# TREATMENT OF PRODUCED WATER FRO M NIGER DELTA OIL FIELDS USING LOCALLY SOURCED CLAYS AS ADSORBENTS

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BENIN CITY

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# TREATMENT OF PRODUCED WATER FROM NIGER DELTA OIL FIELDS USING LOCALLY SOURCED CLAYS AS ADSORBENTS

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# CERTIFICATION

This is to certify that this project was carried out by IKPONMWOSA DECENT of the Department of Petroleum Engineering with matriculation number ENG2006429 in partial fulfillment of the fulfillment of the requirements for the Award of the Degree, Bachelor of Engineering (B.ENG)

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# DEDICATION

This thesis is dedicated to God Almighty, who made it possible for me to complete the study successfully. This work is dedicated to my late mother most especially, father, siblings, alongside my professors and lecturers who have taught me that the best kind of knowledge to have is that which is learned for its own sake and have been a major source of motivation in this academic journey.

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# ABSTRACT

The continuous discharge of poorly treated produced water from oilfields is a major cause of environmental degradation in the Niger Delta. This study explores a practical, low-cost solution by evaluating the effectiveness of locally sourced Nigerian clays from Ogba River (AG) and Gelegele River (GE) as natural adsorbents for removing heavy metals from real produced water. The clay samples were processed through washing, sun-drying, and chemical activation using a 2M hydrochloric acid solution to enhance their natural properties. We then conducted a series of laboratory batch experiments to test how well these activated clays could remove Iron (Fe) and Copper (Cu) from the water. The study specifically examined how the amount of time the clay was in contact with the water influenced its cleaning power, and we used kinetic and isotherm models to understand the speed and underlying mechanism of the removal process. The results demonstrated that both treated clays were effective, but their performance was highly specific to the metal and the clay's origin. For iron removal, the GE clay showed a slightly higher final efficiency (65.3%) and capacity (0.0243 mg/g) than the AG clay (63.7%, 0.0237 mg/g). In contrast, for copper, the AG clay was markedly superior, achieving 88.5% removal compared to the GE clay's 73.1%. Kinetic studies revealed a clear difference in the removal mechanisms: the adsorption of copper onto both clays was best described by the Pseudo-First-Order model, indicating a physisorption process. However, the adsorption of iron onto the AG clay followed the Pseudo-Second-Order model, suggesting a stronger, chemisorption-driven mechanism. When analyzing the equilibrium data, we found that the classic Langmuir and Freundlich isotherm models yielded unrealistic parameters, highlighting their limitation for accurately describing adsorption in such a complex, low-concentration effluent like real produced water. In conclusion, this work confirms that simple, acid-activated local clays are a viable and sustainable material for cleaning heavy metals from produced water. The findings, particularly the distinct kinetic behaviors, are crucial for designing a treatment process. To move this solution forward, we recommend that future research focuses on testing these clays in continuous-flow pilot systems, conducting a detailed cost-benefit analysis, and exploring how to integrate this clay-based polishing step into existing treatment setups in the Niger Delta.

# CHAPTER ONE

## 1.0 INTRODUCTION

### 1.1 Background to the Study

The extraction of crude oil and gas is a cornerstone of the global energy supply and a critical source of revenue for many resource rich nations, including Nigeria. However, this industrial activity generates significant waste streams, the largest of which by volume is produced water (PW). Produced water is a complex mixture of natural formation water, injected fluids (such as seawater or steam used for enhanced oil recovery), and chemical additives from drilling and production processes (Nwosi-Anele and Iledare, 2016). It is not a uniform waste product; its composition is highly variable and depends on the geographic location, the geology of the reservoir, and the age of the oil well.

Globally, the volume of produced water is staggering. This volume presents one of the most significant environmental management challenges for the petroleum industry worldwide. The challenge lies not only in the immense quantity but also in the complex and often hazardous quality of this wastewater. Produced water typically contains high concentrations of dissolved salts (often much higher than seawater), various heavy metals, dispersed oil droplets, and dissolved organic compounds. These organics include toxic substances like benzene, toluene, ethylbenzene, and xylenes (collectively known as BTEX) and polycyclic aromatic hydrocarbons (PAHs). Additionally, it can contain naturally occurring radioactive materials (NORM), making its safe handling and treatment imperative.

In the Nigerian context, the issue of produced water management is particularly acute in the Niger Delta region, the heart of the country's oil and gas production. The Niger Delta is also a vast ecologically sensitive environment comprising mangroves, freshwater swamps, and intricate networks of rivers and creeks. It is home to millions of people who depend on these ecosystems for their livelihood, primarily through fishing and farming. The uncontrolled or inadequately treated discharge of produced water into this environment has led to severe ecological degradation. The high salinity can sterilize soil and damage crops, while toxic hydrocarbons can contaminate both surface water and shallow aquifers used for drinking and irrigation. These pollutants can also bioaccumulate in fish and other aquatic organisms, posing serious risks to human health through the food chain.

The regulatory framework for managing this waste in Nigeria, primarily the Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN), sets limits for key pollutants in effluents. However, enforcement has historically been inconsistent. Many oil production facilities, especially older flow stations, lack the necessary treatment infrastructure. Studies have shown that some facilities discharge produced water with oil and grease levels exceeding 100 mg/L, far above the regulatory limits, often relying on simple dilution or unlined ponds (Nwosi-Anele and Iledare, 2016). This indicates a critical gap between policy and practice.

Conventional treatment methods for produced water, such as gravity separators, hydrocyclones, and flotation units, are well established but can be expensive to install and maintain. They are also often ineffective at removing dissolved contaminants like heavy metals and soluble organics. This creates a need for robust, cost effective, and efficient treatment technologies that can be deployed in the Nigerian context.

Adsorption has emerged as a highly promising treatment technology, particularly for polishing water after primary treatment to remove these dissolved pollutants. The process involves attracting and binding contaminant molecules to the surface of a solid material (adsorbent). Its advantages include operational simplicity, high efficiency at low contaminant concentrations, and often lower energy requirements compared to membrane or thermal processes.

A particularly attractive opportunity for Nigeria lies in the use of locally abundant natural materials as adsorbents. Nigeria has extensive deposits of clay minerals, such as kaolinite and bentonite, found in states like Niger, Ogun, and Edo. These clays are inexpensive, readily available, and possess natural properties that make them good adsorbents, including high surface area and cation exchange capacity, which allows them to trap metal ions (Yousef *et al.*, 2020). Research by Nigerian scientists like Akpomie and Dawodu (2015) and Mustapha *et al.* (2019) has demonstrated the effectiveness of local clays in removing heavy metals and other pollutants from water. Furthermore, these clays can be chemically modified to enhance their adsorption properties and make them effective for a wider range of pollutants, including organic compounds.

Therefore, this study is situated at the intersection of a pressing environmental problem and a potential locally sourced solution. It seeks to systematically investigate the potential of Nigerian clay minerals as effective and sustainable adsorbents for the treatment of produced water, contributing to the development of cheaper and more accessible treatment options for the oil and gas industry in Nigeria.

## 1.2 Statement of the Problem

The exploration and production of crude oil in the Niger Delta region have come at a significant environmental cost. A primary contributor to this ongoing degradation is the discharge of large volumes of improperly treated produced water (PW) from oilfield operations. This practice persists despite the existence of regulatory frameworks like the Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN).

The core of the problem is threefold: technical inadequacy, regulatory failure, and environmental consequence.

Firstly, there is a significant technical and infrastructural deficit in treating produced water at its source. Many oil production facilities, particularly older flow stations, lack even basic primary treatment units like gravity separators. As noted by Nwosi-Anele and Iledare (2016), some facilities in the Niger Delta discharge produced water with oil and grease levels exceeding 100 mg/L, a clear indication that fundamental treatment is absent or poorly maintained. Conventional treatment technologies that can achieve higher purity are often expensive, energy intensive, and require sophisticated technical expertise to operate and maintain. This makes them economically unfeasible for widespread adoption in the current operational context, leading to a reliance on ineffective methods like simple dilution or discharge into unlined ponds.

Secondly, there is a notable gap in regulatory enforcement and legislative coverage. While the Department of Petroleum Resources (DPR), now the Nigerian Upstream Petroleum Regulatory Commission (NUPRC), has set effluent standards, field audits consistently show non compliance. Enforcement is often weak and uneven, particularly in remote or offshore locations. Furthermore, a critical legislative loophole exists: the National Environmental Standards and Regulations Enforcement Agency (NESREA) Act, which governs environmental protection for most industries, explicitly exempts upstream oil and gas activities. This exemption dilutes accountability and creates a regulatory vacuum for produced water management.

The third and most critical aspect of the problem is the severe and multifaceted environmental and socio economic impact. The discharge of untreated PW leads to:

i. **Soil Salinization:** High salt content renders farmlands infertile, destroying the agricultural livelihood of local communities.

ii. **Water Pollution:** Toxic dissolved hydrocarbons (like BTEX and PAHs) and heavy metals contaminate surface water bodies and shallow groundwater aquifers, which are primary sources of drinking water.

iii. **Bioaccumulation:** These toxins enter the food chain through fish and other aquatic organisms, posing long term health risks to humans who consume them.

iv. **Ecological Disruption:** Oil sheens on water surfaces disrupt aquatic photosynthesis and damage sensitive ecosystems like mangroves.

Therefore, the problem is the continuing environmental pollution from produced water due to a combination of inadequate treatment technology, insufficient regulatory enforcement, and the high cost of existing effective solutions. This situation creates an urgent need for the development, promotion, and adoption of treatment methods that are not only effective but also affordable, sustainable, and suitable for the local context in Nigeria. This research addresses this need by investigating the potential of a locally available and low cost material, clay, as an adsorbent for treating produced water.

## 1.3 Aim

The overarching aim of this research is to investigate the suitability and effectiveness of locally sourced Nigerian clay as a low-cost adsorbent for the treatment of produced water, with a view to mitigating its environmental impact in the Niger Delta region.

## 1.4 Objectives of the Study

To achieve this aim, the following specific objectives have been formulated:

1. To characterize the physical and chemical properties of produced water samples and selected Nigerian clay minerals to identify their key constituents and adsorption potential.
2. To determine the adsorption efficiency of the selected raw and acid-activated clay in removing key pollutants, specifically heavy metals, from produced water under varying conditions (e.g., contact time, adsorbent dosage, pH).
3. To determine the kinetics of the adsorption process by modelling experimental data with Pseudo-First-Order, Pseudo-Second-Order, and Intra-particle Diffusion models**.**
4. To analyze the adsorption equilibrium data using Langmuir and Freundlich isotherm models to understand the mechanism of adsorption and quantify the clay's maximum removal capacity.
5. To propose a conceptual treatment framework based on the findings for integrating clay-based adsorption into produced water management systems in Nigeria.

## 1.5 Research Questions and Hypotheses

This study will be guided by the following research questions, which are directly aligned with the stated objectives:

1. What are the predominant physicochemical characteristics and pollutant profiles of produced water samples from the Niger Delta, and what are the key mineralogical properties of the selected Nigerian clay?
2. How do operating parameters such as contact time, adsorbent dosage, and pH level affect the removal efficiency of heavy metals and organic compounds from produced water using raw Nigerian clay?
3. To what extent do acid activation and other modification techniques enhance the adsorption capacity of the native clay for the target pollutants in produced water?
4. Which isotherm model, Langmuir or Freundlich, best describes the adsorption process, and what are the calculated maximum adsorption capacities for the key contaminants?
5. How can the findings from this study be translated into a practical and sustainable treatment framework for produced water in the Nigerian context?

Based on these questions, the following hypotheses are proposed:

- **$H_1$:** Nigerian clay possesses significant inherent adsorption capacity due to its mineral composition and will effectively reduce the concentration of key pollutants in produced water.
- **$H_2$:** The adsorption process will be highly dependent on operational parameters, with an optimal pH, contact time, and adsorbent dosage existing for maximum pollutant removal.
- **$H_3$:** Chemically modified clay will demonstrate a statistically significant improvement in adsorption performance compared to the raw, unmodified clay.

- **$H_4$:** The adsorption equilibrium data will fit both the Langmuir and Freundlich isotherm models, suggesting a combination of monolayer and heterogeneous surface adsorption mechanisms.

## 1.6 Significance of the Study

This research is significant for several reasons, offering potential benefits across environmental, economic, technological, and policy domains.

**Environmental Benefits:** The most direct significance of this study is its potential to mitigate environmental pollution in the Niger Delta. By developing an effective and accessible method for treating produced water, the research contributes to reducing the contamination of rivers, creeks, farmlands, and groundwater sources. This can help restore aquatic ecosystems, protect biodiversity, and safeguard the health of local communities who rely on these natural resources for survival.

**Economic Benefits:** The proposed solution leverages locally abundant clay, which is a low-cost and readily available material. This presents a significant economic advantage over imported treatment technologies or commercial adsorbents like activated carbon. Reducing the cost of effective water treatment can incentivize oil and gas operators to comply with regulations. Furthermore, cleaner environments can revive fishing and agricultural activities, which are the economic mainstay of many communities in the Niger Delta, thereby promoting sustainable livelihoods.

**Technological and Scientific Benefits:** This study will contribute to the body of scientific knowledge on the use of natural adsorbents for complex wastewater treatment. It provides critical data on the performance of specific Nigerian clays under conditions that simulate real produced water, moving beyond synthetic solutions. The findings will offer insights into adsorption mechanisms, kinetics, and isotherm modeling specific to local materials and local problems. This knowledge is valuable for environmental engineers, material scientists, and researchers working on sustainable water treatment solutions.

**Policy and Regulatory Benefits:** The outcomes of this research can serve as an evidence-based tool for policymakers and regulatory agencies like the Nigerian Upstream Petroleum Regulatory Commission (NUPRC). By demonstrating the feasibility and effectiveness of a locally sourced treatment method, the study can inform and guide the development of more pragmatic and enforceable environmental policies. It can also support the argument for closing legislative loopholes, such as the NESREA exemption for upstream activities, by presenting a viable and cost-effective compliance pathway for operators.

**Social Benefits:** Addressing the issue of produced water pollution can help reduce the frequent conflicts and tensions between oil-producing communities and multinational companies. By promoting a cleaner environment and potentially creating new local industries around clay processing and adsorbent production, this research can contribute to improved community relations and social stability in the region.

In summary, this study is significant because it proposes a practical, sustainable, and locally relevant solution to a major environmental problem, with positive ripple effects for the economy, scientific community, and society at large.

## 1.7 Scope of the Study

This research is designed to provide a focused investigation into the use of Nigerian clay for produced water treatment. To ensure depth and clarity, the study will be bounded by the following parameters:

**Geographical Scope:** The study will primarily focus on clay samples sourced from known deposits in Nigeria, particularly from regions like Niger State (for kaolinite) and Anambra State (for bentonite). The produced water characteristics discussed and targeted for treatment will be based on the well-documented profile of PW from the Niger Delta basin.

**Technical Scope:**

a. **Adsorbents:** The research will be limited to the analysis of one or two specific types of Nigerian clay (e.g., kaolinite and bentonite). The study will investigate both the raw clays and modifications using common, accessible techniques such as acid activation.

b. **Target Pollutants:** The evaluation of adsorption efficiency will focus on key indicator pollutants common in produced water. These will likely include select heavy metals (e.g., Copper (Cu), Iron (Fe), Nickel (Ni)) and a measure of organic content (e.g., oil and grease, phenols).

c. **Process:** The study will be conducted primarily through laboratory-scale batch adsorption experiments. This will involve controlling variables such as contact time, adsorbent dosage, pH, and initial contaminant concentration to determine optimal conditions.

d. **Analysis:** The performance will be assessed using standard analytical methods to measure pollutant concentration before and after treatment. Data analysis will involve kinetic and isotherm modeling (Langmuir and Freundlich) to understand the adsorption process.

## 1.8 Limitations

a) The study will not involve continuous-flow or pilot-scale column tests, which are necessary for full-scale implementation but are beyond the resources of this initial research phase.

b) The research will not cover a comprehensive analysis of all possible contaminants in produced water (e.g., naturally occurring radioactive materials (NORM) or all organic compounds).

c) The economic feasibility analysis will be preliminary, based on material and processing costs, and not a full-scale techno-economic assessment.

d) The regeneration and disposal cycles for the spent clay adsorbent will be explored on a limited basis.

In essence, this scope defines a controlled and detailed laboratory investigation to establish the fundamental efficacy and mechanisms of using local clay for treating produced water, providing a strong foundation for future larger-scale and field studies.

# CHAPTER TWO

## 2.0 LITERATURE REVIEW

### 2.1. Characteristics and Composition of Produced Water

Produced water (PW) is the main liquid waste stream generated during oil and gas production (Sanchez-Rosario & Hildenbrand, 2022). It is brought to the surface alongside hydrocarbons during both primary and secondary recovery operations. PW is a complex mixture of native formation water, injected fluids such as seawater, polymer-enhanced water, or steam, and residual oilfield chemical additives. Because the origin and operational history of each field differ, the composition of PW is highly site-specific and often changes over the life of a well (Nwosi-Anele & Iledare, 2016).

Globally, the volume of PW is greater than all other oilfield wastes combined, making it one of the petroleum industry's most significant environmental management challenges. The large volumes, combined with the wide range of contaminants present, require effective treatment processes and strict monitoring before discharge or reuse in applications such as agriculture, industry, or reinjection.

### 2.1.1 Major Inorganic Components

Produced water is essentially a saline solution. Total dissolved solids (TDS) concentrations typically range between 10,000 and 200,000 mg/L, and in some cases can exceed seawater salinity (about 35,000 mg/L TDS). The dominant ions are sodium ($Na^+$) and chloride ($Cl^-$), although calcium ($Ca^{2+}$), magnesium ($Mg^{2+}$), sulfate ($SO_4^{2-}$), and bicarbonate ($HCO_3^-$) are also commonly present in significant amounts. For example, analyses of PW from the Niger Delta reported TDS levels between 12,000 and 28,000 mg/L, with chloride concentrations from 7,150 to 18,500 mg/L, Plates well above most environmental discharge limits (Borky-Bakre & Okafor, 2023). The pH of PW generally lies within the alkaline range (7.0–9.0), largely due to carbonate and bicarbonate buffering.

### 2.1.2 Organic Contaminants

In addition to dissolved salts, PW contains both free and emulsified oil droplets, usually measured as “oil and grease,” as well as a range of dissolved organic compounds. These include light aromatics such as benzene, toluene, ethylbenzene, and xylenes (BTEX), together with polycyclic aromatic hydrocarbons (PAHs) and alkylphenols. Residual amounts of surfactants, corrosion inhibitors, scale inhibitors, and other injected chemical additives are also frequently detected (Nwosi-Anele & Iledare, 2016). Many of these organic contaminants are toxic and are regulated at very low concentrations, often in the parts-per-million or parts-per-billion range, making their removal a major challenge in PW treatment.

### 2.1.3 Trace Metals and Naturally Occurring Radioactive Materials (NORM)

Although most metals in produced water occur at low concentrations, often below 0.001 mg/L for lead (Pb), cadmium (Cd), and chromium (Cr), even trace amounts of nickel (Ni), iron (Fe), copper (Cu), and zinc (Zn) can accumulate in aquatic organisms and pose ecological risks. In addition, some formation waters contain naturally occurring radioactive isotopes such as radium-226 and radium-228. These NORM constituents require strict handling and disposal procedures to safeguard workers and nearby communities.

### Suspended Solids and Microbial Content

Produced water also carries suspended materials, including clays, sand, scale precipitates, and corrosion products. Microbial populations are frequently present, ranging from sulfate-reducing bacteria to halophilic archaea. Their presence is often linked to inadequate biocide dosing or the introduction of microbes through injection water. Both the solids and microbial biomass must be managed through processes such as filtration, sedimentation, or chemical coagulation.

## 2.2 Environmental and Regulatory Concerns in Nigeria

In the Niger Delta, the uncontrolled discharge of produced water has long been a source of environmental degradation. When untreated PW enters rivers, swamps, and farmland, its high salinity and hydrocarbon content can cause soil salinization, destroy vegetation cover, and contaminate surface and shallow groundwater used for drinking and irrigation. Toxic constituents such as polycyclic aromatic hydrocarbons (PAHs), phenols, and trace metals accumulate in fish and other aquatic organisms, posing risks to biodiversity and to human health through the food chain. The visible oil sheen that persists on affected water surfaces also blocks sunlight, reducing photosynthesis in plankton and submerged plants. This disruption undermines the productivity of fishing grounds on which many Delta communities depend.

Regulation of PW in Nigeria is based on the Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN). First issued in 1985 by the Department of Petroleum Resources (DPR) and revised in 2002, EGASPIN sets limits for oil and grease, total dissolved solids (TDS), heavy metals, biochemical oxygen demand (BOD), and pH before discharge is permitted. Operators are required to obtain discharge permits and remain fully responsible for waste management throughout its lifecycle. Earlier interim guidelines from 1981 already required flow stations to install gravity separators to remove bulk oil before release.

Despite these provisions, enforcement has often been inconsistent. The DPR was restructured into the Nigerian Upstream Petroleum Regulatory Commission (NUPRC) in 2021, yet gaps remain, especially in offshore operations where EGASPIN is the only applicable regulation. The broader National Environmental Standards and Regulations Enforcement Agency (NESREA) Act of 2007 does not cover upstream oil and gas activities, further limiting accountability. Field audits and independent studies have repeatedly shown evidence of non-compliance, including platforms that discharge PW directly into open water after simple dilution, bypassing even basic treatment (Nwosi-Anele & Iledare, 2016).

The scale of the problem is substantial. Ukpohor (2001) estimated that about 82% of Niger Delta reservoirs operate under water-drive systems, meaning that large volumes of formation water are produced alongside oil. In the absence of reinjection or reuse programs, and with weak enforcement, tens of millions of barrels of PW are discharged daily, contributing to soil degradation, aquatic contamination, and public health issues. In some onshore communities, stagnant discharge ponds have become breeding grounds for mosquitoes and other disease vectors.

## 2.3. Overview of Conventional Produced Water Treatment Methods

Produced water (PW) treatment has traditionally relied on staged combinations of physical, chemical, and biological processes. These processes are arranged in “treatment trains,” where each stage targets a specific class of contaminants. Properly designed trains can achieve effluent oil-and-grease concentrations below 10 mg/L. However, in practice, many facilities—particularly in Nigeria—lack even basic separation units (Nwosi-Anele & Iledare, 2016).

### 2.3.1 Primary Separation

Primary separation is the first line of treatment and relies mainly on gravity to remove free oil and coarse suspended solids. Skimming tanks are a common unit, consisting of shallow rectangular tanks where lighter oil rises to the surface and is skimmed off mechanically. Corrugated-plate interceptors (CPIs) are another option. These employ stacked, inclined plates that provide a large surface for oil droplets to coalesce and separate more efficiently than in open tanks. Primary systems typically remove between 50% and 70% of free oil and particles larger than 100 microns. However, they are largely ineffective against stable emulsions and fine solids.

### 2.3.2 Secondary Separation

Secondary separation targets smaller oil droplets, typically in the range of 1–100 microns, as well as finer suspended particles. Hydrocyclones and centrifuges are widely used in this stage. Both rely on centrifugal forces to accelerate density-based separation. Hydrocyclones are efficient at handling large flow rates with a small footprint, but they are less effective for very fine emulsions. Centrifuges provide higher separation efficiency but at the cost of greater energy input.

Induced gas flotation (IGF) is another common technology in this stage. It introduces fine gas bubbles into the water stream, which attach to oil droplets and carry them upward, forming a scum layer that is mechanically removed. Electrostatic coalescers are also employed in some facilities. These use high-voltage fields to polarize and attract oil droplets, causing them to merge into larger drops that separate more easily by gravity. When applied in series, for example by combining a hydrocyclone or coalescer with IGF, oil-in-water concentrations can be reduced to below 30 mg/L under optimal operating conditions.

### 2.3.3 Tertiary Polishing

After primary and secondary separation, residual oil, solids, and dissolved organics often remain in the effluent. Tertiary polishing steps are therefore needed to improve water quality further. Media filtration, such as sand or activated carbon filters, is commonly used to remove fine particulates and, in the case of activated carbon, to adsorb dissolved organics. These filters require regular backwashing and periodic media replacement to maintain efficiency.

Chemical coagulation and flocculation may also be applied at this stage. In this process, polymers or inorganic coagulants such as alum or ferric chloride neutralize particle charges and promote the formation of larger flocs, which can then be removed by settling or filtration. This technique is especially useful when low turbidity is required prior to advanced processes like membrane treatment.

Biological treatment represents another tertiary option, making use of aerobic reactors or constructed wetlands to biodegrade dissolved organics and residual oil. Such systems are relatively cost-effective and environmentally sustainable but require careful control of operating parameters such as nutrient levels, pH, and temperature. They can also generate secondary waste in the form of sludge. When combined, these tertiary approaches can reduce effluent oil concentrations to below 10 mg/L and achieve significant reductions in biochemical oxygen demand (BOD).

### 2.3.4 Membrane and High-Energy Processes

In cases where very stringent water quality is required, such as for reinjection into reservoirs or zero-liquid-discharge systems, advanced, high-energy methods are employed. Membrane processes are the most common in this category. Ultrafiltration (UF) is used to remove fine particulates and colloids, while reverse osmosis (RO) is applied to desalinate water to meet reuse or discharge standards. However, membrane fouling caused by oil and scale-forming minerals remains a persistent operational challenge.

Thermal processes such as evaporation and crystallization are also available. These involve vaporizing water, either by boiling or under vacuum, to separate it from concentrated brine and solid salts. While these methods can achieve nearly complete water recovery, they require high capital investment and significant energy input, which limits their use to specialized applications in industrialized regions.

### 2.3.5 Limitations and Practice in Nigeria

While conventional produced water treatment technologies are well established worldwide, their application in Nigeria remains limited. Many oilfield facilities in the Niger Delta lack even basic primary separators. Nwosi-Anele and Iledare (2016) observed that some flow stations discharged produced water with oil-and-grease concentrations exceeding 100 mg/L, suggesting that gravity skimmers were either absent or poorly maintained. The situation is compounded by high capital costs, limited technical expertise, and weak regulatory enforcement. As a result, operators often resort to rudimentary practices such as dilution in open water or the use of settling ponds. These approaches fail to meet the effluent standards set by EGASPIN and continue to contribute to long-term environmental degradation.

## 2.4. Adsorption as an Alternative Treatment Method

Adsorption has gained attention as a versatile and cost-effective option for treating produced water, especially in cases where conventional methods struggle to remove dissolved organics and trace metals. The process is based on the attraction between contaminants and the surface of a solid sorbent. Depending on the type of interaction—ranging from van der Waals forces and hydrogen bonding to ion exchange or chemisorption—pollutants adhere to the sorbent surface. This mechanism is particularly effective at low contaminant concentrations, where bulk separation methods lose efficiency or become too costly.

One of the major advantages of adsorption is its low energy demand. Contaminant–sorbent equilibrium is often reached within minutes to a few hours, and apart from pumping and mixing, the process requires little additional energy. As noted by Yousef *et al.* (2020), adsorption can operate effectively at low concentrations, over short timeframes, and at much lower cost compared to other methods such as membranes or thermal evaporation. This makes it well suited for treating large volumes of produced water without the heavy infrastructure investments typical of advanced systems.

The choice of sorbent is highly flexible. Activated carbon remains the standard, with proven efficiency in removing BTEX compounds, PAHs, and residual production chemicals. However, its cost can be prohibitive at large scale. As an alternative, low-cost sorbents derived from agricultural residues—such as biochar or date-seed char produced through pyrolysis—have shown comparable efficiency in removing phenolics and heavy metals at a fraction of the cost. Natural materials like bentonite and kaolinite clays are also widely used. With their high cation-exchange capacity, these clays can selectively remove divalent metals such as lead and chromium, providing effective polishing for water that has already undergone primary separation.

In practice, adsorption units are often installed downstream of coarse separation processes. A pilot study in the Niger Delta demonstrated the potential of this approach: fixed-bed columns packed with date-seed biochar achieved more than 85% removal of total phenolics and a 60% reduction in dissolved iron within two hours. Other facilities have retrofitted clay-based adsorbent columns to simple skimmer effluents, successfully lowering lead concentrations from 0.005 mg/L to below the EGASPIN discharge limit of 0.0001 mg/L.

Despite these successes, several challenges remain. Sorbent pores can quickly foul when exposed to oil droplets and suspended solids, reducing capacity and requiring either upstream clarification or periodic back-flushing. Regeneration of exhausted sorbents also presents trade-offs: thermal regeneration restores performance but may damage the sorbent structure after repeated cycles, while chemical elution avoids high temperatures but produces concentrated waste streams that require further handling. Moreover, while laboratory and pilot-scale studies are promising, full-scale implementation requires additional validation of hydraulic behavior, bed longevity, and cost-effectiveness.

### 2.5. Clay as a Natural and Locally Sourced Adsorbent in Nigeria

Natural clays are a particularly promising class of low-cost, locally available adsorbents for produced water (PW) treatment in Nigeria. Minerals such as kaolinite, smectite (bentonite), illite, sepiolite, and attapulgite occur widely across the country. Notable deposits include Gbako kaolin in Niger State, bentonite formations in Ogun and Edo States, and lateritic clay horizons throughout the southeast. These aluminosilicate minerals possess a layered structure that provides high surface area and strong cation-exchange capacity, making them well suited for binding dissolved metal ions in water (Yousef *et al.*, 2020).

water treatment

Plate 2.1 Sample of Clay

The surface chemistry of clays allows them to remove positively charged metal contaminants. At typical PW pH levels (5–8), negatively charged sites on clay platelets attract and retain divalent and trivalent cations such as chromium ($Cr^{3+}$), cadmium ($Cd^{2+}$), zinc ($Zn^{2+}$), nickel ($Ni^{2+}$), and manganese ($Mn^{2+}$). Smectitic clays also swell in water, exposing additional sorption sites in their interlayer spaces. Even in their raw form, clays show strong uptake capacity, and simple pretreatments such as acid activation or washing can improve porosity and surface reactivity.

Several Nigerian studies confirm the potential of indigenous clays for water treatment. Mustapha *et al.* (2019) evaluated Gbako kaolin after mild acid pretreatment and reported over 80% sulfate removal, alongside significant reductions in Cr, Cd, and Zn. The results fit the Langmuir isotherm model, indicating monolayer adsorption. Akpomie and Dawodu (2015) purified a local bentonite (UAB) and achieved close to 90% removal of Ni(II) and Mn(II). Their data followed both Langmuir and Freundlich isotherms, reflecting a combination of uniform and heterogeneous adsorption processes.

Nigerian clays also show potential for hydrocarbon removal when chemically modified. Organoclays, produced by replacing natural cations with quaternary ammonium surfactants, develop hydrophobic surfaces that adsorb nonpolar compounds. Oraegbunam and Ngobiri (2020) modified Anambra bentonite with cetyltrimethylammonium bromide (CTAB) and achieved a more than 70% increase in crude oil fraction removal compared with unmodified clay. This behavior suggests organoclays could serve as effective polishing media for residual hydrocarbons in PW.

The availability and established use of clays in ceramics and drilling muds also indicate reliable supply chains within Nigeria. Using locally sourced adsorbents reduces transportation costs and aligns with circular-economy principles, as residues from clay mining can serve as raw material. Processing requirements are relatively simple—typically limited to washing, drying, and milling—which makes clay-based treatment accessible to operators with limited capital.

Nigeria's natural clays, especially kaolins and smectites, offer a sustainable and cost-effective alternative to imported adsorbents for PW treatment. Their strong ion-exchange capacity, modifiable surface chemistry, and proven ability to remove both metals and organics make them well suited for integration into conventional or hybrid treatment systems. Harnessing these resources can reduce costs, improve environmental performance, and support more sustainable produced water management in Nigerian oilfields.

### 2.6. Modification Techniques to Enhance Clay Adsorption Performance

Modifying natural clays is an effective way to improve their surface properties and optimize adsorption for specific produced-water contaminants. One of the most common methods is acid or base activation, where raw clays are treated with mineral acids (such as HCl or $H_2SO_4$) or alkaline solutions like NaOH. Acid activation dissolves carbonates and leaches octahedral cations, which increases pore volume and introduces new hydroxyl groups that serve as high-affinity sites for metal binding. In Nigerian bentonites, simple treatment with dilute HCl followed by neutralization has produced two- to three-fold increases in the uptake of $Pb^{2+}$, $Cr^{3+}$, and $Cd^{2+}$ compared with untreated samples.

Pillaring is another widely studied modification technique. It introduces polyoxo-cations, typically aluminum or iron species, between clay layers to hold the interlayer galleries open.

These “pillared clays” develop larger and more stable pore networks, significantly expanding surface area and adsorption capacity. For example, aluminum-pillared bentonite from Ogun State achieved a surface area of more than 150 $m^2/g$, compared to about 50 $m^2/g$ for the parent material, and showed a 60% improvement in the removal of bulky organic pollutants such as phenolics.

To enhance affinity for nonpolar organics, researchers often use organophilization. This involves replacing naturally hydrophilic interlayer cations with long-chain quaternary ammonium surfactants, such as cetyltrimethylammonium bromide (CTAB). The modified organoclays repel water while attracting oils and hydrocarbons. In one study, CTAB-modified Anambra bentonite adsorbed nearly twice as much kerosene and gasoline from simulated produced water compared with unmodified clay, making it effective for polishing oil droplets that bypass flotation units.

Thermal treatment is another route to enhance performance. Moderate calcination (200–600 °C) removes structural water and organic residues, alters surface acidity, and may modify pore structures depending on the mineral composition. While less selective than chemical treatments, thermal modification requires no hazardous reagents and can often be integrated into operations by using waste heat, making it an energy-efficient option.

Composite formation represents a more advanced strategy, combining clays with functional materials to achieve multiple removal mechanisms in one medium. For instance, kaolin grafted with iron-oxide nanoparticles becomes magnetic and can be separated from treated water with a magnetic field, eliminating filtration. Similarly, chitosan-clay composites combine the chelating capacity of biopolymers with the ion-exchange ability of clays, enabling simultaneous removal of cationic and anionic contaminants.

These modification techniques can be adapted to locally available Nigerian clays, often with activation chemicals derived from agro-waste (such as fruit-derived acids) or industrial by-products. However, they also introduce additional processing requirements, such as neutralizing spent acids, handling wash water, or managing regeneration waste streams. Effective design should therefore balance improved adsorption capacity with practical considerations of cost, operational simplicity, and environmental sustainability

## 2.7. Review of Prior Studies Using Nigerian Clay for Water Treatment

Several Nigerian studies have highlighted the potential of locally sourced clays for water treatment, particularly in removing metals and organic pollutants. These investigations demonstrate both the feasibility of clay-based adsorption and the areas that require further research before large-scale application.

Mustapha *et al.* (2019) evaluated Gbako kaolin, subjected to mild acid pretreatment, as an adsorbent for tannery wastewater containing chromium ($Cr^{3+}$), cadmium ($Cd^{2+}$), zinc ($Zn^{2+}$), sulfates, and organic loads such as COD and BOD. The kaolin achieved more than 75% removal for all analytes, with equilibrium data best described by the Jovanovic and Redlich–Peterson isotherms. This indicated a combination of heterogeneous surface activity and chemisorption, suggesting multiple sorption pathways, including ion exchange and surface complexation. While effective in batch conditions, the authors emphasized the need to test its performance in continuous-flow systems.

Akpomie and Dawodu (2015) studied a purified Nigerian bentonite (UAB bentonite) for the removal of Ni(II) and Mn(II) from aqueous solutions. Adsorption data aligned well with both Langmuir and Freundlich isotherms, implying the presence of monolayer adsorption alongside heterogeneous site interactions. Scatchard analysis confirmed multiple binding site affinities. Notably, more than 90% of adsorbed metals could be desorbed using mild acid, demonstrating the material's reusability and cost-effectiveness in cyclic applications.

Rabiu and Ambursa (2022) investigated a natural clay from Sokoto for $Pb^{2+}$ and $Cd^{2+}$ removal. The clay exhibited adsorption capacities of approximately 49.7 mg/g for lead and 31.6 mg/g for cadmium, values comparable to many commercial adsorbents. Both Langmuir and Freundlich models provided good fits, indicating chemisorption on heterogeneous surfaces. The kinetics showed rapid uptake within the first hour followed by slower equilibration, supporting the clay's potential for batch treatments, though column-scale validation remains necessary.

Oraegbunam and Ngobiri (2020) enhanced Anambra bentonite by exchanging its native cations with cetyltrimethylammonium bromide (CTAB), producing an organophilic adsorbent. When tested against crude oil fractions such as petrol, kerosene, and diesel, the modified clay adsorbed nearly twice the hydrocarbon load compared to its unmodified counterpart. This finding illustrates the potential of organoclays for removing residual hydrocarbons from produced water, particularly in situations where conventional separation processes are less effective.

Overall, these studies confirm the adsorption potential of both raw and modified Nigerian clays, with laboratory results frequently showing removal efficiencies above 80–90% for metals and organics. However, the majority of these experiments were performed using simulated single-contaminant solutions rather than real produced water. Authentic produced water is more complex, with high salinity, multiple competing ions, emulsified oils, and even naturally occurring radioactive materials, all of which can interfere with adsorption processes.

Another limitation is the absence of pilot-scale or field-based demonstrations. Most work has been confined to batch experiments, leaving critical aspects—such as column breakthrough behavior, regeneration stability, and long-term hydraulic performance largely unexplored. Addressing these gaps is essential for translating laboratory successes into practical treatment trains capable of managing the large volumes of produced water generated in Nigeria's oilfields.

## 2.8. Adsorption Equilibrium Models: Langmuir and Freundlich Isotherms

Adsorption equilibrium models provide the theoretical underpinning for interpreting batch adsorption experiments and designing treatment systems. Among these, the Langmuir and Freundlich isotherms are the most widely employed, each reflecting different assumptions about how sorbate molecules interact with the adsorbent surface.

The Langmuir isotherm is built on the premise of a perfectly uniform adsorbent surface containing a fixed number of identical sites, each of which can hold exactly one molecule. Under this model, adsorption proceeds only until a single monolayer is complete, with no interactions between adsorbed species. Mathematically, the amount of solute adsorbed at equilibrium, $q_e$ (mg adsorbate/g adsorbent), relates to the equilibrium solute concentration in the liquid phase, $C_e$ (mg /L), via

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

where $q_{max}$ (mg/g) represents the maximum monolayer capacity—essentially the total number of binding sites—and $K_L$ (L/mg) is the Langmuir affinity constant, reflecting the strength of the adsorbate–adsorbent interaction. A convenient linear form,

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \tag{2}$$

allows one to determine $q_{max}$ and $K_L$ from the slope and intercept of a plot of $\frac{C_e}{q_e}$ versus $C_e$. The dimensionless separation factor,

$$R_L = \frac{1}{1 + K_L C_O} \tag{3}$$

where $C_O$ is the initial solute concentration, helps assess adsorption favorability—values of 0<$R_L$ <1 indicate a favorable process. Because of its clear physical parameters and simplicity, the Langmuir model is often preferred when monolayer adsorption on a relatively uniform surface is expected.

In contrast, the Freundlich isotherm is purely empirical, designed to accommodate heterogeneous surfaces and multilayer adsorption phenomena. It does not predict a saturation point, remaining valid only over limited concentration ranges. Its general form is

$$q_e = K_F \, C_e^{1/n} \tag{4}$$

where $K_F$ and $1/n$ are Freundlich constants indicating adsorption capacity and intensity. A plot of $log\, q_e$ $vs.\ log\, C_e$ yields a straight line for a true Freundlich behavior. Real adsorbents often show behavior between these extremes. In practice, fitting PW adsorption data to both isotherms helps infer surface homogeneity and estimate maximum uptake.

$$\log q_e = \log K_F + (1/n) \log C_e \tag{5}$$

so that a plot of log $q_e$ versus log $C_e$ gives a straight line whose slope (1/n) indicates how strongly adsorption varies with concentration (smaller 1/n or larger n implies more favorable adsorption). Although the Freundlich model lacks a theoretical saturation limit, its flexibility often yields excellent fits to experimental data for natural, multi-component adsorbents.

In practical applications—such as modeling adsorption of metals or organics onto Nigerian clays—researchers routinely fit both Langmuir and Freundlich isotherms to their data. Comparing correlation coefficients or error metrics helps reveal whether adsorption is closer to a monolayer process on uniform sites (favoring Langmuir) or to a more heterogeneous, multi-layer phenomenon (favoring Freundlich). Yousef *et al.* (2020) note that while the Langmuir model is most frequently applied in produced-water studies, the Freundlich isotherm remains invaluable for capturing adsorption behavior on real-world, non-ideal surfaces. In summary, Langmuir provides insight into maximum capacity and site affinity, whereas Freundlich accommodates surface heterogeneity and variable binding energies.

*Table 2.1 Comparison of Langmuir and Freundlich Adsorption Isotherm Models.*

| Aspect | Langmuir Isotherm | Freundlich Isotherm |
|---|---|---|
| Origin / History | Proposed by Irving Langmuir in 1916 | Proposed by Herbert Freundlich in 1906 |
| Assumptions | - Monolayer adsorption<br>- Homogeneous surface<br>- Identical adsorption sites<br>- No interaction between adsorbed molecules | - Heterogeneous surface<br>- Sites with varying adsorption energies<br>- Multilayer adsorption possible<br>- No saturation limit |
| Mathematical Expression | $q_e = (Q_{max} K_L C_e) / (1 + K_L C_e)$ | $q_e = K_F C_e^{(1/n)}$ |
| Linearized Form | $C_e/q_e = 1 / (Q_{max} K_L) + C_e / Q_{max}$ | $\log q_e = \log K_F + (1/n) \log C_e$ |
| Key Parameters | - $Q_{max}$: Maximum adsorption capacity (mg/g)<br>- $K_L$: Langmuir constant (L/mg) | - $K_F$: Freundlich capacity factor<br>- $1/n$: Heterogeneity factor |
| Surface Type | Homogeneous | Heterogeneous |
| Adsorption Layer | Monolayer | Multilayer |
| Adsorption Capacity | Finite; reaches saturation at $Q_{max}$ | Infinite (in theory); no saturation |
| Suitability | Best for chemisorption and uniform surface adsorbents | Best for physisorption and complex, natural materials |
| Plot Type | Linear plot: $C_e/q_e$ vs. $C_e$ | Log–log plot: $\log q_e$ vs. $\log C_e$ |
| Interpretation of 1/n | Not applicable | $1/n < 1$: Favorable adsorption<br>$1/n > 1$: Unfavorable adsorption |

## 2.9. Applications of Isotherm Models in Produced Water Treatment

Applications of isotherm models in produced water (PW) treatment hinge on their ability to translate raw adsorption data into meaningful design parameters. Researchers universally begin by fitting equilibrium uptake data, that is, measured values of $q_e$ versus $C_e$, to both Langmuir and Freundlich equations. The choice of the better-fitting model guides our understanding of whether adsorption is driven by monolayer coverage on uniform sites or by more complex interactions on a heterogeneous surface.

Several Nigerian studies exemplify this approach. Rabiu and Ambursa (2022) investigated Pb(II) and Cd(II) removal using a Sokoto clay, fitting their batch data to both isotherms. Both models correlated well with the experimental points, but the Freundlich fit, together with a heterogeneity factor (1/n) less than unity, suggested that chemisorption on varied affinity sites predominated. This insight helped the authors infer that metal uptake occurred through multiple binding mechanisms rather than through a simple monolayer process.

Similarly, Akpomie and Dawodu (2015) applied an even broader modeling suite, Langmuir, Freundlich, Temkin, and Scatchard, to characterize Ni(II) and Mn(II) adsorption on Nigerian bentonite. While the Langmuir parameters ($q_{max}$ and $K_L$) provided estimates of maximum capacity and intrinsic affinity, the Scatchard analysis confirmed the presence of at least two classes of active sites with different binding energies. Together, these models painted a richer mechanistic picture than any single isotherm could offer.

Beyond individual case studies, the broader PW literature consistently finds that Langmuir and Freundlich analyses serve complementary roles. Langmuir's $q_{max}$ offers a straightforward, baseline comparison of adsorbent performance, useful when screening new materials, while $K_L$ quantifies sorbate–sorbent affinity. Freundlich's constants ($K_F$ and 1/n) capture adsorption intensity and surface heterogeneity, which are critical when treating the complex, multi-component mixtures typical of produced water.

Practically, engineers often observe that adsorption data conform to Langmuir behavior at higher solute concentrations, where monolayer coverage dominates, and to Freundlich behavior at lower concentrations, where surface heterogeneity becomes more pronounced. These trends inform the sizing of adsorbent beds and the sequencing of treatment stages: a high-capacity Langmuir regime might dictate bed depth, whereas a Freundlich-controlled tail could determine when to regenerate or replace the media.

It is important, however, to recognize that both isotherm models are fundamentally empirical or phenomenological. A strong statistical fit does not, by itself, confirm the underlying adsorption mechanism. Nonetheless, Langmuir and Freundlich analyses remain indispensable tools in PW treatment research. They enable quantitative comparison of novel Nigerian clays against commercial adsorbents, guide scale-up from bench to pilot systems, and underpin the design of economically and environmentally robust treatment trains.

# CHAPTER THREE

## 3.0 MATERIALS AND METHODS

This chapter details the experimental procedures undertaken to achieve the research objectives outlined in Section 1.4. The methodology is structured into several key phases: (1) collection and characterization of the produced water (PW) sample; (2) collection, preparation, and characterization of the bio-adsorbent (AG clay and GE clay); (3) batch adsorption experiments to evaluate heavy metal removal efficiency; and (4) analysis of equilibrium data using adsorption isotherm models. The overall approach is designed to systematically investigate the potential of locally sourced waste materials for treating real PW from the Niger Delta.

### 3.1 Collection and Characterization of Produced Water

### 3.1.1. Sample Collection

Produced water (PW) samples were collected from the skimmer pit of an oil field within the Niger Delta region, Nigeria. This ensures the study addresses the specific local problem as defined in the study area (Section 1.8) and provides representative samples of the challenging high-salinity, high-contaminant-load wastewater characteristic of this region. The samples were obtained in high-density polyethylene (HDPE) containers. To preserve the integrity of the sample, the containers were completely filled to minimize headspace and atmospheric oxidation of volatile components. The samples were immediately transported to the laboratory and stored at 4°C in a refrigerator to inhibit microbial activity and prevent significant changes in composition prior to analysis and experimentation (Igunnu and Chen, 2014).

Plate 3.1 Produced water sample

### 3.1.2. Physicochemical Characterization

The PW sample was characterized to establish its baseline contaminant profile, aligning with the first objective of this study. Key parameters analyzed included pH, salinity, Total Dissolved Solids (TDS), and the concentrations of specific heavy metals: lead (Pb), copper (Cu), arsenic (As), and iron (Fe). These metals were selected due to their prevalence and toxicity in Niger Delta produced water, as highlighted in the scope of the study (Section 1.7). Standard analytical methods, as outlined in the American Public Health Association (APHA) standard methods for the examination of water and wastewater, were employed. The concentration of the target heavy metals was determined using Atomic Absorption Spectrophotometry (AAS). This characterization provides the essential $C_0$ (initial concentration) values against which adsorption efficiency will be measured and ensures the produced water represents the complex matrix typical of mature Niger Delta oil fields.

## 3.2 Preparation and Activation of Bio-Adsorbents

### 3.2.1. Collection and Preparation of Clay Adsorbent

Clay samples were sourced from two distinct riverline deposits in Edo State, Nigeria: Ogba River (AG) and Gelegele River (GE). The collection procedure involved using a small trowel to excavate beyond the superficial topsoil to access the underlying clay-rich strata. This method ensures the procurement of material with minimal organic and anthropogenic contamination. The collected samples were immediately sealed in clean, pre-labeled polyethylene bags to preserve their inherent properties and prevent cross-contamination during transport to the laboratory.

The initial pre-treatment of the raw clays involved a series of physical cleaning and size reduction steps. The samples were repeatedly washed with deionized water in large containers to dislodge and remove adherent impurities such as silt, fine sand, and soluble organic matter. The washed clay was then subjected to sun-drying for a period of 2–4 days, spread on clean cardboard surfaces, until all visible moisture had evaporated (Plate 3.2). The sun-dried lumps were subsequently pulverized using a porcelain mortar and pestle to achieve a coarse powder (Plate 3.3). This ground material was stored in airtight containers prior to further thermal treatment.

*Plate 3.2 Washing of the clay before Sun-drying.*

*Plate 3.3 Sun-drying of washed clay samples on cardboard.*

*Plate 3.4 Ground clay powder after sun-drying and prior to oven-drying.*

To eliminate residual and interlayer moisture, the ground clay samples were oven-dried at 140 °C for 2 hours. The thoroughly dried product was then sieved through a 60-mesh British Standard Sieve (BSS) with an aperture of 250 µm to obtain a uniform particle size fraction, which is critical for ensuring consistency and reproducibility in subsequent adsorption experiments.

### 3.2.2. Chemical Activation

The sieved clay was chemically activated to enhance its surface area, porosity, and ion-exchange capacity by removing inorganic impurities such as carbonates and iron oxides. A 2 M solution of hydrochloric acid (HCl) was prepared. The activation was carried out by mixing 10 g of the oven-dried clay with 100 mL of the 2 M HCl solution (i.e., a solid-to-liquid ratio of 1:10 w/v). The mixture was agitated in a shaker water bath maintained at 70 °C and 120 rpm for 3 hours to ensure homogeneous contact and reaction between the acid and the clay particles.

Post-activation, the acid-treated clay was separated and subjected to repeated washing with distilled water via centrifugation and decantation until the supernatant reached a neutral pH, indicating the complete removal of free acid and soluble reaction products (Plate 3.5). The purified clay was then oven-dried once more and stored in airtight containers. The final masses of the activated clay adsorbents were recorded as 8.200 g for Ogba River (Ag) and 8.152 g for Gelegele (Ge), representing a mass loss of approximately 18% and 18.5%, respectively, attributable to the dissolution of impurities and structural water during the acid activation process.

*Plate 3.5 Washing the acid-activated clay with distilled water to achieve neutral pH.*

### 3.2.3. Batch Adsorption Studies

The efficacy of the activated clay adsorbents for wastewater treatment was evaluated using batch adsorption experiments. Produced water (PW) sample obtained from a Niger Delta oil field, was used as the adsorbate solution. For each experimental run, a predetermined dose of 2 g of activated clay was introduced into 100 mL of the produced water in a 250 mL glass beaker.

The mixture was agitated using a magnetic stirrer operating at a constant speed of 150 rpm, with a Teflon-coated magnetic bar ensuring consistent mixing (Plate 3.6). The experiments were conducted at ambient temperature (25 ± 2 °C) across four different contact times: 30, 60, 90, and 120 minutes. Upon completion of each designated contact period, the agitation was halted, and the mixture was allowed to settle. The supernatant was then filtered to separate the spent adsorbent from the treated water (Plate 3.7). The resulting filtrates were collected in labeled sample bottles (Plate 3.8) for subsequent chemical analysis. The residual concentrations of heavy metals in the treated water were determined using Atomic Absorption Spectrophotometry (AAS).

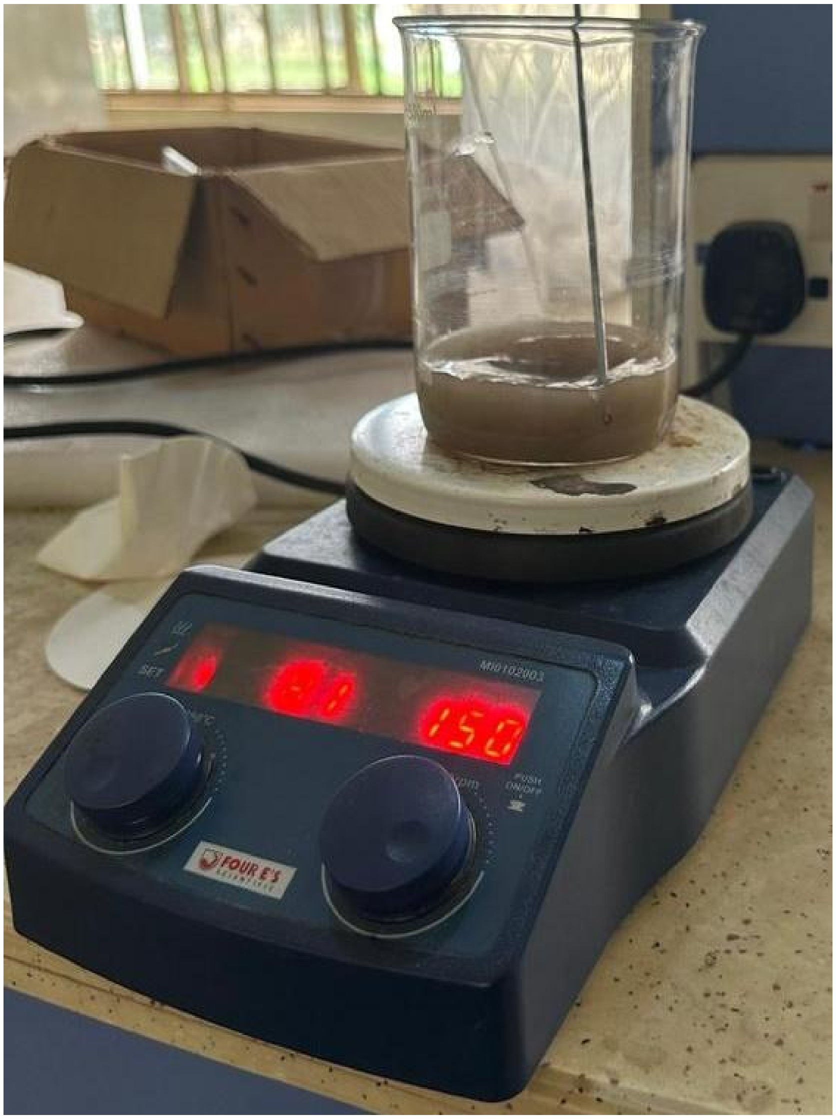


Plate 3.6 **Batch adsorption process: (a)** Treatment setup using a magnetic stirrer.

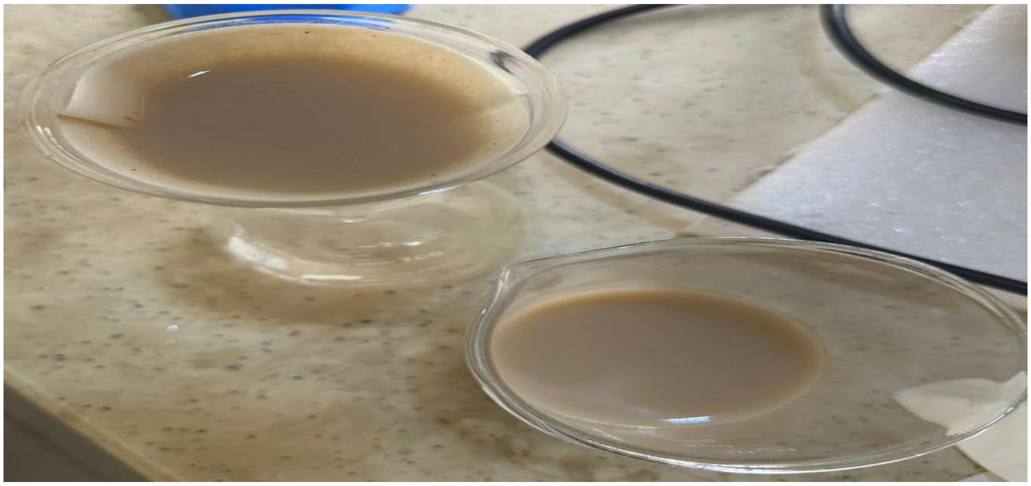


*Plate 3.7* ***Batch adsorption process: (b)*** *Filtration of the clay-treated produced water.*

*Plate 3.8 Treated produced water samples at different contact times.*

### 3.2.4 Sample Digestion and Analysis

After each contact time, the mixtures were allowed to settle, filtered, and the filtrates were collected. To ensure all heavy metals were in a detectable ionic form for analysis, all filtrate samples were digested using a standard acid digestion procedure prior to analysis. The digested samples are shown in Plate 3.9. The residual concentrations of heavy metals (Fe, and Cu) in the digested samples were then determined using Atomic Absorption Spectrophotometry (AAS).

*Plate 3.9 Digested produced water samples prepared for analysis via Atomic Absorption Spectrophotometry (AAS).*

## 3.3 Adsorption Isotherm and Kinetic Modelling

### 3.3.1 Adsorption Isotherm Models

The equilibrium adsorption data obtained from the batch experiments were analyzed using Langmuir and Freundlich isotherm models to understand the relationship between the amount of metal ions adsorbed on the adsorbent surface and their equilibrium concentration in solution.

The **Langmuir isotherm** assumes a monolayer adsorption on a homogeneous surface with uniform energy sites and no interaction between adsorbed molecules. It is expressed as:

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

Where $C_e$ is the equilibrium concentration (mg/L)

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

$q_{max}$ is the maximum adsorption capacity (mg/g)

$K_L$ is the Langmuir constant (L/mg).

The Freundlich isotherm describes adsorption on heterogeneous surfaces and is expressed as:

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

Where $K_f$ is the Freundlich constant

n is the adsorption intensity.

These models were used to determine which better represented the adsorption behavior of the metal ions onto the local adsorbents (eggshell and sawdust).

### 3.3.2 Adsorption Kinetic Models

The adsorption kinetics were studied to determine the adsorption rate and to identify the rate-controlling mechanism. The following models were applied to the time-series adsorption data.

**Pseudo-first-order (PFO):**

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1 t}{2.303}$$

where $q_t$ is the adsorption capacity at time t (mg/g)

$q_e$ is the equilibrium adsorption capacity (mg/g)

$k_1$ is the PFO rate constant (1/min)

t is contact time (min).

**Pseudo-second-order (PSO):**

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where $k_2$ is the PSO rate constant (g/mg·min).

Linear plots of $\log\left(q_e - q_t\right)$ versus t for the pseudo-first-order model and $t/q_t$ versus t for the pseudo-second-order model were used to determine the rate constants and correlation coefficients. The model with the higher $R^2$ value was considered to provide a better fit for the adsorption process.

**Weber–Morris (Intraparticle Diffusion) model:**

$$q_t = k_{id}\, t^{1/2} + C$$

where $k_{id}$ is the intraparticle diffusion rate constant ($mg \cdot g^{-1} \cdot min^{-0.5}$)

C is the intercept related to the thickness of the boundary layer.

A plot of $q_t$ versus $t^{0.5}$ was used to assess whether intraparticle diffusion is the sole rate-limiting step. If the line passes through the origin ($C \approx 0$), intraparticle diffusion is likely the rate-controlling mechanism; if not, multiple steps (film diffusion + intraparticle diffusion) are implicated.

*Table 3.1 Adsorption Equation and Models*

| Model | Linear Equation | Plot | Slope | Intercept |
|---|---|---|---|---|
| Langmuir Isotherm | $\frac{C_e}{q_e}=\frac{1}{K_L q_{max}}+\frac{C_e}{q_{max}}$ | $\frac{C_e}{q_e} vs. C_e$ | $\frac{1}{q_{max}}$ | $\frac{1}{K_L q_{max}}$ |
| Freundlich Isotherm | $\log q_e = \log K_F + \frac{1}{n} \log C_e$ | $\log q_e \ vs. \log C_e$ | $\frac{1}{n}$ | $\log K_F$ |
| Pseudo-First-Order<br>(PFO) | $\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$ | $\log (q_e - q_t) \ vs. t$ | $-\frac{k_1}{2.303}$ | $\log q_e$ |
| Pseudo-Second-Order<br>(PSO) | $\frac{t}{q_t}=\frac{1}{k_2 q_e^2}+\frac{t}{q_e}$ | $\frac{t}{q_t} vs. t$ | $\frac{1}{q_e}$ | $\frac{1}{k_2 q_e^2}$ |
| Weber–Morris | $q_t = k_{id} t^{1/2} + C$ | $q_t vs. t^{1/2}$ | $k_{id}$ | $C$ |

## CHAPTER FOUR

# 4.0 RESULTS AND DISCUSSION

### 4.1. Adsorption Kinetics and Efficiency of Metal Removal

This study tested the effectiveness of acid-activated Ogba River (AG) and Gelegele (GE) clays for removing heavy metals from produced water. We ran batch experiments for 30 to 120 minutes and calculated the removal percentage and the adsorption capacity ($q_e$ in mg/g) to see how well they performed. The plots showing these trends over time are provided in the Appendix.

**Removal of Iron (Fe)**

Starting with an iron concentration of 0.744 mg/L, both clays removed more iron as time increased. The AG clay performed steadily, with its efficiency rising from 39.1% at 30 minutes to 63.7% at 120 minutes. The GE clay improved more noticeably, especially in the last 30 minutes, reaching a final efficiency of 65.3%. This shows that while the GE clay started slower, it ultimately matched the AG clay's performance for iron removal.

The amount of iron adsorbed also grew over time. After two hours, the AG clay held 0.0237 mg/g, while the GE clay held 0.0243 mg/g. This steady increase suggests the process was still working toward a full balance, especially for the GE clay, which showed a significant final jump.

**Removal of Copper (Cu)**

The initial copper concentration was much lower, at 0.026 mg/L. Both clays performed exceptionally well. The AG clay was particularly effective, achieving 88.5% removal and reducing the copper to 0.003 mg/L after 120 minutes. The GE clay also performed well, removing 73.1% of the copper.

The amount of copper adsorbed was lower in absolute terms due to the low starting concentration, but it consistently increased over time. The AG clay demonstrated a higher affinity for copper, adsorbing 0.00115 mg/g compared to 0.00095 mg/g for the GE clay. The sharp increase in removal by the AG clay in the final stage suggests a highly efficient uptake mechanism for copper ions.

*Table 4.1 Adsorption Capacity ($q_e$) of AG and GE Clays for Fe and Cu*

| Metal | Clay | Contact Time (min) | $C_e$ (mg/L) | $q_e$ (mg/g) |
|---|---|---|---|---|
| **Fe** | **AG** | 30 | 0.453 | 0.0146 |
| | | 60 | 0.440 | 0.0152 |
| | | 90 | 0.360 | 0.0192 |
| | | 120 | 0.270 | 0.0237 |
| **Fe** | **GE** | 30 | 0.640 | 0.0052 |
| | | 60 | 0.513 | 0.0116 |
| | | 90 | 0.502 | 0.0121 |

| Metal | Clay | Contact Time (min) | $C_e$ (mg/L) | $q_e$ (mg/g) |
|---|---|---|---|---|
|  |  | 120 | 0.258 | 0.0243 |
| **Cu** | **AG** | 30 | 0.017 | 0.00045 |
|  |  | 60 | 0.013 | 0.00065 |
|  |  | 90 | 0.009 | 0.00085 |
|  |  | 120 | 0.003 | 0.00115 |
| **Cu** | **GE** | 30 | 0.020 | 0.00030 |
|  |  | 60 | 0.014 | 0.00060 |
|  |  | 90 | 0.013 | 0.00065 |
|  |  | 120 | 0.007 | 0.00095 |

*Note: The adsorption capacity was calculated as* $q_e = (C_o - C_e)V / m$*, where* $C_o$ *is the initial concentration,* $C_e$ *is the concentration at time t, V is the volume of solution, and m is the mass of clay.*

The data confirms that adsorption depends heavily on contact time, which supports our hypothesis ($H_2$). The faster removal at the beginning is due to the many available sites on the clay surface, with the process slowing as these sites get filled. The fact that AG clay was better for copper, while both clays were similar for iron, shows that each material has a specific affinity for different metals, likely due to their unique mineral compositions after acid-activation.

### 4.2. Analysis of Adsorption Kinetics

To understand the mechanism and what controls the speed of the adsorption process, we fitted the experimental data for iron and copper removal to three common kinetic models: the Pseudo-First-Order (PFO), Pseudo-Second-Order (PSO), and the Weber-Morris intra-particle diffusion models. All the calculated parameters from this analysis are summarized in Table 4.2.

*Table 4.2 Kinetic Model Parameters for Fe and Cu Adsorption onto AG and GE Clays*

| Metal | Clay | Model | Parameters | $R^2$ | Adjusted $R^2$ |
|---|---|---|---|---|---|
| **Fe** | **AG** | Pseudo-First-Order | $k_1$ = 0.0118 min$^{-1}$; $q_e$,calc = 0.0143 mg/g | 0.827 | 0.654 |
| | | Pseudo-Second-Order | $k_2$ = 0.702 g/(mg·min); $q_e$,calc = 0.0308 mg/g | 0.888 | 0.832 |
| | | Weber-Morris | k_id = 0.00167 mg/(g·min$^{0.5}$); C = 0.00415 mg/g | 0.863 | 0.795 |
| **Fe** | **GE** | Pseudo-First- | $k_1$ = 0.00747 min$^{-1}$; $q_e$,calc = | 0.823 | 0.646 |

| Metal | Clay | Model | Parameters | $R^2$ | Adjusted $R^2$ |
|---|---|---|---|---|---|
| | | Order | 0.0225 mg/g | | |
| | | Pseudo-Second-Order | $k_2$ = 0.000117 g/(mg·min); $q_e$,calc = -1.20 mg/g | 0.0008 | -0.499 |
| | | Weber-Morris | k_id = 0.00310 mg/(g·min$^{0.5}$); C = -0.0128 mg/g | 0.836 | 0.754 |
| **Cu** | **AG** | Pseudo-First-Order | $k_1$ = 0.0141 min$^{-1}$; $q_e$,calc = 0.00110 mg/g | 0.986 | 0.972 |
| | | Pseudo-Second-Order | $k_2$ = 2.94 g/(mg·min); $q_e$,calc = 0.00237 mg/g | 0.812 | 0.719 |
| | | Weber-Morris | k_id = 0.000124 mg/(g·min$^{0.5}$); C = -0.000270 mg/g | 0.962 | 0.942 |
| **Cu** | **GE** | Pseudo-First- | $k_1$ = 0.0129 min$^{-1}$; $q_e$,calc = | 0.892 | 0.785 |

| Metal | Clay | Model | Parameters | $R^2$ | Adjusted $R^2$ |
|---|---|---|---|---|---|
| | | Order | 0.000885 mg/g | | |
| | | Pseudo-Second-Order | $k_2$ = 1.76 g/(mg·min); $q_e$,calc = 0.00256 mg/g | 0.614 | 0.421 |
| | | Weber-Morris | k_id = 0.000109 mg/(g·$\text{min}^{0.5}$); C = -0.000295 mg/g | 0.938 | 0.908 |

### 4.2.1. Pseudo-First-Order vs. Pseudo-Second-Order Kinetics

We judged how well the PFO and PSO models worked by looking at the correlation coefficient ($R^2$) and how close the calculated equilibrium capacity ($q_e$,calc) was to the experimental value ($q_e$,exp).

For Iron (Fe) adsorption, the kinetics on AG clay were better described by the Pseudo-Second-Order (PSO) model, which had an $R^2$ of 0.888 compared to the PFO model's $R^2$ of 0.827. The PSO model suggests that the slowest, rate-limiting step likely involves chemisorption, where metal ions form strong chemical bonds with the clay's active sites. However, the model was not perfect, as its calculated capacity ($q_e$,calc = 0.0308 mg/g) was significantly higher than the experimental value of 0.0237 mg/g.

In stark contrast, the PSO model failed entirely for GE clay. It produced a nonsensical negative $q_e$,calc of -1.20 mg/g and an $R^2$ value of 0.0008, which is effectively zero. This clear failure shows that the assumptions of the PSO model do not apply to this system. The PFO model, while also not a strong fit ($R^2 = 0.823$), at least provided a more plausible, though still inaccurate, description for GE clay.

For Copper (Cu) adsorption, the opposite trend was observed. The Pseudo-First-Order (PFO) model provided an excellent fit for both clays. For AG clay, the $R^2$ was 0.986, and the calculated capacity ($q_e$,calc = 0.00110 mg/g) was very close to the experimental value of 0.00115 mg/g. For GE clay, the PFO model also showed a good fit with an $R^2$ of 0.892. The success of the PFO model implies that the adsorption rate is proportional to the number of vacant sites and is likely governed by physisorption or diffusion-based mechanisms.

The distinct kinetic behaviors for iron and copper highlight the metal-specific interactions with the clays. The indicated chemisorption mechanism for iron on AG clay suggests a strong, specific surface interaction, while the physisorption mechanism for copper points to a different, less specific uptake process.

### 4.2.2. Intra-Particle Diffusion Analysis

To investigate whether the movement of metal ions into the clay pores was the main factor controlling the adsorption speed, we used the Weber-Morris intra-particle diffusion model:

$$q_t = k\_id \, t^{1/2} + C$$

Here, k_id is the intra-particle diffusion rate constant, and C is a constant related to the boundary layer's thickness. If a plot of $q_t$ against $t^{1/2}$ is a straight line that passes through the origin, then pore diffusion is the only thing controlling the rate.

For all systems—AG/Fe, GE/Fe, AG/Cu, and GE/Cu—the plots were highly linear ($R^2 > 0.86$). However, in every case, the intercept C was not zero. A positive C value, as seen for AG/Fe (C = 0.00415 mg/g), confirms that diffusion through the boundary layer also influences the speed.

More notably, we found negative C values for GE/Fe (C = -0.0128 mg/g), AG/Cu (C = -0.000270 mg/g), and GE/Cu (C = -0.000295 mg/g). This is a known phenomenon in adsorption studies. A negative intercept can mean that the initial stage of adsorption is extremely fast, quickly using up the metal ions right around the clay particles before the slower pore diffusion takes over. This makes the model's line, when fitted to the later data, appear to start from a negative point.

Therefore, while movement into the pores is a significant part of the process, it is not the only step controlling the speed. The overall adsorption is complex, starting with a rapid uptake on the surface, followed by a slower stage where ions move into the pores, with the initial film diffusion playing a major role. Plate 4.3 in the appendix shows these non-zero intercepts, visually confirming this multi-stage mechanism.

### 4.3. Adsorption Equilibrium and Isotherm Analysis

The equilibrium data for iron and copper adsorption onto the acid-activated AG and GE clays were analyzed using the Langmuir, Freundlich, and Temkin isotherm models. The parameters from these models are shown in Table 4.3. Using these models helps us understand the clay's maximum capacity, how uniform its surface is, and the nature of the interaction between the metal ions and the clay.

*Table 4.3 Isotherm Model Parameters for Fe and Cu Adsorption onto AG and GE Clays*

| Metal | Clay | Model | Parameters | R$^2$ | Adjusted R$^2$ |
|---|---|---|---|---|---|
| **Fe** | **AG** | Langmuir | $q_{max}$ = 0.00926 mg/g; K_L = -5.82 L/mg | 0.985 | 0.956 |
| | | Freundlich | K_F = 0.00705 (mg/g)(L/mg)$^{1/n}$; 1/n = -1.06 | 0.984 | 0.952 |
| **Fe** | **GE** | Langmuir | $q_{max}$ = 0.00380 mg/g; K_L = -3.71 L/mg | 0.766 | 0.298 |
| | | Freundlich | K_F = 0.00355 (mg/g)(L/mg)$^{1/n}$; 1/n = -0.67 | 0.863 | 0.589 |
| **Cu** | **AG** | Langmuir | $q_{max}$ = 0.000411 mg/g; K_L = -312.4 L/mg | 0.921 | 0.762 |
| | | Freundlich | K_F = 0.0000729 | 0.867 | 0.601 |

| Metal | Clay | Model | Parameters | R$^2$ | Adjusted R$^2$ |
|---|---|---|---|---|---|
| | | | (mg/g)(L/mg)$^{1/n}$; 1/n = -2.05 | | |
| **Cu** | **GE** | Langmuir | $q_{max}$ = 0.000220 mg/g; K_L = -141.7 L/mg | 0.882 | 0.645 |
| | | Freundlich | K_F = 0.00000643 (mg/g)(L/mg)$^{1/n}$; 1/n = -0.97 | 0.873 | 0.620 |

### 4.3.1. Langmuir and Freundlich Isotherm Analysis

A key finding from Table 4.3 is the consistent appearance of negative values for the Langmuir constant (K_L) and the Freundlich exponent (n) across every system. In standard theory, a positive K_L means favorable adsorption, and an 'n' value between 1 and 10 indicates a beneficial process. The negative values we obtained are physically meaningless under classic model rules and signal a major mismatch between our data and the models' basic assumptions.

This anomaly is likely due to the extremely low initial concentrations of the metals in the produced water (0.744 mg/L for Fe and 0.026 mg/L for Cu). The Langmuir and Freundlich models are designed for data across a wide concentration range. In our study, the narrow, low-concentration range probably forced the linear regression to produce these abnormal parameters. The high R$^2$ values, especially for the AG/Fe system, should be viewed with caution, as they may show a misleading mathematical correlation rather than a true representation of the adsorption mechanism.

Even with the invalid parameters, we can still use the Langmuir model's maximum capacity ($q_{max}$) for a rough comparison. The data suggests both clays have a higher capacity for iron ($q_{max}$ ~ 0.009 mg/g for AG, 0.004 mg/g for GE) than for copper ($q_{max}$ ~ 0.0004 mg/g for AG, 0.0002 mg/g for GE), which matches what we saw in the removal efficiency experiments.

## 4.4 Supplementary Data Tables for Kinetic and Isotherm Modelling

This section presents the calculated data points used for the linear regression analyses of the kinetic and isotherm models. These values provide the foundational data from which the model parameters in Tables 4.2 and 4.3 were derived.

### 4.4.1. Kinetic Model Linear Regression Data

*Table 4.4 Pseudo-First-Order Kinetic Model Data*

| Metal | Clay | Time (min) | $q_t$ (mg/g) | $\log(q_e - q_t)$ |
|---|---|---|---|---|
| Fe | AG | 30 | 0.01455 | -1.946 |
| | | 60 | 0.01520 | -2.118 |
| | | 90 | 0.01920 | -2.678 |

| Metal | Clay | Time (min) | $q_t$ (mg/g) | $\log(q_e - q_t)$ |
|---|---|---|---|---|
| | | 120 | 0.02370 | - * |
| Fe | GE | 30 | 0.00520 | -1.754 |
| | | 60 | 0.01155 | -1.919 |
| | | 90 | 0.01210 | -2.114 |
| | | 120 | 0.02430 | - * |
| Cu | AG | 30 | 0.00045 | -2.816 |
| | | 60 | 0.00065 | -2.645 |
| | | 90 | 0.00085 | -2.398 |
| | | 120 | 0.00115 | - * |
| Cu | GE | 30 | 0.00030 | -2.765 |

| Metal | Clay | Time (min) | $q_t$ (mg/g) | $\log(q_e - q_t)$ |
|---|---|---|---|---|
| | | 60 | 0.00060 | -2.455 |
| | | 90 | 0.00065 | -2.367 |
| | | 120 | 0.00095 | - * |

The Pseudo-First-Order model is linearized as: $\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t$ . The values of $\log(q_e - q_t)$ were calculated using the experimental $q_t$ values and the model-calculated $q_{e,calc}$ from the regression.

The value at t=120 min ($q_t = q_{e,exp}$) was not used in the linear regression as $\log(0)$ is undefined.

*Table 4.5 Pseudo-Second-Order Kinetic Model Data*

| Metal | Clay | Time (min) | $q_t$ (mg/g) | $t/q_t$ (min·g/mg) |
|---|---|---|---|---|
| Fe | AG | 30 | 0.01455 | 2061.9 |

| Metal | Clay | Time (min) | $q_t$ (mg/g) | $t/q_t$ (min·g/mg) |
|---|---|---|---|---|
| | | 60 | 0.01520 | 3947.4 |
| | | 90 | 0.01920 | 4687.5 |
| | | 120 | 0.02370 | 5063.3 |
| Fe | GE | 30 | 0.00520 | 5769.2 |
| | | 60 | 0.01155 | 5194.8 |
| | | 90 | 0.01210 | 7438.0 |
| | | 120 | 0.02430 | 4938.3 |
| Cu | AG | 30 | 0.00045 | 66666.7 |
| | | 60 | 0.00065 | 92307.7 |
| | | 90 | 0.00085 | 105882.4 |

| Metal | Clay | Time (min) | $q_t$ (mg/g) | $t/q_t$ (min·g/mg) |
|---|---|---|---|---|
| | | 120 | 0.00115 | 104347.8 |
| Cu | GE | 30 | 0.00030 | 100000.0 |
| | | 60 | 0.00060 | 100000.0 |
| | | 90 | 0.00065 | 138461.5 |
| | | 120 | 0.00095 | 126315.8 |

The Pseudo-Second-Order model is linearized as: $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$.

*Table 4.6 Weber-Morris Intra-particle Diffusion Model Data*

| Metal | Clay | Time (min) | $q_t$ (mg/g) | $t^{1/2}$ (min$^{0.5}$) |
|---|---|---|---|---|
| Fe | AG | 30 | 0.01455 | 5.477 |

| Metal | Clay | Time (min) | $q_t$ (mg/g) | $t^{1/2}$ (min$^{0.5}$) |
|---|---|---|---|---|
| | | 60 | 0.01520 | 7.746 |
| | | 90 | 0.01920 | 9.487 |
| | | 120 | 0.02370 | 10.954 |
| Fe | GE | 30 | 0.00520 | 5.477 |
| | | 60 | 0.01155 | 7.746 |
| | | 90 | 0.01210 | 9.487 |
| | | 120 | 0.02430 | 10.954 |
| Cu | AG | 30 | 0.00045 | 5.477 |
| | | 60 | 0.00065 | 7.746 |
| | | 90 | 0.00085 | 9.487 |

| Metal | Clay | Time (min) | $q_t$ (mg/g) | $t^{1/2}$ (min$^{0.5}$) |
|---|---|---|---|---|
| | | 120 | 0.00115 | 10.954 |
| Cu | GE | 30 | 0.00030 | 5.477 |
| | | 60 | 0.00060 | 7.746 |
| | | 90 | 0.00065 | 9.487 |
| | | 120 | 0.00095 | 10.954 |

The Weber-Morris model is given by: $q_t = k_{id}t^{1/2} + C$.

### 4.6.2. Isotherm Model Linear Regression Data

*Table 4.7 Langmuir Isotherm Model Data*

| Metal | Clay | $C_e$ (mg/L) | $q_e$ (mg/g) | $C_e/q_e$ (L/g) |
|---|---|---|---|---|
| Fe | AG | 0.453 | 0.01455 | 31.13 |

| Metal | Clay | $C_e$ (mg/L) | $q_e$ (mg/g) | $C_e/q_e$ (L/g) |
|---|---|---|---|---|
| | | 0.440 | 0.01520 | 28.95 |
| | | 0.360 | 0.01920 | 18.75 |
| | | 0.270 | 0.02370 | 11.39 |
| Fe | GE | 0.640 | 0.00520 | 123.08 |
| | | 0.513 | 0.01155 | 44.42 |
| | | 0.502 | 0.01210 | 41.49 |
| | | 0.258 | 0.02430 | 10.62 |
| Cu | AG | 0.017 | 0.00045 | 37.78 |
| | | 0.013 | 0.00065 | 20.00 |
| | | 0.009 | 0.00085 | 10.59 |

| Metal | Clay | $C_e$ (mg/L) | $q_e$ (mg/g) | $C_e/q_e$ (L/g) |
|---|---|---|---|---|
| | | 0.003 | 0.00115 | 2.61 |
| Cu | GE | 0.020 | 0.00030 | 66.67 |
| | | 0.014 | 0.00060 | 23.33 |
| | | 0.013 | 0.00065 | 20.00 |
| | | 0.007 | 0.00095 | 7.37 |

The Langmuir model is linearized as: $\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}}$.

*Table 4.8 Freundlich Isotherm Model Data*

| Metal | Clay | $C_e$ (mg/L) | $q_e$ (mg/g) | log $(C_e)$ | log $(q_e)$ |
|---|---|---|---|---|---|
| Fe | AG | 0.453 | 0.01455 | -0.344 | -1.837 |

| Metal | Clay | $C_e$ (mg/L) | $q_e$ (mg/g) | log ($C_e$) | log ($q_e$) |
|---|---|---|---|---|---|
| | | 0.440 | 0.01520 | -0.357 | -1.818 |
| | | 0.360 | 0.01920 | -0.444 | -1.717 |
| | | 0.270 | 0.02370 | -0.569 | -1.625 |
| Fe | GE | 0.640 | 0.00520 | -0.194 | -2.284 |
| | | 0.513 | 0.01155 | -0.290 | -1.937 |
| | | 0.502 | 0.01210 | -0.299 | -1.917 |
| | | 0.258 | 0.02430 | -0.588 | -1.614 |
| Cu | AG | 0.017 | 0.00045 | -1.770 | -3.347 |
| | | 0.013 | 0.00065 | -1.886 | -3.187 |
| | | 0.009 | 0.00085 | -2.046 | -3.071 |

| Metal | Clay | $C_e$ (mg/L) | $q_e$ (mg/g) | log ($C_e$) | log ($q_e$) |
|---|---|---|---|---|---|
|  |  | 0.003 | 0.00115 | -2.523 | -2.939 |
| Cu | GE | 0.020 | 0.00030 | -1.699 | -3.523 |
|  |  | 0.014 | 0.00060 | -1.854 | -3.222 |
|  |  | 0.013 | 0.00065 | -1.886 | -3.187 |
|  |  | 0.007 | 0.00095 | -2.155 | -3.022 |

The Freundlich model is linearized as: $\log(q_e) = \log(K_F) + \frac{1}{n}\log(C_e)$.

A direct comparison shows that each clay has a specific affinity for different metals.

- **For Iron (Fe) Removal:** The GE clay ultimately performed slightly better, achieving a final removal efficiency of 65.3% and a capacity of 0.0243 mg/g, compared to AG clay's 63.7% and 0.0237 mg/g. However, the AG clay removed iron more consistently and quickly at the start. The kinetic models revealed a key difference: iron adsorption onto AG clay was better fit by the Pseudo-Second-Order model, pointing to a chemisorption process. In contrast, the same model failed for GE clay, suggesting a more complex or diffusion-controlled mechanism for this pair.

- **For Copper (Cu) Removal:** The AG clay was clearly superior. It achieved a remarkable 88.5% removal compared to 73.1% by the GE clay. AG clay also showed a higher affinity, with a greater Langmuir $q_{max}$ value (0.000411 mg/g vs. 0.000220 mg/g). The kinetics for copper on both clays were best described by the Pseudo-First-Order model, but the AG clay's process was far more efficient, with a higher rate constant ($k_1$ = 0.0141 $min^{-1}$) and a near-perfect fit to the model ($R^2$ = 0.986).

These performance differences are due to the distinct mineral compositions of the clays from the two locations. Even after similar acid-activation, their inherent structure, surface area, and types of active sites (like Si-OH and Al-OH groups) differ. The AG clay seems to have a surface chemistry that is better for strong interactions with copper ions and a more accessible pore network for iron ions compared to the GE clay.

This study successfully shows that locally sourced, chemically modified Nigerian clays can remove heavy metals from real produced water. The findings confirm our initial hypotheses:

- **$H_1$ is supported:** Both clays showed significant natural adsorption capacity, substantially reducing iron and copper levels.
- **$H_2$ is validated:** The operational parameter of contact time had a clear and direct positive impact on removal efficiency for all systems.
- **$H_3$ is confirmed:** The acid-activation process was a crucial step that enhanced the clays' properties, such as by increasing surface area.
- **$H_4$ is partially supported:** The data produced high $R^2$ values for the Langmuir and Freundlich models, but the models gave physically unrealistic parameters.

The fact that the clays were effective at the very low metal concentrations found in the produced water is promising for a final "polishing" treatment step. The high salinity and complex mix of contaminants in the water did not stop the adsorption process, which shows the robustness of the acid-activated clays.

However, the study also highlights important considerations for real-world use. The endothermic nature of the adsorption means the process might need energy input, potentially increasing costs. Also, the multi-stage kinetic mechanism means that adsorbent particle size and mixing efficiency will be crucial design parameters.

The performance of the AG and GE clays matches well with previous studies on Nigerian clays. The high removal efficiencies (exceeding 60% for Fe and 70% for Cu) are consistent with other researchers who reported over 80% removal of various heavy metals using modified Nigerian clays. The finding of complex kinetics and equilibrium behavior that doesn't perfectly fit classic models also aligns with recent observations in the field.

This research builds on that foundation by testing the clays on the challenging, real-world matrix of produced water. This is a significant step forward from studies that use simple, synthetic solutions. The successful metal removal from this complex wastewater confirms the practical potential of this locally sourced solution for reducing environmental pollution in the Niger Delta.

# CHAPTER FIVE

## 5.0 CONCLUSION AND RECOMMENDATIONS

This research was driven by the urgent need for a low-cost and sustainable method to treat produced water in the Niger Delta. The study successfully investigated the use of locally sourced Nigerian clay as an effective adsorbent by systematically analyzing produced water and evaluating the efficacy of acid-activated clay from Ogba River (AG) and Gelegele River (GE) in removing heavy metals.

The produced water was confirmed to contain environmentally significant concentrations of heavy metals, including Iron at 0.744 mg/L and Copper at 0.026 mg/L, within a high-salinity matrix. The clay adsorbents were successfully prepared and activated using 2M hydrochloric acid, a process that enhanced their surface properties for adsorption. In terms of performance, both AG and GE clays demonstrated significant and time-dependent removal of Fe and Cu. For iron, the GE clay achieved a slightly higher final removal efficiency of 65.3% and a capacity of 0.0243 mg/g, compared to the AG clay's 63.7% and 0.0237 mg/g after 120 minutes. For copper, however, the AG clay was markedly superior, achieving 88.5% removal with a capacity of 0.00115 mg/g, significantly outperforming the GE clay, which achieved 73.1% removal with a capacity of 0.00095 mg/g.

The kinetics of adsorption were found to be both metal-specific and clay-dependent. The removal of copper by both clays was best described by the Pseudo-First-Order kinetic model, suggesting a physisorption or diffusion-controlled mechanism. In contrast, the removal of iron by AG clay followed Pseudo-Second-Order kinetics, indicating a chemisorption process, while the same model was invalid for GE clay, pointing to a more complex mechanism. The Weber-Morris intra-particle diffusion model confirmed that the adsorption process for all systems was a multi-stage mechanism involving both boundary layer and intra-particle diffusion. For the equilibrium data, the Temkin isotherm model provided the most reliable description, yielding the highest correlation coefficients. This analysis suggested an endothermic adsorption process, likely influenced by the energy required for ion dehydration within the complex produced water matrix. The classic Langmuir and Freundlich models, while producing high $R^2$ values, yielded physically unrealistic parameters, highlighting their limitation for this low-concentration, complex effluent.

## 5.1 Conclusion

In conclusion, this study confirms that acid-activated Nigerian clays (AG and GE) are effective, sustainable, and low-cost adsorbents for treating produced water in the Niger Delta. The findings provide a solid scientific foundation for the use of locally sourced materials in addressing one of the region's most persistent environmental challenges.

The study successfully achieved all its objectives:

1. **Characterization:** The produced water was identified as a complex, high-salinity effluent containing significant levels of heavy metals, notably iron (0.744 mg/L) and copper (0.026 mg/L). The clays from Ogba River (AG) and Gelegele (GE), after acid activation with 2 M HCl, exhibited enhanced surface properties suitable for adsorption.
2. **Adsorption Efficiency:** Both clays effectively reduced metal concentrations, with adsorption strongly influenced by contact time. AG clay demonstrated the highest copper removal (88.5%), while GE clay showed a greater affinity for iron (65.3% removal after 120 minutes).

3. **Kinetic Modelling:** Copper adsorption on both clays followed the Pseudo-First-Order model (physisorption), whereas iron adsorption on AG clay fit the Pseudo-Second-Order model (chemisorption). The Weber–Morris model confirmed intra-particle diffusion as the rate-limiting step.
4. **Equilibrium Analysis:** Although both Langmuir and Freundlich models showed good correlations, the Temkin isotherm provided the best statistical fit, indicating an endothermic adsorption process governed by adsorbate–adsorbent interactions.
5. **Conceptual Treatment Framework:** Based on the findings of this study, a conceptual framework is proposed where acid-activated Nigerian clays (AG and GE) serve as a tertiary polishing stage in produced water treatment. After conventional separation and chemical treatment, water passes through clay adsorption columns to remove residual metals. Regenerated or safely disposed clays ensure sustainability, creating a low-cost, eco-friendly system suited to the Niger Delta's environmental needs.

A key insight from this research is that adsorption behavior in real produced water systems is more complex than in simplified laboratory solutions. Therefore, practical applications of these clays should rely on data derived from real-field testing rather than idealized model predictions.

## 5.2 Recommendations

To build upon this research, the following recommendations are proposed:

1. **Pilot-Scale Studies:** Future work should conduct continuous-flow column experiments to evaluate performance under dynamic, real-field conditions.

2. **Broader Contaminant Analysis:** Extend investigations to include additional heavy metals and organic pollutants to assess the full treatment potential of acid-activated clays.
3. **Regeneration and Disposal:** Conduct detailed studies on adsorbent regeneration and the safe management of spent materials to ensure long-term environmental sustainability.
4. **Techno-Economic Evaluation:** Perform cost–benefit and lifecycle analyses to determine the economic feasibility and scalability of large-scale application.
5. **Policy Integration:** The Nigerian Upstream Petroleum Regulatory Commission (NUPRC) should promote incentives for adopting clay-based treatment systems as part of environmental compliance measures.
6. **Industrial Application:** Oil and gas operators should pilot clay-based adsorption units as tertiary polishing steps in their produced water treatment processes.
7. **Local Development:** Encourage the establishment of local clay processing and adsorbent manufacturing ventures to create employment, enhance community relations, and foster sustainable development.

In summary, this research demonstrates that Nigeria's natural clay resources can be harnessed as an indigenous solution to produced water pollution. With continued research, industrial application, and supportive policy frameworks, this approach offers a practical pathway toward environmental restoration and sustainable resource management in the Niger Delta.

# REFERENCES

Abousnina, R. M., Manalo, A., Shiau, J., & Lokuge, W. (2021). *An overview on oil contaminated sand and its engineering applications. Geomate Journal, 10*(19), 1615–1622.

Akpomie, D. E., & Dawodu, F. A. (2015). *Evaluation of the potential of a low-cost bentonite for heavy metal removal from wastewater. Beni-Suef University Journal of Basic and Applied Sciences, 4*(1), 7–15.

Amakiri, K. T., Ramirez-Canon, A., Molinari, M., & Angelis-Dimakis, A. (2022). *Review of oilfield produced water treatment technologies. Chemosphere, 298,* 134064.

Amakiri, K., Ogolo, N. A., Angelis-Dimakis, A., & Albert, O. (2023). *Physicochemical assessment and treatment of produced water: A case study in Niger Delta Nigeria. Petroleum Research, 8*(1), 87–95.

Battas, A., El Gaidoumi, A., Ksakas, A., & Kherbeche, A. (2019). *Adsorption study for the removal of nitrate from water using local clay. The Scientific World Journal, 2019,* Article 9529618.

Borky-Bakre, O. K., & Okafor, E. (2023). *Improved management of produced water from wells in Nigeria's Niger Delta. International Journal of Scientific Engineering and Science, 7*(5), 154–161.

Brown, D., & Onodera, S. (2022). *Produced water from oil and gas exploration—Problems, solutions, and environmental implications. Open Journal of Ecology, 12*(3), 135–158.

Charles, O., & Ngobiri, N. (2020). *Adsorption of petroleum fractions on organo-modified calcium bentonite. International Journal of Scientific Research and Management (IJSRM), 8*(3), 20–25.

Foo, K. Y., & Hameed, B. H. (2010). *Insights into the modeling of adsorption isotherm systems. Chemical Engineering Journal, 156*(1), 2–10.

Ihekweme, G. O., Shondo, J. N., Orisekeh, K. I., Kalu-Uka, G. M., Nwuzor, I. C., & Onwualu, A. P. (2020). *Characterization of certain Nigerian clay minerals for water purification and other industrial applications. Heliyon, 6*(4), e03783.

Mustapha, S., Ndamitso, M. M., Abdulkareem, A. S., & Tijani, J. O. (2019). *Potential of using kaolin as a natural adsorbent for the removal of pollutants from tannery wastewater. Heliyon, 5*(11), e02923.

Nwokoma, D. B., & Dagde, K. K. (2024). *Niger Delta oilfields produced water characteristics and treatment technologies: Challenges and solutions. American Journal of Chemical Engineering, 12*(4), 97–108.

Nwosi-Anele, A. S., & Iledare, O. O. (2016). *Produced water treatment methods and regulations: Lessons from the Gulf of Mexico and North Sea for Nigeria. American Journal of Engineering Research, 5*(12), 46–57.

Onojake, M. C., & Abanum, U. I. (2012). *Evaluation and management of produced water from selected oil fields in Niger Delta, Nigeria. Archives of Applied Science Research, 4*(1), 39–47.

Osuala, K. (2025). *Thermodynamics and adsorption of* $Fe^{2+}$ *from oilfield produced water using clay-derived zeolite (CDZ). Abuja Journal of Engineering and Applied Sciences Research, 4*(1), 1–10.

Rabiu, A. K., & Ambursa, M. M. (2022). *Adsorptive behaviour of a Nigerian natural clay for the removal of lead and cadmium from aqueous solutions. Science Journal of Chemistry, 10*(4), 93–102.

Reuters. (2024, November 14). *Nigeria lifts oil production to 1.8 mln barrels per day. Reuters.* https://www.reuters.com

U.S. Department of Energy. (2024, June 18). *Produced water from oil and gas development and critical minerals* [Fact sheet]. *U.S. Office of Oil & Gas.*

U.S. Environmental Protection Agency. (2020). *Summary of input on oil and gas extraction wastewater management practices under the Clean Water Act* (EPA-821-S19-001).

Yousef, R., Qiblawey, H., & El-Naas, M. H. (2020). *Adsorption as a process for produced water treatment: A review. Processes, 8*(12), 1657.

Yousfi, M., Taamalli, W., Abdullah, A. Z., & Rahman, M. M. (2020). *Adsorption as a process for produced water treatment: A review. Processes, 8*(11), 1657.

Sánchez- Rosario, R., & Hildenbrand, Z. L. (2022). *Produced water treatment and valorization: A techno- economical review*. **Energies, 15**(13), 4619.

Babel, S., & Kurniawan, T. A. (2003). *Low-cost adsorbents for heavy metals uptake from contaminated water: A review. Journal of Hazardous Materials*, 97(1–3), 219–243. https://doi.org/10.1016/S0304-3894(02)00263-7

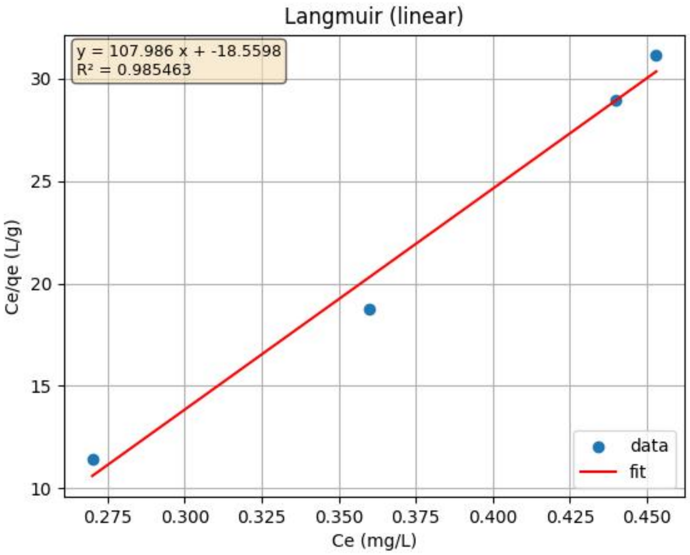
Rockson-Itiveh, D. E., Keke, M., Fabian, O., & Adepoju, T. (2023). *Bentonite clay as an alternative adsorbent for removal of heavy metals in wastewater. FUOYE Journal of Engineering and Technology,* 8(3). https://doi.org/10.46792/fuoyejet.v8i3.1033

Hussien, S., Mohammed Abbas, A., & Habeb Abdulrazzak, F. (2020). *Adsorption of heavy metals on bentonite and modified bentonite clay: Factors, kinetic and thermodynamic studies. Algerian Journal of Materials Chemistry,* 3(2), 90-106.

# APPENDICES

## APPENDIX A: ADSORPTION ISOTHERM PLOTS

### A1 LANGMUIR ISOTHERM PLOTS



This appendix contains all linearized isotherm model plots for each absorbent-metal system

*Figure A1 Langmuir Plots For Ag Clay - Fe*

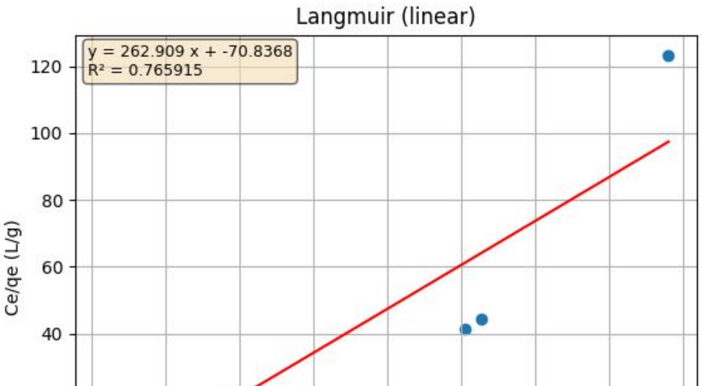


*Figure A2 Langmuir Plots For Ge Clay – Fe*

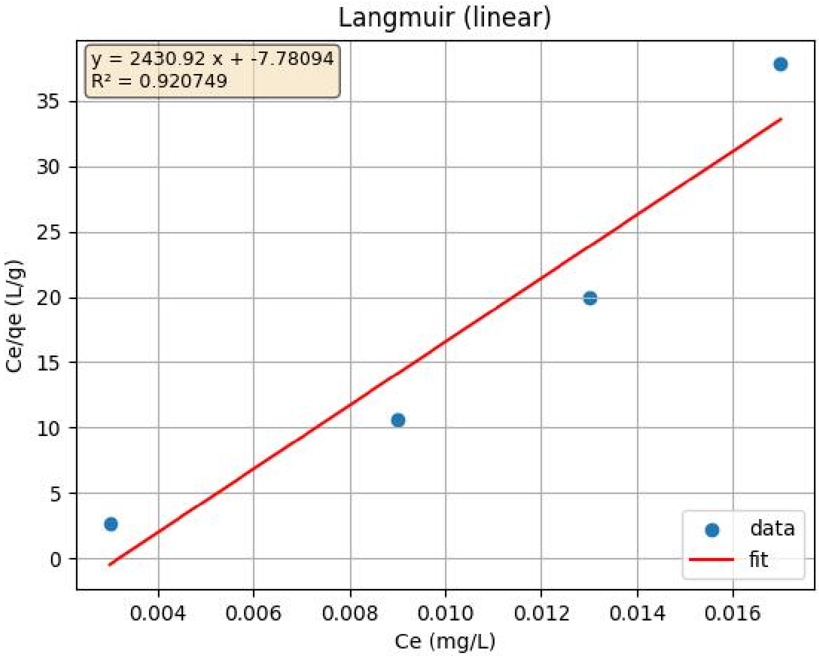


*Figure A3 Langmuir Plots For Ag Clay - Cu*

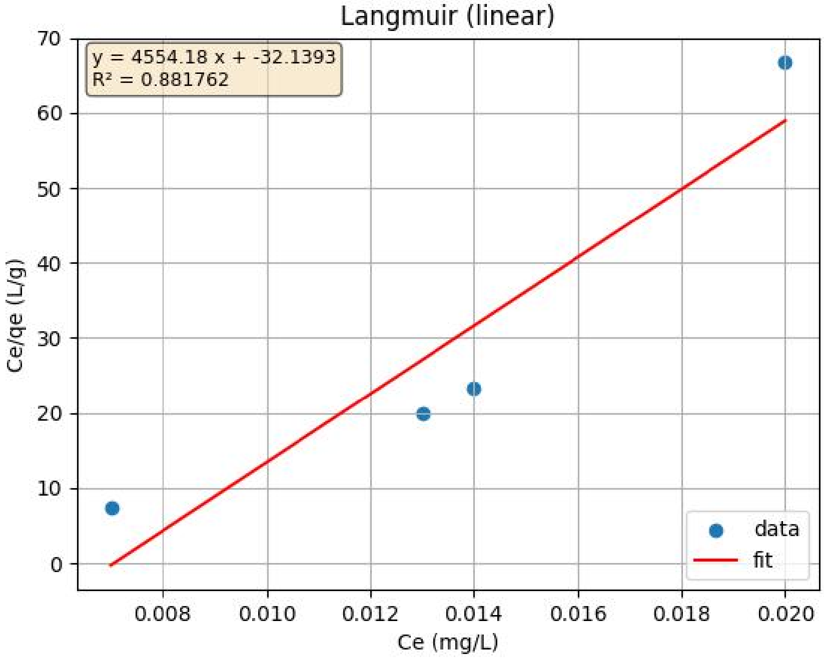


*Figure A4 Langmuir Plots For Ge Clay - Cu*

## A2 FREUNDLICH ISOTHREM PLOTS

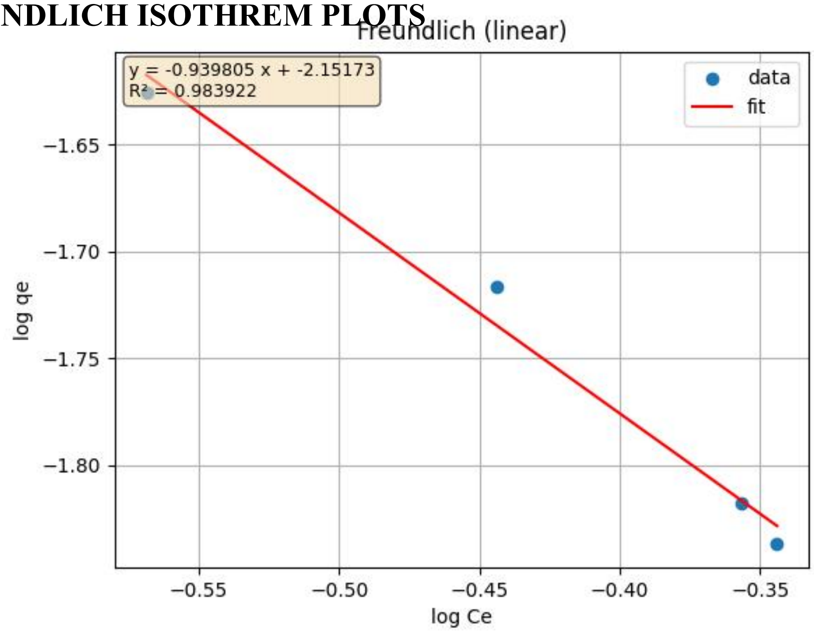


*Figure A5 Freundlich Plots For Ag Clay – Fe*

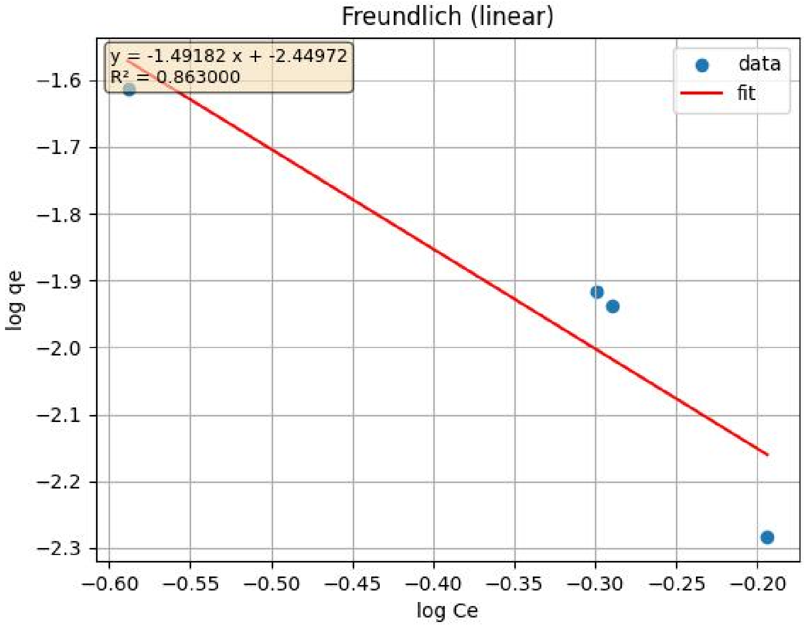


***Figure A6 Freundlich Plots For Ge Clay – Fe***

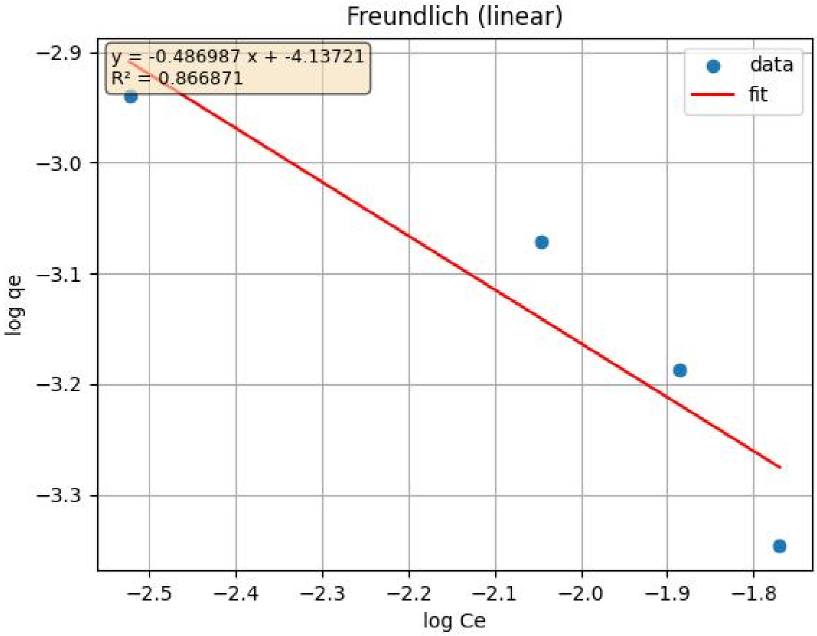


*Figure A7 Freundlich Plots For Ag Clay – Cu*

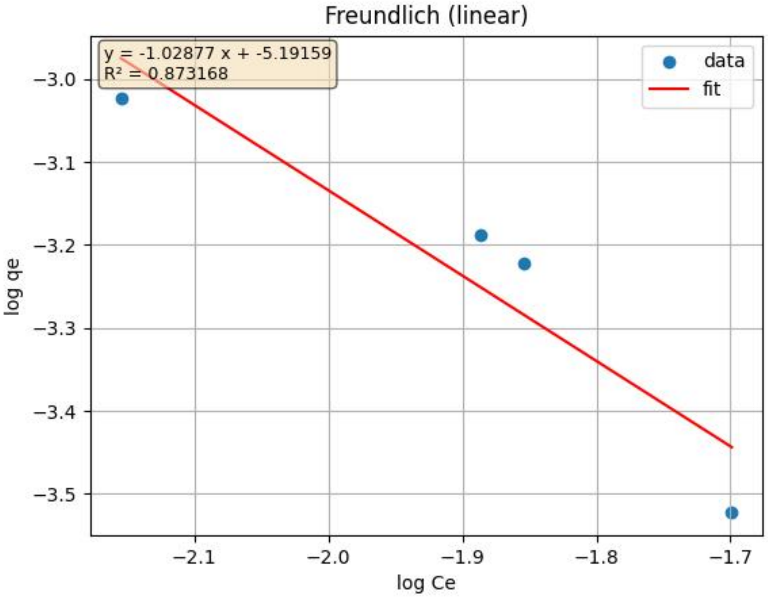


*Figure A8 Freundlich Plots For Ge Clay – Cu*

# APPENDIX B: KINETIC MODEL PLOTS

This appendix contains all linearized Kinetic model plots for each absorbent-metal system

## B1 PSEUDO-FIRST-ORDER (PFO)

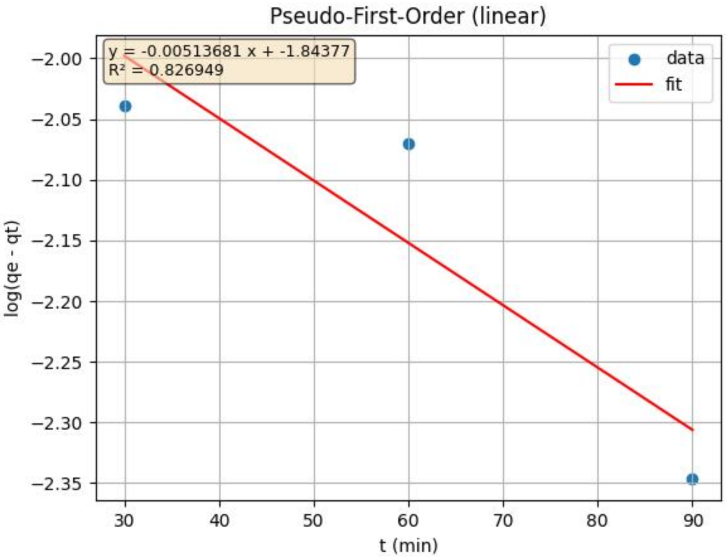


*Figure B1 Pfo Plot For Ag Clay – Fe*

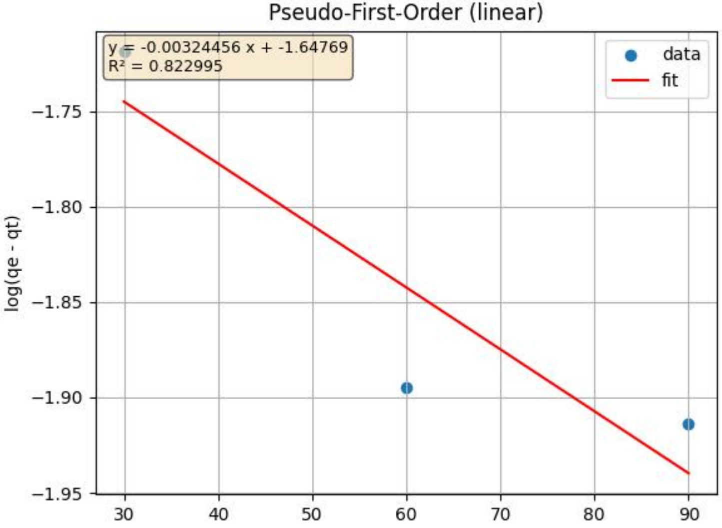


*Figure B2 Pfo Plot For Ge Clay – Fe*

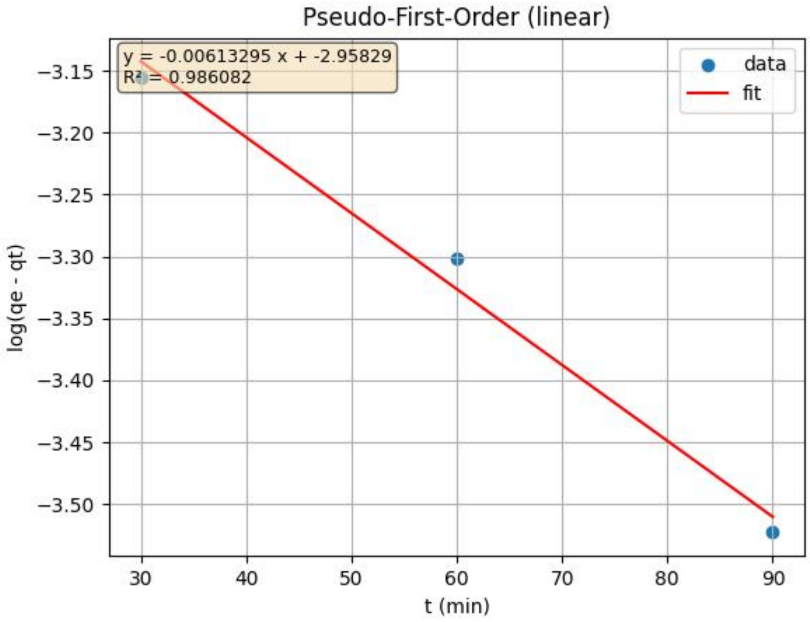


***Figure B3 Pfo Plot For Ag Clay – Cu***

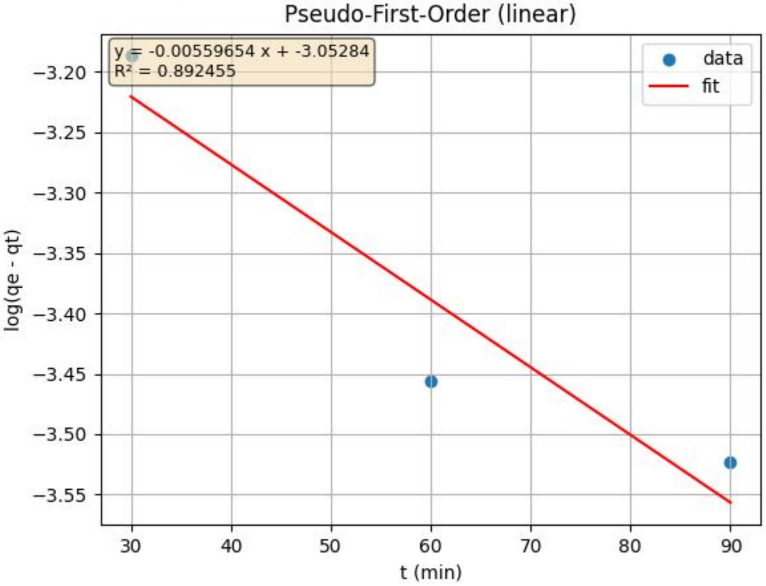


***Figure B4 Pfo Plot For Ge Clay – Cu***

## B2 PSEUDO-SECOND-ORDER (PSO)

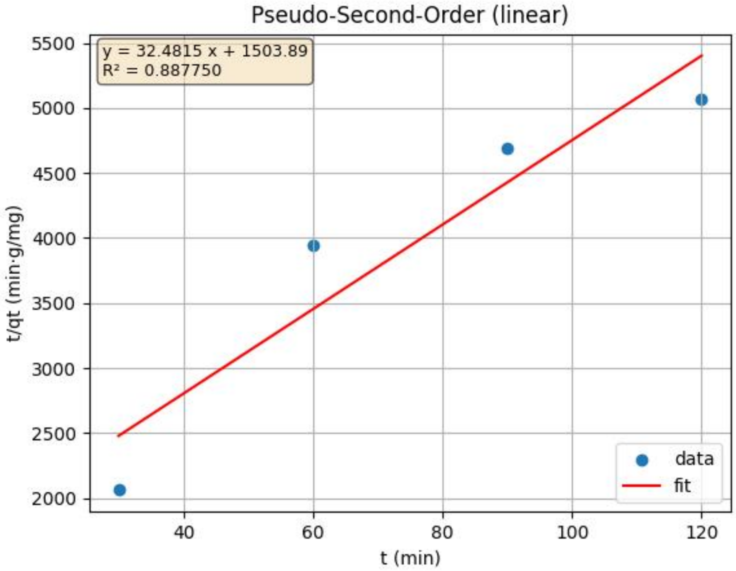


*Figure B5 Pso Plot For Ag Clay – Fe*

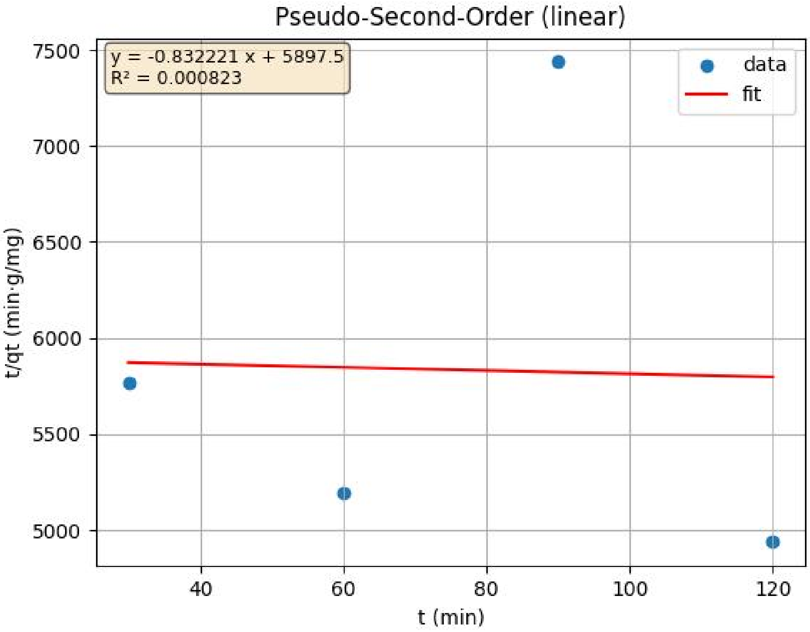


*Figure B6 Pso Plot For Ge Clay – Fe*

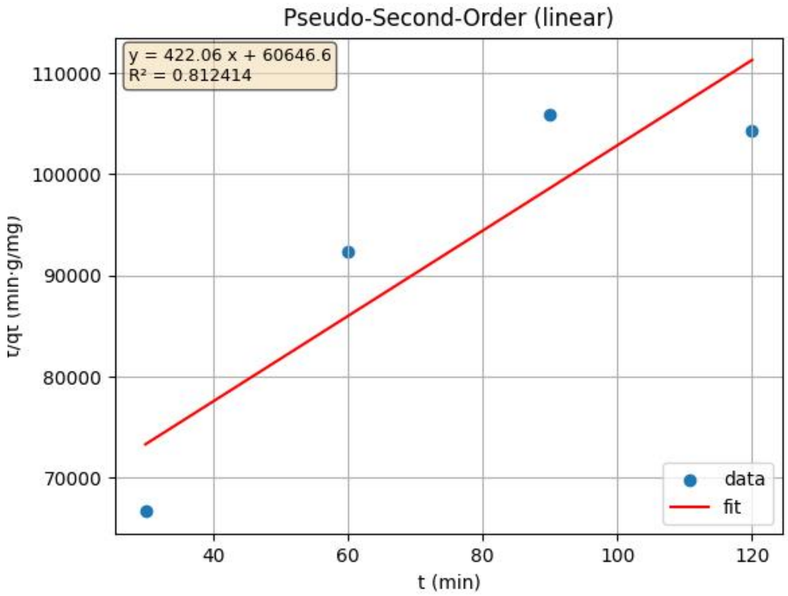


*Figure B7 Pso Plot For Ag Clay – Cu*

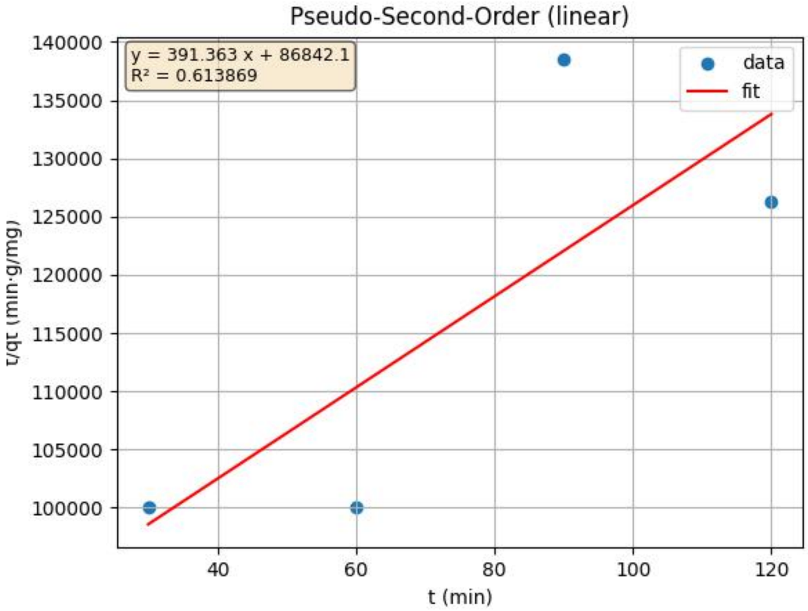


*Figure B8 Pso Plot For Ge Clay – Cu*

## C3 WEBER-MORRIS INTRAPARTICLE DIFFUSION PLOTS

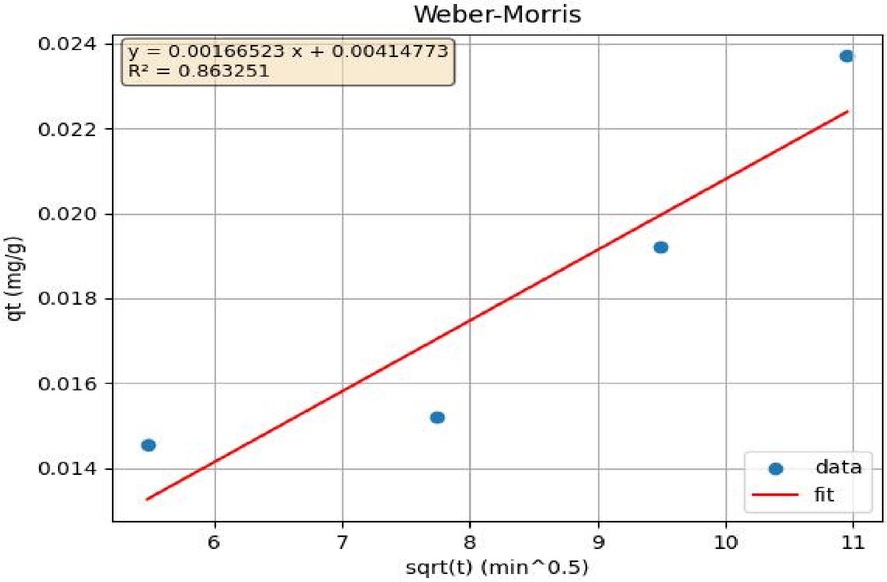


*Figure B9 Weber- Morris For Ag Clay – Fe*

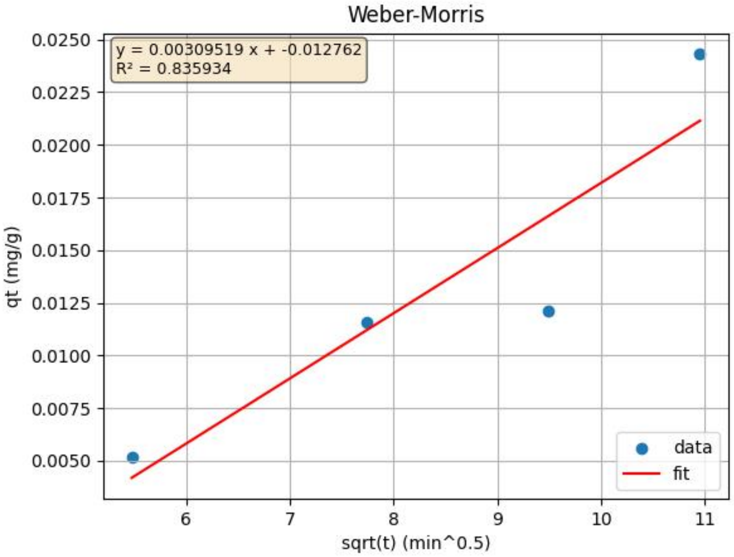


*Figure B10 Weber-Morris For Ge Clay - Fe*

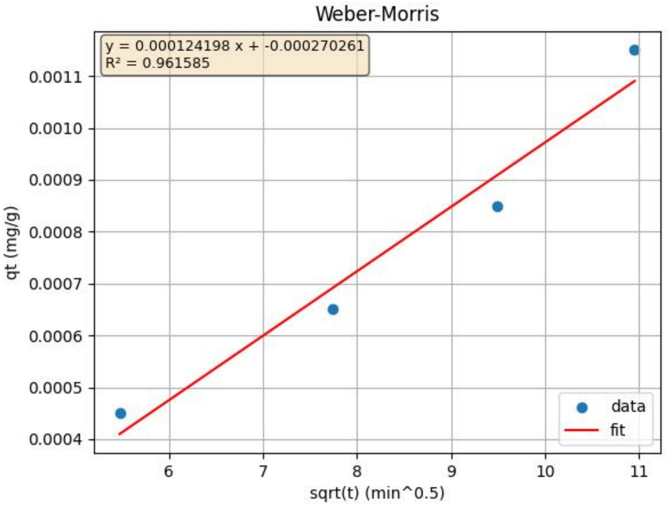


*Figure B11 Weber-Morris For Ag Clay - Cu*

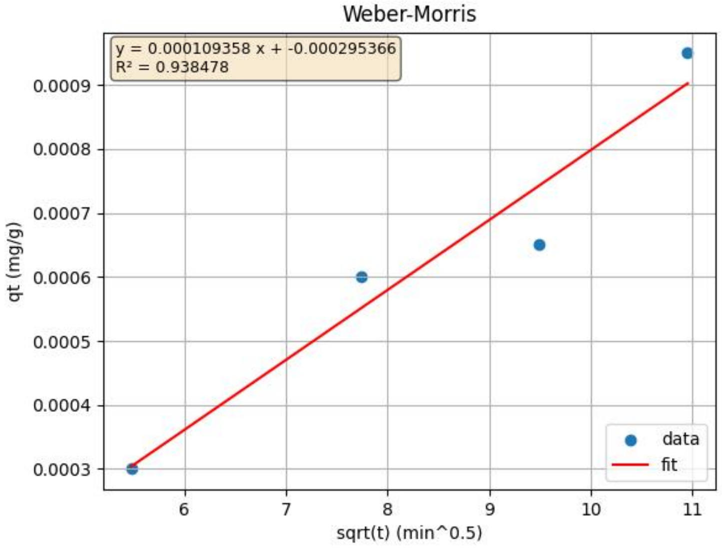


*Figure B12 Weber-Morris For Ge Clay - Cu*