AN ASSESSMENT OF THE EFFICIENCY OF ADSORBENTS PRODUCED FROM A MIX OF LEMON AND ORANGE SKINS IN THE REMOVAL OF METALS FROM WASTEWATER

By

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Submitted in accordance with the requirements
for the degree of
Master of Environmental Science
in the

COLLEGE OF AGRICULTURE AND ENVIRONMENTAL SCIENCES
DEPARTMENT OF ENVIRONMENTAL SCIENCES
at the
University of South Africa
FLORIDA CAMPUS

SUPERVISOR:
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October 2023

DEDICATION

I dedicated this dissertation to my parents Richard Kadiambuji Mbaya and Ntumba Ngalula Mbaya, and my precious wife Angelique Mbaya.

DECLARATION

This Research Report is my own work, and it has neither been copied from any other person's work whether published or unpublished, nor has it been previously submitted for assessment at UNISA or any other institution. I confirm that I have read and understood the learning unit on plagiarism and the University regulations on plagiarism in the UNISA policy on research ethics.

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DATE: -------01 October 2023------------------------

ACKNOWLEDGEMENTS

I Thank My Lord and Saviour, Jesus Christ, for giving me the strength to sail through this academic journey. Your Grace is always sufficient for me.

This study became a reality because of the following people to whom I owe my sincere appreciation.

1. My supervisor Prof. VM Ngole-Jeme for the support and guidance provided and for encouraging me throughout this work. What an inspirational leader!
2. My wife Angelique Mbaya, and offsprings Abigail Ntumba Mbaya, Micah Kabongo Mbaya and Asante Ntumba Kabedi Mbaya for the support and inspiration. It was not easy, but they understood the challenges that I faced and supported me throughout this journey.
3. My brother and sisters, Lukusa Mbaya, Rodia Mudibu, Nseya Ngoie, Job Mbaya and Jean Kalala for the support I received from them during the period of this study.
4. Dr Denga for her immeasurable assistance in the laboratory.
5. University of South Africa for the financial assistance.

LIST OF ABBREVIATIONS

AC	Activated carbon
Al	Aluminium
BET	Brunauer–Emmett–Teller
Cd	Cadmium
C_e	final metal concentration at equilibrium (mg/L)
C_i	Initial metal concentration (mg/L)
CAC	Commercial Activated Carbon
Fe	Iron
FTIR	Fourier Transform Infrared Red
g	gram
HM	Heavy Metal
Kf	Freundlich constant
KL	Langmuir constant
L	litre
Mg	milligram
Ni	Nickel
Pb	Lead
q_e	Adsorption capacity at equilibrium (mg/g)
q_t	Adsorption capacity at time t (mg/g)
R	Ideal gas constant (kJ/mol.K)
R2	Correlation factor
RL	separation factor or equilibrium parameter
T	Temperature (K)
V	Volume (L)
w	Weight of the adsorbent (g)
Zn	Zinc

ABSTRACT

Waste materials generated from various agricultural products, processes, and activities have been widely investigated as potential biomass to produce adsorbents with the capacity to remove heavy metals from effluents of various sources because they are cheap. The mechanisms associated with using agricultural waste as adsorbents include ion exchange, chemisorption, complexation, adsorption, and diffusion through pores. These pores have characteristics that may vary with the type of agricultural waste used to prepare the adsorbent. The use of agricultural-waste-derived activated carbon to recover potentially toxic metals including aluminium (Al), cadmium (Cd), iron (Fe), lead (Pb), nickel (Ni), and zinc (Zn) from aqueous solution could play an imperative role in the economy of industries since it could reduce the financial and environmental cost associated with disposal of waste containing these metals. It also encourages recycling through re-utilization of the agricultural waste. This study looked at the effectiveness and selectivity of raw and phosphoric acid-activated adsorbents made from a mixture of orange and lemon skins in the recovery of Al, Cd, Fe, Pb, Ni, and Zn from Acid Mine Drainage (AMD).

The morphology of the mixed orange and lemon skins-derived adsorbent was characterized using a scanning electron microscope (SEM) whereas functional groups present on the surface of the prepared adsorbent and their crystallinity were identified using Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) respectively. Batch experiments to find out how time, pH, adsorbent dosage, and temperature affected Al, Cd, Fe, Pb, Ni, and Zn removal from aqueous solutions using the activated lemon and orange skins were also carried out. The Freundlich and Langmuir isotherm models were used to study the equilibrium kinetics, adsorption isotherms, and the nature of the adsorption process associated with the use of the prepared adsorbent. The optimized parameters were used with the prepared adsorbent to remove Al, Cd, Fe, Pb, Ni, and Zn from AMD samples.

The activated lemon and orange skins had mean pore size and BET surface area of 5.180 nm and 169.28 m^2/g, respectively. It had visible pores on the surface which may indicate high surface area, high efficiency and good adsorption capacity and could be described as mesoporous in nature. Using the optimised conditions with the prepared adsorbent, percentage removal of Al, Cd, Fe, Pb, Ni, and Zn from the AMD were 90.0%, 95.5 %, 99.9 %, 66.0 %, 72.5 %, and 93.0 %, respectively. The data acquired corresponded well with the Langmuir isotherm model with R^2 varying from 0.976 to 0.991, indicating a homogeneous uniform adsorption process. The kinetic investigations revealed that the process of adsorption of metals on the prepared adsorbent was most accurately described by a pseudo-second-order model. Additionally, the adsorbent was capable of being reused up to five times indicating a high potential of recycling them after use.

The findings from this study indicate that adsorbents made from a mixture of orange and lemon skins have the potential to be cost-effective and can be used in the removal of HM's from industrial wastewater, as was demonstrated with AMD. To find out how much metal can be retrieved under optimal conditions, desorption of the metals from the prepared adsorbent needs to be investigated. Further research also needs to be carried out to determine the elemental content, proximal characteristics, and the yield percentage of the adsorbent to understand how to improve Its characteristics as an adsorbent.

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CHAPTER ONE

INTRODUCTION

1.1. Introduction

The discharge of wastewater rich in organic and inorganic pollutants including metals in water bodies results in the contamination of these waterbodies, affecting their use for various purposes. Recovery of these metals from industrial wastewater effluents is therefore a necessity because they have the potential to pollute water bodies and they also impact many life forms negatively due to their toxicity. Heavy metal (HM) recovery from wastewater has been hampered by the costs of the various processes involved. This first chapter of this report on the study carried out to determine how orange and lemon skins can be utilized in the recovery of metals in industrial effluents presents the background upon which the study was formulated and the problems that the study is aiming to provide solutions to. This is followed by the main aim and objectives of the study, the research questions, and the hypothesis that is being tested in the study. The chapter concludes with a justification on why such a study is necessary.

1.2. Background and Motivation

Due to the continuous increase in world population and the establishment of diverse industries to meet the demands of this growing population, environmental pollution has increased in recent years and has become a major concern to environmentalists (Roser et al., 2013). These industries generate wastewaters which may be too acidic or alkaline and rich in suspended, colloidal, and dissolved (inorganic and organic) solids, inert materials, HM, organic pollutants including dyes, and pathogenic bacteria. The wastewater may be discharged into sewers with the hope that they will not affect the sewers, or the effectiveness of the processes used to treat the wastewater with which they are mixed, or they could be discharged into surface water bodies.

In recent years, HM concentrations in wastewater, besides other pollutants, have increased to levels that could be dangerous for humans and the physical environment (Briffa et al., 2020). Metals such as aluminum (Al), arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), mercury (Hg), nickel (Ni), silver (Ag), and zinc (Zn), which are also naturally occurring components of the earth's crust are among the elements that fall under the category of HMs (Briffa et al., 2020). Some of them (Fe, Cu, Se, and Zn) are involved in the control of certain human physiological and biochemical functions (Roohani et al., 2013) whereas others such as Pb, Ni, Cd, and antimony (Sb) which are widely used in industrial processes have no known function in the human body. They are toxic even at low concentrations and could cause significant environmental pollution and human health complications.

The concentrations of HMs often contained in industrial wastewaters is considerable because of their extensive use for different purposes. Industrial processes that produce effluents with high concentrations of HMs include mining, electroplating, conversion coating, anodizing cleaning, milling, etching, wood processing, petroleum refining and photographic operations (Musapatika et al., 2010). Mining activities produce acid mine drainage (AMD) which is a low pH liquid containing high amounts of HMs. AMD is formed when mining activities expose large amounts of pyrite and other sulphide minerals to water and oxygen. The reaction equations involved in AMD generation as indicated by Coetzee et al. (2017) and Ngole-Jeme and Ndava (2023) are presented in Equations 1.1 – 1.4:

$$2FeS_2(s)+7O_2+2H_2O \rightarrow 2Fe^{+2}+4SO_4^{-2}+4H^+ \qquad (1.1)$$

$$2Fe^{+2}+\tfrac{1}{2}O_2+2H^+ \rightarrow 2Fe^{+3}+H_2O \qquad (1.2)$$

$$2Fe^{+3}+6H_2O \leftrightarrow 2Fe(OH)_3(s)+6H^+ \qquad (1.3)$$

$$14Fe^{+3}+FeS_2(s)+8H_2O \rightarrow 2SO_4^{-2}+15Fe^{2+}+16H^+ \qquad (1.4)$$

This HM rich liquid could be discharged into rivers as effluents, potentially increasing the HMs contents of such rivers with negative health consequences on humans and other animals that may get exposed to them through their various activities.

Some HMs are beneficial to man but excessive consumption of even the essential metals could lead to serious toxicological problems such as vomiting, seizures, convulsions or even death (Mitra et al., 2022). According to Hou et al., (2013), Pb causes lung, kidney, gastrointestinal, liver, reproductive system, brain, skeletal dermal and central nervous system complications, and infant intellectual abnormalities. Antimony and Cr are incriminated as carcinogens (Mitra et al., 2022; Talha Bin Emran et al., 2022) with Hg and Cd toxicities being responsible for Minamata and *itai-itai* diseases respectively (Mitra et al., 2022). Therefore, it is mandatory to remove HMs from industrial wastewater before they are discharged into receiving waters to reduce possible human exposure to these HMs and the prevalence of associated health risks.

Various chemical, physical, and biological methods including precipitation, reduction, flocculation, filtration, evaporation, solvent extraction, absorption, adsorption, ion exchange, electrodialysis, and membrane separation are commonly utilized to remove HM from industrial wastewater (Al-Zoubi et al., 2015), but most of these methods are not feasible for developing countries due to the high cost and high energy consumption involved in their use. In addition, some of them have low feasibility at small scale, and the possibility of regenerating the material is low (Al-Zoubi et al., 2015). These techniques are also limited by the fact that they produce large amounts of sludge that require further processing and disposal.

Ion exchange is among one of the very effective methods commonly used for removing HM from wastewaters due to its efficiency, but this efficiency is reduced when the metal concentrations in solution are high because the matrix becomes clogged with organic matter and other solids in the wastewater. Moreover, it is non-selective and may be impacted by the solution's pH (Zewail and Yousef, 2015). Electrolytic recovery, sometimes known as electro winning is also another method where an aqueous metal carrying solution with a cathode plate and an insoluble anode passes an electrical current in the effluent. Metal cations get attached to the cathode, leaving a deposit of metal that may be retrieved (Zewail and Yousef, 2015). The corrosion of the electrodes is a major limiting factor with this method because they need to be replaced frequently.

Adsorption which is a process where contaminants in solution (solute) are adsorbed onto solid surfaces by physical forces or weak chemical bonds is an inexpensive, convenient, and easy operating technique for removing HMs from aqueous solutions (Khulbe and Matsuura 2018). The solute which is attached to the solid surface is called the adsorbate whereas the solid surface onto which the contaminant is attached is known as the adsorbent. High HM removal efficiency is achieved with adsorption, and it is used as a rapid method for the removal of metals from all types of wastewaters (Naef et al., 2021). It is growing in popularity because it is easy to use, and a wide range of adsorbents are available (Zahrim et al., 2019). In addition, the adsorbents utilized can be recycled and the HM can be recovered from the adsorbent (Ouyang et al., 2020). Though considered a viable method of recovering HM from wastewater, the use of adsorption in the treatment of commercial wastewater is limited due to the lack of high-capacity adsorbents. The benefits of this technology are highly dependent on the development of efficient adsorbents (Ouyang et al., 2020).

An effective adsorbent is characterized by high porosity and high surface area, and it should be able to remove contaminants from solution within the shortest possible time (Singh et al., 2018). Activated carbon (AC) is the preferred choice among known adsorbents because it displays most of these properties in addition to being inert, thermally stable, and having active free valences (Soni et al., 2021). It has several notable advantages such as its low operating costs, and it is very stable with a surface structure that can be manipulated (Bagha & Balchi, 2018). However, it is expensive.

Efforts to create affordable AC made from agricultural waste have been expended (Franco et al., 2021). Agricultural waste contains lignin, cellulose, lipids, hemi-cellulose, starches, simple sugar proteins, polysaccharide, and hydrocarbons as the main constituents. The polar functional groups including alcohols (OH-), aldehydes (RCHO), ketones (RRCO), carboxylic acids (RCO_2H), phenolic (ArOH), and ether (ROR) found in these constituents may aid in metal adsorption (Kushwaha and Sudhakar, 2013) by forming complexes with the metal ions in solution. The naturally occurring and abundant surface functional groups present in agricultural wastes therefore make them potentially excellent precursors for adsorbents (Altun and Pelhlivan, 2012).

Studies that have focused on agricultural wastes as adsorbents for HMs (Singh et al., 2018; Kwikima et al., 2021) have used lemon stalk, rice husk, potatoes peel, peanut hull either in their natural state or modified form. These materials are economical and environmentally friendly due to their chemical composition and abundance, and furthermore, they are effective in removing ions from aqueous solutions (Singh et al., 2018). In this study lemon and orange skins were used in the preparation of adsorbents for the recovery of Al, Cd, Fe, Pb, Ni, and Zn from an aqueous solution. These HMs are frequently used in many industries for a variety of processes and products and hence are likely to be present in most industrial wastewaters (Zahrim et al.,2019).

Lemon and orange are major fruit crops grown worldwide and recent advances in biotechnology and the health benefits associated with intake of fruits have increased the yields of these citrus fruits globally. A significant proportion of orange production is destined for juice and jam production and other related products. The production of these items from lemons and oranges generates a considerable amount of lemon and orange skin residue whose valorization could be beneficial environmentally and financially. Due to their availability and affordability, these wastes are promising raw materials for adsorbent production (Rosas et al., 2010). The skins of oranges and lemons are rich in cellulose, pectin, hemicellulose, lignin, chlorophyll pigments, and other hydrocarbons, many of which have several functional groups that could be instrumental in the separation of HMs from wastewaters (Rosas et al., 2010).

To improve the performance of adsorbents produced from agricultural wastes, they need to be activated chemically or physically. The physical activation of agricultural wastes involves partial gasification of the carbonized raw material followed by activation using CO_2 or steam (Fernandez et al., 2014). Due to the high cost involved in physical activation, the use of chemical activation, which makes use of a chemical agent such as phosphoric acid (H_3PO_4) at a temperature that is lower than what is used in the physical activation process is widely advocated for (Ahmadpour et al., 2012). It is believed that chemical activation improves the characteristics of adsorbents, especially their porosity and increases the number of mesopores it contains (Ahmadpour et al., 2012). In addition to the type of adsorbent used and its characteristics and whether it is activated or not, the temperature and pH of the solution containing the contaminants to be removed, the contaminant concentration, the contact time between the adsorbent and the adsorbate, and the particle size of the adsorbent are other factors which determine the performance of adsorbents in the removal of contaminants (Rashed, 2013). This research study investigated the performance of adsorbents produced from chemically activated lemon and orange skins to determine their potential as low-cost HM adsorbents for use in industrial wastewater treatment.

1.3. Problem Statement

The demand to reduce contaminants in aqueous solutions from industries seems to be incessant because of the associated human and environmental impacts. The adverse effects of HM's on human health are widely reported. Metal rich effluents from industry are sometimes deliberately or accidentally allowed to flow into surface water bodies which become contaminated because of the high concentrations of HM. Some of these rivers play a vital role in the sustenance of communities within their catchment. The Elsburgspruit River, a tributary of the Natalspruit, which runs into the Riet spruit and, ultimately, into the Vaal River for example is a river which plays a significant role in the provision of potable water to many communities in South Africa. Accidental drainage of AMD from The East Rand Proprietary Mines which is located close to the Elsburgspruit River could result in the contamination of these rivers with HMs, which may present a significant risk to human health, plants, and animals. Reducing the concentrations of HMs in industrial wastewaters including AMD would reduce the concentrations of HMs released into surface water bodies receiving these effluents and consequently the HM exposure risk to humans and other organisms.

Commercial activated carbon is a very effective adsorbent for HM (Mu'azu et al., 2017) but because it is expensive to produce, attempts are being made by researchers to develop low-cost adsorbents that would provide an alternative. A variety of low-cost adsorbents made from several natural or modified waste materials have recently been developed and used to remove HMs from metal-contaminated wastewater (Mu'azu et al., 2017; Saleem et al., 2019). However, using a combination of lemon and orange skins as biomass for the production of adsorbents and the ratio at which they should be combined have received very little attention, if at all. Orange and lemon skins are mostly composed of organic compounds with functional groups which could contribute to their effectiveness as metal adsorbents.

One of the problems associated with low-cost adsorbents is their performance which is linked to the pH of the solution containing the adsorbate, the contact time between the adsorbent and the adsorbate, the amount of adsorbent (adsorbent dose) which should be used, and initial adsorbate concentration. The optimum parameters for the effectiveness of adsorbents produced from lemon and orange skins are unknown. To ascertain their potential as a possible adsorbent for the removal of HM from contaminated industrial wastewaters, it is necessary to determine the ratio at which lemon and orange skins should be combined to produce adsorbents, and the optimum conditions required for the performance of the adsorbent. The recovery of Al, Cd, Fe, Pb, Ni, and Zn from aqueous solution using lemon and orange skins as adsorbents could also play an imperative role in the economy of the industries producing such wastes since it will reduce the financial and environmental cost associated with their disposal, as well as encourage recycling through their reutilization.

1.4. Research Aim and objectives

The primary aim of this study was to determine the efficiency of adsorbents produced from a mixture of orange and lemon skins for the recovery of Al, Cd, Fe, Pb, Ni, and Zn from AMD.

The objectives included:

- To determine the ratio at which orange and lemon skins should be mixed when using them as raw material for the preparation of low-cost adsorbents.
- To investigate the kinetics, and adsorption characteristics of adsorbents made from orange and lemon skins.
- To identify optimum conditions under which the prepared adsorbents should be used for the recovery of HM’s from aqueous solutions.
- To determine the efficiency of the adsorbent prepared from lemon and orange skins relative to that of commercial activated carbon.
- To determine which adsorption isotherm best describes the adsorption of HM at optimum operation parameters.
- To determine the reusability and regeneration of the prepared adsorbent.

1.5 Research questions

- Which is the best ratio at which lemon and orange skins should be combined when used in the production of low-cost adsorbents?
- How effective are adsorbents made from orange and lemon skins in the removal of Al, Cd, Fe, Pb, Ni, and Zn from AMD?
- How does the efficiency of the adsorption of these metals by adsorbents made from lemon and orange skins compare with that of commercial activated carbon?
- What are the optimum conditions under which the prepared adsorbent should be used for the recovery of HM's?
- Which of the two main equilibrium isotherms is the most likely observed during the adsorption of metals at the optimum operation parameters?
- Can the prepared adsorbent be regenerated after use?

1.6 Hypothesis

H_0: Low-cost adsorbents made from a combination of orange and lemon skins are not efficient in the removal of HMs from AMD
H_1: Low-cost adsorbents made from a combination of orange and lemon skins could be used to remove HMs from wastewater.

H_0: The efficiency of adsorbents prepared from a combination of orange and lemon peels is lower than that of commercial activated carbon in the removal of HM from AMD
H_1: The efficiency of adsorbents prepared from a mixture of orange and lemon skin is comparable with that of commercial activated carbon.

1.7 Justification

The conversion of agricultural waste into adsorbents to recover HM ions from industrial wastewaters will not only solve the problems associated with the disposal of this wastes but it will also provide a solution to the reduction of the toxicity of many industrial effluents. Low-cost solutions are likely to increase economic gain in industries where disposal of aqueous solutions rich in HM is posing a challenge. The materials that are used in the preparation of the adsorbents are easily found locally and internationally, hence the method may be economically feasible even for small scale industries who are currently relying on service providers to dispose of metal rich effluents as the raw materials are available. Recycling of these wastes offers numerous benefits, such as reducing greenhouse gas emissions from the degradation of the wastes, preserving natural resources, prolonging the lifespan of landfills as less waste will be taken to the landfill, and conserving energy.

CHAPTER TWO

LITERATURE REVIEUW

2.1 Introduction

Several efforts have been made in the search for low-cost adsorbents that could remove heavy metals from aqueous solutions. This chapter gives a summary of literature on recent research that have been undertaken around the globe on the removal of HM from wastewater using adsorbents. Various methods used in the treatment of wastewater contaminated with HM are also reviewed. The chapter provides a synopsis of the environmental consequences of HMs and the various materials used to prepare adsorbents that are used for heavy metal recovery. The chapter also discusses the use of agricultural wastes that have been used as adsorbents and the factors affecting their efficiency in the removal of HMs from aqueous solutions.

2.2 Wastewater types and composition

Wastewater includes urban/municipal wastewater (sewage), agricultural wastewater, stormwater runoff, industrial and commercial wastewater. Urban/municipal wastewater is derived from domestic wastewater which consists of night soil (human and animal waste) and grey water which is generated from various household activities such as washing (32.5%) and bathing (67.5%) (Oteng-peprah et al., 2018). It may also contain traces of food, grease, hair, dirt, and household cleaners (Oteng-peprah et al., 2018), many of which contain a variety of HMs. Agricultural wastewater comprises wastewater produced by farming (pastoral and arable), and other agricultural activities. Due to the heavy use of pesticides and fertilizers, agricultural wastewater is becoming an increasingly important source of organic and inorganic pollution (Saxena & Bharagava, 2020). Stormwater comprise runoff generated from various surfaces during rainstorm and its composition is highly variable because of its diverse origins. It however usually contains nitrogen, phosphorus, antifreeze, lubricating substance, toxic elements and HMs from automobiles, plant nutrients, insecticides and other substances from gardens, residences and commercial establishments, microorganisms from animal excreta and malfunctioning sewage systems, and particulate matter from construction and industrial sites. Industrial wastewater consists of effluents from various industrial and manufacturing processes and comprises of salts, acids, and various chemicals. The sources of these industrial wastewaters vary greatly, as does the composition of the effluents produced by them, which often require specific treatment to meet emission regulations. Industrial wastewater is generally divided into inorganic wastewater, which is dominated by chlorides, nitrogen, phosphorus, sulphur, toxic inorganic compounds, and HMs (Bharagava, 2017), and organic industrial wastewater which include pesticides, herbicides, endocrine disruptors, dyes, polychlorinated biphenyls, phenolic compounds, and phthalates among others, (Saxena & Bharagava, 2020; Bharagava, 2017).

2.3 Sources of HMs in wastewater

Among the components of wastewater, HMs have generated a lot of interest to environmentalists and various healthcare sectors because they do not biodegrade in the environment, and they have the ability to cause negative health outcomes in humans and other animals upon exposure. The extraction of mineral resources during industrial and mining processes, and their use in various industries and economic development projects have resulted in the generation of HM rich effluents which are eventually discharged into rivers or into the sewer system to be treated with wastewater, thereby increasing the concentrations of HMs in the environment (Ali et al., 2018). The exposure of mine wastes such as tailing dams and waste rocks to oxidation and leaching is one of the sources of HM release into the environment from mining (Ali et al., 2018). AMD which is acidic and contains high concentrations HMs is generated when pyrite and water reacts under the earth’s surface. Table 2.1 presents various HM and their sources to wastewater. It can be seen that the anthropogenic sources of HM are diverse, and some sources are incriminated in the release of more than one HM into the wastewater stream.

Table 2. 1 : Main sources of certain HM ions in wastewater

HM	Type of industries where produced	Industrial process releasing HM
Cu	Iron steel industry, metal finishers, dying & textile industry, Agricultural industry	Leather Tanning, Fertilizers, photovoltaic cells
Zn	Dying & textile industry, iron steel industry, metal finishers	Soldering, cosmetics, pigments
Ag	Mining, power plant, manufacturing industry	Industrial process and mining.
Cr	Power plant, dying & textile industry, metal finishers	Tanning, of leather, chrome plating industries
As	Mining, Iron steel industry, Agricultural industry	Discharge of unprocessed sewage effluent.
Hg	Mining, manufacturing of battery, paint industry, Domestic wastewater plant	Municipal waste incineration process, Combustion of coal at power station.
Cd	Metal finishers, power plants	Manufacturing process such Paints, pigments, and electroplated parts.
Pb	Power plant, metal finishers, dying & textile industry, mining, manufacturing of battery, agricultural industry	Production of pipes, agricultural process, and manufacturing of lead batteries etc.

(Modified after Singh et al., 2022)

2.4 Effects of HMs in wastewater on the environment

2.4.1 Effects on aquatic organisms

Organism, such as fish and invertebrates absorb HMs from various sources which results in various impacts that can vary from insignificant to fatal. Even though some metals, like Cu, Zn, Fe, Mn, Co, Molybdenum (Mo), Cr, and Selenium (Se), are crucial for organisms at low concentrations, at higher concentrations, they could affect the organism's growth, metabolism, or reproduction with dire consequences on entire food chains (Stankovic et al., 2014). Lead, Cd, Ni, As, and Ag are non-essential HMs that even at low amounts are harmful to living organism. Elevated levels of Al are toxic to gill-breathing fish and could cause the plasma and haemolymph ions to be destroyed, which can result in osmo-regulatory failure (Jaishankar et al.,2014). Cadmium due to its high-water solubility, can affect aquatic organism such as diatoms, amphibians, and fish. The tadpoles of the frog (*Rana luteiventris*) from Colombia were shown to be affected by Pd, Al, Cd, Fe, and Ni in terms of their survival, growth, and metamorphosis (Stankovic et al., 2014). Therefore, elevated levels of HMs in the aquatic environment can seriously threaten the functioning of aquatic ecosystems due to their toxic effects, long-term persistence, bioaccumulation properties, and bioaccumulation in food chains (Stankovic et al., 2014).

2.4.2 Effects on soils and plants

High concentrations of HMs in wastewater may find their way to soils through irrigation or seepage where they could affect important soil microbial processes and activities (Chibuike and Obiora, 2014) with consequences on various biogeochemical cycles. This may affect the breakdown and availability of organic nutrients in soils and eventually plant growth. Some HMs are necessary for the development and growth of plants, but they should not be excessive in concentrations in the soil as they may poison the plant (Chibuike and Obiora, 2014). High Cd concentrations in soil for example can reduce the ability of plants to photosynthesize and absorb protein, resulting in cell membrane damage (Okereafor et al., 2020). Similarly, elevated level of Zn in soil suppresses the metabolic activity of plants, inhibits growth, and causes senescence (Okereafor et al., 2020) even though it is an essential element for plant growth. The phytotoxic effects of Zn and Cd are also manifested by the performance of the pea plant, enzymes, and developmental delay. and oxidation-induced damage in several other plant species (Okereafor et al., 2020). Lead adversely affects plant growth by interfering with important enzymes and therefore reduces the germination of seeds (Okereafor et al., 2020). Other impacts of heavy metals on soils and plants can be found in Okereafor et al. (2020).

2.4.3 Effects on humans

Humans are exposed to HMs in wastewaters daily due to the various industrial process and activities which they control and participate in. Human exposure to HM could lead to a reduction in energy levels and may affect the lungs, brain, kidneys, liver and composition of the blood and other organs. It could also in the long term induce progressive physical, muscular and neurological diseases with prolonged exposure potentially leading to cancer (Jarup, 2003). Cadmium can seriously harm human kidneys and cause osteoporosis. Copper poisoning can induce vomiting, pain in the abdomen, and other gastrointestinal issues (Jarup, 2003). In severe situations, it can also result in organ failure and even death. Zinc causes internal bleeding, cramping in the abdomen, and nausea (Jarup, 2003). Lead poisoning can cause harm to the neurological and brain systems, excessive blood pressure, and kidney complications (Jarup, 2003). Table 2.2 presents some of the human health challenges caused by heavy metals of interest in this study.

Table 2. 2: Health effects of selected metals in humans

Metal	**Health Effect**	**Reference**
Al	Nausea, mouth ulcer, skin ulcer, brain damage and loss of memory	Jaishankar et al. 2014,
Cd	Osteoporosis, lung damage and kidney disease.	Jaishankar et al. 2014, Chakraborty et al. 2013
Fe	Bleeding of the intestine and diarrhoea	Jaishankar et al. 2014
Ni	Harm lungs, harm stomach & harm kidney.	Jaishankar et al. 2014,
Zn	Lethargy, respiratory disorder, vomiting /nausea, and diarrhoea	Plum et al., 2010

2.5 Techniques used in HM recovery from wastewater

The most used methods to remove HMs from toxic effluents are chemical precipitation, ion exchange, electrolysis, and adsorption.

2.5.1 Chemical precipitation

Chemical precipitation is widely utilized in industry and is regarded as an important method for removing HMs in wastewater by Naef et al. (2021). In this process, a reagent is used to alter the pH or electro-oxidation potential of a solution containing dissolved metal ions, causing the metal ions to precipitate. Precipitation is usually done with a hydroxide as per the reaction represented in Reaction Equation 2.1 due its simplicity, low cost, and tenable pH (Naef et al.,2021).

$$\text{Metal(Ca) (OH)2} \Leftrightarrow \text{Metal (OH)n}\downarrow + Ca^{2+} \qquad 2.1$$

Calcium hydroxide ($Ca(OH)_2$) is one of the most used hydroxide precipitates for heavy metals in inorganic effluents (Kurniawan et al., 2006). Most metals including Zn^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Cr^{3+} are successfully removed by this method (Naef et al.,2021). A pH value of 9 - 11 has been discovered to improve the precipitation reaction according to Kurniawan et al., (2006) and Naef et al., (2021) but a high pH is regarded as a disadvantage of chemical precipitation because a large dose of coagulant is needed to increase the pH (Naef et al.,2021).

2.5.2 Ion exchange

Ion exchange is a process whereby a reversible chemical reaction is used to replace unwanted metal ions with safe, harmless, and environmentally friendly alternatives (Dąbrowski et al., 2004; Naef et al., 2021). In this procedure, HM ions are extracted from wastewater solutions by binding them to immobile solid particles such as inorganic zeolites or organic resins. As stated by Dąbrowski et al. (2004) and Naef et al. (2021), ion exchange has been successfully used to remove Pb, Hg, Cd, Ni, V, Cr, Cr, Cu, and Zn from wastewater. The advantages of the ion exchange process include the fact that the resin used can be regenerated, it is cheaper than other methods, and it is very efficient in inorganic ions removal from wastewater. However, it has some disadvantages which include the high long-term costs of running ion exchangers, and the fact that while ion exchange beds can be recycled, the process discharges salt water directly into the environment. Despite these disadvantages, ion exchange is the most widely used industrial effluent treatment method due to its high removal efficiency and kinetics (Mishra et al., 2021).

2.5.3 Electrodialysis

Electrodialysis (ED) can be described as a form of membrane filtration that segregates ions in a solution using electrical discharge across exchange membranes (Mishra et al., 2021). It uses charged membranes and potential difference to separate ions from aqueous solutions and other uncharged components (Mishra et al., 2021). Electrodialysis has emerged as a future technology with tremendous potential for concentrating and recovering metals from toxic effluent (Mishra et al., 2021). The Cu removal rate of electroplating in industrial wastewater effluent was studied and the results obtained with a 5-unit cell electrodialysis experiment from synthetic electroplating water achieved 85 % removal efficiency (Caprarescu et al., 2021). In another study, electrodialysis successfully removed 96.9, 99, and 99.9% of Ni^{2+}, Pb^{2+}, and K^{+} respectively from a synthetic solution (Nemati et al., 2017). Results from studies using electrodialysis to remove HM from AMD show that electrodialysis has some potential with a contaminant removal percentage of more than 97% (Buzzi et al., 2013).

2.5.4 Adsorption

Adsorption is one of the most widely used techniques for removing metal ions from aqueous solutions. Adsorption is a surface occurrence (Hussain et al., 2021) where molecules (absorbate) are attracted to, and retained on the surface of the adsorbent until a state of equilibrium is reached between the molecules on the surface of the adsorbent and those in the solution. Processes associated with the interactions between the adsorbent and adsorbate include chemical bonding, hydrogen bonding, hydrophobic forces, and van der Waals interactions (Hussain et al. 2021). Adsorption can be divided into physisorption and chemisorption, each with different binding properties. "Physisorption" which is caused by van der Waals forces is said to occur when the electronic structure of the atom or molecule involved is not altered during adsorption whereas “Chemisorption” is facilitated by the chemical reactions that take place on exposed surfaces of the adsorbent (Hussain et al.,2021). Adsorption processes are relatively new processes and have emerged as preferred alternatives for HM removal due to their design flexibility, efficiency reversibility and ability to regenerate adsorbents (Demey et al., 2018). Despite being highly effective, adsorption as a HM removal technique possesses inherent limitation or drawbacks such as significant sludge generation, delicate operational requirements, and expensive disposal cost (Demey et al., 2018). Most of the sludge generated is disposed of in landfills with little or no treatment. This aggravates the solid waste disposal problem in some developed and developing countries (Moosavi et al., 2020). Several variables, including contact time, adsorbent surface area, particle size, pore size, pH, and the solubility of the adsorbate in solution influence the efficiency of the adsorption process. Adsorption is often defined by an isotherm that elucidates the correlation between the amount of substance adsorbed by a known weight of adsorbent and the concentration of adsorbate left in solution at equilibrium under constant temperature (Demey et al., 2018). The Langmuir and Freundlich isotherm models are commonly employed to illustrate the adsorption of different metal ions to adsorbents.

2.5.4.1 Langmuir isotherm

The Langmuir isotherm proposed by Langmuir (1916) is a semi-empirical isotherm derived from a proposed kinetic mechanism and is based on four assumptions:

- The adsorbent's surface is uniform, meaning all adsorption sites are the same.
- The molecules which might be adsorbed do not interact.
- The mechanism of adsorption of the molecules is the same.
- During maximum adsorption, just a monolayer is created because the adsorbent molecules only deposits on the free surface of the adsorbent, not on other adsorbate molecules that have previously been adsorbed.
- The rates of adsorption and desorption are equal at equilibrium.

The following equation (Equation 2.2) is the mathematical representations of the Langmuir model:

$$q_{e\,(mg/g)} = \frac{Q_m b C_e}{1 + bC_e} \qquad (2.2)$$

Where; q_e*(mg/g) is the amount of metal ion adsorbed per weight of the adsorbent at equilibrium.* Q_m *is the monolayer adsorption capacity (mg/g).* C_e *is the equilibrium concentration of HM in solution (mg/l) and* b *is the Langmuir constant (L/g) (Langmuir 1916).*

Since the Langmuir isotherm has numerous uses in surface kinetics and thermodynamics, it is one of the most widely used models of adsorption.

2.5.4.2 Freundlich isotherm

The Freundlich adsorption isotherm establishes a connection between the amount of adsorbate on the surface of an adsorbent and the amount of adsorbate in the liquid that the adsorbent is in contact with (Freundlich 1906). The underlying principle of the isotherm is that as adsorption rate increases, the size of the heat of adsorption decreases (Callery et al., 2016). There is an exponential distribution of the adsorption sites with respect to adsorption energy, which is indicated by the logarithmic decline of the heat of adsorption with increasing extent of adsorption (Freundlich 1906; Callery et al. 2016). The Freundlich model is empirical and there are no assumptions made when deriving it. The Freundlich isotherm is mathematically shown as in Equation 2.3:

$$\mathrm{q_e} = \mathrm{K_f}(\mathrm{C_e})^{1/\mathrm{n}} \qquad (2.3)$$

Where K_f and n are the equilibrium constants representing the adsorption capacity and the adsorption intensity, respectively. With increasing temperature, the constants K_f and n change, reflecting the empirical observation that the amount of adsorption increases more slowly, and a higher pressure is required to saturate the surface of the adsorbent (Freundlich 1906).

To study the equilibrium data of adsorbents composed of varied materials, Langmuir and Freundlich isotherms can be used. Langmuir's model suggests that sorption occurs on a homogeneous surface of the adsorbent, producing a saturated monolayer in contrast to Freundlich's equation which is based on adsorption on a heterogeneous surface (Khayyun & Mseer, 2019). Nonetheless, the Langmuir isotherm has frequently been used to understand the adsorption of HMs on heterogeneous adsorbents.

2.6 Type of adsorbents used to remove HMs from wastewater

Adsorbents are characterised by high porosity, and a large surface area that allows substances to be adsorbed onto its surface by intermolecular forces (Moosavi et al., 2020). Industrial sorbents are divided into three classes as follows:

- Polar and hydrophilic oxygen containing materials like zeolite, silica gel, and alumina.
- Compounds made of carbon that are hydrophobic and are not polar including graphite and activated carbon.
- Materials where polar or non-polar functional groups in a porous polymer matrix are used.

The most popular industrial adsorbents are those belonging to the first two groups and include silica gel, zeolites, alumina, and activated carbon because of their extraordinarily large surface area per unit weight.

2.6.1 Silica Gel

This is a three-dimensional polymer made up of four-dimensional highly porous SiO_2 units (Tso and Chao 2012). It has a network of interconnecting pores and channels that can transfer many substances, including water, alcohols, phenols, and amines (Tso and Chao 2012). Silica gels contain large pores with large diameters and a high adsorption capacity at low temperatures, both of which may be adversely impacted by a high moisture content according to Pourhakkak et al (2021). Due to its exceptional chemical stability at higher acidity levels, silica gel plays a key role as an adsorbent for the removal of HM ions even though the silanol groups (Si-OH) on its surface are very reactive chemically (Pourhakkak et al., 2021). Li et al. (2019) studied the removal of Pb^{2+}, Cu^{2+}, and Cd^{2+} from aqueous solutions using silica gels and found adsorption capacities of 63.5, 53.14, and 76.22 mg/g for each respectively with removal efficiency of between 96% to 99% at the same concentration of 20 mg/l. According to Etale et al. (2014), mesoporous silica nanoparticles (NPs) were used in batch studies to adsorb Cu(II), Mn(II), and U(VI) ions to test the viability of employing NPs to clean up AMD-contaminated water. It was discovered that the adsorption response was quick, reaching equilibrium for Cu in 5 minutes and for Mn and U in under 1 minute. Nevertheless, elimination of Cu was slowed down in 1:2 Cu: Mn solutions. These studies indicate that silica gel could be successfully used as an adsorbent for HMs. However, silica gels are disadvantaged by their low water exchange because adsorption requires a remarkably high relative pressure (Henninger et al., 2009).

2.6.2 Zeolite

Silicon, Al, and O make up the crystalline solids known as zeolites. They are produced in an autoclave using the hydrothermal synthesis of sodium aluminium silicate or another silica source followed by ion exchange with sodium or lithium or calcium ions (Khaleque et al., 2020). Zeolites have the capacity to selectively sort molecules by size due to a very uniform pore structure. They are used as ion exchange beds in water purification (Khaleque et al., 2020). Yang (2003) studied the exchange capacity of zeolite and showed that the enhancement of the cation exchange capacity of zeolites depends on the pre-treatment method. In Zeolites that were treated with NaOH to improve their adsorption efficiency, their Mn^{2+} adsorption capacities were more than 100 mg/g higher than those of untreated zeolites (Khaleque et al., 2020). According to Wulandari et al. (2020), the removal efficiencies of Cu and Zn by natural and synthetic zeolites were 98.16% and 93.98% at optimal adsorbent dose of 1.5 g/l and 21 g/l, respectively. The optimal contact time for both adsorbents was 120 minutes which highlights its potential as an adsorbent. Zeolites have the potential to replace AC as a widely used adsorbent, but they need to be artificially transformed because of their low permeability before they can be used.

2.6.3 Alumina

Chemical grade alumina that has been enhanced with surface activity and high levels of porosity is known as "activated alumina," and it is the ideal adsorbent according to Yang (2003). The surface chemistry and pore structure of activated alumina can be adjusted for a range of purposes by applying acid or alkali treatment, as well as controlled heat treatment. Inorganic pollutants like Cd, Pb, As, and Fe are removed from water by alumina-based sorbents, which are employed in wastewater treatment (Yang, 2003). The adsorption behaviour of aluminium oxide is significantly influenced by the pH of aqueous environments. For instance, at pH 5–6, alumina can effectively adsorb Se(VI), and over 90% of As (V) from surface and groundwater when the pH is 7. Because of the chemical bonding of As to alumina which stops further leaching of As into the environment, As in sludge can be removed inexpensively and safely with alumina. It has also been demonstrated that the high exchange capacity of this ion, which is immune to SO_4^{2-} or Cl^- present in water efficiently removes fluoride from water. Furthermore, phosphorus, a significant contributor to eutrophication in ponds and lakes, is effectively removed by alumina (Kim et al., 2013). According to Kim et al.

(2013), a new composite material made from activated alumina and recycled collagen fibre in an alginate gel was created to tackle the problem of HM pollution in AMD. The quantity of Cd (II) eliminated was 32.2 mg/kg, while the quantities of Cu (II) and Pb (II) removed were 1690 mg/kg and 414 mg/kg, respectively.

2.6.4 Activated Carbon

A highly porous, non-polar, amorphous material made up of micro crystallites with a graphite lattice, activated carbon is comprised of small granules or powders (Putshaka and Adamu 2010) formed from bituminous and lignite, oil cake, sawdust, burk, and wood products (Putshaka and Adamu 2010). Activated carbon can be produced either by physical or chemical activation (Putshaka and Adamu 2010). The production process consists of carbonation and elevated temperature activation (Campbell et al., 2012). Exposure of the crystals to an oxidizing agent such as carbon dioxide or a steam environment activates carbonized particles (Campbell et al., 2012) creating a pore-blocking structure which is burned away by a chemical, leaving behind a porous three-dimensional graphite network (Campbell et al 2012). The length of time taken for carbonation affects the size of the pores that are created upon activation as the size of the pore increases with exposure time.

Activated carbon is used as an adsorbent to remove HM from wastewaters due to the high surface area, microporous nature, and surface chemical makeup. Its large interior surface area, (500 $m^{2/}g$ to 1500 m^2/g), makes it a good adsorbent (Campbell et al. 2012). According to Abdulrazak et al. (2017), AC showed great ability in removing Cd, Cu, Ni and Pb from wastewater with removal rates at a temperature of 80°C of 93.23 ± 0.035%, 96.71 ± 0.097%, 92.01 ± 0.018%, and 95.42 ± 0.067% for Cd, Cu, Ni and Pb, respectively. An investigation was conducted by Suliestyah et al., (2020) to investigate how effectively coal-based AC removes metals from AMD. Iron and Mn had maximum adsorption values of 100% and 56% respectively, with a maximum pH increase from 3 to 6.2.

The use of AC as an adsorbent is a known technique for eliminating or reclaiming metals from industrial wastewater but adsorbent-grade AC is expensive and recycling of spent carbon is often difficult making it less affordable for small-scale industries (Campbell et al., 2012). As a result, there is rising interest in the production of adsorbents utilizing less expensive materials including clay, fly ash, and agricultural waste. In general, an adsorbent is described as "cheap" if minimal processing is required in its production, it is plentiful in the environment, or it is a by waste product from industry (Campbell et al., 2012). Agricultural waste is commonly available and affordable.

2.7 Agricultural waste as low-cost adsorbents

Agricultural wastes have distinct chemical composition, they are abundant, renewable, inexpensive, and widely accessible making them one of the favourable raw materials for inexpensive adsorbents (Acharya et al., 2018). The biodegradability, non-toxicity, and environmental friendliness of these materials are further advantages. Recent studies have revealed a focus on the utilization of agricultural waste materials in the production of adsorbents used for wastewater treatment (Othmani et al., 2022; Karic et al., 2022). These materials have potential adsorption efficiencies comparable to those of commercial AC and they are affordable (Acharya et al. 2018). The variety of functional groups present in agricultural wastes including hydroxyl and carboxyl groups play crucial roles in their adsorption capabilities due to the high affinity of these functional groups for metal cations (Acharya et al. 2018). Studies show that various agricultural wastes such as rice husks, tree bark, coconut shells, apricot kernels, tea leaf waste, sugarcane, apple, banana, orange peel, grape stalks, sugar beet pulp, cotton stalks have been used as raw materials for adsorbents. (Bulut and Tez 2007; Skodras et al. 2007; and Lafka et al. 2007).

A study by Abdel Salam et al. (2011) revealed that, in descending order, fly ash, natural zeolites, coal fly ash, and peanut shell charcoal all have the capacity to remove HMs from industrial effluents. Sekhula et al., (2009) also showed a 56.7-73.2% range of recovery of HM from synthetic industrial wastewater using corn brush, an agricultural waste material. According to Bulut (2006), walnut sawdust may also be an effective adsorbent for metal ions in aqueous solutions. The stem of *Amaranthus hybridus (African spinach)* and the seeds of *Carica papaya (pawpaw)* were also found to successfully remove Mn (II) and Pb (II) ions from an aqueous solution (Egila et al., 2011) with the seeds of C*. papaya* showing a consistently higher capacity for adsorption than the stem of *A. hybridus*. This demonstrates that the adsorption effectiveness varies with the waste utilized in producing the adsorbent and the kind of HM that needs to be removed. However, plant materials when used as an adsorbent without pre-treatment release soluble organic compounds which may cause low adsorption capacity, high chemical, and biological oxygen demand (BOD), and total organic carbon (TOC) (Iqbal et al 2008). Therefore, plant waste must be modified before it is used for removing metals.

2.7.1 Factors which affect the efficiency of agricultural waste as adsorbents

The effectiveness of agricultural waste as HM adsorbents is influenced by several factors among which are contact time, ion concentration and ion type, the pH of the metal ion solution, and agitation rate (Sekhula et al., 2009). In a study by Abdel Salam et al, (2011) the optimum pH for Cd and Zn removal was pH 6 when using peanut husk charcoal whereas for natural zeolite, a pH of 8 was identified as the optimum pH. Batch experiments by Sekhula et al. (2009) indicated that the proportion of Cd^{2+} removed from a 20-ppm solution varied between 29.5 and 33.9% at pH 1 and between 56.7 and 73.2% at pH 4, indicating that the recovery of Cd by maize tassel is pH dependant. These studies highlight the significance of pH in the adsorption of HMs by agricultural waste.

Experiments conducted by Abdel Salam et al. (2011) revealed that an equilibrium time of 2 h was needed by peanut husk charcoal and fly ash for the adsorption of Cu(II) and Zn(II) whereas up to 3 h were needed for the adsorption of the same ions onto natural zeolite. Equilibrium was achieved within a period of 30 min in a study involving the recovery of Cd^{2+} from aqueous solutions using maize tassel (Sekhula et al., 2009). Bulut & Tez (2007) attained equilibrium within 60 min using walnut sawdust in the adsorption of Pb, Cd, and Ni from aqueous solution by the sawdust of walnut. These results highlight the necessity of identifying optimum, parameters that should be used when agricultural wastes are used as absorbents for HMs. In another experiment conducted by Putra et al. (2014), the amount of coconut tree sawdust (CTS), eggshell (ES) and sugarcane bagasse (SB) used to remove Cu(II), Pb(II) and Zn(II) ions from an aqueous solution at a pH of 6.0 was found to affect removal efficiency.

2.8 Conclusion

The extraction of HMs from industrial effluents has been accomplished using a variety of techniques, such as adsorption, coagulation, and electrocoagulation (Simeonidis et al. 2019). However, the cost of these procedures and the amount of sludge that must be disposed restrict their use. Adsorption of HMs has become a popular technology for removing HM from aqueous solutions since it is easy to use, inexpensive, ecologically beneficial, and reversible. For the adsorption of HMs, a variety of adsorbents including activated carbon, zeolites, charcoal, and silica are utilized. However, the high production cost has prompted researchers to investigate low-cost, eco-friendly substances that can be employed as adsorbents or as raw materials to produce an adsorbent that is more reasonable in terms of cost. A sustainable, effective, and cost-effective way of recovery of metals from effluents is the use of biosorbents manufactured from municipal solid waste and agricultural by-products.

CHAPTER THREE
MATERIALS AND METHODS

3.1 Introduction

This chapter focuses on the approach that was used to carry out the study. The chemical activation of lemon and orange skins using dilute phosphoric acid (H_3PO_4), as well as the methods used to characterize the prepared activated material are explained in this chapter. The chapter also includes the experimental procedures used in testing the efficiency of Al, Cd, Fe Ni, Pb and Zn adsorption using the adsorbent prepared from lemon and orange skins. The optimization of parameters such as contact time, initial concentration, adsorbent mass, pH, reaction kinetics and the test to determine whether the adsorbate can be regenerated from the adsorbent are also included in the chapter. The chapter concludes with a presentation of the quality assurance measures taken to ensure the accuracy of the data, and data analyses, and the ethical considerations surrounding the study.

3.2 Description of the study area

This research was a laboratory-based study where samples collected from an AMD treatment plant were brought to the laboratory and used in the experiments. The AMD samples were taken from the Central Basin Acid Mine Drainage treatment plant located in the western portion of the East Rand Proprietary Mines (ERPM) in Gauteng Province, South Africa with geographical coordinates S 26° 13` 02.6" and E 28° 10' 57.1" (Figure 3.1). The site treats AMD from ERPM and releases the treated water into the Elsburgspruit River whereas the sludge is discharge through an existing pipeline to Brakpan tailings dam. The AMD treatment facility is currently treating wastewater containing substantial amounts of toxic metals, particularly Al, Cd, Fe Ni, Pb and Zn. The technology utilized for treatment entails neutralizing the acidity of the AMD to facilitate the precipitation and removal of the HMs.

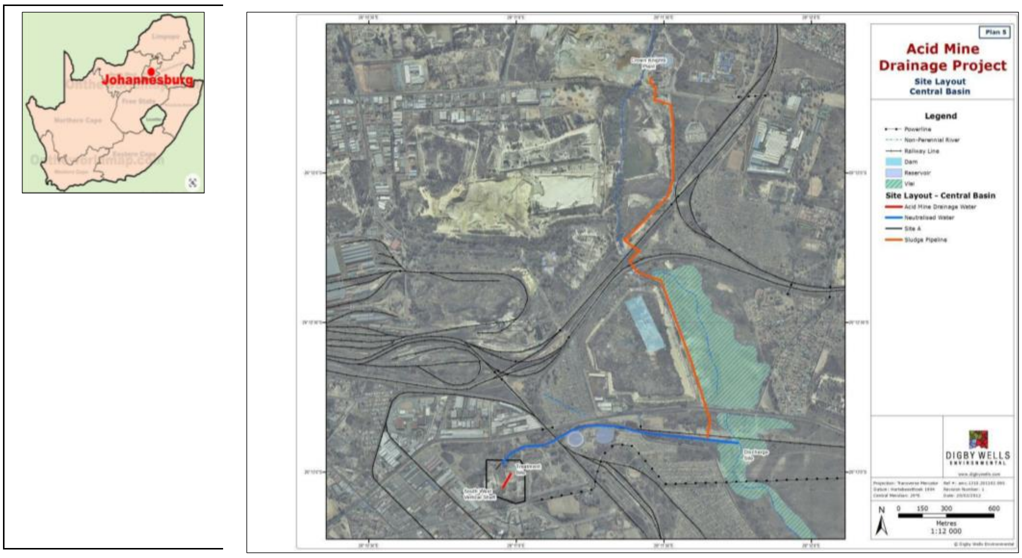


Figure 3. 1 : Locality map of study area (Grant Beringer and Graham Trusler 2012)

3.3 Research Methods

3.3.1 Research design and approach

For this study, a quantitative research design with an experimental approach was employed. Quantitative research focuses on numbers or facts that can be converted into numbers (Williams, 2014). Statistics and figures are often used to communicate objective findings from quantitative studies (Williams 2014). In this research design, the researcher manipulates or controls the independent variable to observe how it impacts one or more dependent variables. This research involved several laboratory tests to determine how effectively HM could be removed from industrial effluent using adsorbents made from a mixture of lemon and orange skins.

3.3.2 Collection of orange and lemon skins and preparation of adsorbent

Orange and lemon skins weighing about 2kg each were purchased from Tshwane Fresh Produce Market in Pretoria, Gauteng Province. The treatment and activation of the orange and lemon skins were done following a method described by Amela et al. (2012) and Temesgen et al. (2018) with some modifications. The skins were cleaned in distilled deionized water and dried in an oven at 95°C for 24 hours to eliminate moisture. The dried skins were then crushed with a mixer to a particle size range of between 200 and 600 µm. Three weight percent ratios of the dried orange and lemon skins (1:1, 4:1 and 1:4) were constituted and placed in separate containers after which they were each impregnated with 1 M H_3PO_4. The impregnation was done by adding a mixture of 50 g of 1 M phosphoric acid (H_3PO_4) and 150 ml of distilled water into the different combinations of lemon and orange skins in a glass container. The mixed material was drained and dried at 110 ^{o}C in an oven for 24 hours. To enhance the adsorption of the H_3PO_4 by the skins, ultrasonic assistance was utilized in cycles of 10 minutes, followed by a 10-minute pause (Amela et al. 2012). Afterwards, the glass container with the mixtures were placed on a shaking device set at 60 revolutions per minute at a temperature of 30°C for 24 hours. The mixtures were then drained and dried at 110 ℃ in an oven for 24 hours after which they were transferred into a furnace under inert atmosphere and heated to a temperature of 650℃ and held at this temperature for 3 hrs (Amela et al. 2012). The chemically activated materials henceforth referred to as the adsorbent were then cooled down, and then rinsed with distilled water, dried at 110 °C, and crushed into particles that ranged in size from 200 to 600 m (Fernandez et al., 2014). This was repeated for each of the three combinations of lemon and orange skins.

3.3.3 Sampling and characterisation of AMD

Acid mine drainage samples were collected from two AMD reactors at the study site using two five litre containers which had been cleaned with distilled deionised water to eliminate all impurities. The samples were kept in a cooler box at normal temperature and transported to the laboratory where the concentrations of the HMs of focus in the study (Al, Cd, Fe, Pb, Ni, and Zn) were determined. These metals were chosen due to their persistence in most wastewater streams (Wilschefski and Baxter, 2019). Inductively coupled plasma-optical emission spectroscopy (ICP-OES) using a Shimadzu ICPE-9001 was employed in the quantification of these metals in the AMD sample solutions after calibration using standard solutions of the metals (Wilschefski and Baxter, 2019). The equipment conditions used for the analyses of these HM were as indicated in Table 3.1.

Table 3. 1 : ICP-EOS operating parameters

Parameters	Conditions
RF generator power/W	1150
Coolant gas flow rate/L min^{-1}	12
Frequency of RF generator/MHz	40
Pump rate/rpm	51
Viewing configuration/touch mode	Axial
Replicates	2
Flush time/s	31

3.4 Characterisation of the adsorbent

Properties of the adsorbents characterised included the total surface area, pore diameter and pore volume, morphology, functional groups present on the surface of the adsorbent, the elemental composition, and the crystal structure of the adsorbent.

3.4.1 Determination of the absorbent morphology

The prepared adsorbent was freeze-dried and pre-coated with a carbon/gold alloy in high vacuum to induce conductivity (Yacob et al., 2011) before analysing with a TESCAN VEGA 3 XMU LMH scanning electron microscopy combined with energy-dispersive X-ray spectroscopy (SEM-EDX). An accelerated voltage of 20kv was applied to the SEM for the determination of the morphology of the adsorbent whereas elemental composition of the adsorbent was determined using the energy dispersive X-ray spectroscopy (EDX). The micrographs produced from the SEM were used to obtain visual information on the particles size and the phase characteristics of the adsorbent surface (Yacob et al., 2011).

3.4.2 Determination of surface area

The surface area, pore diameter, and pore volume of the adsorbents were measured using the Brunauer-Emmett-Teller (BET) method. Before performing the BET analysis, 0.2 g of the adsorbent was put into a BET tube and degassed using a N_2 micrometric degassing equipment at 120°C for 10 hours (Gregg and Sing, 1982). The surface area and pore size of the adsorbent were measured using a Micromeritics TriStar 3020 3.00 at 120°C following degassing (BET ASAP 2020 porosimeter; Norcross, GA, USA).

Nitrogen adsorption/desorption isotherms were used to record the pore size distribution of the adsorbents as described by Sinha et al. (2019).

3.4.3 Determination of functional groups in the adsorbent

Fourier transformation infrared analysis (FTIR) was employed to determine the principal functional groups found on the surface of the prepared adsorbent. The adsorbent was dried at 100 °C for 12 h and thereafter, 300 mg mixed with KBr discs and pelletized for analysis using an IRPrestige-21 Shimadzu FTIR. The FTIR spectra were obtained in the 500–4000/cm range with an average of 33 scans (El-Azazy et al., 2022). The spectra resolution was maintained at 16/cm.

3.4.4 Determination of the crystal structure of the prepared adsorbent

X-ray powder diffraction analysis of the pulverized adsorbents was performed as per the method of Céspedes et al. (2021) to determine whether the adsorbents were crystalline or amorphous. The powdered adsorbent was densely packed into an Al frame and pressed into the XRD mould with no further treatment prior to analysis. The adsorbent was then scanned with a Cu-K radiation source at an energy of 8.04 keV and a wavelength of 1.5406 nm at different angles (2θ) ranging from 0° to 90°. To produce diffraction patterns, the XRD was run at 40 mA and 40 kV. The crystalline phases of the adsorbent were subsequently identified using the XRD diffraction patterns (Céspedes et al., 2021). Analysis of the XRD patterns provided information on the structure of the adsorbent (Ali et al., 2022).

3.5. Selection of the orange: lemon skin mixing ratio

Three different ratios of orange and lemon skins (1:1, 1:4 and 4:1) were tested for their efficiency in the removal of Al, Cd, Fe, Pb, Ni, and Zn from synthetic water with a view of understanding how these peels should be combined to produce an efficient adsorbent. In this experiment, a 50 ml solution containing 30 mg/l of Al, Cd, Fe, Pb, Ni, and Zn was prepared, and the pH adjusted to 7 using diluted NaOH. In the experiment, 0.2 g of the adsorbent prepared from lemon and orange combined at a ratio of 1:1 was added to the solution after which it was agitated through sonication at 150 RPM for 60 minutes at room temperature. An aliquot was then taken from each solution and analysed for the different metals using ICP-OES. This procedure was repeated with the adsorbents containing orange and lemon skins at a ratio of 1:4 and 4:1.

3.6 Batch adsorption experiment

For the batch adsorption studies, a glass vessel was filled with 100 mL of a model solution which contained 30 mg/l of Al, Cd, Fe, Pb, Ni, and Zn. The pH of the solution was adjusted to 7 using diluted NaOH. 0.2 g of the adsorbent prepared from the combination of lemon and orange skins with the best adsorption of metals determined in Section 3.5 was then added to the solution. The mixture was sonicated at room temperature for 5 –180 minutes at a rate of 150 revolutions per minute until equilibrium was attained (Mahmoud et al., 2012). Filtration was used to separate the adsorbent from the solution, and an ICP-OES was used to determine the concentration of different metals in the filtrate. The difference between the initial (C_i), and final (C_{eq}) metal concentrations in the solution was calculated to determine the amount of metal sorbed on the adsorbent. Equation 3.1 and Equation 3.2 were utilized to calculate the specific adsorption and adsorption percentage, (%S) by the adsorbent respectively (Ramutshatsha et al., 2019).

$$\% S = \frac{(C_i - C_{eq})}{C_i} x100 \tag{3.1}$$

$$q_e = (C_i - C_{eq}) \frac{V}{m} \tag{3.2}$$

Where C_{eq} and C_i are the equilibrium and initial concentrations of the metals in mgL^{-1} respectively, m is the mass of the adsorbent in grams, and V, is the solution volume in litres and q_e is the equilibrium uptake (mg/g).

3.6.1 Effect of contact time and initial concentration of heavy metal on adsorption

100 ml of a solutions containing 50, 75, 100, 125, 150, 175, and 200 mg/L of Pb, Al, Cd, Ni, Zn, and Fe, respectively, were prepared in a series of 500 ml flasks to determine the effect of initial metal concentration and contact time with adsorbent on the removal of metals by the adsorbent. 0.2 g of the prepared adsorbent was added separately into each flask and with a magnetic stirrer, the mixture was swirled at a constant temperature of 30℃ at a pH of 7. A sample was taken from each flask at different time intervals (20, 40, 60, 80, 100 and 120 min) and filtered through 0.4 µm

cellulose filter paper, after which the concentrations of the various metals in the filtrate were determined. Calculating the difference between the initial (C_i) and final (C_{eq}) metal concentrations in the solution as shown in Equation 3.1 allowed the computation of the concentrations of the metal sorbed on the adsorbent (Ramutshatsha et al., 2019). The same procedure was carried out on the commercial activated carbon (CAC) to compare the performance of the prepared adsorbent relative to CAC.

3.6.2 Effect of pH on adsorption

The effect of solution pH on adsorption of metals was carried out by mixing 0.2g of adsorbent with the appropriate initial concentration of metals and contact time determined in section 3.6.1 but varying the pH of the solutions such that solutions of pH 2, pH 4, pH 6, pH 8 and pH 10 were used at 30°C. The pH was adjusted to these various levels with 0.1 M NaOH or 0.1 M HCl solutions to raise or decrease the pH of the solution as was necessary and the mixtures stirred. A sample was taken from each flask at different time intervals (20, 40, 60, 80, 100 and 120 min) and filtered through 0.4 µm cellulose filter paper, after which the concentrations of the various metals in the filtrate were determined. The calculation of percentage heavy metal removal by the adsorbents at different pH levels was determined as in Equations 3.1 (Fernandez et al., 2014). The same procedure was also carried out using the CAC.

3.6.3 Effect of mass (dose) of adsorbent

The effect of adsorbent mass on adsorption was carried out by adding different masses of adsorbent ranging from 0.10 to 0.60 g of adsorbents into 100 ml of solution containing Al, Cd, Fe, Pb, Ni, and Zn at concentrations and contact time determined in section 3.6.1 and at pH determined in section 3.6.2 (Fernandez et al., 2014). The mixtures were stirred, filtered, and the concentrations of the metals of concern in samples from the different solutions determined as indicated in section 3.6.1. The percentage of the heavy metal removed using different amounts of adsorbents was then determined (Fernandez et al., 2014). The same procedure was conducted using the CAC in place of the prepared adsorbent.

3.7 Reaction kinetics

The kinetic studies of Al, Cd, Fe, Pb, Ni, and Zn adsorption was carried out by batch adsorption at optimum conditions determined from the previous experiments at a temperature of 30°C. Samples were taken from the mixture of adsorbent and adsorbate at regular time intervals beginning at 20 up to 120 minutes and the concentrations of the different adsorbates determined. The remaining concentration of adsorbate in the solution after adsorption were measured and the amount of adsorption at time t, and qt (mg/L) were calculated as in Equation (3.3) (Kumar and Jain 2013).

$$q_t = \left(\frac{(C_0 - C_t)V}{M}\right) \text{……………………….. (3.3)}$$

Where qt (amount of metal adsorbed at any time (t), c_o is the initial concentration (mg/l) of Al, Cd, Fe, Pb, Ni, and Zn, C_t is the concentration (mg/l) of the same metals at a specified time, V is the volume (in litres) of solution, and M denotes the mass of adsorbent in grams (Kumar and Jain, 2013; Santiago et al, 2018). The reaction is said to exhibit a zero-order kinetics if an increase in the reactant lengthens the half-life and a first-order kinetics if there is no impact. However, if the half-life shortens as the reactant concentration rises, the process is said to exhibit a second-order kinetics.

3.8 Batch sorption experiments and adsorption isotherms

A series of Al, Cd, Fe, Pb, Ni, and Zn solutions with various concentrations (ranging from 50 to 200 mg/L) were prepared and used in batch adsorption studies at 30 °C under optimal conditions obtained in previous experiments. The concentrations of Al, Cd, Fe, Pb, Ni, and Zn in the solution after adsorption were measured. The adsorption of each HM at equilibrium, q_e (mg/g) was calculated as detailed by Kumar and Jain (2013) using Equation 3.4.

$$q_e = \left(\frac{(C_0 - C_{qe})V}{M}\right) \text{………………………………… (3.4)}$$

Where C_0 and C_{eq} represent the concentrations (mg/l) of Al, Cd, Fe, Pb, Ni, and Zn at initial and equilibrium respectively, M is the mass (g) of adsorbent used and V is the volume (L) of the solution. The adsorption efficiency of Al, Cd, Fe, Pb, Ni, and Zn were calculated as in Equation (3.1) (Kumar and Jain 2013).

Adsorption isotherms were then used to determine the relationship between absorbent and absorbates. Al, Cd, Fe, Pb, Ni, and Zn adsorption isotherm data were obtained by mixing 0.2 g adsorbent with 100 ml of solution that contained metal ions at concentrations ranging from 50 to 200 mg/l. For 45 hours, the flasks were shaken at 150 rpm on a shaking platform in an incubator set to 30°C. After this time, the concentrations of the Al, Cd, Fe, Pb, Ni, and Zn ions in the solution were measured and the equilibrium uptake (qe) determined. The results were fitted to the Langmuir (Equation 3.5) and Freundlich isotherms (Equation 3.6) to determine the most appropriate model that explained metal adsorption by the adsorbent (Zhou et al., 2012).

$$\frac{1}{q_e} = \left[\frac{1}{K_L\, q_{max}}\right] \frac{1}{C_e} + \frac{1}{q_{max}} \qquad (3.5)$$

where: q_e is the adsorption capacity at equilibrium (mg/g)

q_{max} is the theoretical maximum adsorption capacity of the adsorbent (mg/g)

K_L is the Langmuir affinity constant (ℓ/mg) 0.00367 ℓ/mg

C_e is the supernatant equilibrium concentration of the system (mg)

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \qquad (3.6)$$

where:

K_F is the Freundlich constant related with adsorption capacity in (mg/g).

n is the heterogeneity coefficient

3.9 Removal of heavy metals in AMD samples

Batch sorption studies were carried out to ascertain the efficacy of the adsorbent made from a combination of orange and lemon skins in the adsorption of metals in the AMD samples. The optimised reaction conditions determined in section 3.6.1 – 3.6.3 were used. The concentrations of adsorbates in the AMD after the batch experiment using the prepared adsorbent were compared to determine the effectiveness of the adsorbent in the removal of metals from AMD.

3.10 Regeneration studies

In this experiment, 0.2 g of adsorbent was used to adsorb Al, Cd, Fe, Pb, Ni, and Zn in a solution containing 100 ml/L of each in 80 ml of solution for 6 hours. The adsorbent was washed with 3M HNO_3 to achieve desorption of the metals from the adsorbent, which was then cleaned with 0.3 M HNO_3, repeatedly rinsed with deionized water, and then dried for 24 hours at 60 °C in an oven. The desorption-sorption process was repeated for successive cycles until it became difficult to reuse.

3.11 Quality control

All experiments were repeated thrice to ensure reliability and validity of the data generated. To determine percent metal recovery by ICP-OES, the concentrations of the elements studied in a standard of known concentration were determined by ICP-OES and the percent element recovery calculated. All glassware and sample bottles were pre-soaked in 1% HNO_3, washed, and rinsed with deionised water. All reagents used were Analar grade reagents obtained from Merck chemicals. To ensure sufficient quality of the analysis, all equipment were calibrated, and safety measures taken into consideration to minimize errors.

3.12 Data analyses

To investigate the ratio at which orange and lemon skins should be mixed when using them as raw material for low-cost adsorbents, the metal adsorption efficiencies of adsorbents prepared with orange and lemon skins mixed at the three different ratios were compared. The ratio with the highest metal removal efficiency during batch experiments was identified as the best ratio at which the orange and lemon skins are to be used in the preparation of adsorbents.

To identify optimum conditions under which the prepared adsorbents should be used for the recovery of metals from aqueous solutions, the amount of HMs in the filtrates that had been shaken with different weights of the absorbent for different lengths of time, under different pH conditions, were determined and used to determine the percentage metal removal under these different conditions. The conditions with the highest percentage removal were identified as the optimum conditions for using the adsorbent.

To determine the efficiency of the adsorbents prepared from lemon and orange skins in the removal of heavy metals from AMD samples, the concentrations of the heavy metals in the AMD were compared before and after batch experiments using the prepared adsorbents. The reusability of the adsorbent was determined by comparing the number of times that it can be used before its removal efficiency drops.

In the analyses of data, ANOVA was used to determine whether the percentage removal of heavy metals observed at different contact times, different pH and different absorbent masses were significant or not. ANOVA was also used to evaluate whether the removal efficiency of the metals from AMD by the prepared adsorbent was better than the removal efficiency of the same metals using commercial activated carbon under the same conditions. To test the hypothesis that adsorbents prepared from a mixture of orange and lemon skins was effective in removing the metals under study from AMD, the removal efficiencies of the prepared adsorbent was compared with what has been reported for commercial adsorbents. The software used for ANOVA analyses was XLSTAT.

3.13 Ethical considerations

The research was conducted with integrity, sincerity and in conformance with acceptable standards.

- Written permission to collect wastewater from the Trans-Caledon Tunnel Authority were obtained.
- Considering that contaminated wastewater was involved in this study, steps were taken to ensure safe handling of the wastewater by persons involved in the research. All packages containing contaminated wastewater were clearly labelled. Synthetic gloves were also used in the handling of wastewater throughout the experiment.
- Some of the metal solutions used in this research are toxic. Measures including the use of protective clothing and goggles as well as gloves were ensured throughout the research to avoid contact with toxic solutions/chemicals. Principles

of safe laboratory use as directed by the laboratory administrators was abided to at all times.

- All the toxic reagents and waste materials that were generated during the research were disposed of safely according to the procedure for disposal of chemicals in the laboratory.

The study was given an ethical clearance certificate which can be found in **Appendix B**

3.14 Delimitations and limitations of the study.

The study focused on identifying the ratio at which orange and lemon skins should be mixed to give an adsorbent with high surface area. It also looked at characterising the prepared adsorbent in terms of surface area, functional groups present and morphology. Optimizing the pH, contact time and amount of absorbent to be used were also part of the study.

The study did not include Thermogravimetric and proximate analyses of the lemon and orange skins before and after carbonization. It also did not look at the recovery of the removed metals from the prepared adsorbents or investigated methods that could be used to dispose of the spent adsorbents.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Introduction

This study aimed to develop environmentally friendly, inexpensive, and selective adsorbents for the removal of Al, Cd, Fe, Ni, Pb and Zn, from aqueous solutions. This chapter discusses the characterization results of the prepared adsorbent. Furthermore, a discussion on the optimized parameters and optimal conditions under which the adsorbent should be used are presented. Moreover, results from the kinetic, isotherm and regeneration studies are discussed in this chapter.

4.2 Orange: lemon skin mixing ratios

Results from this experiment showed that the 1:1 ratio of lemon and orange skins had the largest surface area (Table 4.1) and showed an 80% efficiency in the removal of Al, Cd, Fe, Pb, Ni, and Zn from solution **(**Figure 4.1). Further experiments were therefore only carried out with the adsorbent prepared using a ratio of 1:1 lemon skin: orange skins.

Table 4. 1 : Surface area ratio results on orange and lemon skins adsorbent

Ratio of orange skin: Lemon skin	Surface area m^2/g
1:1	168.292
1:4	116.552
4:1	1.7932

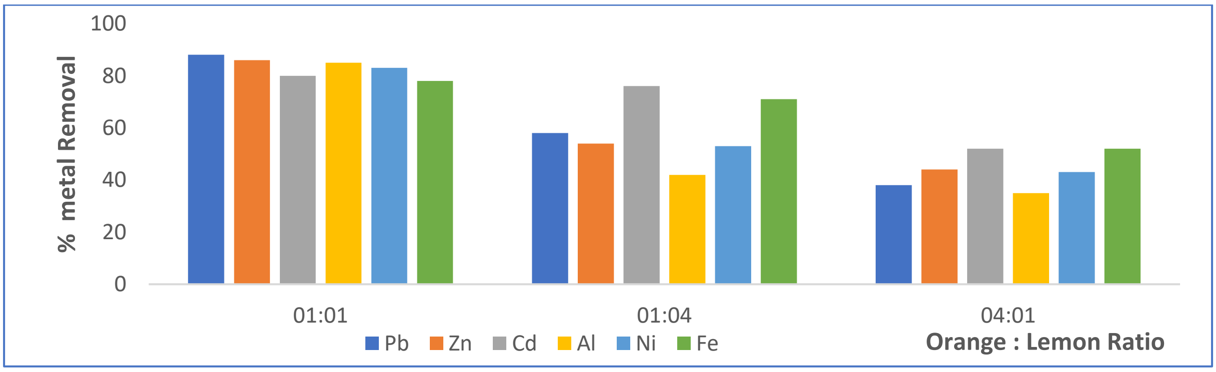


Figure 4. 1 : Removal of Pb, Zn, Cd, Al, Ni and Fe by 0.2 g of adsorbent prepared from mixed lemon and orange skins at different ratios at a pH of 7 and initial concentration of 30 ppm.

4.3 Adsorbent Characteristics

4.3.1 Pore size

The specific surface area of the synthesized adsorbent was 168.29 cm^3/g with an average pore volume of 0.269 cm^3/g. The N_2 adsorption-desorption isotherm curves of the synthesized adsorbent shown in Figure 4.2 (a) displayed a type IV isotherm with a prominent H1 hysteresis loop, indicating the adsorbent was mesoporous according to Nasrullah et al. (2017) and Hassan et al. (2014). From Figure 4.2 (b), the average pore size of synthesized adsorbent is approximately 0.34 cm^3/g, and the bulk of the pores were categorized as mesoporous according to the IUPAC pore size categorization (Sing et al., 2018).The surface area of the adsorbent produced from the orange and lemon skins was within the lower boundaries of the surface area of adsorbents prepared using other agricultural wastes including banana peels (Temesgen et al., 2018; Hashem et al., 2020), pomelo peels (Li et al., 2016; Huang et al., 2018), orange skins (Pandiarajan et al., 2018; Dey et al., 2021) and rice husks (Lewoyehu, 2021) which had surface areas ranging from 168 – 1892 cm^3/g. All these values are however well below the surface areas of CAC, which typically has pore size varying between 500 and 1500 cm^3/g and can reach values of 3000 cm^3/g (Dimpe and Nomngongo, 2017). The availability of sites on which sorption can occur is therefore lower for the adsorbent prepared from agricultural waste compared to CAC.

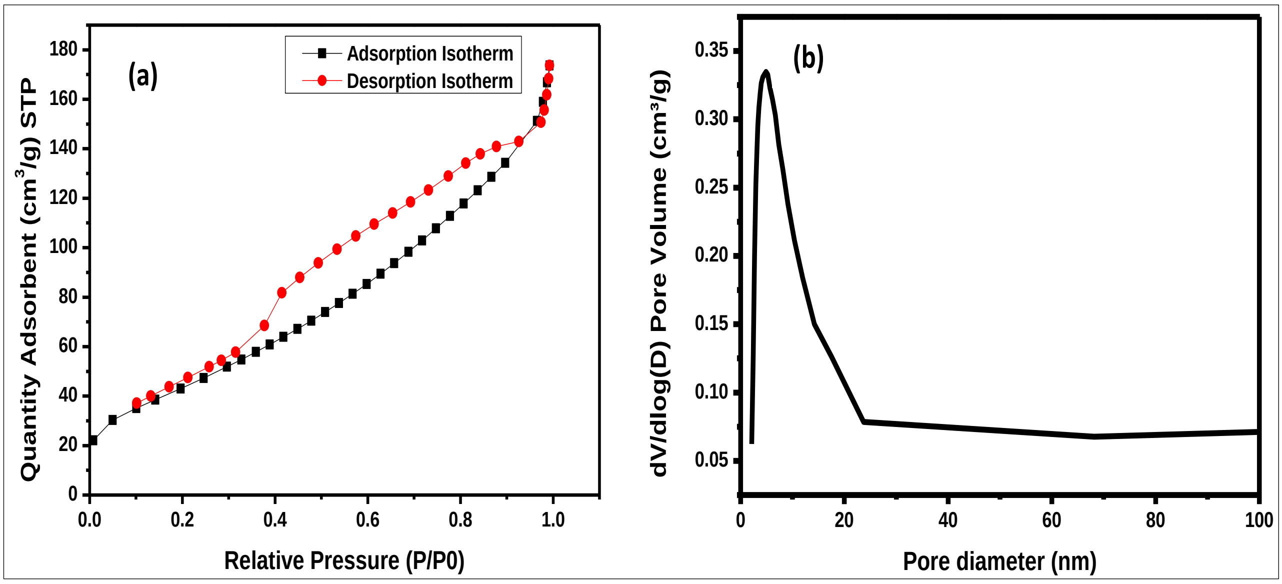


Figure 4. 2 : BET isotherms (a) and pore size distribution curves(b) of adsorbent made from orange and lemon skins.

4.3.2 *Microstructure*

The XRD analysis of the synthesised adsorbent (Figure 4.3) shows two broad peaks at 2θ angles of 22.8° and 43.8°, which corresponds to (002) and (100) planes, respectively (Li et al., 2016). These results are consistent with the XRD results of adsorbents made from banana and pomelo peel waste (de Lima et al., 2020). This peak resembles the disordered carbon sheet and could represents carbon and organic matter from the orange and lemon skins.

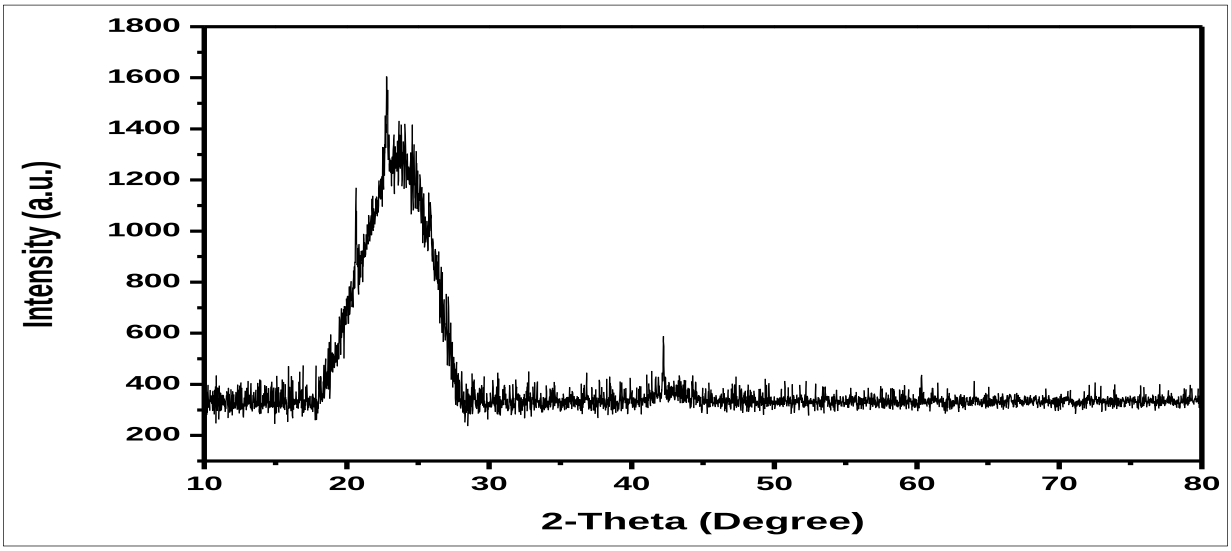


Figure 4. 3 : The XRD diffractogram of adsorbent prepared from mixed orange and lemon skins.

The double peaks are part of the low crystalline carbon. Lignin and cellulose could potentially be the chemical compounds represented by these peaks as they are significant components of biosorbents derived from agricultural wastes. The broad peaks which according to de Lima et al. (2020) increases with increasing calcination temperature indicated the amorphous nature of the adsorbent. The increasingly amorphous nature of the adsorbent makes it ideal for metal adsorption because of higher specific surface area (de Lima et al., 2020).

4.3.3 *Functional groups identified in prepared adsorbent*

The FTIR spectrum of the prepared adsorbent is shown in Figure 4.4. The broad peak at 3282 cm-1 demonstrates the presence of a surface hydroxyl (-OH) moiety originating possibly from phenol, alcohol, and carboxylic acid structures in the adsorbent. The C=C stretch and the C=O stretches of the carboxyl and carbonyl groups respectively were represented by the bands at 1572 cm-1 and 1389 cm-1. While the weak peak at 1019 cm has been attributed to the presence of C-O stretches vibrations, the adsorption peaks at 2871 cm1 can be assigned to the aliphatic, symmetric, and asymmetric, C-H stretches (Dey et al., 2021; Akawa et al., 2021; Pandiarajan et al., 2018).

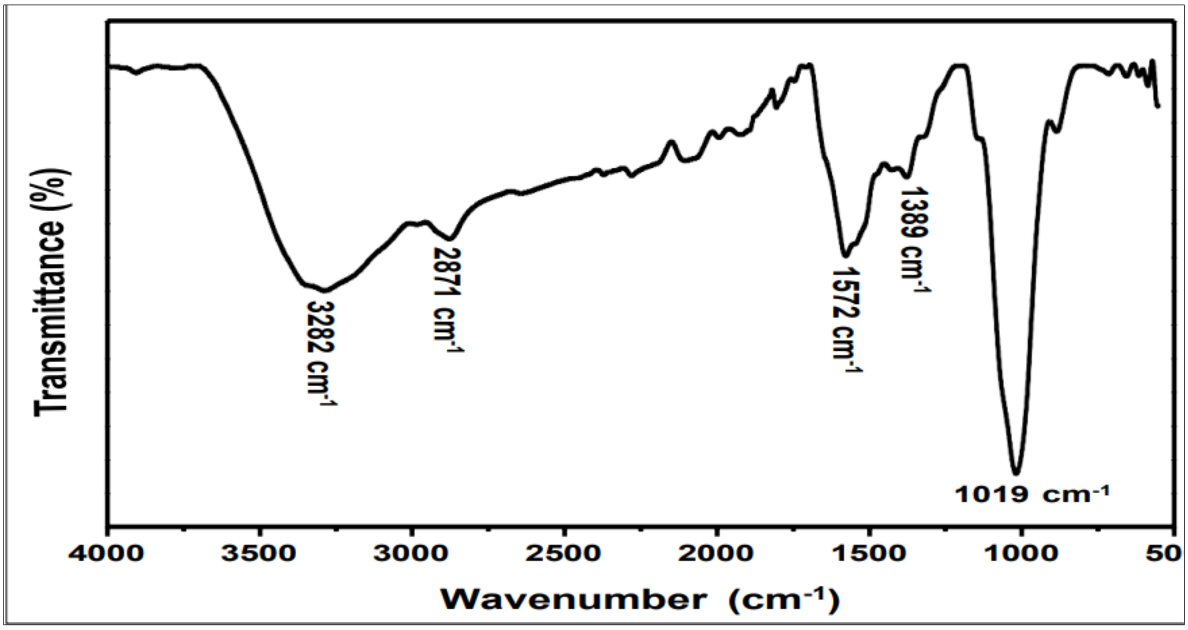
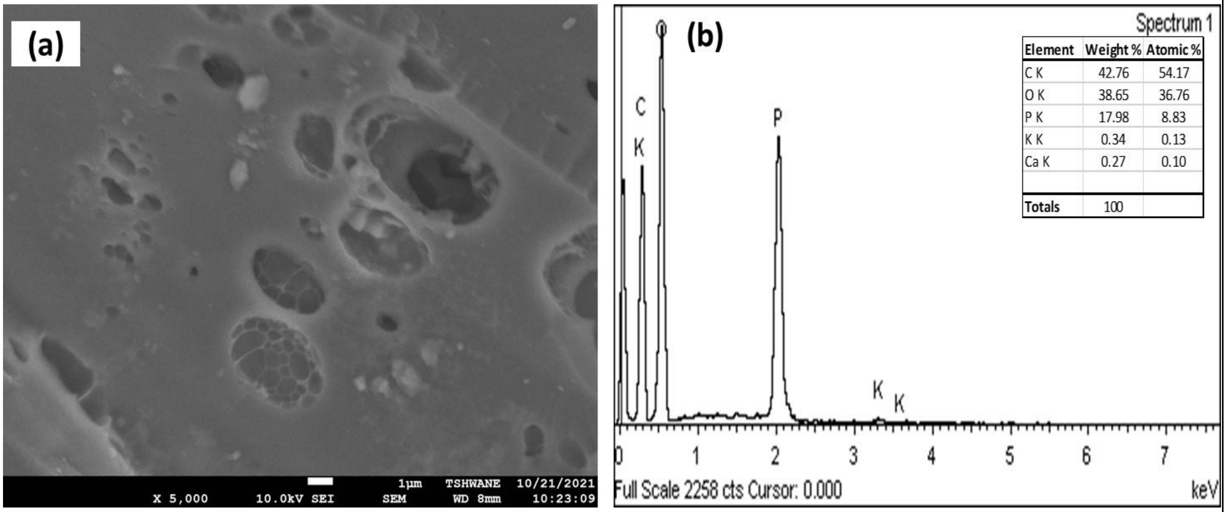


Figure 4. 4 : FTIR spectrum of adsorbent from mixed orange and lemon**.**

The results of the FTIR analyses suggest that the prepared adsorbent contains the –OH, C=O, C=C, C–H and C–O functional groups, which are typical bonds found in adsorbents prepared from biowastes (Li *et al.,* 2016; Lee and Choi, 2018; Pandiarajan *et al.,* 2018; Temesgen et al., 2018; Ahmadi and Ganjidoust, 2021). The carboxyl group is generally considered to be the functional group with the highest heavy metal adsorption capability (Lee and Choi, 2018). The HM are effectively adsorbed from the aqueous solution when the carboxyl group dissociates into H^+ and $-COO^-$ and the zeta potential of the adsorbent reaches a specific pKa value (Lee and Choi, 2018; Li et al., 2016).

4.3.4 Surface morphology and elemental composition

The SEM image of the adsorbent (Figure 4.5a) shows an adsorbent with a smooth surface, which is highly porous, with clearly visible surface pores. The structure and the surface pores are advantageous for molecular diffusion and offer enough open spaces for analyte adsorption. The presence of C and O was primarily confirmed by the EDX spectrum of the synthetic material in Figure 4.5 (b). The activating agent used was H_3PO_4 which is the most likely reason for the presence of P in the adsorbent.



Element	Weight %	Atomic %
C K	42.76	54.17
O K	38.65	36.76
P K	17.98	8.83
K K	0.34	0.13
Ca K	0.27	0.10
Totals	100	

Figure 4. 5 : **(a)** SEM image and **(b)** EDS spectrum of adsorbent from mixed orange and lemon

The results from the adsorbent prepared using a combination of orange and lemon skins reveal that the surface area of the adsorbent is much lower than what is reported in other adsorbents but has the potential of serving as a low-cost adsorbent that could be used for heavy metal removal from industrial effluents. It has functional groups which have the potential to form complexes with metals thereby increasing the possibility of the metals being sorbed from solution.

4.4 Batch adsorption studies

4.4.1 Effect of contact time on adsorption of metals by adsorbent

The results from batch sorption experiments using the prepared adsorbent showed that the adsorption of Pb, Al, Cd, Ni, Zn and Fe increases with time from 0 to 60 minutes, then significantly decreases as the reaction time surpasses an hour (Figure 4.6a).

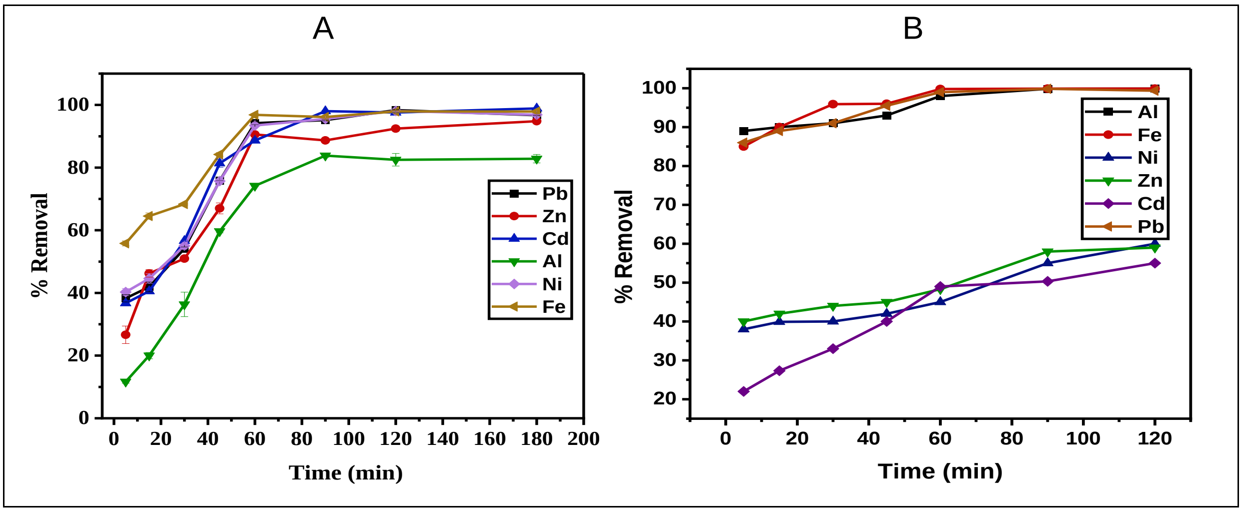


Figure 4. 6 : Adsorption of Ni, Cd, Al, Pb, Fe and Zn on adsorbent made from mixed orange & lemon (A) and Commercial Activated Carbon (B).

This initial rapid adsorption of the metals could be due to the availability of sorption sites on the adsorbent which become saturated with time as more cations get adsorbed (Ramutshatsha et al., 2022). For all the metals studied, the adsorption generally occurred in three steps. Between 0-60 min which can be described as the first step, adsorption of the metals on the adsorbent was fast as reflected by the rapid increase in the rate of metal removal with time by the adsorbent (Figure 4.6a). The second stage occurred between 60-90 min where adsorption progressed at a slower rate. This may have been caused by intra particle diffusion of the adsorbate into the adsorbent's inner matrix. The third stage occurs after 90 mins where the adsorption stops indicating equilibrium (Changwei Hu et al., 2017). These results indicate that adsorption of metals on the adsorbent prepared from a mixture of orange and lemon skins takes place within the first 90 mins after which the adsorption sites become saturated.

Percentage removal of Al, Fe, and Pb by CAC after 5 minutes reached 80% and at 60 minutes, removal was 99 % whereas percentage removal of Ni and Zn increased from 40 to 65% between 5 and 60 minutes and up to 55% within 90 minutes (Figure 4.6b). These results indicate that the adsorbent was able to remove higher amounts of Zn, Cd and Ni within 90 minutes from the solution compared to the CAC whereas the removal of Fe, Pb and Al was better with the CAC within the same length of time which highlights the selectivity of adsorbents (Figure 4.6b). ANOVA analyses indicates that there were significant differences in the removal of metals by the adsorbent and CAC ($P < 0.05$).

4.4.2 Effect of pH of solution on adsorption of metals by adsorbent

Figure 4.7 illustrates the impact of pH on the removal of Al, Cd, Ni, Pb, Zn, and Fe by 0.2 g of the prepared adsorbent. Since Fe precipitated at pH levels higher than 3, the pH of the Fe containing solution was left at 3. As the pH of the other solutions increased from 2 to 5, an increase in the % removal of Pb and Ni was seen, followed by a significant reduction as the pH of the solution increased from 5 to7 (Figure 4.7a).

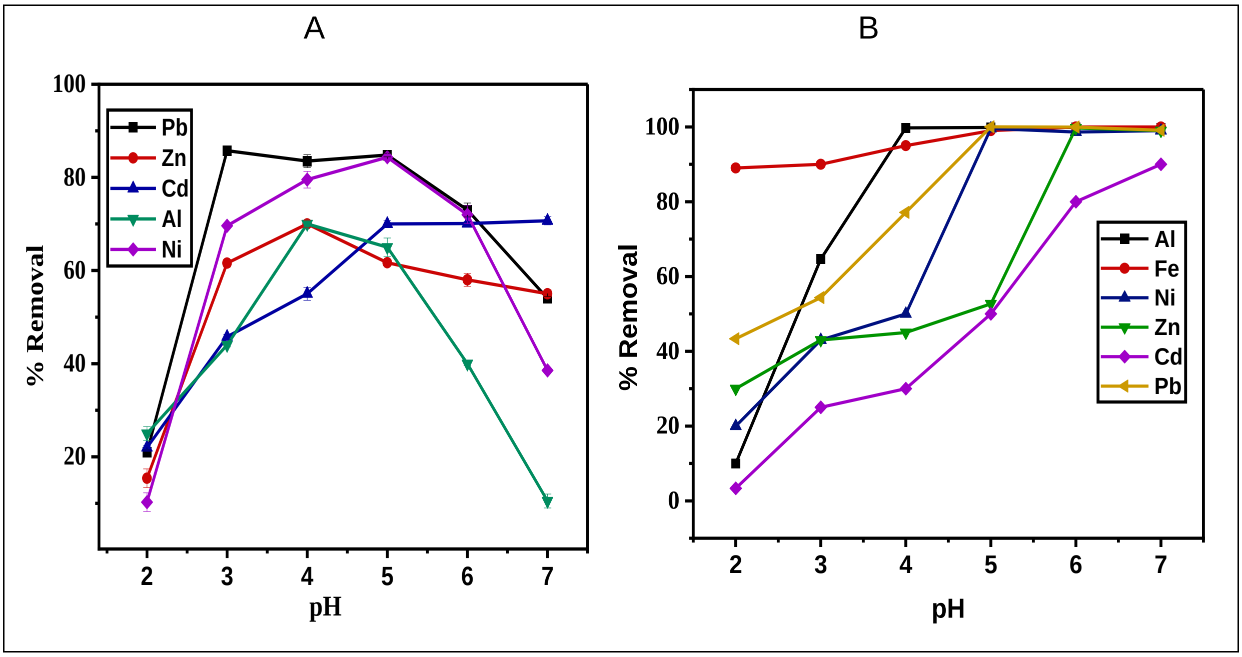


Figure 4. 7 : Adsorption of Al, Cd, Ni, Pb, Zn and Fe on prepared adsorbent (A) and commercial activated carbon (B) at different pH levels

Maximum removal of Al and Zn were achieved at pH of 4 whereas for Cd, the percentage removal increased slowly from pH 2 - 7. These results indicate that the optimal pH for removal of Ni and Al using adsorbents prepared from orange and lemon skin is pH 5 whereas for Pb and Zn, it is pH 4. Increasing the pH beyond these values is not likely to increase the amount of metals removed from solution. With the CAC, an increase in pH from 2 to 7 resulted in an increase in percentage removal of all the elements (Figure 4.7b). Aluminium reached maximum removal of 98 % at pH 4, Zn reached maximum removal of 98 % at pH 6, Cd reached maximum removal of 98 % at pH 7, whereas Fe, Pb, and Ni reached maximum removal of 98 % at pH 5 (Figure 4.7b). The removal of Fe ranged from 80 to 98 %. A study was undertaken by

Lakshmikandhan and Ramadevi (2019) to examine if CAC could be used to extract Pb (II) from aqueous solutions and the findings of batch tests demonstrated that the influence of initial pH on the removal of Pb (II) by CAC was only efficient for quantitative Pb (II) removal at a limited pH of 5. At lower pH levels, the increased proportion of hydrogen ions competes with the positively charged metal ions for adsorption sites, which reduces the uptake of metal ions whereas at higher pH, the sorption sites become accessible, and the adsorption of ions increases (Bayramoglu and Arica, 2017). According to Bayramoglu and Arica (2015), alterations in the surface characteristics of the adsorbent could explain changes in sorption capacity at various pH values.

4.4.3 Effect of adsorbent mass on prepared adsorbent

When deciding whether to utilize adsorbents to extract metals from wastewater, the adsorbent dose is an important consideration. Figure 4.8 illustrates the impact of adsorbent mass on the removal of metals by the adsorbent. The results show that as the adsorbent mass of both the prepared adsorbent (Figure 4.8a) and CAC (Figure 4.8b) increases, so does the percentage removal of Al, Cd, Ni, Pb, Zn and Fe. Based on the results obtained, the minimum mass of the prepared adsorbent to be used in the removal of the metals studied is 0.2 g. Similar trends were achieved by Ratan et al (2018) using adsorbents made of rice husk, wheat straw as well as corn cob. The removal efficiency of Cd and Pb from the solution increased considerably when the mass of CAC used increased from 0.02 to 0.2 g. Al, Fe and Pb reached maximum removal of 98 % at with adsorbent mass of 01.5 g. The increase in adsorption with increase in adsorbent mass is most likely due to the higher number of adsorption sites present with increased adsorption mass. Several researchers (Esmaeili et al. 2019; Ratan et al. 2018) have reported similar results.

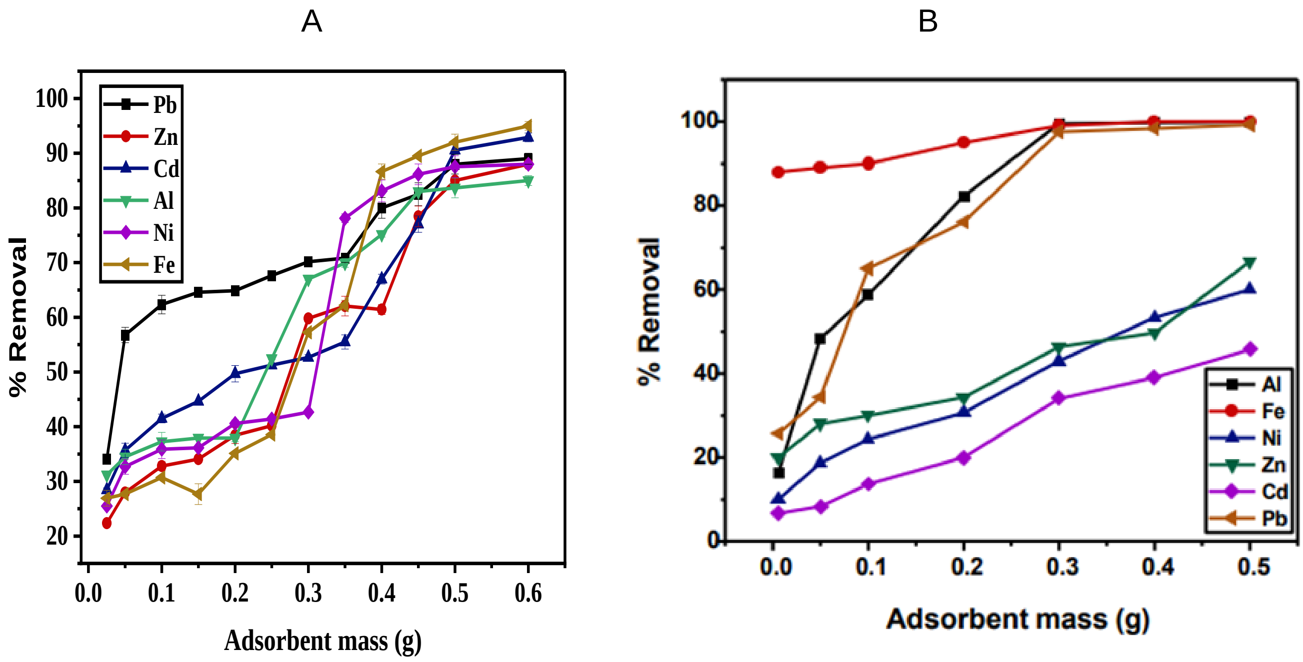


Figure 4. 8 : Adsorption of Al, Cd, Ni, Pb, Zn and Fe on different masses of adsorbent prepared from mixed lemon and orange skins (A) and commercial activated carbon (B)

Results from optimization studies indicate that the prepared adsorbent yields good percentage removal of metals when the pH of the solution is at about 5.5 whereas CAC works best at a pH of 7. The highest percentage removal was obtained when a mass of 0.5 g was used for the prepared adsorbent and 0.25 when commercial activated carbon was used whereas for optimum contact time, 90 min was the time required for maximum removal using both the prepared adsorbent and the CAC. Even though the optimum time is similar, the prepared adsorbent achieved a higher percentage removal of the metal ions from solution (80-95) compared to the CAC (45-95).

4.5 Kinetic Study

To calculate the residence time to reach equilibrium as a function of the initial concentration of Al, Cd, Fe, Pb, Ni, and Zn by the adsorbent, the adsorption kinetics of these metals and the adsorbent were examined, and the results are presented in Figures 4.9 and 4.10. During the first 60 minutes of the adsorption process, analytes were taken up quickly, but thereafter adsorption was slower before reaching equilibrium. Pseudo-first order and second order are the well-known models of adsorption kinetics used to fit experimental data. Kinetics are presented in Table 4.2. Compared to the R^2 value produced when a pseudo first order model was applied, a higher R^2 coefficient was obtained using a pseudo second order model (Figure 4.9 and Table 4.2).

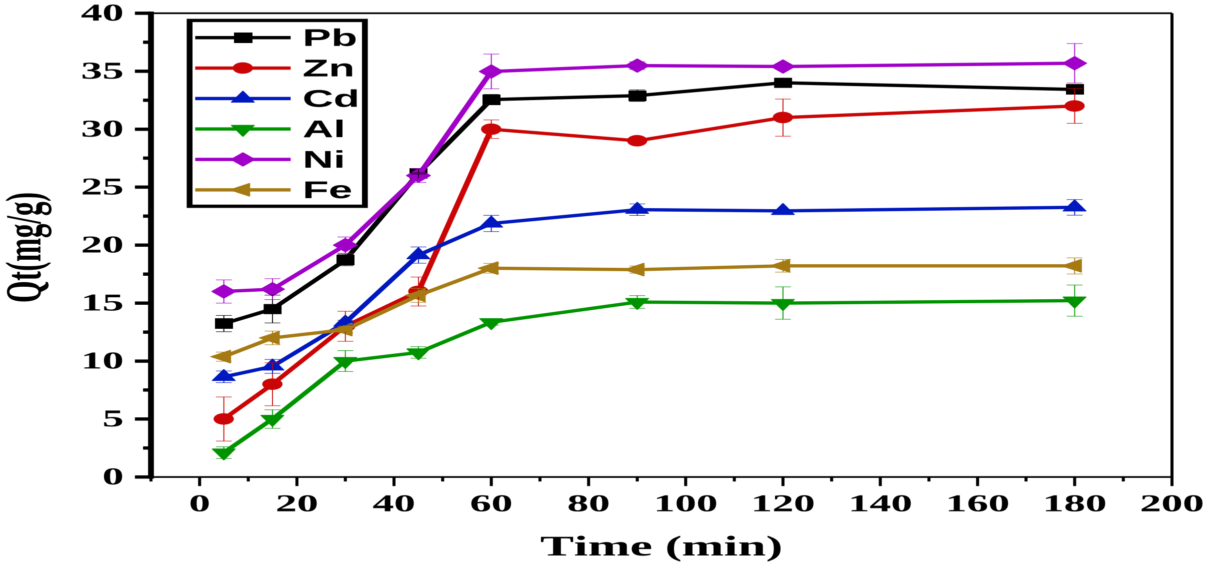


Figure 4. 9 : Adsorption capacity of 30-ppm starting concentration of Al, Cd, Ni, Pb, Zn and Fe on 0.2 g of adsorbent prepared from lemon & orange skins at pH of 5, Fe (pH 2)

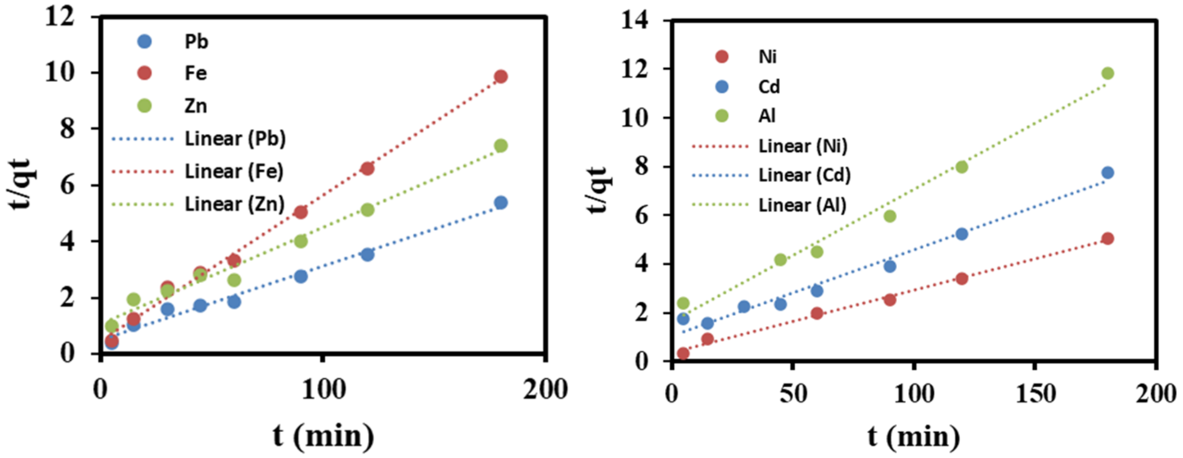


Figure 4. 10 : Pseudo second order graphs of Al, Cd, Ni, Pb, Zn and Fe

A pseudo-second order model was therefore the most likely model that explained the removal of Al, Cd, Fe, Pb, Ni, and Zn by the prepared adsorbents as shown in Table 4.2. Similar observations have been made by Ramutshatsha et al., (2022). According to Li et al., 2022), the adherence to the second order kinetic model is an indication that the reaction processes that are taking place on the adsorbent are chemical adsorption processes which involve the sharing or replacement of electrons between the adsorbent and the heavy metals.

Table 4. 2 : Adsorption Kinetic model parameters

Pseudo-first order				
Ions	Q_{exp}	K_1	Q_{est} (mg/g)	R^2
Al	15.09	0.037	19.298	0.927
Cd	23.25	0.041	23.259	0.908
Ni	35.68	0.046	51.69	0.829
Pb	33,42	0.067	57.57	0.900
Zn	23.0	0.029	21.917	0.883
Fe	18.2	0.046	12.125	0.783
Pseudo-second order				
Ions	Q_{est}	K_2	Q_{est}(mg/g)	R^2
Al	18.0	0.002	same as 1st order	0.984
Cd	28.4	0.002	same as 1st order	0.978
Ni	38.7	0.001	same as 1st order	0.993
Pb	36.0	0.002	same as 1st order	0.974
Zn	28.0	0.001	same as 1st order	0.981
Fe	19.2	0.006	same as 1st order	0.996

4.6 Isotherm study

Both Freundlich and Langmuir isotherms are used to determine how the adsorption capacity of an adsorbent varies with initial concentration of adsorbates. Parameters for both Langmuir and Freundlich isotherms as well as from associated gradients and intercepts are presented in Table 4.3. The results showed a high R^2 coefficient when the data were fitted to the Langmuir model as opposed to the Freundlich model. In addition, Langmuir's maximum adsorption capacity data correlated with data obtained from the batch experiment on the removal of Al, Cd, Ni, Pb, Zn and Fe by the adsorbent (Table 4.3). The constant factor (RL) shown in Table 4.3, can be used to represent the Langmuir isotherm, which reveals crucial model properties.

Table 4. 3 : Modelling parameters for the adsorption isotherm

Langmuir

Ions	Q_{exp}	K_L	Q_e (mg/g)	R_L	R^2
Al	0.00	0.00	0.00	0.00	0.000
Cd	53.4	0.086	60	0.10	0.978
Ni	29.58	0.047	35	0.16	0.985
Pb	42	0.1387	50.2	0.06	0.992
Zn	30	0.1070	34	0.08	0.985
Fe	29.4	0.38	33	0.023	0.975

Freundlich

Ions	K_F	n	R^2
Al	0.00	0.00	0.00
Cd	7.2	2.05	0.991
Ni	0.8	0.24	0.954
Pb	1	3.39	0.968
Zn	0.6	1.8	0.982
Fe	0.77	2.42	0.954

The RL results provide information on the adsorption process's favourability. Adsorption of Al, Cd, Fe, Pb, Ni, and Zn on the adsorbent made from lemon and orange skins was favourable ($R_L<1$) (Ramutshatsha et al., 2022) since the calculated RL value was less than 1 and the value of n was more than 1. The experimental data on the adsorption capacity attained upon removal of Al, Cd, Fe, Pb, Ni, and Zn by the adsorbent correlate with the Langmuir maximum adsorption capacity data and indicate that adsorption of the metals on the adsorbent are explained by monolayer adsorption.

4.7 Use of prepared adsorbent to remove metals from AMD water samples

The initial concentrations of Cd, Pb, Fe, Zn, Ni, and Al in the AMD sample were 0.03, 2.0, 0.04, 0.02, 0.43 and 220 mgL$^{-1,}$ respectively. The synthesized adsorbent was able to remove 66.67%, 95.5%, 90.0%, 72.5%, 93.0%, and 99.9% of Cd, Pb, Fe, Zn, Ni, and Al respectively from the AMD samples (Table 4.4).

Table 4. 4 : Percentage removal of Al, Cd, Fe, Ni, Pb and Zn from AMD wastewater using prepared adsorbent

Analytes	Initial concentrations mg L^{-1}	Final concentration (mg L^{-1})	%Removal
Cd	2.0±0.34	0.089±0.58	95.5
Pb	0.02±0.9	0.0055±0.90	72.5
Fe	220±1.8	0.002±01.45	99.9
Zn	0.43±0.34	0.03±0.74	93.0
Al	0.03±0.34	0.01±0.10	66.67
Ni	0.04±0.34	0.004±1.79	90.0

The element which was removed at a high rate was Fe and the least removed element was Al. These observations confirm that the adsorbent has potential in the removal of HM from effluents rich in HM as it compares with values that have been reported in other studies using different effluents. For example, Suliestyah et al. (2020) reported an Fe removal efficiency of 100% using coal based activated carbon. Lakshmikandhani and Ramadevi (2019) reported a 98% percent efficiency in the removal of Pb using CAC. Similarly, Musapatika (2010) reported an efficiency of 85% when removing Ni from industrial wastewaters.

4.8. Regeneration Study

As shown in Figure 4.11, all the targeted metals were effectively removed by the adsorbent in the first cycle (>80%). The percentage removal rate of Al, Cd, Ni, Pb, Zn and Fe by the adsorbent was kept at 80% up to the fifth cycle. This was followed by the sixth cycle with less removal of metals such as Al and Zn.

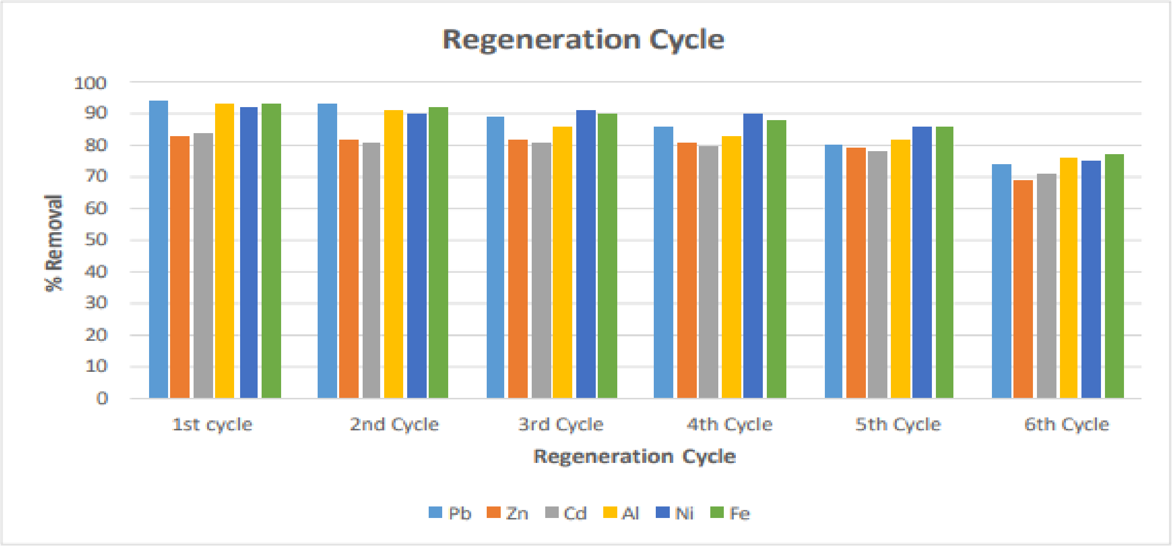


Figure 4. 11 : Regeneration and reusability studies of the absorbent from mixed orange & lemon adsorbent in adsorption of Al, Cd, Ni, Pb, Zn and Fe

It was found that the mass of the adsorbent decreased to 0.17 g from 0.2 g after the sixth reusability tests indicating that some of the adsorbent was lost during the wash-off process. The decrease in the removal efficiency after several adsorption-desorption cycles could therefore be attributed to the reduction of available functional groups that formed chelates with the metals, reduction in the surface area due to filling of pores by other non-target pollutants or loss of the adsorbent during the wash cycles which could have reduced the surface area and sites available for adsorption. However, considering that this low cost and environmentally friendly adsorbent can be reused up to five times with such high efficiency, the mixed orange and lemon skin adsorbent can be considered as an adsorbent of good potential. A major challenge that may arise from the use of adsorbents made from orange and lemon skins could therefore be the disposal of the adsorbent after five cycles of use. Possible solutions could be the desorption of the absorbate from the absorbents after which the absorbents could be disposed of through landfilling or incineration. The desorbed adsorbents could also be recycled but further studies on how this could be done are necessary.

4.9 Feasibility of using lemon and orange skins in the removal of HM from industrial wastewaters

Results from this study show that it may be feasible to use orange and lemon skins as raw materials for the preparation of absorbents for industrial use. They are widely available at an affordable price. Currently they are being disposed at a cost to juice and jam making factories which use massive amounts of these products. Using them as a raw material for adsorbents would reduce the cost of disposal and this encourages recycling which may increase the profit margin of these industries. High HM concentrations in industrial wastewaters are a concern in many industries. The adsorbent prepared from the orange and lemon skins has displayed enormous potential as a heavy metal removal absorbent that could be used in place of commercial activated carbon.

The adsorbent prepared from mixed orange and lemon skins were found to be capable of removing Al, Cd, Ni, Fe, Pb and Zn ions with high efficiency. The adsorbents had a strong affinity and high selectivity toward Al, Cd, Ni, Fe, Pb and Zn ions due to the presence of functional groups on the surface and the adsorption process is fast (within 90 minutes). The other benefit is that the prepared adsorbent can be recycled /regenerated up to six times. This treatment effectively decreases pollutants in wastewater in an environmentally friendly manner and is therefore aligned with the principles of efficient, innovative, and sustainable waste management.

Cost benefit analysis is an important factor when selecting agricultural waste as an adsorbent, it can be estimated that the cost of the adsorbent prepared was much lower (R 2900.00) than the commercial adsorbent which cost R6500.00. based on preliminary cost benefit analyses that took into consideration the cost of the lemon skins, and the reagents used for its activation. However, the energy required for activation was not included but further studies which take into consideration every aspect of the production of the adsorbent needs to be undertaken. Based in this preliminary estimate, adsorbents produced from a mix of lemon and orange skins could be described as low-cost adsorbents.

CHAPTER FIVE

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.1 Introduction

In this study, a mixture of orange and lemon skins have been used to prepare low-cost adsorbents which can be used to reduce the HM concentrations in industrial effluents. In this chapter, the results of the investigations carried out are used to conclude on the objectives of the study. The chapter also presents recommendations on what needs to be done to enhance the potential of the adsorbents made from orange and lemon skins for use in industry.

5.2 Conclusions

The following conclusions were drawn from the investigations:

1. Where orange and lemon skins are to be used in the preparation of adsorbents, a 1:1 weight percent mixture is recommended as this ratio seems to produce adsorbents with the highest total surface area.
2. Chemical activation with phosphoric acid is necessary in the preparation of such adsorbents due to the higher final carbon yield, and it is a one-step process, utilizing generally lower activation temperatures.
3. Batch adsorption experiments of Al, Cd, Ni, Pb, Zn and Fe on an adsorbent prepared from lemon and orange peel were completed by evaluating variables such as contact time and initial concentration, pH and absorbate mass.
   From the experimental results, it was observed that.
   - Increasing the contact time between adsorbent and adsorbate resulted in an increase in the removal of Al, Cd, Ni, Pb, Zn and Fe using the adsorbents prepared from a 1:1 weight percent lemon and orange skins, a contact time of 90 minutes seems to be the maximum time required for the adsorption of metals from wastewater.

- The effect of pH studies showed that the removal of Al, Cd, Ni, Pb, Zn and Fe using the prepared adsorbents is highly dependent on the pH of the solution with a pH of 5.5 being the maximum pH recommended for using this adsorbent to remove heavy metals from solution.
- An increase in adsorbent mass favoured the removal of heavy metal ions but the minimum mass that could be used with reasonable heavy metal removal efficiency is 0.5g for prepared adsorbent and 0.25 for commercial activate carbon meaning double the quantity of the prepared adsorbent is required to achieve the same efficiency of metal removal as CAC
- The adsorption was investigated using the Langmuir and Freundlich isotherms, and it was determined by the correlation coefficient that the Langmuir isotherm model was more favourable for the adsorption of Ni, Cd, Al, Pb, Fe, and Zn. Hence, the nature of the latter adsorbents is homogeneous.
- The comparison of the regression factors of the first and second order pseudo-kinetic models demonstrated that pseudo-second-order kinetics was the likely order for the adsorption of the Al, Ni, Zn, Cd, Pb, and Fe ions by the adsorbent.
- The average removal efficiency of metals from AMD by the adsorbent were 66.67%, 95.5%, 90.0%, 72.5%, 93.0%, and 99.9% for Cd, Pb, Fe, Zn, Ni, and Al, respectively.
- The adsorbent can be recycled up to six times as per the results of the study.
- The adsorbent showed good percentage removal (>80%) of all targeted metals in the first cycle of the regeneration cycle. This was done until the sixth cycle, the absorbent's percentage removal rate of Al, Cd, Ni, Pb, Zn and Fe was maintained at 80%.

5.3 Recommendations

The following recommendation should be considered in future work:

- When making adsorbents using a mixture of lemon and orange skins, a weight percent ratio of 1:1 should be used to achieve a metal removal efficiency of 80%.
- When using adsorbent prepared from mixed orange and lemon skin 0,2 g and a pH of 2 -7, is recommended for metal concentrations of up to 30 mg/L in in aqueous.
- When using adsorbent prepared from mixed orange and lemon skin 0,2 g and a pH of 2 -7, is recommended for metal concentrations of up to 30 mg/L in in aqueous.
- Further studies are needed to:
    - characterize the adsorbent in terms of elemental content, yield percentage and other methods that could be used to enhance the properties of the adsorbent.
    - find out how the adsorbents could be desorbed and recycled to reduce the waste management demands related to the used adsorbents could have been undertaken in future.
    - evaluate other lemon skin and orange skin ratios to see if they could perform better.
    - determine the proximate properties of the prepared adsorbent.
- Studies on the cost benefit analyses of using orange and lemon skin derived adsorbent in place of commercial activated carbon that take into consideration every aspect of the production of the low-cost adsorbent are necessary.

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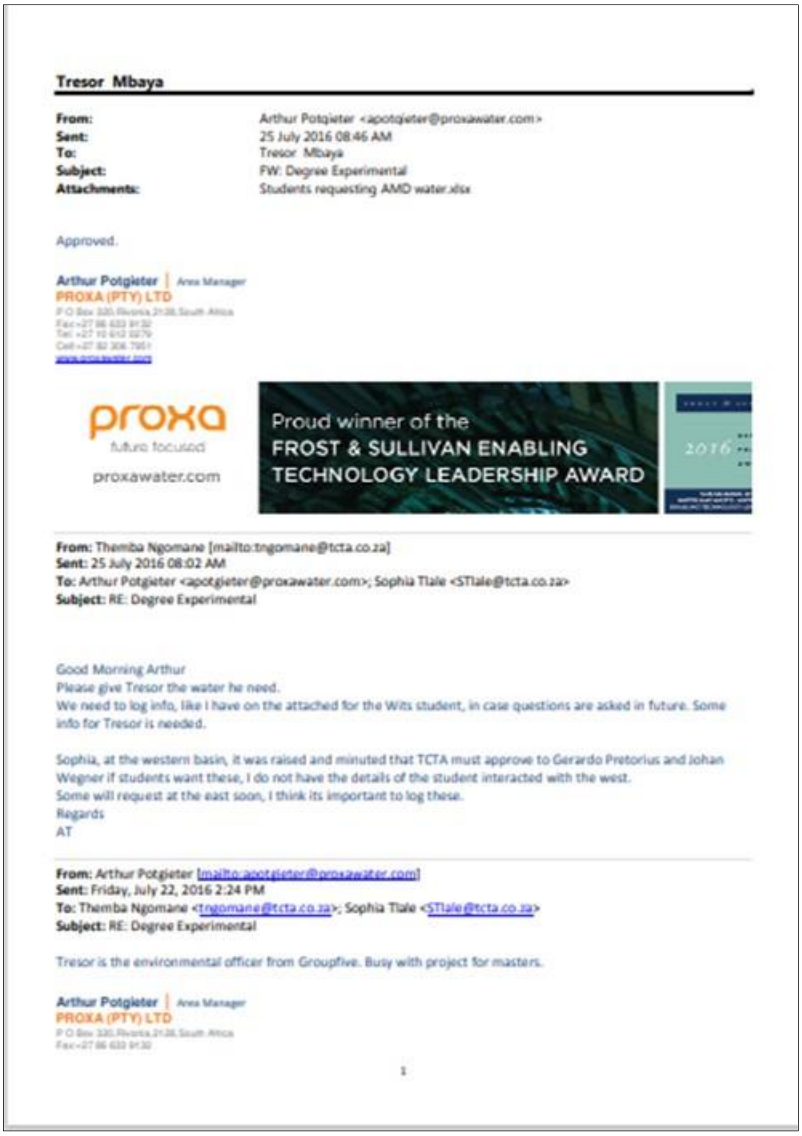
APPENDICES



Tresor Mbaya

From: Arthur Potgieter <apotgieter@proxawater.com>
Sent: 25 July 2016 08:46 AM
To: Tresor Mbaya
Subject: FW: Degree Experimental
Attachments: Students requesting AMD water.xlsx

Approved.

Arthur Potgieter | Area Manager
PROXA (PTY) LTD

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From: Themba Ngomane [mailto:tngomane@tcta.co.za]
Sent: 25 July 2016 08:02 AM
To: Arthur Potgieter <apotgieter@proxawater.com>; Sophia Tlale <STlale@tcta.co.za>
Subject: RE: Degree Experimental

Good Morning Arthur
Please give Tresor the water he need.
We need to log info, like I have on the attached for the Wits student, in case questions are asked in future. Some info for Tresor is needed.

Sophia, at the western basin, it was raised and minuted that TCTA must approve to Gerardo Pretorius and Johan Wegner if students want these, I do not have the details of the student interacted with the west.
Some will request at the east soon, I think its important to log these.
Regards
AT

From: Arthur Potgieter [mailto:apotgieter@proxawater.com]
Sent: Friday, July 22, 2016 2:24 PM
To: Themba Ngomane <tngomane@tcta.co.za>; Sophia Tlale <STlale@tcta.co.za>
Subject: RE: Degree Experimental

Tresor is the environmental officer from Groupfive. Busy with project for masters.

Arthur Potgieter | Area Manager
PROXA (PTY) LTD

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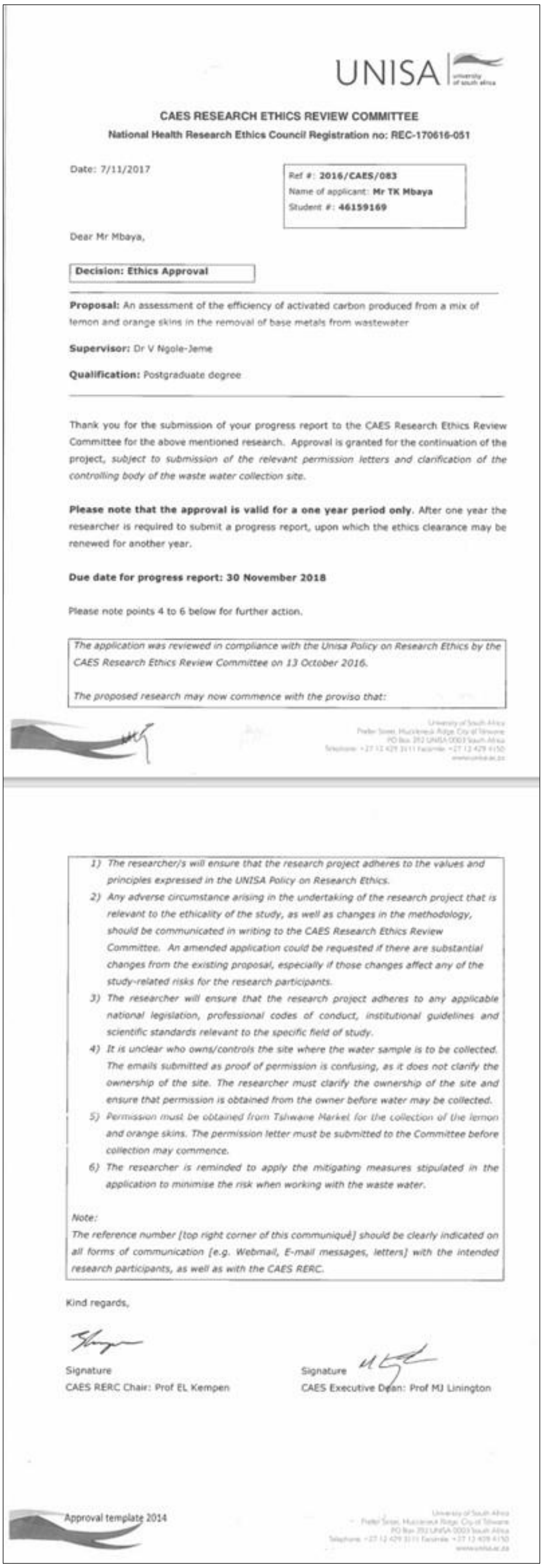
- **Appendix B:** Ethics Clearance certificate 79



UNISA university of south africa

CAES RESEARCH ETHICS REVIEW COMMITTEE

National Health Research Ethics Council Registration no: REC-170616-051

Date: 7/11/2017

Ref #: **2016/CAES/083**
Name of applicant: **Mr TK Mbaya**
Student #: **46159169**

Dear Mr Mbaya,

Decision: Ethics Approval

Proposal: An assessment of the efficiency of activated carbon produced from a mix of lemon and orange skins in the removal of base metals from wastewater

Supervisor: Dr V Ngole-Jeme

Qualification: Postgraduate degree

Thank you for the submission of your progress report to the CAES Research Ethics Review Committee for the above mentioned research. Approval is granted for the continuation of the project, *subject to submission of the relevant permission letters and clarification of the controlling body of the waste water collection site.*

Please note that the approval is valid for a one year period only. After one year the researcher is required to submit a progress report, upon which the ethics clearance may be renewed for another year.

Due date for progress report: 30 November 2018

Please note points 4 to 6 below for further action.

The application was reviewed in compliance with the Unisa Policy on Research Ethics by the CAES Research Ethics Review Committee on 13 October 2016.

The proposed research may now commence with the proviso that:

University of South Africa
Preller Street, Muckleneuk Ridge, City of Tshwane
PO Box 392 UNISA 0003 South Africa
Telephone: +27 12 429 3111 Facsimile: +27 12 429 4150
www.unisa.ac.za

1) *The researcher/s will ensure that the research project adheres to the values and principles expressed in the UNISA Policy on Research Ethics.*
2) *Any adverse circumstance arising in the undertaking of the research project that is relevant to the ethicality of the study, as well as changes in the methodology, should be communicated in writing to the CAES Research Ethics Review Committee. An amended application could be requested if there are substantial changes from the existing proposal, especially if those changes affect any of the study-related risks for the research participants.*
3) *The researcher will ensure that the research project adheres to any applicable national legislation, professional codes of conduct, institutional guidelines and scientific standards relevant to the specific field of study.*
4) *It is unclear who owns/controls the site where the water sample is to be collected. The emails submitted as proof of permission is confusing, as it does not clarify the ownership of the site. The researcher must clarify the ownership of the site and ensure that permission is obtained from the owner before water may be collected.*
5) *Permission must be obtained from Tshwane Market for the collection of the lemon and orange skins. The permission letter must be submitted to the Committee before collection may commence.*
6) *The researcher is reminded to apply the mitigating measures stipulated in the application to minimise the risk when working with the waste water.*

Note:
The reference number [top right corner of this communiqué] should be clearly indicated on all forms of communication [e.g. Webmail, E-mail messages, letters] with the intended research participants, as well as with the CAES RERC.

Kind regards,

Signature
CAES RERC Chair: Prof EL Kempen

Signature
CAES Executive Dean: Prof MJ Linington

Approval template 2014

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