

**REMOVAL OF SELECTED HEAVY METALS FROM WASTEWATER USING
MODIFIED AGRICULTURAL WASTE**

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DECLARATION

I, Maureen Nomaxhosa Msimango, declare that the thesis submitted for the degree of Master of Applied Science in Chemistry at the Durban University of Technology is the result of my investigation and has not already been accepted in substance for any degree and is not being concurrently submitted for any other degree. All the work was done by the author.

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DEDICATION

First and foremost, I dedicate this work to God for giving me the strength and hope through the entire process. I also dedicate this thesis to my supervisors Dr LQ Qwabe and Dr P Ntola. My dedication also goes to Mr FM Makhanya, Mr ST Dube, my laboratory family for their unwavering support that they have shown throughout my studies and to my family for supporting me through tough times and the sacrifices they have made to give up family time for my studies.

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LIST OF ABBREVIATIONS

SCB:	Sugarcane bagasse
SCBC:	Sugarcane bagasse cellulose
CMC:	Carboxymethylcellulose
WHO:	World Health Organization
USEPA:	United States Environmental Protection Agency
LOD:	Limit of detection
MCL:	Maximum contaminant limit
FTIR:	Fourier Transform Infrared
COD:	Chemical oxygen demand
BOD:	Biological oxygen demand
AWB:	Agricultural waste biosorbents
AAS:	Atomic absorption spectroscopy
XRD:	X-Ray diffraction spectroscopy
SEM:	Scanning electron microscope
EDS:	Energy dispersive X-Ray spectroscopy
TEM:	Transmission electron microscope
BET:	Brunauer- Emmett -Teller
TOC:	Total organic content

ABSTRACT

This study explores the potential of utilizing inexpensive adsorbent materials derived from agricultural waste to eliminate Zn (II), Ni (II) and Cd (II) from water-based solutions. Sugarcane bagasse was chemically modified to extract cellulose and further functionalize extracted cellulose to prepare carboxymethyl cellulose which were used as biosorbents. The biosorbents were characterized using XRD, FTIR (ATR), and SEM for confirmation of physical and chemical properties and surface morphology of the adsorbents. In batch experiments, the effect of various parameters such initial concentration (10-300 mg/L), pH (2-8), adsorbent mass (0.1-1.7 g), and contact time (5-150 min). Adsorption was poor for all metals below pH 4 and reached maximum removal efficiency at pH 6. The increase in initial concentration favoured the increase in removal efficiency but reaches a maximum beyond 100 mg/L. The increase in biosorbent mass shows favours increase in removal efficiency for Ni (II) and Cd (II) but a decrease was observed for Zn(II). The removal efficiency increased with contact time and reached equilibrium at 60 minutes for all metals and biosorbents. The maximum adsorption capacities of Zn(II), on SCB, SCBC, and CMC were 12.3, 20.9 , and 33.5 mg/g respectively. Ni (II) adsorption capacities on SCB, SCBC, and CMC, were 41.9, 25.4, and 125.7 mg/g respectively. The maximum capacities of Cd(II) on SCB, SCBC, and CMC, were 11.3, 20.8, and 21.6 mg/g respectively. The performance of CMC superseded SCB and SCBC. Kinetic experiments showed that the adsorption process followed pseudo second order whereas the equilibrium studies showed that the adsorption process followed the Langmuir adsorption isotherm.

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CHAPTER 1: INTRODUCTION

1.1 Background

Water is one of the precious resources in the world, however it is becoming scarce due to different human activities polluting the environment (Karnitz Jr *et al.* 2007). Fauna and flora cannot survive without water; hence its scarcity might disturb the ecosystem, therefore it requires preservation. Water is necessary for domestic and industrial use, and it generates domestic and industrial wastewater. Heavy metals such as cadmium (Cd), chromium (Cr), arsenic (As), zinc (Zn), and lead (Pb) are amongst the pollutants that are affecting the environment through rapid urbanization (Nghah and Hanafiah 2008). Industrialization is a major culprit in polluting the universe through various processes such as mining, smelting, battery, tannery, pesticides, paint manufacturing, metallurgy, textile printing, photography and metal plating (Zhang *et al.* 2017; Nghah and Hanafiah 2008; Karnitz Jr *et al.* 2007). The waste generated by these industries ends up in the municipality's effluent and might directly or indirectly pollute the surrounding water bodies. Heavy metal waste, unlike the organic waste does not degenerate through biological activities and can amass in the living tissues giving rise to various illnesses and disorders to both fauna and flora (Nghah and Hanafiah 2008 ;Gupta *et al.* 2016). Unlike some contaminants, heavy metals are non - biodegradable, hence their persistence in the environment (Karnitz Jr *et al.* 2007). Consequently, the elimination of the heavy metals has become a critical and a worldwide environmental priority (Zhang *et al.* 2017). Exposure to heavy metals can cause serious effects for both animals and plants even if the concentrations are at micro levels (Nguyen *et al.* 2013).

Okeola *et al.*, (2011) reported the existence of different water treatment techniques such as electrolytic extraction, coagulation, ion exchange, bioremediation, reverse osmosis, chemical precipitation, and adsorption (Yu *et al.* 2013). Amongst these techniques adsorption is widely employed, and commercial activated carbon is the commonly utilized adsorbent for the

wastewater treatment because of its effectiveness in both removal of cations and cost when compared to other techniques (Eletta *et al.* 2020). It is of high importance that heavy metals are eliminated from the environment and or reduced to acceptable levels due to their toxicity. Arsenic (As), Nickel (Ni), Lead (Pb), Chromium (Cr), Cadmium (Cd), Copper (Cu) and Mercury (Hg) are the most common heavy metals listed by the Environmental Protection Agency (Khayatzadeh and Abbasi 2010), hence Zn, Ni and Cd are investigated in this study. Human exposure to As, Pb, Ni, Cr and Cd causes adverse illnesses particularly cancer. The target organs by these heavy metals are the lungs, kidneys, liver, and bladder. Due to the evidence of widespread of heavy metals and the impact they present, the United States Environmental Protection Agency listed As, Ni, Pb, Cr and Cd as priority control pollutants. USEPA has also risen the bar on their environmental policies due to the high presence of these heavy metal in the environment (Masri *et al.* 2021). Adsorption capacities of sugarcane bagasse, sugarcane bagasse extracted cellulose and its derivative carboxymethylcellulose (CMC) with respect to heavy metals Nickel (Ni), Zinc (Zn) and Chromium (Cr) were evaluated in this study.

1.2 Effect of nickel in humans and the environment

Nickel is a heavy metal widely used in many fields such as electrical, jewelry, engineering and medicine (Zdrojewicz, Popowicz and Winiarski 2016). Industries involved in mining, tannery, electroplating and cadmium batteries are generators of nickel containing waste (Genchi *et al.* 2020). Nickel is also an essential micronutrient responsible for proper functioning of the human body as it increases the activity of the hormones and is involved in lipid metabolism. It contributes to the growth and development of plants and facilitates seed germination and productivity (Genchi *et al.* 2020). The route of entry to the human body is respiratory tracts, skin and digestive system (Zdrojewicz, Popowicz and Winiarski 2016). In plants, if it is present in high levels, nickel inhibits enzymatic activity like photosynthesis and chlorophyll

biosynthesis. In humans it causes acute and chronic diseases such as cardiovascular, lung fibrosis, dermatitis, and lung cancer.

1.3 Effect of zinc on humans and the environment

Smelting, galvanizing, pharmaceutical, and mining industries are major contributors to zinc waste. Other sources of zinc waste are companies that produce zinc-based alloys, semiconductors, and chemicals. Zinc becomes widespread in the environment through sewage sludge, industrial emission, vehicle emission and from weathering of zinc based rocks (Yin *et al.* 2016). Zinc is a multipurpose trace element that acts as a binding agent for greater than 300 enzymes and approximately 2000 transcriptional factors. It is required for the synthesis of protein and collagen, hence it contributes to wound healing and healthy skin (Chasapis *et al.* 2020). It is critical for zinc to be present at acceptable levels as it is responsible for major biological uses such as being a catalyst, structural and regulatory agent. In high levels heavy metals are toxic to animals and humans, however zinc is one of the most important micronutrients necessary for human health. Zinc deficiency in humans is a cause of chronic diseases such as neurological disorders, atherosclerosis, autoimmune disease, aging, and Wilson's disease. In mammals its deficiency is associated with pregnancy complications, structural birth defects, prematurity, low birth weight, behavioral and immunological abnormalities (Chasapis *et al.* 2020). Zinc in elevated levels is toxic because it affects respiratory tracts, causes gastrointestinal tracts, focal neurological deficit and elevated risk of prostate cancer (Plum, Rink and Haase 2010).

1.4 Effect of cadmium on humans and the environment

In the environment cadmium does not usually exist in a pure form but as zinc, copper and lead ores (Remelli *et al.* 2016). Natural sources of cadmium are rocks and soil, air and anthropogenic activities like mining, fuel combustion, sewage sludge, landfills and the companies involved in the production of metals and fertilizers. High levels of Cd^{2+} cause neurological disorders, renal failure, anosmia and cancer (Evans *et al.* 2021). Agricultural and industrial sectors are the main source of cadmium waste to produce batteries, alloy production, coatings, electroplating and stabilizers for plastics. Kumar *et al.* 2021 suggests that male workers that work in the cadmium rich environment are at high risk of developing prostate cancer. He further explains that both men and women in this environment are susceptible to chest pains, anxiety and breathing problems. Planting of crops in cadmium contaminated soil or Irrigating crops with cadmium contaminated water leads to accumulation of cadmium in plants, hence humans can be exposed to diet containing cadmium (Remelli *et al.* 2016). Cadmium can accumulate in human lungs through air dust and cigarette smoke. Table 1.1 shows acceptable concentration as per WHO and USEPS standards.

Table 1.1: WHO and USEPA maximum contaminant levels for zinc, nickel and cadmium (Organization 2022).

METAL	MCL (WHO)	MCL (USEPA)
Nickel	0.02 mg/L	0.1 mg/L
Zinc	3 mg/L	5 mg/L
Cadmium	0.003 mg/L	0.005 mg/L

In this study, biomass waste sugarcane bagasse (SCB) and its derivatives have been chosen as alternative adsorbents for the removal of the above mentioned heavy metals (Nickel, zinc and

cadmium) due to reported success of other agricultural waste materials in the adsorption of heavy metals (Nguyen *et al.* 2013).

1.5 Rationale

Contamination of wastewater and surface waters by pollutants like dyes, pesticides and heavy metals amongst other harmful contaminants is a worldwide problem (Isa *et al.* 2020). The presence of heavy metals in wastewater streams is attributed to industrial processes such as mining, metal plating operations, tanneries, power generation facilities, and electronic device manufacturing (Farghali *et al.* 2013). Since heavy metals are naturally occurring components of the earth's crust, they can enter wastewater by acidic rain breaking down the soil leading to their release to various waterbodies (Raval, Shah and Shah 2016). Unlike organic compounds, the toxic heavy metal ions are non-degradable and tend to bioaccumulate causing harm not only to aquatic organisms but also to land animals including humans and plants through food chain transfers (Farghali *et al.* 2013). This study focuses on the removal of heavy metals from domestic and industrial wastewater using excess agricultural waste, namely sugarcane bagasse and its derivatives. Various industrial applications that involve heavy metal use have increased significantly, leading to possible discharge of untreated industrial wastewater containing heavy metals (Raval, Shah and Shah 2016). The adverse effects that come with heavy metals is undesirable and governments must enforce environmental laws driving industries to perform adequate treatment before disposal (Isa *et al.* 2020). South Africa is amongst countries that cannot supply potable water to its entire population, hence some rural communities rely on natural water sources for their daily activities. The need for good quality water arises and can be achieved by employing efficient water treatment methods. A number of techniques have been used for the removal of heavy metals in wastewater such as chemical precipitation, ultrafiltration, reverse osmosis, ion exchange, solvent extraction and adsorption (Ali 2017). Adsorption has been found by most researchers to be the most preferable method for

wastewater treatment because of its low cost, ease of operation, less sludge production (Ali 2017) and good removal performance (Isa *et al.* 2020). Other processes have limitations such as being uneconomical, secondary sludge production (Raval, Shah and Shah 2016) and ineffective at low metal concentrations such as those below 100 ppm of metal ion concentration (Ali 2017).

In the adsorption technique, activated charcoal gained popularity due to its high surface area, high pore volume and larger number of active sites, but it is expensive and produces a secondary sludge which requires further treatment (Supong *et al.* 2020). The activated charcoal restrictions caused the researchers to investigate alternative adsorbents generated from agricultural activities either as waste or byproducts. Biomass materials are considered viable adsorbents because they are cheaper and abundantly available in nature. (Supong *et al.* 2020). Agricultural waste biosorbents are mostly produced from Rice straws, eggshells, fruit peels, corncob, nut shells, and sugarcane bagasse (SCB) but not limited to these. There are various adsorbents derived from agricultural waste, however SCB outperformed other biomass adsorbents because it is widely accessible and is considered economical agro-industrial waste (Raj, Chauhan and Pal 2022). Another advantage is that amongst agricultural waste, sugarcane bagasse is generated in large volumes. Sugarcane bagasse produced per annum is approximately 540 million metric tons globally (Khatri and Pandit 2022). The leading country in the production of sugarcane is Brazil followed by India, China, Colombia and Mexico (Bezerra and Ragauskas 2016; Raj, Chauhan and Pal 2022). South Africa (SA) is the largest producer of SCB in Africa followed by Sudan, Kenya, and Swaziland. There is a total of fourteen milling companies in SA of which 86% are in KwaZulu Natal and the remaining 14% are in Mpumalanga Province. SA produces about 28% of sugarcane globally and generates around 7 million tons of sugarcane bagasse per annum. Industries that produce sugar generate sugarcane bagasse and molasses as waste. These residues are used in generating energy for

powering plants, in production of industrial ethanol, pulp and paper production and animal feed (Mohlala *et al.* 2016). The sugarcane bagasse composition is, cellulose 40% to 50%, hemicellulose 25% to 35% and lignin 15% to 20% (Asl, Mousavi and Labbafi 2017). Sugarcane bagasse is rich in hydroxyl and phenolic groups because of these biological polymers. Hydroxyl and phenolic groups can be chemically modified to produce adsorbent materials with new properties (Yu *et al.* 2013). In this study natural and modified sugarcane bagasse generated biosorbents were investigated for the removal of heavy metals from wastewater.

1.6 Problem statement

Agricultural and industrial sectors generate a lot of waste that pollutes the environment, therefore the waste disposal methods available must be able to keep the environment clean. The most environmentally preferred waste disposal approach is reducing, reusing, and recycling. Waste that is generated by the agricultural sector will be beneficial in treating the heavy metal waste generated by industries. Pollution of the environment by heavy metals and biomass waste threatens the well-being of mankind and therefore requires prompt scientific innovative interventions. This study seeks to investigate the use of biomass and its derivatives as a cheaper but effective adsorbent in the eradication of heavy metals environmental pollution (Nghah *et al.* 2013). Water and soil contamination can cause adverse effects in the ecosystem. For example, human exposure to heavy metals can be through air, drinking water and diet. Exposure to heavy metals can present acute and or chronic illnesses like Liver and kidney damage, cancer, headache, nausea, vomiting, protein degeneration and the paralysis of the nervous system, alter enzyme activities and disrupt cellular function (Ezeonuegbu *et al.* 2021).

1.7 Aim

The aim of the study is to use natural and modified sugarcane bagasse, a bio sorbent derived from agricultural waste to remove selected heavy metals from wastewater.

1.7.1 Objectives

- To extract cellulose from sugarcane bagasse by alkalization, acidification, followed by bleaching with hydrogen peroxide.
- To chemically modify the sugarcane bagasse extracted cellulose into one of its derivatives, carboxymethylcellulose.
- To characterize sugarcane bagasse, sugarcane bagasse cellulose and carboxymethylcellulose using ATR-FTIR, XRD, and SEM and to evaluate their potential as bio sorbents.
- To investigate the efficacy of SCB, SCBC and CMC in removing heavy metals from wastewater.

1.8 Dissertation layout

The dissertation is structured into five chapters. Below is the brief presentation of each chapter.

Chapter 1: Introduction

This chapter includes the introduction of the wastewater treatment contaminated by heavy metals and the background to the topic, problem statement, justification and study objectives.

Chapter 2: Literature review

This section discusses literature reviews related to the study by various researchers.

Chapter 3: Theoretical principles

Under this section theoretical principles of the analytical instruments used are discussed.

Chapter 4: Methodology

Consists of the methodology and techniques used in preparing the bio sorbents, sugarcane bagasse, sugarcane bagasse extracted cellulose and carboxymethylcellulose. Methods used in preparing heavy metal solutions. The parameter employed in the determination of adsorption efficacy of sugarcane bagasse, sugarcane bagasse cellulose and carboxymethylcellulose.

Chapter 5: Results and discussion

This chapter presents the experimental results and examines them in detail.

Chapter 6: Conclusion and recommendations

The chapter discusses the research findings and states if they are aligned with the objectives. Limitations and recommendations for future work are also discussed in this section.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

This chapter discusses the effects of urbanization and industrialization which improved people's lives but the pollution that came with it is not desirable for the environment (Hegazi 2013). Herein the industrial processes that generate heavy metal waste that ends up in the effluent that needs to be treated before it is released into water streams are discussed.

Heavy metals, unlike organic waste, are non-biodegradable and tend to build up in the environment as well as in fauna and flora (Sheick *et al.* 2018). Sheik *et al.* (2018), reported that heavy metals may cause cancer, central nervous system breakdown, liver damage, kidney failure, pulmonary fibroses and skin dermatitis to humans. Elimination or reduction of metals like Arsenic (As), Chromium (Cr), Zinc (Zn), Nickel (Ni), Cadmium (Cd), Mercury (Hg) and Lead (Pb) in effluent may be achieved by employing techniques such as chemical precipitation, ion exchange, membrane processes and electrolytic methods (Hegazi 2013). These techniques are, however, expensive, and not very effective. Biomass waste from agricultural processes and forestry on the hand is also on the increase and proving difficult to remove, hence researchers have sought to find a solution by using it as a cost effective and environmentally friendly alternative adsorbent in the removal of heavy metals in water systems (Chand *et al.* 2009; Zhang *et al.* 2017; Chambon *et al.* 2018).

2.2 Sources of heavy metals

In developing countries access to potable water remains a challenge, hence pollutants exacerbate the problem. World Health Organization (WHO) reports that a population of about 844 million do not have access to basic drinking water. It further states that approximately 230 million spend more time collecting water from enhanced boreholes, tap water, springs and protected wells (Joseph *et al.* 2019). Heavy metals can come from both manmade and natural

sources (Wei and Yang 2010; Muhammad, Shah and Khan 2011). The primary natural source is the weathering of metal-containing rock and volcanic eruptions. Heavy metal pollution due to volcanic eruptions is through explosive volcanic activities, sporadic emissions and continuous low emissions (Zamora-Ledezma *et al.* 2021). There are physical, chemical, and biological processes that occur during weathering. The rock surface weakens during this (Garcia-Sanchez *et al.* 2009) breakdown which results to erosion, hence contaminating the environment (Moses, Robinson and Barlow 2014). Industrial output such as mining and smelting, fertilizer use and sewage outflow are examples of anthropogenic sources (Ntengwe and Maseka 2006; Bhuiyan *et al.* 2011; Zhou *et al.* 2020; Garcia-Sanchez *et al.* 2009). Heavy metal concentrations in biogeochemical cycles have increased as a result of mining and industrial processes used to extract mineral resources and use those resources in industry and agriculture (Zhou *et al.* 2020). In affluent countries such as Europe and North America, the levels of heavy metals and the number of heavy metals with concentrations below the threshold limits for both WHO and USEPA criteria, whereas the developing countries like Africa, Asia and South America had higher heavy metal concentrations (Zhou *et al.* 2020).

Major culprits in generating heavy metal waste are the industries involved in mining, galvanizing, smelting, tanneries, recycling, and solid waste activities. The United Nations (UN) suggested that almost 80% of the industrial and municipality effluent does not get treated before it is released to the environment. Other contributors to water pollution include, urban stormwater runoff and agricultural runoffs that are contaminated by heavy metals (Joseph *et al.* 2019). Industries that generate wastewater streams containing Cd, Ni, Cu, Cr, Ag, Pt, V, Pb and Tn are the ones involved in electroplating, electrolysis depositions, coating, milling, and anodizing-cleaning. A large amount of Tn, Pb and Ni waste comes from Printed Circuit Boards (PCB). Wood processing industries that use chromated copper-arsenate wood treatment techniques produce arsenic, copper, and chromium waste. Cadmium and chromium waste is

mostly generated by companies involved in inorganic pigmentation production. High levels of silver and ferrocyanide come from the waste generated by photographic companies. Petroleum refiners generate Ni, V and Cr through their catalytic conversion processes. There are different wastewater treatment techniques that are employed to prevent heavy metals from harming the environment, however they have their advantages and drawbacks.

2.3 Various techniques used in water treatment

Inorganic effluent generated by different industries can be treated using conventional processes. Heavy metals in wastewater are removed by various methods including chemical precipitation, coagulation, complexation, solvent extraction, ion exchange, cementation, foam floatation, electrode deposition, membrane separation and activated carbon adsorption (Gunatilake 2015). These methods are efficient but to a certain extent.

Some industries use chemical precipitation as one of the wastewater treatment methods for the removal of heavy metals in inorganic effluent due to ease of operation. This technique requires the addition of a substance that will react with dissolved metal in solution to produce insoluble precipitates of heavy metals such as hydroxides, sulfides, phosphates, and carbonates. During this process, very fine particles are produced which in turn are enhanced to large particles by means of a sedimentation technique and removed as a sludge (Renu, Agarwal and Singh 2017). Lime is the preferred precipitant due to its low cost in several countries, availability and the pH can be controlled with ease (Gunatilake 2015). Coagulation and flocculation process involves the addition of a coagulant resulting in destabilized particles that are further agglomerated (Saleh, Mustaqeem and Khaled 2022). It uses coagulants and flocculants which cannot be recovered and generates large amounts of sludge (Chai *et al.* 2021).

Solvent extraction is suitable for the removal of heavy metals and is popular in electronic and chemical industries. In this technique, there is a possibility of cross contamination between

aqueous streams which results in poor effluent quality (Crini and Lichtfouse 2019; Chai *et al.* 2021). Since organic solvents are used, there is a high risk of exposure to toxic substances which is in violation of occupational Health and Safety Act.

Ion exchange is a technique that employs resins that are capable of adsorbing heavy metals efficiently. It is simple to operate and relatively cost effective, but it works efficiently only if the concentrations of heavy metals in wastewater are low. This technique is limited if there are high levels of heavy metals because it quickly reaches the heavy metal saturation point requiring recurrent substitution (Fu *et al.* 2022).

Membrane filtration is a semi-permeable separation technique which is nondestructive. There are different types of membrane technologies which are divided into three, mainly ultrafiltration, nanofiltration and reverse osmosis. Ultrafiltration is efficient when working with macro particles such as colloids and solutes of high molecular weights. Liquid is enforced in a semi permeable membrane using hydrostatic pressure. Reverse osmosis cleans wastewater under high pressure using a semi-permeable membrane. The high pressure forces the water to flow to the opposite direction restricting the flow resulting in the ions being trapped in a semi-permeable membrane. Nanofiltration is suitable for use in treating ground water, surface water, organic substances, and heavy metals in wastewater. All these wastewater treatment techniques have disadvantages that either make them costly, less efficient or production of a secondary sludge which might be toxic. In the adsorption technique, the advantages outweigh the disadvantages.

Adsorption is a physical or chemical interaction process that involves molecular, atomic, or ionic mass transfer to the solid surface. This process is easy to operate, highly effective with fast kinetics and can be used for a variety of pollutants (Chai *et al.* 2021). Adsorption could either be physical or chemical. In physical adsorption the adsorbate and the adsorbent are bound

by van der Waals forces whereas chemisorption involves a chemical reaction between the adsorbate and an adsorbent resulting in new bonds which are either covalent or ionic. Physical adsorption is favorable at low temperatures. (Tripathi and Ranjan 2015). Physical adsorption is reversible and has small thermal effects. On the other hand, chemisorption is irreversible and its thermal effect is huge (Burakov *et al.* 2018). Adsorption is a popular wastewater treatment technique globally in which the adsorbent can be regenerated with a possibility of recovering the metal (Malik, Jain and Yadav 2018). There are different adsorbents available for the removal of heavy metals in wastewater such as zeolites, clay minerals, industrial by-products, activated carbon, charcoal and resins but adsorbents have been reported to be costly (Sepehrian *et al.* 2010; Chand *et al.* 2014; Wang *et al.* 2018).

2.4 Adsorbents used in wastewater treatment

2.4.1 Zeolites

Zeolites are aluminosilicates which occur naturally or can be synthesized by industries. They consist of oxygen atoms mutually binding their tetrahedral molecules (Shcherban *et al.* 2018; Belova 2019). One of the properties of zeolites that contribute to their effectiveness in heavy metal removal is their ion exchange capabilities (Tripathi and Ranjan 2015). Their large surface areas and hydrophilic nature make them suitable for extracting heavy metals (Burakov *et al.* 2018). Zeolites exist in various species such as chabazite and clinoptilolite. The ion exchange capabilities of the most naturally occurring clinoptilolite has made it the most effective adsorbent amongst other species. Burakov *et al.* (2018) reported on the heavy metal selectivity of the sodium form zeolite to ascend in the following order $Pb^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Cr^{6+} > Zn^{2+} > Ni^{2+} > Hg^{2+}$. Clinoptilolite has been widely evaluated by researchers and has exhibited high selectivity for Zn (II), Pb (II), Cd (II), and Cu (II). Modified zeolites were found to be more effective than the natural form. Replacing Si^{4+} and Al^{3+} based zeolites with K^+ , Na^+ , Mg^{2+} or Ca^{2+} has proved to significantly enhance the efficiency of the zeolites. According to Burakov

et al. (2018) when modified zeolite was used to remove Cd^{2+} at the optimum pH of 5.0, the maximum adsorption capacity was found to be 838.7 mg/g and a removal percentage of 80% was achieved. Tahoon *et al.* (2020), also concur that modified clinoptilolite zeolite exhibited excellent removal of cadmium from water with an adsorption capacity of 138.9 mg/g.

2.4.2 Clay minerals

Clay minerals are divided into three classes namely, bentonites, kaolinite, and mica. They have ion exchange capabilities and bentonite have the greatest ion exchange capabilities amongst mineral adsorbents (Burakov *et al.* 2018). Although clay mineral adsorbents do not have the greatest removal capacity their advantages of having high surface area, low cost, plasticity, large zeta potential and resistance to wear keeps them as efficient adsorbents. They cost 0.03 to 0.12 USD/kg which is 20 times cheaper than activated carbon, however their cost is higher than that of agricultural waste. In one of the studies, clay proved to be effective in the removal of copper, nickel, and zinc with the adsorption capacities of 83.3 mg/g, 80.9 mg/g and 63.2 mg/g respectively (Meez, Rahdar and Kyzas 2021).

2.4.3 Industrial by-products

Industries involved in certain activities during their operations, produce solid waste and by-products. These by-products, which are infrequently used, can be used to remove heavy metals from wastewater and reduce environmental pollution and disposal costs. Fly ash, red mud, waste sludge, lignin from paper production and blast furnace are amongst the industrial solid waste that have been used by researchers to effectively remove heavy metals from wastewater (Burakov *et al.* 2018). Industries using coffee beans, tea leaves, grapes, sugar beet, olives and many other agricultural products as their raw material generate waste that can be utilized as low-cost adsorbents. (Zwain, Vakili and Dahlan 2014) in their study reported the use of various adsorbents such as lignin, waste sludge, cassava waste, bentonite and dried marine green macroalgae for the removal of zinc in wastewater. Powdered waste sludge achieved a

maximum adsorption capacity of 168 mg/g which was higher than that of marine green macroalgae which was 128mg/g. Maximum adsorption capacities of lignin, cassava waste and bentonite were 73.2 mg/g, 55.82 mg/g and 52.91 mg/g respectively. Red mud has benefits of possessing high metal adsorption capacity. Though dealing with sludge generated and the wastewater treated with red mud was found difficult, nevertheless (Chi, Zhu and Langdon 2007) obtained novelty in using red mud adsorbent for the removal of Cd²⁺ in wastewater.

2.4.4 Activated carbons

Commercial activated carbon (CAC) is currently the most used adsorbent not solely due to its efficiency in removing heavy metals but because of its capacity to remove other pollutants in wastewater (Malik, Jain and Yadav 2018). Coal, wood, and coconut are generally the originators in the production of activated charcoal, and this makes it costly. Activated carbons have been extensively used adsorbents due to their structural characteristics, namely, highly porous structure, fairly large surface area, and various functional groups such as hydroxyl, carboxyl, phenol, carbonyl and a few others (Burakov *et al.* 2018). (Gupta 2009; Gupta *et al.* 2016) refers to commercial activated carbon as the best adsorbent in treating heavy metals in effluent till to date. However, due to activated carbon drawbacks such as secondary sludge generation and being costly, several researchers have embarked on investigating agricultural waste activated carbon, agricultural waste in their origin or modified forms or by-products for the removal of heavy metals in wastewater as a viable alternative.

2.5 Agricultural waste adsorbents

Several researchers have reported that agricultural waste products are a form of low-cost adsorbents that have proven to be effective in the removal of heavy metals in wastewater. Adsorbents derived from agricultural waste have gained worldwide popularity due to their abundance in nature, low or no cost at all and the potential to effectively remove heavy metals from wastewater. A variety of biomass materials such as sugarcane bagasse (SCB), sawdust,

rice hulks, coconut shells, palm shells, apple pomace, fruit peels and other agricultural waste have been investigated as adsorbents in the removal of heavy metals in wastewater (Chand *et al.* 2014; Zhang *et al.* 2017; Sheick *et al.* 2018). It has however been established that the modified plant wastes present increased adsorption capacities in comparison to their unmodified counterparts (Pham *et al.* 2015). Khoramzadeh, Nasernejad and Halladj (2013) demonstrated that the efficiency for the removal of Hg in water was greater for the modified SCB than unmodified SCB. Ngah and Hanafiah (2008), reports that the use of unmodified biomass wastes as adsorbents often present several concerns such as low adsorption capacities, high chemical oxygen demand (COD), biological chemical demand and total organic carbon.

Low efficacy for the unmodified plant wastes is attributed to the presence of organic compounds in the plant which escalates COD, BOD and TOC which depletes oxygen leading to the demise of aquatic organism instead of heavy metal removal (Ngah and Hanafiah 2008). Unmodified SCB for example contains about 40 to 50% cellulose, 25 to 35% hemicellulose and 15 to 20% lignin (Rezende *et al.* 2011; Asl, Mousavi and Labbafi 2017). The presence of high content of highly reactive functional groups such as hydroxyl groups makes modification of agricultural waste such SCB viable thereby improving the adsorption capacity (Wei *et al.* 2013; Ferreira *et al.* 2015; Sun, Wen and Yan 2018). SCB is rich in hydroxyl and phenolic groups making it an interesting candidate for modification. Other studies investigated the use of rice husks (Hegazi 2013), modified and unmodified sawdust (Ngah and Hanafiah 2008), modified and unmodified fruit peels or pulps of bananas, avocado, pineapples, dragon, and watermelon (Lasheen, Ammar and Ibrahim 2012; Chand *et al.* 2014; Mallampati *et al.* 2015; Romero-Cano *et al.* 2017) for the removal of metal ions such Pb, Cu, Zn, As, Cd and Co. Other biomass materials such as modified and unmodified *Tithonia Diversifolia* commonly known as Mexican sunflower due to their origin were reported to be effective in the removal of Ni (Okoronkwo, Igwe and Ogbonna 2008).

Sheick *et al.* (2018), however noted that while the sawdust was effective as an adsorbent in the removal of Cu, Co, and Zn ions from water, the adsorption of Zn and Co ions were severely affected by the presence of Cu ions. It becomes apparent then that to assess the adsorption capacity of the adsorbent in the removal of any ion in water, single metal ions must first be investigated to eliminate the possibility of interference with other ions. The type of biomass waste really depends on its local availability. KwaZulu-Natal, South Africa, is the leading producer of sugar and alcohol in Africa which in turn produces abundant SCB. Notwithstanding the use of SCB by the alcohol industry and sugar mills as the source of energy, a sizeable amount that still needs to be disposed remains (Chambon *et al.* 2018).

2.5.1 Low-cost adsorbents derived from agricultural products

The relevance of utilising industrial and agricultural leftovers as manufacturing starting materials is highlighted by the latest trends in the material world. Reusing and recycling these wastes can cut back on the usage of noble starting materials while minimizing the environmental issues caused by their build-up. The use of conventional biomaterials, such as natural lignocellulosic fibres instead of synthetic polymers, for example, has been given some thought due to their superior performance (Karnitz Jr *et al.* 2007). Agricultural residues are commonly employed for adsorption purposes, either in their original form or after undergoing modification. Even in their natural state, these residues can exhibit effective adsorption properties. Scientists are investigating new biosorbents that could retrieve metals, while keeping expenses low and reducing the need for secondary waste treatment resulting from the adsorption process. Agricultural residues, which contain a significant amount of cellulose, are suitable for adsorption purposes. However, there are operational challenges associated with using them as adsorbents. These issues include low adsorption capacity in their natural state and the leaching of colour, as seen in peanut skins. To address these problems, the adsorbent can be modified chemically or physically (Jamshaid *et al.*, 2017).

2.5.2 *Fruit peels*

Several researchers have assessed fruit peels as cheap adsorbents due to their abundance. Orange peel, banana peel, and pineapple peel are the most popular biomass wastes that researchers investigate. Fruit peels contain cellulose, hemicellulose and pectin substances and they contain hydroxyl and carboxyl groups which are good binding sites for metals. (Lasheen, Ammar and Ibrahim 2012), reported that oranges represent about 75% of the citrus family, hence they generate enormous amount of waste, and they cause a major disposal problem. (Lasheen, Ammar and Ibrahim 2012) successfully removed cadmium, lead and copper from synthetic water using modified and unmodified orange peels. Removal of copper using orange and pineapple peels treated with Instant Controlled Pressure Drop (DIC) and some further functionalized with citric acid was assessed. The fruit peel adsorbent that was physically treated with DIC and then chemically treated with citric acid resulted in a maximum adsorption capacity of 163 mg/g and an enhanced capacity of 4.19 times was observed compared to the fruit peels that were only treated with DIC (Annadurai, Juang and Lee 2003; Romero-Cano *et al.* 2017). Annadurai, Juang and Lee (2003), utilized acid and alkali modified orange and banana peels for the removal of Pb^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} and Co^{2+} in water. Adsorption capacities descended in the order of Pb^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} , Co^{2+} for both orange and banana peels. According to this study, banana peels displayed a higher adsorption capacity for heavy metals in relation to orange peels (Meez, Rahdar and Kyzas 2021).

2.5.3 *Saw dust*

Saw dust is a biodegradable low-cost material that is generated by sawmills as their waste. Like most agricultural waste, saw dust constitutes cellulose, hemicellulose, and lignin. Sawdust is a readily available and cost-effective adsorbent that can effectively remove heavy metals from water and wastewater (Wang *et al.* 2018). Sawdust contains functional groups such as COOH and OH that bind with metal ions, causing them to release H^+ ions. The various mechanisms

by which metal ions bind to cellulosic sorbents such as sawdust include chelation, ion exchange, complexation with functional groups, and hydrogenic bonding. Studies have shown that cellulosic materials, including sawdust, can accumulate heavy metals such as Cu (II) in the secondary septum of wood, which is rich in cellulose and poor in lignin. Several researchers have investigated the efficacy of sawdust and wood-derived materials such as poplar, willow, fir, oak, and black locust sawdust, pulp, and kraft lignin for removing toxic heavy metals such as Cd (II) and Ni (II) from aqueous solutions (Asadi, Shariatmadari and Mirghaffari 2008).

2.5.4 Rice husks

Large amounts of agricultural waste, particularly rice husk, which is a by-product of the rice milling industry, are created which causes environmental issues. Rice husk is appropriate for the fixation of metallic cations since it mostly comprises of crude protein (3%), ash (containing silica 17%), lignin (20%), hemicellulose (25%), and cellulose (35%) (Krishnani *et al.* 2008). Rice husks has a unit weight of 125 kg/m³ and can absorb up to 15% of water by weight. The ash from rice husks contains 90% silica and is very porous, light, and has a large surface area (Baiju *et al.* 2022). The removal of several heavy metals and metalloids such as Pb, Cd, Zn, Ni, and As, from both groundwater and surface water has been extensively explored using rice husk (RH), a low-cost agricultural by-product, bio adsorbent (Lata and Samadder 2014). Compared to untreated adsorbent, rice husk treated adsorbent is better at removing heavy metals from wastewater. This is due to the untreated adsorbent having low adsorption capacity, high chemical oxygen demand, biological oxygen demand and total organic carbon because of the release of soluble organics compounds in plant materials (Lata and Samadder,2014). According to Sobhanardakani *et al.* (2018) the pH range of 2 to 5 showed the largest increase in the sorption rate of Cr and Cu ions on husk. The author also noted that as pH increased, Cr(III) or Cu(II) sorption percentages increased as well, reaching maximums of 55 and 65%, respectively at pH 6.0. With a pH increase from 1.0 to 7.0, the percentage of Cr(III) removal

increased from 7 to 55%. Cu(II) sorption percentage increased as pH increased, peaking at pH 6.0 at 67%. With a pH increase from 1.0 to 7.0, the percentage of Cu(II) removal increased from 7 to 66%. This is in line with the conclusions of other researchers, including (Wong *et al.* 2003).

2.5.5 *Sugarcane bagasse*

Saccharum Officinarum is one of the most significant crops in the world and is commonly known as sugarcane bagasse. It ranked as the 12th most significant crop globally in 2016 with a total harvest of 26,774,304 ha, or 1.93% of the world's harvested area. In the same year, 1,890,661,751 tons of sugarcane were produced, making it the world's most significant crop in terms of volume and accounting for 2101 of all crop production globally (Figueroa-Rodriguez *et al.* 2019). The world's largest producer of sugarcane for the alcoholic beverage and sugar sector in Brazil (41%), followed by India (16%), China (6%), Thailand (6%) and the remaining 31% is shared amongst other 100 sugarcane growing countries (Figueroa-Rodríguez *et al.* 2019). Sugarcane bagasse is the residue in the form of pulp that remains when the sugar has been extracted from sugarcane (Khoramzadeh, Nasernejad and Halladj 2013). Sugarcane bagasse is produced in vast quantities by these sectors, and even though it is burned to provide energy for sugar mills, leftovers are still substantial. Thus, there is a lot of interest in creating chemical processes for recycling sugarcane bagasse due to its significance as an industrial waste. Bagasse made from sugarcane has around cellulose, polyoses, and lignin (Karnitz Jr *et al.* 2007). The glucose polymer cellulose, which makes up around 40–50% of SCB and is largely crystallized, is present. Hemicelluloses, an amorphous polymer often made of xylose, arabinose, galactose, glucose, and mannose, make up the remaining 25–35%. The remaining material is mainly made up of lignin, with minor amounts of wax, mineral, and other substances (Sun *et al.* 2004). With estimations of 1011 tonnes of global biosynthesis every year, cellulose, the primary component of all plant materials, makes up around half to one third of plant tissues.

The biopolymers present in sugarcane bagasse are polysaccharides that contain numerous hydroxyl, and or phenolic groups. These groups can be subjected to chemical modification, leading to the creation of novel compounds with altered properties. For example, the hydroxyl groups in cellulose and hemicellulose can be modified to introduce new functional groups such as carboxyl, amino, or sulfonic acid groups. These modifications can improve the solubility, reactivity, and other properties of the polysaccharides, making them more useful for various industrial applications. In addition, the phenolic groups in lignin can be modified to create value-added products such as adhesives, resins, and antioxidants. Lignin-based compounds can also be used as renewable precursors to produce high-value chemicals such as vanillin, syringaldehyde, and others (Homagai, Ghimire and Inoue 2010). Overall, the chemical modification of polysaccharides from sugarcane bagasse can provide a sustainable source of novel compounds with various industrial applications (Homagai, Ghimire and Inoue 2010).

2.6 Cellulose

Cellulose is the major component of plants, specifically wood, cotton, sugarcane bagasse, flax, hemp, jute, ramie, cereal straws, etc. It has sparked a lot of scientific interest due to its abundance and a potential biosorbent in wastewater treatment. Cellulose possesses interesting qualities such as strong mechanical properties, low density, thermal stability, biocompatibility, and biodegradability (Saelee *et al.* 2014). Various types of cellulose with distinct mechanical and pharmaceutical characteristics are obtainable in the market in diverse forms. The variability in the properties of these forms is linked to the shape, size, and level of crystallization of their particles, either in a fibrous or agglomerated state. Microcrystalline cellulose (MCC) is the cellulose type that is widely recognized and utilized in the pharmaceutical sector (Oprea and Voicu 2020).

Due to their advantageous characteristics, isolated cellulosic fibers, and their derivatives have attracted interest for their applications ranging from paper, packaging, sensors, water

purification, and textiles to biomedical devices and drug delivery (Melesse, Hone and Mekonnen 2022). Chemically, cellulose is a linear natural polymer made up of anhydroglucose units joined by -glycosidic linkages at the one and four carbon atoms. This is supported by the production of several strong intermolecular and intramolecular hydrogen bonds as well as the presence of three hydroxyl groups with varying reactivity: secondary OH at position C-2, secondary OH at position C-3, and primary OH at position C-6 (Sun *et al.* 2004; Saelee *et al.* 2014).

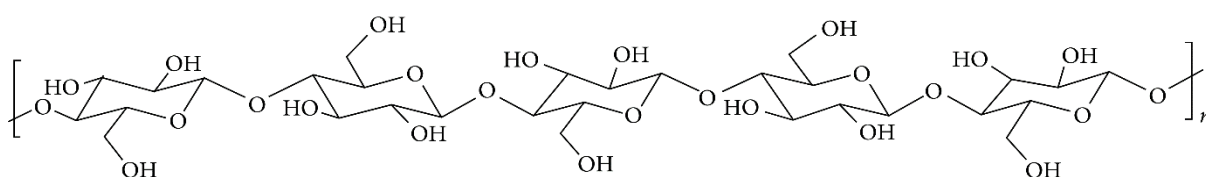


Figure 2.1: Chemical structure of cellulose (Melesse, Hone and Mekonnen 2022)

The general equation for the adsorption of heavy metals by cellulose can be represented as follows:



In this equation, R-OH represents the hydroxyl groups present in the cellulose molecule, which serve as the adsorption sites for heavy metal ions ($\text{M}(\text{H}_2\text{O})_m$). When the heavy metal ions come into contact with the cellulose, they bind to the hydroxyl groups through coordination bonds, forming a complex (R-M). The number of hydroxyl groups available for adsorption depends on the degree of polymerization of the cellulose, which refers to the number of glucose units in the polymer chain. Generally, cellulose with a higher degree of polymerization has more hydroxyl groups available for adsorption, resulting in a higher adsorption capacity for heavy metals. The adsorption process is pH-dependent, and the optimal pH for adsorption varies depending on the type of heavy metal and the type of cellulose used. At pH values lower than the optimal pH, there may be competition between protons and heavy metal ions for the

adsorption sites, leading to a decrease in adsorption efficiency. At pH values higher than the optimal pH, the hydroxyl groups may become deprotonated, resulting in a decrease in the adsorption capacity.

As a biopolymer, cellulose has been employed in various ways, including as a construction material, such as intact wood, cotton or flax fibers in textiles, and paper and board. Furthermore, cellulose is a versatile raw material that can undergo chemical transformations, leading to the production of cellulose-based threads and films, as well as a broad range of stable cellulose derivatives used in numerous industries and daily activities (Hokkanen, Bhatnagar and Sillanpää 2016). The cellulose derivatives have the potential to increase the effectiveness of the wastewater treatment procedure, particularly in eliminating heavy metal ions. Compared to its unmodified form, chemically altered versions of cellulose provide greater adsorption capacities. Numerous approaches are available for the modification of cellulose, which comprise but are not confined to techniques such as esterification, halogenation, etherification, oxidation, and grafting. These methods can be accomplished by using a diverse range of agents, including mineral and organic acids and bases, organic and inorganic compounds, and oxidizing agents.

2.6.1 Cellulose derivatives

Cellulose ethers and cellulose esters are the two primary categories of cellulose derivatives, each possessing distinct physicochemical and mechanical characteristics. These polymers are widely employed in the development of dosage forms and healthcare items. They also have significant applications in various pharmaceuticals, including extended and controlled release matrices, osmotic drug delivery systems, bioadhesives and mucoadhesives, compression tablets as compressibility enhancers, thickening agents and stabilizers in liquid dosage forms,

binders in granules and tablets, gelling agents in semisolid preparations, and many more (Shokri and Adibkia 2013).

2.6.2 Cellulose ether derivatives

Cellulose ethers are large molecules generated by substituting the hydrogen atoms of hydroxyl groups within the anhydroglucose units of cellulose with alkyl or substituted alkyl groups (Oprea and Voicu 2020). According to Shokri and Adibkia (2013) the most utilized types of cellulose ethers include methyl cellulose (MC), ethyl cellulose (EC), hydroxyethyl cellulose (HEC), hydroxypropyl cellulose (HPC), hydroxypropylmethyl cellulose (HPMC), carboxymethyl cellulose (CMC), and sodium carboxymethyl cellulose (NaCMC).

2.6.3 Carboxymethyl cellulose

Hassan *et al.* (2014) states that carboxymethylcellulose, which is considered a significant type of cellulose ether, is produced through a series of steps involving the treatment of raw cellulose with a sodium hydroxide solution, extraction of the resultant alkali cellulose, and subsequent reaction with monochloroacetic acid or sodium monochloro-acetate in an alcohol-based medium. Upon completion of the etherification procedure, a lengthy, linear polysaccharide chain with exposed carboxyl and hydroxyl groups is generated. This distinctive chemical composition grants carboxymethyl cellulose the ability to react chemically and dissolve in water (Zulkifli, Rani and Shahitha 2019).

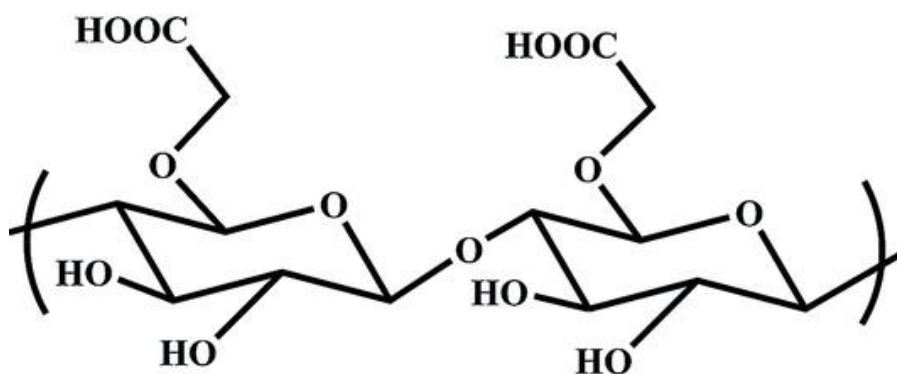


Figure 2.2: Chemical structure of carboxy methyl cellulose (Melesse, Hone and Mekonnen 2022)

The presence of numerous hydroxyl and carboxyl groups in CMC has made it an effective adsorbent for the removal of heavy metal ions (Hu *et al.* 2022). According to Sun *et al.* (2022), the CMC hydrogels that were prepared has a promising potential for use in wastewater treatment and removal of heavy metal ions. The highest efficiency of adsorption was observed within 180 minutes, with maximum adsorption capacity values of 200.44 mg/g and 192.28 mg/g for Cu (II) and Zn (II) respectively. Additionally, Godiya *et al.* (2019) observed that the pristine CMC hydrogel exhibits a maximum adsorption capacity of 99.01 mg/g, 86.95 mg/g, and 172.41 mg/g for Cu(II), Pb(II), and Cd(II) ions, respectively. Table 2.1 shows the comparison of the effectiveness of SCBC with other adsorbents for the removal of Ni (II), Zn (II), Cd(II) from wastewater.

Table 2.1: Comparison of the effectiveness of sugarcane bagasse cellulose with other adsorbents for Ni (II), Zn (II), and Cd (II) from wastewater

Adsorbent	Modifying agent	Heavy metal	Q_{\max} (mg g ⁻¹)	Reference
Unmodified SCB	-	Zn ²⁺	107.9	Singh <i>et al.</i> 2019
Sugarcane bagasse cellulose		Cd ²⁺	92.6	(Karnitz Jr <i>et al.</i> 2007)
Sugarcane bagasse cellulose	NaOH, H ₂ SO ₄	Cd ²⁺	250	(Homagai, Ghimire and Inoue 2010)
(2010)		Ni ²⁺	167	(Homagai, Ghimire and Inoue 2010)
(2010)		Zn ²⁺	200	(Homagai, Ghimire and Inoue 2010)
Zeolite from flash		Zn ²⁺	34.40	(Hui, Chao and Kot 2005)
		Ni ²⁺	52.12	(Hui, Chao and Kot 2005)
Rice husk ash		Cd ²⁺	3.02	(Taieban <i>et al.</i> 2012)
		Ni ²⁺	4.87	(Taieban <i>et al.</i> 2012)
Bagasse fly ash		Ni ²⁺	6.51	(Taieban <i>et al.</i> 2012)
Tea factory waste	-	Ni ²⁺	15.26	(Torab-Mostaedi <i>et al.</i> 2013)
Corn stalk	Acrylonitrile	Cd ²⁺	12.73	(Gou <i>et al.</i> 2019)
Coffee husk	-	Zn ²⁺	5.6	(Gou <i>et al.</i> 2019)
Agave bagasse	-	Cd ²⁺	14.0	(Gou <i>et al.</i> 2019)
	-	Zn ²⁺	8.0	(Gou <i>et al.</i> 2019)
Parthenium hysterophorus - 2009)		Ni ²⁺	17.24	(Motsi, Rowson and Simmons 2009)
Zeolite (clinoptilolite)	-	Zn ²⁺	2.21	(Motsi, Rowson and Simmons 2009)
Synthetic zeolite flash	NaOH	Ni ²⁺	52.12	He <i>et al.</i> 2015
		Zn ²⁺	34.40	He <i>et al.</i> 2015
Synthetic zeolite	L-carnitine	Ni ²⁺	78.94	Hong <i>et al.</i> 2019

CHAPTER 3: THEORETICAL PRINCIPLES

In this chapter, the theoretical principles of instruments used in this study were briefly explained.

3.1 Atomic Absorption Spectroscopy (AAS)

Atomic absorption spectroscopy (AAS) is a technique used to analyse the concentration of specific elements in a sample. It is based on the principle that atoms absorb light at specific wavelengths, which correspond to their electronic energy levels. The process involves passing a beam of light, typically from a hollow cathode lamp, through the sample containing the element of interest. The light source emits radiation at a characteristic absorption wavelength of the element. When the light passes through the sample, the atoms of the element absorb the light energy at specific wavelengths.

The absorption of light by the atoms is measured using a detector, such as a photomultiplier tube or a photodiode. The detector quantifies the amount of absorbed light, which is directly proportional to the concentration of the element in the sample. By comparing the absorption to a calibration curve generated from standards of known concentrations, the exact concentration of the element in the sample can be determined. Atomic absorption spectroscopy is widely used in various fields, including environmental analysis, pharmaceuticals, agriculture, food and beverage industry, and forensic sciences. It is particularly useful for the analysis of trace metals and is known for its high sensitivity and selectivity (García and Báez 2012).

3.1.1 *Flame Atomic Absorption Spectroscopy (FAAS)*

Flame atomic absorption spectroscopy (FAAS) is a technique used in AAS that utilizes a flame as the atomization source. It is one of the most common and widely used methods for elemental analysis in various fields. In FAAS, the sample is typically dissolved in a suitable solvent and introduced into a flame. The flame serves two main purposes: atomization and excitation.

Atomization: The primary function of the flame is to convert the analyte in the sample into atomic form. As the sample enters the flame, it undergoes vaporization, desolvation, and ultimately decomposes into individual atoms. This process is facilitated by the high temperature of the flame, which breaks down the chemical bonds in the sample and converts the analyte into atomic species.

Excitation: Once the analyte is in atomic form, a hollow cathode lamp (HCL) is used as the light source. The HCL emits light at the characteristic absorption wavelength (s) of the element being analysed. The emitted light is focused into a beam and passed through the flame containing the atomized analyte. Atoms of the element in the flame absorb the specific wavelengths of light corresponding to their electronic transitions, resulting in the attenuation of the light intensity and the absorbed light is then quantified using a detector.

Flame atomic absorption spectroscopy offers several advantages, including relatively low cost, simple instrumentation, high sensitivity, and wide elemental coverage. It is commonly used for the analysis of metals and metalloids in various samples, such as environmental samples, pharmaceuticals, food and beverages, and clinical specimens (Welz and Sperling 2008; García and Báez 2012).

3.2 Fourier Transform Infrared (FTIR)

FTIR spectroscopy is an experimental method that was initially developed for the purpose of qualitatively and quantitatively analysing organic compounds. It offers valuable insights into molecular structure, chemical bonding, and the molecular environment, thereby providing specific and detailed information.

The fundamental principle of an FTIR spectrometer involves splitting an incoming infrared light beam into two separate beams using an optical beam splitter. These beams have their optical path difference adjusted by a movable mirror for one beam and a fixed mirror for the

other. The two beams are then combined using an optical combiner, resulting in interference. This process generates an interference signal that relies on the optical path difference and can be detected using standard infrared detectors. In the case of a monochromatic emission line, the interference signal takes the form of a cosine function based on the optical path difference. For polychromatic light sources, a more complex function called the interferogram is obtained. It can be demonstrated that this interferogram, which represents the detector signal as a function of the optical path difference (usually measured in centimetres), corresponds to the Fourier transform of the original spectrum. The original spectrum represents the signal as a function of inverse wavelengths (usually measured in units of cm^{-1} , commonly referred to as wavenumbers). To retrieve the original spectrum from the measured interferogram, a numerical Fourier transformation is performed using a fast Fourier transform algorithm (Anderson, Bendell and Groundwater 2004; Kötting *et al.* 2010)

3.3 X-Ray Diffraction (XRD)

X-ray diffraction is an effective method that does not cause damage to materials and is used to examine the properties of crystalline substances. It offers insights into structures, phases, preferred crystal orientations (texture), as well as other structural characteristics including average grain size, crystallinity, strain, and crystal defects. X-ray diffraction peaks occur when a monochromatic X-ray beam scatters at particular angles from sets of lattice planes within a sample, resulting in constructive interference. The intensity of these peaks reflects the arrangement of atoms within the lattice. As a result, the X-ray diffraction pattern serves as a unique identifier of the periodic atomic structure present in a specific material (Bunaciu, UdrişTioiu and Aboul-Enein 2015).

X-rays are created using a cathode ray tube, then filtered to generate monochromatic radiation. They are further collimated to concentrate the beam and directed towards the sample. When

these incident X-rays interact with the sample, they undergo constructive interference, resulting in a diffracted ray. This phenomenon follows Bragg's law, which states that constructive interference occurs when the conditions of the equation (1)

$$n\lambda = 2d \sin \theta \quad 1$$

are met. Where, n represents an integer, λ stands for the X-ray wavelength, d is the interplanar spacing responsible for the diffraction, and θ represents the angle of diffraction (Epp 2016; He 2018).

3.4 Scanning Electron Microscope (SEM)

SEM is a highly adaptable and sophisticated tool commonly used to study the surface characteristics of various materials. In a SEM, the sample is subjected to high-energy electrons, and the resulting electrons or X-rays are examined. These emitted electrons or X-rays provide valuable insights into the topography, morphology, composition, grain orientation, crystallographic details, and other properties of the material (Akhtar *et al.* 2018; Kannan 2018a). Topography refers to the surface characteristics of an object, including its appearance and texture, which are directly linked to properties such as hardness and reflectivity. Morphology pertains to the shape and size of the particles comprising the object, and these structures have a direct impact on properties such as ductility, strength, and reactivity. Composition denotes the elements and compounds present in the object, along with their relative amounts, and this composition directly influences properties such as melting point, reactivity, and hardness. Crystallographic information refers to the arrangement of atoms within the object, and these arrangements have a direct relationship with properties such as conductivity, electrical properties, and strength (Kannan 2018a). In some instances, SEM is coupled with Energy-Dispersive X-ray (EDX). EDX spectroscopy is utilized in the identification of the elemental composition of a substance through the use of a scanning

electron microscope. EDX is capable of detecting elements with atomic numbers higher than boron, and these elements can be detected even at concentrations as low as 0.1%. The application of EDX encompasses various areas, including material evaluation and identification, identification of contaminants, spot detection analysis of regions up to 10 cm in diameter, quality control screening, and more (Abd Mutalib *et al.* 2017).

3.5 Transmission Electron Microscope (TEM)

In TEM, a high-voltage electron beam is generated by heating a tungsten filament (cathode). The electrons are then guided towards an anode using magnetic lenses and pass through an aperture. After traversing the aperture, the electron beam goes through electromagnetic condenser, objective, intermediate, and projector lenses. The concentrated electron beam is directed through an extremely thin specimen (with a size of 50nm), which is partially transparent to electrons and contains valuable structural information. The specimen is placed on a grid within the beam path and can be adjusted using a goniometer. A portion of the beam is absorbed, scattered, or transmitted through an objective aperture, and it is eventually projected onto a fluorescence screen after being corrected by intermediate lenses and focused by a projector lens.

The beam is divided into different components: some are absorbed, some are scattered, and some are transmitted through an objective aperture. These components are then projected onto a fluorescence screen after being corrected by intermediate lenses. The resulting image can be observed using an optical binocular connected to the viewing window. To enhance the spatial details in the image, a series of magnetic lenses magnify the image until it is captured by striking a fluorescent screen or a light-sensitive sensor like a CCD camera. This camera can be positioned either on the side or at the bottom of the photographic plate. The contrast in the image is primarily generated through electron scattering instead of differences in absorbance. Scattering occurs when the electrons of the illuminating beam interact with the atoms in the

specimen. The repulsion between the negatively charged electron clouds surrounding atomic nuclei leads to the scattering of electrons. This scattering effect becomes more pronounced as the electrons come closer to the specimen atoms. Nuclei with higher atomic numbers, such as those found in heavy metals like lead and uranium, cause more significant scattering. Transmission electron microscopes (TEMs) generate black and white, two-dimensional images. With the TEM, it is possible to achieve high-resolution imaging of structures such as ribosomes, microtubules, microfilaments, and large molecules like proteins. In fact, under specific operating conditions, it is even possible to capture images of individual heavy metal atoms. The main components in a typical SEM include the electron source, column which contains electromagnetic lenses, electron detector, sample chamber, and the computer display (Abd Mutalib *et al.* 2017; Tanaka 2017; Kannan 2018b).

CHAPTER 4: EXPERIMENTAL

4.1 Materials and characterization

The following chemicals and reagents were purchased from Merck, Germany; Sulphuric acid (98%), Sodium hydroxide (99%), Hydrogen peroxide (30V), Ethanol (99,9%), Magnesium sulphate, (98%), Nickel sulphate (99%), Zinc chloride (99%), Cadmium chloride (98%). Monchloroacetic acid (MCA) was purchased from Sigma-Aldrich.

Surface areas of adsorbents was studied using the Burner, Emmer and Teller (BET) method using N₂ as the gas at 77 K using Micromeritics Tristar II instrument. Thermogravimetric studies were done using the SDT Q600 thermal analyser in static air atmosphere at a heating rate of 10°C min⁻¹. The functional groups of adsorbents were studied using a Perkin Elmer Spectrum 100 FT-IR (ATR) equipped with a diamond crystal scanning from 300 to 4000 cm⁻¹. Crystallinity, phases, and diffraction patterns of materials was studied using the Bruker D8 XRD operating CuK α radiation source with wavelength, $\lambda = 1.54056 \text{ \AA}$, generated at 40 kV and 40 mA. Signals corresponding the 2θ values were recorded between 5° and 90°.

4.2 Preparation of adsorbent material

Sugarcane bagasse (SCB) was collected from the Council of Scientific and Industrial Research (CSIR) site located in the University of KwaZulu-Natal (UKZN), Howard College Campus. SCB was washed with hot water at approximately 60 C. It was then dried in an air oven at 70 °C for 24 hours. A heavy-duty blender purchased from Lasec was used to grind the SCB.

4.3 Preparation of cellulose from sugarcane bagasse

Isolation of cellulose from sugarcane bagasse was achieved by exposure to acid pretreatment, alkaline pretreatment, and bleaching. The experimental procedure below was adopted from Candido and Gonçalves 2019.

4.4 Acid pre-treatment

A 5-L glass beaker flask was used to combine 100 g of SCB and 1 L of H₂SO₄ solution with a concentration of 10% (v/v). The mixture was stirred at 100 °C for 1 hour. After the reaction time elapsed, the mixture was subjected to vacuum filtration and then rinsed with distilled water until a neutral pH was reached. The resulting material was air-dried at room temperature and kept for future procedures and characterization (Candido and Gonçalves 2019).

4.5 Alkaline pre-treatment

A polypropylene beaker with a capacity of 5 L was used to combine 50 g of acid-treated SCB and 500 mL of NaOH solution with a concentration of 5% (m/v). The mixture was stirred at 100 °C for 1 hour. After the reaction time elapsed, the mixture was subjected to vacuum filtration and then rinsed with distilled water until a neutral pH was reached. The resulting material was air-dried at room temperature and kept for future procedures and characterization (Candido and Gonçalves 2019).

4.6 Bleaching

The bleaching process was performed by utilizing polypropylene bags containing a solution consisting of 5% (v/v) hydrogen peroxide (H₂O₂) and 0.1% magnesium sulphate (MgSO₄). The bags were maintained at a temperature of 70 °C for a duration of 1 hour. The consistency of the mixture was 5% (w/v), and the pH level was adjusted to 12 by adding concentrated sodium hydroxide (NaOH). Once the designated time had elapsed, the material underwent filtration and was subsequently rinsed with distilled water at 70 °C until reaching a neutral pH (Candido and Gonçalves 2019).

4.7 Preparation of carboxymethylcellulose

In a 500 mL three-neck flask, the following components were introduced: 5 g of sugar cane bagasse cellulose (SCBC), 92.5 g of ethanol, 3.7 g of water, and a solution containing about 5 g of sodium hydroxide (NaOH) dissolved in about 8 g of water. The mixture was then stirred for one hour at a temperature of 15 °C. Subsequently, a solution consisting of MCA and ethanol (50% w/w) was added, resulting in an MCA-to-cellulose mole ratio of 8.8:1. The temperature was then raised to 60 °C, and the reaction was allowed to proceed for three hours. After this period, the suspension was filtered, and the resulting carboxymethylated product was washed with a mixture of methanol and water before drying at room temperature (Candido and Gonçalves 2019).

4.8 Preparation of stock solutions for single metal ion

4.8.1 Preparation of Ni (II), Zn (II), and Cd (II) solutions

A 1000 mg/L stock solutions of Ni(II), Zn (II), and Cd (II) were prepared by weighing of a precise amount of NiSO₄·6H₂O, ZnCl₂, and CdCl₂ respectively. The weighed amounts were then dissolved in deionized water and stored in a refrigerator set at a temperature of 3°C. Subsequently, working standards with concentrations ranging from 50 to 350 mg/L Ni (II), 20 to 120 mg/L Zn (II), and 1 to 60 mg/L Cd (II) were obtained by diluting the stock solution.

4.9 Adsorption studies

4.9.1 Effects of optimization conditions for adsorption

Single metal ions of 100 mg/L of nickel, zinc, and cadmium were prepared as sorbates. The pH range chosen in this study was 2 – 8 adjusted using either 0.1 mol/L NaOH or 0.1 mol/L HCl. Batch samples of a metal ion solution with a concentration of 100 mg/L were used. The pH of the solution was adjusted to 6.5 for Ni (II), 5.5 for Cd (II), and 6.0 for Zn (II) by adding either 0.1 mol/L NaOH or 0.1 mol/L HCl. These samples were then placed in 250 mL stoppered flasks and subjected to shaking on a Stuart SSL1 orbital shaker for one hour at room temperature.

The single metal ion concentrations of 10, 20, 30, 40, 50, 100, 150, 200, 250, and 300 mg/L were used to determine the optimal concentration for each metal ion. The effect of adsorbent dosage was conducted using 0.1, 0.3, 0.5, 0.7, 0.9, 1.1, 1.4 and 1.7 g to determine the optimal dose. The effect of contact time was studied at different time intervals 5, 10, 15, 20, 25, 30, 60, 90, 120, and 150 minutes.

In a typical experiment, 0.10 g of SCB, SCBC, and CMC adsorbents were individually added to each flask containing 50 mL of metal ion, followed by stirring at 250 rpm for different durations. Once the shaking was complete, the solid materials were separated by centrifugation using a Hettich Rotofix 32A centrifuge. The concentration of the metal ions was determined using Agilent 55B flame atomic absorption spectrophotometry (FAAS) at specific wavelengths: Zn at 213.9 nm, Cd at 228.8 nm, and Ni at 232 nm. All experiments were carried out in duplicate.

The removal efficiency and quantity of metal adsorbed were calculated using Equation 2 and 3 below:

$$\% \text{ Removal efficiency} = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (2)$$

Adsorption capacity of the adsorbent is expressed as:

$$\text{Quantity of metal ion adsorbed (mg/g)} = \left(\frac{C_i - C_f}{m} \right) (V) \quad (3)$$

Where C_i and C_f are the initial concentration and final concentration (mg/L) respectively, m is the mass of adsorbent (g) and V is the volume of the metal ion solution (L) (Alomá *et al.* 2012; do Carmo Ramos *et al.* 2016; Ezeonuegbu *et al.* 2021).

Kinetics studies were performed using two models, the pseudo first-order and pseudo second order based on the following equations,

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

$$\text{and } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

The equilibrium conditions were investigated using Langmuir Freundlich adsorption isotherms:

$$\frac{c_e}{q_e} = \frac{1}{KQ_{max}} + \frac{c_e}{Q_{max}} \quad (6)$$

$$\text{and } \ln q_e = \ln k_f + \frac{1}{n} \ln c_e \quad (7)$$

where, K (in L/g) is the equilibrium adsorption constant, Q_{max} (mg/g) is the maximum amount adsorbed per unit mass of adsorbent, k_f and n are Freundlich constants related to adsorption capacity and adsorption intensity

CHAPTER 5 : RESULTS AND DISCUSSION

5.1 Characterization of adsorbents

5.1.1 Fourier Transform Infrared Spectroscopy

Figure 5.1. below exhibits the FTIR spectra of sugarcane bagasse (Fig. 5.1a), sugarcane bagasse cellulose (Fig. 5.1b) and carboxymethyl cellulose (Fig. 5.1c). The spectra of all three adsorbents show a strong and broad absorption peak at $3300 - 3500 \text{ cm}^{-1}$ which is attributed to stretching vibration of -OH groups in cellulose. The spectra of all adsorbents showed a peak at a region of $2800 - 3000 \text{ cm}^{-1}$ indicating C-H stretching vibrations of alkyl and methoxy groups. The peaks observed in $1722 - 1737 \text{ cm}^{-1}$ indicate the C=O stretching of uronic and acetyl groups of pectin in hemicellulose or the ester linkages of carboxylic groups of p-coumaric and ferulic acids of hemicellulose and lignin (Linganiso, Buthelezi and Motaung 2019).

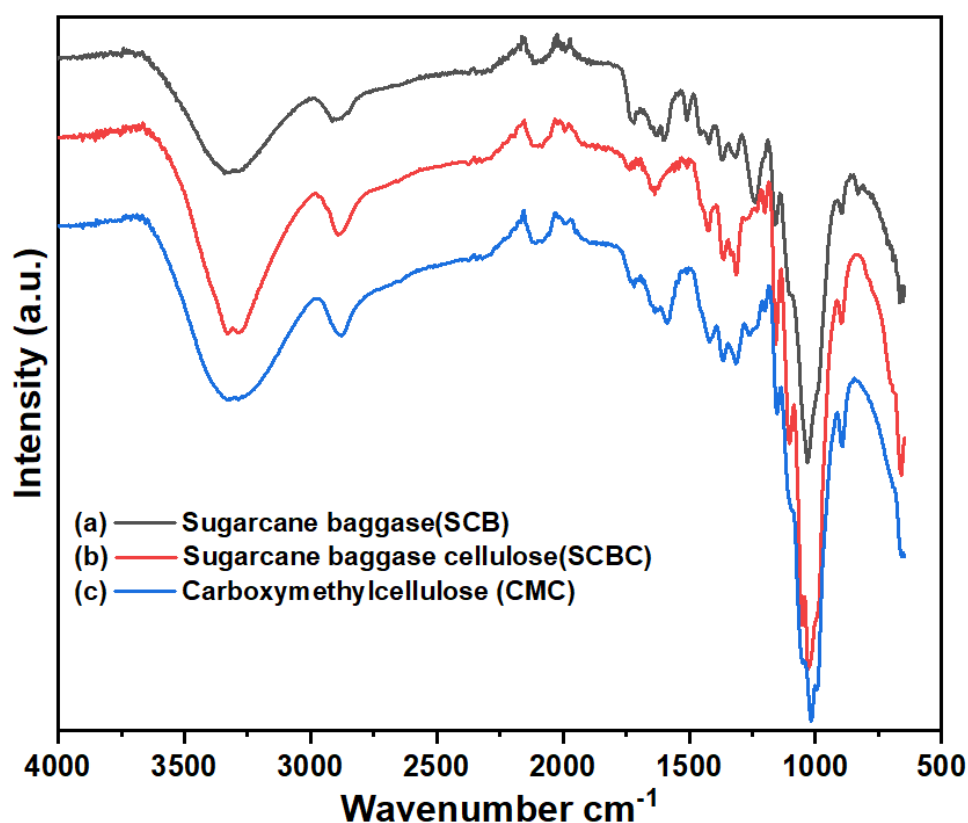


Figure 5.1: FTIR spectra of (a) SCB, (b) SCBC and (c) CMC

The stretching vibration at 1730 cm^{-1} may be present in cellulose derivatives or residual hemicellulose. The peaks observed in the region of $1050 - 1100\text{ cm}^{-1}$ represents the C-O stretching in glycosidic linkages between glucose units in cellulose. Peaks 1423 cm^{-1} and 898 cm^{-1} shows significant cellulose I content (Kumar *et al.*, 2014). The peak observed at 1105 cm^{-1} shows the presence of C-O-C glycosidic ether bands. The bands at 1032 cm^{-1} and 894 cm^{-1} correspond to C-O-C pyranose ring vibration and the stretching C-O-C of the β -(1 - 4)-glycosidic linkage between the glucose units, respectively. The C=O group is represented by the two peaks observed at 1722 cm^{-1} , while the stretching vibration of the (COO-) group is identified by the peaks at 1636 cm^{-1} .

Table 5.1 below shows the experimental frequencies for the sugarcane bagasse, sugarcane bagasse cellulose and carboxymethyl cellulose.

Table 5.1: FTIR spectra frequency for SCB, SCBC and CMC

Wavenumber (cm^{-1})	Experimental value			Functional group
	SCB	SCBC	CMC	
3300-3500	3343	3332	3321	-OH group vibration stretching in cellulose
2800-3000	2915	2892	2878	C-H vibration stretching
1600-1700	1603	1636	1623	COO- Carboxylate group
1730	1722	1737	1722	C=O stretching of acetyl ester groups
1500-1600	1509	-	1588	Aromatic C=C in plane symmetrical stretching vibration found in lignin
1430-1420	1423	1423	1420	-CH ₂ scissoring motion in cellulose
1105	1103	1105	-	C-O-C glycosidic ether bands

1050-1100		1051		C-O-C pyranose ring stretching
902-893	898	898	894	Cellulosic β -glycosidic linkages

5.1.2 Powder X-ray diffraction

Figure 5.2 (a), (b) and (c) below show the XRD diffraction for SCB, SCBC and CMC respectively. Fig. 5.2 (a) indicates a broad and intense peak at 2θ around 22° corresponding to (200) crystal lattice plane. The diffractogram for SCB has a broad background or halo diffraction patterns indicative of a material that is either amorphous or a mixture of amorphous and crystalline material. Figure 5.2 (b) indicates diffracted peaks at 2θ around 15.6° , 22.5° , and 34.7° which correspond to the (110) (200) and (004) crystal planes. This in agreement with the diffraction peaks for cellulose I which gives diffraction peaks at $2\theta = 16.5^\circ$, 22.5° and 34.5° with the characteristic assignments of (110) (200) and (004) planes respectively (Kumar *et al.* 2014; Plermjai *et al.* 2018). The SCBC shows improved diffraction peaks indicating that the modified SCB has more cellulose content than the raw SCB. Fig. 5.2 (c) for the CMC shows a smooth background and narrow peaks indicating improved crystallinity. CMC has a broad peak at 2θ equal to 20.5° which agrees with the study conducted by (Teotia, Ikram and Gupta 2012). Fig. 5.2 (c) also shows a narrow peak at $2\theta = 37^\circ$ indicating the semi crystalline structure of CMC (El-Lateef, Albokheet and Gouda 2020).

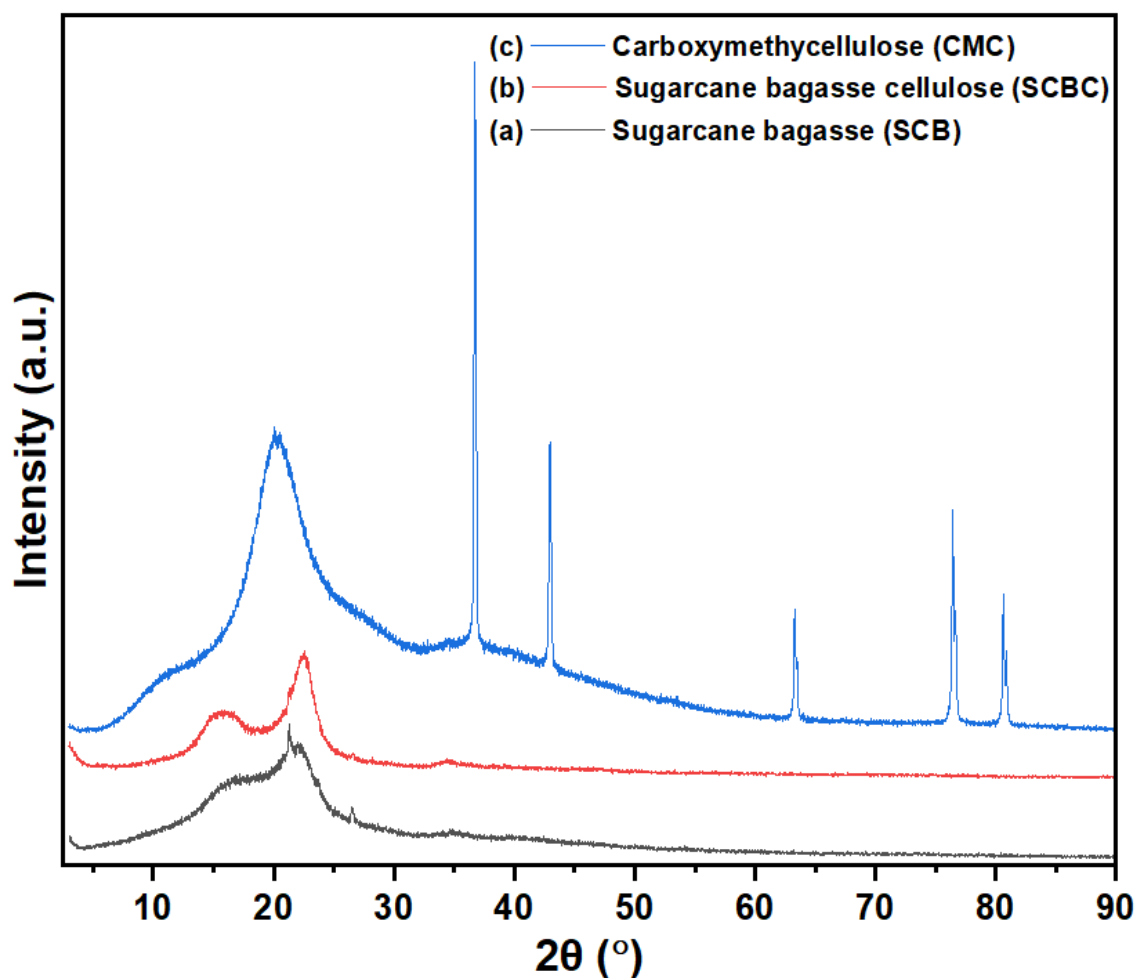


Figure 5.2: XRD diffractograms (a) Sugarcane bagasse, (b) Cellulose and (c) Carboxymethyl cellulose

5.1.3 Scanning electron microscopy

Figure 5.3 (a) shows the surface of the sugarcane bagasse fibers observed in the SEM images and it displays different features, including roughness, cracks, pores, and irregularities (Driemeier *et al.* 2011; Rezende *et al.* 2011). These features are important for understanding the physical properties and potential applications of sugarcane bagasse. For example, the roughness of the fiber surface can influence the adhesion properties and interactions with other materials in various applications. Fig. 5.3 (b) exhibits the SEM image of cellulose that show an interconnected network of fibrous structures. These fibers, composed of long chains of cellulose molecules, are arranged in a hierarchical manner, forming microfibrils. The SEM

images can provide details about the size, shape, and orientation of these microfibrils, which contribute to the mechanical properties of cellulose-based materials. Fig. 5.3 (c) is the SEM image of CMC indicating a fibrous structure like native cellulose. These fibers consist of interconnected microfibrils composed of carboxymethyl cellulose chains (Driemeier *et al.* 2011; Rezende *et al.* 2011).

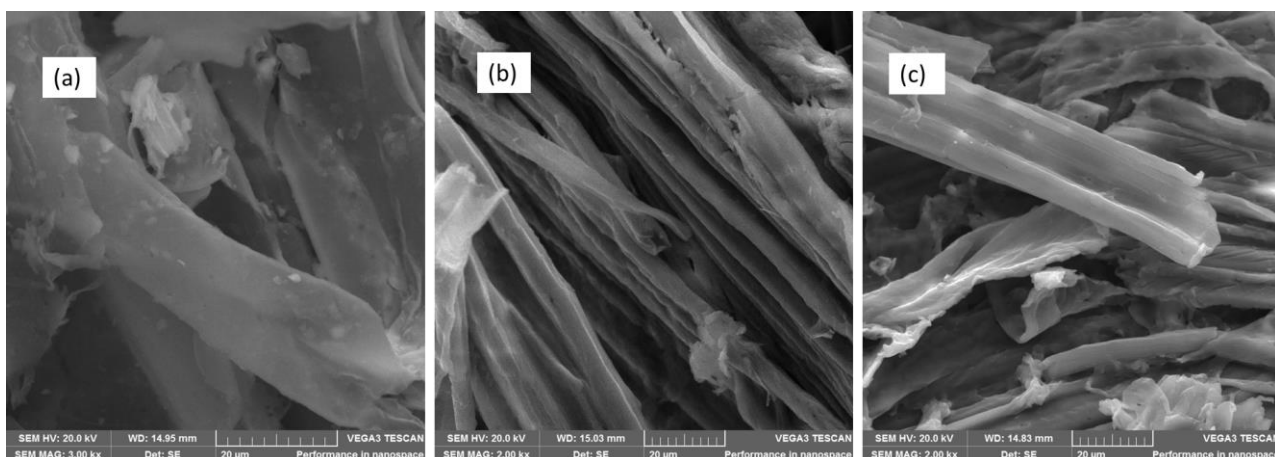


Figure 5.3: SEM (a) images for Sugarcane bagasse, (b) Sugarcane bagasse cellulose and (c) Carboxymethyl cellulose

5.2 Adsorption studies

5.2.1 Effect of pH on zinc, nickel, and cadmium removal by SCB, SCBC and CMC

Optimization of pH for Zn(II), Ni(II), and Cd(II) was performed from a pH range of 2 to 8. This specific range was selected because previous studies show that some metal hydroxides precipitate after pH 6, hence most studies adopt a pH range of 2 to 7 when conducting pH optimization studies for heavy metals (Nguyen *et al.* 2013). The optimal pH for Zn (II), Ni (II) and Cd(II) on SCB, SCBC and CMC in Figs 5.4 ranges between 5 and 6.5. Removal of metal ions in the lower pH regions is poor until at about pH 4 when it begins to improve in SCBC and CMC. The lower pH region is dominated by hydrogen ions which create competition for adsorption sites with the metal ions. The increase in pH avails negative sites on the surface of

adsorbents which favours the metal ion uptake due to electrostatic attraction (Nguyen *et al.* 2013). While the adsorption of Zn (II) is poor before pH 4 on SCB and SCBC, it shows considerable increase on CMC. Contrastingly SCB shows dismal adsorption for Ni (II) before pH 4 while SCBC and CMC show that at pH 4 removal efficiency was approximately 40% and 80% for SCBC and CMC respectively. At pH 6 Ni (II) is comparable SCBC and CMC. SCB and SCBC showed similar trend in the adsorption of Cd (II) with maximum removal efficiency of about 35%. CMC was superior in the removal of Cd(II) similar to Zn (II) and Ni (II). The superior performance of CMC may be attributed to the dominance of hydroxyl and carboxyl groups. CMC showed the best removal efficiency at pH 6.

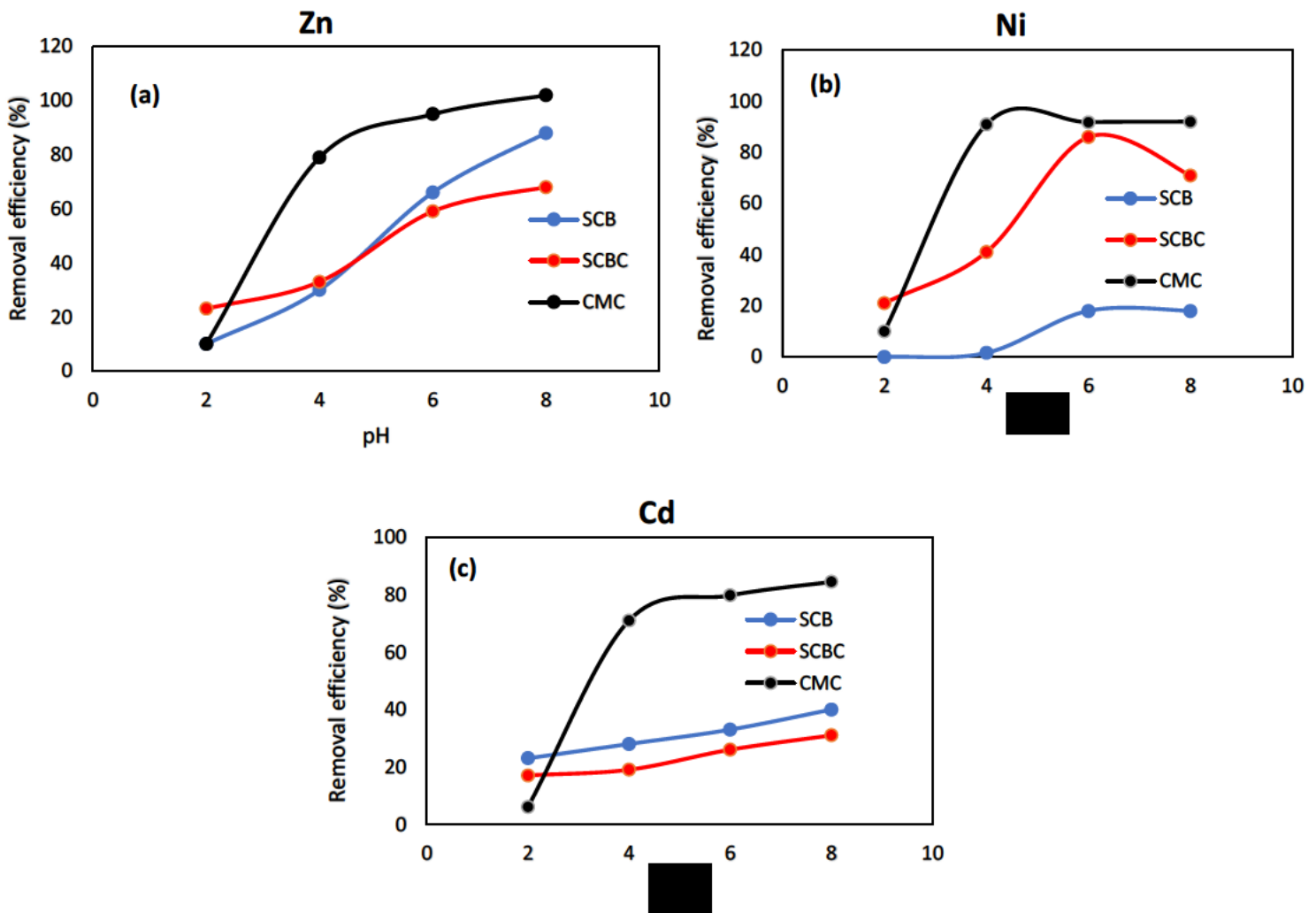


Figure 5.4: Effect of pH on adsorption of (a) Zn (II), (b) Ni (b), and (c) Cd (II) using 0.1 g of SCB, SCBC, and CMC at 25 °C and 250 rpm.

5.2.2 *Effect of initial concentration*

The effect of initial concentration on the removal of metal ions was investigated using SCB, SCBC, and CMC. Figs 5.5 (a), (b), and (c) indicate that there is an increase in the removal efficiency as the initial concentration increases. One frequently observed result by researchers is that the maximum capacity for adsorption of certain biosorbents derived from agricultural waste tends to rise as the initial concentration increases (Nguyen *et al.* 2013). The removal of Zn (II) appears to reach maximum at 100 mg/L on all adsorbents with cellulose giving best results at 79 % removal. SCB and CMC both gave a removal efficiency of about 70%. The optimum concentration for Cd (II) is 50 mg/L on all adsorbents even though CMC produced the highest adsorption at around 78% followed by cellulose at 60% and SCB at 50%. The optimal concentration of Ni (II) was 250 mg/L on CMC producing 70% adsorption efficiency. SCB and cellulose did not give maximum adsorption even concentrations above 250 mg/L. The optimal concentration in the adsorption of Zn (II) on all adsorbents was 100 mg/L with an adsorption efficiency of around 80% on cellulose and 70% on both bagasse and CMC.

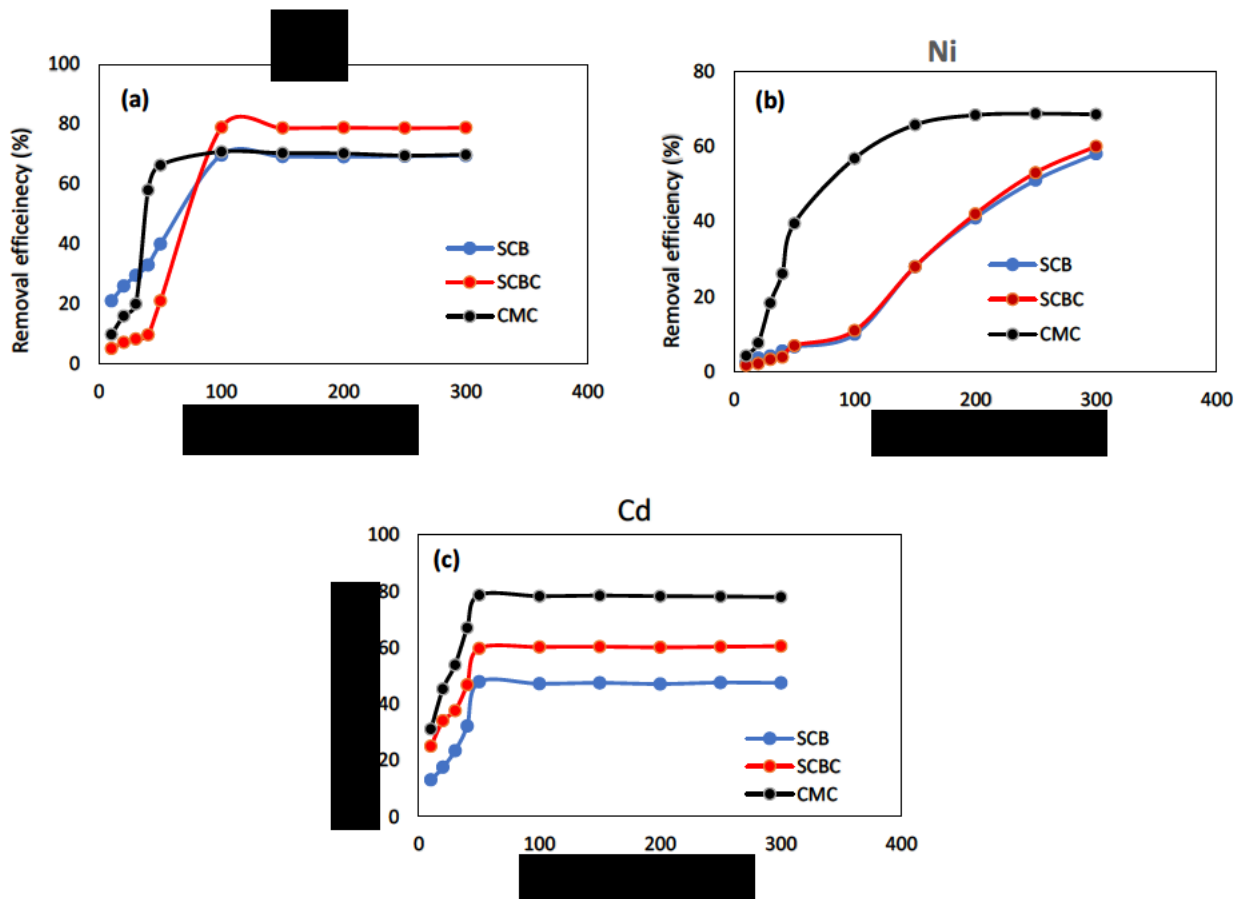


Figure 5.5: Effect of initial concentration on adsorption of (a) Zn (II) at pH =6, (b) Ni at pH=6 (b), and (c) Cd (II) at 6 using 0.1 g of SCB, SCBC, and CMC at 25 °C and 250 rpm.

5.2.3 Effect of contact time

The contact time experiments were conducted to investigate the equilibrium time required for Zn(II), Ni(II), and Cd(II) ion adsorption on SCB, SCBC, and CMC at optimum experimental conditions. Figure 5.6 (a) indicates rapid adsorption of Zn (II) ions in the first 30 minutes and then reached equilibrium state within this time period. On the other hand, Fig. 5.6 (b) and (c) show that the adsorption of Ni (II) and Cd (II) ions attained equilibrium state within 60 minutes. The rapid adsorption of these metal ions in the initial stages is due to the availability of sufficient vacant sites at the surfaces of SCB, SCBC and CMC. This concurs with the findings made by (Gupta *et al.* 2016).

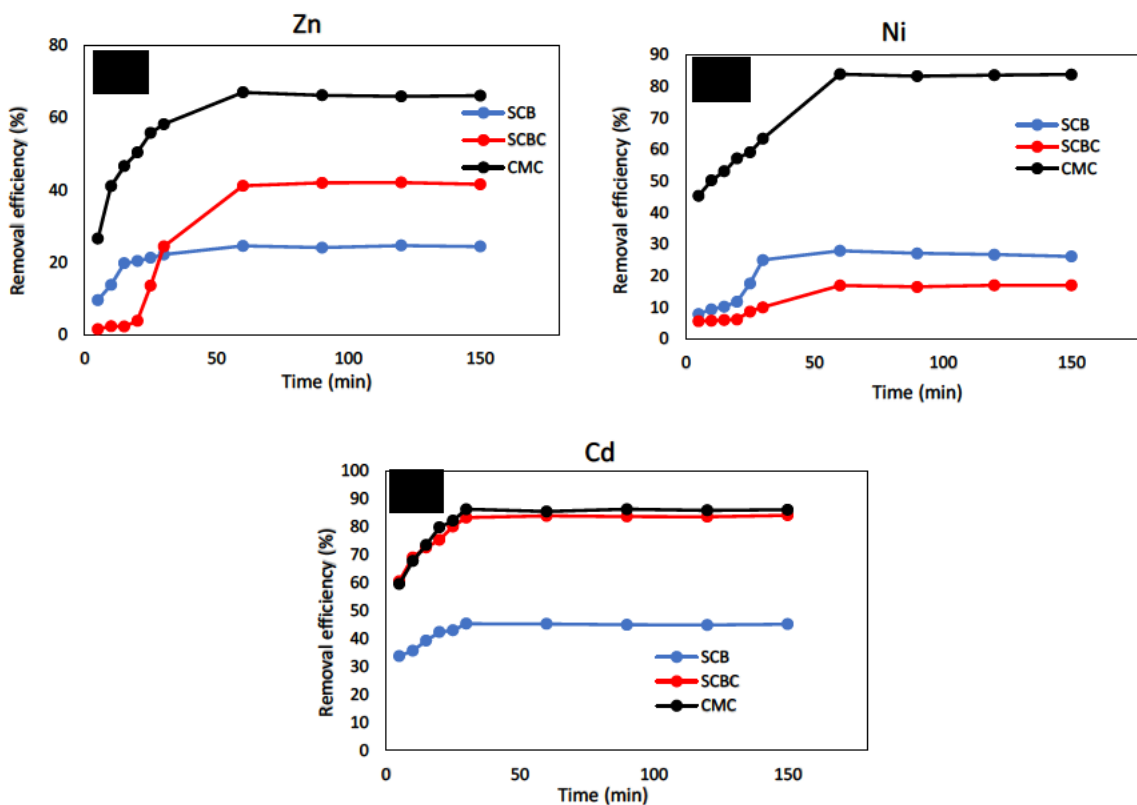


Figure 5.6 Effect of contact time on adsorption of (a) Zn (II), (b) Ni (II) and (c) Cd (II) at pH = 6 using 0.1 g of SCB, SCBC, and CMC at 25 °C and 250 rpm.

5.2.4 Effect of adsorbent dosage

Figures 5.7 (a), (b) and (c) show that the removal efficiency increase with an increase in a bio sorbent dosage for all adsorbents. This behavior can be attributed to the higher number of adsorption sites available. According to various researchers, the percentage of metal ion removal shows an upward trend as the dosage of agricultural waste bio sorbent increases (Kumar *et al.* 2014). Gupta *et al.* (2016) also concur with this finding as the Cr (IV) ions increased sharply as the adsorbent dose increases. Figure 5.7 shows that the adsorption of Zn (II) differs in trend from other adsorbates, and this may be attributed to the fact that the zinc ions might be affected by the overlapping of adsorption sites leading to a decrease in the total surface area. This different and unusually trend was also found by (Boota, Bhatti and Hanif 2009) (Nguyen *et al.* 2013).

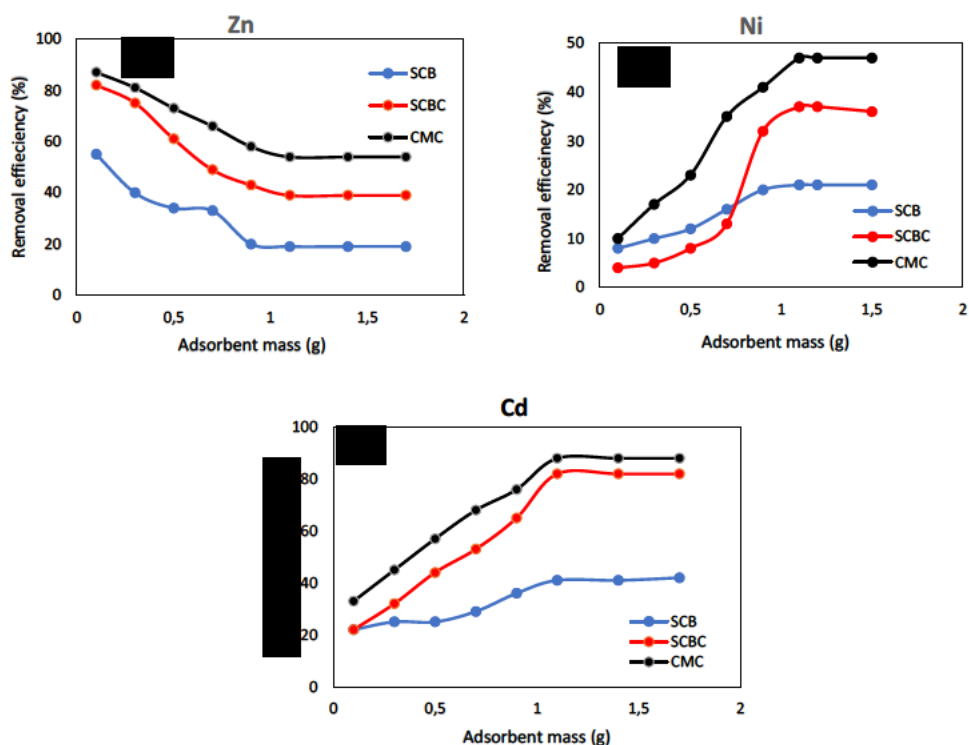


Figure 5.7: Effect of adsorbent mass on adsorption of (a) Zn (II) at pH=6, (b) Ni at pH=6.5 (b), and (c) Cd (II) at pH = 5.5 using SCB, SCBC, and CMC at 25 °C and 250 rpm.

5.3 Adsorption kinetic studies

The equilibrium time in adsorption of pollutants in wastewater is an important parameter and is often expressed as adsorption capacity of the adsorbent. The adsorption capacities of SCB, SCBC, and CMC for Zn (II), Ni(II), and Cd(II) is shown in Figure 5.8 (a), (b), and (c). The adsorption capacity for all metals rapidly increases over time until it reaches maximum (Q_{max}) at about an hour. The rapid removal of cations in the solution can be attributed to the availability of many adsorption sites owing to the negative surface charge of the adsorbents. The rapid adsorption process is quickly followed by slow adsorption which could be attributed to the saturation of the adsorption surface (Siqueira et al., 2019). Similar results are reported by El-Sheikh et al., (2018) but his studies concerned competitive adsorption of metal ions in a solution containing a mixture of cations. The Q_{max} values are for each metal in different adsorbents are given in Table 5.2. The adsorption capacity of CMC for all metal ions was higher

than SCB and SCBC because of its high functionalization (Siqueira et al., 2019 and El-Sheik et al., 2018). Table 5.2 shows a summary of maximum adsorption capacities.

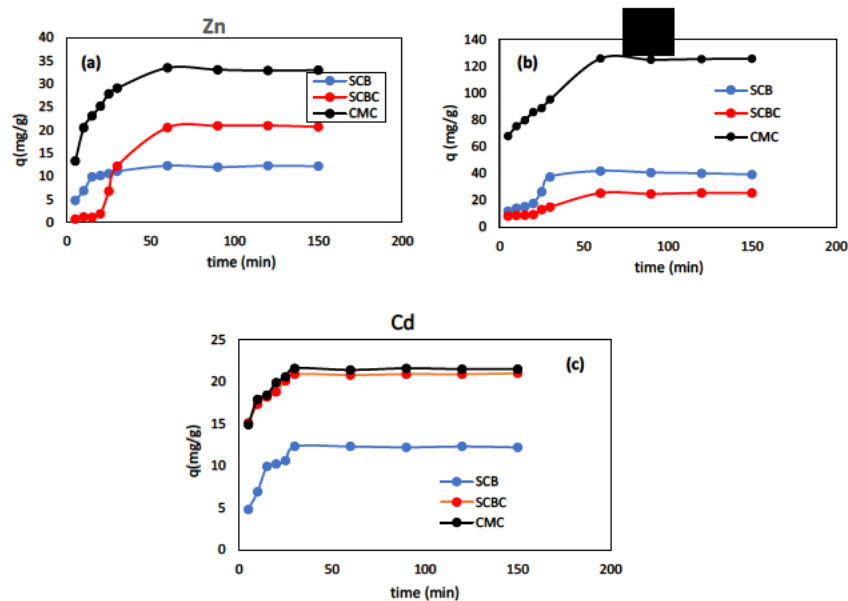


Figure 5.8: Adsorption capacities of SCB, SCBC, and CMC using 50 mg/L of Cd (II), 100 mg/L of Zn (II) and 300 mg/L of Ni (II) and 100 mg of adsorbent at pH =6, and respectively at 25 °C and 250 rpm.

Table 5.2 : Maximum adsorption capacities for Zn (II), Ni (II) and Cd (II) each adsorbent

Metal ion	Maximum adsorption capacity(mg/g) on each adsorbent		
	SCB	SCBC	CMC
Zn (II)	12.3	20.9	33.5
Ni (II)	41.9	25.4	125.7
Cd (II)	11.3	20.8	21.6

5.4 Kinetic models

The kinetic studies for the adsorption of Zn (II), Ni(II), Cd(II) onto SCB, SCBC, and CMC was studied using two models, the pseudo first-order and pseudo second order based on the equations below:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where q_e and q_t represent the amount adsorbed at equilibrium and at time t , k_1 and k_2 the first order and second order rate constant of adsorption, respectively (Lasheen *et al.* 2012; Siqueira *et al.* 2019). The first order model is based on Lagergren model (Lagergren 1898) which assumes the rate of adsorption is proportional to number of free sites. The model suggests that if the adsorption process follows pseudo first-order kinetics the plot of $\ln(q_e - q_t)$ vs time should be linear. In such a plot k_1 and q_e can be determined from the slope and the intercept of the plot respectively. Similarly, when the adsorption follows second order kinetics a plot of t/q vs time should be linear in which k_2 and q_e can be obtained from the slope and intercept respectively (Lasheen *et al.* 2012; Siqueira *et al.* 2019). The second order model assumes that the rate of adsorption is proportional to the square of the number of available or unoccupied sites (Lasheen *et al.* 2012).

Figure 5.9 below show plots for both pseudo first-order and pseudo second order kinetics for all metals in different adsorbents. The results show that adsorption data fitted well with the second order model with R^2 values > 0.99 . The pseudo first-order plots were non-linear for all metals confirming that the adsorption followed pseudo second order kinetics for all metals and adsorbents as shown by the respective correlation coefficients that were low (less than 0.7).

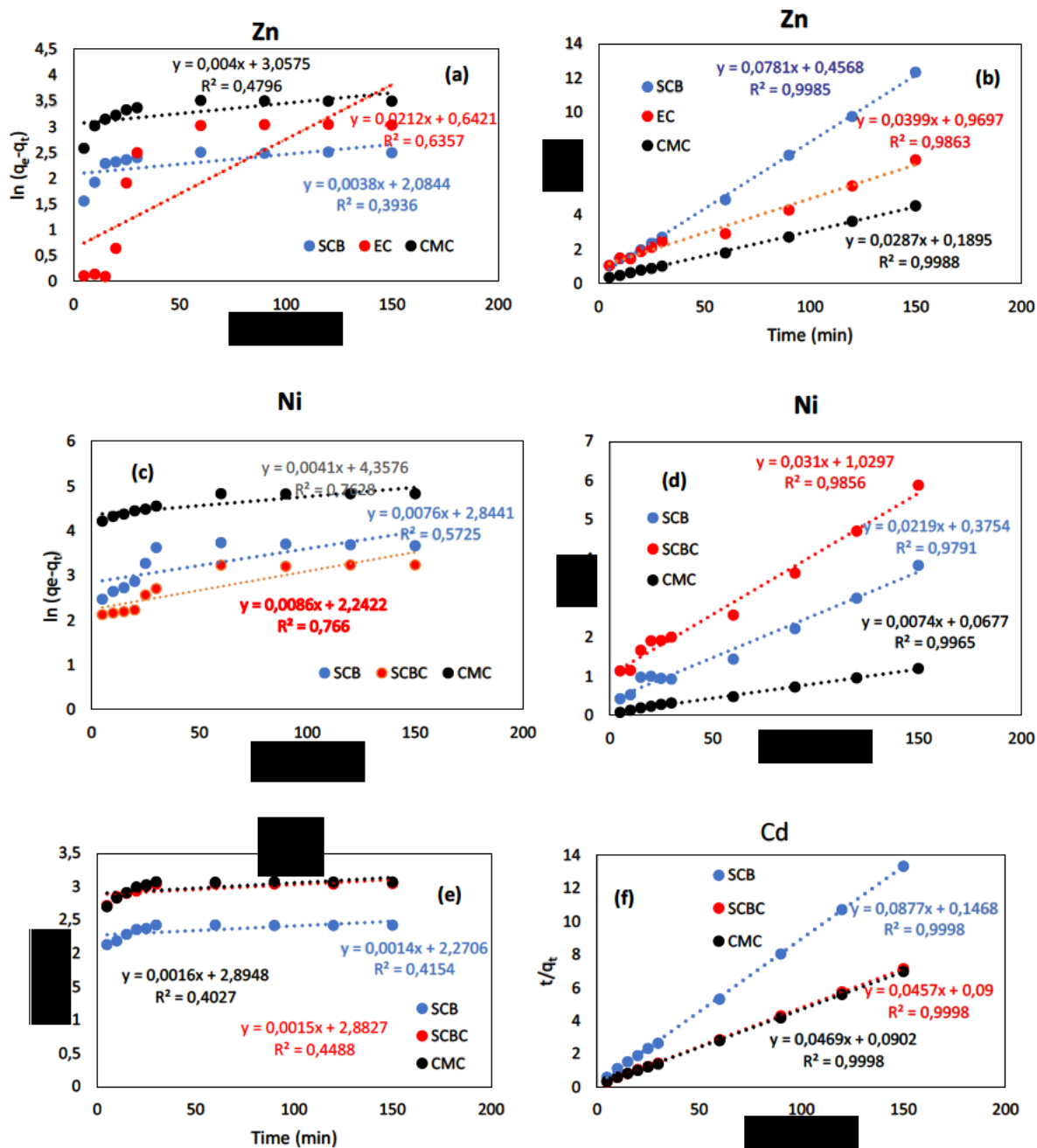


Figure 5.9: Kinetic models pseudo-first order (a) Zn (II), (c) Ni (II), (e) Cd (II), and pseudo second order (b) Zn(II), (d) Ni(II), (f) Cd(II) on SCB, SCBC, and CMC at 25 °C and 250 rpm.

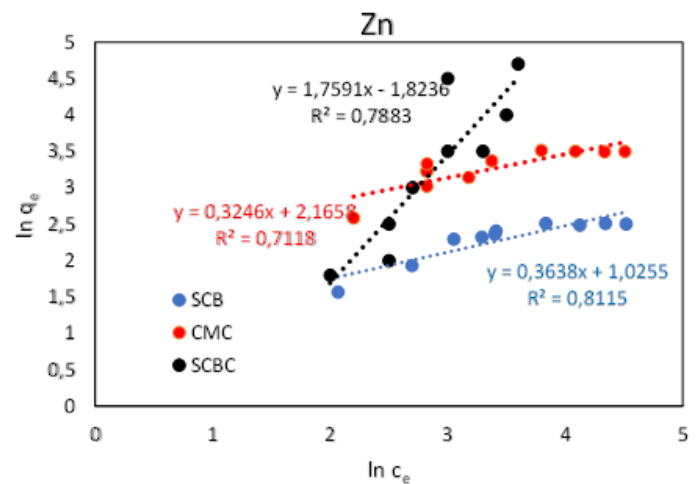
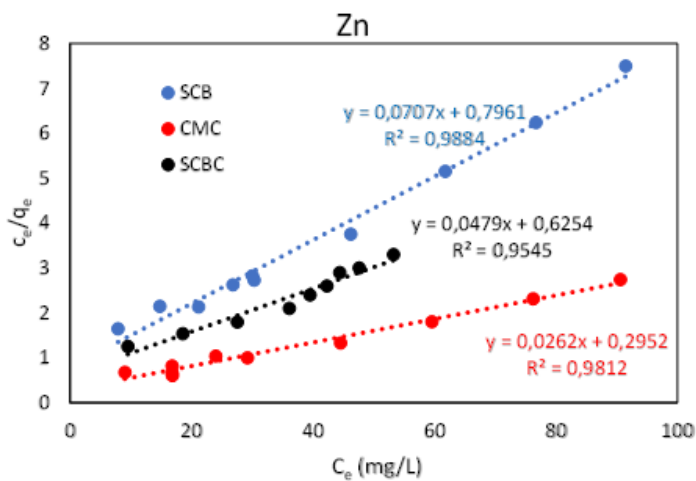
5.5 Adsorption isotherms

The mechanism of adsorption can be understood through the analysis of adsorption data in relation to equilibrium adsorption isotherms (Lasheen, 2012). This study considered two isotherms, Langmuir and Freundlich. The Langmuir adsorption and Freundlich adsorption parameters are obtained from the equations:

$$\frac{c_e}{q_e} = \frac{1}{KQ_{max}} + \frac{c_e}{Q_{max}} \quad (6)$$

$$\ln q_e = \ln k_f + \frac{1}{n} \ln c_e \quad (7)$$

Where, K (in L/g) is the equilibrium adsorption constant, Q_{max} (mg/g) is the maximum amount adsorbed per unit mass of adsorbent, k_f and n are Freundlich constants related to adsorption capacity and adsorption intensity (Lasheen, 2012). If the plot of c_e/q_e vs time is linear the adsorption favours the Langmuir model whereas if the plot of $\ln q_e$ vs $\ln c_e$ is linear the adsorption favours the Freundlich model. The adsorption of the metals was studied as a function of concentrations on various adsorbents and the results are shown in Figure 5.10.



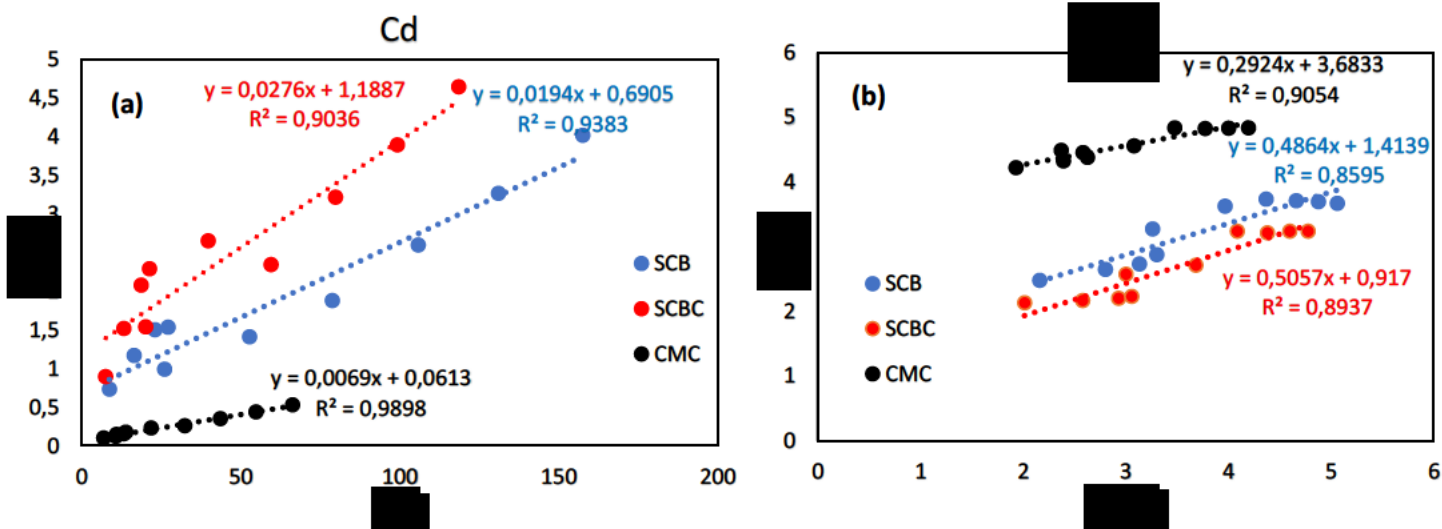


Figure 5.10: Langmuir ('a graphs') and Freundlich ('b graphs') adsorption isotherms at 25 °C.

The results show that data fitted the Langmuir model which assume the monolayer adsorption.

The correlation coefficient (R^2) in Langmuir model for all metals on different adsorbent were greater than 0,9 when compared to their counterparts in the Freundlich model which mostly less than 0,9 which in agreement with the Langmuir model proposal. On all adsorbents, SCB, SCBC, and CMC, the order of adsorption capacities is Ni (II) > Zn (II), and Cd (II) whereas the order of adsorbent efficiency is CMC > SCBC >, and SCB. The higher adsorption capacity of CMC may be attributed to higher hydroxyl and carboxylic groups acquired during modification. The same argument applies to SCBC when compared to SCB. This was expected because modification of SCB removed the lignin content producing material with more cellulose containing more hydroxyl groups that are useful in the adsorption of metals. Lasheen (2012) however found that both Langmuir and Freundlich models were applicable in the adsorption of Pb (II), Cu (II) and Cd (II) on modified orange peels. Table 5.3 shows all Langmuir and Freundlich parameters and related correlation coefficients.

Table 5.3: Langmuir and Freundlich parameters for Zn, Ni and Cd at 25 °C

Zn (II)							
Adsorbents	Langmuir Q _m (mg/g) (Exp.)	Langmuir Q _m (mg/g) (Calc.)	K	R ²	Freundlich K _f (mg/g)	n	R ²
SCB	12.3	14.2	0.102	0.988	9.00	3.00	0.712
SCBC	20.9	20.9	0,076	0,955	0.161	0.568	0,788
CMC	33.5	38.2	0.0887	0.981	2.80	2.70	0.812
Ni (II)							
SCB	41.9	33.4	0.0384	0.910	30.0	3.0	0.902
SCBC	25.4	51.5	0.0102	0.939	3.90	2.10	0.880
CMC	125.7	145	0.0549	0.967	2.49	2.30	0.886
Cd (II)							
SCB	11.3	36.2	0.040	0.904	40.0	3.40	0.905
SCBC	20.8	51.5	0.0163	0.938	4.10	2.10	0.860
CMC	21.6/144.9	144.9	0.113	0.990	2.50	1.97	0.894

5.6 Post adsorption characterization

To show that adsorption took place one sample of the adsorbent on which Ni (II) was adsorbed was analyzed using the SEM-EDX and XPS post adsorption and the results are presented in figure 5.11 and 5.12, respectively. The EDX results show that Ni was adsorbed on the surface of the adsorbent, but the intensity is low. The low intensity of the metal was expected considering the concentrations the adsorbent was expose to. The SEM/EDX data were corroborated by X-ray photoelectron spectroscopy (XPS) that showed binding energies of the Ni 2p_{1/2} and Ni 2p_{3/2} at about 874 and 855 eV as shown in figure 5.12 (a) and (b). These binding energies are indicative of Ni in the +2-oxidation state. This evidence proves that Ni

(II) was indeed adsorbed on the surface of the adsorbent. The intensity of C and O peaks is enhanced indicative of carbon and oxygen materials that form the chemical makeup of the adsorbent.

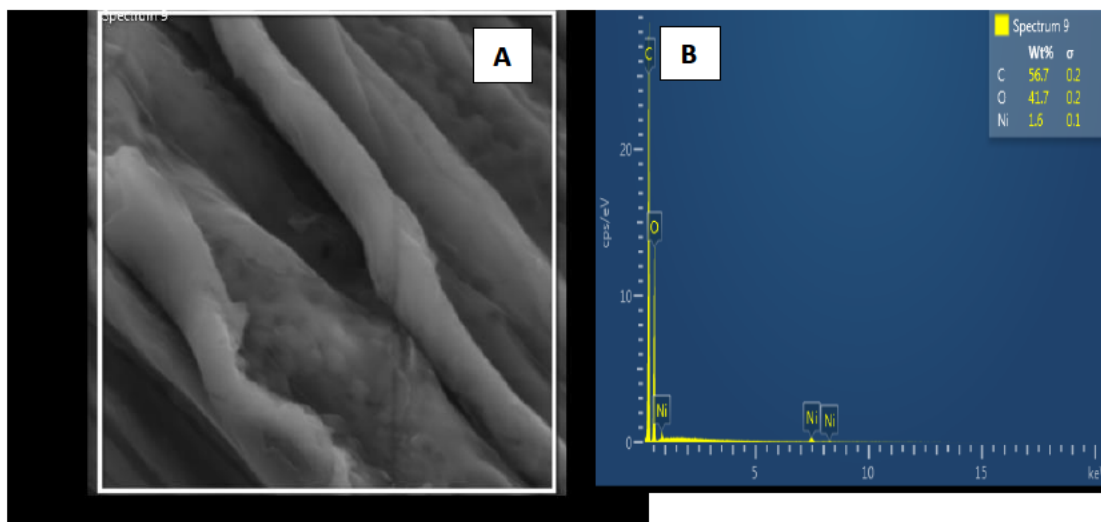


Figure 5.11: SEM/EDX image showing Ni micrograph adsorbed on SCBC.

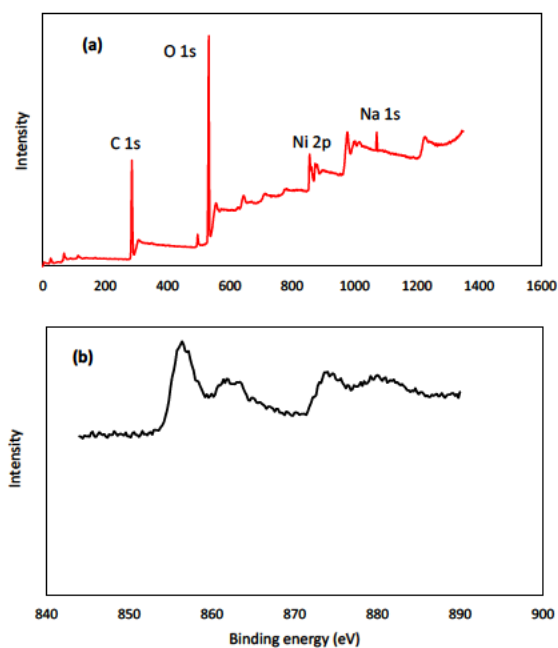


Figure 5.12: XPS profile of SCBC (a) full spectrum of SCBC post Ni (II) adsorption (b) Ni 2p core levels post adsorption.

CONCLUSIONS AND RECOMMENDATIONS

The study undertook to investigate the use of agricultural waste in particular sugar cane bagasse and its derivatives obtained through chemical modification. The modification of sugar cane bagasse as shown through characterization techniques to cellulose and carboxymethyl cellulose was successful. FTIR, SEM, and XRD confirmed the success of chemical modification of sugarcane bagasse and its functionalization during the synthesis of carboxymethyl cellulose.

Adsorption studies undertaken using the materials was also successful. The adsorption experiments were conducted for removal of Ni (II), Zn (II), and Cd (II). The adsorption process was much better on carboxymethyl cellulose followed by cellulose and sugar cane bagasse for all metals investigated evidenced by order of adsorption capacities following the same order for all metals. Adsorption depended on the pH, adsorbent dosage, time, and initial concentrations as expected. It became evident that modification of sugarcane bagasse improved its adsorption capacity. The adsorption data suggested that the adsorption process followed the second order kinetics and favoured the Langmuir adsorption isotherm.

There is still more work that can be done with respect to material design using agricultural waste for cleaning the wastewater systems. A further study may look at the adsorption experiments that involve mixtures of metal ions using such materials and also study the industrial effluents to understand the rigor of these materials in dealing with real samples.

REFERENCES

- Abd Mutalib, M., Rahman, M., Othman, M., Ismail, A. and Jaafar, J. 2017. Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectroscopy. In: *Membrane characterization*. Elsevier, 161-179.
- Akhtar, K., Khan, S. A., Khan, S. B. and Asiri, A. M. 2018. Scanning electron microscopy: Principle and applications in nanomaterials characterization. *Handbook of materials characterization*, Article ID: 113-145.
- Ali, A. 2017. Removal of Mn (II) from water using chemically modified banana peels as efficient adsorbent. *Environmental Nanotechnology, Monitoring & Management*, 7: 57-63.
- Alomá, I., Martín-Lara, M., Rodríguez, I., Blázquez, G. and Calero, M. 2012. Removal of nickel (II) ions from aqueous solutions by biosorption on sugarcane bagasse. *Journal of the Taiwan Institute of Chemical Engineers*, 43 (2): 275-281.
- Anderson, R. J., Bendell, D. J. and Groundwater, P. W. 2004. *Organic spectroscopic analysis*. Royal Society of Chemistry.
- Annadurai, G., Juang, R.-S. and Lee, D. 2003. Adsorption of heavy metals from water using banana and orange peels. *Water science and technology*, 47 (1): 185-190.
- Asadi, F., Shariatmadari, H. and Mirghaffari, N. 2008. Modification of rice hull and sawdust sorptive characteristics for remove heavy metals from synthetic solutions and wastewater. *Journal of hazardous materials*, 154 (1-3): 451-458.
- Asl, S. A., Mousavi, M. and Labbafi, M. 2017. Synthesis and characterization of carboxymethyl cellulose from sugarcane bagasse. *Journal of food processing and technology*, 8 (8).

- Baiju, V., Abhishek, P., Priya, K. and Mohammed, S. P. 2022. Performance investigation of silica gel based consolidated composite adsorbents effective for adsorption desalination systems. *Materials Today Communications*, 32: 104015.
- Belova, T. 2019. Adsorption of heavy metal ions (Cu^{2+} , Ni^{2+} , Co^{2+} and Fe^{2+}) from aqueous solutions by natural zeolite. *Heliyon*, 5 (9): e02320.
- Bezerra, T. L. and Ragauskas, A. J. 2016. A review of sugarcane bagasse for second-generation bioethanol and biopower production. *Biofuels, Bioproducts and Biorefining*, 10 (5): 634-647.
- Bhuiyan, M. A. H., Suruvi, N. I., Dampare, S. B., Islam, M., Quraishi, S. B., Ganyaglo, S. and Suzuki, S. 2011. Investigation of the possible sources of heavy metal contamination in lagoon and canal water in the tannery industrial area in Dhaka, Bangladesh. *Environmental monitoring and assessment*, 175 (1-4): 633-649.
- Boota, R., Bhatti, H. N. and Hanif, M. A. 2009. Removal of Cu (II) and Zn (II) using lignocellulosic fiber derived from *Citrus reticulata* (Kinnow) waste biomass. *Separation Science and Technology*, 44 (16): 4000-4022.
- Bunaciu, A. A., UdrişTioiu, E. G. and Aboul-Enein, H. Y. 2015. X-ray diffraction: instrumentation and applications. *Critical reviews in analytical chemistry*, 45 (4): 289-299.
- Burakov, A. E., Galunin, E. V., Burakova, I. V., Kucherova, A. E., Agarwal, S., Tkachev, A. G. and Gupta, V. K. 2018. Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: A review. *Ecotoxicology and environmental safety*, 148: 702-712.
- Candido, R. and Gonçalves, A. 2019. Evaluation of two different applications for cellulose isolated from sugarcane bagasse in a biorefinery concept. *Industrial Crops and Products*, 142: 111616.

- Chai, W. S., Cheun, J. Y., Kumar, P. S., Mubashir, M., Majeed, Z., Banat, F., Ho, S.-H. and Show, P. L. 2021. A review on conventional and novel materials towards heavy metal adsorption in wastewater treatment application. *Journal of Cleaner Production*, 296: 126589.
- Chambon, C. L., Mkhize, T. Y., Reddy, P., Brandt-Talbot, A., Deenadayalu, N., Fennell, P. S. and Hallett, J. P. 2018. Pretreatment of South African sugarcane bagasse using a low-cost protic ionic liquid: a comparison of whole, depithed, fibrous and pith bagasse fractions. *Biotechnology for biofuels*, 11 (1): 1-16.
- Chand, P., Shil, A. K., Sharma, M. and Pakade, Y. B. 2014. Improved adsorption of cadmium ions from aqueous solution using chemically modified apple pomace: mechanism, kinetics, and thermodynamics. *International Biodeterioration & Biodegradation*, 90: 8-16.
- Chand, R., Watari, T., Inoue, K., Kawakita, H., Luitel, H. N., Parajuli, D., Torikai, T. and Yada, M. 2009. Selective adsorption of precious metals from hydrochloric acid solutions using porous carbon prepared from barley straw and rice husk. *Minerals Engineering*, 22 (15): 1277-1282.
- Chasapis, C. T., Ntoupa, P.-S. A., Spiliopoulou, C. A. and Stefanidou, M. E. 2020. Recent aspects of the effects of zinc on human health. *Archives of toxicology*, 94: 1443-1460.
- Chi, Q.-q., Zhu, G.-w. and Langdon, A. 2007. Bioaccumulation of heavy metals in fishes from Taihu Lake, China. *Journal of Environmental Sciences*, 19 (12): 1500-1504.
- Crini, G. and Lichtfouse, E. 2019. Advantages and disadvantages of techniques used for wastewater treatment. *Environmental Chemistry Letters*, 17: 145-155.
- do Carmo Ramos, S. N., Xavier, A. L. P., Teodoro, F. S., Gil, L. F. and Gurgel, L. V. A. 2016. Removal of cobalt (II), copper (II), and nickel (II) ions from aqueous solutions using phthalate-functionalized sugarcane bagasse: mono-and multicomponent adsorption in batch mode. *Industrial Crops and Products*, 79: 116-130.

Driemeier, C., Oliveira, M. M., Mendes, F. M. and Gómez, E. O. 2011. Characterization of sugarcane bagasse powders. *Powder technology*, 214 (1): 111-116.

El-Lateef, H. M. A., Albokheet, W. and Gouda, M. 2020. Carboxymethyl cellulose/metal (Fe, Cu and Ni) nanocomposites as non-precious inhibitors of C-steel corrosion in HCl solutions: synthesis, characterization, electrochemical and surface morphology studies. *Cellulose*, 27: 8039-8057.

Epp, J. 2016. X-ray diffraction (XRD) techniques for materials characterization. In: *Materials characterization using nondestructive evaluation (NDE) methods*. Elsevier, 81-124.

Evans, L., Rhodes, A., Alhazzani, W., Antonelli, M., Coopersmith, C. M., French, C., Machado, F. R., McIntyre, L., Ostermann, M. and Prescott, H. C. 2021. Surviving sepsis campaign: international guidelines for management of sepsis and septic shock 2021. *Intensive care medicine*, 47 (11): 1181-1247.

Ezeonuegbu, B. A., Machido, D. A., Whong, C. M., Japhet, W. S., Alexiou, A., Elazab, S. T., Qusty, N., Yaro, C. A. and Batiha, G. E.-S. 2021. Agricultural waste of sugarcane bagasse as efficient adsorbent for lead and nickel removal from untreated wastewater: Biosorption, equilibrium isotherms, kinetics and desorption studies. *Biotechnology Reports*, 30: e00614.

Farghali, A., Bahgat, M., Allah, A. E. and Khedr, M. 2013. Adsorption of Pb (II) ions from aqueous solutions using copper oxide nanostructures. *Beni-Suef University Journal of Basic and Applied Sciences*, 2 (2): 61-71.

Ferreira, C. I., Calisto, V., Santos, S. M., Cuerda-Correa, E. M., Otero, M., Nadais, H. and Esteves, V. I. 2015. Application of pyrolysed agricultural biowastes as adsorbents for fish anaesthetic (MS-222) removal from water. *Journal of analytical and applied pyrolysis*, 112: 313-324.

- Figuroa-Rodríguez, K. A., Hernández-Rosas, F., Figuroa-Sandoval, B., Velasco-Velasco, J. and Aguilar Rivera, N. 2019. What has been the focus of sugarcane research? A bibliometric overview. *International Journal of Environmental Research and Public Health*, 16 (18): 3326.
- Fu, Z.-J., Jiang, S.-K., Chao, X.-Y., Zhang, C.-X., Shi, Q., Wang, Z.-Y., Liu, M.-L. and Sun, S.-P. 2022. Removing miscellaneous heavy metals by all-in-one ion exchange-nanofiltration membrane. *Water Research*, 222: 118888.
- Garcia-Sanchez, A., Ania, C. O., Parra, J. B., Dubbeldam, D., Vlugt, T. J., Krishna, R. and Calero, S. 2009. Transferable force field for carbon dioxide adsorption in zeolites. *The Journal of Physical Chemistry C*, 113 (20): 8814-8820.
- García, R. and Báez, A. 2012. Atomic absorption spectrometry (AAS). *Atomic absorption spectroscopy*, 1: 1-13.
- Genchi, G., Carocci, A., Lauria, G., Sinicropi, M. S. and Catalano, A. 2020. Nickel: Human health and environmental toxicology. *International journal of environmental research and public health*, 17 (3): 679.
- Godiya, C. B., Cheng, X., Li, D., Chen, Z. and Lu, X. 2019. Carboxymethyl cellulose/polyacrylamide composite hydrogel for cascaded treatment/reuse of heavy metal ions in wastewater. *Journal of hazardous materials*, 364: 28-38.
- Gou, X., Zhao, X., Singh, S. and Qiao, D. 2019. Tri-pyrolysis: A thermo-kinetic characterisation of polyethylene, cornstalk, and anthracite coal using TGA-FTIR analysis. *Fuel*, 252: 393-402.
- Gunatilake, S. 2015. Methods of removing heavy metals from industrial wastewater. *Methods*, 1 (1): 14.

- Gupta, V. 2009. Application of low-cost adsorbents for dye removal—a review. *Journal of environmental management*, 90 (8): 2313-2342.
- Gupta, V. K., Chandra, R., Tyagi, I. and Verma, M. 2016. Removal of hexavalent chromium ions using CuO nanoparticles for water purification applications. *Journal of colloid and interface science*, 478: 54-62.
- Hassan, M. L., Abou-Zeid, R. E., Fadel, S. M., El-Sakhawy, M. and Khiari, R. 2014. Cellulose nanocrystals and carboxymethyl cellulose from olive stones and their use to improve paper sheets properties. *International Journal of Nanoparticles*, 7 (3-4): 261-277.
- He, B. B. 2018. *Two-dimensional X-ray Diffraction*. John Wiley & Sons.
- Hegazi, H. A. 2013. Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents. *HBRC journal*, 9 (3): 276-282.
- Hokkanen, S., Bhatnagar, A. and Sillanpää, M. 2016. A review on modification methods to cellulose-based adsorbents to improve adsorption capacity. *Water research*, 91: 156-173.
- Homagai, P. L., Ghimire, K. N. and Inoue, K. 2010. Adsorption behavior of heavy metals onto chemically modified sugarcane bagasse. *Bioresource Technology*, 101 (6): 2067-2069.
- Hu, P., Wang, S., Wang, J., Jiang, S., Sun, Y. and Ma, Z. 2022. Scale-up of open zeolite bed reactors for sorption energy storage: Theory and experiment. *Energy and Buildings*, 264: 112077.
- Hui, K., Chao, C. Y. H. and Kot, S. 2005. Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash. *Journal of Hazardous Materials*, 127 (1-3): 89-101.
- Isa, Y. M., Harripersadth, C., Musonge, P., Sayago, A. and Morales, M. G. 2020. The application of eggshells and sugarcane bagasse as potential biomaterials in the removal of

heavy metals from aqueous solutions. *South African Journal of Chemical Engineering*, 34 (1): 142-150.

Joseph, L., Jun, B.-M., Flora, J. R., Park, C. M. and Yoon, Y. 2019. Removal of heavy metals from water sources in the developing world using low-cost materials: A review. *Chemosphere*, 229: 142-159.

Kannan, M. 2018a. Scanning electron microscopy: Principle, components and applications. *A Textbook on Fundamentals and Applications of Nanotechnology; Springer: Berlin/Heidelberg, Germany*, Article ID: 81-92.

Kannan, M. 2018b. Transmission electron microscope—Principle, components and applications. *A textbook on fundamentals and applications of nanotechnology*, Article ID: 93-102.

Karnitz Jr, O., Gurgel, L. V. A., De Melo, J. C. P., Botaro, V. R., Melo, T. M. S., de Freitas Gil, R. P. and Gil, L. F. 2007. Adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugarcane bagasse. *Bioresource technology*, 98 (6): 1291-1297.

Khatri, P. and Pandit, A. B. 2022. Systematic review of life cycle assessments applied to sugarcane bagasse utilization alternatives. *Biomass and Bioenergy*, 158: 106365.

Khayat-zadeh, J. and Abbasi, E. 2010. The effects of heavy metals on aquatic animals. In: *Proceedings of The 1st International Applied Geological Congress, Department of Geology, Islamic Azad University–Mashad Branch, Iran.* 26-28.

Khoramzadeh, E., Nasernejad, B. and Halladj, R. 2013. Mercury biosorption from aqueous solutions by sugarcane bagasse. *Journal of the Taiwan Institute of Chemical Engineers*, 44 (2): 266-269.

- Kötting, C., Suveyzdis, Y., Bojja, R. S., Metzler-Nolte, N. and Gerwert, K. 2010. Label-free screening of drug–protein interactions by time-resolved fourier transform infrared spectroscopic assays exemplified by ras interactions. *Applied spectroscopy*, 64 (9): 967-972.
- Krishnani, K. K., Meng, X., Christodoulatos, C. and Boddu, V. M. 2008. Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk. *Journal of hazardous materials*, 153 (3): 1222-1234.
- Kumar, A., Negi, Y. S., Choudhary, V. and Bhardwaj, N. K. 2014. Characterization of cellulose nanocrystals produced by acid-hydrolysis from sugarcane bagasse as agro-waste. *Journal of materials physics and chemistry*, 2 (1): 1-8.
- Lasheen, M. R., Ammar, N. S. and Ibrahim, H. S. 2012. Adsorption/desorption of Cd (II), Cu (II) and Pb (II) using chemically modified orange peel: Equilibrium and kinetic studies. *Solid State Sciences*, 14 (2): 202-210.
- Lata, S. and Samadder, S. 2014. Removal of heavy metals using rice husk: a review. *International Journal of Environmental Research and Development*, 4 (2): 165-170.
- Linganiso, L. Z., Buthelezi, T. and Motaung, T. E. 2019. A comparative study of sugarcane bagasse and soft wood. *Wood Res*, 64: 273-280.
- Malik, D. S., Jain, C. K. and Yadav, A. K. 2018. Heavy Metal Removal by Fixed-Bed Column– A Review. *ChemBioEng Reviews*, 5 (3): 173-179.
- Mallampati, R., Xuanjun, L., Adin, A. and Valiyaveetil, S. 2015. Fruit peels as efficient renewable adsorbents for removal of dissolved heavy metals and dyes from water. *ACS Sustainable Chemistry & Engineering*, 3 (6): 1117-1124.

- Manzoor, K., Ahmad, M., Ahmad, S. and Ikram, S. 2019. Removal of Pb (ii) and Cd (ii) from wastewater using arginine cross-linked chitosan–carboxymethyl cellulose beads as green adsorbent. *RSC advances*, 9 (14): 7890-7902.
- Masri, S., LeBrón, A. M., Logue, M. D., Valencia, E., Ruiz, A., Reyes, A. and Wu, J. 2021. Risk assessment of soil heavy metal contamination at the census tract level in the city of Santa Ana, CA: Implications for health and environmental justice. *Environmental Science: Processes & Impacts*, 23 (6): 812-830.
- Meez, E., Rahdar, A. and Kyzas, G. Z. 2021. Sawdust for the removal of heavy metals from water: a review. *Molecules*, 26 (14): 4318.
- Melesse, G. T., Hone, F. G. and Mekonnen, M. A. 2022. Extraction of Cellulose from Sugarcane Bagasse Optimization and Characterization. *Advances in Materials Science and Engineering*, 2022.
- Mohlala, L. M., Bodunrin, M. O., Awosusi, A. A., Daramola, M. O., Cele, N. P. and Olubambi, P. A. 2016. Beneficiation of corncob and sugarcane bagasse for energy generation and materials development in Nigeria and South Africa: A short overview. *Alexandria Engineering Journal*, 55 (3): 3025-3036.
- Moses, C., Robinson, D. and Barlow, J. 2014. Methods for measuring rock surface weathering and erosion: A critical review. *Earth-Science Reviews*, 135: 141-161.
- Motsi, T., Rowson, N. and Simmons, M. 2009. Adsorption of heavy metals from acid mine drainage by natural zeolite. *International journal of mineral processing*, 92 (1-2): 42-48.
- Muhammad, S., Shah, M. T. and Khan, S. 2011. Health risk assessment of heavy metals and their source apportionment in drinking water of Kohistan region, northern Pakistan. *Microchemical journal*, 98 (2): 334-343.

- Ngah, W. W. and Hanafiah, M. M. 2008. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review. *Bioresource technology*, 99 (10): 3935-3948.
- Ngah, W. W., Teong, L., Toh, R. and Hanafiah, M. 2013. Comparative study on adsorption and desorption of Cu (II) ions by three types of chitosan–zeolite composites. *Chemical Engineering Journal*, 223: 231-238.
- Nguyen, T., Ngo, H., Guo, W., Zhang, J., Liang, S., Yue, Q., Li, Q. and Nguyen, T. 2013. Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater. *Bioresource technology*, 148: 574-585.
- Ntengwe, F. and Maseka, K. 2006. The impact of effluents containing zinc and nickel metals on stream and river water bodies: The case of Chambishi and Mwambashi streams in Zambia. *Physics and Chemistry of the Earth, Parts A/B/C*, 31 (15-16): 814-820.
- Okoronkwo, N. E., Igwe, J. C. and Ogbonna, H. I. 2008. Detoxification of Hg²⁺, Cd²⁺ and Fe²⁺ from aqueous solution using waste boiler fly ash. *Terrestrial and Aquatic Environmental Toxicology*, 2 (1): 49-53.
- Oprea, M. and Voicu, S. I. 2020. Recent advances in composites based on cellulose derivatives for biomedical applications. *Carbohydrate Polymers*, 247: 116683.
- Organization, W. H. 2022. *Guidelines for drinking-water quality: incorporating the first and second addenda*. World Health Organization.
- Pham, T. T., Hoang, M. T., Nguyen, M. K., Dinh, T. H., Han, L. and Bruggen, B. 2015. Evaluation of chemical modified sugarcane bagasse for cadmium removal in aqueous environment. *International Proceedings of Chemical, Biological and Environmental Engineering*, 88 (2): 6-10.

- Plermjai, K., Boonyarattanakalin, K., Mekprasart, W., Pavasupree, S., Phoohinkong, W. and Pecharapa, W. 2018. Extraction and characterization of nanocellulose from sugarcane bagasse by ball-milling-assisted acid hydrolysis. In: *Proceedings of AIP Conference Proceedings*. AIP Publishing LLC, 020005.
- Plum, L. M., Rink, L. and Haase, H. 2010. The essential toxin: impact of zinc on human health. *International journal of environmental research and public health*, 7 (4): 1342-1365.
- Raj, V., Chauhan, M. S. and Pal, S. L. 2022. Potential of sugarcane bagasse in remediation of heavy metals: A review. *Chemosphere*, Article ID: 135825.
- Raval, N. P., Shah, P. U. and Shah, N. K. 2016. Adsorptive removal of nickel (II) ions from aqueous environment: A review. *Journal of Environmental Management*, 179: 1-20.
- Remelli, M., Nurchi, V. M., Lachowicz, J. I., Medici, S., Zoroddu, M. A. and Peana, M. 2016. Competition between Cd (II) and other divalent transition metal ions during complex formation with amino acids, peptides, and chelating agents. *Coordination Chemistry Reviews*, 327: 55-69.
- Renu, Agarwal, M. and Singh, K. 2017. Methodologies for removal of heavy metal ions from wastewater: an overview. *Interdisciplinary Environmental Review*, 18 (2): 124-142.
- Rezende, C. A., De Lima, M. A., Maziero, P., deAzevedo, E. R., Garcia, W. and Polikarpov, I. 2011. Chemical and morphological characterization of sugarcane bagasse submitted to a delignification process for enhanced enzymatic digestibility. *Biotechnology for biofuels*, 4 (1): 1-19.
- Romero-Cano, L. A., García-Rosero, H., Gonzalez-Gutierrez, L. V., Baldenegro-Pérez, L. A. and Carrasco-Marín, F. 2017. Functionalized adsorbents prepared from fruit peels:

Equilibrium, kinetic and thermodynamic studies for copper adsorption in aqueous solution. *Journal of cleaner production*, 162: 195-204.

Saelee, K., Yingkamhaeng, N., Nimchua, T. and Sukyai, P. 2014. Extraction and characterization of cellulose from sugarcane bagasse by using environmental friendly method. In: *Proceedings of Proceedings of the 26th annual meeting of the thai society for biotechnology and international conference, Mae Fah Lunag University (School of Science), Thailand.* 26-29.

Saleh, T. A., Mustaqeem, M. and Khaled, M. 2022. Water treatment technologies in removing heavy metal ions from wastewater: A review. *Environmental Nanotechnology, Monitoring & Management*, 17: 100617.

Sepehrian, H., Ahmadi, S., Waqif-Husain, S., Faghihian, H. and Alihanbari, H. 2010. Adsorption studies of heavy metal ions on mesoporous aluminosilicate, novel cation exchanger. *Journal of hazardous materials*, 176 (1-3): 252-256.

Shcherban, N. D., Barakov, R. Y., Mäki-Arvela, P., Sergiienko, S. A., Bezverkhyy, I., Eränen, K. and Murzin, D. Y. 2018. Isomerization of α -pinene oxide over ZSM-5 based micro-mesoporous materials. *Applied Catalysis A: General*, 560: 236-247.

Sheick, R., Serra, S., De Franceschi, P., Dondini, L. and Musacchi, S. 2018. Characterization of a novel self-incompatibility allele in Malus and S-genotyping of select crabapple cultivars. *Scientia Horticulturae*, 240: 186-195.

Shokri, J. and Adibkia, K. 2013. Application of cellulose and cellulose derivatives in pharmaceutical industries. In: *Cellulose-medical, pharmaceutical and electronic applications.* IntechOpen.

- Sobhanardakani, S., Jafari, A., Zandipak, R. and Meidanchi, A. 2018. Removal of heavy metal (Hg (II) and Cr (VI)) ions from aqueous solutions using Fe₂O₃@ SiO₂ thin films as a novel adsorbent. *Process safety and environmental protection*, 120: 348-357.
- Sun, J., Sun, X., Zhao, H. and Sun, R. 2004. Isolation and characterization of cellulose from sugarcane bagasse. *Polymer degradation and stability*, 84 (2): 331-339.
- Sun, N., Wen, X. and Yan, C. 2018. Adsorption of mercury ions from wastewater aqueous solution by amide functionalized cellulose from sugarcane bagasse. *International journal of biological macromolecules*, 108: 1199-1206.
- Supong, A., Bhomick, P. C., Karmaker, R., Ezung, S. L., Jamir, L., Sinha, U. B. and Sinha, D. 2020. Experimental and theoretical insight into the adsorption of phenol and 2, 4-dinitrophenol onto Tithonia diversifolia activated carbon. *Applied Surface Science*, 529: 147046.
- Tahoon, M. A., Siddeeg, S. M., Salem Alsaieri, N., Mnif, W. and Ben Rebah, F. 2020. Effective heavy metals removal from water using nanomaterials: A review. *Processes*, 8 (6): 645.
- Taieban, S. M. R., Torabi, E., Najafpoor, A. A., Alidadi, H. and Zezoli, M. A. 2012. Survey of Biosorption Chromium and Cadmium from industrial effluent, by using agricultural waste material-A Review Article. *Navid No*, 16 (58).
- Tanaka, N. 2017. *Electron Nano-Imaging*. Springer.
- Teotia, A., Ikram, S. and Gupta, B. 2012. Structural characterization of chitosan and oxidized carboxymethyl cellulose based freeze-dried films. *Polymer bulletin*, 69: 175-188.
- Torab-Mostaedi, M., Asadollahzadeh, M., Hemmati, A. and Khosravi, A. 2013. Equilibrium, kinetic, and thermodynamic studies for biosorption of cadmium and nickel on grapefruit peel. *Journal of the Taiwan Institute of Chemical Engineers*, 44 (2): 295-302.

Tripathi, A. and Ranjan, M. R. 2015. Heavy metal removal from wastewater using low cost adsorbents. *J Bioremed Biodeg*, 6 (6): 315.

Wang, T., Ai, S., Zhou, Y., Luo, Z., Dai, C., Yang, Y., Zhang, J., Huang, H., Luo, S. and Luo, L. 2018. Adsorption of agricultural wastewater contaminated with antibiotics, pesticides and toxic metals by functionalized magnetic nanoparticles. *Journal of Environmental Chemical Engineering*, 6 (5): 6468-6478.

Wei, B. and Yang, L. 2010. A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. *Microchemical journal*, 94 (2): 99-107.

Wei, H., Deng, S., Huang, Q., Nie, Y., Wang, B., Huang, J. and Yu, G. 2013. Regenerable granular carbon nanotubes/alumina hybrid adsorbents for diclofenac sodium and carbamazepine removal from aqueous solution. *Water research*, 47 (12): 4139-4147.

Welz, B. and Sperling, M. 2008. *Atomic absorption spectrometry*. John Wiley & Sons.

Yin, N.-H., Sivry, Y., Benedetti, M. F., Lens, P. N. and van Hullebusch, E. D. 2016. Application of Zn isotopes in environmental impact assessment of Zn–Pb metallurgical industries: a mini review. *Applied Geochemistry*, 64: 128-135.

Yu, J.-X., Wang, L.-Y., Chi, R.-A., Zhang, Y.-F., Xu, Z.-G. and Guo, J. 2013. Competitive adsorption of Pb²⁺ and Cd²⁺ on magnetic modified sugarcane bagasse prepared by two simple steps. *Applied Surface Science*, 268: 163-170.

Zamora-Ledezma, C., Negrete-Bolagay, D., Figueroa, F., Zamora-Ledezma, E., Ni, M., Alexis, F. and Guerrero, V. H. 2021. Heavy metal water pollution: A fresh look about hazards, novel and conventional remediation methods. *Environmental Technology & Innovation*, 22: 101504.

Zdrojewicz, Z., Popowicz, E. and Winiarski, J. 2016. Nickel-role in human organism and toxic effects. *Polski Merkuriusz Lekarski: Organ Polskiego Towarzystwa Lekarskiego*, 41 (242): 115-118.

Zhang, X., Hao, Y., Wang, X. and Chen, Z. 2017. Adsorption of iron (III), cobalt (II), and nickel (II) on activated carbon derived from *Xanthoceras Sorbifolia* Bunge hull: mechanisms, kinetics and influencing parameters. *Water Science and Technology*, 75 (8): 1849-1861.

Zhou, Q., Yang, N., Li, Y., Ren, B., Ding, X., Bian, H. and Yao, X. 2020. Total concentrations and sources of heavy metal pollution in global river and lake water bodies from 1972 to 2017. *Global Ecology and Conservation*, 22: e00925.

Zulkifli, F. H., Rani, N. A. M. and Shahitha, F. 2019. Carboxymethyl cellulose nanofibres impregnated with silver nanoparticles for tissue engineering applications. *Materials Today: Proceedings*, 16: 1715-1721.

Zwain, H. M., Vakili, M. and Dahlan, I. 2014. Waste material adsorbents for zinc removal from wastewater: a comprehensive review. *International Journal of Chemical Engineering*, 2014.