



Institute for Water  
and Energy Sciences  
(incl. Climate Change)



**PAN-AFRICAN UNIVERSITY  
INSTITUTE FOR WATER AND ENERGY SCIENCES  
(including CLIMATE CHANGE)**

# **Master Dissertation**

Submitted in partial fulfillment of the requirements for the Master degree in  
**WATER ENGINEERING**

Presented by

**GOBUSAONE MOKOKWE**

**ADSORPTIVE REMOVAL OF HEAVY METAL IONS FROM WASTEWATER  
UTILIZING FAYALITE SLAG AS A LOW-COST ADSORBENT: BATCH  
STUDIES, ARTIFICIAL NEURAL NETWORKS AND ADAPTIVE NEURO-  
FUZZY INFERENCE SYSTEM MODELING AND OPTIMIZATION**

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## **DEDICATION**

This dissertation is dedicated to all of my friends, fellow researchers and my family.

## **DECLARATION**

I, Gobusaone Mokokwe, declare that this thesis is my own original work and it has not been presented and will not be presented by me to any other university for similar or any other degree award. I also declare that all information and sources of material used for this thesis have been fully cited and referenced in accordance with the academic rules and ethics.

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This is to certify that the thesis entitled “**Adsorptive removal of heavy metal ions from wastewater utilizing Fayalite slag as a low-cost adsorbent: Batch studies, Artificial Neural Networks and Adaptive Neuro-Fuzzy Inference System modeling and optimization**” submitted in partial fulfillment of the requirements for the degree of Master of Science in Water Engineering, the Graduate Program of the Pan Africa **Institute for Water and Energy Sciences (incl. Climate Change)**, and has been carried out by **Gobusaone Mokokwe ID. No PAUWES/2023/MWE08**, under my supervision. Therefore, I recommend that the student has fulfilled the requirements and hence hereby can submit the thesis to the Water Program for defense.

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## ACRONYMS

ANFIS	Adaptive Neuro-Fuzzy Inference Systems
ANN	Artificial Neural Networks
BCL	Bamangwato Concessions Limited
BOS	Botswana Bureau of Standards
$\text{Cu}^{2+}$	Divalent copper ion
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	Hydrated salt of Copper Sulphate
EU	European Union
FAO	Food and Agriculture Organization
FS	Fayalite slag
$\text{Fe}^{2+}$	Ferrous ion
$\text{Fe}_2\text{O}_3$	Iron oxide
MCL	Maximum Contamination Level
$\text{Ni}^{2+}$	Divalent Nickel ion
SEM	Scanning Electron Microscopy
SDG	Sustainable Development Goal
$\text{SiO}_2$	Silica
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

## ABSTRACT

This study investigated the adsorptive removal of three heavy metal ions ( $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$ ) from wastewater using fayalite slag (FS), a low-cost industrial by-product. The media was characterized using XRD, XRF, SEM, batch adsorption studies were conducted, and the adsorption process was further optimized and predicted adsorption efficiency by developing Artificial Neural Network (ANN) and Adaptive Neuro-Fuzzy Inference System (ANFIS). Comprehensive characterization revealed that FS was suitable as an adsorbent, with a particle size distribution ( $d_{10} = 0.3\text{mm}$ ,  $\text{Cu} = 5.36$ ), high porosity (50%), and significant iron oxide content ( $\text{Fe}_2\text{O}_3 = 45.44\%$ ). Batch adsorption experiments demonstrated optimal removal efficiencies at a dosage of 2.0 g/100mL, near-neutral pH (6-8), and a contact time of 40 minutes, achieving approximately 3.5 mg/ g adsorption capacity (35% removal efficiency) for each metal. The adsorption kinetics aligned with the pseudo-second-order model ( $R^2 \geq 0.994$ ), indicating chemisorption as the rate-limiting step. Langmuir and Freundlich isotherm models effectively described the adsorption behavior. Thermodynamic studies confirmed that the process was endothermic ( $\Delta H^\circ > 0$ ) and spontaneous ( $\Delta G^\circ = -9.023$  to  $-10.294$  kJ/mol). Reusability studies showed a gradual decline in recovery efficiency, from approximately 30% in the first cycle to less than 20% by the third cycle. The ANFIS model, with six fuzzy rules, exhibited superior performance ( $R^2 = 0.823$ ,  $\text{RMSE} = 11.87$ ), demonstrating a high correlation between predicted and experimental data. Thus, FS proved to be an effective, sustainable adsorbent, warranting further research into regeneration optimization, continuous flow applications, and real wastewater treatment, alongside cost-benefit and pilot-scale assessments for industrial implementation.

**Keywords:** Adsorption, Artificial Neural Networks, Artificial Neuro-Fuzzy Inference System, Fayalite Slag, Heavy metals, Wastewater

# 1. CHAPTER ONE: INTRODUCTION

## 1.1 Background of the study

Heavy metal ions are prevalent form of environmental contaminants found particularly in water sources, and represent a significant global environmental concern (Hama Aziz *et al.*, 2023). These toxic, non-biodegradable metals originate mainly from industrial waste, posing risks to human health as they enter the food chain through aquatic organisms and drinking water (Chan *et al.*, 2021). Efforts to alleviate water scarcity by using treated industrial wastewater for irrigation have been adopted by many developing countries including Botswana. Such effluents are laden with nutrients suitable for plant growth and soil fertility (Usman *et al.*, 2012; Mokokwe and Letshwenyo, 2022a). However, such effluents are also loaded with contaminants such as heavy metals including copper, hence the need for treatment prior to discharge. Sources of these heavy metals also include natural phenomena like rock erosion, and volcanic eruptions (Torres *et al.*, 2023). Prior to releasing industrial waste like metallurgical waste into the environment, industries are obligated to comply with established limits on the permissible metal content. Base metals from such waste, notably iron and copper, can lower soil pH, and elevated levels of these metals in disposed waste may lead to soil pollution and toxicity, negatively impacting plant growth and animal health (Gabasiane *et al.*, 2021).

High concentrations of heavy metals can also lead to detrimental health effects in humans, including neurotoxicity, mutagenicity, and carcinogenicity, therefore a significant concern for environmental protection (Mitra *et al.*, 2022). Though copper is needed by our bodies in minimal amounts, it can pose hazards to human health when present in the environment. Copper's harmful effects span a range of health challenges such as gastrointestinal problems in nausea and abdominal pain (Taylor *et al.*, 2020), liver damage and Wilson disease (Khan *et al.*, 2017). Certain vegetables have been found to bioaccumulate heavy metals sourced from both irrigation water and soil, ultimately becoming part of the human diet (Balkhair and Ashraf, 2016). To address the risk of heavy metal ingestion through food, organizations like the Food and Agriculture Organization (FAO) have implemented stringent policies, including of water quality standards, to manage and control heavy metal contamination in irrigation water. The World Health Organization (WHO) has approved limit for copper in drinking water, with thresholds set at 0.05 to 1.5 mgL<sup>-1</sup>. These standards differ from those established by the United States Environmental Protection Agency (USEPA), which sets limit at 1.3 mgL<sup>-1</sup> for copper.

Exceeding the set thresholds may result in harmful health effects, hence the need to adhere to stringent regulations imposed by these organizations.

Researchers across the globe are dedicated to finding better solutions to guarantee continuous water access and address the challenge of water scarcity in line with the sustainable development objective of providing clean water and sanitation to everyone by 2030 (SDG 6). Various wastewater treatment techniques, including, chemical precipitation, ion exchange, membrane filtration, and adsorption, have been explored for their efficacy in removing heavy metals (Srivastava et al., 2006; Lekgoba et al., 2020). Prior to selecting a technique, it is essential to assess cost-effectiveness and efficiency of the technology from an engineering standpoint (Hafsa *et al.*, 2020). The drawbacks of these methods have spurred efforts to find more effective and eco-friendly technologies to tackle the growing concern over future water security (Shemer, Wald and Semiat, 2023). Among these aforementioned technologies, adsorption stands out as a preferred option due to its effectiveness, minimal waste generation, high extraction efficiency, and cost-effectiveness. Industrial solid wastes are particularly favored as adsorbents due to their economic benefits and contribution to waste reduction. Numerous media were discovered over the past years and were applied in the removal of toxic metals from wastewater; for instance, water treatment sludge and red mud (Zhou and Haynes, 2012), activated rubber wood saw dust (Biswas and Mishra, 2015), cement brick waste (Mokokwe and Letshwenyo, 2022b), activated fly ash (Xiyili, Çetintaş and Bingöl, 2017) and iron oxide- coated eggshell powder (Ahmad, Kumar and Haseeb, 2012).

Copper mining industries in Botswana produce significant amounts of Fayalite slag and other by products as a solid waste, contributing to environmental pollution. Globally, a substantial amount of Fayalite or copper slag is generated, with an estimated 2.2 tonnes of slag produced for every tonne of copper manufactured (Gorai and Jana, 2003). The annual worldwide production of slag stands at around 24.6 million tons in the early 21st century, with a growth rate of 11% per year. According to (Gorai and Jana, 2003; Gabasiane et al., 2021), in Africa, including regions like Botswana, the annual slag production amounts to approximately 2.3 million tonnes. In Botswana specifically, this slag, initially considered metallurgical waste, was typically disposed of by stockpiling into heaps at designated mining areas after processing. The availability and abundance of such materials present an opportunity to explore their potential as adsorbents. Fayalite slag from such mining industries emerges as a promising material for the adsorption of heavy metals and other contaminants due to its promising physicochemical

properties. It constitutes oxide minerals such as silica, iron oxide suitable for the surface reaction; adsorption of heavy metals due to their noteworthy catalytic properties (Egodawatte *et al.*, 2015), (Singh, Sharma and Basu, 2018). While recent research has focused on high-cost media with high affinity and retention capabilities, there is still lack of investigation into practical aspects such as mechanical or structural strength, porosity, and environmental friendliness of such media (Sarma, Sen Gupta and Bhattacharyya, 2019), (Lata, Singh and Samadder, 2015). Additionally, exploring the individual physicochemical parameters affecting the adsorption process is both costly and labor-intensive. This highlights the need for more comprehensive studies that consider both the performance and practical applicability of adsorption media.

Modeling the adsorption process can enable the assessment of individual parameter effects and simulate metal ion removal with fewer experimental works, thus conserving resources. The effect of operational conditions on the process typically exhibits non-linearity, complicating the use of non-linear statistical models for development and outcome resolution. Recent advancements highlight Artificial Neural Networks (ANN) and Adaptive Neuro-Fuzzy Inference Systems (ANFIS) as superior techniques for addressing complex engineering problems and relationships (Ghaedi *et al.*, 2015). Many scientific applications rely on artificial neural networks (ANNs) due to their impressive capacity for representing complex nonlinear connections (Fiyadh *et al.*, 2023). In recent decades, there has been a significant increase in the utilization of artificial neural networks for adsorption modelling. Particularly in the realm of water purification, these AI models have been employed to establish correlations and predict the kinetics, isotherms, and breakthrough curves of various adsorbents and adsorbates (Fiyadh *et al.*, 2023). ANN has been used to predict the performance of different adsorbents in various adsorption processes, such as the removal of pollutants from water, air, and industrial effluents. Consequently, this study employs robust optimization and heuristic computational intelligence techniques, that is, ANN and ANFIS to model adsorption, enhancing understanding of behavior and facilitating critical decision-making regarding the process. Furthermore, this research investigates the potential of using Fayalite slag (FS) as a low-cost adsorbent for removing divalent copper, nickel and ferrous iron ions from aqueous solutions. The study investigates various adsorption-physicochemical factors such as contact time, initial solution pH, adsorbent dosage, and thermodynamic processes on the adsorption process. Additionally, the study delves into kinetic and isotherm models to deepen understanding of adsorption mechanisms. To the

best of our knowledge, this research presents, for the first time in the literature, the development of ANN and ANFIS models for the adsorption of divalent Cu, Ni and Fe ions onto FS.

## **1.2 Statement of the problem**

The contamination of water resources by heavy metals, such as divalent copper, nickel and iron ions, poses significant environmental and public health risks due to their toxicity and non-biodegradability. Conventional methods for removing heavy metals from wastewater are often costly, inefficient, or environmentally detrimental. Fayalite slag, an abundant industrial by-product, presents a promising low-cost adsorbent for heavy metal removal. However, the effectiveness and optimization of fayalite slag in adsorbing divalent copper, nickel and ferrous iron ions from wastewater require thorough investigation and advanced modelling techniques to enhance process efficiency and predict outcomes accurately.

## **1.3 Research questions**

This research intends to address the following research questions;

1. How are the adsorption process parameters influencing the removal of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Ni}^{2+}$  ions from wastewater?
2. Is there possible regeneration potential of FS and what are the environmental effects of using FS as an adsorbent?
3. Which artificial intelligence model will best predict and optimise the adsorption process?

## **1.4 Objectives of the study**

### **1.4.1 General objective**

The overall objective of this study was to investigate the effectiveness of locally available low-cost adsorbents (Fayalite slag) in the adsorptive removal of divalent copper, iron and nickel ions from wastewater and optimize the process using ANN and ANFIS models.

### **1.4.2 Specific objectives**

The specific objectives addressed to accomplish this main objective are:

1. To investigate the effects of different process (pH, adsorbent dosage, contact time) parameters influencing the removal of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Ni}^{2+}$  ions from wastewater.
2. To investigate and understand the regeneration potential and environmental effects FS as adsorbent through leaching test.

3. To optimize the adsorption process utilizing ANN and ANFIS models.

## 2. CHAPTER TWO: LITERATURE REVIEW

### 2.1 Water Contamination

Water is a vital resource essential for life and environmental sustainability. Many developing countries, including Botswana, face significant challenges due to unreliable rainfall patterns, leading to persistent droughts and water scarcity (Rao *et al.*, 2017). Globally, researchers have been exploring innovative solutions to ensure uninterrupted access to high-quality water. One such approach is the reuse of treated industrial effluents for irrigation, as they often contain nutrients beneficial for plant growth. However, these effluents frequently harbor toxic heavy metals, such as iron (Fe), nickel (Ni), and copper (Cu), which must be removed before discharge into aquatic systems (Tytła, 2019). High concentrations of these metals are linked to severe health effects: excessive iron can cause hemochromatosis, neurotoxicity, and organ damage (Bełcik *et al.*, 2024), nickel exposure can lead to carcinogenicity, dermatitis, and cognitive impairments, and elevated copper levels are associated with gastrointestinal distress, liver and kidney damage, and neurodegenerative conditions like Wilson's disease (Farooq *et al.*, 2010). Moreover, the accumulation of these metals in soil and water disrupts ecosystems, contaminates crops, and introduces toxins into the food chain, affecting both humans and animals. To address these risks, developing cost-effective and sustainable water treatment technologies, such as adsorption using locally available materials, is crucial for ensuring public health and environmental sustainability in resource-constrained regions.

#### 2.1.1 Sources of Water Contamination

Water contamination arises from diverse sources, which can be broadly categorized as natural and anthropogenic. Natural sources include rock weathering, volcanic eruptions, and forest fires, which release heavy metals such as mercury (Hg) and arsenic (As) into water bodies (Farooq *et al.*, 2010). Anthropogenic activities, on the other hand, significantly exacerbate contamination levels. Industrial discharges, agricultural runoff, and urban wastewater are major contributors. For instance, electroplating industries release cadmium (Cd), nickel (Ni), and chromium (Cr), while agricultural practices introduce pesticides and fertilizers containing lead (Pb) and zinc (Zn). Mining activities, particularly for gold and coal, contribute to the leaching of toxic metals into nearby water sources (Gebrekidan *et al.*, 2024). Another instance is mercury (Hg) from fossil fuel combustion and mining activities causes neurological damage, while cadmium (Cd) from electroplating and plastics manufacturing can lead to kidney damage and hypertension (Boening, 2000). **Table 2.1** provides an overview of heavy metals, their sources,

and associated health impacts. Additionally, improper waste disposal and inadequate treatment facilities in urban areas amplify the contamination problem. Heavy metals from municipal solid waste and e-waste leach into groundwater, further worsening the quality of water resources (Gebrekidan *et al.*, 2024). Addressing these sources requires stringent regulations, advanced treatment technologies, and public awareness campaigns.

**Table 2.1:** Summary of health effects on humans and sources of various heavy metals

Heavy metals	Sources	Health Impacts	References
Lead (Pb)	Batteries, pigments, electroplating, construction materials, ammunition, and radiation shielding.	Anemia, lack of appetite, anorexia, fatigue, developmental delays, and high blood pressure, brain damage	(Flouty and Estephane, 2012)
Mercury (Hg)	Volcanic eruptions, coal combustion, mining (especially gold mining), wastewater discharge, and the burning of hazardous waste	Renal and neurological damage, dermatitis, liver damage, kidney damage, respiratory issues, developmental delays, and memory loss.	(Manohar, Krishnan and Anirudhan, 2002)
Chromium (VI) (Cr VI)	Metal plating, leather tanning, cement production, and the discharge of industrial effluents.	Mutagenic, lung cancer, respiratory problems, skin irritation, kidney damage, and gastrointestinal issues.	(Mridul and Gupta, 2015)
Arsenic (As)	Sediment rock weathering, energy production from fossil fuels, mining, enamels.	Liver tumor, encephalopathy, polyneuropathy, hemolysis, melanosis in bones, damage to cardiovascular and nervous system, gastrointestinal symptoms	(Rahman and Hashem, 2019)
Nickel (Ni)	Thermoelectric, coated porcelain, electroplating, formulation of paints, mineral processing, non-ferrous materials.	Lung cancer, reduced lung function, chronic bronchitis.	(Öztürk, 2007)
Copper (Cu)	Wood preservation, printing, paints production, galvanizing, electronics coating.	Diarrhea, sleep disturbances, neurotoxicity, develops acute toxicity.	(Papandreou <i>et al.</i> , 2007; Chuah <i>et al.</i> , 2005)
Cadmium (Cd)	Refinery, mining, plastics, pigments production, enamel, electroplating.	Loss of appetite, hypertension, bone injury, kidney damage, carcinogenic.	(Godt <i>et al.</i> , 2006)
Iron (Fe)	Industrial emissions, mining activities, vehicle exhaust, agricultural runoff, and corrosion of infrastructure.	Hemochromatosis, neurotoxicity, and organ damage	(Belcik <i>et al.</i> , 2024)

### 2.1.2 Heavy metals and regulatory bodies for policies

Heavy metals, such as lead (Pb), chromium (Cr), and arsenic (As), have been the subject of extensive scientific research due to their known toxicological effects on human health, ecosystems, and the environment (Gebrekidan *et al.*, 2024). These metals, which are naturally occurring but also introduced into the environment through industrial activities, agricultural runoff, and improper waste disposal, are classified as persistent pollutants. Once released into the environment, heavy metals can accumulate in soils, water, and biota, leading to long-term exposure risks (Wang *et al.*, 2024). In particular, when food crops are irrigated with water contaminated by these metals, the pollutants can enter the food chain through plant uptake, bioaccumulation, and biomagnification. This process poses a significant threat to human health, as ingestion of heavy metals through contaminated crops can result in chronic poisoning, cancer, kidney damage, and neurological disorders, especially in vulnerable populations such as children and pregnant women (Kumar *et al.*, 2019).

To mitigate the risks associated with heavy metal contamination, international regulatory bodies like the Food and Agriculture Organization (FAO), United State Environmental Protection Agency (USEPA), European Union (EU), World Health Organization (WHO) and national organizations such as Botswana Bureau of Standards (BOS) have developed stringent guidelines that set permissible limits for the concentration of heavy metals in drinking water and irrigation water (**Table 2.2** and **Table 2.3**). These guidelines are designed to minimize human exposure to harmful substances and ensure that the quality of water remains within safe thresholds for agricultural and consumption purposes (Sarker *et al.*, 2022). The FAO, in particular, has established maximum allowable concentrations for heavy metals in food crops and drinking water, taking into account factors like the toxicological profile of the metals, their bioavailability in different environmental matrices, and the potential for human exposure (Scutarașu and Trincă, 2023).

These limits are based on extensive toxicological data and scientific research, which assesses the risks posed by long-term exposure to these metals. Regulatory frameworks like these are essential not only in reducing the direct health risks associated with contaminated water but also in promoting sustainable water management practices that protect both human populations and the surrounding environment (Mitra *et al.*, 2022). Furthermore, research on heavy metal contamination in irrigation water highlights the importance of regular monitoring, risk assessments, and the adoption of best agricultural practices to prevent the uptake of these

harmful metals by crops. This includes utilizing alternative, cleaner water sources, improving irrigation techniques, and developing soil management practices that reduce the mobility and bioavailability of heavy metals. By combining stringent regulations, scientific research, and effective management strategies, it is possible to mitigate the risks of heavy metal contamination, ensuring food safety and public health protection for current and future generations.

**Table 2.2:** Maximum threshold of some heavy metal ions in portable water set by different regulatory bodies

Heavy metals	EU standards	USEPA	WHO	Botswana Standards (BOS)
Nickel (Ni)	0.020	0.100	0.020	0.020
Lead (Pb)	0.010	0.015	0.010	0.010
Zinc (Zn)	-	5.000	3.000	0.01
Chromium (Cr)	0.050	0.100	0.050	0.050
Arsenic (As)	0.010	0.010	0.010	0.010
Copper (Cu)	2.000	1.300	2.000	1.000
Cadmium (Cd)	0.005	0.005	0.003	0.003

**Table 2.3:** Maximum Contaminated Level (MCL) of heavy metals in wastewater set by USEPA (Babel and Kurniawan, 2003)

Heavy metal (mgL <sup>-1</sup> )	USEPA
Arsenic (As)	0.050
Cadmium (Cd)	0.010
Chromium (Cr)	0.050
Copper (Cu)	0.250
Nickel (Ni)	0.200
Zinc (Zn)	0.800
Lead (Pb)	0.006
Mercury (Hg)	0.00003

## 2.2 Water for Irrigation in Developed Countries

In developed nations, advanced water treatment technologies and robust regulatory frameworks ensure the safe reuse of treated wastewater for irrigation. These countries benefit from significant investments in research and infrastructure, enabling the implementation of sophisticated techniques such as reverse osmosis, ultrafiltration, and advanced oxidation processes (Maura, Atreya and Arshi, 2023). Such methods effectively remove heavy metals and

other contaminants, ensuring compliance with stringent safety standards. Moreover, public awareness campaigns and education programs have encouraged sustainable water practices, further enhancing the efficiency of water management systems. The integration of technology with precision agriculture has also optimized irrigation, reduced water wastage and enhancing crop yields (Li *et al.*, 2024). In developed nations, advanced water treatment technologies and robust regulatory frameworks ensure the safe reuse of treated wastewater for irrigation. For instance, countries such as Portugal, and Canada have established their own recommended MCL for heavy metal ions for irrigation water (**Table 2.4**). These practices not only conserve water but also enhance agricultural productivity by supplying essential nutrients.

**Table 2.4:** Recommended MCL for some heavy metals in irrigation water formed by Canada and Portugal (Vareda et al.,2019)

Heavy metal concentrations ( $\mu$ g/L)	Canada	Portugal
Arsenic	100	100
Cadmium	5	10
Copper	-	200
Nickel	200	500
Zinc	1000 pH < 6.5	2000
Lead	200	5000

### 2.3 Irrigation Water in Developing Countries

In contrast, developing countries often face significant challenges in managing water resources due to financial constraints, inadequate infrastructure, and limited access to advanced technologies (David, 1993). Untreated or partially treated wastewater is frequently used for irrigation, as it provides a readily available and cost-effective water source. However, this practice often leads to the accumulation of heavy metals in agricultural soils and crops, posing serious health and environmental risks (Li *et al.*, 2024). Efforts to address these issues include the introduction of low-cost, decentralized treatment systems and the promotion of natural methods such as constructed wetlands. International collaborations and funding initiatives are also helping to bridge the gap by providing technical expertise and resources to improve wastewater treatment facilities and irrigation practices in these regions. In contrast, developing countries often face limitations in implementing advanced wastewater treatment methods due to financial constraints and inadequate infrastructure (Jayaraj, 2024). Consequently, untreated

or partially treated wastewater is frequently used for irrigation, leading to potential health risks and environmental degradation.

## **2.4 Wastewater Treatment Technologies**

### **2.4.1 Biological Methods**

Biological treatment methods utilize microorganisms to degrade and remove contaminants from wastewater. This approach is considered environmentally friendly and cost-effective compared to physical and chemical methods. Key biological processes include activated sludge systems, anaerobic digestion, and constructed wetlands;

#### **2.4.1.1 Activated sludge systems**

Activated sludge systems rely on diverse microbial communities to metabolize organic pollutants and heavy metals, facilitating the breakdown of harmful substances present in wastewater. These systems consist of a suspension of microorganisms, primarily bacteria, that are responsible for digesting organic matter, including pollutants, in the wastewater (Shchegolkova *et al.*, 2016). By converting these contaminants into simpler, less harmful substances, activated sludge systems significantly reduce the environmental impact of wastewater discharges. As a result of their ability to effectively treat a wide range of contaminants, activated sludge systems are widely used in urban wastewater treatment plants around the world (Singh, Chakraborty and Sehgal, 2023). Their high efficiency in removing both organic pollutants and heavy metals makes them a crucial technology in the management of wastewater, contributing to improved water quality and environmental sustainability. Additionally, the adaptability of these systems allows them to be scaled for various plant sizes, making them suitable for both small and large urban areas (Shchegolkova *et al.*, 2016).

#### **2.4.1.2 Anaerobic digestion**

Anaerobic digestion, in contrast to aerobic processes, utilizes anaerobic bacteria to break down organic matter in the absence of oxygen, producing biogas as a valuable by-product. This process occurs in sealed, oxygen-free environments called digesters, where microorganisms decompose complex organic compounds into simpler substances such as methane and carbon dioxide (Ngan *et al.*, 2020). The biogas produced, primarily methane, can be harnessed as a renewable energy source, making anaerobic digestion an environmentally sustainable method of wastewater treatment. This technique is especially effective for treating industrial wastewater with high organic loads, such as that from food processing, dairy, and pharmaceutical industries,

where large amounts of biodegradable material are present. In addition to reducing the organic content of the wastewater, anaerobic digestion significantly minimizes the volume of sludge produced, making it an efficient and cost-effective alternative for managing high-strength wastewater (Jameel *et al.*, 2024). The process also contributes to reducing greenhouse gas emissions, as the methane produced can be captured and used for energy generation, further enhancing its sustainability.

#### **2.4.1.3 Constructed wetlands**

Constructed wetlands are an eco-friendly alternative that combines vegetation, soil, and microbial activity to treat wastewater (Hassan *et al.*, 2021). Plants like cattails and reeds absorb heavy metals, while microbial communities in the soil aid in the degradation of organic matter. However, the efficiency of biological methods can be influenced by environmental factors such as temperature, pH, and the presence of toxic substances. Despite their advantages, these methods may require extensive land and have longer treatment times. Biological treatment employs microorganisms to remove contaminants from wastewater (Maddison *et al.*, 2009). Overall, biological techniques like activated sludge, anaerobic digestion, and constructed wetlands are widely used. These methods are cost-effective and environmentally friendly but require significant labor and maintenance (Gunatilake, 2015).

### **2.4.2 Physical Treatment Methods**

Physical treatment methods involve the separation of contaminants from wastewater through physical processes. These methods are often used as preliminary or tertiary treatments in wastewater management systems. They include:

#### **2.4.2.1 Membrane filtration techniques**

Membrane filtration techniques, including microfiltration, ultrafiltration, and reverse osmosis, are commonly used to remove suspended solids, microorganisms, and dissolved contaminants from water (Aziz *et al.*, 2024). Microfiltration and ultrafiltration filter larger particles and bacteria, while reverse osmosis (RO) is more advanced, effectively removing smaller dissolved substances like salts and heavy metals by forcing water through a semi-permeable membrane under high pressure. Reverse osmosis is particularly efficient in removing heavy metals, such as lead and mercury. However, these methods come with challenges, including high operational costs due to energy demands, especially for reverse osmosis, which requires significant

pressure. Additionally, membrane fouling can increase maintenance costs, making large-scale applications economically challenging despite their high effectiveness (Qu *et al.*, 2023).

#### **2.4.2.2 Sedimentation and flotation**

Sedimentation and flotation are widely used physical methods for wastewater treatment due to their simplicity and effectiveness, especially in large-scale operations. Sedimentation relies on gravity to separate heavier particles, such as dirt, sand, and other solid matter, from wastewater. As the wastewater flows through a tank or basin, these heavier particles naturally settle to the bottom, forming a sludge layer, while the cleaner water remains on top. This method is cost-effective and works well for removing larger particles, but it may not be sufficient for finer or dissolved contaminants (Oladimeji *et al.*, 2024). Flotation, in contrast, introduces air bubbles into the wastewater, which attach to lighter contaminants, such as oils, grease, or fine suspended solids, causing them to float to the surface. These floated materials can then be skimmed off for removal. This method is particularly useful for treating wastewater with high levels of lighter contaminants and can be more efficient than sedimentation in some cases. While both sedimentation and flotation are simple, reliable, and well-suited for large-scale operations, they have limitations (Oladimeji *et al.*, 2024). They may not fully remove all types of contaminants, particularly dissolved substances or smaller particles. As a result, these methods are often used as pre-treatment steps, with additional chemical or biological processes required for more thorough purification and to meet regulatory standards for water quality.

#### **2.4.3 Chemical Treatment Methods**

Chemical treatment methods involve the use of chemical reactions to remove contaminants from wastewater. These methods are highly effective but often require precise control and management to minimize secondary pollution. The following subsections outline the key chemical methods applied for wastewater treatment:

##### **2.4.3.1 Chemical precipitation**

Chemical precipitation is one of the most widely used methods for the removal of heavy metals from wastewater. This process involves adding precipitating agents, such as lime, sodium hydroxide, or sulfides, which react with metal ions in the wastewater to form insoluble compounds. These compounds then aggregate into larger particles, known as precipitates, which can be easily separated from the water through sedimentation or filtration. The metal ions are effectively removed from the water, making it safer for discharge or further treatment (Pohl,

2020). The efficiency of chemical precipitation is influenced by several factors, including the pH of the water, the specific type of metal ions present, and the choice of precipitating agents. For instance, lime is commonly used to precipitate metals like calcium, magnesium, and some heavy metals, while sodium hydroxide is effective for removing metals such as aluminium and copper. The pH level is a crucial factor in determining the solubility of the metal ions and the effectiveness of the precipitating agents (Kowalski, 2002). An optimal pH must be maintained to ensure the successful formation of precipitates and efficient removal of metals.

While chemical precipitation is effective in removing a wide range of heavy metals from wastewater, it does have some drawbacks. One of the primary challenges is the large amount of sludge that is generated during the precipitation process. This sludge consists of the precipitated metal compounds and often requires proper disposal or treatment to avoid environmental contamination. The disposal of such sludge can be costly and presents environmental concerns, particularly if the sludge contains hazardous levels of heavy metals (Y. Zhang and Duan, 2020). Concluding, chemical precipitation is a highly effective and widely used method for removing heavy metals from wastewater. By adding precipitating agents, metal ions are converted into insoluble compounds that can be easily separated from the water. However, the generation of large amounts of sludge poses disposal challenges, and careful consideration must be given to the pH, type of metal ions, and choice of chemicals to optimize the process and minimize environmental impact.

#### **2.4.3.2 Coagulation and flocculation**

Coagulation is a water treatment process that involves the addition of chemicals such as alum (aluminum sulphate) or ferric chloride to destabilize suspended particles in wastewater. These chemicals cause the particles to clump together, forming larger aggregates known as flocs (Iwuozor, 2019). This destabilization process is crucial in removing various contaminants, particularly in turbid water with high levels of suspended solids, such as sediments, organic matter, and microorganisms. By adding coagulants, the small, dispersed particles are neutralized, making it easier for them to aggregate and settle. Following coagulation, the flocculation process takes place, which involves gentle mixing of the water to encourage the formation of larger flocs. During flocculation, the destabilized particles collide and stick together, forming larger, heavier particles that are easier to remove through sedimentation or filtration. The flocs are then allowed to settle at the bottom of a sedimentation tank, or they can be filtered out using various filtration techniques, depending on the specific treatment system

in place (Tahraoui *et al.*, 2024). Coagulation and flocculation are particularly effective for treating water with high turbidity, which often contains a high concentration of suspended solids that are difficult to remove through simple filtration, hence not effective for heavy metal removal. This method is widely used in municipal water treatment, as well as in industrial wastewater treatment processes, where the removal of suspended particles is essential for ensuring water quality.

However, while coagulation and flocculation are effective, they require careful control and dosing of chemicals to avoid the formation of excessive residues or chemical waste. An overuse of coagulants can result in high concentrations of chemical by-products, which may not only affect the quality of the treated water but also increase the costs of disposal and treatment (Tahraoui *et al.*, 2024). Additionally, the efficiency of the process can be influenced by factors such as the type and concentration of contaminants, pH levels, and water temperature. Therefore, precise dosing and close monitoring are essential for achieving the desired water quality while minimizing the environmental impact of excess chemicals. In conclusion, coagulation and flocculation are highly effective methods for treating turbid water with high levels of suspended solids. By destabilizing particles and forming larger flocs that can be easily removed through sedimentation or filtration, these processes play a vital role in improving water quality. However, the success of this method depends on careful management of chemical dosing and process conditions to ensure that the treatment remains efficient and environmentally sustainable (Tahraoui *et al.*, 2024).

#### **2.4.3.3 Oxidation-reduction**

Oxidation-reduction (redox) reactions are widely used in water treatment to transform harmful contaminants into less toxic or more easily removable forms. These reactions involve the transfer of electrons between chemical species, resulting in the reduction of one substance and the oxidation of another. In the context of environmental remediation, redox processes are particularly effective for addressing contaminants such as heavy metals, halogenated compounds, and other harmful chemicals in water.

A prime example of a redox reaction in water treatment is the transformation of hexavalent chromium (Cr (VI)), a highly toxic form of chromium, into trivalent chromium (Cr (III)), which is far less toxic and easier to remove through filtration or precipitation. This reduction of Cr (VI) to Cr (III) is achieved by adding reducing agents such as ferrous sulphate ( $\text{FeSO}_4$ ) or

sodium sulfite ( $\text{Na}_2\text{SO}_3$ ), which donate electrons to the chromium, thereby lowering its toxicity and making it more manageable in treatment processes. Redox reactions can also be employed to neutralize other contaminants, such as organic compounds and pathogens. Oxidizing agents like chlorine ( $\text{Cl}_2$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and ozone ( $\text{O}_3$ ) are frequently used in these processes. These agents function by accepting electrons during the reaction, thereby breaking down or neutralizing pollutants. For example, chlorine can be used to disinfect water by oxidizing harmful microorganisms, while hydrogen peroxide and ozone are effective in breaking down organic contaminants and removing color or odor from water sources.

Although redox processes are highly effective in treating a wide range of contaminants, they do require careful control and monitoring to ensure optimal results. The precise dosing of oxidizing and reducing agents is critical to achieving the desired chemical transformations while avoiding the formation of secondary pollutants or unintended by-products. For example, overuse of chlorine can lead to the formation of harmful chlorine by-products, such as trihalomethanes (THMs), which are regulated due to their carcinogenic potential.

Additionally, redox reactions may require sophisticated equipment, such as advanced dosing systems, reaction chambers, and real-time monitoring devices, to maintain the proper balance of chemicals and ensure efficient treatment. This can increase the complexity and cost of the process, especially in large-scale applications. Overall, oxidation-reduction reactions are a powerful and versatile tool in water treatment, enabling the conversion of harmful contaminants into less toxic or more easily removed forms. The use of oxidizing agents like chlorine, hydrogen peroxide, and ozone, along with reducing agents such as ferrous sulphate and sodium sulfite, can effectively treat a variety of pollutants, including heavy metals and organic contaminants. However, the need for precise control and the potential for secondary pollution means that this method often requires sophisticated equipment and expert management to ensure optimal performance.

#### **2.4.3.4 Ion exchange**

Ion exchange is a water treatment process that involves the exchange of undesirable ions in wastewater with more desirable ones using ion exchange resins. This process relies on the principle that certain resins contain functional groups capable of attracting and exchanging specific ions. During treatment, contaminant ions, such as nitrates, arsenic, and heavy metals, are attracted to the resin, while beneficial ions like sodium or hydrogen are released in exchange

(Zhao and Wang, 2021). As a result, the target contaminants are removed from the water, making it cleaner and safer for use or discharge. Ion exchange is particularly effective for removing specific contaminants, including highly toxic metals such as lead (Pb), chromium (Cr), and arsenic (As), as well as other pollutants like nitrates, which are common in agricultural runoff. The selectivity of ion exchange resins allows for the targeted removal of these contaminants without affecting other elements in the water. This method has proven to be an essential tool in treating water sources contaminated with heavy metals and providing high-quality water in industrial and drinking water systems (Zhao and Wang, 2021).

Despite its effectiveness, ion exchange has some limitations that must be considered. One of the major drawbacks is the high cost of ion exchange resins, which can make the process expensive, particularly in large-scale applications. The resins require periodic regeneration, as they become saturated with contaminant ions after prolonged use. Regeneration involves using chemical solutions to remove the accumulated contaminants from the resin and restore its ability to exchange ions (Gao, Cui and Deng, 2021). This process adds to the operational costs and can generate waste products that require proper disposal.

Additionally, the effectiveness of ion exchange can be influenced by factors such as water pH, the presence of competing ions, and the concentration of contaminants, which can complicate the treatment process. Despite these challenges, ion exchange remains a widely used and reliable method for removing specific contaminants, particularly in situations where high levels of precision and effectiveness are required (Shemer, Wald and Semiat, 2023). Overall, while ion exchange is a powerful and efficient method for removing specific contaminants like heavy metals, arsenic, and nitrates, its high operational costs and need for periodic resin regeneration limit its widespread use in large-scale applications. Continued advancements in resin technology and regeneration techniques may help reduce the costs associated with this method, making it more accessible for large-scale environmental and industrial water treatment systems.

#### **2.4.3.5 Advanced oxidation processes (AOPs)**

Advanced Oxidation Processes (AOPs) are a group of highly efficient water treatment methods that involve the generation of highly reactive hydroxyl radicals ( $\bullet\text{OH}$ ). These radicals are capable of degrading both organic and inorganic pollutants, including heavy metals, by breaking down complex contaminants into simpler, less toxic substances (Deng and Zhao, 2015). AOPs

are particularly effective in treating water or wastewater that contains a wide range of pollutants, as they can degrade stubborn contaminants that are resistant to conventional treatment methods.

Common techniques used in AOPs include Fenton's reagent, UV photolysis, and ozone oxidation. Fenton's reagent, which consists of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and iron salts (usually ferrous sulfate), generates hydroxyl radicals in the presence of an acidic environment. These radicals then interact with contaminants, breaking them down into less harmful compounds (Amor *et al.*, 2021). UV photolysis involves the use of ultraviolet (UV) light to activate chemical reactions that produce hydroxyl radicals, which are effective at degrading both organic and inorganic substances. Ozone oxidation uses ozone ( $\text{O}_3$ ), a powerful oxidizing agent, to generate hydroxyl radicals and directly degrade pollutants, including heavy metals, through oxidation (Amor *et al.*, 2021).

AOPs are particularly useful in breaking down complex and hazardous contaminants that are often difficult to treat using traditional methods. In the context of heavy metal removal, these processes can effectively reduce the toxicity of metals by promoting the oxidation of soluble metal ions into insoluble forms, which can then be easily removed by filtration or precipitation. Additionally, AOPs are capable of breaking down organic compounds such as solvents, pesticides, and pharmaceutical residues, which may co-exist with heavy metals in wastewater (Amor *et al.*, 2021).

However, despite their effectiveness, AOPs have certain limitations. One of the major drawbacks is their high energy requirement, particularly for processes like UV photolysis and ozone oxidation, which require significant amounts of electricity or ozone generation. The need for precise control and careful handling of chemicals, such as hydrogen peroxide and ozone, can also increase the complexity and cost of the process. Additionally, AOPs may produce intermediate by-products during the degradation of pollutants, which may require further treatment to ensure complete removal and avoid secondary pollution (Ma *et al.*, 2021). Overall, Advanced Oxidation Processes (AOPs) are a powerful and efficient tool for removing heavy metals and other complex pollutants from water. By generating highly reactive hydroxyl radicals, AOPs can break down both organic and inorganic contaminants, including heavy metals, into less toxic forms. However, their high energy requirements and the need for careful handling of chemicals make AOPs more suitable for specific applications where high treatment efficiency is required, despite the associated operational costs.

#### 2.4.4 Adsorption

Adsorption is a widely preferred technique due to its cost-effectiveness, high efficiency, and minimal secondary waste generation. The process has gained significant attention for its ability to remove heavy metals, organic compounds, and other pollutants from wastewater (Satyam and Patra, 2024). Industrial waste materials, such as coal fly ash (Ankrah, Tokay and Snape, 2022), copper slag (Wu *et al.*, 2021), cement kiln dust (Elmaadawy *et al.*, 2025) and many others, are being increasingly explored as alternative low-cost adsorbents, addressing both waste management and water treatment needs. Additionally, the simplicity of adsorption processes makes them adaptable to a wide range of operational conditions, from large-scale industrial applications to decentralized water treatment systems.

##### 2.4.4.1 Types of adsorbents

Various adsorbents have been investigated for their ability to remove heavy metals and other pollutants effectively. These include:

- **Natural materials:** Natural adsorbents, such as clay, zeolites, and activated carbon derived from agricultural waste, are widely studied for their potential to remove heavy metals. These materials are abundant, cost-effective, and eco-friendly, making them attractive for environmental remediation (Xie *et al.*, 2024). Clay and zeolites, for example, have a high surface area and contain ion-exchange sites that facilitate the adsorption of metal ions. Activated carbon made from agricultural waste, such as coconut shells or rice husks, also shows significant potential for adsorbing heavy metals due to its high surface area and porosity (Kainth, Sharma and Pandey, 2024). However, while natural materials offer environmental benefits, they may require pre-treatment, such as acid washing or thermal activation, to enhance their adsorption capacity and optimize their effectiveness in removing pollutants (Kainth, Sharma and Pandey, 2024).
- **Industrial by-products:** Industrial by-products, such as fly ash, copper slag, and cement kiln dust, have gained attention as low-cost, abundant adsorbents. These materials are often produced in large quantities as waste from industrial processes, making them highly available for use in environmental applications (Pallewatta *et al.*, 2023). Fly ash, a by-product of coal combustion, is rich in silica and alumina, which provide active sites for metal ion adsorption (Lekgoba, Ntuli and Falayi, 2020). Copper slag, a waste material from copper smelting, contains iron oxide and silicate minerals that can adsorb heavy metals, including lead, arsenic, and chromium (Letina and

Letshwenyo, 2018). Similarly, cement kiln dust, produced during cement manufacturing, has functional groups that facilitate the uptake of metal ions (Elmaadawy *et al.*, 2025). While these industrial by-products are cost-effective and widely available, they may need to be treated or modified to improve their adsorption capacity and minimize potential leaching of toxic components.

- **Synthetic materials:** Synthetic adsorbents, including functionalized polymers, graphene oxide, and nanomaterials, have gained considerable attention due to their exceptional adsorption capacities and ability to target specific contaminants (Zarenezhad *et al.*, 2021). Functionalized polymers, such as polyethyleneimine and polystyrene derivatives, can be tailored to enhance metal ion binding through the introduction of specific functional groups, such as amines or carboxyl. Graphene oxide, a derivative of graphene, exhibits a high surface area, numerous oxygen-containing functional groups, and an ability to adsorb a wide range of pollutants, including heavy metals (Zarenezhad *et al.*, 2021). Nanomaterials, such as magnetic nanoparticles and carbon nanotubes, have shown remarkable potential for adsorbing heavy metals due to their large surface-to-volume ratio, high porosity, and tunable properties (Al-senani and Al-fawzan, 2018). However, the production of synthetic adsorbents often involves higher costs and more complex synthesis processes, which may limit their widespread use in large-scale applications. Overall, a variety of adsorbents, including natural materials, industrial by-products, and synthetic materials, have been explored for the removal of heavy metals and other pollutants. Each category offers distinct advantages in terms of cost, availability, and adsorption capacity. Natural materials are abundant and eco-friendly, though they may require pre-treatment to optimize their efficiency. Industrial by-products are promising due to their low cost and high availability, while synthetic materials, although costly, offer exceptional adsorption capacities and are highly tailored to specific applications. The choice of adsorbent depends on the specific contaminants to be removed, the treatment goals, and the available resources.

#### **2.4.4.2 Factors affecting adsorption efficiency of adsorbents**

The effectiveness of the adsorption process is influenced by several critical factors such as pH of solution, temperature, contact time, dosage, ion concentration and many more. Such factors include:

- **Solution pH:** The pH of the solution plays a vital role in the adsorption process as it affects both the ionization state of the adsorbate and the charge on the adsorbent surface. Different pollutants may ionize to different extents at varying pH levels, which impacts their interaction with the adsorbent (Haghseresht, Nouri and Lu, 2002). For example, in acidic conditions, metal ions like lead or cadmium may exist in their cationic form, which could be more easily adsorbed by negatively charged adsorbents. Conversely, in alkaline conditions, the adsorbate may become negatively charged, reducing the interaction with the adsorbent surface (Gerçel and Gerçel, 2007). Therefore, maintaining an optimal pH is crucial for maximizing adsorption efficiency.
- **Contact Time:** The contact time between the adsorbent and the solution is a key factor in determining the overall adsorption capacity. Sufficient contact time allows the system to reach adsorption equilibrium, ensuring that the maximum amount of pollutant is adsorbed. If the contact time is too short, the adsorbent may not have enough time to adsorb the pollutants effectively (Murphy *et al.*, 2023). However, excessively long contact times beyond equilibrium may not result in significant improvements in adsorption efficiency and could lead to unnecessary resource use.
- **Adsorbent Dosage:** The dosage of the adsorbent is another crucial factor in the adsorption process. Increasing the adsorbent dosage provides more active sites for adsorption, which can lead to a higher removal capacity (Murphy *et al.*, 2023). However, if the dosage is too high, the adsorbent particles may aggregate, leading to a reduction in surface area and, consequently, a decrease in adsorption efficiency (Sabela *et al.*, 2019). Therefore, determining the optimal adsorbent dosage is essential to achieve effective pollutant removal without wastage or loss of efficiency.
- **Initial Metal Concentration:** The initial concentration of metal ions in the solution significantly impacts the adsorption process. At high concentrations, the adsorbent may become saturated with metal ions, leading to a decrease in removal efficiency (Soço and Kalembkiewicz, 2013). When there are more metal ions than available active sites on the adsorbent, the system can no longer effectively remove additional pollutants. Therefore, in cases of high initial metal concentration, the adsorbent's capacity to remove contaminants may be reduced, and the process may need to be optimized through increased dosages or pre-treatment methods (Ali, 2014).
- **Temperature:** Temperature has a temperature-dependent effect on the adsorption process. In general, higher temperatures can enhance the diffusion of adsorbate molecules into the pores of the adsorbent, improving the rate of adsorption (Zafar *et al.*,

2019). Elevated temperatures can also increase the kinetic energy of both the adsorbent and adsorbate, which may promote stronger interactions. However, excessively high temperatures may lead to the desorption of previously adsorbed contaminants or cause damage to the adsorbent material. Therefore, maintaining an optimal temperature is important to ensure efficient adsorption while avoiding potential degradation of the adsorbent (Bamal *et al.*, 2025). In conclusion, the efficiency of the adsorption process is influenced by various factors, including the solution pH, contact time, adsorbent dosage, initial metal concentration, and temperature. Careful optimization of these parameters is essential to maximize pollutant removal and ensure the effectiveness of the treatment process. Understanding the specific conditions that favor adsorption for a given pollutant is key to achieving the desired outcomes and maintaining efficient, cost-effective water treatment.

#### **2.4.4.3 Adsorption mechanisms**

The adsorption process involves a series of interactions between the adsorbate (contaminants) and the adsorbent surface. These interactions can be categorized into physical adsorption and chemical adsorption (Agboola and Benson, 2021). Physical adsorption is governed by Van der Waals forces and is typically reversible, while chemical adsorption involves the formation of covalent or ionic bonds between the adsorbate and the adsorbent. Mechanisms such as ion exchange, surface complexation, and pore diffusion contribute to the overall adsorption efficiency. Factors like pH influence the surface charge of the adsorbent, while temperature can affect the rate of adsorption and equilibrium (Akhtar *et al.*, 2024). **Table 2.5** summarized different adsorbents with different parameters from previous studies.

**Table 2.5:** Distinct adsorbents and their performance from different studies

Heavy metal ions	Adsorbents	Optimal solution pH	Initial concentration (mgL <sup>-1</sup> )	Maximum Removal efficiency (%)	Maximum Adsorption capacity (mgg <sup>-1</sup> )	Batch isotherms models used	Equilibrium contact time (hrs)	Mode of adsorption	References
Ni (II)	Coal fly ash	8	5 -100	99.6	-	Langmuir and Freundlich	1	Batch	(Sočo and Kalemkiewicz, 2013)
Cu (II)		8 – 10		90.9			2		
Cu (II)	Coal dust	4	5 -100	100	-	Langmuir, Freundlich and Redlich - Peterson	1	Batch	(Kapur and Mondal, 2014)
Ni (II)									
Pb	Cement kiln dust	6 -9	20 -200	98	-	Langmuir and Freundlich	4	Batch	(Elmaadawy et al., 2024)
Zn				94					
Cu				92					
Cd				90					
As	Water treatment sludge and Red mud	2 -12	1mM	-	-	Langmuir and Freundlich	2	Batch	(Zhou and Haynes, 2012)
Se									
Cu (II)	Groundnut seed cake powder, Sesame seed cake, and Coconut cake powder	5	10	-	4.24	Langmuir and Freundlich	0.5	Batch	(Kumar et al., 2019)
Ni (II)	Sugarcane bagasse, Passion fruit waste, Orange peel, Pineapple peel, Commercial activated carbon	6	50, 100, 150, 200 and 300	-	14.75 – 63.50	-	6	Batch	(Souza, Dotto and Salau, 2018)

#### 2.4.4.4 Regeneration and reusability of adsorbents

The sustainability of adsorption processes depends on the ability to regenerate and reuse the adsorbent. Regeneration involves restoring the adsorbent's adsorption capacity using techniques such as thermal treatment, chemical washing with acids or alkalis, and solvent extraction (Badran *et al.*, 2023). Effective regeneration ensures the economic feasibility of adsorption systems and minimizes waste generation. For example, acid washing has been successfully used to desorb metal ions from fly ash, restoring its adsorption efficiency for subsequent cycles (Satyam and Patra, 2024). Reusability studies have shown that many adsorbents retain their efficiency for multiple cycles, making them suitable for long-term applications (Table 2.6).

**Table 2.6:** Regeneration of distinct adsorbents from previous studies

Adsorbent	Heavy Metals ions	Eluents Used	Remarks	References
Iron oxide coated eggshell powder	Cu (II)	0.01 M and 0.1 M of HCl, HCOOH, EDTA, and NaOH	The highest regeneration capacity was observed with 0.1 M HCl, followed by 0.1 M HCOOH, 0.1 M EDTA, and 0.01 M NaOH. Further research is needed to determine the appropriate disposal methods for the media.	(Ahmad, Kumar and Haseeb, 2012)
Water Treatment Sludge and Red Mud	As (III), As (V), Se (IV) and Se (VI)	0.5M NaOH, HNO <sub>3</sub>	The safe disposal of the adsorbent is a significant concern. Considering the recovery of metals as an alternative should be prioritized.	(Zhou and Haynes, 2012)
Coal dust	Cu (II) and Ni (II)	HCl, HNO <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub> and distilled water	Spent coal dust can be utilized as fuel and recovered metal solutions may be used in industries.	(Kapur and Mondal, 2014)
Cement brick waste	Cu (II), Ni (II) and Fe (II)	0.1M Na OH	Spent adsorbent can be repurposed for backfilling.	(Mokokwe and Letshwenyo, 2022)

#### 2.4.4.5 Environmental impacts of adsorbents

The environmental safety of adsorbents, particularly their leachability and toxicity, must be evaluated. Regulatory standards mandate that the materials used should not release harmful

substances into the environment during or after use. Adsorption is a widely preferred technique due to its cost-effectiveness, high efficiency, and minimal secondary waste generation. Industrial waste materials, such as coal fly ash and copper slag, are increasingly being explored as alternative low-cost adsorbents (Liu *et al.*, 2024). Studies have demonstrated their potential in removing metals like Cu and Ni from wastewater with high adsorption efficiencies (Zhang and Wang, 2015).

## **2.5 Artificial Neural Networks (ANNs) and Adaptive Neuro-Fuzzy Inference Systems (ANFIS) models in Adsorption Technology**

Advanced computational tools like Artificial Neural Networks (ANNs) and Adaptive Neuro-Fuzzy Inference Systems (ANFIS) have gained significant attention in the modelling and optimization of complex systems, including adsorption processes in wastewater treatment (Souza, Dotto and Salau, 2018). These tools are highly effective due to their ability to capture nonlinear relationships and interactions among multiple variables, enabling precise predictions and informed decision-making for process optimization. ANNs are inspired by the human brain's structure and function, consisting of interconnected nodes (neurons) arranged in layers. These networks are trained using experimental data to recognize patterns and relationships between input variables (e.g., pH, contact time, adsorbent dosage, initial pollutant concentration) and output variables (e.g., adsorption efficiency or pollutant removal percentage) (Costa *et al.*, 2025). By adjusting the network's weights and biases during the training process, ANNs can accurately predict system behavior under varying conditions. This capability makes them invaluable for identifying optimal process parameters and predicting adsorption performance across a wide range of operating conditions, even for untested scenarios (Fiyadh *et al.*, 2023). On the other hand, ANFIS combines the learning capability of ANNs with the reasoning ability of fuzzy logic. Fuzzy logic is based on "if-then" rules that describe complex systems in a human-readable format, incorporating uncertainty and imprecision. ANFIS models use fuzzy inference systems to map inputs to outputs, while the neural network component optimizes the membership functions and rules through iterative learning (Walia, Singh and Sharma, 2015). This hybrid approach allows ANFIS to handle highly nonlinear processes, making it particularly suitable for adsorption systems where variables often interact in complex ways. ANFIS not only provides accurate predictions but also offers interpretability by outlining the fuzzy rules governing the process, aiding in a deeper understanding of system dynamics (Souza, Dotto and Salau, 2018).

Both ANNs and ANFIS excel in optimizing adsorption processes by analyzing large datasets and identifying the most influential factors affecting adsorption efficiency. These tools have been applied to optimize key parameters such as adsorbent dosage, contact time, initial concentration, and temperature (Onu *et al.*, 2021a). For example, ANNs can evaluate the synergistic effects of these variables to determine optimal operating conditions that maximize pollutant removal while minimizing adsorbent usage and energy consumption. Similarly, ANFIS can identify optimal parameter ranges by incorporating linguistic rules, providing insights into the trade-offs between competing objectives such as cost-effectiveness and environmental performance (Onu *et al.*, 2021a).

Moreover, these computational models reduce the need for extensive experimental work, saving time and resources in the development of adsorption-based wastewater treatment technologies. By integrating experimental data, ANNs and ANFIS can simulate adsorption processes under different conditions, predict the behavior of new adsorbents, and explore the effects of process modifications without the need for physical trials (Souza, Dotto and Salau, 2018). This not only accelerates the research and development process but also enhances the scalability and adaptability of adsorption systems for real-world applications. Overall, ANNs and ANFIS are powerful tools for modeling and optimizing adsorption processes, providing accurate predictions, reducing operational costs, and enhancing the efficiency of wastewater treatment technologies. Their ability to handle complex, nonlinear systems makes them indispensable for advancing sustainable water treatment solutions, particularly in scenarios requiring high precision and adaptability (Fiyadh *et al.*, 2023).

## **2.6 Research Gaps Identified from the Review**

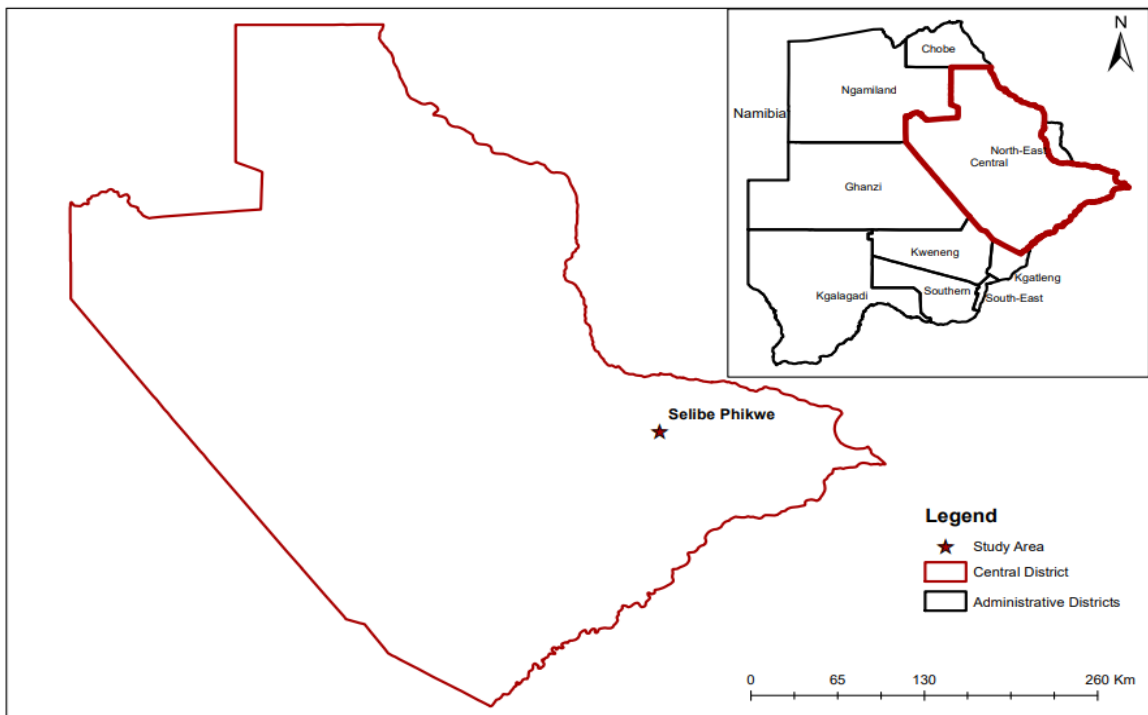
Despite significant advancements in wastewater treatment technologies, several gaps remain. First, while adsorption has been widely recognized as an effective method, there is limited research on the performance of novel low-cost adsorbents such as fayalite slag. Key parameters like adsorption kinetics, thermodynamics, and regeneration potential require further investigation. Additionally, the influence of competing ions in wastewater on adsorption efficiency has been inadequately studied. Second, although ANNs and ANFIS have demonstrated potential in optimizing treatment processes, their application in modeling adsorption using industrial waste materials remains underexplored. A comprehensive understanding of how these models can predict multi-ion adsorption scenarios would be beneficial. Lastly, there is insufficient data on the environmental impact and leachability of

adsorbents, particularly concerning heavy metal desorption under varying pH conditions. Future studies should focus on evaluating the long-term sustainability and environmental safety of these materials.

### 3. CHAPTER THREE: RESEARCH METHODOLOGY

#### 3.1 Description of Media and Sampling Site

Selebi-Phikwe town (**Figure 3.1**), situated in the northeastern region of Botswana, was home to the major copper and nickel mining company known as BCL (Bamangwato Concessions Limited). As reported by (Motswaiso *et al.*, 2019), 90% of the 418 mm of annual rainfall that Selebi-Phikwe receives is concentrated between the months of October and March. The average maximum temperature ranges from 13.0°C in June to 39°C in October. Between July and January, the mean low temperature varies from 5°C to 20°C. BCL mined the region's abundant mineral reserves for copper and nickel ores using both open-pit and underground techniques. The important metals (copper and nickel) were extracted from these ores by a variety of on-site processing methods. BCL copper-nickel mine generated a large amount of Fayalite slag (FS) waste as a byproduct of its operations. It is generated when impurities in the ore, such as iron and silica, react with fluxes and oxidizing chemicals during the smelting process. Fayalite slag typically contains significant levels of iron oxide ( $\text{Fe}_2\text{O}_3$ ) and silica ( $\text{SiO}_2$ ), as well as trace amounts of other elements. The mine has been operational since August 1956. By August 2016, the BCL (Ltd) mine produced 81,000 tonnes of slag per month (Letina and Letshwenyo, 2018).



**Figure 3.1:** Media sampling site

### **3.2 Analytical Instrumentation**

The fresh and spent FS was ground and analyzed using various techniques to determine its mineralogical structure, elemental composition, and morphology. These techniques included X-Ray Diffraction (XRD) using a Bruker D8 Advance diffractometer, X-Ray Fluorescence (XRF) with a Delta Professional system, and Scanning Electron Microscopy (SEM) with a Carl Zeiss FEGSEM Gemini 500. Ionic concentrations of the adsorbates and filtrates were quantified using a calibrated Inductively Coupled Plasma-Optical Emission Spectrometer (iCAP 7000 SERIES). The FS and solutions were agitated with an Orbital shaker from Thermo Scientific, supplied by Lamworld Technologies Pty Ltd. Functional groups present in FS before and after heavy metal adsorption were identified using a Fourier Transform Infrared Spectrometer (FTIR, Vertex 70V model) manufactured and supplied by Bruker GmbH in 2018.

### **3.3 Chemical Reagents Used**

A simulated industrial effluent was created to mimic the ionic concentrations of divalent copper, nickel, and iron typically present in the effluents from metal refinery operations. Stock solutions were prepared using hydrated salts, specifically nickel sulphate ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ) with 99% purity, ferrous sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) with 99% purity, and copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) with 99.5% purity, sourced from Glass World, Minema, and Rochelle Chemicals, respectively. To preserve the samples and control hydrolysis, as well as to adjust pH, 65% nitric acid and sodium hydroxide (NaOH) solutions were utilized, both provided by Sigma-Aldrich.

### **3.4 Preparation of FS**

Fayalite scoria samples were collected from the waste heaps of BCL (Ltd) mine. Seven vertical test holes were excavated on each waste heap using picks and shovels. Samples from each hole were collected, thoroughly mixed through quartering, and stored in plastic bags prior to use as per (Letina and Letshwenyo, 2018). The scoria was thoroughly washed with deionized (DI) water to remove soluble organic materials, dust, and other surface impurities. After washing, the samples were air-dried in a controlled, contamination-free environment to ensure no external contaminants affected the results. Once dried, the scoria was carefully inspected to remove oversized or irregular fragments, and then crushed into smaller, uniform particles using a jaw crusher to enhance surface area, which is essential for efficient adsorption. The crushed material was sieved through mesh screens to obtain particles of the desired size range of 0.6mm to 4.75mm diameter and stored in airtight containers to maintain integrity and prevent exposure

to moisture or contaminants, ensuring the fayalite scoria was clean, uniform, and optimized for use as an adsorbent in pollutant removal studies.

### **3.5 Physical characterization of FS**

#### **3.5.1 Particle size distribution of FS**

The particle size distribution of FS was assessed using mechanical sieving, following the standard procedure outlined by the American Society for Testing and Materials (ASTM C136). The coefficient of uniformity (Cu) for the media was calculated after grinding the brick waste. For copper smelter slag, the particle size distribution and uniformity coefficient were determined directly, as the material was already in granular form. To evaluate the uniformity of particle distribution, the coefficients of uniformity (Cu) of the media were calculated using the specified equation (1):

$$Cu = \frac{D_{60}}{D_{10}} \quad (1)$$

where, Cu represents the uniformity coefficient, D10 refers to the particle size corresponding to 10% finer by weight on the particle size distribution curve (with 90% being larger), and D60 indicates the particle size at which 60% of the particles are finer (and 40% are larger). The gradation coefficient (Cc) of the media was calculated using the equation (2) provided below:

$$Cc = \frac{(D_{30})^2}{D_{60} \times D_{10}} \quad (2)$$

where in this equation, D30 corresponds to the particle size at which 30% of the material is finer by weight (and 70% is larger). The definitions of D10 and D60 remain as previously described.

#### **3.5.2 Saturated Hydraulic conductivity of FS**

The saturated hydraulic conductivity test evaluates the rate at which water flows through the pores of FS. This was carried out by applying water at a constant pressure to a media sample with known dimensions, enabling the flow rate to be measured. The saturated hydraulic conductivity of FS was determined using the constant head method, which is well-suited for granular materials. The procedure involved allowing water to flow through the media under steady-state conditions, with the volume of water passing through the media recorded over a specific time period. The hydraulic conductivity (K) was calculated using the following equation, as described by (Letina and Letshwenyo, 2018):

$$K = \frac{QL}{Ath} \quad (3)$$

where, in this equation, K represents the saturated hydraulic conductivity, Q is the water discharge, L is the distance between the manometers, A denotes the cross-sectional area of the media, t is the total discharge time, and h is the head difference between the manometers.

### 3.5.3 Bulk, particle densities, porosities of FS

The bulk density of the adsorbent was measured by placing 50 g of the material into a 100 mL measuring cylinder. The material was allowed to settle within the cylinder, facilitated by tapping the cylinder three times. The final volume of the settled material was carefully noted. The bulk density was then calculated according to the method described by (Dan-Asabe *et al.*, 2013) using the equation provided (4):

$$\rho_b = \frac{\text{mass of media (g)}}{\text{volume of media (mL)}} \quad (4)$$

where  $\rho_b$  is the denotes bulk density of the media.

Particle density ( $\rho_p$ ) is defined as the ratio of the total mass of solids to their solid volume. To determine particle density, 60 mL of water was poured into a 100 mL measuring cylinder, and the initial volume was recorded, assuming water's density to be 1.0 g/cm<sup>3</sup>. Next, 50 g of the adsorbent was added to the water in the cylinder. The mixture was gently stirred to eliminate any air trapped between the water and the particles. The final volume of the mixture was recorded, and the difference between the initial and final volumes was taken as the volume of the adsorbent particles. The particle density was calculated using the following mathematical equation (5):

$$\rho_p = \frac{\text{mass of media (g)}}{\text{particles volume (mL)}} \quad (5)$$

Porosity is the portion of adsorbent occupied by the pores. It is computed utilizing the values of bulk and particle density using the following equation (6):

$$n = 1 - \frac{\rho_b}{\rho_p} \times 100 \quad (6)$$

where; n shows porosity (%),  $\rho_b$  represents bulk density and (g cm<sup>-3</sup>),  $\rho_p$  represents particle density (g cm<sup>-3</sup>) of FS.

### 3.6 Adsorbent Leaching Test

The leaching behavior of FS was investigated by agitating the adsorbents for 24, 48, and 72 hours in deionized (DI) water with a pH of 6.81. After each contact time, the mixtures were filtered to separate the leachates, which were then analyzed for metal ion concentrations using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, iCAP 7000 SERIES). The filtrates were tested for concentrations of heavy metals. Target elements were

identified using an X-Ray Fluorescence Analyzer (Delta Professional). Batch experiments were performed in duplicate, with mean values and standard deviations calculated. The ICP-OES was calibrated before each analysis following standard method. The measured concentrations of borderline metals were compared to the threshold values established by the United States Environmental Protection Agency (USEPA) to assess the potential toxicity of the media.

### 3.7 Adsorbate Preparation

In deionized water (DI), hydrated salt of Copper Sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), weighing 3.9060 g,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  weighing 4.484g and 4.975 g respectively were dissolved to simulate or mimic wastewater with a concentration of  $1000 \text{ mgL}^{-1}$ . By diluting the stock solution with DI water, the various concentrations were created. Initial concentrations of the adsorbates were fixed at  $200 \text{ mgL}^{-1}$  to mimic industrial effluents generated in base metal refineries. As suggested by (Haile and Fuerhacker, 2018), 65% Nitric acid ( $\text{HNO}_3$ ) was employed as a preservative to prevent the hydrolysis of the prepared adsorbate.

### 3.8 Adsorption Studies

Adsorption experimental tests were conducted using batch adsorption mode. The initial pH of the prepared stock solution was adjusted using  $0.1 \text{ molL}^{-1} \text{ HNO}_3$  to be in acidic condition or  $0.1 \text{ molL}^{-1} \text{ NaOH}$  as per (Sulaiman *et al.*, 2021) to be alkaline. The initial and final concentrations of the target adsorbates ( $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Ni}^{2+}$ ) were determined using a calibrated ICP-EOS. All adsorption experimental operations were conducted in a 250mL Erlenmeyer flasks, where varying amounts of FS (ranging from 0.6mm to 4.75mm diameter) were combined with 100 mL of solution and orbitally shaken at 120 rpm using an orbital shaker. The predetermined contact times were ranging from 5 to 90 minutes and tests were conducted at room temperature ( $20^\circ\text{C}$ ). The initial solution pH was varied at 2-12 pH units by homogeneously adding dilute  $\text{HNO}_3$  and  $\text{NaOH}$  for pH adjustment. Preliminary tests indicated that the sorption process reached an equilibrium stage after 30 min. To investigate the effect of dosage that influenced the adsorption capacities, different FS dosage, ranging between 0.5 and 6.0 g, was used. The adsorbent removal efficiency (%R) as well as adsorption capacity at the time,  $t$  (qt) of media were respectively calculated using equations (7 and 8) as reported by (Ouyang *et al.*, 2019) and (Sanad *et al.*, 2021).

$$\%R = \frac{(C_i - C_t)}{C_i} \times 100 \quad (7)$$

where %R denotes removal efficiency of media,  $C_i$  and  $C_t$  represent initial concentration and concentration at time,  $t$  respectively.

$$qt = \frac{(C_i - C_t) V}{M} \quad (8)$$

where  $qt$  symbolizes adsorption capacity at time,  $t$ ,  $C_i$  and  $C_t$  represent initial concentration and concentration at time,  $t$  respectively,  $V$  represent the volume of solution and  $M$  denotes mass of the media.

### 3.9 Adsorption Kinetic and Isotherm Models

The progression of adsorption with time is clarified through the examination of adsorption kinetics, offering insight into the dynamics of the process (Kapur and Mondal, 2014). Understanding these kinetics is pivotal in determining the rate at which adsorption occurs and the mechanisms controlling it. To delve into the rate-controlling mechanisms, various kinetic models such as Lagergren pseudo first order, pseudo second order, and intra-particle diffusion were compared. The linear representations of these mathematical models, facilitating analysis and interpretation of reaction mechanisms involved are shown in equations 9 to 11 as applied by (Mishra *et al.*, 2017):

$$\log (q_e - q) = \log q_e - \frac{K_1}{2.303} t \quad (9)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) and  $q$  ( $\text{mg g}^{-1}$ ) represent the quantities of heavy metals adsorbed at equilibrium and at a specific time  $t$  (in minutes), respectively. A linear graph of  $\log (q_e - q)$  versus  $t$  was generated using equation (9). Additionally, the experimental data were analyzed using the pseudo-second-order kinetic model, expressed in the following form:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

where here,  $k_2$  ( $\text{g} / (\text{mg min})$ ) represents the rate constant of the second-order equation,  $q$  ( $\text{mg/g}$ ) is the amount of adsorption at time  $t$  (minutes), and  $q_e$  ( $\text{mg g}^{-1}$ ) is the quantity of heavy metals adsorbed at equilibrium. A plot  $t/q_t$  against  $t$  was created, and the  $R^2$  values were derived from the graphs. The equation for the intraparticle diffusion model is expressed as follows:

$$q = K_{id} t^{0.5} + C \quad (11)$$

where in this context,  $q$  ( $\text{mg g}^{-1}$ ) represents the adsorption capacity at time  $t$  (minutes),  $K_{id}$  ( $\text{mg}/(\text{gmin}^{-0.5})$ ) is the rate constant for intraparticle diffusion, and  $C$  is the intercept, which provides insight into the boundary layer thickness. If intraparticle diffusion is the only rate-determining step, the plot of  $q$  versus  $t^{0.5}$  should be linear and pass through the origin.

In case of isotherm models, it is noteworthy to understand that optimization of parameters such as capacity of media, adsorption pathway mechanisms, and effective adsorption system design is achieved through the analysis of adsorption kinetic and isotherms, which are influenced by the specific characteristics and nature of the process (Sočo and Kalembkiewicz, 2013). In this case, a comparison between the Langmuir and Freundlich isotherm models was done to ascertain the adsorption capacity of the adsorbent. The Langmuir model posits that adsorption takes place at distinct, uniform active sites within the adsorbent, while with Freundlich model, adsorption occurs in heterogenous sites (Kapur and Mondal, 2014). The linear representation of Langmuir model and mathematical expression for Freundlich isotherm model in logarithmic form are as respectively represented (Equations 12 and 13):

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} K_L C_e} \quad (12)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) represents the amount of contaminant adsorbed per unit weight of the media,  $C_e$  ( $\text{mg L}^{-1}$ ) is the equilibrium concentration of the adsorbate,  $q_{\max}$  ( $\text{mg g}^{-1}$ ) denotes the monolayer adsorption capacity of the adsorbent, and  $K_L$  ( $\text{L mg}^{-1}$ ) is the Langmuir adsorption constant associated with adsorption free energy (Kargi and Cikla, 2006). According to the Langmuir model, adsorption occurs on homogeneous active sites of the adsorbent, while the Freundlich model describes adsorption on heterogeneous, multilayer surfaces. The Freundlich isotherm is expressed in the following equation (Equation 13):

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (13)$$

where in this equation,  $(1/n)$  represents the adsorption intensity, and  $K_f$  is the Freundlich constant associated with the adsorption capacity  $\{(\text{mg g}^{-1}) (\text{mg L}^{-1})^n\}$ . The adsorption intensity was determined from the slope and intercept of the plotted data as per (Flouty and Estephane, 2012).

### 3.10 Adsorption Thermodynamic Studies

The objective of this study was to determine the energy requirements of an adsorbate to migrate from the solution to the adsorbent surface. In this study, the linearized thermodynamic equations were applied to determine thermodynamic parameters, which were computed using the equations provided by (Al-Ghouti and Al-Absi, 2020). From these equations, the thermodynamic parameters, namely the Gibbs free energy change ( $\Delta G^\circ$ ), entropy ( $\Delta S^\circ$ ) and enthalpy ( $\Delta H^\circ$ ), were derived. Additionally,  $\Delta S^\circ$  and  $\Delta H^\circ$  of the adsorption process were evaluated using the Van't Hoff's equation (Aljeboree, Alshirifi and Alkaim, 2017). The

alteration in entropy and enthalpy values was obtained from the slope as well as intercept of the Van't Hoff's plot. Equation 14 to 16 were applied in this thermodynamic study;

$$\text{Ln}K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (14)$$

$$\Delta G^0 = -RT \text{Ln}K_d \quad (15)$$

$$K_d = \frac{C_i - C_e}{C_e} \times \frac{V}{M} \quad (16)$$

where T (K) represents the absolute temperature,  $K_d$  ( $\text{Lg}^{-1}$ ) denotes the distribution coefficient whereas R ( $\text{J.molK}^{-1}$ ) represents the universal gas constant.

### 3.11 Reusability Studies

The objective of adsorbent reusability operation is to restore the exhausted active pore sites utilizing desorption solvents (Sulaiman *et al.*, 2021). Herein, an effective regeneration eluent,  $0.1 \text{ molL}^{-1}$  NaOH was used to desorb or recover metals. The test was conducted by mixing 2.0 g of FS with 100mL stork in 250 mL Erlenmeyer flasks. The mixture was subjected to agitation for a day (24hr) at 120 rpm. Thereby, the mixture was filtered through a 0.45 microns filter paper. The used FS was rinsed with distilled water to attain neutral pH, air-dried, and reused in the next cycle. A  $0.1 \text{ molL}^{-1}$  NaOH and FS were then mixed and agitated for 24 hrs again. Then physical separation of used residue (FS) and the solution was done through filtration with filter paper. The same method was repeated for 3 regeneration cycles. The reusability efficiency (RE) was computed using mass balance equation (Equation 17).

$$\text{RE} = \frac{C_i - C_t}{C_i} \times 100 \quad (17)$$

where RE (%) denotes removal efficiency of FS,  $C_i$  and  $C_t$  represent initial concentration and concentration at the time, t respectively.

### 3.12 Statistical and Error Analysis

Batch adsorption tests were performed in triplicate, and mean values were computed using Microsoft Excel's XLSTAT statistical analysis package. While linearization of models may introduce variations between theoretical and experimental values, leading to potential errors, the coefficient of determination ( $R^2$ ) may not effectively reflect the model's accuracy in such cases. Therefore, to account for these fractional errors, the Root Mean Square Error (RMSE) is employed as a more reliable method for model validation. RMSE provides a better measure of how well the model fits the observed data by quantifying the average magnitude of the errors between experimental and predicted values. A lower RMSE value indicates better model

performance, as it signifies a smaller deviation between observed and predicted data (Lekgoba, Ntuli and Falayi, 2020).

$$\text{RMSE} = \sum \left( \frac{q_{e,\text{exp}} - q_{e,\text{model}}}{q_{e,\text{model}}} \right)^2 \quad (18)$$

where RMSE is Root Mean Square Error,  $q_{e, \text{exp}}$  is the experimental adsorption capacity, and  $q_{e, \text{model}}$  is the model adsorption capacity.

### 3.13 Development of ANN and ANFIS models

The Artificial Neural Network (ANN) tool in MATLAB (R2021b) was used to model and optimize the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Ni}^{2+}$  ions onto FS. ANN is a powerful predictive modeling technique that mimics the functioning of the human brain and nervous system to establish complex relationships between inputs and outputs (Khan *et al.*, 2020). In this study, the ANN model was constructed with four input variables: adsorbent dosage, particle size, contact time, and initial pH. The output variables were the removal efficiency (%R) and adsorption capacity (mg/g) of FS. The input-output relationships in the ANN model were trained using the data from experimental adsorption tests. The training set consisted of experimental data obtained through batch adsorption tests, where real-world conditions were replicated. To ensure that the model is robust, a portion of the data was used for validation and testing, which helped assess the accuracy and generalizability of the model.

Additionally, ANFIS was integrated into the modeling approach to account for the inherent uncertainties and complexities in the adsorption process. ANFIS or Fuzzy Logic allows for modeling imprecise or vague input-output relationships, which are often present in real-world systems. This technique is particularly useful when the data exhibits non-linearity or when the system's behavior cannot be precisely described by traditional mathematical models (Walia, Singh and Sharma, 2015). By integrating both ANN and Fuzzy Logic, this study aimed to provide a more comprehensive understanding of the adsorption process, accounting for both clear patterns and uncertain elements in the data. The combination of these techniques allowed for a more accurate and adaptable model compared to traditional linear models.

#### 3.13.1 Validation and Comparison with Observed Data

To validate the performance of both the ANN and ANFIS models, the predicted adsorption capacities and removal efficiencies were compared against experimental data obtained from batch adsorption tests. The models were validated using the correlation coefficient (R) and Root

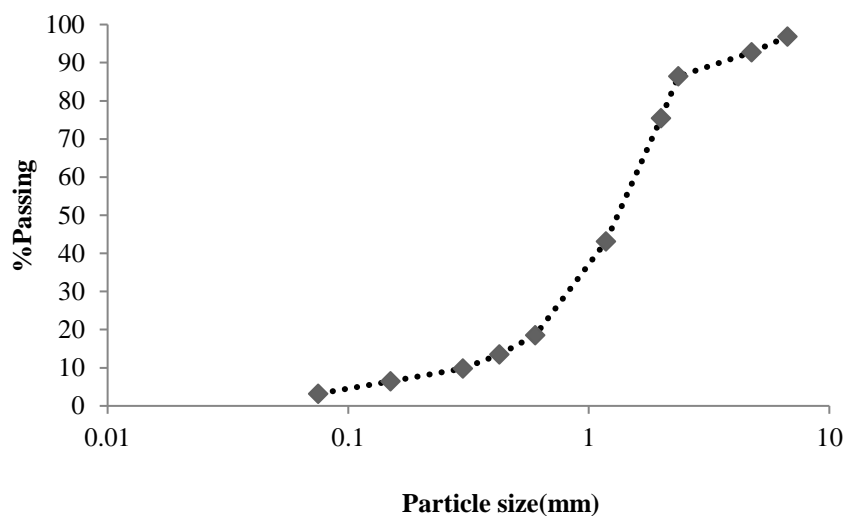
Mean Square Error (RMSE), which measures the strength and direction of the linear relationship between the observed and predicted values. A high correlation coefficient (R close to 1) indicates that the model accurately predicts the experimental results, a low R value suggests poor model performance, while vice versa with RMSE (Kumari *et al.*, 2025). Both models were assessed for their ability to predict the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Ni}^{2+}$  ions onto FS accurately. The correlation coefficient provides a reliable measure of the agreement between the modeled and observed data sets, guiding the evaluation of the models' effectiveness and their potential for future use.

## 4. CHAPTER FOUR: RESULTS AND DISCUSSIONS

### 4.1 Characterization of FS

#### 4.1.1 Particle Size Distribution (PSD) of FS

The results of grain size distribution of the adsorbent measured using American Society for Testing Materials method (ASTM D 422) is shown in **Figure 4.1**. The effective grain size (D10) of FS was found to be 0.300 mm (**Table 4.1**). It has been reported that, the European guidelines for the design of slow sand filters recommended the effective size range of 0.15mm to 0.35mm (Logan et al., 2001; Abdiyev et al., 2023). This implies that FS was within the recommended effective size range with D10 of 0.3mm thus suitable for use in replacement of sand in slow sand filtration systems. On the other hand, others have reported an effective grain size to be 0.3-0.45mm, and coefficient of uniformity ( $C_u$ ) to be 0.15-0.3mm (Healy, Rodgers and Mulqueen, 2007) and was still within the range of D10 in this study. The coefficient of uniformity of the Fayalite slag (FS) was determined to be 5.36 mm, which exceeds the recommended size. A  $C_u$  value of 1.0 indicates a monodisperse particle size distribution, where all particles are of equal size. In contrast, a  $C_u$  value greater than 1.0, as observed in this case, indicates a broader, more heterogeneous particle size distribution. Enhanced filtration efficiency is positively correlated with increased particle uniformity, meaning that a more uniform particle size distribution typically results in better filtration performance (Abdiyev et al., 2023). Given the relatively high  $C_u$  value of FS, its more varied particle size distribution could reduce hydraulic conductivity and may hinder fluid flow, particularly at higher loading rates (Healy, Rodgers and Mulqueen, 2007), (Abdiyev *et al.*, 2023). These variations in particle size can fill the spaces between larger particles, contributing to clogging.



**Figure 4.1:** Particle Size Distribution of FS

**Table 4.1:** Summary of sieve analysis of FS

Media	D10	Cu
FS	0.3	5.36

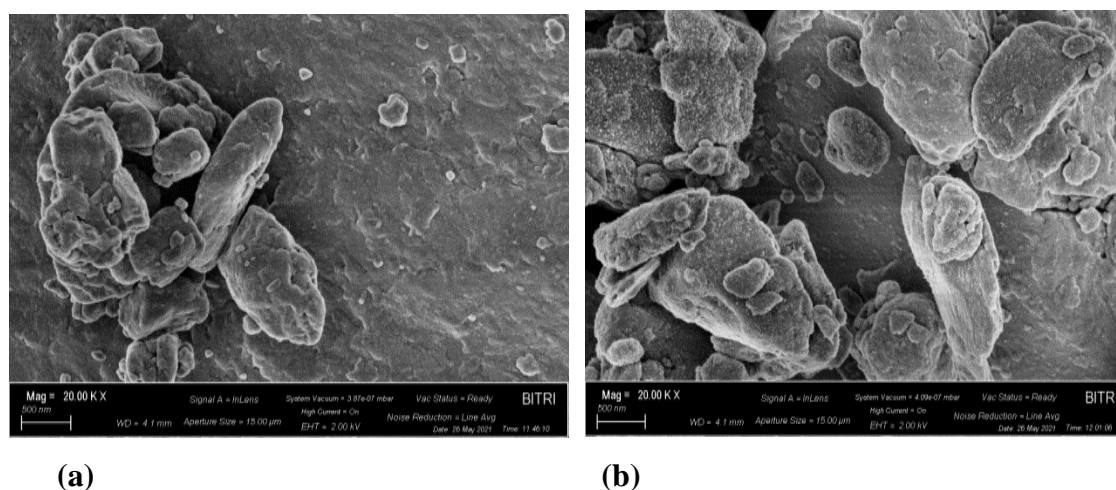
#### 4.1.2 Physical Properties of FS

The physical characteristics of FS are represented in **Table 4.2**. The results indicated that FS is characterized by bulk density of  $1.90 \text{ gcm}^{-3}$  and notably high particle density of  $13.0 \text{ gcm}^{-3}$ , exhibiting a substantial porosity of 50%, alongside a hydraulic conductivity of  $8.04 \times 10^{-4} \text{ m/s}$ . The high bulk density ensures a significant mass of the material can be packed into treatment systems, enhancing its overall adsorption capacity. The exceptionally high particle density indicates that the individual particles are dense and heavy, contributing to the stability and durability of the adsorbent in various environmental conditions (Worch, 2012). The 50% porosity is particularly influential, as it suggests a considerable internal surface area available for the adsorption process, facilitating more interaction sites for heavy metal ions. This porous nature of FS also aids in the efficient diffusion of contaminants into the adsorbent matrix (Raji *et al.*, 2023). The hydraulic conductivity value indicates adequate permeability for water flow, ensuring uninterrupted contact between the adsorbent and the aqueous phase, thereby promoting efficient heavy metal ion transport to adsorption sites (Wang *et al.*, 2015). The hydraulic conductivity value of  $8.04 \times 10^{-4} \text{ m/s}$  reflects the material's ability to allow water to flow through it, ensuring that heavy metal ions can reach the active sites within the adsorbent easily. Surface morphology plays a pivotal role in the performance of FS as an adsorbent. The irregular and rough surfaces observed in imaging studies (**Figure 4.2**) create a high specific

surface area, which is a crucial factor for effective adsorption (Mane *et al.*, 2024). These surface characteristics provide numerous active sites that facilitate the binding of contaminants. The presence of micropores and mesopores within the structure further supports the material's capacity for both rapid adsorption kinetics and significant adsorption capacity (Mane *et al.*, 2024). Collectively, the combination of bulk and particle densities, high porosity, favorable surface morphology, and sufficient hydraulic conductivity underscores the suitability of FS as an effective adsorbent.

**Table 4.2:** Physical properties of FS

Physical Properties	FS
Bulk density( $\text{gcm}^{-3}$ )	$1.9 \pm 0.07$
Particle density( $\text{gcm}^{-3}$ )	$13 \pm 0.04$
Porosity (%)	$50 \pm 5$
Hydraulic conductivity ( $\text{ms}^{-1}$ )	$8.04 \times 10^{-4}$



**Figure 4.2:** SEM morphology of (a) Fresh FS (b) Loaded FS at 2.00kV with magnification of 20.00KX

#### 4.1.3 Mineralogical and Elemental properties of FS

The elemental and mineralogical analysis of Fayalite Slag (FS) is indicative of its stable composition and suitable application as an adsorbent for heavy metals. The major elements that the media constitutes such as iron (Fe), silicon (Si), and aluminum (Al) play a significant role in its adsorption capabilities, with iron contributing to binding pollutants via mechanisms such as surface complexation as well as ion exchange (Raji *et al.*, 2023). It is noteworthy that, minimal differences between fresh and loaded FS highlight limited leachability and structural degradation, underscoring its durability and reusability properties. Key trace elements such as

chromium (Cr) and zinc (Zn) (**Table 4.3**) exhibit slight reductions post-adsorption, indicating their involvement in the adsorption process, whilst the negligible presence of toxic metal like arsenic (As) guarantees environmental safety. Overall, these properties make FS a robust and sustainable media for water treatment applications mainly in adsorption.

**Table 4.3:** Elemental composition of fresh and used FS

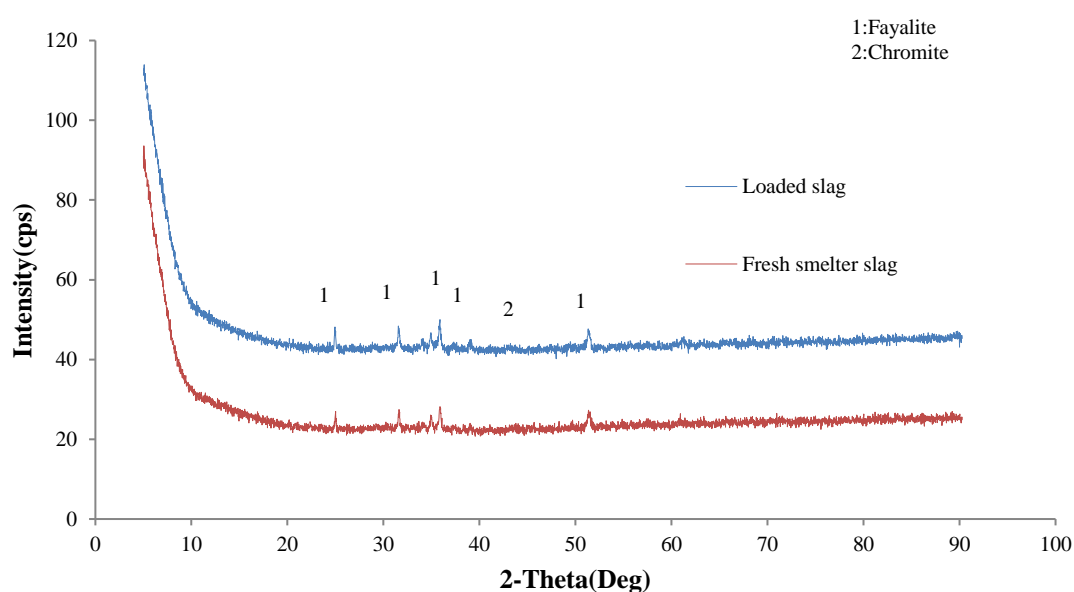
Elements(mgg <sup>-1</sup> )	Fresh FS	Used FS
Al	0.00531	0.00601
Si	0.00611	0.00577
K	0.0004907	0.0004271
Cu	0.0017777	0.0018156
Ti	ND	ND
Cr	0.0000755	0.0000310
Mn	0.0001270	0.0000985
Fe	0.03373	0.03117
Co	ND	ND
Ni	0.0000267	0.0000254
Cu	0.0003076	0.0002799
Zn	0.0000392	0.0000374
Pb	0.0000038	0.0000031
As	ND	ND

ND means Elements were not detected by analytical instrument.

#### 4.1.4 X-ray diffraction (XRD) patterns of FS

The XRD patterns and mineralogical composition of FS highlights an important insight into its ability as a low-cost adsorbent for divalent  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Fe}^{2+}$  metal ions. It has been reported that the amorphous and crystalline phases in the XRD pattern are represented by broadened and sharp peaks (Kapur and Mondal, 2014). It can be observed that the XRD analysis (**Figure 4.3**) reveals distinct peaks corresponding to fayalite ( $\text{Fe}_2\text{SiO}_4$ ) and chromite phases, which indicate the crystalline structure of FS. The presence of these phases suggests high structural stability, making FS effective for adsorption under varying environmental conditions. The comparison between fresh and loaded FS shows minor changes in intensity, implying that the adsorption process involves surface interactions without significant alteration to the bulk mineral structure (Lekgoba, Ntuli and Falayi, 2020). From **Table 4.4**, the mineralogical composition highlights high levels of  $\text{Fe}_2\text{O}_3$  (45.44%) and  $\text{SiO}_2$  (14.88%), with smaller amounts of  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ , and  $\text{MgO}$ . The iron oxide content plays a critical role in the adsorption of divalent metal ions

through ion exchange and surface complexation mechanisms (Raji *et al.*, 2023). Additionally,  $Mg_2Fe_2SiO_4$ , comprising 12.88%, contributes to active sites for binding adsorbates. The presence of CaO and MgO also suggests potential enhancement of adsorption capacity due to their ability to facilitate charge interactions with the adsorbates (Perera *et al.*, 2024), and (Wu *et al.*, 2025). In conclusion, the XRD and mineralogical results indicate that FS is a highly stable and versatile material for adsorbing divalent metal ions, with its crystalline structure and mineral composition playing pivotal roles in the adsorption efficiency.



**Figure 4.3:** XRD patterns of Fresh and loaded FS

**Table 4.4:** Compositions of some major minerals in fresh FS

Minerals	Fresh FS (%)
$Al_2O_3$	3.27±0.07
$SiO_2$	14.88±0.02
$Fe_2O_3$	45.44±0.43
CaO	2.34±0.21
MnO	1.38±0.02
$SO_3$	0.043±0.003
MgO	1.78±0.057
$(Mg, Fe)_2SiO_4$	12.88±0.002
$FeCr_2O_4$	0.89±0.001

#### 4.1.5 Leachability of FS

Leaching tests conducted on Fayalite Slag (FS) revealed a time-dependent release of Cu, Fe, and Ni, with concentrations increasing over 72 hours (**Table 4.5**). Cu and Ni exhibited a gradual release, potentially due to surface dissolution or ion exchange processes (Eksteen, Oraby and Nguyen, 2020). However, Fe showed a significant spike at 48 hours ( $28.1 \pm 0.001$  mg/L) compared to 24 hours ( $0.192 \pm 0.001$  mg/L) and 72 hours ( $3.314 \pm 0.003$  mg/L). This anomalous Fe release could be attributed to the dissolution of a metastable Fe-rich phase within the FS, a change in the redox conditions of the leaching environment favoring Fe oxidation and dissolution, or the formation of a secondary Fe-bearing precipitate that subsequently re-dissolves (Brar *et al.*, 2024). Further investigation into pH dependence, long-term leaching behavior, and speciation analysis is crucial to assess environmental risks and explore mitigation strategies, such as surface modification, to minimize heavy metal release.

**Table 4.5:** Leaching results of the adsorbent

Adsorbent	Heavy metal (mg/L)	Leaching time (h)		
		24	48	72
FS	Cu	0.122±0.041	0.23±0.016	2.34±0.025
	Fe	0.192±0.001	28.1±0.001	3.314±0.003
	Ni	0.061±0.003	0.358±0.001	1.276±0.001

## 4.2 Batch Adsorption Studies

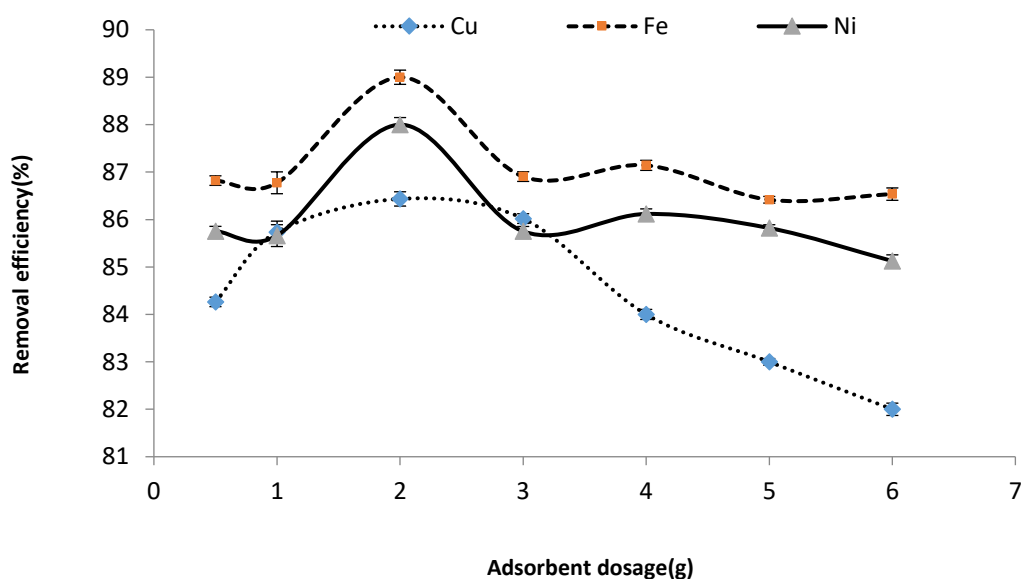
### 4.2.1 Effect of adsorbent dosage on heavy metal adsorption

The effect of adsorbent dosage on the adsorption of  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Fe}^{2+}$  ions onto FS demonstrates distinct trends, highlighting the interplay between active site availability and adsorption efficiency (**Figure 4.4**). For  $\text{Ni}^{2+}$ , the removal efficiency increased with dosage, peaking at approximately 88% at 2.0 g/100mL, followed by a gradual decline likely due to active site saturation and particle agglomeration reducing surface area (Badhai and Behera, 2016). Similarly,  $\text{Fe}^{2+}$  exhibited a maximum removal efficiency of just over 88% at 2.0 g/100mL, but unlike  $\text{Ni}^{2+}$ , its efficiency remained relatively stable at higher dosages, indicating a stronger affinity or less competition for adsorption sites. In contrast,  $\text{Cu}^{2+}$  showed a consistent removal efficiency at lower dosages, peaking at 3.0 g/100mL before declining sharply, which may be attributed to weaker interactions with active sites or increased competition among metal ions (Ali, 2014). The declining efficiency at higher dosages for  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  can also be explained by site shielding effects and decreased ion availability relative to the adsorbent

surface area (Onundi *et al.*, 2010). These results underscore the critical role of optimizing adsorbent dosage to balance adsorption site utilization and material removal efficiency, as overdosing does not enhance performance and may lead to inefficiencies. Moreover, comparative results of initial concentration of metals with final concentrations at optimal media dosage was indicated in **Table 4.6** with final concentrations exceeding BOS threshold. Overall, the observed trends align with adsorption principles, suggesting the need for further investigation into isotherm and kinetic models to elucidate the mechanisms governing metal uptake onto fayalite slag.

**Table 4.6:** Comparative results of initial concentration of metals with final concentrations at optimal media dosage

Media	Solution Initial concentration of Cu, Fe and Ni ( $\text{mgL}^{-1}$ )	Solution Final concentration ( $\text{mgL}^{-1}$ )			BOS Public sewer discharge standards ( $\text{mgL}^{-1}$ , max)		
		Cu	Fe	Ni	Cu	Fe	Ni
FS	200	27.130	26.188	27.570	5.0	20	20

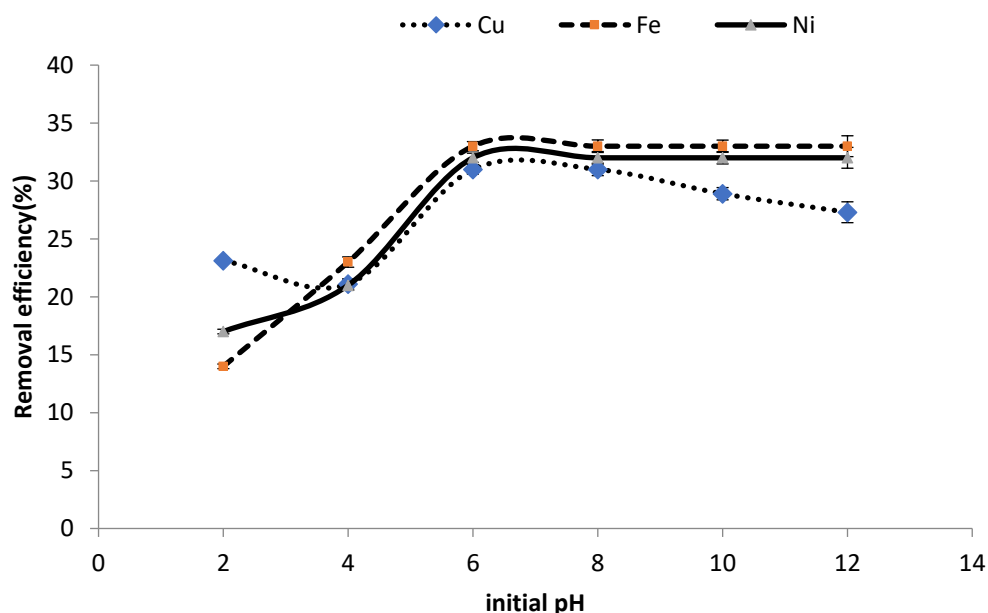


**Figure 4.4:** The effect of adsorbent dosage on heavy metal ion removal using FS

#### 4.2.2 The effect of initial pH on adsorption

The effect of initial pH on the adsorption of divalent Ni, Cu, and Fe onto FS reveals significant variations in removal efficiency across the tested pH range (**Figure 4.5**). For all three metals, the removal efficiency is lower at acidic pH values (pH 2–4), likely due to competition between  $\text{H}^+$  ions and metal ions for adsorption sites on the slag surface (Malandrino *et al.*, 2006). As the

pH increases, the removal efficiency improves markedly, reaching a maximum at near-neutral pH values (6–8), where the metals achieve removal efficiencies of approximately 35%. This improvement can be attributed to reduced protonation of the adsorbent surface and increased availability of negatively charged functional groups, which enhance electrostatic interactions with the divalent cations (Lesbani *et al.*, 2024). At pH values beyond 8, a slight decline in Cu removal efficiency is observed, potentially due to the precipitation of metal hydroxides rather than adsorption, while Ni and Fe maintain relatively stable efficiencies (Abbar *et al.*, 2017). These results emphasize the critical role of pH in influencing metal adsorption onto fayalite slag, where near-neutral conditions favor maximum adsorption efficiency. Further investigations involving speciation analysis and surface characterization are necessary to better understand the adsorption mechanisms and the pH-dependent behavior of each metal.

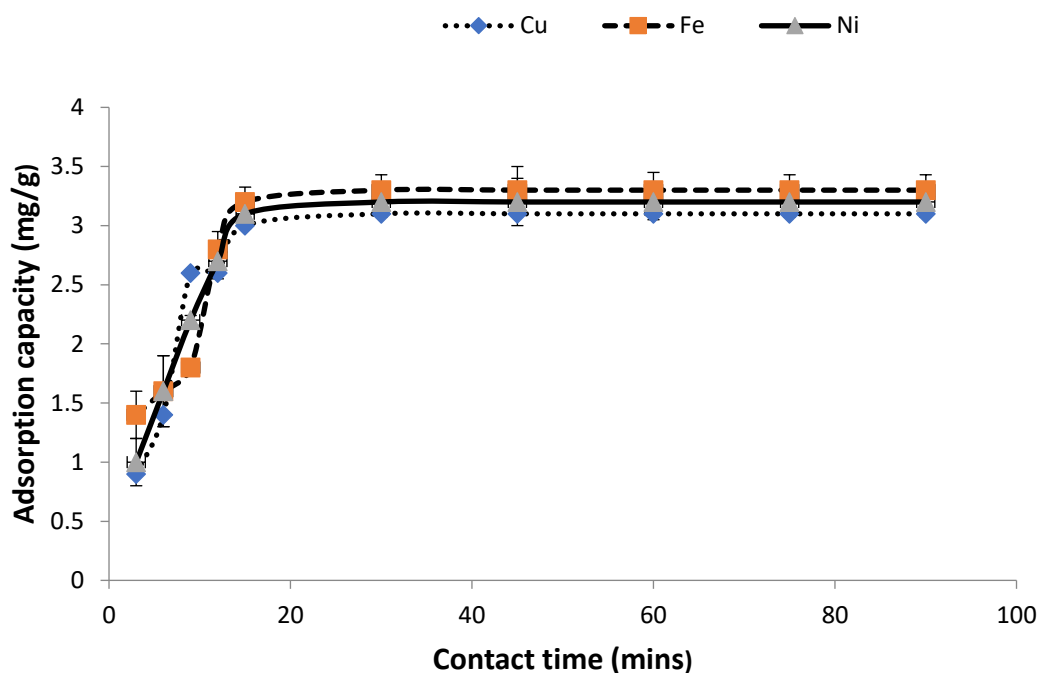


**Figure 4.5:** Effect of initial pH on heavy metal adsorption

#### 4.2.3 The effect of contact time on adsorption

The effect of contact time on the adsorption of divalent Ni, Cu, and Fe onto fayalite slag indicates rapid adsorption during the initial stages, followed by a plateau as equilibrium is reached (**Figure 4.6**). For all three metals, the adsorption capacity increases sharply within the first 20 minutes, achieving approximately 90% of the maximum adsorption capacity. This rapid uptake can be attributed to the high availability of active sites on the surface of the adsorbent and the strong driving force for mass transfer between the metal ions in solution and the

adsorbent (Qasem, Mohammed and Lawal, 2021). Beyond 20 minutes, the adsorption rate slows significantly, and equilibrium is achieved by 40 minutes, with maximum adsorption capacities of approximately  $3.5 \text{ mgg}^{-1}$  of Fayalite Slag for each metal. The plateau phase indicates saturation of the active sites and suggests that the adsorption process is governed by the gradual filling of remaining less accessible sites (El Hajam *et al.*, 2020). The similarity in adsorption behavior across Ni, Cu, and Fe reflects uniform adsorption characteristics of the slag surface and suggests a monolayer adsorption mechanism (Abdel Ghafar *et al.*, 2020). These results highlight the efficiency of Fayalite slag as an adsorbent for rapid metal ion removal and provide critical insights for optimizing contact time in practical adsorption applications. Further kinetic studies are recommended to clarify the adsorption mechanism and identify the rate-limiting step, whether due to mass transfer, diffusion, or chemical interactions. Additionally, conducting series batch tests alongside kinetic analysis will provide a better understanding of adsorption behavior and help optimize the process for practical applications.



**Figure 4.6:** Effect of contact time on adsorption

### 4.3 Batch Kinetic Models

#### 4.3.1 Batch kinetic models (PFO and PSO)

The results from **Table 4.7** reveal that the adsorption kinetics of FS for  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Ni}^{2+}$  ions align more closely with the pseudo-second-order kinetic model compared to the pseudo-first-order model. This is evident from the higher  $R^2$  values ( $\geq 0.994$ ) and lower RMSE values for

the pseudo-second-order model, indicating better accuracy in predicting the experimental  $q_e$  values. Martins et al., 2014 stated that adsorption takes place via interface diffusion when the process aligns with the PFO kinetic model. However, (Mishra *et al.*, 2017) proposed that chemisorption is the rate-controlling mechanism when the process follows the PSO model. In this case, the process followed the pseudo-second-order model suggesting that chemisorption is the rate-limiting step, involving electron sharing or exchange between the adsorbate and the adsorbent's surface. The alignment of  $q_e$  experimental and model values underscores the reliability of FS as an adsorbent and the predominance of chemisorptive interactions in the adsorption process.

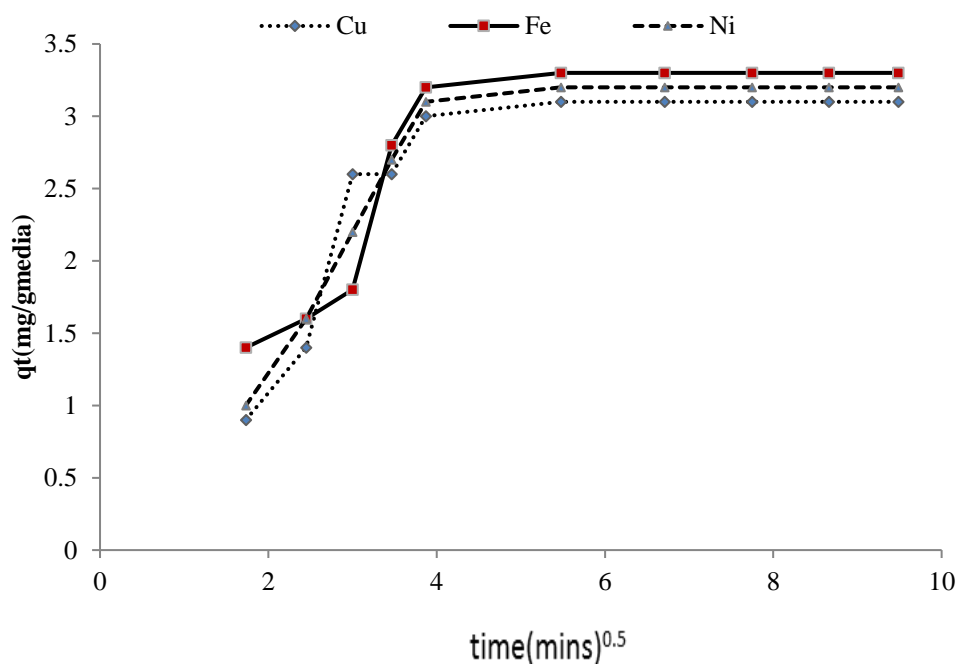
**Table 4.7:** PFO and PSO kinetic models

Pseudo-First Order Kinetic Model						Pseudo-Second Order Kinetic Model					
Adsorbents	Metal Ions	$q_e$ model (mgg <sup>-1</sup> )	$q_e$ experimental (mgg <sup>-1</sup> )	$k_1$ (min <sup>-1</sup> )	$R^2$	RMSE	$q_e$ model (mgg <sup>-1</sup> )	$q_e$ experimental (mgg <sup>-1</sup> )	$k_2$ ((g/mg)min)	$R^2$	RMSE
FS	Cu <sup>2+</sup>	6.504×10 <sup>8</sup>	3.1	0.569	0.885	0.9999	3.3	3.1	61.22	0.995	0.0037
	Fe <sup>2+</sup>	5.727×10 <sup>8</sup>	3.3	0.546	0.811	0.9999	3.3	3.3	70.64	0.994	0.0000
	Ni <sup>2+</sup>	5.806×10 <sup>8</sup>	3.2	0.564	0.896	0.9999	3.3	3.2	70.64	0.996	0.0009
Intra-particle Diffusion kinetic Model											
		$K_{id}$ (mg/(gmin <sup>-0.5</sup> ))	C		$R^2$						
FS	Cu <sup>2+</sup>	0.2151	1.4685		0.5511						
	Fe <sup>2+</sup>	0.2327	1.5061		0.6425						
	Ni <sup>2+</sup>	0.2275	1.4632		0.6161						

### 4.3.2 Intraparticle Diffusion Model

The graph depicting  $qt$  (mgg<sup>-1</sup>) versus time<sup>0.5</sup> for Cu<sup>2+</sup>, Fe<sup>2+</sup>, and Ni<sup>2+</sup> suggests that the adsorption process onto FS involves multiple stages, consistent with the intra-particle diffusion model (**Figure 4.7**). The initial high gradient in  $qt$  indicates rapid adsorption, likely dominated by external surface adsorption or boundary layer diffusion (Gupta *et al.*, 2021). This is followed by a lower gradient phase, where intra-particle diffusion becomes the rate-limiting step as the adsorbate molecules penetrate the adsorbent's pores. The plateau observed for all ions signifies equilibrium, where adsorption sites are saturated. The values of  $K_{id}$  (mg/(g·min<sup>-0.5</sup>)); 0.2151 for Cu<sup>2+</sup>, 0.2327 for Fe<sup>2+</sup>, and 0.2275 for Ni<sup>2+</sup> (**Table 4.7**) indicate the diffusion rates of the metal

ions within the adsorbent pores.  $\text{Fe}^{2+}$  demonstrates the highest  $K_{id}$ , suggesting faster intra-particle diffusion compared to  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ . The C values, representing the intercepts of the intra-particle diffusion model, were 1.4685, 1.5061, and 1.4632 for  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Ni}^{2+}$ , respectively. These values, with units of mg/g, provide an indirect indication of the boundary layer thickness. Although C does not directly represent thickness, it reflects the resistance to mass transfer at the external surface, which influences the initial phase of adsorption (Foo and Hameed, 2010). The comparable C values suggest similar levels of external mass transfer resistance for all three metal ions. According to Fierro and Torne, (2008) intraparticle diffusion governs the adsorption process only if the function intersects the origin. Based on the graph (**Figure 4.7**), it is evident that intraparticle diffusion was not the sole rate-limiting step in this case. However, the  $R^2$  values of 0.5511 for  $\text{Cu}^{2+}$ , 0.6425 for  $\text{Fe}^{2+}$ , and 0.6161 for  $\text{Ni}^{2+}$  suggest that the intra-particle diffusion model does not fully account for the adsorption process. This implies that while intra-particle diffusion is significant, other mechanisms, such as film diffusion or chemical interactions, also influence the adsorption kinetics.



**Figure 4.7:** Intra-particle diffusion model for FS

#### 4.4 Adsorption Isotherm Models

The adsorption isotherm results for FS (adsorbent) across three heavy metal ions ( $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ) and temperatures indicate a strong dependence of adsorption parameters on temperature

and metal type (**Table 4.8**). The Langmuir constant  $q_{\max}$  which represents the maximum adsorption capacity, decreases slightly with increasing temperature for  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$ , suggesting an exothermic adsorption process. Conversely, for  $\text{Ni}^{2+}$ ,  $q_{\max}$  increases with temperature, implying endothermic adsorption, potentially due to enhanced molecular motion at higher temperatures improving metal ion access to active sites (Aziam *et al.*, 2024). The dimensionless separation factor  $R_L$  remains less than 1 across all cases, confirming favorable adsorption conditions (Ajenifuja, Ajao and Ajayi, 2017). Freundlich constants  $K_f$  and  $1/n$  suggest the heterogeneity of the adsorbent surface and metal ion affinity, with  $1/n$  values less than 1 indicating adsorption intensity decreases with increasing concentration (Salim *et al.*, 2021). Overall, the correlation coefficients  $R^2$  for both models demonstrate a moderate fit, validating the reliability of Langmuir and Freundlich equations in describing the adsorption behaviors. These results underscore the potential of FS as an effective adsorbent, with adsorption efficiency influenced by temperature and specific metal ion properties.

**Table 4.8:** Adsorption isotherm models

Adsorbent	Heavy metal ions	Temp (K)	Langmuir constants				Freundlich constants		
			$q_{\max}$ ( $\text{mgg}^{-1}$ )	$K_L$ ( $\text{Lmg}^{-1}$ )	$R^2$	$R_L$	$K_f$ ( $\text{mgg}^{-1}$ )	$1/n$	$R^2$
FS	Cu (II)	293	1.515	0.1305	0.726	0.0369	0.217	0.581	0.8152
					4		8		
		303	1.4108	0.1235	0.721	0.0389	0.1885	0.603	0.8309
				1		9			
		313	1.3046	0.1291	0.699	0.0373	0.1842	0.584	0.8167
					8		5		
FS	Fe (II)	293	1.5805	0.1013	0.713	0.0470	0.1846	0.633	0.7996
					5		6		
		303	1.6093	0.0886	0.706	0.0534	0.1723	0.643	0.7900
				6		8			
		313	1.5830	0.0827	0.692	0.0570	0.1627	0.648	0.7789
					6		2		
FS	Ni (II)	293	1.0004	0.7163	0.535	0.0069	0.3402	0.509	0.7518
					9		4		
		303	0.9977	0.6439	0.546	0.0077	0.3280	0.496	0.7475
				5		9			
		313	1.2455	0.2070	0.657	0.0236	0.2369	0.576	0.7739
					3		7		

#### 4.5 Adsorption thermodynamic studies

The thermodynamic parameters for the adsorption of Cu, Fe, and Ni divalent ions on the adsorbent FS were determined at temperatures of 293 K, 303 K, and 313 K to evaluate the spontaneity, enthalpy, and entropy changes of the adsorption process (**Table 4.9**). The negative values of  $\Delta G^\circ$  (ranging from -9.023 to -10.294 kJ/mol) at all temperatures indicate that the adsorption process is spontaneous and thermodynamically favorable (Wu, Joo and Lee, 2005). The increase in  $\Delta G^\circ$  magnitude with rising temperature suggests enhanced spontaneity, which could be attributed to the higher mobility of metal ions and improved interaction with the adsorbent surface at elevated temperatures. The positive  $\Delta H^\circ$  values (5.798 kJ/mol for Cu<sup>2+</sup>, 2.001 kJ/mol for Fe<sup>2+</sup>, and 7.912 kJ/mol for Ni<sup>2+</sup>) confirm that the adsorption process is endothermic, signifying that heat energy is absorbed during adsorption, likely due to chemical interactions or bonding (Aziam *et al.*, 2024). The negative  $\Delta S^\circ$  values (-0.051, -0.038, and -0.058 kJ/mol·K for divalent Cu, Fe, and Ni, respectively) reflect a decrease in randomness at the solid-liquid interface, consistent with the formation of an organized adsorbate layer on the adsorbent surface (Özcan, Erdem and Özcan, 2005). These findings highlight the potential of FS as an effective adsorbent for the removal of divalent metal ions under varying temperature conditions, with thermodynamic properties favoring its application in wastewater treatment.

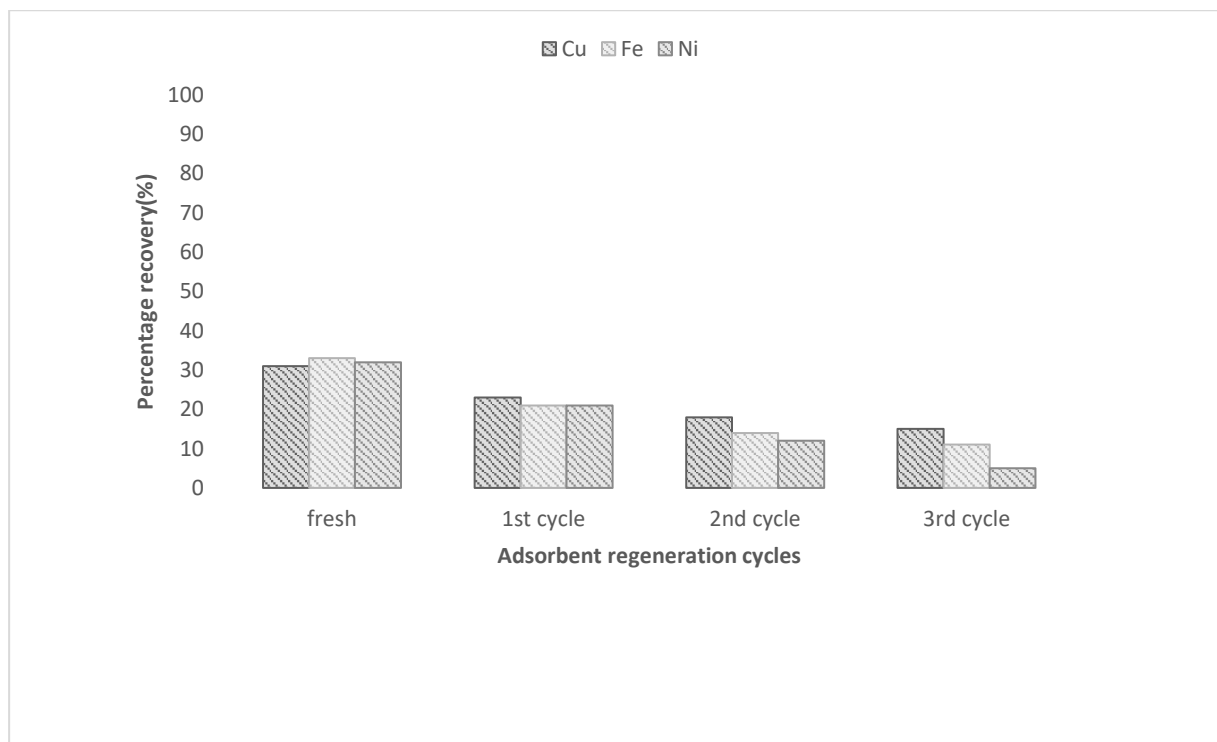
**Table 4.9:** Parameters of Adsorption thermodynamic studies

Adsorbent	Metal ion	Temperature (K)	$\Delta G^\circ$ (kJmol <sup>-1</sup> )	$\Delta H^\circ$ (kJmol <sup>-1</sup> )	$\Delta S^\circ$ (kJmol <sup>-1</sup> K <sup>-1</sup> )
FS	Cu (II)	293	-9.247		
		303	-9.651	5.798	-0.051
		313	-10.276		
	Fe (II)	293	-9.023		
		303	-9.399	2.001	-0.038
		313	-9.775		
	Ni (II)	293	-9.134		
		303	-9.876	7.912	-0.058
		313	-10.294		

#### 4.6 Batch reusability studies

The regeneration efficiency of the adsorbent was evaluated for divalent metal ions (Ni, Cu, and Fe) over three regeneration cycles using 0.1 mol L<sup>-1</sup> NaOH as the desorption eluent. Initially, the fresh adsorbent exhibited a recovery percentage of nearly 30% for Cu, Fe, and Ni,

highlighting its better adsorption capacity and efficient desorption (**Figure 4.8**). However, after the first regeneration cycle, the recovery efficiency dropped to approximately 23% for Cu, 21% for Fe and for Ni, indicating a reduction in available active sites (Bayuo, Abukari and Pelig-Ba, 2020). In the second cycle, the recovery efficiency further decreased to around 18% for Cu, 14% for Fe, and 12% for Ni, likely due to partial irreversible binding, or ion exchange as reported by (Ahmad, Kumar and Haseeb, 2012). By the third cycle, the recovery efficiency was reduced to less than 20%, with values of approximately 15% for Cu, 11% for Fe, and 5% for Ni. Despite this progressive decline, the adsorbent demonstrated reusability potential for at least two cycles, which is advantageous for cost-effective and sustainable water treatment applications (Zhang and Wang, 2015). The significant reduction in performance after the third cycle emphasizes the need for appropriate strategies for the disposal or repurposing of spent adsorbent. Effective management approaches, such as incorporating spent adsorbents into construction materials or recovering the adsorbed metals for recycling, could minimize environmental impact and enhance sustainability within circular economy practices.



**Figure 4.8:** Reusability studies

## 4.7 Artificial Neural Network and Adaptive Neuro-Fuzzy Inference System Modeling

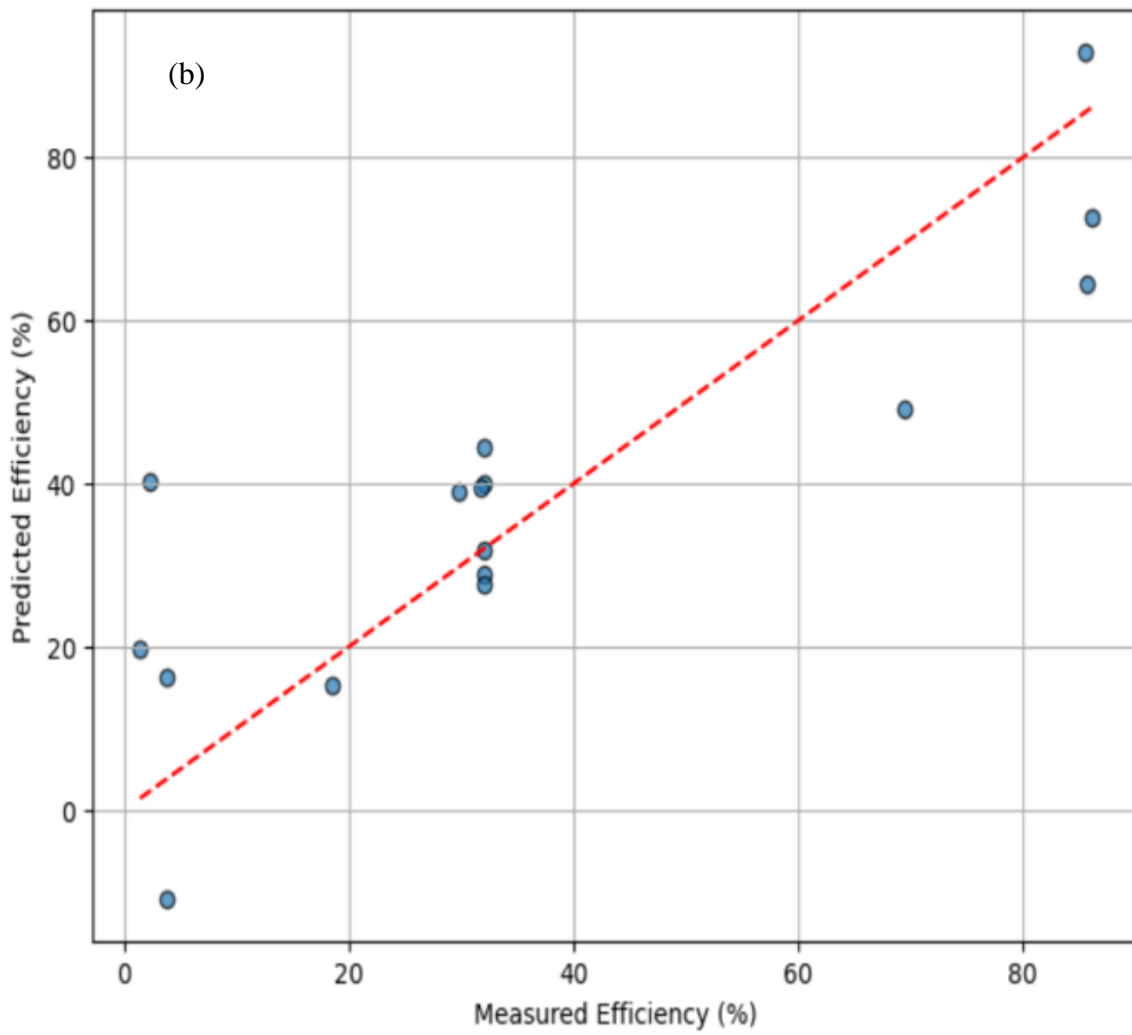
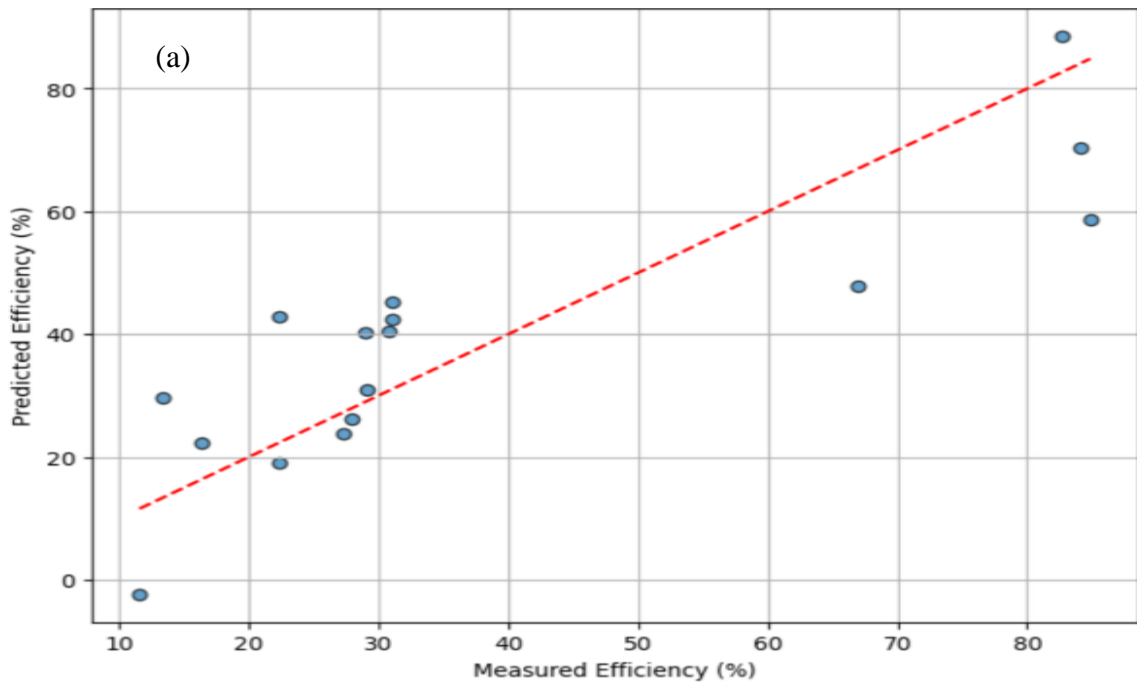
### 4.7.1 Artificial Neural Network (ANN)

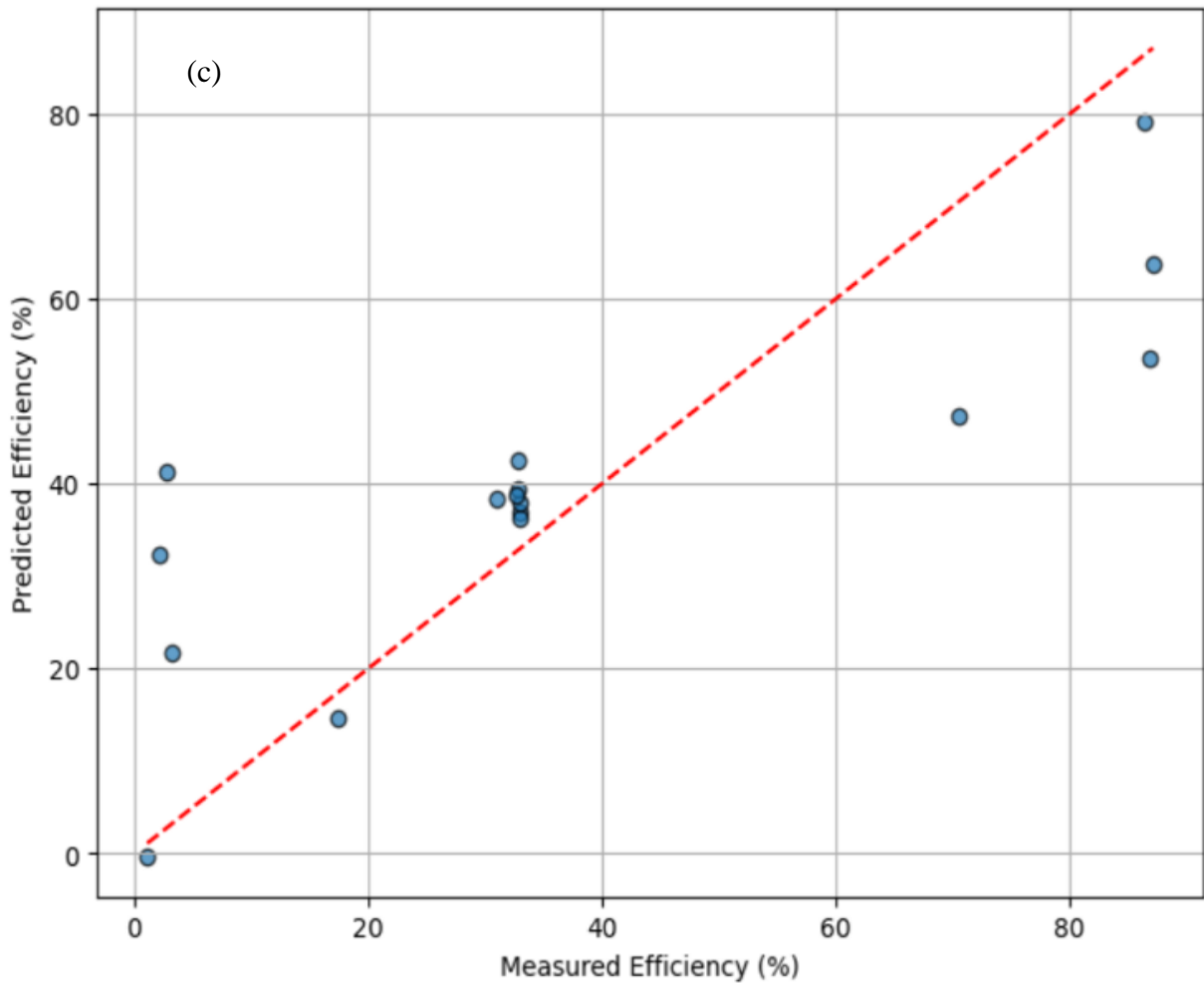
The adsorption efficiency of divalent  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Fe}^{2+}$  onto fayalite slag was predicted using an Artificial Neural Network (ANN) model, with results presented in scatter plots and

performance metrics summarized in the table (**Table 4.10** and **Figure 4.9**). The ANN performance, measured by the coefficient of determination ( $R^2$ ) and root mean square error (RMSE), improved as the number of neurons increased up to 20, where the highest  $R^2$  (0.778) and lowest RMSE (13.15) were observed, indicating optimal model performance. Beyond this,  $R^2$  values fluctuated, suggesting overfitting or diminishing returns in prediction accuracy. The scatter plots show a reasonable correlation between measured and predicted adsorption efficiencies, with better accuracy in the mid-efficiency range (20 – 40%) but deviations at extreme values, particularly for  $\text{Cu}^{2+}$ , where underprediction was observed at high adsorption efficiencies.  $\text{Ni}^{2+}$  and  $\text{Fe}^{2+}$  exhibited similar trends, with ANN predictions aligning well in moderate efficiency ranges but deviating at lower and higher values. The results can be compared and contrasted with studies reported by (Onu *et al.*, 2021), (Pavan Kumar *et al.*, 2019), (Souza, ANDotto and Salau, 2018). These results suggest that while ANN effectively models adsorption efficiency, further optimization, such as incorporating additional adsorption-related parameters, could enhance prediction accuracy.

**Table 4.10:** ANN performance metrics for adsorption

Neurons	$R^2$	RMSE
5	0.348212	22.102632
10	0.681513	15.467113
15	0.581606	18.083434
20	0.778481	13.151172
25	0.694588	15.482393
30	0.729334	14.578571





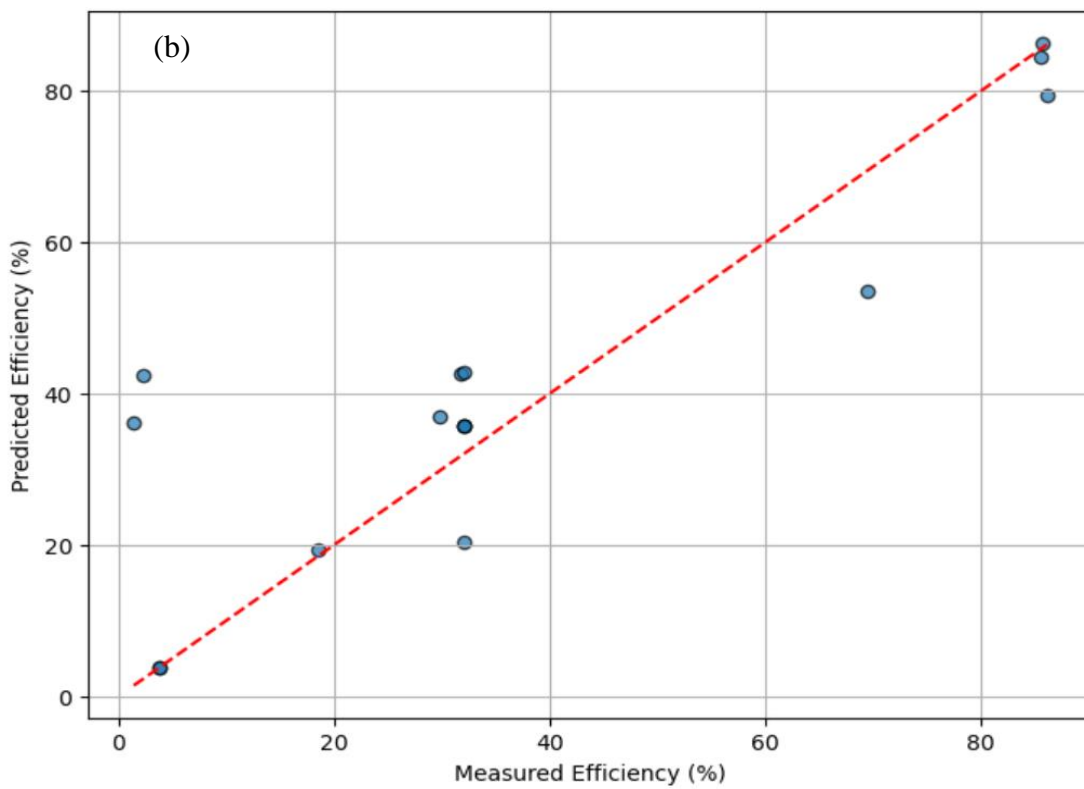
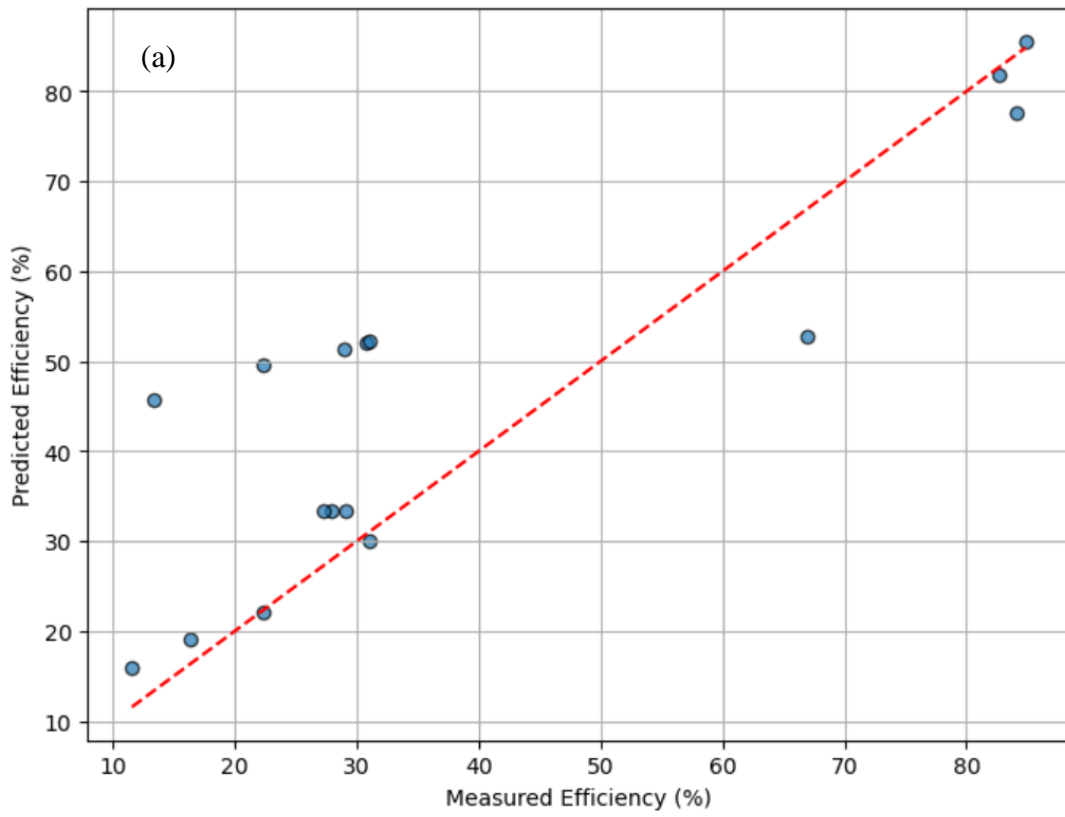
**Figure 4.9:** Predicted versus measured adsorption efficiencies for Cu (a), Ni (b) and Fe (c) using A

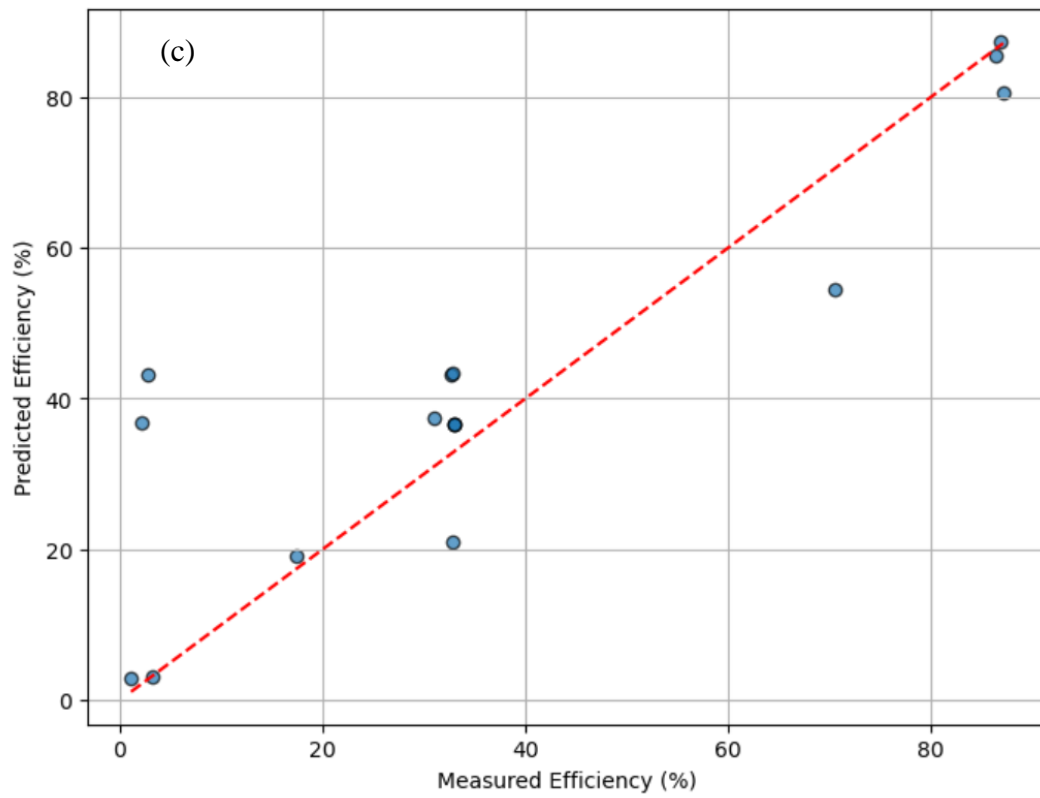
#### 4.7.2 Adaptive Neuro-Fuzzy Inference System (ANFIS)

The adsorption efficiency of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Fe}^{2+}$  onto fayalite slag was modeled using the Adaptive Neuro-Fuzzy Inference System (ANFIS), with its predictive performance evaluated through the coefficient of determination ( $R^2$ ) and root mean square error (RMSE) (**Table 4.11** and **Figure 4.10**). The results indicate that as the number of fuzzy rules increased, the model's accuracy improved, with the best performance observed at six fuzzy rules ( $R^2 = 0.823$ , RMSE = 11.87). The measured vs. predicted adsorption efficiency plots for  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Ni}^{2+}$  further validate the model, as most data points align well along the 1:1 reference line, demonstrating a strong correlation between experimental and predicted values. However, minor deviations at lower efficiency levels suggest some limitations in capturing complex adsorption dynamics. A comparison can be made between this study and studies reported by (Souza, Dotto and Salau, 2018) where nickel adsorption onto agro-wastes and commercial activated carbon was conducted, and (Onu *et al.*, 2021) where black-T dye was adsorbed using modified clay. Overall, the findings confirm ANFIS as a robust predictive tool for modeling heavy metal adsorption onto fayalite slag, with significant potential for optimizing adsorption processes for wastewater treatment applications.

**Table 4.11:** ANFIS performance metrics for adsorption

Fuzzys rules	$R^2$	RMSE
2	0.512364	19.87412
3	0.643217	16.5411
4	0.725489	14.76231
5	0.798214	12.98452
6	0.823678	11.87436





**Figure 4.10:** Predicted versus measured adsorption efficiencies for Cu (a), Ni (b) and Fe (c) using ANFIS

## **5. CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS**

### **5.1 CONCLUSION**

The following conclusions were aligned respectively with the objectives of this research; Optimizing process parameters such as pH, adsorbent dosage, and contact time enhanced the removal of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Ni}^{2+}$  from wastewater using fayalite slag, with near-neutral pH, optimal dosage, and rapid initial adsorption achieving the highest efficiency, though further refinements are needed to fully meet discharge standards. The study revealed that fayalite slag (FS) demonstrated moderate regeneration potential for removing  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Ni}^{2+}$ , with efficient adsorption and desorption observed during the initial cycles. However, regeneration efficiency declined significantly after two cycles due to reduced active sites and partial irreversible binding. Leaching tests further showed that FS released metals, particularly Fe, into the environment over time, raising concerns about its environmental impact. The adsorption of Cu, Ni, and Fe divalent ions onto Fayalite slag was well modelled and optimized using an Adaptive Neuro-Fuzzy Inference System (ANFIS) better than Artificial Neural Network (ANN).

### **5.2 RECOMMENDATIONS FOR FUTURE WORKS**

The following should be done as recommendations for future works to improve this study;

- Further studies should explore advanced modifications to the slag, such as surface activation or blending with other adsorbents, to improve efficiency and ensure compliance with discharge standards.
- It is recommended to improve the regeneration efficiency of fayalite slag (FS) by exploring advanced desorption techniques and surface modifications to reduce active site loss during reuse. Additionally, strategies should be developed to minimise metal leaching, such as coating the adsorbent or combining FS with stabilising agents. Regular monitoring of environmental metal concentrations is also advised to ensure safe application and mitigate potential ecological impacts.
- It is also recommended that enhancement of the ANN and ANFIS model can be achieved by expanding the dataset, optimising hyperparameters, incorporating advanced feature selection, and applying regularisation techniques to improve accuracy and generalisation. Additionally, integrate external factors, hybrid approaches, and real-world validation to ensure robustness and practical applicability in adsorption studies.

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