



Wastewater treatment and photo-reduction of CO₂ using an integrated magnetized TiO₂ anaerobic- photocatalytic system

Submitted in fulfillment of the academic requirements for the degree of **Doctor of Engineering** in the **Department of Chemical Engineering under the Green Engineering Research Group**, Faculty of Engineering, and the Built Environment at the Durban University of Technology

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MEng (Cum Laude)

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Preface

This doctoral study was carried out under the conjunction of DUT's Green Engineering Research Group, under the Department of Chemical Engineering and the Water Research Commission (WRC), South Africa. The candidate was the principal investigator for the WRC project (C2019/2020-00212) aimed to develop "an integrated anaerobic-photocatalytic-magnetic wastewater treatment system" under the project leadership and supervision of Prof Sudesh Rathilal. This project proof of concept resulted in WRC project (WRC2021/2022-00958) to develop smart integrated AD-AOP magnetised pilot plant for the valorisation of wastewater into bioenergy. The investigation was carried out using effluent from the Umgeni water, eThekweni municipality, and a local sugar and oil refinery industries, located at the Kwazulu Natal province of South Africa. This thesis has six chapters compiled and discussed with the author's published and unpublished journal papers.

Declaration

I, **Emmanuel Kweinor Tetteh**, the undersigned candidate declares that

- (i) The research reported in this thesis, except where otherwise indicated, is my original work.
- (ii) This thesis has not been submitted for any degree or examination at any other university.
- (iii) This thesis does not contain other persons' data, pictures, graphs, or other information unless specifically acknowledged as being sourced from other persons.
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Sign:

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As the candidate supervisor, I do agree to the submission of this thesis.

Prof. Sudesh Rathilal

Sign:

Date: 16 September 2022

Dedication

This work is dedicated to my family for their resilience prayers, support, and encouragement through it all. And to the next generation, remember that life is a journey and that with God's Grace, you will get there.

And to you my precious jewel, we made it together!!! Cosmic take off !!! Shalom!!!

“Be the change that you wish to see in the world”

Mahatma Gandhi

Acknowledgment

Praise and Glory be to our God who makes provision even in the wilderness, I am most grateful for your Grace in this journey.

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I wish to thank DUT for offering me this PhD position, the South Africa National Research Foundation for their partial grant (138046), and South Africa Water Research Commission (WRC) for funding this research (C2019/2020-00212). I also acknowledge the support, advice, and thought-provoking discussions instigated by the WRC Reference Group:

My warmest thank you to my father in the Lord (Pastor Obed Obeng –Addae DrApol, PhD), Pastor Daniel Kusi-Boateng, Pastor Dr David Antwi-Agyei, Pastor Ebenezer Offery (Christ Cosmopolitan Incorporated, Kumasi Ghana), and the CCI family worldwide; “Our year of Cosmic take off” Shalom !!!

Lastly, I would like to acknowledge my family (the Tetteh’s and Amoah’s) and all my loved ones who remain unnamed. Thank you for your love, understanding, and support on this path that ends with Glory be to God!!! Shalom !!!

Abstract

Conventionally, the treatment of municipal wastewater involves a sequence of treatment units aimed at reducing pollutants to acceptable discharge levels. Herein wastewater treatment plants in South Africa's municipalities are being challenged recently due to emerging contaminants (nanomaterials, pesticides, antibiotics, COVID-19 RNA, etc.) that impede their efficiency. This calls for robust technological water solution systems targeted at promoting sustainable water supply and mitigating anthropogenic gas (CO₂) emission via biogas production. Against this background, the novel of this study is aimed to develop an integrated AD-AOP (anaerobic digestion – advanced oxidation process) magnetized system to improve wastewater for reuse with biogas production and nanoparticles recoverability benefits.

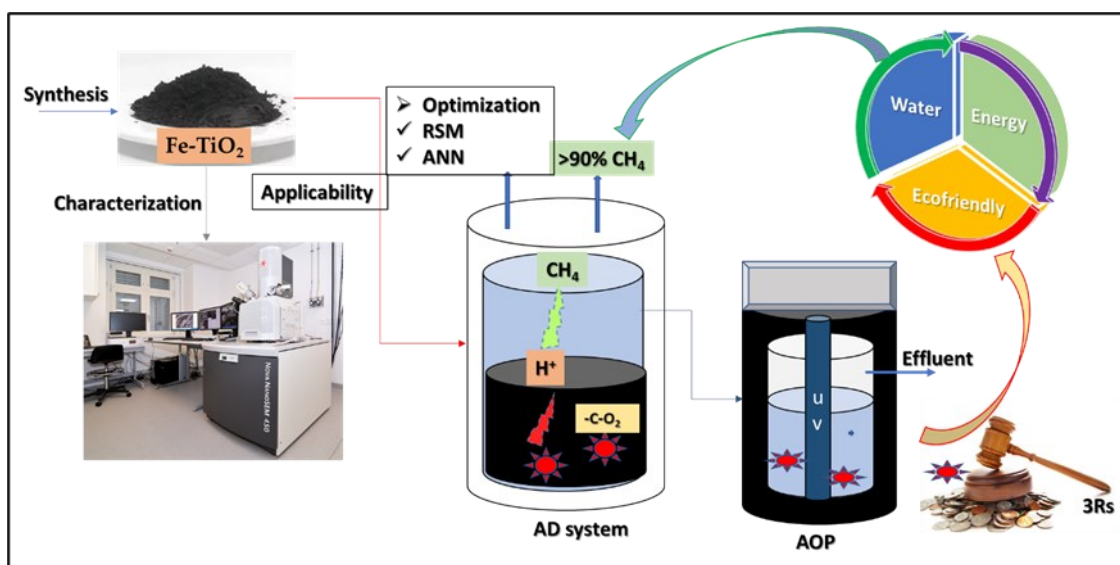
To obtain an optimal balance between robustness and cost-effectiveness of the integrated system, a series of feasibility and engineering works were explored. The first phase involved the synthesis via a co-precipitation technique, characterization, and applicability of the magnetized-photocatalysts (MPCs) for wastewater treatment. Analytically, the scanning electron microscopy and energy dispersive X-ray (SEM/EDX), Fourier transforms infrared spectra, X-ray diffraction (XRD), and Brunauer- Emmett-Teller (BET) techniques showed the tailored MPCs were successfully magnetized. Among the MPCs studied, Fe-TiO₂ (with a BET surface area of 62.73 m²/g) was found as the best with greater potential for above 75% decontamination of the wastewater and methane yield.

In the technological design and evaluation, Fe-TiO₂ was examined using biochemical methane potential (BMP), biophotocatalytic (BP), biomagnetic (BM), and biophotomagnetic (BPM) systems. Due to the external magnetic field influence on the BPMs, it was found very promising for future adventures. Above all, the novel integrated AD-AOP magnetized system proof of concept showed great potential for recoverability of the MPCs for reuse, reducing the

toxicological effects of trace metals (27 elements considered), and improving water and biogas quality. The bioenergy economy of the integrated AD-AOP magnetized system demonstrated net energy being able to subsidize the energy required by the UV-lamp of the AOP system.

Conclusively, this finding provides an insight into synthesizing novel MPCs and their applicability for wastewater remediation and biogas production. Also kinetics modeling and response surface methodology (RSM) optimization coupled with artificial neural network (ANN) predictability showed the potential to develop an optimized integrated AD-AOP magnetised system towards the treatment of industrial wastewater, biogas production, and CO₂ emission reduction. The prospects necessitate a techno-scientific revolution to upscale the current integrated system into a pilot scale with smart-online monitoring towards improving the wastewater circular economy.

Graphical abstract



Research outputs and knowledge dissimulation

This thesis is based on the author's published journal Papers (1-20), book chapters (1- 6), unpublished works under consideration for publication, and technical reports (I- IV). The author was the corresponding author in all the papers, while the co-authors assisted in writing by making valuable comments and corrections. The present author was also the principal investigator for the technical reports (I- IV) and a presenter at both local and international conferences (I - XI) with many accolades and awards (I - XI) to his name.

List of journal publications

Out of the published journal articles listed below, Papers (1-10) as referred were linked to the objectives of this study as supporting information to compile the Chapters of the thesis.

1. **Kweinor Tetteh, E.**, Rathilal, S., Asante-Sackey, D. and Chollom, M.N., 2021. Prospects of Synthesized Magnetic TiO₂-Based Membranes for Wastewater Treatment: A Review. *Materials*, 14(13), 3524. <https://doi.org/10.3390/ma14133524>
2. **Kweinor Tetteh, E.**, Opoku Amankwa, M., Armah, E.K., Rathilal, S., 2020. Fate of COVID-19 Occurrences in Wastewater Systems: Emerging Detection and Treatment Technologies—A Review. *Water*, 12, 2680. <https://doi.org/10.3390/w12102680>
3. **Kweinor Tetteh, E.** and Rathilal, S., 2021. Adsorption and Photocatalytic Mineralization of Bromophenol Blue Dye with TiO₂ Modified with Clinoptilolite/Activated Carbon. *Catalysts*, 11(7). <https://doi.org/10.3390/catal11010007>
4. **Kweinor Tetteh, E.**, Obotey Ezugbe, E., Asante-Sackey, D., Armah, E.K. and Rathilal, S., 2021. Response Surface Methodology: Photocatalytic Degradation Kinetics of Basic

Blue 41 Dye Using Activated Carbon with TiO₂. *Molecules*, 26(4), 1068.
<https://doi.org/10.3390/molecules26041068>

5. **Kweinor Tetteh, E.** and Rathilal, S., 2020, Kinetics and Nanoparticle Catalytic Enhancement of Biogas Production from Wastewater Using a Magnetized Biochemical Methane Potential (MBMP) System. *Catalysts*, 10, 1200.
<https://doi.org/10.3390/catal10101200>
6. **Kweinor Tetteh, E.**, Amo-Duodu, G. and Rathilal, S., 2021. Synergistic Effects of Magnetic Nanomaterials on Post-Digestate for Biogas Production. *Molecules*, 26 (21), 6434. <https://doi.org/10.3390/molecules26216434>
7. **Kweinor Tetteh, E.** and Rathilal, S., 2021. Biogas Production From Wastewater Treatment-Evaluating Anaerobic And Biomagnetic Systems. *Water-Energy Nexus*, 4, 165-173. <https://doi.org/10.1016/j.wen.2021.11.004>
8. **Kweinor Tetteh, E.**, Rathilal, S. and Amo-Duodu, G., 2022. Exploring CO₂ Bio-Mitigation Via Bio-Photo-Magnetic System For Wastewater Treatment And Biogas Production, *Biomass Conversion and Biorefinery (MDPI Journal of Applied Science , Accepted)*
9. **Kweinor Tetteh, E.**, and Rathilal, S., 2022. Response Surface Optimization of Biophotocatalytic Degradation of Industrial Wastewater for Bioenergy Recovery, *Bioengineering*. 2022; 9(3):95. <https://doi.org/10.3390/bioengineering9030095>
10. **Kweinor Tetteh, E.**, and Rathilal, S., 2022, Biophotocatalytic Reduction Of CO₂ in Anaerobic Biogas Produced from Wastewater Treatment Using an Integrated System. *Catalysts*. 12(1), 76. <https://doi.org/10.3390/catal12010076>

Additional supporting papers:

11. **Kweinor Tetteh, E.** and Rathilal, S., 2021. Application Of Biomagnetic Nanoparticles For Biostimulation Of Biogas Production From Wastewater Treatment. *Materials Today: Proceedings*. 45, 5214-5220. <https://doi.org/10.1016/j.matpr.2021.01.720>
12. **Kweinor Tetteh, E.**, Rathilal, S. and Amo-Duodu, G., 2022. Biogas Production From Wastewater: Comparing Biostimulation Impact of Magnetized-Chitosan and -Titania Chitosan,. *Materials Today: Proceedings*. <https://doi.org/10.1016/j.matpr.2022.02.092>
13. **Kweinor Tetteh, E.**, Rathilal, S. and Naidoo, D.B., 2020. Photocatalytic Degradation of Oily Waste And Phenol from a Local South Africa Oil Refinery Wastewater Using Response Methodology. *Scientific Reports*, 10(1), 1-12. <https://www.nature.com/articles/s41598-020-65480-5>
14. **Kweinor Tetteh, E.**, and Rathilal, S., 2021. Application Of Magnetized Nanomaterial for Textile Effluent Remediation Using Response Surface Methodology. *Materials Today: Proceedings*, 38, 700-711. <https://doi.org/10.1016/j.matpr.2020.03.827>
15. **Kweinor Tetteh, E.**, Obotey Ezugbe, E., Rathilal, S. and Asante-Sackey, D., 2020. Removal of COD and SO_4^{2-} from Oil Refinery Wastewater Using a Photo-Catalytic System-Comparing TiO_2 and Zeolite Efficiencies. *Water*, 12(1), 214. <https://doi.org/10.3390/w12010214>
16. **Kweinor Tetteh, E.**, Naidoo, B.D. and Rathilal, S., 2019. Optimization of Photo-Catalytic Degradation of Oil Refinery Wastewater Using Box-Behnken Design. *Environmental Engineering Research*, 24(4), 711-7. <https://doi.org/10.4491/eer.2018.216>

Other contributions:

17. Amo-Duodu, G., **Kweinor Tetteh, E.**, Rathilal, S., Armah, E. K., Adedeji, J., Chollom, M. N. and Chetty, M., 2021. Effect of Engineered Biomaterials and Magnetite on Wastewater Treatment: Biogas and Kinetic Evaluation. *Polymers*, 13 (24), 4323. <https://doi.org/10.3390/polym13244323>
18. Amo-Duodu, G., Rathilal, S., Chollom, M.N. and **Kweinor Tetteh, E.**, 2021. Application of Metallic Nanoparticles for Biogas Enhancement Using the Biomethane Potential Test. *Scientific African*, 12, e00728. <https://doi.org/10.1016/j.sciaf.2021.e00728>
19. Sibiya, P.N., Rathilal, S. and **Kweinor Tetteh, E.**, 2021. Coagulation Treatment Of Wastewater: Kinetics and Natural Coagulant Evaluation. *Molecules*, 26(3), 698. <https://doi.org/10.3390/molecules26030698>
20. Madondo, N. I., **Kweinor Tetteh, E.**, Rathilal, S. and Bakare, B. F., 2021. Synergistic Effect of Magnetite and Bioelectrochemical Systems on Anaerobic Digestion. *Bioengineering*, 8(12), 198. <https://doi.org/10.3390/bioengineering8120198>

List of book chapters

The book chapters (1-6) enlisted below assisted the author in the conceptualization development of this project.

1. **Kweinor Tetteh, E.**, Asante-Sackey, D., Armah, E. K., and Rathilal, S., 2022. Tapping Wastewater Resource: Why And How? In Sanjay S (ed), *Handbook of Biofuels*, Academic Press, <https://doi.org/10.1016/B978-0-12-822810-4.00006-3>

2. **Kweinor Tetteh, E.**, Opoku-Amankwa M., Rathilal S., 2021. Microbial Degradation of Oils. In: Inamuddin ., Ahamed M.I., Prasad R. (eds), Recent Advances in Microbial Degradation. Environmental and Microbial Biotechnology. Springer, Singapore., https://doi.org/10.1007/978-981-16-0518-5_16
3. **Kweinor Tetteh, E.**, Rathilal S., Amankwa Opoku M., Amoah I.D., Chollom M.N., 2021 Molecular Imprinting Technology: A New Approach for Antibacterial Materials. In: Inamuddin, Ahamed M.I., Prasad R. (eds), Advanced Antimicrobial Materials and Applications. Environmental and Microbial Biotechnology. Springer, Singapore. https://doi.org/10.1007/978-981-15-7098-8_15
4. **Kweinor Tetteh, E.** and Rathilal, S., 2019. Application Of Organic Coagulants In Water And Wastewater Treatment, In Arpit S and Elsayed Z (eds), Organic Polymers, IntechOpen, DOI: 10.5772/intechopen.84556
5. **Kweinor Tetteh, E.**, Rathilal S, Chetty M, Armah EK., and Asante-Sackey, D., 2019. Treatment of Water and Wastewater for Reuse and Energy Generation-Emerging Technologies, In Murat E (ed), Water and Wastewater Treatment, IntechOpen, DOI: 10.5772/intechopen.84474
6. Armah, E. K., Chetty, M., Rathilal, S., Asante-Sackey, D., and **Kweinor Tetteh, E.**, 2022 Lignin: Value Addition Is Key To Profitable Biomass Biorefinery. In Sanjay S (ed), Handbook of Biofuels. Academic Press. <https://doi.org/10.1016/B978-0-12-822810-4.00011-7>

List of technical reports

The following are a list of technical reports (I-IV) submitted to the South Africa's Water Research Commission as being part of deliverables for the ongoing project (WRC: C2019/2020 – 00212), where the author was the principal investigator.

- I. Synthesis of magnetic nanoparticles: characteristics and application for wastewater treatment, (Submitted 22/01/2021)
- II. Design and fabrication of anaerobic-photocatalytic system for municipality wastewater treatment - biogas production (Submitted, 30/06/2021)
- III. Monitoring and evaluation of the integrated anaerobic-photocatalytic system for municipality wastewater treatment (Submitted, 29/10/2021)
- IV. An integrated anaerobic-photocatalytic-magnetic wastewater treatment system (Under preparation)

List of conference presentations

The author was the main presenter at both the local and international conferences (Papers I-XI)

- I. **Kweinor Tetteh, E.,** and Rathilal, S. Biostimulation of biogas production from wastewater: comparing magnetized- chitosan/titania biocatalyst impact, Science, Engineering & Technology (ICISSET-21), December 13-15, 2021. Lisbon (Portugal), <http://fenp.org/conference/277>
- II. **Kweinor Tetteh, E.,** Rathilal, S. and Amo-Duodu, G. Application of magnetized photocatalyst for municipality wastewater treatment using the biophotocatalytic

- system, International Conference On Sustainable Development, December 7-9, 2021, Durban, South Africa, [international conference on sustainable development \(dut.ac.za\)](http://international.conference.on.sustainable.development.dut.ac.za)
- III. **Kweinor Tetteh, E.,** Amo-Duodu, G. and Rathilal, S. Synergistic effect of functionalized Zn-FeTiO₂ and Cu-ZnFeTiO₂ on biostimulated methanation process. Southern African Sustainable Energy Conference (SASEC 2021). 17-19 November 2021, Stellenbosch, Capetown, Western Cape Province, South Africa. [Home - SASEC 2021](http://Home-SASEC2021)
 - IV. **Kweinor Tetteh, E.,** and Rathilal, S. Magnetic induction and nanoparticles effects on anaerobic digestion of industrial wastewater for biogas production, South African Chemical Engineering Congress 2021, September 21-22, 2021. <https://www.sacec.co.za/>
 - V. **Kweinor Tetteh, E.** and Rathilal, S. Application of biophotocatalytic system for CO₂ mitigation in anaerobic biogas production, 8th Edition of Global Conference on Catalysis, Chemical Engineering & Technology (Virtual), September 27-28, 2021 <https://www.youtube.com/c/MagnusGroupLLC/playlists>
 - VI. **Kweinor Tetteh, E.,** Rathilal, S. and Amo-Duodu, G. Exploring CO₂ bio-mitigation via the bio-photo-magnetic system for wastewater treatment and biogas production. International Conference on Advances in Sustainable Research for Energy and Environmental Management (ASREEM-2021). August 6-8, 2021. Virtual, Gujarat, India <https://sites.google.com/view/asreem-2021/home>
 - VII. **Kweinor Tetteh, E.** and Rathilal, S. Application of nanoparticles (NPs) oxides (CuO, Fe₃O₄ and TiO₂) for methanation enhancement in anaerobic digesters. Green Technologies for Sustainable Development-2021. March 9-11, 2021. Dharmsinh

Desai University, Nadiad-387 001, Gujarat, India.

<https://www.youtube.com/watch?v=C2kt7sReujk>

- VIII. **Kweinor Tetteh, E.** and Rathilal, S. Biogas production from wastewater treatment – evaluating anaerobic and biomagnetic systems. Green Technologies for Sustainable Development-2021. March 9-11, 2021. Dharmsinh Desai University, Nadiad-387 001, Gujarat, India. <https://www.youtube.com/watch?v=C2kt7sReujk>
- IX. **Kweinor Tetteh, E** and Rathilal, S 2020, Magnetic coagulant for wastewater treating to enable biogas production from sludge, World Sustainable Energy Days 2020, Young Energy Researchers Conference, Wels/Austria 04 - 06 March 2020, <http://p353980.webspaceconfig.de/en/reviews/wsed-2020/young-energy-researchers.html>
- X. **Kweinor Tetteh, E** and Rathilal, S 2019, Evaluation of magnetic coagulants for industrial wastewater treatment, UNESCO Engineering Conference, Hosted by NorthWest University, Mahikeng, South Africa 25 September 2019 <https://engineering.nwu.ac.za/engineering/programme>
- XI. **Kweinor Tetteh, E** and Rathilal, S. Biogas production using an integrated coagulation-anaerobic magnetized system. DUT, 5th Interdisciplinary Research and Innovation Conference 2020, 15 – 17 September 2020, Virtual, South Africa. <https://www.dut.ac.za/events/interdisciplinary-research-and-innovation-virtual-conference/>

List of awards and honours

The author is the recipient of the followings awards and accolades

- I. Doctoral Student of the year award by the Durban University of Technology ,SA , June 2022
- II. Best oral paper presentation of 30th International Conference on Innovations in “Science, Engineering & Technology” (ICISSET-21) Lisbon, Portugal, December 13-15, 2021.
- III. National Research Foundation (NRF) 2021 Research Excellence Award for the Next Generation Researchers held in Pretoria, South Africa, November 2, 2021
- IV. Top Doctoral 2020 published student in the department of chemical engineering. at the Durban University of Technology, South Africa, 5 November 5, 2021
- V. Best oral paper presentation of the International Conference on Advances in Sustainable Research for Energy and Environmental Management (ASREEM-2021) held in India, August 6-8,2021
- VI. Best oral paper presentation of Green Technologies for Sustainable Development- 2021 conference, Dharmsinh, Desai University, Nadiad, Gujarat, India, March 9-11, 2021
- VII. 1st Runner Up oral paper presentation of SAIChE KZN Research Day. Mangosuthu University of Technology, SA, August 28, 2019
- VIII. Durban University of Technology award in recognition of receiving the Eni Award in the Category: Young Talents from Africa, November 12, 2019

- IX. Eni Award Debut Researcher: Young Talent from Africa 2019 presented by the President of the Italian Republic, Sergio Mattarella, ceremony held at the Quirinal Palace in Rome, Italy, October 10, 2019
- X. 1st Runner Up oral paper presentation of SAIChE KZN Research Day. Mangosuthu University of Technology, SA , August 28, 2019
- XI. Best oral presenter of Three Minutes PhD Thesis Competition, Hosted by Durban of University of Technology, SA. August 13, 2019

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Abbreviations

AD	Anaerobic digestion
AN	Anoxic/buffer system
ANN	Artificial neural network
ANOVA	Analysis of variance
AOP	Advanced oxidation process
BBD	Box–Behnken design
BMP	Biochemical methane potential test
BP	Biophotocatalytic system
COD	Chemical oxygen demand
EDX	Energy dispersive X-ray
FTIR	Fourier transform infrared spectrometer
HRT	Hydraulic retention time
MPCs	Magnetic photocatalysts
Ms	Magnetic filter
NPs	Nanoparticles
OLR	Organic loading rate
RSM	Response surface methodology

SEM	Scanning electron microscopy
UV	Ultra -violet
UV-vis	Ultra-violet visible
XRD	X-ray diffraction
WWTPs-	Wastewater treatment plant

Chapter 1 - Introduction

1.1 Background

The development of centralized wastewater treatment systems, which are energy efficient to mitigate emerging pollutants and environmental challenges associated with the water sector is globally gaining attention (Adetunji and Olaniran, 2021; Divyapriya et al., 2021). Meanwhile, there is a considerable risk of freshwater and energy resource depletion due to upsurging population growth and industrialization along with anthropogenic CO₂ emissions (Adetunji and Olaniran, 2021; Ángeles et al., 2021; Divyapriya et al., 2021). Herein, the world's population is estimated to increase from 7.7 billion in 2019 to 9.7 billion people in 2050 (Hube et al., 2020). This appears to increase the demand for freshwater supply significantly as 70% of the world's water resources is already accounted for agricultural irrigation (Naddeo et al., 2019; Izadpanah et al., 2021). Meanwhile, the operation of conventional wastewater treatment plants (WWTPs) coupled with disposal and distribution systems comes with high costs to meet stringent demands (Kamuti 2022; Lin and Sai 2021; Russo and Von Blottnitz 2017). Therefore, utilizing the wastewater treated residue as an energy resource for biogas production, to compensate the WWTP energy utilization, comes in handy.

Conventionally, WWTPs are also being challenged with high organic strength and emerging contaminants (ECs) such as pharmaceuticals (antibiotics), COVID-19 RNA, personal care products, food additives, and customized nanomaterials (Papers 1-2). Subsequent advancement of scientific environmental assessments reveal recalcitrant contaminants (like antibiotics) after a long period can still be detected in the wastewater streams (Lin and Sai 2021; Maghari et al. 2022). This has drawn the attention of many stakeholders in the water sector to improve the efficacy of WWTPs.

In view of this, advanced oxidation processes (AOPs) is considered a viable wastewater treatment technology for eliminating high strength organics and ECs that are difficult to be handled by conventional methods due to their high chemical stability and/or limited biodegradability (Chong et al., 2010; Xu et al., 2019; Adetunji and Olaniran, 2021). However, AOPs, as reported in our previous works (Book chapter 5; Paper 2) and other studies (Lin et al. 2022; Mahtab et al. 2021), have many setbacks, including difficulty to recover the photocatalyst and its energy-driven tenacity makes it expensive to operate (Della Rocca et al., 2021; Bica et al., 2022).

On this basis, incorporating a magnetized photocatalyst (Fe-TiO₂) with a high surface-volume ratio and magnetic properties reported in our Papers (1, 2 and 7) have shown great potential for magnetic separation technology in wastewater settings. Therefore, the novelty of this study was inline with the development of integrated AD-AOP magnetised system for wastewater treatment with bioenergy production and nanomaterials recoverability potential.

1.2 Wastewater treatment challenges

Wastewater treatment is a critical performance area as it impacts directly on human health, indirectly on downstream drinking water purification systems, and also communities settled downstream who use these waters for their daily activities (Samer 2015). With a projected 9.7 billion people by 2050, water pollution is expected to rise with an increase in demand and therefore requires taking drastic measures (Ramakrishna and Jose 2022; Sahani et al. 2022).

Pollutants in wastewater can be organic, inorganic, or biological (Adetunji and Olaniran 2021; Russo and Von Blottnitz 2017; Sahani et al. 2022). Water pollution endangers human health and the aquatic ecology, making it one of the world's biggest environmental issues

today (Sahani et al. 2022). As highlighted in our Book chapters (1-6), conventional wastewater treatment systems involve primary, secondary, tertiary, and advanced methods of treatment. However, most of these conventional methods do not completely remove emerging contaminants (ECs). This is due to their high polarity and solubility in water (Bhadra et al. 2016; Mlunguza et al. 2019). Herein, magnetized nanoparticles with separation and reusability benefits were proposed (Papers 1-2) to be given attention for advanced treatment processes like AOP and membrane technology.

Recently, as industries strive to meet the needs of increasing human activities, more recalcitrant contaminants are introduced into the environment, compounding global efforts to reduce pollution and make the planet more sustainable (Adamek et al. 2016; Mecha et al. 2016). This comprises waste resources that contribute to industrial wastewater and CO₂ emissions. South Africa, being known as a water scarcity country, is also faced with chemical pollutants of high strength organics emerging from industries such as pharmaceuticals, petrochemical, agrochemicals, mining, textiles, pulp and paper, etc. posing threats to the water bodies (Adetunji and Olaniran 2021; Griggs et al. 2013; Russo and Von Blottnitz 2017). The end route of these recalcitrant pollutants offers significant treatment hurdles in South African municipality WWTPs (Stafford et al., 2013; Ponce-Robles et al., 2020), as this has resulted in sub-optimal operation and high energy utilization in treating polluted water before discharge (Beumer, 2018). So, most of the municipalities require huge investments and more robust technology to alleviate their treatment deficits and satisfy strict discharge constraints (Kamuti 2022).

Consequently, the Department of Water Affairs developed the National Water Resource Strategy (NWRS) II in June 2013, intending to ensure equitable and sustainable access to and use of water for all South Africans while also safeguarding the country's water resources.

According to the same NWRS report, an investment of around R700 billion is required over the next decade to address the technical requirements of the affected water value chain (Van Niekerk and Schneider 2013). To address this problem will make most conventional technologies to be expensive and energy intensive to operate on a daily basis and therefore, warrants alternate robust technologies.

1.2.1 Emerging contaminants

Emerging contaminants (ECs) are defined as synthetic or naturally occurring substances that can interfere with the functionality of endocrine systems due to the endocrine-disrupting properties of pharmaceuticals, personal-care products, steroid sex hormones, illegal substances, flame retardants and perfluorinated compounds (Gogoi et al. 2018; Lin et al. 2022; Sahani et al. 2022). These have great environmental concerns in the wastewater settings as they are mostly unregulated compounds with variations in real-time data monitoring resources (Chollom et al. 2020; Gogoi et al. 2018; Sahani et al. 2022).

The residual pharmaceuticals in sewage streams, mostly in aquatic systems, pose great challenges (Gogoi et al. 2018). Thus, they are highly resistant to biological degradation and can easily escape from conventional treatment plants and therefore, requires sophisticated analytical tools for their accurate detection and treatment (Papers 1-2). Also, soluble pesticides are one of the most harmful substances in the environment, posing a serious hazard to surface and groundwater (Demir et al. 2019). The use of AOPs to degrade ECs has been extensively researched (Chollom et al. 2020; Kanakaraju et al. 2018; Sahani et al. 2022; Sivaranjanee and Kumar 2021; Wang and Zhuan 2020), however, there are very few cost-effective integrated AD-AOP treatment alternatives. In essence, most of the advanced processes (AOP, membrane) are employed in the water and wastewater sectors as polishing steps, generally for the abatement of ECs (Kanakaraju et al. 2018; Mahtab et al. 2021; Wang

and Zhuan 2020). Herein, the AOP system considered was more advantageous than the membrane process, as some of its setbacks are highlighted in Paper 1.

1.2.2 Conventional wastewater treatment technologies

Conventionally, treatment of wastewater involves a series of treatment steps designed to remove domestic and industrially generated pollutants to desirable discharge limits (Adetunji and Olaniran 2021; Rajesh Banu et al. 2008; Rout et al. 2021). Some of these phases in municipal or sewage WWTPs include primary (physio-chemical processes involving coagulation/sedimentation), secondary (activated sludge digesters or trickling filters) and tertiary (filtration, chlorination, disinfection), as well as advanced processes (advanced oxidation processes (AOPs), membrane filtration and adsorption) (Book chapters 1-6).

Diversity of wastewater resources is not only associated with the industries (textile, refining, mining, agrochemical, pharmaceutical, pulp and paper, food industry, etc.) that generate them but also the concentration level of the contaminants (Sahani et al. 2022; Sivaranjanee and Kumar 2021). Generally, compositions of industrial wastewater are more diverse than domestic wastewater, which makes their treatment processes highly complex, such that their composition and volume are subjected to change with time within the industry as well as the downstream (Adetunji and Olaniran 2021; Kamuti 2022; Sahani et al. 2022). Consequently, meeting discharge limits and remediation of the wastewater for reuse requires a combination of cost-effective treatment technologies (Demir et al. 2019; Kamuti 2022; Russo and Von Blottnitz 2017). This makes the selection of the best treatment process to be a very immersive task in wastewater settings. Therefore, some factors which can be considered by decision-makers in selecting the best wastewater treatment technology are presented in Figure 1.1. The use of a hybridized/integrated system that combines biological, chemical,

and physical treatment approaches is beneficial (Apollo et al. 2013, 2016; Sudarjanto et al. 2006; Wang et al. 2021). Notwithstanding, this combination must be used to save energy, recover resources, and improve overall system efficiency.

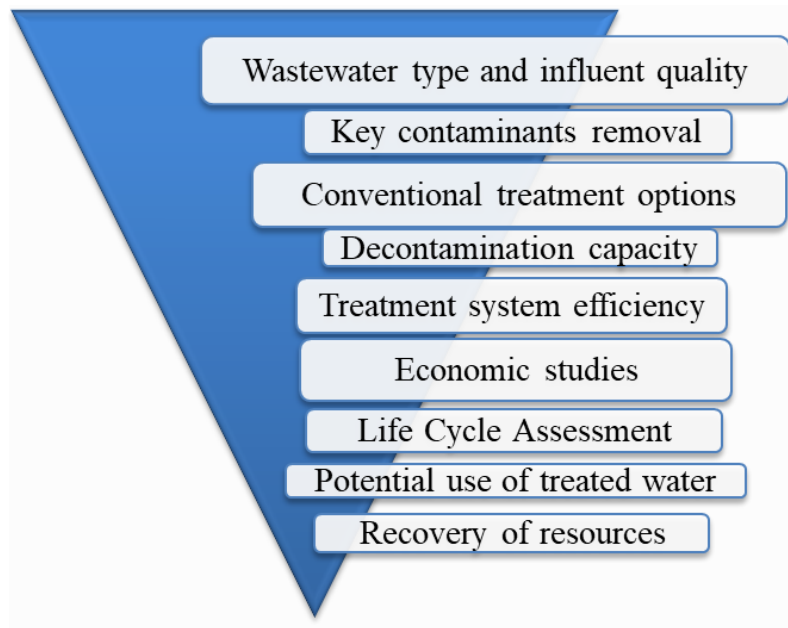


Figure 1.1: Schematic diagram of factors to be considered in selecting wastewater treatment technologies; Adapted from Fermoso et al. (2019)

1.3 Water-energy nexus

Global warming and waste management have driven greener and more eco-friendly technologies (Mostafaeipour et al. 2022; Nguyen et al. 2021). Reducing fossil fuels usage or replacing it with environmentally acceptable, renewable energy sources has been a hotly debated subject (Demirbas 2005; Finance 2011; Goli and Sahu 2018; Kumar et al. 2021; Mostafaeipour et al. 2022; Popp et al. 2014; Wang et al. 2021). It is possible to reduce energy consumption and pollution without compromising economic growth in countries such as South Africa (Lin and Sai 2021). As a developing country, South Africa has a lot to lose if

it keeps using fossil fuels and depleting its large coal reserves. Meanwhile, electricity represents about 75% of the total energy demand in South Africa, where petroleum and natural gas are the most commonly used fossil fuels (Kamuti 2022; Lin and Sai 2021; Russo and Von Blottnitz 2017).

Amidst this challenge, investing in renewable energy sources to subsidize the country's energy demand comes with a cost (Chai et al. 2021; Zhao et al. 2021a). This necessitates balancing energy demands with minimizing wastewater pollution, which is a better option to mitigate the combustion of coal with its environmental risk (Nguyen et al. 2021). However, reducing sludge-water content in wastewater is highly complex, since it can compromise both the water and bioenergy quality (Ángeles et al. 2021; Russo and Von Blottnitz 2017; Zhao et al. 2021b). The technological, legislative, socioeconomic, environmental, and political issues might affect the decision-maker to consider wastewater as an energy resource (de Andrade Guerra et al. 2021; Wang et al. 2021). So, to improve sustainable energy and the environment, future technologies should consider recycling and reusing wastewater with a resourceful potential (Book chapter 1).

1.3.1 Wastewater as a bioenergy resource

Wastewater is generated by households, agriculture, and industries. However, it is generally treated in constructed wetlands, which end up producing odorous gases (Nguyen et al. 2021; Rajesh Banu et al. 2008; Rout et al. 2021). In essence, freshwater besides being an essential commodity for human metabolism is also a medium for deriving useful resources for industries (Apollo et al. 2013; Chai et al. 2021; Nguyen et al. 2021; Rout et al. 2021). Meanwhile, natural resources are depleting owing to population growth estimated to populate 9.7 billion people by 2050 (Griggs et al. 2013; Ramakrishna and Jose 2022; Van Niekerk and Schneider 2013). The need for alternative cheap and affordable energy is

therefore inevitable as this is paved by the United Nations development goals for 2050 (Griggs et al. 2013; Ramakrishna and Jose 2022; Russo and Von Blottnitz 2017).

Reclamation of wastewater for reuse is becoming more environmental and economically sustainable by adding value to their by-products. Such as agricultural purposes and energy (biogas) generation (Nguyen et al. 2021; Russo and Von Blottnitz 2017; Zhao et al. 2021b). Therefore, considering the urban water chain, which is a pool of liquid waste streams, has many opportunities to recover resources such as organic matter, phosphorus, nitrogen, and heavy metals for reuse (Book chapter 1). For example, biogas rich in methane (CH_4) can be used to produce green gas, heat and electricity, using combined heat and power technology (Durán et al. 2021; Nguyen et al. 2021). The use of AD under various reactor designs for the dual purposes of energy recovery and wastewater treatment can reduce the cost of disposing of WWTPs sludge (Ángeles et al. 2021; Fernández-Polanco et al. 2021). Herein, these works present anaerobic biogas production from wastewater to complement the UV post-treatment system's energy demands.

1.3.2 Biogas production upgrading

Biogas production process can be classified into two categories such as thermo-chemical (e.g. gasification) and biochemical production (AD) (Wu et al. 2021). Biogas from WWTPs characteristically constitutes a valuable bioenergy product such as methane (CH_4) of 40–75% carbon dioxide (CO_2) of 25–60% and others (Fuentes et al. 2021; Lin and Sai 2021). France produced 84% of its annual energy from AD biogas utilizing non-hazardous waste (De Clercq et al. 2017). Also, Germany developed agricultural biogas plants exploiting biowaste and wastewater sludge to generate electricity via a combined heat and power (CHP) mechanism (Hijazi et al. 2016). However, the high concentration (25-60%) of CO_2 can affect the overall methane potential of the AD biogas produced (Fuentes et al. 2021; Lin

and Sai 2021), where CO₂ emissions into the atmosphere coupled with fossil fuel combustion could pose high threats to civilization. This necessitates CH₄ enrichment and upgrading of the biogas (Durán et al. 2021; Zhao et al. 2021b). Water scrubbing, organic solvent scrubbing, ammonia scrubbing, pressure swing adsorption, and membrane applications are among the common techniques used for biogas upgrading (Bauer et al. 2013). Advanced water gas shift (WGS) reactions can be employed with a catalyst to convert the excess carbon into methane (Pastor-Pérez et al. 2017). Therefore, this study focused on using novel magnetized photocatalysts (MPCs) as a biocatalyst to enhance the AD process.

1.4 The integrated system conceptualization

To provide sustainable energy and water supply for socioeconomic growth and activities warrants cost-effective technologies (De Clercq et al. 2017; Popp et al. 2014). However, societal and industrial activities are upsurging wastewater and combusted fossil fuel CO₂ levels in the atmosphere (Lin and Sai 2021; Nguyen et al. 2021; Popp et al. 2014). So, focusing on wastewater/biomass treatment to establish a bio-based economy gave this novel integrated AD-AOP magnetised system concept to develop.

Anaerobic digestion (AD) has been a common approach for converting high organic material into biogas (Bauer et al. 2013; Russo and Von Blottnitz 2017; Zhao et al. 2021b). However, the AD process is mainly governed by the oxidation state of the organic waste digested, environmental conditions, and the AD reactor configurations (Apollo et al. 2013; Rojo et al. 2021; Zhao et al. 2021b). The enactment of AD processes is inadequate in removing some recalcitrant micropollutants emerging from oil refineries (soap oil grease), mines (heavy metals), textile (dyes), agriculture (pesticides) and pharmaceutical (antibiotics) industries entering the Municipality WWTPs (Papers 1-2).

With the recent South African energy-driven economy, meeting the country's high energy demand warrants upgrading of WWTPs capacity to balance their energy throughput and utilization (Lin and Sai 2021; Russo and Von Blottnitz 2017). In essence, the paradigm shift of WWTPs into the bioeconomy involves the use of AD to degrade complex organic matter into biogas (Rojo et al. 2021). Notwithstanding, the AD process has proven to be advantageous in terms of adding value to wastewater as a bioenergy resource (Durán et al. 2021; Russo and Von Blottnitz 2017; Zhao et al. 2021b). The AD mechanism, which includes hydrolysis, acidogenesis, acetogenesis, and methanogenesis to produce methane potential is very slow (Ajay et al. 2020; Apollo et al. 2013; Rojo et al. 2021). In addressing these setbacks, this study proposed an AD process coupled with photocatalytic technology coupled with magnetic separation as a wastewater abatement technology option for bioenergy production.

1.4.1 Magnetic separation

A recent surge in research into superparamagnetic nanomaterials has hastened the development of magnetically recoverable catalysts (Jiang et al. 2022; Maghari et al. 2022; Nakhband et al. 2022; Watson et al. 2002). For the development of high-quality magnetically recoverable catalysts, the choice of support and immobilization method is critical. Some of the synthesis methods commonly used include co-precipitation, microemulsion, thermal decomposition, solvothermal, sonochemical, microwave-assisted, chemical vapour deposition, combustion, carbon arc, and laser pyrolysis (Jacinto et al. 2020; Jiang et al. 2022; Watson et al. 2002; Xu et al. 2012).

Magnetic photocatalysts (MPCs) are a class of nanomaterials with a size less than 100 nm and can be influenced by an external magnetic field (Jacinto et al. 2020; Lamichhane et al. 2022; Nakhband et al. 2022). In addition to size effects, surface-to-volume ratios,

interaction, magnetic separation, selectivity, and surface chemistry make MPCs very intriguing (Jacinto et al. 2020; Lamichhane et al. 2022).

Magnetic separation has been researched to improve the handling and recovery of the enzymes, organometallics, and nanoparticle catalysts in medication delivery, molecular biology, diagnostics, catalysis and environmental remediation (Jacinto et al. 2020; Jiang et al. 2022; Lamichhane et al. 2022; Limthin et al. 2022; Nakhband et al. 2022). A common application of magnetic nanoparticles is to remove heavy metals from wastewater (De Latour 1973; Kemsheadl and Ugelstad 1985). This purification technique yields no secondary waste and all materials are recyclable. Magnetic nanoparticles adsorb pollutants via ionic exchange and other weak forces commonly known as magnetically induced chemical separation (De Latour 1973).

Currently, heterogeneous photocatalysis based on titanium dioxide (TiO_2) nanomaterials in an AOP has been a remarkable post-treatment technique for eliminating a wide range of recalcitrant (inorganic and organic) pollutants (Kanakaraju et al. 2018; Mahtab et al. 2021; Wang and Zhuan 2020). Unfortunately, the use of conventional TiO_2 nanoparticles is difficult to separate after photocatalytic activity and inactive in solar energy utilization for large-scale production (Abdulhameed et al. 2019; Riaz and Park 2020; Thakre et al. 2021; Zhao et al. 2021c). This is a major problem in water and wastewater treatment since it increases costs and limits the treatment efficiency. In addressing this setback, this study employed the co-precipitation technique to synthesize the novel MPCs with magnetically recoverable benefits.

1.4.2 The novel integrated system proposed

Generally, the efficacy of an integrated wastewater treatment system is commonly revealed by the distinctive nature of the individual units involved in the process (Apollo et al. 2013;

Rajesh Banu et al. 2008). In essence, the position of AOP (pre-or post-treatment) in a sequence of physical, chemical, and biological wastewater treatment processes can have an impact on AD efficiency, whether it's for biogas production or improving water quality (Apollo et al. 2013; Nguyen et al. 2021). Using AOP as a pre-treatment process can partially oxidize recalcitrant compounds to produce biodegradable intermediates for further breakdown by the AD process (Apollo et al. 2013, 2016; Sudarjanto et al. 2006). However, this can increase the cost of operation and therefore should be avoided based on the following reasons:

- a. During AOP pre-treatment, there is a lack of selectivity for preferential confrontation on the more bioresistant fractions of the effluent.
- b. Stable intermediates are formed that become less biodegradable than their original molecules.
- c. If treatment options are not selected with precision, excessive pre-oxidation can produce an effluent that is not nourished enough for microbes.
- d. An excessive amount of oxidant and/or catalysts such as metals, metal oxides, and metal salts employed in the oxidation process can poison the microorganisms in the AD process.
- e. Excessive TiO_2 photocatalysts are difficult to be separated from the reaction solution, hence magnetizing it for easy separation is valuable.

To address the above-mentioned limitations, the need to establish a step-by-step evaluation of each process comes in handy along with optimizing the operating conditions of the system such as contact time, catalyst type and dose, toxicity, temperature, etc. (Apollo et al. 2013; Kushwaha 2015; Rajesh Banu et al. 2008; Ratna et al. 2021). This approach should be

encouraged to deduce the reaction mechanisms, the degradation pathway, and kinetics of evaluating the toxicity of the wastewater matrix.

Figure 1.2 presents a summary of the diverse steps taken to warrant the feasibility study of the integrated AD-AOP system for the municipality wastewater. This depicts not just the physiochemical analysis of the wastewater, but also the biodegradation and toxicity of the performance of each process.

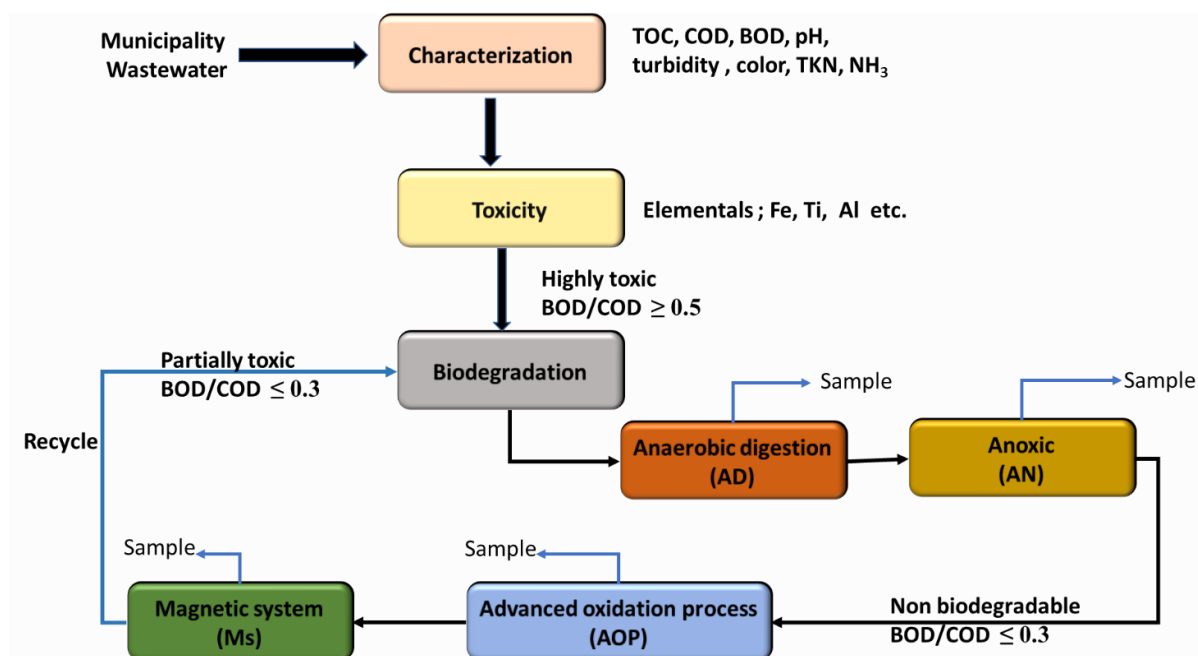


Figure 1.2: Strategy for the selection of the best treatment option for a specific toxic and/or non-biodegradable industrial wastewater adapted from Fermoso et al. (2019)

As observed (Figure 1.2), the variables commonly used to describe the high strength organics are the chemical oxygen demand (COD), biological oxygen demand (BOD), and the total organic compounds (TOC). Estimating their ratios ($0.3 \leq \text{BOD/COD} \leq 0.5$) provides an index of the amount of biodegradable and nonbiodegradable organic compounds contained in the effluent. Also, monitoring the daily biogas production can be used to

estimate the biodegradability performance of the AD process. Whereas the anoxic/buffer system (AN) as shown Figure 1.2 drives the nitrification- denitrification process. Apart from this measurement, another series of parameters related to the process conditions were monitored. In this design, introducing magnetized photocatalysts into the system can be recovered by the magnetic system (MS). To demonstrate that, the toxicity level (especially the elementals or inorganics) after the AOP-MS process is reduced and admissible for discharge. Further biotoxicity testing to ascertain the success of the treatment is encouraged.

1.4.3 Process optimization techniques

As engineering process involves the interactive effect of input factors on the process response (Abdulhameed et al. 2019; Khataee et al. 2011). Notwithstanding, the complexity of an integrated system operation, robust optimization is required to maximise the process efficiency. In this integrated system, the standalone AD and AOP processes are energy-driven with multi-operational factors. For instance, hydraulic retention time (HRT), organic loading rate (OLR), feed-substrate ratio, carbon-nitrogen ratio (C/N), and temperature (mesophilic, thermophilic) are key operational factors of the AD process (Ajay et al. 2020; Apollo et al. 2016; Rojo et al. 2021). Likewise, the AOP process is faced with energy intensity, catalyst loading, and reaction rate (Kanakaraju et al. 2018; Wang and Zhuan 2020).

Response surface methodology (RSM) was employed to model their key operational factors as a function of the response. Thus, RSM is a mathematical and statistical technique that is useful in modelling, improving, and optimization processes (Abdulhameed et al. 2019; Chelladurai et al. 2021; Deriase et al. 2021). Generally, the process optimization using RSM involved the following steps; (a) identification of response/s; (b) screening of multivariate according to the design of experiment; (c) building of an empirical response surface model; (d) and the application of various response optimization through mathematical modelling

(Abdulhameed et al. 2019). Therefore, to understand the geometrical dynamics and operational parameters that govern the integrated system, the RSM prediction was compared with an artificial neural network (ANN) as a computational prediction and validation tool.

1.5 Aim and objectives

The recent societal and industrial activities reliance on fossil fuels and water demand have intensified environmental problems. These problems directly undermines the United Nations (UN, 2015) Sustainable Development Goals (SDGs) especially those associated with clean water and sanitation (SDG 6), health (SDG 3), and sustainable management of waste (SDG 11) as well as clean and affordable energy (SDG 7). Against this background, transforming the sewage management sector in South Africa into a circular economy asset will necessitate the development of wastewater treatment technologies with sustainable benefits. This study aimed to develop an integrated AD-AOP magnetized system for the valorisation of industrial wastewater into bioenergy with the beneficiation of reducing WWTP's anthropogenic gas (CO₂) emission. Additionally, magnetized photocatalysts (MPCs) were synthesized to ease the recoverability of TiO₂ photocatalysts and also improve AD biogas production and methane quality. To achieve this aim, the study was carried out under the following four (4) specific objectives;

1. Synthesis and characterisation of the TiO₂ magnetized photocatalyst (MPC) for industrial wastewater treatment and biogas enhancement

2. Technological evaluation and applicability of the synthesized TiO₂ MPCs for industrial wastewater treatment using biological (AD), biomagnetic (BM), biophotocatalytic (BP), and Biophotomagnetic (BPM) systems
3. Design, monitor, and evaluate the lab-scale integrated anaerobic-photo-catalytic-magnetic system for municipality wastewater treatment
4. Modeling and optimising the integrated AD-AOP magnetised system for municipality wastewater treatment with estimated energy produced and CO₂ emission reduction.

The novelty of this work was carried out in two folds; (i) synthesising of the novel MPCs as an alternative to the conventional TiO₂ photocatalyst with recoverability potential, and (ii) developing an optimised integrated AD-AOP magnetized system for the treatment of wastewater, biogas production and recovery of nanomaterials. Aside this scope, this project is expected in the future, to develop a smart integrated AD-AOP magnetized for the abatement of wastewater as useful resources for the valorization of biogas to promote a sustainable wastewater management system in South Africa.

1.6 Thesis framework and layout

This thesis comprises of six chapters with a framework presented in Figure 1.3. This was compiled as chronological journal articles linking the study objectives with listed journal Papers (1-10) in Chapters as supporting information.

The introduction Chapter 1 provides a comprehensive overview, background, problem statement and conceptualisation, justifying the need to develop an integrated AD-AOP magnetised system for the wastewater treatment sector. Adding to that is the four (4) specific objectives of the study, which are expanded in Chapters 2-5.

In Chapters 2-5, the author offers brief introductory remarks to help readers grasp the articles' content and their connection to the Chapters. These include theoretical and pre-experimental motivations, methodology and discussions of unpublished findings.

Chapter 6 summarizes the findings and recommends future research directions to develop smart integrated systems. Except for the main published Papers, all cited articles are in the Reference section.

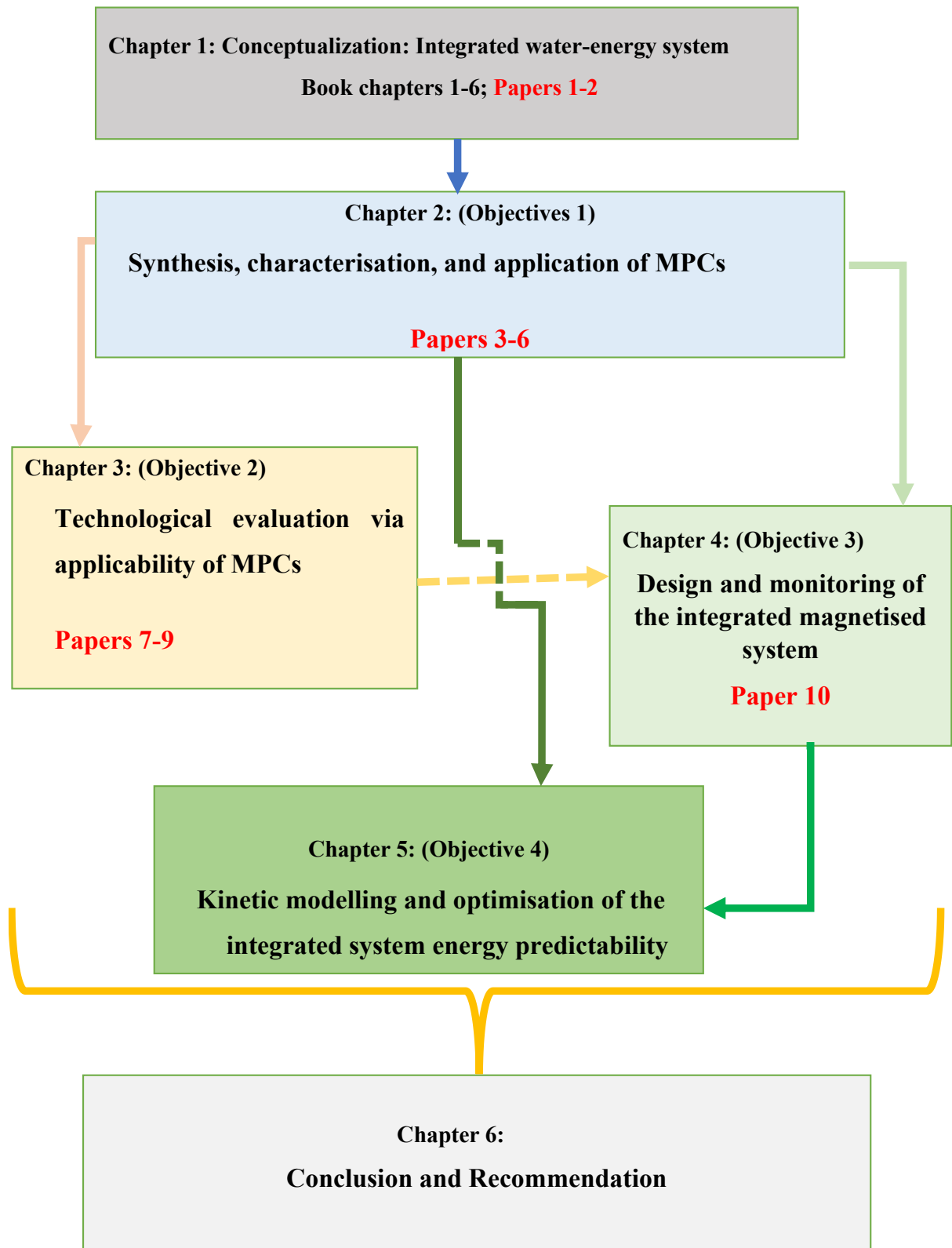


Figure 1.3: Framework of thesis layout connecting objectives and published papers to chapters

1.7 Additional information

This section presents two of our published journal Papers with their short titles as supporting information to this Chapter and conceptualization development of the project.

Paper1: Prospects of magnetized TiO_2 photocatalysts



Paper 1.pdf

Paper 2: Advanced treatment of emerging contaminants



Paper 2.pdf

Review

Prospects of Synthesized Magnetic TiO₂-Based Membranes for Wastewater Treatment: A Review

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Abstract: Global accessibility to clean water has stressed the need to develop advanced technologies for the removal of toxic organic and inorganic pollutants and pathogens from wastewater to meet stringent discharge water quality limits. Conventionally, the high separation efficiencies, relative low costs, small footprint, and ease of operation associated with integrated photocatalytic-membrane (IPM) technologies are gaining an all-inclusive attention. Conversely, photocatalysis and membrane technologies face some degree of setbacks, which limit their worldwide application in wastewater settings for the treatment of emerging contaminants. Therefore, this review elucidated titanium dioxide (TiO₂), based on its unique properties (low cost, non-toxicity, biocompatibility, and high chemical stability), to have great potential in engineering photocatalytic-based membranes for reclamation of wastewater for re-use. The environmental pathway of TiO₂ nanoparticles, membranes and configuration types, modification process, characteristics, and applications of IPMs in water settings are discussed. Future research and prospects of magnetized TiO₂-based membrane technology is highlighted as a viable water purification technology to mitigate fouling in the membrane process and photocatalyst recoverability. In addition, exploring life cycle assessment research would also aid in utilizing the concept and pressing for large-scale application of this technology.

Keywords: advanced oxidation process; titanium dioxide (TiO₂); photocatalysis; magnetic TiO₂; membranes; wastewater treatment



Citation: Tetteh, E.K.; Rathilal, S.; Asante-Sackey, D.; Chollom, M.N. Prospects of Synthesized Magnetic TiO₂-Based Membranes for Wastewater Treatment: A Review. *Materials* **2021**, *14*, 3524. <https://doi.org/10.3390/ma14133524>

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1. Introduction

In a growing economy, clean and drinkable water, free from toxic chemicals, carcinogenic substances and harmful microorganisms are essential for human health and sustainability [1,2]. However, the fast population growth associated with urbanization, irrigated agriculture and industrialization have driven the environmental concern of wastewater and demand for fresh water globally [3,4]. This opioid epidemic, be it due to insufficient accessibility to clean water, poor water quality or waterborne diseases, has seriously threatened human lives in many underdeveloped and developing countries [4–6]. The result has been an upsurge of stringent environmental standards to provide clean water with high quality and sustainable waste management facilities [4–7]. In addition, conventional technologies (coagulation, flocculation, biological) are limited when it comes to complete decontamination of water containing emerging contaminants (hormones, persistent organic pollutants, antibiotics, pharmaceuticals, heavy metals, nano plastics, etc.) [6,8–10], and to avoid secondary pollution problems an advanced treatment technology is required. It is therefore valuable to explore the development of advanced wastewater treatment technologies to effectively purify water in a more ecofriendly and economical routine.

In recent years, advances in nanoengineering and nanotechnology to develop nanosorbents, nanocatalysts, bioactive nanoparticles, and filtration systems coupled with nanoparticles have been seen to be very promising in wastewater treatment settings [1,9,11–15].

Most of the nanotechnology-based materials can exhibit distinctive physical and chemical properties at a nanoscale (1–100 nm) as compared to their bulk complements [9,12]. Intensive research devoted to understanding the fundamental mechanism of nano-based materials has revealed that semiconductor photocatalysts, such as TiO_2 , possess high surface-to-volume ratios, chemical stability, hydrophilicity and high photo-reactivity with antireflection and self-cleaning abilities [13,16,17]. Semiconductor photocatalysis is driven by energy sources (UV light, ultrasonic, heat or sunlight) to activate metal oxides (TiO_2 , ZnO , and Fenton reagent) in order to generate radical species (OH^- , H^+) in the occurrence of wet or air oxidation states like ozone or hydrogen peroxide [10,18–21].

Heterogeneous photocatalysts and semiconductors assisted with UV light for photodegradation of organic pollutants in water and wastewater settings have been reported by many researchers [9,11,16,22,23]. These include BiVO_4 , TiO_2 , $\text{Fe-ZnIn}_2\text{S}_4$, WO_3 , BiOBr , BiFeO_3 , Fe_2O_3 , CuS , and ZnO [11,17,24]. Among these photocatalysts and nanoparticles, titanium dioxide (TiO_2), being cheap, commercially available, nontoxic and chemically stable, has been the most extensively researched in water settings [25–27]. Aside from water and wastewater treatment applications, the TiO_2 photocatalyst has been widely used in air purification and other biological applications [25,28–33]. Notwithstanding, there are several setbacks associated with TiO_2 industrial applications at a large scale via the advanced oxidation process (AOP) [11,18,25,34,35]. Some of these include high cost of energy resources and chemicals as oxidants and their potential to handle large amounts of wastewater with high organic strengths [11,34,35]. The separation, recovery, and re-use of TiO_2 nanoparticles is also a major constraint to its industrial applications [34,36,37].

In general, most chemicals or nanoparticles used in conventional systems end up converting contaminants from one form to another [11,15]. For instance, generation of biosolids or sludge becomes the new pollutant, which requires further treatment before discharge. Additionally, in the application of TiO_2 photocatalysis, the low rate of electrostatic interaction to oxygen and high rate of electron-hole recombination significantly slows its adsorption of organic contaminants onto its surface [11,38]. Yet, there are still some research gaps associated with TiO_2 nanoparticle applications, which include low quantum efficiency due to inefficient visible light harvesting, acceptable photoreactor design, recovery, re-use, scale-up, etc. [25]. Thus, in conjunction with unaddressed concerns of emerging contaminants [1], the search for ecofriendly techniques capable of degrading pollutants rather than simply converting them from one form to another becomes essential. Consequentially, many researchers have pursued to develop new heterogeneous photocatalysts with a suitable crystal structure, high specific surface area, and easy separation and re-use capabilities [18,26,30,39]. This includes synthesizing metal/ TiO_2 nanocomposites as an efficient way to improve TiO_2 photocatalytic efficiency by enhancing its electron-hole separation [18,30,40]. In addition, the embedding of Fe_3O_4 has been proven to be very useful in order to provide TiO_2 with magnetic separation ability [41–43].

Research Approach

Conventionally, post-treatment of wastewater with membrane filtration or TiO_2 immobilization via AOP has been applied and reported by many researchers. These processes, however, face problems such as membrane fouling and loss of effective catalysts [30,44,45]. Although substantial progress has been made in developing membrane technologies at a large scale, much work is expected for TiO_2 photocatalysis to become a commercialized technology in wastewater treatment settings. Therefore, in this review the basics of photocatalysis are discussed with TiO_2 nanoparticles and recombination with membrane technology as well as the mechanisms involved to prioritize their usage in the water and wastewater treatment sector [46–48]. This was carried out via a desktop approach, where a search of literature with keywords such as membrane, TiO_2 photocatalyst, advanced oxidation process (AOP) and integrated photocatalytic membrane (IPM) was conducted utilizing Google scholar, Web of Science, PubMed, and the ScienceDirect database, as shown in Figure 1. The data obtained from 2011–2021 were refined based on the following categories: subscribed journals, article type, publication title, subject area and access type

(open access or achieve). Even though the progression of membrane technology (Figure 1a) as of 20 April 2021 seems to be low (<60,000), its publication supersedes AOP (Figure 1b; <25,000), followed by IPM (Figure 1c; <2500), and then TiO₂ photocatalysis (Figure 1d; <1000). Apparently, the knowledge of IPM is still limited and therefore should be given attention.

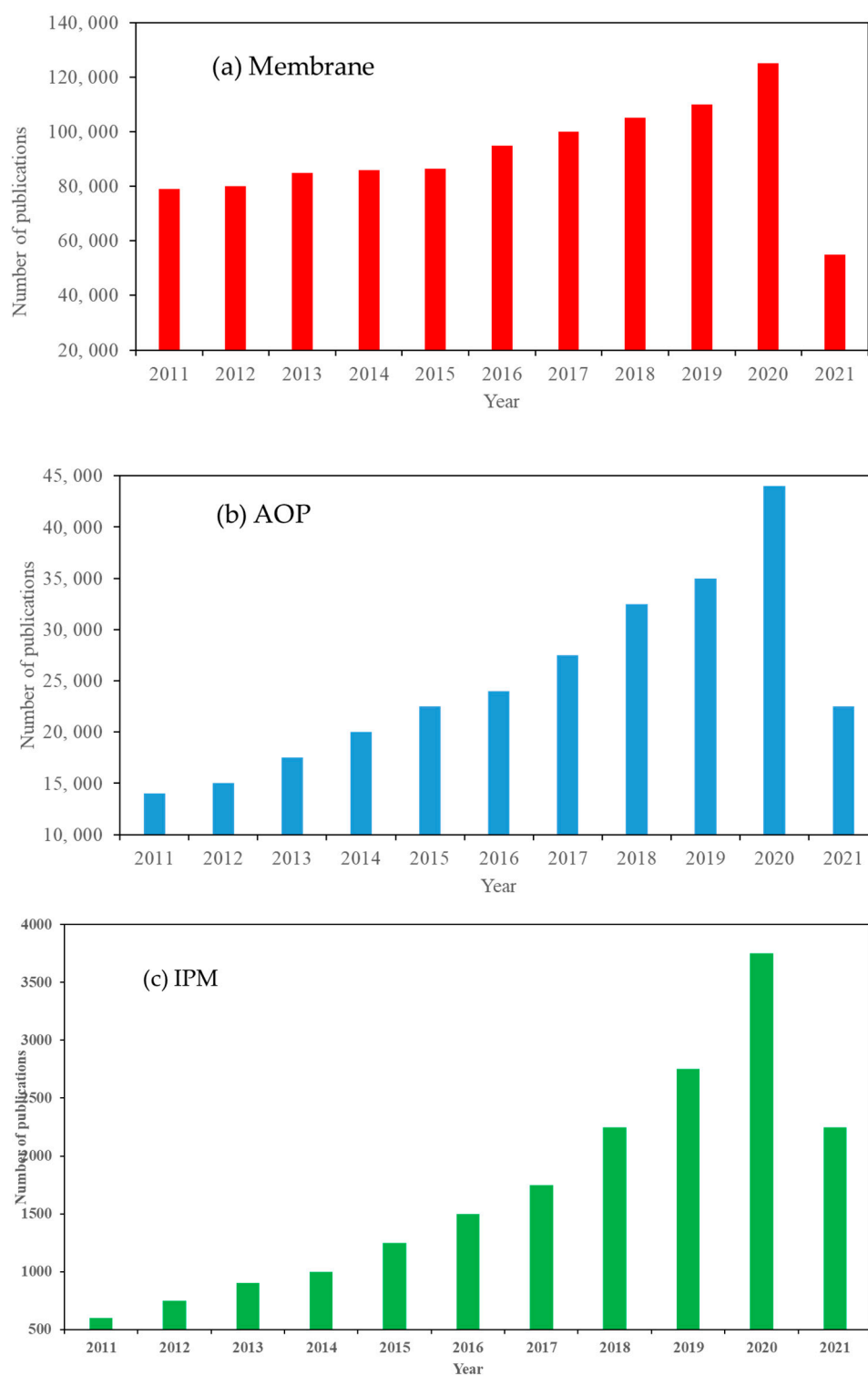


Figure 1. Cont.

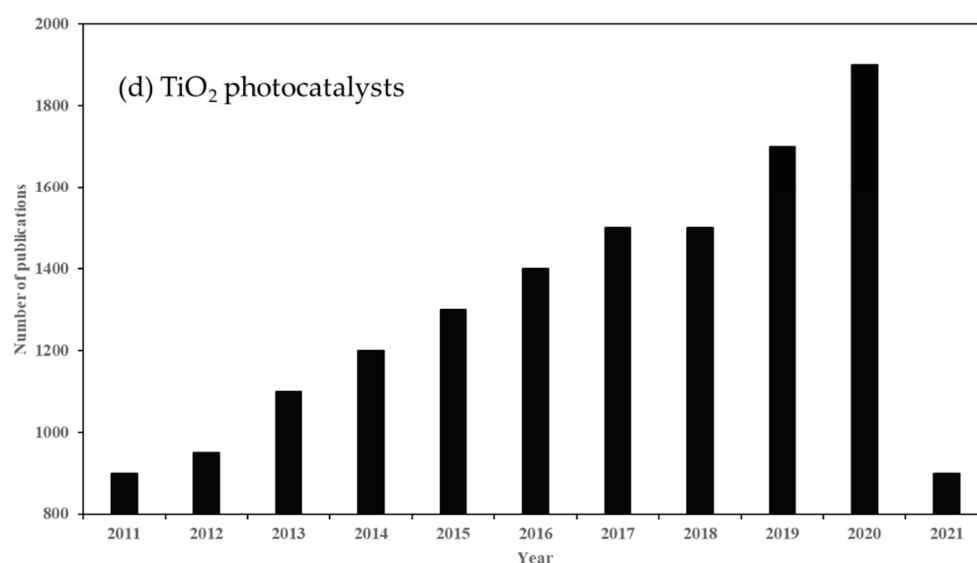


Figure 1. Publication trend of (a) membranes, (b) advanced oxidation processes (AOP), (c) integrated photocatalytic processes (IPM), and (d) TiO_2 photocatalysts, from 2011–2021 (Web of Science database, 20 April 2021).

2. Advanced Oxidation Process (AOP)

Advanced oxidation processes (AOPs) have attracted a great deal of attention of stakeholders in the water and wastewater treatment sector. Photocatalytic degradation technology, being one of the AOPs, involves the use of a semiconductor photocatalyst and photogeneration of highly oxidative hydroxyl radicals [22,34]. In addition, the chemical reactions in AOPs caused by the absorption or desorption of photocatalysts remains unchanged in both photocatalysis and photoelectrochemical splitting of water using titanium [19,22,49]. Furthermore, AOPs differ from conventional chemical and biological wastewater treatment systems as their produced hydroxyl radicals are potent oxidants used to degrade toxic and recalcitrant contaminants into simple and harmless inorganic molecules without creating a secondary excess [46,50,51]. Additionally, AOPs are very robust so as to enhance precipitations and elimination of heavy metals as metal hydroxides, and subsequently, based on the irradiation period, can lead to total mineralization [19,34,52]. AOPs are classified into two categories, namely homogeneous and heterogeneous systems, that can be carried out with or without UV radiation. Table 1 presents some of the reported AOPs commonly used in wastewater treatment settings. The thermal Fenton reaction process is a homogeneous process that involves Fe^{2+} reacting with H_2O_2 . The aforementioned phase ($\text{Fe}^{2+}/\text{Fe}^{3+}$, H_2O_2 , UV-Vis) is commonly termed as a photo-Fenton reaction [19]. Heterogeneous photocatalysis involves a photoinduced reaction accelerated by the presence of TiO_2 photocatalysts [53,54]. This process stands out among the heterogeneous AOPs because UV irradiation of TiO_2 creates hydroxyl radicals. This facilitates the oxidation and more efficient mineralization of organic material present in the effluent when it is photocatalyzed [55]. In contrast with other AOPs and biological treatments, TiO_2 photocatalysis offers significant advantages [19,46]. Thus, the TiO_2 /UV system can handle contaminants in both the gas and solution phases. Furthermore, TiO_2 is inexpensive, practically insoluble in water, and biologically and chemically inert [19,22,46].

Table 1. Types of advanced oxidation processes; adapted from [19,46].

Chemical Process	Photochemical Process
Wet air oxidation	Photo-Fenton reaction
Supercritical water oxidation	UV/ultrasound system
Ultrasound/H ₂ O ₂ system	UV/O ₃ /H ₂ O ₂ system
Ultrasound/Sonolysis	UV/H ₂ O ₂ system
Fenton reaction	UV/O ₃ system
Ozonation in alkaline	UV photolysis
O ₃ /H ₂ O ₂ system	UV/O ₂ /TiO ₂ system
Electron—Fenton reaction	UV/H ₂ O ₂ /TiO ₂ system

2.1. TiO₂ Photocatalyst

TiO₂ is the most widely used photocatalyst because of its strong physical and chemical stability, insolubility in water, resistance to acids, inertness to most chemicals and long-term photostability [25,40,47]. TiO₂ exhibits three main crystal structures such as rutile (stable), anatase (metastable), and brookite structures (Table 2).

Table 2. Chemo-physical properties of TiO₂ (adapted from [49,54]).

Crystalline Forms	Anatase	Rutile	Brookite
Crystalline structure	Tetragonal	Tetragonal	Rhombohedral
Lattice constants (nm)	a = b = 0.3733 c = 0.9370	a = b = 0.4584 c = 0.2953	a = 0.5436; b = 0.9166 c = 0.5135
Density (g.cm ^{−3})	3.83	4.24	4.17
Bravais lattice	Simple, body-centered	Simple, body-centered	Simple
Melting point (°C)	Turning into rutile	1870	Turning into rutile
Boiling point (°C)	2927	-	-
Band gap (eV)	3.2	3.0	-
Refractive index (ng)	2.5688	2.9467	2.809
Standard heat capacity (cp)	55.52	55.60	-
Dielectric constant	55	110–117	78

The tetragonal structure consists of both rutile and anatase, while brookite has a rhombohedral structure [48–50]. In addition to their shape and nanoscale or size, the unique physicochemical properties of TiO₂ crystals are a result of their intrinsic electronic structure and crystal structures [17,25,51]. Anatase has been found to be more active than rutile, but both forms of TiO₂ have been reported to be photoactive. Additionally, a mixture of anatase and rutile for photocatalysis has been found to exhibit synergy due to the photoinduced interfacial electrons of anatase that can be transformed into rutile [27,39].

Rutile and anatase, with 3.0 eV and 3.2 eV band gaps, respectively, are the most common polymorphs of TiO₂ [49,50]. In Figure 2, the large TiO₂ energy band means that higher UV light energy is required to excite electrons to create hydroxyl radicals, which is the key to the photodegradation of contaminants in the presence of oxygen [20,27,52].

The crystalline phase of anatase is desired because of its maximum efficiency under UV irradiation [20]. The photogenerated electrons form superoxide radicals in the rutile conduction band and the holes in the anatase valence band play a significant role in oxidation reactions. In addition, the 3.2 eV anatase band gap (Figure 2) corresponding to the light wavelength of 388 nm means that only UV light will activate TiO₂. This limits the use of sunlight and greener energy for the activation of TiO₂, as only around 5% of sunlight is formed by UV radiation. Thus, during the photo activation step, TiO₂ undergoes a rapid recombination of electrons and holes, which then reduces photoactivity. Hence, by doping the TiO₂ with inert supports, the electron–hole recombination and wide band gap can be addressed while increasing the TiO₂ nanoparticle size [20,25].

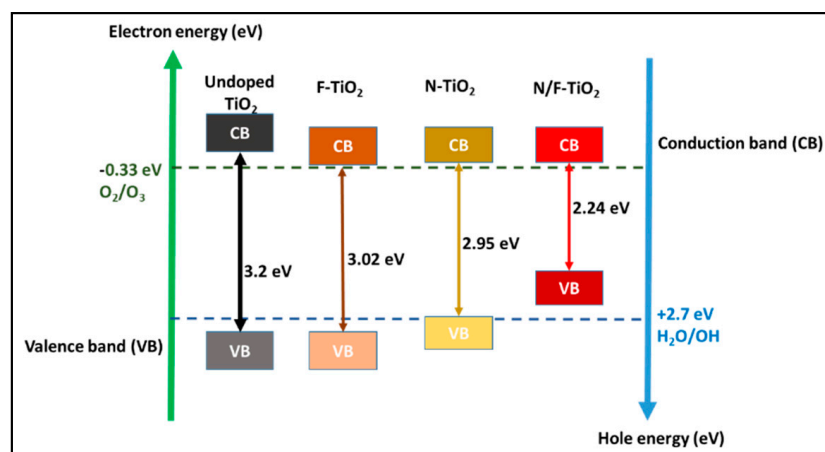


Figure 2. Schematic diagram of TiO_2 with different valence and conduction band levels; adapted from [49,53].

Furthermore, in photocatalytic activities, TiO_2 with a valence band (VB) and conduction band (CB) levels of +2.9 and -0.33 eV can result in a band gap energy of 3.2 eV. As shown in Figure 2, the TiO_2 VB and CB levels are more positive and negative than the distinctive redox potential of $\text{O}_2/\text{H}_2\text{O}$ (1.23 eV). The presence of Ti^{3+} defects beneath the CB surface causes the band gap reduction in F-doped TiO_2 (3.02 eV), while in N-doped TiO_2 (2.95 eV) the mid-band states are created as the N species fill voids as impurities above the VB. However, there is a doping-induced effect and a transition in the VB tail; co-doping N and F into TiO_2 results in the greatest band gap reduction, from 3.2 eV to 2.24 eV (Figure 2).

2.1.1. TiO_2 Modification Supports

In wastewater treatment settings, TiO_2 photocatalysis in practical applications is very limited due to low quantum efficiency under visible radiations as well as difficulties of being separated in suspensions [18,55,56]. To ensure that TiO_2 will work optimally without any complexity, modification becomes essential [6,54]. Filtration following photocatalytic activities is very costly and, therefore, catalyst supports can be explored. Some of the supporting materials of TiO_2 reported include glass beads, fiber, glass, silica and zeolite mater [6,20,25,53,57]. Consequently, there are diverse techniques used to modify TiO_2 , where doping of pure TiO_2 with either anions or cations remain one of the most common methods for enhancing its sensitivity to visible light and lowering the rate of charge carrier recombination [20,39,53,54]. Furthermore, photocatalysts synthesized via chemical doping or ion implantation with metals and nonmetals result in a narrowing of the TiO_2 band gap as well as the crystal lattice or structure [20,25,39]. Therefore, in selecting these metals and nonmetals, their sensitivity should be considered.

- Cationic doping of TiO_2

To dope TiO_2 , cations like rare earth metals, noble metals, weak metals and transition metals have been used [26]. In addition, when a metallic ion is doped with TiO_2 , the light absorption range expands, whereas the redox potential of the photogenerated radicals increases [58–60]. This generally results in the transfer of photoexcited electrons from the TiO_2 conduction band to metal particles deposited on the TiO_2 surface. Cationic doping can also decrease the probability of electron–hole recombination, leading to an effective separation of the charge and thus improved photocatalytic activity [61]. However, the nature and concentration of the dopant inducing the charge surface together with the corrosion mechanism can affect the photocatalytic property of the materials [20,40]. Thus, cationic dopants have a distinctive impact on the catalyst lattice. Some of these metal dopants (Ag, Fe, Mn, Ni, Cu, Pt, Rh, and Pd) act as free electrons, which facilitates the conjugation of the photogenerated carriers [26]. Conversely, metal-doped materials have

been reported to be thermodynamically unstable, which can be captured on the TiO₂ band gap at the d-level and can subsequently shift the redox potential [26,30,62,63]. However, by removing the electron hole, TiO₂ doped with metallic cations with lower oxidation states can maintain electron stability [30]. In addition, TiO₂ doped with metallic cations with higher oxidation states, by adding electrons to the already empty conduction band, can also enhance the electron stability [20,40].

- Anionic doping of TiO₂

Doping TiO₂ with anionic nonmetals, including carbon, sulfur, nitrogen, and iodine, has been found to be more efficient in ensuring higher photocatalytic activity under visible light [26]. Anionic dopants result in p-state substitution in TiO₂ by altering the atomic level in the valance band and subsequent shift of the conduction band. For instance, incorporation of carbon into TiO₂ contributes to the formation of carbonaceous species on the surface, which increases the visible light absorption [18,58,60]. Furthermore, the presence of more reactive sites, which facilitate the adsorption of more target contaminants, is another explanation for the increase in photocatalytic activity of C-doped TiO₂ due to its higher surface area [26]. Nitrogen doping in TiO₂ adjusts the stiffness, elastic modulus, refractive index, electrical conductivity, and photocatalytic behavior of TiO₂ under visible light absorption activity [18].

Subsequently, silica is reported to have higher surface area, which provides the effective adsorption and catalyst support structure for heterogeneous photocatalysis. According to Ghosh and Das [26], silica modified TiO₂ is more effective as a photocatalyst than TiO₂ alone. Thus, doping TiO₂ with silica can enhance and stabilize both the external and internal surfaces of the catalyst within the silica-based matrix, where contaminants are adsorbed. Zeolite is also found to play an important role in charge and electron transfer during the photocatalytic reaction [20,34]. Due to uniform pores and straight paths, zeolites have been found to be good photocatalyst supports. The zeolite acts as a supporting material for the homogeneous dispersion of TiO₂ particles on its surface, which improves TiO₂-based zeolite composites. Activated carbon (AC), due to its pore structure, also has benefits as a photocatalyst support for promoting the photocatalytic process [25,53,64]. AC is commonly used as a supporting material to extract organic and inorganic pollutants from water and wastewater. Contrariwise, the surface chemistry of AC carbon may obstruct effective coating of TiO₂ photocatalysts [64]. However, the application of AC–TiO₂ photocatalysts in wastewater treatment settings comes with a cost and, therefore, necessitates the use of a reactor to effectively expose the photocatalytic surface to light photons [2,53,64].

- Other supporting metallic oxides

Coupling TiO₂ with other semiconductors to increase its photocatalytic activity is another way to produce photoinduced electron–hole pairs [26]. A good match between the conduction and valence bands of two semiconductors ensures a potential charge carrier movement from one to the other. Several studies have indicated that TiO₂ photocatalytic activity can be enhanced by the presence of metal oxides like CdS, ZnO, ZrO₂, Cu₂O, CeO₂, SnO₂, WO₃, and Fe₃O₄ [17,18,26,62,65,66]. Among them, Fe₃O₄ has been studied extensively due to its ability to facilitate magnetic separation of the nanocomposite from the aqueous medium [39,67]. Ahangar et al. [60] prepared a Fe₃O₄-embedded SiO₂ nanocomposite and compared its magnetic properties with pure Fe₃O₄. It was found that the Fe₃O₄ nanoparticles embedded in SiO₂ have a much higher photocatalytic efficiency. Furthermore, the photocatalytic performance of the resulting nanocomposite was nearly identical. As a result, the core–shell framework is an efficient way to incorporate the desirable properties of two or more nanomaterials into a single nanocomposite. However, adding semiconductor dopants can alter the surface properties of TiO₂ catalysts, such as surface area and surface acidity [16,41]. Wang et al. [68] used a hydrothermal method followed by co-precipitation to develop anatase-structured TiO₂ nanoparticles (Fe/TiO₂) with elongated morphological characteristics.

2.1.2. Mechanism of TiO₂ Photocatalysis

The heterogeneous photocatalysis mechanism involves the ability of semiconductors to produce charge carriers under light irradiation, preceded by the production of free radicals such as OH[•], which contributes to further reactions, eventually forming CO₂ and H₂O [32]. Excitation, bulk diffusion, light-induced surface transfer, and photon absorption with a potential energy greater than the band gap are all part of the basic photocatalytic activation mechanism [30,47]. As shown in Figure 3, when UV light with an energy greater than the band gap energy of TiO₂ is irradiated, electrons in the valance band are excited to the conductance band, which leaves positive charge holes (h⁺) in the valance band.

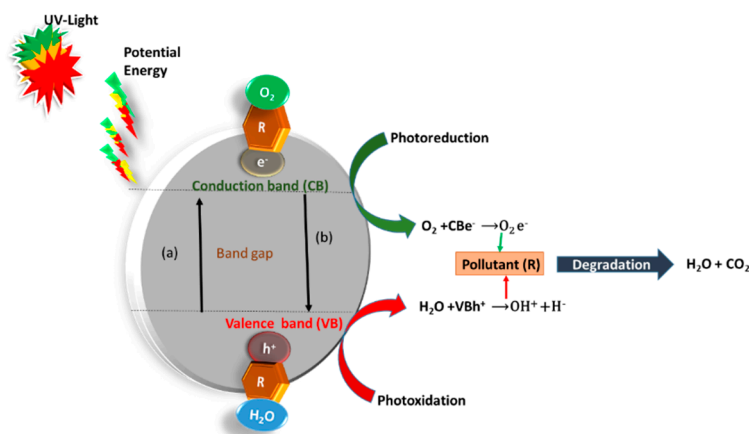
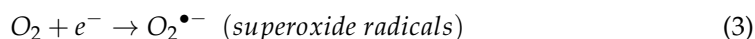
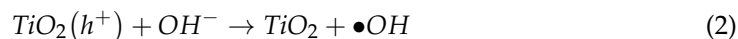
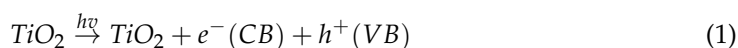


Figure 3. Schematic presentation of the photocatalysis mechanism; adapted from [26].

The electrons extracted from the VB are passed to the CB, which then react with the absorbed oxygen (O₂) on the TiO₂ surface. As a result, a positive area (h⁺) forms in the VB holes and causes free electrons (e⁻) to form in the CB. Simultaneously, the holes (h⁺) react with water molecules (H₂O) adsorbed on the TiO₂ surface to create hydroxyl radicals (OH[•]), as shown in Figure 3 and Equations (1)–(4). Furthermore, the CB electron reduces oxygen to superoxide ions (O₂^{•-}). This reaction prevents the e⁻/h⁺ from recombining, which happens when other electron acceptors such as pollutants are absent [30,40]. Organic pollutants (R) in wastewater can be oxidized to carbon dioxide (CO₂) and water (H₂O) by oxygen reactive radicals.



2.2. Operational Parameters in Photocatalysis

The photocatalytic system's oxidation rates and semiconductor catalyst performance coupled with a photoreactor are all highly dependent on several operational parameters that regulate the kinetics [18,26,69]. Outstanding studies of the different parameters affecting the photocatalysis process, including pH, catalyst loading, amount of oxygen, contaminant loading, light intensity and duration of light irradiation, preparation method of the catalyst, its calcination temperature, and amount and type of dopant, have been carried out and reported in the literature [18,25,26,51,53,70,71]. In comparison to immobilized films, photocatalysts mostly take the form of suspended powder (slurries), giving higher efficiency [25]. However, separating photocatalysts from treated water in this form is difficult, implying that a recovery step for photocatalyst re-use is required [72–74]. Pho-

photocatalysts based on TiO_2 with a large surface area have a high photocatalytic efficiency, so nano-sized TiO_2 particles have been used in most studies [25,74].

- pH

pH affects the surface charge or isoelectric point of the photocatalyst directly as well as the catalyst particles, size of catalyst aggregates, and the positions of conductance and valence bands [75,76]. The point of zero charge (PZC) of TiO_2 is the main parameter used to study the effect of pH in photocatalyst reactions. PZC is a condition where the surface charge of TiO_2 is zero or neutral in the range of 4.5–7.0 [69,75]. The catalyst surface will be negatively charged and repel the anionic compounds in water, which can affect the charge densities [75]. At pH = PZC, the neutral surface charge of the catalyst particles will not be able to produce the interactive rejection necessary for the separation of the solid liquid. When this happens, the catalyst becomes larger, thereby leading to the sedimentation of the catalyst. Since this can induce the aggregation of the catalyst, optimization becomes necessary [76].

- Catalyst loading

One of the key factors affecting photodegradation efficiency and overall cost is the amount of catalyst used. Increasing the TiO_2 load does not only increase the number of active sites for pollutant adsorption, but it also increases the number of e^-/h^+ pairs, which speeds up the reaction rate [18,19,75]. However, if the amount of TiO_2 is increased above a saturation level, the catalyst may agglomerate, resulting in a light screening deficiency [69,75]. This makes the excess TiO_2 particles reduce the active surface area of the TiO_2 exposed to illumination and consequently reduces the photocatalytic efficiency. Thus, the absence or obstruction of the irradiated light prevents it from penetrating the effluent's interior mass, hence hindering photocatalysis [69]. Therefore, in order to avoid excessive usage and gain optimal photonic efficiency, an optimal value of catalyst dosage must be used [76].

- Light intensity

The light intensity ensures that sufficient photons of energy are delivered to the TiO_2 surface-active sites. This should be significant enough to achieve a reasonable photocatalytic reaction rate, particularly in water treatment [51,69]. This is usually limited to photons with wavelengths that are smaller than the absorption edge of nearly 400 nm [51]. However, attenuation of radiation reaching the photocatalyst is one of the reasons for lower efficacy. Attenuation can occur for a variety of reasons, including insufficient light spatial distribution within the reactor, reflection losses, transmission losses, scattering, and so on [18,25]. According to Naldoni et al. [51], the rate of reaction can be associated with the high thermodynamic efficiency of reactor photons distributed within it.

- Catalyst type and temperature

The development of visible/solar light-active photocatalysts has been a continued effort in recent years [19,25,77,78]. Some of these photocatalysts have been synthesized and their efficacy in wastewater treatment has been determined. Additionally, most of the early photocatalysts developed were UV-only active and, therefore, research into photocatalysts' physical and chemical properties is required to support their future prospective use. Modification of TiO_2 with promising results has been reported as a solution. Some researchers have worked on incorporating activated carbon, graphite, graphene oxide, nanosheets, and other elements into TiO_2 while others have focused on the incorporation of various metallic and nonmetallic additives [18,19,25,51,77,79,80]. Furthermore, doping metals and nonmetals into conventional photocatalysts enhances photoreactivity, and thus quantum efficiency, by altering the intrinsic and surface properties in a favorable approach [51]. In photocatalytic activity, temperature seems to have no effect. The ideal temperature range initiated by photon adsorption reaction is reported to be 20 to 80 °C [25]. Meanwhile, the activation energy, being relatively stable at these temperatures, makes it possible for a wide

range of photon-induced reactions. However, an increase in temperature above 80 °C has been reported to have negative consequences on the overall photocatalytic process [25,51].

- Dissolved oxygen and contaminant concentration

The presence of dissolved oxygen (DO) is critical in TiO₂ photocatalysis. The DO ensures that there are enough electron scavengers present to aid in the trapping of the excited conduction-band electrons during the recombination step [18,51,77]. The presence of DO has no effect on the adsorption onto the TiO₂ catalyst surface since the reduction reaction occurs at several sites separate from where the oxidation occurs. The DO influences the formation of reactive oxygen species, the stabilization of radical intermediates, mineralization, and direct photocatalytic reactions [77]. The total amount of DO produced in a reactor is determined by a few factors such as the environmental condition, the catalyst type and concentration, the contaminant, and so on [80]. The pollutant's initial concentration has a significant impact on its photodegradation. The effectiveness of photodegradation decreases as the initial concentration increases for two reasons: (i) equilibrium adsorption of the pollutant rises with increasing concentration and thus competes with adsorption of OH[−] on the same site, and (ii) high-concentration pollutants absorb more than the photocatalyst itself, which tends to prevent degradation [25].

3. Integrated Photocatalytic Membrane (IPM) Reactors

Membrane separation has become one of the most improved technologies for water treatment in recent decades due to its small carbon footprint, high separation efficiency, and ease of operation [2,39,71]. Membrane fouling is caused by the formation of a cake layer on the membrane surface and results in pore blocking in conventional membrane processes [81]. As a result, water flux is reduced significantly, and energy consumption and treatment costs are increased. Furthermore, membrane filtration can only concentrate contaminants into a high concentration retentate, which requires additional treatment prior to discharge [39,81,82]. Therefore, advancements in membrane science and technology are useful in developing a cost-effective membrane process. In essence, membrane technology has progressed to the point where there is a plethora of membranes made for specific pollutants as well as membrane configurations and technologies tailored for specific industries (milk production, beer production, desalination, solvent separation) and material regeneration [2,4,18,25,83].

Moreover, membranes are classified according to their pore sizes as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), which determine their selectivity [25,82,83]. Nanoporous membranes (0.1–1 nm) are made up of a thin film through which molecules are transported via solution diffusion. The driving forces across such membrane transport include pressure, concentration, or potential gradient [2,25,61]. Reverse osmosis (RO), NF and most recently forward osmosis (FO) are processes that use nonporous membranes. Microfiltration (MF) and ultrafiltration (UF) are two pressure-driven processes that use microporous membranes. MF membranes can separate particles with diameters ranging from 0.1 to 10 µm, while UF membranes can remove particles with diameters ranging from 1 to 100 nm [2,84].

Generally, to meet strict wastewater discharge standards, a conventional activated sludge process is used to biologically treat wastewater for organic/nutrient removal, accompanied by an MF/UF process to produce high-quality permeate water (i.e., removing particles and bacteria/viruses, etc.) Furthermore, membrane filtration can only trap contaminants in a high concentration retentate, which requires additional post-treatment prior to discharge. In contrast, photocatalytic membrane processes may degrade contaminants in feed solutions by producing oxygen-reactive radicals in the presence of UV light, preventing the formation of a cake layer on the membrane surface [3,45]. As a result, pore blocking is reduced, pollutant concentrations in the filtrate are reduced, and permeate quality is improved [3,45]. This section delves into the different types of membranes used as supports as well as related photocatalytic membrane types, preparation, attributes and applications of TiO₂ photocatalytic membranes in removing contaminants in wastewater settings.

3.1. Types of IPM Reactors

Simple photocatalytic reactors that use TiO_2 -coated glass beads and a UV lamp to illuminate and activate sites are referred to as slurry/immobilized photocatalytic reactors or fixed-bed photocatalytic reactors [16,48,82]. In recent years, photocatalytic reactors have been upgraded in a variety of ways to increase the irradiated surface area and boost performance. Consistently, the difficulty in separating nano sized TiO_2 particles from treated water has been attributed to its restricted use. To solve the separation problem, some researchers have attempted to salvage nano sized TiO_2 particles from suspensions using membrane filtration [20,39,48,63,82,85].

IPMs are classified into four different configurations: (Figure 4a) a membrane inserted inside a photoreactor with internal walls coated with a photocatalyst such as TiO_2 ; (Figure 4b) a pure TiO_2 porous photocatalytic membrane; (Figure 4c) a slurry photocatalytic reactor followed by a membrane filtration unit; (Figure 4d) an inorganic or polymeric membrane submerged in a slurry photocatalytic reactor.

Among these four configurations, the photocatalytic membrane (Figure 4b) has potential advantages over the other three configurations [26,53]. Here, both the separation membrane and the TiO_2 photocatalytic degradation of the organics occurs in a single unit [26]. In addition, photocatalytic membranes generally outperform conventional membranes in terms of reducing membrane fouling and improving permeate quality [85,86]. Even though the reactor configuration covers a broad range, the reactor design should ensure that the catalyst is irradiated uniformly [25]. This is because the photocatalytic surface available for the possible solutions can decrease and cause a loss in the photocatalytic efficiency.

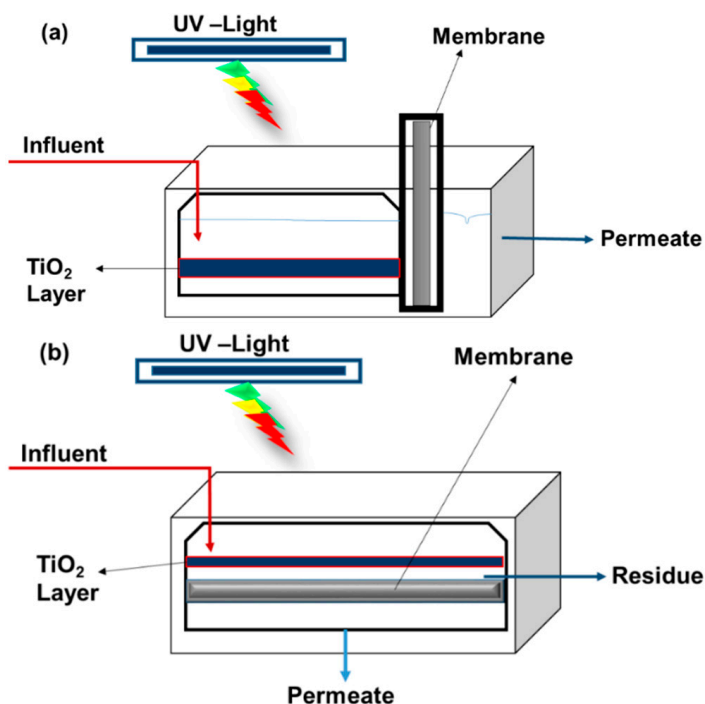


Figure 4. Cont.

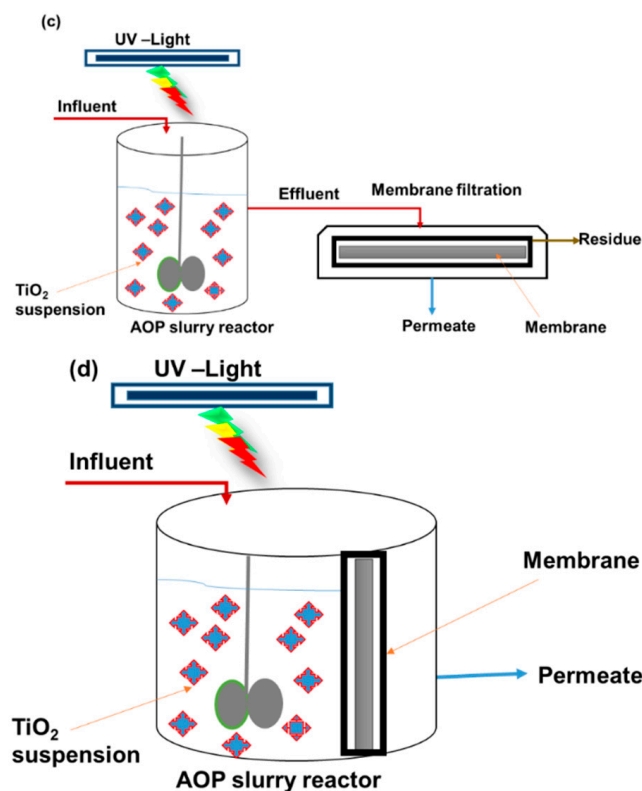


Figure 4. Schematic diagram of TiO₂-based membrane reactor types: (a) a membrane inserted inside a photoreactor with internal walls coated with a photocatalyst such as TiO₂, (b) a pure TiO₂ porous photocatalytic membrane, (c) a slurry photocatalytic reactor followed by a membrane filtration unit, and (d) an inorganic or polymeric membrane submerged in a slurry photocatalytic reactor; adapted from [18,26,32].

Notwithstanding, IPMs have proven to be very promising in wastewater treatment settings, however, they are still limited in a large-scale application. In response, several organic, inorganic, metallic, and polymeric materials have been used as support materials in the fabrication of TiO₂-based photocatalytic membrane reactors [25,26,53,70,87,88]. In contrast to immobilized TiO₂ membranes, TiO₂ nanofibers, nanowires, and nanotubes are also used to make pure TiO₂ photocatalytic membranes. These are classified into two major categories: (i) freestanding pure TiO₂ photocatalytic membrane reactors and (ii) composite TiO₂ photocatalytic membrane reactors [87,89,90].

3.2. Freestanding Pure TiO₂-Based Membrane Reactors

Engineered TiO₂ nanoparticles have various properties that allow them to bind specific pollutants or catalyze degradation reactions when deposited or embedded on membrane surfaces [26,88,90]. However, the nanomaterial loading, matrix content, particle dispersion, nanoscale phase size, shape and orientation, as well as interactions between the phases all affect the hybrid material's overall properties [26,90]. This has inspired interest in making TiO₂-engineered membranes for a variety of applications, including self-cleaning, antimicrobial thin film coatings, photocatalysis, gas sensing and dye-sensitized solar cell nanofibers with well-controlled morphology [25,26,87–90]. One-dimensional freestanding TiO₂ membrane reactors with various TiO₂ morphologies, such as nanotubes (NTs), nanofibers (NFs), and nanowires (NWs), have been developed to improve photocatalytic activity and reduce membrane fouling [31,45].

3.2.1. TiO₂ Nanotube-Based Reactors

The photocatalyst surface-to-volume ratio of synthesized TiO₂ NTs make them more advantageous for wastewater treatment. Some reported applications are presented in Table 3.

Table 3. Removal of pollutants using TiO₂ nanotubes.

TiO ₂ Nanotubes	Pollutant	Removal Efficiency (%)	Reference
TiO ₂ arrays	Acid orange 7	77	[91]
TiO ₂ -Au/Ag	Acid orange 7	85	[91]
TiO ₂	Acid orange 7	99	[91]
TiO ₂	Oil	99	[92]
TiO ₂ /CdS	Rhodamine B	60	[75]
Ag-TiO ₂ /HPA/Al ₂ O ₃	Humic acid	88	[47]
TiO ₂	Humic acid	98	[47]
Si-doped TiO ₂	Reactive Red ED-28	40	[83]
TiO ₂	Methylene blue	68	[83]
Silica/TiO ₂	Direct black 168	85	[83]

Although TiO₂ NTs are available in both crystalline and amorphous forms to enhance performance, high-temperature annealing is required to convert the amorphous form to crystalline [83,91]. For example (Figure 5), from a two-electrode electrochemical cell with titanium foil as the working electrode, a freestanding TiO₂ NT was synthesized using an anodization method.

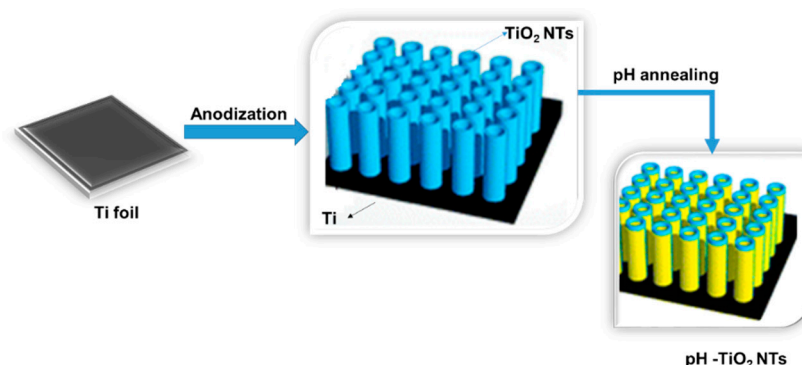


Figure 5. Schematic modification of TiO₂ nanotubes; adapted from [83,92].

In the preparation of TiO₂ NTs, Cai et al. [83] stated that voltage pulses were applied for a short time at the end of the anodization process to achieve open nanochannels; this was a quick and successful bottom-opening method that did not involve the use of engraving solutions. Another method for creating a TiO₂ nanotube alumina membrane was represented by Wang et al. [89], where the TiO₂ NTs were developed by immersing the alumina membrane in a 2.2 pH titanium tetrafluoride (TiF₄) aqueous solution. Their reported SEM image results showed that the TiO₂ NTs were grafted and lined inside the channels of the alumina membrane. Chong et al. [84] reported that the effect of nanotube packing and grafting was highly dependent on the pH of the solution. Additionally, grafting time can be used to monitor TiO₂ NT inner diameter, with a longer grafting time resulting in a smaller internal diameter and therefore, a lower pure water flux [91,92].

3.2.2. TiO₂ Nanofiber-Based Membranes

Many methods of synthesis of TiO₂ nanofibers (NF) have been developed, including sol-gel, hydrothermal, and electrospinning techniques (Figure 6).

Electrospinning is a versatile and efficient technique for synthesizing uniform fibers with a broad specific surface region [28,89,93]. In electrospinning, a polymer solution or melt containing a precursor salt of metal oxide in a syringe is subjected to a high

static voltage [94,95]. The properties of nanofibers can be tweaked to provide more versatility in the end-product's surface functionalities. Many studies use Ti-alkoxides and Ti-halides as TiO_2 precursors, but these are insoluble in water [65,89,94–98]. TiO_2 nanofibers made from water-soluble precursors make it possible to combine TiO_2 with other metal oxides via water-soluble precursors [99]. At a voltage of 30 kV, nanofibers are electrodeposited, collected and dried at a temperature of 25 °C. Liu et al. [100] fabricated silver (Ag) nanoparticle-decorated TiO_2 nanofiber (TiO_2/Ag NF) membranes using the polyol synthesis mechanism. The Ag-decorated membrane ($\text{TiO}_2/\text{Ag}/\text{CdS}/\text{Ag}$ NF) was obtained by immersing $\text{TiO}_2/\text{Ag}/\text{CdS}$ nanofibers in an algae solution for 72 h [98,100].

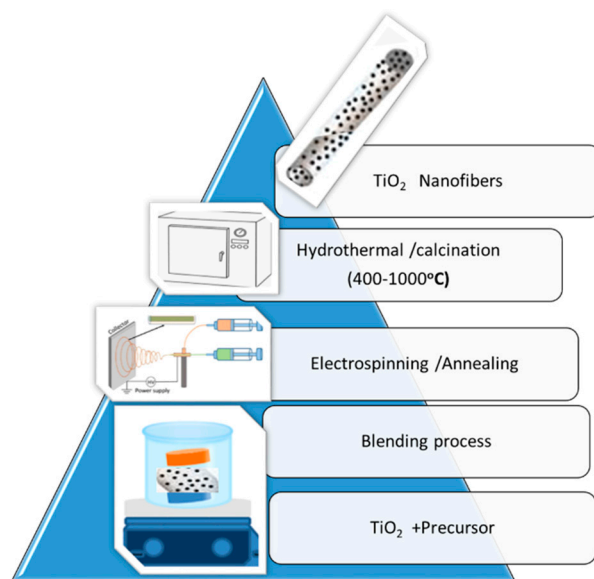


Figure 6. Schematic modification of TiO_2 nanofibers using electrospinning and hydrothermal techniques; adapted from [98,100].

3.2.3. TiO_2 Nanowires

The successful synthesis of titanium dioxide nanowires (NWs) was achieved using a novel approach based on a hydrothermal process [101,102]. A novel TiO_2 nanowire nanostructure (Figure 7) was developed by hydrothermally treating TiO_2 nanopowder as a precursor for 6 h with highly concentrated sodium hydroxide [102]. In the thermal evaporation processes reported in the literature, the sputtering of a Ti buffer layer and the evaporation of Ti at high temperatures are considered mandatory [102–104]. These processes require a lot of energy and a sophisticated setup for the nanostructures to expand [101]. The thermal oxidation method has been used to produce TiO_2 NWs in recent studies [102,103]. The development of TiO_2 NWs with a stable rutile phase is possible with this method. Zhang et al. [102] demonstrated that a direct oxidation of a Ti foil in an organic atmosphere was possible to develop a membrane filtration process and photocatalytic degradation of humic acid in wastewater.

3.3. Composite TiO_2 Photocatalytic Membrane Reactors

TiO_2 composite membrane reactors are classified based on the types of support materials used on the membrane. Among these are TiO_2 polymer composite membranes, TiO_2 ceramic composite membranes and TiO_2 -inorganic/organic materials composite membranes [82,105]. The TiO_2 NPs can either be deposited onto the membrane surface or dispersed in the polymer dope solution prior to membrane casting.

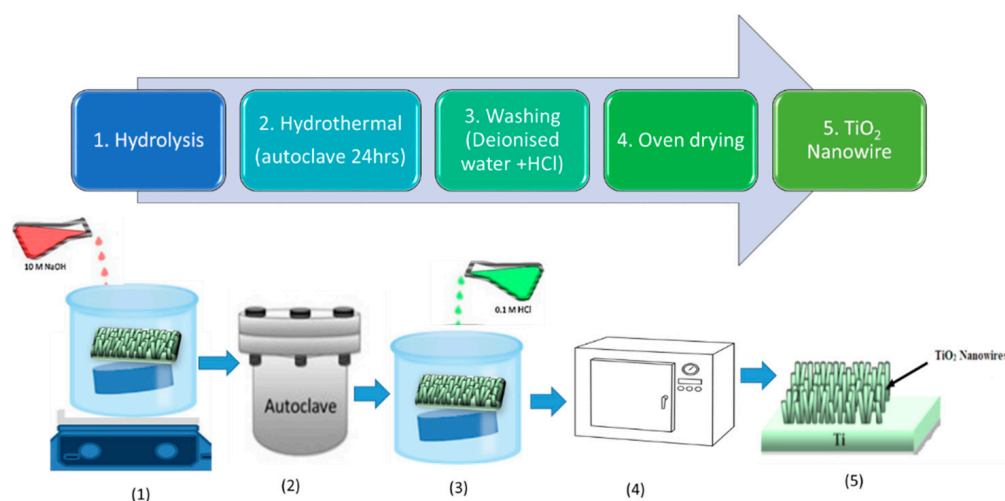


Figure 7. Schematic modification of TiO₂ nanowire using hydrothermal techniques. (1) Hydrolysis, (2) Hydrothermal, (3) Washing, (4) Oven drying and (5) TiO₂ nanowire.

3.3.1. TiO₂ Nanoparticle-Coated Polymer Membranes

In photocatalytic membranes, nanoscale inorganic/organic photocatalysts are embedded in a membrane matrix to improve the properties of the resulting polymer [82,105–107]. Hamed et al. [108] elucidated that TiO₂ nanoparticles can coordinate with the surface of the polymer membrane and Ti⁴⁺ makes ion connections with oxygen atoms of carboxylic groups of polymers or by making H-bonding with carbonyl or hydroxyl groups on the TiO₂ surface. Hyeok et al. [109] increased the hydrophilicity of a commercial membrane via plasma immersion in a nitrogen-purged aqueous acrylic acid solution at various concentrations. The plasma treatment irradiated the membrane surface, causing radicals to form and promoting grafting reactions. TiO₂ was then successfully deposited onto the functionalized membrane surface [82,105].

Some researchers have investigated the photocatalytic behavior of TiO₂ nanoparticles photografted onto commercial polymer membranes, such as polyester membranes [24,82,108,110]. Dong et al. [98] used the activation reaction to coat TiO₂ nanotubes on a polyurethane (PU) membrane surface. The TiO₂ nanotube suspension was formed by ultrasonically dissolving salinized TiO₂ nanotubes in toluene for 10 min. The activated PU membrane was added to the coating process, which was then heated to 60 °C. Furthermore, the TiO₂ nanotube–PU hybrid membrane was collected and washed in ethanol before being dried in a vacuum oven. When the membranes were modified with diethanolamine (DEA), Hamed et al. [108] found that a high concentration of TiO₂ coated on the polyvinylidene fluoride (PVDF) membrane improved pure water flux. Although embedding nanoparticles onto membranes remove unwanted nanoparticles after treatment, the polymer phase material covering the nanoparticles can reduce the active usable surface area [107]. Owing to the blockage of the membrane pores by TiO₂ nanoparticles, the photocatalytic membrane's pure water flux usually decreases as the concentration of TiO₂ in the coating phase rises [58,107,109,111].

3.3.2. TiO₂-Based Polymeric Membranes

Polymer membranes are one of the most popular membranes used in wastewater treatment and water purification (Table 4).

Table 4. Polymer membranes with different TiO₂ types.

Polymer Membrane	Types of TiO ₂	Deposition Time (min)	Reference
Polyethersulfone (PES) Ultrafiltration membrane	Degussa 25	15–30 60	[112]
Poly (vinylidene fluoride) Plasma-grafted poly acrylic acid (PAA)	TiO ₂ suspension	30	[113]
Polyamide thin film supported on polysulfide	TiO ₂ colloidal solution	60	[107]
Polyether sulfone (PES) Polyimide blend membrane (PI)	Degussa 25	15	[109]

Polymers reported as support membranes of photocatalysts include polyamide, polyvinylidene fluoride (PVDF) [23], polyethersulfone (PES), poly (vinylidene fluoride) (PVDF) [24], sulfonated polyethersulfone (SPES), poly (vinylidene fluoride) [105–108], polyurethane (PU) [98], polyethylene terephthalate (PET) [82], polyester [58], polyacrylonitrile (PAN) [43] and polytetrafluoroethylene (PTFE) [109–114]. Polymer–inorganic nanoparticle composite membranes can be divided into two groups based on their structure: (a) polymer and inorganic phases linked by covalent bonds, and (b) polymer and inorganic phases linked by van der Waals forces or hydrogen bonds [113]. The TiO₂ nanoparticles coalesce with the surface of the polymer membrane during the membrane preparation process. Likewise, Ti⁴⁺ makes ion connections with oxygen atoms of carboxylic groups of polymers or by making H-bonds with carbonyl or hydroxyl groups on TiO₂ surfaces [107,111].

3.3.3. TiO₂ Ceramic Membranes

Ceramic membranes, especially Al₂O₃ membranes, have been extensively investigated as supports for photocatalyst immobilization in membrane photocatalytic processes (Table 5).

Table 5. Synthesized TiO₂ ceramic membranes.

Type of Membrane	Type of TiO ₂ Precursor	Calcination Conditions	Reference
Al ₂ O ₃	Tetra-n-butyl titanate	400 °C for 6 h by 100 °C/h	[18]
Al ₂ O ₃	Tetraethyl orthosilicate	400 °C for 2 h by 100 °C/h	
ZrO ₂	Tetrabutyl orthotitanate	530 °C for 1 h by 100 °C/h	[20]
Al ₂ O ₃	Tetra-n-butyl titanate	500 °C for 2 h by 2 °C/min	[115]
Al ₂ O ₃ -ZrO ₂	Tetraisopropoxide titanium	510 °C for 2 h by 5 °C/min	
Al ₂ O ₃	Titanium tetraisopropoxide	500 °C for 15 min by 3 °C/min	[20]
Activated carbon filter	Tetra-n-butyl titanate	200 °C for 15h	[18]
Al ₂ O ₃	Tetraisopropyl orthotitanate	450 °C by 10 °C/h	[20]
Al ₂ O ₃	Commercial TiO ₂	450 °C by 0.5/min	[115]

These are more chemically, thermally and mechanically stable than polymeric membranes. A summary of comparing the ceramic and polymeric membranes is presented in Table 6.

Polymeric membranes are commonly used for the treatment of industrial wastewater due to their availability [115]. On the other hand, ceramic membranes have an advantage over other wastewater treatment options because of their chemical and thermal stability [18,20,115]. Ceramic membranes, for example, can withstand high chlorine doses and work between pH levels of 1 to 14 and temperatures of up to 500 °C. Despite the advantages of ceramic membranes over polymeric membranes, their use has been restricted due to their high initial cost [20].

Table 6. Comparison of different types of membranes; adapted from [116].

Membrane Type	Polymeric Membrane		Ceramic Membrane
Membrane morphology	Hollow fiber	Flat sheet	Tubular membrane
Stability	Medium	Medium	Good
Price	Less expensive	Less expensive	Expensive
Configuration mode	Internal or external	Internal or external	Internal or external
Module processing	Quite simple	Easy	Hard

3.4. TiO₂-Based Membrane Modification Techniques

TiO₂-based catalysts can be deposited on structured membranes through aqueous or gaseous routes [117]. Membranes with desired morphology and properties are prepared using sol–gel, immersion precipitation, vapor-mediated phase separation and immersion precipitation, electrospinning, dip-coating, sintering, track-etching, stretching, template-leaching, and phase-inversion techniques [71,86,87,90,108,112,113]. Aqueous or gaseous routes can also be used to deposit TiO₂-based catalysts on standardized membranes. The advantages and drawbacks of various methods for immobilizing TiO₂ catalysts on membranes are summarized in Table 7.

Table 7. Advantages and disadvantages of different methods used for immobilizing TiO₂ photocatalysts [116,117].

Synthesis Technique Type	Advantage	Disadvantage
Chemical vapor deposition	Processing time is short. Suitable for high-deposition-rate uniform films.	High deposition temperature (>600 °C) is required. Due to varying evaporation times, deposition of many sources of precursors is difficult. When a vacuum system is used, the price skyrockets.
Physical vapor deposition	Low-to-medium deposition temperature (<600 °C) required. Does not involve complex chemical reactions.	Expensive as vacuum systems are used. Deposition of multiple sources of precursors are difficult.
Sol–gel	High purity of materials Homogeneity is achievable. Versatile means processing and control of parameters. Large surface area materials are produced. Chemical bonding results in strong adherence of coating to the substrate.	Hydrolysis rate is difficult to control. Longer processing time required. Calcination at higher temperatures is required.

Among them, the sol–gel method is the most used method for making TiO₂ photocatalysts and subsequent incorporation of membrane matrices. This method is notable for producing unique stable structures at low temperatures as well as for its excellent chemical homogeneity [85,108,113]. Controlling the precursor chemistry and processing conditions will tailor the compositional and microstructural properties of nano-sized samples. As precursors, inorganic metal salts such as titanyl sulphate, titanium tetrachloride and others (non-alkoxide), and metal alkoxides such as titanium (IV) butoxide are commonly used [90,118]. The pH of the reaction medium, the water/alkoxide ratio, and reaction temperatures can influence the sol–gel phase. Horovitz et al. [119] prepared a TiO₂ sol by stirring an ethanol solution in an ice bath while adding a specific amount of TiO₂ precursor.

The second solution was gradually added with a 50:1:3 volume ratio of ethanol, water, and acetic acid. The mixed solution was held at 20 °C for 30 min before being ultrasonicated to produce a visible TiO₂ sol. Dip-coating was achieved by immersing a substrate membrane in the sol for a set period and then drying the coated membrane [71,86]. Penboon et al. [85] made a distinction between TiO₂-coated membranes and TiO₂-blended polymer membranes. It was deduced that the TiO₂-blended membranes had a more porous structure, but the coated TiO₂ composite membranes had greater antifouling properties and long-term flux stability. They went on to say that TiO₂ nanoparticles, which were spread on the membrane's surface using the coating process, could minimize pore blockage. Furthermore, TiO₂-coated membranes are more hydrophilic than TiO₂-blended membranes.

3.5. Characteristics of Photocatalytic Membranes

Characterization of photocatalytic membranes is based on two parameters, membrane morphology and efficiency (permeability, flux, rejection, and separation factors), which are used to describe the membranes (pore size, pore size distribution, thickness of membrane, charge density and pore shape, chemical properties, and physical properties) [3,18,120]. Improving the hydrophilicity of the membrane surface for TiO₂ nanoparticle deposition involves the introduction of functional groups to the membrane matrix (Table 8).

On the other hand, little research has been done on the impact of immersion time on the properties of photocatalytic membranes. According to Zhang et al. [121], longer immersion periods resulted in more TiO₂ nanoparticles coating the membrane surface, which appeared to clog the membrane pores and reduce flux. Nanomaterials and membranes must be characterized in order to understand their structure, chemistry, morphology, surface charge, wet potential, tensile strength and selectivity for a particular application [39,71,82,112]. Notwithstanding, membrane efficiency degrades over time due to a variety of factors such as fouling, chemical contamination, disintegration and cleaning. Therefore, characterization in this case using particular techniques provides useful information about membrane structure and topography in order to gain insight into performance loss or affected membrane structure.

Similarly, modified membranes (modification with nanomaterials) are also characterized in order to better understand the modified surface layer and how it affects membrane performance. Commonly used techniques and methods for characterization include scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photo electron spectroscopy (XPS), thermogravimetric analysis (TGA), energy dispersive X-ray spectroscopy (EDX), dynamic light scattering (DLS), contact angle, porosity, and zeta potential (Table 8). Thiruvengkatachari et al. [19] reported that after 30 min of reverse osmosis-pressurized activity, some TiO₂ particles detached from the membranes, but no further loss occurred after 7 days that was evidently noticeable in SEM images. Koseoglu-Imer and Koyuncu [105] eluded that diethanolamine increased the hydroxyl groups on the membrane surface, lowering the steric hindrance for attracting TiO₂ nanoparticles. The content of TiO₂ on the DEA-modified membrane was three times higher than on the membrane without DEA, according to the results of energy disperse X-ray spectroscopy.

Furthermore, membrane fouling is the accumulation of macromolecules (polysaccharides, proteins), colloids, microorganisms (bacteria, viruses) and salts (multivalent/monovalent) on the surface or within the pores of a membrane [45,113]. Fouling has a few significant drawbacks in membrane technology, including a reduction in permeation flux, a change in selectivity, and a reduction in membrane life during filtration. Membrane fouling is categorized into inorganic fouling, colloidal fouling, organic fouling and biofouling [45,113,118,122]. Therefore, developing photocatalytic membranes (fouling resistant membranes) are a safer alternative for fouling mitigation since they reduce foulant coagulation on the membrane surface, which contributes to clogging.

Table 8. Modification and characterization techniques of TiO₂-based membranes.

Membrane Types	Modification Methods	Characterization Methods	Reference
TiO ₂ -Polysulfone (PS)	Blending	FTIR, SEM/EDS. XRD, contact angle, zeta potential	[105]
TiO ₂ -Polyethersulfone (PES)	Sol-gel	FTIR, XRD, SEM/EDS	[118]
TiO ₂ /PES	Phase inversion	Contact angle, FT-IR, TGA, pore size distribution, SEM	[123]
TiO ₂ /Cellulose Acetate	Dip-coating	Contact angle, viscosity, SEM, FTIR	[113]
ZrO ₂ PVDF	Blending	SEM, TEM, AFM, XPS, TGA, contact angle	[95]
Cellulose acetate-Polyurethane (CA-PU)	Blending	SEM, TEM, AFM, XPS, TGA, contact angle	[19]
Polyvinylchloride (PVC)	Sol-gel	SEM, FTIR, DLS, TGA	[105]

3.6. Application of TiO₂-Based Membranes

Photocatalytic membranes, which combine membrane filtration with photocatalytic degradation of organics and subsequent antibacterial treatment in a single system, have shown great prospects in water and wastewater treatment settings [12,123–127]. Furthermore, membrane flux is a critical parameter for the photocatalytic membrane system, as it can be enhanced by multilayered deposition of TiO₂ nanoparticles on the membrane surface, but pore blockage can minimize water flux in some cases [20,87]. In order to achieve the best overall performance of the membrane, the optimal balance between photocatalytic activity and membrane flux must be considered.

3.6.1. Wastewater Treatment

Photocatalytic membranes are becoming more prominent to deal with emerging contaminants (antibiotics, pharmaceuticals, nanoplastics, and so on) re-routed to wastewater treatment plants, as well as pre- and post-treatment concerns [128–130]. Increased attempts to eliminate toxic contaminants and pathogens from water have come about from the need for high-quality drinking water [12,15]. Photocatalytic membranes have proven to be more effective in removing recalcitrant organic matter than conventional wastewater treatment processes such as coagulation and filtration [131]. Therefore, they have been the subject of comprehensive research over the last few decades for the removal of toxic organic and inorganic compounds from water (Table 9).

Table 9. Application of TiO₂-based membranes in wastewater settings.

Hybrid Membranes.	Pollutants	Removal Efficiency (%)	Reference
UV-ZrO ₂ /TiO ₂ -Al ₂ O ₃	Methylene blue	95	[25]
Solar-Ag/TiO ₂	Methylene blue	80	[18]
UV-TiO ₂ /Al ₂ O ₃	Direct black 168	63	[97]
UV-ZrO ₂ /TiO ₂ -Al ₂ O ₃	Methyl orange	95	[132]
UV-TiO ₂ /PVDF	Reactive black 5	99	[51]
UV-TiO ₂ -Al ₂ O ₃	Reactive black 5	70	[97]
UV-TiO ₂ nanotube	Rhodamine B	70	[131]
TiO ₂ nanotube	Humic acid	28	[112]
UV-TiO ₂ nanowire	Humic acid	60	[102]
UV-TiO ₂ /Al ₂ O ₃	Humic acid	97	[112]
UV-TiO ₂ nanotube	Humic acid	95	[102]

Zheng [20] reported on photocatalytic membranes for the removal of heavy metals such as mercury, lead, mercury, and cadmium from wastewater settings. Other researchers have reported that multilayered nanocomposite membranes have promising properties

for heavy metal ion adsorption, photocatalysis, self-cleaning, enhanced dye rejection performance and reduced fouling [39,61,81,82]. Batch reactors and photocatalytic polycrystalline TiO₂ membrane reactors were used by Shetty et al. [131] to degrade various pharmaceuticals from water at various pH levels. Due to the catalysts' different hydrophilicity/hydrophobicity at different pH levels, the substrates showed different adsorption on catalyst surfaces when the system was in recirculation mode. The treated water had a permeate flux of 31.5–60.0 L/h.m² in both the alkaline and acidic mediums, with a rejection percentage of 10–60% for furosemide and 5–30% for ranitidine [131]. Table 9 summarizes the removal of pollutants using different types of photocatalytic membranes.

3.6.2. Other Industrial Applications

The development and production of simple and responsive biosensors have sparked a lot of interest due to their wide range of applications, including disease detection, drug discovery, food protection and environmental monitoring [82,85,106,133,134]. Due to the small active surface area of microelectrodes and the low recognition signal, electrochemical biosensors have a difficult time working [125]. As a result, chemical and thermal stability with good biocompatibility makes TiO₂ appear to be a promising biosensor material [48]. Therefore, combining it with membranes would improve its suitability for environmentally friendly designs and applications. Examples of these materials include TiO₂ nanotubes, nanosheets, solgel matrices, and three-dimensional microporous matrices [48,71,98,125]. Chen and Zhao [39] reported their first study on the production of a Fe₃O₄@TiO₂ magnetic NP-based disposable test strip immunosensor that uses a multienzyme labeled amplification strategy to detect organophosphorus (OP) pesticides in human plasma.

4. Challenges and Future Prospects of Photocatalytic Membranes

Membrane-based technologies are gaining worldwide popularity in wastewater treatment settings due to their high separation efficiencies, low cost, small carbon footprint and ease of operation. This process can also be used to eliminate a wide variety of harmful pollutants, including pesticides and herbicides used in agriculture, as well as dyes and toxic metal ions used in industry. Despite extensive research and thorough studies of photocatalytic semiconductors (TiO₂), many aspects of this process remain unsolved. One of the pressing issues as to whether the photocatalytic process should be used as a pretreatment or as a standalone form of water purification is the operating conditions that pose major constraints. Consequentially, the chemical composition and pH of industrial wastewater vary by region. Therefore, efforts should be made to develop photocatalytic membrane materials that can be used under a wide range or optimized operating conditions such as temperature, pH and contaminant concentrations. Furthermore, to achieve continuous irradiation with visible light over a wider range of operating conditions, a significant amount of research should be devoted to the doping and modification of TiO₂ and other semiconductors. However, catalyst immobilization is an obstacle that must be overcome in order to maximize the photocatalysts' irradiated surface area. This is needed to avoid issues such as catalyst recovery and agglomeration, which are very common in slurry-based photoreactors.

4.1. Photocatalytic Membranes

Membrane fouling, which is caused by the accumulation of anthropogenic organic contaminants and microorganisms on the membrane pores' surface, results in poor water quality, high operating costs, and a limited membrane life. In order to perform equal photocatalytic operation with minimal water flow consequences, an adequate level of photocatalysts should be incorporated into the membrane. In addition to TiO₂ loading, light intensity and irradiation time influence membrane quality.

In order to execute reasonable photocatalytic activity with minimal water flow repercussions, an appropriate level of the photocatalyst should be incorporated into the membrane. Membrane performance is also influenced by light intensity and irradiation time in

addition to TiO₂ loading. Addressing this, photocatalytic membranes have been reported to have better fouling resistance as well as antimicrobial properties. Two-dimensional nanosheets with graphene have been reported to be useful for membrane applications. Additionally, combinations of nanowires with graphene sheets have also gained attention recently. Such types of structures provide antifouling and antimicrobial properties as well as hydrophilicity and aqueous stability.

4.2. Magnetized TiO₂ Photocatalytic Membranes

In order to implement heterogeneous photocatalysis into practical water and wastewater treatment applications, the overall cost of the process should be minimized. One of the ways to decrease the cost is to improve the recyclability of the photocatalyst. This can be achieved by introducing magnetic constituents into the photocatalytic nanocomposite to enhance recoverability by the application of an external magnetic field. Magnetic components (Fe₃O₄) can benefit in the recovery of photocatalyst particles by preventing them from clumping together [39,67]. Magnetite (Fe₃O₄) NPs, maghemite (Fe₂O₃) NPs and nanorods, and hexagonal ferrites are examples of ferritic nanomaterials that are simple to recover by magnetic fields and are re-usable due to their long-term stability.

In some studies, Fe₃O₄ and TiO₂ nanoparticles have also been successfully used as a filler for composite membranes. This opens a broad spectrum of recycling possibilities in the form of magnetized photocatalytic membrane applications (Table 10).

Table 10. Examples of magnetite heterojunction photocatalyst performance.

Composition	Pollutant	Operating Condition	Efficiency (%)	Reference
Fe ₃ O ₄ (0.075 gL ^{−1})	<i>E. coli</i>	UV @ <i>t</i> = 60 min	50.5	[41]
Fe ₃ O ₄ –TiO ₂	Bisphenol (10 ppm)	UV @ <i>t</i> = 60 min	92	[106]
Fe ₃ O ₄ –ZnO	Rhodamine B (7 ppm)	UV @ <i>t</i> = 60 min	99.3	[52]
Fe ₃ O ₄ –ZnO–rGO	Methylene violet (408 ppm)	UV vis @ <i>t</i> = 120 min	83.5	[52]
Bi ₂ O ₃ –Fe ₃ O ₄	Ibuprofen (2.1 ppm)	UV vis @ <i>t</i> = 120 min	>95	[39]
Fe ₃ O ₄ –CuO–ZnO–nano graphene	Methylene blue (30 ppm)	UV @ <i>t</i> = 120 min	93	[67]
Fe ₃ O ₄ –ZnO–CoWO ₄	Rhodamine B (4.8 ppm)	UV vis @ <i>t</i> = 405 min	98.3	[134]
Fe ₃ O ₄ –Bi ₂ O ₃	Ciprofloxacin	UV vis @ <i>t</i> = 240 min	98.3	[131]

Thus, Fe₃O₄ NPs display exceptional superparamagnetic behavior, which provides an additional benefit of a much easier magnetic separation of the semiconductor and the solution. The coprecipitation method or thermal decomposition method is widely used to make Fe₃O₄ nanoparticles, with minor variations such as room temperature (25–80 °C). The exemplary adsorption potential for toxic metal ion removal was achieved by the finite-size effect of magnetic nanoparticles with high surface-to-volume ratios [118]. Magnetite has also been used as an additive due to its unique features, such as physicochemical properties and high biocompatibility. Many polymeric-based membranes, such as polysulfide and polyether sulfone, had their membranes magnetized with magnetite to strengthen antifouling properties. However, knowledge of magnetized TiO₂ photocatalytic membranes is still limited and therefore requires more attention.

4.3. Life Cycle Assessment (LCA)

A life cycle assessment (LCA) is needed to incorporate TiO₂ photocatalytic-based membrane technology on a large scale [3,84]. LCA is one of the most useful instruments for

determining a process's environmental effects as well as its viability and costs. Although there is a large amount of information in the literature about the recyclability and reusability of TiO₂ photocatalysts, there is still limited knowledge about their end of life [3,19]. The photocatalytic process performance, on the other hand, is highly dependent on the feed water's consistency, the operating conditions and type of treatment configuration. Apart from the environmental impacts of high organic wastewater, the amount of energy required has a major impact on the photocatalysis process [3,84]. This is one of the reasons why solar photocatalysis has received so much attention in recent years. Consequently, the toxicological and environmental impacts of a wastewater treatment facility can be detected and minimized using LCA.

5. Conclusions

This review study presents the photocatalytic membrane process as a game-changing technology to mitigate fouling and other drawbacks of membrane processes in addressing water scarcity and major environmental challenges. Characteristics of TiO₂-based photocatalytic membranes with insight into their types, fabrication techniques, operational conditions and applications in water settings are discussed. As a result, the advancement of photocatalytic membrane reactors based on a wide range of nanomaterials and TiO₂ photocatalyst phase modification is anticipated to have an unparalleled future in water and wastewater treatment settings. The development of magnetite TiO₂ photocatalytic membranes was found to be an ecofriendly choice to increase photocatalytic and recoverability activities as well as reduce membrane fouling. Additionally, incorporating magnetized TiO₂ photocatalytic membranes as a post-treatment to an existing biological system can reduce eutrophication potential while increasing biomethane potential for energy usage. The prospects of life cycle assessment, research and development of magnetic photoactive-based membranes is foreseen to be economically viable with the possible potential to resolve the current membrane setbacks and bring the application of this technology to industrial scale.

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Review

Fate of COVID-19 Occurrences in Wastewater Systems: Emerging Detection and Treatment Technologies—A Review

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Abstract: The coronavirus (COVID-19) pandemic is currently posing a significant threat to the world's public health and social-economic growth. Despite the rigorous international lockdown and quarantine efforts, the rate of COVID-19 infectious cases remains exceptionally high. Notwithstanding, the end route of COVID-19, together with emerging contaminants' (antibiotics, pharmaceuticals, nanoplastics, pesticide, etc.) occurrence in wastewater treatment plants (WWTPs), poses a great challenge in wastewater settings. Therefore, this paper seeks to review an inter-disciplinary and technological approach as a roadmap for the water and wastewater settings to help fight COVID-19 and future waves of pandemics. This study explored wastewater-based epidemiology (WBE) potential for detecting SARS-CoV-2 and its metabolites in wastewater settings. Furthermore, the prospects of integrating innovative and robust technologies such as magnetic nanotechnology, advanced oxidation process, biosensors, and membrane bioreactors into the WWTPs to augment the risk of COVID-19's environmental impacts and improve water quality are discussed. In terms of the diagnostics of COVID-19, potential biosensors such as sample-answer chip-, paper- and nanomaterials-based biosensors are highlighted. In conclusion, sewage treatment systems, together with magnetic biosensor diagnostics and WBE, could be a possible way to keep a surveillance on the outbreak of COVID-19 in communities around the globe, thereby identifying hotspots and curbing the diagnostic costs of testing. Photocatalysis prospects are high to inactivate coronavirus, and therefore a focus on safe nanotechnology and bioengineering should be encouraged.

Keywords: advanced oxidation process; biosensors; magnetic nanoparticles; membrane bioreactor; wastewater-based epidemiology; ribonucleic Acid (RNA); SARS-CoV-2

1. Introduction

The severe and acute respiratory syndrome, coronavirus-2 (SARS-CoV-2), has been an etiological agent of COVID-19, which, according to the World Health Organization (WHO), is transmitted via respiratory droplets and contact routes [1,2]. According to Hart and Halden [3], SARS-COV-2 belongs to the coronvirinae subfamily made of positive-sense Ribonucleic Acid (RNA) viruses. Additionally, in human cells, this virus uses an angiotensin-converting enzyme (ACE2) as a receptor which is very high in the gastrointestinal system as a courier of ACE2 RNA. SARS-CoV-2 detections in human stools and urine of COVID-19 carriers have been reported to be potent [4]. Successive studies of finding the RNA of this virus in sewage systems raises notable concerns about COVID-19 faecal transmission and its pathogenic effects on sanitation and wastewater systems [3,4].

Municipal wastewater is typically observed as one of the main end routes of different types of emerging contaminants such as pharmaceuticals, endocrine disruptors, antibiotics, microplastics, pesticide and heavy metal residues associated with antimicrobial resistance (AMR) [5]. Sewage streams from the municipal system contain a large number of recalcitrant compounds which are usually excreted by humans and other activities. Notwithstanding, global hotspots for drug-infested countries where drug deals and usages are widespread are usually identified through the sewage systems [6]. Despite this, there are various measures surrounding the movement restriction of about 93% global population to monitor the COVID-19 spread and advisory interventions [3]. As such, extensive testing is required to understand the possible routes of the viral contagion, which is very expensive. Therefore, monitoring the spread of COVID-19 early stages in communities through the wastewater-based epidemiology (WBE) approach is useful [5,6]. Additionally, this could possibly provide rapid results for effective and urgent interventions in the fight against COVID-19.

Conversely, the COVID-19 pandemic has led to a paradigm shift of the world's societal and essential activities with a profound transformation of human life, which poses a global threat to socio-economic growth and development [4,7]. The risk and routine of waste collection and wastewater as an ecological response to address COVID-19 complications in water and wastewater settings has received little attention [8]. In response, this study introduces WBE to monitor the COVID-19 spread and its threats to public health, while analyzing the populated pooled wastewater to mitigate COVID-19 complications. In essence, over the past years, over 1500 pathogens have been discovered, with almost 40 of them emerging from communicable diseases with a major impact on communities [7,9]. These include severe and acute respiratory syndromes (SARS) (2002–2003), H1N1flu/swine flu (2009–2010), Ebola (2014–2016), Zika virus (2015–2016), and COVID-19 (2019–2020) [9]. As it stands, the search of vaccines for recurrence of communicable disease prevention and their treatment, in terms of COVID-19, seems far-reaching. This has triggered an international ban at various airports and seaports on travel and social gathering, practicing quarantine protocols, school and church closures, and closures of non-essential industries [10]. According to the WHO report, as of 29 May 2020, over 5 million cases of Covid-19 cases were identified globally with 362,614 deaths and 2,596,004 people recovering [11].

Eventually, SARS-CoV-2 prevention interventions which consist of personal cleanliness, accurate sanitation, hand washing and sanitizing cannot be separated from a safe supply of water. Hence, water and wastewater industries amidst of addressing this global pandemic are going to revel in widespread economic impacts [12]. As a direct consequence of COVID-19 to the global economic system, countries along with South Africa and the United States of America are expected to suffer from huge financial losses of billions of dollars because of revenue discounts of their water utilities [13]. Upon this foundation and many extra anticipated in days to return, studies into figuring out and developing a strong era within the water and wastewater remedy settings to diminish the COVID-19 complications are useful.

Therefore, this paper seeks to discuss the cutting-edge state of the COVID-19 virus in terms of its fate, occurrence and removal from wastewater together with inter-disciplinary and technological procedures as a roadmap for water and wastewater sectors to sign up for the combat against COVID-19 and the future water crisis. The study in addition identifies magnetic nanotechnology, biosensors, and membrane bioreactors as progressive and robust techniques to enhance the purification of wastewater whilst at the same time minimizing the environmental impacts of COVID-19.

2. Current State of COVID-19 in Wastewater

The public health provides significant concentrations of SARS-CoV-2 arriving at WWTPs and the consequent discharge into the wider environment is alarming, even though no substantial studies have been done [14]. The spread of COVID-19 among human populaces might be identified too late, and the virus can only be detected when an enormous scale of human testing is accessible, or when clinical COVID-19 cases are accounted for by health experts, because the carriers are believed to exhibit no symptoms, or few non-specific symptoms [15]. Therefore, there have been investigations

into the virus circulation among developed countries and emerging economies, including China, Netherlands, and Australia using stool samples [16]. The WHO (2020) reported that as of March 3, 2020, only two studies had been able to detect the viral RNA fragments of COVID-19 in the faecal matter of infected patients and that the transmission of the virus through faecal matter was low. In a study, COVID-19 viruses in 10 sampled stools in sewage plants in the Paris area in France were detected [17]. Scientists in the Netherlands also reported on a detected virus RNA in a WWTPs in Amersfoort, a city located 32 miles from southeast of Amsterdam [18]. SARS-CoV-2 RNA in wastewater from 19 communities in Australia, a median range of 171 to 1090 infected people were identified in the communities [19]. In the same study, they further stated that the viral RNA copies were enumerated using the reverse transcriptase quantitative polymerase chain reaction (RT-qPCR), resulting in two positive detections within a six-day period from the WWTPs [20–24].

2.1. Wastewater-Based Epidemiology (WBE) Monitoring of COVID-19

Wastewater-based epidemiology (WBE) is a promising approach to better understand the occurrence of viruses in WWTP catchment population since the WW contains viruses excreted from symptomatic and asymptomatic individuals in a particular location under study [25]. Wastewater monitoring has a greater potential to provide early warning signs on how broadly SARS-CoV-2 is circulating in the community especially in the case of individuals showing mild symptoms or no symptoms at all [23,24]. Despite the applications of WBE in monitoring the outbreaks of enteric viruses such as norovirus, hepatitis virus, and poliovirus for public health interventions [25], there are still few studies documented on the concentration and detection of SARS-CoV-2 in wastewater settings [26]. Zhang et al. [27] reported binary RTqPCR data, while another recent study reported ~250 copies/mL SARSCoV-2 in wastewater in Massachusetts, USA. The authors of these studies further acknowledged that the estimated concentration was much greater (5% of all fecal samples in the catchment) than the confirmed cases (0.026%). Several factors were proposed by the author on the discrepancies and considered their results conservatively. The estimated numbers of SARS-CoV-2 in the study by Ahmed et al. [4] were found to be 3–4 orders of magnitude lower than that reported by Hamidouche and Belmessabih [28].

Furthermore, Kozitsina et al. [29] assessed the stability of drug biomarkers in municipal WWTP as a major factor to influence the estimation of drug consumption using sewage epidemiology and their possible transformation in a sewer. The stability was conducted at 10 and 20 °C in order to simulate typical winter and summer temperature conditions in the sewer system. It was found that among the 14 substances tested, the most unstable compounds were morphine-3- β -D glucuronide (MG), 6-acetyl morphine (6-AM), cocaine (COC) and 6-acetyl codeine (6-AC), while all other investigated compounds appeared to be relatively stable over a period of 72 h. It was also reported in the same study that the transformation processes for all degradable compounds followed pseudo-first-order kinetics with significantly longer half-times during winter. The first detection of SARS-CoV-2 in untreated wastewater in Australia was confirmed by sequencing after shedding the virus in the stool of humans [4]. Their preliminary findings demonstrated the applicability of WBE for COVID-19 surveillance as a potential tool for public health monitoring at the community level. SARS-CoV-2 RNA was concentrated from a wastewater catchment in Australia, and viral RNA copies were numbered using the reverse transcriptase quantitative polymerase chain reaction (RT-qPCR), which resulted in two positive detections within a six-day period from the same WWTP [4]. Currently, it has been reported that RT-qPCR assays developed for clinical specimen testing are being used for SARS-CoV-2 RNA detection in wastewater samples. The Monte Carlo simulation predicted a median number of infections ranging from 171 to 1090 in the catchment basin in their study [4,7].

A major challenge encountered in some of the above studies has been the establishment of quantitative predictions from the viral RNA concentrations measured in the sewage to the actual number of cases in the community. For the application of WBE of SARS-CoV-2 infections, further systematic research possibly will be required in governing these aspects from effective sampling and preservation

via data interpretation. This could be beneficial in remote communities and confined populations, which makes it very crucial. The development and/or identification of enveloped virus concentration methods and local data on the prevalence and concentration of SARS-CoV-2 in patients is, therefore, recommended [29]. Additionally, virus concentration should be considered as an essential factor with much attention to improving the sensitivity of SARS-CoV-2 detection in wastewater [4,28]. Idumah et al. [30] recounted that, contingent upon localized conditions, discovery in such a society's sewage and wastewater of one asymptomatic or symptomatic infected case per 100 to 2,000,000 non-contaminated individuals is hypothetically achievable. This is owing to some viable successes presently being accounted for from around the globe. Thus, with about 105,600 sewage plants that can be placed under surveillance, 2.1 billion people could be monitored globally [28–30]. The European Centre for Disease Prevention and Control (ECDC) (2020) informs that as of 9 September 2020, they were able to report about 27,609,408 cases of COVID-19 with 898,087 deaths globally (Figure 1) [8].

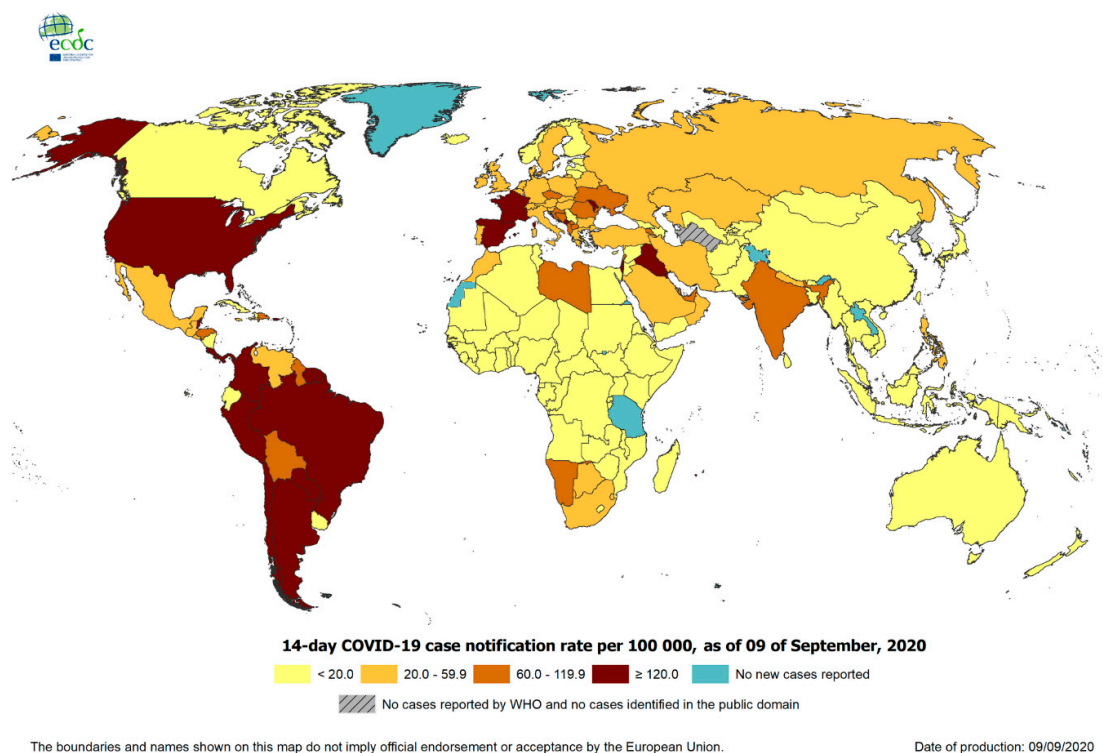


Figure 1. European Centre for Disease Prevention and Control report on the coronavirus (COVID-19) situation worldwide as of 9 September 2020 [8].

2.2. Community Surveillance of the Virus Load

Developed countries tend to have advanced infrastructure as compared to developing countries [31]. Similarly, in the detection of COVID-19 in sewage treatment systems, the method could be quickly adapted to detect viral loads in stools of asymptomatic and symptomatic patients in catchment areas because of the interconnectedness and properly constructed sewage systems linked to a community sewage treatment center [32]. However, in most developing countries, some communities do not have interconnected and centralized sewage systems to put into effect the WBE method of spotting the virus in sewage systems. For instance, BBC World reported on 14 March 2020, that nearly half of 1.2 billion people in India lacked access to toilet facilities (BBC News, 2020). While 49.8% practiced open defecation, 46.9% had access to lavatories as the remaining 3.2% had access to public toilets. Upon investigation of the presence of the virus in sewage systems and possible signs of an imminent outbreak, the rundown of South Africa's municipal sewage systems poses a risk of infection to residents and nearby communities [33]. With streamlined and properly constructed sewage systems in developed countries, WBE is observed to be very consistent with the findings of other

researchers [32–34]. For instance, wastewater was sampled at the Amsterdam Airport once a week in the first quarter of 2020 with results showing a positive detection of the virus RNA using a quantitative RT-PCR methodology four days after recording cases in the Netherlands [34]. Sodré et al. [35] further corroborate these findings, stating that “the detection of the virus in sewage, even when the COVID-19 prevalence is low gives an indication that sewage surveillance could be used to monitor the circulation of the virus in the population.”

Further studies conducted showed that out of the 74 COVID-19 patients, 55% showed a prolonged presence of SARS-CoV-2 in their faecal matter [36]. A mean value of 27.9 days as compared with a mean of 16.7 days in the respiratory samples of the 55% in China was reported [34–36]. The clinical and WBE per-assay costs of screening may differ significantly depending on the geospatial regions, the labor cost differentiation prices, existing infrastructure, safety requirements, among others. Mao et al. [34] discovered that the cost per kit of clinical testing of the virus in patients could cost between USD 10 to 20 depending on the location of the patient with an average mean of USD 15 globally. As it stands now, approximately 30,000–600,000 of SARS-CoV-2 viral genomes per mL of human excreta with a faecal load of 100–400 g has been reported [3,20]. Sodré et al. [35] also reported that the SARS-CoV-2 load to municipal wastewater is estimated to be associated with lower and upper bound estimates of 56.6 million to 11.3 billion viral genomes per infected person per day. This translates into concentrations of 0.15 to 141.5 million viral genomes per liter of wastewater generated in North America and Europe.

2.3. Prevention of COVID-19 in Humans

Appallingly, up until this point, there seems to be no viable formula for medicating the combination or use for SARS-CoV-2 disease cure, with the possible outcomes resulting in fatal provocative reactions and acute lung injury [37]. There have been several pieces of research conducted to remediate and control the absolute collapse of the immune system of infected patients. Hamidouche and Belmessabih [28] suggested that SARS-CoV-2 Mpro protease establishes one of the most appealing antiviral medication targets, particularly in the structure and advancement of SARS drugs. Further, Borges do Nascimento et al. [38] also noted that the Chinese treatment guidelines and the WHO's Centre for Disease Control and Prevention (CDC) had recommended drugs including one of the investigational agents (remdesivir), ritonavir or lopinavir. Up until now, there is no cure for the virus and, therefore, the WHO presents some guidelines as safety protocols for human protection and prevention of the virus as depicted in Figure 2. These include social distancing; lockdown (which is an extreme form of social distancing); hand hygiene practices, such as hand washing and sanitizing; symptom screening; cloth mask and cough etiquettes; testing, isolation, quarantine and contact tracing; and frequent fumigation and cleaning of the environment. As earlier stated, COVID-19 has unknown vaccine or cure, and its death rates are rising steeply. It is, therefore, imperative that precautionary measures are taken for the safety of the whole population [28]. Recent studies suggest that COVID-19 is aerosol or airborne and can stay in the air for more than 8 h; hence, the wearing of masks is very important [28,37,38].

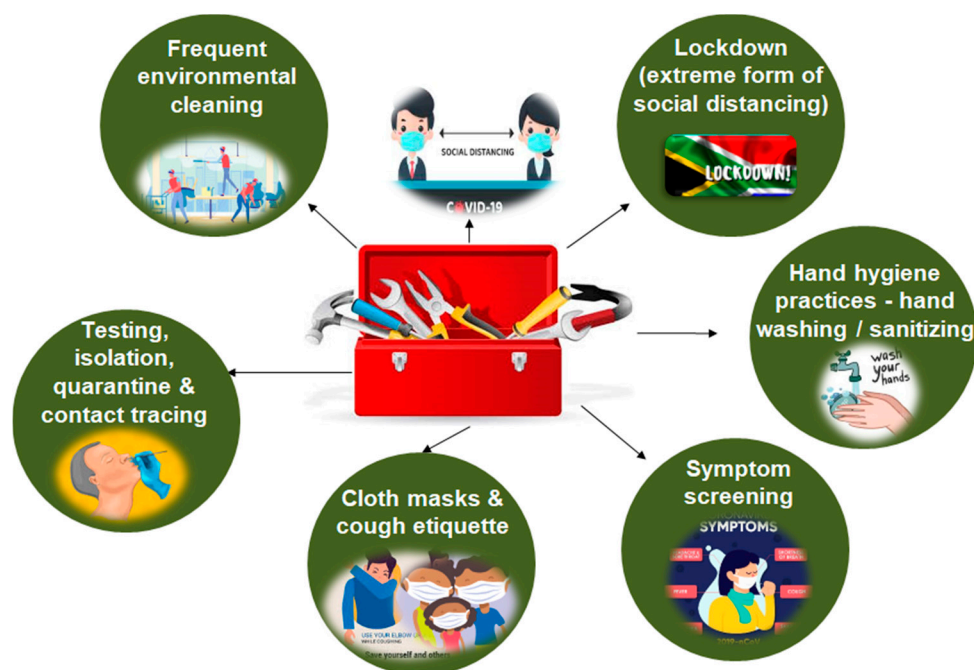


Figure 2. Safety protocols and etiquettes during COVID-19.

3. SARS-COV-2 in Wastewater Possible Treatment Technologies

As the end route of sanitization steps, excretion of COVID-19 patients and other administrative pre-requisites of COVID-19 are the sewage treatment plants and WWTPs. This has prompted the USA Occupational Safety and Health Administration (OSHA) to release new stringent rules and guidelines for wastewater and sewage workers based on data obtained from healthcare settings earlier this year [36–38]. Ahmed et al. [4] reported that coronaviruses, including SARS-COV2, responsible for the COVID-19 pandemic, could possibly remain infectious for days or even longer in sewage and drinking water. Apart from the cleansing and disinfection techniques applied in such as hospitals and clinics such as sterilization by ultraviolet radiation, and chlorination with peracetic acid or hypochlorous acid. This section presents possible wastewater treatment technologies and detection technologies of SARS-COV-2 in wastewater settings.

3.1. SARS-COV-2 Possible Detection Techniques

3.1.1. Magnetic Nanotechnology

Magnetic nanoparticles (Ferromagnetite) have been reported as good substrates for heavy metal adsorption from aqueous solutions [9,34]. The chemistry behind this mechanism could be attributed to the four unpaired electrons in the 3d shell with an iron atom having a strong magnetic moment. Fe^{2+} ions have 4 unpaired electrons in their 3d shell, and Fe^{3+} ions have five unpaired electrons in their 3d shell. Magnetite nanoparticles are susceptible to air oxidation and can be easily aggregated in aqueous systems. The stabilization of the iron oxide nanoparticles by adding surfactants as a type of surface modification is desirable. In this context, ongoing application of magnetic nanoparticles in wastewater settings, which includes the removal of non-magnetic water pollutants like dissolved pollutants, algae, and viruses via magnetic separation has appeared to be very promising techniques [9].

For instance, a study conducted by Mao et al. [34] showed effective use of aptamer-conjugated magnetic nanoparticles for the removal of HCV particles from human plasma samples. Furthermore, magnetic particles coupled with biosensors have been employed for detecting viruses of biofilms in the sewage treatment system [2]. This presented an easy modification with functional groups which leads to the possibility to control their orientation after immobilization [24]. The improved

utilization of established methods and the changing analytical techniques began incorporating nano- or micro-sized magnetic beads (MBs) [39]. Randazzo et al. [6] indicated that the presence of surface functional groups creates a speedy response to an applied magnetic field, uniform and high magnetite content, homogenous size distribution and colloidal stability of magnetic nanoparticles which are some of the specific properties of MBs in the analytical applications. The magnetic behavior associated with magnetic nanoparticles, mostly of ferromagnetic materials, enhances simple isolation of analytes from complex matrices such as environmental and biological samples [39]. This is carried out by connecting specific ligands on the outside of MBs and isolating the MB-bound analytes with the guide of an outer magnetic field. Additionally, with specifications, MBs could then function with different responsive groups, like tosyls, epoxys, carboxyls, and amines which can be utilized to immobilize ligands with high affinity including antibodies, proteins, aptamers, among others, based on the accepted applications [6,39].

Recently, applications of magnetic separation have been introduced in biotechnology for analytical applications, separation of cells, sewage treatment, protein digestion and purifications [6,9,34,39]. Furthermore, integrating MBs with aptamers opens up additional opportunities in various applications including disease diagnosis using biosensors, cell imaging and labelling and magnetic resonance imaging, disease therapy, water purification, wastewater treatment, sewage treatment, and sample preparation [34,39]. As earlier stipulated, in aptamer-modified MB-based assays, aptamers are utilized as MBs and binding ligands generally utilized for separating the analyte from complex matrices. In aptamer-modified MBs, Surface-Enhanced Raman Scattering (SERS) sensing is employed in the analytical applications of diverse sensor designs (Figure 3).

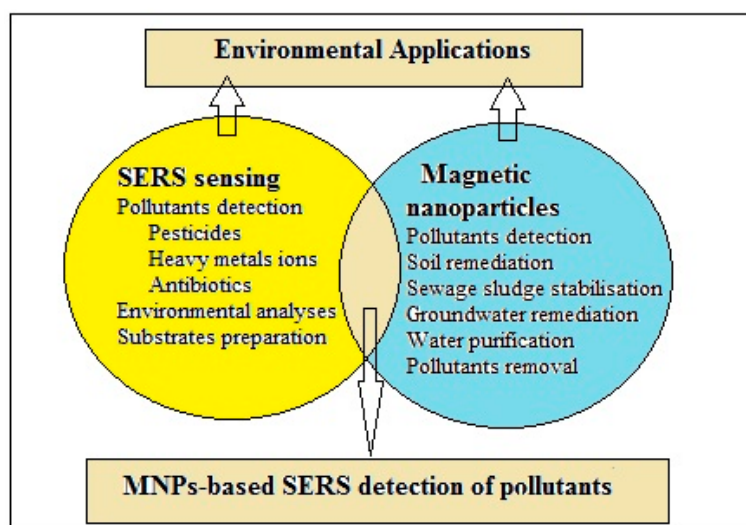


Figure 3. MNP-based SERS detection of pollutants adapted and modified from Pant et al. [39].

3.1.2. Biosensor Technology

Biosensors, as powerful and innovative analytical devices with biological sensing elements, have been employed in many potential fields, which includes drug discovery, diagnosis, biomedicine, food safety, environmental monitoring and security [1,30,40]. For instance, the term “contour” for glucose determination and that of “OneTouch” for glucose and cholesterol determination [40], is a lactose biosensor [30] and a portable system for enzyme immunoassay and polymerase chain reaction analysis [29]. It is reported that the first biosensor was invented by Clark and Lyons [41]. Additionally, the technical revolution in biosensors was found to be the discovery of genetically encoded or synthetic fluorescent biosensors in analyzing molecular mechanisms of biological processes [1,2,29,42]. The development of biosensors is limited by their low stability and the rapid degradation of biological components during storage and use [29]. This makes calibration difficult and reduces reliability. In contrast to biological components, their synthetic equivalents are chemically and thermally stable.

Additionally, the utilization of biosensors has acquired paramount significance in the field of drug discovery, food safety standards, biomedicine, defense, security, and environmental monitoring [43]. For decades, it has led to the invention of precise and powerful analytical tools using biological sensing elements such as biosensor [42].

It is found that the topical advances in biological techniques and instrumentation involving fluorescence tagged to nanomaterials have increased the sensitivity limit of biosensors [42,44]. The adoption of aptamers or nucleotides, peptide arrays, antibodies, and molecule imprinted polymers could provide tools to develop innovative biosensors over classical methods [43]. The integrated approaches provide an improved perspective for the development of specific and sensitive biosensors with high regenerative potentials. Several biosensors ranging from nanomaterials, polymers to microbes could provide broader potential applications. The integrated strategies also involve multiple technologies ranging from electrochemical, electromechanical, and fluorescence with optical-based biosensors and genetically engineered microbes [29,42,43]. The majority of these biosensors have tremendous applications with prospects in disease diagnosis and medicine. The mandate and necessity for the use of biosensors for rapid analysis with cost-effectiveness require bio-fabrication that will pave the way to identify cellular to whole organism activity with a detection limit of high accuracy for single molecules [43]. Previous studies have reported that the rapid diagnosis of infectious diseases and apt initiation of appropriate treatment are typically assigned as determinants for the promotion of optimal clinical outcomes and that of the health of the public [7,20,23]. Other studies have reported that the conventional in vitro diagnostics for infectious diseases are time-consuming, requiring centralized laboratories, experienced personnel, and bulky equipment [32].

Recent advances in biosensor technologies have the potential to deliver point-of-care diagnostics that match or exceed conventional standards with regards to time, accuracy, and cost [7,29,42]. Despite the clinical need, the translation of biosensors from research laboratories to clinical applications remains limited to a few notable examples, such as the glucose sensor [42]. Some of the reported clinical challenges that are overcome by biosensors include sample preparation, matrix effects and system integration [28,29]. The vast range of sewage microbial diseases have been found to cause remarkable morbidity and mortality everywhere throughout the world. Sewage gives a perfect developing condition to various sorts of micro-organisms, including yeasts, fungi, algae, protozoa, viruses, and bacteria [6]. According to Mishra et al. [44], the level of heterotrophic, autotrophic, saprophytic, non-pathogenic, and pathogenic forms varies with their sources. Tobore [45] predicted that the concentration of some pathogenic viruses and parasites like *Giardia* and *Cryptosporidium* in wastewater is directly connected with the disease rate in the populace. This could narrow the general medical issues, other non-pathogenic faecal bacterial like RNA bacteriophages, total coliforms and *E. coli* mostly found in wastewater with a negligible effect on the lives of people [35,46]. Therefore, monitoring SARS-CoV-2 in sewage treatment facilities with biosensors in the sewage is useful. Leustean et al. [47] also added that the identification of waterborne infections is crucial to kill and control their harmful impact as pathogens. In essence, the recent invention of biosensors can be applied with magnetic nanomaterials to improve the precision and effectiveness of detecting several pollutants, including viruses in the sewage systems.

Types of Biosensors

Recently, different types of COVID-19 potential biosensors have been reported for point-of-care (POC) diagnosis of infectious diseases. These include sample-answer chip-, paper- and nanomaterial-based biosensors [1,2,42]. The chip-based biosensors are made of poly-methyl methacrylate (PMMA) for the detection of pathogens [42,43]. These biosensors have a high throughput of analysis by minimizing reagent consumption, owing to being automated and enhances the flow of a fluid with a small volume of samples to be manipulated with precision [43]. Additionally, their cost-effectiveness, high transparency and biocompatibility properties have attracted the attention of many researchers for advancement [7,20,29]. For instance, an integrated digital sample-answer

chip-based biosensor to quantify nucleic acids is to be customized for future diagnosis of COVID-19 in wastewater [29,42].

Paper-based biosensors are also gaining significant usage attention for POC than the chip-based biosensors [2,42]. Due to their cost-effectiveness, user-friendliness and biodegradability, they can be applied on-site for POC testing in remote settings to achieve rapid results [2]. For instance, using a test strip to detect COVID-19 in patients' blood, serum and plasma samples [43]. These test strips consist of the following: (i) a sample pad to add patients samples; (ii) a conjugate pad containing antigen-coated COVID-19 with gold nanoparticles (gold-COVID-19); (iii) a nitrocellulose membrane that consists of a control line (coated with goat anti-rabbit IgG, an IgG test line coated with anti-human IgG, an IgM test line coated with anti-human IgM); and (iv) an absorbent pad that absorbs waste [7,42,43].

Further advancement of biosensors has led to the introduction of nanomaterials-based biosensors such as textile-based, film-based, magnetized nanomaterials (gold, iron, zinc), carbon and nanotubes-based (nanowire) biosensors for the detection of COVID-19 in wastewater settings [2,7,29,43]. The assay development is to improve the functionality and detection sensitivity of the conventional biosensors for commercialization and curbing of the economic threat of COVID-19 [42,43]. For instance, to increase the tunable hydrophobicity and interactions between integrated gold nanoparticle antibodies (AuNP-Ab) and the target for analysis [43].

3.2. SARS-COV-2 Possible Wastewater Treatment Technologies

3.2.1. Membrane Bioreactor

Membrane technology has emerged as a preferred choice for reclaiming water from different wastewater streams for reuse. With a significant reduction in the size of equipment, energy requirement and low capital cost, membrane technology offers many prospects in wastewater treatment [48]. According to Obotey Ezugbe and Rathilal [49], membrane technology has the potential of bridging the economic and sustainability gap, amid possibilities of low or no chemical usage, environmental friendliness, and easy accessibility to many. Thus, membrane technology has proven to be a more favorable option in wastewater treatment processes in recent times. Figure 4 shows the schematic representation of the different paths of the membrane process.

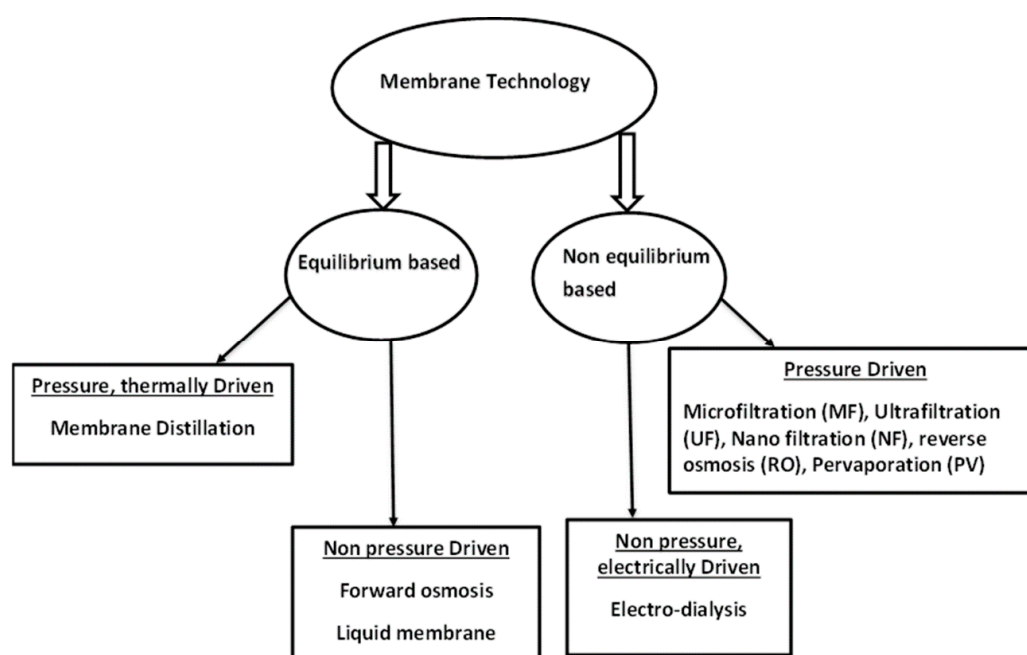


Figure 4. Schematic representation of the membrane processes adapted and modified from Obotey Ezugbe and Rathilal [49].

Over the past decades, membrane bioreactors (MBRs) have reached a significant market share in water and wastewater settings, which is expected to grow at a compound annual growth rate (CAGR) of 13.2% [13,49]. This seems to be higher than that of other advanced technologies, thereby increasing its market value from USD 337 million in 2010 to USD 627 million in 2015 [13]. The main limitation for their widespread application is their high energy demand between 0.45 and 0.65 kWh.m⁻³ for the highest optimum operation from a demonstration plant, according to recent studies [42,50]. Past research articles had reported that, although MBR technology did not come into play when it was earlier introduced by Smith and his co-workers in the late 1960s, it has been playing an important role in wastewater treatment for reuse since the mid-1990s [42]. Rigorous regulations on effluent discharge and the reduction of membrane capital cost could be regarded as the principal drivers for the present widespread use of this technology worldwide [50]. The present emergence in the wastewater treatment market of the membrane bioreactors gives a clue of the degree of maturity reached by this technology. The most cited market analysis report indicates an annual growth rate of 9.0% and predicts a global market value of USD 3.7 billion by 2023 [2]. Predominantly outstanding in this case are China and some European countries with an implementation rate of over 50% and 20%, respectively. The technological advancement in the urban wastewater market is also reflected under two major categories: the diversity of technology suppliers and the upward trend in plant size. It has been found that since 1990, the number of MBRs have grown exponentially with an estimate of over 50 different providers by the end of 2009 [48]. MBR processes make use of their microbiological and metabolic potential for treating wastewater. In relation to that, MBR processes are analogous to conventional activated sludge (CAS) processes [27,48]. These are designed and operated with much longer solids retention times (SRT) than that of CAS processes. Longer SRT operations result in different treatment performances and other associated situations [48]. Table 1 shows the advantages and disadvantages of MBR over CAS.

Table 1. Advantages and disadvantages of MBR over CAS; adapted from [27,48].

Advantages	1. Production of high-quality treated water that is reusable in addition to removal of most of the pathogenic bacteria and some viruses. 2. Low footprint due to the obviation of a secondary sedimentation tank and smaller bioreactor size. 3. Reduces WAS production 4. Fine control of SRT
Disadvantages	1. Greater operational and process complexity 2. Higher capital and operational costs 3. Greater foaming propensity.

Limitations of MBR

The fundamental frameworks associated with an MBR includes microbiology, kinetics, stoichiometry and mass balance that is substantially different from CAS plant bioreactors with respect to design and operations [51]. MBR processes make use of microfiltration or ultrafiltration membranes to separate treated water from activated sludge (Figure 5), replacing gravity sedimentation tanks (or secondary sedimentation tanks) in CAS processes [48,51]. For simplicity, some advantages of MBRs include its compactness, higher effluent quality, a higher rate of degradation and the possibility to convert from existing conventionally active sludge purification. The disadvantages arise from aeration limitation, stress on sludge in external MBRs, fouling and higher costs in pricing [51]. Additionally, at low growth conditions, as is demanded in MBRs, other processes apart from microbial growth have to be taken into consideration. This is recognized as the maintenance energy requirement, endogenous respiration, and subsequent cryptic growth [52]. The commercialization of the largest MBRs with a peak design capacity higher than 50 MLD (mega liters per day) [42] and other plants are presented in Table 2. Conventionally, this involves activated sludge treatment together with a process filtration through a membrane with a pore size between 10 nm and 0.4 microns (micro/ultrafiltration),

which enhances the sludge separation [42,52]. The membrane as a barrier retains all particles, colloids, bacteria, and viruses to provide complete treated water [13].

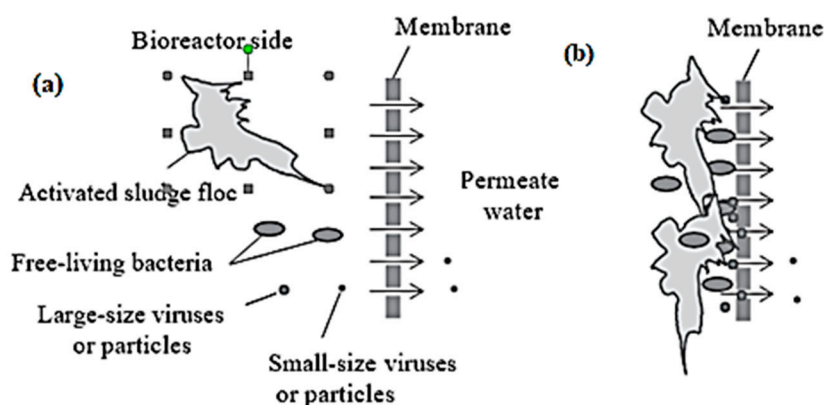


Figure 5. Schematic representation of the principles of the MBR process: (a) membrane filtration in MBR and (b) membrane fouling in MBR modified and adapted from [3].

Table 2. The largest 8 MBR plants adapted and modified from [13].

Project	Technology	Date	* DMDF (MLD)
Wenyu River, China	Asahi K/Beijing Origin Water	2007	100
Shending River, China	Beijing Origin Water	2010	120
Johns Creek, GA	GE Zenon	2009	94
Beixiaohe, China	Siemens	2008	78
Sabadell, Spain	Kubota	2009	55
Peoria, USA	GE Zenon	2008	76
Cleveland Bay, Australia	GE Zenon	2007	75

* DMDF: Design maximum daily flow (MLD: Megaliters per day)

Furthermore, there is limited information on the morphology and extracellular polymeric substance (EPS) production for total sludge retention and low ratios [53]. Additionally, the limitation of gravity sedimentation, which produces nearly particle-free clean effluents could be overcome with membrane separation technology. However, there have been reported cases of severe membrane fouling [49,53]. There is a continuous modification in membrane modules and membrane elements in enhancing the reduction in membrane fouling, which is a major challenge for membrane processes [54]. The leeway of combining two or more membrane processes, or with other forms of technology like coagulation, in an amalgam fashion is continuously being explored, advanced, and applied in many wastewater treatment facilities [54–56].

MBR Configurations

There are two major configurations of MBRs that are currently being used: side stream MBRs and immersed MBRs (Figure 6). The side stream MBR was the first to be introduced in the past decades [51–56]. It is important to understand that with the side stream MBR, the membranes are mounted outside the bioreactor, requiring an intermediate pumping system which transfers the biomass for filtration and residue from the filtration set up back to the bioreactor [51]. This principle is advantageous, in that the membrane module is easily accessible for cleaning; however, due to the high energy and pressure requirements, the side stream MBRs have had limited application in recent years compared to the submerged MBR [56]. The side stream configuration produces very high-quality effluent as the technology was applied to very limited cases such as industrial and leachate wastewater. Higher energy costs associated with mixed liquor recirculation, membrane fouling and high membrane capital costs restrained the spread of this technology to general applications such as the treatment of municipal wastewater [51,56,57].

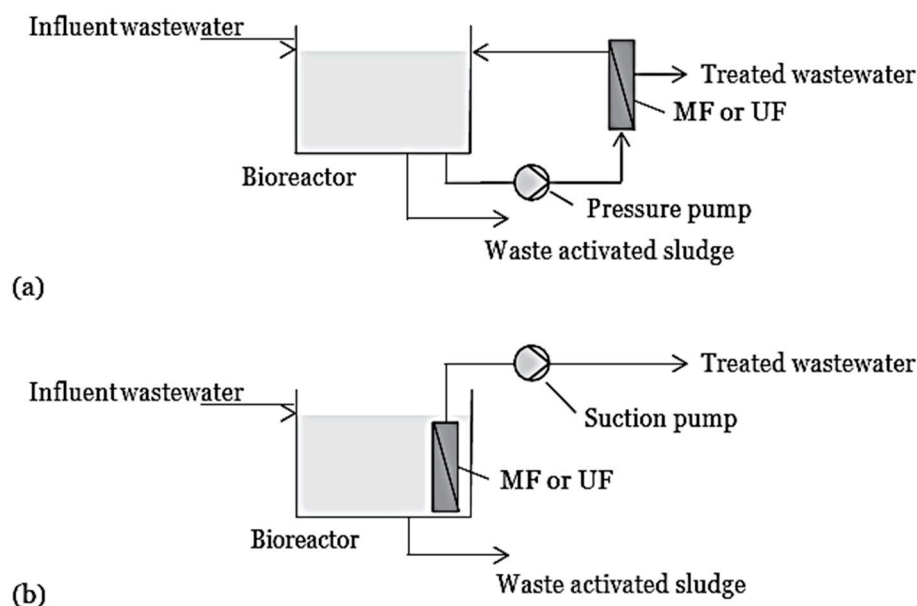


Figure 6. Two operational types of MBR technology: (a) side-stream configuration and (b) submersed configuration [5,51].

Micro-Organisms in Bioreactors

Micro-organisms are commonly defined as small life forms that cannot be easily identified by the naked eye but are observed with the help of a microscope [58,59]. Traditionally, micro-organisms are classified into prokaryotic and eukaryotic micro-organisms based on the existence of a membrane-bound nucleus. Eukaryotic micro-organisms have an intracellular membrane-bound nucleus that contains nuclear materials, while prokaryotic micro-organisms have their nuclear materials spread in the cytoplasm (e.g., no membrane-bound nucleus). A comparison between these kinds of micro-organisms is presented in Table 3. Additional properties that differentiate them include cell size, membrane-bound organelles, cell wall, cell division, and sexual reproduction. Prokaryotic micro-organisms include bacteria and archaea, while eukaryotic micro-organisms include fungi, algae, protozoa, and animals. These micro-organisms play a vital role in bioreactors, such that organic pollutants are mostly oxidized into carbon dioxide and water, while ammonia (an inorganic pollutant) is oxidized into nitrate [60]. Various types of micro-organisms can exist in bioreactors. One main feature of micro-organisms in environmental engineering systems, including MBR, is that they are structured into communities consisting of diverse species in an open system, where diverse micro-organisms are continuously fed into a bioreactor via influent wastewater and from the atmosphere [57,61]. Nevertheless, specific types of micro-organisms can be enriched in bioreactors by imposing specific reactor designs and operational conditions. The microbial community structure is believed to be important in determining the function, performance, and stability of bioreactors [61,62].

Table 3. Comparison between Prokaryotic and Eukaryotic Microorganisms [58].

Micro-Organisms	Prokaryotes	Eukaryotes
Membrane-bound nucleus	Absent	Present
Cell size	0.1–2 μm	10–100 μm
Membrane-bound organelles	Absent	Present (e.g., mitochondria, chloroplast, and Golgi complex)
Cell wall	Present	Not all
Pili	Present	Absent
Cell division	Binary fission	Mitosis, meiosis
Sexual reproduction	Asexual	Sexual, asexual

Application of MBR on Viral Loads in Wastewater

Membrane-coupled bioreactors have been used as one alternative to the conventional anaerobic digestion process. Thus, MBR has the ability to retain microbial community to degrade organics, produce high solid and pathogen-free effluents as well as the capacity to recover the energy potential of soluble organic matter [51,61]. MBR technology has demonstrated to be a more effective system in removing pathological micro-organisms, including SARS-COV-2 [63]. Researchers have determined the diameter of SARS-COV-2 to range between 60 and 140 nm [62–64], where viral load in WWTP has been found to range between 2 and 3.10^3 copies/mL, depending on the level of the epidemic [64,65]. MBR has been reported to efficiently remove viral loads as low as 27 μm [66], which is 60 times smaller than SARS-COV-2 in WWTP [63]. Therefore, its efficiency in removing the viral load is expected to be higher. This technology can also shorten the reaction time (approximately 1.5 min, 2.5 to 5% of traditional wastewater treatment process), viably save disinfectant consumption (chlorine addition can diminish to 1.0 mg/L), and achieve a decent impact of inactivation of micro-organism [63,65]. Higher disinfection viability is accomplished in MBR effluents at a lower dose of disinfectant with fewer disinfection by-products (DBPs) [66]. In the past, MBR was considered inappropriate in WWTP due to its high operating cost; however, decreasing cost and stringent standards are making the use of MBR systems more economically viable [61,63]. For instance, when the limit of MBR plants is increased from 20 to 1000 m^3/d , their operating cost is projected to reduce sharply [67].

3.2.2. Advanced Oxidation Process

Current emerging micropollutants contaminants (RNA of COVID-19, pesticides, antibiotics, endocrine disrupting compounds) in WWTPs discharges impacts on the likelihood to reuse these waters after treatment [68,69]. When aquatic animals inject the micropollutants contaminants, they alter their endocrine system due to the endocrine-disrupting compounds [70,71]. A possible prospect for removing micropollutants from tertiary WWTP is hydrogen peroxide (H_2O_2)/ultraviolet (UV) as an advanced oxidation process (es) (AOPs) [72]. Recently, the Gold Bar Wastewater Treatment Plant applied this method in Edmonton, Canada, to treat secondary sewage [73]. Since then, the process has received much attention because it uses hydroxyl radical ($\bullet\text{OH}$), which is highly reactive to destruct intractable chemicals found in wastewater [74]. Hydroxyl radicals are known to bombard organic molecules nonselective and rapidly. Additionally, the process offers other diverse approaches of producing hydroxyl radicals making it more versatile and consequently gives a better approach to adhering to strict guidelines during wastewater treatment. AOPs which include Photocatalysis, ultrasonic process, Fenton and photo-Fenton processes ($\text{Fe}_2^+/\text{UV}/\text{H}_2\text{O}_2$ and $\text{Fe}_2^+/\text{H}_2\text{O}_2$), $\text{H}_2\text{O}_2/\text{UV}$, ozone combined with catalysts ($\text{O}_3/\text{catalysts}$), UV irradiation (O_3/UV) and ozone combined with hydrogen peroxide ($\text{O}_3/\text{H}_2\text{O}_2$) or both ($\text{UV}/\text{H}_2\text{O}_2/\text{O}_3$) have been effectively utilized in treating wastewater [68,69,74,75]. A remarkable feature realized during the process was the eco-friendliness of the end-product, giving it a more efficient outlook to mineralize a broad spectrum of organic pollutants, including COVID-19. The process is eco-friendly, which can rely on solar energy instead of artificial light sources which is hazardous and costly [69,75]. Furthermore, due to the highly reactive nature of $\bullet\text{OH}$, it can attack almost any organic materials without any discernment. The advantages and disadvantages of AOPs in WWTPs are tabulated in Table 4.

Application of AOP on Viral Loads in Wastewater

As AOP generates high influential oxidative agents such as hydroxide (OH^-), yet more explicitly, a neutral variant of hydroxyl radical ($\bullet\text{OH}$) [68,69]. In essence, AOP oxidation potential is twice that of chlorine (commonly used disinfectant), therefore employing AOP as a polishing step in WWTPs is useful [10]. Hydroxyl radicals are the main impetuses behind many AOPs. UV, H_2O_2 and O_3 are regularly utilized in different combinations to create $\bullet\text{OH}$ in adequate quantities to debase organic and some inorganic pollutants [72,73]. The process can diminish these pollutant concentrations,

conceivably from hundreds of parts per million (ppm) to only a couple of parts per billion (ppb) [73,74]. These radicals are non-selective; therefore, they practically attack all organic materials. After, they form intermediates with the $\bullet\text{OH}$ radical [74]. Thereafter, the intermediates react with the oxidants and mineralize into stable compounds. For instance, platinized sulfated TiO_2 (TiO_2/Pt) and undoped TiO_2 was investigated with micro-organisms loaded over photocatalyst films from aerosols to load influenza A (H_3N_2), vaccinia virus, *Bacillus thuringiensis* and *Mycobacterium smegmatis* [76]. The study showed that 90% of the inactivation was reached in 30 min UVA irradiation on TiO_2 and to 99.8% on TiO_2/Pt . TiO_2/Pt showed increased mineralization rate and inactivation was likely due to charge carrier separation in doped semiconductor photocatalyst. The OH molecule has a very fast reaction rate of the total oxidants used to treat wastewater due to their non-selective nature and its high oxidation potential [75,77]. The fast reactions led to much lower retention times than other traditional treatment processes. One of the issues with chlorine disinfection is the profoundly toxic byproducts (DPBs) that can result after treatment. To forestall these results, an additional de-chlorination step is frequently required. The $\bullet\text{OH}$ molecule can combine to produce water. The most significant issue would be with excess peroxide and bromate formation, nevertheless, these can be managed in a well-structured AOP system [10,76]. Concerning the treatment of SARS-COV-2 in wastewater treatment plants, some of these experimental observations about SARS-COV-2 or other derivatives of CoVs in WWTPs have been shown in Table 5. Wurtzer et al. [78] and Randazzo et al. [79] found positivity of treating wastewater with a viral load of 5.40 $\log_{10}$ copies/L.

3.3. Summary

In summary, from the extant literature on the current pandemic which has held the world in an apocalyptic predicament, the paper found that sewage treatment systems could be a possible arena to keep a surveillance on the outbreak of the SARS-CoV-2 in communities around the globe. Nevertheless, most of the sewage systems appear oblique in impoverished regions, and appreciable in developing and developed countries due to their centralized and organized sewage systems. Additional studies showed that the virus could remain infectious for days in sewage and drinking water and, therefore, an effective method of eradicating the virus loads should be adopted. Additionally, there is cost, delay and unrelenting issues of insufficient diagnostic testing of COVID-19 in poor regions; therefore, this study found the science of wastewater-based epidemiology (WBE) as a viable approach to help identify hotspot areas of COVID-19 in remote communities and populated cities. Thus, by effective sampling and monitoring of the viral RNA in wastewater to assess virus occurrences, early warning and the spread in defined populations seem very promising and economical. However, there is still limited knowledge on the optimized and standardized protocol to enhance the detection and quantification of the SARS-COV-2 in wastewater, which calls for future works. Furthermore, the conventional RT-PCR techniques used for quantitative analysis was found to be time-consuming, labor-intensive and remotely unavailable. Therefore, biosensors were explored, and due to its cost-effectiveness, simplicity, rapidity and portability, was found to be the alternative to real-time monitoring (RT-PCR) of the COVID-19 infections. This included chip-, paper- and nanoparticle-based biosensors, which have been employed to detect nucleic acids of pathogens and human antibodies against the pathogens by integrating sample-answer process units of a biosensor. Additional assay sensitivity, simplicity and performance of the biosensors can be improved by either magnetic nano-based materials (gold, iron, graphene, and nanotubes) or enzyme-based materials to enhance the stability of the RNA in the sample.

With the pressing need for a breakthrough to develop a cure or vaccine for COVID-19, the remediation of wastewater cannot be left out. Thus, the end route of wastewater and human excretion is the wastewater treatment plants. This study found the WBE approach as a possible way to monitor the spread of the COVID-19. Additionally, integrating emerging and robust technologies like magnetic nanotechnology, biosensing and membrane bioreactors or AOPs into the conventional treatment systems could possibly mitigate the threat posed by emerging contaminants as well as the SARS-COV-2 RNA (Table 5).

Table 4. Advantages and Disadvantages of AOPs in WWTPs.

Advantages	Disadvantages
Converts organic materials into stable inorganic compounds	Residual peroxide removal may need to be considered
Treat nearly all organic compounds and remove some heavy metals	Complex chemistry tailored to specific contaminants
Do not introduce new harmful substances theoretically into the water	Relatively high capital and maintenance
No sludge production as with biological or chemical processes	Energy intensive
Does not concentrate waste for further treatment	
Disinfection of pathogens especially using UV	
Rapid and robust technology	

Table 5. Experimental observations about SARS-COV-2 or derived from other CoVs in WWTPs; Adapted from [65,78,79].

Technology	Experimental Observations about SARS-CoV-2 or Derived from Other CoVs	Laws, Mechanisms and Principles
Membrane Biological Reactor (MBR)	3.9, 5.1 and 5.5 log reduction of human norovirus and enterovirus and human adenovirus, respectively was obtained in MBRs with absolute pore size of 0.1 μm	Microfiltration (greater than 0.1 μm) is partially effective and might need a further step of disinfection. ultrafiltration (greater than 0.01 μm), is advised in virus separation
Disinfection with chlorine dioxide or free chlorine	Free residue chlorine of over 2.2 mg/L is required for chlorine dioxide for totally inactivating SARS-CoV (nevertheless, <i>E. coli</i> is not totally inactivated). The dosage of free chlorine (hypochlorous acid) should ensure free residue chlorine over 0.5 ppm, to affirm that chlorine has not been totally exhausted and guarantee total inactivation of SARS-CoV to control the virus. SARS-CoV in wastewater is more susceptible to chlorine dioxide and sodium hypochlorite than <i>Escherichia coli</i>	Inactivation is because of the reaction with proteins in the nucleocapsid rather than membrane lipids or the genome
UVC light	Non-enveloped viruses appear to have higher susceptibility to UVC light than enveloped viruses Inactivation in sludge is akin to wastewater (3 log in 2–4 days)	Inactivation essentially focuses on the genome, while lipid film do not shield viruses from the radiation
Primary and Secondary settling	a huge part of CoVs, is probably going to be available in the primary or secondary sludge 6% of non-enveloped viruses absorbed to solids, compared to 26% of enveloped viruses	The hydrophobicity of the viral envelope makes it less soluble in water and they will in general adhere to solids and concentrate in sludge.
Thermophilic and mesophilic anaerobic digestion	Ammonia may act as a virucidal agent and poliovirus lose infectivity in anaerobic digestion at 28 °C. For anaerobic digestion, SARS-CoVs infectivity is lost at temperature of 56 °C for 90 min Human CoV was detected in sludge's pre and post anaerobic digestion	Mesophilic digestion is much less effective against non-enveloped viruses than thermophilic aerobic digestion higher inactivation of CoVs is normal in anaerobic digestion in light of the fact that CoVs are substantially more delicate to warm temperature than poliovirus

4. Conclusions and Recommendations

This paper reviewed recent literature on the fate of COVID-19 in wastewater treatment systems and its emerging wastewater treatment technologies. In the midst of COVID-19 wastewater remediation, magnetic nanomaterials were found to be promising (biomagnetic separation, immunoassays,

and medical imaging techniques) to provide opportunities to effectively target emerging contaminants that the conventional systems fail to remove. Thus, contaminant-loaded magnetic particles could be easily separated from the solution via an external magnetic field. Thereby, employing them in the wastewater treatment settings can enhance the stability of the viral RNA and other pathogens for the biosensor detections. Comprehensive studies on the toxicity of magnetic nanoparticles have proven to have little or no negative environmental impacts. Hence, integrating magnetized nanomaterials into the wastewater treatment settings, due to their super-magnetic properties, could facilitate the treatment and separations, while the rest of the composite is meant to provide a high surface area for the adsorption of the virus RNA for detection and quantification. Therefore, integrating magnetic biosensor diagnostics into wastewater treatment systems, via wastewater-based epidemiology (WBE) could be a possible way to investigate the spread of COVID-19 in communities around the globe for health policy development and to minimize the diagnostic cost of testing. Additionally, the long-term assessment of AOP (UV/H₂O₂) has proven to be economically viable for degrading endocrine-disrupting compounds and removing them in wastewater which gives hope for UV/magnetized TiO₂ photocatalysis to inactivate RNA of COVID-19 on adsorbed surface of sludge.

Other recommendations and future works include:

- In the application of WBE, which requires routine sampling for diagnostic testing, all safe work protocols and effective personal protective equipment are encouraged to be used to protect personnel from SARS-CoV-2 exposure.
- To avoid discrepancy of results, future work of developing optimized and standardized protocols for detection and quantification of SARS-CoV-2 in wastewater is crucial. This assay needs to be compared and connected with centralized hospital laboratories to help generate effective regional reports.
- To improve the assay of biosensors with the aforementioned capabilities to mitigate and safeguard COVID-19's spread, its sensitivity and detection with magnetic nano-based materials are recommended. Future work can focus on integrating biosensors with biosecurity coupled with smart-phone apps connected to a centralized hospital database to help track carrier status.
- The prospects of photocatalysis to inactivate SARS-CoV-2 in wastewater settings is very high, owing to its appreciable used for sterilization of clinical devices, degradation of protein and virus RNA. Therefore, future research should focus on its safe nanotechnology and bioengineering line to combat the COVID-19 pandemic.

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Chapter 2 - Synthesis, characterization, and application of MPCs

Overview of objective 1:

- Synthesizing and characterizing the TiO_2 magnetized photocatalyst (MPC) for industrial wastewater treatment.

This chapter presents the co-precipitation technique of synthesizing the novel magnetized photocatalysts (MPCs) with beneficiation of recoverability for reuse. Generally, photocatalysis involves photo-absorption and excitation of electrons from valance band to conduction band of semiconductor material (TiO_2). Based on this band gap theory, to increase the exciation energy level of the electrons whereby the electron-hole recombination is been suppressed. For the betterment of this ressearch and magnetic functional properties of MPCs, binary (Fe-TiO_2) and tenary ($\text{Fe-TiO}_2 / \text{Al}$ or Cu or Ch) were synthesised. Among them, the Fe-TiO_2 was extensively explored in the study. And this was due to its excellent surface area, magnetic charge seperation ability, UV-light utility and remarkable for the enhancement of biogas production and degradability of organic content. The materials and assay protocol used together with the analytical techniques to attest to the success of the engineered MPCs are discussed. To understand the applicability of MPCs and other magnetized nanoparticles (MNPs), a series of feasibility studies and engineering works were explored. These included adsorption and photocatalytic studies for textile effluent (Papers 3, 4, and 14), kinetics and biostimulation of AD biogas production (Papers, 5, 6, 11, 12, 17 and 18), optimization and photocatalytic degradation of oily effluent (Papers 13, 15 and 16), coagulation process (Paper 19), and bioelectrolysis (Paper 20). The above studies elucidated that tailored MPCs have great potential to improve wastewater and biogas quality and are easily recovered with an external magnetic field. Further discussions on technological evaluation and application of MPCs are presented in Chapter 3.

2.1 Introduction

Titanium dioxide (TiO_2) has been utilized as a photocatalyst since the 1970s because of its stable semiconductor properties for natural applications (Guo et al. 2019; Riaz and Park 2020). In environmental activities like water splitting to make hydrogen and treating contaminated air and water, TiO_2 has been the most used semiconductor as a photocatalyst (Ge et al. 2021; Guo et al. 2019; Kaur et al. 2021). The TiO_2 polymorphs (Figure 2.1) exhibit different properties as rutile (stable at a higher temperature), brookite (usually found in minerals with an orthorhombic crystal structure), and anatase (stable at low temperature).

Conventionally, TiO_2 application is limited to ultraviolet (UV) light due to wide bandgaps (3.2 eV for anatase, 3.0 eV for rutile, 3.4 eV for brookite). Several efforts have been undertaken to produce visible-light-active photocatalysts (VLAPs) that can capture most of the solar spectrum (400 nm) by changing large bandgap semiconductors or by finding a suitable low bandgap material (Guo et al. 2019; Riaz and Park 2020). Modification of TiO_2 by doping metal (Fe, Cu, Al, Ni, Zn) or non metals (Chitosan) or other lower bandgap semiconductors (Fe_2O_3 , Cu_2O , CuO , CoO , Bi_2O_3 , CuBiO_4) have been reported for wastewater purification, antibacterial, and solar-energy conversion applications (Ge et al. 2021; Guo et al. 2019). The modification of TiO_2 enhanced surface area for adsorption of targeted species, direct pathways to transport photogenerated charge, and good chemical stability in water (Ge et al. 2021; Guo et al. 2019). Unsaturated bonds trap photogenerated charge carriers, and can also allow charge separation. This necessitates the transformation of the TiO_2 to have a high surface area and morphological and physiochemical stability (Riaz and Park 2020; Xu et al. 2021).

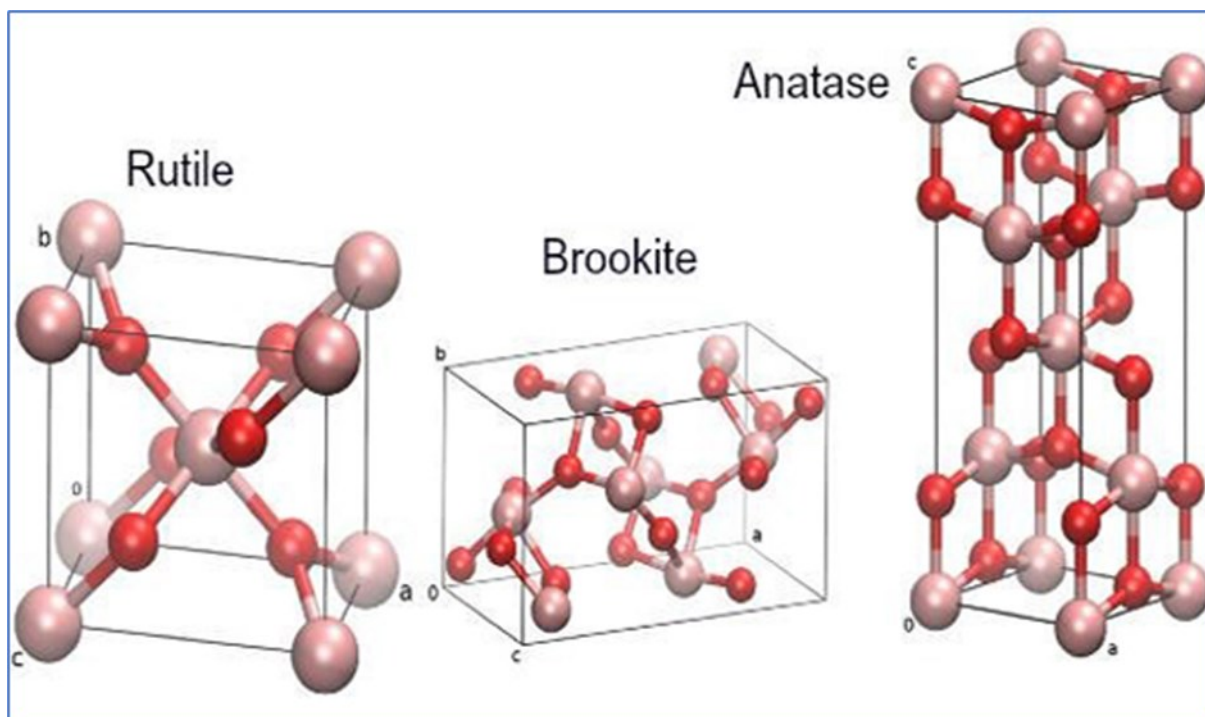


Figure 2.1: Crystal structure of TiO₂ rutile, brookite and anatase; adapted from Kim et al. (1996)

Consequently, the activation energy intensity is the main drawback of TiO₂ industrial application. In our published journal Papers (1 and 2), we proposed ways to mitigate some of these setbacks via the use of MPCs in the membrane technology, biomembrane reactors, and advanced oxidation processes. Table 2.1 shows various chemical synthesis routes for tailoring monodisperse superparamagnetic NP structure, size, surface composition, and aggregation state. Chemical co-precipitation, microemulsion synthesis, thermal decomposition, and hydrothermal synthesis were identified as effective techniques (Jacinto et al. 2020; Jiang et al. 2022; Watson et al. 2002; Xu et al. 2012). Among them, the co-precipitation method was considered a convenient way to synthesize MPCs. In line with this study objective, there is a possibility to introduce a novel photocatalyst characterized to influence catalytic activity in both biological and photocatalytic systems. Therefore, in this chapter, the characteristics of the tailored MPCs and their feasibility studies in our published Papers (3-6) are presented.

Table 2.1: Synthesis techniques and their properties, adapted from Kiser et al. (2009) and Lu et al. (2007)

Method of synthesis	Co-operation	Microemulsion	Thermal decomposition	Hydrothermal synthesis
Techniques	Very simple, ambient condition	Simple	Simple, inert atmosphere	Simple, high pressure
Reaction period	Hours	Hours	Hours -days	Hours
Component	Water	Organic compound, water	Organic compound	Water -ethanol
Reaction temperature (°C)	20-90	20-50	100-320	220
Size distribution	Relatively narrow	Relatively narrow	Very narrow	Very narrow
Shape control	good	good	Very good	Very good
Yield	High	low	high	Medium

2.2 Materials and methods

2.2.1 Chemicals and stock solution preparation

All chemicals enlisted in Table 2.2, unless modified, were of analytical grade obtained from Sigma Aldrich, South Africa. These include oleic acid (surfactant) and ethanol (95%). Firstly, 1 L stock solution of the chemicals was prepared based on their mass (g) and molecular weights as presented in Table 2.2. For instance, to prepare 0.4 M Fe^{3+} , 0.2 M Fe^{2+} and 3 M NaOH stock solutions, respective measured masses of 108.12 g, 55.61 g and 199.99 g were dissolved in 1 L distilled water. With a known concentration and volume, the Sigma Aldrich mass molarity calculator was used to determine each mass of the chemicals.

Table 2.2 Chemicals and masses to prepare the stock solutions

Chemical	Molecular weight (g/mol)	Mass (g)
Ferrouschloride hexahydrates ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$)	270.29	108.12
Ferroussulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)	287.55	55.61
sodium hydroxide pellets (NaOH)	39.997	199.99
Copper (II) nitrate trihydrate	241.6	48.32
Aluminium sulphate hexadecahydrate	630.38	126.08
Chitosan	1526.5	305.3
Titanium oxide	79.87	15.96

2.3 Co-precipitation synthesis

The MPCs were prepared using the co-precipitation assay adapted from El Ghandoor et al. (2012). Table 2.3 and Figure 2.2, respectively depict the stock composition and schematic route for the synthesis. Before the binary and ternary nanocomposite preparation, a precursor of bimetallic magnetite (Fe_3O_4) was prepared. In brief, the precursor constituted a 1:1 volume ratio (0.5 L/0.5 L) of Fe^{3+} and Fe^{2+} stock solutions that were poured into a 2 L beaker. The solution was then constantly agitated (at 15 rpm, under 70°C for 6 hours) on a magnetic hotplate while 2 mL oleic acid was added dropwise. This resulted in a pH drop to 2 and the formation of a microemulsion. The pH was then adjusted to 10-12 with 250 mL, 3 M NaOH with continuous stirring (15 rpm) until a black precipitate was formed.

The resultant precipitate was then heated at a temperature of 70°C for 2 hours (ageing) and subsequently allowed to cool at room temperature. The supernatant was decanted (2.1), and the granules were washed thrice with distilled water and ethanol to remove undesirable particles (NaCl and Na_2SO_4). Afterward, the precipitate was oven dried for 12 hours at 70°C , followed by calcination at 550°C for 1 hour. The resulted Fe_3O_4 was allowed to cool and a sample was then bagged for characterisation. The same procedure was repeated for the binary and ternary MPCs, respectively using a volume ratio of 3:2:1 ($\text{Fe}^{3+}/\text{Fe}^{2+}/\text{TiO}_2$) and

3:2:1:1 for $\text{Fe}^{3+}/\text{Fe}^{2+}/\text{TiO}_2/\text{Al}$ or Cu or Ch). The iron oxide magnetic nanoparticles (Fe_3O_4) were formed from the aqueous Fe^{2+} and Fe^{3+} salt solutions by the addition of the NaOH according to reaction equation (2.1).

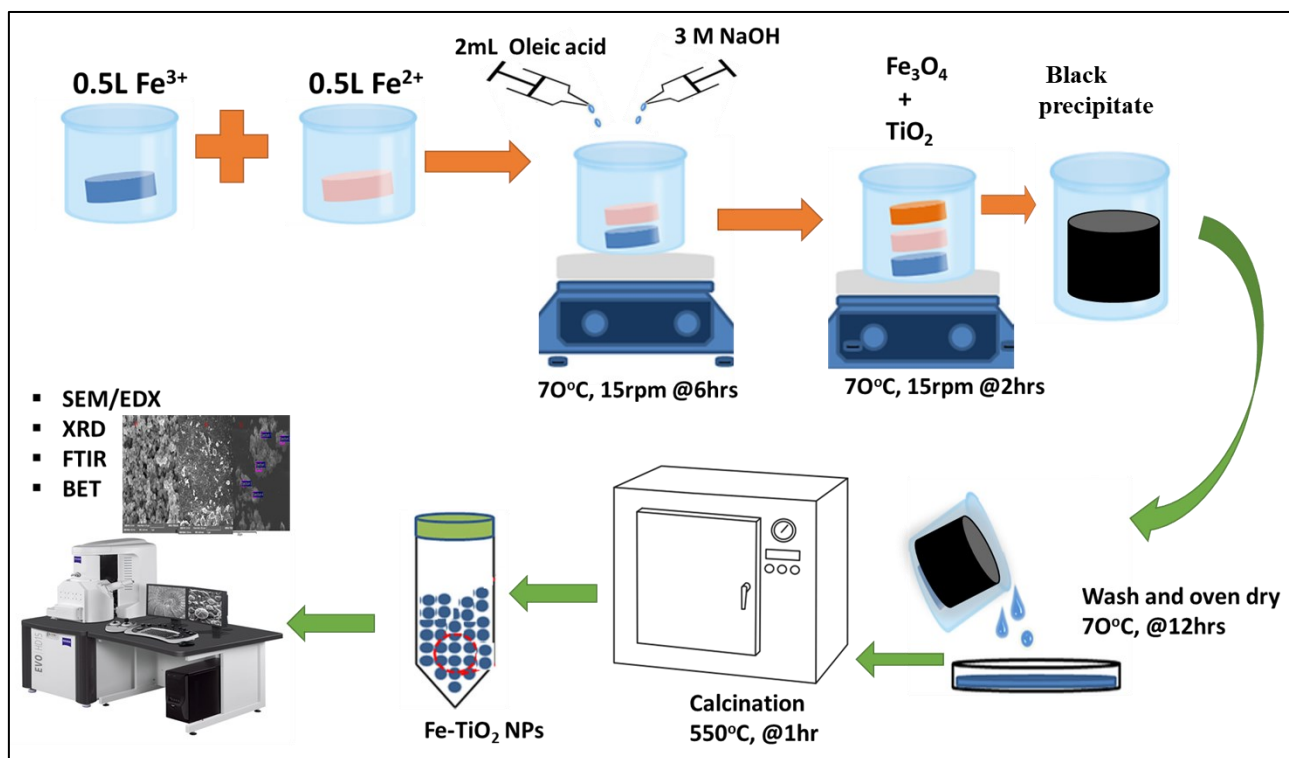
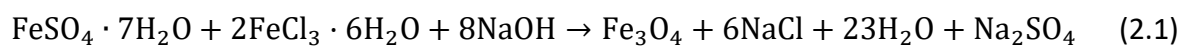


Figure 2.2: Schematic flow diagram for the co-precipitation synthesis of the magnetic nanoparticles

Table 2.3: Composition of the magnetic nanoparticles prepared via co-precipitation

Type	Nanocomposite (s)	Volume (mL)
Single	Fe_3O_4	$\text{Fe}^{3+} = 500$ $\text{Fe}^{2+} = 500$
Binary	Fe-TiO_2	$\text{Fe}^{3+} = 500$ $\text{Fe}^{2+} = 333$ $\text{TiO}_2 = 167$
Ternary	Fe/Al-TiO_2	$\text{Fe}^{3+} = 500$ $\text{Fe}^{2+} = 350$ $\text{Al} = 75$ $\text{TiO}_2 = 75$
Ternary	Fe/Cu-TiO_2	$\text{Fe}^{3+} = 500$ $\text{Fe}^{2+} = 350$ $\text{Cu} = 75$ $\text{TiO}_2 = 75$
Ternary	Fe/Ch-TiO_2	$\text{Fe}^{3+} = 500$ $\text{Fe}^{2+} = 350$ $\text{Chitosan} = 75$ $\text{TiO}_2 = 75$

2.4 Characterisation of MPCs

2.4.1 Scanning electron microscopy / energy-dispersive X-ray (SEM/EDX) analysis

The morphology and elemental analysis of the MPC samples were carried out using scanning electron microscopy and energy dispersive X-ray (Figure 2.3) at the Electron Microscope Unit of University of Cape Town, South Africa. A thin layer of the sample was double-sided taped to the carbon specimen holder. To avoid charging effects (sputter-coating), the samples were coated with a thin film of gold with a thickness of around 30 nm. This was operated at an acceleration voltage of 5 kV with a magnification in the range of 10–50 k.

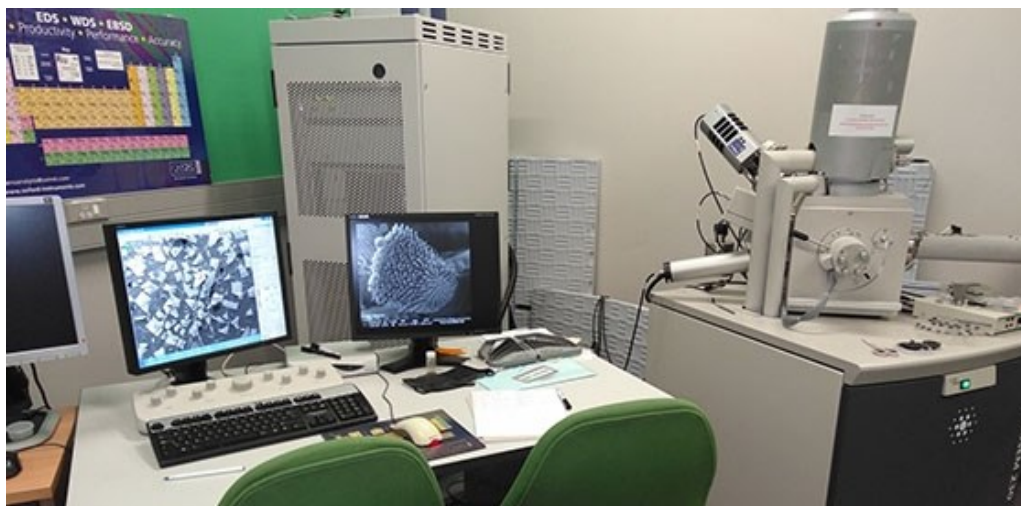


Figure 2.3: SEM/EDX; Nova NanoSEM coupled with EDT and TLD detector

2.4.2 X-ray-diffraction (XRD)

The crystallographic structure and chemical composition of the MPCs were determined by using the X-ray diffraction (XRD) (Bruker AXS, D8 Advance, Germany) coupled with PANalytical software (Empyrean, PRO MPD, Netherlands) at the iThemba LABS, Materials Research Department, South Africa.

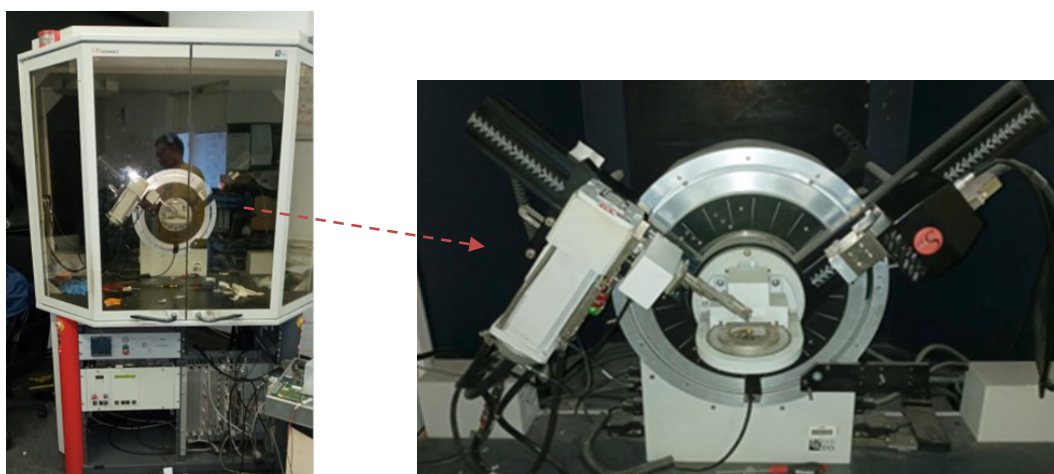


Figure 2.4: Pictorial view of X-ray diffraction (XRD) equipment at iThemba LABS, South Africa

As shown in Figure 2.4, the XRD was operated at 40 kV with a target current of 40 mA. The sample was mounted in the centre of the sample holder on a glass slide, levelled up to the correct height and then scanned with a J-J scan coupled with the copper anode (Cu-K α radiation: $\lambda = 1.5406 \text{ \AA}$) and Bragg-Brentano configuration. The measurements ran within a range of 5 to 85 (2θ) defined with a typical step size speed of 0.0340 min^{-1} . A position-sensitive detector, Lyn-Eye, was used to record diffraction data at a typical speed of 0.5 sec/step which is equivalent to an effective time of 92 sec/step for a scintillation counter. Using the Debye-Scherrer equation (2.2), phases were found from the match of the calculated peaks with the measured ones until all phases have been identified within the limits of the resolution of the results.

$$(D = \frac{k\delta}{\beta \cos \theta}) \quad (2.2)$$

Where D is the particle size of the crystal, δ is the wavelength of X-ray radiation (CuK $\alpha = 0.15406 \text{ nm}$), k is the Sherrer constant (0.98), β is the line broadening in radians obtained from the full width at half maximum height (FWHM) of the peak (determined using Origin software), and θ is the Bragg diffracting angle of the XRD diffraction patterns.

2.4.3 Fourier Transform Infrared (FTIR) spectrometer

The molecular structures and functional groups of the MPCs were identified by a Fourier Transform Infrared (FTIR) spectrometer (Shimadzu FTIR 8400) equipment (at the School of Chemical & Metallurgical Engineering, University of the Witwatersrand, South Africa). The samples were analysed over the range of $400 - 4000 \text{ cm}^{-1}$ against the background of the NIST Quantitative Infrared Database, SRD 79.

2.4.4 Brunauer-Emmett-Teller (BET) analysis

The specific surface areas, pore volumes, and pore size of the MPCs were determined with a BET (Figure 2.5) Micrometric analyser (TriStar II Plus, GA, USA) at the Department of Chemical Engineering, Durban University of Technology, South Africa. Using the weighing balance a measured mass of about 2 g of the MPCs was poured into a known mass of a glass sample tube. The samples were then degassed using the Micromeritics (Figure 2.5a) coupled with flowing gas (Nitrogen) and heat to remove atmospheric contaminants, such as water vapour and adsorbed gas, from the surface and pores of the samples. This was operated at a temperature of 400°C for 24 hours. The samples were then taken and allowed to cool under a nitrogen degassing pressure of < 5 mmHg. By observing all safety protocols, liquid nitrogen from non-pressurized storage was fractionated into the smaller container of the BET experimental setup (Figure 2.5b). Using the system software (TriStar II Plus version), it was then switched on and all required input parameters were defined according to the sample port ID. The system was then allowed to run under helium and nitrogen gas coupled with a vacuum pump for 24 hours. The recorded data was then converted into Excel sheets for interpretation and assessment.



Figure 2.5: Micromeritics (a) Degasser (FlowPrep 060) and (b) BET analyser (TriStar II Plus, GA, USA)

2.5 Results and discussion

The morphology and elemental composition of the MPCs were defined by the scanning electron microscopy and energy dispersive X-ray detector (SEM/EDX) analysis. X-ray diffraction results indicated the phase and crystal structures of the MNPs, whereas the Fourier Transform Infrared (FTIR) spectrometer was used to determine their functional groups. The BET revealed their surface area, pore size and pore volume.

2.5.1 Morphology and elemental composition of the MPCs

The SEM was utilized to characterize the morphology and texture of the MPCs with their contents defined in Table 2.3. Figure 2.6 shows the SEM images of the (a) Fe/Al-TiO₂, (b) Fe/Cu-TiO₂ (c) TiO₂ (d) Fe/Ch-TiO₂ (e) Fe₃O₄ (f) Fe-TiO₂.

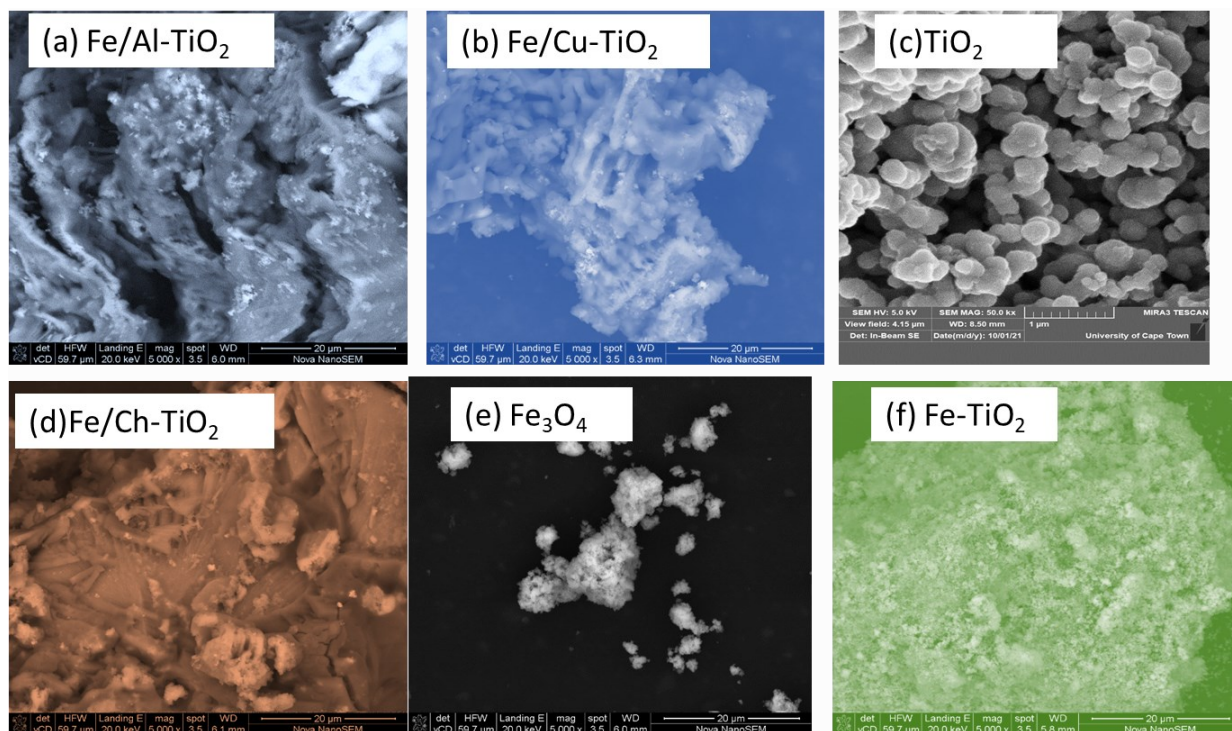


Figure 2.6: SEM images of (a) Fe/Al-TiO₂, (b) Fe/Cu-TiO₂, (c) TiO₂, (d) Fe/Ch-TiO₂, (e) Fe₃O₄ and (f) Fe-TiO₂

The raw TiO₂ (Figure 2.6c) under a microscale of 1 μm, showed irregular cubic shape structures with good monodispersed uniform particles. Conversely, the hybridized MPCs (Figure 2.6 a; b; d; f) revealed the presence of Fe₃O₄ with compressed and irregular shaped fragmented structures with monodispersed structures under a microscale of 20 μm. This was obtained under a magnification of 5000 kx and landing energy capacity of 20 keV within a width distance (WD) of 5 - 6.8 mm. As observed in Figure 2.6e, there is a less dense fragmented structure with good monodispersed uniform particles (Guo et al. 2019; Watson et al. 2002; Zhao et al. 2021c). Also, the slight aggregates observed might be due to the agglomeration of other particles with the surfactant (oleic acid) molecules (El Ghandoor et al. 2012).

Furthermore, to warrant an effective photocatalytic activity, good dispersion of the Fe₃O₄ and TiO₂ across the MPC surfaces was observed. Small aggregates of the Fe₃O₄ and TiO₂

that are uniformly dispersed on the MPCs are considered to be more advantageous because they provide more active sites than the agglomerated particles (Keane et al. 2010).

Figure 2.7a-f represents the EDX spectrum and elemental composition of the MPCs. The dominating elements of Fe_3O_4 and TiO_2 as Ti, O and Fe suggest the successfulness of the MPCs. Likewise, the composition of the chitosan (Table 2.3) with surface spectra in Figure 2.7d. The binding energies of Fe_3O_4 with Fe as key elements ($\text{O} > \text{Fe} > \text{C}$) are associated with the peaks around 0.8, 6.3, and 6.8 keV in all the MPC's EDX spectra (Petcharoen and Sirivat 2012). Also, the presence of C infers the coating of the MPCs during the sample preparation with a carbon thin film.

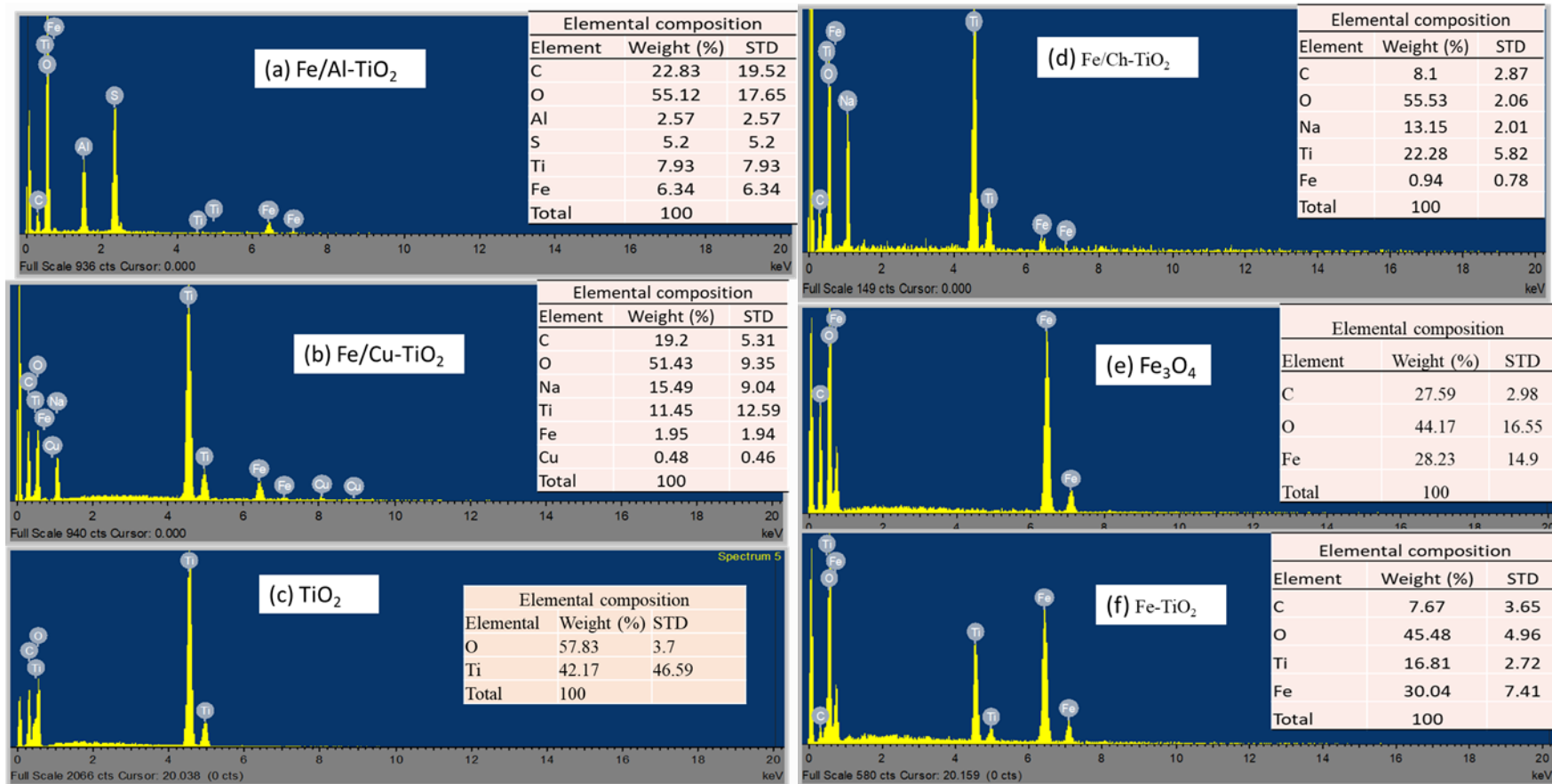


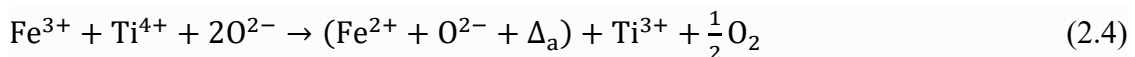
Figure 2.7: EDX images (a-f) of MPCs) with their compositions defined in Table 2.3

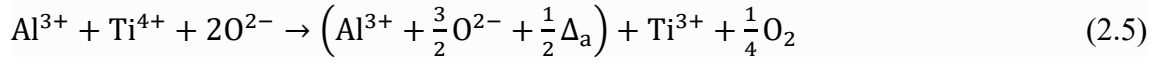
The EDX spectra (Figure 2.7) confirmed the formation of oxygen vacancies in TiO₂ via Fe valence transformation. Thus, the inclusion of Fe in the oxidation of the MPCs (Fe/Al-TiO₂, Fe/Cu-TiO₂, Fe/Ch-TiO₂, Fe-TiO₂) expedited their paramagnetic phase transformation reaction (2.3). This valence change might also be due to the heating, whereby the Fe reduction promoted the oxidation reaction (2.4). Similarly, the cationic dopants (Al/Cu) have many valences and hence the possibility for reduction-oxidation processes (2.5). This increased oxygen vacancies (promoted phase change via lattice relaxation) and/or Ti³⁺ bridging formation (inhibition of the phase transformation through lattice constraint). The fact that Al³⁺ has the same valence as Fe³⁺ may explain why it inhibits the phase change (2.5).



Where Δ_a denotes an anion vacancy.

The generation of oxygen vacancies by the reduction of dopant Fe/Al in the TiO₂ lattice may assist the anatase to rutile phase transition (2.4-2.5). Also using the divalent Cu²⁺ has the tendency of producing tenorite (CuO) or cuprite (Cu₂O) photocatalysts (β-Cu/TiO₂), with some complexity. Likewise, the use of chitosan with Na⁺ dominancy can also produce sodium oxide (Na₂O) photocatalysts (γ-Na-TiO₂). The phase transformation for ternary MPCs mixed-effects is revealed by the EDX spectra (Figure 2.7) with the presence of Fe/Cu/Al/Ch. In this mixed phase of the MPCs, the photogenerated electrons (e⁻) and hole (h⁺) are expected to migrate towards the active surface and to initiate the redox reaction with adsorbed organics and water splitted molecules. Moreover, the confirmation of their lattice phases are being presented in Table 2.4.





2.5.2 Crystal structures of the MPCs

The X-ray diffraction (XRD) was used to determine the MPC crystallinity and polymorphic phases (Table 2.4). Figure 2.8 shows the MPCs crystal diffractograms corresponding to their peaks found in the JCPDS files (Joint Committee on Powder Diffraction Standards) presented in Table 2.4.

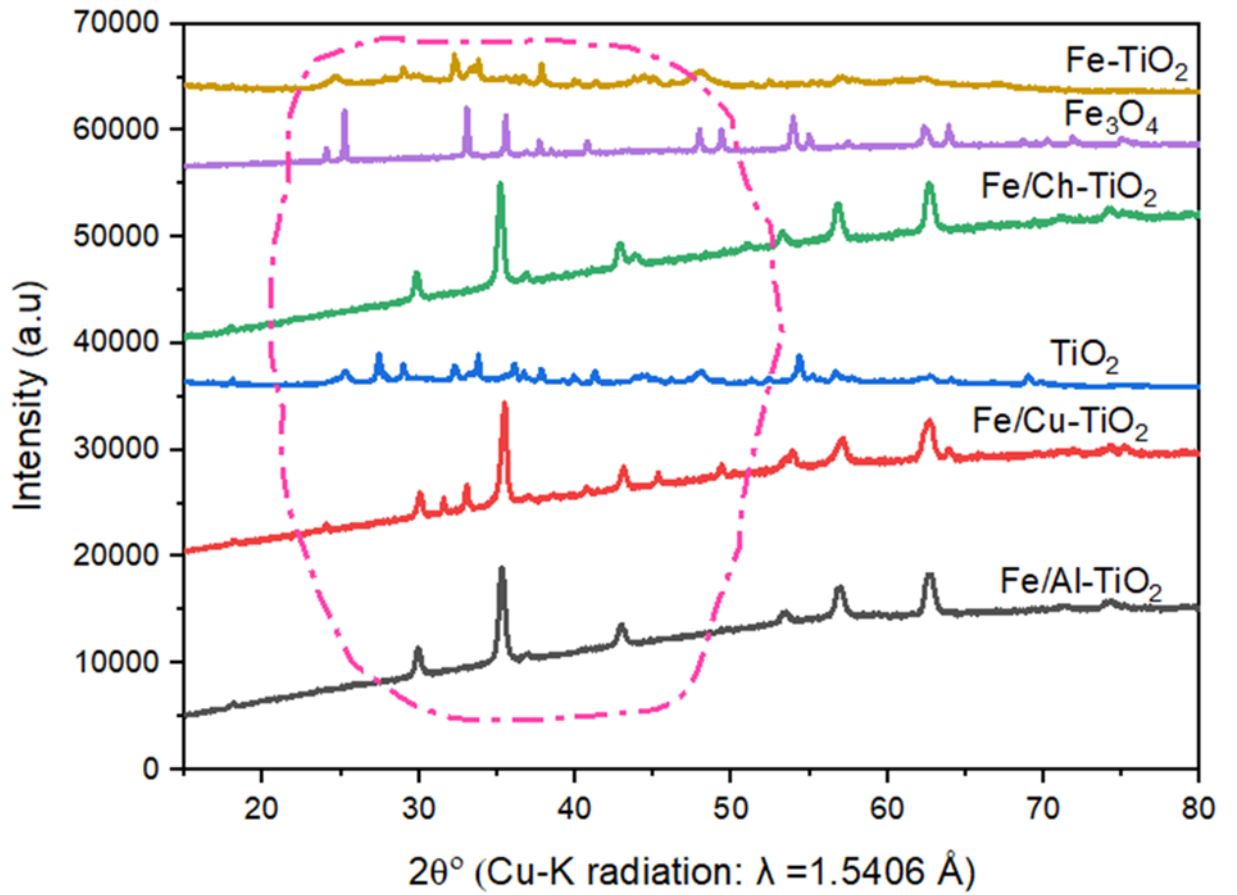


Figure 2.8: XRD spectra of MPCs with their compositions defined in Table 2.3

For instance, in JCPDS 00-070-2091, the reflection (14) of ferrimagnetism has an interplanar distance of 3.893 Å and diffractogram at 21.398° (2θ). Also, magnetite (Fe₃O₄) dominating at 35.423° (227) has an interplanar distance of 5.197 Å index at JCPDS 00-019-

0629. The MPCs' strong crystalline structure (227) agrees with the EDX pictures (Figure 2.7), which show magnetite (Fe_3O_4) in all modified MPCs. The TiO_2 embedded in the MPCs exhibited similar crystalline structures with peaks corresponding to (101), (004), (200), (211), (204), (116), (220), (215), and (224).

Conversely, 25.281° (2θ) resembles the reflection (141) of anatase with an interplanar distance of 3.893 Å. (JCPDS 00-021-0428) with a body-centred tetragonal structure. In addition, the sharp peaks suggest the MPCs have a good crystalline structure with a small particle size and well-indexed structure of cubic spine Fe_3O_4 (El Ghandoor et al. 2012; Kobwittaya and Sirivithayapakorn 2014).

The diffractogram of the rutile had weak signals with overlapping peaks of the anatase, which affirms conventional TiO_2 composition of 75-80% anatase and 20-25% rutile (Chong et al. 2010). The crystal structures of transition metal oxides, silicates, and carbonates associated with the hydrolysis and condensation reactions of their metal ions are depicted in Table 2.4. Additionally, the forms of iron oxides, classically ferrimagnetite, ferromagnetite, maghemite, mikasite, magnesioferrite, thermonatrite, sylvite and so on were also identified (Table 2.4). Among them, magnetite and maghemite are reported to be very promising with good biocompatibility and superparamagnetic potential (El Ghandoor et al. 2012; Kobwittaya and Sirivithayapakorn 2014).

Table 2.4: Physio-chemical properties of the MPCs obtained from the XRD JCPDS file

2 θ (degree)	Miller indices (hkl) plane	d _{hkl} (nm)	Crystal structure	Nanostructure	JCPDS pattern
24.865	(62)	3.549	Orthohombic	β -FeSO ₄	00-033-0682
28.294	(0)	2.297	Monoclinic	Calcium sulfite	00-038-0701
14.686	(0)	0.233	Monoclinic	Calcium sulfate hydrate	00-047-0964
24.482	(225)	1.988	Face-centered cubic	Sylvite	00-41-1476
46.8	(148)	3.157	Rhombohedral	Mikasaite	00-047-1774
83.568	(15)	6.505	Base-centered monoclinic	Tenorite (CuO)	00-048-1548
21.398	(14)	3.202	Monoclinic	ferrimagnetite	00-070-2091
25.432	(63)	2.961	Base-centered orthohombic	Calcium sulfate (CaSO ₄)	01-070-0909
74.365	(227)	4.498	Face-centered cubic	Magnesium -iron oxide	01-071-1254
48.491	(12)	2.106	Monoclinic	Clinoptilolite	01-071-1425
76.561	(59)	3.606	Orthohombic	Iron oxide chloride	01-072-0619
47.197	(63)	3.654	Base-centered orthohombic	Iron sulfate	01-073-1057
36.989	(15)	3.102	Base-centered monoclinic	Szomolnokite	01-074-1332
51.44	(44)	2.162	Base-centered orthohombic	Sodium nitrate	01-075-2073
65.976	(227)	5.42	Face-centered cubic	Copper iron oxide	01-077-0010
84.582	(148)	2.856	Rhombohedral	Aluminium sulfate	01-077-0385
53.755	(227)	5.547	Face-centered cubic	Nickel iron oxide	01-080-0072
22.337	(12)	2.174	Monoclinic	Heulandite	01-082-1228
40.224	(152)	2.635	Hexagonal	Quartz	01-083-0539
27.589	(15)	1.572	Monoclinic	Sodium oxide hydrate	01-083-0597
69.934	(139)	3.232	Body-centered tetragonal	Calcium oxide	00-003-0865
29.406	(167)	2.711	Rhombohedral	Calcite	00-005-0586
27.335	(225)	2.163	Face-centered cubic	Halite	00-005-0628
32.497	(29)	2.263	Orthohombic	Thermonatrite	00-008-0448
20.212	(13)	1.96	Monoclinic	Iron chloride hydrate	00-016-0123
35.525	(227)	4.523	Face-centered cubic	Magnesioferrite	00-017-0464
35.423	(227)	5.197	Face-centered cubic	Magnetite (Fe ₃ O ₄)	00-019-0629
27.335	(53)	3.336	Orthohombic	Iron sulfate	00-021-0428
25.281	(141)	3.893	Body -centered tetragonal	Anatase (TiO ₂)	00-021-1272
14.63	(0)	2.613	Hexagonal	Calcium sulfate hydrate	00-023-0128
41.806	(150)	1.712	Hexagonal	Antarcticite	00-026-1053
33.837	(15)	2.124	Monoclinic	Trona	00-029-1447
17.374	(160)	3.065	Rhombohedral	Hydroniumjarosite	00-031-0650
33.153	(167)	5.27	Rhombohedral	Hematite (α -Fe ₂ O ₃)	00-033-0664
24.717	(148)	3.06	Rhombohedral	Mikasaite	00-033-0679
35.631	(213)	4.858	Cubic	Maghemite (γ -Fe ₂ O ₃)	00-039-1346

2.5.3 Functional and molecular groups of MPCs

The MPCs' FTIR spectra (Figure 2.9) revealed their functionality in terms of stability, oxidation, and reactivity.

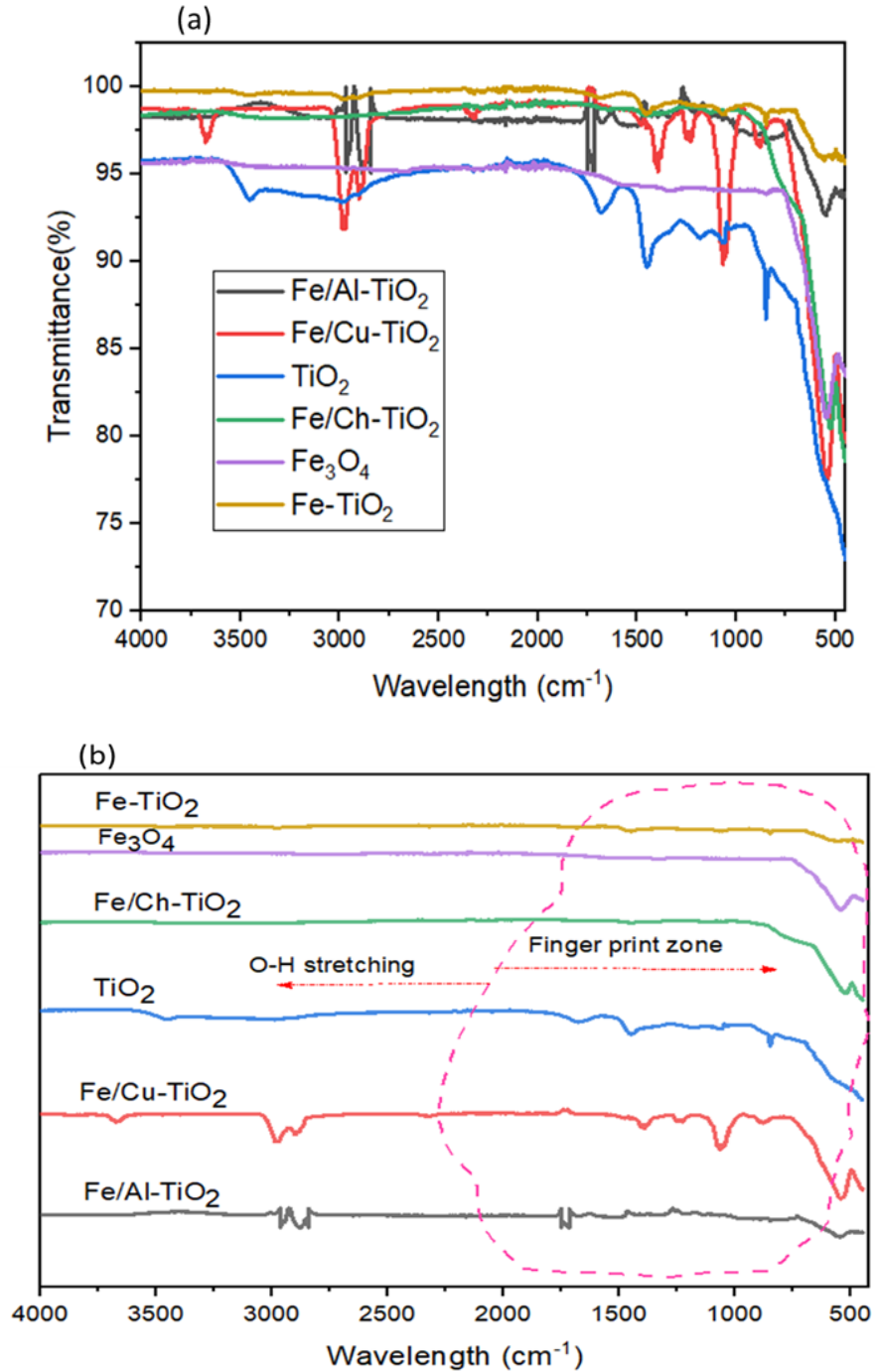


Figure 2.9: FTIR spectra of (a) unstretched and (b) stretched MPCs with their compositions defined in Table 2.3

As shown in Figure 2.9 b, most of the chemical and functional groups are found within the fingerprint region of wavenumber $2000 - 400 \text{ cm}^{-1}$. Also, the spectrum region $4000 - 1500 \text{ cm}^{-1}$ are bands that appear at 3600 cm^{-1} , 3000 cm^{-1} and 1620 cm^{-1} have been associated with the O-H vibrations of water (El Ghandoor et al. 2012; Kobwittaya and Sirivithayapakorn 2014). The asymmetric and symmetric CH_2 stretching can be attributed to the absorption peaks at 2924 cm^{-1} and 2854 cm^{-1} , respectively (Daou et al., 2006). The asymmetric and symmetric CH_2 stretching bands shifted to 2921 cm^{-1} and 2850 cm^{-1} , respectively, in most MPCs with significant carbon content (Figure 2.9). This suggests that in the crystalline phases, the hydrocarbon chains encircling the MPC monolayers were tightly populated (El Ghandoor et al. 2012; Finance 2011; Kobwittaya and Sirivithayapakorn 2014; Watson et al. 2002).

The region $1500 - 900 \text{ cm}^{-1}$ corresponds to the area of vibrations in line with the surfactant and NP molecules appearance. Thus, the broad bands detected at 1394 and 1120 cm^{-1} can be assigned to the C-vibrations coming from the MNPs. In addition, the intense overlapping peaks within $1250 - 1000 \text{ cm}^{-1}$ reveal vibration stretch of the carboxyl groups (C-OH / C-H), hydroxyl groups (H-O-H) and double bonds (C=C) of the MNPs. Furthermore, between 850 and 500 cm^{-1} , the bands observed at 584 cm^{-1} and 629 cm^{-1} can be assigned to the magnetite and maghemite in their oxidized form (El Ghandoor et al. 2012; Finance 2011; Kobwittaya and Sirivithayapakorn 2014; Watson et al. 2002). This affirms Kobwittaya and Sirivithayapakorn (2014) report, where the absorption peaks at 530 cm^{-1} corresponding to Fe-O vibrations are related to the magnetite phase.

2.5.4 Surface area, pore size, and pore volume of MPCs

The BET surface area, pore-volume, and mesopore diameter distribution estimated by the Barret-Joyner-Halenda (BJH) are depicted in Table 2.5. It was observed that the BJH pore

size of the Fe_3O_4 (1.484 nm) decreased slightly in the modified MPCs (Fe/Al- TiO_2 , Fe/Cu- TiO_2 , Fe/Ch- TiO_2 , Fe- TiO_2), whereas that of the TiO_2 (0.16 nm) seems increased in the modified MPCs. This increase in the MPCs BJH pore size is reflected in their surface area, as the Fe- TiO_2 was found as the highest (62.73 m^2/g). The success of the TiO_2 transformation and surface area modified with the Fe_3O_4 , affirms other reported studies (Álvarez et al. 2010; Askari and Salarizadeh 2020; Debnath et al. 2014; Kamal et al. 2017; Rezlescu et al. 2014; Saiz et al. 2014).

Table 2.5: BET surface morphology

Catalyst type	BET Surface area (m^2/g)	Pore volume (cm^3/g)	BJH pore size (nm)
Fe_3O_4	27.6	0.008	1.484
Fe- TiO_2	62.73	0.017	1.337
TiO_2	25.7	0.11	0.16
Fe/Ch- TiO_2	54.85	0.004	0.286
Fe/Al- TiO_2	30.02	0.009	1.144
Fe/Cu- TiO_2	28.85	0.008	1.453

2.6 Summary and additional information

This study demonstrated the potential of using co-precipitation assay to synthesize MPCs for biogas production from wastewater treatment towards environmental sustainability. All the operational parameters of the co-precipitation technique were kept constant, the TiO_2 phase modification was examined by doping with different metallic (Fe/Cu/Al) and non-metallic (chitosan) materials. The MPCs functional properties was used as a model to assess the success of the syntheses. Analytically, characterization of the MPCs via SEM/EDX, XRD, FTIR and BET techniques revealed successful modification of the TiO_2 in its binary (Fe- TiO_2) and ternary (Fe/Al- TiO_2 and Fe/Cu- TiO_2 , Fe/Ch- TiO_2) forms. In essence, the distribution of the Fe_3O_4 on the TiO_2 surface was affirmed with the SEM/EDX, whereas the XRD and FTIR spectra, respectively revealed the crystalline structure and functional monomers of the MPCs. Among the MPCs, the BET showed that Fe- TiO_2 had the highest surface area ($62.73 \text{ m}^2/\text{g}$) with a pore volume of $0.017 \text{ cm}^3/\text{g}$ and pore size of 1.337 nm . Therefore, to improve the MPCs, especially the Fe- TiO_2 found to be more competitive than its commercialised counterparts (TiO_2) should be given attention.

Additional information supporting the objective of this chapter feasibility study can be found in our published journal Papers (3-6).

Paper 3: Adsorption and photocatalysis



Paper 3.pdf

Paper 4: Photocatalytic degradation optimisation



Paper 4.pdf

Paper 5: Magnetised biokinetics



Paper 5.pdf

Paper 6 : Biocatalysis of post-digestate into bioenergy



Paper 6.pdf

Article

Adsorption and Photocatalytic Mineralization of Bromophenol Blue Dye with TiO₂ Modified with Clinoptilolite/Activated Carbon

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Abstract: This study presents a hybridized photocatalyst with adsorbate as a promising nanocomposite for photoremediation of wastewater. Photocatalytic degradation of bromophenol blue (BPB) in aqueous solution under UV-irradiation of wavelength 400 nm was carried out with TiO₂ doped with activated carbon (A) and clinoptilolite (Z) via the co-precipitation technique. The physiochemical properties of the nanocomposite (A–TiO₂ and Z–TiO₂) and TiO₂ were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier-transform infrared (FTIR) spectroscopy. Results of the nanocomposite (A–TiO₂ and Z–TiO₂) efficiency was compared to that with the TiO₂, which demonstrated their adsorption and synergistic effect for the removal of chemical oxygen demand (COD) and color from the wastewater. At an optimal load of 4 g, the photocatalytic degradation activity (Z–TiO₂ > A–TiO₂ > TiO₂) was found favorably by the second-order kinetic model. Consequently, the Langmuir adsorption isotherms favored the nanocomposites (Z–TiO₂ > A–TiO₂), whereas that of the TiO₂ fitted very well on the Freundlich isotherm approach. Z–TiO₂ evidently exhibited a high photocatalytic efficacy of decomposition over 80% of BPB (COD) at reaction rate constant (k) and coefficient of determination (R²) values of $5.63 \times 10^{-4} \text{ min}^{-1}$ and 0.989, respectively.

Keywords: activated carbon; adsorption; bromophenol blue dye; clinoptilolite; nanocomposite; photocatalysis; titanium dioxide



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1. Introduction

The recent uprising of industrialization is being associated with the depletion of water resources owing to its consumption rate, making it essential to maintain healthy living [1,2]. Notwithstanding, the impact of anthropogenic activities and socio-economic development has resulted in poor sanitation and inadequate freshwater supply for drinking, even in countries or regions considered as water-rich [1]. Water shortages in many developing countries have been reported as one of the most significant political and societal problems confronting them [1,3].

South Africa, like many African countries, continues to suffer from the fresh water supply, which is declining in quality because of an increase in the pollution index and impeding of river catchments being caused by urbanization, deforestation, industrial and agricultural activities [4–6]. Furthermore, dyes and pigments produced by various industries such as cosmetics, textile, paper, leather, pharmaceutical, nutrition, and plastics are the foremost common contaminants in wastewater [7]. Distinctively, with a yearly estimation of over 70,000 tons of dyes produced, during the dyeing processes, 15% are being misapplied [8,9]. The release of these dyes and other organic pollutants into wastewater and the aquatic environment, even at low concentrations, are noticeable to be highly toxic with low transparency [9,10]. Additionally, emerging contaminants (antibiotics, pesticides, nanoplastics) complexity opposing water quality poses a great threat to aquatic life and

human health [7,11]. Therefore, it is essential to develop a viable technology for the treatment of wastewater, most especially textile effluent.

Conventionally, decontamination technologies such as coagulation, ion flotation, sedimentation, filtration, biological treatment, and chlorination are limited in handling dye effluents [11–15]. Furthermore, most of the technologies end up generating secondary pollutants associated with complex sludge and toxic byproducts, which requires further treatment [6,16]. These setbacks make most of the treatment technologies to be cost-ineffective and time and energy-intensive in nature [11,14,17]. Therefore, a balanced technology is required to simultaneously improve water quality and debase dyes in wastewater settings.

Currently, advanced oxidation processes (AOPs) emerges as the needful technology to remediate poor water quality associated with conventional wastewater treatment technologies to mitigate high strength organic pollutants [18–22]. Among the different AOPs, heterogeneous photocatalysis as a principal component of green chemistry has inspired extensive research on designing eco-friendly and effective photocatalysts [23,24]. These photocatalysts are primarily semiconductors, which include TiO_2 , ZnO , Fe_2O_3 , CdS , and ZnS [7,23]. Among them, TiO_2 has been the most widely used due to its ability to break down organic pollutants to achieve complete mineralization with high reactivity, reduced toxicity, low cost, and being chemically stable [25,26]. Conversely, photodegradation of dyes under ultra-violet (UV) irradiation with TiO_2 is reported to have some setbacks [27,28]. Thus, the presence of dye on the surface of TiO_2 induces its negative charge ions by reducing the energy required for their excitation, hence extends its adsorption efficiency under a visible region of the spectrum. Even though TiO_2 powders are easy to agglomerate, their adsorption capacity is very poor, with difficulties in recycling and separation [27,28]. Adsorbents, on the other hand, after regeneration, reduces their adsorption capacity as compared to photocatalysts [29–31]. To overcome these setbacks, a combination of photocatalysts and adsorbents have been reported to be very promising for wastewater treatment. One such way is by catalyst fixation onto a support such as gold nanoparticles, activated carbon, and zeolites (e.g., ZSM-5) [31,32].

However, only a few reports have cited the use of TiO_2 nanocomposite doped on clinoptilolite (Z) or activated carbon (AC) for the mineralization of bromophenol blue dye (BPD) from wastewater. BPD was selected as the functional model for the wastewater simulation because of the role it plays as a dye and pigments for the wide usage in art decoration and textile industries, with the end product being wastewater [8,9]. Therefore, this study presents photocatalytic degradation of BBD using the TiO_2 /UV system. Furthermore, the influence of Z, AC, and hybridized photocatalysts (Z- TiO_2 and AC- TiO_2) loading rate (1–6 g), as well as their adsorption capacity, was investigated. Decolonization and degrading of the organics in the form of color, turbidity, and chemical oxygen demand (COD) was considered as the performance criteria.

2. Results and Discussion

2.1. Physiochemical Properties of TiO_2 -Based Composite (A- TiO_2 /Z- TiO_2)

2.1.1. Crystalline Size

The change in the crystallographic structure of TiO_2 after being modified into A- TiO_2 and Z- TiO_2 nanocomposites were determined by X-ray diffraction (XRD). As can be seen (Figure 1), the XRD results showed the presence of crystalline phases in phase mixtures, with most of the TiO_2 structures as the anatase phase. Comparatively, the change in the intensities of the TiO_2 peaks to that of A- TiO_2 and Z- TiO_2 signpost the effect that the isomorphic interaction may have occurred during the modification mechanism [32,33]. Notwithstanding, the dominating phase of the TiO_2 pattern in all the samples by the XRD peaks (Figure 1) within the angle range of 2θ ($5^\circ > 2\theta > 70^\circ$) is anatase corresponding to the JCPDS Files No.21-1272 [33,34]. The peaks observed at 2θ values of 25.28° , 38.68° , 48.16° , 54.05° , 62.87° , and 68.98° , respectively, are attributed to 101, 112, 200, 105, 211 and 116 crystalline structures of the anatase (Λ) plane. The lowest Bragg angle of the anatase (Λ) phase is around 25.28° , and that of rutile ($\Re$) is about 27.45° . Activated carbon being an

amorphous material is being revealed (Figure 1) by the broad bump of A-TiO₂ around $2\theta = 25.28^\circ$. Adding to this, the reflection peak in the A-TiO₂ of the anatase around $2\theta = 25.67^\circ$ decreased, whereas the rutile peak at $2\theta = 27.45^\circ$ (002) became sharper and stronger. However, the anatase peak in the Z-TiO₂ remained unchanged, even though the rutile peak intensity heightened. The most intense reflection of clinoptilolite (Z) was found at $2\theta = 9.88^\circ$. Conversely to this result, Zhong et al. [33] suggested the steadiest rutile polymorph of TiO₂ observed at $2\theta = 27.45^\circ$ of the Z-TiO₂ displayed the same signal characterized for natural zeolite (clinoptilolite). In terms of A-TiO₂, there is no peak at the $2\theta = 24.67^\circ$ position, which is generally characterized as a crystalline plane (002) of activated carbon (A), which seems to be isolated by the TiO₂ (anatase peak at 25.28°). This makes A-TiO₂ be in an amorphous state, by its carbon suppressing the TiO₂ (anatase peak at $2\theta = 25.45^\circ$) transition to reveal the rutile peak at $2\theta = 27.45^\circ$. Additional, peaks at 2θ values of 52.06° (004), 55.2° (211) and 58.68° (204) of A-TiO₂ and Z-TiO₂, aside it being rutile, might also be attributed to reflections of crystallographic phases of impurities as some are depicted in Table 1. Additionally, the anatase being the predominant phase, therefore, expedited the nanocomposite for the photocatalytic activity [35]. Furthermore, the dominant crystal size (22–34 nm) of TiO₂ present in the nanocomposites (A-TiO₂ and Z-TiO₂) as anatase was calculated by using the Scherer's Equation (1) and the diffraction peak at the $2\theta = 25.28^\circ$ (101) plane [27], where δ is the wavelength of X-ray radiation (CuK $\alpha = 0.15406$ nm), K is a constant taken as 0.98, β is the first line width at half maximum height (FWHM) of the peak (determined using Origin software, version 2018), and θ is the diffracting angle ($2\theta = 25.28^\circ$ for 101 planes).

$$\left(D = \frac{K\delta}{\beta \cos \theta} \right) \quad (1)$$

where δ is the wavelength of X-ray radiation (CuK $\alpha = 0.15406$ nm), K is a constant taken as 0.98, β is the first line width at half maximum height (FWHM) of the peak (determined using Origin software), and θ is the diffracting angle ($2\theta = 25.28^\circ$ for 101 planes).

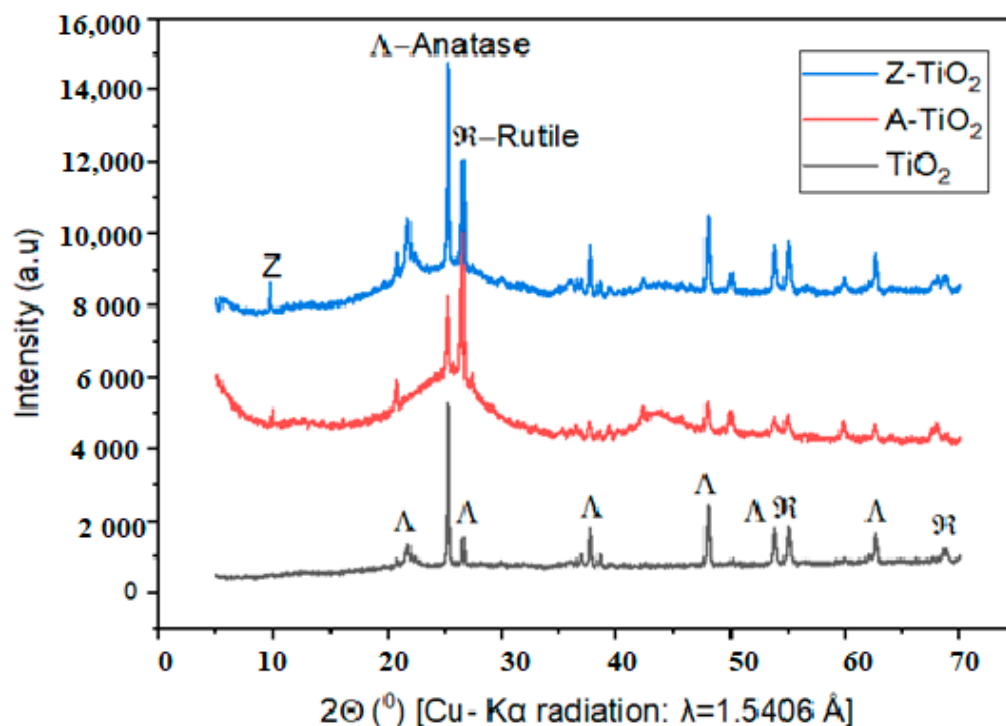


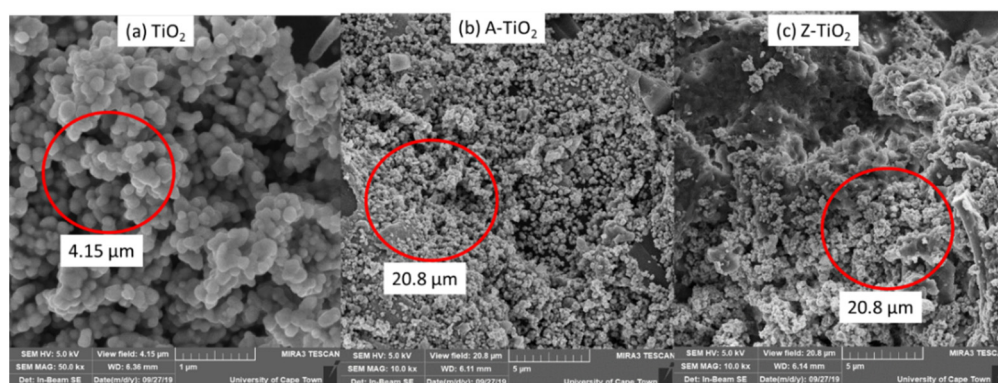
Figure 1. XRD pattern of TiO₂ (black), A-TiO₂ (red) and Z-TiO₂ (blue); Λ—anatase, and ℞—rutile.

Table 1. Elemental distribution of TiO₂, A-TiO₂, and Z-TiO₂ for their average spectra (Figure 3).

Elemental Composition	TiO ₂		A-TiO ₂		Z-TiO ₂	
	Weight (%)	Std. Dev.	Weight (%)	Std. Dev.	Weight (%)	Std. Dev.
C	13.08	3.69	17	1.1	19.72	6.74
O	45.64	2.41	31.4	11.41	35.64	6.59
Na	10.73	1.35	0.27	0.21	1.01	0.55
Ti	30.55	5.78	16.02	0.26	23.15	1.69
Mg			0.4	0.08	0.64	0.63
Al			2.66	0.6	1.18	1.11
Si			0.86	0.14	16.57	1.94
K			23.23	2.17	1.6	0.51
Ca			0.48	0.33	0.49	0.64
P			1.17	0.36		
S			0.28	0.07		
Cl			6.23	2.17		
Total	100		100		100	

2.1.2. Morphological Analysis

Scanning electron microscopy (SEM) at the University of Cape Town, South Africa was employed to characterize the surface morphologies of the TiO₂, A-TiO₂, and Z-TiO₂ nanocomposites, and the results obtained are presented in Figure 2. It is observed (Figure 2a) that the TiO₂ with no covering has very hexagonal and unformulated structures with abundant pores to accommodate other materials [31,33,35]. The average grain size (Figure 2a) of the pores was 4.15 µm under the scale of 1 µm with a magnification of 50 kx and a working distance (WD) of 6.36 mm. Conversely, for the A-TiO₂ and Z-TiO₂ representing a WD of 6.11 mm (Figure 2b) and 6.14 mm (Figure 2c), respectively, a grain pore size of 20.8 µm under the same scale of 5 µm and magnification of 10 kx was obtained.

**Figure 2.** SEM images of (a) TiO₂, (b) A-TiO₂ and (c) Z-TiO₂.

Subsequently, the EDX images at 100 µm for the TiO₂ (Figure 3a), A-TiO₂ (Figure 3b), and Z-TiO₂ (Figure 3c) revealed the possible hybridization with well-dispersed TiO₂ on the A-TiO₂ and Z-TiO₂ nanocomposites. Evidently, the hexagonal structure (Figure 3a) of TiO₂ nanoparticles was well dispersed and intertwined on the surface of A-TiO₂ or Z-TiO₂ [33], which transformed their surface structures (Figure 3b,c). The porous and agglomerated structures are revealed in the A-TiO₂ (Figure 3b) and Z-TiO₂ (Figure 3c). However, the surface chemistry of A-TiO₂ or Z-TiO₂ with other elements present, as shown in Table 1, may have obstructed the TiO₂ surface coating and photocatalytic activities. The elemental compositions of the TiO₂, A-TiO₂, and Z-TiO₂ nanocomposites, is shown in Table 1. This revealed the elements in the TiO₂ (O > Ti > C > Na) were distinctively present in the A-TiO₂, and Z-TiO₂ which proofed the success of hybridizing the nanocomposite. Considering the elemental structures, Z-TiO₂ contained O > Ti > C > Si > K > Al > Na > Mg > Ca, where Si,

Al, O and other cationic elements forms the internal framework of Z [34,35]. The unique pores of Z provided a large surface area and improved the homogeneous dispersion of TiO₂ nanoparticles on the surface (Figure 3c) of A-TiO₂ constituted O > K > C > Ti > Cl > Al > P > Si > Ca > Mg > S, whereby most of the cationic carriers suppressed the presence of the Ti composition (Figure 3b). In addition, the strong synergy between Al and Si decreased the charge carriers of the Ti as there is a high possibility of forming composite oxides [33,35].

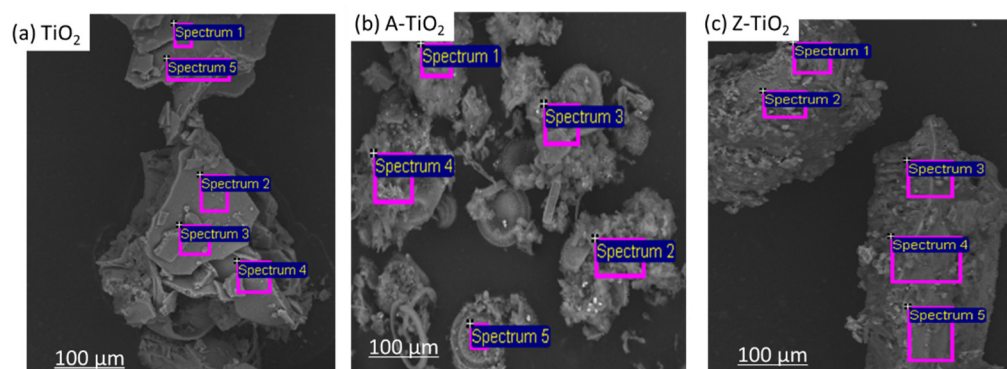


Figure 3. EDX images of (a) TiO₂, (b) A-TiO₂ and (c) Z-TiO₂.

2.1.3. Molecular Structures and Functional Groups

The nanocomposites (A-TiO₂ and Z-TiO₂) and TiO₂ were furthermore analyzed by Fourier-transform infrared (FTIR) spectroscopy. The chemical bonds and functional groups within a fingerprint region of wavenumber of 400–2000 cm^{−1} revealed by the FTIR spectra are presented in Figure 4. The spectrum also reveals the vibration bands between the reactive hydroxyl groups, as well as the hydrophilic nature of the TiO₂ [28,36]. The peaks observed around 3250 cm^{−1} was attributed to the strong vibrations of OH groups bonded with water or TiO₂, where the shift in the OH bonding or the overlayer might be due to the combined A or Z with the TiO₂. The peaks detected around 1630–1820 cm^{−1} were ascribed to the OH and C=O vibration band. The single band around 1635 cm^{−1} associated with the vibration mode of the Ti-O bond and other oxygenated functional groups [30,33]. The weak absorption band around 1590 cm^{−1} and 1450 cm^{−1} for the A-TiO₂ and Z-TiO₂ were attributed to the carboxyl (C-OH/C-H) and hydroxyl (H-O-H) bending vibration mode, which might have occurred by the nanocomposite adsorbing moisture during the preparation [36]. Furthermore, the broad and weak peaks observed around 1070 cm^{−1} for the A-TiO₂ and Z-TiO₂ might also be due to the modification of the TiO₂ spectrum being attributed to the C-O-C stretching vibrations [36,37]. Finally, the broad peaks within the range of 400 cm^{−1} to 1000 cm^{−1} may be instigated by the vibration stretch of Ti-O and -OH, as observed in all the samples [35].

2.2. Photocatalytic Degradation

2.2.1. Effect of pH on Photocatalytic Degradation

The pH of an effluent strongly plays an important role in photocatalytic degradation of organic compounds, such as dyes in an aqueous suspension with TiO₂ NPs. First and foremost, the pH of the BPB synthesized effluent was investigated to ascertain the TiO₂, Z-TiO₂, and A-TiO₂ photocatalytic activities on COD removal. This was carried out by varying the pH of the effluent from 5–9 while keeping the catalyst load and reaction time constant at 2 g and 30 min, respectively. Figure 5 shows the degradation efficiency obtained by the TiO₂, Z-TiO₂ and A-TiO₂ on the COD removal. Evidently, the pH affected the adsorption shift of the organic substrates onto the surface of the photocatalyst as well as their photodegradation efficiency from the neutral to the acidic and basic mediums. The degradation efficiencies recorded for the acidic medium (pH 5–6) were 75–79%, 75–77%, and 77–80% for TiO₂, Z-TiO₂ and A-TiO₂, respectively. Under the neutral medium, almost the same degradation efficiency of about 63% was recorded for all the catalysts.

In the basic or alkaline medium (pH 8–9), the degradation efficiency of 66%, 64%, and 63% was, respectively recorded for the TiO_2 , Z– TiO_2 , and A– TiO_2 . The results confirm the occurrence of photocatalysis on the surface of NPs are mostly influenced by their charged ions and the pH of the solutions [18,24]. Thus, the charged ions and change in pH promoted the pollutant's stability, neutralization, agglomeration, and adsorption onto the photocatalyst surface [24]. The high acidic medium-efficiency can be attributed to the presence of negatively charged contaminants in the effluent, which were attracted and adsorbed onto the surface of the positively charged photocatalysts (TiO_2 , Z– TiO_2 and A– TiO_2) [21,24]. In addition, the low-efficiency exhibited within the basic medium (pH 8–9) may be due to the electrostatic repulsion between the positively charged NPs and the cationic charges in the solution.

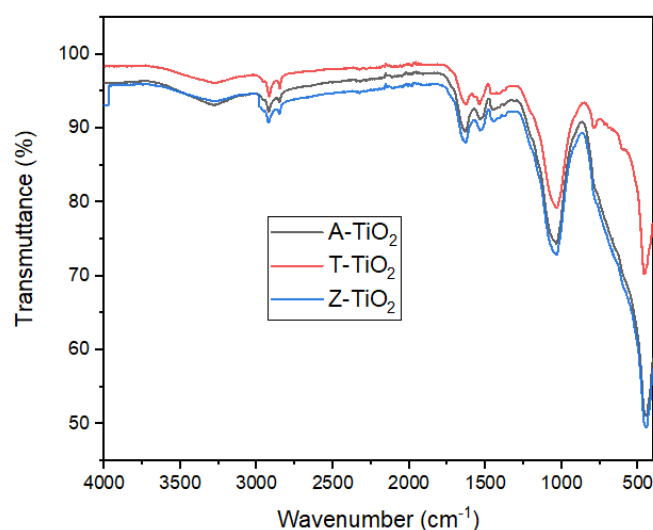


Figure 4. FTIR spectra of TiO_2 (red) < A– TiO_2 (black) < Z– TiO_2 (blue).

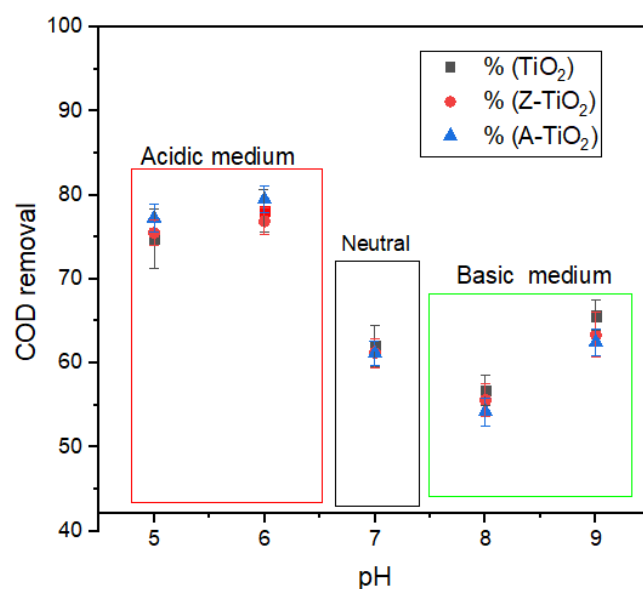


Figure 5. Effect of pH on photocatalytic degradation of chemical oxygen demand (COD) at a catalyst load of 2 g and reaction time of 30 min.

2.2.2. Effects of Photocatalyst Dosage

The photocatalytic performance of single (A, Z, TiO_2) and binary nanocomposites (A– TiO_2 and Z– TiO_2) were investigated by measuring catalyst-load-dependent degradation of the COD (367.7 mg/L), and color (458 Pt. Co) initial concentrations from the BPD simulated

effluent under a UV-light. The effluent pH was kept constant at an acidic medium of 6.5 to enhance the protonation of the active sites of the catalyst. Subsequently, to ascertain the optimal dosage (2–4 g) of the nanocomposites (A–TiO₂ and Z–TiO₂), first, the load (1–6 g) of a single catalyst (A, Z, and TiO₂) was investigated at the reaction time of 30 min.

Figure 6 shows that photocatalytic degradation efficiency increased with an increase in the catalyst load until an optimal dosage is attained. As seen (Figure 6a,b), an increase in the catalyst load (1–5 g) promoted the photodegradation rate with more active sites, whereby after the optimal load (5 g), there was a degeneration as compared to the A and Z loads at 6 g. Thus, an increase in the active sites of the catalyst surfaces was too dense to interact with the contaminant, thereby destabilizing and deactivating them as they agglomerate [20,30]. At a single catalyst load of 5 g, about 60–80% and 65–90% of the initial concentration of color (Figure 6a) and COD (Figure 6b) was respectively removed. In addition, the increasing order of the single catalyst loads was observed for the color (Z > TiO₂ > A) and COD removal (TiO₂ > Z > A).

Evidently, the single catalyst load results favored the TiO₂ due to its high active sites and hydroxyl radicals, which entrapped the contaminants [31,32]. This affirms that the photocatalytic nature of TiO₂, once activated by UV radiations, produces a very reactive species, which led to the degradation of the organic substance in the solutions [29,36]. However, in the subsequent investigation of the nanocomposites in 1:1 ratio (A–TiO₂ and Z–TiO₂) loads (2–4 g), there is a prompt increase in the contaminant removal efficiency (Figure 6c,d) as compared to the individual components (Figure 6a,b). Thus, the TiO₂ in the nanocomposite was photo-activated by producing a high amount of the hydroxyl radicals [30,36]. Thus, an increase in the nanocomposite load to a high level (4 g) produced more of the photogenerated electron holes [37]. This increased the removal efficiency of the A–TiO₂ by 20% as compared to the TiO₂, for the removal of color and COD, as shown in Figure 6c,d, respectively. In addition, the increasing order of color ((Figure 6c) and COD (Figure 6d) removal by the catalyst was found as A–TiO₂ > Z–TiO₂ > TiO₂. However, among the nanocomposites, activated carbon (A) is recounted as a good electron acceptor, whereas TiO₂ is also known to be an effective electron donor [33,34]. Consequently, the A–TiO₂ was found to be very effective in suppressing the photogenerated species from destabilization during overload as compared to that of the TiO₂ [35,37]. Therefore, the synergistic effect of hybridizing A–TiO₂ (Figure 6) eventually reduced the destabilization of the hole-pair electrons at the high dosage which increased its efficiency [36].

2.3. Adsorption and Photocatalysis

Figure 7 presents the adsorption and photocatalytic degradation performance of the nanocomposites (A–TiO₂ and Z–TiO₂) and TiO₂, which were simultaneously achieved with a catalyst load of 4 g by monitoring the removal of COD. Firstly, the dark adsorption (no UV-light) was carried out within a stipulated time interval of 60 minutes, after which the solution was illuminated for another 60 minutes to enhance the photodegradation. However, the adsorption and photocatalytic activities of the supported TiO₂ (A–TiO₂ and Z–TiO₂) under the irradiation time of 60 min led to higher degradation (>85% COD) as compared to the unsupported TiO₂ (80% COD). In the dark adsorption experiment, TiO₂ was seen to be less efficient because of its deactivated reactive sites, which makes it slow to react with other complex compounds. Even though the increasing order (Z–TiO₂ > A–TiO₂ > TiO₂) of the photocatalytic degradation efficiency favored Z–TiO₂ (Figure 7b), the hybridized A–TiO₂ also had effective adsorptive (Figure 7a) capacity owing to its low density and surface area [33,35]. Thus, the support on TiO₂ with A and Z increased the irradiated surface area and adsorption capacity of the TiO₂. According to Zhong et al. [33], the high specific surface area of the nanocomposite creates an interface, which tolerates immobilization and destabilization of the photocatalyst to trap the organic pollutants. Results obtained have also confirmed the three steps of the decomposition mechanism of TiO₂, such as (i) movement of the excited radicals, (ii) adsorption and photodegradation of the organic pollutants from the bulk solution onto the photocatalyst surface [34].

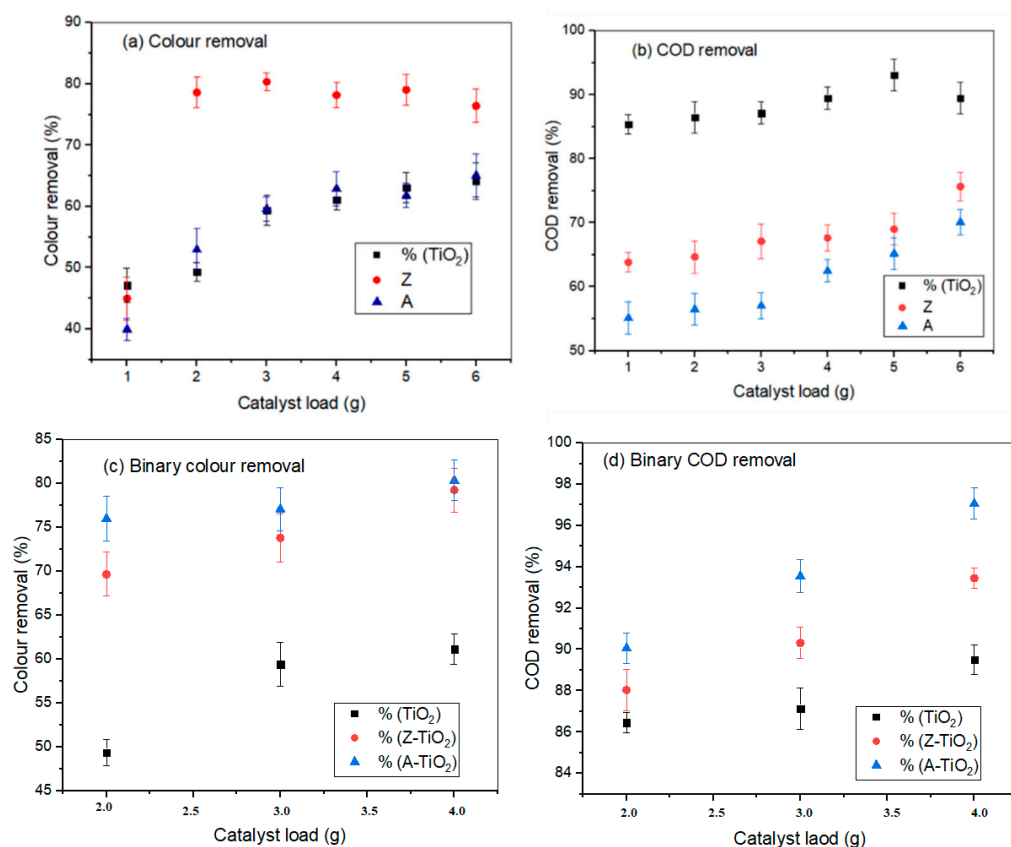


Figure 6. Effects of catalyst load at 1–6 g for the removal of (a) color (458 Pt. Co) and (b) COD (367.7 mg/L) with subsequent binary catalyst load effect of 2–4 g (c,d) at a reaction time of 30 min.

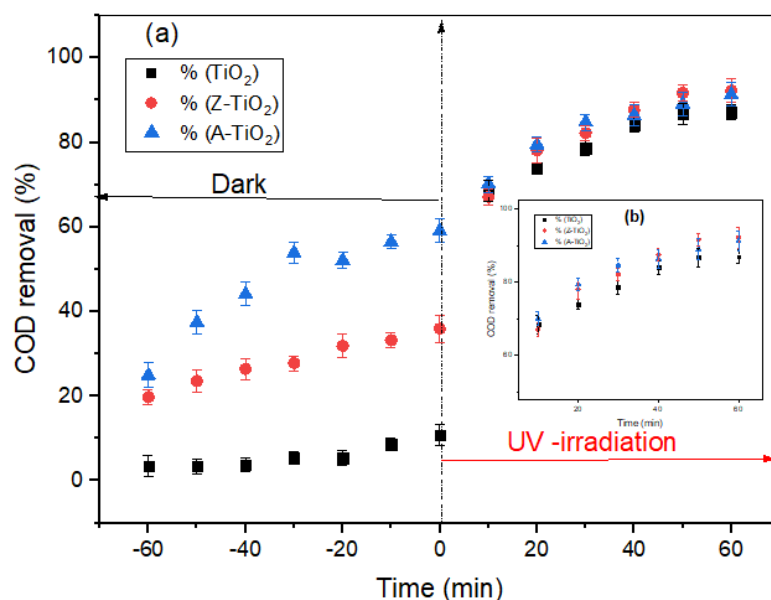


Figure 7. Adsorption (a) and photocatalytic (b) degradation of COD (367.7 mg/L) at 4 g catalyst loading of TiO₂ (black) < A-TiO₂ (blue) < Z-TiO₂ (red).

2.3.1. Kinetic Models

The kinetics of heterogeneous photocatalyst reactions in the slurry is usually described by the Langmuir–Hinshelwood model expressed in (2). However, the degradation and

adsorption processes can be monitored either by a first-order (3) or the second-order kinetic models (5) [38,39].

$$r = \frac{K_r K_a C_e}{1 + K_a C_e} \quad (2)$$

where r , K_r and $K_a C_e$ represents the reaction rate, the rate constant (mg/min) and adsorption constant (mg⁻¹), respectively. Assuming $K_a C_e$ is negligible at a low concentration, the rate of degradation in (2) can then be expressed as a first-order model (3).

$$r = \frac{-dC}{dt} = K_r K_a C_e = k_1 C \quad (3)$$

where k_1 is the first-order rate constant (min⁻¹). Equation (3) can then be integrated into (4).

$$\ln \frac{C_0}{C} = k_1 t \quad (4)$$

$$\frac{1}{C} - \frac{1}{C_0} = k_2 t \quad (5)$$

To estimate the rate of reaction constants for the first and second-order kinetic models, $\ln \frac{C_0}{C}$ vs. t (Figure 8a) and $\frac{1}{C} - \frac{1}{C_0}$ vs. t (Figure 8b), respectively, was plotted. Where, k_2 is the second-order rate constant (min⁻¹), C_0 is the initial COD concentration, t is time, and C is the concentration at the specified time.

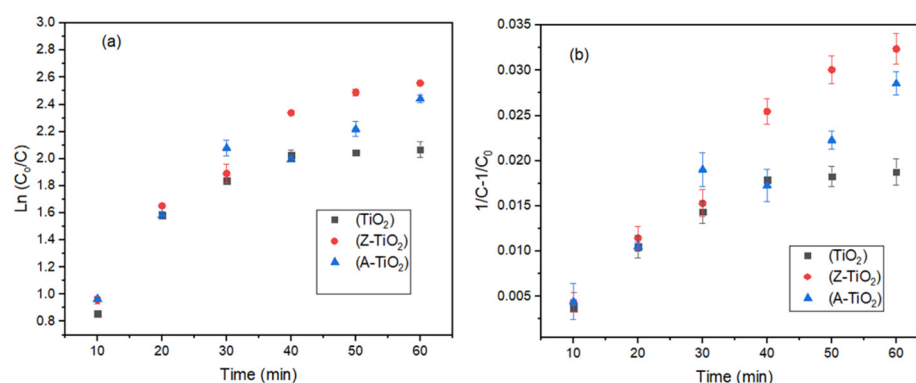


Figure 8. Photocatalytic degradation of COD (367.7 mg/L) as a function of time; (a) first-order and (b) second-order kinetic models.

Table 2 presents the kinetics data obtained, indicating that the reactions do not fit well on the first-order kinetic model. However, all the reactions fitted well on the second-order kinetic model as observed based on their rate constants (k) and coefficient of determination (R^2) values. A 95% confidence level with a difference of less than 0.2 between the R^2 and Adjusted R^2 , also suggests the significance and accuracy of the model predictability. Additionally, the probability functions ($p < 0.05$) were significantly different from the zero levels. The increasing order of the k and R^2 values were seen as Z-TiO₂ > A-TiO₂ > TiO₂, whereby Z-TiO₂ had the highest k and R^2 values of $5.63 \times 10^{-4} \text{ min}^{-1}$ and 0.989, respectively. This validates the trend observed for the highest removal of the COD by photocatalytic degradation (Z-TiO₂ > A-TiO₂ > TiO₂), as shown in Figure 7, the data obtained favored the second-order kinetic model. In addition, the adsorbates (A) presence in the nanocomposites (A-TiO₂) suppressed the TiO₂, which made it more favorable for adsorption [40,41].

Table 2. Kinetics data for the removal of COD with a catalyst load of 4 g.

Photocatalyst Type	TiO ₂	Z-TiO ₂	A-TiO ₂
First-order Model			
k ₁ (min ^{−1})	0.0218	0.0313	0.0269
R ²	0.872	0.955	0.927
Adjusted R ²	0.769	0.912	0.869
Sum of squares	0.832	1.714	1.212
Second-order Model			
k ₂ (min ^{−1})	0.000327	0.000563	0.000415
R ²	0.952	0.989	0.973
Adjusted R ²	0.916	0.978	0.945
Sum of squares	1.926	1.346	1.564

2.3.2. Kinetic Isotherms

Figure 9 presents Freundlich and Langmuir isotherms best fits of the data obtained from the adsorption of COD. The adsorption was done in the dark until equilibrium was achieved, whereas the photocatalytic degradation was carried out under UV-irradiation for 60 min. The Langmuir isotherm defined by (6) is expressed in a linearized form as (7).

$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \quad (6)$$

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m} \quad (7)$$

where, q_e is the adsorbate at equilibrium (mg/g), q_m is the theoretical maximum adsorption capacity (mg/g), K_L is the Langmuir adsorption constant (L/mg) and C_e is the supernatant concentration at equilibrium (mg/L). From (7), a plot of $\frac{C_e}{q_e}$ vs. C_e gives a straight line (Figure 9b) with slope $\frac{1}{q_m}$ and intercept $\frac{1}{K_L q_m}$. The Freundlich isotherm described in (8) is expressed in a linear form as (9), where K_f and n are the Freundlich isotherm constants representing the adsorbate capacity (mg/L) and intensity, respectively.

$$q_e = K_f C_e^{\frac{1}{n}} \quad (8)$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (9)$$

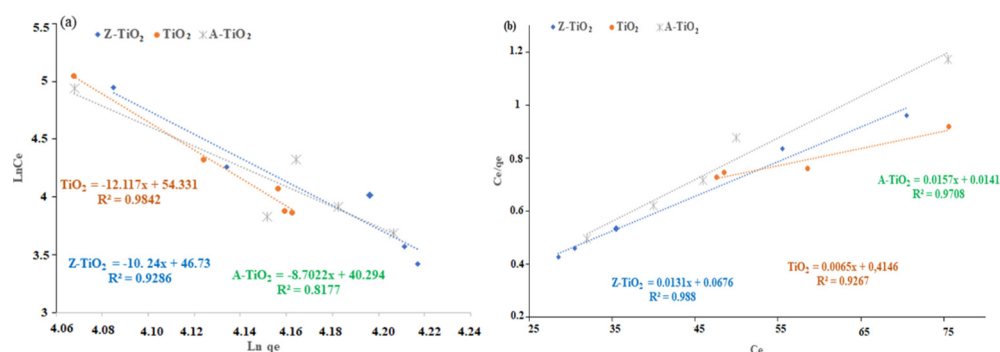


Figure 9. Freundlich (a) and. Langmuir (b) adsorption isotherms for the degradation of COD (367.7 mg/L) using 4 g of Z-TiO₂ > A-TiO₂ > TiO₂.

A plot of $\ln q_e$ vs. $\ln C_e$ gives a straight line (Figure 9a) with $\frac{1}{n}$ as the slope and $\ln K_f$ as the intercept. The Freundlich isotherm (Figure 9a), which is used for non-ideal adsorption containing heterogeneous surfaces with different affinity, was preferred for the TiO₂ adsorption. The order of increasing the deactivated sites towards adsorption in the Freundlich

isotherm (Figure 9a) was $\text{TiO}_2 > \text{Z-TiO}_2 > \text{A-TiO}_2$, whereby TiO_2 fits well with the R^2 value of 0.984. This confirms that adsorption occurred at reactive sites with different strengths of affinity, whereby the adsorption efficiency reduced (Figure 7) as the reactive sites being occupied increased [38,39]. Conversely, the nanocomposites ($\text{Z-TiO}_2 > \text{A-TiO}_2$) were well fitted with the Langmuir isotherms (Figure 9b), which assumes unchanging monolayer adsorption with no interaction between the adsorbates as compared to TiO_2 . However, Z-TiO_2 was found to fit on both Freundlich ($R^2 = 0.929$) and Langmuir ($R^2 = 0.988$) isotherms. This can be attributed to the heterogeneous surface of Z-TiO_2 which, with the presence of the TiO_2 , makes it possible to exhibit different energy or affinity levels [36–38]. Wolf [39], therefore itemized that (i) monolayer adsorption occurs on the adsorbent surface, which has a finite number of similar active sites, (ii) the interaction does not take place between adjacent adsorbed molecules, (iii) the active sites have equal affinities towards the adsorbate molecules and finally (iv) the adsorption process is reversible.

3. Materials and Methods

3.1. Chemicals and Synthetic Effluent

A locally manufactured TiO_2 used in this study was supplied by Huntsman Tioxide, South Africa (Pty). Its crystal structure composes of anatase (75%) and rutile (25%) with a mean particle size of 25 nm, specific surface area and density of $48 \text{ m}^2/\text{g}$ and $4.26 \text{ g}/\text{cm}^3$, respectively. AC with a specific surface area, pore-volume and ash content of $1576 \text{ m}^2/\text{g}$, 0.967, and 3%, respectively, was supplied by a local South Africa industry (RTB Chemicals). Natural zeolite powder (95–98% of clinoptilolite balanced with silica, 125–250) was supplied by Pratley Minerals, South Africa.

Synthetic textile effluent for the experiment was simulated according to a modified protocol of ISO (9887;1992) to mimic a local South African textile effluent based in Kwazulu Natal province. The constituents of the effluent included bromophenol blue (BPB) dye ($505 \pm 15 \text{ mg}/\text{L}$) and other metal salts of ionic and inorganic derivatives such as Zn ($9 \pm 75 \text{ mg}/\text{L}$), Fe ($18 \pm 3 \text{ mg}/\text{L}$), Cu ($25 \pm 53 \text{ mg}/\text{L}$), Mg ($5 \pm 15 \text{ mg}/\text{L}$), Mn ($24 \pm 13 \text{ mg}/\text{L}$), Al ($3 \pm 25 \text{ mg}/\text{L}$), Ca ($33 \pm 8 \text{ mg}/\text{L}$) and Na ($34 \pm 22 \text{ mg}/\text{L}$) dissolved with deionized water (25 L) [42]. All chemicals used were of analytical grade supplied by Sigma-Aldrich, Johannesburg, South Africa.

Nanocomposite Synthesis (A-TiO_2 and Z-TiO_2)

The composites (A-TiO_2 , Z-TiO_2) were synthesized based on a modified low-temperature co-precipitation method [31,35]. First, 30 g of AC and 10 g of TiO_2 was added to 200 mL of deionized water and sonicated (45 kHz at 80°C) for 1 h. After the sonication, the samples were oven-dried at 80°C for 24 h, which resulted in A-TiO_2 . This was then washed with deionized water, filtered, and dried for 1 hour at 110°C . Prior to usage, the A-TiO_2 was calcined at 600°C for 1 h at a ramp speed of $15^\circ\text{C}/\text{s}$. The above procedure was also repeated for the Z-TiO_2 .

3.2. Characterization of Composite (A-TiO_2 and Z-TiO_2)

3.2.1. X-Ray Diffraction (XRD) Analysis

X-ray diffractometer equipment (Bruker AXS, D8 Advance) coupled with PANalytical software (version 6.01) (Empyrean, PRO MPD, Almelo, The Netherlands) operated at 40 kV with a target current of 40 mA was used for the analysis. The samples were closely packed in a rectangular glass cell and scanned with a J-J scan coupled with the copper anode ($\text{Cu-K}\alpha$ radiation: $\lambda = 1.5406 \text{ \AA}$) and Bragg–Brentano configuration. This was carried out at a room temperature with a speed of $0.033^\circ \text{ min}^{-1}$ over a region of 5 to $70 (2\theta)$ [43].

3.2.2. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR spectra of the samples were obtained by using an FTIR-spectrometer (Shimadzu FTIR 8400) in the wavenumber range of $400\text{--}4000 \text{ cm}^{-1}$ with a resolution of

4 cm^{-1} [43]. This method provided information about the molecular structure and functional groups of the composite.

3.2.3. Scanning Electronic Microscope (SEM) Analysis

A Scanning electronic microscope at the University of Cape Town, South Africa (Nova NanoSEM coupled with EDT and TLD detector) was used to analyze the morphological structure of the samples. This was operated at an acceleration voltage of 5 kV with a magnification in the range of 10–50 kx [43].

3.3. Experimental Procedure

The adsorption and photocatalytic experiments were carried out with a modified jar tester reactor, which consisted of six 1 L beakers, stirred at a speed of 150 rpm. At a distance less than 2 cm, the setup was exposed to a UV light of wavelength 400 nm and power rating of 18 W (T8 blacklight-blue bulb 400 nm, 18 W, Philips, and Netherland). Three sets of experiments, as presented in Table 3, were used to investigate the effects of single catalyst load (1–6 g), binary catalyst load (2–4 g), and reaction time (10–60 min). Furthermore, the adsorption capacity of the binary composites was investigated without the UV radiation for the 60 min reaction time, whereas samples were collected in 10 min intervals. The supernatant samples collected with a syringe were filtered through a Whatman filter (Grade 5; $2.5\text{ }\mu\text{m}$). The effluent was initially characterized for COD (367.7 mg/L) and color (458 Pt. Co) using HACH DR 3900 within the wavelength of 455–635 nm (Hach Company, Loveland, CO, USA) as well as turbidity (14.48 NTU) using HI 98,703 portable turbidimeter (Hanna Instruments, Veneto, Italy). Likewise, the Hannah pH-meter (HI98130, Hanna Instruments, Woonsocket, RI, USA) was used to measure the pH (7.5) of the effluent. Based on primary studies, the pH (6.5) was kept constant by adjusting it with 1 M HCl and NaOH. Upon analyzing the treated samples, the contaminants removal efficiency was calculated using the following Equation (10).

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_f}{C_0} \times 100\% \quad (10)$$

where C_0 and C_f are initial and final concentrations of contaminants before and after treatment. The removal rate of COD obtained by the Z-TiO₂ and A-TiO₂ composites contributed to the adsorption and photocatalysis process. All the experiments were carried out in triplicates, and the average values obtained were reported.

Table 3. Adsorption and photocatalysis experimental design.

Category	Investigating Factor	Purpose	Single Material (A, TiO ₂ , and Z)	Binary Composite (A-TiO ₂ and Z-TiO ₂)
1	Single dosage (1–6 g)	Photocatalysis	All	N/A
2	Binary dosage (2–4 g)	Photocatalysis	TiO ₂	All
3	Reaction time ($\pm 60\text{ min}$)	Adsorption and photocatalysis	TiO ₂	All

4. Conclusions

In this study, the treatability of bromophenol blue (BPB) dye in aqueous solution by adsorption and photocatalytic degradation with and without UV light of wavelength 400 nm and a power rating of 18 W, was investigated. This was carried out under different catalyst loads (1–6 g) and reaction times (10–60 min) for the removal of COD, color, and turbidity. Furthermore, nanocomposites (A-TiO₂ and Z-TiO₂) were synthesized, where their physicochemical analyses (SEM, FTIR, and XRD) demonstrated large pore size ($20.8\text{ }\mu\text{m}$) and crystalline size (22–34 nm) with high surface area and chemical stability improvement as compared to the uncoated TiO₂. At the optimal single catalyst load of 5 g, above 70%

removal of color ($Z > \text{TiO}_2 > A$), turbidity ($\text{TiO}_2 > A > Z$) and COD ($\text{TiO}_2 > Z > A$) with their respective increasing order index were observed, whereby TiO_2 demonstrated the highest photocatalytic activity. In comparing the nanocomposite loads (2–4 g), at an optimal load of 4 g, the photocatalytic efficiency increased by 20% with an increasing order index for color and COD removal as $A\text{-TiO}_2 > Z\text{-TiO}_2 > \text{TiO}_2$, whereas $\text{TiO}_2 > Z\text{-TiO}_2 > A\text{-TiO}_2$ was observed for turbidity removal. The hybridized $A\text{-TiO}_2$ and $Z\text{-TiO}_2$ maximized the adsorption and photocatalysis as a viable prospect for remediation of BPB as compared to the TiO_2 . Kinetically, the photodegradation of the COD by $Z\text{-TiO}_2 > A\text{-TiO}_2 > \text{TiO}_2$ were well fitted on the second-order kinetic model, of which $Z\text{-TiO}_2$ had the highest k and R^2 values of $5.63 \times 10^{-4} \text{ min}^{-1}$ and 0.989, respectively. Under the same operating conditions, the Langmuir adsorption isotherms favored the nanocomposites ($Z\text{-TiO}_2 > A\text{-TiO}_2 > \text{TiO}_2$), whereas that of the TiO_2 fitted on the Freundlich isotherm ($\text{TiO}_2 > Z\text{-TiO}_2 > A\text{-TiO}_2$). Above all, hybridization of the photocatalyst with the adsorbent ($Z\text{-TiO}_2$) was found to be potentially effective for photoremediation of wastewater for future work of separation and recovery of the TiO_2 photocatalyst.

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Article

Response Surface Methodology: Photocatalytic Degradation Kinetics of Basic Blue 41 Dye Using Activated Carbon with TiO₂

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Abstract: Water decontamination still remains a major challenge to some developing countries not having centralized wastewater systems. Therefore, this study presents the optimization of photocatalytic degradation of Basic Blue 41 dye in an aqueous medium by an activated carbon (AC)-TiO₂ photocatalyst under UV irradiation. The mesoporous AC-TiO₂ synthesized by a sonication method was characterized by X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) spectroscopy for crystal phase identification and molecular bond structures, respectively. The efficiency of the AC-TiO₂ was evaluated as a function of three input variables viz. catalyst load (2–4 g), reaction time (15–45 min) and pH (6–9) by using Box-Behnken design (BBD) adapted from response surface methodology. Using color and turbidity removal as responses, a 17 run experiment matrix was generated by the BBD to investigate the interaction effects of the three aforementioned input factors. From the results, a reduced quadratic model was generated, which showed good predictability of results agreeable to the experimental data. The analysis of variance (ANOVA), signposted the selected models for color and turbidity, was highly significant ($p < 0.05$) with coefficients of determination (R^2) values of 0.972 and 0.988, respectively. The catalyst load was found as the most significant factor with a high antagonistic impact on the process, whereas the interactive effect of reaction time and pH affected the process positively. At optimal conditions of catalyst load (2.6 g), reaction time (45 min), and pH (6); the desirability of 96% was obtained by a numerical optimization approach representing turbidity removal of 93% and color of 96%.

Keywords: activated carbon; box-behnken design; dye; response surface methodology; TiO₂ photocatalyst



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1. Introduction

With the recent industrial revolution, large volumes of wastewater produced by textile industries containing high levels of pollutants such as dyes and pigments, pose a great threat to human health and the environment. Globally, it has been estimated that about 800,000 tons of dyes and pigments are produced per year, whereby about 25% of them end up in the environment via wastewater discharges [1,2]. This poses a great threat to the environment and a serious health concern. Thus, in the textile industries, during the dyeing processes, large volumes of water are used with the end-product wastewater containing high levels of organics and toxic compounds. These wastewaters, when discharged into water bodies without treatment, end up affecting the dissolved oxygen levels for aquatic life [3].

Subsequently, dyes at concentrations even as low as 1 ppm can contribute to high strength color associated with reduced oxygen dissolution and sunlight diffusion which is

necessary for aquatic life [3–5]. Therefore, there is the need to treat these colored effluents to remove the dyes before discharging them into water bodies [5]. Basic Blue 41 dye (BB41) is a dye typically used for dyeing wool and silk [4,6]. Discharges of effluents with the dye has recently been reported as a public health concern causing eye burns, nausea, vomiting, and diarrhea [2,7].

Finding an effective treatment method for wastewater-containing dyes is paramount as numerous treatment technologies have been established for the discoloration and degradation of dyes in wastewater [8–10]. Some of these techniques include adsorption, reverse osmosis, ultrafiltration, chlorination [9,10] and biological methods, such as aerobic and anaerobic treatments [11]. Nonetheless, most of these traditional techniques eliminate pollutants by simply transferring them from one phase to another without any conversion into environmentally-friendly end products [12,13]. These created intermediates usually require some form of secondary treatment or polishing step. Advanced oxidation processes (AOPs) such as Fenton, photo-Fenton catalytic reactions, UV/H₂O₂, and UV/O₃ are effective methods for treating wastewater-containing dyes [14,15]. Comparatively, the removal of organic contaminants via photocatalytic degradation has proven to be more efficient than these conventional processes as it results in the total mineralization of a wide range of organic pollutants and the fact that it produces harmless compounds such as CO₂ and H₂O [13,15].

Among the numerous semiconductors (TiO₂, ZnO, WO₃, etc.), titanium dioxide (TiO₂) is a promising photocatalyst due to its unique biological and chemical stability, low price and ready availability [9,16–18]. Narayanasamy and Murugesan [19] and Nataraajan, et al. [20], reported photocatalytic degradation of yellow dye using TiO₂ thin films under visible light, where the degradation efficiency decreased with an increase in catalyst load. Similarly, other studies have exposed TiO₂ photocatalysts to UV light for discoloration of different types of dyes in wastewater such as Direct Red 23, Toluidine Blue, Safranin Orange, and Methylene Blue [21–23]. Apart from the catalyst load, several other factors which includes pH, temperature, wavelength, reaction time, and the pollutant concentration can influence the photocatalytic efficiency [24–26]. In response to this fact, optimization becomes an option to improve photocatalytic degradation efficiency. Herein response surface methodology (RSM) is proven as an effectual tool for process optimization with multi-complex operational factors [26–28]. A Box Behnken design (BBD), a type of RSM, has shown to be very efficient as compared to the central composite design (CCD) in estimating the correlation coefficient (R^2) for a specified model, reduced experimental errors and good data fitness in the design, modeling and optimization of a process [24,28].

However, after degradation it is difficult to settle immobilized TiO₂ nanoparticles in solution, so enhancing water clarity requires an extended period of time [21,23]. The probability of this resulting in the formation of non-degradable toxic intermediates seems very high, which is, therefore, increasing environmental and human health concern [18,22]. Ideally, due to the adsorption potential of activated carbon (AC), combining AC and photocatalytic systems [19] is an option for treating pollutants and minimizes the cumulative cost of disposal of wastewater residue. To the best of our knowledge, there is little knowledge in the literature on the use of activated carbon (AC) doped with TiO₂ for photocatalytic degradation of BB41 via RSM optimization techniques. Therefore, this study presents the optimizing of photocatalytic degradation of BB41 in an aqueous medium by AC-TiO₂ photocatalyst under UV light irradiation using RSM. Furthermore, the kinetic degradability of raw TiO₂ and AC-TiO₂ is comparatively explored.

2. Materials and Methods

2.1. Reagents and Materials

2.1.1. Chemicals

Basic Blue 41 (BB41, CAS Number 12270-13-2) of 40% dye with absorbance ($\lambda = 617$ nm) and molecular weight (C₂₀H₂₆N₄O₆S₂) of 482.57 g/mol, hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from Sigma Aldrich (Durban, South Africa).

All chemicals used, unless otherwise stated, were of analytical grade. The locally manufactured TiO₂ supplied by Huntsman Tioxide (Durban, South Africa), is made up of anatase (75%) and rutile (25%) with mean particle size of 25 nm, specific surface area and density of 48 m²/g and 4.26 g/cm³, respectively. Activated carbon (AC) with specific surface area, pore-volume, and an ash content of 1576 m²/g, 0.967, and 3%, respectively, were supplied by a local South African industry (RTB Chemicals, Pietermaritzburg, South Africa).

2.1.2. Synthetized Textile Effluent

A stock solution of 2.5 M BB41 was prepared by diluting 30.16 g of the dye in 5 L deionized water coupled with 20 L of local wastewater [3]. HCl and NaOH were used for pH adjustment, measured with a Hannah pH—meter HI98130 (Hanna Instruments, Woonsocket, RI, USA). The main composition of the synthesized effluent was pH (7.55), COD (176.87 mg/L), color (54.8 Pt.Co) and turbidity (12.28 NTU). The COD and color was measured with a HACH DR 3900 (Hach Company, Loveland, CO, USA), while turbidity was measured by using a HI 98703 Portable Turbidimeter (Hanna Instruments, Veneto, Italy).

2.1.3. AC-TiO₂ Composite Preparation and Characterization

The AC-TiO₂ nanocomposite was prepared by the co-precipitation method assisted with a low temperature of 90 °C [29]. In brief, 30 g and 10 g of AC and TiO₂, respectively was added to 200 mL of deionized water and sonicated at 45 kHz for 1 h. Successive overnight drying at 100 °C resulting in the AC-TiO₂ composite was washed with deionized water/ethanol, filtered, and dried for 1 h at 110 °C to remove any excess impurities. Preceding, the AC-TiO₂ was calcined at 600 °C for 1 h at a ramp speed of 15 s. The mineralogical constituent and phase magnitude of the composite was determined by X-ray diffraction (XRD) equipment (D8 Advance AXS, Bruker, Elmford, NY, USA) coupled with J-J scan and copper anode filter (Cu-K α radiation: $\lambda = 1.5406 \text{ \AA}$) at the rate of 0.033°/min over a range of 5 to 70° (2 θ). Fourier Transform Infrared spectroscopy (FTIR) analysis was carried out to identify the functional groups of the AC-TiO₂ composite. This was carried out with a FTIR 8400 FTIR-spectrometer (Shimadzu, Columbia, MD, USA) in the wave-number range of 300–4000 cm^{−1} with a resolution of 4 cm^{−1}.

2.2. Experimental Procedure

2.2.1. Photocatalytic Degradation

The photocatalytic degradation experiment was carried out in batch-wise mode using six 1 L reactors coupled with UV-T8 blacklight—blue bulb of wavelength 400 nm and power of 18 W, (Philips, Eindhoven, The Netherlands), under constant stirring at a speed of 150 rpm [24]. The reactor was placed in a closed chamber with the UV-light placed at a distance of less than 2 cm. To establish the photocatalytic kinetics, 3 g of each catalyst (TiO₂ and AC-TiO₂) was added to 500 mL dye solution. The irradiation time (10–60 min) was varied while the solution was constantly stirred. At each time interval of 10 min, supernatant samples were collected with a syringe and filtered through a Whatman filter (Grade 5; 2.5 μm). The kinetics degradation efficiency was monitored in terms of the COD removal, by using Equation (1). To estimate the rate of reaction constants for the first-order kinetic model (2), a plot of $\ln \frac{C_0}{C}$ vs t was developed:

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_f}{C_0} \times 100 \quad (1)$$

$$\ln \frac{C_0}{C} = k_1 t \quad (2)$$

where, k_1 is the first-order rate constant (min^{−1}), C_0 is the initial COD concentration, t is time and C_f is the concentration at the specified time.

2.2.2. Design of Experiments

The photocatalytic efficiency (Figure 1) was investigated based on the experimental design with the three operating factors (Table 1). This was carried out by using the Box-Behnken design (BBD) by Design-Expert software (version 11.1.0.1) (Stat-Ease, Inc., MN, USA). The BBD is a factorial combination with a minimum of three factors that were studied under the randomized response surface methodology. The effect of three independent factors such as A: catalyst load (2–4 g), B: reaction time (15–45 min), and C: pH (6–9) was examined on photocatalysis with turbidity (Y_1) and colour (Y_2) as the responses. All the experiments were carried out in duplicate and average values obtained are reported.

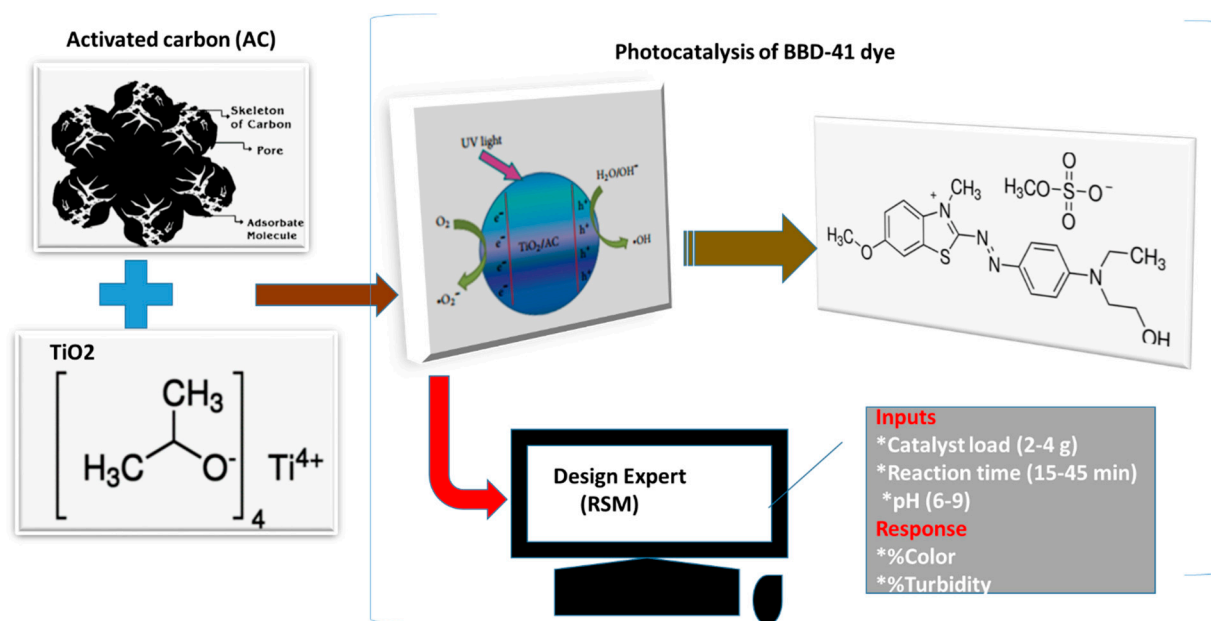


Figure 1. Schematic representation of the photocatalytic process via response surface methodology.

Table 1. Box-Behnken design matrix for input variables.

Factor	Low Level (−1)	Medium (0)	High (+1)	Ref
A: Catalyst load (g)	2	3	4	[24]
B: Reaction time (min)	15	30	45	[26]
C: pH	6	7.5	9	[28]

From Table 1, the total number of the experiments was estimated by Equation (3). Seventeen experimental runs were obtained according to a three-level scale such as low (−1), medium (0), and high (+1) coupled with five center points (Cps). The responses (Y_1 and Y_2) were expressed as a function of the input variables (A, B, and C) by fitting the data obtained on a polynomial quadratic model (4). The empirical model developed depicts the influence of the input variables on the response within the design space [24]. Analysis of variance (ANOVA) was employed to evaluate the significance of the results statistically by considering $p < 0.05$ [26]:

$$NE = k^2 + k + Cp \quad (3)$$

where NE , k and Cp represents the total number of experiments, the number of factors, and the replicated number of center points. To analyze the pivotal relationship between the dependent and independent variables, the polynomial quadratic expressed in Equation (4) was utilized:

$$Y = \beta_0 + \sum_{i=1}^K \beta_i x_i + \sum_{i=1}^K \beta_{ii} x_i^2 + \sum_{i=1}^{K-1} \sum_{j=2}^K \beta_{ij} x_i x_j + \varepsilon \quad (4)$$

where, Y is a response variable, β_0 is a constant, β_i is the regression coefficient, k is the number of independent variables, and ε is the unknown error constant. Also, the coded values of the independent variables were expressed by Equation (5):

$$x_i = \frac{X_i - X_{i0}}{\Delta X_i}, i = 1, 2, 3, \dots k \quad (5)$$

where, x_i are the coded values and X_i the real values of independent variables, X_{i0} the real value in the center plane, and ΔX_i the step change. The model's overall prediction efficiency is commonly assessed by the coefficients of determination (R^2), which can be calculated by Equation (6):

$$R^2 = \frac{SS_{\text{residual error}}}{SS_{\text{total}}} \quad (6)$$

This coefficient is used to measure the total response variation of predicted values from the mean response. However, the addition of variables to the model increases R^2 values irrespective of its statistical significance.

3. Results and Discussion

In this study, photocatalytic degradation of BB41 dye with a hybridized photocatalyst (AC-TiO₂) was optimized using response surface methodology. This feasibility study was carried out to strengthen the knowledge of using TiO₂ for photocatalysis and absorption processes. The results obtained are presented under Sections 3.1–3.3, respectively, denoting the physiochemical properties of the AC-TiO₂ composite, photocatalytic kinetics, and response surface methodology.

3.1. Physiochemical Properties of the Photocatalyst

Figure 2 presents the physiochemical results obtained. The XRD (Figure 2a) and FTIR (Figure 2b) spectra of the TiO₂ and AC-TiO₂ composite, confirm the successful impregnating of the TiO₂ on the AC surface [15,30]. The crystalline phase of the catalysts (TiO₂ and AC-TiO₂) as observed by the XRD (Figure 2a) was seen to be very prominent, with anatase corresponding to the JCPDS Files No. 21-1272. At the scanning range of $2\theta > 2\theta > 70^\circ$, the peaks observed at various diffractions of 27.47° , 36.07° , 37.80° , and 69.0° assigned to (001), (021), (210) and (220) reflects the rutile phase of TiO₂. Whereas, the reflections of the peaks at 2θ of 25.4° , 48.02° , 50° , 54.19° , 55° and 62.72° were dispensed to (101), (110), (200), (211) (105) and (103) of the anatase plane. The rutile phase intensity is considerably less than that of the anatase phase [29,30]. The average crystalline size (28 nm to 22 nm) was then determined by Scherrer's equation (Equation (7)) with the crystalline plane of (101) and (001) for anatase and rutile, respectively:

$$D = \frac{K\delta}{\beta \cos \theta} \quad (7)$$

where δ is the wavelength of X-ray radiation ($\text{CuK}\alpha = 0.15406 \text{ nm}$), k is a constant taken as 0.9. β is the line width at half maximum height (FWHM) of the peak (determined using Origin software), and θ is the diffraction angle of the most intense peaks of rutile (27.47°) and anatase (25.4°).

Figure 2b presents the FTIR spectra ranged with a wavenumber of $400\text{--}2200 \text{ cm}^{-1}$. The spectrum also reveals the adsorption bands between the reactive hydroxyl groups and the hydrophobic and hydrophilic nature of TiO₂ [12,15]. This is associated with the vibration and stretching modes of the TiO₂ and different oxygenated functional groups. The peaks at $1400\text{--}1600 \text{ cm}^{-1}$ represent the stretching of hydroxyl (OH) and carboxyl (C=O) groups which might have been caused by either water moisture or the titanium carboxylate [8,30]. There is evidence of a shift in the OH vibration band towards a lower wavenumber ($<800 \text{ cm}^{-1}$) of the AC-TiO₂ spectra as compared to the TiO₂ [15,29]. This might be due to the acid-base interaction of the OH group used in synthesizing the AC-

TiO₂ composite [29]. Lastly, the broad stretching peaks around 400–600 cm^{−1} is also the representation of the TiO₂ bonding in the composite [8,12]. The surface morphology of the AC-TiO₂ is represented by the SEM (Figure 2c) and EDX (Figure 2d) images. With scanning microscopy magnification (Figure 2c) of 50 kx and binding energy of 5 kV, grain size of 4.15 µm was viewed under the scale of 1 µm and working distance (WD) of 6.11 mm. EDX image (Figure 2d) under scale of 1mm revealed the TiO₂ spectra (Figure 2e) at the binding energy of 0.5, 4.5 and 5 keV. This affirmed the success of incorporating the TiO₂ with the AC. Also the elemental composition of the composite (AC-TiO₂) was distinctively defined as Ti (41.88%) > C (32.89%) > O (21.2%) > Si (2.07%) > Al (1.96%).

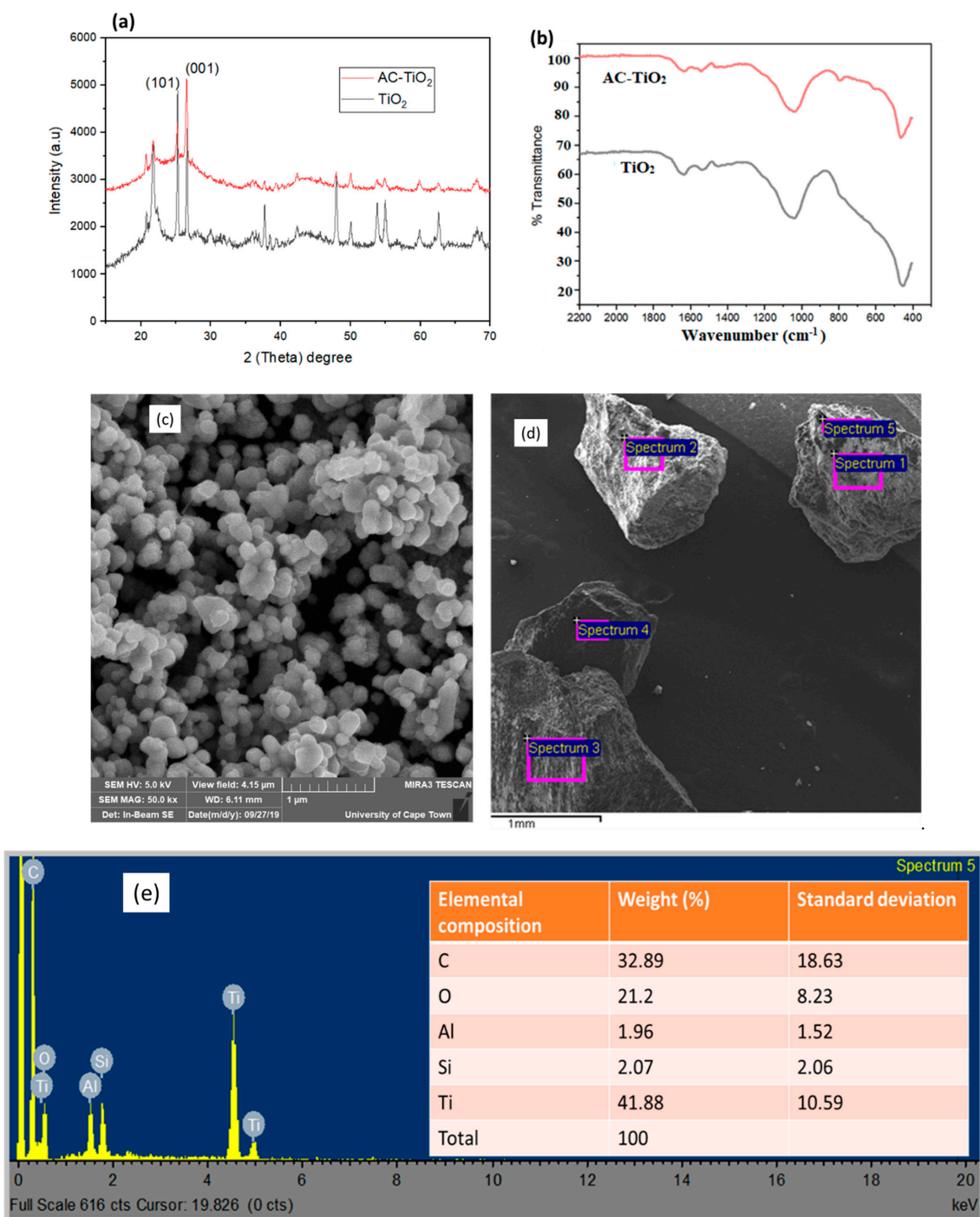


Figure 2. Spectra of (a) XRD and (b) FTIR analysis for TiO₂ (black) and AC-TiO₂ (red); (c) SEM and (d) EDX image of AC-TiO₂ and (e) EDX spectra and elemental composition of AC-TiO₂.

3.2. Photocatalytic Degradation Kinetics

Figure 3 presents the comparative effects of TiO_2 and AC- TiO_2 (Figure 3a), as well as their photocatalytic kinetics (Figure 3b) on the removal of COD from the effluent. Chemical oxygen demand (COD) as the organic strength of effluent, in this instant, was used to measure the efficacy of the catalyst. This is also attributed to the amount of oxygen required for the oxidation of the dye into CO_2 and H_2O , with the possible reactions presented in (8) and (9) [31,32]. To estimate the reduction values of the COD, the before and after treatment results obtained were used. Figure 3 denotes the mineralization of the dye organics (COD) along with an increase in the reaction time (10–60 min). However, rapid degradation was observed after the 30 min irradiation (Figure 3a), where it became stabilized within 40–50 min with a slight drift towards 60 min. The maximum degradation of 93% and 96% COD removal, respectively, by TiO_2 and AC- TiO_2 was obtained at the 50 min irradiation:

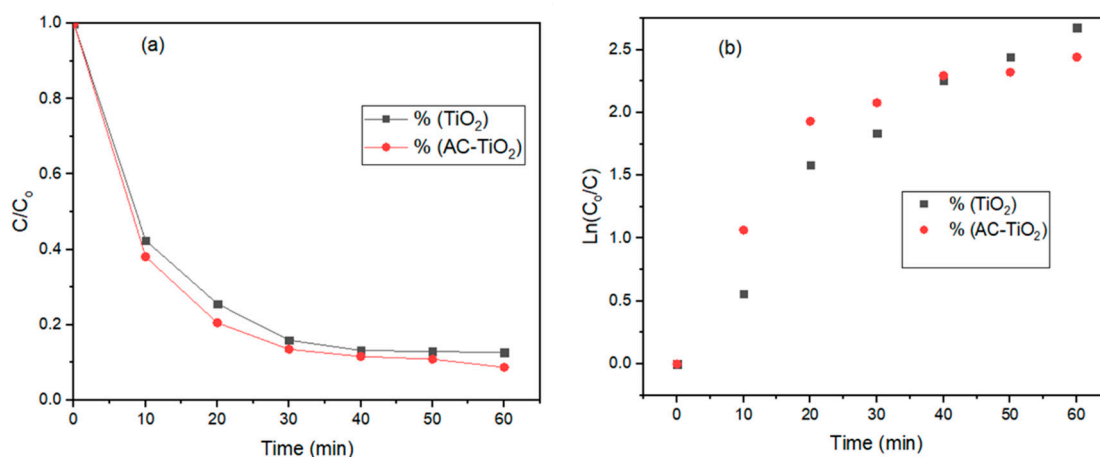
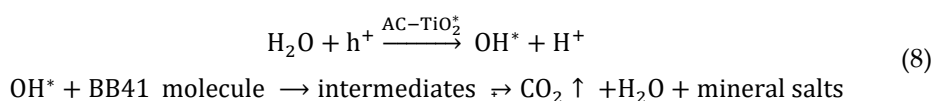


Figure 3. Comparative effect of TiO_2 (black) and AC- TiO_2 (red) on (a) decomposition of COD and (b) First-order kinetic model.

Consequently, activation of TiO_2 nanoparticles by the UV-light produced reactive species (OH^*), which facilitated the degradation of organics in the solution [12,33]. As shown in Figure 3b, the degradability followed the first-order kinetics for irradiation time less than 60 min. The kinetic rate constants were estimated as 0.0322 min^{-1} and 0.0366 min^{-1} for TiO_2 and AC- TiO_2 , respectively, at regression coefficient (R^2) values of 0.889 and 0.9188. The recorded residual sums of squares (SSR) were 0.7704 and 0.691 for TiO_2 and AC- TiO_2 , respectively. It was found that the degradability of COD was a function of the irradiation time, thus confirming previous kinetic studies on the degradation of organic pollutants in wastewater that generally followed Langmuir-Hinshelwood (L-H) kinetics [12,31].

3.3. Response Surface Methodology (RSM)

The experimental runs, as mentioned earlier, were designed by the RSM via the BBD to investigate the key operating parameters such as catalyst load (A), reaction time (B), and pH (C). The BBD matrix obtained with 17 randomized sets of experimental runs, along with the response and predicted results obtained, is presented in Table 2. The maximum removal of the contaminants (colour and turbidity) obtained was within the range of 90–95% for the actual results with a deviation of less than 5% from the predicted values. The experimental data (Table 2) was fitted to a reduced quadratic model (Equations (10) and (11)) and their

statistical significance and validity were tested via the analysis of variance (ANOVA) detailed under Section 3.3.1. The model Equations (10) and (11) are expressed with the actual values of the input parameters (A, B, C), their interaction (AB, AC), and quadratic (B^2 , C^2) terms as a function of the responses (Y_1 and Y_2). The positive sign represents the synergistic effect of the term on the response, whereas, the negative sign points out an antagonistic effect. In this view, the increasing order of the effect of the terms for the removal of colour follows $AC > B^2 > AB > B > A > C$, whereas that of the turbidity removal is $AC > AB > B > C^2 > A > C$. Also, the optimal values of the parameters are obtained by estimating the regression equation and the analysis of the surface response:

$$\text{Color } (Y_1) = 148.575 - 8.4385A - 1.04B - 8.668C - 0.1631AB + 2.288AC + 0.0256B^2 \quad (9)$$

$$\text{Turbidity } (Y_2) = 143.429 - 9.3017A - 0.2023B - 9.472C + 0.0876AB + 2.667AC - 1.807C^2 \quad (10)$$

Table 2. Results of Box-Behnken design with experimental and predicted values.

Run	Factor 1	Factor 2	Factor 3	Y ₁ : Colour (%)		Y ₂ : Turbidity (%)	
	A: Catalyst Load (g)	B: Reaction Time (min)	C:pH	Exp	Pred	Exp	Pred
1	2	15	7.5	85	86.32	86	86.16
2	3	30	7.5	86.88	87.00	90.04	90.04
3	4	30	9	90.87	91.59	92	92.51
4	2	30	9	77.31	77.00	80	79.54
5	3	45	9	88.98	90.22	88.08	88.74
6	3	30	7.5	86.88	87.00	90.04	90.04
7	2	30	6	90.3	89.28	92	91.96
8	3	30	7.5	86.88	87.00	90.04	90.04
9	4	30	6	90.13	90.13	88	88.93
10	4	15	7.5	98.61	98.90	89.31	88.50
11	2	45	7.5	91.92	91.50	85	85.35
12	3	30	7.5	86.88	87.00	90.04	90.04
13	3	45	6	95	95.63	94.02	93.16
14	4	45	7.5	95.8	94.35	93.57	92.95
15	3	30	7.5	86.88	87.00	90.04	90.04
16	3	15	6	95.09	95.31	90.9	91.34
17	3	15	9	91.73	89.90	87.18	86.92

3.3.1. Analysis of Variance (ANOVA)

The model robustness in this study is evaluated by both the coefficient of determination R^2 and adjusted- R^2 with an estimated difference of less than 0.2 (Table 3). The fit statistics, as presented in Table 3, show that the predicted R^2 of 0.886 and 0.893 for color and turbidity, respectively, were in reasonable agreement with the adjusted R^2 of 0.966 and 0.975, where their difference is less than 0.2, suggesting good predictability of the models. Considering the acceptable threshold value of R^2 , which should be greater than or equal to 0.8, it becomes more relevant when it is closer to 1 [27,28]. The statistical significance ($p < 0.05$) of the model and its validity are tested by using the ANOVA (Tables 4 and 5), with additional information such as the Fisher variation ratio (F-value), adequate precision, coefficient of variance (CV), probability value (Prob > F) and lack of fit. As shown in Tables 4 and 5, the F-value and Prob > F values for the models and their independent parameters were found to be significant because of their p -values < 0.05. Also, there is only a 0.01% chance that an F-value this large could occur due to noise. Therefore, model terms with their p -values > 0.05 (insignificant), were not considered via model reduction to improve the models because they are not required to support the model hierarchy [34].

Table 3. Analysis of variance (ANOVA) results for the response quadratic models.

Parameter	Colour	Turbidity
Standard deviation	1.06	0.63
Mean	89.71	89.19
Coefficient of variance (CV, %)	1.18	0.71
Coefficient of determination (R^2)	0.972	0.988
Adjusted R^2	0.966	0.975
Predicted R^2	0.886	0.893
Adequate precision	32.33	33.67

Table 4. Analysis of variance (ANOVA) results for color quadratic models.

Source	Sum of Squares	Degree of Freedom	Mean Square	F-Value	p-Value	
Model	389.44	6	64.91	58.28	<0.0001	significant
A-Catalyst load	119.20	1	119.20	107.02	<0.0001	
B-Reaction time	0.2016	1	0.2016	0.1810	0.0495	
C-pH	58.48	1	58.48	52.51	<0.0001	
AB	23.67	1	23.67	21.25	0.0010	
AC	47.13	1	47.13	42.31	<0.0001	
B ²	140.77	1	140.77	126.39	<0.0001	
Residual	11.14	10	1.11			Non-significant
Lack of Fit	11.14	6	1.86	12.32	0.132	
Pure Error	0.0000	4	0.0000			
Cor Total	400.58	16				

Table 5. Analysis of variance (ANOVA) results for the turbidity quadratic models.

Source	Sum of Squares	Degree of Freedom	Mean Square	F-Value	p-Value	
Model	179.76	6	29.96	75.42	<0.0001	significant
A-Catalyst load	49.40	1	49.40	124.36	<0.0001	
B-Reaction time	6.62	1	6.62	16.68	0.0022	
C-pH	38.98	1	38.98	98.14	<0.0001	
AB	6.92	1	6.92	17.41	0.0019	
AC	64.00	1	64.00	161.11	<0.0001	
A ²	13.83	1	13.83	34.82	0.0002	
Residual	3.97	10	0.3972			Non-significant
Lack of Fit	3.97	6	0.6621	10.52	0.154	
Pure Error	0.0000	4	0.0000			
Cor Total	183.73	16				

3.3.2. Effects of the Factors and Their Interaction on the Responses

To study the interactive effects of the factors on the response, first one factor was varied at a time while keeping the other two process variables constant. Figure 4a–f shows the visual representation effects of each factor on the response. Figure 4a,d elucidate the effects of the catalyst dosage (2–4 mg/L) on the decrease of colour and turbidity, respectively. Decomposition efficiency increases with an increase in catalyst load up to 3.5 mg/L, beyond which there is a gradual reduction in terms of the removal of turbidity (Figure 4b). Thus, the more active sites made available in turn increases the rate of radical formation which increased the efficiency [35,36]. However, the overdosed catalyst load contributed to the turbidity of the solution by retarding the light penetration to activate the catalyst for collision with the colloids [35,36]. This resulted in the reduction of the turbidity efficiency (Figure 4b). Figure 4b,e, present the development of irradiation time which caused high organics degradation in terms of colour and turbidity, respectively. Mineralization of colour became less efficient within 20–30 min before increasing at 45 min, which might be due to the probability of slow reaction and deactivation of the active sites

caused by the complex intermediaries with OH radicals [35,37]. Conversely, increasing the pH (6–9) decreased the colour (Figure 4c) and turbidity (Figure 4f) efficiency. This affirms that pH affects the pollutant charge neutralization with higher efficiency in the acidic medium ($\text{pH} < 6$) than the neutral ($\text{pH} = 7$) and alkaline conditions ($\text{pH} > 7$) [8,27].

Figures 5 and 6 also confirmed that the interaction relationship between the catalyst load and pH has a significant impact on the photocatalytic activity on both responses (colour and turbidity). The three-dimensional response (3D) surface (Figure 6) was plotted based on the models (10) and (11) predicted removal efficiency, whereas, the reaction time was kept constant. This confirms that the interactive effects (AC) are predominant in comparison with the individual (A and C) and quadratic effects (A^2 , C^2). This is in agreement with other reported studies, whereby the catalyst dosage can be considered as the most influential factor.

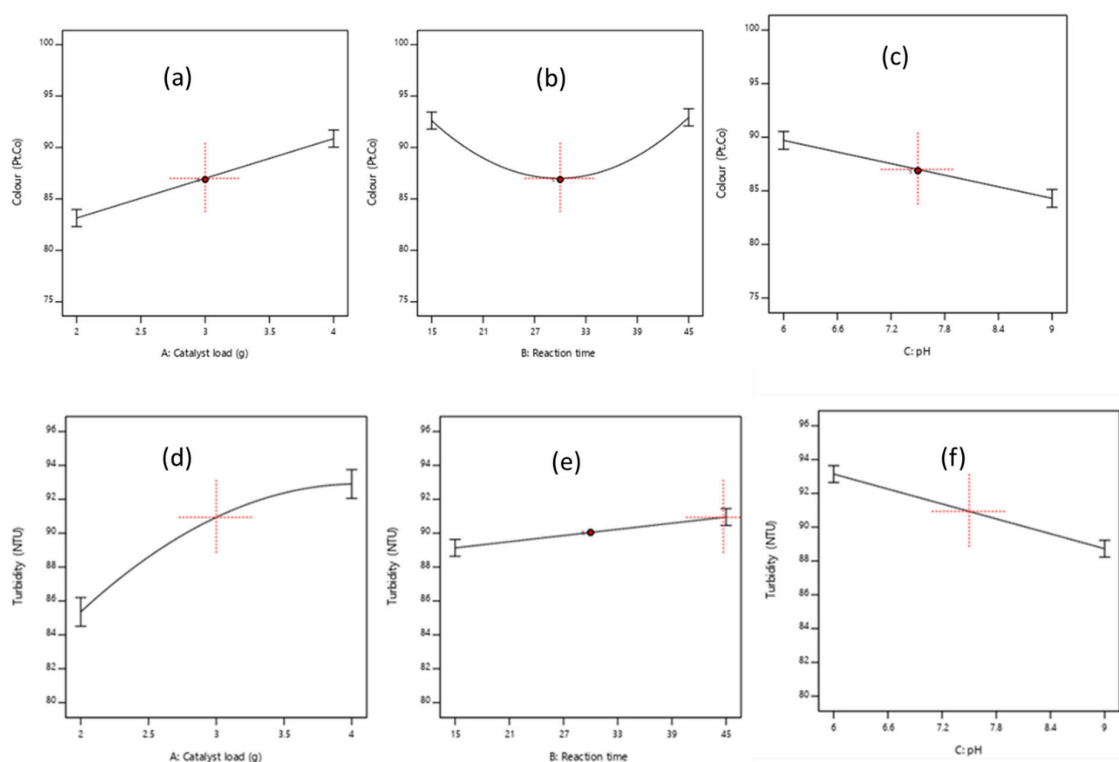


Figure 4. Response representation of individual factors effects on color (a–c) and turbidity (d–f) removal.

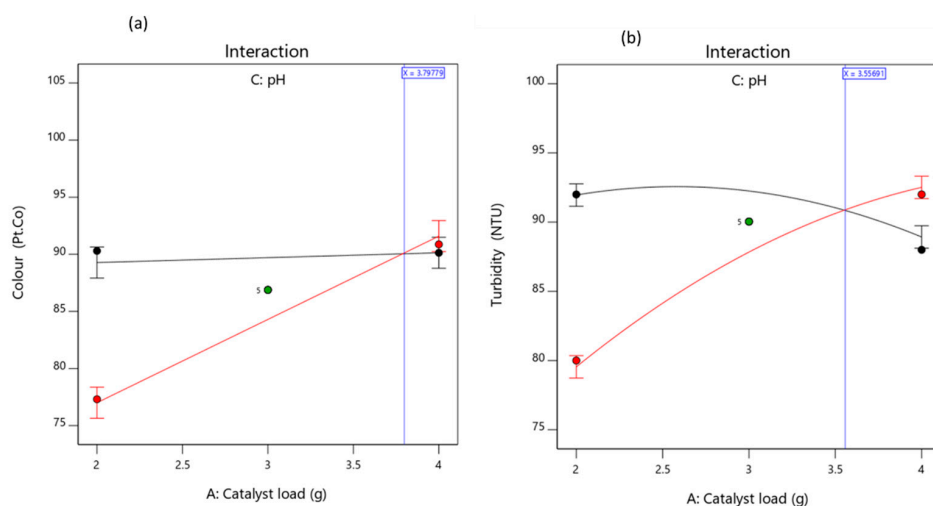


Figure 5. Interactive effect of catalyst load and pH on (a) color and (b) turbidity removal.

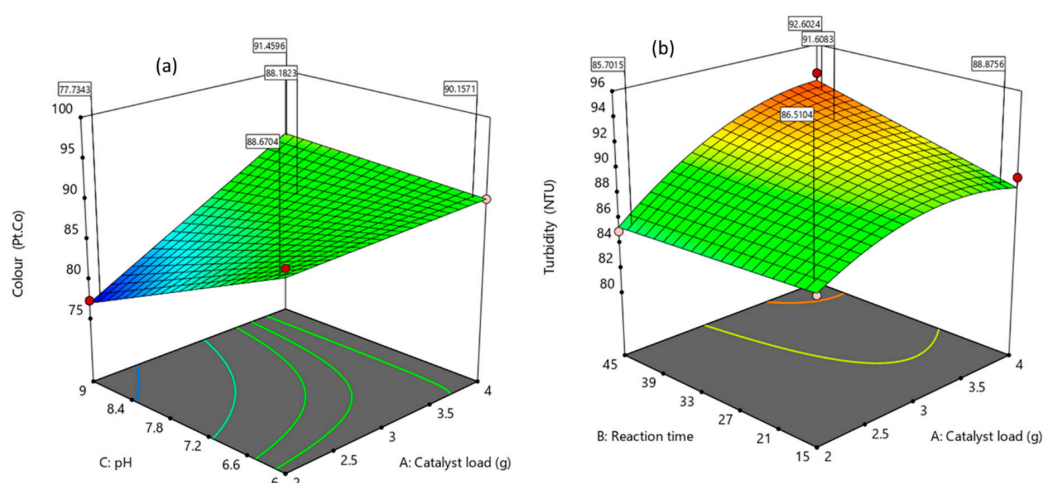


Figure 6. Response surface 3D plot of catalyst load and pH effects on (a) color and (b) turbidity removal.

3.3.3. Numerical Optimization

To maximize the pollutant abatement, the Design-Expert software numerical optimization was carried out by setting individual factor values within their respective range such as catalyst load (2–4 g), reaction time (15–45 min) and pH (6–9), whereas the responses (colour and turbidity) were set at maximum with 95% confidence level. The desirability function approach was carried out, where the optimized conditions obtained are presented in Figure 7. In Table S1, out of 63 sets of solutions obtained, the most desirable (95.4%) and optimum condition selected is presented in Figure 7. Thus an optimum catalyst load of 2.6 g, a reaction time of 45 min and pH of 6 that resulted in 96.5% and 92.9% of colour and turbidity removal, respectively, was established. Additional optimum conditions with parametric constraints and desirability are presented in Table S1. Furthermore, the optimum conditions obtained were confirmed and verified experimentally which was closer to the predicted results with less than 2% deviation. This is agreeable to other studies suggesting RSM is economically viable for experimental optimizations based on its predictability with precision [27,28].

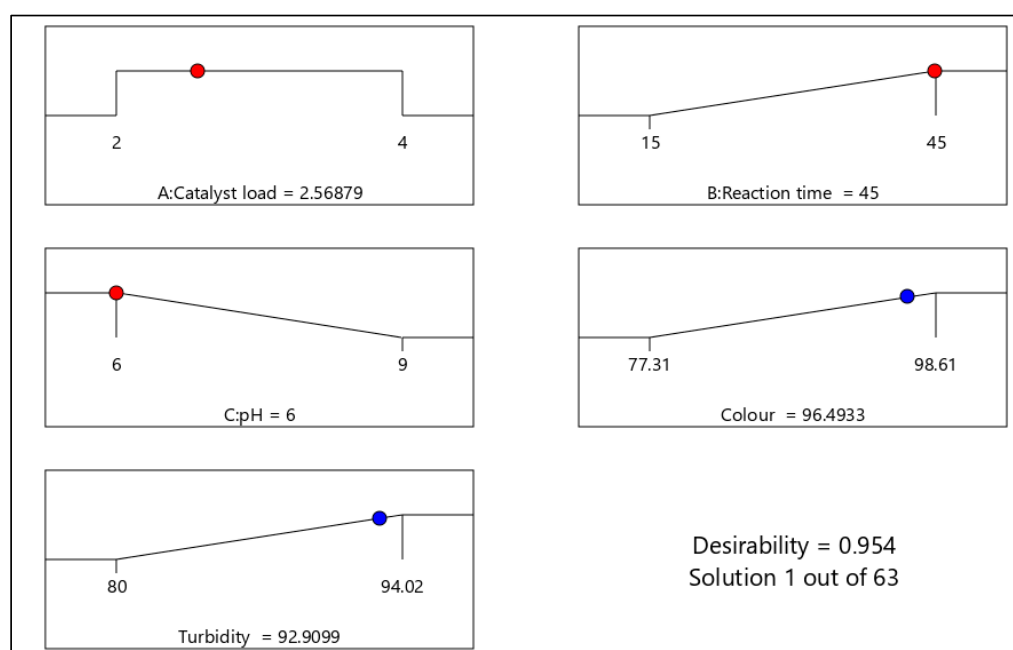


Figure 7. Ramp plot of numerical optimized conditions with the desirability of 95%.

4. Conclusions

This study presented a co-precipitate of TiO₂ impregnated on activated carbon (AC-TiO₂) as a potential photocatalyst for wastewater treatment by optimizing the operating conditions (catalyst load, reaction, and pH) via response surface methodology (RSM). The crystal structure and functional groups were revealed by XRD and FTIR analysis. Furthermore, comparative performance and kinetic degradability between the AC-TiO₂ and raw TiO₂ were explored based on chemical oxygen demand (COD) reduction. First-order kinetic rate constants were estimated as 0.0322 min^{−1} and 0.0366 min^{−1} for TiO₂ and AC-TiO₂, respectively, with regression coefficient (R^2) values of 0.9589 and 0.9828.

Results obtained by the Box-Behnken design (BBD) matrix were employed for modelling and optimization of the aforementioned operating conditions on photocatalytic degradation of colour and turbidity. A reduced quadratic model was developed as a function of the three input parameters and the responses were seen to be highly significant ($p < 0.005$). The models showed good predictability with a high correlation between the experimental values and the model-predicted values at a 95% confidence level. Catalyst load and pH was found to be the factors with the most influential impact on the response. The optimal conditions were found at a catalyst load of 2.6 g, reaction time of 45 min, and pH of 6, respectively, for 96.5% and 92.9% of colour reduction and turbidity removal via a numerical optimization. The optimal conditions were verified and confirmed experimentally to show less than 2% deviation. This confirms the use of BBD via RSM as viable for optimization and modelling photocatalytic systems in wastewater settings.

Supplementary Materials: The following are available online, Table S1. Numerical optimized conditions.

Author Contributions: Conceptualization S.R. and E.K.T.; methodology, E.K.T., E.O.E. and D.A.-S.; validation, E.K.T., and E.K.A.; formal analysis, E.K.T.; resources, E.K.T. and S.R.; writing—original draft preparation, E.K.T., and E.K.A.; writing—review and editing, D.A.-S., E.O.E., and S.R.; supervision, S.R.; project administration, E.K.T. All authors have read and agreed to the published version of the manuscript.

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Article

Kinetics and Nanoparticle Catalytic Enhancement of Biogas Production from Wastewater Using a Magnetized Biochemical Methane Potential (MBMP) System

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Abstract: This study presents magnetized nanoparticles (NPs) as a catalyst to accelerate anaerobic digestion (AD) potential for clean and ecofriendly energy (biogas) from wastewater settings. The effects of iron oxides (Ms) and aluminum sulphate (Alum) were investigated using two chronological experiments: (i) the Jar test technique to generate residue slurry as organic fertilizer potential and (ii) a magnetized biochemical methane potential (MBMP) system for biogas production at mesophilic conditions for 21 days. X-ray diffraction and Fourier Transform Infrared spectroscopy were carried out to establish the Ms Crystallite and active functional groups respectively. Scanning electronic microscopy coupled with energy dispersive X-ray spectrometer and elemental analysis were used to track and confirm NPs inclusion after the post-AD process. Coagulation at 50 mg/L and magnetic exposure time of 30 min showed above 85% treatability performance by Ms as compared to 70% for Alum. Owing to the slow kinetics of the AD process, additional NPs content in the digesters coupled with an external magnetic field improved their performance. Cumulative biogas yields of 1460 mL/d > 610 mL/d > 505 mL/d for Ms > Control > Alum respectively representing 80% > 61% > 52% of CH₄ were attained. The modified Gompertz model shows that the presence of NPs shortens the lag phase of the control system with kinetics rate constants of 0.285 1/d (control) to 0.127 1/d (Ms) < 0.195 1/d (Alum).

Keywords: anaerobic digestion; biogas; catalysis; coagulation; ferromagnetite (Fe₃O₄); wastewater

1. Introduction

With the global concern about freshwater resources depletion, the purification of water and wastewater comes in handy to meet the necessities of humankind and other living organisms. This has sparked significant interest in developing wastewater treatment technologies worldwide, owing to the rapid industrialization and environmental pollution accompanying it [1–4]. The swift utilization of nanomaterials (like coagulants, nanotubes, nanowires, metals) and generation of a huge amount of pollutants such as heavy metals in the wastewater setting cannot be excluded from this industrial evolution [5–7]. However, recovery of valuable products such as energy from wastewater and landfills is gaining much attention through worldwide application of the anaerobic digestion (AD) process [3,4,8]. Owing to the increasing rate of municipality solid wastes and biosolids, the AD process has been one of the cost-effective technologies for biomass conversion to biogas and degradation of high strength organic waste [4]. In spite of managing zero-waste, recovering valuable potentials from wastewater as a renewable energy source (biogas) has attracted considerable attention, aimed at achieving green

energy, clean water and sanitation towards the United Nations sustainable development goals for the year 2030 [9].

Recent advancing technologies such as membrane filtration, ion exchange, magnetic coagulation, adsorption and advanced oxidation processes are emerging to eliminate the contaminants from the wastewater before discharging to the water bodies [4,7,10]. In response, nanotechnology has drawn the attention of many researchers for biotechnological, pharmacological and separation applications [6,10,11]. However, there is limited information on its application in bioenergy from biomass [4,12], and wastewater treatment plants (WWTPs) [6,11]. This has raised global environmental concern of antibacterial resistance and inhibition effects of nanoparticles (NPs) in wastewater settings, especially with the biological systems [13]. Furthermore, the use of fossil fuels poses negative impacts on the environment, contributing to global warming [4,12,14], whereby the need for alternative and renewable sources of energy have become a global concern [14–16].

Biogas (methane and carbon dioxide), which is produced biologically in an oxygen-depleted environment during anaerobic digestion (AD) of organic materials, seems very promising [4,16]. In wastewater settings, biogas is considered as the by-products of AD of sewage sludge treated for the reduction of odors, eutrophics, and landfill residues [16]. Apart from industrial wastewater and that from slaughterhouses and municipalities, biogas can also be produced from high strength organic wastes including water hyacinth, cow dung, poultry litter and breweries, anaerobically [4,17–19]. However, there is still ongoing debate about the use of aluminum and iron-based coagulants, and their safety and toxicity towards biological systems [6,20]. Thus, there is a high possibility of the accumulated nanomaterials to affect the treatability performance of the downstream process and to incur costs of landfill disposal [20,21], notwithstanding the occurrence and transportation routes (Figure 1) of emerging contaminants (nanoplastics, pharmaceuticals, antibiotics) ending up in the WWTP [7,8,16]. These undergo a series of transformations through the different unit operations from physical, chemical to biological treatment processes [4]. Similarly, in the AD process, different domains of microorganisms contribute to the degradation of organic compounds into biogas in sequential steps including hydrolysis, acidogenesis, acetogenesis and methanogenesis [16,17].

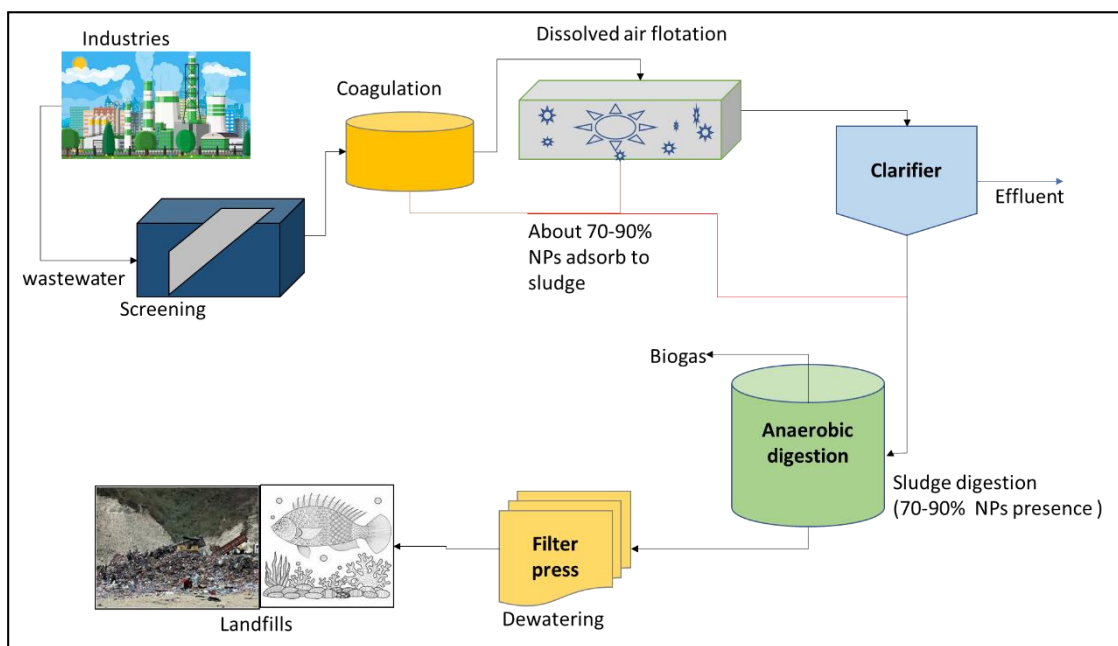


Figure 1. Schematic flow of a conventional wastewater treatment plant.

As a known fact in wastewater settings, there is a high probability of NPs trapped in sludge to be toxic and inhibitory to microbial organisms during biogas production [4,14,22]. A possible way to

overcome this problem is to use carrier materials that can provide large surface areas for microbial growth [23,24]. Brar et al. [23] demonstrated that iron-rich primary sludge increased biogas production in wastewater sludge as compared to iron-poor sludge. On the contrary, the limited effect and pathway of Fe^{3+} - and Al^{3+} -based coagulants on biogas production is not well known [22,23,25]. Therefore, this study aimed to examine the magnetic effect on coagulation using magnetic-based coagulants (Ferro magnetite (Ms) and Alum), and also their coagulated sludge effect on biogas production by the magnetized biochemical methane potential (MBMP) system. In addition, modified Gompertz and first-order Kinetic models of biogas production were compared. This was carried out to improve the AD process, bioenergy, and sludge stability as well as heavy metals removal from wastewater settings.

2. Results

This study investigated coagulation and anaerobic digestion of wastewater as a means to facilitate integration of physiochemical and biological treatment processes with benefits of biogas production and reduction of landfills complexity. The results obtained are presented under Sections 2.2 and 2.3 for coagulated sludge production and BMP respectively, whereas a detailed discussion is presented in Section 3.

2.1. Characterised Ms

The crystalline structure of the Ms is characterized by XRD, with distinctive diffraction peaks as shown in Figure 2. The X-ray diffraction analysis (Figure 2) revealed Ms as the principal dominating component with other phases of hematite (H) and wustite (W). The iron oxide ($\text{Ms} > \text{H} > \text{W}$) phases identified are in agreement with the reference line pattern of JCPDS file No. 19-0629 [5,6]. Their respective peaks–signal index and interlinear (hkl) spacing values are presented in Table 1. The peaks identified (Figure 2) were furthermore analyzed by Fourier Transform Infrared (FTIR) spectroscopy to understand how the Ms interacted with the active functional groups. In Figure 3, even though the FTIR was evaluated within a range of $400\text{--}4000\text{ cm}^{-1}$, the disappearing region represents amines and other radical groups which were bonded to the Ms and sludge surface (Figure 2). In addition, Ms in water could cause water-splitting with more negatively charged ions, resulting in excessive OH groups appearing on the surface of the nanoparticles [6,24,26].

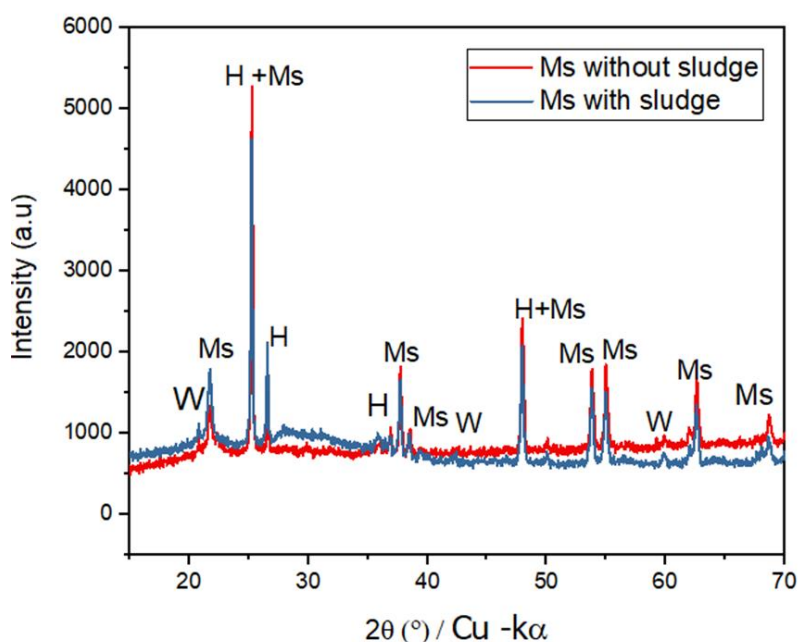
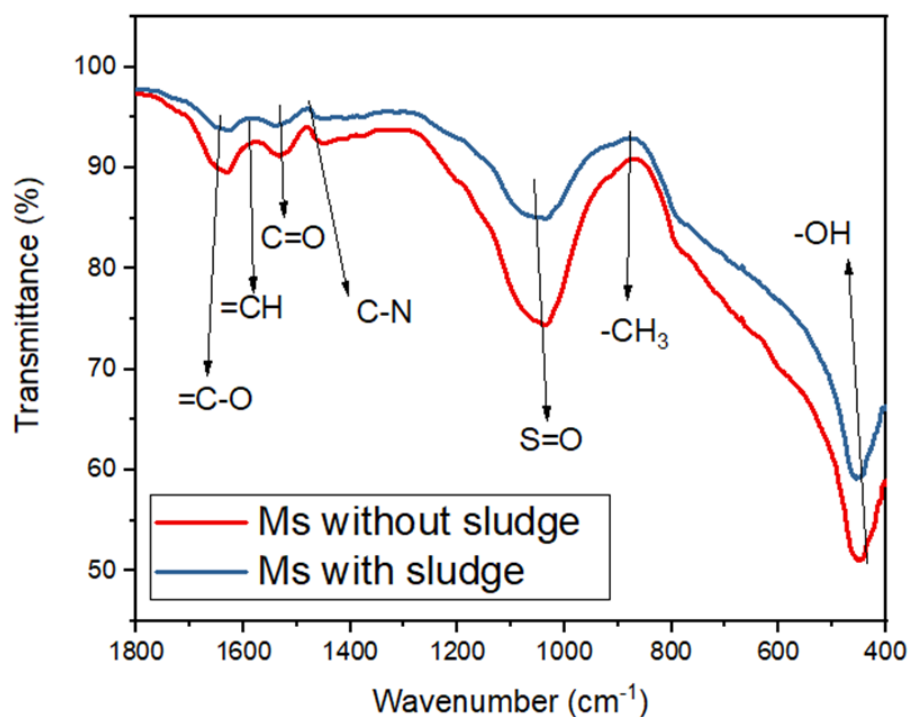


Figure 2. X-ray diffraction iron oxides (Ms) profile with and without sludge corresponding to JCPDS file No. 19-0629 reference line patterns; **Ms** magnetite (Fe_3O_4), **H**: hematite ($\alpha\text{-Fe}_2\text{O}_3$) and **W**: wustite (FeO).

Table 1. X-ray diffraction positions (2θ) and crystal structure of the iron oxide phases identified.

2θ (°)	d (Å)	Interlinear Spacing Values (hkl)	Crystal Structure	Iron Oxides Phase (JCPDS File No. 19-0629)
21.4	6.32	(200)	Orthorhombic	W wustite (FeO)
24.2	4.53	(111)	Cubic	Ms magnetite (Fe ₃ O ₄)
25.3	3.96	(222)	Hexagonal	H: hematite (α -Fe ₂ O ₃)
		(440)	Cubic	Ms
26.5	3.76	(104)	Hexagonal	H
36.5	3.16	(024)	Hexagonal	H
37.8	2.96	(220)	Cubic	Ms
38.4	2.70	(311)	Cubic	Ms
42.6	2.52	(200)	Orthorhombic	W
48.2	2.41	(116)	Hexagonal	H
		(400)	Cubic	Ms
53.6	1.96	(422)	Cubic	Ms
55.1	1.74	(511)	Cubic	Ms
60.1	1.69	(220)	Orthorhombic	W
62.8	1.52	(214)	Cubic	Ms
68.7	1.38	(533)	Cubic	Ms

**Figure 3.** Fourier Transform Infrared (FTIR) spectra of Ms with and without sludge.

2.2. Coagulated Sludge Production

The wastewater sample collected from a local South Africa Sugar refinery industry was firstly coagulated with the coagulants (Alum and Ms). This was carried out at a pH of 6.8 to investigate the effect of coagulant dosage (10–60 mg/L) and magnetic field time exposure (10–30 min) for the removal of color and turbidity. Figure 4 presents the effect of coagulant dosage for the removal of (a) turbidity and (b) color from the wastewater. Likewise, Figure 5 shows the effect of magnetic field exposure on the coagulation process. However, no removal of the contaminant was observed without the addition of the coagulant (Ms and Alum). Summarized results on the coagulation process are presented in Table 2. It was deduced that the longer the magnetic time (30 min) and optimal coagulant dosage (50 mg/L) with high supermagnetic strength, the better the pollutant removal. The subsequent experiment was carried out using the coagulated sludge, spiked with the pure activated sludge (inoculum) towards the biogas production (Section 2.3).

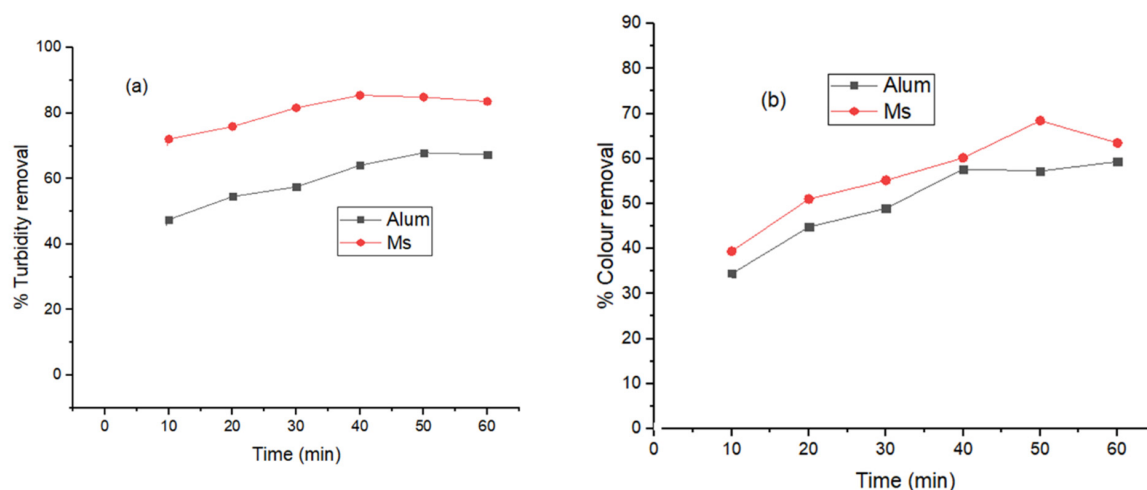


Figure 4. Effects of coagulant dosage (10–60 mg/L) on (a) turbidity and (b) color removal (%); Ms (red) and Alum (black) without any magnetic influence.

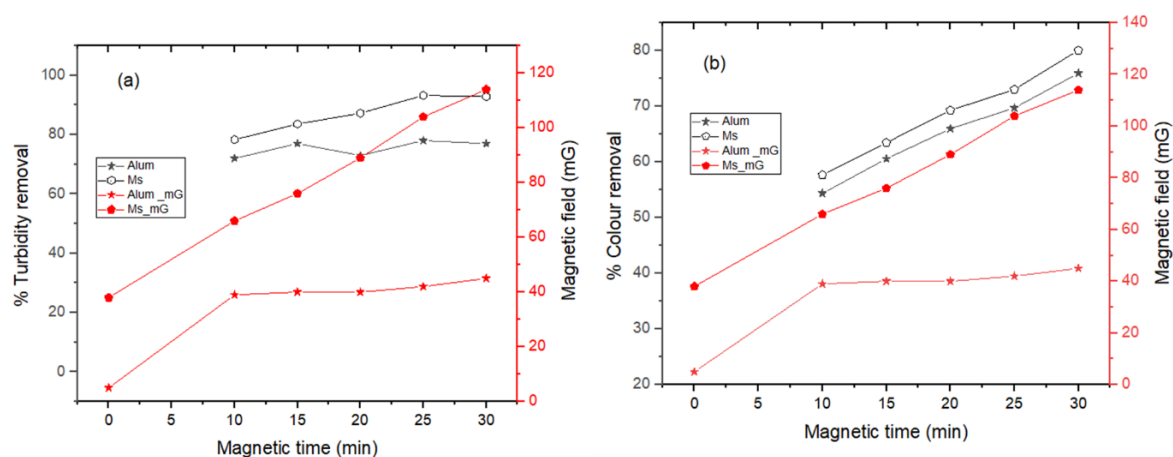


Figure 5. Effect of magnetic field exposure time (10–30 min) on (a) turbidity and (b) color removal (black scale—left) at dosage of 50 mg/L; Ms_mG, Alum_mG; magnetic field (red scale—right).

Table 2. Coagulation summary results with and without magnetic field.

Parameters	N* Ms	W* Ms	N* Alum	W* Alum
Dosage (mg/L)	50	50	50	50
Magnetic time (min)	N/A	30	N/A	30
Magnetic field (mG)	N/A	111.69	N/A	81.05
Turbidity (%)	85	95	70	80
Colour (%)	70	80	60	75

N*—no magnetic field, W*—with magnetic field, N/A—not applicable.

2.3. Biochemical Methane Potential (BMP)

The results for the nanoparticles and magnetic field effects on biodegradability carried out by the BMP test for biogas and methane production are presented in Section 2.3.1. The scanning electron microscopy (SEM)/energy dispersive X-ray spectrometer (EDS) results (Section 2.3.2) present the morphology and elemental composition of the digester sludge after conducting the experiments with Alum (A), Ms (B) and control (C). The kinetics were carried out to make understanding the mechanism of degradation and synergetic interactions of the nanoparticles enhancing the anaerobic chain reaction for the biogas production easier (Section 2.3.3).

2.3.1. Biogas Production

Figure 6 shows the digester set-ups (A, B and C) daily and cumulative biogas volumes produced. The average daily biogas production (Figure 6a) was 70 ± 14 mL/d, 30 ± 5 mL/d and 25 ± 42 mL/d, representing the increasing order of the set-ups as $B > C > A$ respectively. Similarly, the cumulative biogas (Figure 6b) yield was 1460 mL/d, 630 mL/d and 505 mL/d for set-ups $B > C > A$ respectively for the degradability duration of 21 days. Noticeably (Figure 6), the addition of nanoparticles such as Ms increased the biogas production (high peaks) in the set-up (B) as compared to the control set-up (C). However, the alum additives in set-up (A) reduced biogas production (low peaks) by achieving a high peak at the 8th day as against the control (C) (Figure 6a).

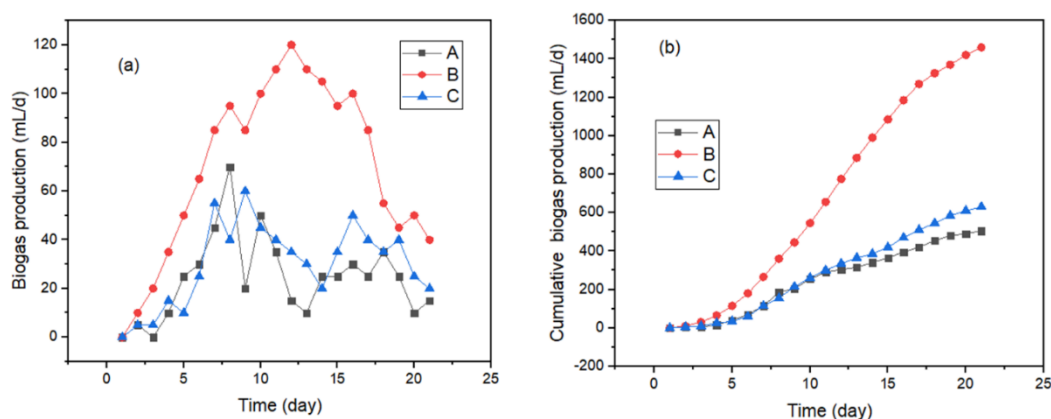


Figure 6. (a) Daily and (b) cumulative biogas production; B—Ms (red) > C—Control (blue) > A—Alum (black).

Figure 7 shows the methane content (Figure 7a) and biogas production (Figure 7b) monitored on a weekly basis (7th, 14th and 21st days). Magnetically, an increase in exposure time to the digester had a significant impact on the degradability of the organic compounds into biogas and methane production, as seen on the 14th day with the highest peak of set-up (B) biogas (105 mL/d) and methane (90%) production, as compared to set-ups ($C > A$) low biogas ($25 > 20$ mL/d) and methane ($76 > 60\%$) production. This revealed that the magnetic field agglomerated the microbial activity as a function of biogas production [23,27]. This phenomenon might be due to the decreased number of active methanogens and structural modification of the bacteria components caused by the impact of the magnetic field [26–28]. In addition, the inactivation of bacterial cells or a decrease in bacterial fission rate along with the nanoparticles could have inhibited the system after the 14th day to the 21st day [28].

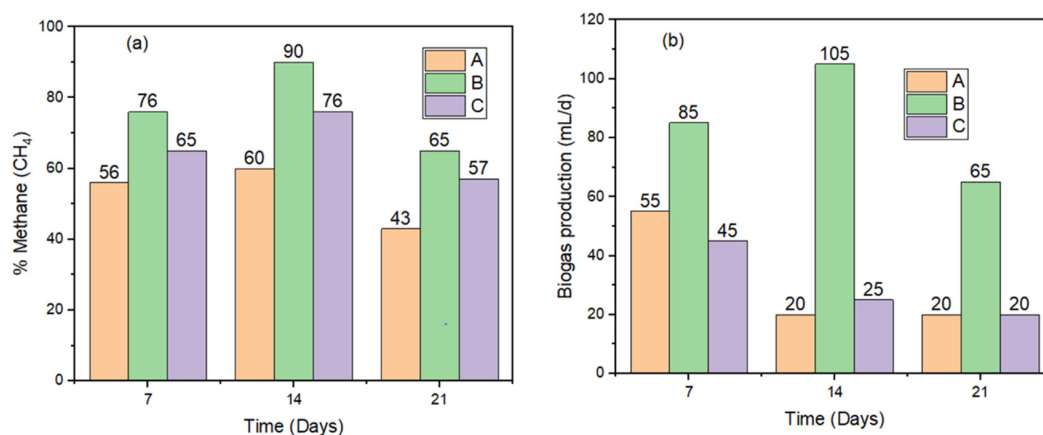


Figure 7. Biochemical methane potential (BMP) weekly monitoring (a) methane content (%), and (b) biogas production (mL/d); B—Ms (green) > A—Alum (brown) > C—Control (violet).

2.3.2. SEM/EDS Results of Digester Sludge

After the 21 days of hydraulic retention time (HRT), 2 g of the sludge obtained was characterized by SEM coupled with an energy dispersive X-ray analyzer (EDX) (Model: EVO HD15, Carl Zeiss, and Germany). Figure 8 represents scanned images of digested sludge surfaces of (A) A—Alum, (B) B—Ms and (C) C—Control. In Figure 8C, the activated sludge had a smooth surface, flawless boundaries, a dense structure and irregular protrusions. Comparing Figure 8A to that of the control (Figure 8C), the regular dense structure of the sludge is destroyed with unclear boundaries, crystallized amorphous and flocculated coalesces observed. Figure 8B shows the activated sludge had agglomerated crystallized particles with heterogeneous, spongy and large surface layers. These layers with abundant pores provided active sites for the adsorption of the Fe-NPs. It appears that the effect of NPs used in the MBMP system depends not only on the size of the NPs, but also on their concentration, the NP type, the substrate and the HRT. Their average surface thickness (Figure 8A–C) appears to be $6.36\text{ mm} > 5.90\text{ mm} > 5.33\text{ mm}$ for $B > A > C$ respectively when viewed at $20.8\text{ }\mu\text{m}$ under a scale of $5\text{ }\mu\text{m}$. This result agrees with Deepanra et al. [29] and Zaidi et al. [30], who stated that supermagnetic and metallic-supported nanoparticles can influence the surface area and consequently adsorptive activities. Additional reports also suggest that nanoparticle size can be of a wide range of 5 nm to 250 nm, which denotes the NPs acted as a catalyst for the bio-degradation [28,30,31].

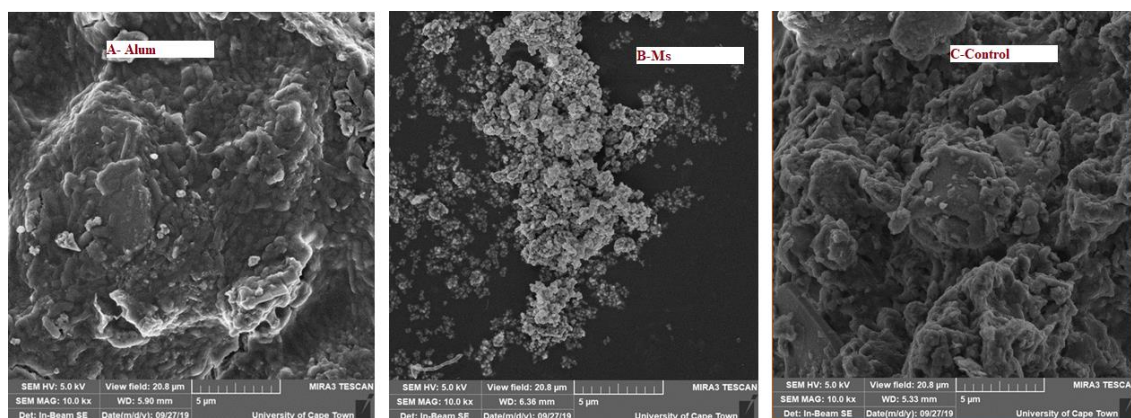


Figure 8. Scanning electron microscopy (SEM) images of digested sludge from magnetized biochemical methane potential (MBMP) setups of (A) Alum, (B) Ms and (C) Control.

Figure 9 shows the EDS results of the activated sludge post-adsorption of the elemental distribution on the surface. The compositions (table), spectrum (EDS images) and peaks of the elementals were elucidated by the adsorption mechanism by electrostatic attraction, agglomeration and the process of oxidation [29,30]. As observed, the elements on the control set-up (C) sludge surface (Figure 8C) were higher than those of set-ups B (Figure 9B) and A (Figure 9A). Spectrum 2 of Alum (Figure 9A) and Ms (Figure 9B) EDS images show the elemental distributions, whereas for that of the control (Figure 9C), represented by spectrum 5, almost similar peaks were observed near 0.7–6.5 keV energy regions. The decreasing order ($C < A < B$) of most of the adsorbed elementals onto the activated sludge surface were towards the NPs with magnetic properties. This adsorption mechanism of the supermagnetic and metal-supported NPs onto the activated sludge surface was due to the presence of the external magnetic field. This conforms to the results obtained by Zhao et al. [28] and Zaidi et al. [30], who reported on the magnetic effect on substrate surface complexation, pore structure, functional groups, ions exchange, hydrogen and chemical bonds.

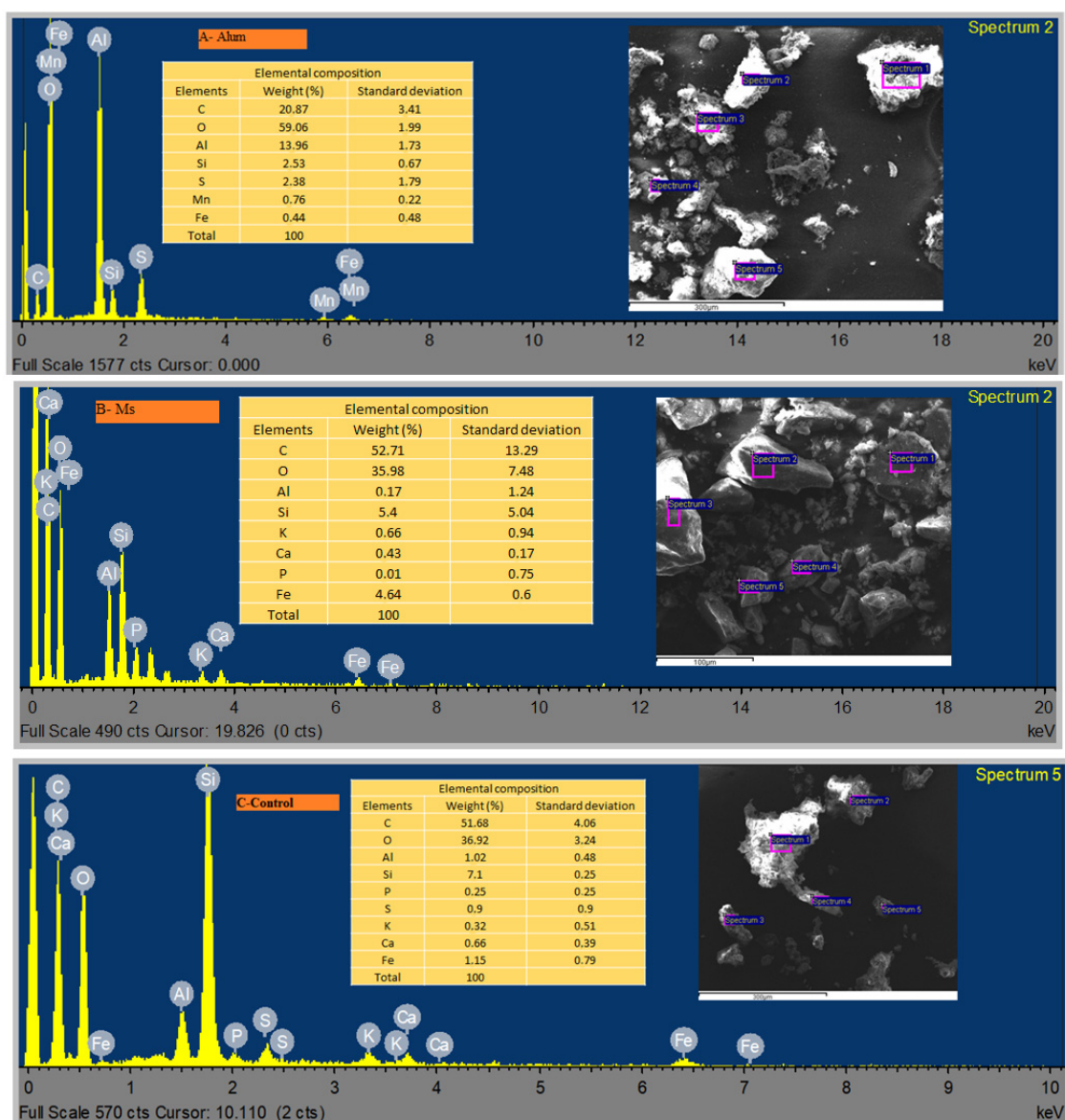


Figure 9. Energy dispersive X-ray spectrometer (EDS) image showing tracing nanoparticles (NPs) in digester sludge of set-up A—Alum (A) increasing order C > O > Al > Si > S > Mn > Fe; set-up B—Ms (B) increasing order C > O > Si > Fe > K > Ca > Al > P and set-up C—Control (C) increasing order C > O > Si > Fe > Al > S > Ca > K > P.

2.3.3. Biogas Kinetics

The cumulative biogas production data obtained was kinetically modelled with the first-order and modified Gompertz kinetic models equations (2) and (3) respectively. The kinetic constants were determined by simulating the data obtained with non-linear regression of OriginLab (2019 version) software. Figure 10 and Table 3 respectively present the modified Gompertz model fitting curves and the parameter values. The aforementioned models predicted different biogas production results, whereby the yield for each set-up (A, B, C) was based on the organic substrate and the nanomaterial additives.

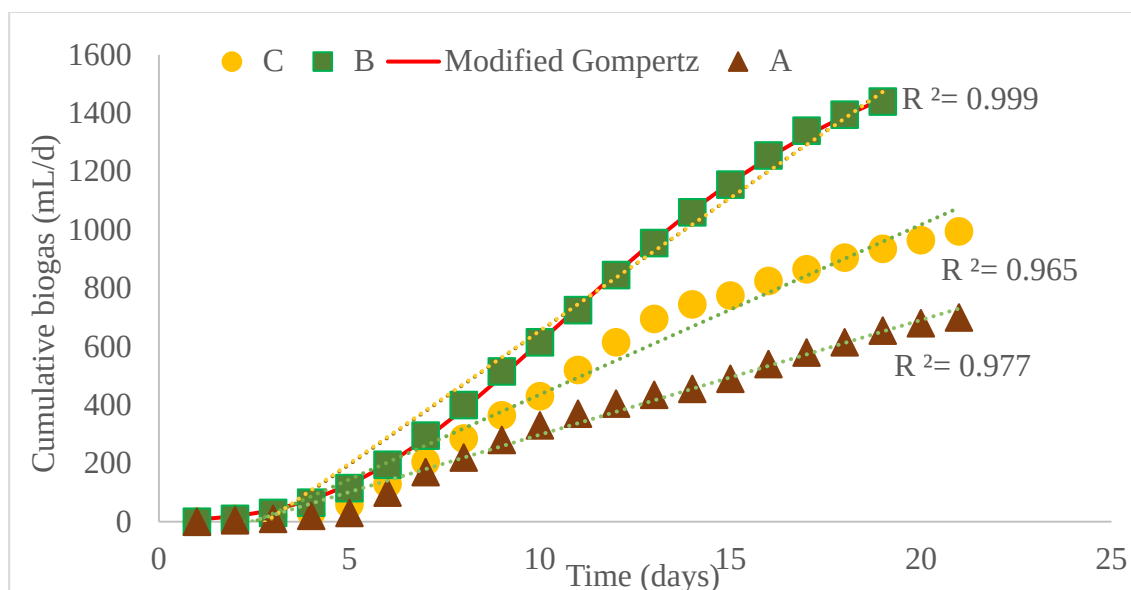


Figure 10. Cumulative biogas production for Modified Gompertz kinetic model.

Table 3. Results of Modified Gompertz and first-order kinetic constants.

Set-Up	A—Alum	B—Ms	C—Control
Modified Gompertz Model			
y	535.28 ± 09	1731.3 ± 58	736.3 ± 67
k (1/day)	0.195	0.127	0.285
c	9.13	10.69	10.97
Actual coefficient of determination (R^2)	0.977	0.999	0.965
Adjustable coefficient of determination (Adj R^2)	0.969	0.996	0.954
Sum of squares residual (SSR)	6075.73 ± 35	2113.63 ± 92	4915.56 ± 41
First-order model			
y	283.65 ± 25	827.33 ± 66	339.44 ± 52
k (1/day)	0.315	0.221	0.329
Actual coefficient of determination (R^2)	0.985	0.983	0.976
Adjustable coefficient of determination (Adj R^2)	0.983	0.981	0.966
Sum of squares residual (SSR)	1170.07 ± 75	932.38 ± 36	1292.89 ± 18

2.3.4. Summary of Results

The BMP test was carried out to estimate the impact of the NPs (aluminum and iron-based additives) on AD digestion of sludge for biogas and methane production. Adding to the credit of the NPs was their ability to dissociate and dissolve organics (proteins, carbohydrates and cellulose) and increase the surface area for sorption of the contaminants, as well as the methanogen activities, under AD conditions for biogas production [4,29,30]. Aside from the biogas production, it is evident that the NPs stimulated the dissolution of the organics and restructuring of the microbe's active surface for adsorption and precipitation, whereby appreciable elementals were found in their activated sludge generated (Figure 9). From the extensive experiments conducted and data analyzed, the summarized results of the MBMP tests are presented in Table 4.

Table 4. Summarized results of the BMP test.

Parameter	A—Alum	B—Ms	C—Control
pH	6.4	6.6	6.8
COD (mg/L)	304 ± 92	157 ± 8	258 ± 72
Turbidity (NTU)	66 ± 44	24 ± 16	105 ± 7
Color (PtCo)	75 ± 2	52 ± 8	112 ± 24
TSS (mg/L)	38 ± 8	22 ± 7	60 ± 8
Al (mg/L)	36 ± 8	8 ± 4	30 ± 4
Fe (mg/L)	60 ± 16	6 ± 7	32 ± 3
Average daily biogas (mL/d)	25 ± 42	70 ± 14	30 ± 5
Cumulative biogas (mL/d)	505	1460	630
% Methane (CH ₃)	51.56	79.8	60.74
% Carbon dioxide (CO ₂)	48.44	20.2	39.26

3. Discussions

The results (Section 2) illustrated effective biogas and methane production by integrated-anaerobic treatability with NPs after a coagulation treatment of local South Africa Sugar refinery wastewater. The experiments were carried out in two steps: (i) coagulation and (ii) MBMP tests, whereby the physiochemical properties of the characterized Ms and other detailed discussion are being presented under this section.

3.1. Characteristics of Ms

Figure 2 shows the crystalline structure of Ms characterized by XRD with and without sludge, whereby most of the peaks identified at 2θ (°) of 24.2, 25.3, 37.8, 38.4, 48.2, 53.6, 55.1, 62.8 and 68.7 were allotted to Ms (magnetite Fe₃O₄). With respect to the diffraction peaks, the Ms Crystals with cubic spine structure were determined to be (111), (440), (220), (311), (400), (422), (511), (214) and (533). As the XRD signals are indexed in Table 1 with phases which are close to iron oxides. This makes it possible to be attracted by the external magnetic field. Generally, the diffraction peaks at (200) are the characteristic peaks of wustite, whereas (222), (104), (024) and (116) represent hematite, such that Ms can easily be oxidized in air to form maghemite (γ -Fe₂O₃), hematite (α -Fe₂O₃) and wustite (FeO) at temperatures above 250 °C. The Ms crystallite size was estimated by using the Scherrer equation with the width at half-maximum of the strongest peak (331) to be 12.9 nm [7,13]. Additionally, the dominant phase was found to be Ms, with an estimated lattice constant of 0.839 nm, which was in agreement with other studies [6,7,13].

The FTIR spectra (Figure 3) of Ms with and without sludge had active functional groups (polymeric hydroxyl, carbonyl and aromatic rings) which were chemisorbed onto their surface. In Figure 3, the minor band at 453 cm^{−1} assigned may be due to the vibration of Fe–OH bonds [7,13]. Thus, the surfactant molecules in the transmission state were being subjected to surface hydroxylation and thereby shifting the bands towards the lower wavenumber region (<800 cm^{−1}). This signifies the hydrocarbon chains were closely packed in their crystalline state, which enhanced the electrostatic force of attraction [6,13]. The broad and sharp bands at 1479 cm^{−1}, 1027 cm^{−1} and 882 cm^{−1} might be due to the overlaid intramolecular hydrogen bond (O–H) ascribed to the symmetric and asymmetric stretching vibrations of the CH₂ [7,13]. Notwithstanding, the absorbance intensity at 1655 cm^{−1}, 1593 cm^{−1} and 1508 cm^{−1} denotes the carbonyl (C=O) and alkene (C=C) stretching vibrations due to the aromatic rings of the Ms with sludge [7,13]. This proves the possible occurrence of esterification between the C=O and C=C on the surface of the magnetite [13].

3.2. Effects of Coagulant Dosage and Magnetic Field on Coagulation

The increase in the coagulant dosage (10–60 mg/L) effectively reduced the pollutant surface charge, which resulted in destabilization and agglomeration of the particles into larger flocs [25,29].

As shown in Figure 4, both coagulants (Alum and Ms) demonstrated potential removal of turbidity and color within three categorical dosages: (i) the dosage of 10 mg/L was too low to coagulate the pollutant effectively (alum 50%; Ms 70%); (ii) an observably optimal range was achieved within 40–60 mg/L for alum (60–80%) and Ms (75–95%) with appreciable larger flocs formed; and (iii) optimal dosage of 50 mg/L, of which increasing it to 60 mg/L had no effect on the treatability performance. This phenomenon might be due to reversal and restability of the charge ions on the particle surface due to an excess of the coagulant molecules [23,25].

Based on Figure 5 and Table 2, it is evident that the combination of coagulation and magnetic field provided over 75% removal of the initial color and turbidity (Table 1) with a pH of 6.5, whereby the iron-based coagulant (Ms) performance was proven to be magnetically more effective than the alum, representing turbidity (95%) and color (80%) removal. Alum showed a slight effect of magnetism for the turbidity (80%) and color (75%) removal. This treatability performance occurred at a dosage of 50 mg/L and magnetic field exposure time of 30 min. As observed (Figure 5), the magnetic field facilitated the strength of the aggregated flocs to settle easily by trapping metalloids and other derivatives, leaving the suspension supernatant clear [6,25]. Meanwhile, the charge neutralization and adsorption of pollutants by Ms is reportedly better, owing to its supermagnetic property and dipole–dipole attraction [25].

Consequently, the issue of disposing hazardous waste, which increases the complexity and operational cost of WWTPs, has become a global concern, whereby coagulation plays a major role as the first pre-treatment step [23,25]. For instance, iron- and aluminum-based coagulants have been reported as contributing to secondary pollutants and generating large volumes of sludge [6,23]. Notwithstanding the fact that conventional ferric chloride is reported to be more effective in the removal of pollutants than alum, in most cases the cheap cost of alum is considered [6,31]. The Ms appeared to be more advantageous than alum, owing to its sludge generated with no or slightly complex elementals (Figure 9A). Also, the presence of multivalent metal ions (Fe^{3+}) enhanced the flocculation of complex metals by bridging most of the microflocs with carboxylate groups into aggregated flocs during the process [28,29]. This stimulated the sulfur species for subsequent degradation in the wastewater [30].

Therefore, using magnetic-based coagulants (Ms) stands a better chance of addressing most of the setbacks associated with conventional coagulation [31,32]. Thus, the dissociated ions (Fe^{3+} and Al^{3+}) behaved as Lewis acids, which reacted with the OH-ions (Lewis base) of the wastewater, thereby precipitating the pollutants in the form of $\text{Fe}(\text{OH})_3$ or $\text{Al}(\text{OH})_3$ [29,30]. These precipitates have positive electrostatic surface charges with large adsorptive surface areas to enhance trapping of the negatively charged particles in the solution [6,29,30]. This phenomenon justified the reason why high amounts of precipitated solids/flocs settled at the bottom of the beaker with magnetic fields [29,30]. A similar occurrence was observed with the use of Ms, whereas the dissociated Al species in the solution were not magnetically attracted due to its non-magnetic property [6,26].

3.3. Effects of Nanomaterials and Magnetic Field on Biogas and Methane Production

With the rapid development and application of nanotechnology towards green energy [30,33], the safety and toxicology of some of these engineered nanomaterials are of environmental concern. In conventional WWTPs, accumulation and adsorption of high amounts of heavy metals or nanomaterials in the sludge might affect the downstream treatment process [6,29,30]. Successively, some of these nanomaterials (iron-based) are likely to be utilized as micronutrients by microbial biomass, whereas others can exhibit an inhibitory impact on the AD process [27–29]. Thus, the substrate variation of content in the sludge during the degradation by the microbes can result in different intermediate end products such as sugars, fatty acids, alcohols, carbonic acids and amino acids [6,30]. This has led to intensive research on the degradation of sewage sludge with other waste streams by AD processes towards environmental protection, economical and eco-friendly energy [27,29]. Nevertheless, this study affirms the presence of heavy metals and nanomaterials in a digester might decrease the AD efficiency [24,27,30]. Thus, the addition of nanoparticles in AD had a synergic effect on the microorganisms for the biogas production [29].

The impacts of the NPs on the setups were ascertained based on the volume of biogas production and methane composition. In Figure 6 and Table 4, it is evident that biogas production increased more with time for the setup (B) with Ms as compared to the control (C), and that of set-up (A) was the lowest. The addition of alum to setup (A) contributed to the production of volatile fatty acids and other organic intermediates (SO_4^-) [30–32]. This mechanism, along with metal toxicity, resulted in methanogenic bacteria inhibition. Additional conversion of the substrate to volatile fatty acid by the acidogenic bacteria also contributed to acidification and system failure in setup (A). Based on Figure 7 and Table 4, an enhancement of the biogas volume of production and methane composition was observed when the systems were exposed to external magnetic fields. Thus, the systems under the anaerobic conditions with the magnetic field influenced the growth and multiplicity of the microbes' activities.

The magnetic field strength of the system reduced the lag phase and increased biogas production and methane composition (Figure 7). This is in accordance with Zhao et al. [28] and Zaidi et al. [30], who reported on the presence of Fe NPs, which provided suitable substrates for methanogenesis enhancement in AD systems. Seyedi et al. [22] and Biswas [33] also reported on the effects of trace metals such as iron and their capacity to reduce the lag phase of mixed culture, which caused the improvement in methane composition and the biogas production. Srekanh and Sahu [34] reported that NPs uptake may stimulate methanogens by increasing their metabolic intermediates and key enzymatic activities involved in the hydrolysis, acidification, and methanogenesis stages of AD. Here, Fe species acted as an active component, and the catalytic activities were governed by the trivalent and zero-valent ($\text{Fe}^{3+}/\text{Fe}^0$) ions ratio and their exposed surface area [30,34,35]. Srekanh and Sahu [34] added 1.4 g of NPs to enhance biogas yield in a portable-food waste digester, while here the waste and environmental conditions of this study are different. Casals et al. [36] reported that an Fe NPs dose of 0.5–16 mg/L increased cumulative CH_4 production, by reducing the CO_2 via a hydrogenation mechanism. This is in agreement with the current study, which confirms that the Ms increased the CH_4 potential by 20% (Table 4). Therefore, there are high prospects of Fe NPs to be used as fuel catalysts to reduce CO_2 into CH_4 through the stability of the autotrophic methanogens [30].

3.3.1. Sludge Surface Complexity and Traced Nanoparticles after Digestion

The SEM images (Figure 8) present the morphology of the activated sludge aggregated with NPs of amorphous shapes with an average diameter less than 10 nm. The addition of the Fe/Al NPs increased the roughness of the activated sludge, with the development of cracks and macrospores. The pores of Ms (Figure 8B) were larger than those of Alum (Figure 8A), which is due to the replaceability of the Fe or Al species as ion donors on the surface of the activated sludge. This observation is in agreement with the EDS results (Figure 9), in which similar peaks for the Fe element between Ms and Alum were observed.

Figure 9 reveals the complexity of the metal ions or organic compounds on the surface of the activated sludge after the complexation reaction and adsorption. This was as a result of the interaction between the electron donors and electron acceptors being bound to the active groups on the activated sludge surface [31,33]. The control system (C) had a substrate without nanomaterials and resulted in a low biogas production volume and methane composition. Also, there were some elemental changes in the set-up systems as depicted in the electoral spectrum (Figure 9), which includes carbonate (C), silicate (Si), sulfur (S), calcium (Ca), potassium (K), phosphorus (P), manganese (Mn), iron (Fe) and aluminum (Al) from the control. The toxicity levels of elementals accumulated in the sludge followed a decreasing order (Figure 9A) in set-up (A); $\text{C} > \text{O} > \text{Al} > \text{Si} > \text{S} > \text{Mn} > \text{Fe}$; Figure 9B for setup (B) as $\text{C} > \text{O} > \text{Al} > \text{Si} > \text{Fe} > \text{K} > \text{Ca} > \text{P}$ and Figure 9C representing set-up (C) as $\text{C} > \text{O} > \text{Si} > \text{Fe} > \text{Al} > \text{S} > \text{Ca} > \text{K} > \text{P}$. It can be seen that the low biogas yield (Table 4) of the alum digester (A) can be attributed to the rapid poisoning of the active microbes in the digester by the SO_4^- species (sulfide), which increased the acidity of the system.

Conversely, some of the elementals in the Ms digester (Figure 10 B) acted as macro-nutrients (Fe, K, Ca, P) for simulating the methanogenic activity, creating active sites and stabilizing surface

intermediate species. According to Casals et al., [36], this can be due to the hydrolysis of soluble proteins and transformational activities of the electron donors, which were driven by redox–proton translocation in a methanogenic species. Furthermore, Zhao et al. [28] indicated magnetic NPs (Ms), which seems to be non-toxic during long-term contact with bacterial activity and has mild toxicity at the initial stage (Figures 8 and 9). However, the magnetic effects of the MBMP system influenced the Ms to enhance the activity of the autotrophic bacteria [29,30]. Thus, the propagation of autotrophic bacteria being attached to a carrier with a proton donor is positive for their growth and enrichment [35,36].

The two key tracing metal ions (Fe and Al) were assessed based on their distribution in the effluent. These were characterized to understand the possible mechanism of the heavy metal impact order in the supernatant. In Table 4, it is shown that B—Ms (Al: 8 ± 4 mg/L; Fe: 6 ± 7 mg/L) affected the system positively, followed by C—control (Al: 30 ± 4 mg/L; Fe: 32 ± 3 mg/L), whereas A—Alum (Al: 36 ± 8 mg/L; Fe: 60 ± 16 mg/L) had a negative impact on the system. The Al active sites, besides the primary Fe sites on the surface of activated sludge (Figure 9C) microspheres, facilitated the creation of Al–peroxide intermediates (Al–OOH), which reduced the apparent activation energy of the decomposition [34–36]. The synergistic effect between the Fe and Al sites acted as reaction promoters for most of the metal oxides being used in CO₂ hydrogenation reactions [34,35].

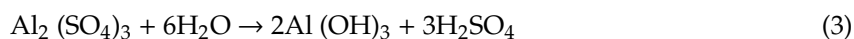
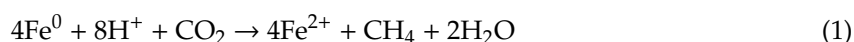
As reported, nanomaterials are inhibitory to biodegradation, nitrification and the AD process [24,33]. Hence, understanding the complex mechanisms by which these particles interacted with the substrate and the microbes to enhance methanogenesis is very important. Notwithstanding their composition, nanoparticles have high surface area to volume ratios and particle size that can influence the rate of adsorption and biodegradation [28,30]. Additional combination of the substrate and the NPs resulted in functional groups containing oxides (Fe₂O₃), which heightened precipitation removal of the contaminants from the effluent [31,33]. According to Zhao et al., [28], the interactions between the Ms and the activated sludge created an anoxic environment, which heterotrophic bacteria prefer, and thereby enhanced their activities. This adds to the advantages of Ms due to the large fraction and highly disperse nature (Figure 8B) of the Fe species on the surface of the activated sludge (Figure 9B), making it reachable for the reactants to adsorb.

3.3.2. Biogas Production Kinetics Using First-Order and Modified Gompertz Models

The availability of substrate for metabolism under anaerobic conditions with active microbial community enhanced the rate of biogas production. This mechanism was attributed to the four steps in the AD process: hydrolysis, acidogenesis, acetogenesis and methanogenesis [30,33]. The inhibitory effect of the nanoparticles in the AD biogas production was evaluated by the BMP test. To monitor the performance in terms of volume of biogas produced per day, the water displacement method was used. The measuring cylinder used for the gas collection was fixed with butyl rubber at the top to enable injection of the gas for analysis. From Figure 6, the average daily biogas production recorded was 25, 70 and 32 mL/day respectively for A—alum, B—Ms and C—Control. In Table 4, organic degradation is also represented as 304 ± 92 , 157 ± 8 and 258 ± 72 mg/L of COD respectively for A—alum, B—Ms and C—Control set-ups. The cumulative biogas production data (Figure 10) obtained was simulated with the first-order kinetic model (5) and modified Gompertz model (6) constants obtained, presented in Table 3.

Additives of the nanomaterials (Ms) enhanced the kinetics process of the acetotrophic and hydrogenotrophic methanogens in the digester for biogas and methane production. Thus, the electrons released or hydrogen generated by the Ms had a significant influence on the biogas and methane production (Figure 3). Subsequently, methanogenic reactions under anaerobic conditions were accelerated by the presence of Fe³⁺, whereas the Al³⁺ retarded or inhibited the methanogens growth rate. The reactions (1 and 3) illustrate the dehydrogenation and hydrogenation pathways of Fe and Al

NPs, which served as catalysts to hinder microbial activities or enhanced the degradation of the toxic organic compounds respectively.



From reaction (1), electrons released (Fe) promoted the CH_4 production and by-products like formic acid whose decomposition resulted in a polymerization chain reaction of CO_2 and H_2 . Also, the zero-valent Fe^0 can be consumed by the inorganic CO_2 and other complex compounds (sulfide) (2) [30]. Table 5 presents reported bio-stimulating effects of Al- and Fe-based salts and NPs additives on AD biogas production, which confirms Ms as the most effective nanocatalyst for the bio-hydrogenation and methanogenesis processes [28,30,33]. In Table 6, Sreekanh and Sahu [35] reported about 21.3% and 35.7% reduction in the biogas volume as a result of using 100 mg/L of Al- and Fe-based salts for municipality sewage treatment respectively. Although previous studies were on mixed sludge with alum and ferric salts, the current study also corroborates reduction of biogas yield from Alum activated sludge [35,36]. Thus, the Al additives promoted the formation of sulfuric acid, and other volatile fatty acids, which were inhibitory to the MBMP process. This retarded the pH level of the AD process to be in acidic medium, thereby affecting the methanogen growth rate and activities for the biogas and methane production [33–35]. However, additives of the Ms reduced not only the lag phase but also the time to achieve the highest biogas production (peak).

Table 5. Study on bio-catalytic effect of Al- and Fe-based salts and nanoparticles on biogas production.

Substrate	Cumulative Biogas Production (mL/d) without Nanoparticles	Cumulative Biogas Production (mL/day) with Nanoparticles	Ref
Algae wastewater + Ni NPs	488	618	[30]
Algae wastewater + Co NPs	488	535	[30]
Algae wastewater + Fe NPs	488	624	[30]
Algae wastewater + Mg NPs	488	529	[30]
Sewage + Al salt	34.91 ± 1.3	24.85 ± 1.3	[35]
Sewage + Fe salt	34.91 ± 1.3	22.46 ± 1.5	[35]
Sugar refinery wastewater + Alum	630	505	* This study
Sugar refinery wastewater + Ms	630	1460	* This study

* Results obtained from this study.

Table 6. Characterized wastewater sample.

Parameter	Units	Value
pH	-	6.6–7.2
Chemical oxygen demand (COD)	(mg/L)	942 ± 180
Turbidity	NTU	302 ± 18
Color	Pt.Co	250 ± 24
Total suspended solids (TSS)	(mg/L)	152 ± 13
* Aluminium ion (Al)	(mg/L)	56 ± 12
* Iron (Fe)	(mg/L)	134 ± 19

* as a result of spiked nano-material residue.

4. Materials and Methods

4.1. Chemicals

All the chemicals and reagents used were of Sigma Aldrich analytical grade purchased from Merck Chemicals (Pty) (Durban, South Africa). Aluminum sulphate hydrate (alum) and ferric chloride hexahydrate ($\text{FeCl}_3 < 5 \mu\text{m}$, $\geq 96\%$) were used as coagulants. Their stock solutions were prepared with MiliQ water (Conductivity of $18.2 \text{ M}\Omega/\text{cm}$ at 25°C). In order to prevent further reactions, the stock solution bottles were wrapped with aluminum foil, stored at room temperature and used within 24 h. In terms of synthesizing Ms, the ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and FeCl_3 were used as the precursors. Ammonium hydroxide (25 wt% NH_4OH) was used as the precipitating agent, whereas deionized water was used to remove the extreme impurities. Successively, the experiments were carried out in two phases: (i) coagulation and (ii) magnetized biochemical methane potential (MBMP).

4.1.1. Synthesis of Ferromagnetite (Ms)

The Ms was prepared via a modified chemical co-precipitation procedure reported in the literature [6,25]. This was carried out by dissolving 5.4 g of FeCl_3 and 2.7 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ with 100 mL MiliQ water followed with intermittent addition of 20 mL of 25 wt% NH_4OH . This was then sonicated (45 KHz at 80°C) for 15 min until the solution color changed from orange to dark brown. The precipitated Ms was filtered and systematically washed with deionized water to remove the chloride ions and at the end oven dried at 80°C for 24 h and calcined at 500°C for 1 h.

4.1.2. Physiochemical Analysis

The crystalline nature and mineralogical composition of the Ms and sludge were identified by X-ray diffraction equipment (Bruker AXS, D8 advance) coupled with Panalytical X'Pert PRO MPD software. This was carried out by firstly metalizing the samples with a gold–palladium alloy using the sputtering technique (Quorum Q15OR ES metallizer). A continuous measurement was done on a J-J scan with copper anode ($\text{Cu-K}\alpha$ radiation: $\lambda = 1.5406 \text{ \AA}$) and Bragg–Brentano configuration. The diffractograms were performed at room temperature with 0.01° (2θ) step size and 10 s step time. To ascertain the functional groups on the Ms and sludge surface, Fourier Transform Infrared spectroscopy (FTIR) by a Perkin Elmer spectrum spectrophotometer was employed. The spectrum obtained was within the wavelength of 4000 to 400 cm^{-1} . Also, scanning electron microscopy coupled with an energy dispersive X-ray analyzer (SEM/EDX) (Model: EVO HD15, Carl Zeiss, Germany) was employed to determine the elemental distribution of sludge.

4.2. Wastewater and Substrate

Both the wastewater and activated anaerobic sludge samples used were obtained from a local South African Sugar processing industry, in the Kwazulu Natal Province (Durban, South Africa). The thickened sludge was allowed to settle in a cold room (5°C) for 24 h, whereby the supernatant aqueous part was removed. The wastewater used as the substrate was rich in organic nutrients (COD), which was spiked with the coagulated residue obtained to serve as inhibitors to the BMP process. The water quality, as presented in Table 6, was characterized based on the American Public Health Association standards for wastewater (APHA) [37]. Al and Fe were characterized using an Agilent Micro-Plasma Atomic Emission Spectrophotometer (MP-AES, MY 18379001).

4.3. Experimental Procedure

4.3.1. Coagulation Process

A jar test apparatus (JTL6) manufactured by Velp Scientifica (Velp Inc, USA) equipped with six 1 L beakers was employed to evaluate the effect of coagulant dosage ($10\text{--}60 \text{ mg/L}$) and magnetic

time exposure (10–30 min). Firstly, the wastewater sample was distributed into the beakers leaving a headspace of 200 mL. After the addition of the specified coagulant dose, the suspension was rapidly mixed (at 150 rpm—quick coagulation) for 2 min, followed by 15 min slow mixing (at 30 rpm—slow coagulation) [6]. The samples were then exposed to a magnetic field for 15 min to enhance settling. At the end of the settling period, 20 mL of the supernatant from the top of the suspension was withdrawn with a syringe for turbidity (Hach 2100N turbidimeter, USA) and color (Hach DR3900 Spectrophotometer) measurement. The above procedure was also used to test the magnetic effect using different magnetic exposure times (10, 15, 20, 25 and 30 min) at the optimum dosage obtained. Removal of the contaminants was calculated according to (4).

$$\%removal = \frac{C_0 - C_I}{C_0} \times 100 \quad (4)$$

where C_0 and C_I are the contaminant initial and final concentrations of the samples.

4.3.2. Biochemical Methane Potential (BMP)

Biochemical methane potential (BMP) tests reported by Tetteh et al. [19] and Armah et al. [17] were followed with modification. The 1000 mL Duran schott bottles used as batch reactors were supplied by CC Imelmann (Pty) Limited in Johannesburg, South Africa. In Figure 11, the working volumes of the bottles were 800 mL; filled with anaerobic sludge (400 mL), substrate (350 mL), coagulated residue (40 mL) and 10 mL of stock solution (alum or Ms). Magnetic bars (stirrers) were placed in each bottle to facilitate mixing of the samples. After all the components were filled, the bottles were air-tightened with the caps. The reactors' headspaces of 200 mL were then purged with N_2 gas for 5 min to flush out the oxygen inside. This was carried out through the two ports of the cap: one side for injecting and the other side for releasing of the gas. Each setup was then placed on a hotplate magnetic stirrer, operated at mesophilic temperature (35 °C) with a mixing rate of 15 rpm. Intermittent mixing was done every 4 h, to ensure contact of constituents and homogeneousness of the samples. The volume of biogas produced was recorded every day at the same time. The experiment was carried out for 21 days, which had enough retention time to digest all the organic content. Every 7 days, the biogas composition was characterized by Gas Chromatography (GC 2014, Shimadzu), whereas the daily biogas production was measured by the liquid displacement method used by other authors [17,19]. The biogas production kinetics was modelled with the modified Gompertz model and first-order models expressed in Equations (5) and (6) respectively [27].

$$y(t) = ym[1 - \exp(-kt)] \quad (5)$$

$$y(t) = y(m) \cdot \exp\left(-\exp\left[\frac{U, e}{y(m)}[\lambda - t]\right] + 1\right) \quad (6)$$

where $y(t)$ represents the cumulative yield of biogas at time t (mL/days) and t the digestion time for biogas production (days). $y(m)$ is the volume of biogas produced (mL), λ is the lag phase period of producing biogas (days), e is the mathematical constant ($= 2.718282$), and k is the biogas rate constant (1/days). In the modified Gompertz model, k is expressed as the maximum biogas production rate per biogas production potential ($\frac{U, e}{y(m)}$; 1/days), where U is the maximum biogas production rate.

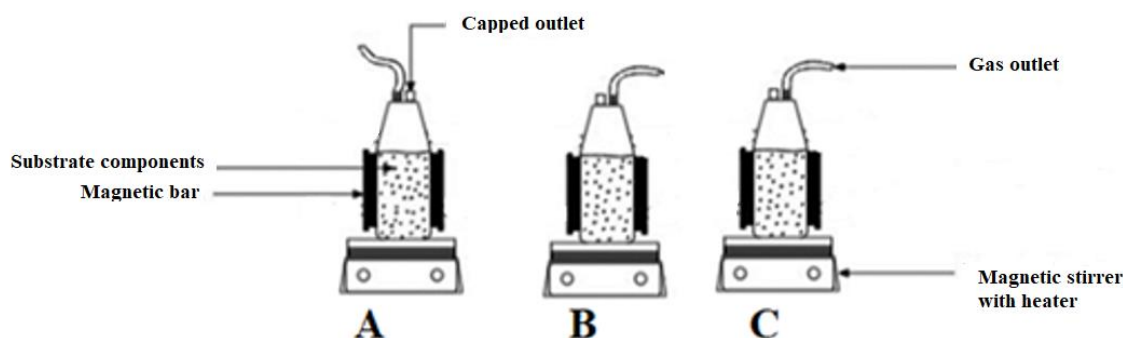


Figure 11. Magnetized biochemical methane potential (MBMP) setups; (A) with Alum; (B) with Ms and (C) Control without any nanomaterials.

5. Conclusions

This study presents coagulation and anaerobic digestion coupled with Ms as effective options for wastewater treatment for reuse as compared to that of alum. Additionally, the potential benefits of a magnetized system for wastewater remediation and biogas production via integration of coagulation and MBMP were explored. The physiochemical analysis by XRD and FTIR validated the crystallite of Ms and its ability to bind to or react with other functional groups. In the coagulated system, the magnetic field influenced the agglomeration and adsorption of the contaminants with easy settling. This yielded turbidity (95%; 80%) and color (80%; 75%) removal representing Fe-NPs and alum performance at a dosage of 50 mg/L and magnetic exposure time of 30 min. The inhibitory effect of the NPs was measured based on the biogas production. Ms increased the daily biogas volume of the control system from 32 mL to 70 mL, whereas the alum inhibitory effect reduced the volume of the biogas to 25 mL. The cumulative biogas production of the Ms and alum were 1460 mL/d and 505 mL/d as compared to the control system of 630 mL/d. The Ms attained the highest amount of methane composition of 80% CH₄, as compared to the control and alum respectively at 61% CH₄ and 52% CH₄. Cumulative biogas data obtained were modelled by the modified Gompertz and first-order kinetic models. The results were well fitted with the modified Gompertz kinetic model, with coefficient determinations (R^2) as 0.965, 0.999 and 0.967 for Control, Ms and alum systems corresponding to kinetic rate constants of 0.285 d⁻¹, 0.127 d⁻¹ and 0.195 d⁻¹ respectively. Subsequent addition of Ms to the MBMP coupled with a magnetic field showed robust enhancement of the biogas production and methane yield, with a reduced lag phase and low kinetic rate. In addition, the magnetized system has proven to be viable for heavy metals removal from wastewater with complex ions and high organic strength. The synergistic effect of integrating magnetized systems into coagulation as pre-treatment to AD in the wastewater setting results in the following research directives being recommended:

- The future prospects of magnetized NPs (Fe NPs) to be used in bioenergy systems for energy conversion are economically viable. This is due to their high surface area, porous structure and supermagnetic properties, which can act as an activator for a degradation catalyst, such as a photocatalyst (Fe/TiO₂).
- The development of magnetized NPs to be used as a coagulant or catalyst should be given research attention for the removal of contaminants and reduction of landfills complexity. This includes methods of recovery of the NPs after the application in the AD process to reduce environmental impact on soil and agricultural crops.
- Kinetically evaluate the effects of magnetic field on AD biogas production by considering different approaches such as substrate pre-treatment, nanoparticles dosage and inoculum mixture with respect to time should be considered.

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Article

Synergistic Effects of Magnetic Nanomaterials on Post-Digestate for Biogas Production

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Abstract: Digestate is characterized by high water content, and in the water and wastewater treatment settings, necessitates both large storage capacities and a high cost of disposal. By seeding digestate with four magnetic nanoparticles (MNPs), this study aimed to recover biogas and boost its methane potential anaerobically. This was carried out via biochemical methane potential (BMP) tests with five 1 L bioreactors, with a working volume of 80% and 20% head space. These were operated under anaerobic conditions at a temperature 40 °C for a 30 d incubation period. The SEM/EDX results revealed that the morphological surface area of the digestate with the MNPs increased as compared to its raw state. Comparatively, the degree of degradation of the bioreactors with MNPs resulted in over 75% decontamination (COD, color, and turbidity) as compared to the control system result of 60% without MNPs. The highest biogas production (400 mL/day) and methane yield (100% CH₄) was attained with 2 g of Fe₂O₄-TiO₂ MNPs as compared to the control biogas production (350 mL/day) and methane yield (65% CH₄). Economically, the highest energy balance achieved was estimated as 320.49 ZAR/kWh, or 22.89 USD/kWh in annual energy savings for this same system. These findings demonstrate that digestate seeded with MNPs has great potential to improve decontamination efficiency, biogas production and circular economy in wastewater management.

Keywords: anaerobic digestion; biogas; digestate; magnetite; renewable energy; wastewater



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1. Introduction

Bioenergy production has been seen as one of the most environmentally friendly solutions available for the degradation of chemically complex digestates [1]. These include wastewater treatment plant sludge, paper mill sludge, organic fraction of municipal solid waste, industrial wastewater and waste streams from the food and pharmaceutical industries, which can undergo microbial metabolic pathways via anaerobic digestion (AD) to produce biogas [2]. In addition, digestate is readily available and exceptionally rich in macro- and micronutrients, propelling its usability for agricultural applications such as NPK fertilizer. Also, ammonia and free phosphorus, which have been freed from their biologically bound states in feedstock, have the potential to be recycled back into the food chain for agricultural farming. However, AD has many reported setbacks [1–3], which warrants trace-element involvement in order to propel its complex reactions and mechanisms in bioenergy production.

Recent complex sludge production from primary, secondary, and tertiary treatment in wastewater treatment plants (WWTPs) has resulted in pressing concerns, as its treatment cost accounts for 20–55% of the total operating costs of WWTPs. This necessitates the possibility of considering an abatement technology for sewage sludge treatment given such sensitive factors as the end product, energy generation, the environment and human health impacts [4,5]. Sewage waste is becoming a major concern in South Africa (SA), since the volume of solid waste produced is escalating daily. This is attributed to rapid population growth and industrialization. In this case, the capability of AD facilities for

processing municipal waste is being overused to reduce waste before it is disposed of in landfills [6,7]. However, due to legal and budgetary constraints, landfill use is dwindling as a conventional approach whereas dumpsites remain limited. In response to the substantial risks involved with municipal solid waste management for final disposal, municipalities are seeking a better option to mitigate these pressing concerns. Of note, several studies on consistent AD operation in treating the organic components of sewage sludge are also being undertaken [6,8].

Subsequently, using sludge as a bioenergy resource is reported to be eco-friendly, with a high caloric value ranging from 21–23.5 MJ/m³, which will help ease the over dependency on fossil fuels to generate bioenergy [3]. In this vein, biogas produced from municipal waste can be used for electricity, fuel for vehicles and heat for cooking, and can therefore offset the limitations that fossil fuels pose [1,3]. Generally, production of biogas via AD involves four processes: (i) hydrolysis of complex organic compounds to manageable soluble compounds; (ii) acidogenesis, which converts the soluble compound to volatile fatty acids; (iii) the acetogenesis stage, where higher organic acids and alcohol from the preceding stage are converted to acetic acids, CO₂ and H₂; and finally (iv) the methanogenesis phase [3,6,7].

To develop AD technology and meet current energy and environmental concerns, it is critical to research wastewater-based biogas production as an alternative option. The use of nanotechnology in the wastewater settings, especially the magnetisation separation coupled with AD process knowledge is still limited. Therefore, this study aimed to employ magnetic nanomaterials (MNPs) as a biostimulant in the AD process for enrichment of the organic fraction of municipal WWTP digestate into methane-rich biogas. The morphological and elemental analysis of the digestate is highlighted. In addition, an existing kinetic model is used to establish the degree of degradation and the biogas production.

2. Results and Discussions

2.1. Digestate Morphological Properties

SEM/EDX was used to investigate the compatibility and morphology of the digestate before and after 30 days of incubation. The interfacial adhesion and dispersion of the MNPs in the digestate is presented in Figure 1. At a micrograph scale of 5 µm, the digestate surface profile was taken at a high magnification of 10k× with a width view size of 20.8 µm. The raw sludge (Figure 1F) shows a porous structure with an irregular shape, revealing the potential of active microbes for biodegradation. However, after 30 days of incubation, the particle surface with Fe₂O₄-TiO₂ (Figure 1A) was found to be much smoother than the original digestate (Figure 1F). The micrograph indicates that the digestate with MNPs (Figure 1A–D) consisted more of cluster cells, while that without (Figure 1B,C) consisted more of filamentous clusters. Figure 1A,D also reveal that the micrograph images include flower-like particles, with many apertures distributed along the surface. This suggest the digestate, which consisted of Fe₂O₄-TiO₂ and Chitosan-Fe₂O₄/TiO₂ in bioreactors A and D, may have increased the contact surface (Figure 1A,D), reactivity and degradation efficiency in reducing contaminants as well as increasing biogas production [6,8].

The electron micrographs showing the spatial distribution of different elemental composition in the sludges are illustrated in Figure 2. Quantitatively, the most predominant elemental distribution on the surface of the digestate was found to be Al, Si, Na and Fe (Figure 2). These elements, aside from the carbonate (C, O), influenced the adsorption ability of the contaminants. Substrates rich in Al or Fe potentially stimulate inter-species reactions that oxidize complex metals (S or P) and remove them via precipitation [6,8]. SEM/EDX (Figure 1) revealed that the mineralisation of the digestate had interactive features which increased the methanogenic pathway of the organics. The EDX (Figure 2), showed that the metabolic pathways were very sensitive to the microbial community, as there was a reduction in their concentration level. The availability of the nutrient-rich trace elements also increased methanogenic activity. The presence of MNPs amplified the strong electrostatic contact between the core NPs and the pollutants present in the wastewater, as

previously observed. Therefore, subsequent study also investigated the role of the MNPs in the removal of specified contaminants from the wastewater.

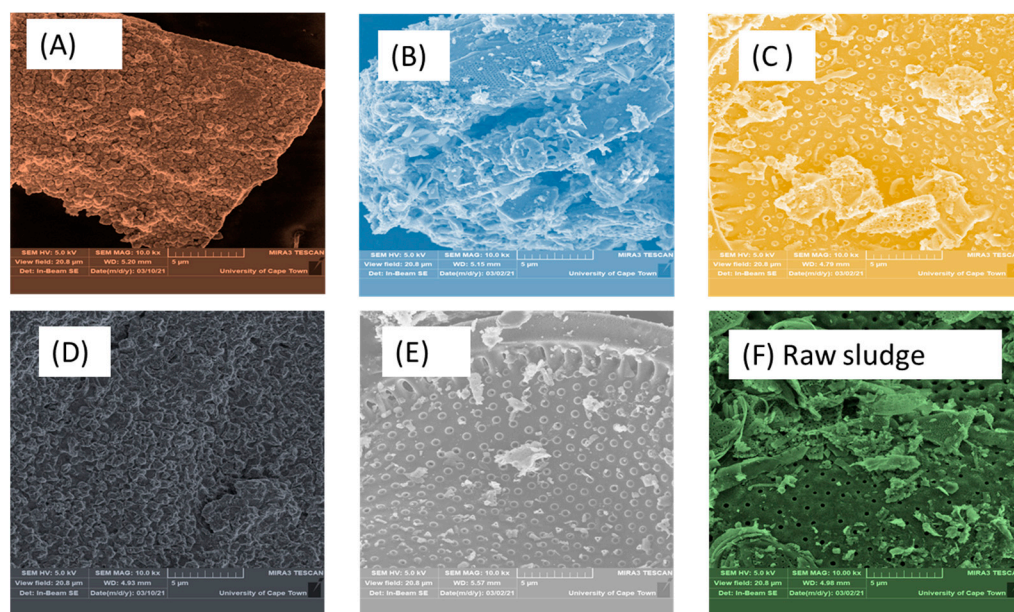


Figure 1. SEM images for post-sludge bioreactors A–D charged with 2 g of (A) $\text{Fe}_2\text{O}_4\text{-TiO}_2$; (B) $\text{Cu-Fe}_2\text{O}_4$; (C) Fe_3O_4 ; and (D) Chitosan- $\text{Fe}_2\text{O}_4/\text{TiO}_2$ MNPs, whereas bioreactor E is a control: (E) no MNPs and (F) raw sludge.

2.2. Decontamination of the Wastewater

In this study, AD was investigated as a medium to degrade high-strength organics and generate biogas with rich methane potential, as well as to decontaminate pollutants to meet the discharge limits of the South African Department of Environmental Affairs [9,10]. This is important due to many parameters in wastewater treatment being identified as posing threats to human health and aquatic life when released in large quantities into the environment [10,11]. Table 1 presents the water quality parameters including COD, colour, and turbidity which were considered in this study to ascertain whether they are aligned with their respective discharge limits [10]. It was found that over 70% of the pollutants were removed by the bioreactors with the MNP additives as compared to that of the control system. Among these bioreactors (A–E), bioreactor A was found to be more dominant in terms of its treatment performance as compared to the others. This affirms other studies where the presence of $\text{Fe}_2\text{O}_4\text{-TiO}_2$ released trivalent ions as electron donors which instigated the agglomeration and neutralisation of pollutants for their removal [12–16].

Table 1. Decontamination efficiency of the bioreactors (A–E).

Parameter	Feed	A	B	C	D	E	Discharge Limit [10]
COD (mg/L)	3570 ± 79	181.5 ± 8	870 ± 12.5	354 ± 4.5	755 ± 5.6	1120 ± 7.6	75
COD removal (%)	-	94.92	75.63	90.08	78.85	68.63	-
Color (Pt.Co)	1340 ± 55	421 ± 25	628 ± 26	520 ± 17	450 ± 23	653.75 ± 23	<15
Color removal (%)	-	68.58	53.13	61.19	66.42	51.21	-
Turbidity (NTU)	200 ± 33	33.62 ± 27	58.35 ± 17	46.77 ± 5	39.77 ± 23	88.03 ± 23	<5
Turbidity removal (%)	-	83.19	70.83	76.61	80.12	55.99	-
VS/TS ratio	0.72	0.49	0.46	0.47	0.46	0.62	-

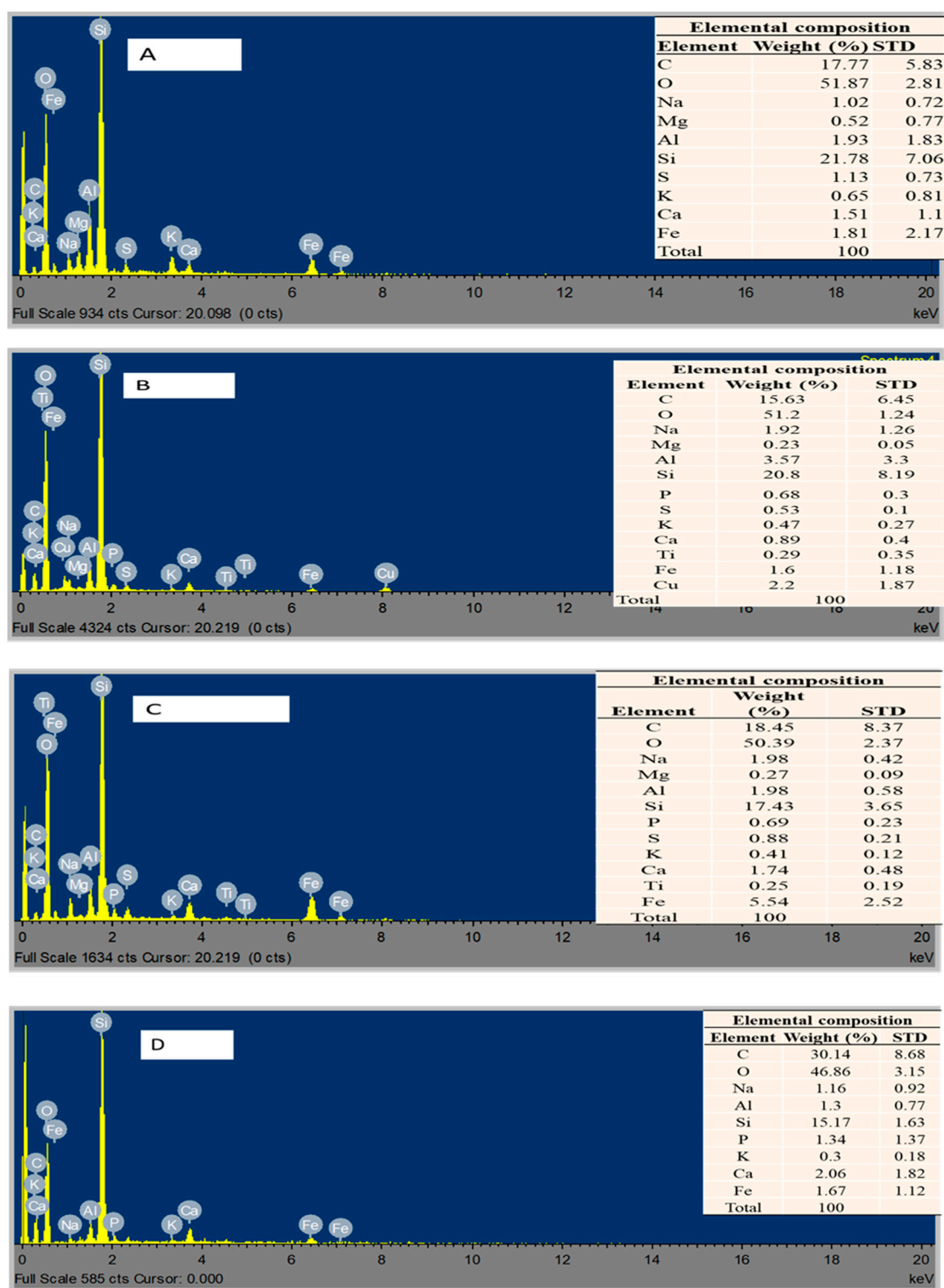


Figure 2. Cont.

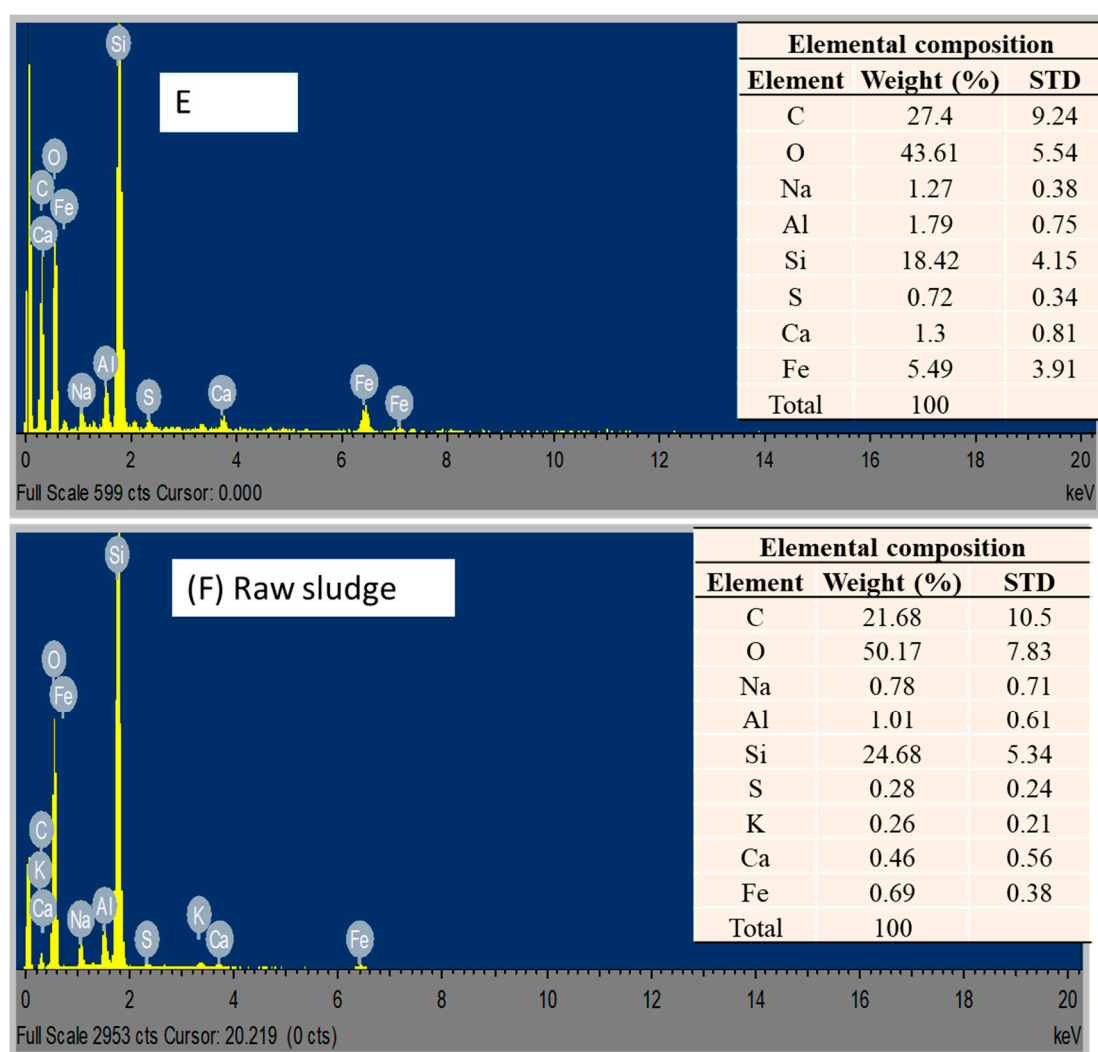


Figure 2. EDX images for post-digestate of bioreactors A–D charged with 2 g of (A) $\text{Fe}_2\text{O}_4\text{-TiO}_2$; (B) $\text{Cu-Fe}_2\text{O}_4$; (C) Fe_3O_4 ; and (D) $\text{Chitosan-Fe}_2\text{O}_4/\text{TiO}_2$ MNPs, whereas bioreactor E is a control: (E) no MNPs and (F) raw sludge.

2.3. Digestate Degradation and Biogas Production

Biogas is constituted by methane, carbon dioxide and other trace gases as the prime component of AD of waste or wastewater along with high-strength organics [1,3]. To improve AD biogas output, the potential biochemical methane system was dosed with different MNPs and their influence was monitored for 30 days. Figure 3 shows the amount of TS compared with the biogas produced by bioreactors A–D charged with 2 g of $\text{Fe}_2\text{O}_4\text{-TiO}_2$, $\text{Cu-Fe}_2\text{O}_4$, Fe_3O_4 and $\text{Chitosan-Fe}_2\text{O}_4/\text{TiO}_2$ MNPs, respectively, whereas bioreactor E had no MNP additives. The considerable TS outputs achieved were as follows: A (142.55 mg TS/L) < C (184.73 mg TS/L) < D (198.66 mg TS/L) < B (205.49 mg TS/L) < E (241.31 mg TS/L).

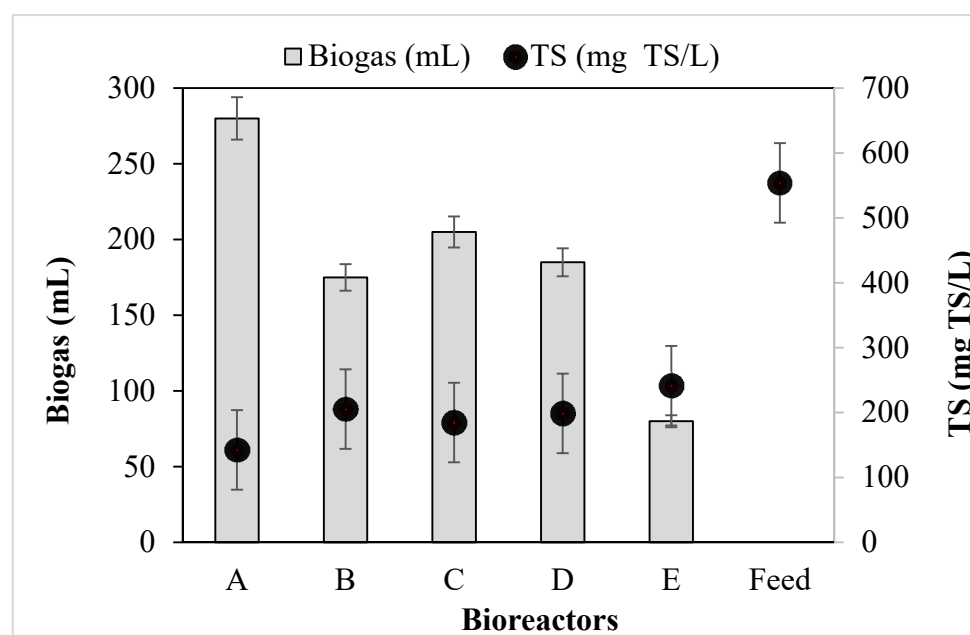


Figure 3. Biogas yield and TS degradation of bioreactors A–D charged with 2 g of (A) $\text{Fe}_2\text{O}_4\text{-TiO}_2$; (B) $\text{Cu-Fe}_2\text{O}_4$; (C) Fe_3O_4 ; and (D) Chitosan- $\text{Fe}_2\text{O}_4/\text{TiO}_2$ MNPs, whereas bioreactor E is a control: (E) no MNPs.

Comparatively, bioreactor A was found with the lowest digestate at 142.55 mgTS/L, corresponding to the highest biogas of 400 mL/d, whereas bioreactor E, being the control system, was found to be the lowest with biogas of 130 mL/day and biomass of 241.31 mg TS/L. Lower yield of the digestate was observed among the bioreactors charged with the MNPs, suggesting that there was significant microbial activity which resulted in the degradation of the organics during biogas production [2,17–20]. Conversely, for bioreactor E (control), the difference in the digestate compared to the other reactors was enormous, such that less microbial activity occurred [2,18].

Furthermore, the digestate can be used as a by-product for fertilizer or soil amendment, depending on the application. This is associated with the quality of the feedstock and the degree of degradation efficiency in the process, as well as the extent to which the post-treatment process was carried out. Significantly, sludge treatment contributes greatly to the total cost of wastewater treatment plants [4,5]. It was observed that the addition of MNPs to the bioreactors were easily separated from the sludge by an external magnet. This suggests that the bioreactors with MNP additives induced the sludge with its super-magnetic properties, which strengthened its degradability [19,21]. Therefore, the low sludge generated (Figure 3) suggests that biostimulation of wastewater systems with magnetic separation processes can help mitigate the costs of treatment and landfill complexity.

Figure 4 presents the cumulative biogas production yield collected over the incubation period of 30 days. Slow or low biogas production was observed during the first week, accompanied by rapid production from the 5th to the 25th day, followed by steady production until the last week when the system was shut down. The slow production observed is in agreement with other reported works which suggest the microbes need to get acclimatised before they begin production [4,5,12]. The overall biogas production was enhanced by the MNP additives to the bioreactors as compared to the control system without any MNP additives. This resulted in an increase in bioreactor production efficiency as follows: A (400 mL/day) > D (339 mL/day) > C (250 mL/day) > B (245 mL/day) > E (130 mL/day). Significantly, the bioreactor charged with $\text{Fe}_2\text{O}_4\text{-TiO}_2$ MNPs positively impacted biogas production ($p < 0.05$) [18]. MNP additives released metal ions into the substrate as nourishment, which stimulated microbial activity via long-term exposure [19].

In addition, the high surface area of the MNPs facilitated agglomeration, which had a great potential impact on the enzymatic activities of the methanogenesis microbes which increased the biogas production [18,19].

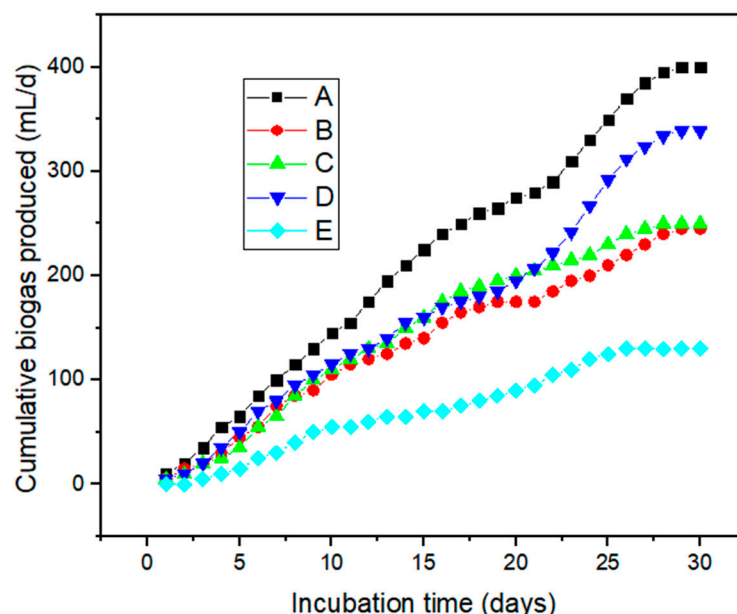


Figure 4. Cumulative biogas yield for 30 days of bioreactors A–D charged with 2 g of (A) Fe₂O₄-TiO₂; (B) Cu-Fe₂O₄; (C) Fe₃O₄; and (D) Chitosan-Fe₂O₄/TiO₂ MNPs, whereas bioreactor E is a control: (E) no MNPs.

2.4. Biomethane Potential

Figure 5 shows the biogas composition as characterised after 30 days of incubation. Here, the direct interspecies electron transfer by the MNPs played an important role in facilitating methanogenesis activity during the digestion period [18,20]. This positively resulted in over 75% degradation of the initial COD of 3570 ± 79 mg COD/L, which resulted in an increase in the methane yield (Figure 5). This result affirms other reported works in that the release of the electron carriers by the MNPs can regenerate into H₂, which serves as an electron donor and combines with CO₂ to produce CH₄ [1,2,18,19,21]; this was observed in bioreactors A–D, which had an increase in methane yield. Additionally, the high surface area of the Fe₂O₄-TiO₂ MNPs had a positive effect on the AD process, which resulted in both biogas enhancement and higher methane yield [18,22]. Evidently (Figure 5), a reduction in COD increased the productivity of the volatile fatty acids, which were then converted into the CH₄ potential by the methanogens as recorded by each bioreactor: A (100% CH₄); B (90% CH₄); C (100% CH₄); D (100% CH₄); and E (65% CH₄). Similar results were reported by other researchers, as MNPs influence biomethane potential [1,18,22,23]. This present study was no different, in that the addition of the MNPs had a significant impact on COD reduction and methane yield.

2.5. Technoeconomic Analysis of the Potential Estimated Energy

To ascertain the effectiveness of this technology and its economic feasibility, the cost of the energy produced was estimated based on the methane yield. Theoretically, the biogas consists of about 60–65% CH₄ and 35–40% CO₂, and 80% of the energy produced is converted into electricity [24,25]. Herein, the cost of energy was estimated based on the volume of biogas produced by the bioreactors: A (400 mL/day) > D (339 mL/day) > C (250 mL/day) > B (245 mL/day) > E (130 mL/day), with the results obtained presented in Table 2. To compare the energy economy of each bioreactor to that of [23] study, an assumed 80% methane potential (Figure 5) observed via the BMP test composition was used. This was based on 0.3 L of sludge, which was used to inoculate the degradation of

the wastewater via methanogenesis to produce the biogas, as well as subsequent characterisation of the methane composition. The calorific values of the substrate as well as that of the digestate were also considered for balancing the energy during the anaerobic digestion process [18,26]. The estimated calorific energy required (E_H) by the waterbath to maintain the digester temperature is given by (1):

$$E_H = Q \times C_p \times p (T_i - T_0) \quad (1)$$

where Q = substrate flowrate (m^3/d), C_p = specific heat of feed ($\text{kJ}/\text{kg } ^\circ\text{C}$), T_i = the digester temperature and T_0 = the substrate temperature from its stock [23].

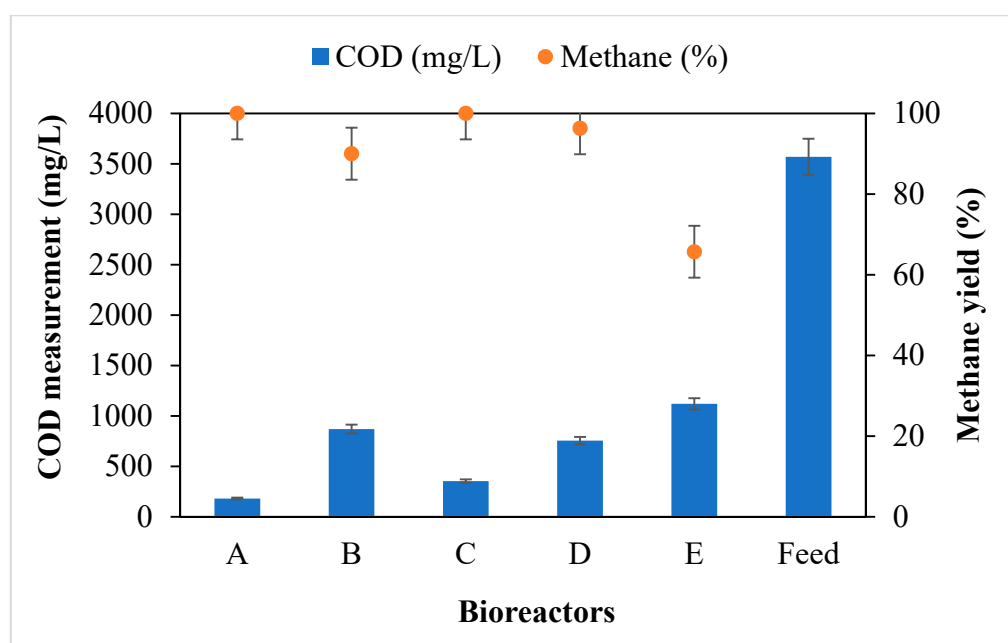


Figure 5. COD measurement and methane yield of bioreactors A–D charged with 2 g of (A) $\text{Fe}_2\text{O}_4\text{-TiO}_2$; (B) $\text{Cu-Fe}_2\text{O}_4$; (C) Fe_3O_4 ; and (D) Chitosan- $\text{Fe}_2\text{O}_4/\text{TiO}_2$ MNPs, whereas bioreactor E is a control: (E) no MNPs.

The daily energy production by each bioreactor E_A (kJ/d) corresponding to that of the methane contained in the produced biogas is given by (2). In addition, the net energy production E_P (kJ/d) is the difference between the produced energy and the energy consumed by the process (3).

$$E_A = (Mp) \times (L.H.V \text{ of methane}) \quad (2)$$

$$E_P = E_A - E_H \quad (3)$$

where Mp = daily methane production rate ($\text{m}^3 \text{CH}_4/\text{d}$) and $L.H.V$ = lower heating value of $35.8 \text{ kJ}/\text{m}^3 \text{CH}_4$ [24].

Table 2. Cost estimation for the energy produced from 0.3 L sludge.

Item No	Item	Unit	A	B	C	D	E	[23]
	Type of sludge		Activated wastewater sludge					
1	Energy content of Methane	m ³ /h	0.0036	0.00198	0.00225	0.00294	0.00077	73.29
2	Energy produced (E_A) (80% CH ₄ to electricity)	kW/h	0.00202	0.00113	0.00148	0.001283	0.00038	671
3	Energy (E_H) used by the waterbath	kW/h	0.00058	0.00032	0.00036	0.00047	0.00012	601.6
4	Net energy (E_P) = $E_A - E_H$	kW/h	0.0023	0.00127	0.00144	0.00188	0.00049	69.4
	Daily net energy cost estimated							
5	Energy cost (3.22 ZAR/kWh)	ZAR	0.00742	0.00409	0.00464	0.00606	0.00158	223.47
6	Energy cost (0.23 USD/kWh)	USD	0.00053	0.00029	0.00033	0.000432	0.00011	15.96
	Annual net energy cost estimated							
7	Energy cost (3.22 ZAR/kWh)	ZAR	320.49	176.67	200.31	261.57	68.43	
8	Energy cost (0.23 USD/kWh)	USD	22.89	12.62	14.30	18.68	4.89	

The main purpose of observing the energy balance in this experiment was to examine the economics of the energy potential of wastewater in terms of sustainable circular economy. Among the bioreactors A–E (Table 2), bioreactor A, charged with 2 g of Fe₂O₄-TiO₂, was found to be the most economically viable system with an estimated net energy profit of 320.49 ZAR/kWh, or 22.89 USD/kWh. Evidently, as observed in Table 2, all the bioreactors charged with the MNPs were found to be more economical than the control system which had no MNPs. This validates the positive role the MNPs charged to the bioreactors played in enhancing biogas production (Figure 4) as well as methanation efficiency (Figure 5). This proves that the use of MNPs to enhance biogas yield will be cost effective and large-scale production will be economically feasible [23,24].

3. Materials and Methods

3.1. Chemicals and Feedstock Collection

3.1.1. Synthesis and Characterisation of MNPs

All chemicals used, unless modified, were of analytical grade and obtained from Sigma Aldrich, South Africa. These included sodium hydroxide pellets (NaOH), ferrous sulphate heptahydrate (FeSO₄·7H₂O), oleic acid (surfactant), ferrous chloride hexahydrates (FeCl₃·6H₂O), titanium oxides, chitosan and ethanol (95%). The magnetised nanomaterials (Fe₂O₄-TiO₂, Cu-Fe₂O₄, Fe₃O₄ and Chitosan-Fe₂O₄/TiO₂) used in this study were engineered via co-precipitation techniques [8] and characterised at the DUT, Chemical Engineering Research Lab, Durban, South Africa. The MNP SEM/EDX micrographs revealed a high magnification of 10–50k× and landing energy capacity of 20 keV with a view size of 20.8 µm and width diameter of 4.5 mm to 6.5 mm.

3.1.2. Inoculum and Wastewater Distribution

The inoculum and wastewater samples were collected from an anaerobic digester operated by a local South Africa municipal wastewater treatment facility in the KwaZulu-Natal province. Using the American Public Health Association (APHA) [27] protocol for wastewater characterisation, the assay of the feedstock was found to constitute pH (6.3 ± 2.6), chemical oxygen demand (3570 ± 78.6 mg COD/L), turbidity (200 ± 32.7 NTU), total solids (554 mg TS/L), volatile solids (419 mg VS/L) and color (1340 ± 55.4 Pt.Co).

3.2. Biochemical Methane Potential (BMP) Test

With a reactor volume of 1 L, working volume of 80% and 20% head space, five bioreactors (1 L Duran schott bottles) were experimentally set up as depicted in Figure 6. Each bioreactor was initiated with homogenised 0.5 L wastewater and 0.3 L inoculum and labelled A–E. Subsequently, bioreactors A–D were charged with 2 g of Fe₂O₄-TiO₂, Cu-Fe₂O₄, Fe₃O₄ and Chitosan-Fe₂O₄/TiO₂ MNPs, respectively, whereas bioreactor E had no MNP additives. To enhance anaerobic conditions, each bioreactor was purged with nitrogen gas. In order to avoid thermal shocks in bioreactors and promote acclimatisation of the microbes, the system was left to stand for two days while adjusting the temperature from 27.5 °C to the mesophilic temperature of 40 °C. By using the downward displacement technique [4],

the biogas produced was collected and monitored daily along with intermittent shaking of the bioreactors. After 30 days of incubation, each bioreactor supernatant sampled was analysed and estimated for the degree of efficiency of contaminant removal (4).

$$\% \text{ degree efficiency} = \frac{\text{initial (feed)} - \text{final (after digestion)}}{\text{initial (feed)}} \times 100 \quad (4)$$

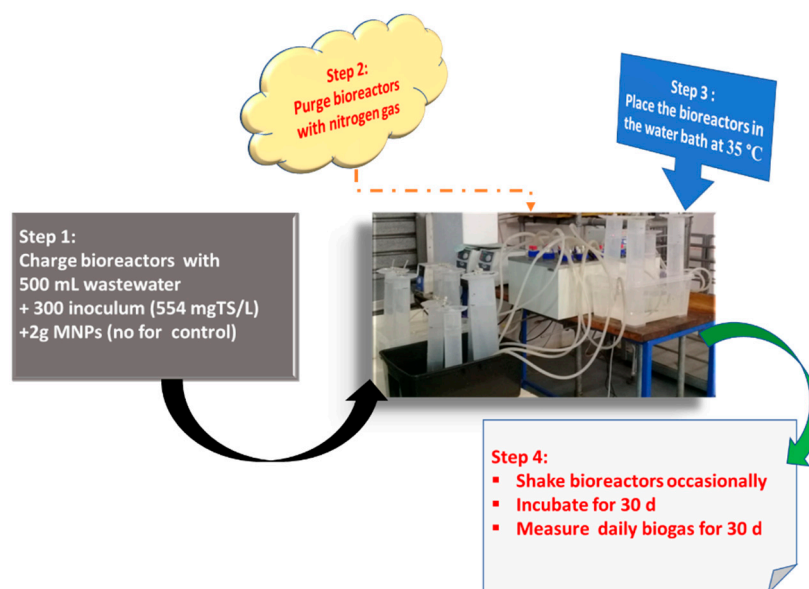


Figure 6. Schematic diagram of experimental procedure.

3.3. Digestate Analysis

The sludge was subjected to solids analysis before charging the bioreactors and after withdrawing the digestate from the bioreactors. Figure 7 represents the component balance of the influent and effluent water quality considered for characterisation using the standard protocols of analysing solids samples of APHA section 2540B [9]. Prior to knowing the mass of the crucibles used, they were first oven dried and allowed to cool in a desiccator. About 25 mL of the digestate was then weighed with the crucible and recorded as Q . At the temperature of 100 °C, the samples were then oven dried for 24 h. After drying, the sample was placed in a desiccator to cool, then immediately weighed with an analytical balance and recorded as R . The volatile solid content of the sample was determined using the furnace ignition at 550 °C for 1 h and the sample weighed and recorded as S . The estimated TS and VS were expressed with Equations (5) and (6), respectively:

$$\text{Total solids (TS)} = \frac{Q - R \times 1000}{V_S} \quad (5)$$

$$\text{Volatile solids (VS)} = \frac{R - S \times 1000}{V_S} \quad (6)$$

where Q is the mass (g) of crucible and sample after drying in oven, R is the mass of the crucible (g), S is the mass of the sample and crucible after calcination (g) and V_S is the volume of the sample (mL).

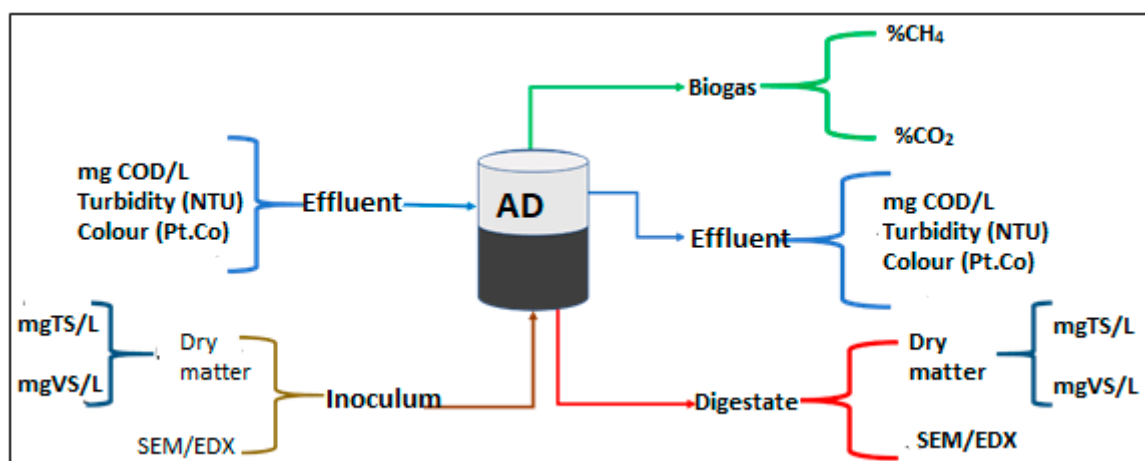


Figure 7. Schematic diagram of the component balance of the digestate input and output analysis.

3.4. Analytical Techniques

The pH was quantified with a Hannah pH-meter (HI98130, Hanna Instruments, Woonsocket, RI, USA). A HACH 2100N turbidity meter (Hach Company, Colorado, CO, USA) HACH DR 3900 within the wavelength of 455–635 nm (Hach Company, Colorado, CO, USA) was used for the COD and TKN measurements. The sludge samples were characterized using scanning electron microscopy and energy dispersive X-ray (SEM/EDX, FEI Nova NanoSEM 450 coupled with EDT and TLD detector) equipment based at the University of Cape Town, South Africa. The biogas composition analysis was carried out with a Geotech Biogas 5000 Portable Biogas Analyser (ISO17025) supplied by Keison Products, (Chelmsford Essex, UK).

4. Conclusions

In this study, the effects of magnetic nanoparticles (MNPs) on digestate for biogas production and decontamination were compared to the conventional treatment of municipality wastewater with no MNPs. This was carried out via biochemical methane potential (BMP) tests for 30 days using five bioreactors, A–D, charged with 2 g of $\text{Fe}_2\text{O}_4\text{-TiO}_2$, $\text{Cu-Fe}_2\text{O}_4$, Fe_3O_4 , and $\text{Chitosan-Fe}_2\text{O}_4/\text{TiO}_2$ MNPs, respectively, while bioreactor E had no MNPs added. SEM/EDX results confirmed the presence of trace elements (MNPs) in the digestate matrix, with distinctive impacts and interactive features in the metabolic pathway via microbial activity. Addition of MNPs to the bioreactors was demonstrated to be efficient for the treatability of the wastewater, with over 75% of the COD, colour and turbidity removed. Comparatively, bioreactor A, which was charged with $\text{Fe}_2\text{O}_4\text{-TiO}_2$ MNPs, showed itself as exceptionally viable in biostimulation of the AD process to increase biogas production (400 mL/day) and methane yield (100% CH_4). Analysis of energy balance and cost were performed based on the influence of the MNPs in generating energy from biogas production. The addition of the MNPs to bioreactors A–D showed a considerable annual net energy profit gain of 170–320 ZAR/kWh, or 12–23 USD/kWh, as compared to the control bioreactor E of 68 ZAR/kWh, or 4.89 USD/kWh. Conclusively, bioreactor A with $\text{Fe}_2\text{O}_4\text{-TiO}_2$ MNPs was estimated to have the highest energy profit (320.49 ZAR/kWh or 22.89 USD/kWh). Above all, the $\text{Fe}_2\text{O}_4\text{-TiO}_2$ MNPs proved to be economically viable and had good potential to improve circular economy in anaerobically managed wastewater and waste management settings.

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Chapter 3 - Technological evaluation via applicability of MPCs

Overview of objective 2:

- Technological evaluation and applicability of the synthesized TiO_2 MPCs for wastewater treatment using biological (AD), biomagnetic (BM), biophotocatalytic (BP), and biophotomagnetic (BPM) systems

In this chapter, the applicability of the MPCs is investigated and compared with different treatment configurations such as AD, BM, BP and BPM systems. The kinetic effect of the MPCs as biocatalysts in the AD process biogas production and methanation yield are discussed. The technological evaluation of the AD, BM, BP and BPM systems as stated were investigated with different goals. This included the understanding of the influence of the UV-Light only (BP), magnetic field (BM, BPM) as well as effect of both on the AD system. In Paper 7, we evaluated and compared the treatability, biogas production, and methanation enhancement performance of the AD and BM systems. It was found that the BM system outperformed conventional AD due to its external magnetic effect and the MPC addition. Likewise, BP and BPM system elucidated in Paper 8 (In appendix) respectively refers to the AD and BM system coupled with UV-light. In this case, a comparative study of the AD, BP and BPM were investigated. This resulted in CO_2 reduction, biogas production, methanation increase, and above 75% organic content (COD) degradability of the wastewater. Furthermore, the upscaled form of the BP system optimised via response surface methodology (RSM) to maximize its desirability is reported in Paper 9.

Herein in this section, the kinetics and energy economy of the upscale BP system is presented, elucidating how to subsidize the energy required by the UV-light via the BP system biogas produced and the effect of the MPCs loading.

3.1 Introduction

In wastewater engineering, mitigating the cost of discharging sludge with water content is becoming more challenging (Chai et al. 2021; Mostafaeipour et al. 2022; Zhao et al. 2021a). This warrants the use of AD for the reduction of sludge while increasing the caloric value of its products (biogas) (Bauer et al. 2013; Durán et al. 2021; Zhao et al. 2021b). AD is a biological treatment method that takes place in the absence of oxygen to degrade organic substrates into biogas (Apollo et al. 2013; Rojo et al. 2021). However, biogas production in the AD process involves a series of phases such as hydrolysis, acidogenesis, acetogenesis and methanogenesis (Apollo et al. 2016; Rojo et al. 2021). Herein, the microorganisms, known as methanogens, utilize and convert intermediate products such as acetic acid and hydrogen into methane, carbon dioxide (CO₂), and water. Kinetically, the AD process is very slow with low methane content (Ajay et al. 2020; Zhao et al. 2021b).

Energy-efficient wastewater treatment options are significantly important, especially for upgrading AD biogas production. This becomes a valuable tool to reduce wastewater pollution and its anthropogenic gas (CO₂) emissions towards a sustainable circular economy (Bauer et al. 2013; Durán et al. 2021; Russo and Von Blottnitz 2017). Subsequently, AD has been recognized as a successful process for converting large amounts of organic waste from wastewater into biomethane and produces large volumes of complicated sludge, whereby its discharge to the environment is of great concern (Hijazi et al. 2016; Russo and Von Blottnitz 2017).

Photocatalysis, on the other hand, has the advantage of mineralizing resistant pollutants but is also energy-intensive (Apollo et al. 2013; de Andrade Guerra et al. 2021; Sudarjanto et al. 2006). The notion of CO₂ photo-reduction via water-splitting mechanism conversion of CO₂ into methane was examined (Paper 8). As a result, using the BP system to recover bioenergy from wastewater can be used to power the UV energy required became the option.

In this study, biocatalyst (microorganisms or enzymes) coupled with photochemical catalyst (Fe-TiO₂) was explored as BP system for the valorisation of wastewater into bioenergy. This involves a bio-photo sequence, by degrading the organic content biologically whereas the nonbiodegradable pollutants were photodegraded. The photogenerated reactive oxidation species (ROSs), including e^- , h^+ , OH^- , OH^* , and O_2^{*-} played different roles in the BP systems. Herein, the addition of the Fe-TiO₂ in the presence of the UV-light facilitated the ROSs production (Fe, OH⁻, OH^{*}, and Ti⁴⁺). This influenced the hydrolysis of the water molecules splitting (H₂ and O₂) as well as the methanation reaction between the CO₂ and H₂. Thermodynamically, the more hydrogenation activity the higher the methane potential of the biogas produced. Herein, the upflow anaerobic sludge blanket (UASB) reactor was coupled with UV-light as an upscaled BP system, effect of the Fe-TiO₂ load was evaluated for degradation of the contaminants along with biomethane enhancement. In addition the kinetic dynamics and cost-benefit analysis was carried out.

3.2 Materials and methods

3.2.1 Magnetic photocatalyst (Fe-TiO₂)

A laboratory-based magnetite-titania photocatalyst (Fe-TiO₂) synthesized via the co-precipitation technique with characteristics detailed in Chapter 2 was employed in this study.

It had a specific surface area of 62.73 m²/g, pore volume of 0.017 cm³/g, and 1.337 nm particle size (Table 2.5).

3.2.2 Wastewater and sludge sample

The wastewater and sludge sample used in this study was obtained from a local South African municipality wastewater treatment plant based in the eThekweni municipality of the KwaZulu-Natal province. By observing the standard protocols for wastewater sample collection and characterization (Chambers 2019), Table 3.1 presents the wastewater characteristics distribution from the biofiltration stream of the wastewater treatment plant.

Table 3.1: Characterization of wastewater and activated sludge samples.

Water quality	value	Analytical instrument
pH	7.42 ± 3.6	Hanna pH/EC/TDS Tester (H198130)
Temperature (°C)	26.4 ± 2.3	Hanna pH/EC/TDS Tester (H198130)
Colour (abs 465 nm, Pt.Co)	570 ± 7.6	HACH Spectrophotometer (DR3900)
Turbidity (NTU)	732 ± 12.5	Turbidity meter (HACH 2100N)
Chemical oxygen demand (mg COD/L)	2380 ± 32	HACH Spectrophotometer (DR3900)
Ammonia (mg NH ₃ /L)	0.739 ± 0.4	HACH Spectrophotometer (DR3900)
Total Kjeldahl nitrogen (mg TKN/L)	30.5 ± 1.4	HACH Spectrophotometer (DR3900)
Nitrate (mg NO ₃ /L)	0.64 ± 0.5	HACH Spectrophotometer (DR3900)
Total nitrogen (mg TN/L)	31.88 ± 7.8	HACH Spectrophotometer (DR3900)
Total suspended solids (mg TS/L)	304.5 ± 23.6	Analytical balance (HCB602H 22 ADAM)
Volatile solids (mg VS/L)	229.5 ± 2.65	Analytical balance (HCB602H 22 ADAM)
Ratio VS/TS	0.75	

3.2.3 Biophotocatalytic (BP) system description

An upflow anaerobic sludge blanket (UASB) reactor constructed with Plexiglass coupled with UV-light was used as the BP system (Figure 3.1). The dimensions of the UASB were 60 cm in height and 20.7 cm in diameter which resulted in a total volume of 10 L and a working volume of 8 L with a headspace of 2 L. Compartments of the BP system included the conical settling zone and the blanket zone. To reduce variations in temperature, continuous recycling of cooling water through the water jacket of the reactor was carried out

using a water bath at constant temperature of 37.5°C at HRT of 30 days . Aside the gas collection and purging port, there are sampling points, which was used for the monitoring of the reactor performance with regards to effluent quality, sludge production as well as desludging of the reactor. The BP system was run for four (4) weeks and a weekly analysis of the water quality and biogas composition was done. The first week had no Fe-TiO₂ addition, followed by the system being dosed with 2 g Fe-TiO₂ every week until the fifth week where the system was shut down.

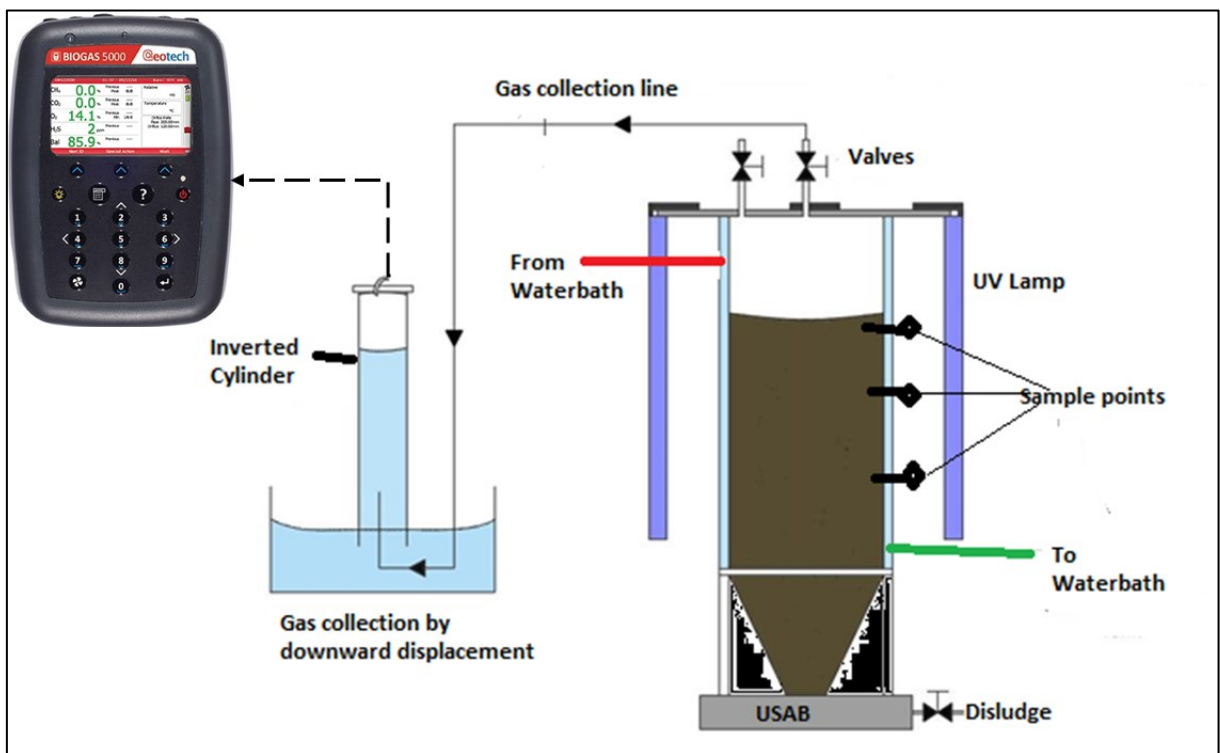


Figure 3.1: Schematic representation of the biophotocatalytic (BP) system consisting of an upflow anaerobic sludge blanket (UASB) reactor coupled with UV-light

Experimentally, the BP system was run for four (4) weeks and weekly analyses of the water quality and biogas composition were done. Thus, with 80% working volume and 20% headspace, the BP was charged with 5 L wastewater and 3 L activated sludge. The system was purged to create anaerobic conditions with nitrogen gas for 2 minutes. UV-light bulbs

(T8 blacklight - blue tube, 365 nm, 18 W, Philips, Netherlands) were placed alongside the BP system to ignite the photons of the Fe-TiO₂ for the degradation of the pollutants. In the first week, there was no addition of Fe-TiO₂. Afterwards, the system was dosed with 2 g Fe-TiO₂ every week until the fifth week when the system was shut down. However, daily monitoring volumes of the biogas was collected via the downward displacement technique and characterised weekly with Geotech Biogas 5000 Portable Biogas Analyser (ISO17025). To establish the rate of degradation, the cumulative biogas obtained was modelled and compared with the pseudo-first-order (3.1) and modified Gompertz (3.2) kinetic models.

$$Y(t) = Y_m [1 - \exp(-kt)] \quad (3.1)$$

$$Y(t) = Y_m \cdot \exp\left(-\exp\left[\frac{2.7183R_{\max}}{Y_m}[\lambda - t]\right] + 1\right) \quad (3.2)$$

Where,

$Y(t)$ is cumulative of specific biogas yield (mL/g COD),

Y_m is maximum biogas production (mL/g COD),

λ is lag phase period or minimum time to produce biogas (days),

t is cumulative time for biogas production (days),

$R_{\max}$ is the maximum specific substrate uptake rate (mL/g COD.day), and

k is a first-order rate constant (1/d)

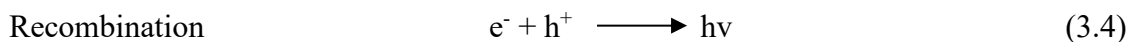
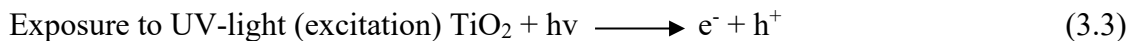
3.3 Results and Discussion

In this section, the effect of Fe-TiO₂ on the biophotocatalytic process for wastewater treatment and biogas production is presented. The biogas production and composition along with the kinetic study is highlighted. Also, the techno-economic analysis of estimating the energy produced to offset the UV-light energy required is underscored.

3.3.1 Effect of catalyst load on contaminant reduction

The effect of the catalyst load was conducted ranging from 2 g to 6 g while keeping other parameters constant with an initial effluent concentration of 2380 mg COD/L of the wastewater of the municipality. Before this, a zero charge of the catalyst load was initially conducted to observe the essence of the catalyst. This was carried out to understand the mechanism of how the catalyst helps with photodegradation by adsorbing pollutants onto its surface.

In essence, the presence of the catalyst Fe-TiO₂, which is made up of Fe and TiO₂ facilitated the degradation of the pollutants (de Oliveira Guidolin et al. 2021; El-Gendy and Nassar 2021). The presence of the UV light caused illumination and excitation on the surface of the Fe-TiO₂ catalyst, whereby the excited radicals/electrons moved from the catalyst valance band to the conduction band creating a hole on the surface for easing adsorption of the pollutants (Guo et al. 2019; Kobwittaya and Sirivithayapakorn 2014; Vargas et al. 2016). With the reaction mechanism presented (3.3-3.6), the hole and electron species created, reacted with the oxygen or water molecules to produce peroxide or hydroxyl species which in turn degraded the pollutants (Guo et al. 2019).



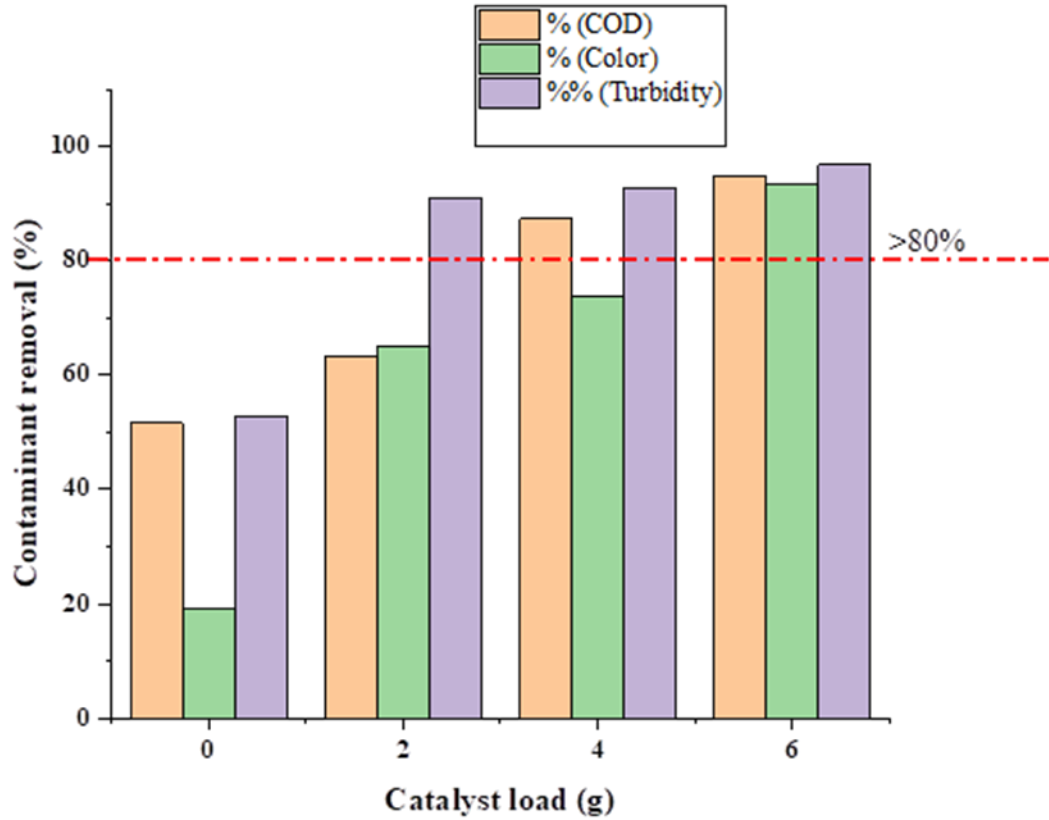
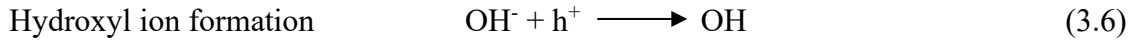
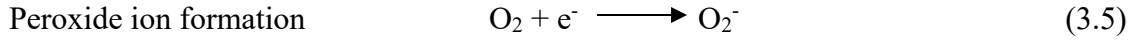


Figure 3.2: Effect of weekly catalyst load of 2 g Fe-TiO₂ on contaminant removal by using the biophotocatalytic system for four weeks.

Figure 3.2 shows that increasing the catalyst load from 2 g to 6 g Fe-TiO₂, increased the photocatalytic activity. This resulted in about 80% decontamination of the COD, colour and turbidity removal. Impressively, the colour removal efficiency was greater than the COD by 5% at a catalyst load of 2 g, implying that there was mineralization of colour-causing bonds (chromophores) in the wastewater (Ghofrani-Isfahani et al. 2020; Kobwittaya and Sirivithayapakorn 2014; Xu et al. 2021). The best efficiency of COD, colour, turbidity, and

reduction of other contaminants was achieved when the reactor had adapted/stabilized in the fourth week (4).

Table 3.2 presents a summary of the final effluent concentration per catalyst load charged per week. The balanced pH within 7.13 to 7.69, COD (12-115 mg COD/L) and VS/TS ratio < 0.5 proves that there was the degradation of organics (Apollo et al. 2013; Sudarjanto et al. 2006).

Table 3.2: Summary of results obtained for the weekly catalyst load of 2 g Fe-TiO₂ on contaminant removal by using the biophotocatalytic system for four weeks.

Parameters	Week 1	Week 2	Week 3	Week 4
Catalytic loading (g)	0	2	4	6
pH	5.59	7.13	7.13	7.69
COD (mg COD/L)	115	87	30	12
NO ₃ -N (mg/L)	24.61	7.26	0.98	2.65
TKN (mg/L)	24.3	6.01	0.80	2.53
NO ₂ -N (mg/L)	0.31	1.25	0.18	0.12
NH ₄ ⁺ (mg/L)	0.89	0.78	0.76	0.74
VS/TS	0.35	0.19	0.32	0.48

*Chemical oxygen demand (COD), Nitrite -Nitrogen (NO₂-N) , Total Kjeldahl nitrogen (TKN), Total Nitrate -Nitrogen (NO₃-N), Ammonia (NH₄⁺), Total solids (TS) and volatile solids (VS)

The nitrates (NO₃) and ammonium (NH₄⁺) during the degradation pathway suggests that there was mineralisation of the recalcitrant nitrogen-containing organic compounds such as TKN, NO₂-N, NO₃-N and NH₄⁺ in different proportions (Apollo et al. 2016; Wang et al. 2021). This infers that there was a reductive pathway, where the high oxidation state as shown Table 3.2 produced more unstable intermediates such as TKN and NH₄⁺ (Apollo et al. 2013).

Likewise, at the oxidation state, most of the elemental nitrogen molecules being detached increased the nitrate (NO_3^-) levels to be more than the NH_4^+ (Kobwittaya and Sirivithayapakorn 2014). So, NO_3^- being more than the NO_2^- and NH_4^+ in this study suggest more nitrogen atoms in the wastewater stream with higher oxidation state were eliminated via the photocatalysis pathway compared to the biological route (Deriase et al. 2021; Joy et al. 2021; Kobwittaya and Sirivithayapakorn 2014).

3.3.2 Biophotocatalytic (BP) reactor system

Figure 3.3 shows the effect of the Fe-TiO₂ load on biogas production for the duration of 30 days corresponding to 5150 mL of cumulative biogas. This cumulative biogas data was well fitted on a modified Gompertz kinetic model (3.2) and information obtained is presented in Table 3.3. The AD process can produce biogas by breaking down the organic molecules. On the other hand, mineralizing the organic molecules via UV photodegradation utilizes the energy produced (Apollo et al. 2013; Joy et al. 2021; Kobwittaya and Sirivithayapakorn 2014).

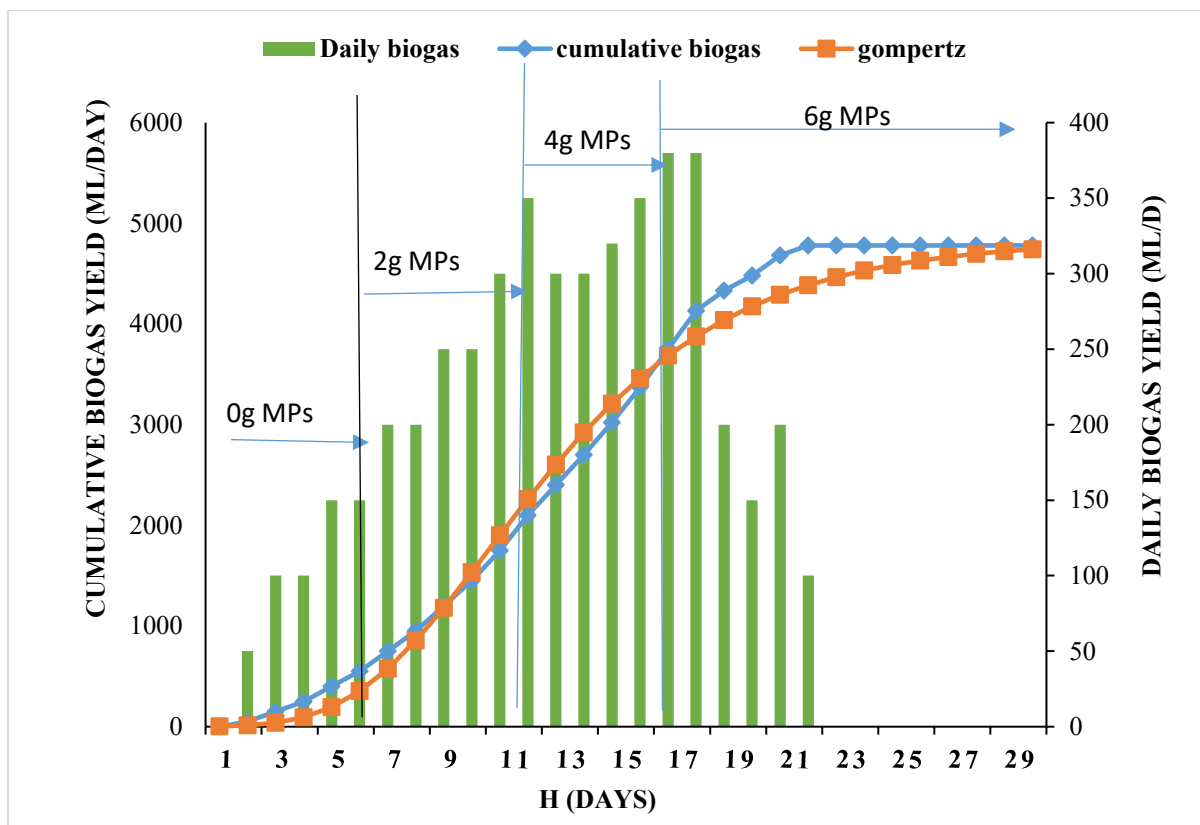


Figure 3.3: Effect of weekly catalyst load of 2 g Fe-TiO₂ on biogas production using the biophotocatalytic system for 30 days

Table 3.3: Summary of the modified Gompertz and first-order kinetic models for the BP system

Terms	Modified Gompertz model	First-order model
Ct (mL/g COD)	4780	4780
Cm (mL/g COD)	4830	3141923
k (1/day)	0.20623	0.00006
λ (day)	10.7	N/A
Sum of square errors (SSR)	1152385	7258214
Correlation Coefficient (R ²)	0.9917	0.9351
Predicted yield (mL/g COD)	4741	5659

The change in the catalyst load of 2 g per week (Figure 3.3), the average biogas produced weekly was 110 mL (zero charges), 270 mL (2 g charge), 285 mL (4 g charge) and 55 mL

(6 g charge), respectively for weeks 1- 4. The biogas production increased from the zero charged catalyst up to the 6 g charged, where there was retardation of the biogas production from the 21st day to the 30th day. The reduction in biogas yield occurring in the fourth week could be due to the substrate consumption and excess and other intermediated compounds generation, which inhibited the biogas production activity (Bauer et al. 2013; Durán et al. 2021; Zhao et al. 2021b). Thus, the microorganism activity was hampered with the high catalyst load from the 21st to the 30th day. Conversely, the highest amount of the catalyst load (6 g) charged increased the methane yield (70% CH₄) of the zero charges to 95% CH₄ as depicted in Figure 3.4. This performance could be a result of the presence of Fe and TiO₂, which served as direct electron transfer species (Ghofrani-Isfahani et al. 2020), which facilitated the CO₂ photoreduction mechanism to generate more methane (>80% CH₄).

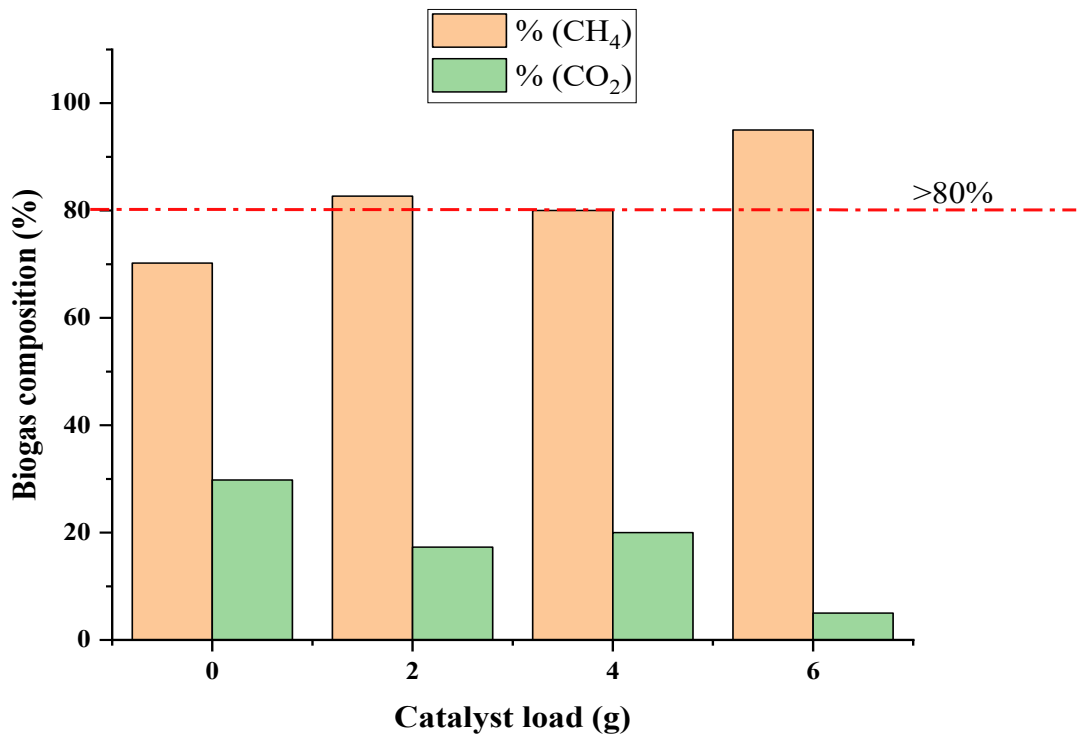


Figure 3.4: Effect of weekly catalyst load of 2 g Fe-TiO₂ on methane yield using the biophotocatalytic system for 30 days

3.4 Energy estimation of the BP System

AD energy production rate and energy consumption rate of the UV photodegradation were determined. Generally, biogas constitutes about 60-65% methane and 35-40% carbon dioxide (Hijazi et al. 2016; Zhao et al. 2021b), hence estimating 60% of 1 m³ biogas produced as energy is equivalent to 6 kWh. Biogas, as a renewable and sustainable energy source, can be used to produce heat, electricity, and vehicle fuel in place of fossil fuel (Fernández-Polanco et al. 2021; Hijazi et al. 2016).

In this study, the energy estimation was carried out to evaluate the amount of electricity that can be produced from the biogas generated and how much of it can be used to offset the UV-light power required. With 0.3 L of activated sludge, cumulative biogas of 0.00515 m³ yielded 90% methane with an energy content of 0.0464 kWh (Table 3.4). Assuming 75% of this energy can be converted into electricity, the result is 0.0348 kW/h. The total energy consumption for UV-light to degrade the unit mass of pollutant above 80% was estimated as 0.0180 kWh, hence the net energy left was 0.0168 kWh. Also, the projected cost was estimated by adopting the basis and energy reports on biogas production from wastewater settings (Mostafaeipour et al. 2022). Herein, the energy cost per hour (3.22 ZAR/kWh*0.0168kWh) was found to be ZAR 0.05 (Table 3.4). This affirms the fact that integrating AD with a photocatalytic process can assist subsidize the energy required by the UV lamp (Apollo et al. 2013; Mostafaeipour et al. 2022).

Table 3.4 Estimated cost of energy produced by biophotocatalytic (BP) process

Item No	Item	Values
	Biogas produced (m ³)	0.00515
1	Energy content of Methane (m ³ /h)	0.0464
2	Methane for electricity (kW/h)	0.0348
3	Energy applied (UV) (kW/h)	0.0180
4	Net energy (2-3) (kW/h)	0.0168
	Cost estimation	
5	Energy cost (3.22 ZAR/kWh)	0.054
	Energy cost (0.23 USD/kWh)	0.0039
6	Net energy cost for 30 days	
	Energy cost (3.22 ZAR/kWh)	38.86
	Energy cost (0.23 USD/kWh)	2.78

3.5 Summary and additional information

The magnetized photocatalyst (Fe-TiO₂) used in the biophotocatalytic (BP) system for the municipality wastewater treatment and bioenergy potential recovery was found viable. Thus, the UASB coupled with the UV-light ignited the Fe-TiO₂ radical species which facilitated the bio-photoreduction of the CO₂ which resulted in methane yield above 80%.

Also, the nitrate (NO₃⁻) and ammonium (NH₄⁺) formed during the biophotodegradation infer effective photodegradation occurrence of biorecalcitrant compounds. The energy analysis showed that the BP system produced 0.0348 kWh electricity out of 75% methane energy (0.0464 kWh) obtained from the 5150 mL of biogas, while the UV-light utilized 0.018 kW of electricity to enhance the treatment of the wastewater. This finding shows energy produced by the BP system can be used to subsidize the energy cost of UV-photodegradation when applied as an integrated system. Additionally, Paper 7 explains the potential of the biomagnetic system for trace elements reduction and enhancement of biogas and methane yield, whereas, in Paper 8, biophotoreduction of CO₂ emission reduction was highlighted. Furthermore, Paper 9 presents the need to understand the dynamics of Fe-TiO₂ load on

biophotocatalytic along with other operational parameters by the use of response surface methodology (RSM). The prospects of the BP system applicability and viability in a large-scale wastewater treatment setting warrant an integrated AD-AOP system coupled with magnetic field lab-scale studies (Chapter 4).

Paper 7: Biomagnetic system



Paper 7.pdf

Paper 8 (Appendix A): Bio-photoreduction of CO₂ emission

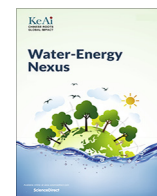


Paper 8.pdf

Paper 9 (Appendix B): Biophotocatalytic system optimization



Paper 9_r.pdf



Biogas production from wastewater treatment-evaluating anaerobic and biomagnetic systems

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ABSTRACT

Biogas, a green and sustainable form of energy produced during the degradation of organic waste anaerobically comes with ecological and economic paybacks when compared to a comprehensive fossil fuel-based energy system. However, the biodiversity of microorganisms and chemical loads for enzymatic and bioconversion reactions impedes the anaerobic digester's (AD) practicality for commercialization. Hence, this study examined the application of titanium dioxide magnetite (Fe-TiO₂) (F) via a synthetic route in AD + F and a biomagnetic system (BMs) as a collective pathway to maximize methane potentials, wastewater treatment, and improve biogas production. The AD + F and BM systems were operated at a working volume of 0.8 L (inoculum to wastewater ratio of 0.6), the mesophilic temperature of 35 °C for an incubation period of 30 days. The results showed in-situ Fe-TiO₂ facilitated the bio-electrolysis and bio-methanation reactions in the AD process which improved its performance as compared to the control (AD only). Above 75% of chemical oxygen demand (1600 ± 16.2 mg/L), Total Kjeldahl Nitrogen (76 ± 6.4 mg/L), total solids (135 ± 12 mg VS/L), volatile solids (94 ± 6.8 mg VS/L), and other inorganic contaminants (28 elementals) contained in the wastewater were removed by the BMs at a pH of 6.5 followed by the AD + F (65–75%) and the AD only (50–65%). On the 20th day, the control system (AD only) had a maximum daily biogas yield of 50 mL/COD.d, whereas the AD + F gave 90 mL/d and BMs 120 mL/d. Compared to the control with a methane yield of 66%, the addition of the Fe-TiO₂ to AD + F and BMs increased the methane yield to 100%. Synergistically, the catalytic and biomagnetic activity of Fe-TiO₂ in the BMs heightened the adsorption and reaction pathway of the contaminant's transformations and degradation. Amidst two kinetic models investigated, the cumulative biogas yield followed the Gompertz kinetic model. In conclusion, combining the magnetic effect with green magnetic catalyst (Fe-TiO₂) in AD and adsorption-based wastewater settings have viable prospects towards environmental purification.

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1. Introduction

Recent energy costs and the decline in the availability of energy resources have become a pressing concern of decision-makers and consumers about their societal activities, environmental and economic impact (Eurostat, 2020; Ning et al., 2013). This has resulted in a paradigm shift of wastewater management experts

reconsidering wastewater treatment plants (WWTPs) as a vital source for a bio-based circular economy rather than end-of-life treatment and disposal facilities (Casas-Godoy et al., 2020; Sanders and Van der Hoeven, 2008; Spierling et al., 2018). Thus, redesigning and operating modernized WWTPs is a valuable pathway for resource optimization and energy recovery in wastewater settings. In essence, wastewater with high-strength organic matter can generate 10 times the energy required for its treatment in the form of biogas to meet on-site power and thermal needs (Casas-Godoy et al., 2020). Notwithstanding, route sources of WWTPs are mostly obtained from livestock farms, slaughterhouses, domestic, industrial, and agricultural activities (Jordan et al., 2007; Maina et al., 2017). Such waste contains large quantities of organic matter which are biodegradable representing a valuable resource for bioenergy.

Abbreviations: WWTPs, Wastewater treatment plants; AD, Anaerobic digester; BMs, Biomagnetic system; COD, Chemical oxygen demand; NPs, Nanoparticles; TS, Total solids; BMP, Biomethane potential; TE, Trace elements; TKN, Total Kjeldahl Nitrogen.

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In wastewater treatment works, anaerobic digestion (AD) has proven to be the most widely used sustainable technology for reduction, recycling, and recovery resources from organic wastes (Bennich and Belyazid, 2017; Casas-Godoy et al., 2020; Jordan et al., 2007). Given South African wastewater management systems, AD processes are incorporated with the benefits of transforming organic solid wastes into more useful organics (fertilizers, dry sludge) (Russo and von Blottnitz, 2017; Stafford et al., 2013). Also, to derive and capture biogas (methane-rich natural gas) as a renewable source of energy for heat, electricity, and biofuel production (Msibi and Kornelius, 2017; Russo and von Blottnitz, 2017). Generally, the AD mechanism involves three main phases (hydrolysis, acidogenesis, and methanogenesis), which require different groups of active microbes at each phase (Budzianowski and Postawa, 2017; Prussi et al., 2019). Concisely, AD is dependent on the number and activities of these microbes, which are associated with several factors such as the reactor operational conditions (presence or absence of oxygen, temperature, pH, hydraulic retention time, etc.), substrate properties, and the digester configuration (Laiq Ur Rehman et al., 2019; Lohani and Havukainen, 2018). To avoid the AD operational failure and poor performance, making provision of nutrients insufficient amount and the right proportion in the substrate to sustain the microbe's growth and activities becomes very critical. Thus, any form of limitations could affect the biogas production efficiency. Meanwhile, some of the microbes required for anaerobic ingesting of organic matter for biogas production have a desire for intake of trace elements (Fe, Cu, Ti, Ni, Mg, Co, Ag, Zn, Pb), nutrients (phosphate, ammonia, nitrate, and nitrite), whereas some can be inhibitory to the AD process (Hagos et al., 2017; Thanh et al., 2016; Zhang et al., 2011; Kweinor Tetteh et al., 2020; Kweinor Tetteh and Rathilal, 2020). Therefore, finding balance in the substrate or nutrient composition and bioavailability of trace metals for biogas production should be given attention.

Today, nanotechnology (nanoparticles, nanomembrane, and nanopowder) offers a great opportunity for the effective removal of pollutants in water and wastewater treatment settings. Meanwhile, the number of nano-scaled materials entering the WWTPs is becoming unbearable to the levels for microbial communities (Kweinor Tetteh et al., 2020; Kweinor Tetteh and Rathilal, 2020). This phenomenon has resulted in anti-microbial resistance as a hinge environmental problem in the water and wastewater treatment sector. To avert this, the use of a magnetic field in anaerobic digestion is drawing attention among researchers for nanomaterials magnetic separation (Abdel Maksoud et al., 2020; Zaidi et al., 2014; Zhang et al., 2016). Extensively, studies on the use of magnetic powder and other electromagnetic regimes have proven to be effective to provide magnetic induction, accelerate the growth and metabolism of microorganisms (Abdel Maksoud et al., 2020). Additionally, biomagnetic effects have been found to depend on the magnetic field strength, frequency, configuration type, and the length of exposure (Abdel Maksoud et al., 2020; Bée et al., 2011; Zaidi et al., 2014). For instance, constant magnetic field exposure was successively employed in wastewater treatment, which enhanced the biological and enzymatic activity (Kefeni et al., 2017; Long et al., 2019; Yadollahpour et al., 2014). Thus, the exposure is accountable for altering the magnetic powder properties as well as the exposed solution polarisation, molecular structure, and change in electronic charge (Yadollahpour et al., 2014).

Apart from the environmental merits of magnetic separation technology, the hypothesis of radical pair mechanism (magnetized microbes) responsible for the changes in reaction kinetics induced by the magnetic field has a significant effect on substrate degradability and microbial growth (Bhatia et al., 2021; Yadollahpour et al., 2014).

Despite the availability of valuable information on the role of magnetic seeding in biological systems and microbial enhancement (Baek et al., 2015; Booker et al., 1991; Ebner et al., 2002; Esfandiari et al., 2020; Horst et al., 2016; Liang et al., 2017; Liu et al., 2015; Navratil and Akin, 2009; Suanon et al., 2016; Xiang et al., 2019). There is still inadequate information on developing a biomagnetic system for biogas production from wastewater treatment. In response to the AD process been kinetically slow in biogas production, hence seeding it with titanium dioxide magnetite (Fe-TiO₂) to be AD + F system or coupling it with the magnetic field to be defined as a biomagnetic system (BMs) will enhance biogas upgrading. Therefore, this study aimed to evaluate the effect of the Fe-TiO₂ as a biostimulant in AD + F (with Fe-TiO₂ additives) and BM (AD with Fe-TiO₂ additives + Magnetic field) systems for the wastewater treatment to produce biogas by comparing it to a control system (AD with no additives and magnetic field).

This comparative study was carried out with three bioreactors (AD only, AD + F, and BM) at a mesophilic temperature of 35 °C for the incubation period of 30 days. In addition, the cumulative biogas data obtained was kinetically modeled to determine the parameters suitable for the stability and upscaling of the reactors. Inclusively, this investigation provides essential information required to explore the technological competitiveness of maximizing methane potential in biogas via the valorization of wastewater treatment. Advancing this technology in wastewater settings and industries can be a potential candidate for the reclamation of wastewater and environmental sustainability.

2. Materials and method

2.1. Wastewater and inoculum used

In this study, the wastewater and anaerobic sewage sludge (inoculum) used was collected from a local South African sugar refinery wastewater treatment plant based in Durban in the KwaZulu-Natal Province. The wastewater and sludge samples were taken from the point source of biofiltration and anaerobic digester units, respectively. The sludge was homogenized, kept under aerobic conditions, and stored at room temperature before use. Table 1 shows the initial results of pH, chemical oxygen demand (COD), Total Kjeldahl Nitrogen (TKN), total solids (TS), and volatile solids (VS) tested by APHA (2012). The pH was quantified with a Hanna pH-meter (HI98130, Hanna Instruments, Woonsocket RI, USA). HACH DR 3900 within the wavelength of 455–635 nm (Hach Company, Colorado – USA) was used for the COD and TKN measurement. The elemental composition of the samples was performed with an Agilent Micro-Plasma Atomic Emission Spectrophotometer (MP-AES, MY 18379001).

2.2. Biomethane potential test

Titanium dioxide magnetite (Fe-TiO₂) used in this experiment was synthesized by co-precipitation of mesoporous Titania coupled with Fe₂O₃ NPs as defined and characterized by Kweinor Tetteh and Rathilal (2020) and Kalan et al. (2016). Three 1 L Duran Schott bottles with a bottom hotplate supported by a stirrer were used in the batchwise digester experiment. As shown in Fig. 1, these reactors were classified as control (AD only), AD + F (AD with Fe-TiO₂), and BMs (AD with Fe-TiO₂ additives + Magnetic field). The BMs magnetic field was generated by two magnetic bars (GMX model 400 – Chino, California, USA). The addition of 2 g of Fe-TiO₂ NPs to the AD + F and BMs was studied to see if there was any biostimulation in terms of biogas production, as compared to the control bioreactor (AD only) with only wastewater and

Table 1
Characteristics of the wastewater sample.

Parameters	Feed	AD	AD + F	BMs
pH	7.5	6.8	6.7	6.5
Total Kjeldahl Nitrogen (mg TKN/L)	76 ± 6.4	60.9 ± 12	57.97 ± 14	42.69 ± 23
Chemical oxygen demand (mg COD/L)	1600 ± 16.2	928 ± 27	432 ± 136	450 ± 125
Total solids (mgTS/L)	135 ± 12	98 ± 18	72 ± 26	66 ± 23
Volatle solids (mgVS/L)	94 ± 6.8	76 ± 8	63 ± 12	57 ± 21

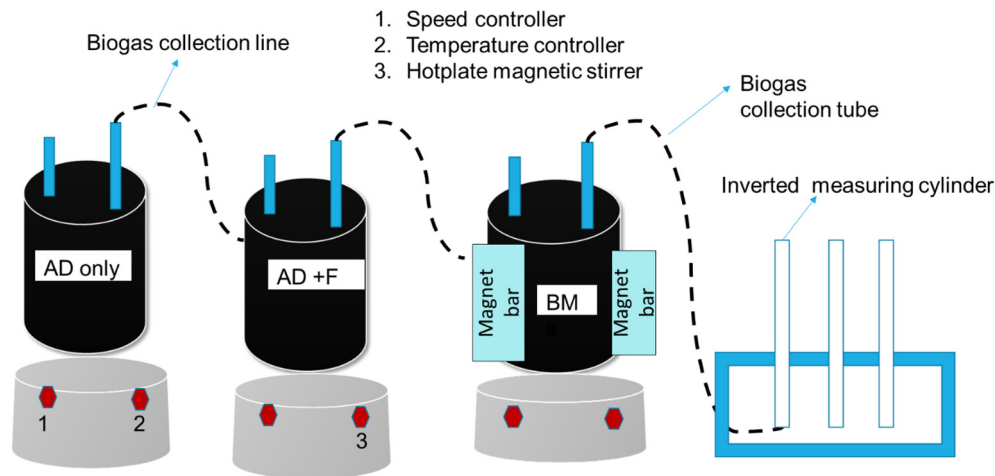


Fig. 1. Schematic flow diagram of the experimental setups on magnetic hotplate stirrers operated at a temperature of 35 °C and mixing rate of 15 rpm for HRT 30 days; Control as AD only (with no additives and magnetic field); AD + F (AD with Fe-TiO₂) and BMs (AD with Fe-TiO₂ additives + Magnetic field).

inoculum. Each module was run for 30 days at a hotplate mixing rate of 15 rpm and a mesophilic temperature of 35 °C. To ensure component contact and uniformity of the samples, periodic mixing was done every 4 h. The reactors substrate to inoculum ratio was fed as 350 mL (wastewater): 450 mL wastewater (inoculum) with allowable headspace of 200 mL for the biogas accumulation. Furthermore, the headspace was purged with N₂ gas for 5 min to deoxygenate the setups. A tube was connected from each of the reactors to the downward displacement collection vessel Gas Chromatography (GC 2014, Shimadzu) was employed for the biogas composition characterization. The reactor efficiency was assessed by monitoring the removal of the contaminants (1). Additional cumulative biogas data obtained were fitted on a modified Gompertz model and first-order kinetics models expressed in (2) and (3).

$$\text{Reactor efficiency} = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (1)$$

where, C_i = Substrate influent and C_f = Substrate effluent. The cumulative biogas production data obtained was evaluated by first-order and modified Gompertz equations (2) and (3), respectively (Kweinor Tetteh and Rathilal, 2020).

$$Y = ym \cdot \exp \left(- \exp \left[\frac{R_{max,e}}{ym} [\lambda - t] \right] + 1 \right) \quad (2)$$

$$Y = ym[1 - \exp(-kt)] \quad (3)$$

where, Y = cumulative specific biomethane (mL/g COD) at time t (days), ym = the methane potential (mL/g COD), λ = lag phase of producing biogas (day), e = mathematical constant (2.718282), R_{max} = the maximum specific substrate uptake rate per maximum biogas production (L/g COD.day) and k is the methane production rate constant (1/d), were in terms of Gompertz, $k = \frac{R_{max,e}}{ym}$.

3. Results and discussions

3.1. Bioreactor performance via effluent analysis

Additives of Fe-TiO₂ NPs characterized under microscale of 20 µm with a magnification of 5000 kx and landing energy capacity of 20 keV within a width distance (WD) of 5–6.5 mm were used as a biostimulant. Its crystalline structure was face-centered cubic with reflection (227) index JCPDS 00-019-0629 at 35.423° (2θ). Also, the reflection (141) of anatase with an interplanar distance of 3.893 Å (JCPDS 00-021-0428) and a body-centered tetragonal structure was determined at 25.281° (2θ). Conventionally, the high organic wastewaters used as feedstock was digested anaerobically to minimize the pollutants as well as the cost of discharging the sludge (Broun and Sattler, 2016). According to Michailos et al., (2020) sludge treatment and disposal constitutes up to 50% of the total cost of most wastewater treatment. Therefore, turning wastewater into an energy-saving economy comes in handy.

In this study, significant reduction and separation of the sludge by an external magnet was observed as tense aggregate with the Fe-TiO₂ additives was found around the magnetic bars which increased the sludge separation from the effluents. To understand the degradability and biostimulation effect of the Fe-TiO₂ NPs, two bioreactors such as AD + F (with Fe-TiO₂) and BMs (AD with Fe-TiO₂ additives + Magnetic field) efficiency was compared to that of a control system (AD with no additives and magnetic field). After the 30 days of incubation, results of the characterized supernatant for each bioreactor and that of the feed are depicted in Table 1. This demonstrated there was significance in the removal of specific contaminants from the wastewater sample in the following order of the bioreactors as AD only > AD + F > BMs. Aside from the degree of reducing chemical oxygen demand (COD) in wastewater as a measure of the performance indicator, TKN, NH₄, TS, VS, and 28 trace elements reduction were also monitored along with the biogas production.

The reduction in nitrate concentration throughout AD is generally attributable to the anaerobic denitrification process. Denitrification of oxidized nitrogen and methanogenic degradation occur simultaneously in the bioreactors (Table 1). A reduction in TKN and NH_4 concentration during the degradation period was also observed in all the wastewater samples treated by the various systems (Table 1). However, respective concentrations of the BMs > AD + F were lower than that of the control system (AD only). This can be accounted by the fact that the Fe-TiO₂ additives in the AD + F and BMs reactors were removed by the ionic -exchange. As Fe-TiO₂ NPs at oxidation state can release trivalent and divalent radical ions, which facilitated the removal of the contaminant.

Monitoring of the pH exhibited similar behavior within the range of 6.5 to 7.5, whereas that of the pH of the BMs was seen to be the lowest. According to Zhai et al., (2015), the pH of AD processes is very sensitive and delicate parameters. So, the low pH variation suggests the stability and buffering capacity of the reactors, especially the BMs with the external magnetic field tended to withstand such fluctuation (Gheraout, 2017; Li et al., 2019; Xu et al., 2020). Kwietniewska and Tys (2014) also reported that the variation in pH beyond the capacity of the reactor can cause system failure, by affecting the methanogenic bacteria activity and degradability performance.

In Fig. 2, the corresponding values to maximize the initial COD of 1600 ± 16.2 mg/L removal efficiency were in order of BMs (68%) > AD + F (62%) > AD only (55%). It was found that the high amount of soluble COD available in the feed nourished the anaerobic microbes for the degradation of the organic matter for biogas production. As the highest degradation was experimental with the BMs followed by the AD + F and AD. As the COD and TKN concentration in the augmented reactors BMs > AD + F remained were lower than that of the control (AD only) (Table 1), affirms the tendency of the TS and VS reduction by the bioreactors. Amani et al. (2010) and Thanh et al. (2016) reported that bioaugmentation of AD with Fe NPs improved the COD removal efficiency.

Fig. 3 shows the degree of total solids (TS) and volatile solids (VS) removal after the degradation of the substrate. It was found the Fe-TiO₂ additives enhanced the reduction of the sludge-water level content (Fig. 3) %VS/TS ratio of 88.4%, 89.3%, and 92% respectively for AD only, AD + F, and BMs reactors. The highest removal efficiency of %VS/TS observed in the BMs > AD + F might be attributed to the inhibitory effect of the Fe-TiO₂ addition (Abdelsalam et al., 2017; Chen et al., 2018; Chen et al., 2019; Omara et al., 2019). These results are harmonized with the Chen et al., (2018)

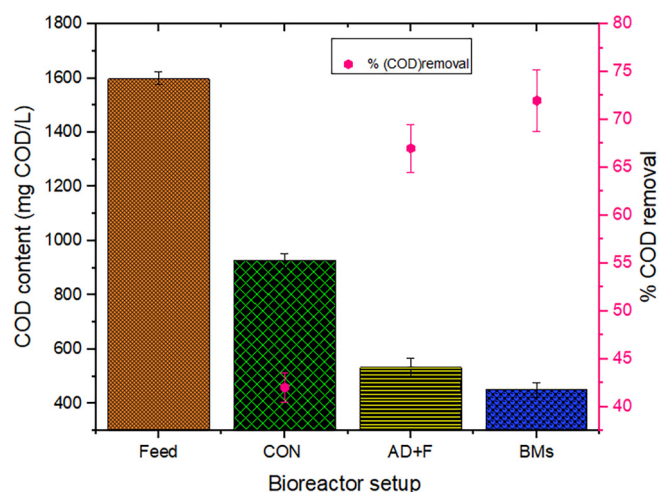


Fig. 2. COD removal and degradation efficiency of the bioreactors (AD only, AD + F and BMs).

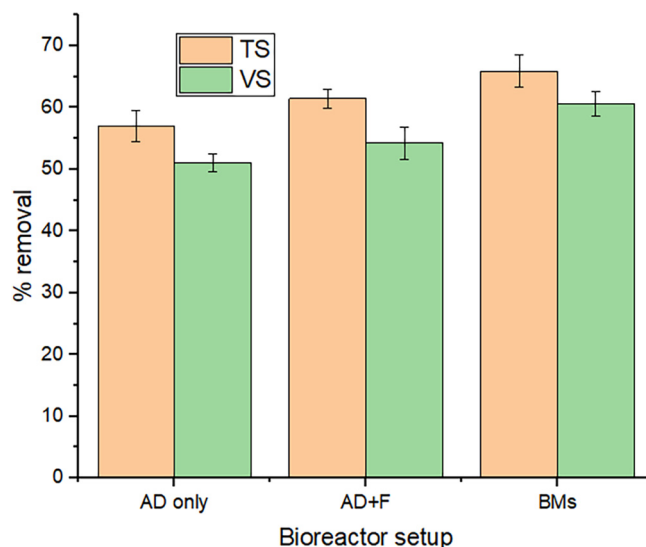


Fig. 3. Percentage removal of TS and VS for the reactors (AD only, AD + F and BMs).

report, where Fe-based additives increased the rate of agglomeration and acclimation of sludge via the microbe's activities which improved the treatment efficiency.

3.2. Trace elements removal

Consequently, the fate and level to which elements are available for interaction with biological systems can be divided into two categories based on their uptake mechanisms: those with (i) active uptake, i.e. internalization processes that require direct metabolic activity from microorganisms to transfer TE through the plasma membrane; and those with (ii) passive uptake, i.e. internalization processes that do not require direct metabolic activity from microorganisms to transfer TE through the plasma membrane. TE bioavailability is also influenced by TE partitioning across liquid and solid phases, as well as TE diffusion to the microbial membrane surface. Also, TE can affect biogas production and methane yield via the intracellular, once absorbed (Fig. 4).

Table 2 shows the trace metals and their concentration in the supernatant after the degradation. Despite the individual differences in the operated reactors (AD only, AD + F, BMs), it is observed that there is bioavailability of trace metal content in the sludge used. Interestingly, most of the trace metals concentration (0.797 mg Fe/L and 0.154 mg Ti/L) in the control (AD only) reactor seems to be very high and their accumulation inhibited the system. According to Chen et al., (2019), accumulation of trace metals are responsibly for volatile fatty acids contribution, which can increase methane yield or cause acidification/alkalinity shock to the reactor system. This affirms the treatability efficiency results obtained (Table 2), where most of the trace metals became chemical species suitable for microbial uptake (Fig. 4). For instance, the trace metal content of Fe-TiO₂ additives in the substrate (Fe and Ti), even if they were not supposed to be, met the microbial requirement sufficient for their activities. This observation is in line with Chen et al., (2018), where addition of Ni to a digester resulted in stabilization of the process and biogas production. Some of these metals which are commonly used for substrate variation in the AD process operational improvement including Fe, Cu, Ni, Mn, Zn, Co, Mo, Se and Ti were identified (Table 2). Despite the nutritional values of most of the trace metals, certain levels of the metal content in the reactors reflect metal surplus or deficiency for the microbial activities in the system (Chen et al., 2019; Tao et al., 2019). This highlights that bioavailability of metal species for microbial uptake

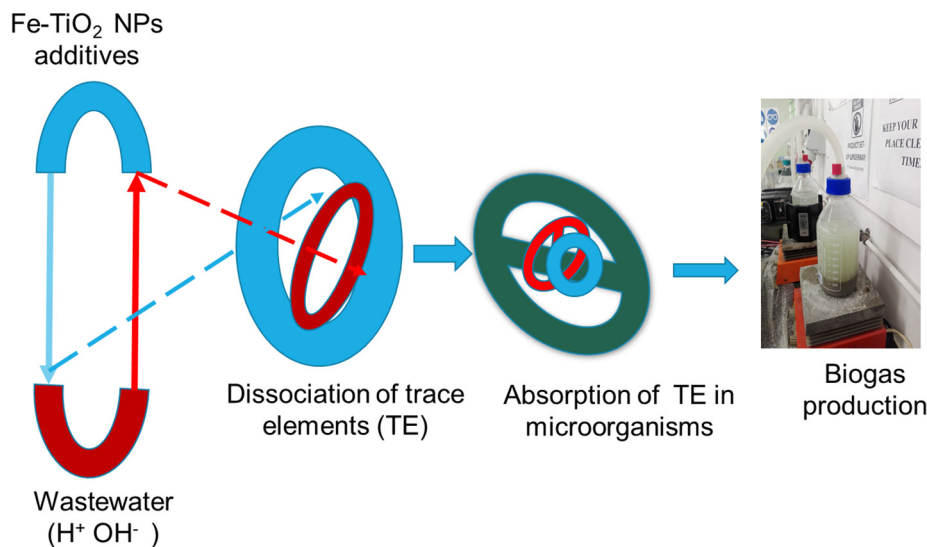


Fig. 4. Schematic and conceptual representation of trace elements bioavailability in a biological system.

Table 2
Reactors performance for the removal of trace metals

Elements (mg/L)	Feed (mg/L)	AD only (mg/L)	AD + F (mg/L)	BMs (mg/L)
Si	0.8325	0.555	N/A	N/A
V	1.599	0.084	1.038	0.952
Zn	0.5925	0.876	0.103	0.11
Ag	58.126	112.697	1.185	2.599
Al	4.6055	2.333	1.853	1.853
As	0.0915	0.15	0.011	0.005
Ba	0.3085	0.008	0.257	0.203
Be	43.835	87.598	0.026	0.024
Ca	97.602	0.015	65.063	58.182
Cd	0.018	0.006	0.01	N/A
Co	0.149	0.289	0.038	0.003
Cr	0.2685	0.264	0.091	0.0329
Cu	0.357	0.075	0.236	0.213
Fe	1.4775	0.797	0.329	0.158
K	282.732	16.812	182.884	117.426
Mg	23.784	0.15	15.806	15.784
Mn	0.1485	N/A	0.099	0.071
Mo	74.178	148.356	N/A	N/A
Na	137.121	1.113	91.043	103.963
Ni	3.0445	0.029	2.02	1.989
Pb	0.0255	0.003	0.016	0.004
Sb	0.0475	0.044	0.017	0.0031
Se	0.0835	0.044	0.041	0.038
Sn	0.0235	0.02	0.009	0.015
Sr	N/A	N/A	N/A	N/A
Ti	0.731	0.154	0.436	0.211
Tl	0.048	0.024	0.024	0.07

in the reactors (AD only, AD + F and BMs) might differ from one to another depending on their considerable chemical and biological conditions (Abdelsalam et al., 2017). Thus, the reactors improvement forms the basic requirement of metals as macro or micro-nutrients for microbial metabolic enzymatic activities and growth. In addition, the nutrient balance facilitated the degree of degradation of the substrate and the biogas production (Abdelsalam et al., 2017; Chen et al., 2018; Chen et al., 2019).

3.3. Biogas production performance

Bioconversion of wastewater into bioenergy anaerobically with NPS additives resulted in methane-rich biogas. Fig. 5 presents cumulative biogas production concerning time. It was found that

the rate of biogas production varied significantly between the augmented reactors with Fe-TiO₂ additives (BMs > AD + F) as compared to the control (AD only). The daily volume of biogas produced by BMs and AD + F were 30 mL/d and 25 mL/d, respectively, in comparison to 20 mL/d of the control reactor (AD only). The reactors containing the Fe-TiO₂ additives showed the highest biogas productivity over the 30 days of measurement with 815 mL, 680 mL and 625 mL for BMs > AD + F > AD only, respectively. Aside from the biogas production, the addition of the Fe-TiO₂ had a positive impact on the methanogenic activity which resulted in a high percentage of methane composition of the biogas (Fig. 6). The methane composition of the reactors was 100% for BMs and AD + F, whereas 66% for the control (AD only). The 100% CH₄ in the BMs system is accounted for the fact that methanogenesis is considered the most metal-rich enzymatic pathway. Dissociation of the Fe-TiO₂ additives resulted in Iron (Fe) species dominant presented Fe-S clusters for catalysis and/or electron transport which augments the hydrogenation and methane content (Fig. 4).

In Fig. 6, the quality of the methane produced during the digestion, which is directly linked to the amount of COD degraded. Significantly, the more methane produced is very resourceful for energy production in terms of heat and power consumption (Abdelsalam et al., 2017; Chen et al., 2018). Interestingly, the measure of methane (Fig. 6) as the final product of degradation of the organic matter showed how well the reactors functioned. The low methane content in the biogas for the control reactor (AD only) can be attributed to its low volatile fatty acid production, as degradation of VS content produced more of the methane content for BMs > AD + F. The best performance of BMs is in line with Abdelsalam et al. (2017), who reported on an increase in biogas and methane content as a result of incorporating magnetic NPs and magnetic field induction in the AD process.

Generally, Fe₃O₄ magnetic NPs additives were proved to increase biogas production. Liu et al., (2015) reported that magnetic NPs could be nontoxic with long-term contact, and only showed slight toxicity to bacteria at an initial stage. In contrast, the addition of 2 g Fe-TiO₂ Fe₃O₄ NPs improved the bacterial activity during the 2nd and 3rd week of biogas production and reduced it during the 4th week. The magnetic field influence on the magnetic NPs could affect the activity of autotrophic bacteria in the existence of the Fe²⁺/Fe³⁺ ions, introduced into the reactor in the form of Fe-TiO₂ NPs. Additionally, Suanon et al., (2016) mentioned

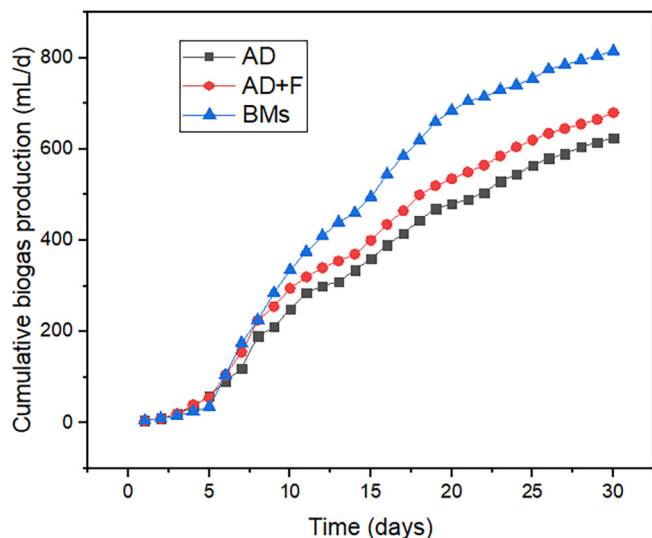


Fig. 5. Cumulative biogas performance of the reactors (AD only, AD + F and BMs).

that Fe_3O_4 NPS is used during the anaerobic digestion bioaugmentation process of the organic fraction of municipal solid waste.

3.4. Kinetics evaluation

The kinetics results obtained based on the cumulative data (Fig. 5) acquisition throughout the HRT of 30 days are presented in Table 3. This depicts the acceptable conditions of the bioreactor and substrate utilization of the microbes for biogas production (Krümpel et al., 2016; Yu and Wensel, 2013). It is observed that most of the predicted biogas values by the First-order kinetic model (3) were relatively higher than the measured biogas (Y), as confirmed by the theoretically derived maximum biogas (ym) produced. Conversely, the difference between the Gompertz model (2) predicted biogas values were agreeable with the measured biogas values with low deviation (<10%). Results of the biogas production rate constants (k) obtained for the First-order kinetic model were very low as compared with that of the Gompertz values. For comparison, the k values of Gompertz > First order for reactors AD only ($0.131 \text{ d}^{-1} > 0.00961 \text{ d}^{-1}$), AD + F ($0.138 \text{ d}^{-1} > 0.015 \text{ d}^{-1}$)

and BMs ($0.159 \text{ d}^{-1} > 0.0131 \text{ d}^{-1}$). In addition, for the augmented reactors, the k values of BMs > AD + F were seen to be higher than the control (AD only). This occurrence might be due to the Fe-TiO_2 additives which enhanced the microorganism's activity in the augmented systems (Biswas et al., 2006; Sarto et al., 2019). This was confirmed by the high regression coefficient (R^2) obtained, representing BMs (0.9954) > AD + F (0.9938) > AD only (0.9917). As the Gompertz kinetic model (2) fitted very well with the data of the system obtained, their lag of phase ($\lambda = 10.6$ days (AD only) > 10.16 days (AD + F) > 10.12 days (BM)) suggest the rapid response for the systems maximize biogas production. Above all, the minimum sum of squares (SSE) denotes the statistical significance ($P > 0.05$) and predictability of the models.

Furthermore, the relationship between degradation of the organic components in wastewater concerning hydraulic retention time (HRT), was determined by the plot of $\ln(\text{COD})$ against the $1/\text{HRT}$ with time (Fig. 7). This validates the Gompertz model (Table 3) in describing the AD, AD + F, and BMs process with their regression coefficient (R^2) as 0.9917, 0.9938, and 0.9954 respectively. The substrate balance around the reactor was formulated with the assumption that they were operated at steady-state conditions with constant effluent substrate concentration. However, a good biodegradability was achieved as the ratio of the BOD_5/COD was found to be in the range of 0.25–0.5 (Brooms et al., 2020), which enhanced the biogas production

3.5. Estimated theoretical methane

Using the biodegradability degree by each bioreactor via the biochemical methane potential (BMP) assay as the characterised effluent COD, the methane productivity by the specified substrate volatile solids (VS) was used to estimate the theoretical methane potential (Nielfa et al., 2015; Shet, and Mutnuri, 2021). This methane potential as expressed as mLCH_4 at standard temperature and pressure conditions per amount of organic material added (VS). Table 4 present the theoretical methane production obtained, which increased with the reduction of the VS content in the substrate. The maximum conversion of the substrate COD to methane, was calculated based on the assumption that, in standard conditions (0°C ; 1 atm), 1 g of COD yields 354 mL of methane (Nielfa et al., 2015). This resulted in 100% methane potential of 265.44 mLCH_4/gVS , 461.36 mLCH_4/gVS and 454.25 mLCH_4/gVS respectively for bioreactors AD, AD + F and BMs. Nielfa et al. (2015) assumed Eqs. (4) and (5) can be used to validate any form of substrate COD conversion into methane via BMP conditions.

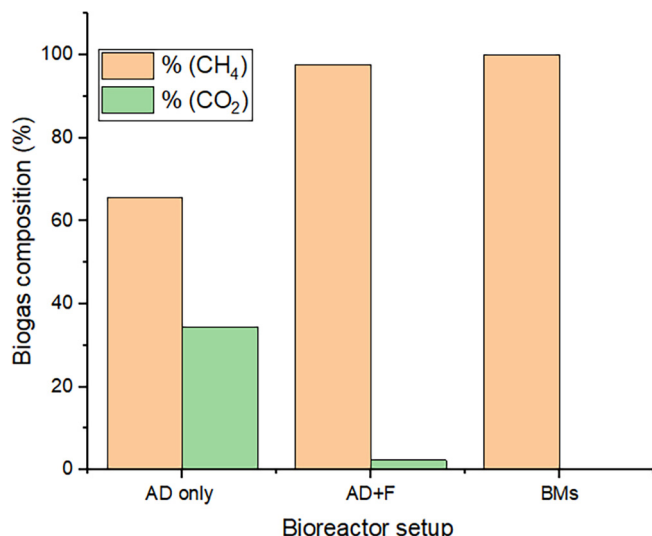


Fig. 6. Biogas composition of reactors (AD only, AD + F and BMs).

Table 3

First order and Gompertz kinetics model parameters

Bioreactor setup	AD only	AD + F	BMs
<i>First-order model</i>			
Measured (Y, mL/g.d COD)	625	680	815
Predicted (Y, mL/g.d COD)	656.26	712.86	879.55
Maximum biogas (ym, mL/g COD)	2619.73	1956.92	2698.35
k (d^{-1})	0.00961	0.015	0.0131
R^2	0.9856	0.983	0.9726
SSE	24833.4	34275.74	87941.87
<i>Gompertz</i>			
Measured (Y, mL/g.d COD)	625	680	815
Predicted (Y, mL/g.d COD)	608.06	659.71	801.32
Maximum biogas (ym, mL/g COD)	658.59	703.21	835.7
k (d^{-1})	0.131	0.138	0.159
λ (d)	10.6	10.16	10.12
R^2	0.9917	0.9938	0.9954
SSE	8102.02	12494.24	11302.68

R^2 -Regression coefficient SSE-Sum of Square errors λ -Lag of phase k -Rate constant.

$$BMP_{Cod} = \frac{n_{ch_4} RT}{PVS} \quad (4)$$

$$n_{ch_4} = \frac{COD}{64(\frac{g}{mol})} \quad (5)$$

where BMP_{Cod} is the theoretical production at laboratory conditions, R is the gas constant ($R = 0.082 \text{ atm L/mol.K}$), T is the mesophilic temperature (313 K), P is the atmospheric pressure (1 atm), VS (g) are distinctive volatile solids of each bioreactor substrate and n_{ch_4} is the amount of molecular methane (mol) determined from (5). Furthermore, the deviation between the experimental and the theoretical production was calculated to obtain the relative error according to equation (6).

$$\text{error} = \frac{BMP_{exp} - BMP_{the}}{BMP_{exp}} \times 100\% \quad (6)$$

3.6. Current trend and future developmental works

With the recent trends as a potential ground-breaking phase of advancement in the biogas upgrading and technologies assimilated in the biorenewable settings (Anaokar et al., 2021). The AD-based biorefineries have the potential to be a game-changer in meeting the world's energy demand. Therefore, promoting sustainable development via process integration in the wastewater settings to allow treatment of wastewater and the production of upgraded biogas and fertilizer comes in handy. Of recent bioavailability of biodegradable lignin in biogas plants, resulting in higher methane generation is gaining attention (Anaokar et al., 2021). Herein, the use of nanoparticles in AD technologies has become a novel concept for improving the biomass bioavailability in microbial consortia in biogas plant and AD performance (Jovičić-Petrović, et al., 2021). The addition of various concentrations of metallic-based nanoparticles (NPs) (Fe, Cu, and Ni) as additives to AD was investigated, and improvements in digestion, intensification of biogas production, and reduction of hydrogen sulphate were noted (H_2S) (Suhel, et al., 2021). Furthermore, the use of biomagnetized nanoparticles with favorable properties as biostimulant in biological activities, waste management, and biogas upgrading operations warrants attention to understand its mechanism for commercialization.

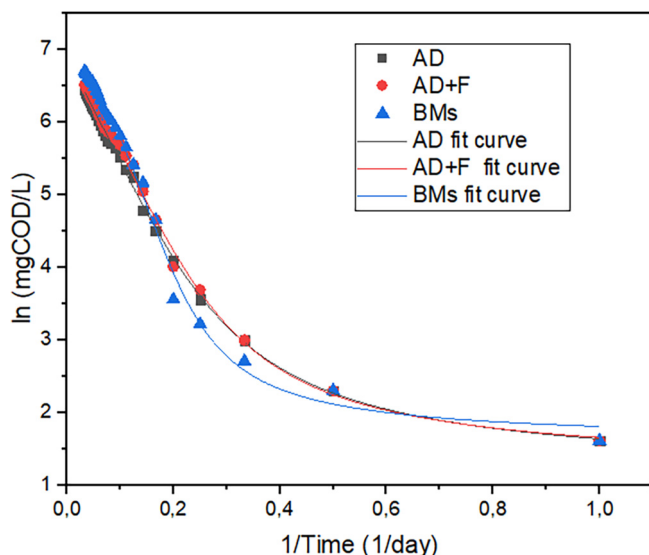


Fig. 7. Cumulative biogas performance of the reactors (AD only, AD + F and BMs).

Table 4
Estimated theoretical methane produced.

Bioreactors	AD	AD + F	BMs
Substrate COD (g/L)	0.672	1.168	1.15
Molecular methane (n_{CH_4})	0.0105	0.01825	0.017969
R (atm L/mol K)	0.082	0.082	0.082
Temperature (K)	313	313	313
Pressure (atm)	1	1	1
Volatile solids (gVS/L)	0.076	0.063	0.057
Theoretical methane production (mLCH ₄ /gVS)	3.545961	7.434992	8.090981
Error (%)	48.05	8.92	18.53

Aside the bioenergy generation and waste management prospects of biomagnetised nanoparticles, they can also enhance the adsorptive removal of contaminants and biogas yield by interacting with bacteria. In addition, the recoverability and reuse of nanoparticles will make the process viable to mitigate environmental risks associated with nanoparticles toxicity (Hoang, 2021). Eventhough, biogas technology has been an interested area of focus via biostimulation of AD process with magnetized nanoparticles, life cycle assessment of microbial community and utilization of digestate slurry to reduce landfills complexity needs to be intensified (Terlouw et al 2021). The applicability of mesophilic/thermophilic bacteria system coupled with magnetized nanoparticles to enhance the AD efficiency and methane yield needs to be explored.

4. Conclusion

The application of magnetized nanoparticles ($Fe-TiO_2$) to the wastewater and inoculum mixture was effectively tested with anaerobic digestion (AD + F) and biomagnetic systems (BM), as compared to the control with no NP additives (AD only). The prospect of inducing a magnetic field in the AD process has been demonstrated to be an eco-friendly technology for wastewater treatment, biogas production, and methane enhancement. Thus, the BM augmented with 2 g of $Fe-TiO_2$ offered the highest treatability (>70% COD, TKN, TS, and VS removal) and biogas (815 mL/d) performance, as compared to the control (625 mL/d). Additional qualitative analysis of the biogas showed 100% methane concentration for the augmented bioreactors (AD + F and BM) as compared to 66% methane for AD only. Also, the toxicity of 28 trace metals in the BM supernatant in comparison with the AD-only reactor was significantly low. The prediction of biogas produced from the cumulative biogas data, among the two kinetic models used showed that the modified Gompertz model was more favored with acceptable conditional limits. Conclusively, a fundamental strategy that considers both the important metabolic cycles of trace elements (TE) and the available analytical techniques is essential. In terms of application, a greater understanding of TE bioavailability in biological systems will aid in the reduction of TE replenishment costs while also increasing the efficacy of anaerobic treatment operations.

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CRediT authorship contribution statement

E. Kweinor Tetteh: Conceptualization, Methodology, Investigation, Writing – original draft. **S. Rathilal:** Supervision.

Declaration of Competing Interest

Not applicable.

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Chapter 4 - Design and monitoring of the integrated magnetized system

Overview of objective 3:

- Design, monitor, and evaluate the continuous integrated anaerobic-photo-catalytic-magnetic system for municipality wastewater treatment

In this chapter, the novel lab-scale integrated AD-AOP magnetic system was designed and monitored for municipality wastewater treatment and biogas production. Also, the applicability of different MPCs were evaluated and compared to select the best MPC. Using the conventional TiO_2 as baseline photocatalysts, the considerable MPCs in this study were the Fe/Al- TiO_2 , Fe- TiO_2 and Fe/Ch- TiO_2 . The toxicological abatement of trace elements and recyclability of the MPC are highlighted. Furthermore, our published Paper 10 expounded the bio-photocatalytic upgrading of biogas utilising carbon dioxide (CO_2) as a potential option for beginning fossil fuel depletion and its associated environmental risks in the pursuit of sustainable development. Additionally, some operational parameters were investigated and optimized to improve the integrated system's desirability which is presented in Chapter 5.

4.1 Introduction

Anaerobic digestion (AD) is an environmentally benign waste disposal technology that is well-suited to address issues such as municipal solid waste, sewage, and other waste disposals (Fermoso et al. 2019; Rajesh Banu et al. 2008; Zhao et al. 2021b). AD waste-to-energy conversion has emerged as a fascinating technology (De Clercq et al. 2017; Popp et al. 2014). Herein, biogas produced by AD can be utilized to generate electricity and heat. Despite these benefits, anaerobic processing cannot be classified as a monolithic (one-step)

treatment technology (Apollo et al. 2013; Fermoso et al. 2019; Ghofrani-Isfahani et al. 2020; Zhao et al. 2021b). Thus, to warrant good water quality discharge limits, its effluent requires post-treatment (Apollo et al. 2013). The quality and efficiency of an integrated system in wastewater settings are based on the possible synergetic effects of the incorporated systems.

In wastewater settings, photocatalysis has been an advantageous post-treatment technology for rapid degradation of most recalcitrant pollutants without generating sludge (Ge et al. 2021; Guo et al. 2019; Kaur et al. 2021), unlike other treatment processes such as adsorption, coagulation, and flocculation (Sudarjanto et al. 2006). Besides, photocatalysis is energy driven which makes it costly as the UV lamp used for irradiation is energy-intensive (Apollo et al. 2013; Kaur et al. 2021).

Amidst exploring the BP system (AD coupled with UV-light), which demonstrated to be very promising for bioenergy production from wastewater treatment (Chapter 3), the recyclability of the Fe-TiO₂ and toxicological reduction of the trace metals needs to be expanded. Therefore, this chapter explores the impact of MPCs as compared to TiO₂ for municipal wastewater treatment using the integrated AD-AOP magnetized system. The magnetized system is employed to facilitate the recovery of the MPCs and improve the treated water quality.

4.2 Materials and methods

4.2.1 Municipality wastewater and sludge used

The wastewater sample used was obtained from a local eThekweni municipal wastewater treatment plant in the KwaZulu-Natal province. This onsite treatment plant involves solid-liquid separation, biofiltration, aeration, clarification, and finally chlorination. The samples collected from the biofiltration process sampling point were characterized and the results

obtained are itemized in Table 4.1. The MPCs synthesized and characterized (Chapter 2) are employed in this study.

Table 4.1: Wastewater sample characteristics and their analytical technique used

Water quality	value	Analytical instrument
pH	7.8 ± 2.3	Hanna pH/EC/TDS Tester (H198130)
Temperature (°C)	28.4 ± 3.6	Hanna pH/EC/TDS Tester (H198130)
Color (abs 465 nm, Pt.Co)	1840 ± 45	HACH Spectrophotometer (DR3900)
Turbidity (NTU)	604 ± 13.6	Turbidity meter (HACH 2100N)
COD (mg/L)	1640 ± 24.2	HACH Spectrophotometer (DR3900)
NH ₃ (mg/L)	5.47 ± 1.2	HACH Spectrophotometer (DR3900)
TKN (mg/L)	38.3 ± 1.7	HACH Spectrophotometer (DR3900)
NO ₃ (mg/L)	7.05 ± 2.3	HACH Spectrophotometer (DR3900)
TN (mg/L)	45.35 ± 8.7	HACH Spectrophotometer (DR3900)

4.2.2 Design and fabrication of the integrated AD-AOP magnetized system

(i) Design factors

The AD-AOP magnetized system was designed based on operational factors that affect the production of biogas and the photocatalysis process. Some of the operational factors considered were the temperature, pH, agitation, type of wastewater, water quality, catalyst type as well as light source (Apollo et al. 2013; de Andrade Guerra et al. 2021; Sudarjanto et al. 2006). Other factors such as maintenance, durability, corrosion, toxicity, separation, and recoverability of the magnetized photocatalyst were also considered for the selection of the materials used for the fabrication. The dimensions of the various components were chosen to minimize the size, based on the availability of effluent load required and operational cost while not jeopardizing the system's efficiency.

(ii) Components required

Aside from the bioreactors, photoreactor (Figure 4.1a) and magnetic filter (Figure 4.1b), biogas analyzer, flexible silicon tubes, flexible Polyvinyl chloride (PVC), plugs, multi-plug, electrical wire, pliers, sealant, valves, and fittings were among the additional resources and machinery used. The pliers were used to help cut the cables and silicon tubes into the required sizes, whereas the sealants were used to hold joints together.



Figure 4.1: Cross-section view of (a) photocatalytic reactor setup and (b) magnetic filter

(iii) Fabricated AD-AOP system:

The lab scale integrated system, involving anaerobic reactor (AD), buffer (AN), photocatalytic reactor (AOP), and magnetic filter (MS) components assembled for the treatment of the eThekweni Municipality wastewater is presented in Figure 4.2. Table 4.2 shows the various component units used for the fabrication and their functionality in the integrated AD-AOP magnetized system.

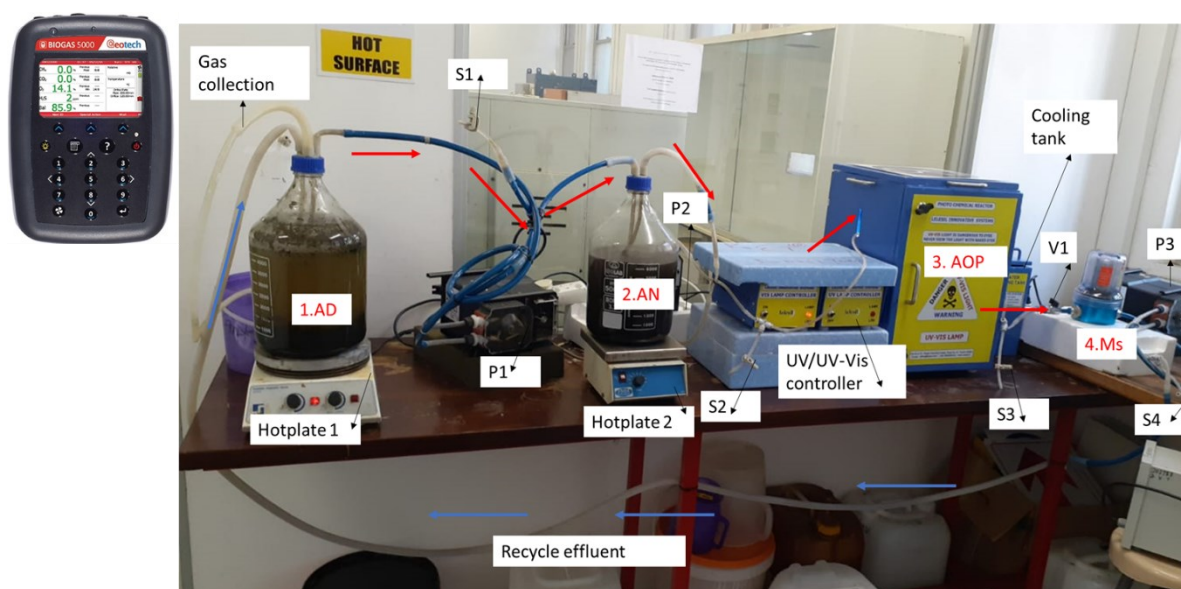


Figure 4.2: Graphical representation of the integrated AD -AOP magnetised system in operation

(iv) Installation and commissioning

After the installation of the system components (Table 4.2), the integrated AD-AOP magnetized system (Figure 4.1) was commissioned with water to check for leaks and make any repairs where necessary. The pumps were calibrated to know their respective flow rates. As presented in Figure 4.1, the low-high pump speed of 10-80% corresponded to average flow rates of 20-200 mL/min for P1 and P3, whereas P2 recorded 23-175 mL/min. The diameter of the silicone tubes was 0.79 cm (ID) by 1.27 cm (OD). The distance between the AD-P1, P1-S1 and S1-AN was 3 cm, 4.5 cm and 10 cm, respectively. The flowrate path via P2 was AN-P2, P2-S2 and S2-AOP through distances of 60 cm, 30 cm and 50 cm,

respectively. Also, the recycled route via the P3 was AOP-S3, S3-MS, MS-P3 and P3-S4 with distances of 25 cm, 27 cm, 30 cm and 60 cm, respectively. Subsequently, to maintain the temperature of the AD process, hotplate 1 was regulated to mesophilic temperature (30 - 45°C), whereas the hotplate 2 was adjusted to an intermittent slow mixing rate of 15 rpm. The AOP reactor was also regulated within 15 - 45 rpm. To ascertain the performance of the system, all conditions were kept constant in this study, while different types of catalysts were investigated.

Table 4.2: Component unit and checklist of the integrated system

Integrated system units	Components	Functionality	Remarks
Anaerobic digestion (AD)	5 L Duran Schott bottle with three-port caps	-AD for biodegradation. -Charged with 3 L inoculum and 1.5 L wastewater -Purged with nitrogen gas for 2 mins -Treat recycled effluent -± 2 g MNP additives	-Ensure the system is airtight with no leaks -Keep AD level at 3.5-4.5 L -Maintain anaerobic conditions at mesophilic temperature -Recycled effluent causes fluidization and mixing. - Charge AN with MNP additives
	Gas collection	Collection and monitoring of biogas produced with 1 L inverted cylinder with flexible tubes	Mark and record levels daily
	Hotplate 1 (Snijders 34532, Holand)	Adjust AD process to mesophilic temperature (30-45°C)	-Intermittent heating to adjust the temperature. -Keep safe from a hotplate
	Pump 1 (P1) Blue-white A - 100N (Flexflo, USA)	P1 ensures a flow of effluent from AD to AN	-Ensure there is enough supernatant before the start of P1 -Avoid cavitation by running pumps at a slow speed (10-35%)
	S1 (Sample point 1)	AD system sampling point for characterization	-Ensure valves are closed after sampling -check water quality after allowing to settle

Buffer system (AN)	5 L Duran Schott bottle with two-port caps	-Denitrification and nitrification of the organics -A working volume of 4.5 L and headspace of 0.5 L - Charged with 2 L inoculum and 2.5 L wastewater	-Maintain AN level at 2.5-4.5 L -Check for leaks
	Hotplate 2 (Magnetic stirrer, FMH Instrument, STR-M0180, SA)	-Intermittent slow mixing (30 rpm and heating)	-Ensure homogeneous mixing after charging with MNP additives
	P2 (Black stone pump, BL3, Romania)	P2 transport effluent from AN to AOP system	-At a high level of AD or low level of AOP run P2 at high speed (40%) -Stop P2 at low AD and high AOP level -Avoid cavitation by running pumps at a slow speed (10-40%)
	S2 (Sample point 2)	AN system sampling point for characterization	-Ensure valves are closed after sampling -check water quality after allowing to settle -Check denitrification efficiency
Advanced oxidation process (AOP)	UV/UV-VIS photoreactor (LELESIL, Model: 1140 – Alpha, India)	-Photocatalytic degradation of organic matter -Charge with photocatalyst	-Always protect your eyes -Ensure there is enough water in the cooling tank -Handle UV/UV-vis lamps with care
	TQR Super 500 ml German Borosilicate Glass Reactor - working volume 100 – 450 ml Central double UV jacket with dip tube, for UV & VIS lamp. Virgin Teflon TQR super taper sealable for sealing quartz to the outer reactor Ports: liquid sampling In, liquid sampling Out, Solid Port. 250 W Visible & 250 W UV lamps with safety resistor with 4 pin connector, single-ended 2 P design Transformer, 2 pins for 250 W Vis and 250 W UV, 3 pins for 230 AC main power.		-Maintain AOP level at 150-450 mL -Ensure intermittent mixing -Switch off and unplug the system after runs

	Eye protect TM safety cabinet with LED lamps, 4" cooling vent fan, PU coating Flexi top lid for inserting lamp. 3 pin for 230 AC main power Magnetic drive: digital display 100-1500 RPM with LED display for RPM.		
	3 L cooling tank with submersible pump	To maintain the temperature of the photoreactor	Ensure there is enough water before starting the reactor
	UV/UV-Vis controller	Lamp controller with pulsating (4 pulses per second) igniter Switch and electronic ballas	Use the right controller for the suitable lamp in use.
	Valve (V1)	Valve and fittings to control level in the AOP system	Close valve if AOP $\leq$ 150 mL
	S3 (Sample point 3)	AOP system sampling point for characterization	-Ensure valves are closed after sampling -check water quality after allowing to settle
Magnetic filter system (MS)	Magnetic filter (0.5 L) (Eclipse, Micromag MM5, UK)	Recovery and separation of the magnetized photocatalyst and other metallic elements	-No cartridge change is required -Clean the core after runs -Ensure there are no leaks -Ensure maintenance after each run -Ensure there is overflow (>0.5 L)
	Pump 3 (P3) Blue-white A -100N (Flexflo, USA)	P3 transport effluent from AN to AOP system	-Ensure V1 is open before starting P3 -Avoid cavitation by running pumps at a slow speed (10-35%)
	S4 (Sample point 3)	AOP system sampling point for characterization	-Ensure valves are closed after sampling -check water quality after allowing to settle

4.2.3 Experimental procedure

The experiment was set up as a semi-batch continuous process with the AD-AOP magnetized system assembled as shown in Figure 4.3.

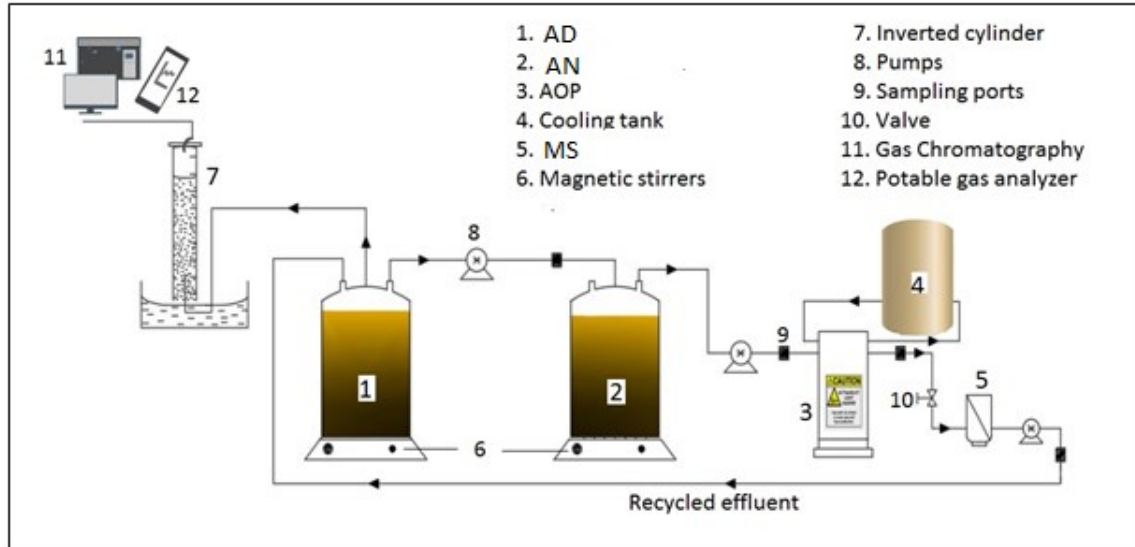


Figure 4.3: Process flow diagram of the integrated AD-AOP magnetized system

(a) Feedstock:

The municipality wastewater sampled from the biofiltration unit was used as a feedstock for the system. Before that, the AD and AN reactors were firstly inoculated with activated sludge of 304.5 ± 23.6 mgTS/L and 229.5 ± 2.65 mgVS/L to aid biodegradability and promote microbial diversity inside the reactor. The amount of inoculum charged was 1.5 L and 2.5 L for the AD and AN reactor, respectively. Aside from the AD and AN being topped with the wastewater sample to a working volume of 4.5 L, the overflow was fed into the AOP (0.45 L) and MS (0.5 L) which was then recycled back to the AD process. The purpose of recirculating was to enhance the homogenisation of the feedstock inside the AD process.

(b) Setup - operation

After establishing good operational conditions via the checklist (Table 4.2), the AD (1) and AN (2) setup was firstly monitored in a batch mode to check their stability and biogas production by collecting the biogas with a water displacement collection technique. Before this, both the AD and AN were purged with nitrogen gas for 2 minutes and left to stand for

48 hrs at a mesophilic temperature of 37-45°C. With the UV-light controller switched on, the system was run in intermittent recycle continuous mode for 5 hours and then switched to batch mode, where all the pumps were set at a speed of 20% corresponding to 35 mL/min, 33 mL/min, and 26 mL/min for P1, P2 and P3, respectively. Samples were taken daily from each unit sample point i.e. AD-S1, AN-S2, AOP-S3, and MS-S4, for characterization. Aside from the no catalyst (No MNPs) charged experimental run, other runs carried out with catalyst charged are summarised in Table 4.3. For example (run 2), before charging the system with fresh feed and 2 g of MPCs to the AD and AOP system, the system was allowed to run and monitored for a week.

Table 4.3: Experimental matrices for the integrated AD-AOP magnetized system

Runs	Magnetised photocatalysts	Symbol	AD	AN	AOP	MS
	Wastewater (L)	BS	3	2.5	0.45	0.5
	Inoculum (L)	AS	1.5	2	-	-
1	No charge (g)	No-MNPs	-	-	-	-
2	TiO ₂	TiO ₂	2	-	2	-
3	TiO ₂ Fe ₂ O ₄ (g)	Fe- TiO ₂	2	-	2	-
4	ChitosanTiO ₂ Fe ₂ O ₄ (g)	Fe/Ch-TiO ₂	2	-	2	-
5	AlTiO ₂ Fe ₂ O ₄ (g)	Fe/Al-TiO ₂	2	-	2	-

(c) Shut down and maintenance.

The system (Figure 4.3) was prepared for shut down, clean up and was prepared for the next set of runs by switching off all the pumps and the UV-light controllers. After emptying and cleaning the AOP vessel, the valve (V1) is closed to prevent backflow from the MS. The MS is also emptied by cleaning the contaminants and MNPs trapped in its core (Figure 4.1b).

4.2.4 Analytical methods

The following physicochemical properties were determined: chemical oxygen demand (COD), volatile solids (VS), total solids (TS), pH, total nitrogen (TN), nitrates-nitrogen

(NO₃-N), and ammonia nitrogen (NH₃-N). COD was determined using close refluxing according to the standard method 5220D. The pH and temperature were measured using Hanna pH/EC/TDS Tester (H198130). The TN, TKN, NO₃-N, and NO₂-N concentration was determined using the HACH kit (Simplified TKN TNT plus, TNT880, method 10242) and Total ammonia nitrogen (TAN) concentration was determined using the HACH kit (Simplified TKN TNT plus, TNT832, method 10205). The elemental composition of the samples was performed with an Agilent Micro-Plasma Atomic Emission Spectrophotometer (MP-AES, MY 18379001).

4.3 Results and discussion

This study discusses a combined process in which photodegradation (AOP) and magnetic (MS) systems were used as post-treatment of a biological (AD-AN) treatment of municipality wastewater and was found to be potentially viable. This system was assessed concerning biogas and methane production, photochemistry of the wastewater (COD, colour, and turbidity), as well as the sequential removal of toxicological trace elements by the MS employed. Also, using the No-catalyst charge as the basis of the system, the performance of TiO₂ photocatalyst was compared to three engineered magnetized photocatalysts herein name as Fe-TiO₂, Fe/Ch-TiO₂, and Fe/Al-TiO₂.

4.3.1 Biogas production and methane content

Figure 4.4 shows the biogas produced after five days with and without MPC additives, whose assay revealed the methane content. This corresponded to a biogas production of 150 mL/d < 350 mL/d < 450 mL/d < 750 mL/d < 820 mL/d for No-charge < TiO₂ < Fe/Al-TiO₂ < Fe/Ch-TiO₂ < Fe-TiO₂ additives impact on the system, respectively. A similar trend was observed for the methane (CH₄) content of the biogas produced by No-charge < TiO₂

$< \text{Fe/Al-TiO}_2 < \text{Fe/Ch-TiO}_2 < \text{Fe-TiO}_2$ additives as $65\% \text{ CH}_4 < 75\% \text{ CH}_4 < 92\% \text{ CH}_4 < 95\% \text{ CH}_4 < 97\% \text{ CH}_4$.

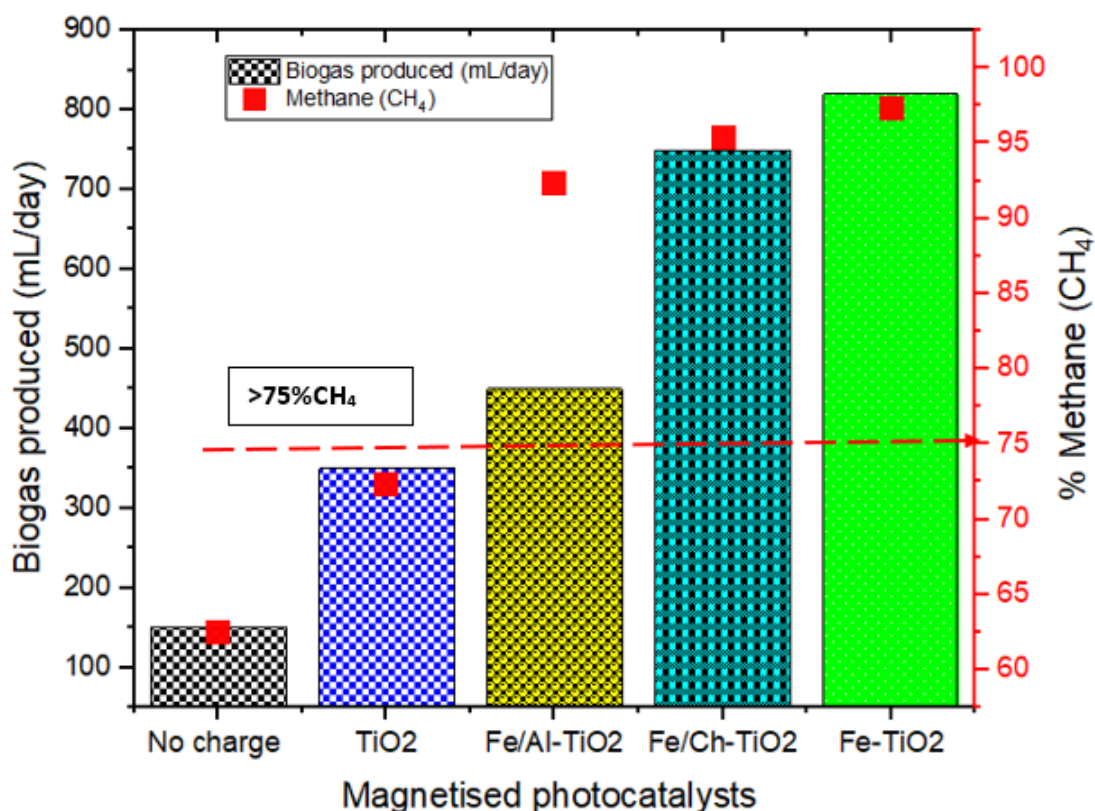


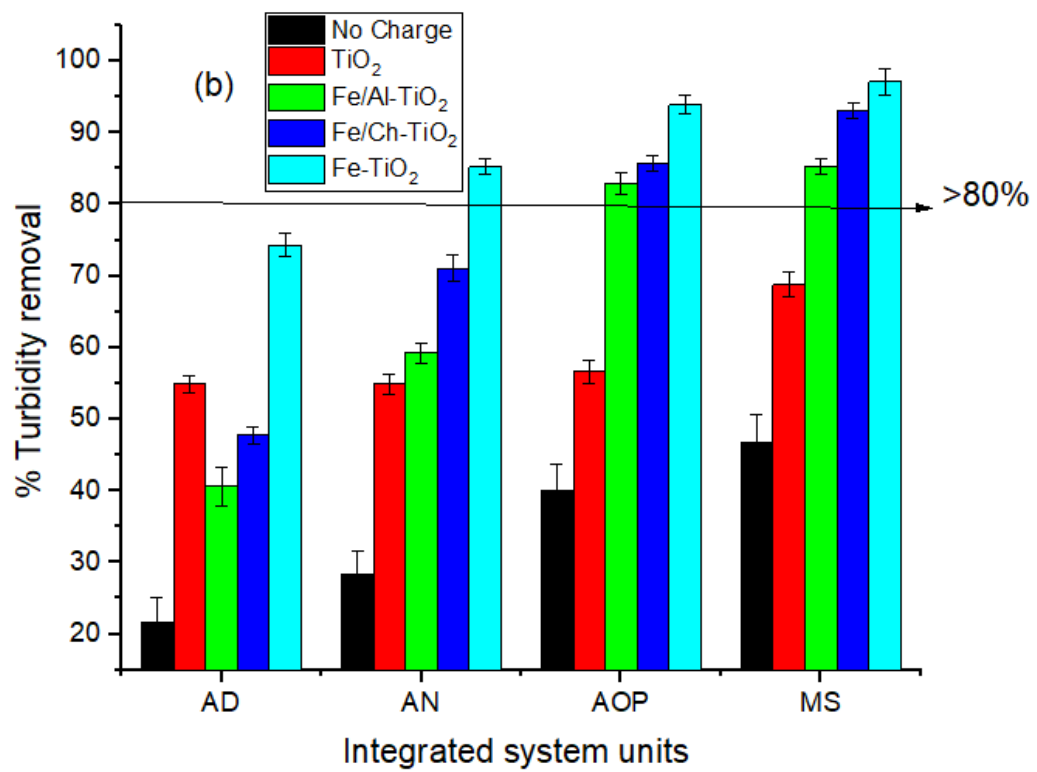
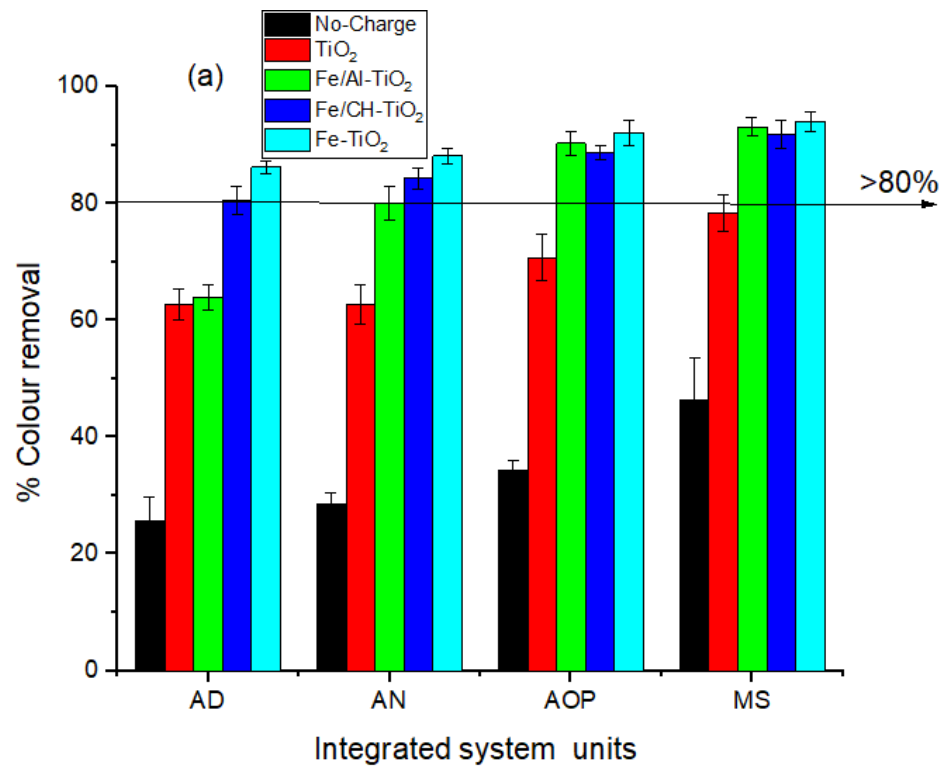
Figure 4.4: Effect of magnetised photocatalysts on biogas production and methane yield using an integrated AD-AOP magnetised system

Evidently (Figure 4.4), the addition of the MPCs enriched the substrate nutrients and energy potential. This stimulated the methanogens during the degradation process to produce biogas with high methane content. Conversely, the substrate deficiency of the MPC additives as macronutrients was not enough for the microorganism activity and resulted in low biogas production in the control system. Similarly, the low methane content of the No-charge (control) can be attributed to the acclimatization of the microorganisms to the fresh organic load. Also, most toxic trace elements presence could have inhibited and retarded the methanogenesis activity during the AD process (Durán et al. 2021; Fermoso et al. 2019; Festel 2008; Russo and Von Blottnitz 2017). However, the presence

of some of the trace elements eventually spikes up the acidogenesis activity (Fermoso et al. 2019). This resulted in more CO₂ being produced rather than enhancing the methane content of the biogas. Generally, the degree of degradation of high organic compounds is expressed as a function of biogas produced with 50-65% methane content (Fuentes et al. 2021). Therefore, in comparing the MPC additives' effect on the methane enhancement in biogas production (Figure 4.4), more than 75% CH₄ was achieved. In this case, the Fe-TiO₂ additives were found to be the best followed by the Fe/Ch-TiO₂ additives. In essence, the high surface area (Table 2.5) and charge magnetic properties of the Fe-TiO₂ increased its reactive oxidation species (ROSs) potential. Thereby increasing the hydrolysis and methanation activity of the biogas production.

4.3.2 Photochemistry analysis (COD, colour, and turbidity removal)

Generally, the degree of degradation of organic compounds depends on the characteristics and operational conditions of the system. Herein, the TiO₂ photocatalyst together with engineered magnetized photocatalyst (Fe-TiO₂, Fe/Al-TiO₂, Fe/Ch-TiO₂) potentials were evaluated for the reduction of the contaminants. The photochemistry (COD, colour, turbidity) results obtained suggest the rate of reduction of the contaminants can be attributed to MPC additives, adsorbing the contaminants to their active sites. Thus, the MPC additives had significant interaction with the contaminants, which increase the contaminant removal as compared with the control system with no MPC (Figure 4.5). Furthermore, the integrated AD-AOP system assisted with the UV-vis radiation was evaluated with Fe-TiO₂ to ascertain its recyclability performance (Paper 10). This infers the possibility of recycling and reusing the MPCs (Ghofrani-Isfahani et al. 2020; Kobwittaya and Sirivithayapakorn 2014; Watson et al. 2002).



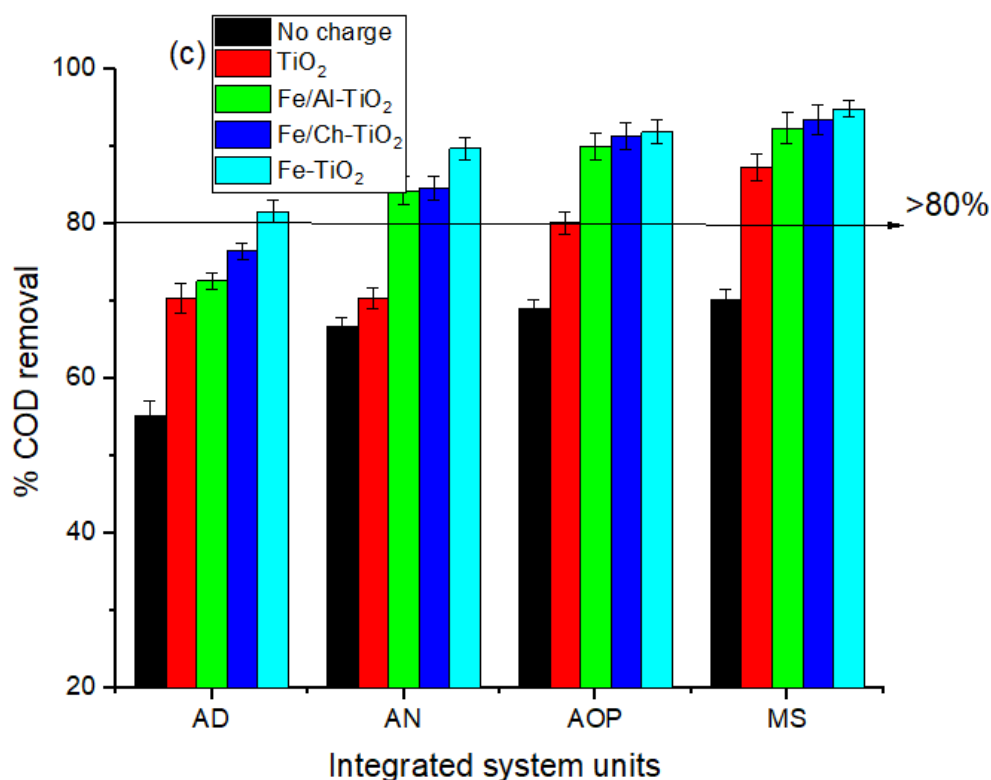


Figure 4.5: Removal of (a) colour, (b) turbidity, and (c) COD by the component units of the integrated AD-AOP magnetized system; AD-anaerobic digester; AN-anoxic; AOP-advanced oxidation process; MS-magnetic filter

4.3.3 Other contaminants removal

Figure 4.6 presents the decolourisation appearance of each component unit as an indicator to assess the treatment performance of the system effluent with (Figure 4.6 a) and without (Figure 4.6 b) Fe-TiO_2 . Summarised results presented in Table 4.4 revealed the magnetized TiO_2 composite catalysts ($\text{Fe-TiO}_2 > \text{Fe/Ch-TiO}_2 > \text{Fe/Al-TiO}_2$) had higher abilities than the TiO_2 for the removal of the contaminants. The pH monitored was within 6.5-7, which makes it a critical parameter in stimulating the metabolic pathways of the stabilised microbial community. In this case, via the recirculation of the effluent, the system was able to buffer the effluent pH, as well as the acid produced during the acidogenesis mechanism to be neutralised by the methanogenesis. The amount of TKN, TN, NH_4^+ and NO_3 recorded

in different proportions suggest the mineralisation of nitrogen-rich compounds that occurred in the degradation pathway produced unstable intermediate compounds . For instance using nitrite (NO_2) as electorn acceptor, ammonia (NH_4) was anaerobically converted into nitrate (NO_3). Herein , the experimental run with No-charge of the MPCs , the TN removal efficieny was increased as the oxidation -reduction bacteria utilised it as a source of reactive species for the transformation and digestion of the organic content (Ghofrani-Isfahani et al. 2020; Kobwittaya and Sirivithayapakorn 2014; Watson et al. 2002).

As shown in Table 4.4 , the high TN removal by No -Charge MPCs might be due to the oxidation-reduction bacteria utilising it as reactive species anaerobically for the degradation of the organic content of the effluent. Whereas the system charge with Fe/Al- TiO_2 , Fe/Ch- TiO_2 and Fe- TiO_2 , the reactive oxidation species (Fe, Al, Ti , e^- , h^+ , OH^- , H^*) override the oxidation-reduction potential by the microbes species. In this case, not all the TN species could be utilised during the denitrification -nitrification process. On the contrary , the high organic content (COD) reduction increased via this path of the charged MPCs as follows $\text{TiO}_2 > \text{Fe/Al-TiO}_2 < \text{Fe/Ch-TiO}_2 < \text{Fe-TiO}_2$.

Table 4.4: Summary of integrated system unit performance for the removal of contaminants

Run	pH	Temp (°C)	Colour (Pt.Co)	Turbidity (NTU)	COD (mg/L)	NH_3 (mg/L)	TKN (mg/L)	NO_3 (mg/L)	TN (mg/L)
Feed	7.8	28.4	1840	604	1640	5.47	38.3	7.05	45.35
No-Charge	7.02	26.54	985.4	321	490.975	1.28	4.62	1.14	5.76
TiO_2	7.02	26.54	398.4	188.8	207.6	1.08	2.236	1.04	3.276
Fe/Al- TiO_2	7.02	26.54	127	88.86	125.4	0.721	1.48	1.23	2.71
Fe/Ch- TiO_2	7.12	26.54	151.6	41.88	106.9	0.0123	11.84	1.1	12.94
Fe- TiO_2	7.02	26.54	109.4	17.14	84.4	0.18	15.3	1.48	16.78

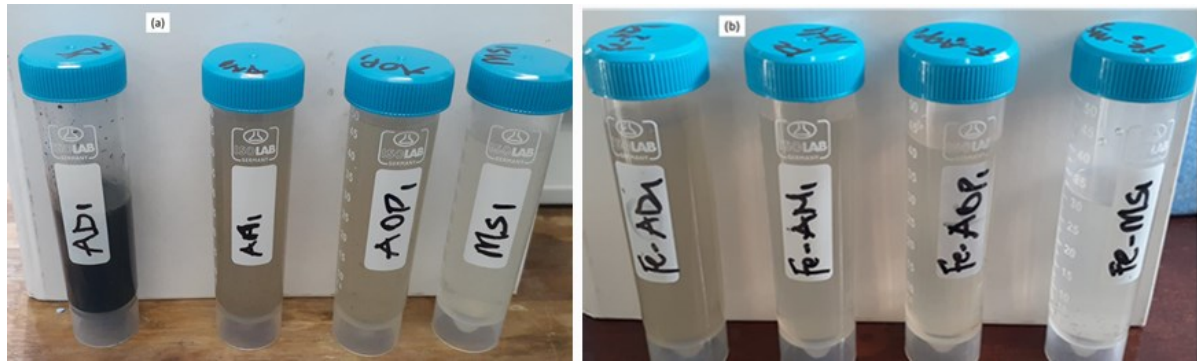


Figure 4.6 : Pictorial view of samples taken from each component unit of the integrated system (a) with no Fe-TiO₂ and (b) with Fe-TiO₂

Evidently, for the system without MPCs, the effluent colour appears to be darkish brown (Figure 4.6a), which is contrary to the system with MPCs being colourless (Figure 4.6b). This affirms that (using 80% treatability performance) (Figure 4.5) the Fe-TiO₂ additives was the most effective of MPCs additives in a sequential order as Fe-TiO₂ > Fe/Ch-TiO₂ > Fe/Al-TiO₂ > TiO₂. Hence, the effluent for the Fe-TiO₂ additives was furthermore characterized to account for the trace elements (Table 4.5), whose agglomeration is associated with the photochemistry as suspended solids and turbidity (Apollo et al. 2013; Sudarjanto et al. 2006).

4.3.4 Toxicological analysis of the trace element

Table 4.5 presents the reduction and deficiency of 27 trace elements detected in the wastewater via the integrated AD-AOP magnetised system (Figure 4.2). The presence of the magnetic filter (MS) facilitated the reduction of most of the trace elements (e.g. Fe, Ti) after the AOP system. Also, impact of trace elements in the wastewater treatment system, especially with the AD process is recently gaining attention for its biostimulation and kinetics improvement (Fermoso et al. 2019; Rout et al. 2021). Conventionally, AD may suffer from low methane yield, instability, and process failure. Also, depending on the

composition of the wastewater and operational system, trace elements can be utilised as micronutrients for microbial activity and redox reduction (Ge et al. 2021; Ghofrani-Isfahani et al. 2020; Guo et al. 2019; Kobwittaya and Sirivithayapakorn 2014; Watson et al. 2002). However, understanding the enzymatic and biocatalytic impact of trace elements require time and sophisticated analytical techniques (Fermoso et al. 2019). Herein, the characterisation of the effluent was considered to account for the potential deficiency of trace elements by the system. Hence, the effluent with the Fe-TiO₂ additives was characterised to account for the trace elements (Table 4.5), whose agglomeration is associated with reduction of trace elements such as desulphurisation depicted in Figure 4.7. As shown in Table 4.5, It can be seen that most of trace element was removed in the AD process , which can be due to the absorption of anaerobic sludge.

Table 4.5: Trace elemental composition and deficiency by each unit of the integrated system

Number	Trace element	Feed (mg/L)	AD (mg/L)	AN (mg/L)	AOP (mg/L)	MS (mg/L)
1	Si	N/A	N/A	N/A	N/A	N/A
2	V	2.775	0.869	0.994	0.964	0.952
3	Zn	0.42	0.107	0.088	0.096	0.11
4	Ag	4.38	2.01	0.827	0.365	0.199
5	Al	32.545	15.805	4.835	5.802	1.779
6	As	0.025	0.031	0.02	0.001	0.005
7	Ba	0.75	0.167	0.212	0.289	0.257
8	Be	0.04	0.022	0.024	0.023	0.026
9	Ca	437.99	65.58	62.39	66.203	58.182
10	Cd	0.075	0.006	0.004	0.006	0
11	Co	0.03	0.003	0.04	0.007	0.038
12	Cr	1.445	0.179	0.122	0.306	0.129
13	Cu	1.32	0.371	0.199	0.147	0.11
14	Fe	0.0375	0.223	0.209	0.068	0.0254
15	K	463.985	154.606	175.714	171.189	177.426
16	Mg	84.06	15.248	15.048	15.979	15.784
17	Mn	0.75	0.09	0.112	0.084	0.071
18	Mo	N/A	N/A	N/A	N/A	N/A
19	Na	741.78	111.346	86.068	97.433	103.963
20	Ni	5.565	0.364	0.701	0.999	1.989
21	Pb	0.145	0.013	0.059	0.052	0.004
22	Sb	0.015	0.016	0.005	0.035	0.031
23	Se	0.22	0.02	0.016	0.005	0.038
24	Sn	0.1	0.003	0.003	0.006	0.015
25	Sr	N/A	N/A	N/A	N/A	N/A
26	Ti	0.77	0.552	0.533	0.274	0.119
27	Tl	0.12	0.029	0.006	0.014	0.007

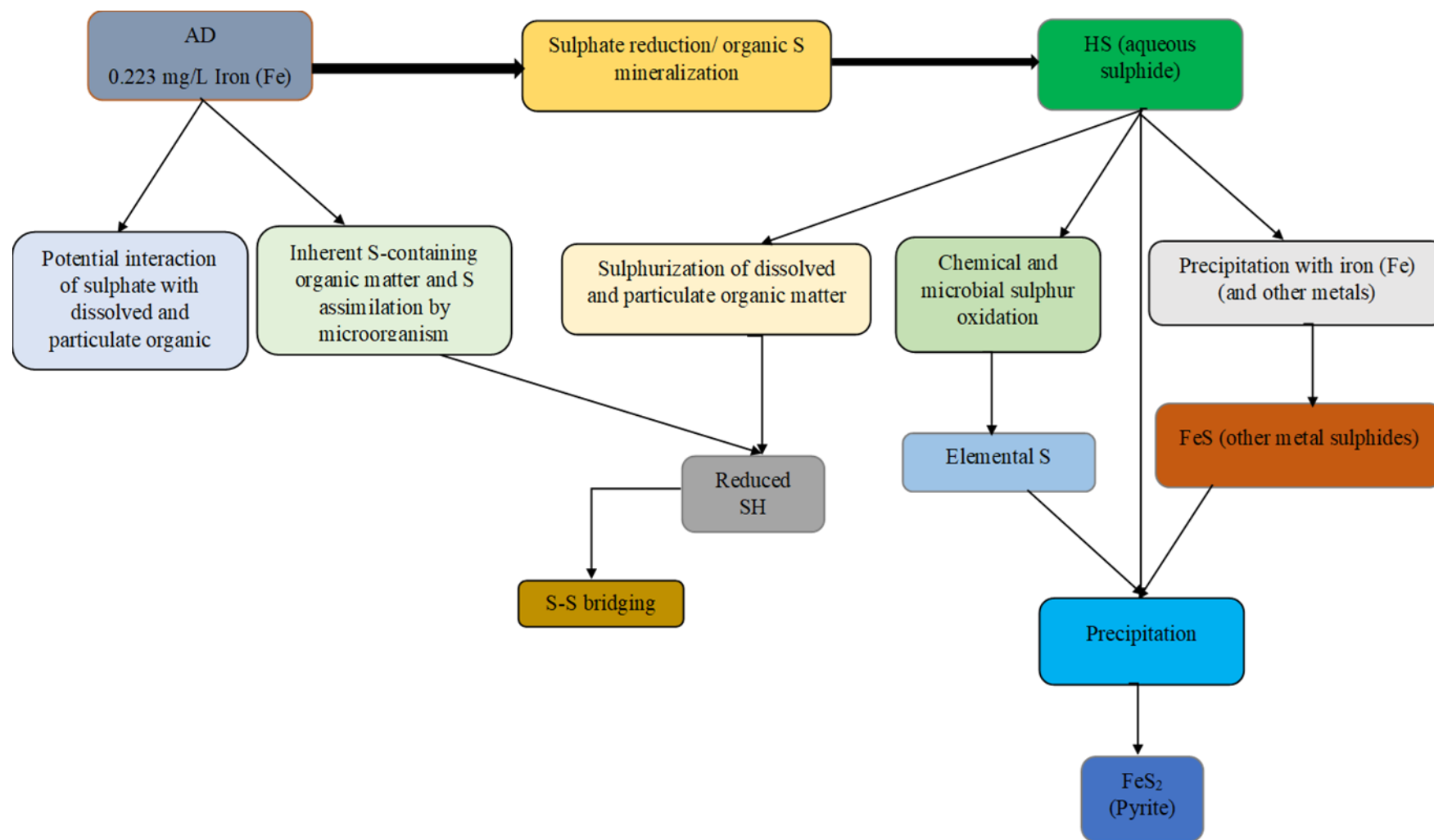


Figure 4.7: Schematic representation of MNP additives such as Fe-TiO₂ enhancing Sulphur reduction

Significantly, to balance the biochemistry of the AD process, intermediate compounds such as carbonates, TKN, TN, NH_4^+ , NO_3 and organic acids produced with the presence of the trace elements can be used to self-control the pH and alkalinity level in the system. For instance, the presence of sulphate can trigger methanogens to compete with sulphate-reducing bacteria for available organic substrates or nutrients, which can lead to system failure (Figure 4.7). The absence of sulphur (S) suggests the possibility of sulphate-reducing bacteria utilising the sulphur (S) as a terminal electron acceptor and iron (Fe) as a proton donor to digest the organic compounds (Figure 4.7). The presence of Fe (0.223 mg/L; 0.068 mg/L) in the AD and AOP processes, respectively favoured the oxidization potentials of the organics into simple compounds. This suggested viability to evaluate the recyclability of MPCs by recovering from magnetic filter and reusing in AD-AOP system cycles. This makes Fe-TiO₂ to be the most advantageous MPCs recommendable for further investigation such that;

- I. It could buffer the oxidation-reduction potential in the system,
- II. It facilitated the enzymatic activities, like Fe-S clusters,
- III. Its reaction with the sulphide and hydrogen molecules improved the system biogas production (820 mL/d) and methane quality (>90% CH₄), while suppressing the hydrogen sulphide and CO₂ levels.

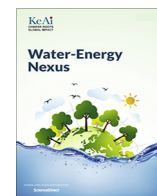
4.4 Summary and additional information

The impact of magnetised photocatalysts ($\text{Fe-TiO}_2 > \text{Fe/Ch-TiO}_2 > \text{Fe/Al-TiO}_2$) tailored via the co-precipitation technique was employed and compared to that of the TiO_2 photocatalyst. The degree of treatability and biogas production by the novel integrated AD-AOP magnetised system was used to ascertain their performance. Among them, the Fe-TiO_2 was found to be the most effective. The degree of treatability of the municipality wastewater was recorded with respect to COD, colour and turbidity removal. Also, the toxicological reduction of the trace elements by the system was highlighted.

Paper 10: Integrated AD-UV-vis system



Paper 10.pdf



Biogas production from wastewater treatment-evaluating anaerobic and biomagnetic systems

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ABSTRACT

Biogas, a green and sustainable form of energy produced during the degradation of organic waste anaerobically comes with ecological and economic paybacks when compared to a comprehensive fossil fuel-based energy system. However, the biodiversity of microorganisms and chemical loads for enzymatic and bioconversion reactions impedes the anaerobic digester's (AD) practicality for commercialization. Hence, this study examined the application of titanium dioxide magnetite (Fe-TiO₂) (F) via a synthetic route in AD + F and a biomagnetic system (BMs) as a collective pathway to maximize methane potentials, wastewater treatment, and improve biogas production. The AD + F and BM systems were operated at a working volume of 0.8 L (inoculum to wastewater ratio of 0.6), the mesophilic temperature of 35 °C for an incubation period of 30 days. The results showed in-situ Fe-TiO₂ facilitated the bio-electrolysis and bio-methanation reactions in the AD process which improved its performance as compared to the control (AD only). Above 75% of chemical oxygen demand (1600 ± 16.2 mg/L), Total Kjeldahl Nitrogen (76 ± 6.4 mg/L), total solids (135 ± 12 mg VS/L), volatile solids (94 ± 6.8 mg VS/L), and other inorganic contaminants (28 elementals) contained in the wastewater were removed by the BMs at a pH of 6.5 followed by the AD + F (65–75%) and the AD only (50–65%). On the 20th day, the control system (AD only) had a maximum daily biogas yield of 50 mL/COD.d, whereas the AD + F gave 90 mL/d and BMs 120 mL/d. Compared to the control with a methane yield of 66%, the addition of the Fe-TiO₂ to AD + F and BMs increased the methane yield to 100%. Synergistically, the catalytic and biomagnetic activity of Fe-TiO₂ in the BMs heightened the adsorption and reaction pathway of the contaminant's transformations and degradation. Amidst two kinetic models investigated, the cumulative biogas yield followed the Gompertz kinetic model. In conclusion, combining the magnetic effect with green magnetic catalyst (Fe-TiO₂) in AD and adsorption-based wastewater settings have viable prospects towards environmental purification.

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1. Introduction

Recent energy costs and the decline in the availability of energy resources have become a pressing concern of decision-makers and consumers about their societal activities, environmental and economic impact (Eurostat, 2020; Ning et al., 2013). This has resulted in a paradigm shift of wastewater management experts

reconsidering wastewater treatment plants (WWTPs) as a vital source for a bio-based circular economy rather than end-of-life treatment and disposal facilities (Casas-Godoy et al., 2020; Sanders and Van der Hoeven, 2008; Spierling et al., 2018). Thus, redesigning and operating modernized WWTPs is a valuable pathway for resource optimization and energy recovery in wastewater settings. In essence, wastewater with high-strength organic matter can generate 10 times the energy required for its treatment in the form of biogas to meet on-site power and thermal needs (Casas-Godoy et al., 2020). Notwithstanding, route sources of WWTPs are mostly obtained from livestock farms, slaughterhouses, domestic, industrial, and agricultural activities (Jordan et al., 2007; Maina et al., 2017). Such waste contains large quantities of organic matter which are biodegradable representing a valuable resource for bioenergy.

Abbreviations: WWTPs, Wastewater treatment plants; AD, Anaerobic digester; BMs, Biomagnetic system; COD, Chemical oxygen demand; NPs, Nanoparticles; TS, Total solids; BMP, Biomethane potential; TE, Trace elements; TKN, Total Kjeldahl Nitrogen.

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In wastewater treatment works, anaerobic digestion (AD) has proven to be the most widely used sustainable technology for reduction, recycling, and recovery resources from organic wastes (Bennich and Belyazid, 2017; Casas-Godoy et al., 2020; Jordan et al., 2007). Given South African wastewater management systems, AD processes are incorporated with the benefits of transforming organic solid wastes into more useful organics (fertilizers, dry sludge) (Russo and von Blottnitz, 2017; Stafford et al., 2013). Also, to derive and capture biogas (methane-rich natural gas) as a renewable source of energy for heat, electricity, and biofuel production (Msibi and Kornelius, 2017; Russo and von Blottnitz, 2017). Generally, the AD mechanism involves three main phases (hydrolysis, acidogenesis, and methanogenesis), which require different groups of active microbes at each phase (Budzianowski and Postawa, 2017; Prussi et al., 2019). Concisely, AD is dependent on the number and activities of these microbes, which are associated with several factors such as the reactor operational conditions (presence or absence of oxygen, temperature, pH, hydraulic retention time, etc.), substrate properties, and the digester configuration (Laiq Ur Rehman et al., 2019; Lohani and Havukainen, 2018). To avoid the AD operational failure and poor performance, making provision of nutrients insufficient amount and the right proportion in the substrate to sustain the microbe's growth and activities becomes very critical. Thus, any form of limitations could affect the biogas production efficiency. Meanwhile, some of the microbes required for anaerobic ingesting of organic matter for biogas production have a desire for intake of trace elements (Fe, Cu, Ti, Ni, Mg, Co, Ag, Zn, Pb), nutrients (phosphate, ammonia, nitrate, and nitrite), whereas some can be inhibitory to the AD process (Hagos et al., 2017; Thanh et al., 2016; Zhang et al., 2011; Kweinor Tetteh et al., 2020; Kweinor Tetteh and Rathilal, 2020). Therefore, finding balance in the substrate or nutrient composition and bioavailability of trace metals for biogas production should be given attention.

Today, nanotechnology (nanoparticles, nanomembrane, and nanopowder) offers a great opportunity for the effective removal of pollutants in water and wastewater treatment settings. Meanwhile, the number of nano-scaled materials entering the WWTPs is becoming unbearable to the levels for microbial communities (Kweinor Tetteh et al., 2020; Kweinor Tetteh and Rathilal, 2020). This phenomenon has resulted in anti-microbial resistance as a hinge environmental problem in the water and wastewater treatment sector. To avert this, the use of a magnetic field in anaerobic digestion is drawing attention among researchers for nanomaterials magnetic separation (Abdel Maksoud et al., 2020; Zaidi et al., 2014; Zhang et al., 2016). Extensively, studies on the use of magnetic powder and other electromagnetic regimes have proven to be effective to provide magnetic induction, accelerate the growth and metabolism of microorganisms (Abdel Maksoud et al., 2020). Additionally, biomagnetic effects have been found to depend on the magnetic field strength, frequency, configuration type, and the length of exposure (Abdel Maksoud et al., 2020; Bée et al., 2011; Zaidi et al., 2014). For instance, constant magnetic field exposure was successively employed in wastewater treatment, which enhanced the biological and enzymatic activity (Kefeni et al., 2017; Long et al., 2019; Yadollahpour et al., 2014). Thus, the exposure is accountable for altering the magnetic powder properties as well as the exposed solution polarisation, molecular structure, and change in electronic charge (Yadollahpour et al., 2014).

Apart from the environmental merits of magnetic separation technology, the hypothesis of radical pair mechanism (magnetized microbes) responsible for the changes in reaction kinetics induced by the magnetic field has a significant effect on substrate degradability and microbial growth (Bhatia et al., 2021; Yadollahpour et al., 2014).

Despite the availability of valuable information on the role of magnetic seeding in biological systems and microbial enhancement (Baek et al., 2015; Booker et al., 1991; Ebner et al., 2002; Esfandiari et al., 2020; Horst et al., 2016; Liang et al., 2017; Liu et al., 2015; Navratil and Akin, 2009; Suanon et al., 2016; Xiang et al., 2019). There is still inadequate information on developing a biomagnetic system for biogas production from wastewater treatment. In response to the AD process been kinetically slow in biogas production, hence seeding it with titanium dioxide magnetite (Fe-TiO₂) to be AD + F system or coupling it with the magnetic field to be defined as a biomagnetic system (BMs) will enhance biogas upgrading. Therefore, this study aimed to evaluate the effect of the Fe-TiO₂ as a biostimulant in AD + F (with Fe-TiO₂ additives) and BM (AD with Fe-TiO₂ additives + Magnetic field) systems for the wastewater treatment to produce biogas by comparing it to a control system (AD with no additives and magnetic field).

This comparative study was carried out with three bioreactors (AD only, AD + F, and BM) at a mesophilic temperature of 35 °C for the incubation period of 30 days. In addition, the cumulative biogas data obtained was kinetically modeled to determine the parameters suitable for the stability and upscaling of the reactors. Inclusively, this investigation provides essential information required to explore the technological competitiveness of maximizing methane potential in biogas via the valorization of wastewater treatment. Advancing this technology in wastewater settings and industries can be a potential candidate for the reclamation of wastewater and environmental sustainability.

2. Materials and method

2.1. Wastewater and inoculum used

In this study, the wastewater and anaerobic sewage sludge (inoculum) used was collected from a local South African sugar refinery wastewater treatment plant based in Durban in the KwaZulu-Natal Province. The wastewater and sludge samples were taken from the point source of biofiltration and anaerobic digester units, respectively. The sludge was homogenized, kept under aerobic conditions, and stored at room temperature before use. Table 1 shows the initial results of pH, chemical oxygen demand (COD), Total Kjeldahl Nitrogen (TKN), total solids (TS), and volatile solids (VS) tested by APHA (2012). The pH was quantified with a Hanna pH-meter (HI98130, Hanna Instruments, Woonsocket RI, USA). HACH DR 3900 within the wavelength of 455–635 nm (Hach Company, Colorado – USA) was used for the COD and TKN measurement. The elemental composition of the samples was performed with an Agilent Micro-Plasma Atomic Emission Spectrophotometer (MP-AES, MY 18379001).

2.2. Biomethane potential test

Titanium dioxide magnetite (Fe-TiO₂) used in this experiment was synthesized by co-precipitation of mesoporous Titania coupled with Fe₂O₃ NPs as defined and characterized by Kweinor Tetteh and Rathilal (2020) and Kalan et al. (2016). Three 1 L Duran Schott bottles with a bottom hotplate supported by a stirrer were used in the batchwise digester experiment. As shown in Fig. 1, these reactors were classified as control (AD only), AD + F (AD with Fe-TiO₂), and BMs (AD with Fe-TiO₂ additives + Magnetic field). The BMs magnetic field was generated by two magnetic bars (GMX model 400 – Chino, California, USA). The addition of 2 g of Fe-TiO₂ NPs to the AD + F and BMs was studied to see if there was any biostimulation in terms of biogas production, as compared to the control bioreactor (AD only) with only wastewater and

Table 1
Characteristics of the wastewater sample.

Parameters	Feed	AD	AD + F	BMs
pH	7.5	6.8	6.7	6.5
Total Kjeldahl Nitrogen (mg TKN/L)	76 ± 6.4	60.9 ± 12	57.97 ± 14	42.69 ± 23
Chemical oxygen demand (mg COD/L)	1600 ± 16.2	928 ± 27	432 ± 136	450 ± 125
Total solids (mgTS/L)	135 ± 12	98 ± 18	72 ± 26	66 ± 23
Volatle solids (mgVS/L)	94 ± 6.8	76 ± 8	63 ± 12	57 ± 21

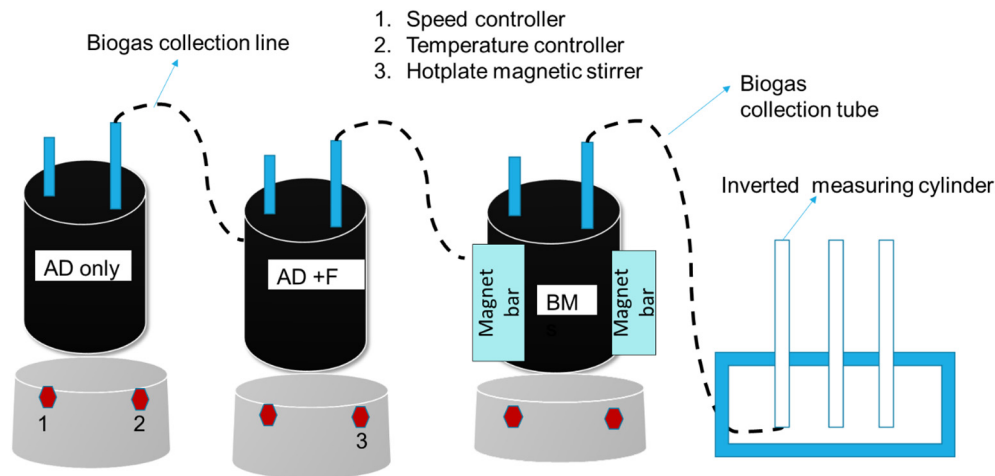


Fig. 1. Schematic flow diagram of the experimental setups on magnetic hotplate stirrers operated at a temperature of 35 °C and mixing rate of 15 rpm for HRT 30 days; Control as AD only (with no additives and magnetic field); AD + F (AD with Fe-TiO₂) and BMs (AD with Fe-TiO₂ additives + Magnetic field).

inoculum. Each module was run for 30 days at a hotplate mixing rate of 15 rpm and a mesophilic temperature of 35 °C. To ensure component contact and uniformity of the samples, periodic mixing was done every 4 h. The reactors substrate to inoculum ratio was fed as 350 mL (wastewater): 450 mL wastewater (inoculum) with allowable headspace of 200 mL for the biogas accumulation. Furthermore, the headspace was purged with N₂ gas for 5 min to deoxygenate the setups. A tube was connected from each of the reactors to the downward displacement collection vessel Gas Chromatography (GC 2014, Shimadzu) was employed for the biogas composition characterization. The reactor efficiency was assessed by monitoring the removal of the contaminants (1). Additional cumulative biogas data obtained were fitted on a modified Gompertz model and first-order kinetics models expressed in (2) and (3).

$$\text{Reactor efficiency} = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (1)$$

where, C_i = Substrate influent and C_f = Substrate effluent. The cumulative biogas production data obtained was evaluated by first-order and modified Gompertz equations (2) and (3), respectively (Kweinor Tetteh and Rathilal, 2020).

$$Y = ym \cdot \exp \left(- \exp \left[\frac{R_{max,e}}{ym} [\lambda - t] \right] + 1 \right) \quad (2)$$

$$Y = ym[1 - \exp(-kt)] \quad (3)$$

where, Y = cumulative specific biomethane (mL/g COD) at time t (days), ym = the methane potential (mL/g COD), λ = lag phase of producing biogas (day), e = mathematical constant (2.718282), R_{max} = the maximum specific substrate uptake rate per maximum biogas production (L/g COD.day) and k is the methane production rate constant (1/d), were in terms of Gompertz, $k = \frac{R_{max,e}}{ym}$.

3. Results and discussions

3.1. Bioreactor performance via effluent analysis

Additives of Fe-TiO₂ NPs characterized under microscale of 20 µm with a magnification of 5000 kx and landing energy capacity of 20 keV within a width distance (WD) of 5–6.5 mm were used as a biostimulant. Its crystalline structure was face-centered cubic with reflection (227) index JCPDS 00-019-0629 at 35.423° (2θ). Also, the reflection (141) of anatase with an interplanar distance of 3.893 Å (JCPDS 00-021-0428) and a body-centered tetragonal structure was determined at 25.281° (2θ). Conventionally, the high organic wastewaters used as feedstock was digested anaerobically to minimize the pollutants as well as the cost of discharging the sludge (Broun and Sattler, 2016). According to Michailos et al., (2020) sludge treatment and disposal constitutes up to 50% of the total cost of most wastewater treatment. Therefore, turning wastewater into an energy-saving economy comes in handy.

In this study, significant reduction and separation of the sludge by an external magnet was observed as tense aggregate with the Fe-TiO₂ additives was found around the magnetic bars which increased the sludge separation from the effluents. To understand the degradability and biostimulation effect of the Fe-TiO₂ NPs, two bioreactors such as AD + F (with Fe-TiO₂) and BMs (AD with Fe-TiO₂ additives + Magnetic field) efficiency was compared to that of a control system (AD with no additives and magnetic field). After the 30 days of incubation, results of the characterized supernatant for each bioreactor and that of the feed are depicted in Table 1. This demonstrated there was significance in the removal of specific contaminants from the wastewater sample in the following order of the bioreactors as AD only > AD + F > BMs. Aside from the degree of reducing chemical oxygen demand (COD) in wastewater as a measure of the performance indicator, TKN, NH₄, TS, VS, and 28 trace elements reduction were also monitored along with the biogas production.

The reduction in nitrate concentration throughout AD is generally attributable to the anaerobic denitrification process. Denitrification of oxidized nitrogen and methanogenic degradation occur simultaneously in the bioreactors (Table 1). A reduction in TKN and NH_4 concentration during the degradation period was also observed in all the wastewater samples treated by the various systems (Table 1). However, respective concentrations of the BMs > AD + F were lower than that of the control system (AD only). This can be accounted by the fact that the Fe-TiO₂ additives in the AD + F and BMs reactors were removed by the ionic -exchange. As Fe-TiO₂ NPs at oxidation state can release trivalent and divalent radical ions, which facilitated the removal of the contaminant.

Monitoring of the pH exhibited similar behavior within the range of 6.5 to 7.5, whereas that of the pH of the BMs was seen to be the lowest. According to Zhai et al., (2015), the pH of AD processes is very sensitive and delicate parameters. So, the low pH variation suggests the stability and buffering capacity of the reactors, especially the BMs with the external magnetic field tended to withstand such fluctuation (Gheraout, 2017; Li et al., 2019; Xu et al., 2020). Kwietniewska and Tys (2014) also reported that the variation in pH beyond the capacity of the reactor can cause system failure, by affecting the methanogenic bacteria activity and degradability performance.

In Fig. 2, the corresponding values to maximize the initial COD of 1600 ± 16.2 mg/L removal efficiency were in order of BMs (68%) > AD + F (62%) > AD only (55%). It was found that the high amount of soluble COD available in the feed nourished the anaerobic microbes for the degradation of the organic matter for biogas production. As the highest degradation was experimental with the BMs followed by the AD + F and AD. As the COD and TKN concentration in the augmented reactors BMs > AD + F remained were lower than that of the control (AD only) (Table 1), affirms the tendency of the TS and VS reduction by the bioreactors. Amani et al. (2010) and Thanh et al. (2016) reported that bioaugmentation of AD with Fe NPs improved the COD removal efficiency.

Fig. 3 shows the degree of total solids (TS) and volatile solids (VS) removal after the degradation of the substrate. It was found the Fe-TiO₂ additives enhanced the reduction of the sludge-water level content (Fig. 3) %VS/TS ratio of 88.4%, 89.3%, and 92% respectively for AD only, AD + F, and BMs reactors. The highest removal efficiency of %VS/TS observed in the BMs > AD + F might be attributed to the inhibitory effect of the Fe-TiO₂ addition (Abdelsalam et al., 2017; Chen et al., 2018; Chen et al., 2019; Omara et al., 2019). These results are harmonized with the Chen et al., (2018)

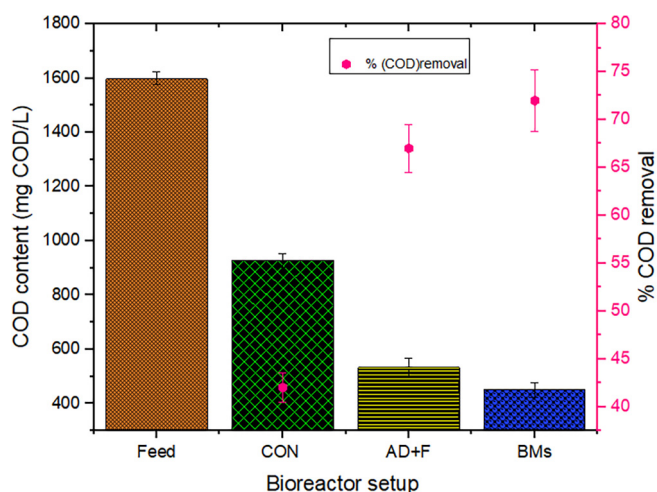


Fig. 2. COD removal and degradation efficiency of the bioreactors (AD only, AD + F and BMs).

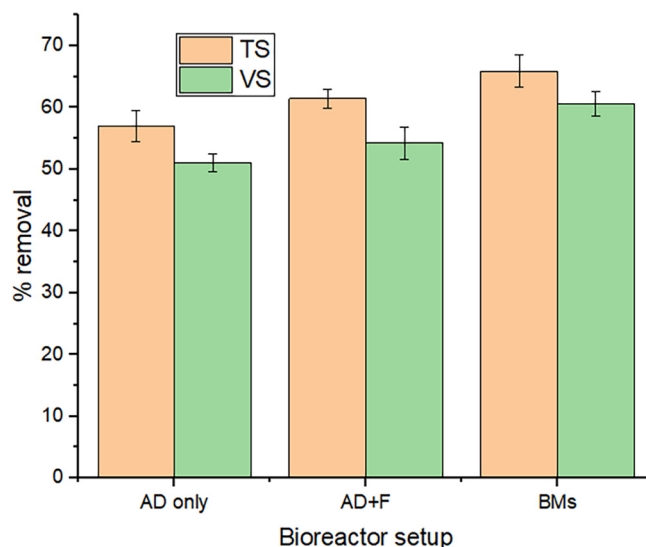


Fig. 3. Percentage removal of TS and VS for the reactors (AD only, AD + F and BMs).

report, where Fe-based additives increased the rate of agglomeration and acclimation of sludge via the microbe's activities which improved the treatment efficiency.

3.2. Trace elements removal

Consequently, the fate and level to which elements are available for interaction with biological systems can be divided into two categories based on their uptake mechanisms: those with (i) active uptake, i.e. internalization processes that require direct metabolic activity from microorganisms to transfer TE through the plasma membrane; and those with (ii) passive uptake, i.e. internalization processes that do not require direct metabolic activity from microorganisms to transfer TE through the plasma membrane. TE bioavailability is also influenced by TE partitioning across liquid and solid phases, as well as TE diffusion to the microbial membrane surface. Also, TE can affect biogas production and methane yield via the intracellular, once absorbed (Fig. 4).

Table 2 shows the trace metals and their concentration in the supernatant after the degradation. Despite the individual differences in the operated reactors (AD only, AD + F, BMs), it is observed that there is bioavailability of trace metal content in the sludge used. Interestingly, most of the trace metals concentration (0.797 mg Fe/L and 0.154 mg Ti/L) in the control (AD only) reactor seems to be very high and their accumulation inhibited the system. According to Chen et al., (2019), accumulation of trace metals are responsibly for volatile fatty acids contribution, which can increase methane yield or cause acidification/alkalinity shock to the reactor system. This affirms the treatability efficiency results obtained (Table 2), where most of the trace metals became chemical species suitable for microbial uptake (Fig. 4). For instance, the trace metal content of Fe-TiO₂ additives in the substrate (Fe and Ti), even if they were not supposed to be, met the microbial requirement sufficient for their activities. This observation is in line with Chen et al., (2018), where addition of Ni to a digester resulted in stabilization of the process and biogas production. Some of these metals which are commonly used for substrate variation in the AD process operational improvement including Fe, Cu, Ni, Mn, Zn, Co, Mo, Se and Ti were identified (Table 2). Despite the nutritional values of most of the trace metals, certain levels of the metal content in the reactors reflect metal surplus or deficiency for the microbial activities in the system (Chen et al., 2019; Tao et al., 2019). This highlights that bioavailability of metal species for microbial uptake

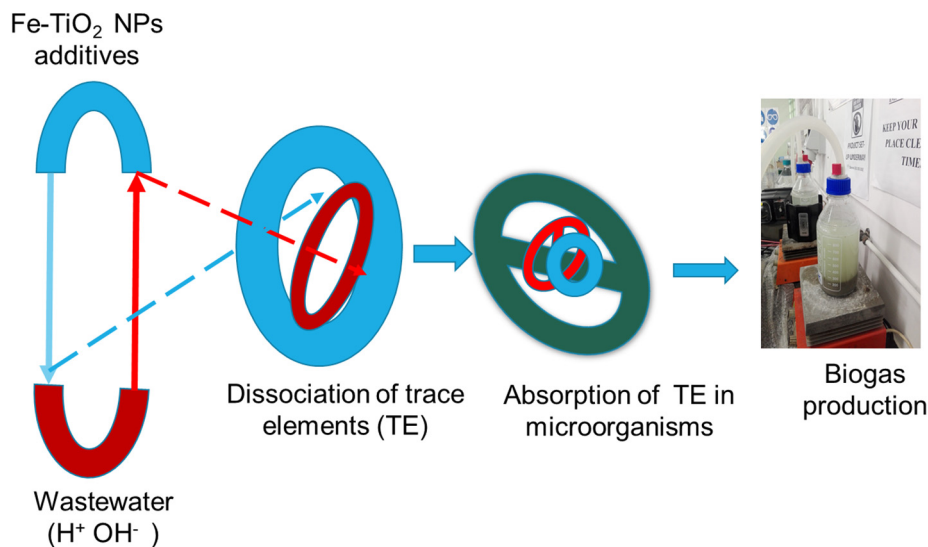


Fig. 4. Schematic and conceptual representation of trace elements bioavailability in a biological system.

Table 2
Reactors performance for the removal of trace metals

Elements (mg/L)	Feed (mg/L)	AD only (mg/L)	AD + F (mg/L)	BM (mg/L)
Si	0.8325	0.555	N/A	N/A
V	1.599	0.084	1.038	0.952
Zn	0.5925	0.876	0.103	0.11
Ag	58.126	112.697	1.185	2.599
Al	4.6055	2.333	1.853	1.853
As	0.0915	0.15	0.011	0.005
Ba	0.3085	0.008	0.257	0.203
Be	43.835	87.598	0.026	0.024
Ca	97.602	0.015	65.063	58.182
Cd	0.018	0.006	0.01	N/A
Co	0.149	0.289	0.038	0.003
Cr	0.2685	0.264	0.091	0.0329
Cu	0.357	0.075	0.236	0.213
Fe	1.4775	0.797	0.329	0.158
K	282.732	16.812	182.884	117.426
Mg	23.784	0.15	15.806	15.784
Mn	0.1485	N/A	0.099	0.071
Mo	74.178	148.356	N/A	N/A
Na	137.121	1.113	91.043	103.963
Ni	3.0445	0.029	2.02	1.989
Pb	0.0255	0.003	0.016	0.004
Sb	0.0475	0.044	0.017	0.0031
Se	0.0835	0.044	0.041	0.038
Sn	0.0235	0.02	0.009	0.015
Sr	N/A	N/A	N/A	N/A
Ti	0.731	0.154	0.436	0.211
Tl	0.048	0.024	0.024	0.07

in the reactors (AD only, AD + F and BM) might differ from one to another depending on their considerable chemical and biological conditions (Abdelsalam et al., 2017). Thus, the reactors improvement forms the basic requirement of metals as macro or micro-nutrients for microbial metabolic enzymatic activities and growth. In addition, the nutrient balance facilitated the degree of degradation of the substrate and the biogas production (Abdelsalam et al., 2017; Chen et al., 2018; Chen et al., 2019).

3.3. Biogas production performance

Bioconversion of wastewater into bioenergy anaerobically with NPS additives resulted in methane-rich biogas. Fig. 5 presents cumulative biogas production concerning time. It was found that

the rate of biogas production varied significantly between the augmented reactors with Fe-TiO₂ additives (BM > AD + F) as compared to the control (AD only). The daily volume of biogas produced by BM and AD + F were 30 mL/d and 25 mL/d, respectively, in comparison to 20 mL/d of the control reactor (AD only). The reactors containing the Fe-TiO₂ additives showed the highest biogas productivity over the 30 days of measurement with 815 mL, 680 mL and 625 mL for BM > AD + F > AD only, respectively. Aside from the biogas production, the addition of the Fe-TiO₂ had a positive impact on the methanogenic activity which resulted in a high percentage of methane composition of the biogas (Fig. 6). The methane composition of the reactors was 100% for BM and AD + F, whereas 66% for the control (AD only). The 100% CH₄ in the BM system is accounted for the fact that methanogenesis is considered the most metal-rich enzymatic pathway. Dissociation of the Fe-TiO₂ additives resulted in Iron (Fe) species dominant presented Fe-S clusters for catalysis and/or electron transport which augments the hydrogenation and methane content (Fig. 4).

In Fig. 6, the quality of the methane produced during the digestion, which is directly linked to the amount of COD degraded. Significantly, the more methane produced is very resourceful for energy production in terms of heat and power consumption (Abdelsalam et al., 2017; Chen et al., 2018). Interestingly, the measure of methane (Fig. 6) as the final product of degradation of the organic matter showed how well the reactors functioned. The low methane content in the biogas for the control reactor (AD only) can be attributed to its low volatile fatty acid production, as degradation of VS content produced more of the methane content for BM > AD + F. The best performance of BM is in line with Abdelsalam et al. (2017), who reported on an increase in biogas and methane content as a result of incorporating magnetic NPs and magnetic field induction in the AD process.

Generally, Fe₃O₄ magnetic NPs additives were proved to increase biogas production. Liu et al., (2015) reported that magnetic NPs could be nontoxic with long-term contact, and only showed slight toxicity to bacteria at an initial stage. In contrast, the addition of 2 g Fe-TiO₂ Fe₃O₄ NPs improved the bacterial activity during the 2nd and 3rd week of biogas production and reduced it during the 4th week. The magnetic field influence on the magnetic NPs could affect the activity of autotrophic bacteria in the existence of the Fe²⁺/Fe³⁺ ions, introduced into the reactor in the form of Fe-TiO₂ NPs. Additionally, Suanon et al., (2016) mentioned

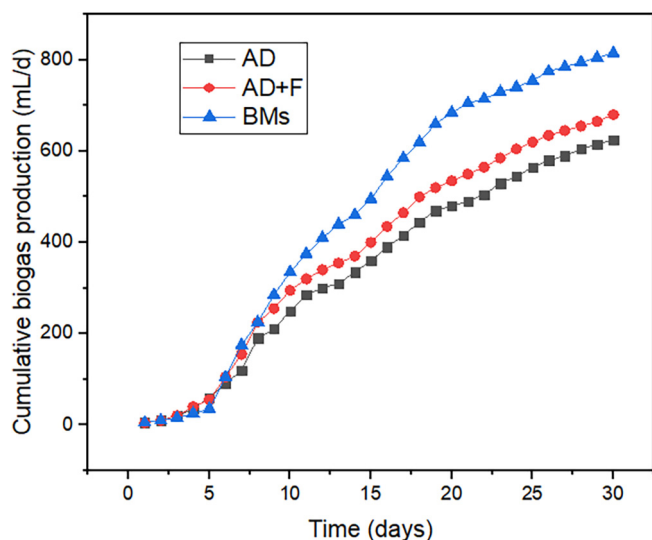


Fig. 5. Cumulative biogas performance of the reactors (AD only, AD + F and BMs).

that Fe_3O_4 NPS is used during the anaerobic digestion bioaugmentation process of the organic fraction of municipal solid waste.

3.4. Kinetics evaluation

The kinetics results obtained based on the cumulative data (Fig. 5) acquisition throughout the HRT of 30 days are presented in Table 3. This depicts the acceptable conditions of the bioreactor and substrate utilization of the microbes for biogas production (Krümpel et al., 2016; Yu and Wensel, 2013). It is observed that most of the predicted biogas values by the First-order kinetic model (3) were relatively higher than the measured biogas (Y), as confirmed by the theoretically derived maximum biogas (ym) produced. Conversely, the difference between the Gompertz model (2) predicted biogas values were agreeable with the measured biogas values with low deviation (<10%). Results of the biogas production rate constants (k) obtained for the First-order kinetic model were very low as compared with that of the Gompertz values. For comparison, the k values of Gompertz > First order for reactors AD only ($0.131 \text{ d}^{-1} > 0.00961 \text{ d}^{-1}$), AD + F ($0.138 \text{ d}^{-1} > 0.015 \text{ d}^{-1}$)

and BMs ($0.159 \text{ d}^{-1} > 0.0131 \text{ d}^{-1}$). In addition, for the augmented reactors, the k values of BMs > AD + F were seen to be higher than the control (AD only). This occurrence might be due to the Fe-TiO_2 additives which enhanced the microorganism's activity in the augmented systems (Biswas et al., 2006; Sarto et al., 2019). This was confirmed by the high regression coefficient (R^2) obtained, representing BMs (0.9954) > AD + F (0.9938) > AD only (0.9917). As the Gompertz kinetic model (2) fitted very well with the data of the system obtained, their lag of phase ($\lambda = 10.6$ days (AD only) > 10.16 days (AD + F) > 10.12 days (BM)) suggest the rapid response for the systems maximize biogas production. Above all, the minimum sum of squares (SSE) denotes the statistical significance ($P > 0.05$) and predictability of the models.

Furthermore, the relationship between degradation of the organic components in wastewater concerning hydraulic retention time (HRT), was determined by the plot of $\ln(\text{COD})$ against the $1/\text{HRT}$ with time (Fig. 7). This validates the Gompertz model (Table 3) in describing the AD, AD + F, and BMs process with their regression coefficient (R^2) as 0.9917, 0.9938, and 0.9954 respectively. The substrate balance around the reactor was formulated with the assumption that they were operated at steady-state conditions with constant effluent substrate concentration. However, a good biodegradability was achieved as the ratio of the BOD_5/COD was found to be in the range of 0.25–0.5 (Brooms et al., 2020), which enhanced the biogas production

3.5. Estimated theoretical methane

Using the biodegradability degree by each bioreactor via the biochemical methane potential (BMP) assay as the characterised effluent COD, the methane productivity by the specified substrate volatile solids (VS) was used to estimate the theoretical methane potential (Nielfa et al., 2015; Shet, and Mutnuri, 2021). This methane potential as expressed as mLCH_4 at standard temperature and pressure conditions per amount of organic material added (VS). Table 4 present the theoretical methane production obtained, which increased with the reduction of the VS content in the substrate. The maximum conversion of the substrate COD to methane, was calculated based on the assumption that, in standard conditions (0°C ; 1 atm), 1 g of COD yields 354 mL of methane (Nielfa et al., 2015). This resulted in 100% methane potential of 265.44 mLCH_4/gVS , 461.36 mLCH_4/gVS and 454.25 mLCH_4/gVS respectively for bioreactors AD, AD + F and BMs. Nielfa et al. (2015) assumed Eqs. (4) and (5) can be used to validate any form of substrate COD conversion into methane via BMP conditions.

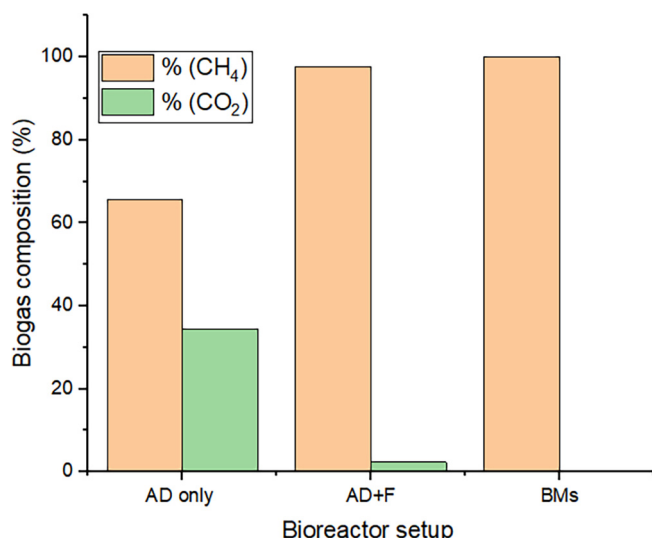


Fig. 6. Biogas composition of reactors (AD only, AD + F and BMs).

Table 3

First order and Gompertz kinetics model parameters

Bioreactor setup	AD only	AD + F	BMs
<i>First-order model</i>			
Measured (Y, mL/g.d COD)	625	680	815
Predicted (Y, mL/g.d COD)	656.26	712.86	879.55
Maximum biogas (ym, mL/g COD)	2619.73	1956.92	2698.35
k (d^{-1})	0.00961	0.015	0.0131
R^2	0.9856	0.983	0.9726
SSE	24833.4	34275.74	87941.87
<i>Gompertz</i>			
Measured (Y, mL/g.d COD)	625	680	815
Predicted (Y, mL/g.d COD)	608.06	659.71	801.32
Maximum biogas (ym, mL/g COD)	658.59	703.21	835.7
k (d^{-1})	0.131	0.138	0.159
λ (d)	10.6	10.16	10.12
R^2	0.9917	0.9938	0.9954
SSE	8102.02	12494.24	11302.68

R^2 -Regression coefficient SSE-Sum of Square errors λ -Lag of phase k -Rate constant.

$$BMP_{Cod} = \frac{n_{ch_4} RT}{PVS} \quad (4)$$

$$n_{ch_4} = \frac{COD}{64(\frac{g}{mol})} \quad (5)$$

where BMP_{Cod} is the theoretical production at laboratory conditions, R is the gas constant ($R = 0.082 \text{ atm L/mol.K}$), T is the mesophilic temperature (313 K), P is the atmospheric pressure (1 atm), VS (g) are distinctive volatile solids of each bioreactor substrate and n_{ch_4} is the amount of molecular methane (mol) determined from (5). Furthermore, the deviation between the experimental and the theoretical production was calculated to obtain the relative error according to equation (6).

$$\text{error} = \frac{BMP_{exp} - BMP_{the}}{BMP_{exp}} \times 100\% \quad (6)$$

3.6. Current trend and future developmental works

With the recent trends as a potential ground-breaking phase of advancement in the biogas upgrading and technologies assimilated in the biorenewable settings (Anaokar et al., 2021). The AD-based biorefineries have the potential to be a game-changer in meeting the world's energy demand. Therefore, promoting sustainable development via process integration in the wastewater settings to allow treatment of wastewater and the production of upgraded biogas and fertilizer comes in handy. Of recent bioavailability of biodegradable lignin in biogas plants, resulting in higher methane generation is gaining attention (Anaokar et al., 2021). Herein, the use of nanoparticles in AD technologies has become a novel concept for improving the biomass bioavailability in microbial consortia in biogas plant and AD performance (Jovičić-Petrović, et al., 2021). The addition of various concentrations of metallic-based nanoparticles (NPs) (Fe, Cu, and Ni) as additives to AD was investigated, and improvements in digestion, intensification of biogas production, and reduction of hydrogen sulphate were noted (H_2S) (Suhel, et al., 2021). Furthermore, the use of biomagnetized nanoparticles with favorable properties as biostimulant in biological activities, waste management, and biogas upgrading operations warrants attention to understand its mechanism for commercialization.

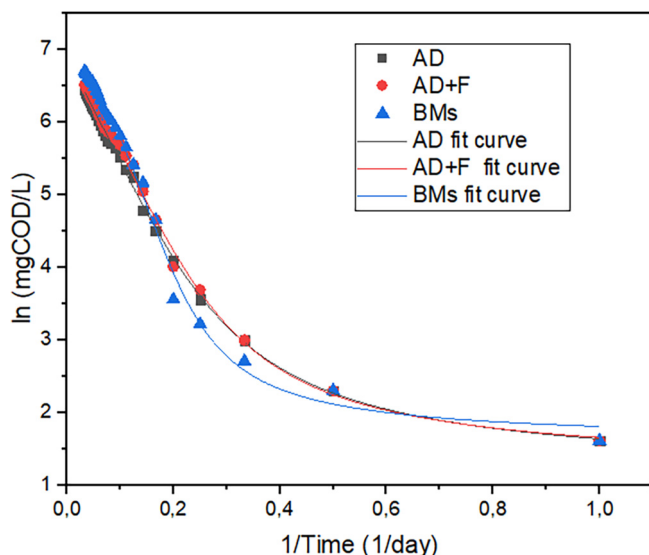


Fig. 7. Cumulative biogas performance of the reactors (AD only, AD + F and BMs).

Table 4
Estimated theoretical methane produced.

Bioreactors	AD	AD + F	BMs
Substrate COD (g/L)	0.672	1.168	1.15
Molecular methane (n_{CH_4})	0.0105	0.01825	0.017969
R (atm L/mol K)	0.082	0.082	0.082
Temperature (K)	313	313	313
Pressure (atm)	1	1	1
Volatile solids (gVS/L)	0.076	0.063	0.057
Theoretical methane production (mLCH ₄ /gVS)	3.545961	7.434992	8.090981
Error (%)	48.05	8.92	18.53

Aside the bioenergy generation and waste management prospects of biomagnetised nanoparticles, they can also enhance the adsorptive removal of contaminants and biogas yield by interacting with bacteria. In addition, the recoverability and reuse of nanoparticles will make the process viable to mitigate environmental risks associated with nanoparticles toxicity (Hoang, 2021). Eventhough, biogas technology has been an interested area of focus via biostimulation of AD process with magnetized nanoparticles, life cycle assessment of microbial community and utilization of digestate slurry to reduce landfills complexity needs to be intensified (Terlouw et al 2021). The applicability of mesophilic/thermophilic bacteria system coupled with magnetized nanoparticles to enhance the AD efficiency and methane yield needs to be explored.

4. Conclusion

The application of magnetized nanoparticles ($Fe-TiO_2$) to the wastewater and inoculum mixture was effectively tested with anaerobic digestion (AD + F) and biomagnetic systems (BM), as compared to the control with no NP additives (AD only). The prospect of inducing a magnetic field in the AD process has been demonstrated to be an eco-friendly technology for wastewater treatment, biogas production, and methane enhancement. Thus, the BM augmented with 2 g of $Fe-TiO_2$ offered the highest treatability (>70% COD, TKN, TS, and VS removal) and biogas (815 mL/d) performance, as compared to the control (625 mL/d). Additional qualitative analysis of the biogas showed 100% methane concentration for the augmented bioreactors (AD + F and BM) as compared to 66% methane for AD only. Also, the toxicity of 28 trace metals in the BM supernatant in comparison with the AD-only reactor was significantly low. The prediction of biogas produced from the cumulative biogas data, among the two kinetic models used showed that the modified Gompertz model was more favored with acceptable conditional limits. Conclusively, a fundamental strategy that considers both the important metabolic cycles of trace elements (TE) and the available analytical techniques is essential. In terms of application, a greater understanding of TE bioavailability in biological systems will aid in the reduction of TE replenishment costs while also increasing the efficacy of anaerobic treatment operations.

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CRediT authorship contribution statement

E. Kweinor Tetteh: Conceptualization, Methodology, Investigation, Writing – original draft. **S. Rathilal:** Supervision.

Declaration of Competing Interest

Not applicable.

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Chapter 5 - Kinetic modelling and optimization of the integrated system energy predictability using RSM and ANN

Overview of objective 4:

- Modelling and optimising the integrated anaerobic-photocatalytic system for municipality wastewater treatment with estimated energy produced and CO₂ emission reduction.

This study, being an extension of previous studies (Chapter 4) employed the novel Fe-TiO₂ photocatalyst and the response surface methodology (RSM) for the experimental design, statistical analysis of the data, modelling and optimisation of the system key operating factors. The Box Behnken design (BBD) of the RSM was used in modelling and optimising three input variables viz organic loading rate (OLR), hydraulic retention time (HRT) and irradiation light source (visible, UV and UV-vis) on four (4) distinctive response variables. The responses included biogas production, COD removal efficiency, bioenergy production (E_{bio}) and the amount of energy consumed (E_{uv}). The degree of the process efficiency was estimated based on the biogas and bioenergy produced by the AD pre-treatment process, and the energy utilised by the light sources (visible/UV-vis/UV) in the photodegradation process as a function of COD degradability.

The interactive effect of OLR, HRT and light source type was applied on the overall process efficiency, and their best-operating conditions with maximum desirability were attained. To estimate and predict the CO₂ emission reduction and energy efficiency under optimal conditions, multi-response modelling and comparative studies of optimization techniques of RSM and artificial neural network (ANN) were also studied. This also had a background of our previous works (Papers 4, 9,13, 14, 16).

5.1 Introduction

Energy is considered as one of the significant benchmarks towards sustainable growth and socio-economic development (Mostafaeipour et al. 2022; Zhao et al. 2021b). Due to the recent economic growth, energy demand is increasing day by day in South Africa, as most of its powers generated relying on coal, has been dominant contributors of greenhouse gas (GHG) emissions in the world (Lin and Sai 2021; Nguyen et al. 2021). Bioenergy production is a long-term sustainable way to mitigate anthropogenic global emission, as it offers a diverse range of options (Ángeles et al. 2021; Nguyen et al. 2021; Zhao et al. 2021b). However, the choice of technology is also a crucial component, as the release of CO₂ from the biogas process should be minimised to reduce its environmental impact (Fuentes et al. 2021; Lin and Sai 2021). Therefore, it is important to improve such technologies to ensure decarbonisation, sustainability, and improvement in the environment, without a disproportionate increase in costs and loss of economic viability.

In this regard, post-treatment photodegradation of AD effluent has proven quite useful for decontamination (Apollo et al. 2013). Herein, the use of the integrated AD-AOP system has shown great potential for energy production and wastewater quality improvement (Chapter 4). This phenomenon could improve the overall efficiency of the integrated process by reducing UV energy requirements and improving AD biogas production (Ghofrani-Isfahani et al. 2020; Guo et al. 2019; Rajesh Banu et al. 2008). Competitively, transforming this technology into sustainable systems necessitate process optimisation of their complex operational parameters (Kaur et al. 2021; Manmai et al. 2021).

As one-factor-at-a-time (OFAT) experimental designs are time consuming and does not account for the interactive effects of multivariables (Abdulhameed et al. 2019; Chelladurai et al. 2021; Khataee et al. 2011; Manmai et al. 2021; Zulfiqar et al. 2019). Synchronously, RSM

allows effective determination of optimal operating conditions via evaluation of the multivariable interactive effect (Abdulhameed et al. 2019; Khataee et al. 2011). Therefore, this current work aimed at optimising the integrated AD-AOP magnetic system for the wastewater treatment and biogas production as well as estimated CO₂ emission reduction and energy predictivity with ANN.

5.2 Materials and methods

5.2.1 Municipality wastewater and sludge used

The wastewater outsourced from a local eThekweni municipal wastewater treatment plant in the KwaZulu-Natal province, South Africa with the characteristics presented in Table 4.1 was used. Also, the magnetite-titania photocatalyst (Fe-TiO₂) as discussed in previous work (Chapter 2) was employed for this study on process optimisation.

5.2.2 Experimental procedure

The integrated AD-AOP magnetic system (Figure 4.2 and Figure 4.3) with a detailed description in previous work (Chapter 4) was applied in this study. A primary investigation was carried out with a constant catalyst load of 4 g Fe-TiO₂ (based on optimum conditions of Paper 9) to the AD and AOP system. At a constant temperature of 37.5°C and 25°C, respectively for the AD and AOP system, OLR was varied between 0.394 kgCOD/L.d and 1.3 kgCOD/L.d.

To ensure HRT and OLR are relevant factors for each component unit, at estimated HRT of 5 days and pump flow rate of 1.2 L/d, 1.4 L/d and 1.1 L/d were employed respectively, for P1, P2 and P3 (Figure 4.2). The organic loading rate was estimated by using equation (5.1) together with an initial organic load of 1.64 kgCOD/L and volume of AD (5 L), AN (5 L)

and AOP (0.5 L). Correspondently, the estimated organic load varied from one component unit to another was 0.394 kgCOD/L, 0.459 kgCOD/L and 3.61 kgCOD/L within HRT of 31 days. Likewise, three different light source types viz visible (vis), Ultraviolet (UV) and UV-vis were investigated. Herein, independent variables and their interactive effect were modelled using RSM-BBD as a function of the wastewater treated (%COD removal), the biogas produced by the AD system (Ebio) and energy use by the UV-light source (Euv). Also, the system energy degree and CO₂ emission reduction was estimated based on the organic load degraded (%COD removal) per effect of the RSM -BBD experimental conditions (Table 5.1).

$$OLR = \frac{C_f \cdot Q}{V} \quad (5.1)$$

where C_f is the feed concentration kg COD/L, Q is the feed flow rate L/d and V is the reactor volume(L)

Table 5.1: Experimental design levels

Factors	Symbol	Low level	Centre points	High level
OLR (kgCOD/Ld	A	0.394 (-1)	0.85 (0)	1.3 (+1)
HRT (d)	B	1 (-1)	16 (0)	31 (+1)
Light source (vis/UVvis/UV)	C	Vis (-1)	UV-vis (0)	UV (+1)

5.2.3 Experimental design and modelling

Design Expert software (version 13.0.7) was used to study the interaction between OLR, HRT, and light source type in terms of biogas production during the AD process and energy usage by the AOP lamp during the photodegradation post-treatment phase (Figure 4.3). With the experimental runs designed to maximise the COD removal and reduce CO₂ emission, the operating parameters as mentioned with their constraints were defined (Table 5.1). In the software, RSM using the Box- Behnken design (BBD) experimental design with three levels (-1, 0, +1) and three replicated centre points was then applied. An experimental design matrix

of 15 randomised runs was generated and the response data obtained were then analysed. Herein, four responses viz biogas production, %COD removal, Ebio and Euv was monitored. Additionally, the energy ratio ($\beta = E_{bio} / E_{uv}$) of the two processes (AD-AOP) and the CO₂ emission reduction were also estimated (Bella and Rao 2021).

Each response data obtained was used to develop a mathematical model that best correlates the input variable and the response in the form of a quadratic polynomial equation (5.2). The response data was analysed with the Design Expert software, and the models were fitted using analysis of variance (ANOVA) (Abdulhameed et al. 2019; Khataee et al. 2011). Parameters such as F-value, probability > F and adequate precision, which is a measure of error or the signal-to-noise ratio, were used as indicators of how the quadratic models fit the experimental values. A probability of F value < 0.05 indicates that the model term is significant while an adequate precision value of ≥ 4 is desirable. The coefficient of regression (R^2) and p-value of the ANOVA was used to determine the acceptability of the model.

$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{i=1}^n \beta_{ii} X_{ii}^2 + \sum_{i < j}^n \beta_{ij} X_i X_j + \epsilon \quad (5.2)$$

Where, the linear parameters Y, β_0 , β_i , X_i and ϵ represents the response, constant term, coefficient, factor, and the residual from the treatment, respectively. In addition, the quadratic terms X_i and X_j represent the factors, β_{ii} and β_{ij} represent the coefficients of the quadratic and the interaction parameters, respectively.

5.2.4 Data collection and response analysis

Four responses were assessed using the RSM-BBD matrix, which includes biogas production, % COD removal, Ebio and Euv. The AD system's biogas production was monitored daily using the downward-water displacement technique, and the cumulative biogas produced was

estimated using the HRT assigned level (Table 5.1). The degree of degradability of the wastewater was estimated based on the %COD removal expressed in equation (5.3).

$$\%COD\ removal = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (5.3)$$

where, C_i = initial COD and C_f = final COD

To estimate the energy produced by the AD process to offset the AOP electricity required for the photodegradation, the energy production by the AD process was calculated by expression (5.4) (Apollo et al. 2013).

$$E_{bio} = LHV_{CH_4} \times E_{COD} \times C_{COD} \times \alpha_{CH_4} \quad (5.4)$$

Where E_{bio} is the AD energy production (kWh/L), LHV_{CH_4} is the low heating value of methane, which is 10.55 kWh/m³ (10.55×10⁻³ kWh/L) (Apollo et al. 2013) E_{COD} is the COD removal efficiency; C_{COD} is the feed concentration (kg COD/L) and α_{CH_4} is the methane production coefficient (L/kg COD removed). The energy consumption of the UV photodegradation process (E_{uv}) was calculated using (5.5) (Apollo et al. 2013).

$$E_{uv} = \frac{P.t}{V.\log\left(\frac{C_i}{C_f}\right)} \quad (5.5)$$

Where P is the AOP lamp power consumption (kW), t is the irradiation time (hours), V is the volume (L) of water treated, and C_i and C_f are initial and final concentrations of the target contaminant. Furthermore, the energy ratio (β), which is the efficiency indicator of the integrated system (AD-AOP) was calculated with equation (5.6)

$$\beta = \frac{E_{bio}}{E_{uv}} \quad (5.6)$$

Where E_{UV} is the UV lamp energy consumption (kWh/L) and E_{bio} is the bioenergy production (kWh/L).

The energy efficiency and environmental impact were estimated based on the conversion rate of the biomethane into electricity. This was estimated based on the assumed 78% of the energy produced, where 33% was electricity generated from the biogas and 45% was estimated as heat in a co-generation process (Apollo et al. 2016; Bella and Rao 2021). Herein, the electricity potential (El_{bio}) can be expressed (5.7) as 33% of the total bioenergy generated per the unit effluent volume treated (kWh/m³). Also, the energy utilised by the pumps was approximated by equation (5.8).

$$El_{bio} = 0.33E_{bio} \quad (5.7)$$

$$Ep = \frac{Qgph}{\omega} \quad (5.8)$$

where Ep is pump power (W), Q is the flow rate of the recycle stream (m³/s), ρ is the fluid density (kg/m³), g is the gravitational acceleration (m/s²), h is the head (m) and ω is the pump efficiency, which was assumed to be 0.6 (Abdullahal., 2017; Mwakasonda & Winkler, 2015). Generally, bioconversion of carbon dioxide to methane of anthropogenic emission from wastewater treatment plants and landfill gases can necessitate the reduction of global warming (Durán et al. 2021; Fuentes et al. 2021; Lin and Sai 2021; Pastor-Pérez et al. 2017). Herein, CO₂ emission reduction (CER) expressed in equation (5.9) was therefore estimated as a function of the electricity produced to power the UV lamp of the photoreactors with respect to the baseline grid emission factor (GEF) of 0.957 kg CO₂ e/kWh (Apollo et al. 2016; Bella and Rao 2021).

$$CER = GEF \times E_{bio} \quad (5.9)$$

5.3 Results and discussion

5.3.1 The integrated system preliminary efficiency

The integrated AD-AOP operating parameters were initially screened to determine the system's overall performance. This included HRT, OLR, and AOP light sources. These variables can influence the AD stability, biogas production, and treated effluent quality before the AOP post-treatment (Apollo et al. 2013; Chong et al. 2010; Qu et al. 2013). Herein, the integrated system stability and efficiency were studied over a fixed HRT of 5 days, OLR of 1.64 kg COD/L with 4 g Fe-TiO₂ under a UV-photodegradation system. Table 5.2 presents the average characterised effluent obtained over the HRT of 5 days. It is observed that the AD-AN system preceding the AOP system as a post-treatment process improved the wastewater treatability efficiency, as the degree of methanogenic activities is being subjected to digested organics (COD) for biogas production (Bauer et al. 2013; Durán et al. 2021; Russo and Von Blottnitz 2017). In this case, the high COD reduction as observed (Table 5.2) in the AD-AN process increased the bioenergy production.

Table 5.2: Treatability summary efficiency of the integrated system component units

Parameter	Feed	AD	AN	AOP	MS
pH	7.8 ± 2.3	7.3 ± 0.23	6.5 ± 0.46	7.19 ± 0.32	7.02 ± 1.2
Temperature (°C)	28.4 ± 3.6	27.88 ± 0.18	26.54 ± 0.126	26.54 ± 0.15	26.04 ± 1.3
Colour (Pt.Co)	1840 ± 45	774.2 ± 14.86	698 ± 8.52	146 ± 2.22	109 ± 1.973
Turbidity (NTU)	604 ± 13.6	155 ± 5.57	89.2 ± 2	36.54 ± 0.93	17.14 ± 1.88
COD (mg/L)	1640 ± 24.2	301.6 ± 7.24	168.2 ± 1.64	133 ± 1.85	84.4 ± 0.702
NH ₃ (mg/L)	5.47 ± 1.2	1.64 ± 1.2	0.726	0.21	0.18 ± 0.02
TKN (mg/L)	38.3 ± 1.7	13.8 ± 1.4	33.68	18.5	15.3
NO ₃ (mg/L)	7.05 ± 1.3	1.94 ± 0.12	3.39	3.4	1.48
TN (mg/L)	45.35 ± 8.7	15.74 ± 1.32	37.07	21.9	16.79
Biogas (mL/d)		820			

*AD-anaerobic digestion; AN-buffer system; AOP-advanced oxidation process; Ms-Magnetic filter system

Figure 5.1 shows that the COD and Colour removal were within 75-80% and 50-60%, respectively for the AD-AN. Conversely, the degree of colour reduction in the AD-AN process

was found not very efficient as compared to the AOP-MS system. Meanwhile, the post-treatment AOP-MS was able to increase the removal efficiency above 85-95%.

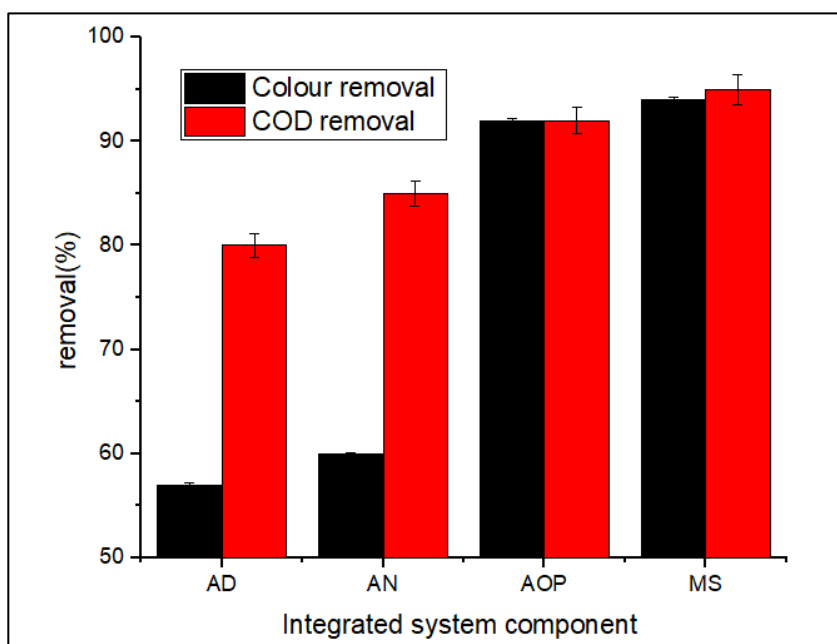


Figure 5.1: Removal of COD and Colour by the integrated system component units; AD-anaerobic digestion; AN-buffer system; AOP-advanced oxidation process; Ms -Magnetic filter system

As shown in Figure 5.1, the degree of colour and COD reduction by the integrated system (AD-AN-AOP-MS) was found to be feasible. The photometric index of the effluent might be due to the degradation of the dissolved organic carbons (C-N, C = C), which might have produced NH₃, TKN, NO₃, and TN, as they increased the colour intensity (Apollo et al. 2016). The COD reduction indeed suggest the degradation of C= C bonds, while NH₃, TKN, NO₃, and TN generation indicated degradation of C–N bonds (Apollo et al. 2013, 2016; Sudarjanto et al. 2006). In Figure 5.1, photodegradation is more effective at reducing colour than COD, however, AD is effective in reducing the COD but not in reducing colour (Table 5.2). Therefore, integrating the AD-AOP system into the wastewater treatment settings is highly appreciable.

5.3.2 The integrated system degradability kinetics

The first-order kinetic model was used to study the integrated system degradability (COD reduction) with respect to HRT of 5 days. Figure 5.2 shows the reduction of (a) COD and (b) colour decreased the downstream of the integrated system from AD-MS. Such that, the organic content (COD) utilisation by the microbes in the AD-AN process was found stable within the stipulated HRT of 5 days. This was reflected in the subsequent photodegradation process (AOP-MS), whereby both COD and colour (Figure 5.2) decreased along with the HRT. The kinetic constant (k) and the regression coefficient (R^2) values respectively are presented in Table 5.3, which correlates with other studies (Fuentes et al. 2021; Kaur et al. 2021).

Table 5.3: Kinetic regression coefficient of the integrated system components

Water parameter	Colour		COD	
	$k(d^{-1})$	R^2	$k(d^{-1})$	R^2
Integrated system component				
AD	0.418	0.998	0.979	0.865
AN	0.23	0.916	0.25	0.876
AOP	0.35	0.893	0.32	0.873
MS	0.76	0.857	0.12	0.981

*AD-anaerobic digestion; AN-buffer system; AOP-advanced oxidation process; Ms - Magnetic filter system, k – kinetic constant

The removal levels of COD and colour at 85-95% in Figure 5.2, affirmed the rate of degradation was lower at the initial state of the system (AD-MS) within the hold-up time from the first to the 5th day. This might be due to the less active sites of the Fe-TiO₂ in the initial reaction period after which the number of active sites in both the AD and AOP increased. A good correlation was observed as the rate-limiting step was observed to be the chemical reaction between the Fe-TiO₂ and that of the organic content of the wastewater in reference to the (Figure 5.2a) COD and (Figure 5.2b) colour reduction.

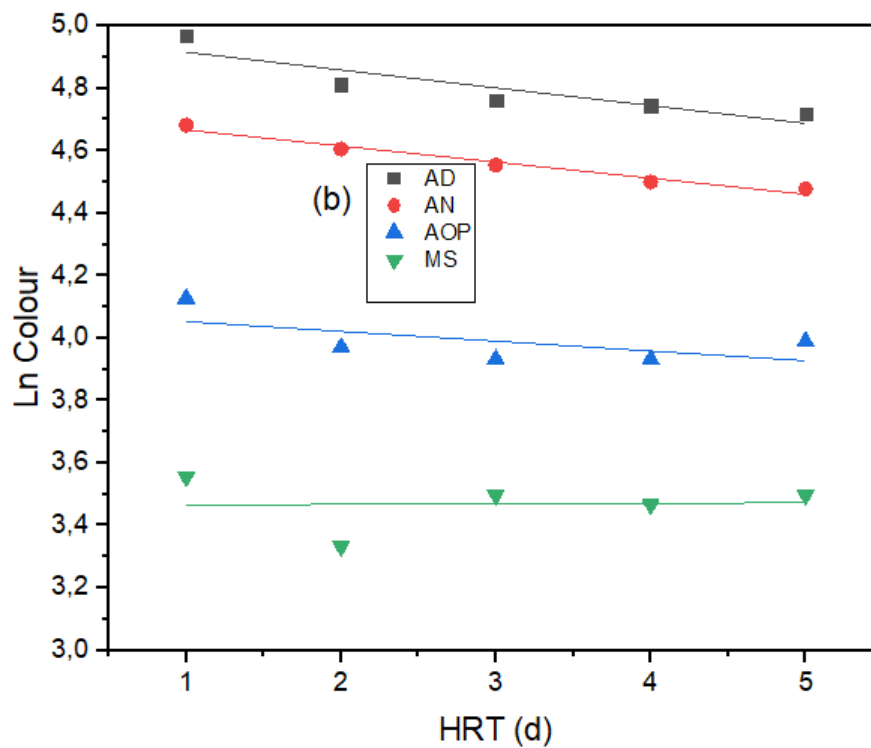
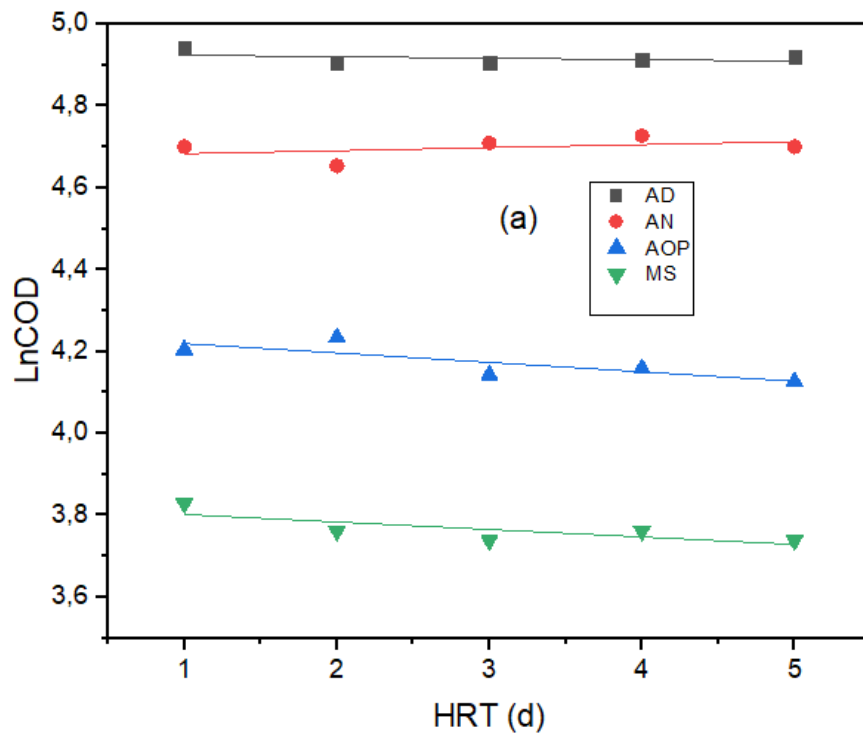


Figure 5.2: Pseudofirst-order kinetic plot of (a) COD and (b) colour removal by the integrated system components; AD-anaerobic digestion; AN-buffer system; AOP-advanced oxidation process; Ms-Magnetic filter system

5.3.3 Comparing photo-irradiation source

As photoactivation of Fe-TiO₂ is energy driven, three artificial light sources viz visible (vis), ultraviolet-vis (UV-vis) and ultraviolet (UV) irradiation were investigated. All the light sources being in a photoactive wavelength range of $\lambda > 400$ nm ignited the Fe-TiO₂ photons, which increased the photoactivity and neutralisation of the intermediate's oxidation products. The degradation rate in terms of COD and colour observed were under the following increasing order as UV > UV-vis > vis. As shown in Figure 5.3, >90% efficiency for the UV-irradiation followed by 80-90% for the UV-vis and lastly 55-75% for the vis -irradiation was achieved. Significantly, the high efficiency by the UV-irradiation can be linked with the high surface area (62.73 m²/g) and porous structures or pore size (1.337 nm) of Fe-TiO₂ which enhanced its light absorption ability. Eventually, the AD process contributed to the high COD degradation and better colour reduction, resulting in a photodegradable effluent with low COD and colour concentration.

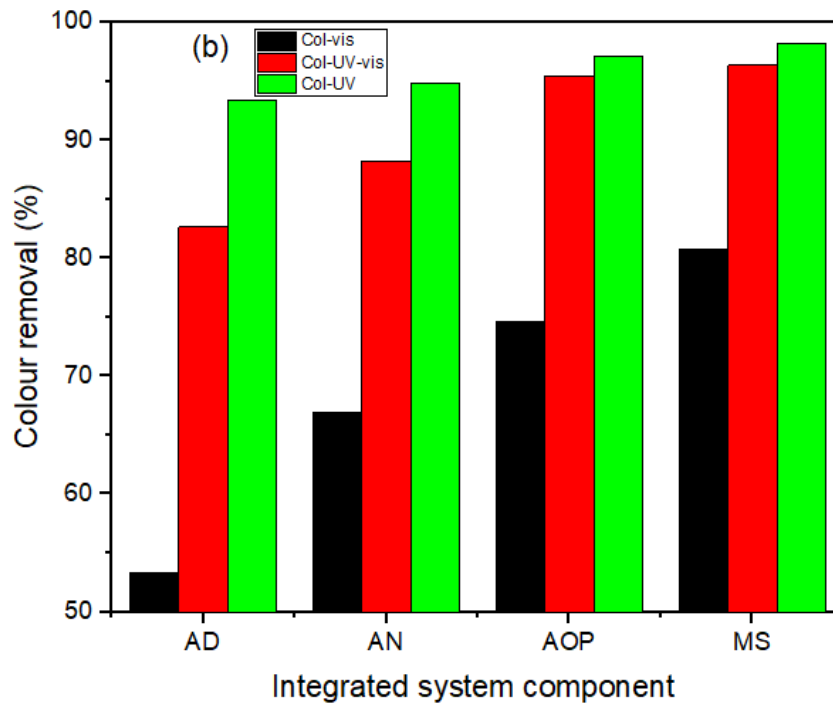
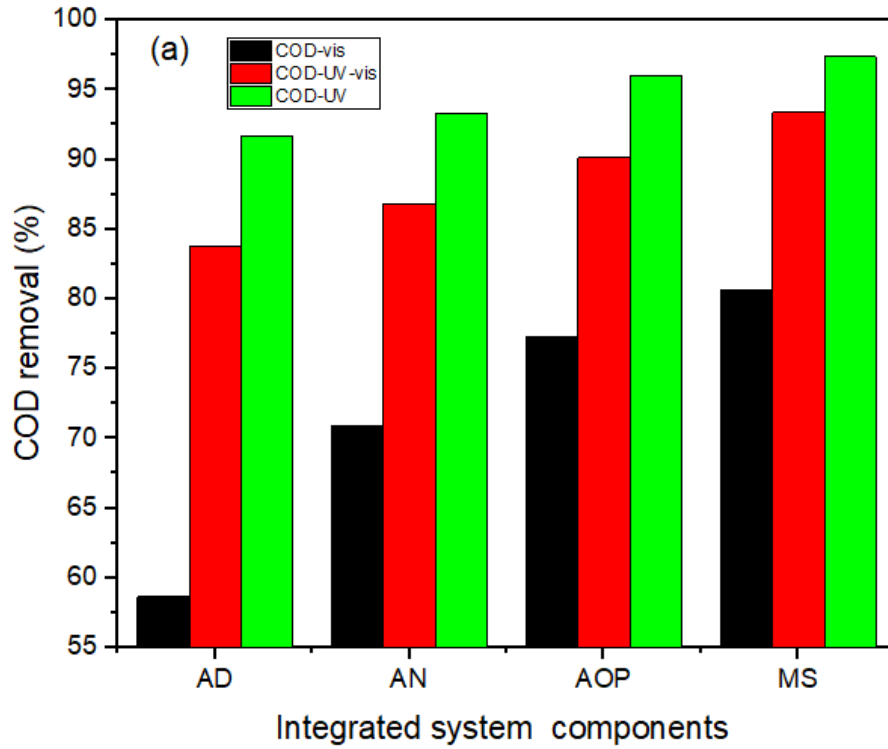


Figure 5.3: Comparing photo-intensity source on (a) COD and (b) colour removal by the integrated system components; AD-anaerobic digestion; AN-buffer system; AOP-advanced oxidation process; Ms-Magnetic filter system

Kinetically, photodegradation of the organic content over the Fe-TiO₂ surface was assumed to occur via the mass transfer of the pollutant across (i) its external boundary layer, (ii) pores and (iii) active sites of the photocatalyst surface (Apollo et al. 2013; Kobwittaya and Sirivithayapakorn 2014; Zulfiqar et al. 2019). Therefore, to ascertain this phenomenon, the pseudo-first-order kinetic model was utilised in checking the photocatalytic activity under the different irradiation sources (vis/UV-vis/UV). Figure 5.4 shows the correlated plot for the photodegradation of COD and colour with respect to the rate-limiting step. As it can be seen in Table 5.4, the goodness of the fit of the linear plot was related in terms of the R² values with kinetic rate constants (k).

Table 5.4: Kinetic regression coefficient of the integrated system components

Water parameter	Colour		COD	
	k (d ⁻¹)	R ²	k (d ⁻¹)	R ²
Light source				
Visible (vis)	-0.418	0.998	0.197	0.986
UV-vis	0.34	0.916	0.56	0.917
UV	0.53	0.893	0.512	0.995

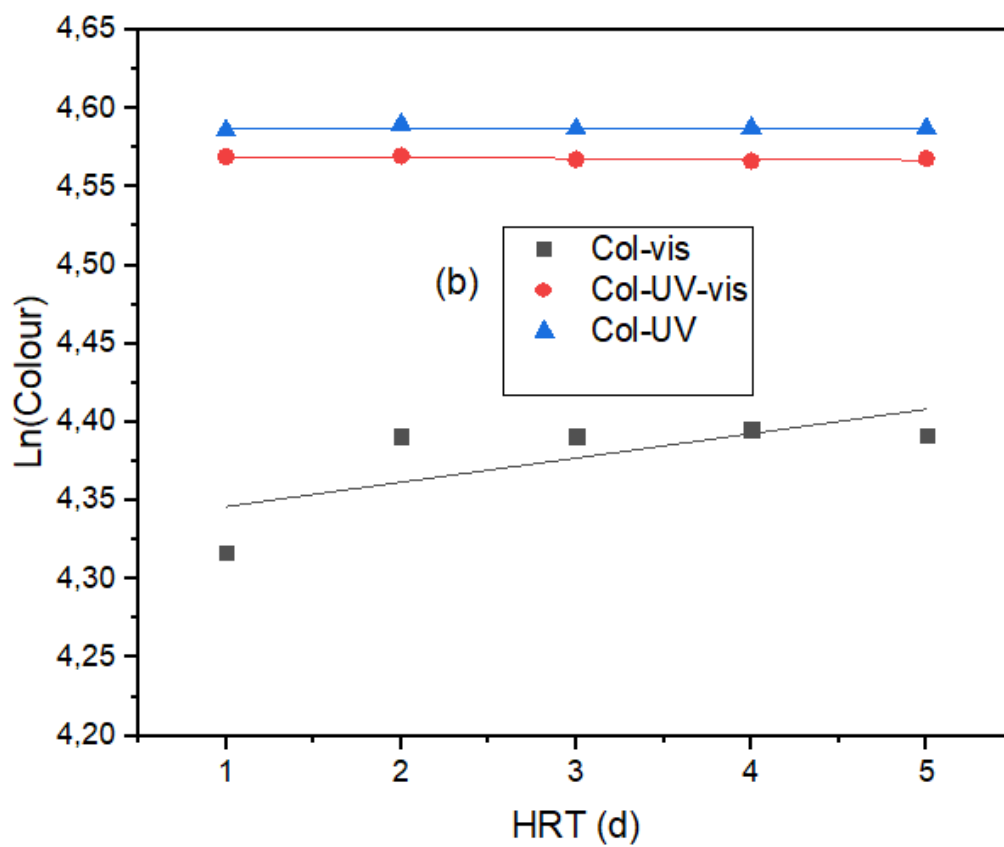
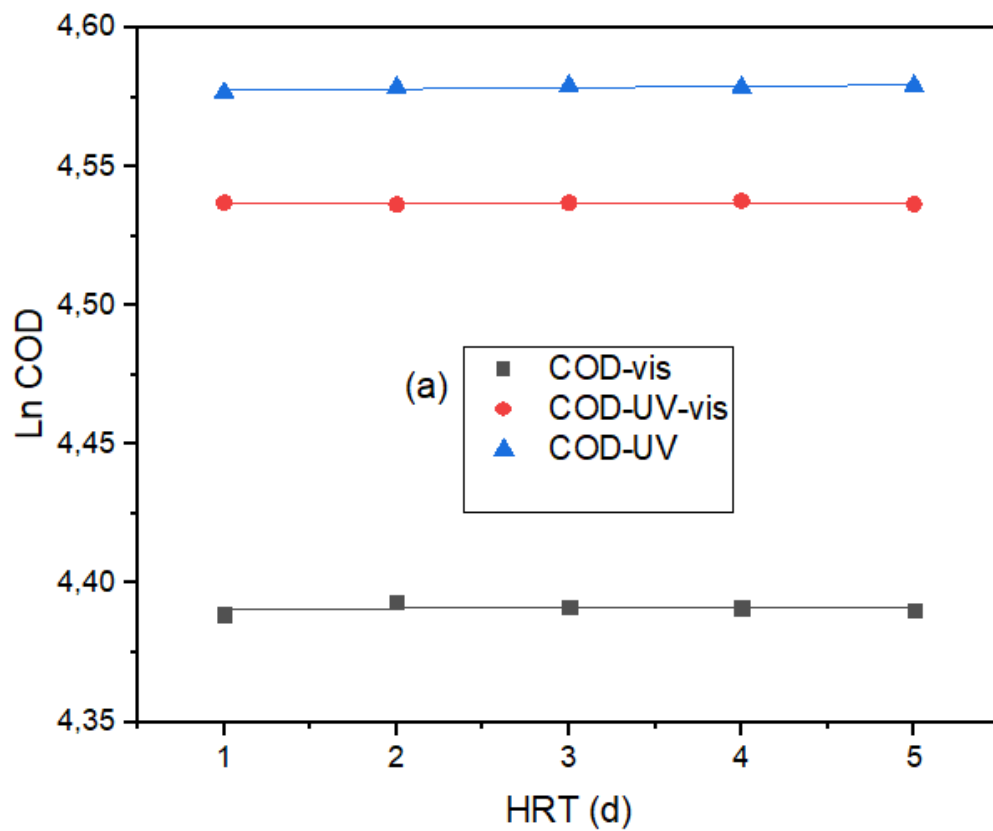


Figure 5.4: Pseudo-first order kinetic plot of (a) COD and (b) colour removal by the photo-intensity source

5.3.4 Integrated system response energy model development

The Box Behnken design (BBD) matrix was used to investigate the effects of the input variables on the process variable and the experimental responses obtained for the process optimisation are shown in Table 5.5. With the randomised run order, the input variables (OLR, HRT and light source) combination was built via the Design Expert software (Version 13.0.7), whereas the response (biogas produced, %COD removal, E_{bio} and E_{uv}) were experimentally generated via the integrated system (AD-AN-AOP-MS) monitoring. The three levelled RSM-BBD had a total of 15 experimental runs with three replicated centre points (run 7, 11, 15). The repeated runs were used as a medium to estimate the reproducibility of the experimental design with limited errors. The residual difference between the experimental values and the RSM-BBD model predicted results over the various-level sequences and were statistically agreeable with low deviation differences. Table 5.6 presents the summary of response ranges with the ratio of minimum to maximum coupled with the mean and the standard deviation (Std Dev) values. This suggested the input variables had a substantial effect on the response, even though some of the responded values were significantly exceptional.

Table 5.5: Experimental and RSM-BBD randomized results obtained from the integrated system

Input variables			Exp Results				RSM-BBD Results			
A:OLR kgCOD/L.d	B: HRT d	C:Light type n/a	Biogas mL/d	COD removal %	Ebio kWh/L	EUV kWh/L	Biogas mL/d	COD removal %	Ebio kWh/L	EUV kWh/L
0.85	31	1	1250	100	38	99	1200	99	37	99
1.30	31	0	1850	100	42	126	1838	100	43	126
0.85	1	1	250	99	36	206	225	99	36	206
1.30	16	-1	1950	96	24	118	1938	96	24	119
0.39	1	0	250	98	42	386	263	98	42	386
1.30	1	0	250	97	42	426	213	97	42	426
0.85	16	0	850	98	42	389	958	98	44	389
1.30	16	1	1250	99	36	235	1313	99	35	235
0.39	31	0	1250	97	42	488	1288	97	43	488
0.85	1	-1	250	96	25	216	300	96	24	215
0.85	16	0	875	98	44	389	958	98	44	389
0.39	16	-1	1550	96	25	395	1488	96	24	396
0.85	31	-1	1950	97	25	126	1975	97	24	125
0.39	16	1	1250	99	144	245	1263	99	143	245
0.85	16	0	1150	99	44	388	958	98	44	389

Table 5.6: Statistical summary of the RSM-BBD responses

Response	Name	Units	Minimum	Maximum	Mean	Std. Dev.	Ratio
R1	Biogas	mL/d	250	1950	1078.33	615.20	7.80
R2	COD removal	%	95.84	99.90	97.84	1.38	1.04
R3	Ebio	kWh/L	24.30	143.73	43.34	28.78	5.92
R4	EUV	kWh/L	98.96	488.13	282.12	131.98	4.93

5.3.5 Response model studies

Using Design Expert 13 software, the RSM-BBD matrices and responses (Table 5.6) were fitted into linear, 2FI, quadratic, and cubic models. The best model was then selected based on each model's significance level (SL), the regression coefficient (R^2) closeness to unity, a low SD (standard deviation), a low PRESS (prediction error of square) and the difference between the predicted and adjusted R^2 values of less than 0.2 as well as the models P-value being below 0.05. Therefore, correlated quadratic models expressed in equations (5.10-5.17) in their coded and actual input factor levels were selected. The impact of the variables linear, squared and 2-way interactions on the responses are ascribed to the coefficient signs in their

empirical quadratic models. The sign convention of the coefficient values of model terms in the final regression model (5.10-5.17) helped predict the nature of the effect of such variables on the responses (Abdulhameed et al. 2019; Khataee et al. 2011; Zulfikar et al. 2019). The positive coefficients in any of the independent variables indicate that increasing interaction terms (OLR and HRT) will benefit the response variable, whereas the negative coefficients will decrease with an increase in those variables. The significance and adequacy of input variables and their interactions were also characterized by their P-values of 0.05, which indicates a 95% confidence level.

$$\text{Biogas}_{\text{coded}}(Y_1) = 958.3 + 125A + 662.5B - 212.5C + 150AB - 100AC - 175BC + 258.33A^2 - 316.67B^2 + 283.33C^2 \quad (5.10)$$

$$\begin{aligned} \text{Biogas}_{\text{actual}}(Y_1) = & 859.94 - 2209.8(\text{OLR}) + 70.51\text{HRT} + 161\text{Light}_{\text{type}} + 22.1(\text{OLR} * \\ & \text{HRT}) - 220.75(\text{OLR} * \text{light}_{\text{type}}) - 11.67(\text{HRT} * \text{light}_{\text{type}}) + 1258.879 * \text{OLR}^2 - \\ & 1.47\text{HRT}^2 + 283.3\text{Light}_{\text{type}}^2 \end{aligned} \quad (5.11)$$

$$\text{COD}_{\text{coded}}(Y_2) = 97.7 - 0.036A + 0.53B + 1.58C + 0.73AB + 0.24B^2 + 258.33AB^2 \quad (5.12)$$

$$\begin{aligned} \text{COD}_{\text{actual}}(Y_2) = & 97.74 - 0.36(\text{OLR}) + 0.061\text{HRT} + 1.59\text{Light}_{\text{type}} - 0.07(\text{OLR} * \text{HRT}) + \\ & 0.0036\text{HRT}^2 + 0.005(\text{OLR} * \text{HRT}^2) \end{aligned} \quad (5.13)$$

$$\begin{aligned} \text{Ebio}_{\text{coded}}(Y_3) = & 44.14 - 27.1A + 0.257B + 6.067C - 56.36AB - 26.68AC + 12.42 A^2 - \\ & 13.94B^2 + 26.5A^2C + 27.04AB^2 \end{aligned} \quad (5.14)$$

$$\begin{aligned} \text{Ebio}_{\text{actual}}(Y_3) = & 104.96 - 142.08(\text{OLR}) + 1.997\text{HRT} + 148.66\text{Light}_{\text{type}} - 14.07(\text{OLR} * \\ & \text{HRT}) - 277(\text{OLR} * \text{light}_{\text{type}}) + 80.5\text{OLR}^2 - 0.084\text{HRT}^2 + \\ & 129.19(\text{OLR}^2 * \text{Light}_{\text{type}}) + 0.0259(\text{OLR} * \text{HRT}^2) \end{aligned} \quad (5.15)$$

$$\text{Euv}_{\text{coded}}(Y_3) = 388.69 - 71.74A - 45B - 8.6C - 34.33AB + 66.75AC - 13.32 BC - 27.37 A^2 - 59.67B^2 - 167.53C^2 - 8.76AB^2 \quad (5.16)$$

$$\begin{aligned} \text{Euv}_{\text{actual}}(Y_3) = & 421.01 - 169.18(\text{OLR}) + 15.42\text{HRT} - 128.86 \text{Light}_{\text{type}} - 12.07(\text{OLR} * \\ & \text{HRT}) + 147.36(\text{OLR} * \text{light}_{\text{type}}) - 0.2835 (\text{HRT} * \text{Light}_{\text{type}}) + \\ & 133.80\text{OLR}^2 - 0.193\text{HRT}^2 - 167.5 (\text{Light}_{\text{type}}^2) + 0.089(\text{OLR} * \text{HRT}^2) \end{aligned} \quad (5.17)$$

5.3.6 Analysis of variance of the response model developed

The ANOVA results show the model equations (5.10-5.17) with quadratic, linear, and interaction variables were statistically significant for the experimental data. Based on the probability > F values, the summary of ANOVA for the quadratic models with their coded variables (Table 5.7), elucidates the interaction of OLR (A) and HRT (B) in the AD process were the most influential variables in all the responses. However, the interaction of the OLR(A) and light_{type}(C) was ascribed to the energy production (E_{bio}) and UV-lamp energy utilisation (E_{uv}). This suggests that the energy required by the UV-lamp in the AOP system can affect the over treatment of the effluent content (OLR) with time (HRT). Notwithstanding, all the models were found significant (P < 0.05). Some of their terms were found insignificant as their probability > F values were found to be greater than 0.05. However, those terms were regarded as hierarchy terms for the final models to enhance their predictivity. Also, the experiment's high reliability and precision were satisfactory, as the coefficient of variance (CV) was found to be less than 10%.

Additionally, the non-significant Lack of Fit (LOF) indicates the models were significant, as their tolerable sufficient precision was greater than 4. This suggests a high signal and therefore the models can be used to navigate within the design space of the input variables levels. The

significance and adequacy of input variables and their interactions were also characterized by their P-values < 0.05 , which indicates a 95 % of confidence level. As illustrated in Figure 5.5, remarkable agreement between actual and predicted respondents suggest the regression model's importance and applicability. It can be inferred that, apart from a few data points, the plot's most produced data points were generally distributed along a straight region provided by the diagonal line (Abdulhameed et al. 2019; Apollo et al. 2016; Khataee et al. 2011). This proves the model's outstanding suitability for predictability within the design space of the input variables levels

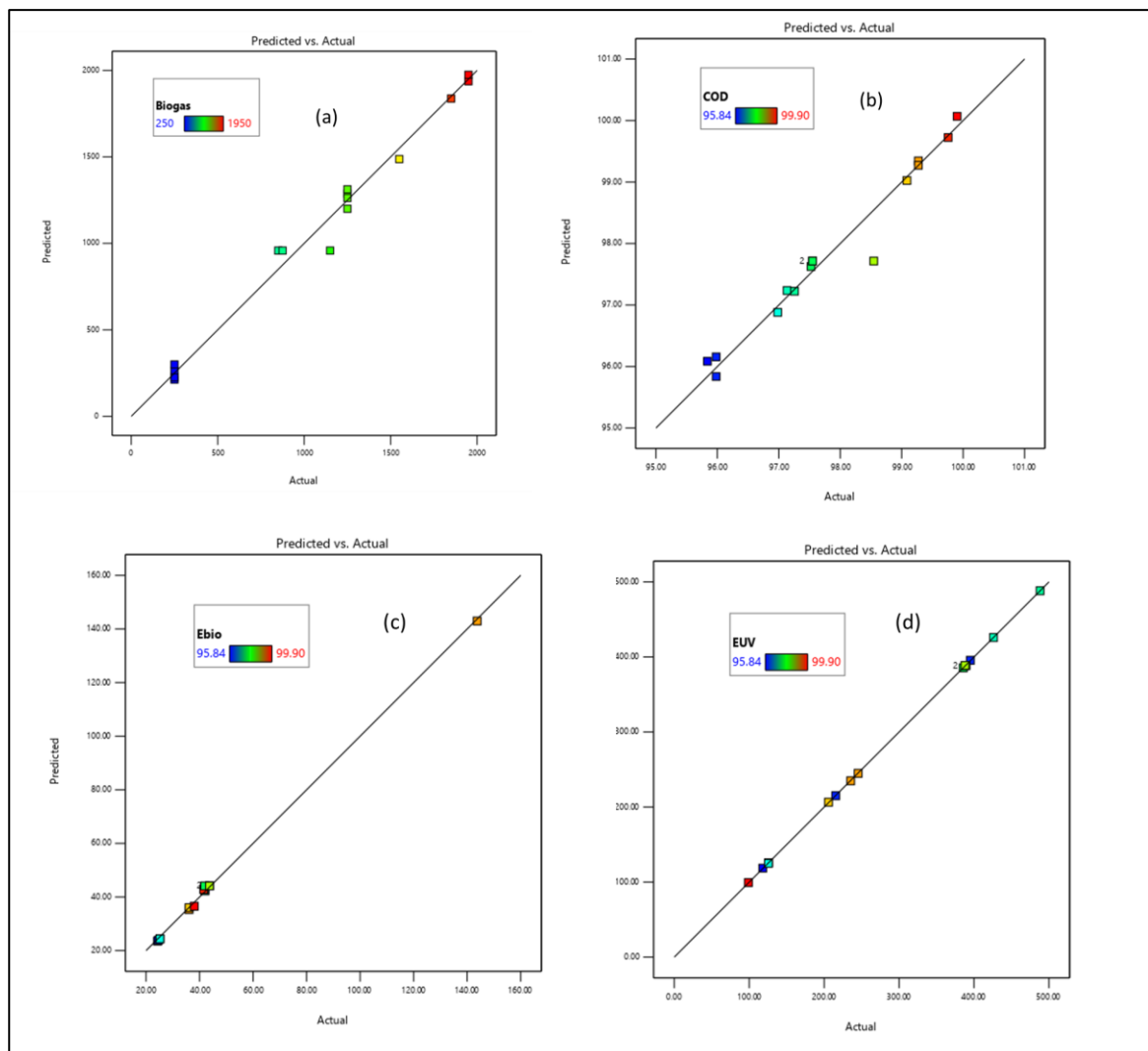


Figure 5.5: Experimental and RSM-BBD predicted results of the integrated system

Table 5.7: Analysis of variance (ANOVA) of integrated system response

Response	Source	Sum of Squares	df	Mean Square	F-value	p-value	R ²	Adeq Precision
Biogas (Y1)	Model	5226000	9	580600	39.81	0.0004	0.9862	17.875
	A-OLR	125000	1	125000	8.57	0.0327		
	B-HRT	3511000	1	3511000	240.77	< 0.0001		
	C-Light type	361200	1	361200	24.77	0.0042		
	AB	90000	1	90000	6.17	0.0556		
	AC	40000	1	40000	2.74	0.0586		
	BC	122500	1	122500	8.4	0.0339		
	A ²	246400	1	246400	16.9	0.0093		
	B ²	370300	1	370300	25.39	0.004		
	C ²	296400	1	296400	20.33	0.0064		
	Residual	72916.67	5	14583.33				
%COD (Y2)	Model	25.91	6	4.32	37.23	< 0.0001	0.9654	18.1822
	A-OLR	0.0051	1	0.0051	0.0437	0.8396		
	B-HRT	2.18	1	2.18	18.77	0.0025		
	C-Light type	20.31	1	20.31	175.13	< 0.0001		
	AB	2.09	1	2.09	18.01	0.0028		
	B ²	0.211	1	0.211	1.82	0.2143		
	AB ²	0.634	1	0.634	5.47	0.0476		
	Residual	0.9279	8	0.116				
Ebio (Y3)	Model	11580.28	9	1447.54	622.88	< 0.0001	0.9988	101.1452
	A-OLR	2946.03	1	2946.03	1267.68	< 0.0001		
	B-HRT	0.5285	1	0.5285	0.2274	0.6503		
	C-Light type	147.23	1	147.23	63.35	0.0002		
	AB	1523.2	1	1523.2	713.02	< 0.0001		
	AC	1326.1	1	1326.1	513.04	< 0.0001		
	A ²	572.57	1	572.57	246.38	< 0.0001		
	B ²	720.14	1	720.14	309.88	< 0.0001		
	A ² C	1405.8	1	1405.8	604.92	< 0.0001		
	AB ²	1462.93	1	1462.93	629.5	< 0.0001		
	Residual	13.94	6	2.32				
Euv (Y4)	Model	243900	10	24385.12	34939.87	< 0.0001	1	543.6355
	A-OLR	20582.21	1	20582.21	29490.92	< 0.0001		
	B-HRT	19457.73	1	19457.73	27879.73	< 0.0001		
	C-Light type	589.96	1	589.96	845.32	< 0.0001		
	AB	40555.92	1	40555.92	58109.97	< 0.0001		
	AC	17823.59	1	17823.59	25538.27	< 0.0001		
	BC	72.34	1	72.34	103.64	0.0005		
	A ²	2766.05	1	2766.05	3963.3	< 0.0001		
	B ²	13148.51	1	13148.51	18839.66	< 0.0001		
	C ²	103600	1	103600	148500	< 0.0001		
	AB ²	153.3	1	153.3	219.65	0.0001		
	Residual	2.79	4	0.6979				

5.3.7 Energy efficiency and carbon emission reduction (CER)

The integrated process energy efficiency and environmental sustainability were assessed based on the electricity generated by the AD process biogas generation and the CER associated with the subsequent photodegradation process. The bioenergy conversion efficiency of 45% heat and 33% power was used in the estimation of CER, whereby a base emission ratio of 0.957 kg CO₂/kWh of power generation was employed (Apollo et al. 2013). The CER attained as compared to energy efficiency, which is a ratio of the energy generated by the AD process to the electricity required by the UV lamp in the photodegradation post-treatment. From the RSM-BBD matrix (Table 5.5) and ANOVA (Table 5.7), the most influential factors identified were the OLR and HRT.

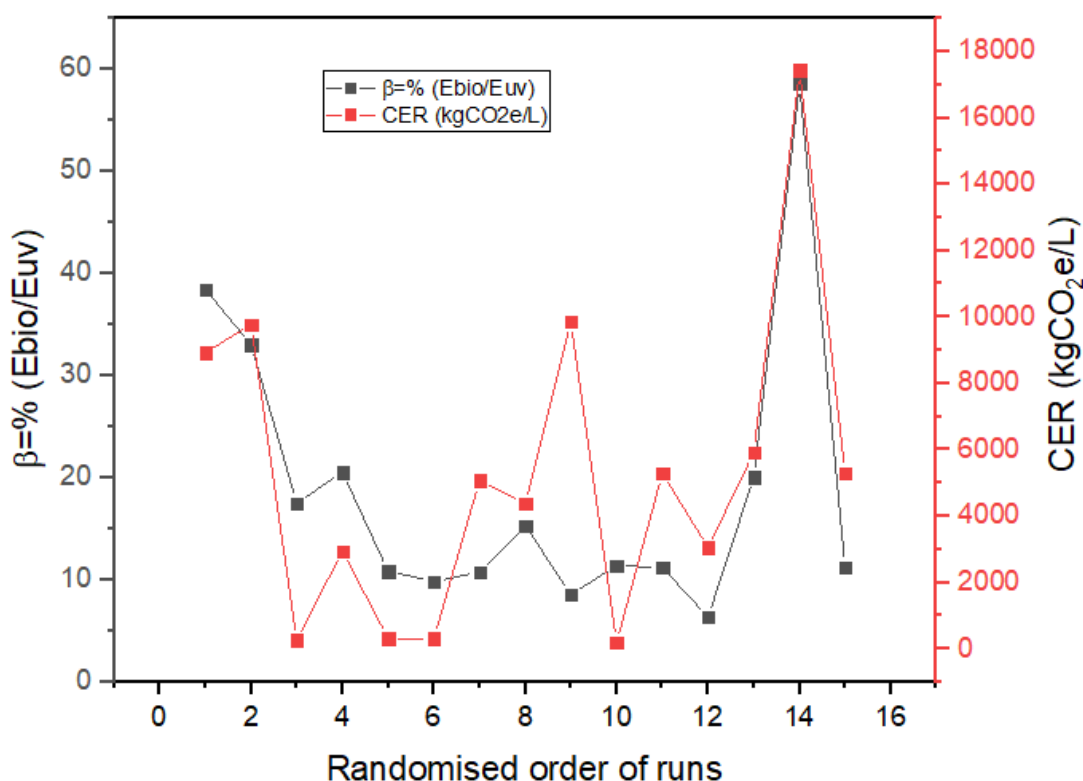


Figure 5.6: Estimated energy efficiency (β) and CO₂ emission reduction (CER) per the RSM-BBD randomised order of runs

The energy efficiency and CER estimated under run 14 conditions (Figure 5.6) was observed as the best. Thus, at a lower OLR of 0.394 kgCOD/Ld and HRT of 16 days with UV-photodegradation, 60% energy efficiency and 17430 kgCO₂e/L were estimated. This corresponds to 1250 mL/d biogas produced with almost 100% COD removal, 144 kWh/L bioenergy produced, and 245 kWh/L energy utilised by the UV-photodegradation. Generally, the energy produced by the AD process was equivalent or lower to the energy required by the UV-photodegradation. Notwithstanding, the bioenergy could be used to subvent the energy required by the UV lamp to photodegrade the high OLR. This elucidates other researcher's findings who also integrated AD and AOP systems for wastewater treatment and biogas production (Apollo et al. 2016; Bella and Rao 2021; Zulfiqar et al. 2019). Therefore, integration of the AD-AOP system gives the insight to produce bioenergy and CO₂ emission reduction with the potency to lower the energy requirement for the photodegradation process while mitigating environmental pollutants in the wastewater settings (Apollo et al. 2013; de Andrade Guerra et al. 2021; Nguyen et al. 2021; Rout et al. 2021).

5.3.8 Three dimensional (3D) interactive response surface

To determine the optimum region to maximize the system's desirability, the 3D response surface revealed quite significant curvatures. These curves demonstrates and infers the correlation that exists between the input variables and the response are quadratic.

Figure 5.7 presents a response surface plot of the interactive effect of OLR and HRTs under UV-photodegradation on (a) biogas produced, (b) %COD removal, (c) E_{bio} - bioenergy produced and (d) E_{uv} - the photodegradation energy required. The generalized representation of the peaks from the 3-D response plots demonstrated the design space or border encompasses the appropriate conditions for optimal response variable performance. This assisted in establishing the optimum level for each process variable by analysing the

interactions between the process variables (Apollo et al. 2016; Khataee et al. 2011). The efficacy of the AD process, for example, could be related to the concave-like peak of the inferring ORL and HRT. These two key operating parameters were found as the most influential factors that facilitated the system overall efficiency in biogas production and organic content degradation.

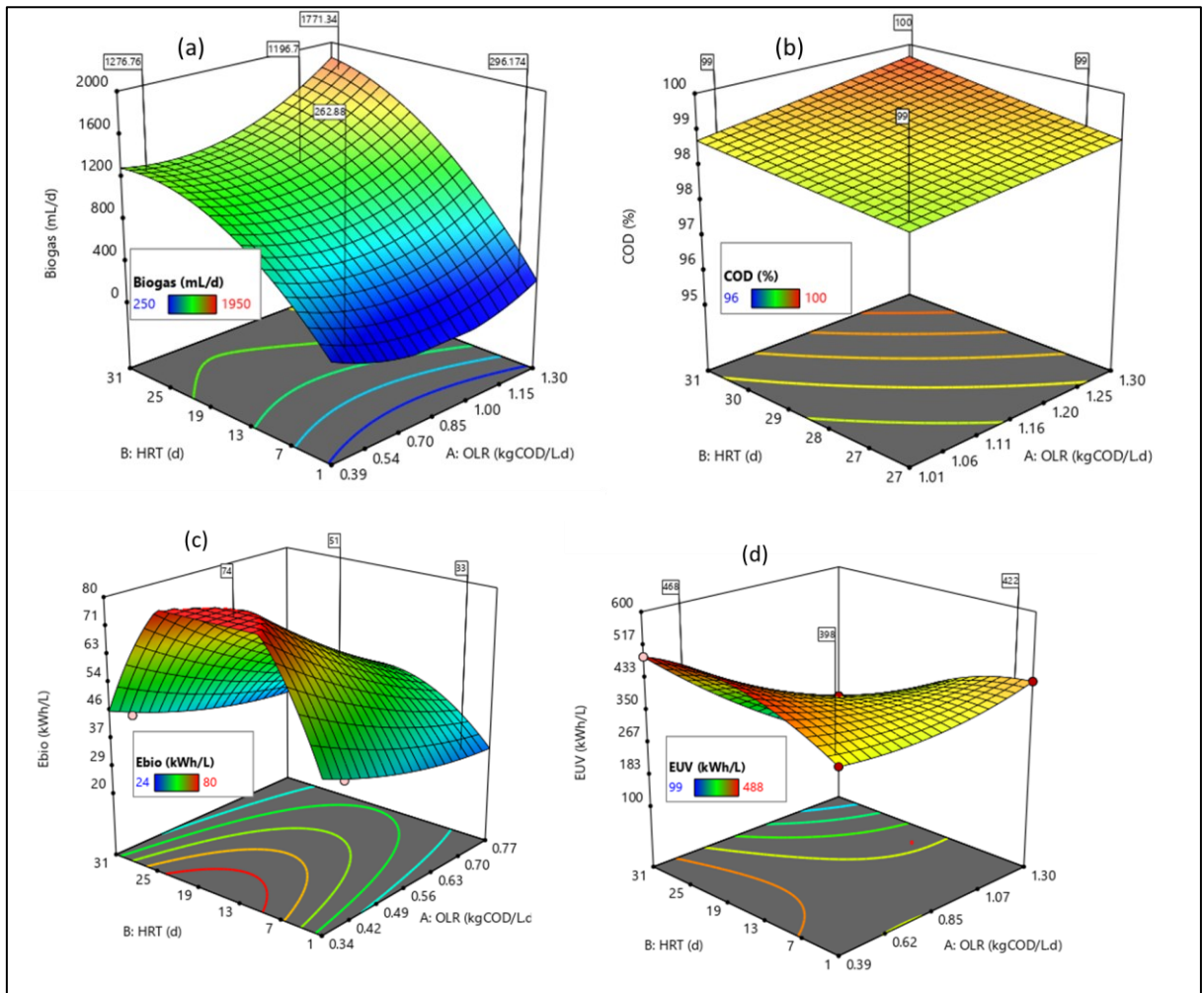


Figure 5.7: Response plots of the interactive effect of OLR and HRT on (a) biogas produced, (b) %COD removal, (c) Ebio - bioenergy produced and (d) Euv - the photodegradation energy

5.3.9 Response optimisation and predictability

Using the response quadratic models (5.10-5.17), the RSM-BBD numerical optimisation projected responses and optimal points at each level of the experimental conditions (Figure 5.8) To maximise the desirability of the responses, the input variables were adjusted within their range with the target goal to maximise the desirability.

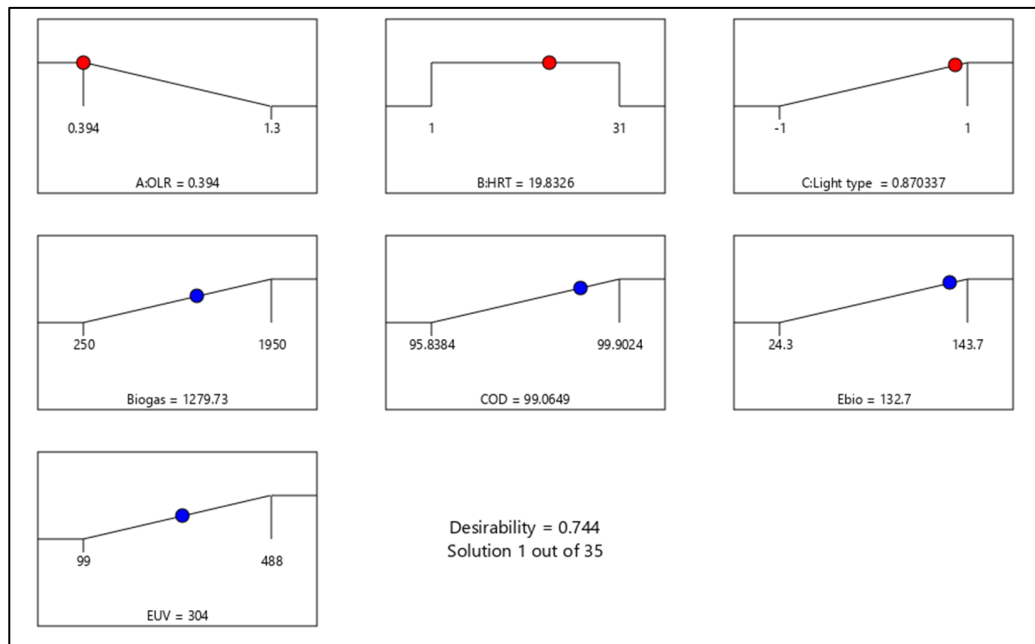


Figure 5.8: Ramp plot of the selected optimum condition of using RSM-BBD for the integrated system

Figure 5.8 presents the selected best optimal conditions chosen from 35 predicted solutions. This ramp plot reveals 1279.73 mL/d of biogas with 99% COD removal, Ebio (132.7 kWh/L) and Euv (304.18kWh/L) at an OLR of 0.394 kgCOD/L.d and HRT of 20 days under UV-photodegradation with 75% overall desirable efficiency. Table 5.8 shows the experimentally validated optimal conditions aggregable with the RSM-BBD predicted results. This affirms the significant and reliable predictability ($P < 0.05$) of the models at 95% confidence levels within the design space of the experiments.

Table 5.8: Experimental validity of the RSM-BBD predicted results at optimal conditions

Solution 1 of 35 Response	Predicted Mean	Observed	Std Dev	SE Pred
Biogas (mL/d)	1279.73	1250	120.761	154.432
COD removal (%)	99.06	98.0	0.341	0.41
Ebio (kWh/L)	132.7	130	1.5	2
EUV(kWh/L)	304	302	1	1

5.3.10 Effect of OLR, HRT and UV-light on biogas production

Figure 5.9 shows the impact of the independent variables on the biogas production as an increase in the OLR (Figure 5.9a) requires longer HRT (Figure 5.9b) to increase the biogas production at UV-light (Figure 5.9c) source in the AOP system. As the AD process was stimulated by the Fe-TiO₂, it influenced its methanogenic activities which increased the biogas production (950-1600 mL/d). Conversely, lower OLR warrants the AOP system with low-light intensity (visible) at a shorted HRT. However, increasing the HRT with low-strength OLR might affect the overall efficiency of the integrated system, as the energy required by the UV-lamp of the AOP system will be higher than the bioenergy produced by the AD system (Apollo et al. 2016).

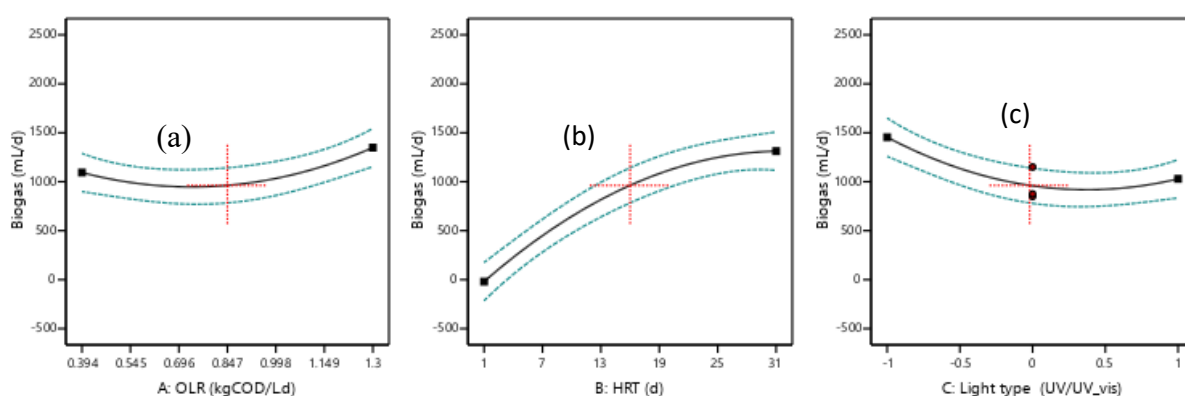


Figure 5.9: OFAT effect on biogas production

5.3.11 Effect of OLR, HRT and UV-light on COD reduction

The COD removal efficiency was based on the extent of OLR degradability. It was observed that a change in the OLR (Figure 5.10a) from 0.394 to 1.3 kgCOD/Ld, maintained almost a constant efficiency of 97-98% with respect to an increase in the HRT (Figure 5.10b) and the use of UV-light (Figure 5.10c) in the AOP post-treatment system. This suggests that the microbial activity became stabilised after the 25th day within the OLR of 1.1 to 1.3 kgCOD/Ld. The longer HRT was due to the fluctuation of the daily biogas production and recycled post-treated effluent from the AOP system (Apollo et al. 2016).

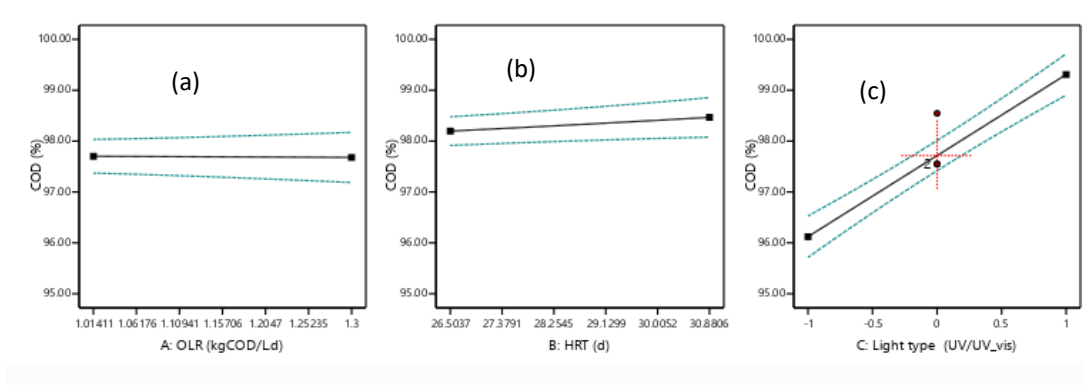


Figure 5.10: OFAT effect on COD removal

5.3.12 Effect of OLR, HRT and UV-light on bioenergy (Ebio) production

Biogas production improves as the high-strength organic content degrades (Figure 5.9). However, the contrary is seen in the bioenergy production (Figure 5.11), as increasing OLR (0.394 - 0.77 kgCOD/L.d) decreased the bioenergy (Ebio) produced. Thus, at high-strength OLR, more energy will be required to degrade the organic content, subsequently affecting the net energy produced. This is observed in the increase of HRT (Figure 5.11b) with UV-light for the AOP system resulting in bioenergy of 20 - 45 kWh/L. Herein, at lower OLR of 0.85 kgCOD/L.d and HRT of 16 days with visible light resulted in 95 kWh/L of bioenergy

produced. Moreover, operating the AD process at fixed HRT, increased the hold-up time between the reactants and the methanogenic activity (Apollo et al. 2013, 2016). Therefore, an AD effluent with low organic intensity degrades faster than one with high-organic intensity, which might cause photodegradation attenuation with an increase in energy consumption.

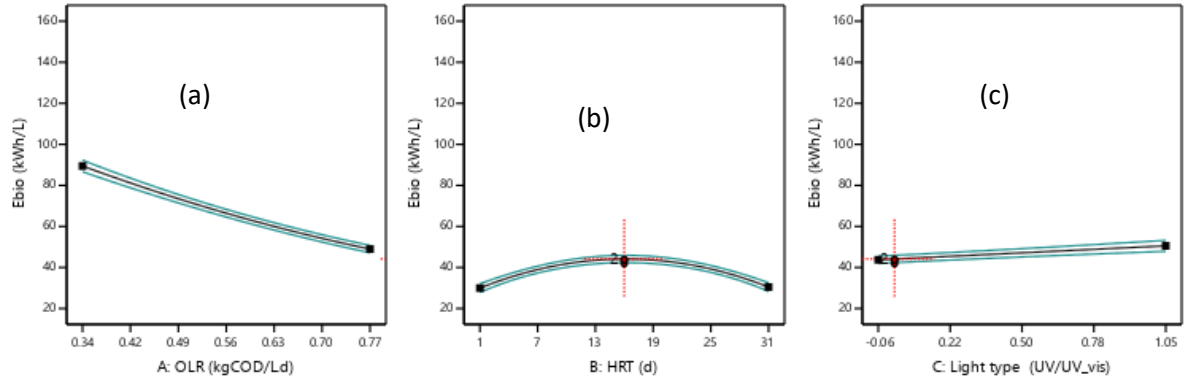


Figure 5.11: OFAT effect on bioenergy production

5.3.13 Effect of OLR, HRT and UV-light energy (Euv) consumption

From the models (5.10-5.17), the interaction of OLR*HRT in the AD process, as well as OLR*Light type in the AOP system, had a significant impact on the overall efficiency. This infers that OLR has a strong effect on the energy consumption of the photodegradation process. Figure 5.12 shows the energy consumption by the UV lamp for the photodegradation post-treatment of effluent with OLR is lower than that of the UV-Vis lamp. Thus, the UV-vis lamp was more energy driven than the UV lamp. At lower OLR of 0.85 kg COD/L.d and HRT of 16 days, an increase in the HRT and the UV-vis (0) photodegradation consumed energy of 400 kWh/L, whereas that of the Vis (-1) and UV (+1) warrants 250 kWh/L resulted in efficient photodegradation and minimal energy requirement (Figure 5.12). On the contrary, biodegradation at high HRT can increase the microbe-pollutant interaction time (Apollo et al. 2013), and therefore more energy will be consumed.

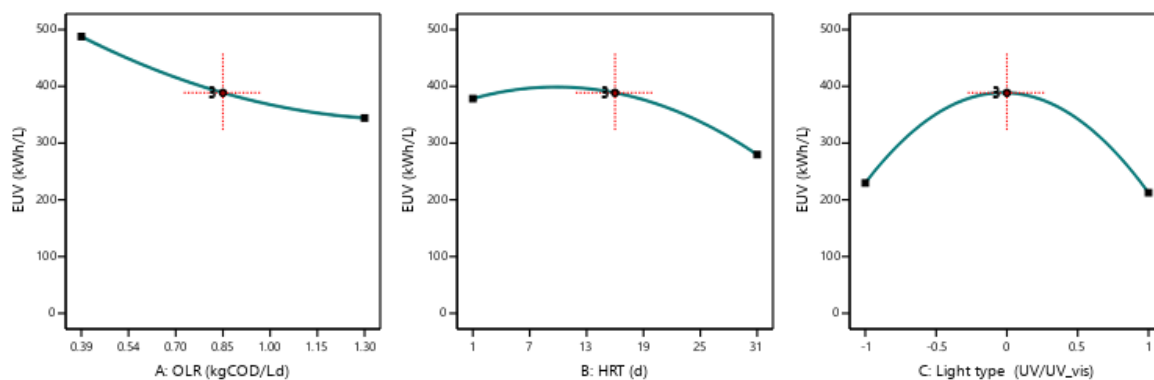


Figure 5.12: OFAT effect on energy consumption

5.3.14 Energy economy

As photocatalysis is an energy intensive process responsible for about 80% of the total energy cost of operation, subsidizing its energy utilisation can improve the economics of the integrated system. Considering the electricity requirement of the UV lamp (which is the major electric component of the photoreactor) and that of the AD unit, the selected optimised condition (Figure 5.8) was cheaper to operate the integrated process. Herein, by applying electricity unit cost of R3.22 (\$0.23) per kWh (Paper 6), the total bioenergy produced (132.7 kWh) was priced R427.29 (\$30.51). This reduced the cost of the energy utilised by the UV-lamp (304.18kWh) from R979.46 (\$69.96) to R552.17 (\$39.45). As illustrated in Figure 5.13, the energy utilised by the AOP system is reduced when the AD-AOP system was integrated. It was necessary to combine the two technologies in such a way that AD preceded the AOP system as it led to a reduction of the energy cost (Figure 5.13) and consumption (Figure 5.12), which is agreeable to Apollo et al. (2013) findings.

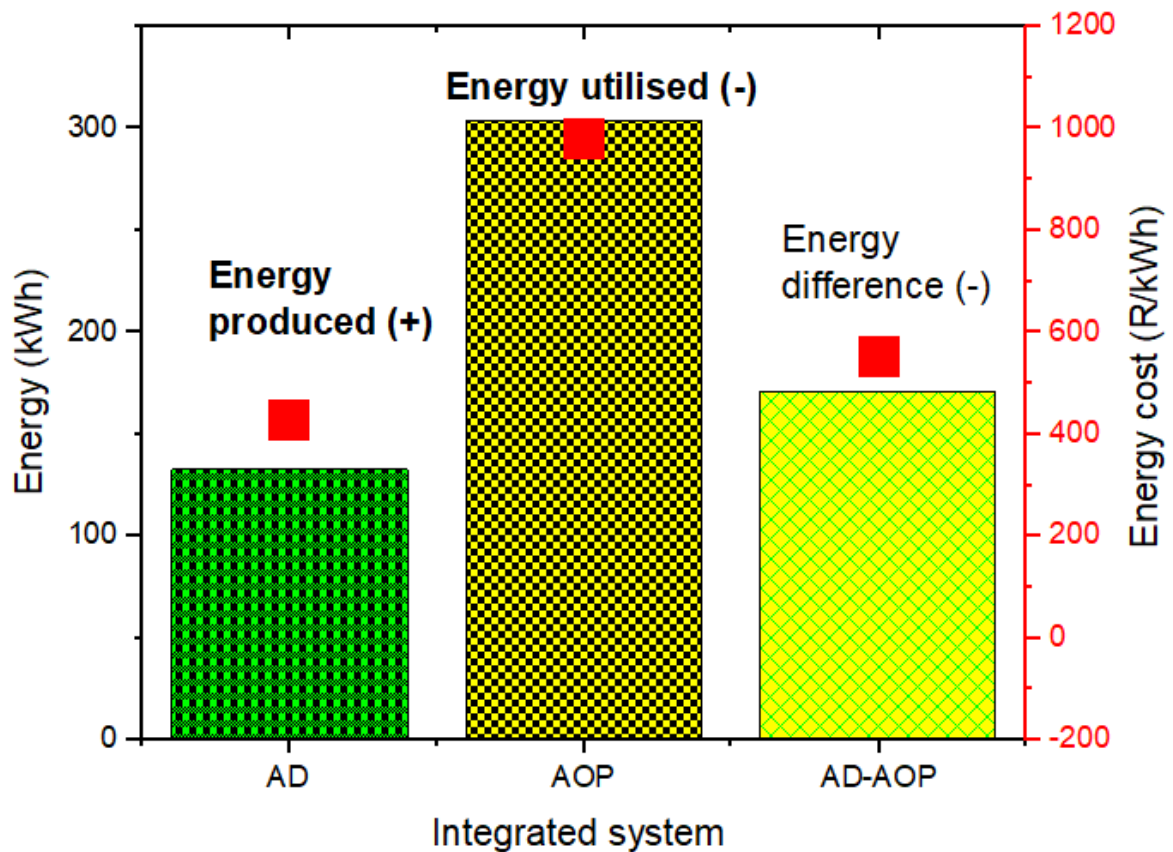


Figure 5.13: Energy estimated cost by applying electricity unit cost of R3.22 (\$0.23) per kWh under the selected optimized conditions (Figure 5.8)

5.4 Predictability and validity of RSM-BBD models with ANN

The experimental data set obtained using the RSM-BBD was adequately used to evaluate the ANN model. However, the ANN modelling performs better with many data sets. Hence, the raw data of 15 experimental sets of runs (Table 5.5) and RSM-BBD predicted results (15 sets) together with its 35 predicted optimal solutions (Figure 5.8) were doubled giving a total of 130 data sets that were utilized in ANN analysis as a technique adapted from Zulfiqar et al. (2019). Matlab software 2020 (R2020b version) was used for ANN modelling. Multi-Layer Perceptron (MPL) was used to train the network. This involved the use of a backpropagation learning algorithm for modelling. The network (Figure 5.14) consisted of 3 input layers, 14 hidden layers (neurons), and 6 output layers. The input variables were OLR, HRT and Light

source types, while the output layers included the Biogas (mL/d), COD (%), Ebio (kWh/L), Euv (kWh/L), $\beta = (\text{Ebio} / \text{Euv})$ and CER (kgCO₂/L). A supervised learning technique called Levenberg-Marquardt (TRAINLM) was randomly used as the training function to regularize the bias value.

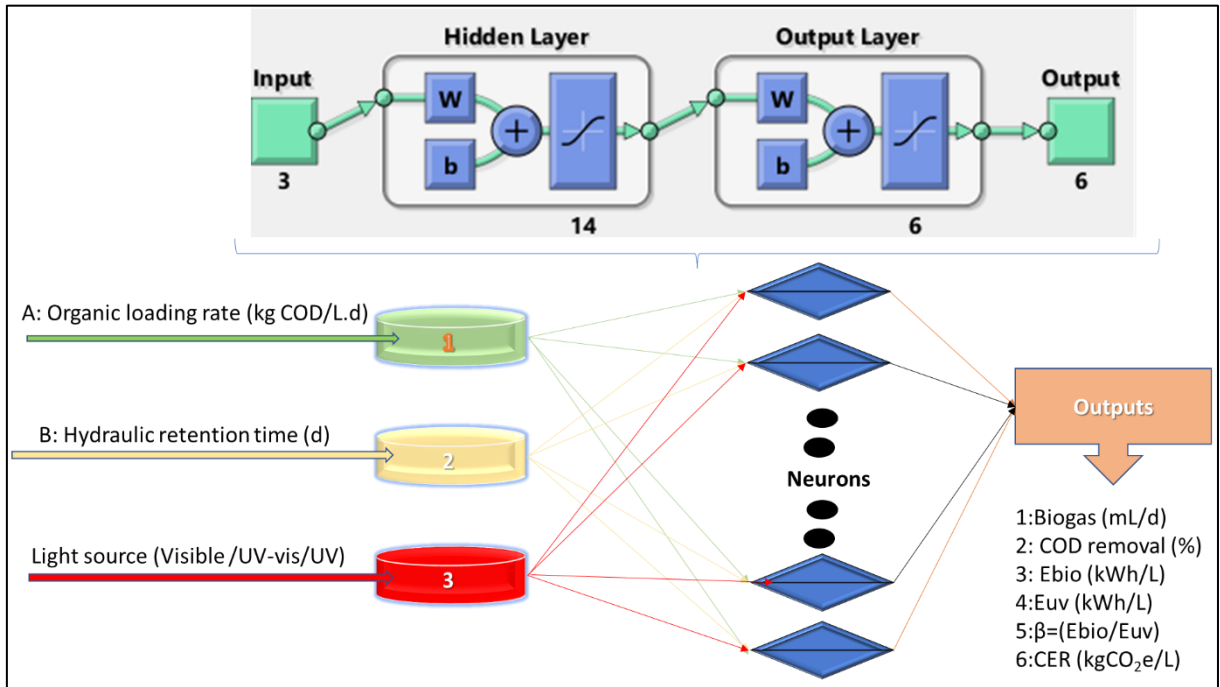


Figure 5.14: ANN architecture of the integrated AD-AOP process

5.4.1 ANN response modelling

The system network was trained and concurrently validated against an undesired rise in validation error (Figure 5.15). With the RSM-BBD matrix (Table 5.5), the ANN multi-input and single-output network system (Figure 5.16) was developed for the response prediction. The MSE and the correlation coefficient were used as performance checks to ascertain the magnitude of the correlation that exists between the independent variables and the dependent outputs as well as a measure of the ANN predictability (Table 5.9). To minimise error, the ANN network was trained using the Levenberg-Marquardt (LM) backpropagation algorithm.

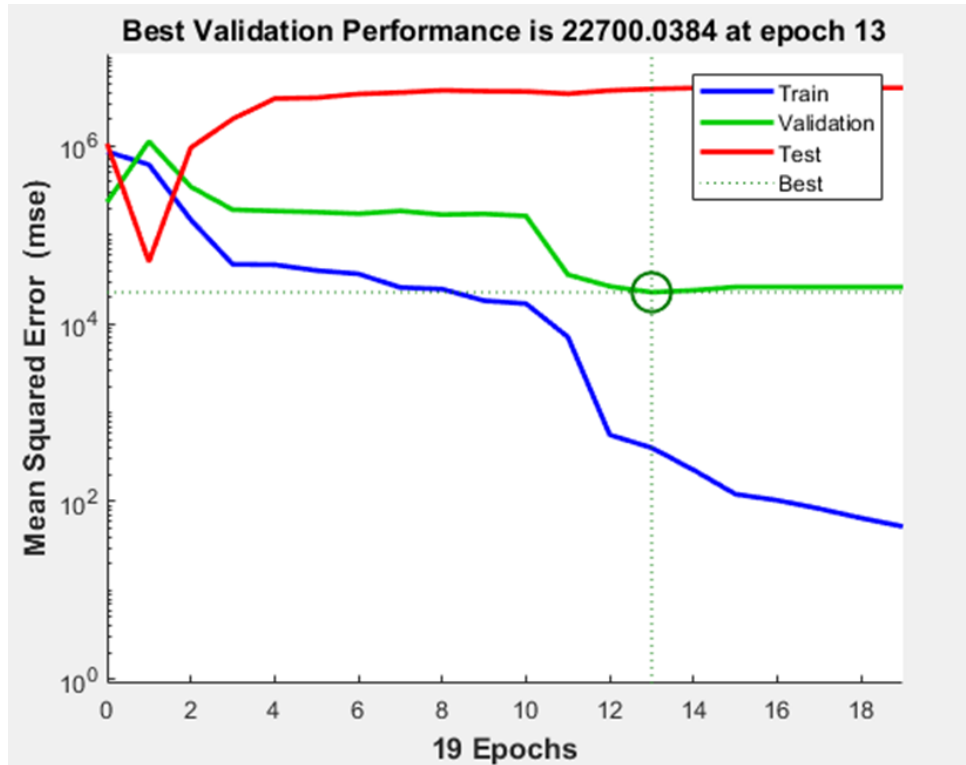


Figure 5.15: Performance plot of training, testing and validation

Figure 5.15 presents the plot of the observed MSE against the epochs. The transition points from stages 1-13 show the best possible network conditions for training, testing and network validation. The best validation performance was obtained at MSE of 2.27×10^4 at epoch 13 (Figure 5.15). This result (validation performance) suggests that after the 13th iteration (epoch 13), the network attained its best learning stage at the lowest possible MSE (2.27×10^4). The MSE attained also suggest the measured correlation between the network predicted responses and the target. Notwithstanding, the MSE seems to be too high suggesting the training network might have experienced over-fitting and so require more data for the training (Zulfiqar et al. 2019).

Figure 5.16 shows the regression plots that display the network target data (RSM -BBD) and the normalized predicted output for training, validation, testing and overall data. The correlation coefficients obtained were 0.9684, 0.9999, 0.9989 and 0.9703 for training, testing, validation, and overall data, respectively while the training means the square error was <0.0005 . Based on the R^2 -values, for training, testing, validation, and All, it could be inferred that the neural networks presented very significant fitting performances in all the stages. The slight shift in fitness observed during the training stage resulted in $R^2 < 0.99$, indicating a lack of sufficient data for the network testing. Although this shift did not affect the overall network performance, it suggests that a learning choice of data for training is insufficient for proper ANN training (Zulfiqar et al. 2019).

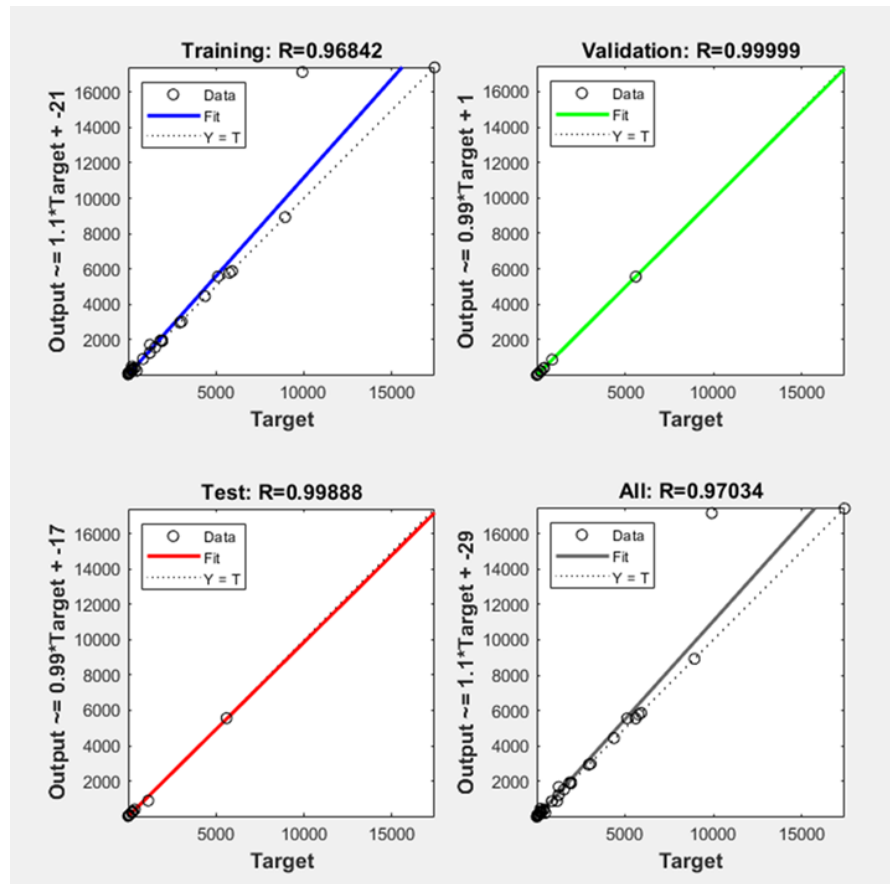


Figure 5.16: Output-target plot of four-in-one network performance

As observed in Figure 5.16, the network outputs using the ANN model are very close to the experimental data sets, implying that all data falls along a 45-degree line. This inferred that the software iteration performed within the hidden layer of the network system revealed a set of equations utilized during the training ($1.1 \times \text{target} - 21$), testing ($0.99 \times \text{target} + 1$), validation ($0.99 \times \text{target} - 17$) and the overall stage ($1.1 \times \text{target} - 29$). However, the extent of accuracy within each stage (training, testing, validation, and All) of the network system was a measure of the order of the RSM-BBD matrix and its correlation coefficient values (R^2). Herein, Figure 5.17 is considered as a representation of the ANN biogas predicted results compared to that of the RSM-BBD and actual experimental data. It was observed that the ANN predicted was aligned with that of the RSM - BBD biogas predicted values (Figure 5.17). In this case, the ANN model seems to perform exceptionally well in the order of the experimental runs.

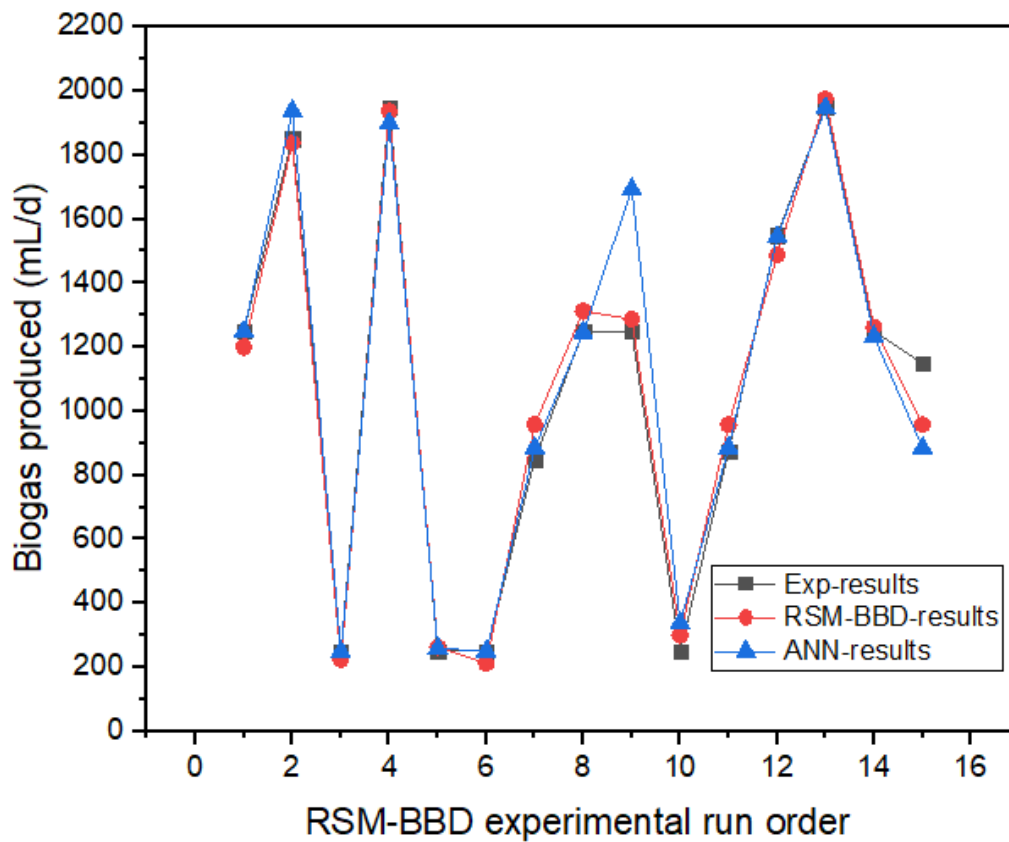


Figure 5.17: Comparative plot of Experimental, RSM predicted, and ANN predicted results

5.5 Summary

The study investigated an integrated AD-photodegradation of wastewater for biogas production and CO₂ emission reduction. It was found that the standalone AD process was noticeably efficient in degradation of the organic content (COD), but not in decolourisation as it was observed in the photodegradation. However, the combined process resulted in above 75% reduction of the COD and colour. Also, the reduction of the nitrate and ammonium were indication of degradation of recalcitrant organic compounds which are of carbon-nitrogen bond based. Kinetically, the correlation that existed between OLR and HRT was found well fitted on the pseudo first-order kinetic model. Also, the use of UV-photodegradation was found very efficient as compared with UV-vis and normal visible -photodegradation. Using the RSM-BBD experimental matrix and response models developed, optimised conditions were attained at OLR of 0.394 kgCOD/Ld and HRT of 20 days under UV-photodegradation with 75% overall desirable efficiency. Energy analysis showed that AD produced 132.7 kWh/L of energy while the UV lamp consumed 304.18 kWh/L to further treat the biodigester effluent. The estimated energy efficiency of 60% resulted in carbon reduction of 17430 kgCO₂e/L. This suggests that the bioenergy produced could subsidise up to 60% of energy required by the UV lamp to further photodegrade 1 L of the wastewater effluent. The economic analysis showed reduction of the cost of electricity utilised from R979.46 (\$69.96) to R552.17 (\$39.45).

Therefore, the prospects of AD bioenergy to subsidise the cost of UV photodegradation when combined in the wastewater settings is economically viable. The interaction

between the OLR, HRT and the type of light source in the AOP system were modelled using the RSM-BBD. The use of the ANN to validate the RSM-BBD predictability was found to be agreeable and comparable in predicting the overall efficiency of the integrated system with good precision. Furthermore, to better assess the potential of the integrated system applicability in large-scale wastewater treatment settings, the OLR and HRT should be key operating parameters of interest. In addition, since the RSM predicted very well as compared to the ANN, future works must generate more data to validate both stimulation tool efficacy with onsite effluent.

Chapter 6 - Conclusion and Recommendation

Overview:

This chapter presents the major findings obtained in this work based on the following specific objectives;

1. Synthesize and characterize TiO₂ magnetized photocatalyst (MPC) for industrial wastewater treatment and biogas enhancement (Chapter 2)
2. Technological evaluation and applicability of the synthesized TiO₂ MPCs for industrial wastewater treatment using biological (AD), biomagnetic (BM), biophotocatalytic (BP), and biophotomagnetic (BPM) systems (Chapter 3)
3. Design, monitor and evaluate the continuous integrated anaerobic-photo-catalytic-magnetic system for municipality wastewater treatment (Chapter 4)
4. Kinetic modelling and optimising the integrated anaerobic-photocatalytic system for municipality wastewater treatment with estimated energy produced and CO₂ emission reduction (Chapter 5)

6.1 Overall findings and conclusion

The novelty of this work presented in this thesis focussed on developing an integrated anaerobic-photocatalytic (AD-AOP) magnetized system as a technological solution for wastewater treatment with bioenergy production benefits. In addition, engineered magnetic photocatalysts (MPCs) with recoverability potentials for wastewater treatment were explored. To obtain an optimal balance between robustness and cost-effectiveness

of the integrated system, a series of feasibility and engineering works were investigated, where some have been reported in our published works (Papers 1-20). Furthermore, the extent to which the aforementioned objectives were met and their main findings are summarised below:

- Firstly, magnetised- photocatalysts (MPCs) of binary (Fe-TiO₂) and ternary (Fe/Ch-TiO₂ and Fe/Al-TiO₂) synthesised via the co-precipitation technique were characterized and applied for wastewater treatment. Analytically, characterisation of the MPCs via the scanning electron microscopy and energy dispersive X-ray (SEM/EDX), Fourier transforms infrared spectra and X-ray diffraction (XRD) and Brunauer- Emmett-Teller (BET) techniques showed that the tailored MPCs were successfully magnetised. Comparatively, the surface morphology (SEM/EDX), crystallinity (XRD), surface area (BET) and functional groups (FTIR) of the MPCs were different from that of the conventional TiO₂. The treatability efficiency of applying the MPCs for biodegradation and photocatalytic degradation of wastewater were found viable. Among the MPCs, Fe-TiO₂ with high surface area (62.73 m²/g), pore volume (0.017 cm³/g) and pore size (1.337 nm) were found as the best for greater than 75% organic content reduction and methane yield (> 85% CH₄). This was due to its functionalised properties with high charge magnetic separation ability and reactive oxidation species , which facilitated the bio-photon and hydrogenation potential.
- Secondly, technological evaluation was carried out with the MPCs to improve the biogas and wastewater qualities. Some of the technologies investigated included biochemical methane potential (BMP), biophotocatalytic (BPs), biomagnetic (BMs) and biophotomagnetic (BPMs) systems. The sequential efficiency order of

the system was AD (without MPCs) < BMP < BMs < BPs < BPMs, where BPMs was recommended as being very promising for future exploits. At a mesophilic temperature of $35 \pm 5^\circ\text{C}$ and hydraulic retention time of 30 days, the addition of 2 g Fe-TiO₂ in the BPMs showed the great potential of generating 1330 mL/d biogas with 95% CH₄ and 80-95% organic content reduction. In essence, both the magnetic field and photo-excited radicals in the BPMs influenced its methanogenic activity. Kinetically, the modified Gompertz model favoured the cumulative biogas data obtained with a high correlated regression coefficient ($R^2 = 0.999$) and kinetic constant (k) of 0.19 d^{-1} . At 33% bioenergy to grid electricity environmental conservation, CO₂ emission reduction of 0.64 kgCO₂ e/L of the BPM was estimated. Furthermore, the cost-benefit analysis of an upscaled 1L BP system to 10 L with 4 g Fe-TiO₂ at organic loading rate (OLR) of 2.38 kgCOD/Ld and HRT of 30 days resulted in 5150 mL/d biogas with 90% CH₄ yield. The BP system net energy profit of 0.0168 kWh at \$2.78 (ZAR 38.86) was estimated as the excess energy produced to subsidize the UV-lamp energy required. Additionally, at an OLR of 1.34 kgCOD/Ld, an optimal catalyst load of 4 g and HRT of 21 days with the desirability of 100% was obtained by using a modified RSM – BBD matrix. The experimental validity was in good agreement with the model predicted results at higher regression ($R^2 > 0.98$) and 95% confidence level.

- Thirdly, the novel integrated AD-AOP magnetised system was developed and evaluated with the MPCs. The proof of concept showed the great potential of the MPCs to reduce the process time complexity, toxicological effect of trace metals (27 elements considered), sludge production and additional usage of chemicals in the wastewater treatment system. Also to mitigate CO₂ emission and

environmental sustainability in the wastewater settings, the findings showed the MPCs can be recovered and reused for the improvement of wastewater and biogas quality.

- Furthermore, the artificial neural network (ANN) and the RSM experimental design and modelling techniques were employed to optimise the system's key operating conditions. At the RSM-BBD optimal conditions of OLR (0.394 kgCOD/L.d), HRT (20 d) and AOP with UV-light irradiation source, biogas (1250 mL/d), 99% COD removal, bioenergy produced (38.02 kWh/L), UV energy used (98.96 kWh/L), net energy efficiency (38.43%) and CO₂ emission reduction of 10859.5 kgCO₂e/L were obtained. Notwithstanding, the limited amount of data for the artificial neural network (ANN) training, its validity and predictability were found considerably agreeable with the RSM-BBD predicted results. A strong correlation was distinctively observed ($R^2 > 0.85$) between the experimental data and RSM-BBD results as well as the ANN results. However, inadequate ANN data and variations in wastewater organic load were observed. Therefore to strengthen these findings with more data, onsite study with a smart pilot-scale or large systems are required.

Conclusively, this finding provides an insight into synthesising and applicability of MPCs, kinetics and RSM modelling and optimization with ANN predictability as a potential to develop an optimized integrated AD-AOP magnetised system towards the treatment of industrial wastewater, biogas, and CO₂ emission reduction. Above all, the prospect to upscale the current integrated system into a pilot- and large-scale unit with a smart-online monitoring system for wastewater treatment towards a circular economy and environmental sustainability is seen viable, hence should be given attention.

6.2 Future prospects and recommendations

Despite this study's milestones, an onsite smart pilot scale and large scale system is warranted to strengthen its findings. As the scope of this study was beyond the MPCs toxicological impact in microbial community shift and quantification, decontamination of specified emerging contaminants (phenols, antibiotics, pesticides , microplastics etc), detailed techno-economic analysis and life cycle assessment necessitates further studies. Also, this work demonstrated successful engineering of MPC, and therefore expanding its potential studies in magnetised coagulation (Paper 19), bioelectrolysis (Paper 20), biocatalysis and bioenergy (Papers 17 and 18) will be of socioeconomic and sustainable environmental benefits. Furthermore, advancing this novel integrated AD-AOP magnetised technology in the wastewater settings will be advantageous to both industrial players and stakeholders including:

- The upscaling of the integrated system into a smart online monitoring system for feasibility, technological evaluation and optimization will be useful to water engineers for wastewater treatment technology capacity development.
- The technological and scientific exploration of this technology for industrial adoption will assist in national/regional action plans and policies by the relevant decision-making stakeholders in the water sector to add value to the wastewater treatment economy.
- The recoverability potential of the MPCs for reuse will reduce the operational cost of the integrated system as well as mitigate the detrimental effect of trace elements complexity in the wastewater settings.

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Appendix A: Bio-photoreduction of CO₂ emission (Paper 8)



Paper 8.pdf

Appendix B :Biophotocatalytic system optimization (Paper 9)



Paper 9_r.pdf

Article

Exploring CO₂ Bio-Mitigation via a Biophotocatalytic/Biomagnetic System for Wastewater Treatment and Biogas Production

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Abstract: Carbon dioxide (CO₂) emissions from fossil fuels have led industries to seek cheaper carbon abatement technologies to mitigate environmental pollution. Herein, the effect of a magnetic photocatalyst (Fe-TiO₂) on biogas production in anaerobic digestion (AD) of wastewater was investigated with three bioreactors coupled with UV-light (18 W). Three experimental setups defined as the control (AD system with no Fe-TiO₂), biophotoreactor (BP), and biophotomagnetic (BPM) systems were operated at a mesophilic temperature (35 ± 5°C) for a hydraulic retention time (HRT) of 30 days. The control system (ADs) had no Fe-TiO₂ additives. The BPMs with 2 g Fe-TiO₂ were exposed to a magnetic field, whereas the BPs were not. The removal rate of the chemical oxygen demand (COD), volatile solids (VS), and total solids (TS), together with biogas production and composition were monitored for each reactor. The degree of degradation of 75% COD was observed for the BPMs at a pH of 6.5 followed by the BPs (65% COD) and the ADs (45% COD). The results showed that the rate of degradation of COD had a direct correlation with the cumulative biogas production of the BPMs (1330 mL/d) > BPs (1125 mL/d) > AD (625 mL/d). This finding supports the use of biophotomagnetic systems (BPMs) in wastewater treatment for resource recovery and CO₂ reduction (0.64 kg CO₂/L) as an eco-friendly technology.

Keywords: anaerobic digestion; biogas; biophotomagnetic; biophotocatalysis; magnetised photocatalysts; CO₂ reduction; nanotechnology; photocatalysis

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1. Introduction

The development of zero waste technology and municipal waste management is critical for sustainable development, as CO₂ emissions from fossil fuel combustion continue to be a global concern [1,2]. In essence, conventional energy sources such as natural gas, coal, and petroleum are continuously exploited. Due to the current overdependence on these fuel sources, which are depleting but have significant ecological impacts, there is a rising need for alternative fuels [3]. Furthermore, anthropogenic CO₂ emissions, which contribute to global warming and climate change, have prompted the globe to seek out alternate actions to mitigate or control CO₂ emissions [4]. The wastewater treatment settings cannot be overlooked in this regard, particularly considering the prospect of boosting its circular economy [5–9]. Herein, energy-saving wastewater treatment systems have become essential, especially with the upgradation of biogas produced by anaerobic digesters (ADs).

Anaerobic digestion (AD) is a technique that transforms organic matter in biomass resources into biogas with methane (CH₄) as a source of sustainable energy [5,10,11]. Of essence, AD creates economic opportunities by producing bioenergy (60–70% methane) and stabilized digestate under suitable conditions to ease pollution [12]. The AD process

utilises microorganisms' degradation potential in an ecologically responsible, odour-reducing, and pathogenic organism-degrading mode, particularly in bioreactors operating at temperatures within the mesophilic (25–45°C) or thermophilic (>45°C) ranges [5,10,13]. Additionally, produced biogas frequently contains pollutants such as H₂S and CO₂, which reduce the calorific value of the biogas and corrode equipment such as pipelines and incineration engines [5,10]. Co-digestion, pre-treatment, reactor design, and additives to stimulate bacteria growth and prevent inhibitory effects are some of the strategies utilized to address this [5,13–15]. In this study, the concept of photoreduction of CO₂, which involves the conversion of the non-energy-rich component of the biogas into methane, is highlighted [11].

In essence, biogas has been exploited as an alternative to fossil fuel for energy generation, and the concept of reducing the CO₂ component to methane is limited. Biogas produced via anaerobic digestion of organic waste is composed of 55–65% methane and 35–45% CO₂ and other gases such as H₂S [16]. To solve the shortcomings, several abatement solutions have been proposed, whereby the AD process coupled with CO₂ photoreduction is gaining attention [12,17,18]. This technology involves the use of a photocatalyst in the presence of UV-light, visible light, or sunlight to convert the CO₂ to methane, which is rich in energy [4,19]. In photocatalytic CO₂ reduction, an incident light (UV, visible light, or sunshine) activates the photocatalyst surface. In doing so, it causes the electrons to shift from the valence band to the conduction band to form a hole and produce electrons [20,21]. The water molecules divide into hydroxyl and hydrogen ions, which then react with the released electron species. For example, CO₂ generated from fossil fuel combustion is absorbed and converted to energy-rich methane by catalytic electrolysis [3]. Subsequently, the addition of nanoparticles to the AD process to enhance biogas production has gained attention [22,23].

Therefore, a biophotocatalytic reduction of CO₂ produced anaerobically into methane by the seeding of a magnetic photocatalyst is shown in this study (Fe-TiO₂). Three distinct configuration systems were explored in this study for reducing sugar refinery wastewater contamination, biogas generation, and methane yield, as well as reducing CO₂ emissions. The modified Gompertz model was utilised to establish the model's operational variables kinematically.

2. Materials and Methods

2.1. Wastewater and Activated Sludge

In this study, The wastewater samples were taken from the biofiltration stream that goes into a bio-digester and clarifier at a sugar refinery wastewater treatment plant in Durban, KwaZulu-Natal, South Africa. This sample point (Figure 1) had a mixture of de-watered centrate with less than 5% solids and biofiltration effluent. The supernatant was employed as substrate in this experiment, whereas the digested sludge was used as inoculum. The magnetite photocatalyst (Fe-TiO₂ NPs) used was engineered and characterised at a high magnification of 10–50 kx and landing energy capacity of 20 keV and, as depicted in our previous studies [5], had a surface and average crystallite size of 6.5 nm and 20 nm [7,24]. Characteristics of the wastewater sample is presented in Table 1.

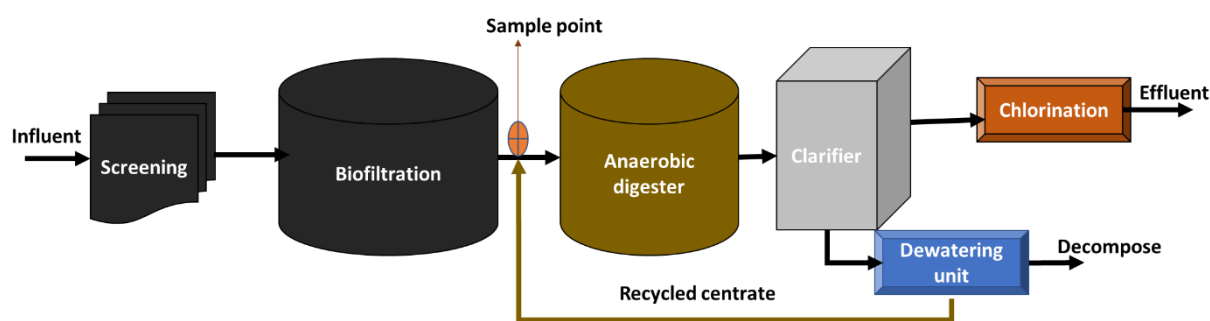


Figure 1. Block diagram of a sugar refinery wastewater treatment plant, Kwazulu Natal, South Afrca

Table 1. Composition of wastewater sample.

Parameters	Value
pH	7.5
Chemical oxygen demand (mg COD/L)	1600 ± 16.2
Turbidity (NTU)	155 ± 2.6
Colour (Pt.Co; 465 nm)	85 ± 3.6
Total solids (mgTS/L)	135 ± 12
Volatile solids (mgVS/L)	94 ± 6.8

2.2. Experimental Setup

Experimental setup protocols were adapted from Kweinor Tetteh and Rathilal [5] and Tetteh and Rathilal [7]. Figure 2 presents the experimental setup employed in this study. Three 1-L Duran Schott bottles used as bioreactors were coupled with UV-light (T8 blacklight-blue bulbs 400 nm, Philips, Netherland), a hotplate magnetic stirrer (temperature regulator), and biogas collection system. Each duplicated reactor was charged with 80% working volume of inoculum to substrate ratio of 3:5 seeded with or without a magnetic photocatalyst of 2 g of Fe-TiO₂ NPs. Herein, these bioreactors, defined as control (AD system with no NPs), biophotoreactor (BP system with NPs) and biophotomagnetic (BPM system with NPs), were operated at a hydraulic retention time (HRT) of 30 days at a temperature of 40°C and intermittent mixing at 15 rpm. Two magnetic bars (GMX model 400) used on the BPM system was obtained from Chino, California, USA. The daily biogas was monitored by downward displacement techniques, while its composition was characterised by Gas Chromatography (GC 2014, Shimadzu). The degree of efficiency of the contaminant removal and the modified Gompertz kinetic model for the biogas production were respectively estimated by Equations (1) and (2).

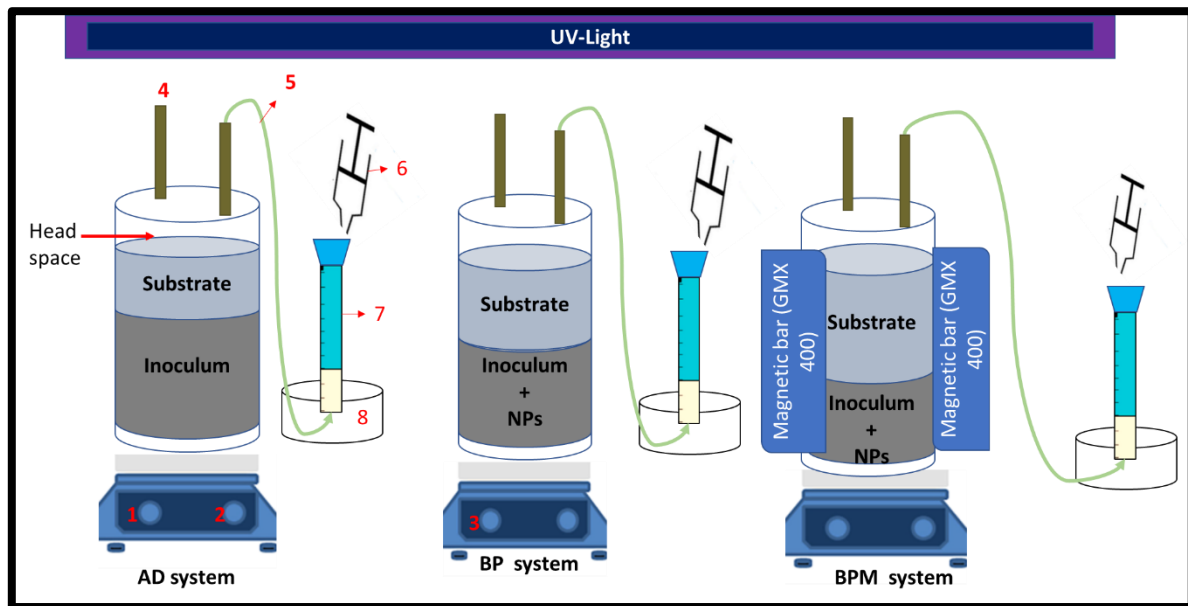


Figure 2. 1: Temperature controller; 2: mixing controller; 3: hotplate magnetic stirrer; 4: purging port; 5: silicon tube; 6: gas sampler; 7: water displacement gas collector; 8: water trough.

$$\text{Reactor efficiency} = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (1)$$

where, C_i = Substrate influent and C_f = Substrate effluent. The cumulative biogas production data obtained were evaluated by the modified Gompertz Equation (2) [5,7].

$$Y = ym \cdot \exp \left(- \exp \left[\frac{R_{max} \cdot Ce}{ym} [\lambda - t] \right] + 1 \right) \quad (2)$$

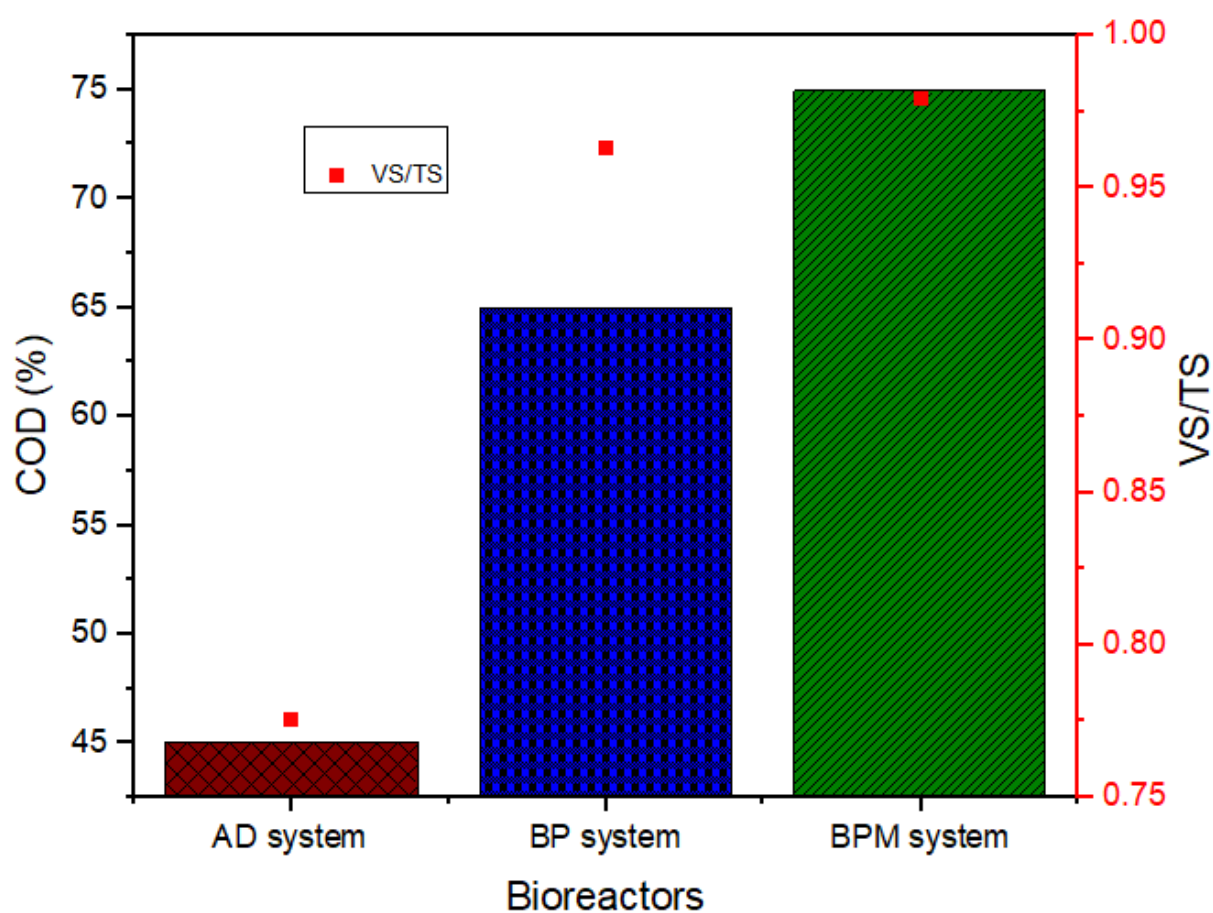
where, Y = cumulative specific biomethane (mL/g COD) at time t (days), ym = the methane potential (mL/g COD), λ = lag phase of producing biogas (day), Ce = mathematical constant (2.718282), R_{max} = the maximum specific substrate uptake rate per maximum biogas produced (mL/g COD.day) and k is the methane production rate constant (1/d), expressed as $k = \frac{R_{max} \cdot Ce}{ym}$.

3. Results

The magnetic field and photocatalyst (Fe-TiO₂) influence on the BPs and BPMs were compared with a control AD system for the degradation of the organic matter (COD), biogas production and methanation (biogas enhancement). Among these bioreactors is the biophotomagnetic (BPM) system, whose efficiency supersedes that of the BP and AD systems. Table 2 presents the comparative summary of results obtained after the 30-day incubation of the three bioreactors by monitoring the degree of degradation in terms of COD reduction to ascertain the treatability performance. Evidently, the rate of degrading the solid content of the wastewater, as revealed by the VS/TS ratio, contributed to the COD reduction (Figure 3). The cumulative biogas data (Figure 4) were also fitted on the Gompertz kinetic model (2), whereby the kinetic conditions obtained are presented in Table 3. Moreover, each bioreactor system achieved distinctive potential for the carbon-based content of the biogas produced and methane yield (Figure 5).

Table 2. Summary of bioreactor performance after 30 days of incubation.

Parameters	AD System	BP System	BPM System
pH	6.8	6.5	6.5
Chemical oxygen demand (mg COD/L)	880	560	400
VS/TS	0.776	0.962	0.979
Cumulative biogas produced (mL)	625	1125	1330
Methane portion (%)	65.5	95	98
Carbon dioxide (%)	34.5	5	2
Total energy produced in 30 days (kWh)	550	1470	2027
Assumed 33% electricity produced (kWh)	182	485	669
CO ₂ emission reduction (kg CO ₂ /L)	0.173	0.464	0.640

**Figure 3.** Bioreactor performance for COD removal (%) and VS/TS reduction ratio after 30 days of incubation.

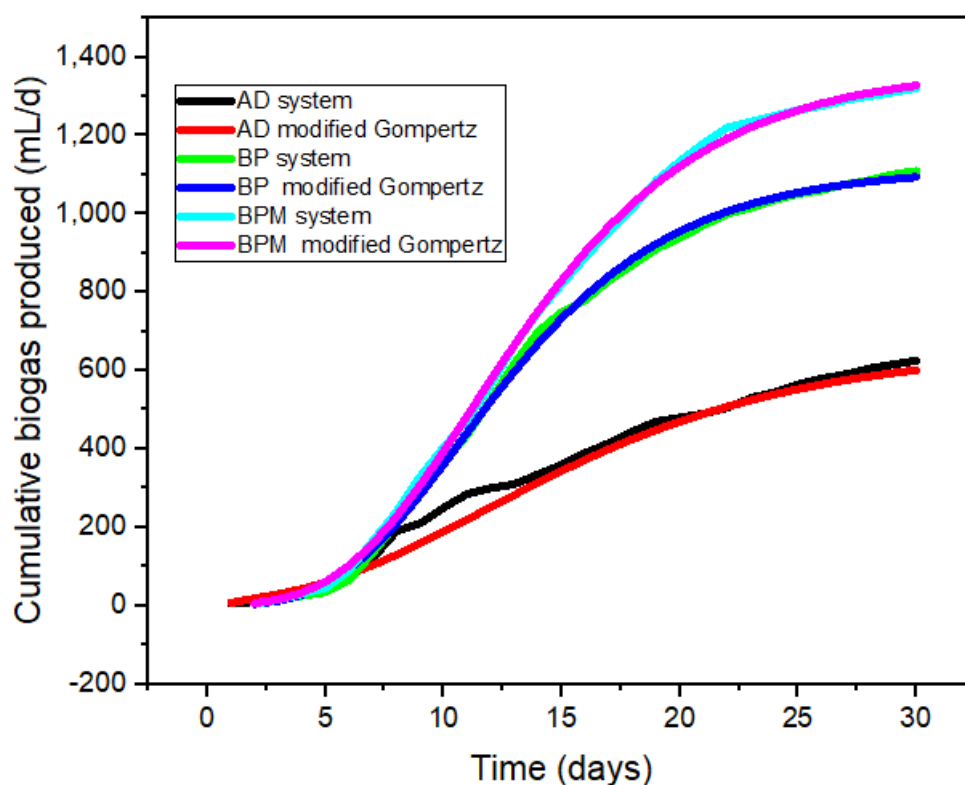


Figure 4. Bioreactor cumulative biogas production fitted with modified Gompertz kinetic model for the 30-day incubation.

Table 3. Summary of modified Gompertz kinetic model parameters.

Bioreactor	AD System	BP System	BPM System
Measured (Y, mL/g.d COD)	625	1125	1330
Predicted (Y, mL/g.d COD)	658.58	1117.828	1370.55
k (d ⁻¹)	0.131	0.189	0.193
λ (d)	10.7	9.62	9.21
SSE	8102.02	5551.23	4131.10
R ²	0.994	0.998	0.999

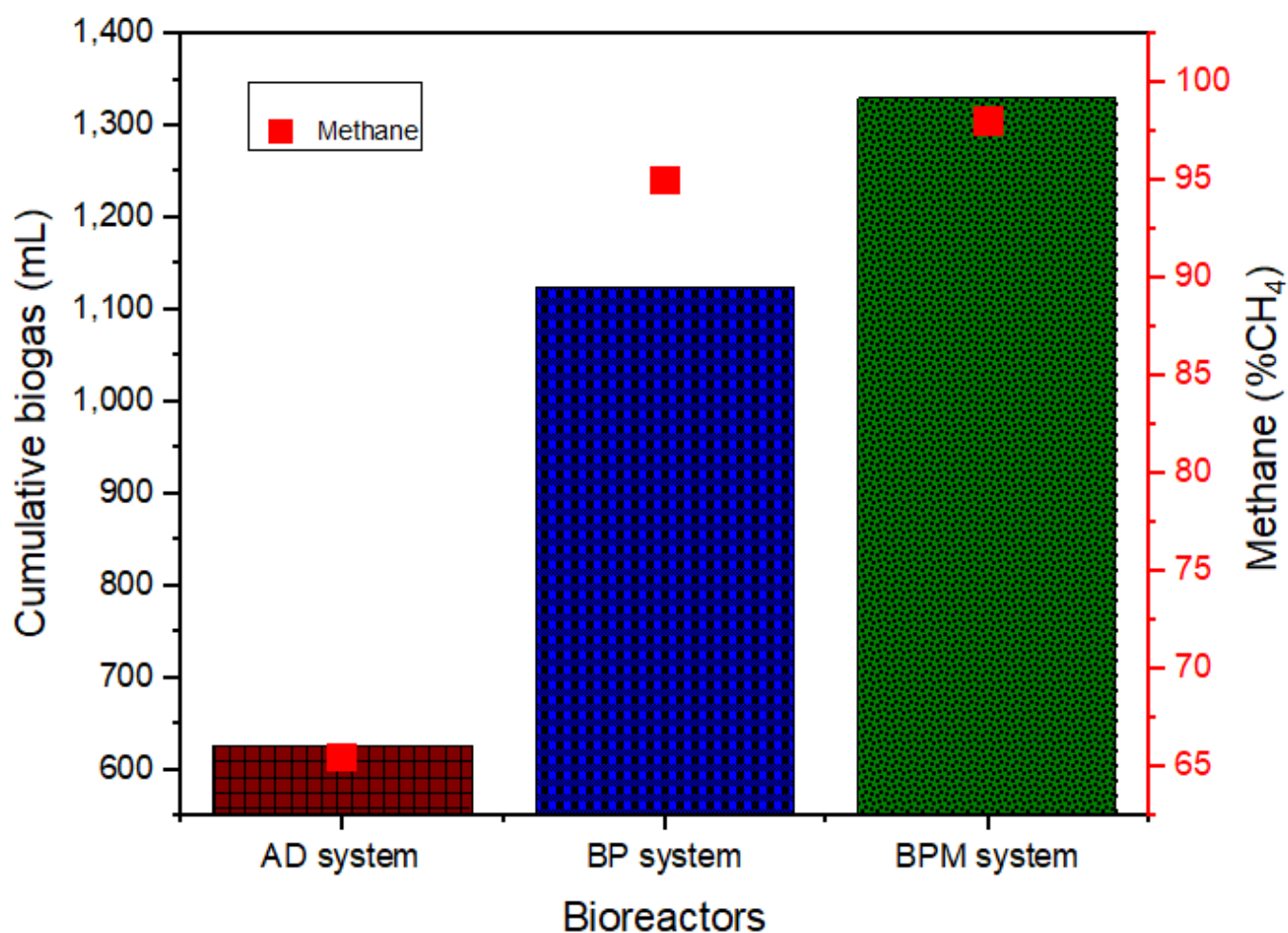


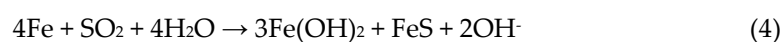
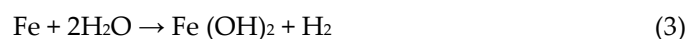
Figure 5. Bioreactor maximum cumulative biogas yield (mL) and methane composition (% CH₄) after 30 days of incubation.

4. Discussion

In this section, the wastewater degradation efficiency, the biogas produced and composition as well as the estimated energy produced, and the CO₂ emission reduction are discussed.

4.1. Degradation of the Organics

The Fe-TiO₂ additions in the BP and BPM systems increased the degradability activity as shown with an increase in the COD removal (Figure 3). Evidently, the anaerobic hydrolysis and methanogenesis were thermodynamically favoured when Fe-TiO₂ was magnetically seeded with electron donors (Fe, OH, H, and Ti species) [5,20]. This electro-receptive reaction expressed in Equations (3) and (4), demonstrated the release of the Fe³⁺ species in the bioreactors facilitated the sulphur-reducing microbes [20,25].



According to Ajay et al. [26], the aggregation of trace metals is responsible for the acidification or alkalinity surge in the reactor system. The microbial activity in the system indicates metal imbalance scorn the nutritional benefits of most metals [25–27]. This shows that bioavailability of metal species for microbial uptake in the reactors (AD alone, BM, and BPM) may vary based on chemical and biological circumstances. Thus, improving the

reactor requires metals as macro or micronutrients for microbial metabolic enzymatic activities and growth. The nutritional balance aided substrate breakdown and biogas production [6,15,22].

4.2. Biogas Production

Generally, biogas constituting hydrogen (H₂), methane (CH₄), and carbon dioxide (CO₂) are the biologically digester end-products of the wastewater substrates. In essence, reducing the CO₂ content into a more ecofriendly gas involves a series of mechanism [15,28]. The methanation reaction between the CO₂ and H₂, was being influenced by the Fe-TiO₂ induced with the activated energy of the UV-light. Herein, the hydrogenation process or hydrolysis of the water molecules splitting (H₂ and O₂) was being ignited by coupled photocatalysis [29]. In addition, the incorporation of the magnetic field influenced the agglomeration of the action of the hydrogenotrophic methanogens in conversion of the CO₂ into methane [5]. This reaction mechanism is expressed in Equation (5).



Figure 4 shows the cumulative biogas production volume at different levels of the three bioreactors operated at the same conditions for 30 days. The maximum cumulative biogas estimated for the biogas produced by the bioreactors (BP = 1125 mL; BPM = 1330 mL) with the Fe-TiO₂ additives were found to be significantly different from that of the control (AD = 625 mL). The BPM system, where 2 g of Fe-TiO₂ additives was added on an average basis, was estimated to be 788 mL/d, followed by the BP system with 671 mL/d and the AD system with 345 mL/d. Kinetically, the cumulative data obtained were well-fitted on the modified Gompertz model (2), where the operating variables obtained are presented in Table 3. There exists a significant correlation (95% confidence level) between the degradation of the carbon content of the wastewater to biogas with a high regression coefficient ($R^2 > 0.9$). These findings correlate with other studies, whereby the Fe-TiO₂ additives increased the surface area of the sludge. This enhanced the microbial activity and hence resulted in high biogas production as compared to the AD system [20,25].

After the HRT of 30 days for methanogenesis, the biogas composition was characterised as showing a high methane yield greater than 65% in the increasing order of the systems as AD < BP < BPM. As shown in Figure 5, there was an impact in both the biogas and methane of the BP and BPM systems. There was partial degradation in the AD system, which is consistent with previous studies that showed the AD process to be kinetically unstable with a general methane potential of 50–65% [7,20,25].

4.3. Energy Estimation and CO₂ Reduction Estimation

The energy efficiency and environmental impact was estimated based on the conversion rate of the biomethane into electricity. This was estimated based on the assumed 78% of the energy produced (Table 2), where 33% was electricity generated from the biogas and 45% was generated from the heat in a cogeneration process. In Expression (6), for the electricity generated (El_{bio}) from the biomethane per unit effluent volume (kWh/m³), the El_{bio} is the total biogas generated [6,26].

$$El_{bio} = 0.33E_{bio} \quad (6)$$

Herein, CO₂ emission reduction was therefore estimated as a function of the electricity produced to power the UV lamp of the photoreactors with respect to the base line grid emission factor of 0.957 kg CO₂ e/kWh as given in Equation (7).

$$CER = GEF \times E_{bio} \quad (7)$$

Generally, the bioconversion of carbon dioxide to methane of anthropogenic emission from wastewater treatment plants and landfill gases can necessitate the reduction in

global warming [15,17,30]. In this case, the maximum CO₂ emission reduction (kg CO₂) was estimated to be 0.640 kg CO₂/L for the BPM system with the rest depicted in Table 2.

Therefore, the BPM system has shown great potential in significantly contributing to decreasing greenhouse gas emissions and mitigating unusual climate change. Additionally, the abatement of greenhouse effects in the wastewater settings can easily be managed with less effort as compared to petrochemical industries. Moreover, the wastewater from the sugar refinery used in this study constitute a high carbon content, which can be used by the BPM system to produce enough energy to offset the photoreactor. Furthermore, the magnetic field incorporated in the BPM, as reported in previous studies [7], has the potential impact for recoverability of the magnetised photocatalyst for reuse. Hence, expanding this technology will also warrant reduction in operation costs such as the pressing cost of chemicals used in the wastewater settings.

5. Conclusions

This study presents a biophotomagnetic system as an energy-saving wastewater treatment option with the upgradation of biogas produced by anaerobic digesters. This study strengthened the knowledge of valorisation of sugar refinery wastewater anaerobically for biogas production and CO₂ emission reduction via photoreduction. Three bioreactor configurations were investigated at the same conditions for 30 days. Among them, the biophotomagnetic (BPM) system seeded with Fe-TiO₂ was found to be the most effective inherent to wastewater treatment (75% COD removal), biogas produced (13,330 mL), and methane yield (98% CH₄) as compared to the ADs of 65.5% CH₄. The good performance of the BPM system has been attributed to the biostimulation influence of the Fe-TiO₂ additives ignited by the UV-light and the magnetic field. Cumulatively, the biogas data were well-fitted on a modified Gompertz kinetic model, and the operational variables defined were found to be significant ($p < 0.05$). It also revealed that the start-up and acclimatisation of the microbes in the BPM system was shorter (9 days; $k = 0.19 \text{ d}^{-1}$) as compared to the BP (10 days; $k = 0.18 \text{ d}^{-1}$) and AD (11 days; $k = 0.13 \text{ d}^{-1}$) processes. To offset the energy demand by the UV-light for the BPM system and environmental conservation, a CO₂ emission reduction of 0.64 kg CO₂ e/L was attained. Conclusively, the BPM system is foreseen to be an eco-friendly technology and therefore integrating its industrial applications must be given attention.

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Article

Response Surface Optimization of Biophotocatalytic Degradation of Industrial Wastewater for Bioenergy Recovery

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Abstract: The continuous combustion of fossil fuels and industrial wastewater pollution undermines global environmental and socio-economic sustainability. Addressing this necessitates a technological revolution to recover the renewable energy potential of wastewater towards a circular economy. Herein, a developed biophotocatalytic (BP) system was examined with an engineered Fe-TiO₂ to ascertain its degradability efficiency and biogas production from industrial wastewater. The response surface methodology (RSM) based on a modified Box-Behnken designed experiment was used to optimize and maximize the BP system's desirability. The parameters investigated included catalyst dosage of 2–6 g and hydraulic retention time (HRT) of 1–31 d at a constant temperature of 37.5 °C and organic loading rate of 2.38 kgCOD/Ld. The modified RSM-BBD predicted 100% desirability at an optimal catalyst load of 4 g and HRT of 21 d. This represented 267 mL/d of biogas and >98% COD, color, and turbidity removal. The experimental validity was in good agreement with the model predicted results at a high regression ($R^2 > 0.98$) and 95% confidence level. This finding provides an insight into RSM modeling and optimization with the potential of integrating the BP system into wastewater settings for the treatment of industrial wastewater and biogas production.

Keywords: anaerobic digestion; bioenergy; biophotocatalysis; magnetite photocatalyst; nanotechnology; wastewater



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1. Introduction

Wastewater treatment concurrently with biogas production via the anaerobic digestion (AD) process has been a universally adaptable technology [1]. However, environmental pollution, water scarcity, food, and energy insecurity have become pressing matters for sustainable development in the twenty-first century [2,3]. Also, greenhouse gas emissions (especially CO₂) being associated with global warming, and fossil fuel combustion, undermine a sustainable environment [4]. Herein, wastewater treatment is envisioned as a renewable energy source that can be used for biogas production as alternative sources of energy [3,5]. Thus, reclaiming wastewater for reuse and biogas production (biogas can be purified and used as an automotive fuel) can ease poor country's standard of living as far as water and energy are concerned [2].

Notwithstanding, treating industrial effluent has become extremely relevant as emerging contaminants (pharmaceuticals, pesticides, nanomaterials, etc.) and toxic chemicals originating from households and industries are posing great threats to human health and the ecosystem when discharged into the environment without proper treatment [6,7]. So, mitigating environmental pollution and its consequences warrant degradation of the high organic constituents of industrial effluents.

Conventionally, treatment of water and wastewater involves the use of physical, chemical, and biological methods [7,8]. The biological treatment involves bacterial and fungal biosorption, anoxic and anaerobic/aerobic processes [2,7]. Membrane filtration,

coagulation-flocculation, flotation, precipitation, ion exchange, adsorption, ultrasonic mineralization, ion-pair extraction, and electrolysis [6,9,10] are some of the physico-chemical treatments. Moreover, these technologies generate by-products during treatment that come with additional treatment costs [9,10]. Thus, it becomes very critical to design and select cost-effective technologies as an option in the water and wastewater treatment settings.

Currently, advanced oxidation processes (AOPs) are being developed to degrade nonbiodegradable contaminants [11]. Heterogeneous photocatalysis is a unique AOP that uses photocatalysts like TiO_2 and UV light to break down pollutants into inoffensive end products like CO_2 , H_2 , and mineral acids [11,12]. The availability, low cost, and photochemical stability of TiO_2 makes it a preferred photocatalytic degradation catalyst for organic contaminants [12]. To stimulate oxidation-reduction potential, photocatalytic reactions use photons with energy larger than the bandgap of a semiconductor, usually TiO_2 [13]. Several researchers have investigated the photocatalytic treatment of hazardous substances in untreated wastewater [7,14–16]. Baseline pollutant concentration, photocatalyst concentration, and pH are among the key parameters that can influence photocatalytic activity [13]. Other parameters including irradiation time, light intensity, light wavelength, catalyst type and temperature can also affect the degradation routes [17]. Similarly, AD processes are influenced by several factors which includes carbon/nitrogen (C/N) ratio, temperature (mesophilic and thermophilic), organic loading rate (OLR), hydraulic retention time (HRT), and pH [1]. This makes it difficult to assess the relative importance of more than a few influencing variables, especially when they have a multifunctional effect on the outputs.

To assess the influence of operating parameters on photocatalytic process efficiency, current research has relied on a conventional one-factor-at-time (OFAT) experimental technique [18,19]. While OFAT techniques are labor-intensive, they do not depict multiple variable interaction effects. Conversely, fewer runs are needed when using response surface methodology (RSM) [20]. Box Behnken (BB), Central Composite Design (CCD), Central Composite Face centered (CCF), and full factorial are some of the most frequent design matrices used in the RSM technique. [18,19]. Environmental remediation studies have shown the great potential of using BBD and CCF for experimental design and optimization [17–20]. This is due to their ability to obtain more information from just a few numbers of their experimental matrix. Generally, using RSM in process optimization involves the following steps: (a) identification of response/s; (b) screening of multivariates according to the design of experiment; (c) building of an empirical response surface model; (d) and the application of various response optimizations through mathematical modeling [17,20].

In essence, AD (kinetically slow) and AOP (energy-intensive) processes are very complex, with limited knowledge of their integrated system (AD-AOP) [21]. Therefore, developing the biophotocatalytic (BP) system as an alternative technology to the AD process comes in handy. Herein, the CO_2 methanation mechanism was carried out by incorporating Fe- TiO_2 into the BP system and was optimized via RSM to maximize its efficacy. Figure 1 presents the light-driven methanation reaction scheme with the dynamic state of water-splitting and CO_2 reduction steps. Ideally, the reactant and its intermediate products emulate natural photosynthesis [22]. Similarly, the presence of the photocatalysts being energy-driven for the initial excitation of its electrons via light absorption also promotes hydro generation potential [21]. However, improper catalyst loading and operating conditions can limit microbial activity and biogas production, yielding poor methane quality. Furthermore, the development of the BP system is still underway, which warrants process modeling, optimization, and control to maximize the process efficiency, as well as support the lab-scale design of a pilot plant. Herein, this study employed experimental data obtained from a modified RSM- BBD matrix with input factors at three levels (−1, 0, +1) with two center points at a constant temperature of 37.5 °C and an organic loading rate of 2.38 kgCOD/Ld. This was aimed at investigating the relationship between the input variable (catalyst dosage and HRT) and the design outputs (biogas, COD, color, and turbidity) via the modified RSM-BBD. Additionally, the analysis of variance (ANOVA) was employed statistically to ascertain the significance of the response models, whereas

numerical optimization was used to optimize and maximize the system desirability for degradation of the organics (COD) for the biogas production.

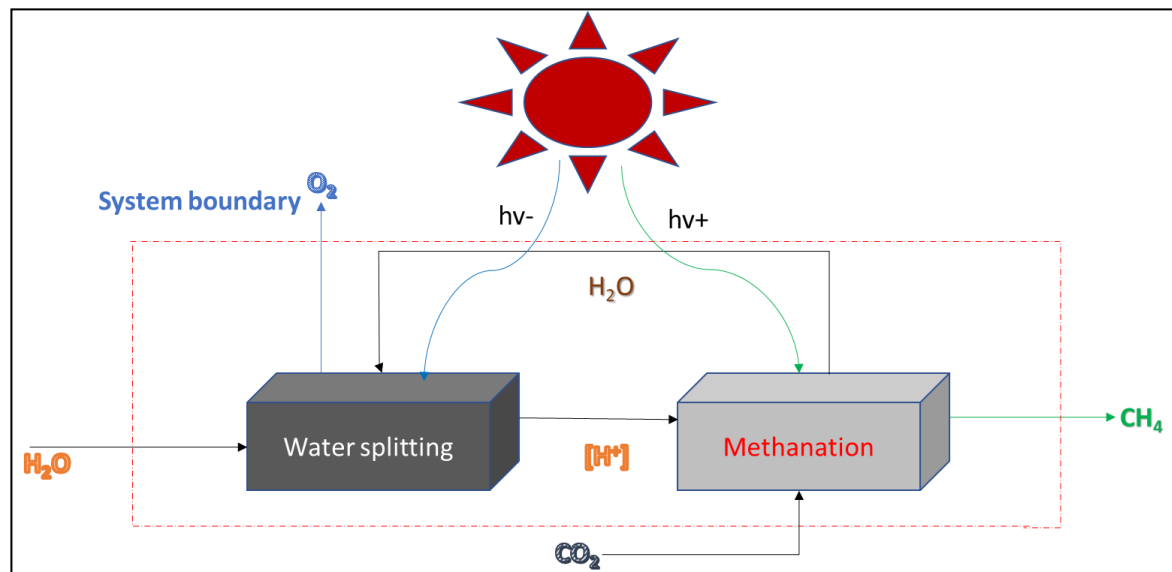


Figure 1. Schematic diagram of light-driven water-splitting with methanation CO₂ reduction.

2. Materials and Methods

2.1. Wastewater and Activated Sludge

The raw wastewater and sludge (anaerobic digested) were obtained from the eThek-wini municipal wastewater treatment plant in the KwaZulu-Natal province, South Africa by observing the standard protocols for wastewater sample collection and characterization [23]. Table 1 presents the wastewater characteristics distribution from the biofiltration stream of the wastewater treatment plant.

Table 1. Wastewater characteristics and analytical technique.

Water Quality	Value	Analytical Units
pH	7.42 ± 2.3	Hanna pH/EC/TDS Tester (H198130)
Temperature (°C)	26.42 ± 3.6	Hanna pH/EC/TDS Tester (H198130)
Color (abs 465 nm, Pt. Co)	570.23 ± 12	HACH Spectrophotometer (DR3900)
Turbidity (NTU)	732.32 ± 14	Turbidity meter (HACH 2100N)
Chemical oxygen demand (mg COD/L)	2380.32 ± 14	HACH Spectrophotometer (DR3900)
Ammonia (mg NH ₃ /L)	0.74 ± 0.4	HACH Spectrophotometer (DR3900)
Total Kjeldahl nitrogen (mg TKN/L)	30.52 ± 1.4	HACH Spectrophotometer (DR3900)
Nitrate (mg NO ₃ /L)	0.64 ± 0.5	HACH Spectrophotometer (DR3900)
Total nitrogen (mg TN/L)	31.88 ± 7.8	HACH Spectrophotometer (DR3900)
Total suspended solids (mgTS/L)	304.53 ± 15.6	Analytical balance (HCB602H 22 ADAM)
Volatile solids (mg VS/L)	229.52 ± 25	Analytical balance (HCB602H 22 ADAM)
Ratio (%VS/TS)	75.37	

2.2. Magnetised Photocatalyst (Fe-TiO₂)

A laboratory-based magnetite-titania photocatalyst (Fe-TiO₂) synthesized via the co-precipitation technique was employed [24], which had a specified BET surface area of 62.73 m²/g, pore volume of 0.017 cm³/g, and 1.337 nm particle size. This was analyzed with Brunauer–Emmett–Teller theory technique equipment (Micromeritics, TriStar II Plus, Norcross, GA, USA).

2.3. Experimental Procedure

The BP system constituted an upflow anaerobic sludge blanket (UASB) reactor coupled with UV-light bulbs (T8 blacklight—blue tube, 365 nm, 18 W, Philips, The Netherlands) as depicted in Figure 2. The BP was operated in batch mode at a working volume of 8 L with a headspace of 2 L at a temperature of 37.5 °C. The effects of catalyst load and hydraulic retention time (HRT) on bio-photodegradation of the wastewater with response biogas production and water quality (COD, color, and turbidity) improvement were studied. The daily monitoring of the biogas produced was obtained via the downward displacement technique as shown in Figure 2, by reading the level of the water displaced by the measuring cylinder. The removal percentage (%R) was evaluated using Equation (1).

$$\text{Reactor efficiency (\%R)} = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (1)$$

where, C_i = Substrate influent and C_f = Substrate effluent.

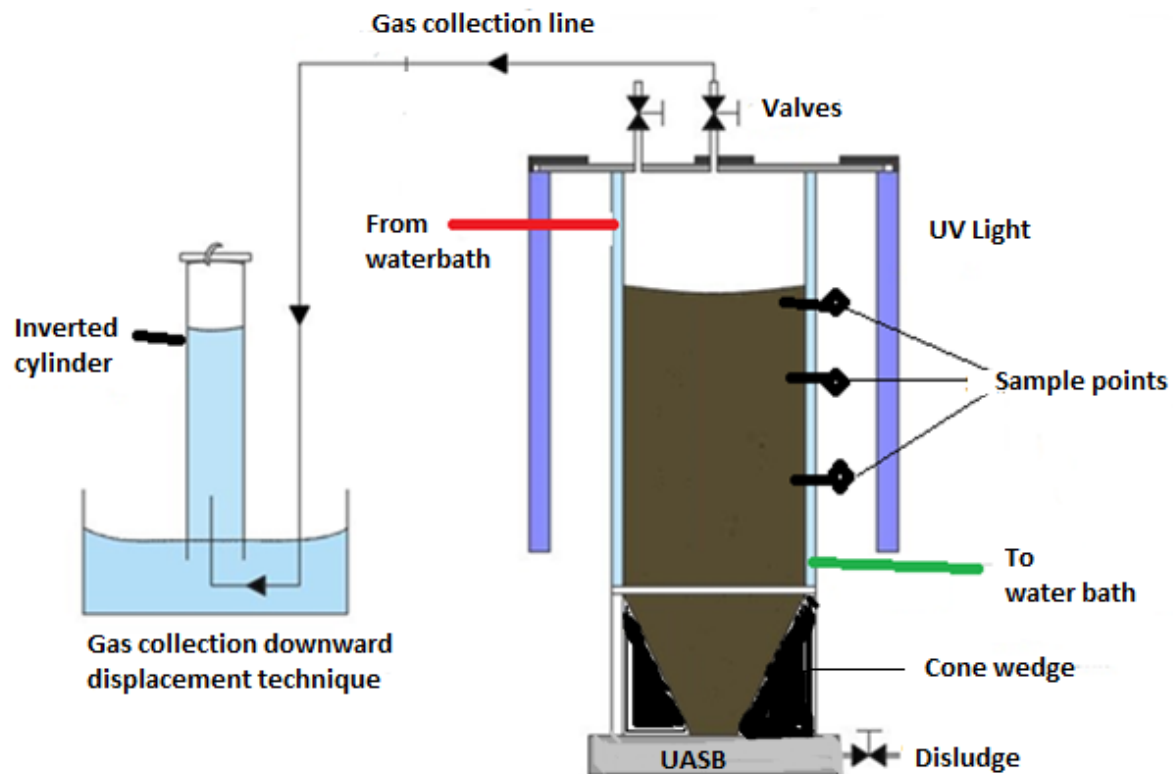


Figure 2. Schematic presentation of the biophotocatalytic system.

2.4. Experimental Design and Modelling

The Design Expert software (version13.0.7) was employed for experimental design, analysis of variance (ANOVA), regression analysis (R^2), and optimization of the process variables of the BP system. The response surface interaction between the catalyst dosage and HRT was investigated using a modified RSM-BBD method. Table 2 depicts the input variable levels considered based on the result of our previous work and other reported literature [17–19]. To avoid systematic mistakes, the experiment was carried out randomly with three levels, four duplicates, and one center point [25]. The response data (biogas, COD, color, and turbidity) obtained were used to develop a mathematical model that best correlates the input variables in the form of a quadratic equation (2). The model's acceptance was also determined by the regression coefficient (R^2) and ANOVA p -value.

$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{i=1}^n \beta_{ii} X_i^2 + \sum_{i < j}^n \beta_{ij} X_i X_j + \varepsilon \quad (2)$$

where the linear parameters Y , β_0 , β_i , X_i and ε represents the response, constant term, coefficient, factor, and the residual from the treatment, respectively. In addition, the quadratic terms X_i and X_j represents the factors, β_{ii} and β_{ij} represents the coefficients of the quadratic and the interaction parameters, respectively.

Table 2. Box- Benhken design matrix.

Symbol	Factor Name	Unit	Type	Low	Middle	High
A	Coded level			−1	0	1
	Catalyst load	g	Factor	2	4	6
	HRT	d	Factor	1	16	31

3. Results and Discussion

In principle, photoexcited catalysts can reduce CO_2 to CH_4 or split water molecules (H^+ ; O^{2-}) via light-induced redox reactions [22,26]. As a result (Figure 1), the H_2 produced during the exergonic metabolism is subsequently utilized by the methanogens to enhance the CO_2 reduction reaction into methane [1,5,27,28]. Results of the characterized municipality wastewater showed a high organic load (2380 ± 14 mgCOD/L) with a VS/TS ratio of 0.75 (Table 1). The VS/TS ratio > 0.5 proves the wastewater used was biodegradable [11,22]. Figure 3 shows the weekly monitoring of the BP system operated under anaerobic conditions, whereby the degraded organic content ($2380 > 115 > 87 > 30 > 12$ mgCOD/L) increased biogas production. The cumulative biogas recorded for week 1 to week 4, were 750, 1950, 1980, and 100 mL/d, respectively as depicted in Figure 3. Also, the activated photons of the Fe-TiO₂ catalyzed the microbes to enhance the degradability of the wastewater organic content. Figure 4 shows the increased methane level of the biogas produced recorded for week 1 to week 4, respectively, like 79%, 83%, 80%, and 95%, with the rest as CO_2 composition. From our preliminary studies, there was the need to investigate the effect of the HRT and catalyst load on the BP system efficiency. Therefore, understanding their individual or interaction effects on the BP system led to the RSM studies at a constant temperature of 37.5 °C, and an organic loading rate of 2.38 kgCOD/Ld.

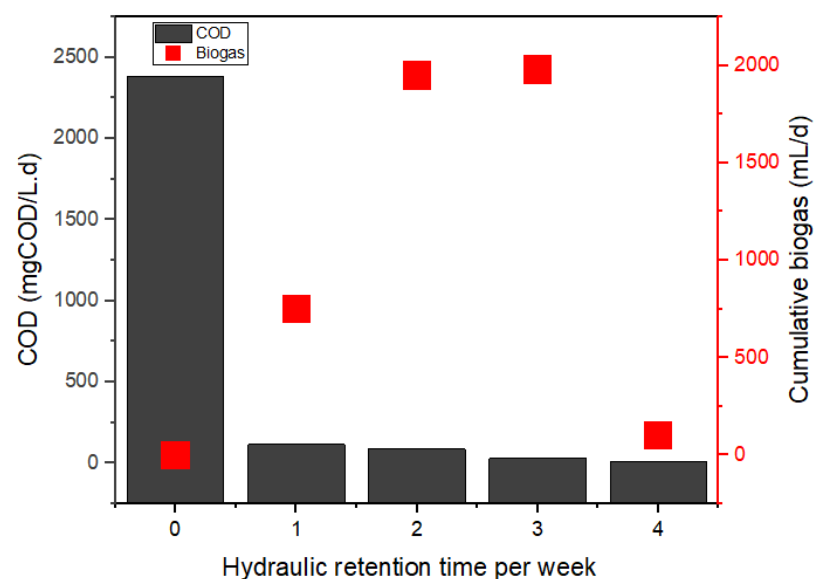


Figure 3. Weekly reduction of the COD and biogas produced by the BP system.

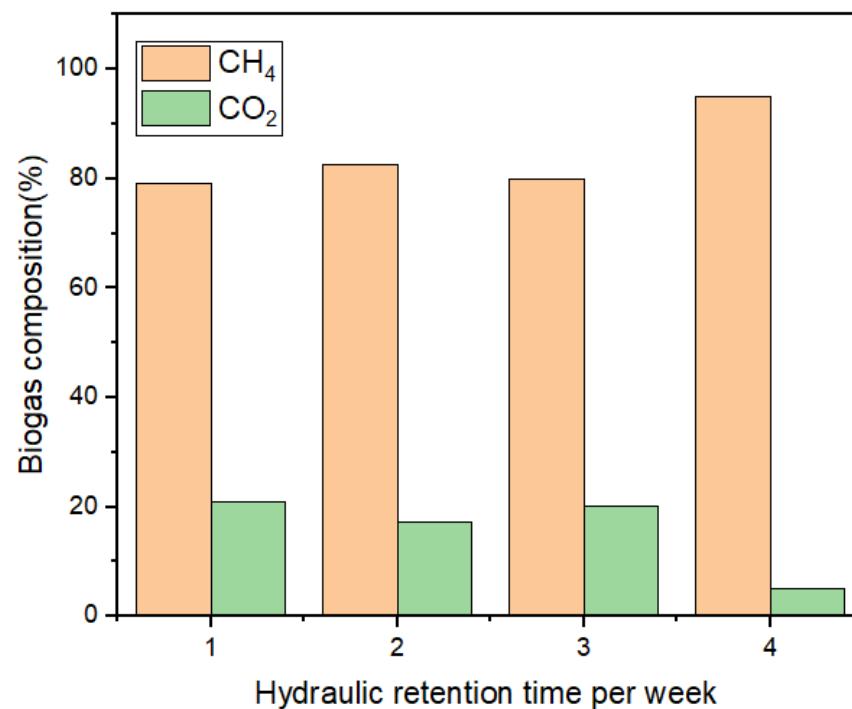


Figure 4. Weekly biogas composition of the BP system.

3.1. RSM Modelling and Statistical Analysis

According to the modified RSM-BBD matrix (Table 2), 13 randomized runs were carried out, including one center point (run 10) and four duplicates (runs 1:3; 2:9; 5:8; and 7:12) as depicted in Table 3 with additional information in Table S1. All the responses of the center point (run 10) showed little variation, indicating the consistency of the experimental runs. In all the experimental conditions, the removal efficiency of COD, color, and turbidity was observed to range from 90–98%. This degradation efficacy corresponded to biogas production of 125–335 mL/d. However, the biogas experimental results (125–335 mL/d) were estimated to deviate by 5% to that of the modified RSM-BBD model predicted results (130–327 mL/d). Subsequently, the significance of the factors was determined by modeling the experimental data as a function of the individual response (Table 3). This resulted in a reduced quadratic model with the Design Expert software that provided equations (3–10) in their coded and actual factors for the distinctive responses. The linear (A, B), interaction (AB), and quadratic (A^2 , B^2) terms represent the hierarchical form of the model, which combined the forward and backward regression option [29]. This regression option augments and eliminates the insignificant variables that do not meet or fall short of the model levels required ($p < 0.05$) [19,29]. The positive and negative coefficients in the predicted models (3–10) denote energetic and antagonistic effects of the process variables, respectively. In essence, the positive coefficient suggests that the response will be favored by an increase in such variable interaction. Conversely, the negative signs implies the response efficiency will decrease with an increase in those variables [29].

$$\text{Biogas}_{\text{coded}}(Y_1) = 267 + 86.37A - 3B - 12.25AB - 50A^2 + 8.75B^2 \quad (3)$$

$$\begin{aligned} \text{Biogas}_{\text{actual}}(Y_1) = & -118.73 + 149.72\text{Catalyst} + 0.189\text{HRT} - 0.41\text{Catalyst} \\ & * \text{HRT} - 12.5\text{Catalyst}^2 - 0.03\text{HRT}^2 \end{aligned} \quad (4)$$

$$\text{COD}_{\text{coded}}(Y_2) = 97.57 + 0.75A + 1.13B - 0.24AB - 1.96A^2 - 1.71B^2 \quad (5)$$

$$\text{COD}_{\text{actual}}(Y_2) = 84.53 + 4.44\text{Catalyst} + 0.35\text{HRT} - 0.0083\text{Catalyst} * \text{HRT} - 0.49\text{Catalyst}^2 - 0.03\text{HRT}^2 \quad (6)$$

$$\text{Color}_{\text{coded}}(Y_3) = 97.86 + 1.5A + 0.99B - 0.75AB - 2.07A^2 - 1.57B^2 \quad (7)$$

$$\text{Color}_{\text{actual}}(Y_3) = 82.12 + 5.29\text{Catalyst} - 0.39\text{HRT} - 0.0249\text{Catalyst} * \text{HRT} - 0.518\text{Catalyst}^2 - 0.00698\text{HRT}^2 \quad (8)$$

$$\text{Turbidity}_{\text{coded}}(Y_4) = 98.57 + 0.8A + 0.49B - 0.37AB - 1.03A^2 - 0.79B^2 \quad (9)$$

$$\text{Turbidity}_{\text{actual}}(Y_4) = 90.61 + 2.67\text{Catalyst} + 0.195\text{HRT} - 0.0125\text{Catalyst} * \text{HRT} - 0.258\text{Catalyst}^2 - 0.034\text{HRT}^2 \quad (10)$$

Table 3. Results of a modified RSM-BBD experiment and model predictions.

Run	Factor 1 A:Catalyst Load (g)	Factor 2 B:HRT (d)	Experimental Results				RSM-BBD Model Predicted Results			
			Biogas (mL/d)	COD (%)	Color (%)	Turbidity (%)	Biogas (mL/d)	COD (%)	Color (%)	Turbidity (%)
1	2	16	135	95	94	96.6	130.6	94.9	94.3	96.7
2	6	16	300	96	97	98.2	303.4	96.4	97.3	98.3
3	2	16	125	95	94	96.6	130.6	94.9	94.3	96.7
4	6	1	335	94	95	97.2	327.4	93.8	95.5	97.4
5	4	31	275	97	97	98.1	272.8	97.0	97.3	98.3
6	2	31	145	94	95	97.1	148.6	94.5	94.5	96.8
7	4	1	275	96	96	97.6	278.8	94.7	95.3	97.3
8	4	31	275	98	97	98.1	272.8	97.0	97.3	98.3
9	6	16	300	97	98	98.7	303.4	96.4	97.3	98.3
10	4	16	275	97	98	98.6	267.0	96.6	96.9	97.6
11	6	31	296	95	96	97.7	296.9	95.5	96.0	97.7
12	4	1	270	93	95	97.1	278.8	94.7	95.3	97.3
13	2	1	135	92	91	95.1	130.1	91.8	91.0	95.1

3.2. Analysis of Variance (ANOVA)

The response data was analyzed with the Design expert software, and the derived models were then fitted using the ANOVA (Table 4). The ANOVA shows how well the quadratic models fit the experimental values, parameters including F-value, probability >F, and adequate precision, which is a measure of error, or the signal-to-noise ratio were used [19,29]. The summary of the ANOVA for the various quadratic models is depicted in Table 4. The models' variables depict the two-factor interactions between the catalyst load (A) and the HRT (B) for the biogas (Y_1), COD (Y_2), Color (Y_3), and Turbidity (Y_4) efficiency. All the variables and their interactions were significant in the proposed models except the interaction of AB of the COD (Y_2) quadratic model (5–6) as indicated by a probability value being more than 0.05 (Table 4). A significant interaction between AB means that the effect of each variable depends on the value of the other variable [20]. Thus, increasing the catalyst load (AD) will require a longer period to reduce its potency. Adequate precision for all the models was greater than 4, suggesting a high signal/noise ratio; hence, the models can be used to navigate the design space [29].

Table 4. A modified RSM-BBD. model analysis of variance (ANOVA).

Response	Source	Sum of Squares	df	F-Value	p-Value	R ²	Adeq Precision
Biogas (Y ₁)	Model	69,092.95	5	289.5	<0.0001	0.9952	42.025
	A-Catalyst	59,685.12	1	1250.42	<0.0001		
	B-HRT	72	1	1.51	0.2591		
	AB	600.25	1	12.58	0.0094		
	A ²	7000	1	146.65	<0.0001		
	B ²	214.38	1	4.49	0.0718		
	Residual	334.13	7				
COD(Y ₂)	Model	29.57	5	20.48	0.0005	0.9360	16.0298
	A-Catalyst	4.5	1	17.65	0.0040		
	B-HRT	10.12	1	25.00	0.0016		
	AB	0.25	1	0.6449	0.4483		
	A ²	10.8	1	49.41	0.0002		
	B ²	8.23	1	25.78	0.0014		
	Residual	7.2	7				
Color (Y ₃)	Model	43.04	5	29.6	0.0001	0.9548	18.8142
	A-Catalyst	18	1	61.89	0.0001		
	B-HRT	8	1	27.51	0.0012		
	AB	2.25	1	7.74	0.0272		
	A ²	12.01	1	41.31	0.0004		
	B ²	6.91	1	23.78	0.0018		
	Residual	2.04	7				
Turbidity (Y ₄)	Model	11.4	5	31.36	0.0001	0.9573	19.0872
	A-Catalyst	5.15	1	70.86	<0.0001		
	B-HRT	2	1	27.51	0.0012		
	AB	0.5625	1	7.74	0.0272		
	A ²	2.99	1	41.11	0.0004		
	B ²	1.73	1	23.78	0.0018		
	Residual	0.5089	7				

Subsequently, the extent of correlation was estimated using experimental-predicted data interactive plots that is represented by plotting the predicted values against the experimental ones (Figure 5). Figure 5a,c,d shows a strong linear correlation between the experimental and the model predicted data with their high regression coefficients (R²) as depicted in Table 4. However, in Figure 5b, only a few data points were frequently scattered around the diagonal line, which could account for the on-and-off degradation of the organics (%COD removal) based on the subjected experimental conditions. The standard error (SE) for the straight line of best fit had insignificant deviation ($p < 0.05$) at a 95% confidence level. As can be inferred in Table 4, the COD (Y₂) model regression is very low, even though all the model's Adjusted R² and Predicted R² values are in reasonable agreement with a difference of less than 0.2. The standard error (SE) for the straight line of best fit shows insignificant deviation (<0.05) at 95% confidence levels.

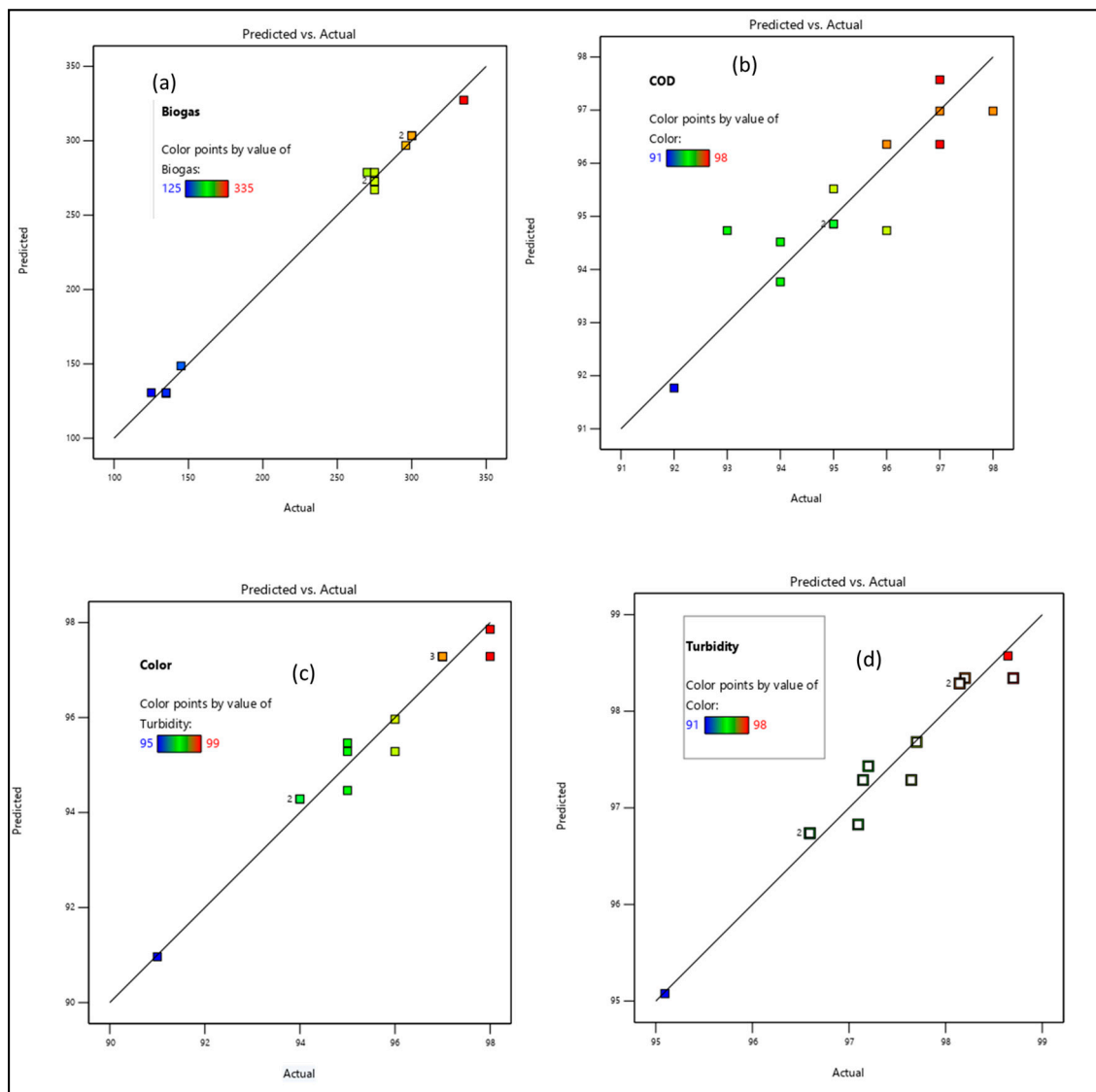


Figure 5. Diagnostic experimental plots against the modified RSM-BBD predicted results; (a) biogas, (b) COD, (c) color, and (d) turbidity. (The numbers on the diagonal line are the data points attained at a specific conditions of the experimental runs as inferred in Table 3).

3.3. One-Factor-At-Time Technique

3.3.1. Effect of Catalyst Load

The impact of the Fe-TiO₂ load over the range of 2–6 g was used to study the degradability of the organic content of the wastewater into biogas. In Figure 6, it is observed that the degradation efficiency as a function of (a) biogas, (b) COD, (c) color, and (d) turbidity increased with an increase in the catalyst load. However, after the optimum regime (>4.5 g) there was a drop in the degradation efficiency. The decrease in efficiency might be due to excess hydroxyl radicals generated which agglomerated and reduced the active surface area [30]. In essence, increasing the catalyst load increased the collision frequency between the hydroxyl radicals and the organic content interspecies, which diminished the photoactivity of the system [27,30]. Also, the exponential growth of the microbial organism and their degradability activity increased biogas production [27]. This suggests that the induction of the catalyst facilitated the conductive electron interspecies transfers, which increased the microbial activity and the methanogenic activity [13,30,31].

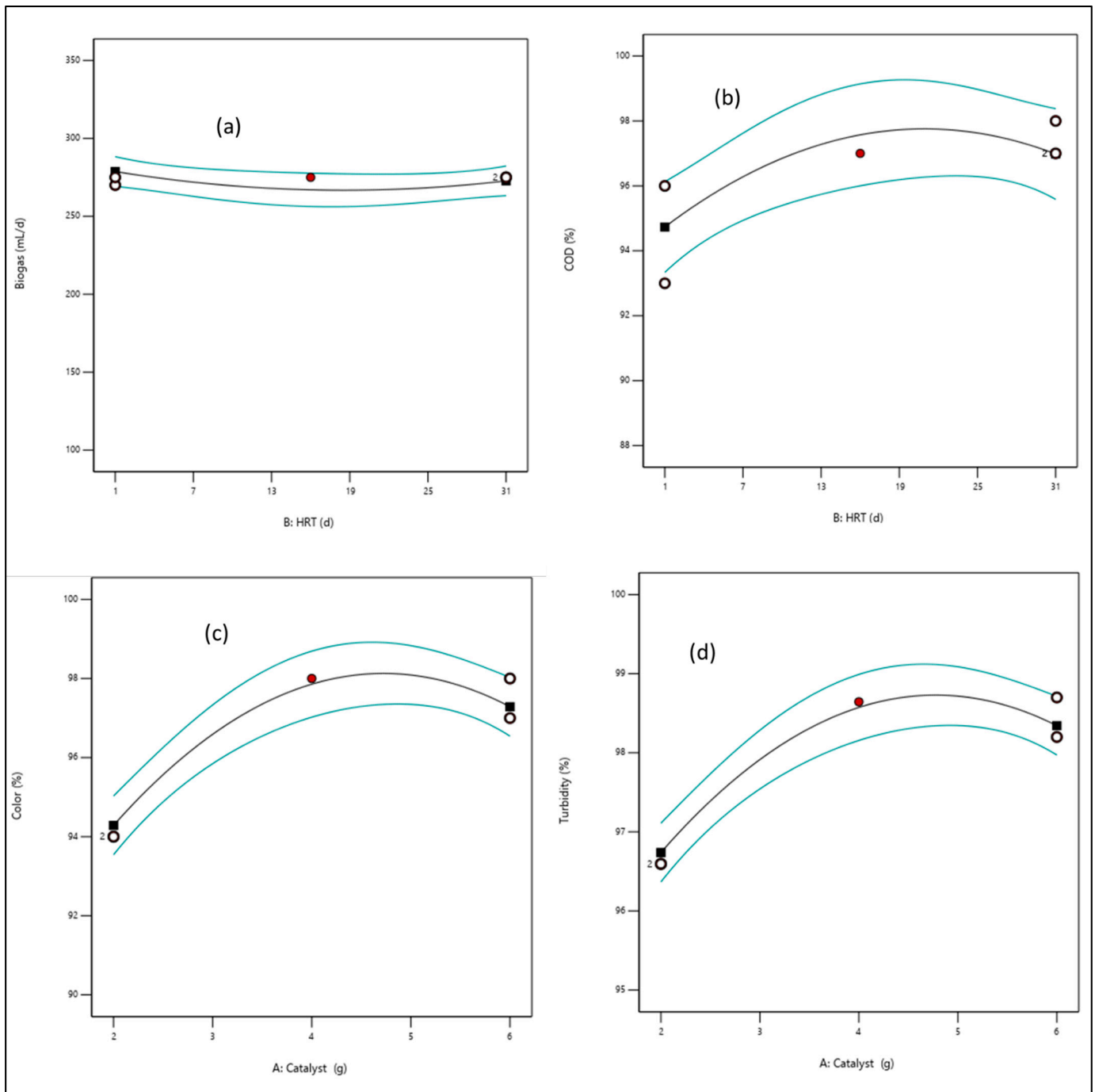


Figure 6. A diagnostic plot of the effect of catalyst load (2–4 g) on (a) biogas, (b) COD, (c) color, and (d) turbidity. The blue lines are the threshold or region of the response. The black is the trend line of the response. The whites and black circles are the level points of the response, whereas the red shows the high levels point.

3.3.2. Effect of Hydraulic Retention Time (HRT)

The HRT investigated from 1–31 days had a significant effect on the digester performance as it facilitated microbial activity to the organic interspecies contact time, which increased its digestibility. Figure 7 shows an initial increase in degradation (COD, color, and turbidity) during the first 5 to 15 days followed by a decline (15–31 days), whereas a fairly constant rate for biogas production (Figure 7a) was observed. This indicates that a longer HRT is required for the methanogens to digest the organic component and convert

it to biogas [32]. In addition, the digestion process will slow down if volatile fatty acids accumulate due to acidic bacteria being dominant with less organic content [26,30,33].

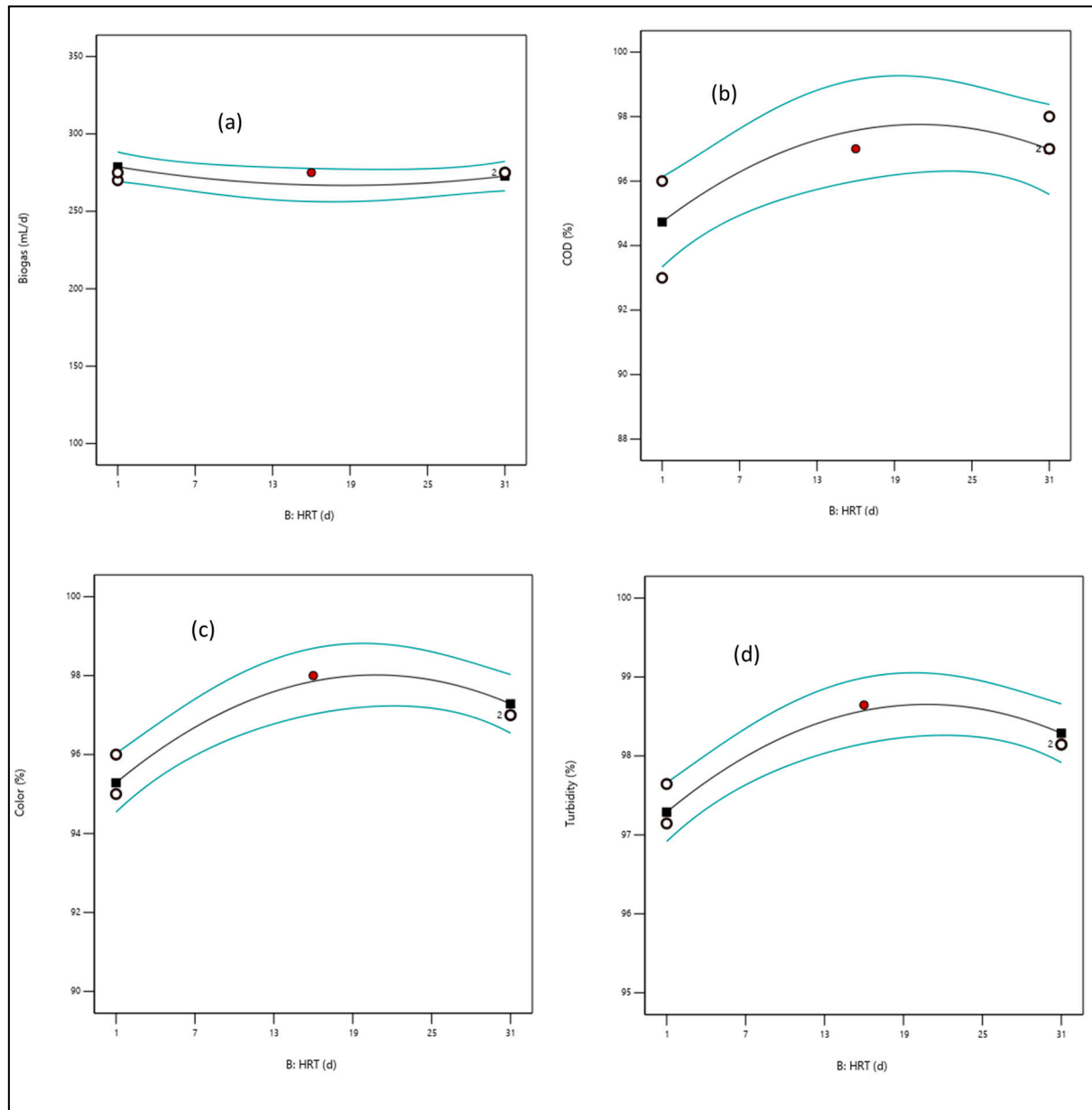


Figure 7. A diagnostic plot of the effect of HRT (1–31 d) on (a) biogas, (b) COD, (c) color, and (d) turbidity. The blue lines are the threshold or region of the response. The black is the trend line of the response. The whites and black circles are the level points of the response, whereas the red shows the high levels point.

3.4. Response Surface Interaction Plots

The modified RSM-BBD was used to illustrate the interactive impact of the factors on the response. Figure 8 shows the presence of interactions between the factors, catalyst load, and HRT (AB) on (a) biogas (b) COD, (c) color, and (d) turbidity. The graphical representation of the three-dimensional (3D) surface plots of the response models was selected based on the influential factors and their interaction that can be utilized to maximize the system desirability. Curvatures of a significant magnitude can be seen in the graphs (Figure 8). These curves indicate that the correlation between the factors (AB) and the response (biogas, COD, color, and turbidity) was well fitted on a quadratic function

(3–10). This elucidates Figure 8 as the degradation efficiency increased to the maximum with an increase in HRT; likewise, with the catalyst load (Figure 6). However, the curvature (Figure 8) highlights an increase in catalyst with dosage from 2 to 4 g and thereafter decreased with a further increase in catalyst load (5–6 g). The trend (Figure 8), observed at higher dosages of the catalyst, can be attributed to particle re-stabilization [30,33]. In addition, an overdose and excess of hydroxyl radicals can also aggregate to decrease the active surface area [30]. In essence, at the stage of re-stabilization, there is a charge reverse between the interspecies [26,30,33]. As illustrated (Figure 8) with an arc-line, the optimum regime can be observed within the HRT of 15–25 days. This validates the positive sign of the response quadratic models (3–10) as reported earlier, which had significant impact on the system predictability (Figure 5).

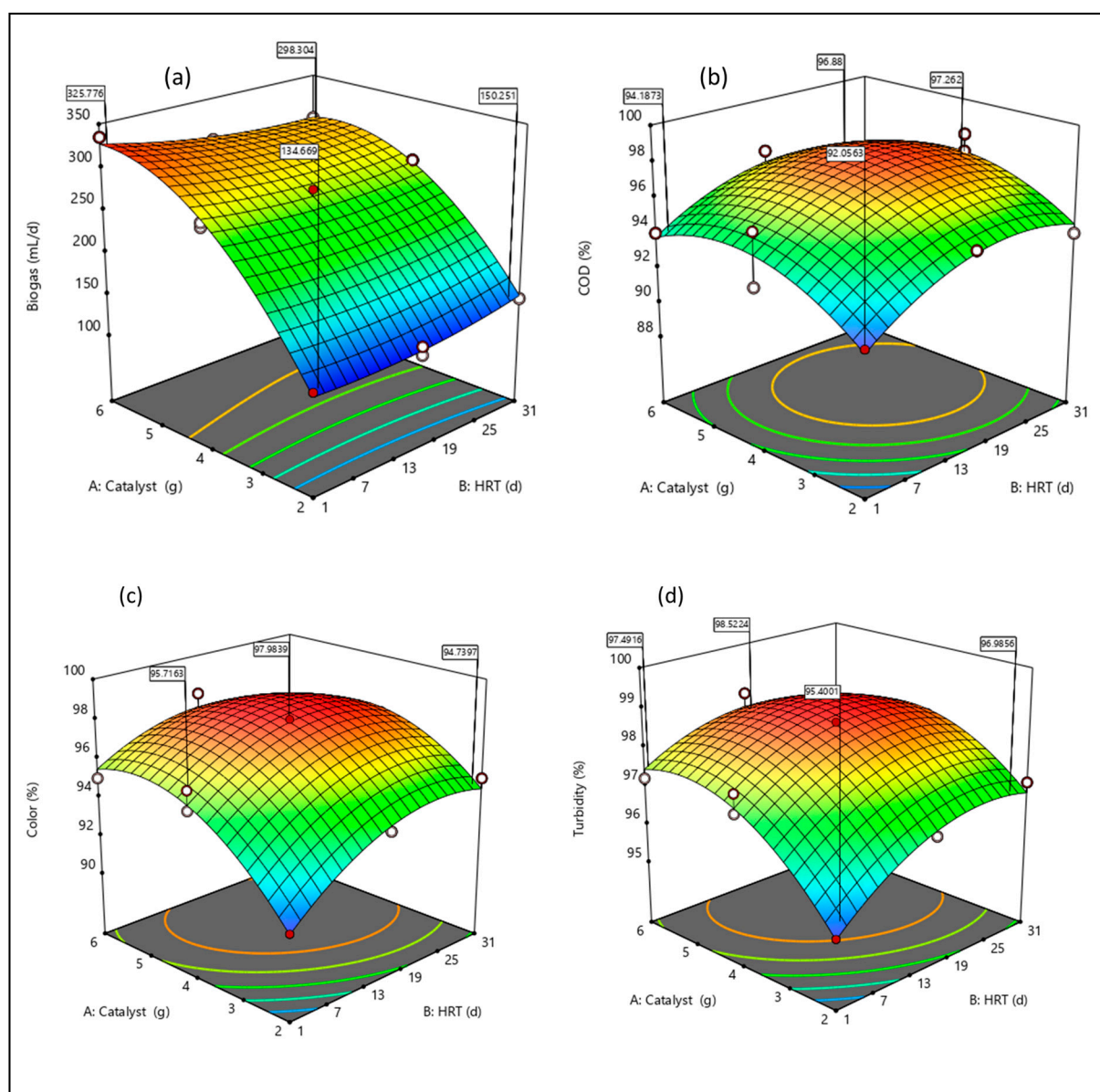


Figure 8. Three-dimensional (3D) plots of (a) biogas, (b) COD, (c) color and (d) turbidity.

3.5. Response Optimization and Confirmation Test

The numerical optimization technique was employed to maximize the responses (biogas, COD, color, and turbidity) and determine the optimal conditions (with respect to the experimental runs) using their respective quadratic equations (3–10). Also, the

comparative evaluation of the experimental and model predicted responses at each level of the experimental conditions (Table 3) showed considerable correlation with the two input variables (A and B) as a constraint. The goal for the optimization was defined as a function of the input variables set within the range of their levels such as low (−1) and high (+1) to maximize the desirability of the responses. The optimal solution selected out of 78 solutions (Table S1) to maximize the responses is presented in Figure 9 with 100% desirability. As it can be inferred from the ramp plot (Figure 9), 267 mL/d of biogas, 97.75% COD, 98% color, and 99% turbidity removal were attained at 4 g catalyst load and HRT of 21 d. The selected optimal conditions validated and confirmed experimentally as presented in Table 5 were in good agreement with the predicted values. This suggests the model's predictability was consistent ($p < 0.05$) at 95% confidence levels with a small standard error (SE) and standard deviation (STD) (Table 5). Also, the results obtained were compared with other studies (Table 6), which showed the appreciable efficacy of the BP system for wastewater treatment and biogas production.

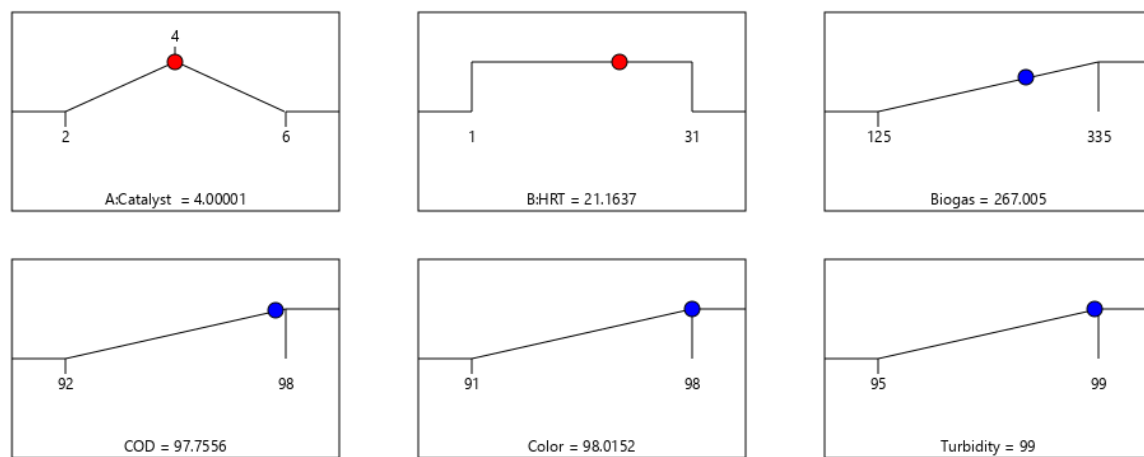


Figure 9. Selected numerical optimized condition ramp plots.

Table 5. Modified RSM-BBD optimum conditions experimental validation.

Response	Predicted	Observed	* Std Dev	* SE Mean
Biogas (mL/d)	267	250	6.95	4.53
COD (%)	98	95	1.01	0.67
Color (%)	98	96	0.53	0.38
Turbidity (%)	99	97	1.87	1.67

* Std Dev—Standard deviation, SE—standard error.

Table 6. Comparing previous and current studies.

Waste Type	Process	Operating Condition	Efficiency	Reference
Blast furnace sludge (BFS) with a Fe-rich residue, as a catalyst	A Laboratory scale differential reactor	Temperature of 300–350 °C, 1 atm, and variable partial pressures of H ₂ (10–50 kPa) and CO (0.25–3.0 kPa)	The methane production and selectivity achieved were 2.63 µmolCH ₄ /gcat/min and 49.5%	[22]
Municipality wastewater seeded with 2 g of Fe ₂ O ₄ -TiO ₂ MNPs	Biochemical Methane Potential (BMP) Test	Temperature 40 °C for 30 days	biogas production (400 mL/day) and methane yield (100% CH ₄)	[24]
Municipality wastewater	Biochemical Methane Potential (BMP) Test	Temperature 40 °C for 30 days	Biogas production (350 mL/day) and methane yield (65% CH ₄).	[24]

Table 6. Cont.

Waste Type	Process	Operating Condition	Efficiency	Reference
Distillery wastewater	Integrated anaerobic-photocatalysis	Organic load rate (OLR) of 3 kg COD/m ³ .d and hydraulic retention time (HRT) of 20 days	98% COD, 50% color, bioenergy of 180.5 kWh/m ³	[25]
Lignocellulosic materials	Anaerobic digestion	0.252 mg of NiO–TiO ₂ /g total solids (TS) and HRT of 4 days	Soluble chemical oxygen demand (COD) and 67% increase in volatile fatty acids (VFAs)	[33]
Municipality wastewater seeded with Fe-TiO ₂	Biophotocatalytic system	4 g catalyst load and HRT of 21 d	267 mL/d of biogas, 97.75% COD, 98% color and 99% turbidity	This study

4. Conclusions

In this study, biogas, and decontamination (COD, color, and turbidity removal) efficiency of biophotocatalytic degradation of municipality wastewater was studied. The lab-scale biophotocatalytic (BP) system operated in batch mode was augmented with Fe-TiO₂ and optimized to treat the wastewater. The results demonstrated both the HRT and catalyst load had positive effects on the BP system efficacy. At an optimal catalyst load of 4 g and HRT of 21 d, the modified RSM-BBD model predicted results were validated experimentally, and 267 mL/d of biogas and >98% COD, color and turbidity removal efficiency were attained. This infers 100% desirability with a high coefficient of regression of >0.98 at 95% confidence. The analysis of variance (ANOVA) suggested the modified RSM-BBD response models developed were significant with high precision, as the predicted results and the experimental results were in good agreement. This study demonstrates the modified RSM-BBD's usefulness and reliability in modeling, optimizing, and monitoring the effectiveness of the BP systems for wastewater treatment and biogas production.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/bioengineering9030095/s1>, Table S1: Modified RSM-BBD optimized conditions of the BP system.

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Response Surface Optimization of Biophotocatalytic Degradation of Industrial Wastewater for Bioenergy Recovery

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Table S1. Modified RSM-BBD optimized conditions of the BP system.

Number	Catalyst Load (g)	HRT (days)	Biogas (mL/d)	COD (%)	Color (%)	Turbidity (%)
1	4	16	267	97.571	97.857	98.574
2	4	31	272.75	96.982	97.286	98.288
3	4	1	278.75	94.732	95.286	97.288
4	4	16.796	266.865	97.626	97.906	98.598
5	4	27.905	270.131	97.384	97.661	98.475
6	4	18.504	266.743	97.711	97.98	98.635
7	4	14.443	267.406	97.436	97.736	98.513
8	4	9.324	270.069	96.731	97.101	98.195
9	4	10.059	269.561	96.857	97.215	98.252
10	4	12.025	268.409	97.153	97.482	98.386
11	4	25.345	268.527	97.607	97.87	98.58
12	4	25.461	268.589	97.599	97.863	98.576
13	4	15.147	267.199	97.502	97.795	98.543
14	4	18.696	266.743	97.718	97.986	98.638
15	4	17.438	266.793	97.664	97.939	98.614
16	4	20.922	266.958	97.756	98.016	98.653
17	4	17.939	266.758	97.688	97.96	98.625
18	4	23.4	267.65	97.709	97.968	98.629
19	4	5.348	273.543	95.908	96.354	97.822
20	4	23.201	267.576	97.716	97.975	98.633
21	4	27.037	269.53	97.471	97.742	98.516
22	4	25.644	268.688	97.586	97.85	98.57
23	4	22.022	267.206	97.747	98.005	98.648
24	4	5.641	273.245	95.977	96.417	97.853
25	4	4.802	274.116	95.776	96.235	97.762
26	4	3.521	275.551	95.449	95.938	97.614
27	4	21.892	267.172	97.749	98.007	98.649
28	4	11.262	268.821	97.045	97.384	98.337
29	4	15.46	267.119	97.529	97.819	98.555
30	4	16.993	266.84	97.638	97.916	98.603
31	4	13.253	267.843	97.308	97.621	98.456
32	4	19.802	266.802	97.746	98.01	98.65
33	4	19.047	266.752	97.729	97.995	98.643
34	4	19.988	266.821	97.749	98.012	98.651
35	4	11.394	268.746	97.064	97.402	98.346

36	4	20.121	266.836	97.751	98.013	98.652
37	4	22.406	267.315	97.739	97.998	98.644
38	4	17.641	266.777	97.674	97.948	98.619
39	4	23.58	267.718	97.702	97.961	98.626
40	4	14.572	267.365	97.449	97.748	98.519
41	4	5.749	273.137	96.002	96.44	97.865
42	4	20.297	266.859	97.753	98.015	98.652
43	4	6.772	272.157	96.23	96.647	97.969
44	4	21.422	267.059	97.754	98.013	98.652
45	4	14.955	267.251	97.485	97.78	98.535
46	4	26.124	268.961	97.55	97.816	98.553
47	4	19.666	266.789	97.744	98.008	98.649
48	4	13.845	267.612	97.374	97.681	98.486
49	4	17.2	266.816	97.65	97.927	98.609
50	4	7.638	271.392	96.411	96.811	98.051
51	4	24.751	268.228	97.644	97.906	98.598
52	4	14.838	267.285	97.474	97.77	98.53
53	4	4.431	274.519	95.684	96.151	97.721
54	4	3.998	275.002	95.574	96.051	97.67
55	4	16.452	266.917	97.604	97.886	98.588
56	4	12.296	268.274	97.189	97.514	98.402
57	4	3.251	275.871	95.377	95.872	97.581
58	4	19.541	266.779	97.741	98.006	98.648
59	4	19.399	266.77	97.738	98.003	98.647
60	4	8.582	270.623	96.596	96.978	98.134
61	4	14.685	267.33	97.46	97.757	98.524
62	4	29.173	271.114	97.237	97.523	98.407
63	4	23.843	267.823	97.691	97.95	98.62
64	4	2.656	276.594	95.214	95.724	97.507
65	4	12.566	268.146	97.224	97.546	98.418
66	4	27.532	269.866	97.423	97.697	98.494
67	4	27.214	269.647	97.454	97.726	98.508
68	4	7.386	271.608	96.36	96.765	98.027
69	4	10.193	269.473	96.879	97.234	98.262
70	4	17.332	266.802	97.658	97.934	98.612
71	4	22.678	267.4	97.733	97.991	98.64
72	4	11.63	268.612	97.098	97.432	98.361
73	3.9	28.75	266.849	97.257	97.523	98.404
74	3.9	18.25	262.395	97.661	97.897	98.591
75	3.9	3.25	270.908	95.324	95.76	97.522
76	4.1	28.75	274.445	97.311	97.61	98.452
77	4.1	18.25	270.849	97.732	98.036	98.666
78	4.1	3.25	280.586	95.42	95.973	97.634