at room temperature. For each experimental run, 100 mL of the pretreated solution was transferred into the reaction vessel and the magnesium source solution was added. NaOH or HCl was used to adjust the pH accordingly, and the solution was continuously handshaken to obtain homogeneity. The reaction mixtures were then placed on an orbital shaker, operated at 150 rpm for 30 minutes, to facilitate mixing and enhance reaction

kinetics. After agitation, the samples were allowed to settle for 2 h, facilitating the formation of struvite crystals freely without disruption. The precipitates were then separated by filtration using Whatman No. 42 filter paper.

The concentrations of phosphate, ammonium, and magnesium in the filtrate were measured by extracting samples (15 mL) of the filtrate and analysing them by an automated Gallery photo-analyser (as described in Section 3.2.2.4). Under isothermal conditions, the filtration residue (precipitates) was dried at 35 °C for 12 h in an oven, following a standard procedure (Zaffar *et al.* 2024). To quantify the elemental composition of the precipitate, the precipitates were dissolved in 1 mL of concentrated HCl and 9 mL of deionised water, and analysed using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) (ICPE 9820, Shimadzu, Tokyo, Japan). All phosphorus and metal analyses were performed on ICP-AES, with method Limit of Detection (LOD) and Limit of Quantification (LOQ) determined as $3\sigma/S$ and $10\sigma/S$, respectively (σ representing standard deviation of the blank or low-level sample; S representing slope of the calibration curve (instrument sensitivity)). Concentrations below LOQ were reported as below quantification limit (BQL) and excluded from the mass balance to avoid bias. This was performed for both the filtrate and the residue (after dissolution in HCl), and changes to the initial concentration were noted. The experiments were duplicated to assess experimental error.

The recovery efficiency for phosphates and ammonium (nutrients) was expressed as the percentage of nutrients in the precipitates in relation to the initial concentration before precipitation. Equation 2.19 illustrates the reaction of pure struvite precipitation occurring in the wastewater stream used to guide the ranges of magnesium source concentrations investigated (Rabinovich and Rouff 2021; Natividad-Marin, Burns and Schneider 2023).

Sequential phosphorus extraction

Sequential phosphorus extraction was performed to fractionate and quantify different forms of phosphorus (P) in sewage sludge, following a modified protocol (Hedley, Stewart and Chauhan 1982; Pokhrel *et al.* 2018). Approximately 1 g of dried sample was sequentially extracted with 20 mL of progressively stronger reagents in 50 mL

polypropylene centrifuge tubes. The steps included: (1) deionised water for readily soluble, bioavailable P ($\text{H}_2\text{O-P}$); (2) 0.5 M NaHCO_3 (pH 8.2) for weakly sorbed organic and inorganic bioavailable P ($\text{NaHCO}_3\text{-P}$); (3) 0.1 M NaOH for strongly sorbed, potentially bioavailable P (NaOH-P); (4) 1 M HCl for non-bioavailable apatite or calcium-bound P (HCl-P); and (5) the residual fraction representing non-bioavailable P (Residual-P). Each step involved shaking at 150 rpm for 16 hours at 25°C, followed by centrifugation at 5000 rpm for 10 minutes, and then filtering the supernatant through a 0.45 μm or equivalent filter. All extractions were performed in duplicate.

Total phosphorus (TP) was determined by combining filtrates and digesting them with acid persulfate to convert all P forms to orthophosphate, followed by colour development using a molybdate-ascorbic acid reagent. Absorbance was measured at 880 nm using a spectrophotometer (APHA 2017; Phansi *et al.* 2022). Inorganic P (IP) was calculated as the sum of $\text{H}_2\text{O-P}$, $\text{NaHCO}_3\text{-P}$, NaOH-P , and HCl-P , while organic P (OP) was obtained by subtracting IP from TP. This method provided detailed P speciation, including bioavailable and non-bioavailable fractions, to characterise phosphorus dynamics in the sludge. Phosphatases are found on the surface of human skin; therefore, gloves must be worn every time to avoid sample contamination (Iammarino *et al.* 2020). Unless noted otherwise, phosphate units are reported by the instrument as PO_4^{3-} . To convert to phosphorus as P, multiply the result by 0.327

5.2.3 Determination of the purity of struvite for its slow-release properties

A dissolution-precipitation analysis method was employed to evaluate the purity of the harvested struvite precipitates (de Figueiredo *et al.* 2021). In this method, the solubility of phosphorus (P) compounds in 2% citric acid is evaluated as a proxy of the solubility of P compounds under conditions relevant to plant nutrient uptake.

The precipitates were first ground to a fine powder with a mortar and pestle to guarantee homogeneity. A sample of about 0.5 g was carefully obtained from a representative subsample for analysis. The subsample was transferred into a 100 mL glass flask, into which 25 mL of a freshly prepared 2% citric acid solution (pH ~2.5) was added. The solubilisation of phosphorus compounds was maximised by stirring the mixture

continuously at room temperature for 1 h. Uniform dissolution of the struvite particles was achieved by stirring, which provided consistent contact with the acid solution.

After filtration, the solution was filtered on Whatman No. 42 filter paper to determine the quantity of the undissolved material. The purity of the harvested precipitate was calculated as the ratio between the soluble phosphorus (P_{soluble}) and the total phosphorus (P_{total}) concentrations in the harvested precipitate. Equation 5.1 was used to express this ratio as a percentage.

$$\text{Struvite Purity (\%)} = \frac{P_{\text{soluble}}(\text{mg/L})}{P_{\text{total}}(\text{mg/L})} * 100\% \quad 5.1$$

The phosphorus content of the pretreated waste-activated sludge (WAS) was characterised before the precipitation process to ensure accuracy. A mass balance was conducted at each stage of the treatment process to account for phosphorus speciation. In this step, the phosphorus fractions of filtrate, precipitate and any discrepancies attributed to unaccounted phosphorus forms, such as those lost by volatilisation or secondary reaction, were measured.

The soluble phosphorus content (P_{soluble}) of the filtrate was then analysed using the molybdenum blue method, as described in the Standard Methods for the Examination of Water and Wastewater (APHA 2017). It was measured at 880 nm using a spectrophotometer following a calibration curve prepared with phosphorus standards using a UV-Vis spectrophotometer, as described in Section 3.2.2.5.

5.3 Effect of operating parameters in the precipitation process

Examining the operating parameters is a critical step in process optimisation, as it identifies the optimal conditions to achieve the most favourable output. This evaluation ensures that the system operates efficiently while maximising desired results. Figure 5.2 and Table 5.1 provide a comprehensive summary of the input parameters and their corresponding ranges, highlighting the variability and measures of spread associated with each parameter. In this section, phosphate and ammonium concentrations were studied as the output responses to determine the quality of the struvite formed. Efforts were made

to minimise the effect of competing ions, such as phosphate and ammonium ions, during the precipitation stages by optimising the chosen operating parameters.

Table 5.1 Summary of input parameters and output responses

Name	Units	Input Factors				Mean	Std. Dev.	Ratio
		Minimum	Maximum	Coded Low	Coded High			
Mg source (20g/L)	mL	0.6893 (0.678 mM)	2.81 (2.76 mM)	-1 ↔ 1.00	+1 ↔ 2.50	1.75	0.6124	4.08
pH		6.17	11.83	-1 ↔ 7.00	+1 ↔ 11.00	9.00	1.63	1.92
Output Responses								
Phosphate in-residue	mg/L	19.5976	74.0756			58.15	19.49	3.78
Phosphate recovered	%	22.8	86.18			67.65	22.67	3.78
Ammonia in-residue	mg/L	4.79938	29.8457			17.87	8.90	6.22
Ammonia recovered	%	5.99667	37.2913			22.33	11.12	6.22

Table 5.2 presents the experimental design matrix generated using RSM under central composite design (CCD). The table outlines the input operating parameters alongside their corresponding output responses. It is important to note that the sludge used during this stage originated from the adsorption unit and had initial phosphate and ammonium concentrations of 85.95 mg/L and 80.03 mg/L, respectively. The magnesium ion concentration was approximately 2.86 mg/L, which was insufficient for an effective precipitation process. Consequently, an external magnesium source was introduced to facilitate precipitation.

Table 5.2 Nutrient distribution after the struvite precipitation

Run	Mg source- 20g/L (mL)	pH	Phosphate in- residue (mg/L)	Phosphate discrepancy (mg/L)	Phosphate recovered (%)	Ammonia residue (mg/L)	in- Ammonia discrepancy (mg/L)	Ammonia recovered (%)	N:P molar ratio
1	2.81	9	55.0±1.2	10.0	63.93±1.4	21.8±3.1	14.1	27.2±3.9	2.09
2	1.75	6.17	19.6±1.1	-3.6	22.8±3.5	8.3±1.2	13.4	10.3±1.5	2.22
3	1.75	9	74.1±1.8	-9.8	86.18±0.7	28.0±1.9	10.2	35.0±2.4	2.00
4	2.5	11	64.5±2.2	-17.6	75.05±2.8	12.1±2.0	10.4	15.1±2.5	0.99
5	1	7	27.3±2.4	-18.8	31.77±2.8	10.5±1.4	10.4	13.4±1.3	2.02
6	1	11	66.3±3.7	-17.8	77.17±4.2	10.7±1.1	16.8	13.1±0.9	0.80
7	1.75	11.8	71.7±2.4	-7.0	83.45±4.2	4.8±0.2	11.4	6.0±0.3	0.35
8	0.69	9	56.1±3.6	-3.9	65.24±2.1	15.5±3.5	9.2	19.3±4.4	1.46
9	1.75	9	72.6±2.4	-11.9	84.52±1.4	26.4±1.2	10.6	33.0±1.4	1.92
10	1.75	9	73.4±3.8	-10.6	85.45±2.1	24.8±1.6	9.9	30.9±2.0	1.78
11	1.75	9	73.3±1.2	-14.7	85.24±0.7	29.8±2.6	9.2	37.3±3.2	2.15
12	1.75	9	70.8±2.4	-11.0	82.36±1.4	28.5±1.0	10.0	35.7±1.2	2.13
13	2.5	7	31.2±2.9	-24.2	36.27±1.7	11.3±2.1	10.8	14.1±2.6	1.91

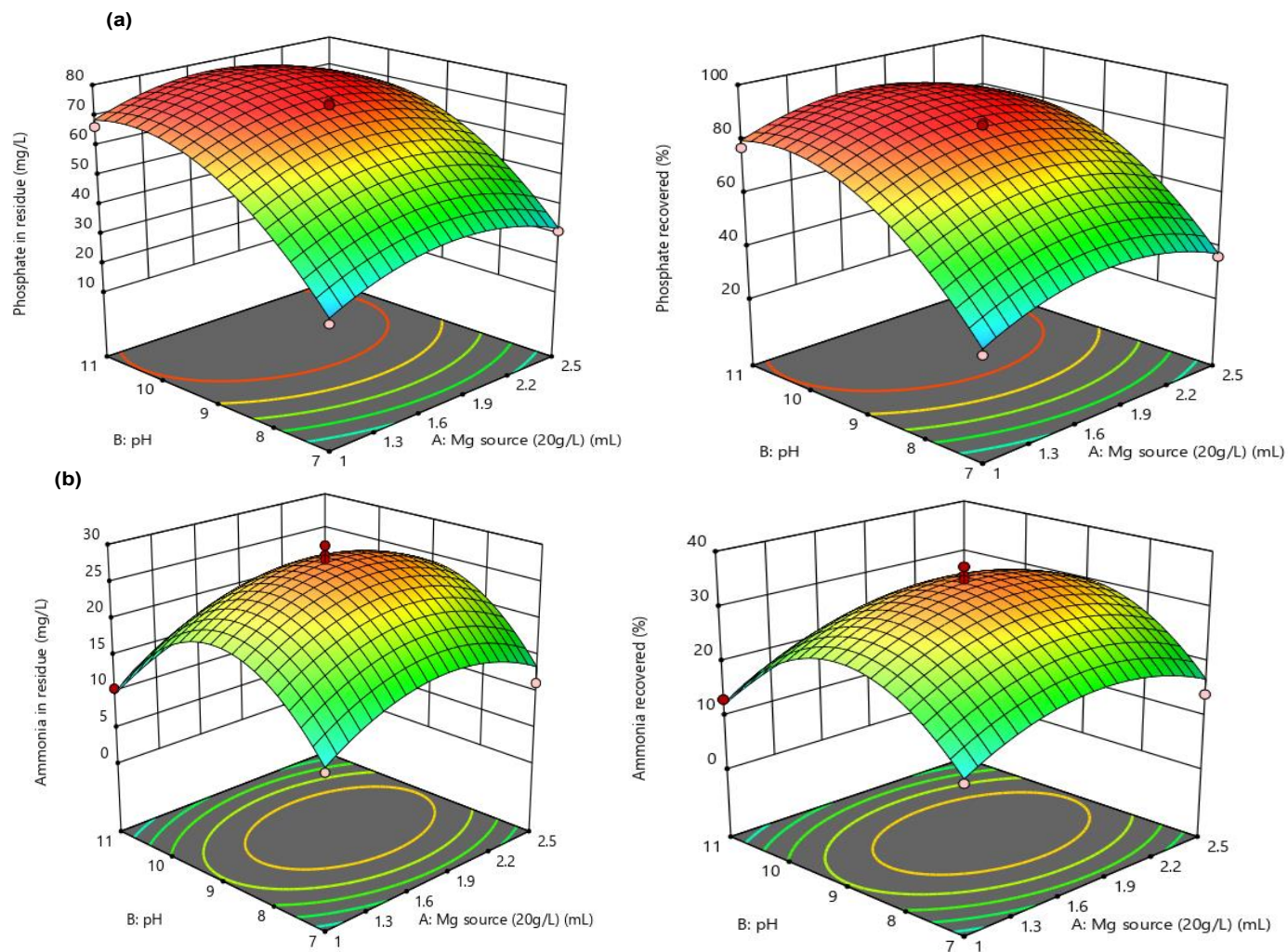


Figure 5.2 Surface plot of the effect of operating parameters on (a) phosphate in-residue and % phosphate recovered. b) ammonium in-residue and % ammonium recovered.

5.3.1 Effect of pH on recovery efficiency

pH played a decisive role in phosphate and ammonium recovery. Lower pH values (e.g., pH 6.17, run 2) resulted in significantly reduced phosphate recovery (22.8%), with high phosphate residue concentrations (19.6 mg/L), as shown in Table 5.2 and Figure 5.2 (a). This is attributed to insufficient supersaturation necessary for struvite crystallisation. Conversely, pH 9.0 (runs 3, 9, 10, and 11) yielded the highest phosphate recovery (85.24% to 86.18%), indicating that a slightly alkaline environment optimises the precipitation process by enhancing the availability of divalent magnesium and the stabilisation of phosphate and ammonium ions (Wu *et al.* 2021).

At pH values exceeding 10 (e.g., pH 11, run 6), phosphate recovery declined slightly to 77.17%. This reduction is due to the formation of $\text{Mg}(\text{OH})_2$, which competes with phosphate for available magnesium ions, thereby hindering struvite precipitation. These findings align with previous studies indicating that optimal phosphate recovery occurs at a narrow pH range of 8.5-9.5, where competing side reactions are minimised (Takaya *et al.* 2016).

Similarly, ammonium recovery varied across the pH spectrum. Under acidic conditions (pH 6.17, run 2), ammonium recovery was 10.3%, with a residue concentration of 8.3 mg/L (Table 5.2 and Figure 5.2 (b)). Acidic pH favours ammonium stabilisation in its ionised NH_4^+ form, minimising volatilisation losses. However, as pH increased, ammonia volatilisation became more pronounced. At pH 7.0 (run 5), ammonium recovery rose to 13.4%, suggesting the onset of ammonia gas formation. At pH 9.0, ammonium recovery peaked (35.0%, run 3), coinciding with optimal struvite crystallisation conditions where the $\text{Mg}:\text{NH}_4:\text{PO}_4$ molar ratio approached stoichiometry.

Beyond pH 10, ammonium recovery significantly dropped, possibly due to enhanced ammonia volatilisation. For instance, at pH 11.8 (run 7), only 6.0% of the ammonium was recovered, with a residue concentration of 4.8 mg/L, confirming extensive loss of ammonium to the gas phase. This observation aligns with prior research demonstrating that high pH conditions (>10) favour ammonia stripping, thereby reducing ammonium recovery efficiency (de Figueiredo *et al.* 2021).

5.3.2 Effect of magnesium dosage on recovery

Magnesium concentration had a direct influence on phosphate and ammonium recovery. As Mg^{2+} availability increased, phosphate recovery improved, as seen in run 1 (pH 9, Mg 2.81 mL), where phosphate recovery reached 63.93%. At lower Mg^{2+} concentrations (e.g., 1.0 mL, run 5), phosphate recovery dropped to 31.77%, demonstrating that insufficient magnesium limits struvite formation. However, excessive Mg^{2+} beyond 2.5 mL (of the 20 g/L MgCl_2 solution) did not enhance phosphate recovery proportionally, as observed in run 4 (pH 11, 2.5 mL Mg), where phosphate recovery stabilised at 75.05%. The diminishing returns at higher magnesium concentrations are attributed to $\text{Mg}(\text{OH})_2$ precipitation, which competes with struvite formation (Hendrix *et al.* 2015; Yesigat *et al.* 2022), as shown in Equation 2.24.

Ammonium recovery exhibited a similar trend (Figure 5.2(b)). At optimal magnesium levels (1.75 mL, pH 9, run 3), ammonium recovery was highest (35.0%). However, at excessive magnesium concentrations, ammonium recovery declined due to $\text{Mg}(\text{OH})_2$ precipitation inhibiting struvite formation. For instance, at 2.5 mL Mg^{2+} (pH 11, run 4), ammonium recovery dropped to 15.1%, indicating that excess magnesium can adversely affect ammonium incorporation into the struvite structure (Rahman *et al.* 2014).

Overall, the analysis of phosphate and ammonium recovery under varying pH and magnesium concentrations reveals that optimal struvite precipitation occurs within a pH range of 8.5-9.5, with a balanced molar ratio of Mg: NH_4 : PO_4 . Higher pH levels (>10) promote $\text{Mg}(\text{OH})_2$ precipitation and ammonia volatilisation, reducing recovery efficiency. These findings emphasise the importance of precise control over operating conditions to enhance simultaneous phosphate and ammonium recovery while minimising nutrient losses.

5.3.3 Interaction of variables

The interaction between magnesium source concentration and pH has a significant influence on phosphate and ammonium recovery, as demonstrated in the interaction plots. In Figure 5.3(a), phosphate recovery exhibits a non-linear trend, where increasing the magnesium source improves recovery up to a certain point, but further increases

beyond the optimal concentration result in a plateau or slight decline. At pH 9 (green points), phosphate recovery is maximised across a range of magnesium source values, aligning with the theoretical optimal conditions for struvite precipitation. This effect diminishes at lower pH levels (e.g., pH 7), where the supersaturation threshold required for crystallisation is not met, as seen in reduced phosphate concentrations in runs with lower pH values.

Conversely, Figure 5.3(b) highlights a more substantial interaction effect for ammonium recovery, which is more sensitive to changes in pH. At pH 9, ammonium retention peaks across intermediate magnesium concentrations (~1.75 mL), reflecting enhanced struvite formation. However, as pH increases towards 11, ammonium recovery decreases despite increasing magnesium levels, likely due to the volatilisation of ammonia gas. This behaviour corresponds with earlier ANOVA findings, where the quadratic term for pH (B^2) was highly significant, suggesting that pH has a dominant role in ammonium recovery over magnesium source. Runs such as run 6 (pH 11, Mg source 1 mL) underscore this trend, where ammonium recovery declined despite favourable magnesium levels.

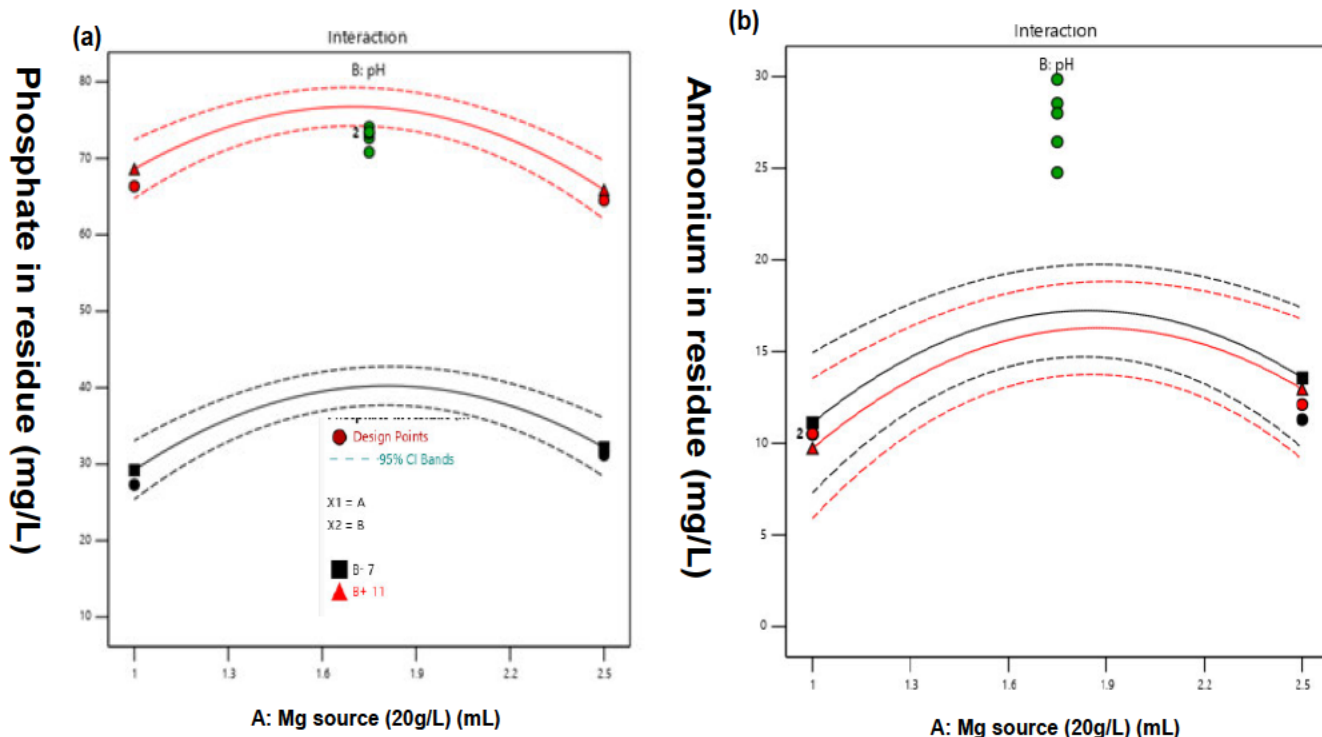


Figure 5.3 Interaction of variables (a) phosphates (b) ammonium in-residue.

The interaction plots collectively reveal that while magnesium concentration influences recovery, pH remains the critical variable. Phosphate recovery is primarily controlled by achieving a balance between supersaturation and competing side reactions, whereas ammonium recovery is strongly impacted by volatilisation at higher pH levels. These findings reinforce the need to optimise both parameters simultaneously, as their interaction directly governs the efficiency of nutrient recovery processes.

5.3.4 Thermodynamic determination of struvite precipitation

Understanding the driving force for precipitation is crucial in determining the thermodynamic favorability of struvite formation, adjusting operational conditions (such as pH and ion concentrations), and preventing competing reactions. This facilitates efficient crystal growth, benefiting nutrient recovery and sustainably operated wastewater treatment processes (Wu *et al.* 2022). Equations 2.26, 2.27, and 2.28 play a crucial role in determining the key parameters for thermodynamic analysis, as outlined below.

$$IAP = [Mg^{2+}][NH_4^+][PO_4^{3-}] = 5.17 \times 10^{10} \text{ mol}^3/L^3$$

This calculation indicates significant supersaturation, making struvite precipitation highly likely.

$$SI = \log \left(\frac{5.17 \times 10^{10}}{13.26} \right) = 9.59$$

$SI > 0$ indicates that the solution is supersaturated, meaning struvite precipitation is thermodynamically favourable.

The driving force, therefore, is computed as follows.

$$F = -\frac{RR_g}{\alpha} \ln \Omega = -\frac{8.314}{3} \times \ln(9.59) = -6.27$$

Supersaturation and thermodynamic parameters are found to be critical factors driving struvite precipitation, as evidenced by results. The IAP of $5.17 \times 10^{10} \text{ mol}^3/L^3$, solubility product (Ksp) of 13.26, and resulting Supersaturation Index (SI) of 9.59 indicate a highly supersaturated solution conducive to crystal nucleation and growth (Natividad-Marin, Burns and Schneider 2023). The calculated driving force ($F = -6.27 \text{ J/mol}$) highlights the

release of free energy necessary for struvite formation. The calculations suggest that pH and the concentrations of reactive ions Mg^{2+} , NH_4^+ and PO_4^{3-} play a dominant role in supersaturation, underscoring the requirement for accurate control of these variables (Wu *et al.* 2021). This is consistent with existing theories that high supersaturation is required for the nucleation barrier to exceed the precipitation of particles (Rahman *et al.* 2014). The results also show that the dynamic equilibrium between ion activity and crystallisation occurs by reducing the supersaturation as the system approaches thermodynamic equilibrium. This thermodynamic framework provides a strong basis for optimising operational parameters in struvite recovery processes to prevent nutrient losses from sewage streams. Based on these insights, the study reaffirms the importance of solubility and supersaturation control in executing sustainable phosphorus recovery.

5.4 Statistical and predictive modelling for precipitation and recovery of phosphate and ammonium

Understanding the precipitation and recovery of phosphate and ammonium is essential for optimising struvite formation. The experiments were conducted to gather data on how various variables, specifically pH and magnesium concentration, affect nutrient recovery. The goal is to develop a predictive framework that enables effective process optimisation.

Table 5.3 ANOVA for quadratic models of phosphate and ammonium in-residue

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	4528.24	5	905.65	215.46	< 0.0001	significant
Quadratic model of Phosphate in-residue						
A-Mg source (20g/L)	0.0257	1	0.0257	0.0061	0.9399	
B-pH	2667.47	1	2667.47	634.62	< 0.0001	
AB	8.09	1	8.09	1.93	0.2078	
A ²	625.29	1	625.29	148.76	< 0.0001	
B ²	1443.70	1	1443.70	343.47	< 0.0001	
Residual	29.42	7	4.20			
Lack of Fit	23.11	3	7.70	4.88	0.0798	not significant
Pure Error	6.31	4	1.58			
Cor Total	4557.67	12				
Quadratic model for Ammonia in-residue						
Model	921.42	5	184.28	44.12	< 0.0001	significant
A-Mg source (20g/L)	16.05	1	16.05	3.84	0.0908	
B-pH	2.02	1	2.02	0.4846	0.5088	
AB	0.1521	1	0.1521	0.0364	0.8541	
A ²	161.43	1	161.43	38.65	0.0004	
B ²	821.39	1	821.39	196.64	< 0.0001	

Residual	29.24	7	4.18			
Lack of Fit	13.80	3	4.60	1.19	0.4189	not significant
Pure Error	15.44	4	3.86			
Cor Total	950.66	12				

Table 5.3 summarises the statistical analysis of phosphate and ammonium recovery based on RSM. The quadratic model for phosphate recovery was highly significant (F-value = 215.46, $p < 0.0001$), indicating that the experimental parameters well explained the variability in phosphate recovery. pH (B) was the most influential factor, with an F-value of 634.62 ($p < 0.0001$), while the magnesium source (A) showed no significant linear effect ($p = 0.9399$). Quadratic terms for both pH (B^2) and magnesium source (A^2) were highly significant ($p < 0.0001$), highlighting strong non-linear effects, particularly for pH, where an optimal range maximises phosphate recovery.

Similarly, the quadratic model for ammonium recovery was also significant (F-value = 44.12, $p < 0.0001$). However, only the quadratic terms for pH (B^2) and magnesium source (A^2) were statistically relevant, confirming a non-linear dependency. The insignificant lack of fit (F-value = 1.19, $p = 0.4189$) suggests that the model was well-fitted to the experimental data with minimal unexplained variance. This reinforces the importance of optimising pH and magnesium concentration to achieve maximum ammonium recovery while minimising losses due to volatilisation.

5.4.1 Mathematical model for predictive estimation

Predictive models were developed to estimate phosphate and ammonium recovery under varying experimental conditions. The fit statistics (Table 5.4) confirm the robustness of the models, with an R^2 value of 0.9935 for phosphate recovery and 0.9692 for ammonium recovery, indicating high predictive accuracy. The adjusted R^2 and predicted R^2 values were in close agreement, demonstrating minimal overfitting and strong generalisability.

Table 5.4 Fit statistics for nutrient recovery

Phosphate recovery			
Std. Dev.	2.05	R^2	0.9935
Mean	58.15	Adjusted R^2	0.9889
C.V. %	3.53	Predicted R^2	0.9618
		Adeq Precision	39.2264
Ammonium recovery			
Std. Dev.	2.04	R^2	0.9692

Mean	17.87	Adjusted R²	0.9473
C.V. %	11.44	Predicted R²	0.8714
		Adeq Precision	16.1644

Final predictive models are presented in Equations 5.2 and 5.3.

Phosphate in residue (coded)

$$= 72.85 + 0.0567A + 18.26B - 1.42AB - 9.48A^2 - 14.41B^2 \quad 5.2$$

Ammonium in residue (coded)

$$= 27.52 + 1.42A - 0.5030B + 0.1950AB - 4.82A^2 - 10.87B^2 \quad 5.3$$

These models illustrate that pH has the most substantial impact on phosphate recovery, while ammonium recovery is primarily influenced by the quadratic effects of both pH and magnesium concentration. The interaction term (AB) was not statistically significant, indicating that pH and magnesium concentration act independently rather than synergistically in this specific design space.

By aligning the experimental data with statistical modelling, this study demonstrates that phosphate and ammonium recovery are optimised within specific pH and magnesium concentration ranges. The developed predictive models offer a practical tool for process optimisation, allowing wastewater treatment facilities to enhance nutrient recovery efficiency while minimising environmental losses. Future improvements could focus on refining the model fitting by incorporating additional parameters or adjusting operational conditions to maximise recovery efficiency in large-scale applications.

5.5 Optimisation of precipitation operating parameters

5.5.1 Molar ratios in optimisation

The N:P molar ratio is a critical parameter in understanding the behaviour of struvite precipitation, as it dictates the stoichiometric balance required for the formation of struvite. Ideally, a molar ratio of 1:1:1 for nitrogen (N), phosphorus (P), and magnesium (Mg) promotes optimal struvite crystallisation under controlled conditions. However, deviations from this ratio influence precipitation efficiency, nutrient recovery, and product purity.

The experimental results in Table 5.2 highlight variability in the $\text{NH}_4\text{:PO}_4$ molar ratios across the tested runs, with values ranging from 0.35 (run 7) to 2.22 (run 2). This range reflects the impact of process parameters, particularly pH and magnesium availability, on the recovery of nutrients. For instance, run 4 ($\text{N:P} = 0.99$) demonstrates a ratio approaching the theoretical ideal, corresponding to a phosphate recovery of 75.05% at pH 11. This indicates near-stoichiometric nutrient availability, facilitating the effective formation of struvite. However, at higher N:P ratios, such as in run 2 ($\text{N:P} = 2.22$) and run 1 ($\text{N:P} = 2.09$), excess ammonium ions are likely to remain unreacted, limiting the precipitation of phosphate despite achieving recoveries of 22.8% and 63.93%, respectively. Such results underscore the significance of optimising the magnesium dosing to balance nutrient recovery.

In contrast, lower N:P ratios, particularly in runs 6 ($\text{N:P} = 0.80$) and 7 ($\text{N:P} = 0.35$), highlight conditions where nitrogen is limiting or the molar excess of phosphorus hinders struvite formation. For instance, run 7, conducted at pH 11.83, achieved a recovery of 83.45% despite a highly deficient N:P ratio, suggesting the dominance of other competing precipitation pathways, such as the formation of Mg(OH)_2 under highly alkaline conditions. This concurs with findings from Wu *et al.* (2021), who reported that elevated pH (>11) reduces the availability of Mg^{2+} for struvite formation, favouring Mg(OH)_2 precipitation instead.

The outcomes also help explain that the optimal level of phosphate removal is attained when N:P ratios stay between 0.99 and 2.00. This range ensures that the key components (Mg , NH_4^+ , and PO_4^{3-}) are sufficiently available to achieve efficient and effective crystallisation. For instance, as highlighted in run 3 ($\text{N:P} \sim 2.00$), a pH of 9 achieved a maximum phosphate recovery of 86.18%, underscoring the importance of molar balance and pH control. The findings align with the literature reports of low N:P ratios, which lead to incomplete precipitation, poor product purity, and significant discrepancies in the mass balance of nutrients (Wu and Vaneeckhaute 2022).

5.5.2 Determination of optimum conditions

The determination of optimum operating conditions is critical for the effective valorisation of waste-activated sludge and the maximisation of nutrient recovery. As discussed, post-adsorption filtrate is particularly enriched in solubilised phosphates and ammonium, yet deficient in magnesium ions, necessitating the external addition of magnesium as a precursor for struvite formation.

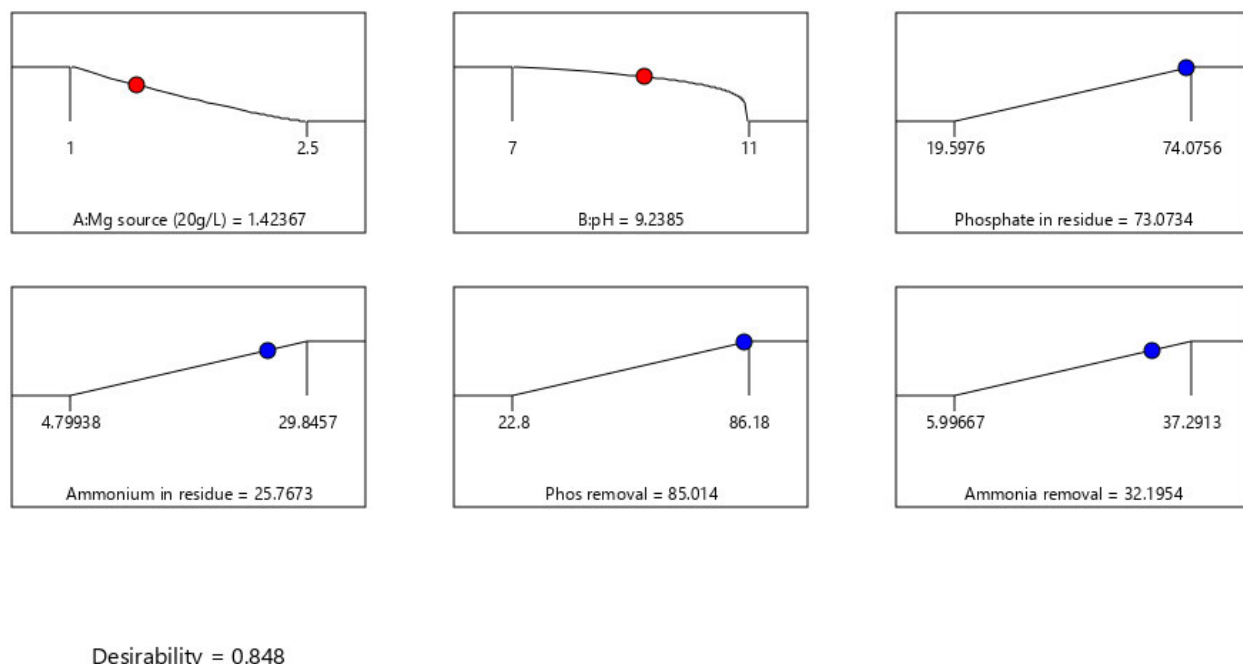


Figure 5.4 Ramp plot for optimisation of the struvite precipitation process

Struvite precipitation remains a sustainable method for phosphorus recovery, producing a crystalline, slow-release fertiliser. However, its efficiency hinges on a delicate balance of pH, magnesium concentration, and the molar ratios of key constituents, all of which must be optimised to prevent competing reactions, such as calcium phosphate formation (Krishnamoorthy *et al.* 2021). The pH adjustment was identified as pivotal in achieving supersaturation conditions, enabling nucleation and crystal growth of struvite. Following 13 experimental runs using an RSM approach, the optimum precipitation parameters were determined to be a pH of 9.24 and a magnesium source concentration of 14.2 mL/L, resulting in a predicted phosphate concentration in the residue of 73.07 mg/L and an

ammonium concentration of 25.77 mg/L. The ramp plots in Figure 5.4 indicate that these conditions yielded phosphate recovery efficiencies of 85.0% and ammonium recovery efficiencies of 25.8%. In the same way, Tong *et al.* (2025) also observed that the optimal pH for struvite crystallisation was 9.0-9.5. Outside of this range, the crystals were formed with impurities such as magnesium hydroxide or carbonates, which decreased the overall recovery efficiency.

The optimisation performed generated a desirability factor of 0.848, indicating that the model is robust and reliable. A higher agreement between the predicted and experimental outcomes is reflected by desirability values closer to 1.0, indicating that the model can be utilised to navigate the design space and predict the optimal responses (Zeeshan *et al.* 2024). The high desirability of this study demonstrates the ability to balance phosphate and ammonium recovery with losses from adsorption and side reactions, which is sufficient to underscore the appropriateness of the chosen parameters. Additionally, the optimised conditions validate well and are highly effective for struvite precipitation and sustainable nutrient recovery.

5.6 Validation of the model and Characterisation at optimum conditions

The optimised conditions of the experimental runs were used to validate the predictive model for struvite precipitation, and values were compared to the model predictions given in Table 5.5.

Table 5.5 Validation of the optimisation of the precipitation process.

Parameter	In-Residue (mg/L)	Predicted In-Residue (mg/L)	% Difference	% Recovery	Predicted Recovery (%)	% Difference
Phosphate	75.3±1.58	73.07	3.05	79.5±3.9	85.0	-6.47%
Ammonium	28.2±1.72	25.77	9.43	36.8±3.3	32.2	14.3%

For phosphate, the experimental in-residue concentration of 75.3 mg/L was close to the predicted value of 73.07 mg/L, with a minor deviation of 3.05%. The recovery percentage achieved was 79.5%, compared to the predicted 85.0%, resulting in a deviation of -6.47%. These slight discrepancies are attributed to operational factors such as ion competition during crystallisation, which are challenging to predict statistically.

In contrast, the experimental ammonium concentration in the residue was 28.2 mg/L, differing from the predicted 25.77 mg/L by 9.43 %. The recovery percentage reached 36.8%, which is higher than the predicted 32.2 %, resulting in a deviation of 14.3 %. The observed variations may stem from competitive interactions with other ions during precipitation (Table 5.5). While the model demonstrates strong predictive capability within the design space, minor deviations are expected due to inherent system complexities and model assumptions.

The ratio of PO_4 : NH_4 : Mg observed in this study was 1:1.98:1.98, which was higher than the ideal molar ratio of 1:1:1 for ideal struvite crystallisation. This discrepancy may be due to competing interactions between phosphate, ammonium and magnesium ions in a naturally organic sludge. Furthermore, observed ratios may be influenced by intrinsic factors (i.e., pH variability, the presence of competing ions such as calcium and iron) or operational factors (inadequate mixing or incomplete reaction time).

Orthophosphate is released from organic and inorganic phosphorus fractions (polyphosphates) during hydrothermal treatment of waste-activated sludge (Dou *et al.* 2024), thereby increasing orthophosphate availability for struvite formation. Nevertheless, in other runs of this study, competing reactions, such as the precipitation of calcium phosphate or magnesium hydroxide under alkaline conditions, could limit the efficiency of magnesium and phosphate utilisation.

In a related study by Tong *et al.* (2025), it was shown that nearly 60% of the phosphorus of the original sludge was recoverable as struvite, with product purity exceeding 90% under optimal conditions. They achieved this recovery using a molar ratio of PO_4 : NH_4 : Mg of 2:1:1.2. Their ratio differed from the theoretical ideal ratio and the one used in this

study, indicating the sensitivity of nutrient recovery efficiency to operational conditions, such as pH control and magnesium dosage.

Validation experiments confirmed the model's accuracy, although there were minor deviations from the model's predicted values (Table 5.5), notably for phosphate recovery (-6.47%). The toxins were given higher priority for removal than the nutrient precipitation, which might explain some of the anomalies. However, nutrient-laden biochar remains a viable source for recovering nutrients and heavy metals through elution processes (Hale *et al.* 2013; Dey *et al.* 2021; Silva 2022). The model validation results demonstrate the effectiveness of the model and provide confidence in applying it for the optimisation of struvite precipitation processes, supporting the feasibility of nutrient recovery from wastewater.

5.6.1 Nutrient analysis and sequential P-extraction in the final product

5.6.1.1 Nutrient analysis

In the struvite precipitation process, the nutrient distribution showed that both PO_4^{3-} and ammonium (NH_4^+) concentrations were significantly reduced, indicating their recovery in the residue. As presented in Table 5.6, the initial phosphate concentration was 94.6 mg/L, which dropped to 26.9 ± 1.4 mg/L in the filtrate (recovery rate: $79.5 \pm 2.2\%$). The residue was found to contain a phosphate concentration of 75.3 ± 2.1 mg/L, resulting in a discrepancy of -7.5 mg/L. A high recovery rate indicates effective struvite crystallisation under optimised conditions, which is an essential process for phosphorus recovery from wastewater streams (Xu *et al.* 2015). Hall *et al.* (2020) attribute the observed discrepancy to the formation of complex phosphorus species or to analytical limitations that prevent the detection of phosphorus.

For ammonium, the feed contained 76.7 mg/L, which was reduced to 48.6 ± 0.7 mg/L in the filtrate, and the residue retained 28.2 ± 1.7 mg/L, giving a lower recovery of $36.8 \pm 2.3\%$. A discrepancy of -0.07 mg/L indicates somewhat low nitrogen losses, likely due to nitrogen volatilisation or entrapment in the precipitate matrix, as also observed in studies on nitrogen volatilisation during struvite precipitation (Afolabi and Sohail 2017). This lower

ammonium recovery is consistent with findings that competitive ion interference, such as calcium interference, can inhibit ammonium recovery (Dey *et al.* 2021).

Table 5.6 Nutrient analyses and balances

Initial (mg/L)	Absolute phosphate (mg)	In filtrate (mg/L)	In-residue (mg/L)	Discrepancy (mg/L)	% recovered (%)	Mass per unit volume (g-P/L)	Moles per unit volume, mol/L
Phosphate							
94.6	1.89	26.9±1.4	75.3±2.1	-7.5	79.5±2.2	0.0015	1.58E-05
Ammonium							
76.7	1.53	48.6±0.7	28.2±1.7	-0.07	36.8±2.3	0.00056	3.13E-05

5.6.1.2 Sequential P-fractionation

Sequential phosphorus (P) fractionation delivers a crucial understanding of the stability and availability of phosphorus in the struvite product. As indicated in Table 5.7, the struvite fertiliser distributes phosphorus over a wide range of fractions, the highest amount of which, 41.22% (17.186±0.315 mg P/g), is classified as HCl-P soluble. This acid-soluble fraction represents phosphorus bound in stable mineral forms that require stringent acidic conditions for release, contingent on its long-term availability in soil (Ran *et al.* 2023; Khalaf 2024). The presence of such mineral-bound P highlights the role of struvite as a slow-release fertiliser ideal for sustained phosphorus delivery in agricultural applications.

The water-soluble P (H₂O-P), constituting 1.18% (0.490 ± 0.016 mg-P/g), represents the immediately bioavailable phosphorus fraction, which is crucial for initial plant uptake. In comparison, the NaHCO₃-extractable P, at 16.99% (7.085 ± 0.277 mg-P/g), corresponds to the loosely bound phosphorus that is moderately plant-available, facilitating short-term nutrient release (Cañas *et al.* 2023). This fraction reflects phosphorus that is weakly sorbed onto mineral surfaces or organic matter.

Table 5.7 P-fractionation of the struvite fertiliser.

Sequence	Struvite (mg-P/g)	Percentage contribution	Synthetic struvite (mg-P/g)	Percentage contribution
H ₂ O - P	0.490±0.016	1.18%	2.241± 0.038	2.10%
NaHCO ₃ - P	7.085±0.277	16.99%	3.363± 0.035	3.15%
NaOH - P	2.696±0.055	6.47%	2.812± 0.027	2.63%
HCl - P	17.186±0.315	41.22%	97.953±0.704	91.71%
P-Residue	14.234±0.225	34.14%	-	0.00%
Total P	41.69		106.81	

The NaOH-extractable P, at 6.47% (2.696 ± 0.055 mg-P/g), indicates phosphorus bound to amorphous iron/aluminium oxides and organic matter, which can become bioavailable over time. However, the high P-residue fraction (34.14%, 14.234 ± 0.225 mg-P/g) confirms that a significant proportion of phosphorus remains in a highly stable form, likely as hydrothermally precipitated salts or crystalline structures, resistant to weak extraction solvents.

The comparison with synthetic struvite, which exhibits a much higher HCl-soluble P (91.71%), suggests that impurities or complex interactions during wastewater-derived struvite precipitation contribute to increased residual and moderately soluble P fractions. This highlights the role of operational conditions in influencing phosphorus partitioning and crystallisation efficiency (Xu *et al.* 2018a).

Sequential P-extraction demonstrates that struvite derived from wastewater contains a balance of immediately available, moderately available, and stable phosphorus fractions, making it an effective slow-release fertiliser while ensuring long-term nutrient supply and reducing environmental risks.

5.6.2 Elemental composition

The results in Table 5.8 highlight key nutrient recovery and precipitation dynamics, particularly when considered in the context of earlier findings in the document.

Magnesium concentrations indicate an effective recovery, decreasing from 296.07 mg/L at the inlet to 207.65 mg/L in the residue, with a molar ratio of 1.42. The excess magnesium observed (a 12.24 molar ratio in the inlet) corroborates earlier findings on the competition between Mg^{2+} and OH^- ions, which form $\text{Mg}(\text{OH})_2$ and potentially reduce struvite crystallisation efficiency under suboptimal conditions.

Table 5.8 Distribution of ions during precipitation

Ion	Concentrations (mg/L)				Molar Ratio of Ion to $\text{PO}_4\text{-P}$		
	<i>Inlet</i>	<i>Residue</i>	<i>Filtrate</i>	<i>Unaccounted for</i>	<i>Inlet</i>	<i>Residue</i>	<i>Filtrate</i>
PO_4^{3-}	94.60	75.27	26.91	-7.57	1.00	1.00	1.00
NH_4^+	76.73	28.20	48.59	-0.07	4.28	1.98	9.53
Mg	296.07	207.65	68.07	20.35	12.24	1.98	9.89

K	12.80	8.23	2.60	1.96	0.33	0.27	0.24
Ca	4.83	1.80	2.35	0.68	0.12	0.06	0.21
Fe	32.30	13.54	14.67	4.09	0.58	0.31	0.93
Na	6.55	4.93	1.97	-0.35	0.29	0.27	0.30

The K: PO₄ molar ratio (0.27 in-residue) supports the hypothesis of K-struvite formation (KMgPO₄·6H₂O). While beneficial as a slow-release fertiliser, K-struvite's lower structural stability compared to NH₄-struvite may pose challenges for long-term agricultural applications, as earlier studies suggest (Yesigat *et al.* 2022). The limited recovery efficiency of potassium (K) and sodium (Na) displays their minor roles in struvite formation as compared to ammonium. This aligns with the importance of optimising the ion competition to minimise product variability.

Calcium (Ca: PO₄ = 0.06 in-residue) and iron (Fe: PO₄ = 0.31) demonstrate limited but notable interactions with phosphate. While calcium's presence appears to have minimal impact on struvite crystallisation, iron's moderate interaction may introduce impurities, as seen in the SEM-EDS analysis in subsequent sections. This reinforces earlier observations regarding the co-precipitation of iron and its impact on product purity, as it typically forms vivianite rather than struvite (Wang *et al.* 2021a).

These observations highlight the interplay of operational parameters, such as magnesium dosing and pH adjustment, as critical factors influencing nutrient recovery and product purity. The data affirms earlier discussions on optimising molar ratios and mitigating competing reactions to enhance struvite formation while minimising losses through volatilisation or secondary reactions.

5.6.3 Functional groups

The FTIR spectra of struvite precipitated under optimum conditions and synthetic struvite (control) reveal significant insights into their structural nature (Figure 5.5). The characteristic peaks observed confirm the formation of struvite (MgNH₄PO₄·6H₂O) in both samples, aligning with findings reported in the literature (Lee *et al.* 2020)

For synthetic struvite, the wide band near 3432 cm⁻¹ corresponds to O-H and N-H stretching vibrations, indicating the presence of water of hydration and ammonium ions

(NH_4^+). A distinct peak around 1440 cm^{-1} arises from the asymmetric N-H bending vibrations of NH_4^+ , a hallmark of struvite formation. The phosphate group (PO_4^{3-}) vibrations are evident at 998 cm^{-1} (antisymmetric ν_3), 572 cm^{-1} (asymmetric bending ν_4), and 450 cm^{-1} (bending vibration ν_2), confirming the tetrahedral structure of PO_4^{3-} in synthetic struvite.

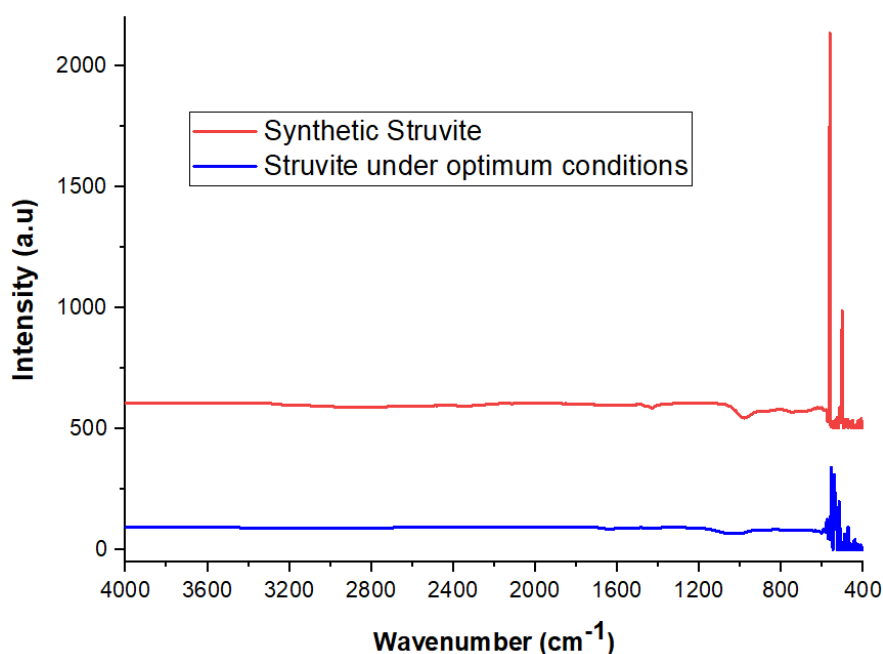


Figure 5.5 FTIR for struvite under optimum conditions and synthetic struvite

Meanwhile, the struvite produced in this study has wavenumbers similar to those of the synthetic struvite, but is only slightly different in some cases, indicating that the two have striking structural similarities. Deviations in intensity in the region between 572 and 450 cm^{-1} suggest that the tetrahedral PO_4^{3-} framework is slightly distorted. Previously reported wastewater-derived struvite suggested that such deviations can arise from the impurities, including calcium or other cations present (Sidorczuk *et al.* 2020).

Interestingly, the reduced peak intensities observed for the recovered struvite at 998 cm^{-1} may also indicate a lower crystallinity or that the phosphate structure is partially substituted in this region due to the effects of the wastewater matrix. Furthermore, barely

discernible peaks observed beyond 400 cm^{-1} support the observation that the main constituents were largely free from interference from non-struvite phases.

FTIR analysis confirms that the hydrothermal treatment process successfully promotes precipitation of struvite, which is comparable to synthetic struvite but with a degree of structural irregularities of struvite that can be attributable to wastewater constituents. These findings are consistent with earlier reports on the effect of hydrothermal treatment on improving phosphate recovery, while accounting for variations observed in the matrix (Zhang *et al.* 2020b).

5.6.4 Crystallography of the struvite

The XRD analysis of struvite produced under optimal conditions confirms its crystalline nature and highlights key similarities and differences when compared to synthetic struvite, serving as the control (Figure 5.6). The characteristic peaks observed align with the typical diffraction pattern for struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), confirming successful crystallisation.

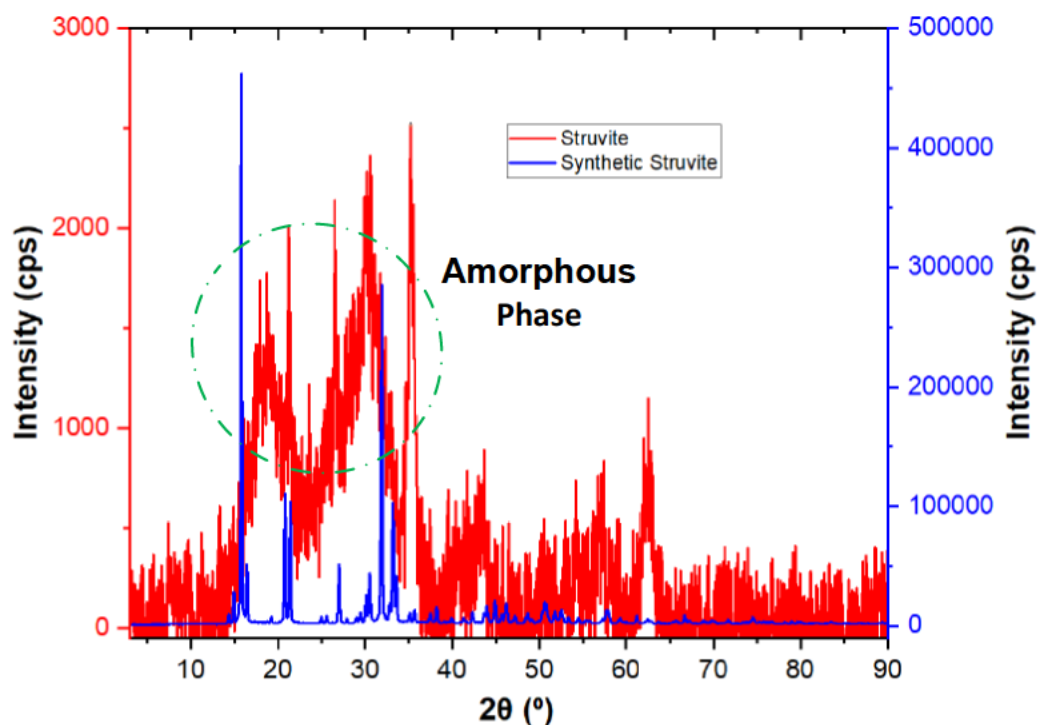


Figure 5.6 XRD for struvite and synthetic struvite

For synthetic struvite, sharp and well-defined peaks are discernible at $2\theta = 14.7^\circ$, 21.2° , 28.5° , and 31.6° , consistent with the standard struvite crystalline structure (Ye *et al.* 2014). These peaks reflect the highly ordered arrangement of atoms within the struvite lattice, which is typical of chemically synthesised samples.

In comparison, the struvite recovered under hydrothermal treatment shows broader and less intense peaks at similar angles, particularly around $2\theta = 14.6^\circ$, 21.1° , and 28.3° . The slight shifts in peak positions and the reduction in intensity suggest lower crystallinity and the potential incorporation of impurities, such as calcium (Ca^{2+}) and other metal ions, during the precipitation process. This is consistent with Gardner *et al.* (2021), who found that impurities can distort the lattice such that the diffraction can have minor angle.

Additionally, further indications of the existence of amorphous phases or incomplete crystal formation are provided by the increased background noise in the hydrothermally treated struvite. This could be due to residual organic matter or operational conditions of the hydrothermal treatment, such as pH fluctuations (Gardner *et al.* 2021; Lu *et al.* 2022). The XRD patterns confirm the crystalline structure of the struvite produced at optimum conditions with slight distortions as compared to synthetic struvite.

5.6.5 Morphological and elemental composition

The SEM-EDS analysis of struvite at optimum conditions, compared to synthetic struvite (control), provides critical insights into the surface morphology and elemental composition of struvite. SEM images of hydrothermally treated struvite (Figure 5.7(a)) show a rough, non-uniform surface covered with irregular granules and minor cracks consistent with impurities and incomplete crystal growth. Alternatively, Sun, Mohammed and Liu (2020) found the synthetic struvite (Figure 5.7(b)) to have a smooth, well-defined morphology characteristic of prismatic or needle-like struvite crystals.

The elemental composition of the samples is further confirmed by EDS analysis. The hydrothermally treated struvite exhibits 24.32 wt% P, 11.92 wt% Mg, with notable amounts of 5.65 wt% Ca and 5.53 wt% Fe, highlighting potential contamination or co-precipitation of Ca and Fe. Conversely, Peng *et al.* (2018b) report that calcium and iron

adsorption onto the struvite surface is usual in wastewater-derived products. They can distort the crystal lattice and lower the purity of the recovered product. Synthetic struvite, on the other hand, features a higher P content (20.74-23.43 wt%) and Mg content (15.48–16.53 wt%), with no impurities like calcium and iron. It emphasises the purer, cleaner struvite due to controlled precipitation conditions.

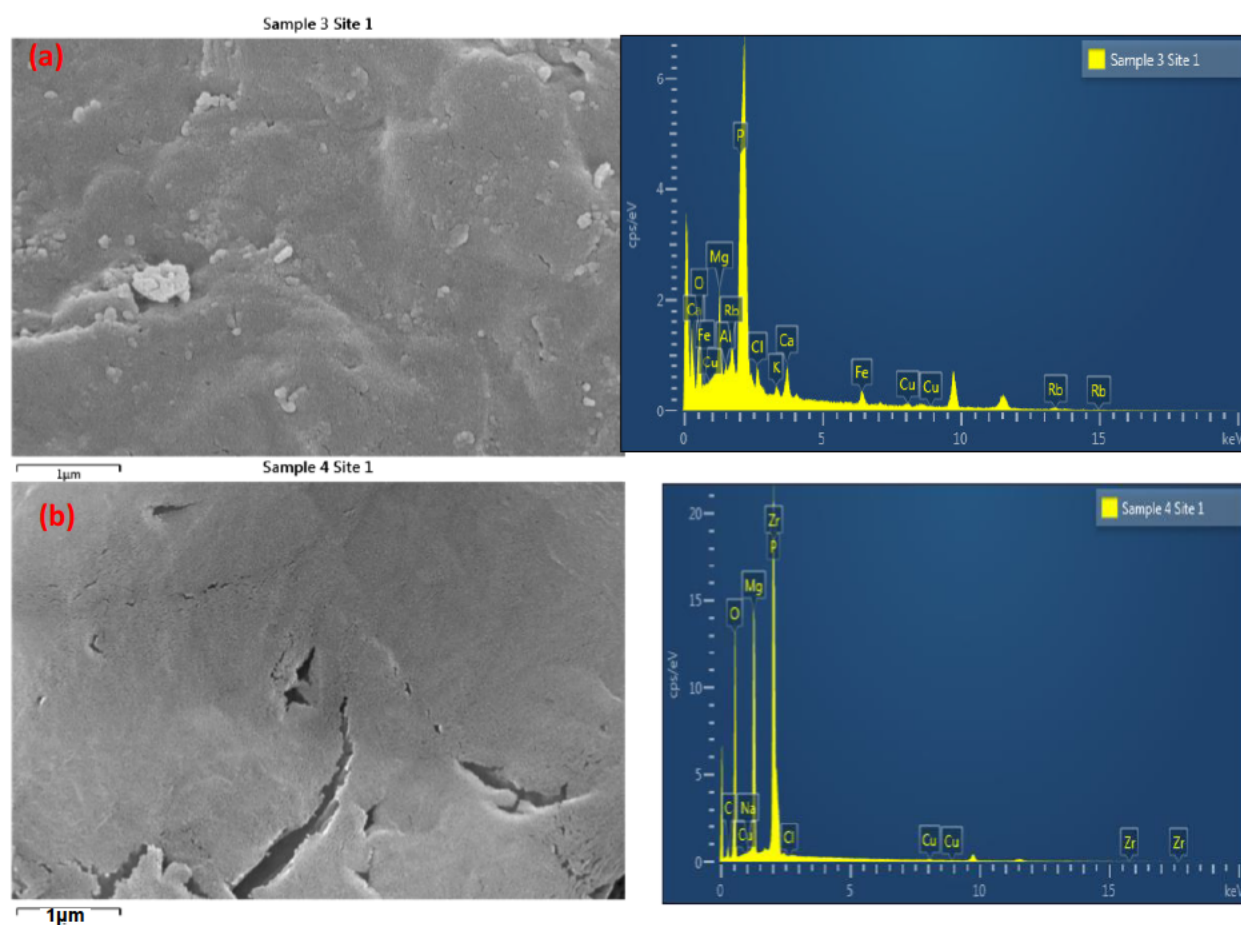


Figure 5.7 SEM images (a) struvite under optimum conditions (b) synthetic struvite under optimum conditions

SEM-EDS results agree with successful struvite precipitation under convective hydrothermal conditions, but with notable impurities such as Ca and Fe present that are not present in synthetic struvite. This aligns with the literature, which acknowledges that real wastewater systems can contain co-precipitating species that alter crystal morphology and composition (Tansel, Lunn and Monje 2018).

5.7 Yield and purity of the struvite

The yield of the struvite powder was found to be 0.98 ± 0.07 g/L of sludge, which translates to a 97.79% recovery from the reaction vessel (the actual yield was 1.002 g/L before scraping off from the reaction vessels). A small fraction of the struvite could not be recovered from the containment vessel, probably because of the struvite's adhesive and sticky nature. The results presented here are consistent with those of Grell *et al.* (2023), who observed the adhesive nature of struvite, resulting in slight recovery loss during collection and even clogging pipes in large-scale industrial operations.

In this study, as shown in Plate 6.1, the coloured struvite produced was greyish brown due to the contribution of residual HT products in the sludge. The brownish organic filtrate of the HT precipitates has been demonstrated to affect the final colouration of struvite, which is characteristically white (Langone and Basso 2020). This is in line with observations by Sirén Ehrnström (2016) that wastewater-derived struvite typically contains impurities that alter the visual and crystalline properties of the struvite and, thus, the conditions of its use.



Plate 5.1 Struvite crystals recovered from hydrothermally treated sludge

The purity of the recovered struvite was $69.06 \pm 1.01\%$, which was lower than the benchmark purity of $\geq 90\%$ usually required for struvite used in fertiliser applications (Santos *et al.* 2024). The presence of competing ions, such as Ca^{2+} and Fe^{3+} or minute particles of hydrochar escaping the filter, was found to reduce the purity. Similar findings were also reported by Shih *et al.* (2017a); Guan *et al.* (2023), with impurities in sludge

matrices and co-precipitation reactions contributing to the low purity of struvite. However, struvite recovered from this process is still suitable for agricultural use, as shown by Le Corre *et al.* (2009); even struvite with moderate purity serves as a slow-release fertiliser.

The findings demonstrate the efficacy of HT in struvite precipitation processes, achieving high recovery yields. The recovered struvite, although slightly less pure, meets the specified requirements of the product and validates its use as an agricultural activity in a manner suitable for sustainable nutrient recovery from wastewater streams.

5.8 Mass balances and recovery efficiency

The material balance of phosphorus recovery in this study highlights significant transitions across the process line, showcasing both the effectiveness and challenges inherent in the integrated hydrothermal treatment, adsorption, and precipitation methodology. As revealed in Figure 5.8 and Appendix B3, phosphorus in the waste-activated sludge (WAS) initially exists predominantly in the apatite phosphorus (AP, HCl-soluble) fraction (33.205 mg-P/g) and residual phosphorus (8.212 mg-P/g), with water-soluble orthophosphate (0.399 mg-P/g) making up only a small portion.

However, hydrothermal treatment (HT) at 220°C significantly enhances phosphorus solubilisation, causing a 79% increase in water-soluble phosphorus (0.715 mg-P/g) and a 23% reduction in HCl-P (to 25.495 mg-P/g). The observed shift suggests that HT disrupts mineral-bound phosphorus, increasing its bioavailability. This transformation aligns with findings by Chauhan (2011); Ewens (2022), who noted similar solubilisation effects of HT on organic and mineral-bound phosphorus fractions.

Following HT, adsorption alters the partitioning of phosphorus. The hydrochar fraction retains 62% of total phosphorus, while 11% is adsorbed onto the recovered adsorbent (MBC), reducing the availability of soluble phosphorus in the filtrate. This highlights the unintended consequence of phosphorus sequestration in solid fractions, which reduces its immediate recoverability. These findings align with the challenges reported by Cheng *et al.* (2023) regarding phosphorus recovery from adsorbents and pyrolysed residues.

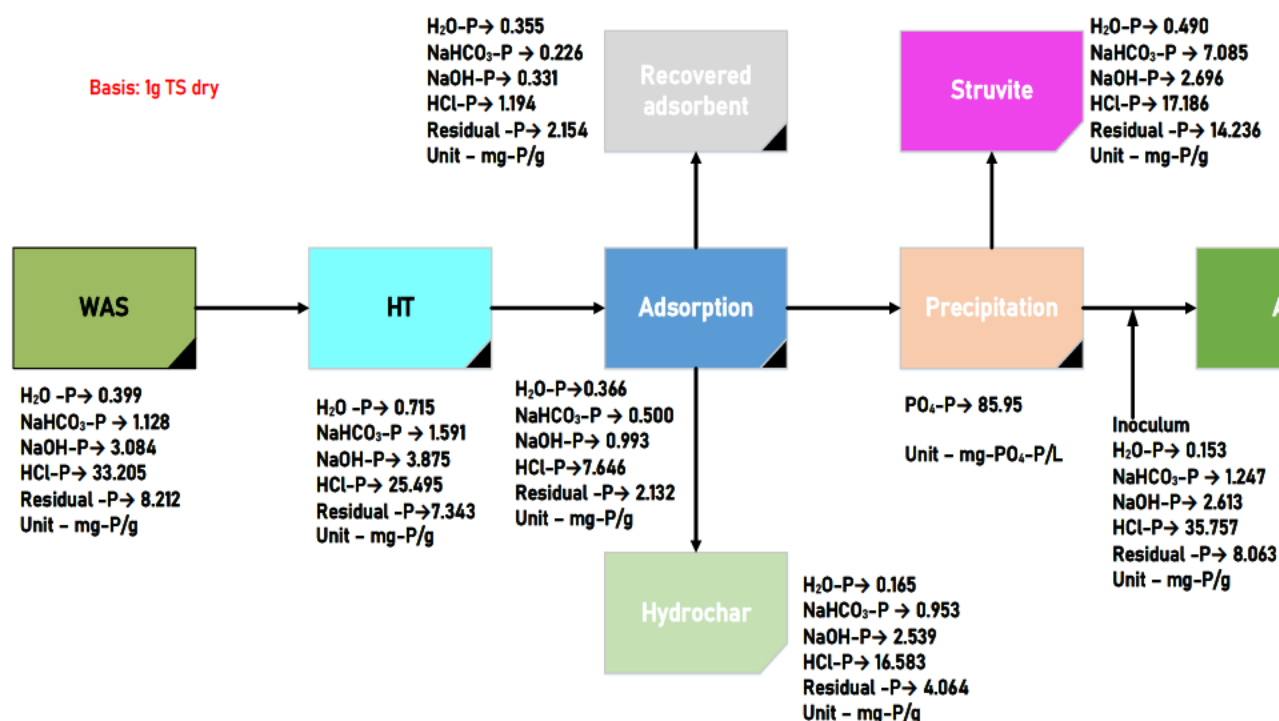


Figure 5.8 Mass balance of phosphorus in the processing line

The precipitation step via struvite formation captures a significant fraction of phosphorus, producing struvite with an HCl-soluble phosphorus concentration of 17.186 mg-P/g, demonstrating its potential as a fertiliser. However, its purity (69.06%) is lower than that of synthetic struvite (97.953 mg-P/g), indicating interference from competing ions such as Fe³⁺ and Ca²⁺. This finding is consistent with a study by Siciliano *et al.* (2020, which documented the detrimental effect of wastewater impurities on struvite quality.

Overall, 85.96 mg/L of orthophosphate was recovered before precipitation, reflecting an efficient but imperfect recovery process. The fractionation of phosphorus (P) could not be performed due to methodological limitations, which are designed to handle only solid samples. The precipitation effluent did not produce sufficient solid material for testing. Discrepancies in mass balance arise primarily from Unaccounted phosphorus retained in hydrochar and adsorbent residues, which could be optimised through desorption techniques; pH and magnesium fluctuations, influencing precipitation efficiency and secondary reactions; and possible volatilisation and complexation reactions, leading to phosphorus loss during filtration and AD.

Discrepancies in phosphorus balance can be attributed to multiple chemical and operational factors. The hydrochar fraction retained a significant amount of phosphorus, particularly HCl-soluble P (16.583 mg-P/g), which limited its direct recovery. Further treatment may be required to mobilise this fraction. The lower purity of recovered struvite is likely due to co-precipitation with Fe and Ca, forming vivianite ($\text{Fe}_3(\text{PO}_4)_2$) or calcium phosphates, as pointed out by XRD analysis, reducing the efficiency of phosphorus crystallisation. Some phosphorus remains unaccounted for in the filtrate, likely due to secondary reactions or limitations in analytical methodologies, which are designed for solid-phase fractionation.

To improve phosphorus recovery efficiency, several strategies can be considered, including optimising pH and magnesium addition by fine-tuning pH levels (9-9.5), which can enhance struvite purity and precipitation efficiency, and minimising unwanted co-precipitation. Implementing desorption or acid-leaching techniques could enhance phosphorus recovery from hydrochar. There is also a need to modify the adsorbent surface chemistry, which could reduce phosphorus sequestration in solid phases and improve release into the filtrate. Advanced analytical techniques (e.g., sequential extraction on filtrates) are crucial, as they can address mass balance discrepancies, providing a more comprehensive picture of phosphorus transformations.

The phosphorus mass balance in this study revealed substantial solubilisation during hydrothermal treatment, notable retention in hydrochar and adsorbent phases, and partial recovery through struvite precipitation. Measurement uncertainty was minimised through

triplicate analyses, blank corrections, and recovery verification, ensuring reliable concentration data across all process streams. The moderate struvite purity ($\approx 69\%$) was primarily influenced by co-precipitation with Fe^{3+} and Ca^{2+} , as well as adsorption losses to solid residues. Mitigation involved optimising pH (9–9.5) and magnesium dosing to reduce competitive precipitation and enhance overall phosphorus recovery efficiency, contributing to improved closure and sustainable wastewater management.

5.9 Chapter summary

This chapter explores the integrated recovery of phosphorus as struvite through HT and precipitation from waste-activated sludge (WAS). The study highlights the optimisation of operational parameters, such as pH and magnesium dosing, to enhance the recovery and purity of struvite, which is a slow-release fertiliser. Under optimal conditions, phosphorus recovery reached up to 85%, demonstrating the feasibility of nutrient recovery while mitigating the risks of eutrophication. However, challenges such as competing ions (e.g., calcium and iron) and impurities in the wastewater matrix slightly compromised product purity, with a struvite purity of $69.06 \pm 1.01\%$.

Key findings also emphasise the role of HT in improving phosphorus solubilisation, enabling efficient struvite crystallisation. Advanced characterisation methods, including FTIR and SEM-EDS, revealed that wastewater-derived struvite retains structural similarity to synthetic struvite, albeit with minor distortions caused by impurities. The chapter concludes by proposing strategies for improving struvite purity, such as optimising reagent dosing, reactor design, and incorporating advanced separation techniques. These findings underscore the environmental and economic benefits of integrating phosphorus recovery into wastewater treatment plants, thereby contributing to a circular economy and addressing global challenges related to nutrient sustainability.

CHAPTER 6: EFFECT OF HYDROTHERMAL TREATMENT AND ITS DERIVATIVES ON ANAEROBIC DIGESTION FOR BIOGAS PRODUCTION

6.1 Introduction

In the case of WWTPs, anaerobic digestion (AD) is a widely used process considered essential for valorising organic waste through biogas production. It is a biological process consisting of a series of microbial-mediated reactions under anaerobic conditions that break down complex organic compounds into simpler, more basic compounds. Biogas is composed mainly of methane (CH_4) and carbon dioxide (CO_2), as well as a small amount of trace gases, including hydrogen sulphide and ammonia. Biogas, when properly harnessed, is a renewable energy source with immense potential to contribute to addressing waste management challenges, reducing greenhouse gas (GHG) emissions, recycling nutrients, and promoting circular bioeconomy principles.

However, the efficacy of AD is limited by the recalcitrant nature of WAS, a by-product of wastewater treatment, which is characterised by dense cellular networks and a complex polymeric structure (Atmakuri *et al.* 2024). Such properties limit the bioavailability of organic substrates for microbial degradation. Given these limitations, several pretreatment technologies, including HT, have been evaluated. HT facilitates the hydrolysis of complex macromolecules, including proteins, carbohydrates and lipids, into simpler, more bioavailable compounds and enables enhanced biodegradability of macromolecules during AD (Li *et al.* 2022b).

As previously discussed in this work (Section 2.1), HT also decreases pathogen loads, enhances nutrient recovery and decreases sludge viscosity, improving the amenability of HT to downstream processing. Nevertheless, the balance between enhanced solubilisation and digestibility and the potential formation of inhibitory by-products such as phenolics and ammonia with process parameters (e.g. temperature, retention time and pH) must be optimised.

This chapter delves into the impact of HT on biogas production through AD, focusing on four treatment streams, which are (1) untreated WAS for establishing a biodegradability

baseline, (2) HT effluent with more solubilised products, (3) adsorption-treated effluent with magnetic biochar for toxin removal, and (4) precipitation of the adsorption effluent for phosphorus recovery.

6.2 Methodology for biogas production through AD

6.2.1 Anaerobic digestion setup.

Bench-scale AD experiments were conducted using 1000 mL Schott bottles operated in batch mode. Each reactor was filled with 700 mL of substrate (300 mL headspace) and inoculum in a 1:1 (v/v) ratio, ensuring the introduction of the same quantity of microbes in each case. The inoculum was sourced from the anaerobic digesters of a local WWTP.

The effluents from four different unit stages were tested for biogas production, with untreated WAS serving as the control against the other three streams. The four feedstock streams were WAS' + inoculum (scenario 1), HT + inoculum (scenario 2), adsorption effluent + inoculum (scenario 3), and precipitation effluent + inoculum (scenario 4). To ensure an anaerobic environment, the 300 mL headspace in the reactors was purged with nitrogen gas for 5 min to eliminate residual oxygen, as illustrated in Plate 7.1.

The temperature of the digesters was maintained at $37\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$ using a circulating water bath. Each experimental setup was conducted in duplicate, and the digestion process was monitored for 21 days. Prior to the biochemical methane potential (BMP) test, the pH of all samples was adjusted to 7 ± 0.5 , the optimal range for methanogenic bacteria, by the dropwise addition of 1 M NaOH or 2 M HCl (all reagent grade).

To prevent stratification and ensure adequate microbial contact with the substrate, the reactors were hand-shaken twice daily. Gas volume was recorded daily, except on weekends when the laboratory was inaccessible. Gas production was measured using a water displacement system with acidified water (pH ~3) to prevent gas losses due to the dissolution of gas units.

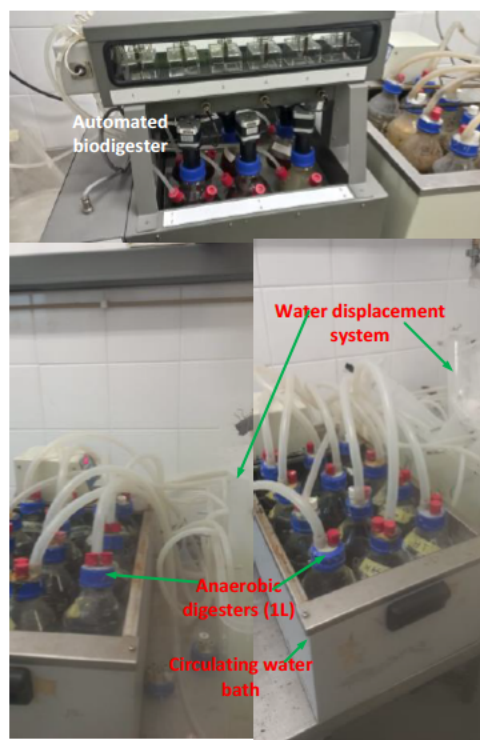
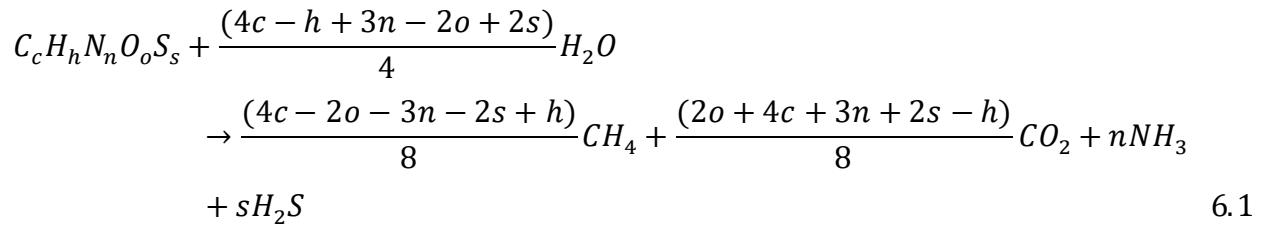


Plate 6.1 Anaerobic digestion set-up

The biogas composition was analysed using gas chromatography coupled with a thermal conductivity detector (GC-TCD, Shimadzu 2014, Japan). The system was equipped with a stainless steel Porapak Q column (1.8 m × 2.1 mm) and operated at injector, column, and detector temperatures of 120 °C, 40 °C, and 250 °C, respectively, with helium as the carrier gas at a flow rate of 8 mL/min. Cumulative gas production and methane yields were recorded for comparative analysis. Sludge characteristics were determined as detailed in Section 3.2.2, following well-documented standard procedures (APHA 2017).

6.2.2 Theoretical gas determination

Theoretical biogas production was calculated using the CHNS/O analysis in conjunction with the Buswell equation, a stoichiometric formula (Yuen and Lau 2023). For a hydrocarbon with the general formula $C_cH_hN_nO_oS_s$, the balanced equation describing the production of methane (CH_4), along with by-products such as carbon dioxide (CO_2), ammonia (NH_3), and hydrogen sulphide (H_2S), is represented in Equation 6.1.



The theoretical methane yield ($CH_{4, th}$), expressed in mL/g-VS under standard temperature and pressure (STP), was determined using Equation 6.2

$$CH_{4, th} = \frac{22400 \left(\frac{4c - 2o - 3n - 2s + h}{8} \right)}{12c + h + 14n + 32s + 16o}
\tag{6.2}$$

where c, h, n, s, and o represent the molar fractions of C, H, N, S and O, respectively. This approach allows for a stoichiometric prediction of methane production based on the substrate's chemical composition.

6.2.3 Kinetic models applied

Various existing kinetic models were modified and evaluated for use in this study, following the approach developed by Xie *et al.* (2016) and presented in Equations 6.3 and 7.4. While several kinetic models are discussed in this thesis (Section 2.7.4), only the First-order and modified Gompertz models were considered as their input variables aligned with those utilised in this work. Additionally, the Gompertz model has been reported to encounter difficulties in accurately describing the hydrolysis phase in anaerobic biodigesters, particularly when studying non-easily biodegradable matter (Lebona *et al.* 2019). For this reason, the modified Gompertz model was selected over the original Gompertz model from the available options. Matlab Software (MATLAB, Version R2023b, MathWorks Inc., Natick, MA, USA) was used to determine kinetic and statistical parameters.

First-order

$$Y(t) = P(1 - e^{(-kt)})
\tag{6.3}$$

Modified Gompertz

$$Y(t) = P \cdot \exp\left\{-\exp\left[\frac{R_m \cdot e}{P} \cdot (\lambda - t) + 1\right]\right\} \quad 6.4$$

$Y(t)$ is the cumulative methane or biogas yield at time t (mL/g-VS); P is the maximum cumulative biogas production (mL/g-VS); R_m is maximum biogas production rate (mL/g-VS/day); λ is the lag phase time (days), representing the microbial acclimation period; t is Time (days) and e is the Euler's number (≈ 2.718).

6.3 Characteristics of the feedstock after hydrothermal treatment

6.3.1 Physicochemical properties

It is essential to recognise that significant changes in the physicochemical properties of the sludge had occurred by the time the AD reactions were conducted. The variations can be attributed to seasonal fluctuations and operational adjustments. Even with these changes, the predictive model remained robust and accurate at predicting the final SCOD resulting from these wastewater characteristics. This shows that the model can be adaptive to the dynamic conditions in the treatment system.

Understanding the behaviour of WAS and its derivatives during AD necessarily depends on the physicochemical properties of WAS. Table 6.1 presents these parameters, including COD, conductivity, TDS, salinity, dissolved oxygen (DO), TS, and VS (Appendix B6), which provide information on the chemical composition, biodegradability and stability of the feedstock. It examines the interplay between pretreatment methods and digestion performance by analysing shifts in these properties before and after AD.

COD represents the total organic load available for microbial degradation (COD). The HT stream prior to AD had a high COD (3035 mg/L), indicating increased solubilisation of organic matter through HT. Nevertheless, COD reductions were observed in all streams upon digestion, with the lowest in the HT + inoculum stream (from 1247 mg/L to 262 mg/L, corresponding to a 79% COD removal efficiency). This COD reduction evidence improved biodegradability and microbial use of organic substrates. COD, being a proxy for organic matter availability, decreases impressively, and this indicates a high conversion to methane, which is discussed later in Section 6.4 of the biogas production.

Although conductivity and TDS reflect changes in solubilisation and nutrient release, they measure both ionic and dissolved mineral content. Initial HT conductivity (1165 $\mu\text{S}/\text{cm}$) and TDS (757 mg/L) were attributed to HT due to the release of soluble organic and inorganic compounds. Post-AD, these values increased further in most streams (e.g., HT + inoculum). This increase (from 2432 to 3037 $\mu\text{S}/\text{cm}$) is likely the mineralisation of organic matter and release of ammonium ions during AD. High conductivity and readily available TDS can enhance microbial activity by supplying readily available nutrients; however, high concentrations may themselves represent osmotic stress (Peng *et al.* 2020; Velmurugan and Pandian 2024).

Salinity, a relatively crucial factor for microbial health, was stable in the streams, with slight increases post-AD, e.g., (from 1.26 to 1.57) in the HT + inoculum stream. The observed stability indicates that salinity levels were within the tolerance range of an anaerobic microbial community, thereby mitigating the risks of osmotic imbalance (Velmurugan and Pandian 2024).

Consistent with both anaerobic and methanogenic conditions, DO levels were low across all streams. A slight change in DO post-AD (as shown in HT + inoculum stream, from 0.31 to 0.36 mg/L) aligns with the anaerobic conditions maintained during digestion, resulting in little to no inhibition of methanogenic activity.

Subsequently, the TS content in all streams was reduced post-AD, with the greatest reduction occurring in the HT + inoculum, from 9818 mg/L to 8430 mg/L. There were also similar reductions in VS, from 6073 mg/L in the HT + inoculum stream to 4745 mg/L. These reductions show that organic matter was effectively biodegraded during AD. Notably, the HT-treated streams consistently exhibited greater VS reductions than the untreated WAS, indicating the ability of HT to enhance the bioavailability of organic substrates.

Table 6.1 shows the distribution of proximate analysis and general characteristics of various streams before and after AD (Appendix B5 and B6).

Table 6.1 Proximate analysis and general characteristics of various streams before and after AD

Stream	Before AD							After AD						
	SCOD (mg/L)	Conductivity (μ S/cm)	TDS (mg/L)	Salinity (μ S/cm)	DO (mg/L)	TS (mg/L)	VS (mg/L)	SCOD (mg/L)	Conductivity (μ S/cm)	TDS (mg/L)	Salinity (μ S/cm)	DO (mg/L)	TS (mg/L)	VS (mg/L)
WAS only	284 $\pm$ 15	621	404 $\pm$ 41	0.3	2.93	5563 $\pm$ 364	4060 $\pm$ 240	0 $\pm$ 0	779	506	0.38	0.89	4588 $\pm$ 18	3233 $\pm$ 39
HT only	3035 $\pm$ 134	1165	757 $\pm$ 16	0.58	0.83	5143 $\pm$ 470	3713 $\pm$ 350	780 $\pm$ 1	1974	1283	1	0.51	4962 $\pm$ 689	3077 $\pm$ 456
Inoculum only	199 $\pm$ 15	3607	2345 $\pm$ 49	1.91	0.77	15893 $\pm$ 74	9230 $\pm$ 247	94 $\pm$ 6	3815	2480	2	0.49	14860 $\pm$ 615	7940 $\pm$ 57
WAS + Inoculum	168 $\pm$ 10	2178	1416 $\pm$ 242	1.12	0.39	9907 $\pm$ 251	6132 $\pm$ 81	34 $\pm$ 3	2513	1634	1.29	0.44	9108 $\pm$ 39	5408 $\pm$ 4
HT + Inoculum	1247 $\pm$ 401	2432	1581 $\pm$ 163	1.26	0.31	9818 $\pm$ 315	6073 $\pm$ 152	262 $\pm$ 4	3037	1974	1.57	0.36	8430 $\pm$ 120	4745 $\pm$ 113
Adsorption + Inoculum	893 $\pm$ 45	2274	1478 $\pm$ 31	1.17	0.48	10273 $\pm$ 95	6215 $\pm$ 78	158 $\pm$ 9	2736	1778	1.41	0.41	9240 $\pm$ 64	5262 $\pm$ 131
Precipitation + Inoculum	1019 $\pm$ 18	2556	1661 $\pm$ 283	1.33	0.34	8515 $\pm$ 78	5155 $\pm$ 141	163 $\pm$ 5	2989	1943	1.55	0.55	7390 $\pm$ 28	4073 $\pm$ 18

Observed changes in physicochemical properties highlight the importance of pretreatment methods in determining AD performance. It was found that HT was an efficient pretreatment process, resulting in a noticeable enhancement of COD solubilisation (over 50 %) and biodegradability index (from 0.1 to 0.25). The improvements resulting from these benefits help to increase system stability by providing a balanced nutrient supply, buffering capacity, and optimal conditions for microbial activity. Furthermore, the TS and VS reductions also signify effective substrate utilisation to prevent the risk of accumulation and subsequent system instability.

6.3.2 Ultimate analysis

As shown in Figure 6.1 (Appendix B2), only the WAS and the HT streams were presented (The adsorption and precipitation streams had insufficient data quality for robust comparative analysis due to errors in analytical equipment).

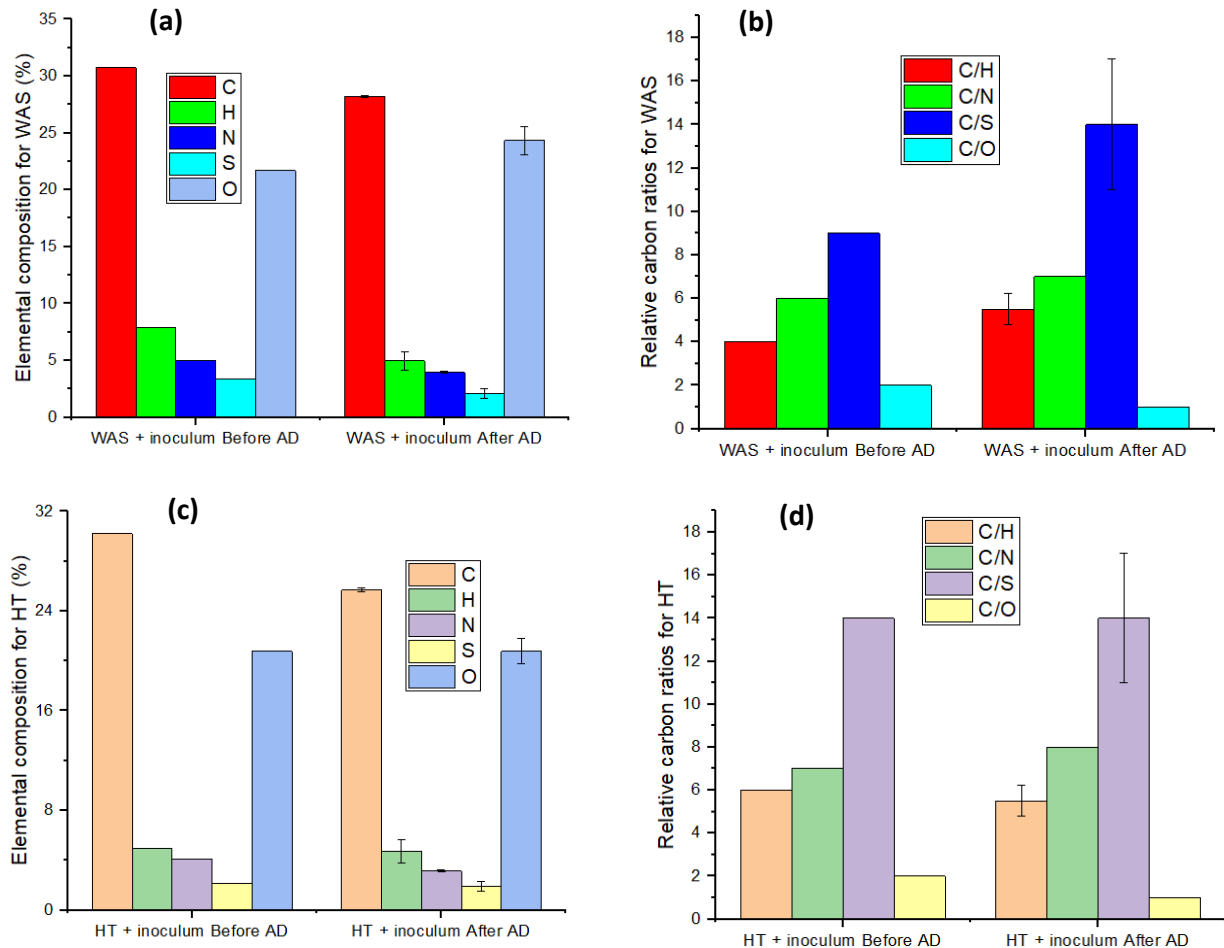


Figure 6.1 Elemental (CHNS/O) composition and relative carbon ratios of waste-activated sludge and hydrothermally treated sludge before and after anaerobic digestion.

The ultimate analysis of WAS and HT-sludge provides a critical foundation for understanding the physicochemical changes that underpin system stability during AD. The CHNOS composition of the inoculated streams was monitored before and after digestion to evaluate how elemental transformations affect microbial activity, nutrient balance, and buffering capacity (Figure 6.1 and Appendix B2).

The carbon content decreased across all streams after AD, with scenarios 1 and 2 showing reductions from 30.73% to 28.20% and from 30.20% to 25.69%, respectively.

This trend reflects the utilisation of organic carbon as a primary substrate by anaerobic microbes for biogas production.

Hydrogen levels exhibited a slight decline post-digestion, consistent with the biochemical conversion of hydrogen-containing compounds into methane (CH_4) and water (H_2O). Scenario 2 retained marginally lower hydrogen content (4.72%) after digestion compared to scenario 1 (4.95%), possibly due to the more advanced hydrolysis achieved in the HT stream prior to AD.

Nitrogen content was also reduced, from 4.96% to 3.95% in scenario 1 and from 4.12% to 3.13% in scenario 2. This reduction likely reflects the conversion of nitrogen compounds into ammonium (NH_4^+), which contributes to alkalinity (as discussed below). The higher initial nitrogen content in HT-sludge (7.01%) suggests that protein breakdown occurs during HT, thereby enhancing the nitrogen pool available for microbial metabolism in AD (Zhong *et al.* 2022).

Sulphur content decreased across all streams, with scenario 2 showing a reduction from 2.11% to 1.89%. This decline corresponds to the microbial utilisation of sulphur-containing compounds and the potential release of hydrogen sulphide (H_2S) gas, which must be monitored to mitigate odour and corrosion risks. Although the levels in this study were below detectable limits, this could be due to the presence of certain sulphur-oxidising bacteria (such as *Thiobacillus*) in the digester, which may convert H_2S into elemental sulphur (S^0) or sulphate (SO_4^{2-}). This occurs under microaerophilic or partially oxidising conditions within the digester. Even small oxygen infiltration or diffusion zones in the reactor could enable this oxidation, and sulphur is retained in non-volatile forms, thereby reducing H_2S emissions (Zhang, Lu and Li 2023).

In scenario 1, oxygen content increased slightly after AD (from 21.69% to 24.32%). This trend may be attributed to the incorporation of oxygen into intermediate and final metabolites, such as CO_2 and water. The increase in oxygen percentage may not represent an absolute rise in oxygen atoms but rather a relative shift due to the degradation of carbon- and hydrogen-rich compounds. As anaerobic microbes break down carbohydrates, lipids, and proteins, the relative proportion of carbon and hydrogen decreases, making the remaining oxygen more pronounced in the elemental composition (Zhang *et al.* 2023b). Also, compounds with lower oxygen content, such

as lipids, are more recalcitrant than carbohydrates, potentially leaving behind residues with higher oxygen content (Scherzinger and Kaltschmitt 2021).

The C/N ratio is a critical determinant of system stability, influencing microbial activity and ammonia accumulation. After AD, the C/N ratio stabilised at 7 for scenario 1 and 8 for scenario 2, indicating balanced nutrient availability. An optimal C/N ratio (6–8) supports efficient methane production while minimising ammonia toxicity (Yellezuome *et al.* 2022). The increase in the C/S ratio post-digestion (e.g., from 9 to 14 for WAS + Inoculum) reflects the preferential utilisation of sulphur-containing compounds, reducing potential odour issues while maintaining biogas quality. The C/H ratio remained stable at approximately 5.5 across streams, signifying consistent energy potential within the system.

A slight decline in the C/O ratio post-AD (e.g., from 2 to 1 for scenario 2) highlights oxygen's role in stabilising reaction intermediates during microbial metabolism. This shift implies that oxidation processes are responsible for degrading complex organic matter to enhance biodegradability and for efficient bioconversion within the AD system.

The ultimate analysis highlights the pivotal role of HT in improving sludge biodegradability, as evidenced by the enhanced carbon and nitrogen solubilisation prior to digestion. The subsequent reductions in elemental concentrations during AD reflect the effective microbial utilisation of substrates. Moreover, the stabilised C/N and C/S ratios post-digestion highlight the balanced nutrient dynamics, which are crucial for sustaining methanogenic activity and minimising the risk of inhibitory by-products, such as ammonia or H₂S.

While biogas production is discussed in later sections, the elemental composition and its changes directly influence the availability of substrates for methanogenesis. The higher nitrogen and carbon content in the HT stream suggests greater potential for biogas yields, underscoring the importance of HT as a pretreatment method for enhancing AD performance.

The ultimate analysis highlights the transformative effects of HT and AD on the elemental composition of sludge, providing insights into the system's stability. By optimising pretreatment conditions and monitoring key elemental ratios, it is possible

to enhance microbial activity, nutrient recovery, and environmental sustainability in AD processes.

6.3.3 VFAs, pH and alkalinity

The stability of an AD system is highly reliant on a fine balance between pH, TA, and VFAs. These parameters are critical indicators of microbial health and system resilience during AD. An imbalance in VFAs, pH, or alkalinity can lead to process instability, which hampers methanogenesis and reduces biogas yield. An interplay between VFAs, pH, and TA across different streams, including untreated WAS, HT-treated effluent, adsorption-treated effluent, and precipitation-treated effluent, was investigated, with the results presented in Table 6.2.

Table 6.2 System stability indicators: variations in pH, volatile fatty acids, and total alkalinity before and after anaerobic digestion.

Stream	pH		pH mV		VFA (mg/L)		TA (mg/L)		VFA/TA
	Before AD	After AD	Before AD	After AD	Before AD	After AD	Before AD	After AD	
Scenario 1	6.98	7.90	0.1	-54.3	4255±22	2413±26	2952±69	3567±40	0.68
Scenario 2	6.90	7.92	4.6	-55.2	1591±22	2215±26	3403±174	4715±90	0.47
Scenario 3	6.88	7.89	5.9	-53.4	1553±20	1934±48	2493±46	4838±116	0.40
Scenario 4	6.97	7.99	0.6	-59.3	1259±96	1487±44	3075±31	3116±48	0.48

6.3.3.1 pH dynamics

Microbial viability generally depends on digester pH, with methanogens being highly dependent on the pH to thrive in the range of 6.8 to 7.5, but can tolerate up to a pH of 8.2 (Okoro-Shekwaga 2019). For this study, pH values across all streams were found to increase steadily from near-neutral values before AD (6.88 to 6.98) to slightly alkaline after digestion (7.89 to 7.99). This rise indicates successful buffering and acid neutralisation, which are necessary to maintain optimal conditions favourable for methanogenesis during AD. Specifically, the pH of scenario 1 increased from 6.98 to 7.90, scenario 2 increased from 6.90 to 7.92, scenario 3 changed from 6.88 to 7.89, and scenario 4 increased from 6.97 to 7.99.

This indicates that the increase in pH has been consistent, representing the efficient conversion of VFAs to methane and carbon dioxide, which prevents unacceptably high acidification. Such a result is consistent with that of Qiu *et al.* (2023), who found that

sufficient alkalinity production compensates for acid accumulation, thereby maintaining stable AD performance. In addition, pH shift represents a stable microbial ecosystem in which extreme pH changes can inhibit particular key microbial groups, such as methanogens (Qiu *et al.* 2023). Zabed *et al.* (2019); Qian *et al.* (2025) also support the observed pH stability by showing that optimal pH buffering capacity enhances methane yields, metabolism and hence improves biogas production efficiency. However, on the contrary, Slezak *et al.* (2020); Sakaveli *et al.* (2024) indicated that if the buffering capacity is inadequate, pH suppression occurs due to high VFA accumulation, and the process fails.

6.3.3.2 Volatile fatty acids

VFAs, including acetic, propionic and butyric acids, are important intermediates of AD and are implicated in shaping microbial community dynamics and methane yield. In this study, only the total VFA concentration, reported as acetic acid, was measured. It was clearly evident that there was a significant reduction in VFA concentration in the scenario 1 stream, from 4255 mg/L to 2413 mg/L, indicating robust methanogenic activity. Zhang *et al.* (2023b) suggest that the conversion of VFAs by methanogenic archaea would be an efficient way to convert VFAs into biogas and maintain process stability. However, scenario 2 had VFAs increasing from 1591 mg/L to 2215 mg/L, possibly because acid utilisation was incomplete or acidogenesis was faster than methanogenesis. Similarly, increased solubilisation increases acidogenesis but may also temporarily inhibit methanogens under hydrothermally treated sludge (Thompson, Young and Baroutian 2021). Despite a modest increase in the streams of scenarios 3 and 4 (from 1553 mg/L to 1934 mg/L and 1259 mg/L to 1487 mg/L, respectively), the complex interaction between substrate availability and microbial consortia dynamics was suggested, as the adsorption of inhibitory compounds selectively removed inhibition (Qiu *et al.* 2023). Excessive accumulation of VFA inhibits methanogens by lowering the pH, which is countered in all streams by strong alkalinity, thereby maintaining a stable pH and preventing acidification (Omine *et al.* 2021).

6.3.3.3 Alkalinity and buffering capacity

The system is buffered against acidification by alkalinity, primarily in the form of bicarbonates, ensuring pH stability. In all streams, alkalinity increased, reinforcing

microbial resilience (Santinello *et al.* 2024). In this study, bulk TA of scenario 1 increased from 2952 to 3567 mg/L, scenario 2 from 3403 to 4715 mg/L, scenario 3 from 2493 to 4838 mg/L, and scenario 4 from 3075 to 3116 mg/L, indicating enhanced buffering capacity.

The amounts of alkalinity increased in the adsorption and HT streams, indicating the potential of pretreatment to increase buffering agents, such as ammonium bicarbonate. This buffering capacity is crucial in preventing the accumulation of VFA, as it can otherwise inhibit AD microbial activity. Similar trends were also reported by Zhang *et al.* (2023b), who found that pretreatment methods, such as hydrothermal or adsorption processes, increase alkalinity and support stable methanogenic activity.

6.3.3.4 VFA/TA ratio

VFA/TA ratio is a key metric in signalling the digester's health, as ratios under 0.4 indicate stable digestion, ratios between 0.4 and 0.8 require close monitoring, and ratios above 0.8 suggest instability (Omine *et al.* 2021). In general, the post-AD ratios in this study were found to have varying stability across streams, ranging from 0.68 in scenario 1, 0.47 in scenario 2, 0.40 in scenario 3, and 0.48 in scenario 4.

The relatively low levels of VFA/TA ratios in scenario 3 indicate a better buffering capacity, stemming from the effectiveness of removing toxic compounds through adsorption. Scenario 2, despite enhanced alkalinity, showed an unexpected rise in VFAs, warranting further investigation into potential inhibitory compounds from HT, such as phenolics and furfurals, or suboptimal methanogenic adaptation (Zhou *et al.* 2024).

In scenario 3, the significant increase in alkalinity and low VFA/TA ratio reinforce the potential of adsorption in stabilising AD systems, a finding consistent with studies by Kim, Lee and Park (2015) who reported that biochar adsorption improves pH buffering and methanogenic activity. However, the residual biochar from adsorption may require further optimisation to avoid unintended microbial inhibition.

The modest alkalinity increase and stable VFA/TA ratio in scenario 4 stream suggest balanced digestion; however, reduced nutrient availability due to phosphorus removal may limit microbial activity, as observed in studies by Zhou *et al.* (2022).

This integrated analysis emphasises the interdependence of pH, VFA, and alkalinity in dictating AD stability and efficiency. The comparison of HT and Adsorption streams indicates the promising role of pretreatment in improving AD performance. However, evidence of VFA accumulation in certain streams suggests a need for targeted process optimisation. Addressing these interactions is crucial for maximising AD performance while advancing sustainable waste management and bioenergy recovery.

6.3.4 Nutrient composition

Nutrient composition plays a significant role in maintaining system stability during AD. However, for all these key nutrients, such as ammonium, nitrate, nitrite, and phosphorus, the process must be carefully managed to avoid toxicity and inhibition, as shown in Table 6.3. Results of this study show striking changes in nutrient profiles before and after AD across multiple treatment streams due to the interplay between HT, adsorption and precipitation processes

Table 6.3 Nutrient composition before and after AD

Stream	Before digestion					After digestion				
	NH ₄	NO ₃	NO ₂	PO ₄	TON	NH ₄	NO ₃	NO ₂	PO ₄	TON
WAS	10.03	14.50	-0.04	64.04	14.46	53.29	-3.62	-0.01	60.61	-3.63
HT	151.6	19.45	-0.05	172.8	19.40	173.4	4.81	-0.08	142.6	4.67
Inoculum	262.53	-3.71	0.12	15.48	-3.60	290.83	-4.11	1.49	7.02	-2.62
WAS + inoculum	166.75	-3.50	0.03	47.78	-3.47	298.68	-6.43	0.03	40.86	-6.40
HT + inoculum	193.86	-4.01	0.05	32.75	-4.61	298.74	-6.48	-0.01	57.50	-6.49

Ammonium bicarbonate is a key buffer in the AD process and provides stable operation under high VFA concentrations. Although the formation of free ammonia nitrogen (FAN) is a concern to system stability, especially under higher pH and temperature conditions, it poses a risk to system stability due to its toxicity to methanogenic archaea. Ammonium concentration for untreated WAS varied from 10.03 mg/L to 151.6 mg/L for the HT stream before AD. These values reflect the release of ammonium during HT due to the hydrolysis of nitrogenous compounds. Ammonium concentrations were greatly enhanced after AD, with the highest concentration in the HT + inoculum stream (298.74 mg/L), indicating higher nitrogen

release during digestion. FAN concentrations remained below the inhibitory threshold of 700-1700 mg $\text{NH}_3\text{-N/L}$ (Marin-Batista *et al.* 2019; Li *et al.* 2021), which confirms that digestibility was stable under ammonium conditions.

The ammonium/ammonia equilibrium is highly sensitive to pH; ammonium prevails at pH levels below 7 and is less toxic, while higher pH values shift the equilibrium towards ammonia, thereby increasing levels of FAN. The system was able to maintain pH values within the favourable range, reducing FAN toxicity risk and maintaining stable methanogenic activity.

AD reduced nitrate and nitrite concentrations significantly in all streams. For instance, in scenario 2, nitrate levels went from -4.01 mg/L to -6.48 mg/L. The near-complete denitrification of nitrate and nitrite in AD is consistent with these reductions, typical of anaerobic conditions favouring the removal of N_2 . AD does not have nitrate and nitrite as limiting nutrients; their minimal presence after digestion indicates efficient nitrogen cycling within the system.

Excessive concentrations of phosphorus can cause eutrophication in effluent streams, and phosphorus is a critical nutrient for microbial growth and energy metabolism (Zhou *et al.* 2022). Most streams showed that phosphorus concentrations decreased after AD, indicating microbial uptake and incorporation into biomass. In scenario 2, phosphorus levels decreased from 47.78 mg/L to 40.86 mg/L. In contrast, phosphorus concentrations in scenario 2 changed from 32.75 mg/L to 57.50 mg/L, which is consistent with the release of organically bound phosphorus during HT.

Precipitation processes for phosphorus recovery represent a sustainable pathway of nutrient recycling. Results show that the precipitation stream achieved effective phosphorus recovery, eliminating the nutrient load in the effluent while minimising phosphorus loss to a level that is necessary for microbial activity during AD.

6.4 Anaerobic digestion comparative study

While trace gases such as H_2S and NH_3 were acknowledged as potential constituents of biogas, their concentrations were below the detectable limits of the analytical instrumentation used in this study. As the primary focus was on energy-related metrics, only methane (CH_4) and carbon dioxide (CO_2), which represent the major

components of biogas, were reported. This approach aligns with established practices in AD research. The organic loading in this study varied between 4 and 7 kg VS/m³ for batch laboratory-scale digesters operating under mesophilic conditions.

6.4.1 Absolute biogas production

AD is a critical process for energy recovery, and methane yield serves as a key indicator of performance. The four feedstock streams (scenarios) exhibited distinct methane yields and production patterns influenced by pretreatment methods and feedstock characteristics, as shown in Figure 6.2.

Background methane production was assessed by running the inoculum alone. Minimal biogas was observed within the first two days, after which production ceased, likely due to the depletion of biodegradable material, as supported by the low SCOD values reported (Appendix B8). Given the negligible volume of methane produced by the inoculum and its rapid cessation, the background biogas contribution was deemed insignificant. Consequently, gas production in the test streams was analysed without subtracting the background biogas from the inoculum, ensuring a straightforward and representative evaluation of the digestion performance.

Methane yields for scenario 1 were the lowest among all the streams. On day 1, the yield was 0.127 mL/g-VS (due to background methane production from the active inoculum), with a gradual increase to a peak of 0.656 mL/g-VS on day 9. The lower yield aligns with the limited solubilisation of organic matter in raw WAS, as evidenced by its lower initial SCOD (284 ± 15 mg/L; Table 6.1).

The complex polymeric structure of WAS slows down hydrolysis, resulting in a prolonged lag phase of up to three days, which is consistent with findings by Campuzano and González-Martínez (2016), who noted slow degradation rates in untreated sludge. Despite its low yield, scenario 1 provides a baseline for assessing the benefits of pretreatment. The low VFA/alkalinity ratio of 0.68 post-AD reflects a stable digestion process but insufficient substrate availability for higher methane production. In scenario 1, the methane content peaked at 11.1% on day 9, lower than the normal range of 54-72% observed in optimised systems (Danso-Boateng *et al.* 2015b). This could have been caused by incomplete adaptation of methanogens and limited hydrolysis and acidogenesis in the early phase.

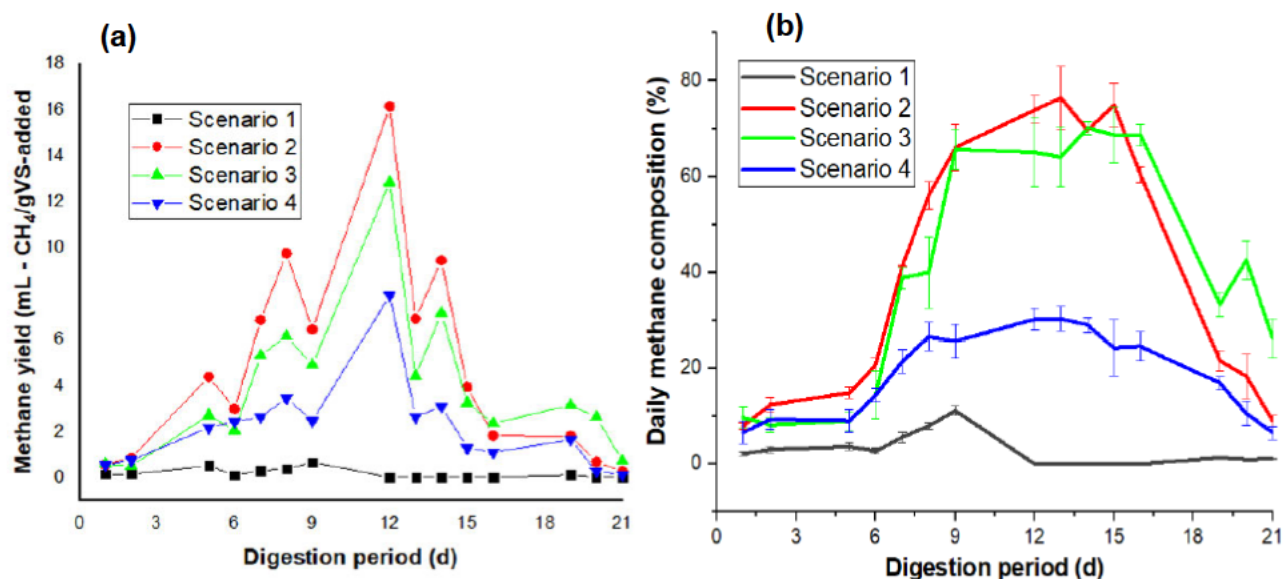


Figure 6.2 Methane production (a) absolute daily yield (b) absolute daily composition

All other streams were outperformed by scenario 2, which produced the highest methane yield and content. The maximum methane yield was observed at 0.54 mL/g-VS on day 1 and peaked at 16.15 mL/g-VS on day 12. This enhanced performance is attributed to the treatment of raw WAS by HT, which increases SCOD from 284 ± 15 mg/L to 3035 ± 134 mg/L. Enhanced solubilisation of substrates was observed, as reported by Aragón-Briceño, Ross and Camargo-Valero (2017a); Svensson *et al.* (2018), who found that hydrothermally treated sludge improves methane yields.

HT tended to shorten the lag phase to 1.2 days due to the presence of readily biodegradable compounds, allowing for faster microbial adaptation. A methane content of 76.4% was observed on day 13, which was within the optimal range of 65-75%, as stated by Villamil *et al.* (2018). Nevertheless, inhibitory by-products (e.g., ammonia, phenolics) present should be monitored to avoid long-term microbial inhibition (Zhou *et al.* 2024).

Moderate methane yields, peaking at 12.85 mL/g-VS on day 12, were seen in scenario 3. Despite a high initial SCOD of 1591 ± 22 mg/L, the adsorption process resulted in SCOD reductions due to the removal of nutrients and contaminants. The yields were likely contributed by residual magnetic biochar (2%) in the effluent, which could catalyse AD through DIET; however, excess biochar residues may inhibit microbial activity (Qi *et al.* 2021). The lowest VFA/alkalinity ratio post-AD for these streams was

0.40, indicating an extremely stable system. The adsorption process was shown to enhance stability, maintaining a mild methane content of 65.7% on day 9, comparable to that of the methane content on HT-treated substrates. Benefits arise from removing phenolic compounds from wastewater sludge to inhibit the AD process because they are highly resistant to biodegradation as an inhibitor (Bispo *et al.* 2018).

The lowest methane yields were obtained in scenario 4 (for pretreated streams), with a maximum of 7.92 mL/g-VS on day 12. Designed to recover nutrients such as phosphorus and nitrogen, this precipitation process reduced essential nutrients needed for microbial growth and maintenance, including ammonium and phosphorus, and consequently microbial activity and methane production. Reduced substrate availability was indicated by the initial SCOD, which was the lowest among the pretreated streams at 1259 ± 96 mg/L. Methane content was only 30.2% on day 12, but the VFA/alkalinity ratio of 0.48 post-AD indicates moderate stability. This finding is consistent with the results of Muys *et al.* (2021), who reported reduced methane yields in nutrient-depleted streams due to impaired microbial growth.

Results are consistent with a clear hierarchy of methane yields in the order of scenario 2 > scenario 3 > scenario 4 > scenario 1, which emphasises the efficacy of HT for improving the biodegradability of sewage sludge. The effectiveness of the microbial community for streams that underwent pretreatment was improved in scenarios 2 and 3, where a short lag phase was exhibited. Methane production followed documented three distinct phases in AD. The initiation phase (days 1-3) has shown rapid production and yields in scenarios 2 and 3 due to high SCOD and soluble substrates, while the peak phase (days 9-12) is characterised by maximum yields in all scenarios, driven by degradation of more complex organic fractions and in the decline phase (days 15-21) has seen reduced yields as substrates were exhausted, which in tandem with a study by Cao *et al.* (2021).

6.4.2 Cumulative biogas production

Cumulative biogas production reflects the efficiency of AD processes in converting organic substrates into biogas over time, as shown in Figure 6.3.

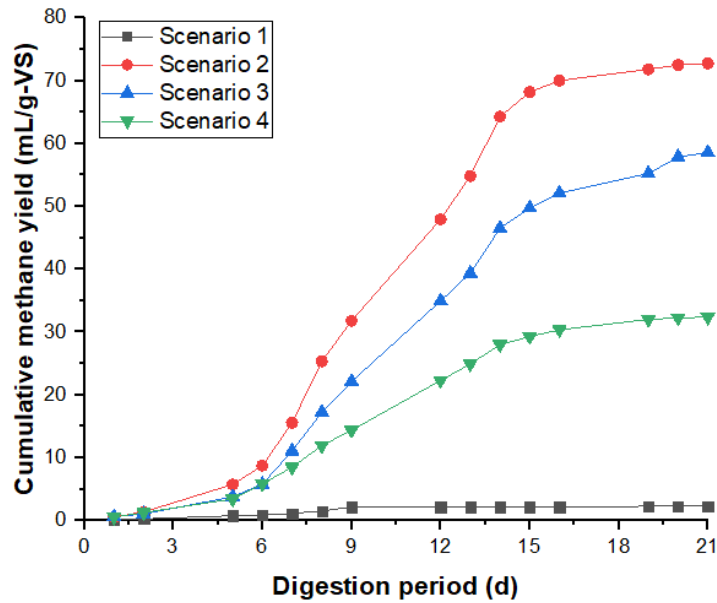


Figure 6.3 Cumulative methane production for various scenarios.

During the initial phase, scenario 2 displayed the highest cumulative biogas production, reaching 8.73 mL/g-VS by day 6, significantly outperforming the other streams. This early surge aligns with the enhanced solubilisation of organic matter due to hydrothermal treatment, which improves substrate availability for microbial metabolism. Scenarios 3 and 4 followed with moderate yields (5.80 mL/g-VS and 5.87 mL/g-VS, respectively). These streams demonstrated slower biogas production, likely due to the adsorption of readily degradable substrates and the nutrient recovery processes reducing the bioavailability of key components. Scenario 1 lagged significantly, producing only 0.85 mL/g-VS by day 6. This highlights the limited biodegradability of untreated WAS, attributable to its dense cellular structure and complex polymeric matrix.

Exponential growth was observed in the peak phase of scenario 2, increasing from 31.8 mL/g-VS on day 9 to 47.9 mL/g-VS on day 12. The rapid production arises from increased solubilisation of VS and enhanced microbial activity in the HT stream. Similar results have also been found, where HT substantially increases the cumulative biogas yield above that of untreated substrates (Choe *et al.* 2021; Scherzinger and Kaltschmitt 2021). Adsorption played a moderate role, although it was significant in the case of scenario 3, with a maximum yield of 58.6 mL/g-VS being achieved. This may be because adsorption eliminates inhibitors such as phenolics, but residual

biochar may potentially reintroduce inhibitory effects through possible elution, slightly curbing the efficiency of microbes. Highest cumulative yields of 32.4 mL/g-VS were observed for scenario 4. The process of precipitation to recover nutrients could have reduced the organic load available for digestion, thereby impacting microbial performance. Observations in scenario 1 indicated the plateauing rate of cumulative biogas production using untreated WAS with 2.17 mL/g-VS, thereby indicating the inefficiency of untreated WAS in sustaining cumulative biogas production with time.

Cumulative production in scenario 2 peaked at 72.7 mL/g-VS in the decline phase or stabilisation phase by day 21, demonstrating that HT-treated feedstock can maintain high biogas yields. This is consistent with the literature, which states that hydrothermal treatment under optimised conditions enhances AD performance (Tommaso *et al.* 2015; Zhou *et al.* 2024). Scenarios 3 and 4 stabilised at 58.6 mL/g-VS and 32.4 mL/g-VS, respectively, representing diminishing returns from adsorption and precipitation. However, these processes are beneficial to the system's stability and nutrient recovery at the expense of biogas yields, resulting in the reduction of bioavailable substrates. Results demonstrated that untreated WAS is a suboptimal feedstock for AD, as indicated by a peak cumulative production of 2.30 mL/g-VS in scenario 1.

The trends in cumulative biogas production from this study are congruent with those of previous studies. For example, as reported in Bougrier, Delgenès and Carrère (2008); Ngo *et al.* (2023), hydrothermally treated WAS showed at least a 20% increase in cumulative biogas yield compared to untreated sludge. This is consistent with the superior performance of scenario 2. The inclusion of biochar in AD systems increased stability, as in scenario 3, albeit with slightly lower cumulative biogas yields, due to the sorption of biodegradable substrates, as observed by Danso-Boateng *et al.* (2015b). As reported by Muys *et al.* (2021), precipitation processes typically increase system stability and nutrient recovery but decrease biogas yields due to the removal of essential nutrients and organic matter, corroborating scenario 4's findings.

6.4.3 Theoretical methane production (TMP)

Theoretical methane production (TMP) is a fundamental aspect of any AD study since it gives insight into the maximum TMP (biogas yield) obtainable with a given substrate. This benchmark is used to evaluate the efficiency of experimental AD processes. Stoichiometric equations, such as the Buswell equation, which predict methane yields

based on the elemental composition of the substrate, serve as the basis for predictive calculations to determine the TMP (Equations 6.1 and 6.2). However, these equations are limited, as they are inherently incapable of discriminating between biodegradable and non-biodegradable fractions of organic (Song *et al.* 2024).

Table 6.4 Comparison of experimental and theoretical methane production

Stream	Experimental Yield (mL/g-VS)	CH ₄ Theoretical (mL/g-VS)	CH ₄ Yield	Experimental CH ₄ composition (%)	Theoretical CH ₄ composition (%)
Scenario 1	2.3±0.3	477±49		11.1±1.0	48.9
Scenario 2	72.7±2.9	515±53		76.4±6.7	52.1

In this study, TMP was calculated for the hydrothermally treated (HT) and untreated waste-activated sludge (WAS) streams; the other streams were not considered due to the inadequacy of the data. The Buswell equation, widely used for such predictions, yielded theoretical methane values that were significantly higher than the experimental results. For instance, as shown in Table 6.4, the HT stream exhibited a theoretical yield of 515 ± 53 mL CH₄/g-VS, whereas the experimental yield was only 72.7 mL CH₄/g-VS (Table 6.4). Similarly, the untreated WAS stream exhibited theoretical and experimental methane yields of 477 ± 49 mL CH₄/g-VS and 2.3 mL CH₄/g-VS, respectively.

There are several reasons for these discrepancies. Since there are recalcitrant components in WAS, the Buswell equation assumes complete biodegradability of organic matter and thus neglects that assumption in its model. This overestimation is confirmed in previous studies by Song *et al.* (2024), who commonly report that a considerable fraction of the organic carbon is inaccessible to microbial activity. The lower experimental yields also reflect the fact that approximately 12% of the organic carbon is used for microbial biomass synthesis rather than methane production (Zabed *et al.* 2019). HT improves solubilisation; however, it may produce inhibitory compounds, such as phenolics and ammonia, which can inhibit methanogenic activity (Erdogan *et al.* 2015).

Interestingly, the methane composition of the HT stream (76.4%) exceeded the theoretical value (52.1%). The phenomenon could be explained by the selective biodegradation of readily biodegradable fractions in the early stages of AD, which consequently results in a higher methane content in the biogas.

HT greatly enhances the biodegradability of WAS by changing its physicochemical properties. SCOD in the HT stream was found to have increased tenfold, indicating an increase in the solubilisation of organic matter. Despite this, its full translation into methane production is not realised because of the formation of recalcitrant products, possibly due to the Maillard reaction at higher temperatures and partial inhibition by soluble ammonia and phenolic compounds.

However, the untreated WAS always had a biodegradability index (experimental to theoretical yield) of ~0.48%, while the HT stream had a value of ~14.1%. This finding is consistent with those of Bougrier, Delgenès and Carrère (2008), who reported that pretreated sludge exhibited improved biodegradability indices. Substrate composition and treatment conditions are found to be important parameters for theoretical predictions of biogas production. For instance, methane yields are directly dependent on the C/N ratio. Compared to the WAS stream with a 5:1 C/N ratio, it has been observed that the HT stream with a 7:1 C/N ratio produces more methane in terms of composition and yield. Barani *et al.* (2018) suggested that optimising this parameter can enhance biogas yields.

This study highlights the need for more accurate predictive models that capture substrate-specific characteristics and microbial dynamics. For example, Buswell's equation accuracy could be improved by the addition of correction factors for biodegradability and for inhibitory effects. In addition, isotopic labelling could be used further to elucidate the fate of organic carbon during AD.

6.5 Kinetic study for anaerobic digestion

The first-order and modified Gompertz kinetic models were employed to evaluate methane production under four scenarios, providing insights into their predictive accuracy and suitability for AD processes. The comparison highlights differences in their abilities to model critical parameters, such as the lag phase (λ) and maximum biogas yield (P), alongside their statistical performance.

The kinetic and biodegradability parameters were evaluated using non-linear regression implemented via MatLab Software, and the results for the estimated parameters are presented in Appendix D. The modified Gompertz model

demonstrated superior predictive accuracy compared to the First-order model (Table 6.5), as evidenced by consistently higher R^2 values across all scenarios of 0.967 (scenario 1), 0.995 (scenario 2), 0.997 (scenario 3), and 0.998 (scenario 4). These values reflect the model's robustness in capturing the dynamics of methane production, including the lag phase and maximum production rates. Conversely, the First-order model exhibited lower R^2 values, particularly in scenario 2 (0.362), which limits its applicability to systems with more complex kinetics.

The relatively high R^2 (0.938) observed for the first-order model in Scenario 4 can be attributed to the simplified kinetics and stable degradation pattern associated with that particular condition. In Scenario 4, the biogas production curve exhibited an exponential trend with minimal lag phase, which aligns closely with the assumptions of the first-order model, that substrate degradation rate is directly proportional to the remaining substrate concentration. Under such conditions, the deviation between experimental and predicted values is reduced, resulting in a higher R^2 . However, the Modified Gompertz model still provided a superior overall fit across all scenarios, as it better captures sigmoidal growth behaviour, substrate inhibition, and lag-phase dynamics that the first-order model cannot fully describe.

Table 6.5 Kinetic model comparison between First order and Modified Gompertz for all scenarios

Parameter	First-order model				Modified Gompertz			
	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 1	Scenario 2	Scenario 3	Scenario 4
P	2.89	40.13	16516.67	4797.89	2.28	76.43	62.34	34.28
R_m					0.35	7.92	5.48	3.20
λ					3.17	5.03	5.10	4.35
k	0.09	0.21	0.00	0.00				
SSR	0.78	7512.61	529.08	133.04	0.29	59.48	19.25	4.67
R²	0.911	0.362	0.925	0.938	0.967	0.995	0.997	0.998
RMSE	0.23	22.38	5.94	2.98	0.14	1.99	1.13	0.56
MAE	0.18	19.87	4.76	2.67	0.10	1.63	0.94	0.46
F- value	132.75	7.37	160.27	195.46	174.37	1181.60	2191.70	2735.36
p-value	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00

The lag phase (λ) is a critical parameter that indicates the microbial acclimation period. The experimental lag phases for scenarios 1, 2, 3, and 4 were 3.5, 1.2, 2.2, and 2.6 days, respectively. In contrast, the modified Gompertz model predicted deviant values of λ of 3.17 (Scenario 1), 5.03 (Scenario 2), 5.10 (Scenario 3), and 4.35 (Scenario 4).

This deviation highlights the challenges of kinetic modelling in accurately capturing early microbial dynamics, particularly under varying substrate characteristics and environmental conditions (Villamil *et al.* 2019; Elagroudy *et al.* 2020). The discrepancy in λ could stem from assumptions in the Gompertz model, such as the symmetrical shape of biogas production curves, which may not align perfectly with experimental realities.

The First-order model, lacking explicit representation of the lag phase, inherently simplifies microbial acclimation, which further explains its poorer performance in scenarios with significant acclimation periods, such as scenario 1. Experimental maximum yields (P) were 2.3, 72.7, 58.6, and 32.4 mL/g-VS for scenarios 1, 2, 3, and 4, respectively; however, both kinetic models showed some deviation in predicting these values. For instance, the modified Gompertz model predicted P values of 2.28, 76.43, 62.34, and 34.28 mL/g-VS, which were closer to the experimental data but still not perfect. The First-order model, on the other hand, predicted P values of 2.89, 40.13, 16,516.67, and 4,797.89 mL/g-VS for scenarios 1, 2, 3, and 4, respectively, demonstrating significant overestimations.

This overestimation by the First-order model is likely due to its assumption of a constant reaction rate, which fails to account for the declining substrate bioavailability and microbial efficiency over time (Xie SiHuang *et al.* 2016). The modified Gompertz model, by incorporating R_m (maximum biogas production rate) and λ , provides a more nuanced approach, though it still cannot fully account for all experimental variations, such as substrate heterogeneity and inhibitory effects.

Key statistical metrics, including root mean square error (RMSE), mean absolute error (MAE), and residual sum of squares (SSR), further corroborate the modified Gompertz model's superior fit. In scenario 3, the RMSE values were 1.13 mL/g-VS (modified Gompertz) versus 5.94 mL/g-VS (First-order), with SSR values of 19.25 and 529.08 mL²/g-VS, respectively. The modified Gompertz model consistently performed with lower RMSE and MAE values in all scenarios, suggesting better predictive precision. The F-statistics and p-values also support this conclusion. In the case of scenario 4, the p-value of the modified Gompertz model turned out to be $p < 0.05$ with F-statistic (2735.36), while the p-value of the First-order model was $p < 0.05$ and the F-statistic

was 195.46. Both models achieve $p\text{-values} < 0.05$, indicating statistical significance (Chicco, Warrens and Jurman 2021).

In scenarios 2 and 3, where pretreated substrates and complex microbial dynamics are present, the modified Gompertz model's ability to incorporate λ and R_m makes it well-suited to these scenarios. This closer alignment to experimental data demonstrates the relevance it has when modelling biogas production under varying conditions (Nguyen *et al.* 2016). Despite this, the deviations in the λ and P predictions indicate the need for further refinement, perhaps by hybrid models that integrate biochemical constraints. Simplistic as it may be, the First-order model can help provide a quick assessment of uniform substrates or systems where no microbial acclimation occurs. At the same time, its broad applicability is limited by significant deviations in scenarios with complex dynamics (Maleki, Bokhary and Liao 2018).

6.6 Chapter summary

In this chapter, the aim was to identify the impacts of HT on adsorption and precipitation processes on AD performance, including methane yield and system stability. The study evaluated biogas production over 21 days using four distinct feedstocks under mesophilic conditions. HT showed the best results as a pretreatment method, increasing solubilisation and biodegradability, which resulted in higher methane yields and shorter lag phases. Stability was only improved by the adsorption of inhibitors, but the yields were moderate, as the adsorbed inhibitors have reduced critical components necessary for AD. While precipitation promotes nutrient recovery, it also reduces methane yields caused by nutrient removal during precipitation. First-order and Modified Gompertz models were used for kinetic modelling, revealing that the latter had superior predictive precision, as evidenced by higher R^2 values and greater agreement with experimental data. Nevertheless, predicted lag phases and maximum yields vary slightly from the predicted results, indicating the limitations of both models.

CHAPTER 7: TECHNOECONOMIC EVALUATION OF INTEGRATED WASTEWATER TREATMENT PROCESSES FOR ENHANCED SUSTAINABILITY AND PROFITABILITY

7.1 Introduction

A significant obstacle lies ahead in the path towards commercialising and expanding waste-to-resource/energy technologies due to their high energy requirements (Kassem *et al.* 2020). Therefore, to successfully commercialise the process, it is crucial to conduct a thorough technoeconomic evaluation. This evaluation will provide valuable insights into early project cost estimating for decision-making on project execution. For economic consideration, it is noteworthy that residual heat can be recovered and used for plant heating purposes.

An analysis was conducted to determine the technical feasibility of the process by examining the energy and mass balance at each unit. An analysis was conducted to compare the economic aspects of various process configurations, focusing on the minimum selling price, NPV, and IRR. A sensitivity analysis was conducted to investigate the impact of various input operating variables on the economic aspects of the studied process configurations, as illustrated in Figure 7.1. The goal of this chapter is to understand the commercial viability and sustainability of this innovative approach to waste management and resource utilisation. Despite the potential of HT, resource recovery, and AD integration, this system has yet to be effectively incorporated into scaled-up WWTPs. It is therefore critical to undertake a technoeconomic analysis to establish its feasibility and identify key drivers of profitability.

A comparison was made against the configuration of AD without HT (WAS only as the control), HT-AD, HT-adsorption of toxins-AD, and HT-toxins removal-struvite precipitation-AD. It has been widely noted and recommended to extract struvite fertiliser after removing toxins to avoid secondary pollution and mitigate the impact of struvite fertiliser on animals in the food chain through adsorption or co-precipitation of detrimental heavy metals (Masomi *et al.* 2014; Li *et al.* 2020a; Wu *et al.* 2020). The study also endeavours to contribute to the growing body of literature on sustainable wastewater management and circular economy approaches.

It is worth noting that the process was designed with a strong emphasis on environmental management, prioritising sustainability and resource recovery over maximising profits using the triple bottom line approach.

7.2 Materials and methods

7.2.1 Process parameters

The source of the sludge and characterisation, HT process and experimental set-up, toxins removal through adsorption, precipitation of struvite and AD were fully covered, mainly in the preceding chapters. The parameters determined helped to compute the mass and energy balances.

To calculate the energy required for the HT process, Equation 7.1 was adopted.

$$Q_{HT} = \frac{m_{WAS} C_{p,WAS} \Delta T}{\eta} + \frac{\tau k_{HTR} A_{HTR} \Delta T_{HTR}}{d_{HTR}} \quad 7.1$$

Q_{HT} represents the total energy required for hydrothermal treatment of sludge, m_{WAS} is the mass of the sludge (in kg), $C_{p,WAS}$ is the specific heat capacity of the sludge (kJ/kg·K), ΔT is the temperature change (in K), and η is the efficiency of the system (1 or below). The second term represents the energy lost, Q_{loss} , to the environment (kJ), with k_{HTR} is the thermal conductivity of the hydrothermal treatment reactor (HTR) material (in W/m·K), A_{HTR} is the surface area of the HTR through which heat is lost (m²), ΔT_{HTR} is the temperature difference between the inside and outside of the HTR (K), τ is the time over which the heat loss occurs (sec), d_{HTR} is the thickness of the HTR wall (m). Heat losses were assumed to occur predominantly through conduction (Mäkelä and Yoshikawa 2016). An efficiency factor of 75-95% for thermal energy recovery from sludge streams via a heat exchanger is recommended in the literature (Akgul, Cella and Eskicioglu 2017). In the current study, an efficiency factor of 80% was considered for the heat exchanger.

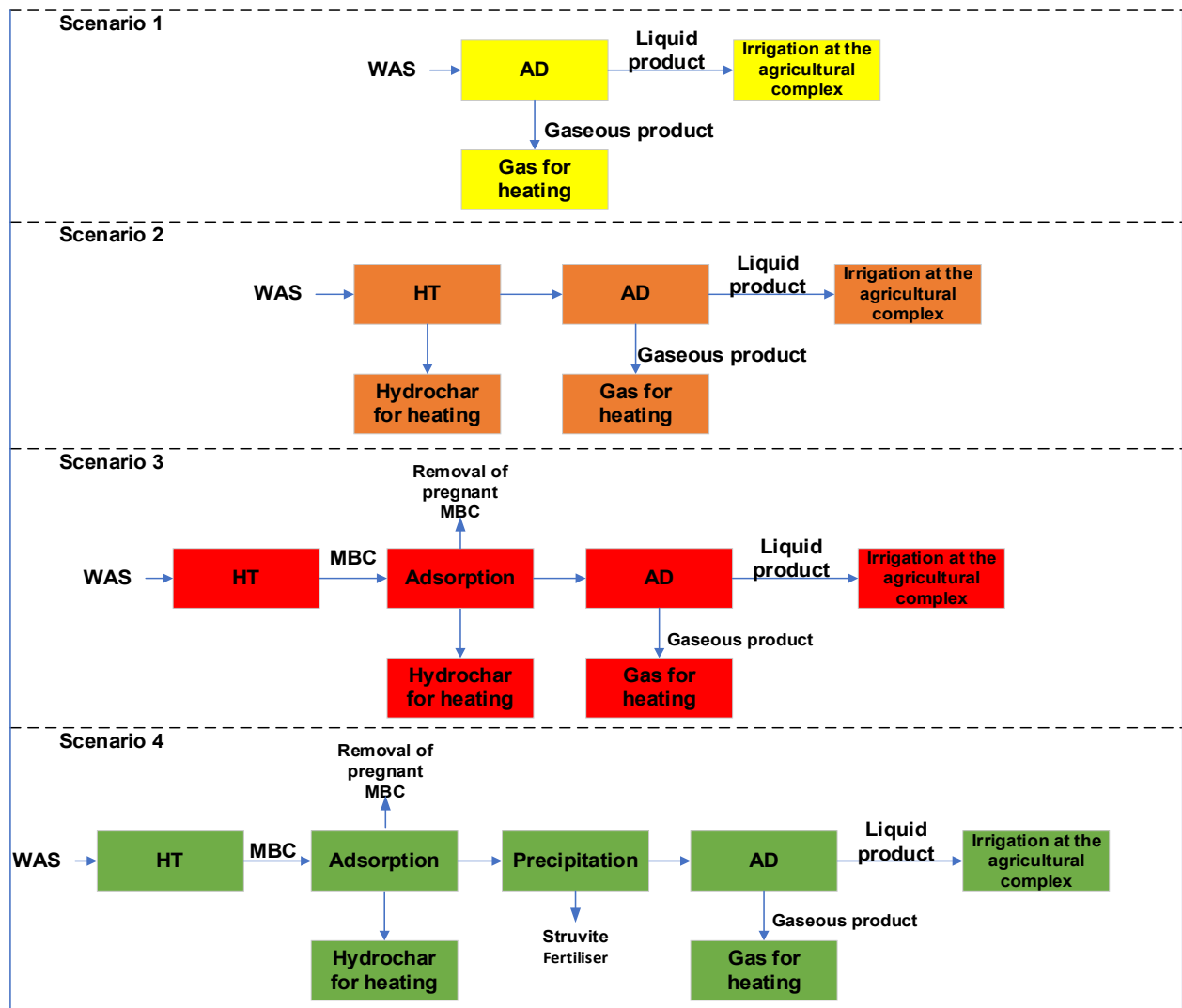
The calculation for determining the heat energy required to maintain the digester's temperature was conducted using Equation 7.2, as postulated by Deublein and Steinhauser (2010).

$$Q_{AD} = [m_{HT} C_p (T_o - T_{HT})] + (k_d A_D \Delta T_D) \quad 7.2$$

The heat energy required for anaerobic digestion is denoted as Q_{AD} . m_{HT} represents the mass of the HT-sludge, while C_p refers to the specific heat capacity of the HT-sludge. T_0 represents the operating temperature of the AD system, and T_{HT} signifies the inlet temperature of the HT-sludge. The C_p of the waste-activated sludge and HT-sludge were experimentally determined to be 3.93 kJ/kg·K and 3.96 kJ/kg·°C, respectively (Section 3.2.4 and 3.8.3). In Equation 7.2, the heat loss from the digester, $Q_{AD-loss}$, is represented by the second term. This term considers the k -factor (Thermal conductivity) of the digester material, the surface area of the digester A_D , and the average temperature difference between the heating medium and the substrate (HT-sludge), ΔT_D . The digester material's k -factor and the outside temperature were chosen as 14.2 W/m.K and 20 °C, respectively (Simmons *et al.* 2020). The surface area of the digester was determined by considering a height-to-diameter ratio of 0.5 to ensure stability and structural integrity, as well as to optimise mixing efficiency, heat transfer, cost-effectiveness, and ease of maintenance.

Figure 7.1 displays the 4 process scenarios discussed in this study. It should be noted that the figures and values quoted in this chapter are optimum values found through bench-scale operations.

- Scenario 1: AD of WAS (without HT); the biogas was combusted for the plant's needs and sold in excess.
- Scenario 2: AD of HT-sludge (Consider hydrochar yielding (pelletisation) and recovery of heat during cooling).
- Scenario 3: AD of HT-sludge after adsorption (removal of toxins). The reuse of biochar was considered.
- Scenario 4: Adsorption and precipitation of HT. Struvite fertiliser/nutrient recovery, heat recovery, and hydrochar recovery were considered.



WAS = Waste-activated sludge, MBC = Magnetic biochar, AD = Anaerobic digestion

Figure 7.1 Process flows for various scenarios.

7.2.2 Evaluation of the technoeconomic aspects

For the economic analysis, it is assumed that the profit will remain consistent throughout the project and that the product will be sold immediately after the initial batch is produced. Additionally, it is commonly assumed that production starts immediately after erecting the critical components, such as the HTR and precipitator; in this case study, the biodigesters are already available.

7.2.2.1 Technoeconomic analysis framework

A spreadsheet model, developed using Microsoft Excel 365 (Microsoft Corporation, Redmond, WA, USA), was created to evaluate the economic performance of all

scenarios. Specifically, the impact of capital expenditures (CAPEX) and operational expenditures (OPEX) on the management of wastewater sludge was examined. It is worth noting that all amounts were quoted in US dollars (\$) as a common international reference, and conversions to the local currency were made at the prevailing exchange rate (Nedbank 2024). The focus of the process was on environmental management rather than prioritising energy and nutrient recovery solely. This viewpoint appears to be a more logical choice, particularly when comparing the prices of levelised cost of methane, 1.75-2.90 \$/kg (Al-Breiki and Bicer 2023), with the price of fossil-derived gas 1.74 to 2.40 \$/kg (Timmerberg, Kaltschmitt and Finkbeiner 2020; Markets Insider 2024), Power-to-gas (P2G) technology from \$1.84 to \$2.44/kg (Gorre, Ortloff and van Leeuwen 2019), gasification 1.21 \$/kg (Li *et al.* 2015), Sabatier process from \$1.50 to \$1.90/kg (Baier, Schneider and Heel 2018).

It is reported that struvite fertiliser sells at approximately \$517/ton (Yetilmezsoy *et al.* 2017). In contrast, popular technologies such as wet process phosphoric acid production and the neutralisation process have produced ammonium and phosphate fertilisers with prices ranging from \$280 to \$330/ton (Ashley, Mavinic and Koch 2009).

Hydrochar has been documented to trade at \$0.08 - \$1.92/kg (Saba, McGaughy and Reza 2019; Sultana and Reza 2022; Nadarajah *et al.* 2024), compared to coal-derived solid fuels priced at \$0.18 - \$0.92/kg (Nyarko *et al.* 2021; Berrocal-Mendéz and Moya 2022).

In addition, it has been widely recognised that wastewater and sewage management projects are often not profitable without public subsidies, even when considering revenues from energy generation (Fersi *et al.* 2015).

In this study, the methodology outlined by Towler and Sinnott (2021) served as the main reference. The study is categorised as a Class 5 estimate with an accuracy of $\pm 50.0\%$, according to the classification by the Association for the Advancement of Cost Estimating International (AACE 56R-08, 2020); the cost data have been updated as of August 2020. First, a thorough analysis was conducted to determine the cost of acquiring each piece of equipment. This involved utilising cost correlations or capacity ratios, such as Williams' rule. These estimates were derived from design parameters obtained from bench-scale experiments and simulations. Considering the potential for clogging by struvite, acidic substances, and corrosive materials, a material factor was

applied as necessary. The construction material for all equipment was selected to be austenitic stainless Steel (304), except for the biodigester, made of reinforced concrete. Afterwards, the Lang factorial method was applied to calculate the total investment cost (TIC). Operational costs were calculated by factoring in a portion of the initial capital expenditure and deducting the revenue generated from product sales. Upon thorough examination, the cost per megalitre of treated sludge was calculated, considering a projected lifespan of 30 years for the plant.

7.2.2.2 Total capital investment

An economic analysis was conducted on the scenarios presented in Figure 7.1 to compare and determine the economic viability of integrating different processes. The mass and energy balances determined in earlier sections were utilised in the scaling up of the equipment to the desired plant capacity, which consequently determined the capital investment required. The cost of the equipment was determined based on information from previous literature (Towler and Sinnott 2021). However, the size of the equipment can vary depending on the plant's operating capacity. Therefore, the final cost for this study was determined using a scaling factor, as shown in Equation 7.3 (Saari *et al.* 2016; Towler and Sinnott 2021).

$$C = C_0 \left(\frac{V}{V_0} \right)^n \quad 7.3$$

Where the variables C and V represent the cost and capacity of the current equipment, while C₀ and V₀ represent the cost and capacity of the base equipment, respectively, the scaling factor is denoted by n, and typically, the n values range from 0.6 to 0.8 (Hendrickson, Haas and Au 2024). For this study, a scaling factor 'n' value of 0.77 was chosen, in line with the previous data collected for waste-activated sludges from plants with capacities ranging from 4 to 450 ML/day (Hendrickson, Haas and Au 2024). The cost of equipment fluctuates from year to year, so it is necessary to adjust the cost data found in the literature to reflect the current year. This calculation was based on data from the Chemical Engineering Plant Cost Index (CEPCI) (Ranganathan, 2023; Hendrickson, Haas, and Au, 2024), using Equation 7.4. This study utilised the cost index data from March 2024 to represent the current year (800.3).

$$Cost_{Cur} = Cost_{Base} \times \frac{CEPCI_{Cur}}{CEPCI_{Base}} \quad 7.4$$

$Cost_{Cur}$ and $Cost_{Base}$ are the costs of equipment to be determined, and similar equipment is known in a certain reference year, respectively. $CEPCI_{Cur}$ and $CEPCI_{Base}$ represent the index for the current year and the reference year, respectively.

In this study, the cost data for various units were estimated from Chemical Engineering Magazine (CE), ICIS, and other online vendors, including Alibaba and Amazon, using Equation 7.4 (Khan 2023; Lozowski *et al.* 2024). Regarding the AD digester, it has been noted in the literature that the cost of the digester can range from \$ 300 to \$ 500 per cubic meter (Deublein and Steinhauser 2011). In this study, only the cost of maintaining the anaerobic digestors was considered since the plant already has reactors. This study did not put much emphasis on upgrading the biogas produced. The total cost of the equipment was determined by adding up the costs of all the major equipment shown in Figure 7.1. The total fixed capital investment (FCI) was calculated by adding capital investment on equipment (CIE) and other capital costs such as startup expenses (15% of CIE), engineering and supervision (25% of CIE) and contingency (10% of CIE) (Hendrickson, Haas and Au 2024).

Aside from the initial investment, sufficient working capital is necessary to establish and sustain the plant until the first revenue is generated. Based on previous studies conducted by Doddapaneni *et al.* (2018); Manthos *et al.* (2024), it has been found that the working capital for chemical plants typically ranges from 15 to 20% of the FCI. For this study, a working capital of 15% was chosen. Ultimately, the total capital investment (TCI) was determined by adding FCI and working capital (Haas *et al.* 2006; Martinovic *et al.* 2018).

7.2.2.3 Production costs

There are different categories of production costs, including direct variable costs, fixed costs, and general expenses. The revenue generated, as well as utilities and other specific costs, are outlined in Table 7.1. The labour needed to run the plant was determined using the methodology outlined in the literature (Towler and Sinnott 2021). It was determined that the plant's availability was 330 days, operating 24 hours a day with three eight-hour working shifts per day. Given the highly automated nature of industrial manufacturing at this scale, a large workforce is not necessary to maintain a high level of processing control. Hence, 8 employees per shift were considered for the additional units, including the supervisors. The costs associated with supervising

staff were determined to be 20% of the expenses related to operating labour (Haas et al., 2006; Turton et al., 2008). 5% of the FCI was allocated for maintenance and repair costs (Apostolakou *et al.* 2009). The other operating costs, such as factory overheads, administration costs, and distribution and selling costs, were calculated using correlations presented by Turton *et al.* (2008); Martinovic *et al.* (2018). The factory overheads comprise various expenses, including payroll, employee benefits, medical services, accounting services, and safety services. The reported cost of wastewater treatment for domestic and industrial effluents (\$ 1-4/m³) was used to calculate the wastewater treatment costs (Riley *et al.* 2020). The depreciation amount was determined using the straight-line method and a zero salvage value over a 30-year lifespan.

Table 7.1 Cost parameters considered in the calculation of production costs and revenue generated.

Parameter	Unit	Cost (US\$)	References
Water ^a	\$/kL	0.48	(Ngobeni and Breitenbach 2020; Ngobeni and Breitenbach 2021)
Electricity (purchase)	\$/kWh	0.044	(Mohlakoana and Wolpe 2023)
Salaries ^b	\$/h	1.47	(CCMA 2024)
Struvite	\$/ton	517	(Yetilmezsoy <i>et al.</i> 2017)
Hydrochar	\$/ton	450	(Saba, McGaughy and Reza 2019; Sultana and Reza 2022; Nadarajah <i>et al.</i> 2024)
Biomethane selling price	\$/kg	2.90	(Al-Breiki and Bicer 2023)
Raw materials: WAS	\$/ML	14.22	(Tesfamariam <i>et al.</i> 2020)

^a National average

^b Minimum wage rate

7.2.2.4 Economic indicators and sensitivity analysis

The economic performance of the AD of the WAS and the other integration approaches was assessed using the payback period, rate on investment (ROI), IRR and NPV.

One way to estimate the payback time is by dividing the total initial capital (fixed capital plus working capital) by the average annual cash flow. Equation 7.5 provides a simple method for calculation (Green and Southard 2019).

$$\text{Payback period} = \frac{\text{Total investment capital}}{\text{Average cash flow per annum}} \quad 7.5$$

The payback period indicated in the cash flow diagrams by Towler and Sinnott (2021) does not align with the assumption that all the investment is made in year zero and revenues begin immediately. For most chemical plant projects, it is often not feasible to expect investments to be fully recovered within the first year of operation. Typically, investments are spread out over one to three years, and it may take until the second year of operation for revenues to reach their full potential. The simple payback time is typically calculated solely based on cash flow. However, to simplify the process, taxes and depreciation are often disregarded, and the average annual income is used as a substitute for cash flow.

The NPV was calculated using Equation 7.6 (Buller *et al.* 2022).

$$NPV = \left(\frac{(1+i)^n - 1}{i \times (1+i)^n} \times \text{net cashflow} \right) - TCI \quad 7.6$$

Where 'i' is the interest rate (8%), n is the plant's lifespan (30 years). The net cash flow can be computed by Equation 7.7:

$$\text{Net Cashflow} = ((R_T - PC_T) \times (1 - \text{tax rate})) + D \quad 7.7$$

R_T represents the total revenue, encompassing the revenue generated from all sources involved in the process. PC_T represents the total production cost, while depreciation (D) is another factor to consider (all costs are quoted in US dollars). A tax rate of 40% was chosen for this study. The IRR (%) value was determined through an iterative process, finding the specific "i" value at which the NPV equals zero in Equation 7.6 (Ross, Jaffe and Kakani 2019).

The evaluation of the impact of integrating bioenergy and bioresource recovery on the selling price of the products was conducted using data on minimum selling prices, as shown in Table 7.1. A methodology presented by Yang and Rosentrater (2019) was used to calculate the minimum selling prices of struvite, biogas, hydrochar, and liquid fertiliser. To achieve the break-even point, the overall costs must be equivalent to the total revenue, as illustrated in Equation 7.8.

$$R_T = PC_T + ROI + IT \quad 7.8$$

$$ROI = CRF \times TCI \quad 7.9$$

$$IT = \text{taxation rate} \times (R_T - PC_T - D) \quad 7.10$$

ROI is the return on investment, whereas IT refers to information technology. The capital recovery factor (CRF) is calculated using Equation 7.11.

$$CRF = \frac{i \times (1 + i)^n}{(1 + i)^n - 1} \quad 7.11$$

A sensitivity analysis was conducted to examine how various cost parameters affect the economic performance of the cases shown in Figure 7.1. For this study, the input parameters were adjusted within a range of $\pm 25\%$ of the base values. These parameters included the fixed capital investment cost of raw materials and the selling price of the products. The parameters that have the most significant impact on economic performance indicators were identified. Parameters causing substantial changes in NPV or IRR when varied were identified as key drivers, as presented in Table 7.2.

Table 7.2 Parameters and related assumptions in costing analysis

Parameters	Comments
Base year	2019 (March) CEPCI (720.1)
Currency and exchange rate	US\$; ZAR/US\$ = 18.86 ^a
Plant site	KwaZulu-Natal (South Africa) Location/site factor (0.85) ^b
Lifespan of the plant	30 years
Material of construction	Austenitic stainless Steel (304) Material Factor, f_m (1.3) ^c
CAPEX estimates	Lang factors for fluid-solid systems
Inside battery limits (ISBL)	$CE + C_{er} + C_p + C_{ic} + C_{el} + C_c + C_s + C_{sf}$
Purchase cost of major equipment (CE)	Total cost of all individual equipment costs
Cost of erecting equipment	$f_{er} = 0.45$; then $C_{er} = CE^* (f_{er}/f_m)$
Cost of pipework	$f_p = 0.45$; then $C_p = CE^* f_p$
Cost of instrumentation and control	$f_{ic} = 0.15$; then $C_{ic} = CE^* (f_{ic}/f_m)$
Cost of Electrical Work	$f_{el} = 0.1$; then $C_{el} = CE^* (f_{el}/f_m)$
Cost of Civils	$f_c = 0.2$; then $C_c = CE^* (f_c/f_m)$
Cost of buildings and structures	$f_b = 0.1$; then $C_b = CE^* (f_b/f_m)$
Cost of surface finishing	$f_{sf} = 0.1$; then $C_{sf} = CE^* (f_{sf}/f_m)$
Outside battery limits (OSBL)	$f_{OSBL} = 0.4$; then $OSBL = ISBL * f_{OSBL}$
Cost of engineering and design	$f_{DE} = 0.25$; then $DE = ISBL * f_{DE}$
Contingency (X)	$f_X = 0.1$; then $X = ISBL * f_X$
Total Investment Cost (TIC)	$TIC = ISBL + OSBL + DE + X$
Fixed production costs	
Operating labour (OL)	
Supervisors' cost	$0.2 * OL$
Direct salary overheads	$0.5 * OL$
Maintenance cost	$0.05 * ISBL$
Tax and insurance	$0.02 * ISBL$
Land rent and buildings	$0.02 * (ISBL + OSBL)$
General plant overheads	$0.65 * (OL + Supervision)$
Environmental tariffs	$0.01 * (ISBL + OSBL)$

Fees and royalties	0.01*TIC
Capital charges	0.01*TIC
Marketing costs	
<i>Estimates of the variable production cost</i>	
Utilities	
Electricity	\$0.044/kWh
Water	\$0.48/kL
<i>Minimum selling price</i>	
Struvite fertiliser	\$517/ton
Hydrochar	\$450/ton
Biomethane	\$2.90/kg
Liquid fertiliser	\$0.14/ton

^a Adapted from Nedbank (2024)

^b Methodology adopted from Intratec (2023)

^c Source of material factor

7.2.3 Ethical considerations

The primary ethical focus of this study's technoeconomic evaluation centres on economic equity, responsible financial decisions, and ensuring fair access to recovered resources. Integrating hydrothermal treatment, struvite precipitation, and AD presents several ethical concerns in relation to cost-benefit distribution, affordability and transparency in commercialisation (Pursell 2013).

First, financial sustainability and cost fairness are two essential ethical aspects for implementing wastewater valorisation technologies. Before capitalising on hydrothermal treatment and nutrient recovery processes, the costs of these technologies, when applied to commercial treatment facilities, will need to be weighed against the long-term financial benefits. The application of such technologies will not disproportionately burden municipalities or taxpayers. In this study, lifecycle costs, revenue generation through biogas, hydrochar, and fertiliser generation, along with cost-sharing mechanisms, are used to ensure that the benefits of wastewater valorisation are accessible to all stakeholders, including low-income communities.

Secondly, fair access to the resources that can be recovered from, for instance, struvite fertiliser and biogas, must be ensured. Recovered phosphorus and bioenergy should not be left monopolised by the few but fairly distributed to maintain sustainable agriculture and local economies. Market regulations and policies that encourage fair trade and stifle the dominance of dominant players will guide the commercialisation strategy of these recovered products.

Worker safety, together with fair labour practices, is an essential element for conducting ethical technoeconomic implementation. In sludge waste management, hydrothermal reactor operation, and biogas plant maintenance expose workers are exposed to hazardous conditions. Organisations must strictly implement worker safety rules, provide proper training, and pay fair wages to achieve proper ethical conduct among their operational personnel.

The process requires both transparency about operations and engagement with stakeholders as fundamental elements. The ethical development of wastewater valorisation processes depends heavily on both public engagement and industry partnership to obtain feedback from regulatory bodies, local communities and industry representatives when planning implementation and assessing financial consequences. The education of communities through public outreach programmes will demonstrate the benefits of wastewater valorisation while building community confidence in price structures and the safety of recovered materials (Van de Poel and Royakkers 2023).

Responsible innovation and regulatory compliance together establish moral principles for the proper integration of these technologies. The entire production line of struvite fertiliser, biogas, and hydrochar requires detailed quality laboratory testing to verify their market and safety suitability before starting commercial sales. The products must comply with agricultural and environmental standards, as this is both an ethical and legal necessity.

7.3 Results and discussion

7.3.1 *Mass and energy balance*

Figure 7.2 illustrates the material and energy flows for various cases that have been examined (scenarios 1, 2 and 3 are presented in Appendix E1). The hydrothermal treatment process, adsorption, precipitation of struvite, hydrochar yield, and AD are significant energy-consuming unit operations.

This study investigates the HT of waste-activated sludge (WAS) in an industrial wastewater treatment plant designed to handle 100 ML/d. For this study, a flow rate of 5 ML/h was used as the basis for calculations and scenario analysis.

The energy requirement for hydrothermal treatment of waste-activated sludge was determined to be 0.98 MJ/kg. This is lower than the values reported by Aragón-Briceño, Ross and Camargo-Valero (2021), which ranged from 3.3 to 5.9 MJ/kg, indicating a more efficient process in the current study. The low value could be attributed to differences in experimental conditions, feedstock variability (including sludge characteristics), energy efficiency of the heating system, and scale of operation, among other causes. The density of the HT-treated sludge was measured at 1010 kg/m³, compared to 1009 kg/m³ for the untreated WAS, indicating compaction and partial dissolution of solids during the treatment process.

At a design flow rate of 5 ML/h, the feed mass flow rate to the HTR unit was approximately 5050 ton/h. The hydrothermal treatment unit was the primary energy consumer in the plant, accounting for over 90% of the energy demands of the valorisation section. The heat losses due to conduction were calculated to be 34.1 MJ/kg, with convection and radiation losses considered negligible. The maximum pressure during HT at 220°C was 3.3 MPa. To protect downstream equipment and prevent undesirable reactions at high temperatures in the presence of oxygen, the valve to the heat exchanger was opened when the bulk liquid temperature had dropped to 150°C, somewhat deviating from the strict definition of hydrothermal treatment.

The heat recovered through the heat exchanger was calculated to be 611.6 MW (Figure 7.2). To achieve this, the mass flow rate of the cooling stream was computed to be 6,562.8 ton/h, sufficient to reduce the HTR contents' temperature to approximately 40°C before the adsorption processes. The cold stream exiting the heat exchanger was divided into two: one stream, at a flow rate of 2,372.3 ton/h, was directed to the anaerobic digester to meet its energy needs, and the other, at 4,190.5 ton/h, was used for preheating and other plant applications. This heat recovery strategy successfully met all the biodigester's energy demands.

After cooling, the post-HT sludge was fed into the adsorption unit at a rate of 2.5 tons/hour, where magnetic biochar (MBC) was used. Experimental data indicated a 98% recovery rate of MBC using an electromagnet. The recovered MBC was then eluted and treated for reuse (not discussed in this study). However, it is anticipated that large-scale operations may encounter lower recovery rates due to different

hydrodynamic behaviours at higher flow rates (Izadi *et al.* 2020). The power consumption of the adsorption unit was calculated to be 0.03 W.

The adsorbed HT-sludge (termed adsorption sludge) was processed through a press filter operating at 500 kPa, with a power consumption of 3.6 MW. This step was essential for yielding hydrochar and removing particulates that could hinder subsequent struvite and hydrochar separation. The hydrochar, after filtration, had a moisture content of 31% w/w and was naturally sun-dried to below 5% before packaging. Its HHV was calculated to be 17.8 MJ/kg from the ultimate analysis of the hydrochar.

The filtered adsorption sludge, with particles less than 25 μm , required flocculation to reduce pumping pressure, enabling the use of larger aperture size filters. The mass flow rate was 5038.9 ton/h, dissipating 3.1 MW of energy for optimal struvite precipitation. To produce 4.1 ton/h of struvite, 1.42 ton/h of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was injected on a dry basis. Sourcing alternative magnesium sources could reduce consumable costs. The resulting sludge, post-filtration, was termed precipitation sludge.

The precipitation sludge, at a flow rate of 5034.6 ton/h, was fed into the anaerobic digester and inoculated with biogas digester sludge from the same WWTP. With a SCOD of 1722 mg/L and a VS of 5155 mg/L, the biogas production rate was calculated to be 1.7 ton/h. The AD temperature was maintained at 37°C using a heating jacket with water circulating from the heat exchanger, entering at 100°C and exiting at 65°C. Experimental observations showed a maximum methane concentration of 71%. After a retention time of 21 days, the AD effluent was pumped to agricultural fields for irrigation purposes.

This study demonstrates the efficiency and practicality of integrating hydrothermal treatment within a wastewater treatment plant. By optimising energy recovery and process parameters, the plant achieves significant reductions in waste volume and energy consumption while producing valuable by-products such as biogas and struvite (Nagarajan *et al.* 2023). These findings highlight the potential of hydrothermal treatment as a sustainable and economically viable solution for wastewater management.

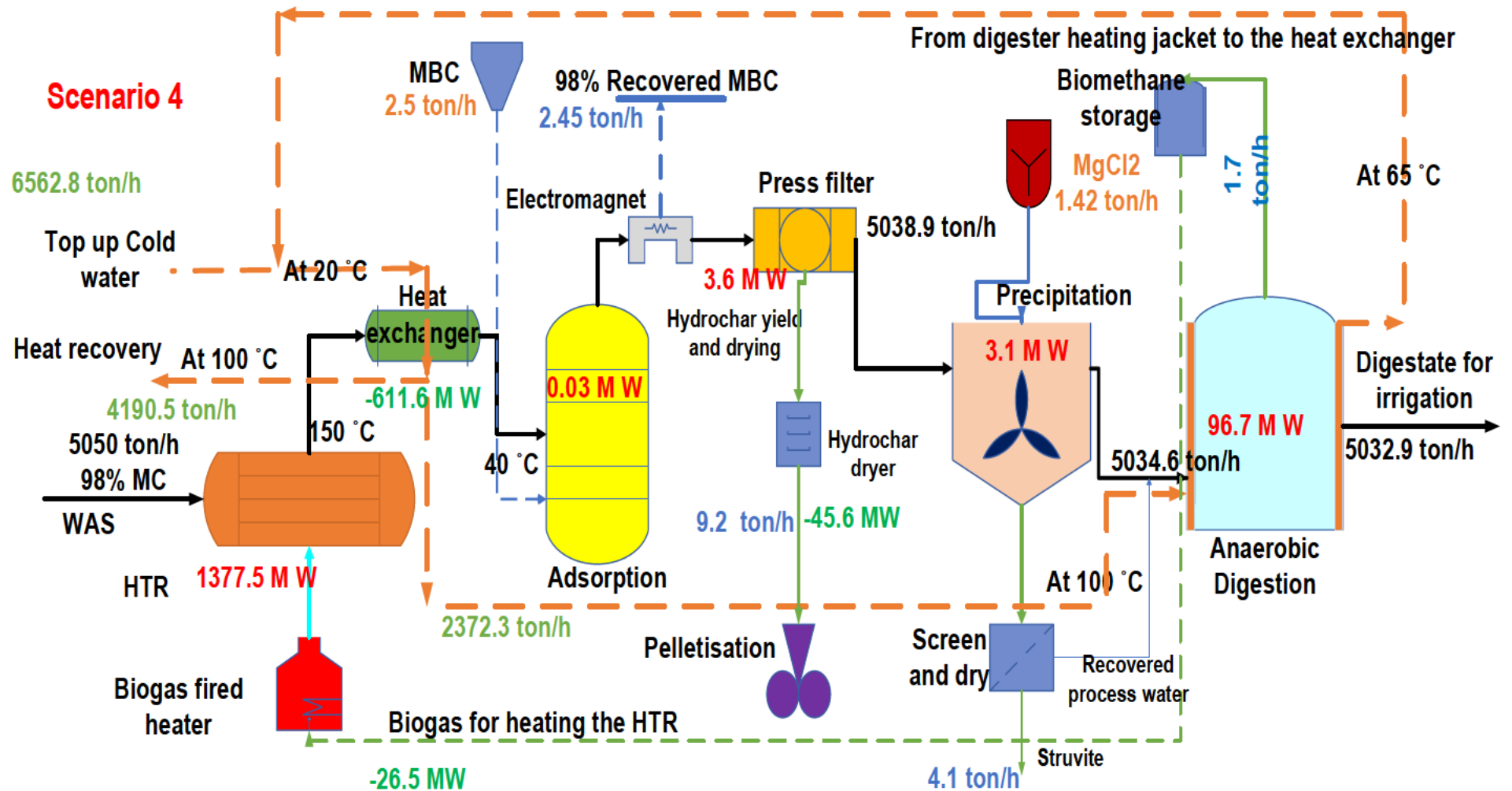


Figure 7.2 Energy and material balances for various scenarios

7.3.2 Profitability analysis

A comprehensive economic analysis was conducted to evaluate the feasibility of valorising WAS through the integration of HT and AD of the HT effluent. To ensure consistency in the economic evaluation, the selling prices of the products, as outlined in Table 7.1, were held constant across all scenarios.

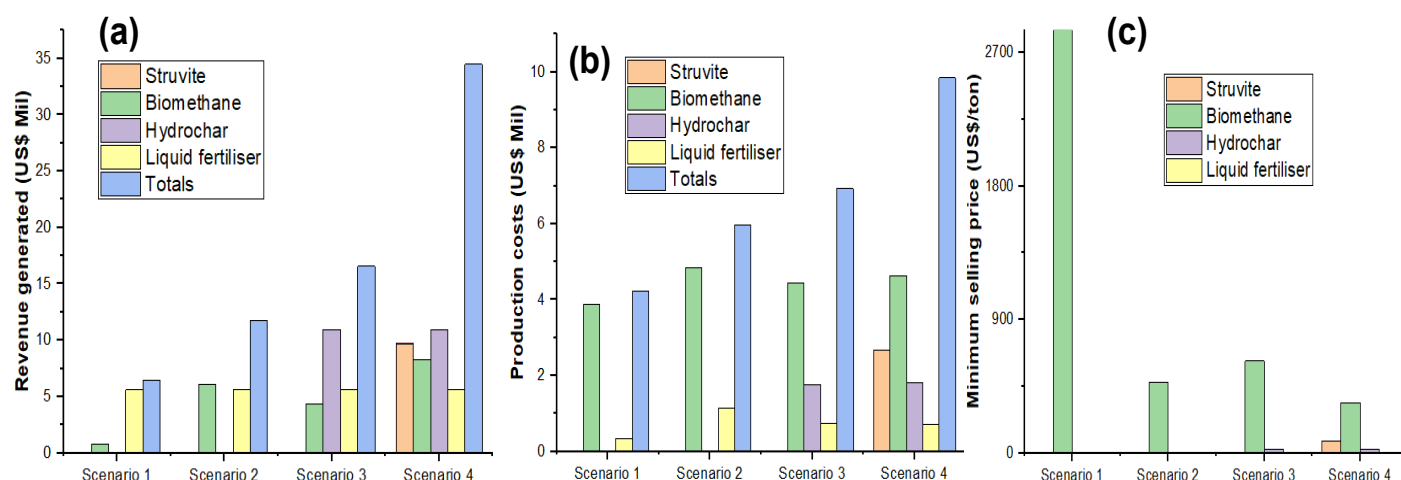


Figure 7.3 Profitability analysis for four scenarios: (a) Revenue generated, (b) Production costs, (c) minimum selling price to break even

Figure 7.3 illustrates the net revenue generated from the sale of struvite, hydrochar, biomethane, and digestate at the established selling prices. Figure 7.3(a) depicts the annual net revenue across various scenarios. All integrated approaches demonstrated higher revenues compared to the standalone AD set-up (scenario 1). Notably, in scenarios 3 and 4, hydrochar sales contributed significantly to the revenue, each generating \$10.9 million. This indicates that excluding the precipitation unit in scenario 3 did not impact the revenue from hydrochar. The total revenue generated in scenarios 1, 2, and 3 was 19%, 35%, and 48% of the total revenue in scenario 4, respectively. These results underscore the substantial profitability gains achieved by integrating hydrochar production and struvite precipitation with traditional AD.

Figure 7.3(b) reveals that the highest production costs were associated with biomethane production across all scenarios, ranging from \$3.8 million to \$4.7 million. The costs related to liquid fertiliser production were also significant due to stringent measures for

ensuring safe sludge disposal. This study allocated more personnel (4 per shift) to this section than to any other. Scenario 4 exhibited the highest total annual production costs, approximately \$9.84 million, largely due to the high usage of MgCl_2 and NaOH , which together accounted for \$2.63 million. This highlights the urgent need for alternative chemicals to either supplement or replace these commercial inorganic raw materials. The total production costs in scenarios 1, 2, and 3 were comparable, ranging between \$4.2 million and \$6.9 million, further emphasising that the chemical costs for struvite precipitation in scenario 4 are a major contributor to operating expenses.

Figure 7.3(c) presents the minimum selling prices of various products across different scenarios required to achieve break-even at a CRF of 9% ($i = 8\%$, $n = 30$ years). The integration of HT, toxin adsorption, and struvite precipitation reduced the minimum selling prices of biomethane, with scenarios 4, 3, 2, and 1 having minimum selling prices of \$337.49/ton, \$619/ton, \$473.72/ton, and \$2883.85/ton, respectively. The observed drop in scenario 2 is attributable to the high SCOD content of the HT effluent feeding the anaerobic digester, which enhances biomethane yield and thus reduces the selling price compared to scenario 3. This finding aligns with existing literature, which suggests that HT significantly improves biomethane yields by approximately 58% compared to untreated sludge (Ahmed *et al.* 2021). The enhanced methane yield from HT-treated sludge not only improves energy recovery but also supports the development of energy-neutral WWTPs. This could substantially reduce the energy burden on municipalities by more than 50% while contributing to circular economy efforts by transforming waste materials into bioenergy and nutrients.

The NPV is a crucial metric for assessing the economic feasibility of a project, representing the cumulative cash flow over its operational lifespan. Figure 7.4(a) illustrates the NPVs for four distinct scenarios over a 30-year plant lifetime. Among these, the standalone process scenario 1 yielded the lowest NPV. In contrast, scenarios 2, 3, and 4 exhibited an exponential increase in NPV, with scenario 4 approaching an NPV of approximately \$2.5 billion. This substantial increase can be attributed to the enhanced production of valuable by-products such as struvite and hydrochar, which significantly

offset the high operating costs typically associated with wastewater treatment plants (WWTPs).

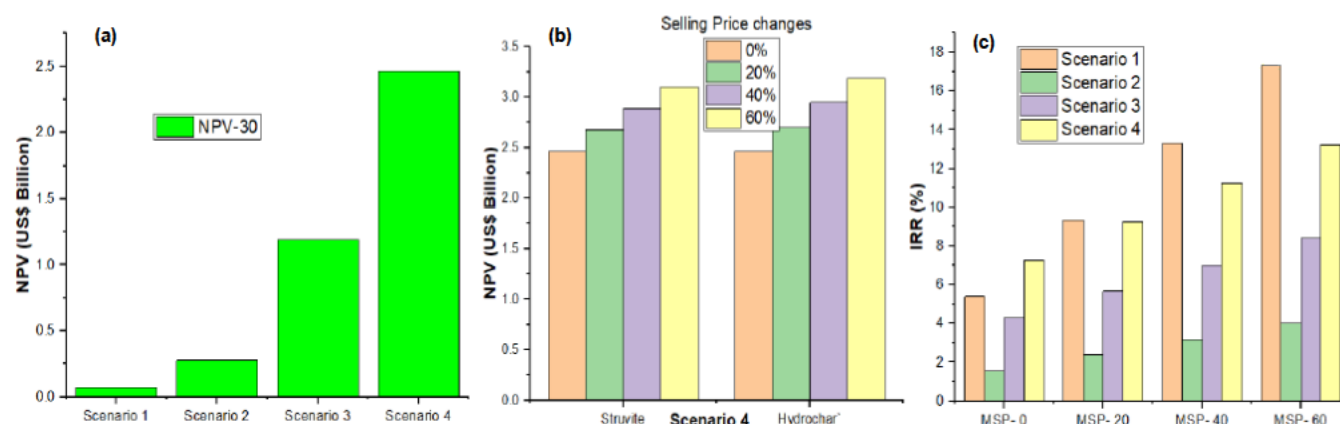


Figure 7.4 NPV and IRR behaviour subject to an increase in the selling prices (a) NPV for various scenarios (b) NPV relative to struvite and biochar price alteration (c) IRR response to MSP increase

Figure 7.4(b) presents a comparative analysis of the NPV behaviour in scenario 4, focusing on the sensitivity to changes in the prices of the two major products. Biomethane production was excluded from this analysis, as the valorisation studies primarily examine struvite and hydrochar. The selling price of struvite was incrementally increased by 0%, 20%, 40%, and 60%, while the hydrochar price was held constant, and vice versa.

The results indicate that increasing the selling price of these products has a positive impact on the NPV across all scenarios. Although the NPVs were generally comparable, hydrochar demonstrated a marginally greater influence on NPV enhancement than struvite. Specifically, price increases of 20%, 40%, and 60% in hydrochar resulted in NPV increases by factors of 1.01, 1.02, and 1.03, respectively. These findings underscore the critical role of product pricing in enhancing the economic viability of the WWTP project, highlighting the potential for optimised by-product utilisation to improve project outcomes substantially.

The IRR is closely tied to NPV and is a crucial financial metric for evaluating the design and construction of plants. Expressed as a percentage, the IRR is pivotal in decision-making, comparative analysis, capital budgeting, and risk assessment.

Figure 7.4(c) presents the IRR for the four scenarios at predetermined minimum selling prices (MSPs). MSPs for each product in the mix were incrementally increased by 0%, 20%, 40%, and 60%. It was observed that price increases for each product had a positive impact on the IRR across all scenarios. Initially, scenario 4 exhibited the highest IRR, followed by scenarios 1, 3, and 2, with IRRs of 7.25%, 5.38%, 4.29%, and 1.56%, respectively. The standalone scenario demonstrated a lucrative IRR due to the simplicity of the process, as it did not necessitate highly specialised equipment. However, this approach does not align with the objective of valorising sewage sludge to extract valuable resources for waste management.

The profitability analysis indicates that scenario 4 was the most economically viable integration route across all price increases, as shown in Figure 8.4(c). This superior performance can be attributed to the inclusion of struvite in the product mix, a feature unique to scenario 4. The other three scenarios did not incorporate struvite. Table 7.3 outlines the major parameters in the economic analysis of the four scenarios. Notably, only scenario 4 achieved a positive rate of return on investment (ROI). The integration of multiple value-added processes, particularly the inclusion of struvite precipitation, had a particularly strong impact on driving positive ROI in scenario 4.

Table 7.3 Major parameters in economic analysis

Parameter	Scenario 1	Scenario 2	Scenario 3	Scenario 4
Total Purchase Cost of Major Equipment (PCE)	\$220 750.80	\$1 976 511.71	\$2 075 319.27	\$2 358 395.13
Variable Costs	\$4 120 131.80	\$6 144 582.22	\$6 592 182.77	\$7 967 622.77
Raw mats and utilities (\$)				
Annual cost of operating labour (\$)	\$90 720.00	\$7 510 881.70	\$191 520.00	\$231 840.00
Direct production cost (\$)	\$4 323 404.91	\$6 689 421.85	\$7 246 615.47	\$8 738 294.09
Indirect Production cost (\$)	\$371 754.87	\$821 459.85	\$932 180.66	\$1 103 657.97
Annual Production Costs (\$)	\$4 695 159.77	\$7 510 881.70	\$8 178 796.13	\$9 841 952.06
Break-even production	\$13 774 382.53	\$15 300 955.85	\$12 240.99	\$13 772 085.63
ROI	-78.29%	-67.65%	-10.37%	45.04%
Simple payback period (years)				5.00

7.3.3 Sensitivity analysis

The cost of resource recovery and energy production in the proposed plant is influenced by numerous parameters, which can be broadly categorised into process-related and cost-related factors. A sensitivity analysis was conducted to pinpoint the key parameters among them. This Section delves into the sensitivity analysis of various parameters that affect the NPV after the end of the equipment's life for optimal capacity. The analysis was performed by varying selected critical parameters by $\pm 25\%$ of their proposed values while keeping all other variables constant. For the process-related parameters, the unit costs of electricity, biochar, and MgCl_2 were considered. Concerning the cost-related parameters, the analysis included fixed capital investment, struvite selling price, and income tax rate. The study aims to determine the order of impact of these parameters on the NPV and gain an understanding of the robustness of the proposed economic performance of the plant.

Figure 7.5 results show the impact of the percentage change in NPV resulting from variations in the cost parameters, exhibiting that responses to the administered changes varied by scenario. However, a 25% alteration of production costs in either direction significantly affected the NPV across all scenarios as well. Specifically, scenarios 1, 2, 3, and 4 showed changes in NPV values by 226%, 92%, 23%, and 13%, respectively. Such results suggest that the annual production cost for scenario 4 is more stable against changes compared to the other scenarios. This is consistent with other studies by Kassem *et al.* (2020), which reported that system scale-up decreases financial parameters, such as the NPV. The robustness of integrated approaches is demonstrated in scenario 4 by the fact that they exhibit lower sensitivity to economic changes compared to standalone setups, due to the economic benefits of a full-capacity valorisation process. This, however, demonstrates that despite this increase in the economic sustainability of integrated approaches in developing regions, it could potentially greatly benefit from continuing to stabilise or increase the market value of by-products.

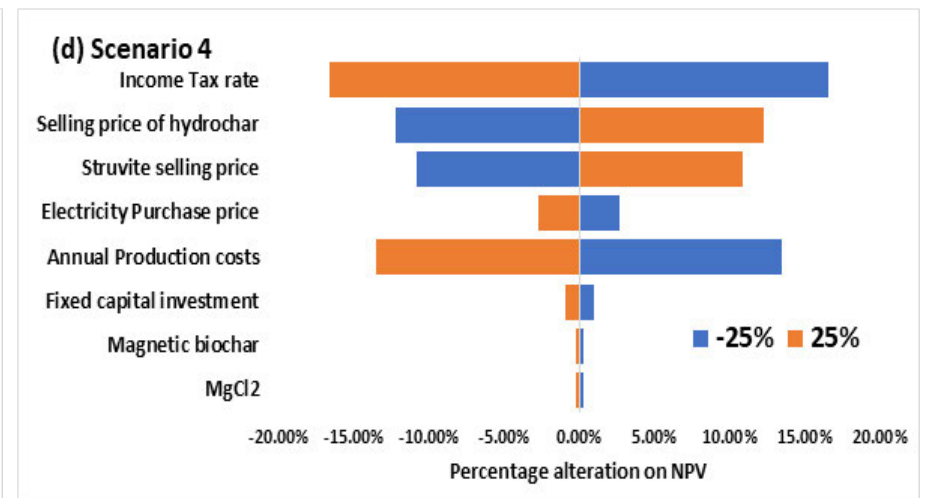
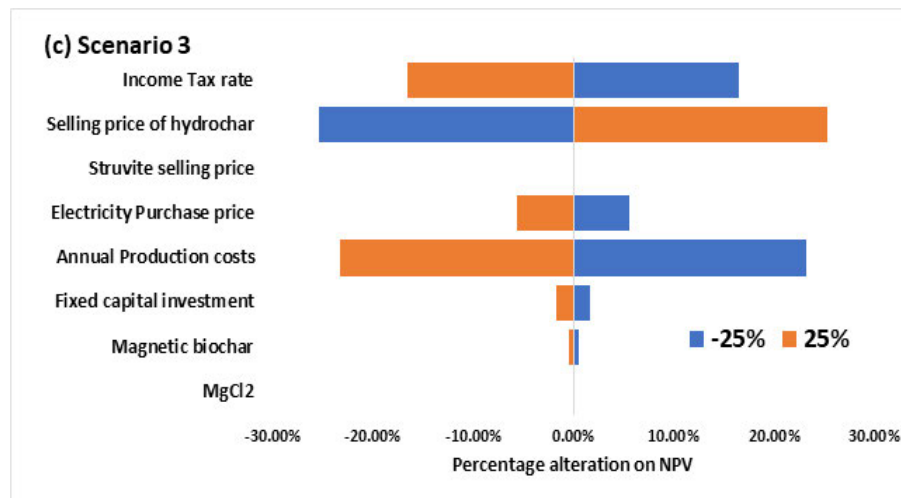
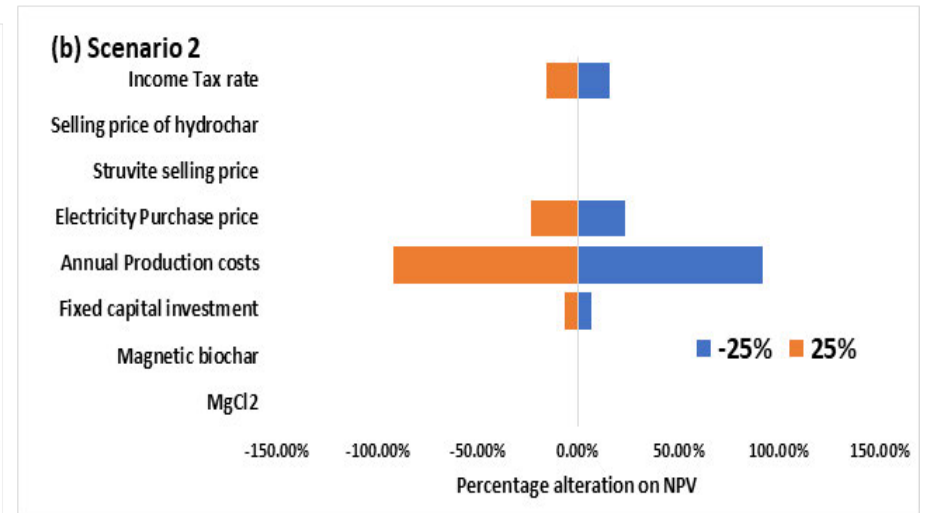
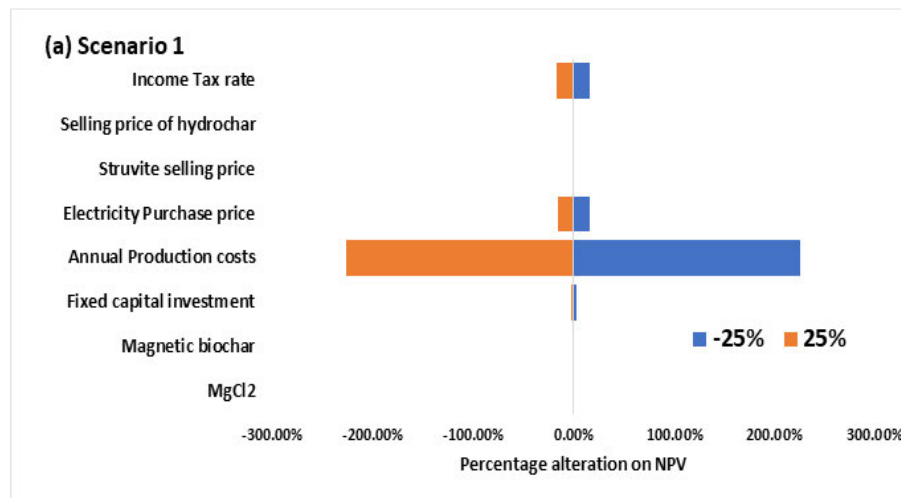


Figure 7.5 Sensitivity analysis for various scenarios (a) Scenario 1 (b) Scenario 2 (c) Scenario 3 (d) Scenario

For all the scenarios, the NPV decreased when all the process-related costs increased by 25%. This implies that processing plants need to keep their utility costs as low as possible to realise profits. However, when the FCI was changed by $\pm 25\%$, there was minimal impact on the NPV with changes of 3%, 7%, 2%, and 1% registered for scenarios 1, 2, 3, and 4, respectively. Such minimal impact only further demonstrates that the project is very robust and relatively insensitive to plant purchasing costs.

Additionally, the NPV did not change significantly (0.2% and 0.3%) in scenario 4, when the costs of magnetic biochar and MgCl_2 were reduced by 25%, respectively. These raw materials were absent in scenarios 1 and 2. Hence, a 0% change was reported for a -25% alteration.

7.4 Pilot-scale implementation plan

To strengthen the techno-economic credibility of the proposed hydrothermal treatment (HT)–adsorption–struvite–anaerobic digestion (AD) integration, a pilot-scale verification is proposed. This plan aims to assess process scalability, heat recovery efficiency, hydrodynamic behaviour, and material handling performance under realistic operating conditions.

7.4.1 Objectives and Scope

The pilot will validate process operability, quantify energy recovery, and confirm nutrient and energy recovery yields at an intermediate scale. Specific goals include:

1. Demonstrating stable, continuous HT operation with effective heat integration.
2. Evaluating magnetic biochar (MBC) separation and reusability under flow conditions.
3. Confirming struvite precipitation efficiency and product purity at scale.
4. Assessing AD stability, methane yield, and synergistic process performance.

7.4.2 Design Basis and Configuration

The pilot is designed for 1 ton/d of wet sludge ($\approx 30\text{--}40$ kg VS/d), diluted to 3–4% TS. Major units and specifications are summarised in Table 7.4.

Table 7.4 Summary of major unit operations, nominal capacities, and key operating specifications

Unit operation	Nominal volume	Operating conditions	Key design notes
HT reactor	100–150 L	220 °C; 20 min HRT; 30 bar	Continuous stirred vessel (316L duplex), recirculation loop, auto-quench; designed for $\geq 70\%$ heat recovery via plate exchanger.
Adsorption (MBC)	200 L	pH 6.5 ± 0.2 ; 5 g/L; 35 min HRT	Agitated tank or moving bed with magnetic drum separator for media retrieval.
Struvite crystalliser	150 L	pH 9.2 ± 0.1 ; $\text{MgCl}_2 \cdot \text{H}_2\text{O}$ 10-25 mL/L sludge; 30–45 min HRT	Agitated vessel with a hydrocyclone for product separation, including a rinsing and drying section.
AD reactor	1–2 m ³	35 ± 1 °C; OLR 2.5-3.5 kg VS/m ³ .d; HRT 20-25 d	Mesophilic CSTR with gas holder and CHP or flare skid.

7.4.3 Hydrodynamics and Material Handling

Residence-time distribution (RTD) studies using salt tracers will verify near-plug-flow behaviour ($\theta/\tau \approx 1$). Mixing intensity will be controlled at $P/V > 2$ W/L, and progressive-cavity pumps will manage sludge transfer. Anti-fouling provisions include back-flush strainers before heat exchangers and desludging ports at each unit. Allowable fouling is limited to a < 0.5 bar pressure increase per 24 h.

7.4.4 Instrumentation and Control

Essential measurements include:

- **HT:** temperature, pressure, flow, ΔP across heat exchanger, energy meters, safety interlocks (PSV, burst disc, emergency quench).
- **Process chemistry:** pH (adsorption/struvite), conductivity, SCOD, $\text{NH}_4^+\text{-N}$, $\text{PO}_4^{3-}\text{-P}$, metals (ICP-OES), phenolics.
- **AD:** biogas flow and composition (CH_4/CO_2), VFA/alkalinity ratio, ORP, and pH. All data will be logged at one-minute intervals to enable energy and mass-balance reconciliation.

7.4.5 Performance Indicators and Acceptance Criteria

A “go” decision will be reached if all key performance indicators are met within $\pm 25\%$ of the techno-economic projections; otherwise, design refinement or reagent optimisation will be required (Table 7.5).

Table 7.5 Performance indicators and corresponding acceptance thresholds for process evaluation

Category	Indicator	Target	Criterion
Heat recovery	Sensible heat across the heat exchanger	$\geq 70\%$	Acceptable energy efficiency
Detoxification	Phenolics removal	$\geq 35\%$	Stable adsorption performance
Metal removal	Cu, Ni, Pb $\geq 75\%$; As $\geq 60\%$	Environmental compliance	Environmental compliance
Nutrient recovery	P $\geq 75\%$; NH_4^+ $\geq 30\%$; purity $\geq 65\%$	Fertiliser-grade struvite	Product quality
AD performance	$\geq 60\text{--}70\text{ mL CH}_4/\text{g-VS}$; VFA/alk < 0.4 ; lag $\leq 1.5\text{ d}$	Stable digestion	Process stability
Operational reliability	Heat exchanger fouling rate $< 5\%$ U loss/ week	Maintainability	Operational continuity
Safety	Zero incidents; no over-pressure events	Mandatory	Regulatory compliance

7.4.6 Safety and Compliance

The pilot loop will undergo a full HAZOP review. Safety systems include high-pressure trips with auto-quench, double containment for thermal oil, flame arrestors, and gas detection for the AD unit. All electrical equipment will conform to relevant ATEX/IECEx classifications.

7.4.7 Implementation Timeline

The implementation schedule outlines the sequential activities required for pilot deployment, from design through performance validation. Activities are distributed over twelve months to ensure adequate time for commissioning, optimisation, and data verification before scale-up assessment. Key milestones include cold and hot

commissioning, baseline establishment, and full operational testing under steady-state conditions (Table 7.6).

Table 7.6 Implementation timeline and major activities for pilot-scale system deployment.

Month	Activity
1-2	Detailed design, procurement, and HAZOP.
3-4	Installation, cold commissioning, and control-loop testing.
5-6	Hot commissioning, RTD and fouling baseline establishment.
7-9	90-day continuous operation and parametric testing.
10-12	Data validation, scale-up correlations, and techno-economic/LCA update.

7.4.8 Expected Outcome

The pilot is expected to verify process stability, quantify energy recovery, and confirm that the integrated configuration can operate safely and economically at semi-technical scale. The results will inform design correlations, equipment sizing, and Class 3 cost estimation for full-scale implementation.

7.5 Chapter summary

This chapter delved into integrated HT, adsorption, struvite precipitation, and AD for wastewater management, analysing technical feasibility and economic viability. Four scenarios, from standalone AD to fully integrated processes, were evaluated. The study's uniqueness lies in its pioneering integration of these processes, optimising nutrient recovery, biogas production, and economic returns, with phosphorus transformation tracked throughout the system, an approach not extensively covered in the existing literature. Key findings indicate that HT significantly enhanced sludge biodegradability, methane yield (a 3000% increase), and nutrient recovery. The economic analysis revealed scenario 4 as the most viable, achieving a positive ROI of 45.04% and the highest NPV of approximately \$2.5 billion over a 30-year period. Sensitivity analysis confirmed the economic robustness of integrated approaches, reducing sensitivity to market fluctuations. Despite energy-intensive requirements,

barriers to adoption include high initial capital costs, process complexity, and limited awareness of HT's long-term economic and environmental benefits. However, energy recovery and resource valorisation partially offset these costs. To translate these findings into practical application, a pilot-scale implementation plan was developed to validate the integrated process under real operating conditions. The twelve-month schedule includes detailed design, installation, commissioning, and a 90-day continuous-operation phase to establish steady-state performance and fouling baselines. The pilot programme is designed to bridge laboratory results and full-scale deployment, providing critical insights into process reliability, energy integration, and techno-economic scalability. Successful completion of this phase will inform future design refinements and facilitate industrial-scale adoption of the integrated HT–AD–struvite recovery system. The study demonstrated that integrated systems are both sustainable and profitable within the framework of a circular economy. Further economic improvements are recommended through optimising chemical usage and sourcing cost-effective raw materials.

CHAPTER 8: LIFE CYCLE ASSESSMENT OF INTEGRATED WASTEWATER MANAGEMENT PROCESSES FOR SUSTAINABILITY AND RESOURCE RECOVERY

8.1 Introduction

The transition to sustainable wastewater management practices has garnered considerable attention from scientists, engineers, and industrialists, especially regarding waste-to-energy initiatives that reduce reliance on natural resources and fossil fuels. This study examines the treatment of waste-activated sludge (WAS) using HT to facilitate energy recovery through AD and to recover nutrients as struvite, a slow-release phosphorus-based fertiliser.

Numerous studies have examined hydrothermal treatment or nutrient recovery in isolation; however, limited research has explored the integration of hydrothermal treatment, nutrient recovery, and biogas production alongside a comprehensive LCA to evaluate the environmental impacts of these processes at a system-wide level (Clift 2013). LCA significantly enhances the understanding of these processes by estimating emissions, energy demand, and overall sustainability, thereby providing a holistic perspective often lacking in many studies. LCA enhances the comprehension of these processes by quantifying emissions, energy demand, and sustainability yardsticks, providing consistent, empirically based information for informed decision-making (Mulya *et al.* 2022). This integrated evaluation allows for the analysis of the trade-off between processes and energy consumption in HT, along with the benefits of resource and bioenergy recovery.

8.2 Materials and methods

8.2.1 Life cycle assessment framework

An LCA study was conducted to evaluate the environmental impact of phosphorus recovery through hydrothermal treatment, aiming to identify the method with a minimal environmental footprint. The assessment procedure utilised SimaPro (SimaPro 9.6.0. PRé Consultants, Amersfoort, Netherlands) and adheres to the standards ISO 14040 (Pappas *et al.* 2023) and 14044 (Heijungs *et al.* 2021). Detailed explanations and

analyses are available in Khoshnevisan *et al.* (2020); Paes *et al.* (2020); Rebello *et al.* (2020) as follows:

- a) The **definition of goal and scope** entails establishing preliminary assumptions related to the study's purpose, the functional unit, and the system boundaries.
- b) **Life cycle inventory (LCI)** involves the collection and analysis of all material and energy inputs and outputs that interact with the environment across the entire life cycle of a product or service system. Inputs and emissions are classified as environmental burdens.
- c) **LCIA** entails the evaluation of environmental effects associated with an activity by applying various impact indicators.
- d) **Life cycle interpretation** seeks to identify potential adjustments or modifications to the system that could reduce its environmental impact.

8.2.2 Goal and scope definition of LCA

The current study is hinged on assessing the environmental impact of the valorisation efforts in an integrated approach at a local WWTP. The consequential LCA approach, using SimaPro software, was employed to achieve this goal due to the potential consequences of altering the waste management system on technology and society.

8.2.2.1 Functional unit and system boundaries

In this study, the functional unit was defined as 1 ton of waste-activated sludge (WAS) on a wet basis, with its physicochemical characteristics described in the preceding chapters. A cradle-to-gate life cycle perspective was adopted, encompassing all processes from the generation and reception of WAS to its final treatment and disposal.

The system boundary, illustrated in Figure 8.1, delineates the flow of materials and energy across all major unit operations. These include sludge pumping, resource recovery facilities (RRF), hydrothermal treatment (HT), adsorption, struvite precipitation, anaerobic digestion (AD), and irrigation. The irrigation of agricultural fields marks the endpoint of the system boundary.

All upstream and on-site processes were considered, including chemical reagents, electricity and heat consumption, consumables, and direct process emissions. Infrastructure construction and maintenance were excluded from the assessment.

Downstream fertiliser substitution resulting from struvite recovery was modelled using an avoided burden approach.

To account for multiple outputs, system expansion was employed to allocate environmental credits to co-products such as struvite fertiliser equivalents and electricity or heat exported to the grid. Where product substitution was uncertain, a cut-off approach with sensitivity bounds was applied. No mass or energy allocation was used unless explicitly stated in Table 8.1.

Each unit operation was quantified based on mass and energy input–output flows, with corresponding emission profiles characterised in the life cycle impact assessment (LCIA). The internal transfer of sludge between unit processes was excluded from the life cycle inventory, as it did not contribute additional environmental burdens.

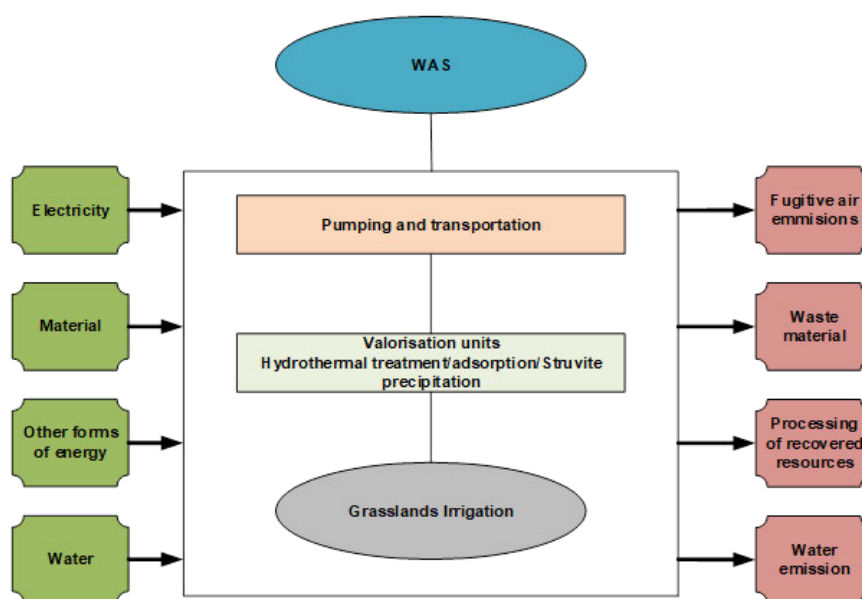


Figure 8.1 System boundary of the base case scenario

The scenario description was well-spelt out under Section 7.2.1. Figure 8.2 outlines the material flow for the four different scenarios used for comparison in this study, and Appendix F presents network diagrams for the scenarios presented in SimaPro software.

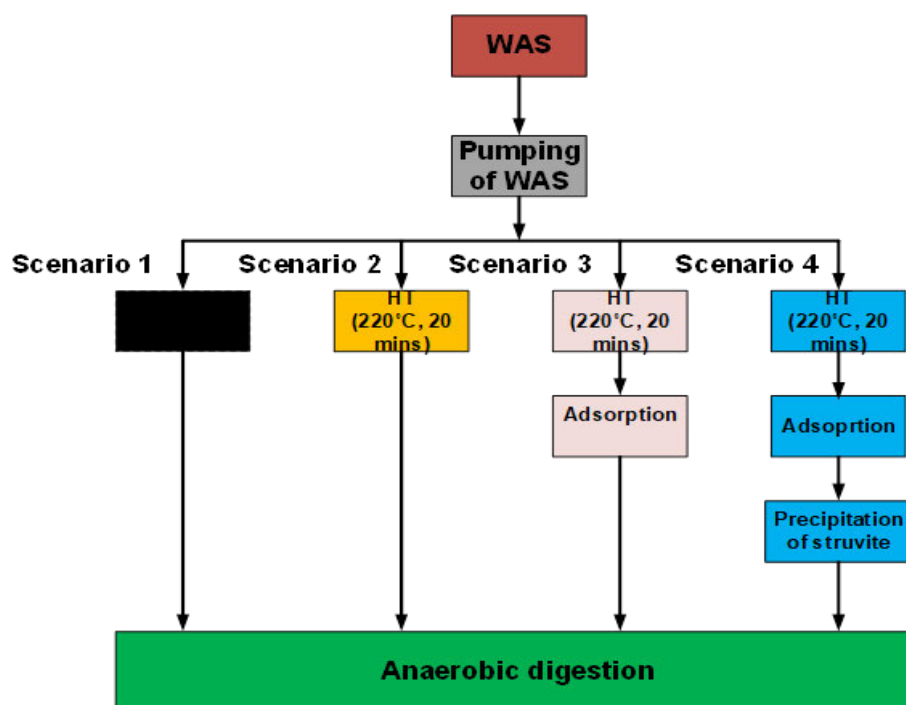


Figure 8.2 Configuration of process scenarios evaluated for wastewater sludge valorisation

8.2.3 Life cycle inventory data collection

This study utilised LCI data that included both background and foreground data. The LCI data were obtained from waste characterisation, experimental procedures involving extrapolation under scaled-up operations, emissions reports from the wastewater treatment plant (WWTP), pertinent literature, and background data concerning the production and processing of materials, chemicals, and energy carriers, which were sourced from the ReCiPe 2016 (Midpoint - H) methodology within the SimaPro software database. The ReCiPe Midpoint (H) method converts LCI results to environmental impact categories (e.g. global warming, eutrophication, human toxicity, etc.) based on the environmental specifications of each emission or resource consumption (characterisation factors). The ReCiPe Midpoint (H) aligns with the research objective of analysing specific environmental burdens relevant to sustainable wastewater management and resource recovery, thereby facilitating replicability (Kakar, Tadesse and Elbeshbishy 2022).

Background processes were modelled in SimaPro using [ecoinvent v3.10] with the system cut-off approach. Regionalisation followed the South Africa profile, where regional data were unavailable; the rest of the world (RoW) datasets were used with sensitivity checks. Bench-scale measurements (materials, energy, yields, and

emissions) were compiled from experimental Sections (Chapters 3-6) and scaled using engineering factors for energy recovery, heat losses, and yields (Table 8.1). Data quality and representativeness were assessed through sensitivity and scenario analyses rather than qualitative pedigree scoring.

All inventory data were normalised to a per-tonne basis of waste. The LCI process entails the systematic identification and quantification of energy and material flows entering and leaving the system boundary. The WWTP in focus processes 100 ML of wastewater daily. Transportation of sludge material is carried out via pumps, while solid materials are conveyed using mechanical systems such as screw conveyors. Additional units for sewage sludge valorisation were designed to be co-located with the existing plant infrastructure or perimeter.

In scenarios 3 and 4, hydrochar recovery was achieved through settling and filtration. In scenario 4, magnetic biochar (MBC) recovery was also incorporated, with the potential for desorption or land application. Water consumption for cooling in the heat exchanger varied across scenarios, with the plant using 0, 85 912.85, and 78 753.44 tonnes annually in scenarios 1, 2, and 4, respectively (scenario 3 mirrored the consumption of scenario 4). Figure 7.2 and Appendix E1 illustrate the material and energy flows of the 4 scenarios. Elemental analysis was utilised to determine the chemical composition of waste-activated sludge (WAS) following hydrothermal treatment, adsorption, and precipitation stages, represented as CHNS/O. These values were instrumental in estimating emissions in conjunction with the Global Protocol for Community-Scale GHG Emissions (GPC) guidelines for biological waste treatment.

In this study, capital equipment, such as construction materials and machinery, was excluded from the inventory analysis. This approach aligns with previous research, which has similarly omitted capital equipment due to its extended service life (Khoshnevisan *et al.* 2020). Furthermore, studies that have incorporated capital equipment into their inventory assessments have consistently concluded that its contribution to the environmental impacts of AD processes and related outputs is negligible (Dastjerdi *et al.* 2021). The foreground data were derived from the bench-scale experiments as described in the preceding chapters. The HHV of spent MBC and residue hydrochar was estimated using the empirical Equation 3.9.

Table 8.1 LCI Data and simulation assumptions

Flow / Process	Foreground/ Background	Source & Citation	Database & Version	System Model	Region	Cut-off/ Boundary Rule	Notes & Uncertainty	Scaling/
WAS at gate (composition, TS/VS)	Foreground	Experimental data (Section 3.7)	–	–	WWTP- specific (Durban)	Functional unit boundary = 1 t WAS (wet basis)	Bench-scale characterisation; ±SD reported for TS, VS, P, N fractions	
HT electricity (kWh)	Foreground Background	to Metered energy balance (Section 3.4)	<i>Ecoinvent</i> v3.10	Cut-off	South Africa grid mix	Included (operational stage)	Sensitivity ±15 % grid emission factor (0.95 kg CO ₂ /kWh)	
HT heat (MJ)	Foreground Background	to Energy balance calc. (Section 3.7)	<i>Ecoinvent</i> v3.10	Cut-off	South Africa	Included	Recovered heat η = 72 % ± 5 %; sensitivity tested ±10 %	
MgCl ₂ production	Background	Ecoinvent dataset: <i>magnesium chloride production, from brine</i> Experimental (Section. 4.3–4.4)	<i>Ecoinvent</i> v3.10	Cut-off	Global	Included	Alternative Mg sources tested in sensitivity analysis (±20 %)	
Magnetic biochar production	Foreground	Experimental (Section. 4.5–4.7)	–	–	Local (SA sugarcane bagasse)	Included	Yield ±SD; transport excluded in base case, included in sensitivity	
Adsorption operation	Foreground	Experimental (Section. 4.5–4.7)	–	–	–	Included	Energy for agitation and magnetic separation included; spent MBC to HT	
Struvite precipitation (chemicals)	Foreground Background	to Experimental (Section 5.2–5.6)	<i>Ecoinvent</i> v3.10	Cut-off	Global	Included	Stoichiometry-based reagent consumption; purity factor 0.69±0.05	
Avoided fertiliser (P, N credits)	Background (avoided)	Ecoinvent datasets: <i>phosphate fertiliser, as P₂O₅; ammonium nitrate</i>	<i>Ecoinvent</i> v3.10	Cut-off	Global	System expansion	Credit bound in sensitivity ±25 % market substitution	
AD electricity/heat export	Foreground Background (avoided)	to Experimental (Section 6.4)	<i>Ecoinvent</i> v3.10	Cut-off	South Africa	System expansion	CHP efficiency η_e = 0.35; η_h = 0.45; displacement of grid power and heat	

8.2.4 Life cycle impact assessment methodology

This study assessed the environmental impacts of waste management systems using key impact categories in SimaPro. The assessed categories encompass GWP, eutrophication potential, ozone depletion potential, terrestrial acidification, toxicity potential, fossil resource scarcity, particulate matter formation, and water consumption. The selected categories are relevant and significant to the wastewater treatment plant under investigation. The characterisation of these impact categories was performed using the LCI results, applying suitable characterisation factors to ensure precise environmental assessment. The sensitivity analysis was performed based on the heating efficiency of the HTR and the seasonal flow variations of the WAS.

8.2.5 Sensitivity and uncertainty analysis

A sensitivity analysis was conducted to examine how various operating parameters affect the environmental impact categories of the scenarios shown in Figure 7.1. For this study, the heating efficiency of the hydrothermal reactor and the WAS flow rates were adjusted within a range of $\pm 10\%$ from baseline values.

The Monte Carlo simulation was conducted with 1,000 iterations in Microsoft Excel 365, using a 95% confidence interval based on ReCiPe 2016 Midpoint-H data for SimaPro software. Log-normal distributions were applied for strictly positive flows (materials/energy), and normal distributions were used for yields. Correlation was applied for linked flows (Table 8.1). This was done to enhance robustness and to identify the most influential parameters for uncertainty. The adopted approach accounts for the variability of input data, stochastic environmental fluctuations, and model assumptions limitations, while improving the reliability of environmental impact estimates (scenario 4 was considered in this analysis for demonstration purposes). Scenario uncertainty (e.g., electricity mix, struvite substitution credit, MgCl_2 sourcing) was explored in a deterministic manner.

8.2.6 Ethical considerations

In conducting this research on nutrient recovery and biogas production from waste-activated sludge (WAS) through HT and AD, several ethical considerations have been addressed to ensure the integrity, transparency, and sustainability of the study.

- **Transparency and reproducibility** - The methodologies employed in this research have been meticulously detailed to ensure replicability and transparency. To prevent ambiguity, all assumptions, such as the ten-year life cycle regulation for physical infrastructure and the exclusion of emissions to soil due to data unavailability, are clearly stated. The limitations of the study are transparently outlined to guide future researchers and prevent misinterpretation while encouraging further exploration of the findings.
- **Data Integrity and usage** - The life cycle impact assessment was conducted using verified data from the SimaPro database, ensuring statistical accuracy throughout. Particular attention was given to maintaining data integrity, ensuring that no significant discrepancies exist. Where assumptions were necessary, such as collection rates across various scenarios, they were grounded in historical data and sound rationale. Data manipulation or selective exclusion of potentially unfavourable results was strictly avoided.
- **Environmental responsibility** - As this study focuses on the environmental and social impact of WAS valorisation, all environmentally relevant consequences of the proposed processes were thoroughly assessed. Although data on emissions to soil are limited, this limitation is clearly acknowledged to ensure that conclusions are drawn within the scope of the available data.
- **Social responsibility and long-term impacts** - The research carefully considered the broader social and economic implications of adopting the proposed sustainable wastewater management techniques. Recognising that changes in waste management practices can impact local communities, the analysis aimed to develop solutions that ensure the long-term sustainability of the local wastewater treatment plant (WWTP) while addressing societal needs.
- **Ethical use of technology** - The application of HT for nutrient recovery and biogas production was evaluated within an ethical framework, considering potential externalities such as material accessibility, energy consumption, and environmental risks. The study ensures that the deployment of these technologies is conducted responsibly, with a clear understanding of their environmental and societal impacts.

8.3 Life cycle assessment results and discussion

The unit operations had their results presented in preceding chapters, and the data were used as input and output to the Technosphere in the LCA. It is crucial to note that the findings presented in this study are influenced by the methodology adopted (ReCiPe 2016 Midpoint-H), the allocation approach, assumptions, functional unit (FU), and the system boundaries established in each scenario.

This study analysed waste management techniques in four distinct scenarios, emphasising the treatment of waste-activated sludge through both traditional and advanced integrated approaches. The initial preparation of input data for the SimaPro software required organising raw primary data in Excel 365, as demonstrated in Appendix F1. This data encompasses various parameters, such as the amounts of waste produced, avoided burdens, and inputs to the Technosphere.

Following this, the outcomes produced by the SimaPro software, encompassing the environmental impacts and assessments of various scenarios, are shown and discussed in subsequent sections. The findings provide a comprehensive overview of the energy usage and emissions impacting soil, air, and water associated with each of the four waste management scenarios. Appendix F2 presents the normalised values, providing a comparative analysis of the environmental impacts associated with each scenario.

8.3.1 Global warming potential (GWP)

Addressing GWP is essential in the context of biogas production, hydrochar combustion, and energy recovery, as these processes are intrinsically linked to GHG emissions. GWP is an essential metric for quantifying emissions, such as CO₂, CH₄, and N₂O, providing a thorough understanding of climate impact across various scenarios.

Figure 8.3 illustrates that scenario 1 had the highest GWP, measuring 6,473,658.88 kg CO₂-eq per FU. Scenarios 3, 4, and 2 followed, contributing 37.4%, 26.6%, and 21.3% of the base case (scenario 1), respectively. Significant contributors to GWP included CO₂ from fossil fuel sources, dinitrogen monoxide (N₂O) produced through microbial processes such as denitrification, thermal degradation of nitrogenous organic matter, and biogenic methane (CH₄) emissions. N₂O is recognised as a highly

potent greenhouse gas, possessing a GWP roughly 298 times that of CO₂ over 100 years (Delre, ten Hoeve and Scheutz 2019; UNFCCC 2024).

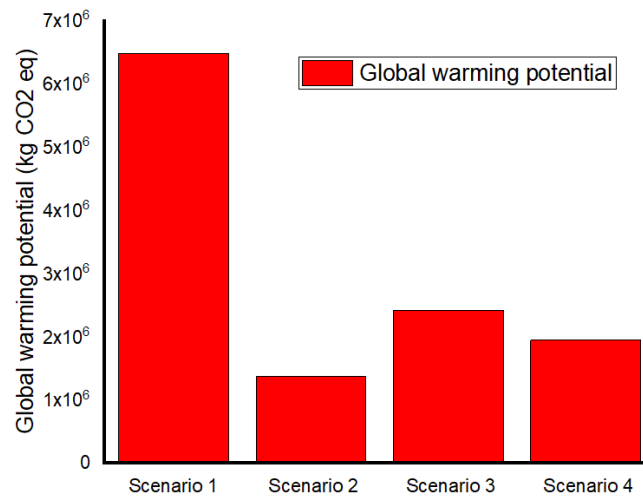


Figure 8.3 Global warming potential (GWP) associated with the four treatment scenarios for waste-activated sludge valorisation

Scenarios 2, 3, and 4 exhibited negative GWP values of -17.7%, -13.1%, and -8.53%, respectively, due to the heat recovered via heat integration. This highlights the significance of heat recovery systems in processing plants, as they reduce energy consumption and substantially mitigate the effects of global warming through reduced emissions.

In all scenarios, digestate was a significant factor in GWP, contributing 62.1%, 38.4%, 31%, and 20.2% in scenarios 1, 2, 3, and 4, respectively. This phenomenon can be attributed to persistent microbial activity following AD, where residual organic matter continues to decompose, resulting in the gradual release of greenhouse gases (Tauber *et al.* 2019). Additionally, not all organic material undergoes complete mineralisation during AD, leading to the gradual decomposition of biodegradable matter and the resultant emissions of greenhouse gases.

This study's observations suggest that HT followed by AD increases biogas yield and decreases the overall carbon footprint by utilising organic-rich sludge produced from HT, consistent with the findings of Ogunleye, Flora and Berge (2024). This synergy is essential in regions pursuing circular economy practices, as it optimises resource efficiency.

8.3.2 Eutrophication potential (EP)

WWTPs are significant reservoirs of N and P compounds, making nutrient recovery a critical element in valorisation strategies. In this study, the recovery of nutrients, specifically in the form of struvite, plays a pivotal role. The impact assessment focuses on the potential for nutrient runoff, which contributes to both freshwater eutrophication (FEP) and marine eutrophication (MEP), phenomena that destabilise aquatic ecosystems and degrade water quality. FEP refers to the enrichment of freshwater bodies, such as lakes and rivers, primarily driven by phosphorus, while MEP is more pronounced in seas, oceans, and coastal waters, where nitrogen pollution predominates.

The results presented in Figure 8.4 illustrate the LCI results for both eutrophication categories. Scenario 1 exhibited the highest eutrophication impact, with FEP reported at 289 kg P eq and MEP at 276 kg N eq. In comparison, scenario 2 showed reductions in FEP by 27.2% and MEP by 17.6%; scenario 3 exhibited decreases of 39.6% and 30.5%, and scenario 4 recorded reductions of 28.7% in FEP and 22.9% in MEP. These percentages are relative to the absolute values observed in scenario 1.

A clear trend emerges, indicating the implementation of valorisation strategies. N and P compounds become more available for biological uptake or chemical extraction via adsorption (as seen in scenario 3) and precipitation (scenario 4). This contrasts with scenario 1, where nutrient recovery was absent.

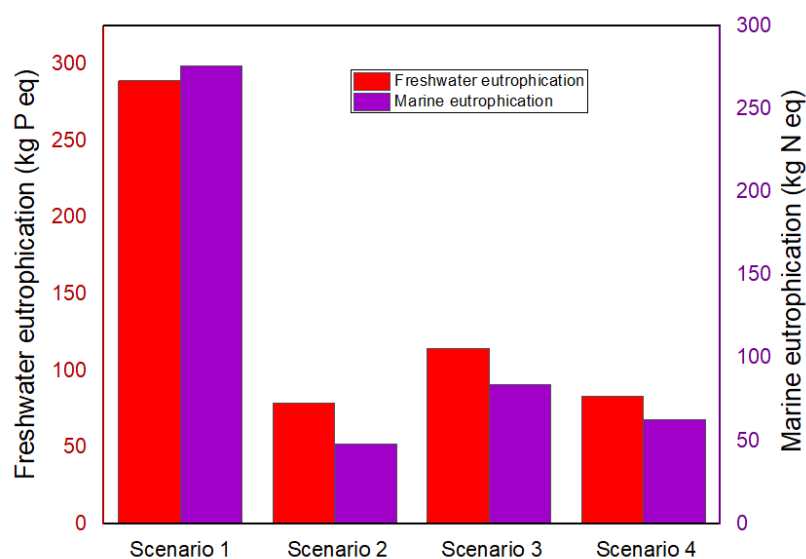


Figure 8.4 Eutrophication potential associated with the four treatment scenarios for waste-activated sludge valorisation

Notably, the COD and BOD₅ contributions to FEP are particularly noteworthy. Scenario 1 exhibited the highest COD (17.2%) and BOD₅ (9.2%) values, while scenario 2 saw a reduction to 10.3% COD and 4.65% BOD₅. Scenario 3 recorded similar reductions (10.3% COD, 4.6% BOD₅), and scenario 4 demonstrated the lowest impacts, with 8.53% COD and 3.46% BOD₅. Elevated levels of COD and BOD₅ intensify eutrophication by supplying organic matter that fosters microbial growth, subsequently leading to oxygen depletion in aquatic environments.

With respect to MEP, nitrate (NO₃⁻) and atmospheric nitrogen deposition played a significant role. In scenario 1, nitrate contributed 61.1% to MEP, while nitrogen deposition accounted for 36.6%. In scenario 4, nitrate contributions rose to 82.1%, while nitrogen deposition decreased to 17.9%. The higher nitrate contribution in scenario 4 can be attributed to the precipitation process, which increases the solubility of N compounds, thereby enhancing nitrate runoff. This shift is further exacerbated by a preference for phosphorus recovery, with relatively lower efforts directed towards nitrogen reclamation in favour of phosphorus recovery.

8.3.3 Ozone depletion and formation potential

The Stratospheric Ozone Depletion Potential (SODP) evaluates the depletion of the stratospheric ozone layer, which is primarily driven by the emission of GHGs. This depletion allows a greater proportion of harmful UV-B radiation from the sun to reach the Earth's surface, leading to adverse environmental and health effects. Ozone formation, impacting both human health (OFHH) and terrestrial ecosystems (OFTE), arises from complex chemical interactions between nitrogen oxides (NO_x) and volatile organic compounds (VOCs) under the influence of heat and sunlight. Ozone, as a secondary pollutant, poses significant health risks, particularly to the respiratory system. It induces inflammation and irritation in the respiratory tract, exacerbating conditions such as asthma and causing symptoms like coughing and chest tightness. From an ecological perspective, OFTE disrupts biodiversity, negatively affecting the natural balance of ecosystems.

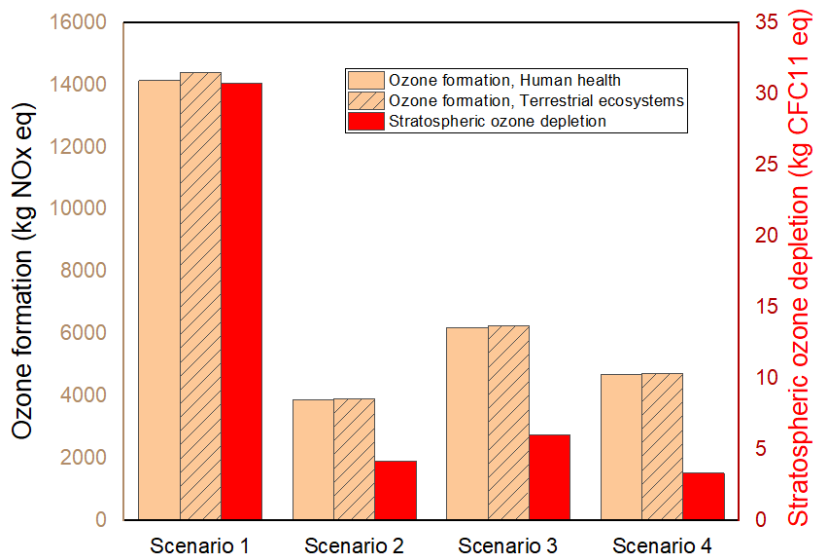


Figure 8.5 Ozone depletion and formation potential associated with the four treatment scenarios for waste-activated sludge valorisation

As demonstrated in Figure 8.5 in scenario 1, the emissions related to OFHH, OFTE and SODP were 14,153 kg NOx eq, 14,410 kg NOx eq, and 31 kg CFC-11 eq, respectively. By contrast, the relative reductions in these impacts for scenarios 2, 3, and 4 were: Scenario 2 (OFHH – 27.5%, OFTE – 27.2%, SODP – 13.6%); scenario 3 (OFHH – 43.9%, OFTE – 43.5%, SODP – 19.7%); and scenario 4 (OFHH – 46.5%, OFTE – 32.9%, SODP – 10.9%). These reductions are expressed as percentages relative to the absolute values recorded for scenario 1 and indicate improved environmental performance, with scenario 4 achieving the most substantial decrease in emissions.

The highest impact observed in scenario 1 was attributed primarily to the absence of hydrothermal (HT) treatment and adsorption processes, resulting in higher emissions of pollutants such as NOx and VOCs due to incomplete degradation of organic material. Dinitrogen monoxide (N₂O) was the predominant contributor to SODP in all scenarios, accounting for more than 99.9% of the impact. Other compounds, including 1,1,2-trichloro-1,2,2-trifluoromethane, 2-chloro-1,1,1,2-tetrafluoromethane, chlorinated hydrocarbons, bromomethane, bromochlorodifluoromethane, bromotrifluoromethane, and chlorodifluoromethane, contributed less than 0.1% combined in each scenario (Appendix F4). These trace substances remain significant

in discussions on ozone recovery and climate change, as their potential to damage the ozone layer varies according to their chemical properties (Bernhard *et al.* 2020).

Scenarios 2 and 4 were identified as the least impactful in terms of ozone depletion potential, though with minor variations, as demonstrated in Figure 8.5. This is largely due to the role of HT treatment in reducing emissions of NO_x and VOCs, which are key precursors to both ozone formation and stratospheric ozone depletion.

8.3.4 Terrestrial acidification

In addressing the environmental impacts of the processes under investigation, it is crucial to evaluate terrestrial acidification (TAc), particularly as a significant by-product of biogas and hydrochar combustion, as well as nutrient recovery. These processes release key pollutants such as nitrogen oxides (NO_x) and sulphur dioxide (SO₂), which are known precursors to acid rain. TAc specifically affects terrestrial ecosystems, causing soil acidification and damaging vegetation (Yadav *et al.* 2020). It is essential to distinguish TAc as a subset of the broader acidification potential (AP), which considers the impact on both terrestrial and aquatic ecosystems, whereas TA narrows the focus to land-based effects.

As illustrated in Figure 8.6, scenario 1 recorded the highest TAc at 18,408 kg SO₂ eq, followed by scenario 3 (10,286 kg SO₂ eq), scenario 4 (7,899 kg SO₂ eq), and scenario 2 (6,577 kg SO₂ eq). The high TAc values in scenario 1 can be attributed to the direct AD of waste-activated sludge without HT, leading to elevated emissions of both NO_x (26.9%) and SO₂ (71.9%). In contrast, scenario 2, which applies HT without resource recovery, shows a 64.3% reduction in TA compared to scenario 1. The lower emissions in scenario 2 highlight the benefits of HT in reducing pollutant release by altering the properties of sludge (Zhang *et al.* 2020d).

Scenarios 3 and 4, which incorporate toxin removal via adsorption and precipitation processes, exhibit intermediate TAc levels, largely due to the partial recovery of toxins by biochar and struvite, which offset some emissions. The decreased TAc in these scenarios is due to the reduced concentrations of NO_x and SO₂ emissions, as toxin removal processes trap harmful elements before combustion (Kapoor, Sharma and Shah 2022; Han *et al.* 2024). These findings underscore the importance of optimising HT and resource recovery processes to mitigate terrestrial acidification, supporting a more sustainable wastewater management strategy. In this context, the potential of a

pollutant to cause acidification is assessed based on its ability to generate H^+ ions; however, the degree of actual acidification can vary depending on the specific locations where these pollutants are deposited.

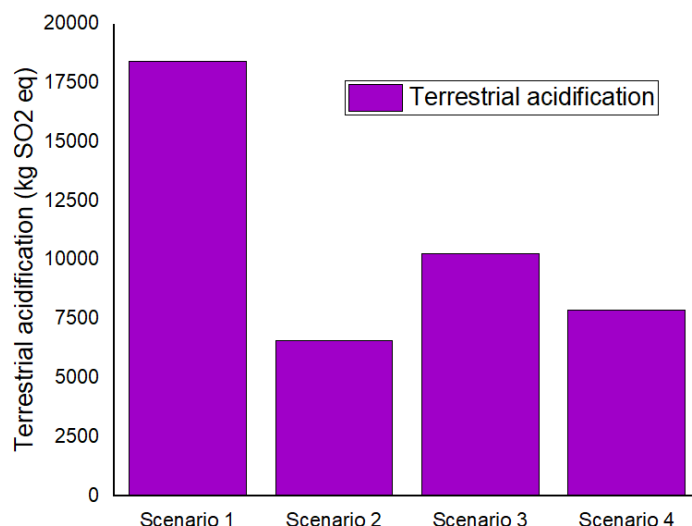


Figure 8.6 Terrestrial acidification associated with the four treatment scenarios for waste-activated sludge valorisation

8.3.5 Toxicity potential

In this Section, we examine the toxicity impacts across various environmental compartments, focusing on Terrestrial (TE), Freshwater (FE), Marine (ME), Human Carcinogenic (HCT), and Human Non-carcinogenic Toxicity (HnCT). These categories encompass the harmful effects of toxic materials discharged into ecosystems, land, freshwater, and marine environments, as well as the impact on human health via both carcinogenic and non-carcinogenic pathways. Such toxic discharges are critical contributors to biodiversity loss and species extinction.

The LCI results depicted in Figure 8.7 highlight significant environmental burdens, with scenario 1 showing the following absolute values: TE - 38 472 716, FE - 8 382, ME - 41 085, HCT - 42 512, and HnCT - 719 778 kg 1,4-DCB eq. Expressed as percentages of these baseline values, scenario 2 presents a marked reduction (TE - 16.1%, FE - 16.8%, ME - 16.3%, HCT - 15%, HnCT - 18.1%). Scenario 3 exhibits even further improvement (TE - 28.2%, FE - 24.3%, ME - 27.9%, HCT - 22.1%, HnCT - 30.2%), while scenario 4 achieves a more substantial decrease in impacts (TE - 21.5%, FE - 15.6%, ME - 20.4%, HCT - 13%, HnCT - 22.3%). These trends emphasise the success

of such strategies in mitigating environmental impacts, suggesting that through process optimisation, there is the potential for sustainable improvements.

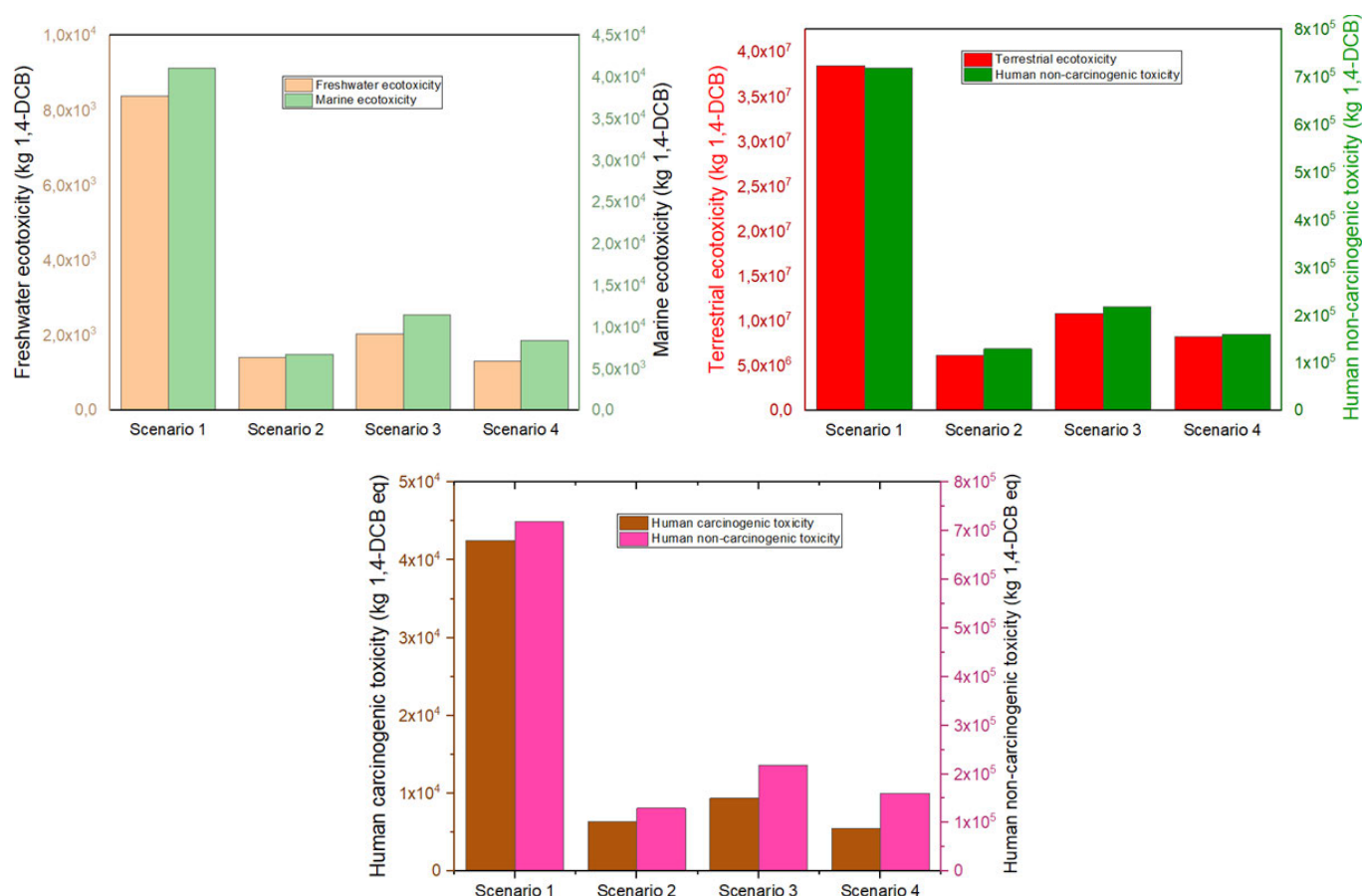


Figure 8.7 Toxicity potential associated with the four treatment scenarios for waste-activated sludge valorisation

These trends suggest that the progressive introduction of resource recovery processes in scenarios 3 and 4, particularly the adsorption and precipitation stages, plays a crucial role in reducing environmental toxicity. For instance, TE, primarily driven by emissions of cobalt and copper, decreases significantly (Appendix F4). Scenario 1 records Co and Cu emissions at 77.2% and 12.6%, respectively, but scenario 4 reduces these figures to 63% (Co) and 20.6% (Cu), underscoring the effectiveness of the enhanced treatment processes.

Likewise, FE and ME exhibit similar declines, particularly in relation to critical toxicants such as 2-methyl-4-chlorophenol and Cr(VI). Scenario 1's high contribution of 2-methyl-4-chlorophenol (51.2%) to FE drops sharply to 10.8% in scenario 4, illustrating the efficacy of adsorption in reducing pollutants from the sludge. Furthermore, HCT

shows a consistent reduction in Cr (VI) contributions, which decreases from 87.8% in scenario 1 to 81.1% in scenario 4. Cr(VI) is highly toxic to aquatic life, causing oxidative stress, DNA damage, and disruption of metabolic processes (Essien *et al.* 2022).

HnCT also improves, with a notable reduction in arsenic (As) and zinc (Zn) contributions. In scenario 1, arsenic accounts for 59.7% of HnCT, whereas in scenario 4, this percentage is reduced to 37.7%. This reduction is primarily due to the advanced adsorption and precipitation techniques employed in scenarios 3 and 4, which effectively mitigate the environmental release of hazardous elements, such as arsenic and zinc (Saravanan *et al.* 2021). These improvements not only minimise ecosystem damage but also present a more sustainable approach to sludge management.

Integrating adsorption phases, often employing magnetic biochar, helps mitigate the release of toxins such as heavy metals and phenolic compounds from wastewater. This study has demonstrated a degree of removal of these toxins, effectively reducing their ecotoxicity potential in downstream applications. This integration not only protects ecosystems but also reduces the impact of secondary pollution.

8.3.6 Fossil resource scarcity (FRS)

FRS measures the depletion of non-renewable energy sources such as coal, natural gas, and crude oil. It quantifies the environmental burden associated with fossil fuel extraction and consumption, where higher values indicate greater reliance on these resources. In this study, hard coal, natural gas (NPG), and crude oil were the primary contributors.

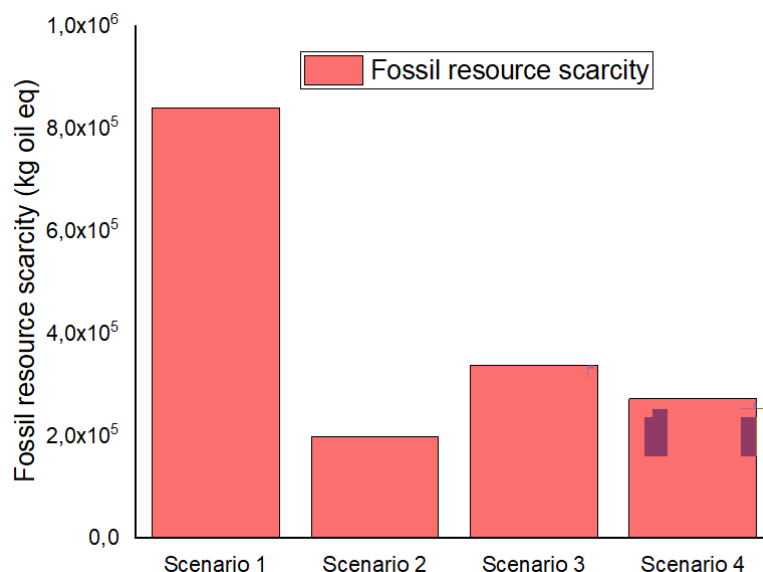


Figure 8.8 Fossil Resource Scarcity associated with the four treatment scenarios for waste-activated sludge valorisation

As shown in Figure 8.8, the LCI results indicate a significant reduction in fossil resource scarcity with the introduction of more advanced resource recovery processes. Scenario 1, the baseline case without HT, exhibits the highest impact at 839,099 kg of oil equivalent, driven by significant coal (55.9%) and crude oil (26.5%) usage. Scenario 2, although applying HT, exhibits inefficiencies, with a 94.4% reliance on coal due to high electricity demands in HT and no resource recovery, resulting in a reduced yet still significant impact of 197,260 kg of oil equivalent.

With the introduction of adsorption and biochar reuse in scenario 3, fossil resource consumption decreases to 338,279 kg of oil equivalent, where coal remains the major contributor (85.1%). Scenario 4, which integrates adsorption, precipitation, and struvite recovery, further reduces the impact to 272,367 kg of oil equivalent, demonstrating the benefits of hydrochar recovery as an energy source. The increasing contribution of crude oil in scenarios 3 and 4 (19.1% and 20.4%, respectively) indicates a shift in the energy mix. Negative NPG values in scenarios 2, 3, and 4 reflect enhanced biogas production, reducing external energy needs. These findings are consistent with studies that highlight the environmental benefits of resource recovery in wastewater treatment (Wu *et al.* 2021; Cavali *et al.* 2022).

8.3.7 Particulate matter formation (PMF)

PMF is a critical environmental impact category, representing the change in ambient $\text{PM}^{2.5}$ concentrations resulting from the emission of specific precursors, such as NH_3 , NO_x , and SO_2 , as well as primary $\text{PM}^{2.5}$. Exposure to fine particulates has significant adverse health effects, ranging from minor irritations to severe respiratory diseases like asthma and, in extreme cases, death (Sharma *et al.* 2024; Yadav *et al.* 2024).

The results from this study, as presented in Figure 8.9, indicate that scenario 1, which involves AD without HT, has the highest PMF at 6,333 kg $\text{PM}^{2.5}$ eq. This is primarily due to the significant contribution of SO_2 (60.6%), NO_x (23.8%), and $\text{PM}^{2.5}$ (15.1%) (Appendix F). Scenario 2, which introduces HT but lacks resource recovery, shows a substantial reduction to 2,061 kg $\text{PM}^{2.5}$ eq, driven by a higher SO_2 contribution (71.6%), reflecting the inefficiency of HT alone without further valorisation. The absence of resource recovery in scenario 2 limits secondary emissions typically associated with material reuse, thus lowering the PMF emissions.

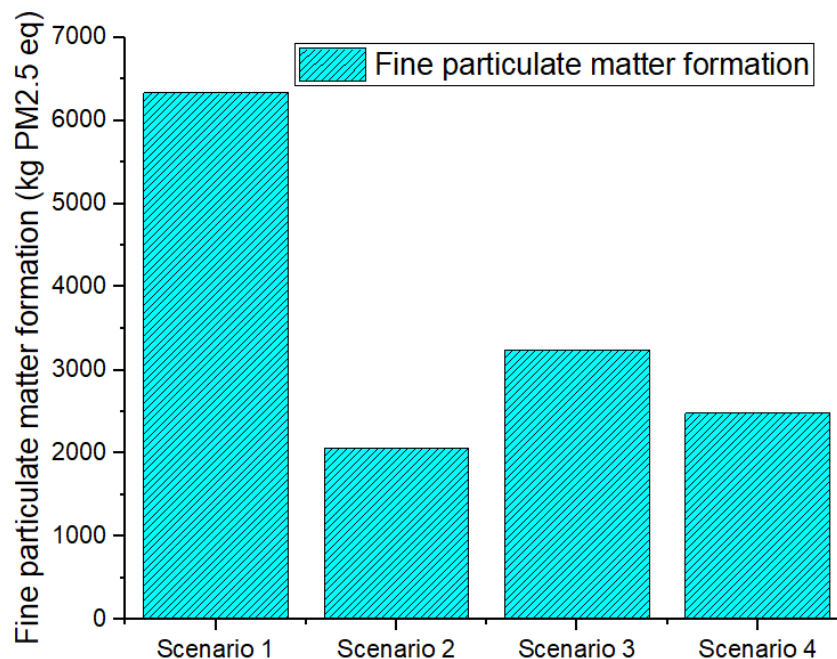


Figure 8.9 Fine particulate formation associated with the four treatment scenarios for waste-activated sludge valorisation

Scenarios 3 and 4, which incorporate the reuse of biochar and hydrochar recovery, further reduce the PMF to 3,238 and 2,481 kg $\text{PM}^{2.5}$ equivalent, respectively. The combustion of hydrochar in these scenarios contributes significantly to SO_2 and NO_x

emissions, which form secondary PM^{2.5} through atmospheric reactions (Xie *et al.* 2019).

Proper post-combustion controls, such as electrostatic precipitators or catalytic converters, are crucial in mitigating this impact. Despite the formation of PM^{2.5}, the overall environmental and economic benefits from resource recovery, particularly in scenarios 3 and 4, support the integration of these processes for sustainable wastewater management.

8.3.8 Water consumption

Water consumption or depletion denotes the utilisation of freshwater resources, whether through direct use or contamination, in relation to the rate at which these resources can be renewed. The water scarcity footprint serves as a method for assessing human impacts on regional water scarcity, considering both local and distant effects throughout global supply chains (Schomberg, Bringezu and Flörke 2021). This underscores the impact of human activities on freshwater resources and ecosystems.

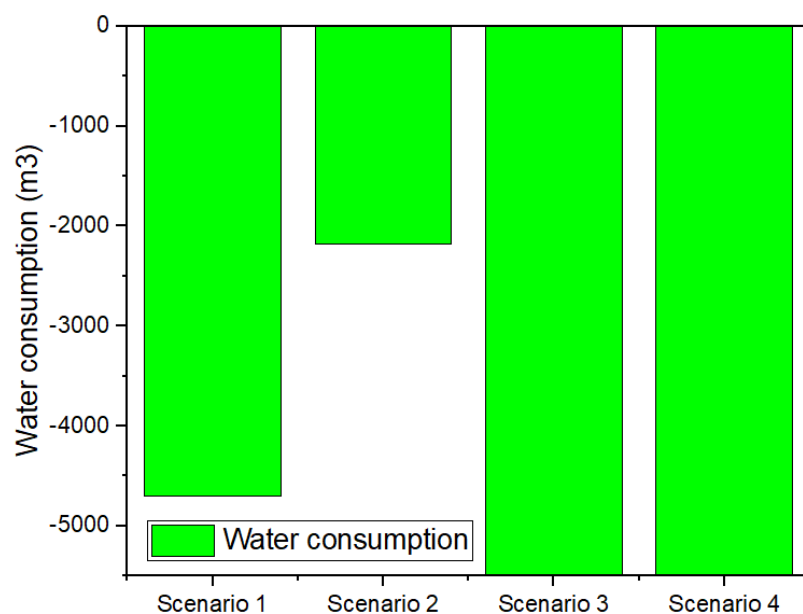


Figure 8.10 Water consumption associated with the four treatment scenarios for waste-activated sludge valorisation

This study indicates that the water depletion metric exhibits negative values in all scenarios, as demonstrated in Figure 8.10. The negative values signify water savings,

primarily attributed to decreased water consumption resulting from heat recovery in the upstream HT process. Scenarios 3 and 4 demonstrate the highest water savings, with reductions of 5,624 m³ and 5,817 m³, respectively. The residual heat from HT is responsible for minimising the requirement for external water to sustain the anaerobic digester's temperature, thereby enhancing overall process efficiency (Zhang *et al.* 2024).

The anomaly noted in scenarios 1 and 2, characterised by reduced water savings, may be attributed to the lack of heat recovery in scenario 1 and the inefficiencies present in scenario 2, which lacks resource recovery measures. Although evaporation may play a minor role, the primary factor in water savings is the effective heat integration from HT, which decreases freshwater consumption in relation to its renewability rate. This efficiency highlights the importance of incorporating resource recovery processes in sustainable wastewater treatment.

8.4 Sensitivity analysis

Sensitivity analysis is crucial in life cycle assessments to evaluate the robustness of results in response to variations in critical variables, including energy recovery rates and sludge composition. This study focused the sensitivity analysis on scenario 4, which embodies the most extensive valorisation effort by incorporating nutrient recovery, heat recovery, and biogas production. Sensitivity analysis is a critical component of LCA, as it assesses the reliability of results and identifies the variables that have the greatest influence on environmental impacts (Bamber *et al.* 2020; Moni *et al.* 2020). The analysis assessed GWP and water consumption as representative impact categories by varying key operational parameters by $\pm 10\%$ from baseline values. The parameters included heating efficiency during hydrothermal treatment and the flow rate of the waste-activated sludge.

Figure 8.11 illustrates that a 10% decrease in the heating efficiency of the hydrothermal reactor has a significant impact on the GWP, resulting in a 4.6% increase from the baseline GWP of 1,945,219.75 kg CO₂-eq. This reduction resulted in a 3.1% decrease in total water consumption (base case: -5,816.79 m³). A 10% increase in heating efficiency in the HTR resulted in a 3.8% decrease in GWP and a 2.5% decrease in water consumption (Appendix F5).

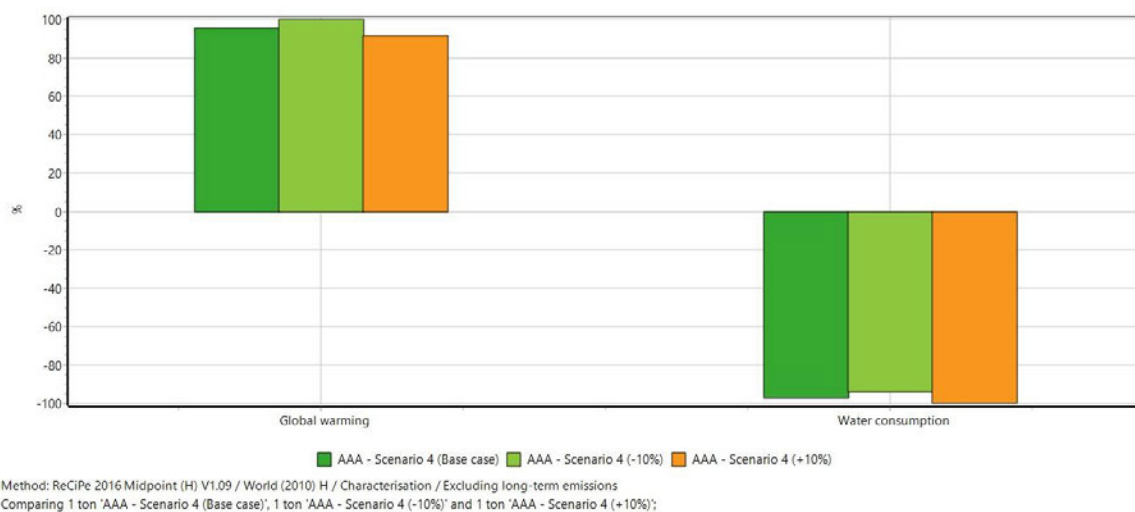


Figure 8.11 Sensitivity analysis showing the effect of heating efficiency variations in the hydrothermal reactor on global warming potential and water consumption

The findings indicate that moderate fluctuations in the heating efficiency of the HTR can lead to alterations in the impact categories, specifically GWP and water consumption, due to their significant dependence on variations in thermal input. Enhanced heating efficiency reduces environmental impacts, aligning with sustainable design goals in wastewater treatment systems, where energy efficiency and minimised resource use are critical. Enhancing the effectiveness of thermal processes decreases greenhouse gas emissions, supporting carbon neutrality goals within the wastewater treatment sector (Sacchi *et al.* 2022).

The quantity of influent waste-activated sludge is influenced by seasonal and operational factors, subsequently impacting environmental effects. Figure 8.12 illustrates that a 10% reduction in sludge flow rate led to a 3.9% decrease in GWP and a 5.7% decrease in water consumption, indicating significant resource savings. A 10% increase in the flow rate resulted in a 4% increase in the GWP and a 5.6% increase in water consumption.

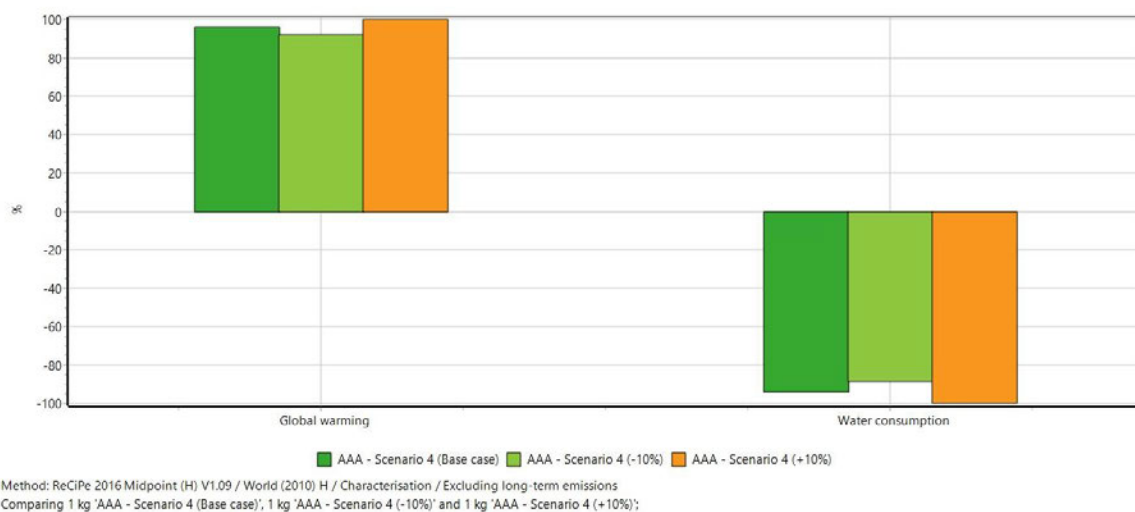


Figure 8.12 Waste-activated sludge flow rate alteration in sensitivity analysis.

The results demonstrate the significant sensitivity of system performance and environmental impacts, such as GWP and water use, to variations in sludge flow rates. Seasonal flow variability is identified as a critical factor in waste management (Comber, Gardner and Ellor 2020; Rashid and Liu 2020). Regulating flow rates through reservoir lagoons in relation to operational capacity can enhance the efficiency of all unit operations, thereby improving both environmental and economic performance (Calabrò, Pangallo and Zema 2024).

8.5 Uncertainty analysis

When using LCA, the identified impacts are subject to various sources of uncertainty, including assumptions made, system boundaries chosen, data quality, and the impact assessment methodology employed, among others (Corcelli *et al.* 2018; Marrucci *et al.* 2022). Hence, to make informed decisions using LCA results, decision-makers must understand the extent to which uncertainty influences the results. These uncertainty sources are always statistically evaluated using methods such as Monte Carlo analysis (Alcazar-Ruiz *et al.* 2022). Thus, stakeholders can make informed, risk-adjusted decisions and improve confidence in adopting new technologies or operating methods. Some interpretations arising from Monte Carlo results pertaining to different impact categories, as shown in Table 8.2, were discussed. The mean GWP value was 1,941,647 kg CO₂-eq, with a standard deviation (SD) of 102,268.8 kg CO₂-eq that translated into a C.V. of 5.27%. CV values below 10 % are considered to define a

system with high precision (Coleman and Steele 2018). This relatively low C.V. implies that even though variation does occur, GWP outcomes are reasonably constant under different simulated conditions. The SEM is 3 234.02 (low relative to its corresponding mean, <0.3), indicating a high degree of precision within the confidence interval (Giuliana *et al.* 2024). In the case of stratospheric ozone depletion, the mean is 3.36 kg CFC-11 Equiv, with minimal variation (SD = 0.18, CV = 5.25%). This low C.V. makes the reliability of the simulation model evident in forecasting the impacts of ozone in varying situations. Freshwater and marine eutrophication, with mean scores of 82.82 kg P-eq and 63.13 kg N-eq, respectively, both demonstrated controlled variability (CV $< 5\%$). The reproducibility of these results suggests that nutrient recovery performance is stable, a crucial factor in mitigating the impact of eutrophication on aquatic ecosystems.

Similarly, freshwater ecotoxicity (mean = 1,311.6 kg 1,4-DCB-eq) had a C.V. of 4.95%, further affirming the consistency of the bioremediation strategies that were utilised. An average scarcity of the fossil resources was 273,090.99 kg oil eq with a C.V. of 4.77%, reflecting the uncertainty of energy needed and the fossil resource used, signifying the reliability of the results. Reductions of PMF outcomes (mean = 4,746.92 kg PM^{2.5}-eq) were characterised by low C.V. (4.94%) and, thus, higher reliability of pollution control strategies. The water consumption metric, which recorded an average saving of 5,825.60 m³, had a C.V. of 5.06%, which signified moderate stability of water recovery efficiency through heat integration and recycling.

Monte Carlo analysis indicates that grid electricity intensity, heat recovery efficiency, and MgCl₂ production dominate the variance across GWP and toxicity-related categories. Median results are robust to distributional assumptions; widening the priors by $\pm 25\%$ increases the 95% CI widths by less than 10%, without altering the scenario rankings. Scenario 4 remains favourable under worst-case bounds (low heat recovery, high MgCl₂ burden), though benefits narrow, underscoring the importance of energy integration and reagent sourcing in full-scale design.

Table 8.2 Uncertainty analysis through Monte Carlo simulation related to the functional unit

Impact Category	Unit	Mean Standard	Median	Max	Min	SD	Coefficient of Variation (C.V.)	Error of the Mean (SEM)
Global warming	kg CO ₂ eq	1941647.09	1941246.29	2373408.14	1617577.28	102268.80	5.27%	3234.021
Stratospheric ozone depletion	kg CFC11 eq	3.36	3.36	3.95	2.84	0.18	5.25%	0.0056
Ozone formation, Human health	kg NOx eq	4688.94	4691.49	5448.18	4041.34	228.14	4.87%	7.21
Ozone formation, Terrestrial ecosystems	kg NOx eq	4729.70	4722.86	5427.05	3998.54	237.51	5.02%	7.51
Fine particulate matter formation	kg PM ^{2.5} eq	4746.92	4740.43	5375.35	4028.06	234.59	4.94%	7.42
Terrestrial acidification	kg SO ₂ eq	7904.06	7908.67	9225.75	6677.44	405.89	5.14%	12.84
Freshwater eutrophication	kg P eq	82.82	82.89	94.73	66.54	4.14	5.00%	0.13
Marine eutrophication	kg N eq	63.13	63.20	72.94	52.33	3.09	4.90%	0.098
Freshwater ecotoxicity	kg 1,4-DCB	1311.60	1310.19	1503.95	1125.62	64.904	4.95%	2.05
Human carcinogenic toxicity	kg 1,4-DCB	5515.58	5525.09	6276.49	4735.49	264.09	4.79%	8.35
Fossil resource scarcity	kg oil eq	273090.99	273232.04	315771.26	236626.57	13036.75	4.77%	412.26
Water saving	m ³	5825.60	5818.82	7005.60	4985.50	294.82	5.06%	9.32

8.6 Chapter summary

This chapter presented a comprehensive LCA of the environmental performance of an integrated wastewater management process, with HT as the focal point alongside adsorption, precipitation, and AD. HT-related results were prioritised, revealing their significant contribution to GWP due to their high energy demand. However, when integrated with adsorption and precipitation, nutrient-related impacts were substantially reduced through enhanced recovery. AD emerged as the most sustainable component, generating renewable energy and mitigating fossil fuel dependency.

Compared to standalone processes, integrated systems demonstrated a lower overall global environmental impact, reinforcing the benefits of a circular economy. This aligns with, and in some cases exceeds, findings from existing literature, confirming HT's potential as a transformative technology. Sensitivity analyses highlighted the influence of energy sources and chemical consumption on environmental performance. Consequently, recommendations focused on improving HT's energy efficiency and optimising chemical inputs to enhance the sustainability of integrated wastewater treatment processes.

CHAPTER 9: CONCLUSION AND RECOMMENDATIONS

9.1 Introduction

This study aimed to develop and optimise an integrated process for the valorisation of waste-activated sludge (WAS) from local WWTPs for harnessing and recovery of energy and critical resources, specifically phosphorus, through struvite while addressing environmental and operational challenges. The specific objectives were the characterisation of various sludge streams for their resource and energy potential, optimisation of the HT process, and evaluation of the use of biochar for toxin removal and struvite precipitation to recover phosphorus, thereby evaluating the WAS resource and energy potential. Furthermore, it evaluated the effect of HT on biogas production by AD with integrated energy production and conducted a technoeconomic assessment to examine the feasibility, sustainability and LCA of the proposed process options.

HT, adsorption, precipitation, and AD integration provide a transformative approach to sustainable wastewater management. This integrated system enables the feedstock conversion of WAS to valuable bioresources and energy, addressing key global challenges, including the depletion of natural phosphate reserves, increasing energy demands and minimising the impacts of environmental effects, particularly eutrophication. This holistic strategy is not only waste-reducing but also offers eco-friendly alternatives to synthetic fertilisers and fossil fuels, fostering a conducive environment for the circular economy.

The novelty of this research lies in its comprehensive focus on tracing the behaviour of phosphorus throughout the production line, from hydrothermal solubilisation to recovery as struvite. Unlike conventional approaches that address individual aspects of wastewater treatment, this study offers an integrated framework that aligns with sustainability goals. By advancing resource-efficient and environmentally sound sludge management, the research contributes to the evolving paradigm of WWTPs as resource recovery hubs rather than mere waste disposal facilities.

9.2 Summary of key findings

9.2.1 *Key findings to objective 1*

The comprehensive characterisation of waste-activated sludge was conducted for the local WWTP, which underscores its substantial potential as a resource for nutrient recovery and bioenergy generation.

WAS exhibited water-soluble phosphorus content of approximately 0.399 mg-P/g and 0.715 mg-P/g dry weight after HT, significantly enhancing the solubility of nutrients. Post-treatment ammonium concentration increased from 10.03 mg/L to 151.6 mg/L, and orthophosphate concentration rose from 64.04 to 172.8 mg/L, supporting nutrient recovery applications such as struvite production.

HT led to a dramatic increase in solubilised organic matter, with soluble COD rising from 284 mg/L to 3,161 mg/L and TOC increasing from 253 mg/L to 2,095 mg/L. Enhanced biodegradability was evidenced by an increase in BOD to 1205 mg/L from 461 mg/L, indicating improved potential for biogas production.

HT improved the macromolecular composition (carbohydrate and protein solubilisation), with carbohydrates increasing from 774 mg/L to 2,692 mg/L and proteins from 1,036 mg/L to 9,101 mg/L. These transformations enhance microbial digestibility, promoting efficient energy recovery.

Although HT enhances resource recovery, it also elevates phenolic compounds from 59.8 mg/L to 119.4 mg/L, necessitating detoxification measures. Heavy metal concentrations were largely within acceptable regulatory limits, ensuring compliance with environmental standards.

HT improved sludge handling properties, including increased bulk density (from 995 to 1044 kg/m³) and fixed solids content, indicating better logistical feasibility for industrial-scale applications.

9.2.2 Key findings to objective 2

The optimisation of HT parameters demonstrated significant advancements in nutrient solubilisation and organic matter biodegradability, paving the way for enhanced resource recovery and energy production from WAS.

The study identified 220°C for 20 min as the optimal conditions for HT, maximising solubilisation efficiency and minimising process energy demands. These parameters resulted in significant improvements in SCOD, ammonium, phosphate, protein, and carbohydrate concentrations.

Under optimal conditions, SCOD increased to 7,951 mg/L, ammonium concentrations reached 175 mg/L, and phosphate concentrations were recorded at 174 mg/L. Proteins and carbohydrates exhibited substantial solubilisation, reaching 11,107 mg/L and 3,408 mg/L, respectively.

HT reduced sludge volume by more than 11%, improving handling and transportation efficiency and contributing to cost-effective sludge management.

There was a marked enhancement in SCOD and organic solubilisation, which improved biogas potential based on the CHNO/S calculations, supporting energy-neutral or energy-positive wastewater treatment operations.

The optimised HT parameters align well with downstream nutrient recovery methods such as struvite precipitation, ensuring sustainable phosphorus recovery for agricultural use. The concentration of soluble phosphates and ammonium was reported to increase, thereby increasing the potential for nutrient recovery.

The HT process generates by-products, such as phenolics, which require post-treatment to mitigate environmental impacts. Nevertheless, heavy metal concentrations remained within acceptable regulatory limits, ensuring compliance and safe application.

9.2.3 Key findings to objective 3

The study demonstrated the effectiveness of biochar in the form of magnetic biochar in mitigating toxins generated during HT, ensuring the compatibility of the effluent for downstream processes.

Magnetic biochar produced from biochar pyrolysed at an optimal temperature of 550°C exhibited superior adsorption properties, with a BET surface area of 99.7 m²/g and a carbon content of 62.44%. This facilitated significant reductions in heavy metals and phenolic compounds, mitigating inhibitory effects on downstream processes like struvite precipitation and AD.

After performing optimisation experiments using a CCD, it was observed that the adsorption process for phenolic compounds was optimised at a pH of 6.57, a contact time of 35 minutes, and a biochar dosage of 5 g/L. These conditions yielded phenol removal efficiencies of up to 37.9 %, with adsorption capacities peaking at 12.91 mg/g. The removal efficiencies of Cu, Ni, Pb, and Zn were 62.4%, 60.4%, 76.8%, and 78.6%, respectively.

While adsorption effectively removed toxins, nutrient retention (e.g., phosphate and ammonium) was prioritised to support downstream recovery. Optimal nutrient retention was achieved at near-neutral pH (6.57), minimising losses while ensuring toxin removal.

Magnetisation of biochar enhanced recovery efficiency and operational feasibility, with iron incorporation improving its separation post-treatment. Although magnetisation reduced the surface area slightly, the trade-off was justified for large-scale wastewater applications.

9.2.4 Key findings to objective 4

The study highlighted the feasibility and sustainability of phosphorus recovery through struvite precipitation, offering a dual solution to resource depletion and environmental challenges.

Under optimised conditions (pH 9.24 and magnesium source concentration of 14.2 mL/L sludge), the process achieved a maximum phosphate recovery of 79.5%, with a phosphate residue (precipitate) concentration of 75.3 mg/L. At the same time, ammonium showed a recovery of 36.8%, corresponding to an ammonium concentration of 28.2 mg/L in the residue. These conditions ensured the efficient utilisation of nutrients for struvite crystallisation, while also considering other upstream and downstream processes.

The recovered struvite was of moderate purity (69.06%), containing phosphorus, ammonium, and magnesium in the recommended stoichiometric proportions, confirming its potential as a slow-release fertiliser. The nutrient composition aligns with sustainable agricultural requirements, reducing reliance on synthetic fertilisers. There was evidence of contamination, as indicated by the XRD and SEM analysis.

The process mitigated nutrient leakage into aquatic ecosystems, addressing eutrophication risks. This aligns with circular economy principles, transforming wastewater into a value-added product while reducing environmental harm.

Discrepancies in nutrient mass balances, primarily due to competing reactions or volatilisation, were observed. Future work should focus on improving process controls, such as pH precision and magnesium dosing, to minimise losses and enhance recovery rates.

The combination of hydrothermal treatment and struvite precipitation proved effective in nutrient recovery, supporting the transition of wastewater treatment plants into multi-product recovery hubs. Further scaling and integration of these technologies are recommended to achieve sustainable wastewater management.

9.2.5 Key findings to objective 5

The integration of HT with AD significantly enhanced biogas production, demonstrating the potential for sustainable energy recovery.

HT pretreatment improved methane yields by over 270 % compared to untreated waste-activated sludge (WAS), with maximum cumulative methane production reaching 72.74 mL/g-VS under optimised conditions.

HT increased the solubilisation of organic matter, elevating soluble COD from 284 mg/L to 3035 mg/L, which facilitated faster microbial adaptation and shortened the lag phase from 3.5 days to 1.2 days.

Alkalinity and pH levels were maintained within optimal ranges post-AD, ensuring resilience against VFA accumulation. VFA/TA ratios in HT-treated streams improved to 0.47, indicating enhanced system stability.

Among the 4 scenarios tested, the HT-treated stream consistently outperformed untreated and other pretreated streams in methane production, with a methane content peak of 76.4%.

The modified Gompertz model provided superior predictive accuracy for methane production, with R^2 values exceeding 0.99 across all scenarios. It effectively captured the dynamics of microbial acclimation and peak production rates.

After AD, both inoculated streams of WAS and HT exhibited increased ammonium concentrations, rising from 166.75 to 298.68 and from 193.86 to 298.74, respectively, which contributed to enhanced buffering capacity and process stability.

9.2.6 Key findings to objective 6

The study demonstrated the technoeconomic viability of integrating HT, adsorption, struvite precipitation, and AD into wastewater treatment processes.

As part of efforts to manage energy and heat, HT energy requirements were measured at 0.98 MJ/kg sludge, with an 80% heat recovery efficiency, thereby reducing operational energy costs. Integrated heat recovery strategies met all biodigester energy demands. Methane yields increased to 72.74 mL/g-VS, with a methane content of 76.4%. This positions the process as an effective energy-harnessing solution for wastewater treatment plants.

Scenario 4 (HT, adsorption, struvite precipitation and AD) achieved the highest ROI of 45.04% and an NPV approaching \$2.5 billion over a 30-year lifespan. The integration reduced biomethane production costs from \$2,883.85/ton in standalone setups to \$337.49/ton.

Struvite precipitation incurred high $MgCl_2$ costs, highlighting the need for alternative, cost-effective magnesium sources. Further research is required to scale magnetic biochar reuse and address by-product management.

9.2.7 Key findings to objective 7

The LCA conducted in this study highlights the environmental benefits of integrating HT, adsorption, struvite precipitation, and AD into wastewater management processes. The

integrated system significantly reduced GWP compared to conventional treatment. Scenario 2 exhibited a 21.3% reduction, scenario 3 a 37.4% reduction, and scenario 4 an 8.53% reduction in GWP, attributed to improved energy efficiency and heat recovery. Digestate contributed substantially to emissions, accounting for up to 62.1% of GWP in conventional systems, while the integrated approach reduced this impact.

Nutrient recovery through struvite precipitation and adsorption reduced freshwater eutrophication potential (FEP) by 27.2-39.6% and marine eutrophication potential (MEP) by 17.6-30.5%. Scenario 4 demonstrated the lowest FEP and MEP, aligning with efficient nutrient recovery and reduced organic matter leakage.

For the toxicity impact categories, scenario 4 achieved a 20-30% improvement across these categories due to enhanced pollutant removal. Scenarios incorporating HT and recovery processes reduced ozone depletion by up to 46.5% and PMF by more than 60% compared to the baseline. The acidification potential was reduced by 64.3% in systems employing HT and resource recovery, due to lower emissions of nitrogen oxides and sulphur dioxide.

Fossil resource consumption decreased by up to 67.5%, with enhanced energy recovery offsetting external energy demands. Water savings reached -5,817 m³ in advanced scenarios, driven by effective heat integration and reduced water use.

The sensitivity analysis conducted signified that variations in hydrothermal reactor efficiency and sludge flow rates are important and that they are optimised to minimise environmental impacts.

9.3 Contributions to knowledge

This research contributes novel insights into the valorisation of waste-activated sludge (WAS) through an integrated hydrothermal treatment (HT) platform tailored for nutrient recovery and bioenergy production, particularly in resource-constrained contexts. By directly addressing the poorly understood phosphorus transformation mechanisms along the HT-adsorption-precipitation continuum, the study fills a fundamental knowledge gap

in the optimisation of phosphorus recovery. It advances prior work by providing a comprehensive characterisation of phosphorus species, revealing how temperature and residence time influence bioavailability and downstream crystallisation, as struvite an area largely overlooked in prior studies.

A key contribution lies in systematically tracing phosphorus behaviour and fate across the HT stream, adsorption phase using magnetic biochar (MBC), and precipitation via struvite. This dynamic tracking enabled the construction of a phosphorus mass balance framework, critical for scaling nutrient recovery in complex, heterogeneous sludge matrices. Unlike previous studies that examine these processes in isolation, this research integrates them holistically, establishing a blueprint for process synergy that balances toxin removal with nutrient conservation.

In addition to nutrient recovery, the investigation into HT's influence on anaerobic digestion (AD) performance yielded significant findings. Methane production increased over 270% with HT pre-treatment, and the lag phase was drastically reduced. These results provide quantitative evidence of the synergistic potential of HT-AD integration, offering a realistic energy recovery pathway in decentralised or underfunded wastewater treatment plants.

Importantly, these technical contributions are embedded within economic and environmental frameworks. The technoeconomic analysis demonstrates that full integration of HT, MBC adsorption, and struvite recovery is financially viable, with a projected ROI exceeding 45% and a payback period under five years at full scale. Concurrently, the life cycle assessment reveals substantial reductions in global warming potential, reinforcing the environmental justification for adopting such integrated systems.

9.4 Policy recommendations

Given the low levels of resources in many parts of the world, policymakers and authorities need to prioritise the use of integrated waste management technologies, such as HT struvite precipitation and AD systems, through effective adoption. These technologies

provide dual benefits in terms of waste reduction and resource recovery, which address critical environmental challenges aligned with SDG 6 (clean water) and SDG 13 (climate action). These systems offer the possibility to make traditional waste management operations into supportive processes that lead to sustainability through enhanced economic resilience.

Government agencies and funding institutions need to establish policies to foster the transfer, procurement, and implementation of HT-Precipitation-AD systems, thereby supporting the deployment of these systems. Financial incentives, such as tax breaks, subsidies, or grants, to offset the high capital costs of these advanced technologies can be included. In developing countries, which are often limited by funding, such measures are particularly important in facilitating the adoption of new waste management solutions.

For scaling up HT-Precipitation-AD systems, policymakers should prioritise access to funding and supportive regulatory frameworks. The more stringent rules on the capture of biomethane would ensure that systems in the facilities incorporated the innovative biogas recovery technology to enhance energy capture and, at the same time, minimise emissions. Additional policies encouraging environmental assessment reports for WWTPs, global reporting initiatives (GRI) and LCAs can also enhance sustainability compliance.

It is imperative to foster effective collaboration with academic and research institutions in refining and optimising HT-Precipitation-AD systems regarding their costs and environmental impacts in various settings within the particular region. Such relationships can contribute to sustaining subsequent research and development of these systems that will further improve their technical feasibility and scalability. This cooperation also highlights the shift in the concept of a circular economy, with a positive impact on both the environment and the economy.

9.5 Recommendations for future research

While this study has provided significant insights, several avenues remain open for further exploration and refinement. Optimising heat integration within hydrothermal systems presents a promising strategy for lowering energy demands and operational costs, especially when excess thermal energy is repurposed for anaerobic digestion (AD). Techniques such as cascading high-grade heat or recovering latent heat from exhausts could reduce environmental burdens while improving overall system efficiency.

On the process side, advancing adsorption technologies, particularly magnetic biochar enhanced through polymer coatings or zeolite layering, can improve the selective removal of heavy metals and persistent organics. Such enhancements are crucial in addressing trace contaminants that are often overlooked in conventional treatment processes. Simultaneously, methane leakage mitigation remains vital; even marginal emissions have disproportionate global warming impacts. Low-pressure flaring, leak detection, and personnel training can enhance the resilience of biogas systems.

Struvite precipitation, a key pillar of nutrient recovery, would benefit from optimisation through fluidised bed reactors, seed crystals, or the use of alternative magnesium sources such as seawater or industrial brines. Notably, the chemical, rather than adsorptive, removal of copper and zinc during struvite formation necessitates upstream interventions to prevent impurity interference and ensure product purity. Further research should also examine the reuse potential of hydrothermal by-products in agriculture and their long-term effects on AD performance and soil rehabilitation.

On the analytical front, high-resolution tools such as Raman spectroscopy, XAS, and AFM can provide a deeper mechanistic understanding of nutrient transformations and by-product characteristics. Meanwhile, predictive modelling using machine learning could support real-time process control, aiding scalability and automation.

To account for sludge variability, the study recommends future multi-site validation to strengthen model robustness and ensure the generalisability of findings across differing wastewater compositions and operational environments.

Ultimately, translating laboratory findings into real-world impact requires pilot-scale validation. Regional wastewater variability, particularly in under-resourced contexts like Sub-Saharan Africa, underscores the urgency for localised life cycle assessment datasets and technoeconomic modelling that reflect real market conditions, energy prices, and infrastructure limitations. Without such contextual grounding, promising innovations risk stagnation at the conceptual stage.

9.6 Limitations of the study

Potential limitations and constraints of this study should be taken into account when interpreting the findings. Despite these limitations, the research presents valuable insights into the integration of hydrothermal treatment (HT) with adsorption, precipitation and anaerobic digestion (AD).

9.6.1 *Experimental and process limitations*

- Laboratory-scale experiments may not fully replicate industrial-scale plant unit operations, which often involve operational challenges, hydrodynamic variations, and heat transfer inefficiencies.
- Scaling up HT presents technical challenges, including maintaining uniform heat distribution, high-pressure control, and efficient mixing, which could affect feasibility and process optimisation.
- Seasonal and influent wastewater variations result in compositional changes in sludge, which affect reproducibility and process efficiency.
- The interdependence of HT, adsorption, precipitation, and AD requires careful optimisation, as minor parameter changes can significantly alter multiple process outcomes.

9.6.2 *Technoeconomic evaluation limitations*

- The study assumes heat losses in the hydrothermal reactor occur only via conduction, which may impact plant profitability estimations.

- Cost estimations were based on unofficial quotations, and import duty taxes were not factored into the analysis, which may have affected the financial assessment.
- Regulatory and market acceptance challenges may hinder the commercialisation of HT due to policy restrictions and uncertainties in adoption.
- The treatment of spent magnetic biochar (MBC) after adsorption was not considered, which may pose secondary pollution risks if not managed properly.

9.6.3 Life cycle assessment (LCA) limitations

- The LCA relied on bench-scale experimental data, which may not fully represent the complexities of large-scale hydrodynamics, potentially leading to estimation discrepancies.
- Soil emissions from nutrient recovery processes were not comprehensively included due to data constraints, which may have led to an underestimation of environmental impacts in agricultural applications.
- The assumption of a constant sludge collection rate throughout the study may not reflect real-world variations influenced by political, regulatory, and technological factors.
- The assumption that hydrochar would be fully utilised for in-plant heating, with any surplus sold, may face practical challenges such as market demand and integration into existing energy systems.
- Some processes in the SimaPro database are region-specific, necessitating estimations for the specific region being studied and introducing uncertainty into environmental impact calculations.

9.7 Conclusion to the study

This study contributes a robust knowledge base for transforming wastewater treatment plants into resource recovery facilities with a call to action toward a circular economy for waste management systems. Thus, based on the identified limitations and prioritising

innovative solutions, further developments in this area can be regarded as promising for improving these processes, enhancing their scalability, and efficiency. The integrated approach implemented not only addresses some of the environmental challenges, including eutrophication and the greenhouse effect, but also allows for the development of renewable energy resources and sustainable fertiliser production. These advancements play a significant role in closing the gap between environmental conservation and resource utilisation, thereby supporting the SDGs. By embracing technology and environmental preservation standards, this research provides direction towards a more resource-efficient and sustainable future for wastewater management systems.

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APPENDICES

Appendix A: General

A1: Turn it in report

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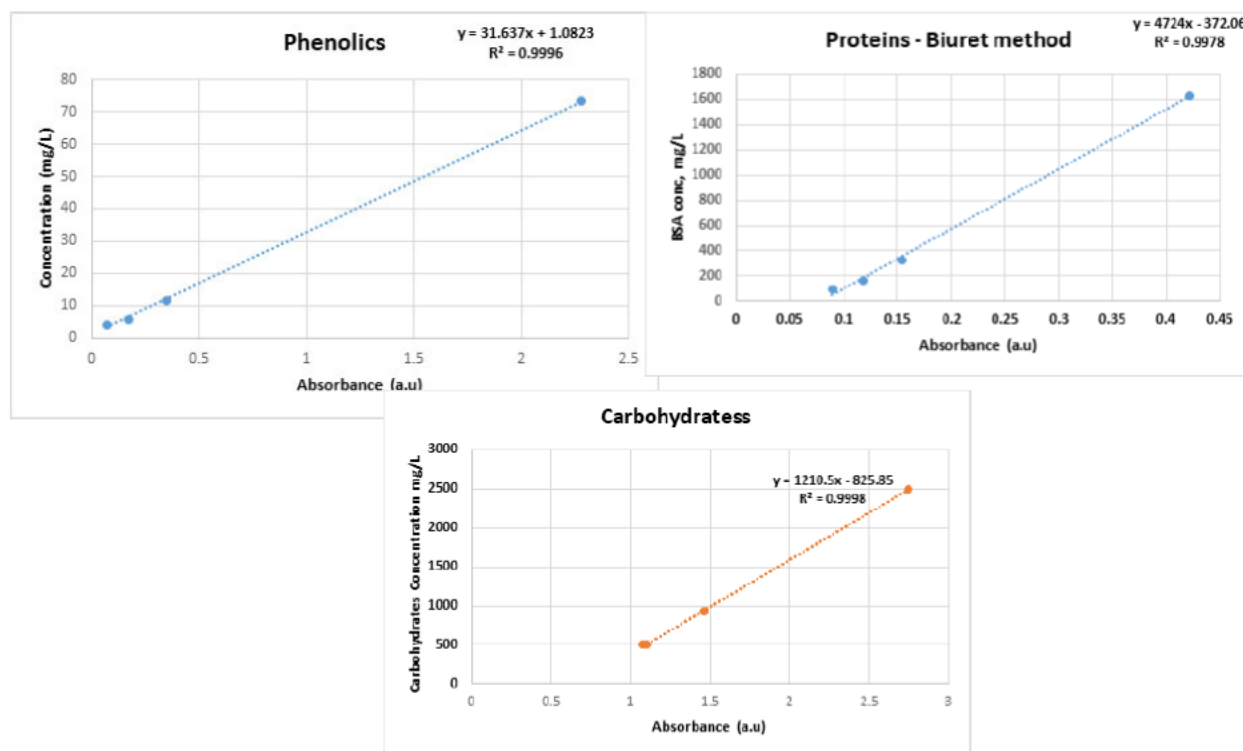


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Appendix B: Characterisation

This appendix presents the comprehensive experimental datasets and supporting analyses that underpin the main findings of this research. It includes calibration curves, elemental analyses, phosphorus fractionation data, and key physicochemical characteristics across various treatment stages. Each table and figure is indexed with clear units and concise descriptions to ensure traceability and reproducibility.

B1: Calibration curves



B2: Ultimate analysis

Material	C (%)	H (%)	N (%)	S (%)	O (%)	C/H	C/N	C/S	C/O
Activated carbon	80.42	1.74	0.71	0.52	16.09	46	113	155	5
T450 (biochar at 450 °C)	54.17	1.65	1.16	0.12	4.52	33	47	451	12
T500	58.23	4.11	1.12	1.64	9.32	14	52	36	8
T550 (optimum)	62.44	4.46	1.61	2.21	8.41	14	39	28	10
T600	32.89	1.82	0.7	0.56	27.47	18	47	59	1

T650			31.71	1.35	0.41	0.22	25.69	23	77	144	1
Magnetic Activated Carbon (MAC)			58.04	1.27	0.51	0.59	16.66	46	114	98	4
Magnetic Biochar (MBC) @ 550 °C (MBC)			50.08	2.56	0.83	1.13	9.88	20	60	44	6
Recovered MAC @ optimum adsorption			59.44	1.5	1.55	0.51	16.09	40	38	117	4
Recovered MBC @ optimum adsorption			47.59	2.17	1.12	0.78	16.60	22	42	61	3
Hydrochar from HT			35.27	5.38	4.18	2.11	19.43	7	8	17	2
Hydrochar after adsorption @optimum			37.74	5.27	4.45	2.27	16.98	7	8	17	3
Inoculum			28.3	4.54	3.3	2	19.87	6	9	14	2
WAS			35.7	6.53	5.88	2.7	30.98	5	6	13	1
HT-sludge			34.8	5.03	7.01	2.04	29.51	7	5	17	1
WAS + inoculum			30.73	7.87	4.96	3.38	21.69	4	6	9	2
HT + inoculum			30.2	4.97	4.12	2.11	20.77	6	7	14	2
Reactor 1 WAS + inoculum after AD			28.16	5.51	3.88	2.37	23.45	5	7	12	1
Reactor 2 WAS + inoculum after AD			28.23	4.38	4.02	1.81	25.19	6	7	16	1
Reactor 1 HT + inoculum after AD			25.59	5.36	3.19	2.17	20.05	5	8	12	1
Reactor 2 HT + inoculum after AD			25.79	4.07	3.06	1.61	21.48	6	8	16	1

B3: Fractionation of phosphorus

Stream	Water-soluble	NaHCO ₃	soluble	NaOH-soluble	HCl-soluble	Residual-P
Inoculum	0.153±0.023	1.247±0.086		2.613±0.003	35.757±1.278	8.063±0.243
WAS	0.399±0.015	1.128±0.051		3.084±0.115	33.205±0.775	8.212±0.055
HT	0.715±0.037	1.591±0.107		3.875±0.098	25.495±1.536	7.343±0.450
WAS + Inoc	0.720±0.024	1.648±0.047		1.922±0.033	37.481±1.086	9.295±0.290
HT+ Inoc	0.622±0.003	1.401±0.070		3.008±0.061	44.992±1.310	7.582±0.548
WAS + Inoc after AD	0.294±0.045	1.436±0.077		2.677±0.019	49.823±1.582	8.235±0.117
HT+ Inoc after AD	1.003±0.114	1.458±0.025		2.093±0.018	64.788±0.659	8.698±0.584

Struvite		0.490±0.016	7.085±0.277	2.696±0.055	17.186±0.315	14.236±0.317
Synthetic struvite		2.241±0.038	3.363±0.038	2.812±0.027	97.953±0.704	3.588±0.018
Hydrochar adsorption	after	0.165±0.004	0.953±0.009	2.539±0.031	16.583±1.559	4.064±0.105
Adsorption effluent		0.366±0.019	0.500±0.107	0.993±0.041	7.646±1.625	2.132±0.16
Adsorbent recovered		0.355±0.050	0.226±0.006	0.331±0.010	1.194±0.334	2.154±0.254
Adsorbent only		*bd	*bd	0.077±0.002	1.115±0.261	2.100±0.253

*The units are expressed as mg-P/g (each sample was in powdered form)

*bd represents the below detectable limit

B4: Heavy metal before and after hydrothermal treatment of WAS

Heavy Metal	Concentration (mg/kg) in Untreated WAS	Concentration (mg/kg) in HT-treated WAS
Arsenic (As)	$2.2 \times 10^{-4} \pm 4.1 \times 10^{-6}$	$9.3 \times 10^{-5} \pm 1.3 \times 10^{-5}$
Copper (Cu)	0.00036±0.00039	0.00098±0.00101
Nickel (Ni)	0.46±0.14	0.47±0.10
Lead (Pb)	$1.0 \times 10^{-4} \pm 1.2 \times 10^{-5}$	$9.2 \times 10^{-5} \pm 8.1 \times 10^{-6}$
Zinc (Zn)	0.0021±0.0001	0.0021±0.0002

B5: Solids content for various streams

Stream	TS (mg/L)	VS (mg/L)	TDS (mg/L)	TSS (mg/L)
WAS only	5563±364	4060±240	404±42	4983±223
HT only	5143±470	3713±350	757±16	4298±173
Ads only	6232±194	4283±74	554±94	5813±53
Precipitation only	2300±14	1727±25	869±90	1403±53
Inoculum only	15893±74	9230±247	2345±496	12867±286
WAS + Inoculum	9907±25	6132±81	1416±242	8220±198
HT + Inoculum	9818±315	6073±152	1581±163	8433±74
Adsorption + Inoculum	10273±95	6215±78	1478±31	8615±311
Precipitation + Inoculum	8515±78	5155±141	1661±283	6517±152

Precipitation effluent with Activated Carbon + Inoculum	9575±64	6395±14	1798±18 5	7470±99

B6: Water quality parameters

Stream	Conductivity (µS/cm)	Salinity	DO %	DO (mg/L)	pH	pH mV
Inoculum	2897	1.51	17.7	1.55	7.15	-9.5
WAS	444	0.21	25.1	2.18	7.23	-26.2
HT	1386	0.69	27.3	2.34	6.92	15.1
HT + Inoculum	2172	1.11	13	1.14	6.97	1
WAS + Inoculum	1769	0.9	10.9	0.96	7.02	-2.2
Adsorption effluent + Inoculum	2254	1.16	11.5	0.99	6.96	1.5
Adsorption effluent with Activ Carb + Inoculum	2324	1.19	8.7	0.74	6.93	3
Precipitation effluent with Activ Carb + Inoculum	2767	1.44	5.3	0.45	7.13	-8.7

B7: Wastewater treatment parameters

Stream	Moisture content (%)	Density (kg/m³)	TS (%)	Organic loading (kgVS/m³)	Fixed solids (%)	Ash (%)
WAS only	99.44±0.037	995±1	0.56±0.037	4.06±0.24	27.00±0.46	21.61±0.02
HT only	99.51±0.033	1044±27	0.49±0.033	3.71±0.35	27.82±0.21	28.00±3.91
Adsorption only	99.38±0.020	1008±1	0.62±0.020	4.28±0.07	31.27±0.95	31.27±0.95
Precipitation only	99.77±0.001	1007±0	0.23±0.001	1.73±0.02	24.89±0.61	24.89±0.61
Inoculum only	98.43±0.005	1015±2	1.57±0.005	9.23±0.25	41.92±1.83	42.74±0.128
WAS + Inoculum	99.09±0.113	1100±139	0.91±0.113	6.13±0.08	38.10±0.67	34.28±0.145
HT + Inoculum	99.03±0.030	1010±1	0.97±0.030	6.07±0.15	38.14±0.43	39.91±0.110
Adsorption + Inoculum	98.99±0.013	1013±4	1.01±0.013	6.22±0.08	39.50±0.19	39.50±0.19
Precipitation + Inoculum	99.16±0.005	1009±3	0.84±0.005	5.15±0.14	39.46±1.11	39.46±1.11
Precipitation effluent with Activ Carb + Inoculum	99.06±0.007	1019±1	0.94±0.007	6.40±0.01	33.21±0.59	33.21±0.59

B8: COD distribution in various streams

Stream	SCOD (mg/L)	TCOD (mg/L)
Inoculum	414±25	8938±58
WAS	284±15	5229±59
HT	3161±45	4778±15
HT + Inoculum	966±59	6847±174
WAS + Inoculum	168±8	6909±87
Adsorption effluent + Inoculum	609±30	6888±116
Adsorption effluent with Activ Carb + Inoculum	704±15	7975±29
Precipitation effluent with Activ Carb + Inoculum	1386±59	8323±174
Adsorption effluent	2085±4	6870±101
Precipitation effluent	1722±8	3273±8

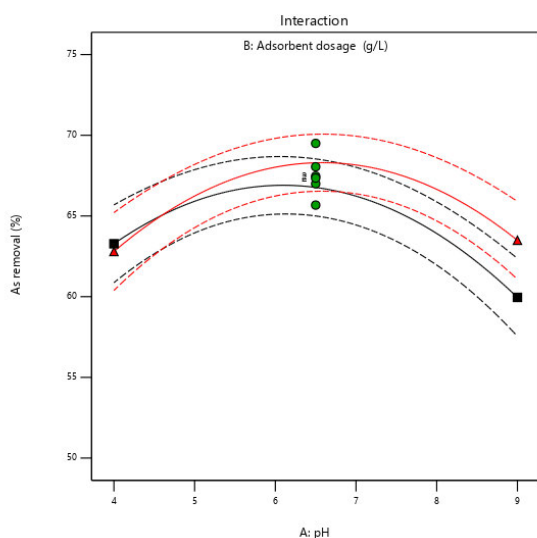
Appendix C: Adsorption studies

This appendix presents the statistical analyses and optimisation models developed to evaluate the removal efficiencies of toxic metals during the adsorption process using magnetic biochar (MBC). The data include ANOVA results, regression statistics, and model equations for individual metals, as well as arsenic (As), copper (Cu), nickel (Ni), and lead (Pb), which show the influence of pH, adsorbent dosage, and contact time on removal performance.

Appendices C1-C4 summarise the model fit statistics (R^2 , adjusted R^2 , predicted R^2), interaction effects, and final predictive equations in both coded and actual terms. The results confirm that the quadratic and interaction models were statistically significant ($p < 0.05$), with high precision values, indicating robust model adequacy and reproducibility.

Collectively, these analyses establish the optimum adsorption conditions applied in Chapter 4 and demonstrate the efficiency of MBC in removing key heavy metals from hydrothermally treated sludge streams.

C1: Arsenic



ANOVA for the Quadratic model

Response 4: As removal

Source	Sum of Squares	df	Mean Square	F-value	p-value

Model	781.94	9	86.88	26.98	< 0.0001	significant
A-pH	5.88	1	5.88	1.83	0.2065	
B-Adsorbent dosage	7.99	1	7.99	2.48	0.1464	
C-Contact time	131.29	1	131.29	40.77	< 0.0001	
AB	8.07	1	8.07	2.51	0.1445	
AC	101.37	1	101.37	31.47	0.0002	
BC	43.46	1	43.46	13.49	0.0043	
A ²	382.64	1	382.64	118.80	< 0.0001	
B ²	0.0000	1	0.0000	9.508E-06	0.9976	
C ²	133.41	1	133.41	41.42	< 0.0001	
Residual	32.21	10	3.22			
	24.31	5	4.86	3.08	0.1213	not significant
Lack of Fit						
Pure Error	7.90	5	1.58			
Cor Total	814.15	19				

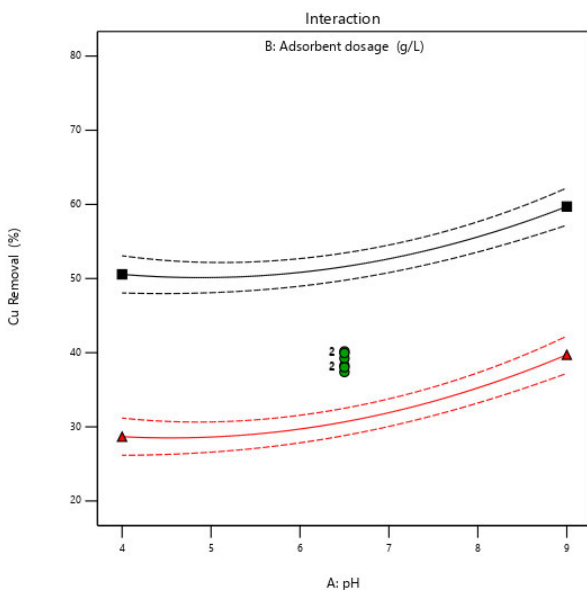
Fit Statistics

Std. Dev.	1.79	R²	0.9604
Mean	61.94	Adjusted R²	0.9248
C.V. %	2.90	Predicted R²	0.7378
		Adeq Precision	14.2266

Final Equation in Terms of Actual Factors

As removal	=
+8.99239	
+12.60897	pH
-1.33642	Adsorbent dosage
+0.625615	Contact time
+0.080361	pH * Adsorbent dosage
-0.043811	pH * Contact time
+0.014344	Adsorbent dosage * Contact time
-0.824444	pH ²
-0.000058	Adsorbent dosage ²
-0.002881	Contact time ²

C2: Copper



ANOVA for the Quadratic model

Response 5: Cu Removal

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	3819.64	9	424.40	121.49	< 0.0001	significant
A-pH	347.95	1	347.95	99.60	< 0.0001	
B-Adsorbent dosage	1496.65	1	1496.65	428.42	< 0.0001	
C-Contact time	409.39	1	409.39	117.19	< 0.0001	
AB	1.81	1	1.81	0.5184	0.4880	
AC	3.98	1	3.98	1.14	0.3112	
BC	637.90	1	637.90	182.60	< 0.0001	
A ²	179.69	1	179.69	51.44	< 0.0001	
B ²	75.20	1	75.20	21.53	0.0009	
C ²	783.13	1	783.13	224.17	< 0.0001	
Residual	34.93	10	3.49			
Lack of Fit	28.67	5	5.73	4.58	0.0603	not significant
Pure Error	6.26	5	1.25			
Cor Total	3854.57	19				

Fit Statistics

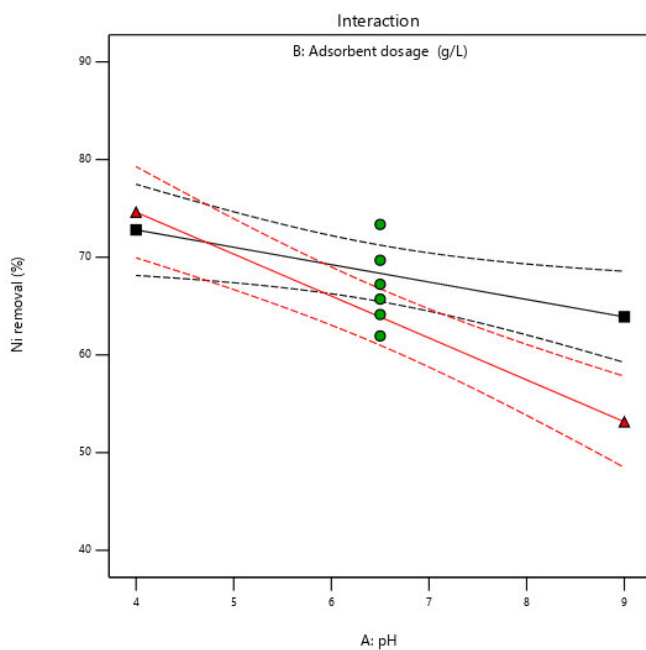
Std. Dev.	1.87	R²	0.9909
Mean	47.86	Adjusted R²	0.9828
C.V. %	3.91	Predicted R²	0.9412
		Adeq Precision	38.0600

Final Equation in Terms of Actual Factors

$$\text{Cu Removal} = +92.03133 - 6.29192 \text{ pH}$$

-0.459397	Adsorbent dosage
-0.617521	Contact time
+0.038061	pH * Adsorbent dosage
+0.008676	pH * Contact time
-0.054951	Adsorbent dosage * Contact time
+0.564978	pH ²
+0.091376	Adsorbent dosage ²
+0.006979	Contact time ²

C3: Nickel



ANOVA for the 2FI model

Response 6: Ni removal

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1590.06	6	265.01	18.25	< 0.0001	significant
A-pH	787.15	1	787.15	54.21	< 0.0001	
B-Adsorbent dosage	68.15	1	68.15	4.69	0.0495	
C-Contact time	278.72	1	278.72	19.19	0.0007	
AB	78.84	1	78.84	5.43	0.0366	
AC	207.09	1	207.09	14.26	0.0023	
BC	170.11	1	170.11	11.71	0.0045	
Residual	188.77	13	14.52			
Lack of Fit	105.60	8	13.20	0.7936	0.6335	not significant
Pure Error	83.17	5	16.63			
Cor Total	1778.83	19				

Fit Statistics

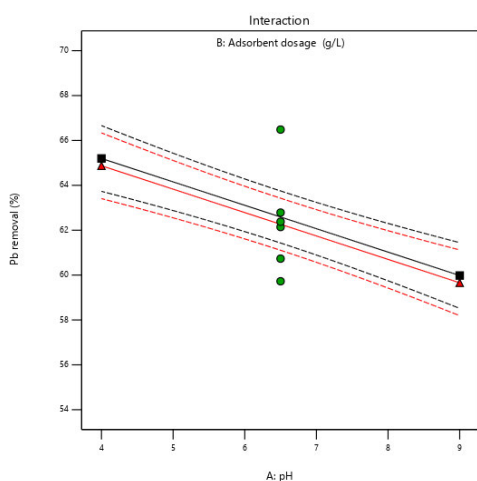
Std. Dev.	3.81	R ²	0.8939

Mean	66.12	Adjusted R²	0.8449
C.V. %	5.76	Predicted R²	0.7415
		Adeq Precision	17.3216

Coefficients in Terms of Coded Factors

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	66.12	1	0.8521	64.28	67.96	
A-pH	-7.59	1	1.03	-9.82	-5.36	1.0000
B-Adsorbent dosage	-2.23	1	1.03	-4.46	-0.0062	1.0000
C-Contact time	-4.52	1	1.03	-6.75	-2.29	1.0000
AB	-3.14	1	1.35	-6.05	-0.2287	1.0000
AC	5.09	1	1.35	2.18	8.00	1.0000
BC	4.61	1	1.35	1.70	7.52	1.0000

C4: Lead



ANOVA for Linear Model

Response 7: Pb removal

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	233.68	3	77.89	32.04	< 0.0001	significant
A-pH	92.90	1	92.90	38.21	< 0.0001	
B-Adsorbent dosage	0.3592	1	0.3592	0.1477	0.7058	
C-Contact time	140.43	1	140.43	57.76	< 0.0001	
Residual	38.90	16	2.43			
Lack of Fit	12.06	11	1.10	0.2043	0.9867	not significant
Pure Error	26.84	5	5.37			
Cor Total	272.59	19				

Zinc

Fit Statistics

Std. Dev.	1.90	R²	0.8241
Mean	77.29	Adjusted R²	0.6658
C.V. %	2.45	Predicted R²	-0.2559
		Adeq Precision	8.6411

No predictive model

Appendix D: Anaerobic digestion

This appendix presents the modelling procedure and statistical validation used to describe methane generation kinetics under the different sludge-treatment scenarios. For demonstration purposes, only the computational code for Scenario 4 (integrated hydrothermal treatment, adsorption, struvite precipitation, and anaerobic digestion) is shown, as it represents the optimal configuration yielding the highest biomethane potential.

Scenario 4

```
% Data for Scenario 4
time = [1, 2, 5, 6, 7, 8, 9, 12, 13, 14,
15, 16, 19, 20, 21];

yield = [0.533856, 1.277205,
3.445349, 5.868593, 8.491968,
11.93215, ...
14.38198, 22.3023, 24.92548,
28.00071, 29.27437, 30.36741, ...
32.00606, 32.26702, 32.38121];

% Parameters provided in Scenario 4
P_given = 250; % Biogas production
potential (mL/g-VS)

Rm_given = 7.920317904; % Max
production rate (mL/g-VS/day)

lambda_given = 2.6; % Lag phase
(days)

% Euler's number
e = exp(1);

% Modified Gompertz model function
gompertz = @(params, t) params(1)
.* exp(-exp((params(2) * e /
params(1)) .* (params(3) - t) + 1));

% Initial guesses for P, Rm, and
lambda
initial_guess = [P_given, Rm_given,
lambda_given];

% Non-linear curve fitting using
lsqcurvefit

options = optimoptions('lsqcurvefit',
'Display', 'off');

params_estimated =
lsqcurvefit(gompertz, initial_guess,
time, yield, [], [], options);

% Extracting fitted parameters

P = params_estimated(1); % Biogas
production potential

Rm = params_estimated(2); %
Maximum production rate

lambda = params_estimated(3); %
Lag phase time

% Model prediction

yield_fitted =
gompertz(params_estimated, time);

% Performance metrics

% 1. R^2
SS_tot = sum((yield -
mean(yield)).^2); % Total sum of
squares

SS_res = sum((yield -
yield_fitted).^2); % Residual sum of
squares

R2 = 1 - (SS_res / SS_tot);

% 2. SSR
SSR = SS_res;

% 3. Root Mean Square Error
(RMSE)
RMSE = sqrt(mean((yield -
yield_fitted).^2));

% 4. Mean Absolute Error (MAE)
MAE = mean(abs(yield - yield_fitted));

% Additional Statistical Metrics
n = length(yield); % Number of data
points

k = length(params_estimated); %
Number of model parameters

F_stat = ((SS_tot - SS_res) / (k - 1)) /
(SS_res / (n - k)); % F-statistic

p_value = 1 - fcd(f(F_stat, k - 1, n - k);
% P-value from F-distribution

% Display results
fprintf('Fitted Parameters:\n');

fprintf('P (Biogas potential, mL/g-VS):
%.4f\n', P);

fprintf('Rm (Max production rate,
mL/g-VS/day): %.4f\n', Rm);

fprintf('lambda (Lag phase, days):
%.4f\n', lambda);

fprintf('\nPerformance Metrics:\n');

fprintf('R^2: %.4f\n', R2);

fprintf('SSR: %.4f\n', SSR);

fprintf('RMSE: %.4f\n', RMSE);
```

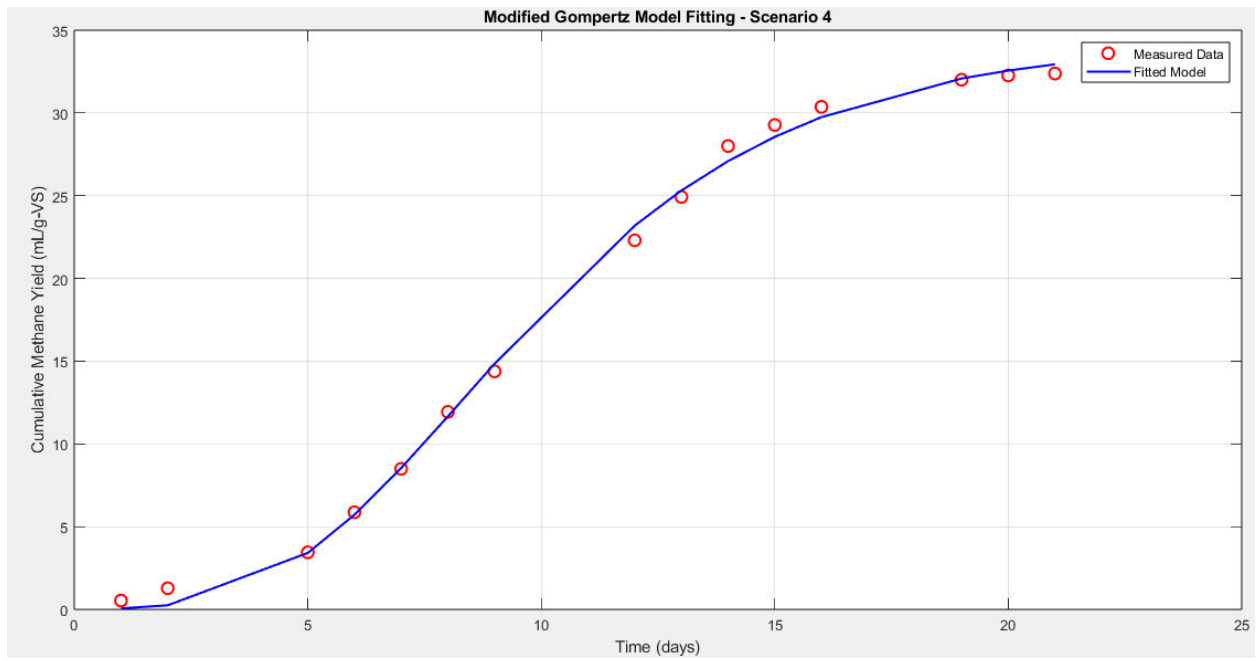
```

fprintf('MAE: %.4f\n', MAE);
fprintf('F-statistic: %.4f\n', F_stat);
fprintf('P-value: %.4f\n', p_value);

% Plotting

figure;
plot(time, yield, 'ro', 'MarkerSize', 8,
'LineWidth', 1.5); hold on;
plot(time, yield_fitted, 'b-', 'LineWidth',
1.5);
xlabel('Time (days)');
ylabel('Cumulative Methane Yield
(mL/g-VS)');
legend('Measured Data', 'Fitted
Model');
title('modified Gompertz Model Fitting
- Scenario 4');
grid on;

```



Appendix E: Technoeconomic evaluation

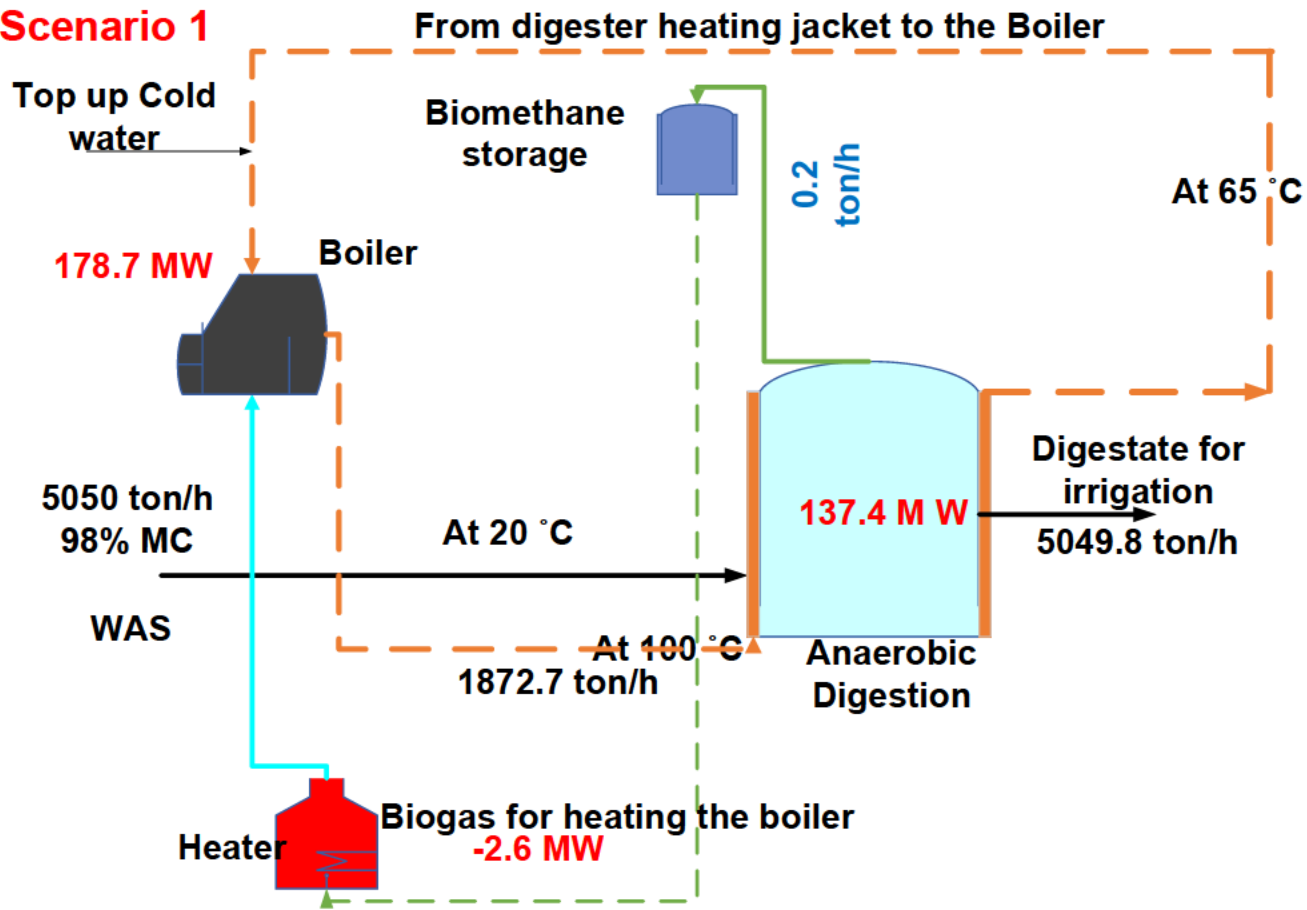
This appendix presents the process flow configurations and energy balance schematics developed for the techno-economic assessment of the proposed wastewater sludge valorisation system. Figures E1–E3 illustrate the process flow diagrams (PFDs) for Scenarios 1, 2, and 3, corresponding respectively to: (i) standalone anaerobic digestion, (ii) hydrothermal treatment integrated with anaerobic digestion and heat recovery, and (iii) the fully coupled system combining hydrothermal treatment, adsorption with magnetic biochar, and nutrient recovery.

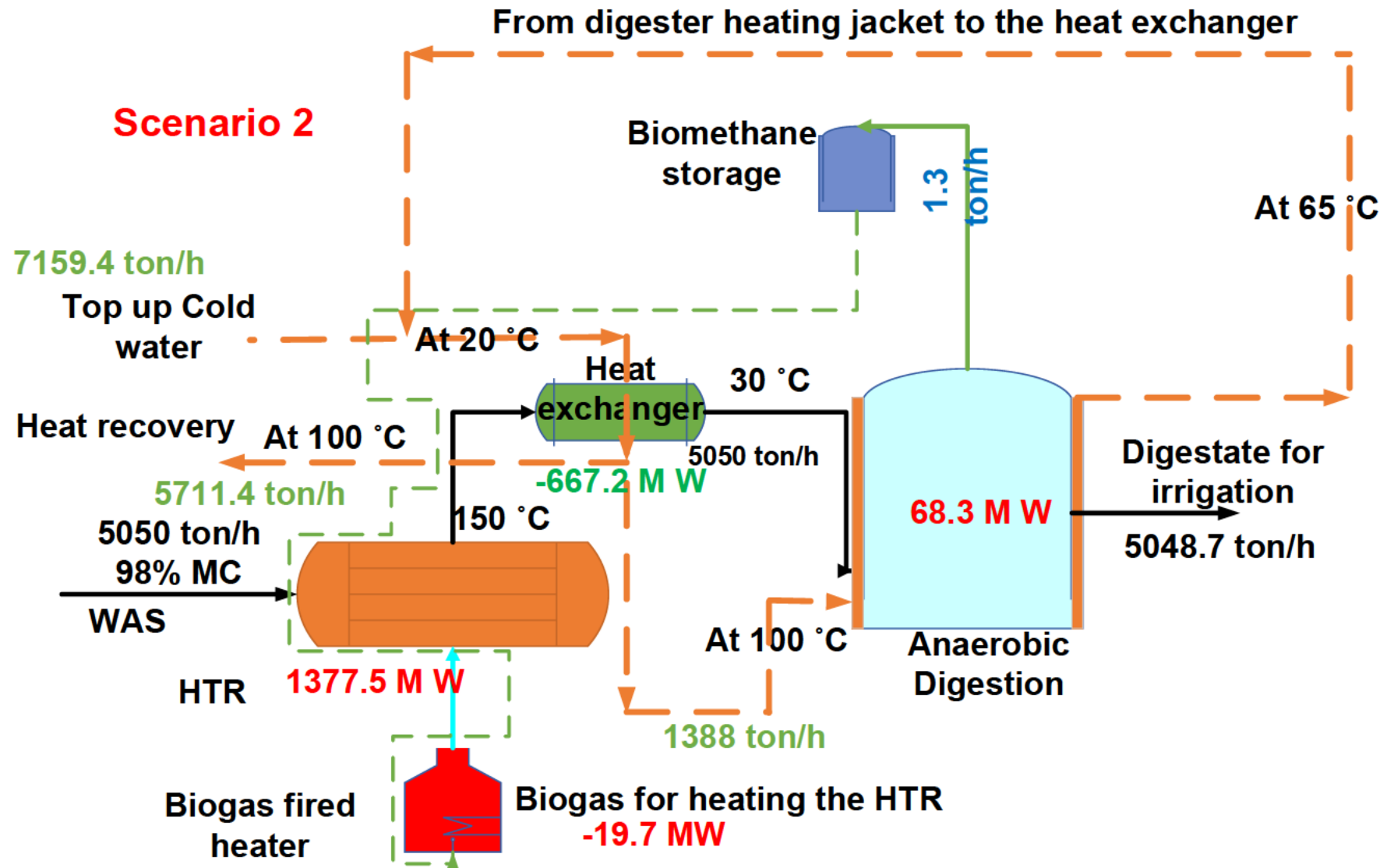
Each diagram quantifies the mass and energy flows, including feed rates, heating demands, heat-recovery contributions, and biomethane outputs. Energy exchanges are represented in megawatts (MW) and tonnes per hour (ton/h) to ensure consistency with process-simulation results. The visual comparison highlights the progressive improvement in thermal integration, energy self-sufficiency, and resource utilisation achieved through process intensification from Scenario 1 to Scenario 3.

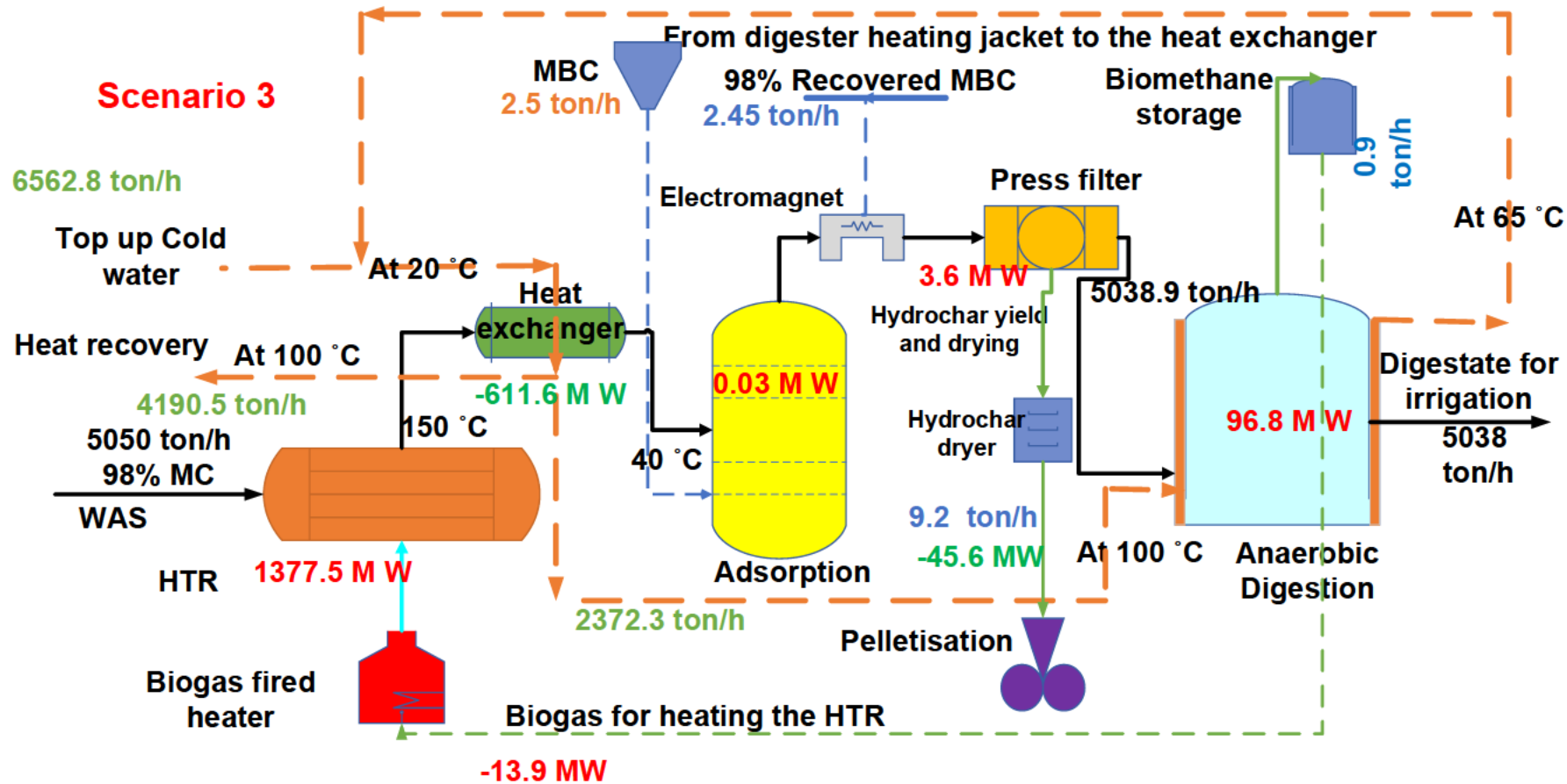
Collectively, these schematics support the life-cycle and economic analyses in Chapter 7, providing a clear visual basis for evaluating system performance, operational feasibility, and sustainability trade-offs across the proposed treatment pathways.

E1: process flow diagrams for scenarios 1, 2 and 3

Scenario 1







Appendix F: Life cycle assessment

This appendix provides the supporting datasets and modelling outputs used for the life cycle assessment (LCA) of the four sludge valorisation scenarios. It includes the inventory data (F1) detailing all material and energy inputs, outputs, and emissions normalised per functional unit, as well as the normalised environmental impact results (F2) across multiple ReCiPe 2016 midpoint categories.

Sections F3 and F4 present the network and emission contribution diagrams generated in SimaPro, illustrating the dominant processes influencing each impact category. Section F5 summarises the sensitivity analysis performed on critical parameters, such as heating efficiency and feed flow rate.

Together, these datasets underpin the comparative sustainability evaluation discussed in Chapter 8, providing full transparency and reproducibility of the LCA modelling framework.

F1: Inventory data for the scenarios

Property	Unit	Scenario 1	Scenario 2	Scenario 3	Scenario 4
Outputs to Technosphere: Products and co-products					
Biogas	ton	4.44E-05	0.000276	0.000194013	0.000412206
Digestate	ton	1.199956	1.199724	1.196895201	1.195947225
Recovered MBC	ton	-	-	2.6953E-05	2.42577E-05
Press filter output (hydrochar)	ton	-	-	0.002436656	0.002192991
After Precipitation sludge	ton	-	-	1.197089214	1.196359431
Struvite	ton	-	-	-	0.000970208
Outputs to Technosphere: Avoided products					
Biomethane	ton	2.88E-05	0.000179	0.000126109	0.000267934
Heat from the heat exchanger	kWh	-	138.7214	125.5098374	145.3271802
Hydrochar fuel recovered	kWh	-	-	12.04109854	10.83698869
MBC for reuse	ton	-	-	2.42577E-05	2.18319E-05
Heat from biogas	kWh	0.677896	4.209337	2.964089489	6.297593139
Inputs from nature					
Water (cooling)		0.001189877	0.00225546	0.002332176	0.002362863
Inputs from Technosphere: materials and fuels					
WAS	ton	1	1	1	1
HT broth to AD	ton	-	1.2	-	-
Inoculum	ton	1.8E-05	2.2E-05	2.20024E-05	1.98022E-05
MBC new	ton	-	-	2.7503E-05	2.47527E-05
HT from adsorption	ton	-	-	1.00000055	1.000000495

HT after precipitation/ AD inlet (plus lost MBC)	ton	-	-	-	1.196359431
MgCl ₂	ton	-	-	-	1.40595E-05
NaOH	ton	2.16E-06	5.28E-06	6.60073E-06	1.18813E-05
HCl	ton	2.16E-06	5.28E-06	6.60073E-06	1.18813E-05
Inputs from Technosphere: Energy/heat					
Boiler heating	kWh	28.81582816	-	-	-
HTR Heating	kWh	-	265.458006	278.6695678	182.0581471
Adsorption electricity	kWh	-	-	0.000812913	0.000799769
Press Filter electricity	kWh	-	-	0.84595072	0.846156418
Precipitation electricity	kWh	-	-	-	0.061698905
Outputs					
<i>Emissions to air (leaks)</i>					
CH ₄ (biogenic)	ton	7.78717E-07	4.83538E-06	3.40493E-06	7.23422E-06
CO ₂ (biogenic)	ton	4.19309E-07	2.60367E-06	1.83342E-06	3.89535E-06
<i>Emissions to water (leaks)</i>					
P and N	ton	3.26279E-06	3.98785E-06	3.29074E-06	5.31637E-06
Phenolics	ton	6.42783E-06	7.85624E-06	4.70075E-06	2.37746E-06
<i>Emissions to soil (leaks)</i>					
Toxins in lost MBC	ton	-	-	5.5006E-07	4.95054E-07

*All units are quoted per FU per year

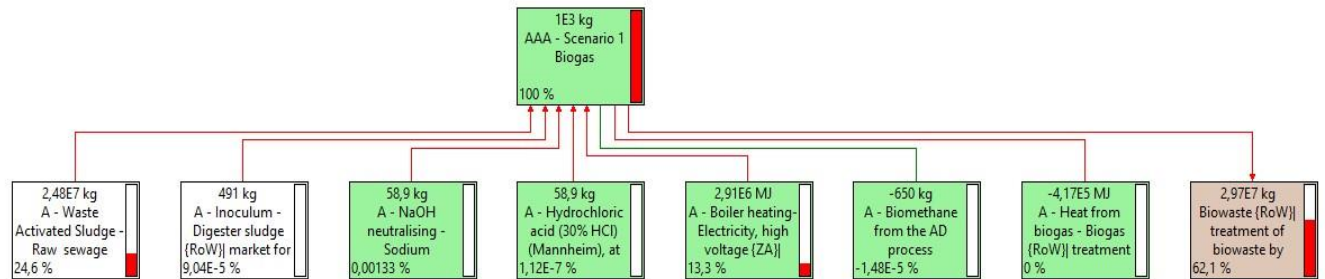
F2: Normalised data for various impact categories.

Impact category	Scenario 1	Scenario 2	Scenario 3	Scenario 4
Global warming	809.2074	172.5	302.5388	243.1525
Stratospheric ozone depletion	513.4829	70.00752	101.0147	56.13702
Ionising radiation	8.97718	3.411546	5.337513	4.170125
Ozone formation, Human health	687.8233	189.1808	301.7605	227.9816
Fine particulate matter formation	247.6376	80.56867	126.6028	97.02332
Ozone formation, Terrestrial ecosystems	811.265	220.6047	352.9871	267.0165
Terrestrial acidification	449.161	160.479	250.9869	192.7281
Freshwater eutrophication	445.6996	121.3986	176.6384	128.0028
Marine eutrophication	59.88504	10.51384	18.25766	13.68855
Terrestrial ecotoxicity	2531.505	406.3298	714.5851	544.1038
Freshwater ecotoxicity	332.7465	55.7455	81.01771	52.01095
Marine ecotoxicity	944.9469	154.0656	263.7176	193.0142

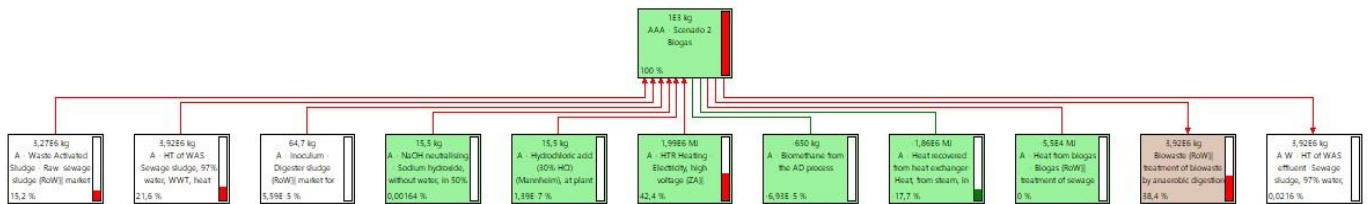
Human carcinogenic toxicity	4127.869	617.24	911.6635	535.0189
Human non-carcinogenic toxicity	23.03291	4.157599	6.946901	5.13116
Land use	15.48386	3.144301	5.265119	3.968827
Mineral resource scarcity	0.049064	0.008188	0.013898	0.01091
Fossil resource scarcity	855.881	201.2049	345.0446	277.8143
Water consumption	-17.6441	-8.18019	-21.0886	-21.8129

F3: Network diagrams for the scenarios presented in Simapro software

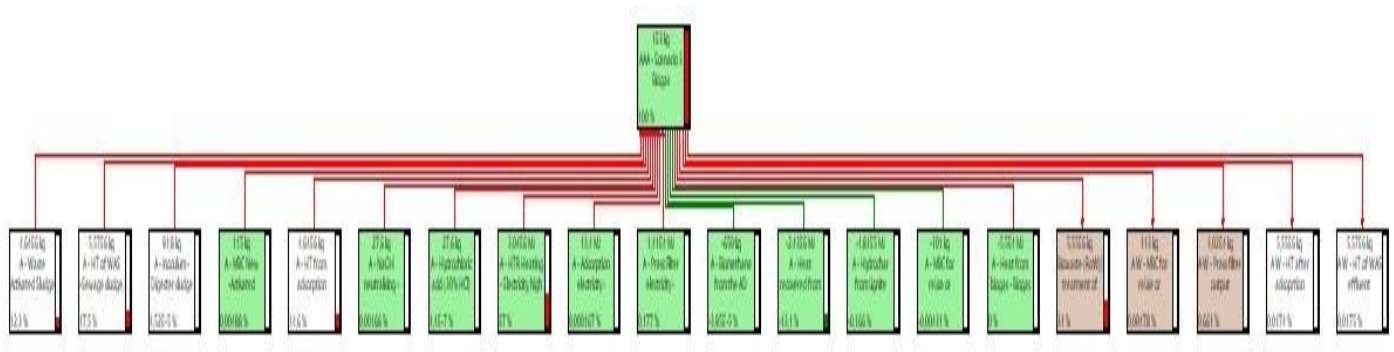
Scenario 1



Scenario 2



Scenario 3



Scenario 4

It had 16000 nodes and was not visible

F4: Emission contributors for various impact categories.

Global Warming

No	Substance	Compartment	Unit	AAA - Scenario 1	AAA - Scenario 2 Biogas	AAA - Scenario 3 Biogas	AAA - Scenario 4 Biogas
	Total of all compartments		%	100	100	100	100
	Remaining substances		%	4,94	1,98	2,24	2,07
1	Carbon dioxide, fossil	Air	%	45,5	67,1	72,6	81,3
2	Methane, biogenic	Air	%	36,7	22,7	18,4	12
3	Dinitrogen monoxide	Air	%	12,9	8,22	6,76	4,68

Terrestrial ecotoxicity

No	Substance	Compartment	Unit	AAA - Scenario 1	AAA - Scenario 2 Biogas	AAA - Scenario 3 Biogas	AAA - Scenario 4 Biogas
	Total of all compartments		%	100	100	100	100
	Remaining substances		%	10,2	14,6	15,1	16,4
1	Cobalt (II)	Air	%	77,2	74,9	69,8	63
2	Copper, ion	Air	%	12,6	10,6	15,1	20,6

Freshwater toxicity

☒ Skip unused
 Category: Freshwater ecotoxicity
☐ Per impact category

No	Substance	Compartment	Unit	AAA - Scenario 1	AAA - Scenario 2 Biogas	AAA - Scenario 3 Biogas	AAA - Scenario 4 Biogas
	Total of all compartments		%	100	100	100	100
	Remaining substances		%	12,2	14,9	17,5	20,8
1	2-Methyl-4-chlorophenol	Water	%	51,2	40,3	26,2	10,8
2	Zinc (II)	Water	%	14,1	17,8	22,4	26,2
3	Chlorpyrifos	Soil	%	9,38	15,1	21	29,2
4	Anthracene	Air	%	7,87	7,4	8,4	9,08
5	Chromium (VI)	Water	%	5,19	4,51	4,52	3,97

Fine particulate matter

No	Substance	Compartment	Unit	AAA - Scenario 1 Biogas	AAA - Scenario 2 Biogas	AAA - Scenario 3 Biogas	AAA - Scenario 4 (Base case)
	Total of all compartments		%	100	100	100	100
	Remaining substances		%	0,46	0,624	0,7	0,806
1	Sulfur dioxide	Air	%	60,6	71,6	70,8	71
2	Particulates, < 2.5 um	Air	%	15,1	7,25	7,78	7,76
3	Nitrogen oxides	Air	%	23,8	20,5	20,8	20,4

Marine ecotoxicity

☒ Skip unused
 Category: Marine ecotoxicity
☐ Per impact category

No	Substance	Compartment	Unit	AAA - Scenario 1	AAA - Scenario 2 Biogas	AAA - Scenario 3 Biogas	AAA - Scenario 4 Biogas
	Total of all compartments		%	100	100	100	100
	Remaining substances		%	21	24,1	27	31,1
1	Anthracene	Air	%	45,8	44,2	42,6	40,4
2	Cobalt (II)	Air	%	33,2	31,7	30,4	28,5

Human carcinogenic toxicity

☐ Per sub-compartment		Category	☒ Exclude long-term emissions				
☒ Skip unused		Human carcinogenic toxicity	☐ Per impact category				
No	Substance	Compartment	Unit	AAA - Scenario 1	AAA - Scenario 2 Biogas	AAA - Scenario 3 Biogas	AAA - Scenario 4 Biogas
	Total of all compartments		%	100	100	100	100
	Remaining substances		%	12,2	14,4	15,6	18,9
1	Chromium (VI)	Water	%	87,8	85,6	84,4	81,1

Human non-carcinogenic toxicity

☒ Skip unused		Human non-carcinogenic toxicity	☐ Per impact category				
No	Substance	Compartment	Unit	AAA - Scenario 1	AAA - Scenario 2 Biogas	AAA - Scenario 3 Biogas	AAA - Scenario 4 Biogas
	Total of all compartments		%	100	100	100	100
	Remaining substances		%	10,4	12,7	14	17,1
1	Arsenic, ion	Water	%	47,8	37,6	32,5	24,8
2	Arsenic, ion	Air	%	11,9	13,6	13,1	12,9
3	Lead (II)	Air	%	10	12,4	12,4	12,7
4	Zinc (II)	Air	%	7,4	5,51	6,18	7,01
5	Zinc (II)	Water	%	6,44	7,51	8,26	8,37
6	Zinc (II)	Soil	%	6,02	10,7	13,5	17,1

Eutrophication

No	Substance	Compartment	Unit	AAA - Scenario 1	AAA - Scenario 2 Biogas	AAA - Scenario 3 Biogas	AAA - Scenario 4 Biogas
	Total of all compartments		%	100	100	100	100
	Remaining substances		%	0,115	0,0406	0,049	0,044
1	Phosphate	Water	%	56	76,5	76,6	81,6
2	Phosphorus	Water	%	17,5	8,54	8,42	6,31
3	COD (Chemical Oxygen Dem	Water	%	17,2	10,3	10,3	8,53
4	BOD5 (Biological Oxygen Der	Water	%	9,2	4,65	4,6	3,46

No	Substance	Compartment	Unit	AAA - Scenario 1	AAA - Scenario 2 Biogas	AAA - Scenario 3 Biogas	AAA - Scenario 4 Biogas
	Total of all compartments		%	100	100	100	100
	Remaining substances		%	2,29	0,968	1,3	1,41
1	Nitrate	Water	%	61,1	71,9	76	82,1
2	Nitrogen, atmospheric	Water	%	36,6	27,2	22,7	16,5

Ozone depletion

No	Substance /	Compartme	Unit	AAA - Scenario 1 Biogas	AAA - Scenario 2 Biogas	AAA - Scenario 3 Biogas	AAA - Scenario 4 Biogas
	Total of all compartments		%	100	100	100	100
1	1,1,1-Trichloroethane	Air	%	0,000967	0,00425	0,00455	0,00643
2	Dinitrogen monoxide	Air	%	99,9	99,9	99,9	99,9
3	Ethane, 1,1,2-trichloro-1,2,2-trifluoro-, CFC-113	Air	%	0,00249	0,00199	0,00206	0,00208
4	Ethane, 2-chloro-1,1,1,2-tetrafluoro-, HCFC-124	Air	%	5,79E-6	5,47E-6	5,99E-6	6,85E-6
5	Hydrocarbons, chlorinated	Air	%	0,00427	0,00493	0,00543	0,00642
6	Methane, bromo-, Halon 1001	Air	%	0,000545	0,000404	0,000552	0,000795
7	Methane, bromochlorodifluoro-, Halon 1211	Air	%	0,0058	0,00187	0,00301	0,00327
8	Methane, bromotrifluoro-, Halon 1301	Air	%	0,0558	0,0159	0,0458	0,0797
9	Methane, chlorodifluoro-, HCFC-22	Air	%	0,000326	0,000375	0,000493	0,000597
10	Methane, dichlorodifluoro-, CFC-12	Air	%	9,89E-5	0,000116	0,000148	0,000203
11	Methane, monochloro-, R-40	Air	%	0,00316	0,0139	0,0149	0,021
12	Methane, tetrachloro-, CFC-10	Air	%	0,0107	0,0109	0,0112	0,0115
13	Methane, trichlorofluoro-, CFC-11	Air	%	1,44E-6	1,73E-6	2,2E-6	3,02E-6

Acidification

No	Substance /	Compartme	Unit	AAA - Scenario 1 Biogas	AAA - Scenario 2 Biogas	AAA - Scenario 3 Biogas	AAA - Scenario 4 Biogas
	Total of all compartments		%	100	100	100	100
	Remaining substances		%	1,24	1,57	1,78	2,05
1	Nitrogen oxides	Air	%	26,9	21,1	21,4	21
2	Sulfur dioxide	Air	%	71,9	77,3	76,8	77

F5: Sensitivity analysis

Contributors

Heating efficiency GWP

No	Substance /	Compartme	Unit	AAA - Scenario 4 (Base case)	AAA - Scenario 4 (-10%)	AAA - Scenario 4 (+10%)
	Total of all compartments		kg CO2 eq	1,95E6	2,04E6	1,87E6
	Remaining substances		kg CO2 eq	1,31E5	1,33E5	1,3E5
1	Carbon dioxide, fossil	Air	kg CO2 eq	1,58E6	1,67E6	1,51E6
2	Methane, biogenic	Air	kg CO2 eq	2,33E5	2,33E5	2,33E5

WAS flowrate

Indicator		C _{yt} -off				
Characterisation		5 %		☐ Default units		
Category				☒ Exclude long-term emissions		
Global warming				☐ Per impact category		
No	Process /	Project	Unit	AAA - Scenario 4 (Base case)	AAA - Scenario 4 (-10%)	AAA - Scenario 4 (+10%)
	Total of all processes		kg CO ₂ eq	1,95E6	1,87E6	2,03E6
	Remaining processes		kg CO ₂ eq	1,37E4	1,41E4	1,41E4
1	A - Heat recovered from heat exchanger- Heat, from steam, in chemi	Hydrothermal treatment ci	kg CO ₂ eq	-1,66E5	-1,66E5	-1,66E5
2	A - HT after precipitation/ AD inlet (plus lost MBC) -Sewage sludge, 9'	Hydrothermal treatment ci	kg CO ₂ eq	2,2E5	2,2E5	2,2E5
3	A - HT from adsorption -Sewage sludge, 97% water, WWT, heat carrie	Hydrothermal treatment ci	kg CO ₂ eq	1,84E5	1,66E5	2,03E5
4	A - HT of WAS -Sewage sludge, 97% water, WWT, heat carrier liquid, 4	Hydrothermal treatment ci	kg CO ₂ eq	2,21E5	1,99E5	2,43E5
5	A - HTR Heating - Electricity, high voltage [ZA]] electricity, high volta	Hydrothermal treatment ci	kg CO ₂ eq	7,03E5	6,8E5	7,27E5
6	A - Waste Activated Sludge - Raw sewage sludge (RoW)] market for ri	Hydrothermal treatment ci	kg CO ₂ eq	1,56E5	1,4E5	1,71E5
7	A W - HT after precipitation/ AD inlet (plus lost MBC) -Sewage sludge	Hydrothermal treatment ci	kg CO ₂ eq	2,2E5	2,2E5	2,2E5
8	Biowaste (RoW)] treatment of biowaste by anaerobic digestion Cut-c	Ecoinvent 3 - allocation, ct	kg CO ₂ eq	3,92E5	3,92E5	3,92E5

Appendix G: List of symbols

This appendix provides a comprehensive list of all symbols, notations, and abbreviations used throughout the thesis. Each symbol is accompanied by its description and unit to ensure clarity and consistency across analytical, modelling, and thermodynamic sections. The definitions encompass parameters from hydrothermal treatment, adsorption, anaerobic digestion, and life cycle assessment models, thereby facilitating the accurate interpretation of equations and process analyses presented in the main text.

Symbol	Description	Unit
A	Surface area	m ²
C	Concentration	mg/L
C₀	Initial concentration	mg/L
C_e	Equilibrium concentration	mg/L
C_e/C₀	Normalised concentration ratio	–
C_p	Specific heat capacity	J/kg.K
E	Energy (electricity or thermal)	MJ or kWh
E_{ht}	Energy input for hydrothermal treatment	MJ/t sludge
η	Efficiency (e.g., recovery, conversion, or heat)	%
HRT	Hydraulic retention time	d or min
k	Reaction or rate constant	h ⁻¹
K_a	Adsorption equilibrium constant	L/mg
K_s	Half-saturation constant	mg/L
LCOE	Levelised cost of electricity	\$/kWh
m	Mass	g or kg
ṁ	Mass flow rate	Kg/s
P	Phosphorus concentration or purity	% or mg/L
P_t	Total phosphorus	mg/L
Q	Heat energy transferred	MJ
Q_{ads}	Adsorbed quantity per unit mass	mg/g
Q_{max}	Maximum adsorption capacity	mg/g
R²	Coefficient of determination	–

R	Gas constant	J/mol.K
S	Entropy or slope (context-dependent)	–
T	Temperature	°C or K
t	Time	s or min
V	Volume	L
VFA	Volatile fatty acids concentration	mg/L
V_{max}	Maximum methane production rate	mL CH ₄ /g VS.d
YCH₄	Methane yield	mL CH ₄ /g VS
ΔH	Enthalpy change	kJ/mol
ΔG	Gibbs free energy change	kJ/mol
ΔS	Entropy change	J/mol.K
ρ	Density	kg/m ³
σ	Standard deviation	–
μ	Specific growth rate or mean	h ⁻¹
λ	Thermal conductivity	W/m. K
Φ	Recovery efficiency or potential	%
