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Removal of Cadmium (II) Ions from Aqueous Solution Using Zebediela Kaolin, Limpopo Province, South Africa

By

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A Masters Dissertation Submitted to the University of Venda, Faculty of Science Engineering and Agriculture, Department of Earth Sciences in Fulfilment of the Requirements for the Master of Earth Sciences in Hydrology and Water Resources

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DECLARATION

I, Ikome Julie Enanga, Student Number 18018316, declare that the dissertation titled - **Removal of Cadmium (II) Ions from Aqueous Solution Using Zebediela Kaolin, Limpopo Province, South Africa -** submitted for the Master of Earth Sciences in Hydrology and Water Resources, to the University of Venda is my own work and has not been previously submitted, in whole or in part, for any degree. All assistance and information from published and unpublished work have been fully acknowledged.

Student Signature:  Date: 24/04/2023

Ikome J.E.

DEDICATION

This work is dedicated to GOD Almighty; I thank Him for strength and direction.

ACKNOWLEDGEMENT

To my supervisors Dr Diko and Dr Bukalo; sincere thanks for guiding me throughout my research journey. I greatly appreciate the knowledge you shared with me.

My sincere gratitude to my family - my husband, children, parents and siblings for their unconditional love, prayers, and support; may the good Lord bless you all abundantly.

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ABSTRACT

Water is central to the life of human beings and the ecosystem, thus, access to clean and safe water for the overall wellbeing of a nation cannot be over-emphasised. In this study, raw kaolin from Zebediela was used to adsorb cadmium (II) ions from aqueous solution. Mineralogical characterization (X-ray diffractometry, Fourier transform infrared spectrophotometry), morphological characterization (scanning electron microscope-energy dispersive using X-ray) and chemical characterization (X-Ray Fluorescence) were done to determine and quantify the minerals present, their morphologies and the elemental composition of the kaolin sample. The mineralogical analyses revealed that the sample was predominantly made up of kaolinite. Morphological analysis showed that the kaolin sample had well developed kaolinite books and stacks with relatively porous aggregates. Furthermore, chemical analysis demonstrated that the kaolin sample is predominantly composed of silica (SiO_2 = 58.39 %), alumina (Al_2O_3 = 28.04 %) and titanium dioxide (TiO_2 = 2.26 %).

Batch adsorption experiments were done to investigate the effect of pH, sorbent dose, contact time and metal ion concentration on the removal of cadmium (II) ions from aqueous solution using Zebediela kaolin. An optimum pH of 7 was observed and was used as the working pH for the other adsorption experiments. Increased adsorption was noted at lower sorbent doses (0.25 - 1 g), however, there was a decline in adsorption at higher sorbent doses (1 – 1.5 g). The adsorption process was initially very fast, and equilibrium was reached after 40 minutes. In addition, there was a rise in percentage removal of Cd (II) ions as initial concentration increased which was followed by a decline after equilibrium was attained. Adsorption isotherm and kinetic models illustrated the adsorption of Cd (II) ions onto the Zebediela kaolin which followed Langmuir isotherm and pseudo second order mechanism, respectively. This study, therefore revealed that raw Zebediela kaolin has the potential to be used as an adsorbent of cadmium (II) ions from aqueous solution.

Keywords: adsorption, cadmium (II) ions, kaolin, water resources, Zebediela

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LIST OF UNITS AND SYMBOLS

%	Percentage
ºC	Degree Celsius
g	Gram
L	Litre
mg/g	Milligram per gram
Mg/L	Milligram per litre
min	minute
ppm	Part per million

LIST OF ABBREVIATIONS

CaO	Calcium oxide
Cd(II)	Cadmium (II)
Cr_2O_3	Chromium oxide
Fe_2O_3	Iron oxide
K_2O	Potassium oxide
MnO	Manganese oxide
MgO	Magnesium oxide
Na_2O	Sodium oxide
P_2O_5	Phosphorus pentoxide
TiO_2	Titanium dioxide
LOI	Loss of ignition
AAS	Atomic adsorption spectrometer
GPS	Global positioning system
pH	Potential of hydrogen
XRF	X ray fluorescence
XRD	X-ray diffractometry
FTIR	Fourier transform infrared spectrophotometry
SEM-EDX	Scanning electron microscope-energy dispersive using X-ray

CHAPTER ONE

INTRODUCTION

1.1 Background

The consumption of unsafe water is fast becoming one of the world's major environmental and health challenges accounting for about 1.2 million deaths per year (Ritchie and Roser, 2021). The utilisation of kaolin in the treatment of contaminated water is very crucial in encouraging alternative, human-friendly innovative techniques to produce clean water for all (Annan *et al*., 2018; Lazaratou *et al*., 2019). Currently there is pressure on the earth's natural resources, including water, due to over exploitation, climate change and pollution (Alade, 2019; Samuel, 2019; Falkland and White, 2020). Additionally, challenges related to access and sustainable management of water resources and sanitation are faced by many nations of the world with about 2.1 billion people lacking access to safe drinking water (Ritchie and Roser, 2020).

According to the Riggs *et al.* (2017), across every state in America there exists different water challenges which include - limited household water supply, faecal contamination, lead contamination of water and unpaid bills. In Europe agricultural practices, over-exploitation of land, presence of industrial and municipal wastewater, droughts, reduction in groundwater levels, physical and structural modification of water bodies - constitute some of the factors adversely affecting countries' water resources (Christian, 2019; du Plessis, 2019). Similarly, in Asia, water resources are also under high pressure due to urbanisation with most of the Asian cities depending on groundwater (Heidari *et al*., 2020; Erkens *et al*., 2015). The over exploitation of groundwater is reported to be contributing to land subsidence in areas like Jakarta, Tokyo, Ho Chi Minh City, Bangkok and Bandung (Erkens *et al*., 2015).

Limited access to safe water in Africa is one of the major factors responsible for infectious diseases including diarrhoea, typhoid, cholera, dysentery, polio, and hepatitis A (Ritchie and Roser, 2020). Childhood stunting, and malnutrition are equally amplified by the consumption of unsafe water (Ishaque *et al*., 2020). Low-income countries, in particular, face serious challenges in providing safe water for their citizens; this leaves many people vulnerable to water-related diseases, which can be lethal as seen in Figure 1.1 below

(Cairncross and Feachem, 2018). Increasing poverty, rapid population growth, limited environmental research, misuse of funds, corruption, inequality, and degradation of the environment are some of the drawbacks to attaining an adequate and reliable water supply system in Africa (Naik, 2017; Hirai and Graham, 2019). Success in providing safe water to communities can be achieved by taking into consideration the beneficiaries needs, customs, beliefs, preferences, political and socioeconomic environment (Hirai and Graham, 2019).

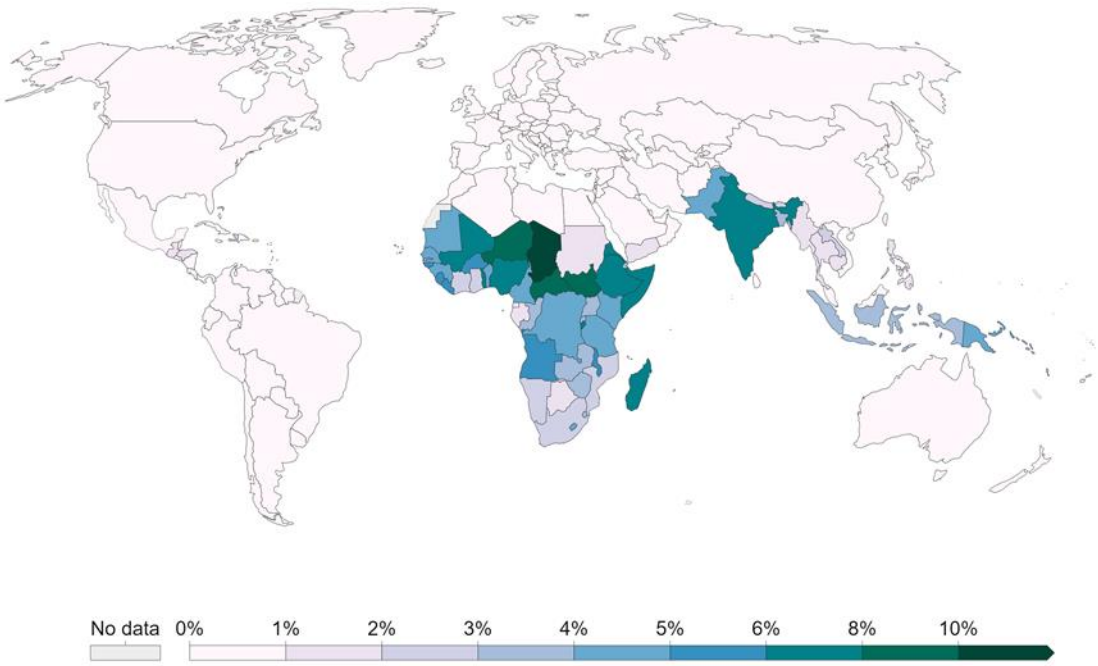

Figure 1.1: The share of total deaths, from any cause, with unsafe water sources as an attributed risk factor (Global burden of disease, Institute for Health Metrics and Evaluation (IHME), 2021)

There exist a variety of water challenges in different parts of South Africa; these include reduction in dams' levels, polluted waters, droughts, flooding, and irregular supply of water, as testaments in places like Eastern Cape, Cape Town, KwaZulu Natal and Limpopo (Bwapwa, 2019; Steyn *et al*., 2019). The decrease in available freshwater resources has necessitated the developing of new ways to treat contaminated water to

help mitigate some of the water challenges and reduce pressure on the available fresh water (Morote *et al*., 2019; Stec, 2020). In addition, the need for good quality water to be used for domestic, industrial, and agricultural activities has led to research for alternative and sustainable water supply (Annan *et al*., 2018). Developing environmental and human-friendly techniques for treating water will enhance the proper use of water and at the same time conserving its quality for future generation (Saleh, 2017; Bhakta and Ali, 2020).

Heavy metal in water is one of the culprits adversely affecting water resources. Cadmium released into aquatic environments (rivers, lakes and streams) occurs through diverse industrial activities (e-waste, incineration and combustion of fuel) and natural volcanic activities (Annan *et al*., 2018; Buba and Maina, 2020). Exposure to cadmium in aquatic environments has adverse effects on humans and other organisms, because cadmium easily accumulates in plants and animals through food chain transfer (Ali *et al*., 2019; Maurya *et al*., 2019). Furthermore, cadmium in aquatic systems can be potentially toxic due to its persistence and high mobility (Park *et al*., 2019), however, kaolin (a clay rich in kaolinite) can be utilized in the removal of heavy metals from water.

The use of kaolin as an adsorbent for the removal of heavy metals is advantageous because of its low cost, abundance, non-toxic nature, good adsorption properties, and its ability to encapsulate toxic matter in its crystal structure (Abdelaal *et al*., 2010; Uddin, 2017). It is in this context that this research will focus on the potential application of Zebediela kaolin in the removal of Cd (II) ions from aqueous solution using the adsorption technique, as it is effective in the removal of toxic pollutants, even at low concentrations.

1.2 Problem Statement

In South Africa the rapid growth of informal settlements, inequality, pollution, urbanisation, climate change, illegal water connections and destruction of river catchments are some of the factors affecting freshwater resources (Ramírez *et al*., 2019; Rawlins, 2019). Currently, the country is challenged by lack of access to potable and sustainable water resources with the consumption of unsafe water accounting for 22.7 deaths per 100,000 individuals in 2019 as seen in Figure 1.2 (Edokpayi *et al*., 2018; Ritchie and Roser, 2021).

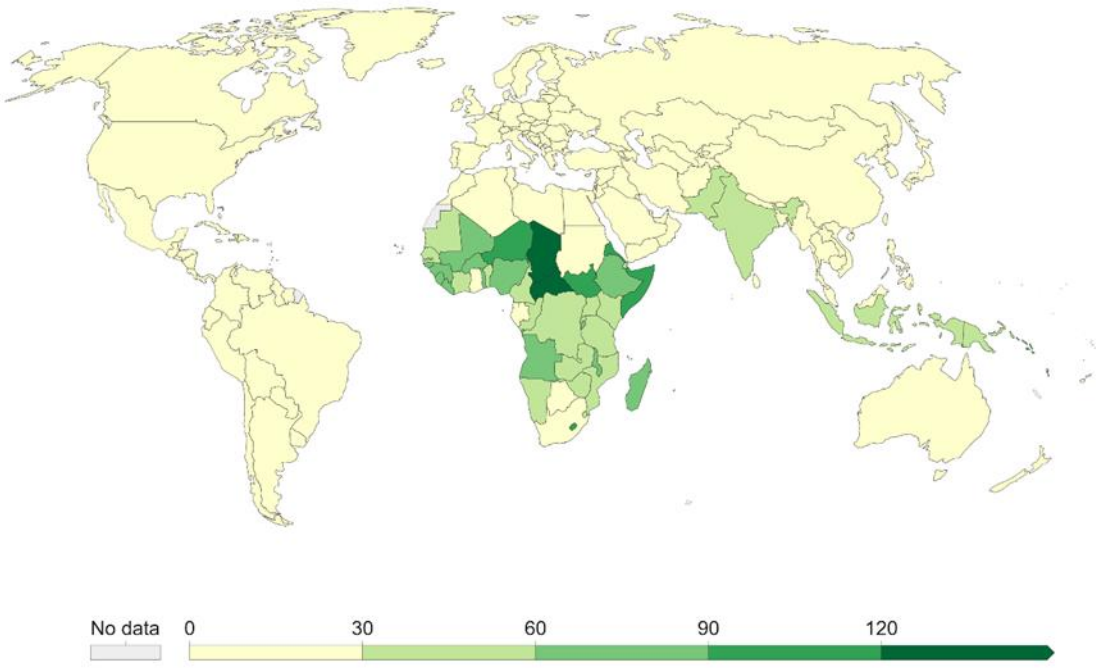

Figure 1.2: Death rates from unsafe water sources measured as number of deaths per 100,000 individuals (Global burden of disease, Institute for Health Metrics and Evaluation (IHME), 2021).

Heavy metals in water are particularly one of the main contaminants because they constitute the major group of inorganic pollutants which contaminate land and water, due to their presence in municipal waste, fertilizers, mine residues, pesticides, smelting industries and sludge (Uddin, 2017; Gu *et al*., 2019). Cadmium in water is a serious threat to humans because of its carcinogenic nature and its potential to cause other diseases such as lung fibrosis, testicular degeneration, and dyspnoea (Annan *et al*., 2018).

Water challenges in South Africa are experienced in different parts of the country, for example, the 2018 drought in Cape Town, water shortages in Limpopo and Eastern Cape, flooding in KwaZulu Natal and Cape Town and raw sewage disposal into water bodies in Gauteng (Bischoff-Mattson *et al*., 2020). Consequently, there is a dire need to invest in alternative water treatment techniques and water sources to address the rising demand for good quality water. Kaolin can be used in its natural state, or it can be modified with acids, heat, chemicals and polymers to remove some of its cationic compounds, heavy

metals, dyes, and to enable it to absorb some organic compounds in water (Ding *et al*., 2012; Zhang *et al*., 2019).

Some research have been done by Diko *et al*. (2016) on the structural order and thermal stability of the Zebediela kaolin. In addition to that, Raphalalani *et al*., (2019) reconstructed the paleoenvironment of the Zebediela kaolin using trace element and stable isotope geochemistry, however, despite the huge economic benefits which can be derived from the Zebediela kaolin, there is limited literature on its potential application in the removal of cadmium (II) from water. This study will, therefore, unearth findings on the removal of Cd (II) ions from aqueous solution using raw Zebediela kaolin.

1.3 Significance of Study

Good quality water is vital for a thriving ecosystem and the proper functioning of all human activities (Srinivasan, 2011). The use of kaolin for water treatment will provide potable water and small-scale mining opportunities in rural areas in South Africa. Also, the realisation of United Nations Sustainable Development Goals One (no poverty), and Six (clean water and sanitation) can be facilitated through the exploitation and processing of Zebediela kaolin to be used as an adsorbent for cadmium.

Furthermore, this research aligns with some development priorities in South Africa namely: (i) community and social development; (ii) local economic and rural development; and (iii) institutional development and financial viability (Makana Municipality Report 2019). This study will put forth findings to encourage sustainable exploitation and beneficiation of kaolin for water treatment, income generation, and reduction of unemployment in local communities and the municipalities.

1.4 Objectives

1.4.1 Main Objective

The main objective of this study was to ascertain the effectiveness of Zebediela kaolin for the removal of Cd (II) ions from aqueous solution. This knowledge will be harnessed to better facilitate the sustainable utilisation of kaolin in water treatment.

1.4.2 Specific Objectives

- To ascertain the mineral makeup of the Zebediela kaolin and how it can impact on the adsorption of Cd (II) ions,
- To determine the chemical composition of Zebediela kaolin and how it can affect the adsorption capacity of Cd (II) ions, and
- To investigate the suitability of Zebediela kaolin in the removal of Cd (II) ions from aqueous solution.

1.5 Research Questions

- How can the mineralogical properties of Zebediela kaolin impact on the adsorption of Cd (II) ions?
- How does the chemical characteristics of Zebediela kaolin affect its adsorption capacity?
- What is the suitability of Zebediela kaolin for the removal of cadmium(II) ions in aqueous solution?

1.6 Expected Outcome

- This study will determine the effectiveness of Zebediela kaolin in the removal of Cd (II) ions from aqueous solution.
- Completion of degree and preparation of manuscript

1.7 Study Area

1.7.1 Geographic Location

Zebediela consist of a group of villages located in the Lepelle-Nkumpi Municipality, Capricorn District, Limpopo Province South Africa. The Municipality covers 3464.00 hectares and Zebediela kaolin is located at longitude 29° 23’ 28’’ S and latitude 24° 16’ 56’’ N (Tilley and Lahiff, 2007). Zebediela is pre-dominantly rural area and is found about 62.8km south-east of Polokwane, which is the main economic centre of the Limpopo Province (IDP, 2018-2019).

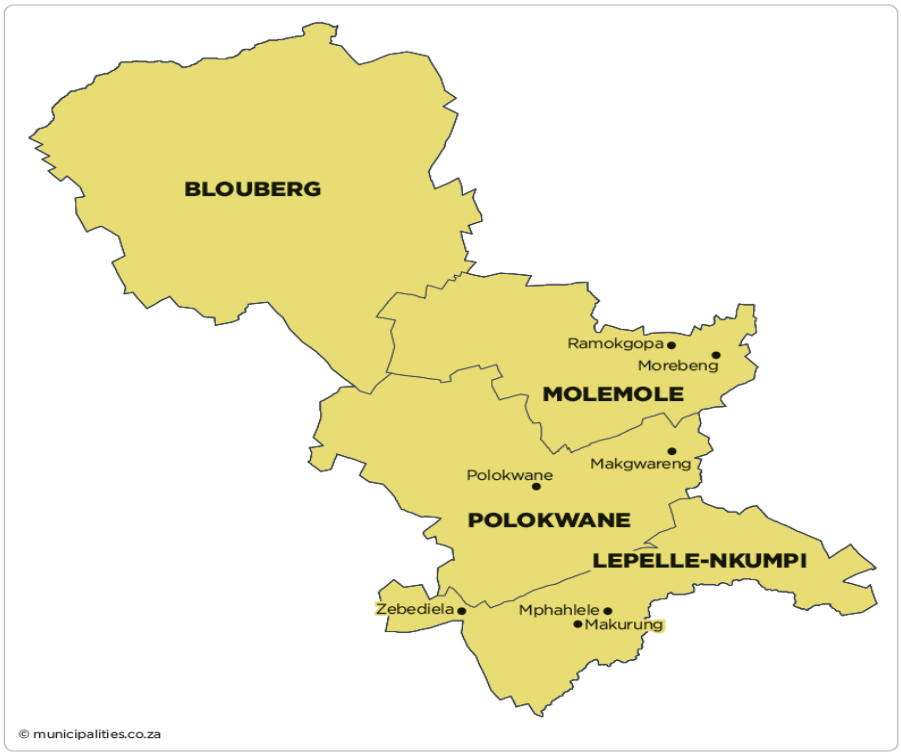

Figure 1.3: Location map for Lepelle-Nkumpi Municipality

1.7.2 Geology of Zebediela

According to a study by Raphalalani *et al*., (2019) the geology of Zebediela is regionally made up of rocks that belong to the Transvaal Supergroup. Eriksson and Reczko, (1995) noted that the Transvaal Supergroup is preserved in three separate structural basins - the Transvaal, Griqualand West and Kanye (Botswana) basins; they also indicated that the supergroup consists of five main lithostratigraphical subdivisions - protobasinal rocks, Black Reef Sandstone Formation, Chuniespoort Group, volcano-sedimentary Pretoria Group and the Bushveld-related Rooiberg Felsite Group. The rocks in the Zebediela area belong to the Wolkberg Group which forms part of the protobasinal successions of the Late Archean-Early Proterozoic Transvaal Sequence (Bosch *et al*., 1993). The Wolkberg Group is succeeded by an unconformity-bound Black Reef Formation which is overlain by the Chuniespoort Group of Proterozoic age (Erikson *et al*., 2001).

Raphalalani *et al*., (2019) suggested that the Zebediela kaolin was formed from an active margin tectonic setting and the kaolin was deposited under suboxic/anoxic conditions.

The Zebediela kaolin was reported to be characterized by a major NNW-SE trending fault truncated by numerous veins and the different colours of the kaolin deposit from different quarries are, white, grey, yellow, reddish brown, light brown pale brown and reddish. The whitish colour of the kaolin may indicate high kaolinite content, however, the other colours - yellowish, reddish brown, light brown and pale brown - are suggestive of high iron content (Kilinc, 2014; Rautureau *et al*., 2017; Raphalalani *et al*., 2019). The stratigraphy of Zebediela and the geologic setting of the Zebediela kaolin are presented in Table 1.1 and Figure 1.3 respectively.

Table 1.1: Stratigraphy of Zebediela

	ERATHEM	GROUP/SUBGROUP	FORMATION	LITHOLOGY
PHANEROZOIC	JURASSIC	KAROO SEQUENCE	Letaba	Volcanic rocks (basalts, pyroclast
	TRIASSIC		Clarens	Red creamy sandstones (fine grained)
PROTEROZOIC	VALINAN	Chuniespoort	Malmani	Dolomite, chert, limestone, chert breccias with interbed shale, sandstone, quartzite
		BLACK REEF		Lava, tuff, quartzite, shale, sandstone, volcanic rocks
		WOLKBERG		Sandy and tuffaceous shale, mudstone, arkose, conglomerate, volcanic rocks.

Source: Diko, 2011

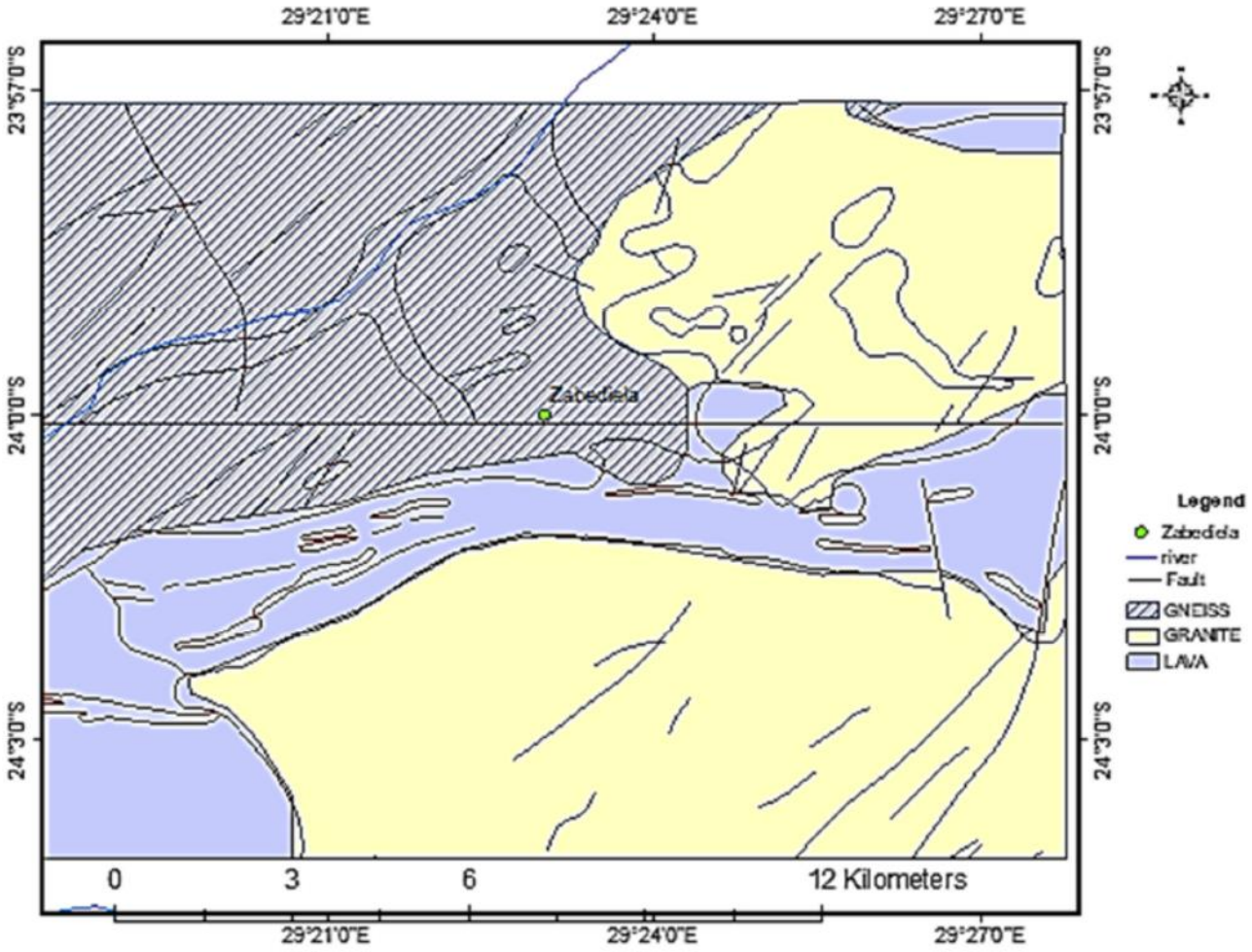

Figure 1.4: Geologic setting of Zebediela kaolin occurrence (Diko, 2011)

1.7.4 Climate

Zebediela has a semi-arid to semi-humid climatic regime, with an average humidity of 52% and an ultraviolet (UV) index of 5 (Web and Media, 2020). Its temperature is affected by the southern Springbok flats and the northern mountainous region with an average annual temperature of 25 °C. The seasons include summer and winter with an average rainfall of 350-650 mm (Diko, 2011)

1.7.5 Soils and Vegetation

Based on the morphological classification of van de Merwe (1940) as cited in Olivier (1968) Zebediela is on a transition of two soil-groups - the Sub-tropic black clay soils and the brown-to reddish brown ferruginous lateritic soils. The soils are normally very deep

and mainly reddish-brown and red sandy loams with very little profile differentiation. The red colour is believed to have emanated from basalts and calcium from dolomites. Olivier, (1968) reported that norite, in combination with titanacious magnetite, granite and sandstones are also suggested as contributors to the red colour of the Zebediela soils. Furthermore, in the South-west of Zebediela, norite intrusions are thought to be responsible for the dark colour of some soil patches.

1.7.6 Land-Use Activities

Some of the land uses include: growing of citrus for local and export markets, livestock farming, health and clinic, mining, dairy production, Zebediela guesthouse, plantations, bloubuffel grass production, primary schools, colleges and stores Zebediela (Tilley and Lahiff, 2007). In addition, Zebediela has been noted to have a potential for tourism development.

1.7.7 Topography and Hydrology

The municipal area is mountainous with the north-eastern quadrant having either the Great Escarpment or Northern Drakensberg as the dominant feature; the Wolkberg and Strydpoort mountain ranges are also located within this quadrant (IDP, 2018-2019). West of Zebediela, towards Mokopane and Magalakwena Local Municipality there exists portions of the Maribashoek Mountains, however, the south-western portion of the municipality is relatively flat. According to the Integrated Development Plan (2018-2019) the Municipality is found in the Oliphants catchment with several tributaries of the Oliphants River transecting the Municipality, including the Hlakaro River, Nkumpi River and Mohlapitse River among others.

1.8 Research Outline

- Chapter Two presents relevant literature on kaolin, adsorption, and heavy metals.
- In Chapter Three, the research methodology employed in this specific project is outlined.
- Chapter Four presents the results and inferences.
- Chapter Five focuses on the conclusion and presents recommendations on the application of the findings for industry and society and offers further research options.

1.9 Summary

This chapter serves as an introduction to water-related challenges globally, in Africa and South Africa. It also elaborates on heavy-metal pollution in water and the use of kaolin to remove them from water, through the adsorption technique. The objectives, research questions, significance of study and expected outcome have been discussed. The subsequent chapter will examine literature on clays, kaolins, adsorption and heavy metals.

CHAPTER TWO

LITERATURE REVIEW

2.1 Preamble

In the last few years in South Africa, there has been an increase demand for good quality water supply following the rise in population, pollution, industrialization, droughts, climate change, reduction of dam levels and floods (Keng *et al*., 2014). This chapter presents relevant literature on heavy metals, clays, kaolin and the use of kaolin as an adsorbent for the removal of heavy metals from water.

2.2 Heavy Metal Pollution in Water

Urbanisation and industrialisation are two main anthropogenic factors responsible for heavy metals in water, although some natural factors, such as erosion, weathering and leaching, contribute to heavy metal pollution in water (see Figure 2.1) (Khatri and Tyagi, 2015). Heavy metals can naturally exist in rocks as ores and can interact with groundwater - one of the major sources of water supply for human consumption (Vetrimurugan *et al*., 2017; Cangemi *et al*., 2019).

The rock-water interaction can cause leaching and weathering of these heavy metals into groundwater, used by humans for drinking, domestic activities, and agriculture (Vetrimurugan *et al*., 2017). Generally, most people consider groundwater as being fit for consumption, therefore, needing little or no treatment, however, the movement of heavy metals into groundwater clearly shows consumers need to be careful when using groundwater (Villa, 2016).

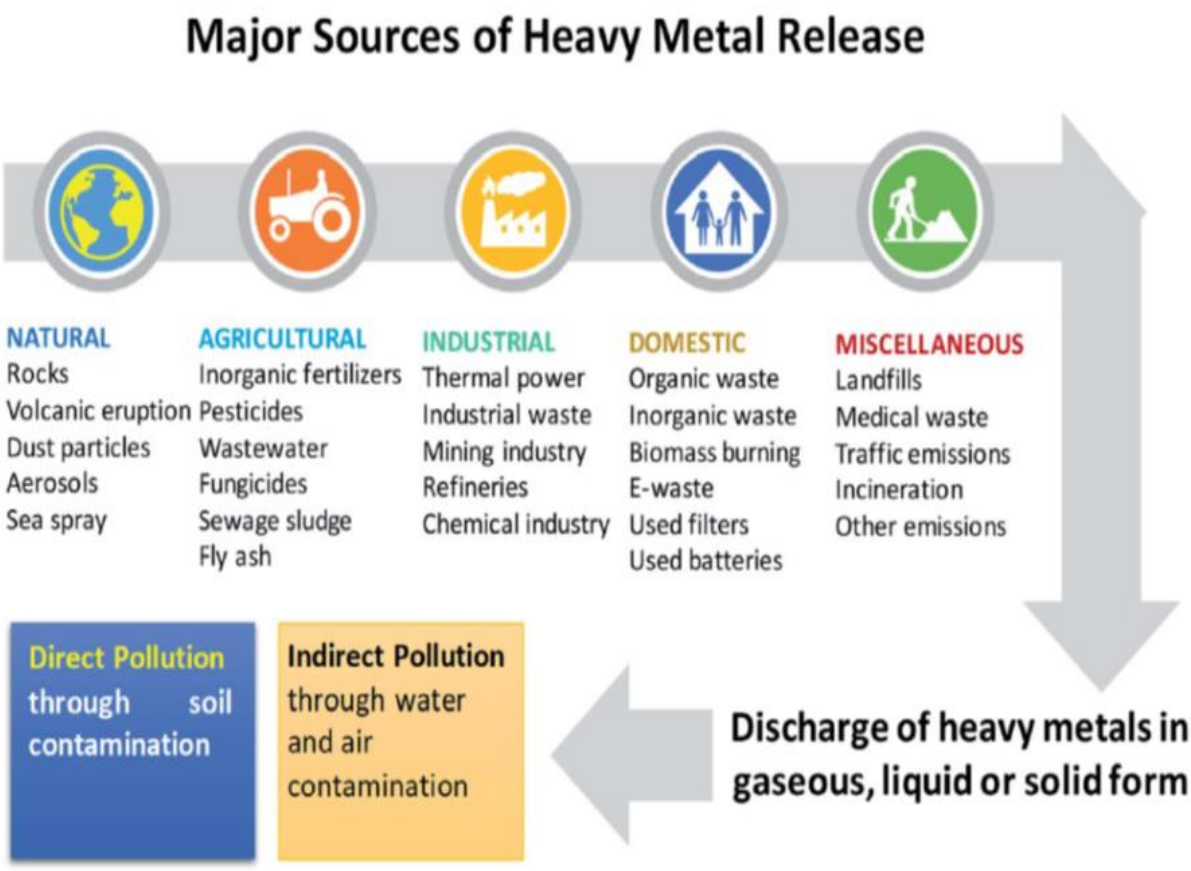

Figure 2.1: Sources of heavy metals in the environment (Rizvi *et al*., 2020)

Furthermore, human activities, improper disposal of industrial and mine wastes, agricultural chemicals, municipal and domestic effluents, pharmaceuticals are some of the culprits responsible for increased heavy metals in surface water resources (Annan *et al*., 2018; Masindi and Muedi, 2018; Buba and Maina, 2020). These metals, once ingested through water, food or air, can bio-accumulate over time causing detrimental health effects to humans and other organisms as seen in Table 2.1 (Sardar *et al*., 2013 Jaishankar *et al*., 2014). Heavy metals cause serious environmental concerns as they cannot be destroyed nor degraded (Jan *et al*., 2015). These metals pose profound health threats because they are carcinogenic, persistent, non-degradable and accumulative in nature (Uddin, 2017).

Table 2.1: Sources and health effects of some heavy metals (Uddin, 2017)

Metals	Uses	Health Effects	Sources (industry)	Sources (natural)
Arsenic	Rat poisons, bronzing, in forming special glass and preserve wood	Carcinogenic, producing liver tumours, and gastrointestinal effects, diabetes	Geogenic/natural processes, smelting operations, thermal power plants, fuel burning	Earth's crust, ground water, geothermal processes, Volcanic action, mineral ore
Cadmium	Electroplating of steel, nickel-cadmium batteries, cellular telephones, Laptop computers and camcorders	Carcinogenic, causes lung fibrosis, dyspnoea, chronic lung disease and testicular degeneration	Zinc smelting, waste batteries, e-waste, paint sludge, incinerations & fuel combustion	Coal combustion, iron and steel production, phosphate fertilizer manufacture and use, and zinc production, volcanic activities and from anthropogenic sources
Chromium	Electroplating, stainless-steel production, leather tanning, textile manufacturing and wood preservation	Nasal and sinus cancers, kidney and liver damage, nasal and skin irritation, ulceration, eye irritation and damage	Mining, industrial coolants, chromium salts manufacturing, leather tanning	Rocks, animals, plants, soil and in volcanic dust and gases
Cobalt	Electroplating, magnet steels and stainless steels, paint pigments	Lung effects such as asthma and pneumonia, Vomiting and nausea, Vision problems, Heart problems, Thyroid damage, hair loss, weight loss	Sewage sludge, phosphate fertilizers, processing of cobalt alloys	Erosion (wind-blown continental dusts), weathering of rocks and soil, seawater spray, volcanoes, forest fires, extraction by plants, continental and marine biogenic emissions
Copper	Electrical wiring,	Stomach ache, irritation of nose,	Mining, electroplating, smelting operations	Wind-blown dust, decaying vegetation,

	stoves, portable CD players, transmission wires, copper alloys and coins	mouth, and eyes, headaches		forest fires and sea spray
Lead	Car batteries, pigments, lead crystal glass, radiation protection, architecture	Carcinogenic, anaemia, abdominal, muscle and joint pains, kidney problems, and high blood pressure	Lead acid batteries, paints, e-waste, smelting operations, coal- based thermal power plants, ceramics, bangle industry	Sea and salt-lake aerosols, forest fires and volcanic eruptions
Nickel	Catalyst and battery manufacture, nickel coating, nickel stainless steel, catalyst and pigment	Causes chronic bronchitis, reduced lung function, cancer of the lungs, intestinal cancer	Electroplating, Ferrous and Nonferrous metal production, Smelting operations, thermal power plants, nickel–cadmium battery industries	wind-blown dust, soil and dust volcanoes, sea salt, forest fires and vegetation
Zinc	Batteries, coating, compound, crops, diecasting alloys	Stomach cramps, skin irritations, vomiting, nausea, respiratory disorders, anaemia and mental fever	Smelting, electroplating, pig and poultry manures	Surface water, soil and rock

2.3 Clay Structure

Clay refers to fine-grained mineral (less than two microns), which are found naturally on the earth's surface, typically made up of alumina, silica, weathered rock, and water (Mana *et al*., 2017; Ural, 2018). They are hydrous aluminosilicates consisting of fine-grained clay minerals and crystals of other minerals, such as metals oxides, quartz, and carbonates (Bhattacharyya and Gupta, 2008; Uddin, 2017). Clays can be plastic in nature or hardened when dried (Rautureau *et al*., 2017).

The mineralogy and size of clays helps to differentiate them from other fine-grained soils. There are two basic structures in clay minerals - (i) The tetrahedron formed through the bonding of silicon ions to oxygen atoms on all four sides Figure 2.2 and (ii) octahedron formed due to magnesium and aluminium ions coordinated on eight-sides with hydroxyl and oxygen ions Figure 2.3 (Ural, 2018).

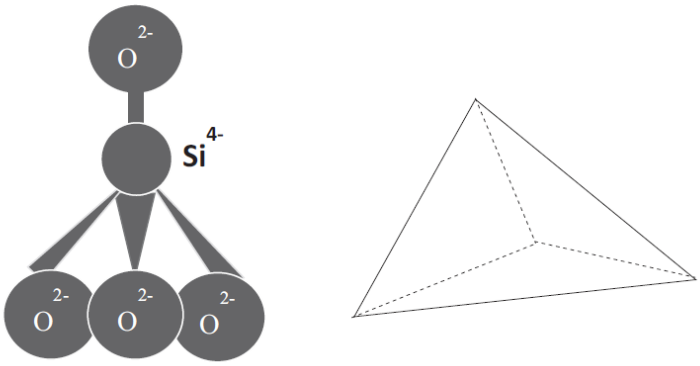

Figure 2.2: The Tetrahedral sheet formed from SiO_4^{2-} tetrahedral connected at three corners creating a hexagonal network in the same direction (Weaver and Pollard, 1973)

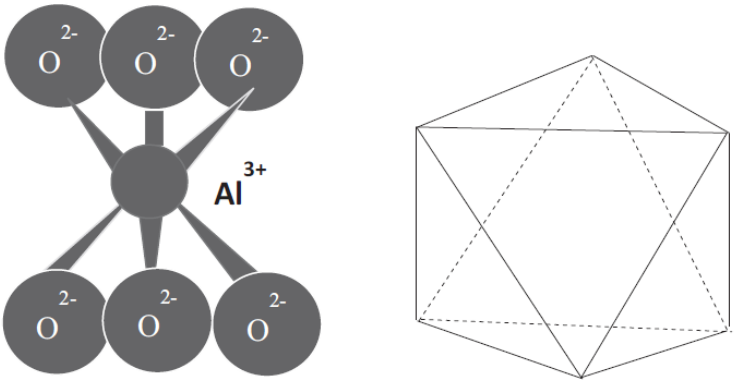

Figure 2.3: Octahedron consist of central cation (Al^{3+}, Fe^{2+}, Mg^{2+}) surrounded by six oxygen or hydroxyls (Weaver and Pollard, 1973)

Various clay mineral groups are formed because of changes in the structures of the tetrahedral and octahedral sheets; these groups include kaolinite, smectite, illite, and chlorite and vermiculite (Adeyemo *et al*., 2017; Gu *et al*., 2019). There are a variety of differences between the various clay groups, and these differences help to evaluate the impact of layer charge and structure on metal ion coordination on permanent charge sites (Adeyemo *et al*., 2017; Kausar *et al*., 2018). The different clay minerals, also provide a variety of arrangement of the aluminol and silanol surface hydroxyl sites (Adeyemo *et al*., 2017). Bhattacharyya and Gupta, 2008 reported that clays have several active sites, which include:

- Lewis acid or electron acceptor sites occurring due to dehydroxylation,
- Bronsted acid or proton donor sites resulting from interactions of adsorbed or interlayer water molecules,
- Reducing sites created due to the presence of some cations such as Fe^{2+},
- Oxidizing sites produced due to adsorbed oxygen on surfaces or due to the presence of some cations like Fe^{3+},
- Surface hydroxyl groups, found mainly in the edges, bound to Si, Al or other octahedral cations.

2.4 Sorption Properties of Clays

Clay minerals and modified clays are efficient adsorbent for the removal of metal ions, dyes, and organic compounds from water (Adeyemo *et al*., 2017). The adsorptive properties of clays are enhanced by their small particle sizes, high specific surface area and complex porous structure which boost their chemical and physical interaction with dissolved species (Uddin, 2017; Xue *et al*., 2020). Clays generally have large surface area (800m^2/g) which facilitates their adsorptive capacity of pollutants in water.

Furthermore, ion exchange capabilities and exchangeable anions (SO_4^{2-}, PO_4^{3-}, Cl^-, NO_3^-) and cations (Na^+, H^+, Ca^{2+}, Mg^{2+}, NH_4^+ and K^+) of clay materials make them efficient adsorbent without affecting their mineral structure (Kausar *et al*., 2018). Also cationic, anionic, non-ionic, and polar pollutants in natural water can be adsorbed by the faces and edges of clay particles (Mukasa-Tebandeke *et al*., 2019). These pollutants, once accumulated on clay surfaces get immobilized through coordination, ion–dipole or ion exchange interactions (Meroufel and Zenasni, 2018).

In addition, depending on the strength of the interactions (weak or strong) the contaminants can be held through hydrophobic bonding, van der Waals forces or H-bonding (Srinivasan, 2011); pre-treatment and modification of clays with heating, chemicals and polymers can improve their adsorptive properties (Gu *et al*., 2019). Table 2.2 below presents permissible limits for some toxic metals in drinking water based on international standards, from different regions of the world. Heavy metal concentrations in drinking water above the standard permissible limits, as recorded in Table 2.2, is a challenge because of its toxicity.

Table 2.2: Permissible limits for some toxic metals in drinking water (mg L^{-1}) based on some standards (Uddin, 2017)

Metal	IS 10500	WHO	USEPA	EU Std	MEP, China	CDW, Canada	NHMRC, Australia
Arsenic	0.010	0.010	0.010	0.010	0.050	0.010	0.010
Cadmium	0.003	0.003	0.005	0.005	0.005	0.005	0.002
Chromium	0.050	0.050	0.100	0.050	0.050	0.050	0.050
Copper	0.050	2.000	1.300	2.000	1.000	1.000	2.000
Lead	0.010	0.010	0.015	0.010	0.010	0.010	0.010
Nickel	0.020	0.020	0.100	0.020	0.000	-	0.020
Zinc	5.000	3.000	5.000	-	-	5.000	-

2.5 General Appraisal of Kaolin

Kaolinite ($Al_2[Si_2O_5](OH)_4$) is an inorganic polymer which is naturally occurring, with layered structures comprising of siloxane and gibbsite-like layers (Cheng *et al*., 2012 Hartanto *et al*., 2016). The siloxane surface comprises of the SiO_4 tetrahedra linked to a hexagonal array while the hydroxylated surface originates from the AlO_6 octahedral layer, Figure 2.4, (Lee *et al*., 2013). It is typically formed by the decomposition of granite, aluminium silicates, feldspars, or weathering processes (Johnson and Arshad 2014).

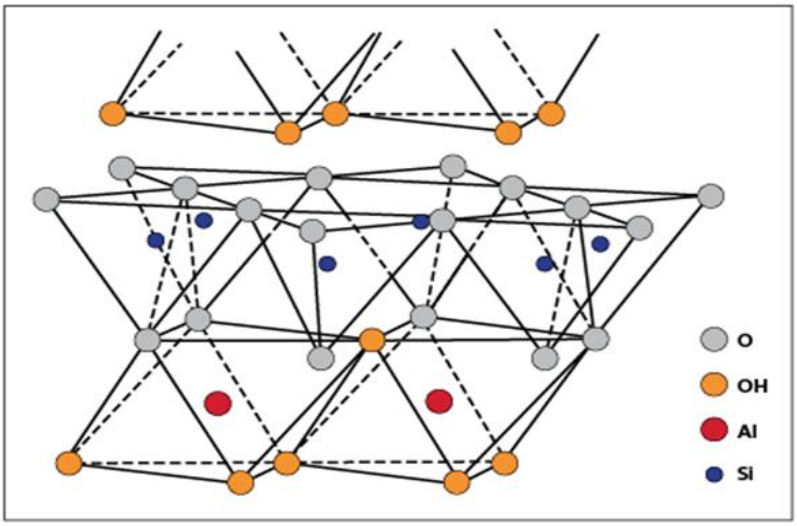

Figure 2.4: Molecular structure of kaolinite (Murray, 2007; Finkelnburg 2017)

The structure of kaolinite comprises of the tetrahedral silica alternating with the alumina octahedral sheet (Brigatti *et al*., 2013). The tetrahedral bases are approximately coplanar and the second layer, consisting of aluminium ions and OH groups (the gibbsite-type layer) are linked to the apical oxygen atoms (Cheng *et al*., 2012). Triclinic-pedial is the crystallographic structure of kaolinite, however, there are symbolic changes in the crystallinity of kaolinite in various kaolin types. This property is closely tied to the origin of the kaolinite and its environment of formation (Dill *et al*., 2015).

About 90% of kaolin deposits possess kaolinite and these may be found in conjunction with various igneous, sedimentary, and metamorphic rocks, with minerals such as smectite, feldspars and goethite (Ekosse, 2012). Kaolinite is generally in abundance in soils that have undergone chemical weathering of rocks in moist and hot climates (Orbovic and Huang, 2012).

2.6 Kaolin Genesis and Environments of Formation

Kaolin minerals are broadly developed in different depositional environments and in a wide range of lithologies (Dill *et al*., 1997; Dill, 2016). The genesis of kaolin, based on the environment of deposition, includes primary (structure bound/magmatic) and secondary (sedimentary) environment of deposition (Dill, 2016). The understanding of the occurrences and environments of formation of clay minerals helps in an efficient exploitation of these minerals to meet the demand from specialized markets (Zhou *et al*., 2016).

2.6.1 Primary Kaolins

Primary kaolins (hydrothermal and residual) refer to those, which are developed *in situ,* by the alteration of pre-exiting feldspar-rich rocks, such as granite and arkose (Figure 2.5) (Bukalo *et al*., 2017). Residual kaolins typically form in high rainfall, subtropical and tropical climates, due to increased rainfall and high temperatures, which favour the rapid breakdown of primary minerals to clay minerals (Bloodworth *et al*., 1993; Harvey and Murray 1997; Bukalo *et al*., 2017). Harvey and Murray (1997) state that the temperature of alteration, climate, permeability of parent rock and topography are some of the major factors that influence the formation of residual kaolins. Residual kaolins are typically of

low plasticity, full of impurities and coarse remains of parent rocks, including unaltered rock minerals and partially-decomposed feldspars.

Hydrothermal kaolins are closely linked to the alteration of the parent rock and the tectonic setting of the deposit (Sayin, 2007) and are formed by the hydrothermal alteration of alumina-silicate rocks (Bloodworth *et al*., 1993; Sayin, 2007). Bloodworth *et al*. (1993) add that during the kaolinization process, the hydrothermal alteration of aluminosilicates is very significant, and the parent rocks need to be sufficiently fractured to allow the free circulation of hot groundwater. Granitic host rocks which have low iron-bearing minerals (biotite) are known to produce high quality kaolins (Bloodworth *et al*., 1993).

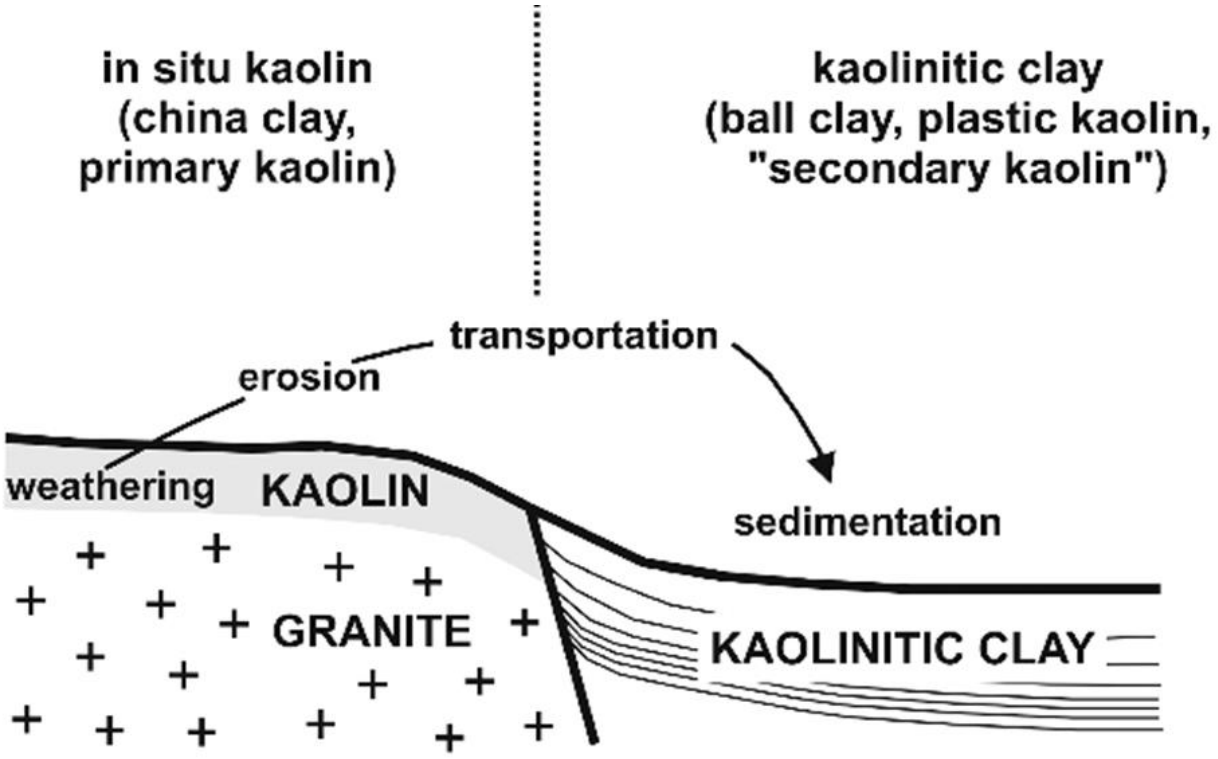

Figure 2.5: Formation of primary and secondary kaolin (Schmitz *et al*., 2011)

2.6.2. Secondary Kaolins

Secondary or sedimentary kaolins are those that have been formed elsewhere and then transported and deposited in lenses and beds with other sedimentary rocks in paludal, deltaic, lacustrine, and lagoonal environments (Figure 2.5 above) (Murray and Keller, 1993; Ekosse, 2010); they are typically fine-grained because of sorting during

transportation and deposition (Kogel, 2014). These sediments may be highly organic (lacustrine deposits) depending on the area of deposition. In the formation of sedimentary kaolins, weathering and diagenetic processes are very significant in their modification and formation (Bloodworth *et al*, 1993).

Baioumy *et al*. (2012) explain that sedimentary kaolins are typically of a complex geologic history with one or several superimposed alteration processes. These deposits usually contain more than 60% of kaolinite, while lower concentrations, due to *in situ* alteration of feldspathic sandstones, are reported in kaolinitic sands (Bloodworth *et al*, 1993). Baioumy (2014) noted that the geochemistry of sedimentary kaolins, is controlled by the following three factors: (i) post-depositional alterations (weathering and diagenesis); (ii) detrital minerals (rutile, feldspars, leucoxene quartz and zircon) and (iii) neo-minerals (non-clay minerals and kaolinite). Additionally, secondary kaolins are important geological-geochemical archives for source areas which have undergone erosion and are significant in unravelling the paleoclimatic data of certain kaolin deposits (Baioumy *et al*.,2012).

2.7 The Kaolinization Process

The formation of kaolin deposits is typically due to the alteration of leucocratic feldspar rich rocks (rhyolite, leucogranite, arkose, granulite and andesite) or illite-rich claystone (Pohl, 2011), however, rocks rich in iron are unsuitable precursors for the formation of kaolins. Kaolinization is a process of kaolin formation through the alteration of minerals into clay mineral kaolinite (Pohl, 2011; Johnson and Arshad 2014). The process of kaolinization is activated by groundwater activity, hydrothermal fluid reactions and surface weathering (Bergaya *et al*., 2011; Huang *et al*., 2011). Kaolinization is facilitated by the presence of acidic solutions; as rainwater dissolves, carbon dioxide in the atmosphere enhances the weathering of granitic rocks (Murray, 1999). In near-surface rocks, aluminium silicates and feldspar are kaolinized by acidic meteoric water which percolates into the ground and reacts with the rocks (Murray, 1999). The reactions below demonstrate the alteration of mica and potassium feldspar into kaolinite (Equations 2.1 and 2.2) (Huang *et al*., 2011):

$2KAlSi_3O_8 + 2H^+ + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2K^+ + 4H_4SiO_4$ Equation 2.1

Muscovite kaolinite

$2KAl_3Si_3O_{10}(OH)_2 + 2H^+ + 3H_2O \rightarrow 3Al_2Si_2O_5(OH)_4 + 2K^+$ Equation 2.2

K-feldspar kaolinite

2.8 Kaolin Mineralogy and Chemistry

The kaolin-group-forming clays are all hydrous aluminium silicates; these are, essentially, kaolinite which is formed by the alteration of aluminous minerals, especially, feldspars (Norman, 2013). Kaolin deposits can be nearly-pure kaolinite (a combination of SiO_2, Al_2O_3 and water in a hydrous crystalline structure) or may contain impurities that affect the characteristics of the clay (Madi *et al*., 2013). Kaolinite occurs as a major mineral phase in most kaolins, while quartz, illite, microcline, goethite, and muscovite usually occur as minor mineral phases (Bukalo *et al*., 2017). Commercial kaolins are generally considered monomineralic clays, however, some small amounts of other minerals are invariably present. The nature and the quantity of these minerals have a significant effect on the abrasiveness, colour and viscosity of the kaolin, which may pose some deleterious effect on the end product, for a particular use (Christidis, 2011).

The term “kaolin” is usually used as a group name for clay minerals, comprising of kaolinite, nacrite, dickite, and halloysite with its metaforms, imogolite and allophane (White and Dixon, 2002; Haowen *et al*., 2018). The minerals can be divided into the 7-Å and 10-Å groups of phyllosilicates and Si-Al complexes (Figure 2.6) (Arkai *et al*., 2002). Dill (2016) reported that the 7-Å group of phyllosilicates is dominant in kaolins and it consists of kaolinite, dickite and nacrite in decreasing order of abundance, as seen in Weaver (1989). They are dioctahedral phyllosilicates with the chemical formula of $Al_2Si_2O_5(OH)_4$ and chemical composition of SiO_2: 46.55 wt %, Al_2O_3: 39.50 wt % and H_2O: 13.96 wt % (Dill, 2016). Polymorphism is typically characterized based on two factors - the location of vacant octahedral site in successive layers, as well as the direction, and the amount of interlayer shift (Weaver, 1990).

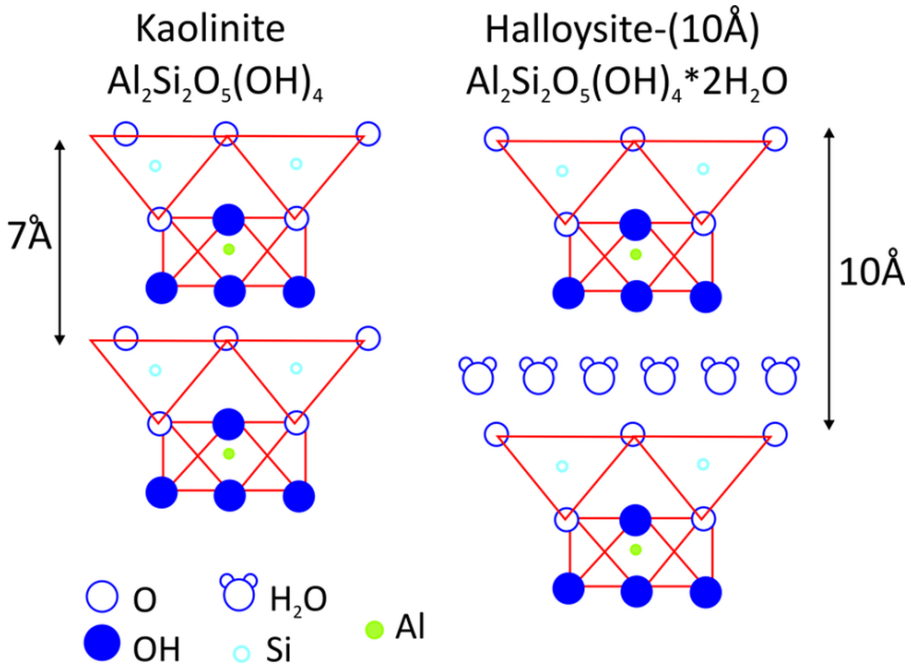

Figure 2.6: Structure of kaolinite and halloysite (Lázaro, 2015)

2.9 Sorption Properties of Kaolinite

Kaolinite is a 1:1 dioctahedral phyllosilicate formed due to the superposition of silicon tetrahedral sheets and aluminium octahedral sheets (Figure 2.7) (White *et al.,* 2009; Lee *et al.,* 2013). The structure of kaolinite provides added advantages in many processes because of its low expansion coefficient, cation exchange capacity and high chemical stability (Uddin, 2017). According to Kausar *et al*., (2018), adsorption in kaolinite can occur on flat exposed planes of alumina and silica sheets. Gu *et al*. (2019) maintained that the H^+ ions which are released from the edge of the layer structure of kaolinite in an acidic environment, enhance the adsorption of heavy metal ions (Pb(II), Cd(II), Hg(II) and Cu(II)) from aqueous mediums.

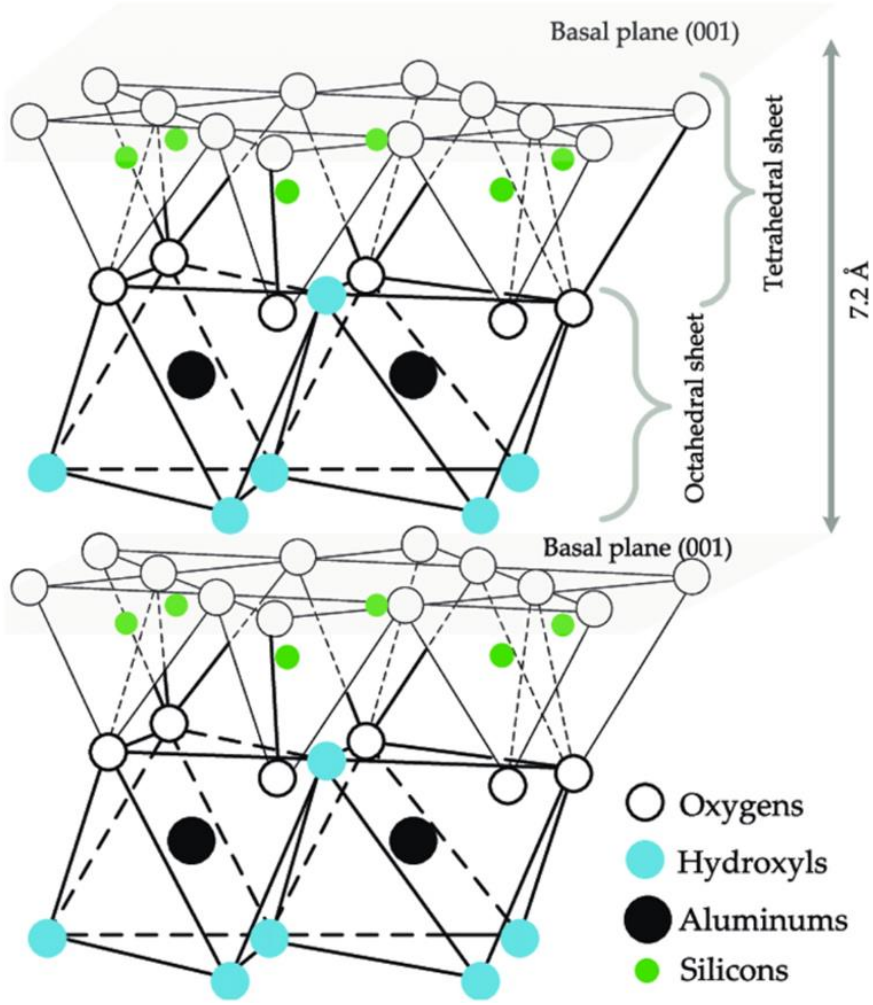

Figure 2.7: Structure of kaolin showing bonding between silicon tetrahedral sheets and aluminium octahedral sheets (Diawara *et al*., 2021)

The adjacent layers in kaolinite are linked by hydrogen bonds and van der Waal forces, however, the hydroxyl groups are the most functional in kaolinites as they can take part in many ion-exchange processes and chemical reactions (Cheng *et al*., 2010). Furthermore, the bonding between the alumina octahedral sheet and the silica tetrahedral sheet of kaolinite is so strong that there is no interlayer swelling (Ural, 2018). The interlamellar aluminol groups, (Al-OH), which can be used for grafting reactions, may experience constricted access, due to the effect of the interlayer (Cheng *et al*., 2012). There is limited isomorphous substitution in kaolinite, because it is non-expanding, thus, has high molecular stability (Brigatti *et al*., 2013). About 40 million tons of kaolinites are consumed in industrial applications (ceramics, paper, paint) because of their favourable

chemical and physical characteristics (acidity and hydrophilicity) (Murray, 2000; Conceicao *et al*., 2005; Ou *et al*., 2007).

2.10 Modification of Clays

The modification of clays involves employing different treatment techniques to improve the adsorption capacity, quality, and characteristics of natural clays. Some of the techniques include, intercalation, pillaring, and acid activation. According to Churchman *et al*. (2006), raw natural clays are hydrophilic and usually show low-adsorption capacity for small non-ionic organic compounds, in aqueous solution. Modification using different salts, acids, surfactants, bases, organic and inorganic chemicals, however, results in clay minerals becoming hydrophobic and organophilic, boosting their adsorption of small non-ionic organic compounds (Churchman *et al*., 2006).

2.10.1 Intercalation

Intercalation refers to the insertion of guest species (atoms, molecules or ions) in the interlayer region of a clay mineral without destruction of the layered structure (Jacobson, and Nazar, 2011). Bruce and Irvine, (2002) reveal that the guest ions can be introduced into the host lattice, via a neutral solvent molecule to impair the degree of reversibility during the process. The resultant material is an intercalated clay which may show increased spacing between adjacent layers under XRD analysis (Bhattacharyya and Gupta, 2008). Intercalation of kaolinite surfaces offers new and novel phases, potential materials for catalysis and provides useful materials which can be incorporated into composite materials. Intercalation followed by deintercalation, can cause particle size reduction and the production of materials with different porosities (Frost and Kristof, 2004); for example, the intercalation of kaolinite with potassium acetate, followed by deintercalation result in the formation of a mesophase-like material which can be used for cation size selection and removal of heavy metals from water (Frost and Kristof, 2004).

2.10.2 Pillaring

According to Schoonheydt *et al*. (1999), pillaring refers to “the process by which a layered compound is transformed into a thermally stable micro- and/or meso porous material with retention of the layer structure”. Cool and Vansant, (1998) maintain that clays have one

main disadvantage - lack of permanent porosity; for instance, in smectites, hydration leads to swelling while severe dehydration (heating) causes layer collapse and inaccessibility of interlayer surface for chemical processes. To avoid this challenge, stable pillars can be introduced in the interlayer region to prop open the clay layers (Figure 2.8) (Asgari and Sundararaj 2021). As a result, there is increased pore volume and maintenance of the porosity of the pillared interlayered clay (PILC) during hydration and dehydration.

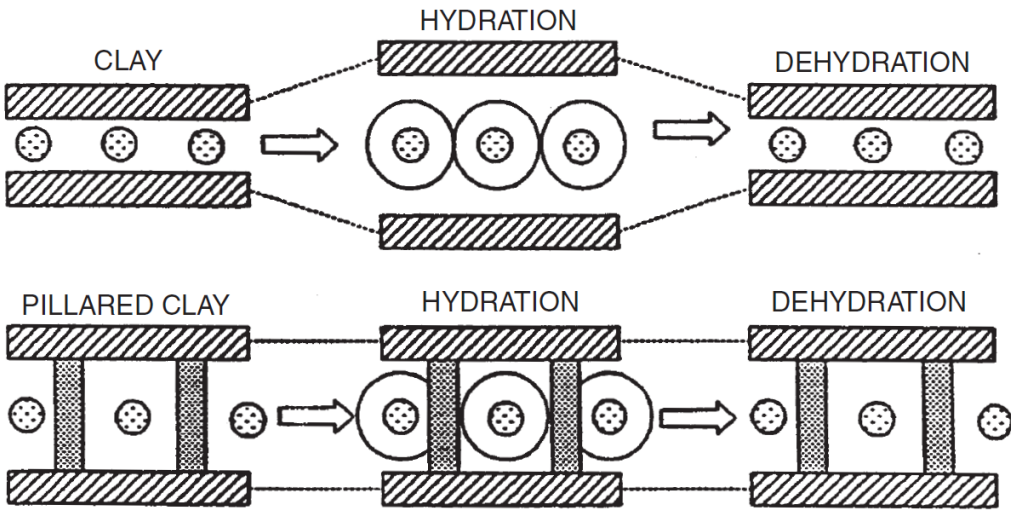

Figure 2.8: Hydration and dehydration behaviour of clay and pillared clay (Cool and Vansant, 1998)

There exists a variety of pillaring species, such as zirconium, metal oxides, aluminium and mixed oxides. Zirconium PILC loses its thermal stability at high temperatures and show a large and poorly defined X-ray diffraction reflection, due to heterogeneity of pillars (Mnasri-Ghnimi and Frini-Srasra, 2019). Mixed oxides are efficient in preventing sintering of the pillared clay and provide increasing stability for the pillars while metal-oxide pillared clays offer high surface area, high thermal stability, and intrinsic catalytic activity (Chauhan *et al*., 2020). Aluminium-pillared clays present a higher adsorption capacity for some heavy metals, compared to natural clays (Mnasri-Ghnimi and Frini-Srasra, 2019).

2.10.3 Acid Activation

Acid activation refers to the chemical treatment of clays with high concentrations of mineral acids (typically hydrochloric and sulphuric acid) at high temperature. It may be one of the most adequate methods to produce active materials for adsorption and catalysis (Komadel and Madejova, 2013, Chai *et al*., 2020). The aim in acid activation is to derive partly-dissolved material of high porosity, specific surface area and acidity. According to Komadel and Madejova, (2013), the resultant product consists of remains of the starting mineral and an amorphous, porous, protonated, and hydrated silica phase, with a three-dimensional cross-linked framework.

The modification in clay properties (surface area and porous structure) due to acid treatment, is dependent on - the type of clay mineral, the non-clay minerals, the other clay minerals present, the type of cations in the interlayer region, the type of acid, the overall chemical composition, the process temperature, the process period - and other environmental factors (Onal *et al*., 2002). Bhattacharyya and Gupta, (2008) discovered that when kaolinite is treated with acid, its crystalline structure is transformed thermally to amorphous Al^{3+} metakaolin and its octahedral ions are released, preferentially, leading to the creation of more Al-OH and Si-OH bonds without modifying the original mineral structure.

2.11 Treatment Methods for Heavy Metal Removal

The pollution of water has created new technologies for the removal of hazardous pollutants from water. Different techniques such as nanofiltration, ultrafiltration, floatation, electrocoagulation, reverse osmosis, electrooxidation, electrodialysis and coagulation flocculation have been employed to remove heavy metals from water. These techniques, however, are not well suited for this study because of their high cost of operation, high energy consumption or membrane fouling (Table 2.3). Kaolin was chosen as the adsorbent because it can be used for the removal of organic and inorganic pollutants from water (Abdelaal *et al*., 2010); secondly, it is capable of encapsulating toxic matter in its crystal structure (Uddin, 2017); thirdly, kaolin is non-toxic, cheap and abundantly available (Keng *et al*., 2014). In this study, adsorption using kaolin (rock rich in kaolinite) was used

for the removal of Cd (II) ions. The choice of the adsorption method was due to the following reasons:

- simple design and ease of operation,
- it is effective and cheap, and
- water can be recycled and reused (Srivastava *et al*., 2015).

Table 2.3: Treatment methods for heavy metal removal from water (Srivastava *et al*., 2015)

Method	Advantage	Disadvantage
Reverse osmosis	Accounts for more than 20% of world desalination capacity Efficient rejection rate	High power consumption due to high operating pressure (20-100 bar) Prone to membrane fouling
Nanofiltration	Easy operation, reliable, low energy consumption Can treat inorganic effluent with metal concentration up to 200 mg/L on a wide range of pH and pressure	Costly Prone to membrane fouling
Ultrafiltration	Low driving force Small space requirement High packing density	Problem of membrane fouling Biodegradation of membrane material
Coagulation flocculation	Can treat wastewater with metal concentration higher than 1000 mg/L Improved sludge settling	High operating cost High chemical consumption and toxic sludge generation
Floatation	Can treat inorganic effluent with metal concentration of more than 150 mg/L Effective for small particle removal Shorter hydraulic retention time, low operation cost	To improve heavy metal removal subsequent treatments are required
Electrocoagulation	No chemical required as coagulant Low operating cost Simple and easy operation	Cannot remove pollutant directly High initial investment
Electrodialysis	Low energy consumption	Feed water pre-treatment required to prevent electrodialysis stack fouling

Electrooxidation	Uses clean reagent as electron No chemical reagent required Simple equipment, easy operation, brief retention time, can treat a wide range of pollutant	High operating cost High energy consumption Risk of electrode fouling

2.12 Adsorption Mechanisms and Models

2.12.1 Adsorption Mechanisms

Adsorption is adhesion of molecules, atoms or ions onto a surface; it involves the separation of a substance in one phase and its accumulation on another surface (McLean and Zarrouk, 2019; Sohi *et al*., 2019). The surface or the material on which adsorption occurs is termed the “adsorbent” and the chemical specie which gets adsorbed is called the “adsorbate” (Sillanpää and Bhatnagar, 2014). Adsorbents can be hydrophilic (forms bond with water molecules) or hydrophobic (repel water molecules) (Macdonald, 2007). Adsorption has its origin in attractive forces between molecules; the exposed surface atoms of the adsorbent can attract the adsorbate molecules (Annan *et al*., 2018).

Adsorption mechanism may involve ion exchange, direct bonding, and surface complexation (Uddin, 2017). Ion exchange involves the interchange of ions of similar or equal charge in solutions (Kumar and Jain, 2013). Direct bonding includes the joining of the adsorbate onto the adsorbent surface. Surface complexation describes the sorption of adsorbate based on surface-reaction equilibrium. Adsorption can be physisorption, chemisorption or biosorption, depending on the nature of the surface forces and the type of adsorbate. Physisorption involves relatively weak intermolecular forces (van der Waals), while chemisorption involves strong chemical bond between the adsorbate and the adsorbent which includes electron transfer (Hu and Xu, 2020). Biosorption is a process of binding of ions from aqueous solutions onto functional groups that are present on the surface of a material of biological origin (Michalak *et al*., 2013).

During adsorption in a solid-liquid system, some solutes are removed from solution and accumulated on the solid surface while the remaining solute in the solution attain a

dynamic equilibrium with those adsorbed at the solid phase (Annan *et al*., 2018). The fundamental equation for adsorption is given below (Equation 2.3) (Ayub *et al*., 2020)

$$q_t = (C_o - C_t)V / m$$

Equation 2.3

where: q_t (mg/g) is the amount of adsorbate at a time (t) per mass unit of adsorbent C_o (mg/L) initial concentration of adsorbate C_t (mg/L) concentration of adsorbate at a time (t) V (L) volume of the solution m (g) mass of adsorbent**.**

2.12.2 Adsorption Isotherm Models

Adsorption isotherms provide useful data on the surface capacity, adsorption capacity and affinity of the adsorbent. This information facilitates the understanding of the binding mechanism of the adsorbate, with the adsorbent (Kentsa *et al*., 2020). The adsorption isotherms utilize the Langmuir and Freundlich models. Table 2.4 presents a summary of equations for some adsorption isotherm models

Table 2.4: Summary of some adsorption isotherms and their equations (Meroufel *et al*., 2013; Batool *et al*., 2018)

Adsorption Isotherms	**Equations**
Langmuir	$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$
Freundlich	$logq_e = logK_F + \frac{1}{n} logC_e$
Brunauer, Emmett and Teller (BET)	$q_e = \frac{q_s c BET^{C_e}}{(C_s - C_e)[1 + (C_{BET} - 1)(C_e/C_s)]}$

2.12.2.1 Langmuir Isotherm

This isotherm was created by Langmuir in 1916, primarily, as a theoretical equilibrium isotherm designed to describe gas-solid phase adsorption (Chowdhury *et al*., 2011). It is based on a uniform, monolayer, and finite adsorption site and it can also be employed to quantify and contrast the adsorptive capacity of different adsorbents (Meroufel *et al*., 2013).

This adsorption isotherm assumes that there exists no interaction among molecules adsorbed on neighbouring adsorption sites and accounts for surface coverage through balancing rates of adsorption and desorption (Bhandari and Ranade, 2014). Adsorption is proportional to the open fraction of the surface of the adsorbent and desorption is proportional to the covered fraction of the adsorbent surface (Ayawei *et al*., 2017). Equation 2.4 represents the Langmuir's isotherm and Equation 2.5 represents the linearized form which will be used to determine the adsorption parameters, in this study.

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$$

Equation 2.4

$$\frac{1}{q_e} = \frac{1}{K_L q_{max} C_e} \times \frac{1}{C_e} + \frac{1}{q_{max}}$$

Equation 2.5

where q_e is the adsorption capacity (mg/g), C_e is the equilibrium concentration of the metal ion (mg/L), C_0 is the initial concentration of the adsorbate (mg g^{-1}), q_{max}, is the maximum adsorption capacity (mg/g), K_L (L/mg) is the Langmuir isotherm constant and R_L is the separation factor. From a graph of $\frac{1}{C_e}$ vs $\frac{1}{q_e}$ the slope, R^2 and the intercept can be gotten.

The essential characteristic of the Langmuir isotherm can be expressed by the separation factor R_L which is a dimensionless constant:

$$R_L = \frac{1}{1 + K_L C_0}$$

Equation 2.6

R_L > 1 implies adsorption is unfavourable; 0< R_L< 1 suggests adsorption is favourable; R_L = 1 indicates adsorption to be linear; R_L= 0 implies adsorption is irreversible (Ayawei *et al*., 2017).

2.12.2.2 Freundlich Isotherm

This adsorption isotherm is based on the adsorption processes being on heterogenous sites and it gives an expression that defines surface heterogeneity, the exponential distribution of active sites and their energies (Batool *et al*., 2018). The process is established on the assumption that binding sites which are stronger are occupied first and the strength of adsorption reduces with the degree of occupation. Equation 2.7 represents the Freundlich's isotherm and Equation 2.8 represents the linearized form which will be used to determine the adsorption parameters.

$$q_e = K_F C_e^{\frac{1}{n}}$$

Equation 2.7

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

Equation 2.8

K_F is the adsorption capacity (L/mg); 1/n is a function of the adsorption strength, and it indicates the affinity between adsorbent and adsorbate. From the plot of log C_e vs log q_e, the values for R^2, the slope, and the intercept can be gotten. A 1/n value below unity suggests that the adsorption process is chemical; a 1/n value above unity implies the adsorption process is more physical; as a 1/n value approaches zero, the more heterogenous the surface (Bhandari and Ranade, 2014).

2.12.2.3 Brunauer, Emmett and Teller BET Isotherm

The BET isotherm is a theoretical equation developed to derive apparent multilayer-adsorption systems which are mainly applied to gas-solid equilibrium system (Foo and Hameed, 2010). Its extinction model related to solid-liquid interface is exhibited as:

$$q_e = \frac{q_s c BET^{C_e}}{(C_s - C_e)[1 + (C_{BET} - 1)(C_e/C_s)]}$$

Equation 2.9

where: C_{BET} is the BET adsorption isotherm (L/mg)

C_s adsorbate monolayer saturation concentration (mg/L)

q_e theoretical isotherm saturation capacity (mg/g)

q_s equilibrium adsorption capacity (mg/g)

the equation is simplified as: C_{BET} and C_{BET} (C_e/C_s) are much greater than 1

$$q_e = \frac{q_s}{1 - (C_e/C_s)}$$

Equation 2.10

2.12.3 Adsorption Kinetic Models

Kajjumba *et al*. (2018) explicates that adsorption kinetics, “is a curve or a line that describes the rate of retention or release of solute from an aqueous environment to solid-phase interface at a given adsorbent dose, temperature, flow rate and pH”. Adsorption kinetics are used to ascertain the rate at which adsorption occurs; solute concentration and flow, surface complexity of the adsorbents are some of the factors which affect adsorption kinetics (Batool *et al*., 2018). The adsorption kinetic models are used to foretell the adsorbent-adsorbate interaction and are essential in the designing of an adsorption system (Mercado-Borrayo *et al*., 2014). The kinetic models include pseudo first-order and pseudo second-order models; Table 2.5 presents a summary of equations for some adsorption kinetic models.

Table 2.5: Summary of some adsorption kinetic models and equations (Kajjumba *et al*., 2018; Kentsa *et al*., 2020)

Adsorption Kinetic models	**Equation**
Pseudo-First-Order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$
Pseudo-Second-Order	$\frac{d_q}{d_t} = k(q_e - q)^2$
Intra-Particle Diffusion (IP)	$q_t = K_p\sqrt{t} + C$
Elovich	$\frac{dq_t}{dt} = \alpha exp^{-\beta q_t}$

2.12.3.1 Pseudo First Order Model (PFO)

Pseudo first-order model referred to as “Lagergren model” depicts the adsorption of solute onto the adsorbent following the first order mechanism (Lagergren, 1898). It illustrates sorption in a solid-liquid system based on the adsorption capacity of solids and it is represented in Equation 2.11 (Ho, 2006) as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

Equation 2.11

where: q_t is the adsorbate adsorbed onto the adsorbent at time t (mg/g), q_e is equilibrium adsorption capacity (mg/g), k_1 is the rate constant per minute. Integrating Equation (2.11) at boundary conditions that is at t = 0, q_t=0 and at $t = t$, q_t=q_t, gives a linear expression of PFO Equation 2.12:

$$In(q_e - q_t) = Inq_e - k_1 t$$

Equation 2.12

The rate constant k_1 can be determined from the slope of a linear plot of $In(q_e - q_t)$ vs t, Kajjumba *et al*., (2018) reported that the rate constant (k_1) is always inversely proportional to the initial concentration of the solute because more time is needed for a large initial solute concentration.

2.12.3.2 Pseudo Second Order Model (PSO)

This model is based on the assumption that the rate of adsorption of a solute is proportional to the available sites on the adsorbent and the driving force $(q_e - q_t)$ is proportional to the number of active sites available on the adsorbent (Kentsa *et al*., 2020). The reaction rate depends on the quantity of solute on the surface of the adsorbent and the model can be affected by - the particle size, pH, temperature and dose amount (Kajjumba *et al*., 2018). The PSO is represented by Equation 2.13, where

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

Equation 2.13

k_2 is the rate constant for the PSO model. Integrating with boundary conditions that at t = 0, q_t=0 and at $t = t$, q_t=q_t gives a linear PSO expression Equation 2.14

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

Equation 2.14

The PSO model evaluates the impact of observable rate parameters and a plot of $\frac{t}{q_t}$ vs t gives a linear relationship which can be used to calculate the PSO constants (k_2 and q_e) (Gandhi *et al*., 2016).

2.12.3.3 Intra-Particle Diffusion (IP) Model

The IP model helps to examine the rate-limiting step during adsorption (Wu *et al*., 2009) In a solution, the adsorption of solute involves surface diffusion, pore diffusion and mass transfer of adsorbate (film diffusion). Surface and pore diffusion may occur simultaneously however film diffusion occur as an independent step; this process can be studied by evaluating the Weber and Morris (1963) model:

$$q_t = K_p\sqrt{t} + C$$

Equation 2.15

where K_p is the rate constant mg/g.min$^{0.5}$ and C is the boundary layer thickness; the higher the values of C the greater the boundary layer effect. The plot of q_t vs $\sqrt{t}$ gives a linear function. IP diffusion controls the adsorption process, if the line passes through the origin, but if the plot does not pass through the origin and it gives multi-linear plots, then two or more steps are responsible for the mechanisms that influence the adsorption process (Gandhi *et al*., 2016).

Kajjumba *et al*. (2018) noted four main mechanisms that illustrate the transfer of solute from a solution to the adsorbent, which include: (i) mass transfer involving the bulk movement of solute particles immediately the adsorbent is placed in the solution; (ii) film diffusion which describes the slow movement of solutes from the boundary layer to the adsorbent's surface; (iii) the movement of the solute on the adsorbent surface to the pores of the adsorbent and (iv) the rapid adsorptive attachment of the solute onto the active sites of the pores. The first and the fourth mechanisms are rapid processes, consequently, they are not considered during the design of kinetic systems and engineering design of kinetics, respectively.

2.12.3.4 Elovich Model

The Elovich model is used to predict the mass and surface diffusion, activation and deactivation energy of a system (Kajjumba *et al*., 2018). This model developed by Zeldowitsch is applied to better comprehend chemisorption and it is based on the

assumption that, the rate of adsorption of solute decreases exponentially as the quantity of adsorbed solute increases as shown in Equation 2.16 (Chen *et al*., 2008).

$$\frac{dq_t}{dt} = \alpha exp^{-\beta q_t}$$

Equation 2.16

where: $q_t \approx 0$, $\frac{dq_t}{dt} \approx \alpha$ is the initial adsorption rate (mg/g.min) and β is desorption constant. Integrating the equation above and applying the limits for t (0,t) and $q_t(0, q_t)$, the Elovich model is linearized as Equation 2.17

$$q_{t=}\frac{1}{\beta} In\left[t + \frac{1}{\alpha\beta}\right] - \frac{1}{\beta} In(\alpha\beta)$$

Equation 2.17

The nature of the adsorption on the heterogeneous surface of the adsorbent is determined by the graph of q_t vs t, whether chemisorption or not. As the system approaches equilibrium $t \gg \frac{1}{\alpha\beta}$, Equation 2.17 becomes

$$q_t = \frac{1}{\beta} In[\alpha\beta] + \frac{1}{\beta} Int$$

Equation 2.18

In summary, the fitness of any model used in an adsorption system is dependent on the Sum of Squared Errors (SSE) or the error level coefficient of determination (R^2). According to Kajjumba *et al*. (2018), the best kinetic model for metal adsorption is evaluated by assessing the error function, and q_e must match with experimental values, q_{ecal} at all initial concentrations of adsorbate with maximum R^2 and minimum X^2 values.

2.13 Review of Heavy Metal Sorption onto Kaolin

2.13.1 Arsenic (As)

Arsenic is amongst the top five dangerous metals which can contaminate water and their rise in wastewater is due to the use of dyes, paints, mining and smelting activities. The adsorption of As onto kaolinite is influenced by temperature and pH. Mohapatra *et al*. (2006) recorded As(v)-kaolinite interactions to be exothermic, with increasing temperature leading to a reduction in the adsorption efficiency. In addition, at pH 5.0, an optimum adsorption capacity of 0.86 mg/g was noted for kaolinite.

Adsorption of As(v) onto kaolinite was found to involve strong specific ion adsorption and inner-sphere surface complexation (Mohapatra *et al*., 2006). Kaolinite intercalated with hexadecyltrimethylammonium ions was reported by Li and Bowman, (2001) as an effective adsorbent for the removal of arsenic and it was noted that an ion exchange mechanism was responsible for the arsenate retention on the intercalated kaolinite. Mudzielwana *et al*., (2019) successfully used inorgano-organo modified kaolin for As (III) and As (V) removal from water. The adsorption of As (III) and As(V) followed the chemisorption process and the arsenic-kaolin interactions were exothermic in nature.

2.13.2 Cadmium

In a single-element system, adsorption of Cd onto kaolinite generally decreases with reducing ionic strength and increases with increasing pH. Also, the interactions of Cd (II) with kaolinite, acid-activated kaolinite, poly(oxo zirconium) (ZrO)and tetrabutylammonium (TBA) derivatives, were found to be influenced by the pH of the aqueous medium; this occurs with the quantity of Cd(II) adsorbed increasing when there is a gradual reduction in acidity (Bhattacharyya and Sen Gupta, 2008). Gupta and Bhattacharyya, (2008) noted that by raising the pH of the solution from 1.0 to10.0, the adsorption rose from 4.3 to 29.5 % for kaolinite and 10.1 to 35.1 % for acid-activated kaolinite.

Also strong endothermic interactions were observed between Cd (II) and kaolinite which were associated with thermodynamically-favourable entropy and Gibbs energy changes. In another study by Mladenović *et al*., (2019) on the removal of cadmium ions from aqueous solution using natural kaolinite and kaolinite modified by amino acids (histidine

and cysteine), it was found that the modified kaolinite offered better adsorption efficiency, with the kaolinite modified with histidine, showing up to 91.8% efficiency. The adsorption process was spontaneous, and chemisorption was the adsorption mechanism for the adsorbents used.

2.13.3 Chromium

Bhattacharyya and Sen Gupta, (2006) and Li *et al*. (2010) observed the adsorption of chromium onto kaolin to be pH-dependent; a decrease in chromium adsorption observed at low pH and increased adsorption at higher pH, could be as a result of the precipitation of metal hydroxide enhancing Cr (III) retention by the clay. Bhattacharyya and Sen Gupta, (2006) recorded that the adsorption of Cr (VI) on kaolinite, ZrO-kaolinite, TBA-kaolinite and acid-activated kaolinite peaks around pH 7.0 with declining trends on both sides of the pH. A reduction in chromium adsorption may be attributed to the formation of hydroxyl complexes of chromium and $Cr(OH)_3$, which may hinder the diffusion of Cr(VI) ions to the clay surface (Bhattacharyya and Sen Gupta, 2006).

Cr(VI)-kaolinite interactions were recorded to be endothermic accompanied by increased entropy and decrease in Gibbs energy. Li *et al*., (2010) noted that the presence of humic acid increased the adsorption of Cr(VI) from aqueous solution on kaolinite. The adsorption process was also endothermic and higher temperatures favoured the adsorption of the metal ions. Another study by Deng *et al*. (2014) on Cr(VI) adsorption by kaolin also revealed similar pH dependency with increased adsorption efficiency within a pH range of 2.5 - 11.5, although, increase in temperature and electrolyte concentration negatively affected adsorption. Also, thermodynamic investigations showed that adsorption was spontaneous and exothermic.

2.13.4 Copper

The adsorption of Cu(II) by kaolinite and its modified forms, were demonstrated by Wang *et al*., (2006) and Alkan *et al*., (2008) to be endothermic in nature, however, exothermic interactions were reported between Cu(II) and Ca-kaolinite (Doula *et al*., 2000). Alkan *et al*., (2008) observed that a rise in pH and temperature lead to an increase in the amount of copper ions adsorbed; conversely it was also noted that a rise in acid-activation, ionic

strength and calcination temperature resulted in a reduction in the amount of copper ions adsorbed.

Bhattacharyya and Sen Gupta, in their study of (2008) discovered that acid activation of kaolinite, increased the adsorption of Cu(II) as opposed to the ZrO- and TBA- derivatives of kaolinite; this was due to increased pore volume and surface area resulting from the acid treatment. In another study by Danková *et al*., (2015) kaolin was modified with manganese dioxide on its surface; this resulted in high values of specific surface area and better affinity for Cu(II). From this study it was observed that in the solutions with lower initial Cu(II) concentrations, the efficiency of Cu(II) removal by the modified kaolin almost reached 100%.

2.13.5 Cobalt

In a study done by Woodward *et al*., (2018), it was observed that the adsorption of Co was dependent on the ionic strength and initial Co concentration being below pH~7. This was attributed to Co binding to kaolinite through outer-sphere surface complexation and surface sorption site, respectively, in the low-mid pH regime. According to Bhattacharyya and Sen Gupta, (2008) adsorption is influenced by initial Co (II) concentration and pH of the aqueous solution (1.0 - 8.0) for a fixed amount of clay, however, beyond this, a pH 8.0 solubility of Co(II) rapidly decreases resulting in separation by precipitation preventing experiments beyond this pH level.

The interactions of Co-kaolinite and acid-activated kaolinite have been reported to be endothermic, associated with increased entropy; these endothermic reactions show high level of randomness at the solid-solution interface following adsorption (Thakur *et al*., 2017). This is most probable by reason of structural changes, adjustments in the adsorbate and adsorbent, as adsorption proceeds. Partial de-solvation of metal ions and the release of ions from the kaolinite surface into the solution are responsible for the structural changes (Bhattacharyya and Sen Gupta, 2008).

2.13.6 Lead

Nenadović *et al*., (2015) reported that mechanically milling kaolinite, decreased the main particle size and modified the ordered crystalline structure which results in enhanced

Pb(II) ion adsorption potential. Their study showed that mechanochemical treatment of kaolinite boosted the adsorption of lead. Bhattacharyya and Sen Gupta, (2008) reported Pb(II)-clay interactions to be strongly exothermic, consequently, with increasing temperature the adsorption of Pb(II) on the clays decreased because the high supply of heat energy, boosted desorption. The report revealed that Pb (II) ions were held more strongly to raw kaolinite surface than the acid-treated kaolinite surface and a maximum adsorption of Pb(II) was recorded within 40 minutes on kaolinite, while equilibrium was reached after approximately 180 minutes (Bhattacharyya and Sen Gupta, 2008).

2.13.7 Nickel

Raw kaolinite was reported to have a lower adsorption capacity and percentage removal efficiency of Ni(II) compared to acid-activated kaolinite by reason of the increased amount of negative charges and metal-ion binding sites on the adsorbent, after acid activation (Chai *et al*., 2020). The adsorption of Ni(II) on kaolinite and its modified forms (TBA-kaolinite, ZrO-kaolinite and acid activated kaolinite) in aqueous medium, has been reported by Bhattacharyya and Sen Gupta, (2008) to be sensitive to alkalinity. An increase in alkalinity results in increased adsorption, albeit at pH 8.0 the experiment had to be stopped because of metal precipitation at this pH value.

In another study by Chai *et al*., (2020) an increase in temperature from 25 to 55 °C was noted to cause a steady reduction in Ni(II) adsorption and the adsorption process was exothermic and spontaneous, indicating that some amount of heat is generated during binding of metal ions on the surface of the adsorbent. A rise in pH, however, enhanced the adsorption capacity of raw and activated kaolinite for Ni(II), but at pH values ranging from 2.0-4.0, the adsorption of Ni(II) onto kaolinite was observed to be low (Chai *et al*., 2020).

2.13.8 Zinc

Arias and Sen (2009) reported that the amount of zinc ions adsorbed on acid-washed kaolin reduces with temperature and the quantity of adsorbent; conversely zinc ion adsorption was noticed to rise with initial metal ion concentration, the solution's pH and contact time. Also kinetic investigations revealed that the adsorption of Zn^{2+} on kaolin was a two-step process "a very rapid adsorption of zinc metal ion to the external surface is

followed by possible slow decreasing intra-particle diffusion in the interior of the adsorbent which has also been confirmed by intra-particle diffusion model'' (Arias and Sen 2009). In another study by Meroufel *et al*., (2013), it was noted that the adsorption of Zn(II) onto natural kaolin increased with a rise in temperature and pH, and that the adsorption process was endothermic and spontaneous in nature.

Table 2.6: Summary of heavy metals, potential adsorbents and optimal experimental parameters

Adsorbent	Adsorbate (metals)	Optimum recovery pH	Conc. of adsorbate (mg/L)	Conc. of adsorbent (g)	Temp °C	Time for maximum adsorption (min)	Adsorption capacity (mg/g)	Ref
Natural Kaolinite	Zn(II)	6.1	10-120	0.2	25	12	12.23	Meroufel *et al*., 2013
	Cu(II)	7.0	100	0.1	25	60	40.01;	Chai *et al*., 2020
	Ni(II)	7.0	100	0.1	25	60	37.64	Chai *et al*., 2020
	As(V)	5.0	10-200	40g/L	25	-	0.86	Mohapatra *et al., 2007*
	Cd(II)	7.0	10-150	0.5	30	30		Jiang *et al*., 2010
	Pb(II)	7.0			30	30		
	Cu(II)	7.0			30	30		
	Ni(II)	7.0			30	30		
	Cd(II)	8	50	2	29.9	40	9.9	
	Co(II)	8	50	2	29.9	40	11.2	

	Cu(II)	6	50	2	29.9	40	9.2	Bhattacharyya and Gupta, 2009(a)
	Pb(II)	6	50	2	29.9	40	11.1	
	Ni(II)	8	50	2	29.9	40	10.4	
Acid Activated kaolinite	Cu(II)	7.0	100	0.1	25	60	41.11	Chai *et al*., 2020
	Ni(II)	7.0	100	0.1	25	60	39.62	Chai *et al*., 2020
	Cd(II)	8	50	2	29.9	40	11.4	Bhattacharyya and Gupta, 2009(a)
	Co(II)	8	50	2	29.9	40	12.1	
	Cu(II)	6	50	2	29.9	40	10.1	
	Pb(II)	6	50	2	29.9	40	12.1	
	Ni(II)	8	50	2	29.9	40	11.9	
TBA Kaolinite	Cu(II)	5.7	50	2	29.9	180	3.2	Bhattacharyya and Gupta, 2006
	Fe(III)	3.0	50	2	29.9	40	3.3	Bhattacharyya and Gupta, 2009(b)
	Co(II)	5.8	50	2	29.9	40	2.5	
	Ni(II)	5.7	50	2	29.9	40	2.3	

ZnO Kaolinite	Cu(II)	5.7	50	2	29.9	180	3.0	Bhattacharyya and Gupta, 2006
	Fe(III)	3.0	50	2	29.9	40	4.3	Bhattacharyya and Gupta, 2008
	Co(II)	5.8	50	2	29.9	40	3.5	
	Ni(II)	5.7	50	2	29.9	40	3.4	

2.14 Factors Affecting Heavy Metal Adsorption

2.14.1 pH

The pH condition is an important variable for the adsorption of heavy metals because it can affect speciation of the adsorbate, specification and ionization degree of the adsorbate and adsorbent surface charge (Imamoglu and Tekir, 2008). The pH of an aqueous solution also regulates cationic adsorption onto clay surfaces as a rise in pH changes the clay surface properties and the metal species (Mnasri-Ghnimi and Frini-Srasra, 2019).

Alkan *et al*., (2008) assert due to the protonation and deprotonation of acidic and basic groups of adsorbents, the adsorption behaviour for metal ions is affected by the pH value, which in turn influences the formation of metal hydroxides, the interaction between sorbents and metal ions and the surface structure of sorbents.

2.14.2 Contact Time

Contact time is a parameter which greatly influences the adsorption process as it is a performance-governing factor. It can affect the adsorption kinetics and the economic efficiency of the adsorption process. Bhattacharyya and Gupta, (2009) illustrated that the adsorption of metal ion on kaolinite was very fast initially, and maximum uptake of the metal ions was achieved within 40 minutes; this was attributed to the large number of adsorption sites at the beginning of adsorption.

The acid-activated kaolinite, however, showed much higher initial uptake, which may have been due to the high surface area and cation exchange capacity. Also discrepancies in equilibrium time for adsorption of some heavy metals could be associated to differences in composition and the exact nature of the clay, environmental conditions and other factors (Bhattacharyya and Gupta, 2008).

2.14.3 Adsorbent Dose

The adsorbent dosage is crucial to the adsorption process because it influences the capacity of an adsorbent for a given initial concentration of the adsorbate. Generally, an increase in the amount of kaolin leads to a rise in the extent of adsorption of a solute

because of increased active exchangeable adsorption sites (Mnasri-Ghnimi and Frini-Srasra, 2019), although, a much higher concentration of kaolin can reduce the overall solute adsorption per unit weight of an adsorbent by reason of interference created through the interaction of the active sites of the adsorbent (Iftekhar *et al*., 2018). The optimum adsorbent dose is mainly linked to the availability of active sites which are interconnected to the presence of surface functional groups (Mustapha *et al*., 2020).

2.14.4 Initial Concentration of Adsorbate

The initial concentration of adsorbate is a significant parameter as it determines the capacity of an adsorbent for a specific initial concentration of the adsorbate. Meroufel *et al*., (2013) assert that increasing Zn(II) concentration expedited the diffusion of Zn^{2+} from solution to the adsorbent surface by reason of a rise in the driving force of concentration gradient. Bhattacharyya and Gupta (2009) revealed that increasing the initial metal concentration led to a gradual rise in the equilibrium amount of metal ions adsorbed per unit mass of clay q_e. This was exemplified by increasing the Co(II) ions from 10mg to 50mg; it led to a rise in q_e from 2.0 mg/g to 5.3mg/g for kaolinite and 2.4 mg/g to 6.3 mg/g for acid-activated kaolinite.

2.14.5 Temperature

Temperature is an important parameter used in conjunction with thermodynamic investigations to ascertain the nature of the adsorption process, whether it is exothermic or endothermic (Chai *et al*., 2020). Alkan *et al*., (2008) revealed that temperature affects the rate and extent of adsorption as well as the adsorbate-adsorbent interactions. Also increased adsorption at high temperature indicates an increase in active surface sites available for adsorption.

In addition, increase temperature can modify pore sizes making them wider, leading to some activation of the surface. According to Mladenović *et al*., (2019) an increase in adsorption capacity by reason of increased temperature can be ascribed to a rise in the mobility of metal cations, however a steep drop in adsorption above 313K suggests the beginning of the desorption process.

2.14.6 Surface Area

Surface area refers to how much exposed area a solid has and is associated with the particle size; smaller particle size shows a greater surface area (Baeza *et al*., 1995). Surface area is significant in chemical kinetics and in adsorption studies because increasing the surface area typically enhances the rate of a chemical reaction and provides more active sites for sorption, resulting in its increased capacity (Mustapha *et al*., 2019).

Meroufel *et al*., (2013) reported that the surface of kaolin becomes negatively charged in alkaline medium (pH > 7) and electrostatic repulsion reduces with increasing pH, due to decrease of positive charge density on the sorption edges, hence, adsorption of metal is increased. On the other hand at low pH, the surface sites experienced an increase in positive charge density; as a result electrostatic repulsion occurs on the surface between metal ions and positively-charged edged groups, leading to low adsorption (Jiang *et al*., 2010; Meroufel *et al*., 2013).

2.14.7 Interfering Substances

Ionic competition between the different ions in a solution can obstruct or boost the adsorption process, based on the affinity of the interfering ion with the adsorbent (Souza and Silva, 2019). According to Chai *et al*. (2020) as the competition between cations and H^+ for available adsorption sites increases, the adsorption capacity of cations decreases because the active sites (silanol and aluminol groups) are highly protonated and insufficient for binding.

At higher pH, it was observed that there was less competition between cations and H^+ for active sites because at a higher pH, the active sites on the adsorbent became more negatively charged increasing the adsorption capacity of cations through electrostatic force of attraction (Chai *et al*., 2020). In another study done by Souza and Silva, (2019) the effect of interfering ions in cobalt solution on the adsorption capacity and cobalt final concentration was investigated. It was observed that the adsorption behaviour of cobalt and chromium followed the same adsorption pattern with a rise in chromium concentration indicating chromium is a competitive ion, however, a rise in iron concentration led to lower

cobalt concentration suggesting that the presence of iron may have enhanced cobalt adsorption (Souza and Silva, 2019).

2.15 Summary

This chapter presented a concise review of the literature related to clays, kaolin genesis, kaolin mineralogy and chemistry, and heavy metal adsorption by kaolinite. Other methods for the removal of heavy metals from water were discussed, however this research will implement batch adsorption for the removal of cadmium (II) ions from aqueous solution using natural Zebediela kaolin.

CHAPTER THREE

MATERIALS AND METHOD

3.1 Preamble

The previous chapter examined the relevant literature related to kaolins and adsorption. Factors which affect heavy metal adsorption and the different adsorption isotherms and kinetic models were also detailed. This chapter describes the methods and procedures employed to achieve the objectives of this research. It covers the sampling techniques, adsorbent and adsorbate preparation, analytical methods, batch adsorption procedure and data analysis. Figure 3.1 depicts a graphical layout of this chapter.

3.2 Desktop Study

Relevant information from books, peer reviewed journal articles, conference proceedings, government publications, online articles and encyclopaedia was used to obtain an understanding of existing knowledge and finding the knowledge gap on kaolins in Zebediela.

3.3 Reconnaissance Survey

Preliminary field visits were done to obtain a general overview of the stratigraphical, lithological, and textural variations of the kaolin deposits. This stage was to facilitate decision-making regarding the specific methods and techniques, which were employed during the field work.

3.4 Field Investigation

Primary field investigation involved recognition of kaolin deposit, mineralogical composition, and colour assessment. Kaolins are identified by their white/off-white colour and a sticky feeling on the tongue (Christidis, 2013), thus, colour and feel were used as a primary consideration in selecting kaolin samples for laboratory assessment (Bloodworth *et al*., 1993). The geographic location and elevation of the kaolin deposits were determined by a Global Positioning System. A measuring tape was used to gauge the distance between sampling points and the thickness of the outcrops. At each sampling site, observations and descriptions of the physical characteristics and lithologies of the outcrop were documented.

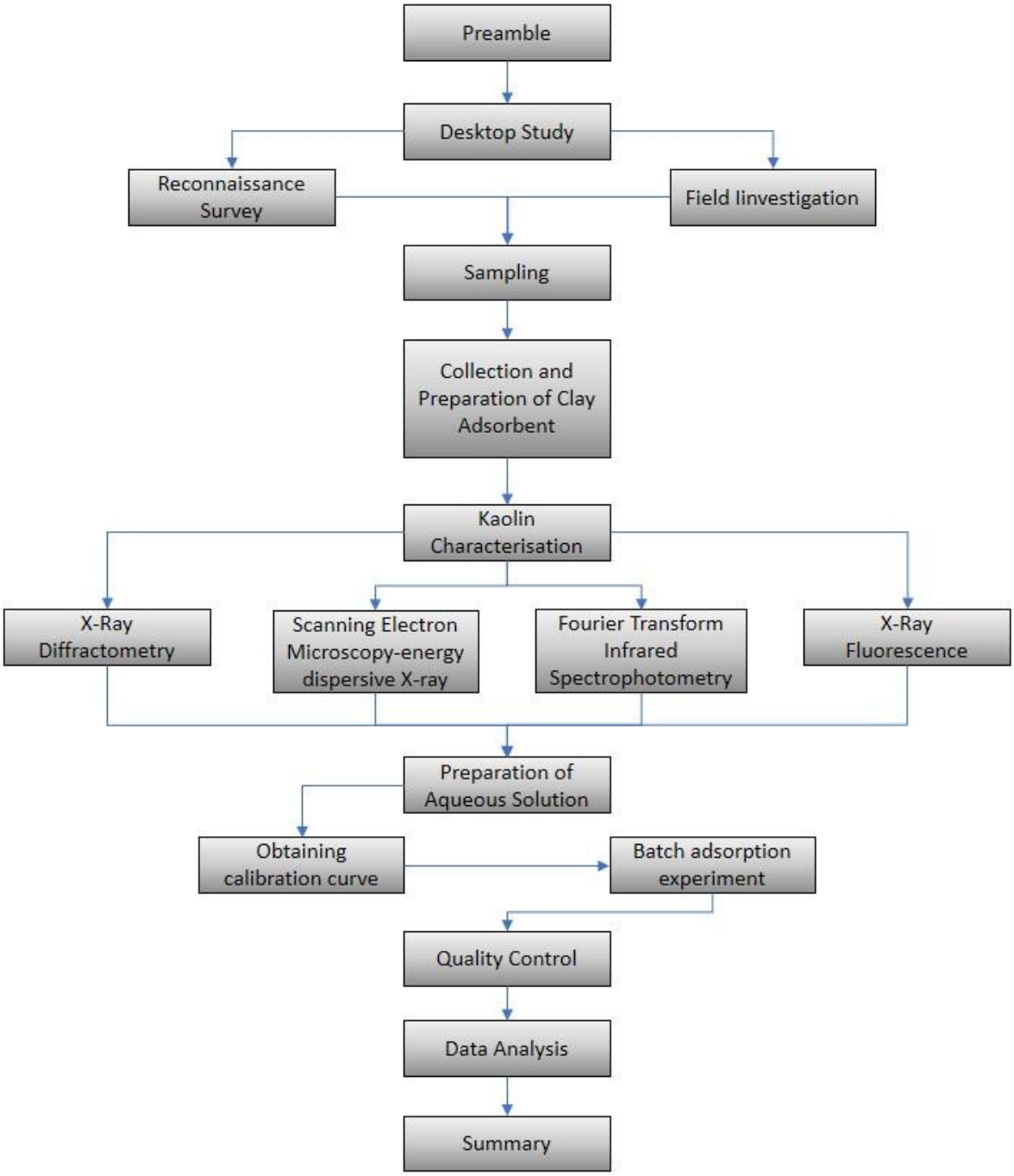

Figure 3.1: Layout of chapter three

3.5 Sampling

Prior to sampling, the outcrop was cleaned to gain access to fresh samples. The outcrop was dug back to at least 60cm to prevent sample contamination from external leached materials and weathered products. The sampling method was judgmental based on the physical characteristics of the kaolin outcrop (Bloodworth *et al.,* 1993; Tan, 1996). The sample was collected using a geologic hammer, chisel and a hand trowel after which it was stored in a labelled airtight field bag and transported to the laboratory for further analyses (van Reeuwijk, 2002).

3.6 Collection and Preparation of Clay Adsorbent

The raw kaolin was obtained from one of the excavation pits within the Zebediela clay deposit, hosted within rocks ascribed to the Transvaal Supergroup (Figure 3.2). The lithostratigraphy of the area comprised rocks of the Wolkberg Group, followed by an unconformity-bound Black Reef formation (BRF), which in turn was overlain by the Chuniespoort Group (Raphalalani *et al.,* 2019). The raw kaolin was crushed and washed thoroughly with distilled water with occasional stirring to remove the soluble inorganic salts, suspended insoluble impurities and other adhering materials attached to its surface (Omar and Al-Itawi 2007). The clay sample was then dried in an oven at 105 ºC overnight, pulverized, sieved through 150 µm mesh sieve and stored in desiccator for further analyses.

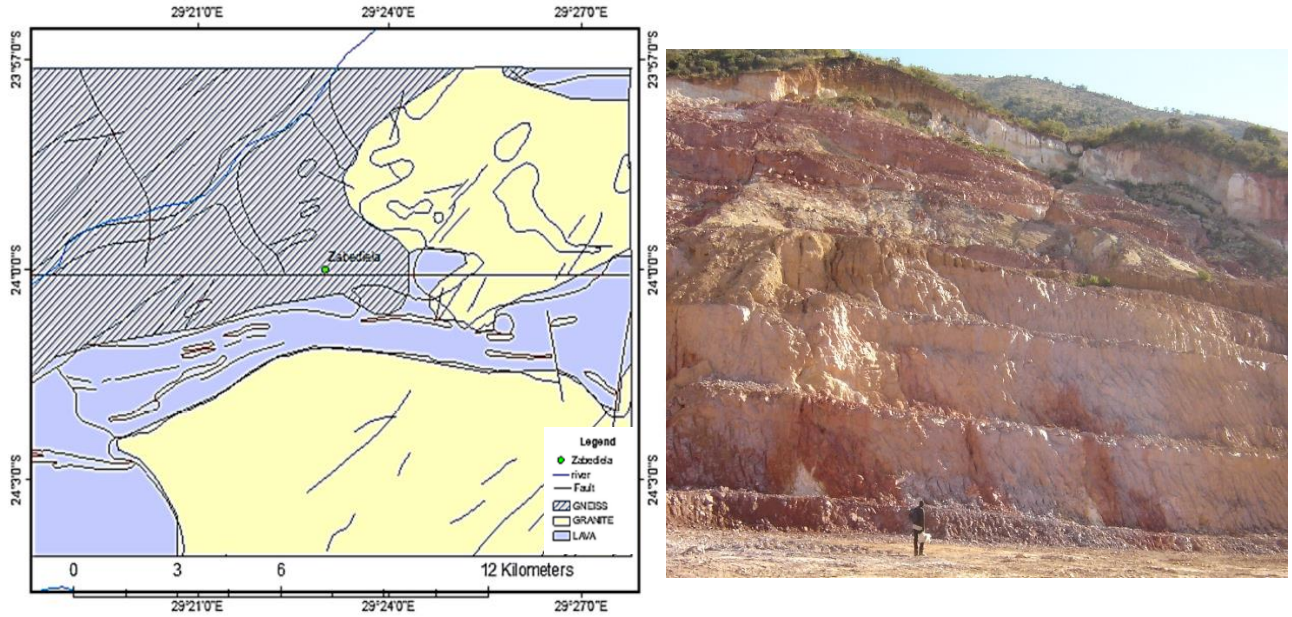

Figure 3.2: Geologic setting of Zebediela kaolin and overview of excavation Pit 1.

3.7 Kaolin Characterisation

The characterization of the raw kaolin was aimed at establishing its mineral phase identification and a description of the micromorphology and geochemistry. In order to achieve this, the following analytical techniques were employed - X-ray diffractometry, Fourier transform infrared spectrophotometry (FTIR), scanning electron microscope equipped with energy dispersive X-ray micro analysis (SEM-EDX) and X-ray fluorescence (XRF) spectroscopy.

3.7.1 X-Ray Diffractometry

X-ray diffractometry (XRD) was used for mineral content identification. Prior to the analysis, the samples were gently ground with the aid of mortar and pestle into powdery form. The ground samples were loaded in sample holders and mounted on a BRUKER D8 Advance diffractometer equipped with a LYNXEYE detector and a Ni-filter (Figure 3.3). Powder mounts were scanned from 2 to 70° 2θ CuK (λ=1.54060) radiation at a speed of 0.05° 2θ steps size per second and generator settings of 40 kV and 40 mA. Overnight glycolation (<24 h) test was performed to distinguish smectites from vermiculite (Yongue-Fouateu *et al.,* 2016).

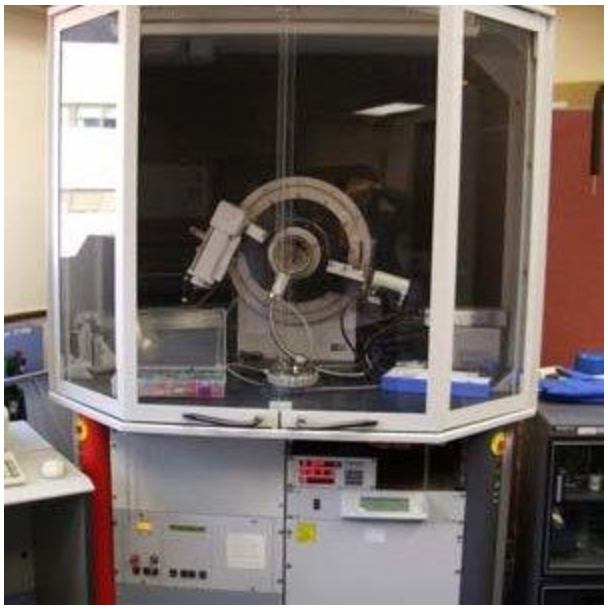

Figure 3.3: Bruker D8 Advance X-ray Diffractometer for mineral identification

Phase identification was based on BRUKER DIFFRAC Plus-EVA evaluation program. Phase concentrations were determined as semi quantitative estimates (with accuracy ± 5%) using Reference Intensity Ratio (RIR) method and relative peak heights/areas proportions (Ekosse *et al.,* 2017).

3.7.2 Fourier Transform Infrared Spectrophotometry

Fourier transform infrared (FTIR) spectrophotometry is an alternative method for determining qualitative/quantitative mineralogy. The mineralogy can be inferred from the FTIR spectrum, given that minerals exhibit most of their fundamental molecular vibration modes in the mid-infrared (400 to 4000 cm^{-1}). The absorbance/transmittance bands of each component in the mixture are proportional to the pure mineral spectrum (Njoya *et al.,* 2006).

The infrared spectra for the raw kaolin were acquired using a Perkin Elmer System 2000 FTIR spectrophotometer at a resolution of 4 cm^{-1} (Figure 3.4). About 5 g of dried powdered sample was homogenized in spectrophotometric grade KBr in an agate mortar and pressed at 3 mm pellets with a hand press. In order not to distort the crystallinity of kaolinite in the sample, the mixing was set to 3 min. allowing for minimal grinding as

suggested by Tan (1996). Peaks were reported based on percentage transmittance to given wavelengths.

Figure 3.4: A Perkin Elmer Spectrum 2000 instrument

3.7.3 Scanning Electron Microscopy-Energy Dispersive X-ray

Morphological analysis was performed using a JEOL JSM – 5800LV scanning electron microscope equipped with energy dispersive X-ray micro analysis (SEM-EDX) (Figure 3.5). The sample for morphological studies were mounted on Al stumps using conductive glue. Excess particulate matter on the Al stumps were eliminated through vacuum spraying in order to minimize interference with the electrode during imaging. The Al stumps were coated with Au and viewed from an analytical scanning electron microscope. Particle images were obtained with the aid of a secondary electron detector.

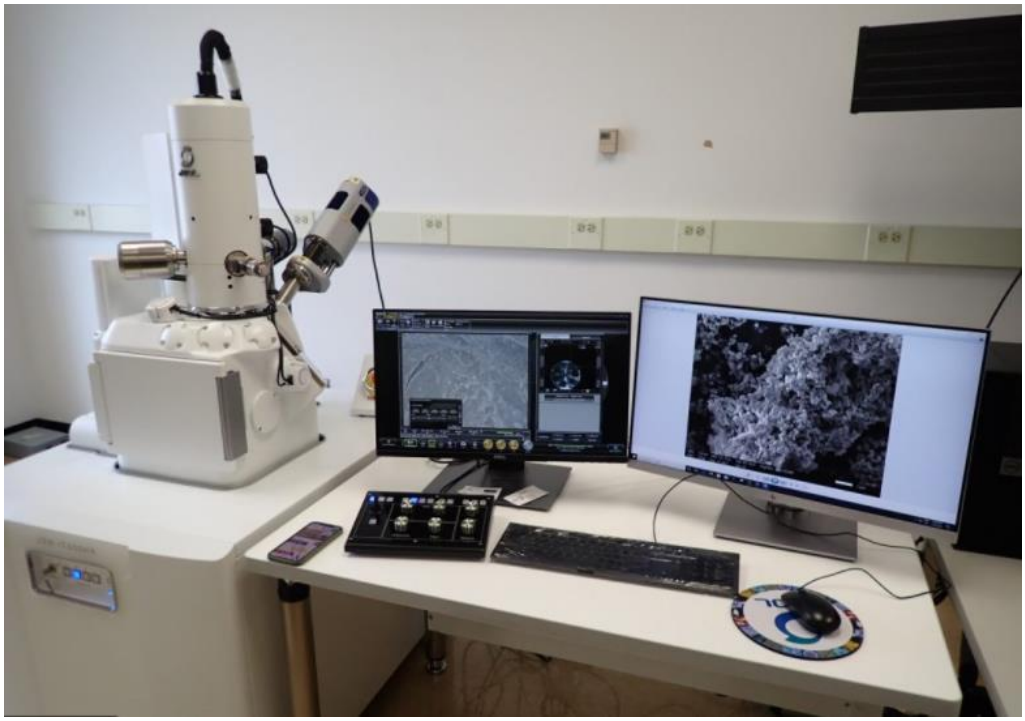

Figure 3.5: Scanning electron microscope for morphological characterization

3.7.4 X-ray Fluorescence

The chemical composition of the bulk sample was determined by X-ray fluorescence spectrometry using a PANalytical Axios WDXRF spectrometer equipped with a 4 kW Rh tube in accordance with the method described by Ekosse *et al.,* (2017) (Figure 3.6). The milled sample with grain size of < 75 µm was heated at 1000 °C for 3 hours to oxidise Fe^{2+} and S and to determine the loss on ignition (LOI). One gram of heated sample and nine gram of flux, consisting of 34% $LiBO_2$ and 66% $Li_2B_4O_7$ were fused at 1050 °C to form stable glass disks. The sample was analysed thrice, and the mean recorded. For quality control, an in-house amphibolite reference material (12/76) was used to ensure accuracy of the data generated.

Figure 3.6: PANalytical Axios WDXRF spectrometer for elemental characterization

3.8 Preparation of Aqueous Solution

An experimental aqueous cadmium (II) stock solution of concentration 1000mg/L was prepared by dissolving 0.2744g of $Cd(NO_3)_2.4H_2O$ salt in deionized water. Other lower concentrations of metal ions (0.5 mg/L 1 mg/L, 1.5 mg/L, and 2 mg/L) were prepared by serial dilution of the stock solution (Ogbu *et al*., 2019). NaOH and/or HCl were used to adjust the pH of the solution.

3.9 Obtaining a Calibration Curve

Cadmium solutions of the following concentrations - 0.5 ppm, 1 ppm, 1.5 ppm, and 2 ppm - were prepared from the stock solution and the absorbance obtained was used to derive a calibration curve (Jiang *et al*., 2010). The solutions were analysed using the atomic adsorption spectrometer (AAS PerkinElmer PinAAcle 900T model) (Figure 3.7). The concentration versus absorbance was plotted on excel to obtain the calibration curve, the equation of the line and the R^2 (coefficient of determination) value. The equation of

the line was used with the batch experiments results to obtain the equilibrium concentration C_e.

$$y = mx - c \qquad \text{Equation 3.1}$$

$$x = \frac{y+c}{m} \qquad \text{Equation 3.2}$$

where x is equilibrium concentration C_e, y is absorbance and c is constant

3.10 Batch Adsorption Experiments

Batch adsorption was done to ascertain the effect of pH, adsorbent dose, contact time and initial metal ion concentration. The experiment was conducted by mixing 0.5 g of kaolinite clay with 50ml of the cadmium (II) ion solution in a clean centrifuge tube at room temperature (25 ºC). The effect of pH was investigated by adding drops of HCl and/or NaOH (Zhang *et al*., 2017). The effect of the adsorbent dose, contact time and initial metal concentration were also studied. During the experiments to assess the effect of any specific parameter, the parameters were varied, while the others were kept constant (Ogbu *et al*., 2019). For each sorption at the end of the agitation time, the mixed solution was filtered and the AAS (Figure 3.7) was used to determine the residual metal ion concentration in the filtrate (DamilolaKayode *et al*., 2019). The percentage removal of metal ions and the adsorption capacity of the adsorbent for metal ions, were calculated as follows (Mustapha *et al*., 2019):

$$\%\, removal = \frac{C_0 - C_e}{C_0} \times 100 \qquad \text{Equation 3.3}$$

$$q_e(mg/g) = v\frac{(C_0 - C_e)}{m} \qquad \text{Equation 3.4}$$

where C_0 (mg/L) is the initial metal ion concentration in the solution, C_e is the metal ion concentration remaining in solution at equilibrium, $q_e(mg/g)$ is the adsorption capacity, v (L) is the volume of solution used in adsorption and m (g) is the mass of the adsorbent.

Table 3.1: Adsorption parameters and levels investigated.

Parameter	**Levels investigated**
Effect of pH	3-10
Effect of dosage	0.25 -1.5 g
Effect of contact time	20-120 mins
Effect of concentration	0.5-2.0 mg/L

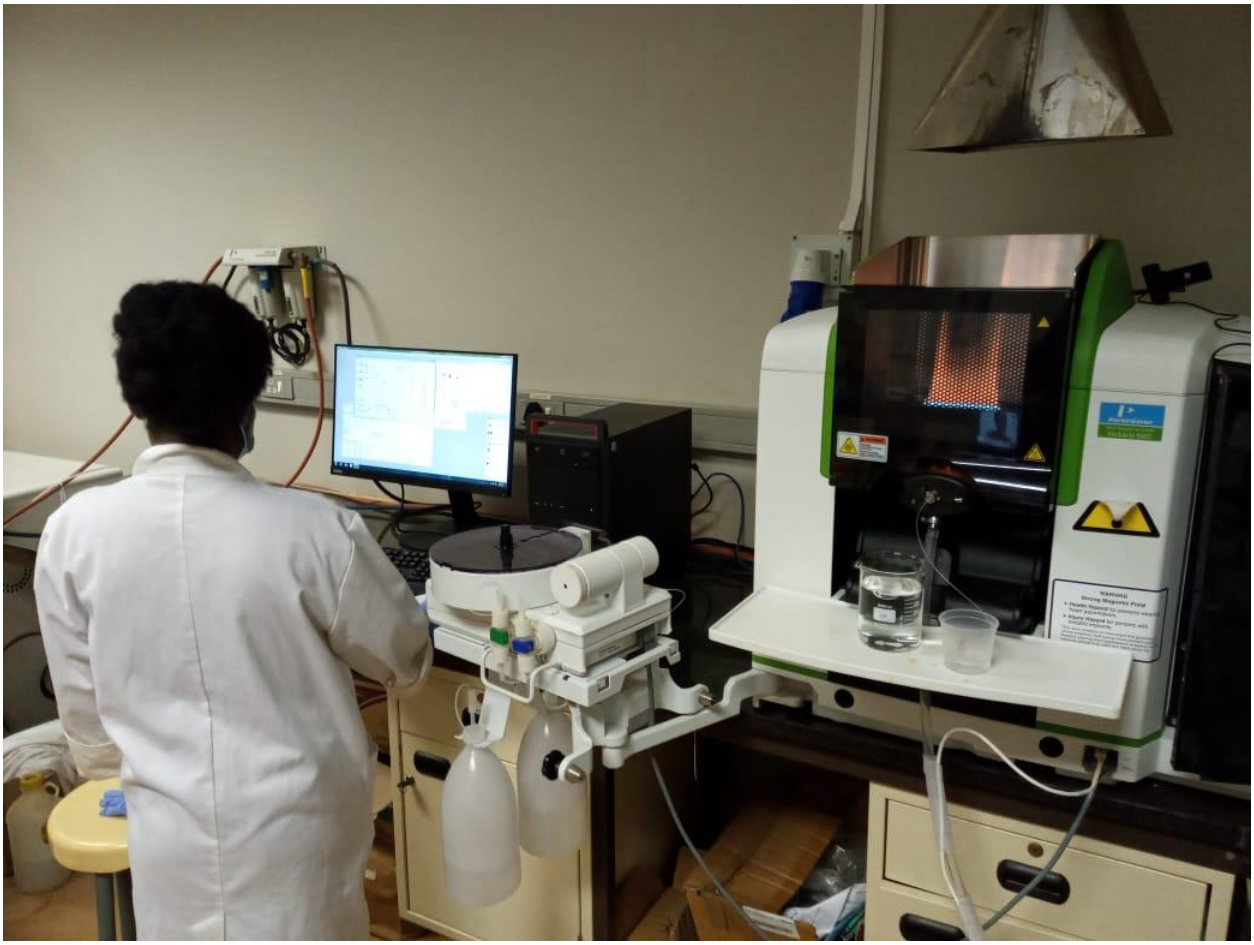

Figure 3.7: Adsorption experiments using AAS machine

3.11 Quality Control

- All glasswares and centrifuge tubes were properly washed and rinsed before usage with deionized water to avoid contamination,
- Deionized water was used as the blank to wash the tube of the AAS machine after each experiment and
- An average of two adsorption tests was taken for each experimental point.

3.12 Data Analysis

This stage involved the analysis of results generated from the laboratory experiments involving the adsorption of Cd (II) ions on the kaolin sample. Isotherm models, kinetic

models, and adsorption optimisation parameters were plotted using Microsoft Excel and OriginLab software.

3.13 Summary

This chapter examines the mineralogical, chemical and morphological characterisation of the Zebediela kaolin. The procedure for batch adsorption experiments and the analysis of experimental data were also reported. The next chapter will discuss inferences drawn from the data obtained.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Preamble

This chapter presents and discusses inferences based on data obtained from Zebediela kaolin characterisation, batch adsorption experiment, isotherm and kinetic models.

4.2 Discussion from Kaolin Characterization

4.2.1 Mineralogical Characterisation

4.2.1.1 Mineral Phase Identification

Results for the mineralogical analysis of bulk and < 2 um fractions are summarized in Table 4.1 and Figure 4.1. The characteristic mineral assemblage comprised of kaolinite + quartz as major phase in all samples, whereas mica (illite/muscovite) + k-feldspar (microcline) occurred in minor to trace quantities. First order kaolinite peaks were observed at either 7.12 Å or 7.07 Å, whereas, second order peaks occurred at either 3.55 Å or 3.56 Å (Figure 4.1). The peaks at 4.24 Å and 3.33 Å corresponded to the second and most intense peaks of quartz. Mica peaks observed at 9.93 Å, 9.90 Å and 9.88 Å were assigned to muscovite.

Table 4.1: Mineral constituents (%) in bulk and clay fractions of Zebediela Kaolin

ZEB1	**Hematite**	**Microcline**	**Plagioclase**	**Quartz**	**Kaolinite**	**Chlorite**	**Mica**
Bulk	-	2	-	21	75	-	1
< 2um	-	-	-	-	95	-	5

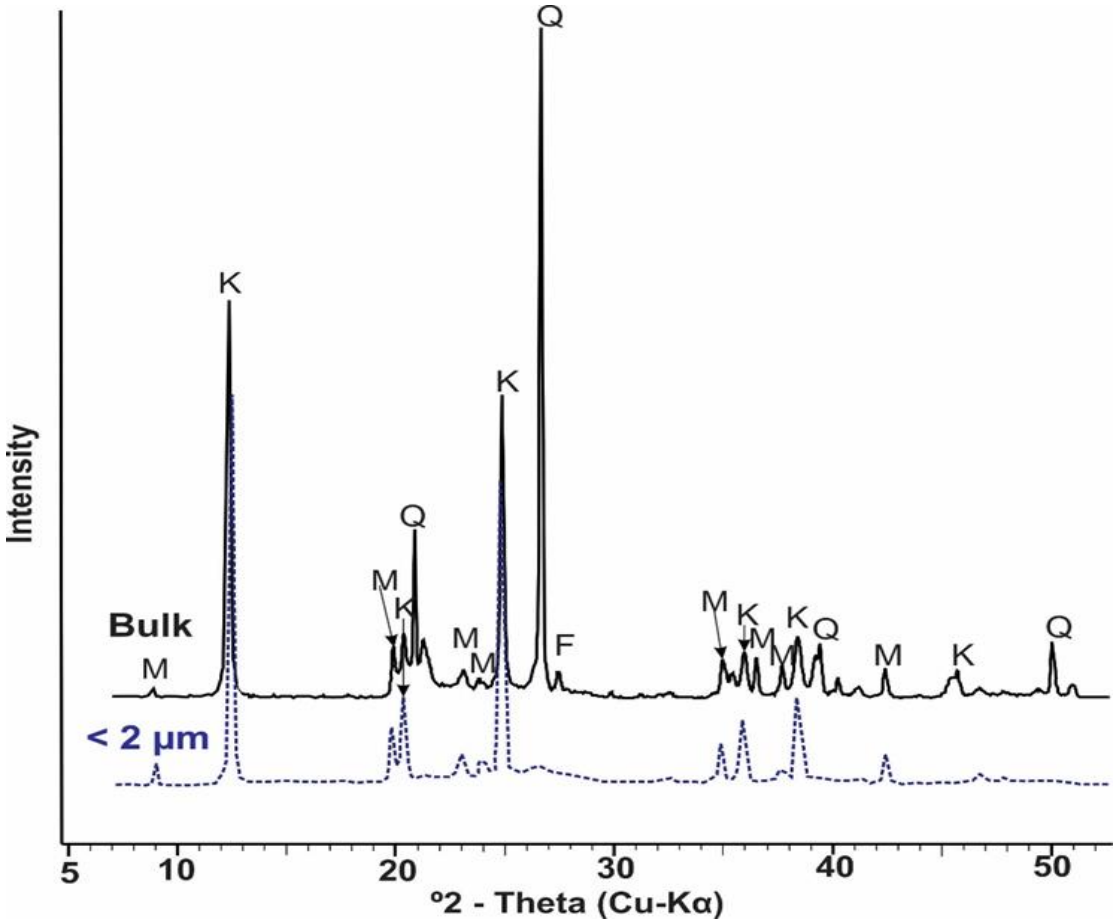

Figure 4.1: XRD pattern of bulk and clay fractions of Zebediela Kaolin: K-kaolinite; Q-quartz; M-mica; Mx-microcline.

4.2.1.2 Functional Group Characteristics

The infra-red (IR) spectra of representative bulk and clay fraction of the kaolin sample from Zebediela are presented in Figure 4.2. The observed bands were assigned as follows: OH stretching bands between 3619 cm^{-1} and 3690 cm^{-1} and Al---O-H deformation within the region 907 cm-1 to 910 cm^{-1} (Figure 4.2). A weak inflexion between the doublet 3619 cm^{-1} and 3690 cm-1 was equally observed. Bands associated with Si-O stretching occurred at, or close to, 1113 cm^{-1}, 1025 cm^{-1}, 998 cm^{-1}, 789 cm^{-1} and 682 cm^{-1} , whereas, Si-O deformation bands were between 402 cm^{-1} and 427 cm^{-1}. The transmittance bands between 522 cm^{-1} and 530 cm^{-1} were assigned to Fe-O, Fe2O3, and Al-O-Si deformation, while, vibration bands from 454 cm^{-1} to 463 cm^{-1} where ascribed to Si-O-Si deformation. Quartz interference peaks were assigned to 1023 cm^{-1}, 791 cm^{-1} and 683 cm^{-1} , whereas, the vibrations at 1023 cm^{-1} were assigned to muscovite.

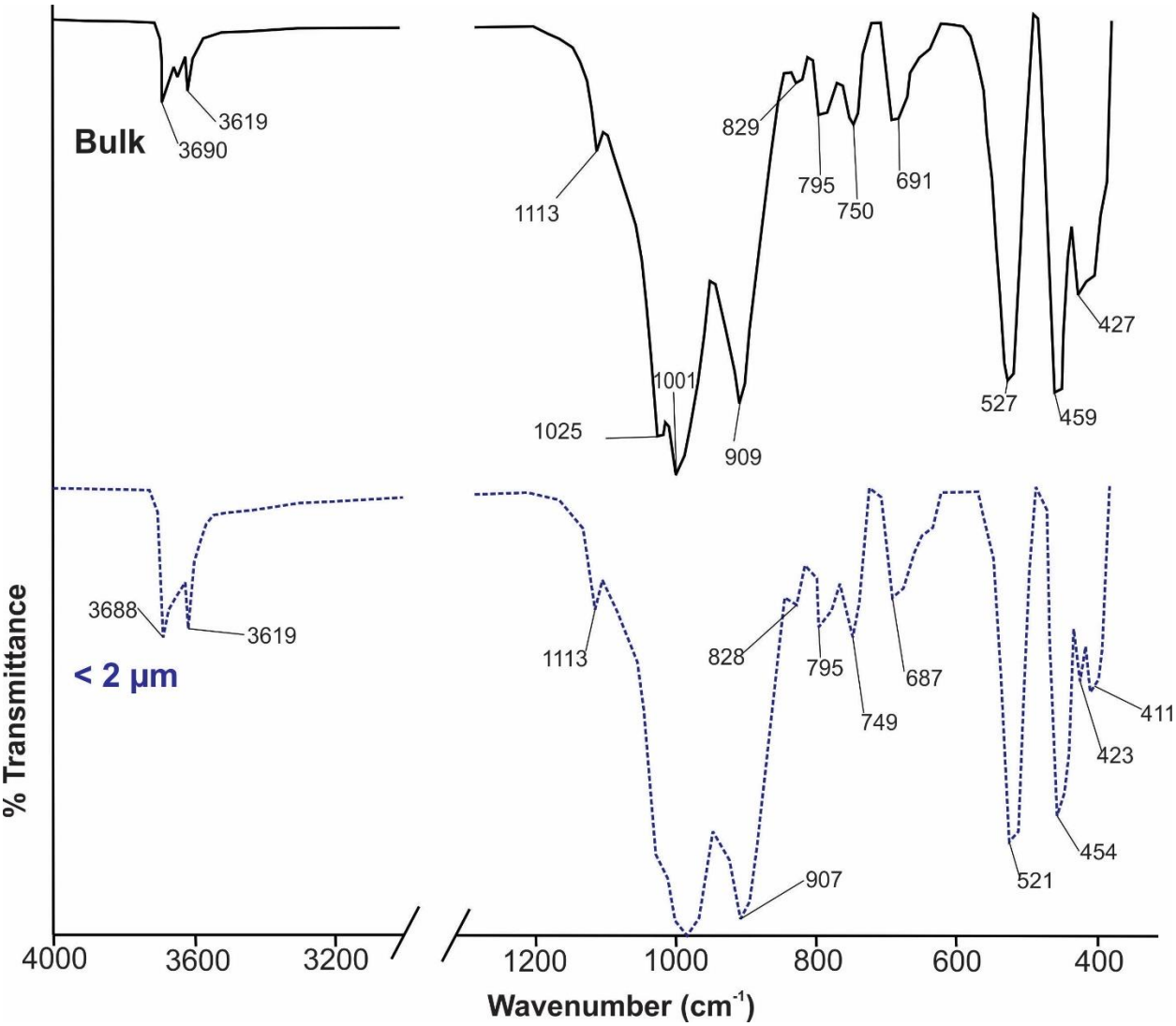

Figure 4.2: Infra-red spectra of bulk and clay fractions of Zebediela kaolin

4.2.1.3 Inferences from Mineralogical Characterisation

From the mineralogical analysis, a higher kaolinite content was observed in the clay fraction compared to the bulk fraction. The kaolinite content for the clay fraction is 95% while the kaolinite content of the bulk fraction is 75% (Table 4.1). The high kaolinite content in the bulk sample is suggestive of strong chemical weathering of the source rock (Raphalalani, 2017). In the bulk sample, which was used for the adsorption studies, kaolinite was the major mineral phase present while quartz, mica and microline occurred as minor mineral phases.

Commercial kaolins are generally considered monomineralic clays, although, this is not usually the case because some small amounts of other minerals are invariably present (Christidis, 2011; Bukalo *et al*., 2017). Kaolin deposits can be nearly pure kaolinite or may contain impurities that can affect the characteristics of the kaolin (Madi *et al*., 2013). In this study the sample used contained 75% kaolinite, 21% quartz, 2% microcline and 1% mica. These other mineral phases (quartz, microcline and mica) constitute impurities which depends on the genesis of the minerals (Balan *et al*., 1999).

The nature and the quantity of these minerals have a significant effect on the abrasiveness, colour, and viscosity of the kaolin, which may have posed some deleterious effect on the adsorption capacity of the kaolin for Cd (II) ions (Christidis, 2011). Furthermore, the impurities in the kaolin affects the particle size and the degree of disorder of the kaolin, consequently impacting on the adsorption characteristics of the kaolin (Balan *et al*., 1999). This suggests that the presence of impurities in the sample used contributed to the low adsorption capacity of the kaolin.

4.2.2 Morphological Characterisation

4.2.2.1 Kaolin Micromorphology

The morphologies of a representative sample from Zebediela depicted in the SEM photomicrographs were indicative of kaolinite. The sample revealed well-developed kaolinite books and stacks with relatively porous aggregates (Figure 4.3). The observed morphological characteristics are consistent with the mineralogy of the sample as suggested by both XRD and FTIR data presented in the previous sections.

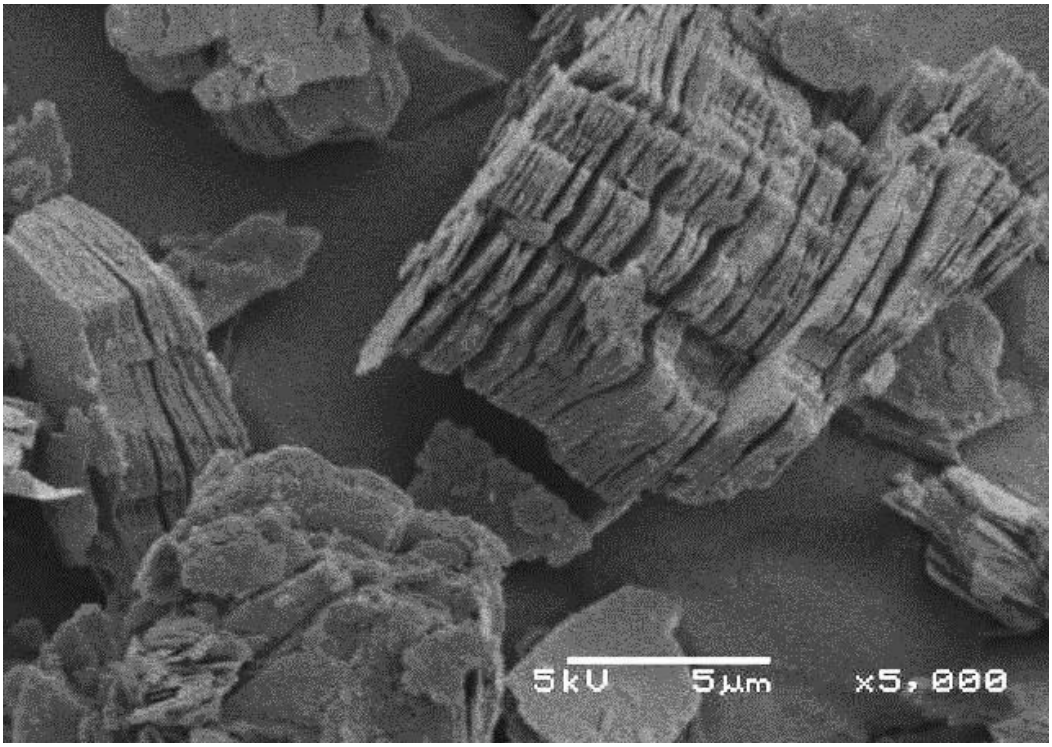

Figure 4.3: SEM photomicrograph of representative sample from Zebediela Kaolin depicting kaolinite books and stacks.

4.2.2.2 Inferences from Morphological Characterisation

The adsorptive properties of clays are enhanced by their complex porous structure and small particles sizes which boost their chemical and physical interaction with dissolved species (Uddin, 2017; Xue *et al*., 2020). Consequently, a kaolin sample with higher porosity will possess a better adsorptive capacity for Cd (II) ions, compared to a less porous kaolin sample (Frost and Kristof, 2004). Furthermore, high porosity in kaolin is very important for the adsorption of heavy metals because such a surface area that has attractive forces indicates that the bonding power between the kaolin and the heavy metal will be high (Uddin, 2017).

In this study, however, the kaolin had relatively porous aggregates; this may have provided a low bonding power between the Zebediela kaolin and Cd (II) ions, hence, the low adsorption capacity of the kaolin for Cd (II) ions. The alumina octahedral and the silica tetrahedral sheets of the kaolinite books were held together very strongly; the adsorption of Cd (II) ions may have occurred on the flat exposed planes of alumina and silica sheets, of the well-developed books and stacks of the sample (Kausar *et al*., 2018). Moreover,

due to hydrogen bonding, the structure of kaolinite is fixed, therefore, there is no expansion between layers and there is low cation exchange capacity (Kumari and Mohan 2021). This also contributed to the low adsorption capacity recorded in this study.

4.2.3 Chemical Characterisation

4.2.3.1 Major Oxide Content

The chemical composition of the Zebediela kaolin is presented in Table 4.2. The results reveal that the kaolin is predominantly made up of silica (SiO_2 = 58.39 wt %), alumina (Al_2O_3 = 28.04 wt %) and titanium dioxide (TiO_2 = 2.26 wt %), whereas, the lost ignition is 9.62 wt % of the remaining oxides (Fe_2O_3, MnO, CaO, Na_2O, K_2O, P_2O_5, Cr_2O_3) which are in trace amounts. High amounts of alumina and silica in the kaolin sample confirm that the kaolin consists mainly of aluminosilicate mineral(s), in this case, kaolinite.

Table 4.2: Chemical composition of Zebediela kaolin

Oxide (Weight %)	Zebediela	Theoretical kaolinite
SiO_2	58.39	46
TiO_2	2.26	
Al_2O_3	28.04	40
Fe_2O_3	0.32	
MnO	0.002	
MgO	0.06	
CaO	0.05	
Na_2O	0.07	
K_2O	0.43	
P_2O_5	0.028	
Cr_2O_3	0.052	
LOI	9.62	14
Total	99.32	

4.2.3.2 Inferences from Chemical Characterisation

Theoretically pure kaolin is made up of 46 wt % silicate, 40 wt % alumina and 14 wt % loss of ignition, however, it is rare to find kaolin that meets this standard due to impurities, such as lime (CaO), titanium (TiO_2), iron (Fe_2O_3) or potassium (K_2O) (Dewi *et al*., 2018). The Zebediela kaolin had a very high weight percentage of silicate (58.39 wt%) compared to the silica standard of pure kaolin (46 wt%). On the other hand, the weight percent of alumina for Zebediela kaolin was far less (28.04 wt%) than the alumina standard for pure kaolin (40 wt%). In addition, the loss of ignition of the pure kaolin (14 wt%) was more than the loss of ignition of the Zebediela kaolin (9.62 wt%).

The disparity between pure kaolin and the Zebediela kaolin is related to differences in the silicate and alumina concentration and the presence of impurities, such as titanium - dioxide (TiO_2), iron oxide (Fe_2O_3), manganese oxide (MnO), magnesium oxide (MgO), calcium oxide (CaO), sodium oxide (Na_2O), potassium oxide (K_2O), phosphorus pentoxide (P_2O_5), and chromium oxide (Cr_2O_3). According to Raphalalani (2017), the presence of these impurities, in minor amounts, can affect the colour and the application of the kaolin.

Additionally, the Ruxton ratio (R) which can be used to determine the weathering index is given below in Equation 4.1 (Ruxton, 1968). The R for the sample used in this study is 2.08. This suggests that the source rock had undergone intense chemical weathering which had resulted in the kaolinite being the dominant mineral phase present in the sample (Oni and Olatunji, 2017).

$$R = \frac{SiO_2}{Al_2O_3}$$

Equation 4.1

$$R = \frac{58.39}{28.04}$$

Equation 4.2

$$R = 2.08$$

Equation 4.3

4.2.3.2.1 Comparison between the chemical composition of Zebediela kaolin and other raw kaolins which have been used for adsorption of Cd (II) ions

Figure 4.4 shows the chemical composition of ZEBK and selected raw kaolin samples which have been used for adsorption of Cd(II) ions from aqueous solution. PK is pure/theoretical kaolin, ZEBK is Zebediela kaolin; KBK is Kribi Kaolin and UBUK represents Ubulu-Ukwu kaolin (Essomba *et al*., 2014; Adebowale *et al*., 2005). It can be noted that the concentration of silica is the highest for all three samples (ZEBK = 58.39 wt %, KBK = 49.52 wt % and UBUK = 65.14 wt %). The concentration of alumina is the second highest in all three samples (ZEBK = 28.04 wt %, KBK = 32.04 wt % and UBUK = 25.62 wt %). The silicate and alumina contents of the KBK sample were close to the pure kaolin sample and the percentage of impurity was low (2.65 wt %) compared to ZEBK and UBUK samples which had 3.272 wt % and 4.44 wt %, respectively.

The kaolins from Zebediela, Kribi and Ubulu-Ukwu do not meet the standard for pure kaolin due to differences in the silicate and alumina content and the presence of impurities such as - TiO_2, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, Cr_2O_3. In addition, differences in the origin and environment of formation of these kaolins may have affected their quality hence their behaviour and interaction with heavy metals in an aqueous media (Dill *et al*., 2015). These kaolins are not up to the standard for pure kaolin, although, they have been successfully used for the removal of Cd (II) from aqueous solution. The raw KBK kaolin was reported to be effective in the removal of Cd(II) ions from aqueous solution. This could be suggestive of its chemical composition being close to the pure kaolin standard and with less impurities, as the adsorption behaviour of the kaolin can be affected by impurities (Essomba *et al*., 2014; Raphalalani, 2017).

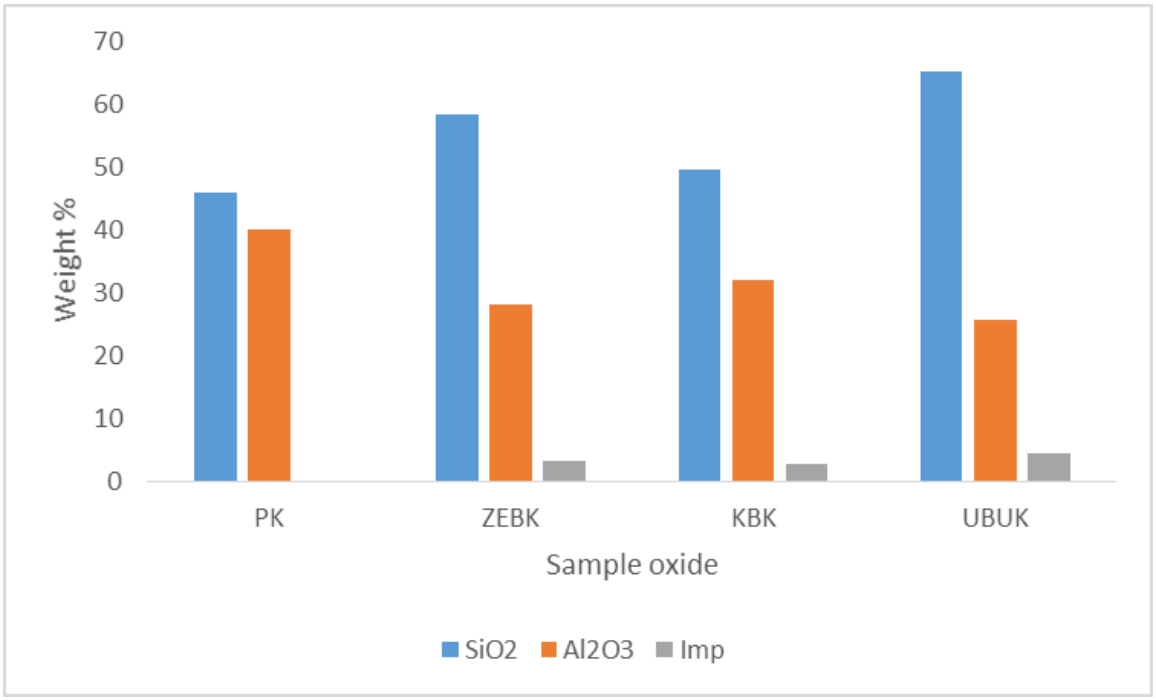

Figure 4.4: Comparison between chemical composition of pure kaolin and the chemical composition of other kaolins used in the adsorption of Cd(II) ions.

4.3 Inference from Batch Adsorption Studies

4.3.1 Effect of pH

Generally, the adsorption of Cd (II) increases with a rise in pH from 3-10 and the amount of Cd (II) adsorbed increases gradually with a decrease in acidity as seen in Figure 4.5. An increase in the solution pH from 3-10 led to a rise in percentage removal of Cd (II) from 57.16% to 89.52%. This finding is consistent with the work of Bhattacharyya and Gupta, (2008) where raising the pH of the solution from 1.0 to10.0, increased the adsorption of Cd (II) on kaolin from 4.3 to 29.5 %.

This behaviour suggests that the surface of the kaolinite clay contains many active sites which may become positively charged at low pH resulting in a rise in competition for available adsorption sites between H^+ and the metal ions (Jiang *et al*., 2010). As pH increases the adsorption of positively-charged metal cations through electrostatic force of attraction is boosted because of the surface-active sites becoming more negatively charged reducing competition (Jiang *et al*., 2010; El Ass, 2018). The optimum pH was

observed at 7 and it was used as the working pH for other adsorption experiments. Bhattacharyya and Gupta, 2009(a); Jiang *et al*. (2010) and Essomba *et al*., (2014) reported optimum adsorption, of pH for Cd (II) ions onto raw kaolin, between pH 7 and 8, however, beyond pH 8, there was precipitation of insoluble cadmium hydroxide from the solution.

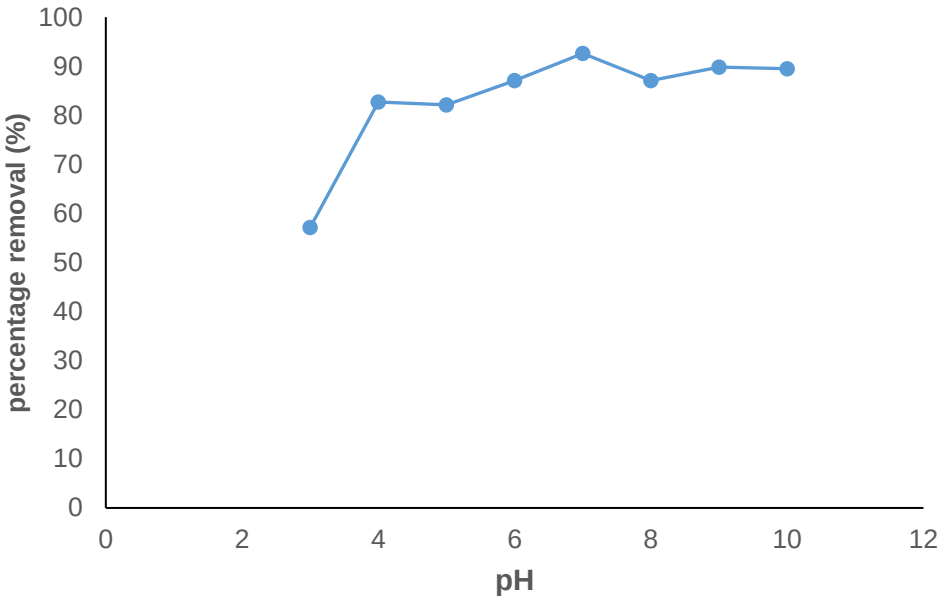

Figure 4.5: Effect of pH on the adsorption of Cd (II) ions on natural kaolinite at initial concentration of 0.5 mg/L, contact time of 60 mins, dosage of 0.5 g at 25 ºC

4.3.2 Effect of dosage

Figure 4.6 depicts the effect of kaolinite dosage (0.25 -1.5 g) on the adsorption of Cd (II) ions. An increase in adsorption was recorded from 0.25 - 1 g, followed by a decrease in adsorption from 1 - 1.5 g with a percentage removal of 80.28 - 94.76 % and 94.76 – 85.21%, respectively. The high adsorption observed between 0.25 - 1 g of the Zebediela kaolin was similar with previous findings of Mustapha *et al*., (2019) where an increase in Cd (II) adsorption was observed between 0.4 -1.4 g of kaolin. The high adsorption at increasing adsorbent dose, is indicative of a greater availability of more active binding sites and an increased surface area of the adsorbent (Mustapha *et al*., 2019).

At higher dosage (1 – 1.5 g), however, a decrease in adsorption was observed; this finding corroborates with the study of Essomba *et al*. (2014) where a decrease in Cd (II) uptake corresponded with increasing kaolin dose. This is suggestive of aggregation of the clay adsorbent, reducing the total surface area and the available active or exchangeable adsorption sites (Bhattacharyya and Gupta 2008). Consequently, the diffusion path length was increased due to the aggregation of the particles leading to decreased adsorption capacity of Cd (II) ions at higher dosage (Shukla *et al*., 2002; Chai *et al*., 2020).

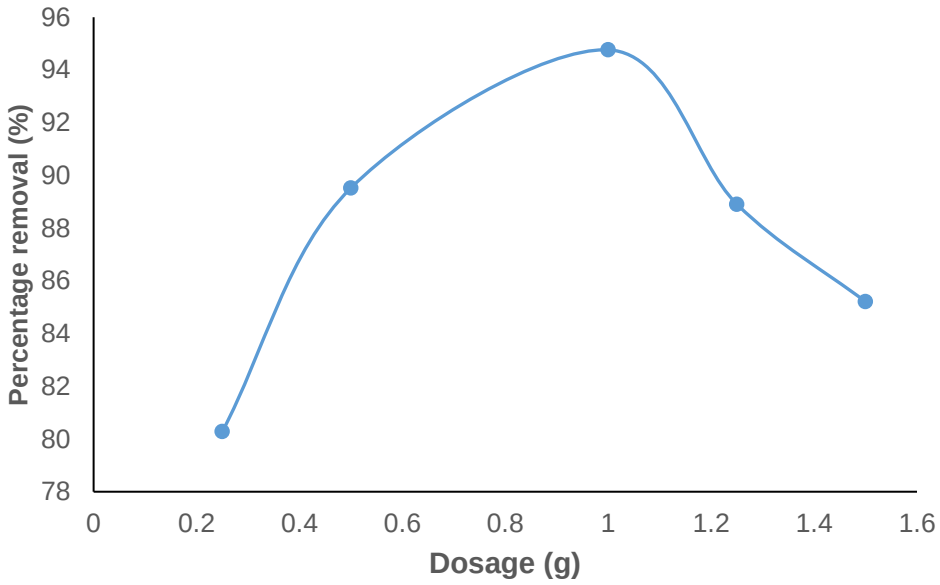

Figure 4.6: Effect of dosage on the adsorption of Cd(II) ions on natural kaolinite at initial concentration of 0.5 mg/L, contact time of 60 mins, pH of 7 at 25 ºC

4.3.3 Effect of Contact Time

The effect of time -between 20 – 120 minutes - was investigated, as illustrated in Figure 4.7. Adsorption was initially very fast and equilibrium was reached after 40 minutes into the adsorption process. This is consistent with the findings of Bhattacharyya and Gupta (2008) and Jiang *et al*. (2010) where the adsorption of Cd(II) by kaolin was fast initially and maximum uptake was attained within 40 and 30 minutes, respectively. The high adsorption rate in the early stage of the adsorption process is suggestive of the availability

of large amounts of active sites on the kaolinite surface resulting in rapid adsorption of Cd(II) ions (Bhattacharyya and Gupta, 2008; Jiang *et al*., 2010). This may be controlled by diffusion of the adsorbate molecules from the bulk solution to the surface of the adsorbent (Mustapha *et al*., 2019).

The slow adsorption rate in the later stages of the adsorption process may be attributed to a decrease in vacant active adsorption sites on the adsorbent and a slower rate of diffusion of Cd(II) ions into the interior of the kaolinite particles (Jiang *et al*; 2009, Kul and Caliskan, 2009). This observation is also consistent with the study of Essomba *et al*. (2014) where there was increased uptake of Cd(II) ions by kaolin with increasing contact time. It was reported that the adsorption was initially very fast but slowed down near equilibrium and this behaviour was attributed to repulsion between adsorbate present in solid and in the bulk phase (Essomba *et al*., 2014).

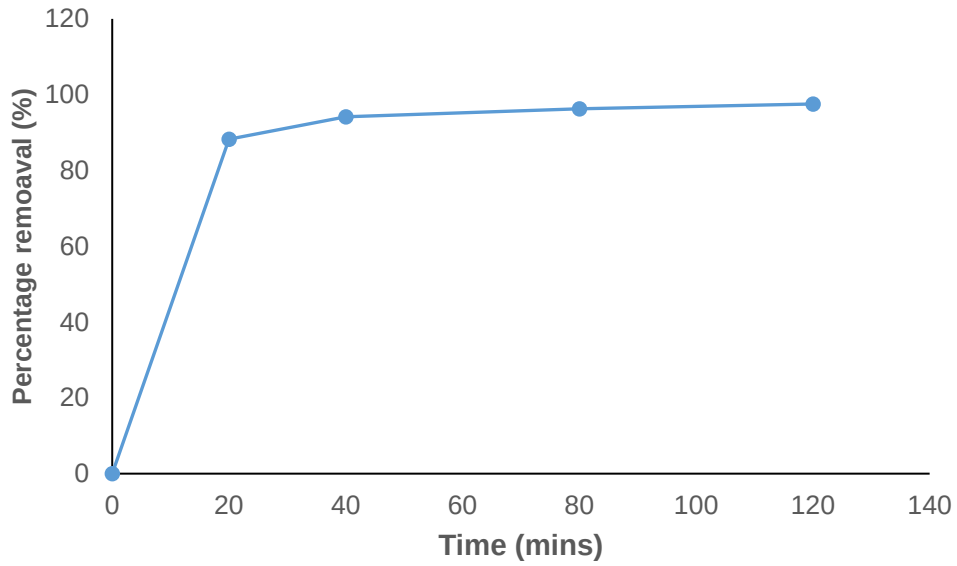

Figure 4.7: Effect of contact time on the adsorption of Cd(II) ions on natural kaolinite at initial concentration of 0.5 mg/L, 1 g of clay, pH of 7 at 25 ºC

4.3.4 Effect of initial concentration

Figure 4.8 presents the effect of initial metal ion concentration on the adsorption of Cd(II) ions on natural kaolinite. There was a rise in percentage removal of Cd(II) ions as initial

concentration increased. The high adsorption rate during the early stages of the process is suggestive of increased diffusion of Cd(II) ions from solution to the binding sites on the kaolinite surface due to a rise in the driving force of concentration gradient (Meroufel *et al*., 2013). After equilibrium was attained, progressing to the later stages of the adsorption process, a slow adsorption rate was observed which is suggestive of a decreased number of active binding sites on the kaolinite surface as more Cd(II) ions were absorbed (Chai *et al*., 2020). Also the slow rate of adsorption may be attributed to the surface of the kaolinite becoming completely saturated with Cd(II) ions at excess at the initial metal ion concentration.

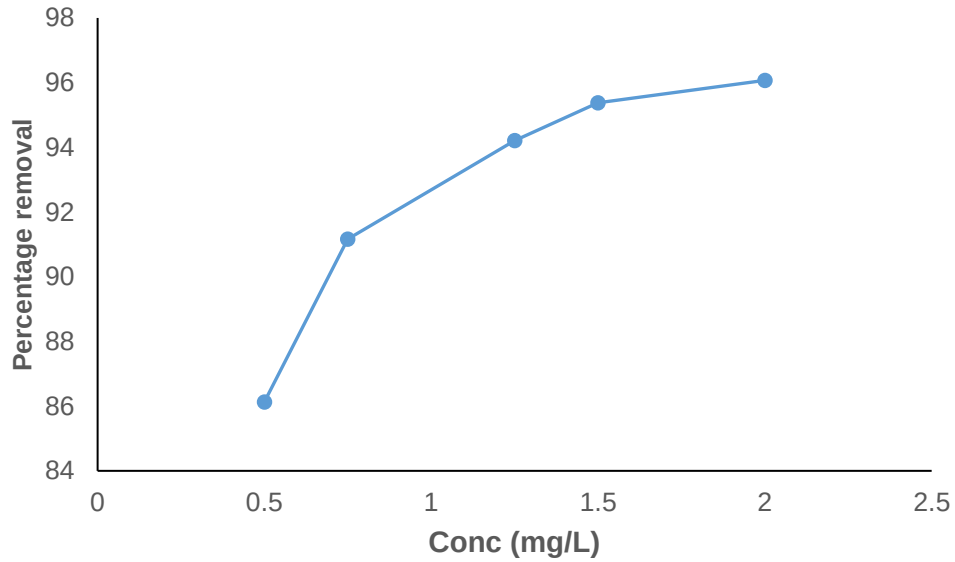

Figure 4.8: Effect of initial concentration on the adsorption of Cd(II) ions on natural kaolinite at pH 7, 1 g of clay for 60 mins at 25 ºC

4.4 Adsorption Isotherms for Cd(II) ions Adsorption onto Natural Kaolinite

Two theoretical models were employed in this study, the - Langmuir isotherm Equation 2.5 and Freundlich isotherm Equation 2.8 - were used to evaluate the equilibrium adsorption characteristics and the adsorption behaviour of the natural Zebediela kaolin. The application of the linearized Langmuir model, as seen in Figure 4.9 was derived from

a plot of $\frac{1}{C_e}$ versus$\frac{1}{q_e}$. The linearized Freundlich model as depicted in Figure 4.10 was obtained from a plot of log C_e versus log q_e.

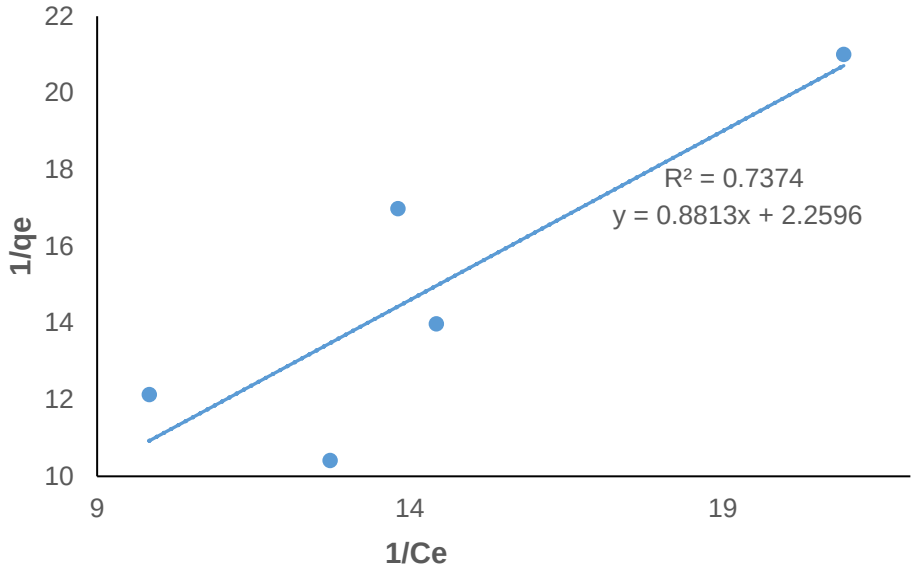

Figure 4.9: Langmuir plots for the adsorption of Cd(II) ions on natural kaolinite at pH 7, 1 g of clay for 60 mins at 25 ºC

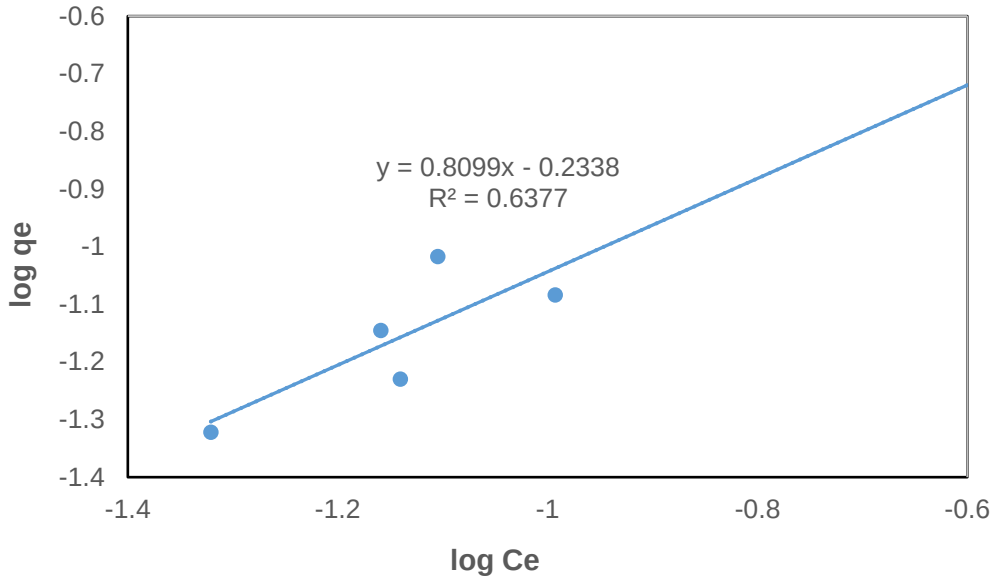

Figure 4.10: Freundlich plots for the adsorption of Cd(II) ions on natural kaolinite at pH 7, 1 g of clay for 60 mins at 25 ºC

The coefficient of determination R^2 for the Langmuir isotherm was 0.7374 while the R^2 for Freundlich isotherm was 0.6377 (Table 4.3). The data obtained from this study yielded a better fitting with Langmuir isotherm, as it had a higher coefficient of determination than the Freundlich isotherm. The essential characteristic of the Langmuir isotherm can be expressed by the separation factor R_L. R_L= 0 implies adsorption is irreversible; R_L = 1 indicates adsorption to be linear; R_L > 1 implies adsorption is unfavourable, while 0< R_L< 1 suggests adsorption is favourable (Ayawei *et al*., 2017). In this study R_L was 0.4383; suggesting the adsorption process was favourable. This indicates that the kaolin sample can adsorb Cd (II) ions, although the adsorption process of Cd (II) on natural Zebediela kaolin was favourable, the adsorption capacity was low. This is because natural kaolins generally show low adsorption capacity for heavy metals, due to low surface area, little isomorphous substitution and low cation exchange capacity. Similar findings have been reported by Essomba *et al*., (2014) and Kumari and Mohan (2021).

Additionally, 1/n value from the Freundlich isotherm is a function of the adsorption strength, and it indicates the affinity between adsorbent and adsorbate. A 1/n value approaching zero, indicates a more heterogenous surface; 1/n value above unity implies the adsorption process is more physical and a 1/n value below unity suggests the adsorption process is chemical (Bhandari and Ranade, 2014). In this study, the 1/n value was 0.8099 suggesting the adsorption process was chemical; this implies a chemical bonding between Cd(II) ions and the kaolin sample. The bonds may have included weak hydrogen bonds between Cd (II) ions and the kaolin.

Furthermore, the Langmuir model is based on the assumptions that the adsorption consists entirely of a monolayer at the surface and that there exists no interaction among molecules adsorbed on neighbouring adsorption sites however, in this study it is likely that there were interactions between the adsorbed Cd(II) molecules on different adsorption sites (Meroufel *et al*., 2013; Bhandari and Ranade, 2014) . On the other hand, the Freundlich model is established on the adsorption processes on heterogenous sites. It assumes that binding sites which are stronger are occupied first and the strength of adsorption reduces with the degree of occupation (Batool *et al*., 2018). This may relate to the adsorption rate of the kaolin reducing as more sites were being occupied leading to a

decrease in vacant active adsorption sites on the kaolin. Also, the relatively low coefficients of determination is related to the low adsorption capacity of the kaolin which can be enhanced by acid treatment, pillaring or intercalation (Mnasri-Ghnimi and Frini-Srasra, 2019; ECETOC, 2023).

Table 4.3: Isotherm parameters for Langmuir and Freundlich isotherm for the adsorption of Cd(II) ions by natural kaolinite at concentration 0.5-2 mg/L; time 60 mins; dosage of 1g; pH 7 at 25 ºC

Adsorbent and Metal Ion	Langmuir				Freundlich		
	q_{max} (mg/g)	K_L (L/mg)	R_L	R^2	K_f	1/n	R^2
Natural kaolinite Cd(II)	0.4426	2.5634	0.4383	0.7374	0.5837	0.8099	0.6377

4.5 Adsorption Kinetics for Cd (II) ions Adsorption onto Natural Kaolinite

Adsorption kinetics were used to ascertain the rate at which adsorption of Cd(II) ions occurred on the kaolinite adsorbent. The pseudo-first-order and pseudo-second-order models were used to determine the kinetic parameters for the adsorption of Cd (II) ions onto natural Zebediela kaolinite. These models were applied to the experimental data following the relationships stated in Equations 2.12 and 2.14. For pseudo-first-order a linear graph of t versus $In(q_e-q_t)$, as depicted in Figure 4.11, was plotted, while for the pseudo-second-order a linear graph of t versus t/q_t, as seen in Figure 4.12, was obtained.

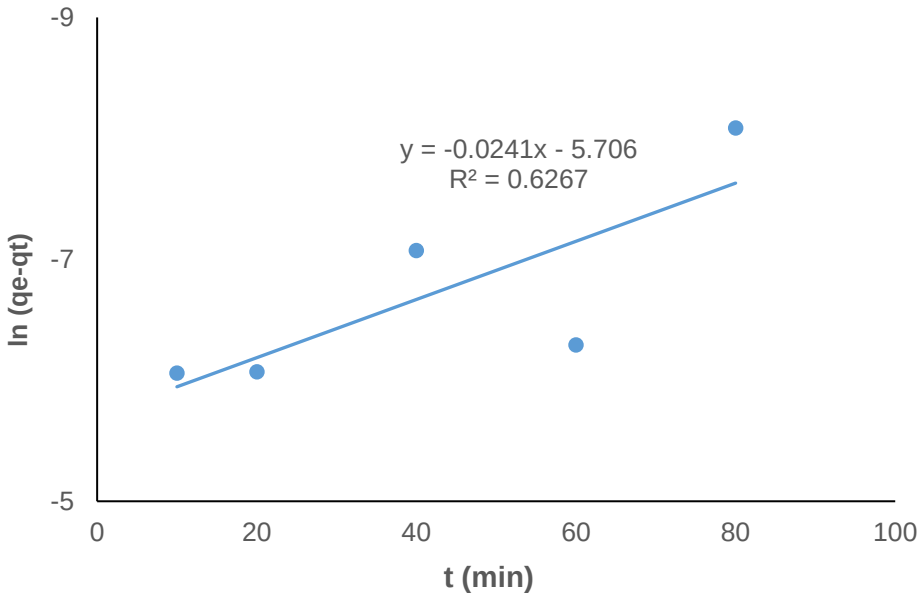

Figure 4.11: Pseudo-first-order plots for the adsorption of Cd(II) ions on natural kaolinite at initial concentration of 0.5 mg/L, 1 g of clay, pH of 7 at 25 ºC

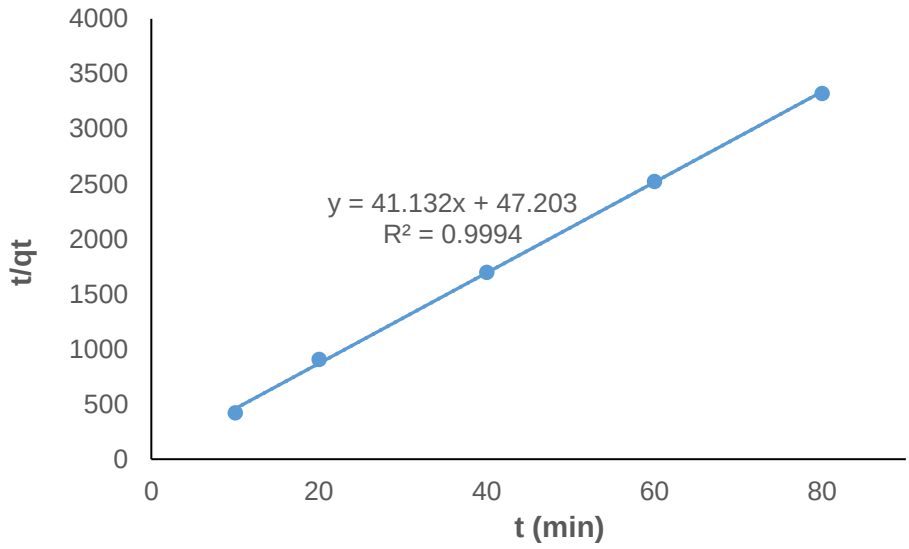

Figure 4.12: Pseudo-second-order (b) plots for the adsorption of Cd(II) ions on natural kaolinite at initial concentration of 0.5 mg/L, 1 g of clay, pH of 7 at 25 ºC

The kinetic parameters for the pseudo-first order (k_1 and q_e) and pseudo-second-order (k_2 and q_e) were calculated from their corresponding slopes and intercepts on the graphs. From the data recorded in Table 4.4, it can be observed that there was no rational agreement between the experimental and the calculated adsorption capacity (q_e) for the pseudo-first-order model and the coefficient of determination R^2 for this model was 0.6267. On the other hand, the application of the pseudo-second-order model yielded similar experimental and calculated q_e values with the R^2 value at 0.9994 This indicates that the pseudo-second-order mechanism is predominant for the adsorption of Cd (II) ions onto the natural Zebediela kaolin.

Moreover, in the pseudo-first-order model, the rate-limiting step involves a diffusion process, and the model is considered to be controlled by physisorption while for the pseudo-second-order model, the rate-limiting step is the surface adsorption that involves chemisorption mechanism. In this study, the chemical process may have involved weak hydrogen bonds between Cd (II) ions and the kaolin (Dariush, 2013; Agbovi and Wilson, 2021). The results of this study corroborate with previous findings of El Ass (2018) who studied the adsorption of cadmium and copper by natural clays.

Table 4.4: Kinetic models for the adsorption of Cd (II) ions by natural kaolinite at initial concentration from 0.5 mg/L; time 60 mins, dosage of 1g, pH 7 at 25 ºC

Adsorbent and Metal Ion	Pseudo-first-order				Pseudo-second-order		
	q_e(exp.) (mg/g)	q_e(calc.) (mg/g)	k_1(min^{-1})	R^2	q_e(calc.) (mg/g)	k_2(min^{-1})	R^2
Natural kaolinite Cd(II)	0.0244	0.0033	-0.0002	0.6267	0.0243	35.97	0.9994

4.6 Sustainable Measures to Prevent Heavy Metal Pollution in Water

The removal of heavy metals from water is a very favourable step, however, it is like treating a symptom of a disease while the root cause is left unattended. Consequently, we need to deal with the root cause of heavy metal pollution in water to ensure clean

water resources for the present and future generations. Some of the root causes, include pollution from industrial, agricultural, municipal, domestic and mine activities (Uddin, 2017; Gu *et al*., 2019). The subsequent points present measures to reduce heavy metal pollution of water and to encourage sustainable management of water resources:

- Integrated management of water resources which would involve all relevant stakeholders (government, communities, businesses, investors, NGOs) in decision-making related to sustainable management of water resources (Bertule *et al*., 2018).
- Implementation of fines to industries, factories, mines, and other defaulters for improper disposal of waste.
- Use of organic fertilizers, such as manure, compost, vermicompost, chicken litter and bone meal, instead of chemical fertilizers will reduce leaching of heavy metals from farmland into water (Hei *et al*., 2016).
- Implementation of water policies and water management strategies which take into consideration the beliefs, policies, socio-economic environment, preferences, and customs of the community (Hirai and Graham, 2019).
- Participation of all water-users in ensuring rivers, streams, lakes, springs, hand-dug wells and boreholes are kept clean.
- Sensitization of all water-users on the dangers and consequences of heavy metal pollution in water.
- Creation of community groups and workshops to teach people on how to dispose of toxic waste properly and how to manage water resources sustainably.
- Incorporation of local and indigenous knowledge in water treatment techniques for heavy-metal removal. This will facilitate acceptance of the treatment methods to be used (Shemsanga *et al*., 2017).

4.7 Summary

This chapter discussed the inferences drawn from the mineralogy, chemistry, and morphology of Zebediela kaolin. Inferences from batch adsorption experiments and adsorption isotherms and kinetic models were presented, as well as sustainable

measures for the prevention of heavy metal pollution of water. The next chapter will discuss the summary of all the findings in this research.

CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

5.1 Preamble

This chapter summarises the findings of this research, based on the specific objectives and research questions stated in Chapter One. It draws conclusion from the inferences derived from Zebediela kaolin's mineralogical composition, chemical composition, and morphological characteristics. Additionally, conclusions were also drawn from batch adsorption experiments. The discussions focus on assessing the suitability of Zebediela kaolin for the removal of Cd (II) from aqueous solution, based on the mineralogy and chemistry of the kaolin. Furthermore, recommendations were made on how to increase the adsorption capacity of the kaolin.

5.2 Conclusions

This study evaluated the adsorption of Cd(II) ions from aqueous solution using natural Zebediela kaolin. The adsorption was influenced by factors such as, the pH, adsorbent dose, contact time and initial Cd(II) ion concentration. The adsorption capacity of the kaolin for Cd (II) ions was established at 0.0244 mg/g.

The mineralogical analysis revealed that the kaolin sample was predominantly made up of kaolinite, followed by quartz, microcline, and mica. The presence of these minerals resulted in low adsorption capacity of the kaolin as they have the potential to affect the particle size, degree of disorder, colour, abrasiveness, and viscosity of the kaolin, hence, having a negative impact on the adsorption characteristic of the kaolin sample.

The morphological analysis revealed that the sample consisted of well-developed kaolinite books and stacks with relatively porous aggregates which may have provided a fairly low bonding relationship between the Zebediela kaolin and Cd (II) ions; consequently, the low adsorption capacity observed. Additionally, the low adsorption capacity can be attributed to low cation exchange capacity of the kaolin and the fixed structure of the kaolinite which did not allow expansion between layers.

The major element in the composition included - silica (SiO_2), alumina (Al_2O_3) and titanium (TiO_2), however other oxides such as - TiO_2, Fe_2O_3, MnO, MgO, CaO, Na_2O,

K_2O, P_2O_5, Cr_2O_3 were present. Low adsorption capacities are usually reported when raw kaolin is used in the removal of heavy metals from water, as was the case in this study. Impurities - TiO_2, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, Cr_2O_3 - may have contributed to the low adsorption capacity of the raw Zebediela kaolin for Cd (II) ions as the impurities could have interfered with the adsorption properties of the kaolin. In addition, the disparity between the silicate and alumina content of the Zebediela kaolin (SiO_2 = 58.39%, Al_2O_3 =28.04) compared to the pure kaolin (SiO_2 = 46%, Al_2O_3 = 40) was substantial; this may have affected its behaviour as an adsorbent.

It can be deduced from the results that maximum percentage removal was attained at pH 7, an adsorbent dosage of one gram, contact time of 40 minutes. The adsorption process was favourable and it followed the Langmuir isotherm. Additionally, the 1/n value from the Freundlich isotherm was less than 1 suggesting a more chemical process, however, the adsorption process showed weak interaction between the kaolin and Cd (II) ions. This indicates the interactions involved relatively weak hydrogen bonds. In addition, the low adsorption capacity recorded was due to low surface area and little isomorphous substitution in natural kaolins.

From the kinetic study, the application of the kinetic models for the adsorption data, suggested that the pseudo-second-order reaction model better describes the mechanism for the adsorption of Cd (II) ions by the natural Zebediela kaolinite. This study has experimentally demonstrated that natural Zebediela kaolin can be used as a low-cost adsorbent for the removal of Cd (II) ions in aqueous solution. The adsorption capacity, however, can be increased by removing the impurities present in the sample and by increasing the surface area and porosity of the kaolin.

5.3 Recommendations

For subsequent studies the following modifications of raw Zebediela kaolin are recommended:

- Acid treatment which increases porosity, specific surface area and transforms crystalline structure without alteration of the original mineral structure (Bhattacharyya and Gupta, 2008).

- Intercalation of the well-developed kaolinite books and stacks with guest species will increase its porosity and adsorption capacity (Frost and Kristof, 2004).
- Pillaring with metal oxides or aluminium to increase the surface area, adsorption capacity, thermal stability and intrinsic catalytic activity (Mnasri-Ghnimi and Frini-Srasra, 2019).

In addition, education should be offered on the proper disposal of toxic waste to ensure an awareness on the sustainable management of water resources is created among water-users (domestic, industrial, municipal, agricultural users) to mitigate against heavy metal pollution of water resources.

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