TREATMENT OF PRODUCED WATER FROM NIGER DELTA OIL FIELDS USING EGGSHELL AND SAWDUST AS LOCALLY SOURCED ADSORBENTS

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NOVEMBER 2025

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A PROJECT SUBMITTED TO THE
DEPARTMENT OF PETROLEUM ENGINEERING
IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE
AWARD OF BACHELOR OF ENGINEERING (B.ENG) DEGREE IN
PETROLEUM ENGINEERING

DEPARTMENT OF PETROLEUM ENGINEERING
FACULTY OF ENGINEERING
UNIVERSITY OF BENIN
BENIN CITY

NOVEMBER 2025

CERTIFICATION

This is to certify that this project was carried out by JIMAH OYAKHILOME JOEL of the Department of Petroleum Engineering with matriculation number ENG2006432 in partial 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 father, mother, 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.

ACKNOWLEDGEMENT

Firstly, to Jehovah God Almighty who sustains life, I would like to express my utmost gratitude for granting me the opportunity, strength, wisdom, and grace to complete my project successfully. Without His divine guidance and favor, this accomplishment would not have been possible.

My sincere appreciation goes to my supervisor, Engr. Dr. Ikponmwosa Ohenhen, for his unwavering support and commitment to the completion of this project. His mentorship, professional feedback, and guidance made this work possible, and I am truly grateful for the sleepless nights and weekend meetings he dedicated to this process.

Special thanks to every member of my family, the Jimah family, for being my backbone, my support system, and for sponsoring my education. They have always provided a safe space for me throughout my academic journey, catering to every one of my academic and emotional needs.

I would also like to thank all my lecturers for training me academically and for helping to develop my character during these years in the Department of Petroleum Engineering. In no particular order, I would like to acknowledge Prof. D.O. Onaiwu, Dr. S.A. Igbinere, Prof. K.O Bello, Prof. O.A Olafuyi, Mr. Frank Edobor, Mr. Isaac A. Ajimosun, Mr. Alonge P. Ibe, and Dr. A.A. Adeniji for their support and contributions toward my education and character development.

I am deeply grateful to the management and staff of Energia Limited for providing me with the opportunity to gain practical exposure and firsthand experience during my internship. My special appreciation goes to Mr. Donald, Mr. Muaz, Mr. Chike, Mr. Obinna, Mr. Akpotu, Mr. Ugo, Mr. Bashorun, and Mr. Uche for their patience, technical insights, and willingness to share knowledge with me. I also wish to acknowledge my colleagues, both interns and corp members, and especially

Benita, Ebube, Fisayo, and Kenneth for their teamwork, cooperation, and encouragement during the training period.

I would also like to acknowledge my friends Hernyz, Zino, Etinosa, Osas, Bolu, Sele, Annah, Jessica, Monica, and Kehinde, for being true friends to me through both the good and the challenging times. Your friendship has been a source of strength.

I extend my gratitude to all my course mates with whom I have shared this academic journey from 100 level till the end. It has been a pleasure learning and growing together with all of you.

A special appreciation goes to Mr. Austin, whose guidance and financial support greatly contributed to the successful completion of this project.

Finally, I acknowledge myself, Jimah Oyakhilome Joel, for showing up every day, even when it was hard, for putting in the work, for not bowing to pressure, for perseverance, discipline, and patience throughout this academic journey.

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ABSTRACT

The extraction of crude oil in the Niger Delta generates vast quantities of produced water (PW), a complex, highly saline wastewater containing hazardous heavy metals. Conventional treatment methods are often prohibitively expensive and inefficient, necessitating the development of low-cost, sustainable alternatives. This research investigates the efficacy of two locally abundant waste materials, thermally-chemically activated sawdust and thermally activated eggshell, as bio-adsorbents for removing iron (Fe) and zinc (Zn) from real produced water sourced from an oil field within the Niger Delta. The study involved preparation and activation of adsorbents, followed by batch adsorption experiments under varying contact times. The produced water was characterized, and experimental data were analyzed using kinetic and isotherm models. Results demonstrated that both adsorbents effectively removed metals. Activated sawdust achieved removal efficiencies of 70.6% for Fe and 95.5% for Zn, while thermally activated eggshell removed 61.4% of Fe and 79.8% of Zn. Kinetic studies revealed that iron adsorption onto sawdust followed a physisorption-driven Pseudo-First-Order model, whereas adsorption onto eggshell followed a chemisorption-driven Pseudo-Second-Order model, indicative of ion exchange with calcium carbonate. Equilibrium isotherm analysis showed that the Freundlich model provided better fit than Langmuir for both adsorbents, suggesting multilayer adsorption on heterogeneous surfaces. However, anomalous parameters in both models underscored the influence of the complex, multi-component nature of real produced water, causing deviation from ideal model behavior. The study concludes that both sawdust and eggshell are viable, low-cost, and sustainable materials for remediating heavy metals from produced water in the Niger Delta, validating a circular economy approach that transforms local waste into valuable resources for environmental cleanup.

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the Study

The extraction of crude oil is invariably accompanied by the production of vast quantities of water, known as produced water (PW). This water, which exists naturally within the pore spaces of subsurface rock formations, is co-produced with oil and gas and represents the largest volume waste stream in the petroleum industry (Clark and Veil, 2009). In mature oil fields, such as those in the Niger Delta region of Nigeria, the water cut (the percentage of water in the extracted fluid) can exceed 80% as the reservoir ages, making water management a central and costly aspect of operations (Igunnu and Chen, 2014).

The chemical composition of PW is complex and highly variable, reflecting its prolonged geological contact with hydrocarbons and the operational chemicals used during extraction. It is characterized by extreme salinity, often with total dissolved solids (TDS) concentrations exceeding 50,000 mg/L, and contains a hazardous mixture of pollutants. These include dispersed oil droplets, dissolved organic compounds like benzene, toluene, ethylbenzene, and xylene (BTEX), heavy metals (e.g., lead, cadmium, copper, arsenic), and naturally occurring radioactive materials (Fakhru'l-Razi *et al*., 2009). The direct discharge of this toxic effluent produced without adequate treatment has devastating consequences for the environment, contaminating soil, surface water, and groundwater, and destroying aquatic ecosystems.

The environmental impact is acutely felt in the Niger Delta, one of the world's largest wetlands and a biodiversity hotspot. Decades of oil production have led to severe pollution, with PW being a significant contributor. Studies in the region have documented alarming levels of contamination;

for instance, Anyanwu *et al*. (2023) reported TPH concentrations in water bodies as high as 889 mg/L and heavy metal levels far exceeding permissible limits. This pollution smothers mangrove roots, depletes oxygen in water, and leads to the bioaccumulation of toxins in fish and shellfish, which are staple food sources for local communities. Consequently, this poses serious risks to human health, including neurological disorders, kidney damage, and cancer.

Conventional treatment methods for PW, such as gravity separation, hydrocyclones, chemical precipitation, and membrane filtration, are often inadequate for the Niger Delta context. They can be prohibitively expensive, energy intensive, and require sophisticated infrastructure and expertise that are frequently unavailable (Jiménez *et al*., 2018). Furthermore, these processes often generate secondary wastes, such as toxic metal hydroxide sludges from precipitation or concentrated brines from membrane systems, which present their own disposal challenges.

This pressing need for cost-effective and sustainable treatment solutions has catalyzed research into alternative technologies. Adsorption, a physicochemical process where dissolved contaminants (adsorbates) are captured and concentrated on the surface of a solid material (adsorbent), has emerged as a highly promising method. Its appeal lies in its simplicity, potential for high efficiency, and the ability to use low-cost materials.

Recent focus has shifted towards utilizing waste-derived, locally available "bio-adsorbents." This approach addresses two problems simultaneously: treating contaminated water and valorizing solid waste. Two particularly promising materials are eggshells and sawdust.

a) Eggshells, an abundant byproduct of the food industry, are composed primarily of calcium carbonate ($CaCO_3$). When ground into a powder, they offer a porous structure and alkaline nature. Their metal removal mechanism is multifaceted: they can exchange calcium ions

(Ca^{2+}) in their matrix for heavy metal ions like lead (Pb^{2+}) in solution (ion exchange), and they can raise the pH of water, causing metals to precipitate out as insoluble hydroxides or carbonates (Park *et al*., 2007; Daniel *et al*., 2022).

b) Sawdust, a waste product from timber operations, is a lignocellulosic material rich in polymers like cellulose and lignin. These polymers contain functional groups such as hydroxyl (-OH) and carboxyl (-COOH) that act as binding sites. Heavy metal ions are removed through mechanisms like surface complexation (forming coordinate bonds) and chelation (Mohan and Chander, 2006; Ehsan *et al*., 2021). Its fibrous structure also makes it suitable for use in packed-bed filters.

The performance of these adsorbents is typically analyzed using adsorption isotherm models, which describe how contaminants partition between the liquid and solid phases at equilibrium. The Langmuir model assumes a monolayer of adsorbate forms on a homogeneous surface, indicating a finite adsorption capacity. The Freundlich model describes adsorption on a heterogeneous surface and is better for multi-layer adsorption. Fitting experimental data to these models allows researchers to quantify adsorption capacity and understand the underlying mechanisms, which is crucial for designing effective treatment systems (Ayawei *et al*., 2017).

Therefore, this study seeks to explore the potential of these two locally sourced, low-cost materials, eggshells and sawdust, for treating the complex contaminant mixture found in Niger Delta PW, contributing to the development of a sustainable and economically viable remediation strategy.

1.2 Statement of the Problem

The Niger Delta region faces a profound environmental crisis, largely driven by the pollution from oil and gas activities. The discharge of untreated or partially treated PW is a major contributor to

this crisis. Despite the known toxicology of its constituents including heavy metals, hydrocarbons, and high salinity; effective and sustainable treatment remains a significant challenge for several interconnected reasons.

Firstly, conventional treatment methods often fail in this context. Technologies like chemical precipitation, advanced oxidation, and membrane filtration (e.g., reverse osmosis) are hampered by high operational costs, substantial energy demands, and the generation of secondary waste streams like toxic sludge (Jiménez *et al*., 2018). These systems require sophisticated technical expertise and reliable infrastructure for maintenance, which are frequently unavailable or unaffordable for many operators in the region. Consequently, a gap exists between the technological solutions available and what is practically implementable on a wide scale in the Niger Delta, leading to the continued discharge of contaminated PW.

Secondly, while the theory of using low-cost, natural adsorbents like eggshells and sawdust is well-established in laboratory settings for synthetic wastewater, a significant research gap exists regarding their application to real, complex PW from the Niger Delta. Laboratory studies often use single-solute systems in distilled water, which do not replicate the challenging conditions of actual PW. Real PW is a complex matrix with high ionic strength, competing ions (like Na^+ and Ca^{2+}), oil emulsions, and organic matter, all of which can interfere with adsorption processes (Foo and Hameed, 2010). It is unclear whether these bio-adsorbents can perform effectively amidst this competition and achieve contaminant removal levels that meet regulatory standards for safe discharge or reuse.

Thirdly, there is a lack of predictive modeling for these materials in such a complex environment. While adsorption isotherm models like Langmuir and Freundlich are standard tools for describing adsorbent behavior, their accuracy and reliability in predicting the performance of eggshell and

sawdust for treating real PW have not been thoroughly validated. Understanding which model best fits the experimental data is crucial for designing and scaling up treatment systems, as it provides insights into adsorption capacity, surface heterogeneity, and the mechanisms at play (Ayawei *et al*., 2017). Without this understanding, the application of these materials remains guesswork rather than engineered science.

Finally, there is a disconnect between waste generation and waste valorization in the region. The Niger Delta produces abundant agricultural and domestic waste, such as eggshells and sawdust, which are often discarded indiscriminately, contributing to solid waste management issues. At the same time, the region is struggling with extensive water pollution. There is a critical need for research that bridges this gap, transforming local waste problems into environmental solutions by systematically testing these materials for a purpose that addresses a pressing local need.

Therefore, the problem this study addresses is the lack of a proven, affordable, and sustainable treatment method for PW in the Niger Delta. It specifically investigates the untapped potential of two locally abundant waste materials as adsorbents, moving beyond idealized lab conditions to test their efficacy on real PW and to reliably model their performance to pave the way for practical, scalable application.

1.3 Aim

The aim of this research is to develop a sustainable and low-cost treatment strategy for PW from the Niger Delta oil fields by using locally available waste materials as adsorbents.

1.4 Objectives of the Study

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

1. To collect PW and characterize the physicochemical properties and contaminant profile of PW samples obtained from selected oil fields in the Niger Delta.
2. To prepare activated adsorbents from locally sourced waste eggshell and sawdust materials.
3. To evaluate the adsorption efficiency of the prepared eggshell and sawdust adsorbents in removing heavy metals from PW through batch equilibrium experiments.
4. To analyze the adsorption data using Isotherm and Kinetic models.
5. To compare the performance, advantages, and limitations of eggshell and sawdust adsorbents based on the experimental results. This will provide a recommendation on their practical applicability and potential for integration into a treatment train for PW remediation in the Niger Delta context.

1.5 Research Questions

This study is designed to answer the following critical research questions:

1. What are the predominant physicochemical characteristics and concentrations of key heavy metal contaminants (e.g., Fe, Zn) in PW samples from the Niger Delta?
2. To what extent can activated adsorbents derived from eggshells and sawdust reduce the concentration of heavy metals in real PW samples?
3. How do operational parameters such as adsorbent dosage and contact time influence the removal efficiency of heavy metals by eggshell and sawdust adsorbents?

4. Which adsorption isotherm model, Langmuir or Freundlich, provides a better fit for the equilibrium data, and what does this reveal about the adsorption mechanism and surface properties of each adsorbent?
5. What kinetic model best describes the adsorption behaviour of eggshell and sawdust during the removal of heavy metals from PW?
6. How does the adsorption performance (e.g., removal efficiency, capacity) of eggshells compare to that of sawdust when treating the same PW sample?

1.6 Hypothesis

Based on the reviewed literature, the following hypotheses are proposed:

- **H_1:** PW from the Niger Delta will contain significant levels of heavy metal contaminants, exceeding national and international environmental discharge standards.
- **H_2:** Activated eggshell and sawdust adsorbents will significantly reduce the concentration of heavy metals in PW.
- **H_3:** The adsorption process will be highly dependent on operational parameters, with removal efficiency increasing with higher adsorbent dosage and longer contact time, up to an equilibrium point.
- **H_4:** The Freundlich isotherm model will provide a better fit to the experimental data than the Langmuir model, indicating multilayer adsorption onto heterogeneous surfaces for both adsorbents.

- **H_5:** Eggshells will demonstrate a higher adsorption capacity for certain cationic metals due to ion exchange and precipitation mechanisms, while sawdust will show a broader affinity for various metal ions due to its diverse functional groups.

1.7 Significance of the Study

The findings from this research are expected to yield significant benefits across environmental, economic, technological, and social domains, particularly for the Niger Delta region.

Environmental Benefits: This study directly addresses a critical source of environmental pollution in the Niger Delta. By developing an effective method to treat PW using waste materials, the research contributes to the restoration and protection of the region's fragile ecosystems, including its mangroves, creeks, and aquatic life. Reducing the discharge of heavy metals and other contaminants helps to mitigate bioaccumulation in the food chain and protects biodiversity.

Economic and Technological Benefits: The proposed solution is designed to be low-cost and sustainable. Utilizing eggshells and sawdust, which are often considered waste with zero or negative economic value, transforms them into a valuable resource for water treatment. This approach can significantly reduce the financial burden associated with conventional treatment technologies, which require expensive chemicals, high energy input, and complex infrastructure. The study provides a practical, accessible, and appropriate technology that is more likely to be adopted by operators in the region, potentially reducing cleanup costs and regulatory fines.

Scientific Knowledge: This research will contribute to the body of scientific knowledge by providing validated data on the efficacy of two specific bio-adsorbents for treating a real-world, complex wastewater stream. It will bridge a critical gap between laboratory studies on synthetic solutions and field application. The analysis using Langmuir and Freundlich isotherms will offer

insights into the adsorption mechanisms of these materials in a competitive environment, information that is valuable for future research and development of similar adsorbents.

Social and Health Benefits: The well-being of local communities in the Niger Delta is intimately tied to the health of their environment. By reducing water pollution, this study indirectly aims to lower the incidence of health issues linked to heavy metal exposure, such as neurological disorders, kidney problems, and cancers, which are prevalent in communities relying on contaminated water and food sources. Furthermore, valorizing local waste materials can inspire community-led initiatives and small-scale enterprises focused on waste collection and adsorbent production, creating green jobs and promoting environmental stewardship.

Policy and Regulatory Support: The results of this study can serve as a evidence-based resource for policymakers and regulatory agencies. It can inform the development of stricter, more realistic guidelines for PW discharge by demonstrating that affordable treatment alternatives are feasible. It can also encourage policies that promote a circular economy, incentivizing the use of waste-derived materials in industrial processes.

In summary, this research offers a holistic approach to a persistent problem, promising not just an engineering solution but also a pathway toward environmental sustainability, economic savings, and improved public health for the people of the Niger Delta.

1.8 Scope of the Study

This research is designed to provide a focused and feasible investigation into the use of local materials for PW treatment. The scope is defined by the following boundaries:

i. **Adsorbents:** The study is limited to the evaluation of two specific bio-adsorbents: chicken eggshells and sawdust (from a commonly available local wood species). Other agricultural or industrial wastes will not be considered.

ii. **Contaminants of Focus:** The primary analysis will focus on the removal of select heavy metal ions, particularly Iron (Fe) and zinc (Zn), due to their prevalence and toxicity in Niger Delta PW. While other parameters like pH, salinity, and total petroleum hydrocarbons (TPH) may be monitored, they are not the central focus of the adsorption efficiency analysis.

iii. **Experimental Scale:** The research will be confined to laboratory-scale batch adsorption experiments. This involves controlled experiments in flasks or beakers. Continuous flow column studies, pilot-scale testing, or field implementation are beyond the scope of this current study.

iv. **Methodology:** The investigation will cover the preparation and activation of the adsorbents, batch equilibrium experiments to assess removal efficiency, and isotherm modeling. It will not include a detailed kinetic study, thermodynamic analysis, or a comprehensive engineering design for a full-scale treatment plant.

v. **Geographical Focus:** The PW samples will be sourced from an oil field within the Niger Delta region, ensuring the study addresses the specific local problem. However, a comprehensive geographical or geological survey of the entire region is not within the scope.

vi. **Economic Analysis:** While the cost-effective nature of the materials is a key motivation, this study will not include a detailed economic feasibility study or a full life-cycle assessment. It will, however, discuss the economic implications based on the findings.

By defining these boundaries, the study remains focused on delivering valid and actionable results regarding the proof-of-concept for using eggshell and sawdust adsorbents for treating Niger Delta PW.

1.9 Study Area

This study will focus on an oil field in the Niger Delta region of Nigeria. The Niger Delta is the largest wetland in Africa and the third-largest mangrove forest in the world, encompassing a vast network of rivers, creeks, and estuaries. It is the heart of Nigeria's petroleum industry, hosting extensive oil and gas exploration and production activities for decades.

The region is characterized by its rich biodiversity and natural resources, which starkly contrast with the severe environmental degradation it has suffered. Oil-related pollution, including frequent spills and the continuous discharge of inadequately treated PW, has profoundly impacted its ecosystems. The communities in the Niger Delta are predominantly reliant on fishing and farming, livelihoods that are directly threatened by the contamination of water and land.

The selection of this area is paramount to the research as the environmental crisis here provides the urgent context for this study. The PW generated here is representative of the challenging high-salinity, high-contaminant-load wastewater that requires a sustainable treatment solution. Furthermore, the local availability of the proposed adsorbents (eggshells and sawdust) within this region makes the research highly relevant and ensures the potential for local application and adoption of the findings.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Empirical Review

Produced water (PW) is the largest waste stream generated from oil and gas extraction (Fakhru'l Razi *et al*., 2009; Liu *et al*., 2021). It is the water that comes to the surface along with hydrocarbons during the drilling process. Globally, the volume is staggering, industry reports estimate that between 10 million and 100 million barrels of this water are produced every day (Yousef *et al*., 2020). In the early days of oil exploration, this water was largely considered a nuisance by-product. The common practice was to dispose of it through surface discharge into ponds or rivers, or through simple reinjection back into the ground without adequate treatment (Sanchez-Rosario & Hildenbrand, 2022).

Our understanding of PW has evolved significantly. It is now recognized as a complex chemical mixture that demands careful management. Its composition is highly variable and depends on factors such as the geological formation of the reservoir, the age of the oil field, and the specific chemicals used during drilling and extraction operations (Liu *et al*., 2021). The consistent feature across most PW samples is high salinity, measured as Total Dissolved Solids (TDS), which includes ions such as sodium, chloride, calcium, and magnesium (Aniakor, 2021). Beyond the salt content, PW typically contains a mixture of hydrocarbons, both dispersed oil droplets and dissolved organic compounds, as well as various chemicals added during production, including corrosion inhibitors, scale preventatives, and biocides (Yousef *et al*., 2020). In some formations, the water also carries heavy metals like lead, cadmium, and arsenic from deep underground, and

occasionally, naturally occurring radioactive materials (NORMs) (Sanchez-Rosario & Hildenbrand, 2022).

The challenge lies in treating this complex mixture to meet environmental discharge standards. Treatment generally follows a multi-stage process. The first stage, called *primary treatment*, focuses on removing free oil and large solid particles. This is usually done through physical separation techniques such as gravity separation in large tanks, where oil floats to the surface, or through mechanical devices like hydrocyclones that spin the water to separate its components (Liu *et al*., 2021).

While these primary methods are effective for removing easily separable contaminants, they cannot handle the dissolved components, emulsified oil droplets, or chemical additives. These residual pollutants make secondary and tertiary treatment stages necessary. Methods such as chemical treatment, membrane filtration, and advanced oxidation require more sophisticated technology, higher energy inputs, and greater operational expertise (Yousef *et al*., 2020). However, in many oil producing regions especially developing countries, these advanced treatment options remain out of reach due to both economic and technical limitations (Sanchez-Rosario & Hildenbrand, 2022).

2.2 Secondary and Advanced Treatment Processes

After the initial separation processes, the water still contains numerous contaminants that require more advanced treatment approaches. This secondary treatment phase targets the emulsified oils, fine suspended particles, and various dissolved substances that make PW so challenging to treat (Liu *et al*., 2021).

Mechanical filtration systems, such as multimedia filters or cartridge filters, are employed to remove remaining fine particles. Chemical treatments involving coagulants and flocculants are often added to aggregate tiny oil droplets and suspended solids, making them easier to remove through sedimentation or filtration (Aniakor, 2021).

Membrane technology has become a crucial tool in PW treatment. Different membrane types serve distinct functions: ultrafiltration membranes effectively remove emulsified oils and microorganisms, while nanofiltration and reverse osmosis membranes target dissolved salts and ions responsible for salinity (Yousef *et al*., 2020). Meeting strict discharge standards for salt content often necessitates the use of reverse osmosis or similar desalination technologies.

The most persistent contaminants dissolved organic compounds such as BTEX (benzene, toluene, ethylbenzene, and xylene) and polycyclic aromatic hydrocarbons, require even more advanced treatment approaches. Advanced Oxidation Processes (AOPs) employ powerful oxidizing agents to degrade complex organic molecules into simpler, less harmful compounds (Sanchez-Rosario & Hildenbrand, 2022). For some applications, biological treatment methods provide a more sustainable alternative by using microorganisms to consume and degrade organic pollutants (Aniakor, 2021).

Modern PW treatment increasingly employs hybrid systems that integrate multiple technologies to address the diverse range of contaminants. Liu *et al*. (2021) categorized these treatment approaches into three tiers: preliminary treatment, main treatment, and advanced polishing. Their research highlights emerging technologies such as improved centrifugal separators, advanced membrane materials, and electrochemical oxidation, developments that represent the evolving landscape of PW management.

The most stubborn contaminants, the dissolved organic compounds like BTEX (benzene, toluene, ethylbenzene, and xylene) and polycyclic aromatic hydrocarbons, often require even more advanced treatment approaches. This is where Advanced Oxidation Processes (AOPs) come into play. These processes use powerful oxidizing agents to break down complex organic molecules into simpler, less harmful compounds. For some applications, biological treatment methods provide a more sustainable alternative, using microorganisms to consume and break down organic pollutants.

Modern PW treatment increasingly uses hybrid systems that combine multiple technologies to address the diverse range of contaminants. Researchers like Liu *et al.* (2021) have categorized these treatment approaches into three tiers: preliminary treatment, main treatment, and advanced polishing. Their work highlights emerging technologies across these categories, including improved centrifugal separators, advanced membrane materials, and innovative electrochemical treatment methods that represent the evolving landscape of PW management.

2.3 Produced Water Treatment Challenges in the Niger Delta

The Niger Delta, which is Nigeria's main oil-producing region, faces particularly difficult challenges when it comes to managing PW. Most of the oil fields in this area are mature, meaning they have been producing for a long time. As oil fields age, they tend to produce much more water relative to oil, a condition known as a high water cut. In the Niger Delta, it is common for the water cut to range from 50 % to over 90 %. This means that for every barrel of oil extracted, several barrels of contaminated water must also be handled and treated (Amakiri *et al*., 2023). This enormous volume of water places a huge strain on treatment facilities, many of which are old and were not designed to handle such high volumes (Nwokoma & Dagde, 2024).

The treatment systems currently in place often rely on basic technology. Gravity separators and gas-flotation units are common. While these can remove some of the oil and solids, they are not effective at removing dissolved pollutants or very fine oil droplets that remain mixed in the water (Amakiri *et al*., 2023). Recent studies confirm that these conventional methods are not enough to make the water safe before it is discharged. For example, a 2024 study by Nwokoma and Dagde tested treated water from several facilities in the Niger Delta and found that the salt content (TDS) remained high, often between 2160 and 2410 mg/L, which exceeds the Nigerian legal limit of 2000 mg/L for discharge into coastal waters (Nwokoma & Dagde, 2024).

The study also found that the levels of Chemical Oxygen Demand (COD), a measure of organic pollutants, averaged between 140 and 153 mg/L, while the regulatory limit is 125 mg/L. Similarly, oil-and-grease levels frequently exceeded the limit of 30 mg/L. These consistent failures to meet standards show that the current treatment methods are not sufficient for the complex and heavily polluted water coming from these mature fields (Nwokoma & Dagde, 2024).

The consequences of this inadequate treatment are serious. Releasing poorly treated water into the region's rivers and creeks harms aquatic life due to the toxicity of hydrocarbons, heavy metals, and other chemicals. From an operational standpoint, the leftover salts can cause scaling and corrosion, damaging pipelines and equipment. This leads to more frequent repairs, higher maintenance costs, and production delays (Amakiri *et al*., 2023).

Researchers such as Amakiri *et al*. (2023) point out that a key part of the problem is that Nigerian regulations have traditionally focused mostly on measuring oil and grease, paying less attention to other dangerous contaminants such as dissolved chemicals and trace metals. Their work shows that even after standard treatment, the water still contains significant amounts of these harmful substances. They argue that the country's environmental standards need to be updated to include

a wider range of pollutants. Furthermore, they recommend adopting more advanced treatment steps such as adsorption, advanced oxidation, and membrane filtration, to properly clean the water.

There is some promising progress. For instance, a pilot project that combined a biological treatment unit with membrane filters showed excellent results, reducing COD, hydrocarbons, and salinity by over 95 % (Amakiri *et al*., 2023). This demonstrates that multi-stage systems, where each stage targets a specific type of pollutant, can be very effective. However, for the Niger Delta, any new technology must be affordable, simple to operate, and easy to scale up. The real challenge is implementing these improved solutions in a region where resources and technical capacity are limited. Many older and remote oil fields still depend on outdated methods, and bridging this gap is crucial for reducing environmental damage in the Niger Delta (Nwokoma & Dagde, 2024).

2.4 Low-Cost Bio-Based Adsorbents for Water Treatment

An increasingly popular approach for treating industrial and oilfield wastewaters, including PW, is the use of low-cost bio-based adsorbents. These materials are commonly derived from agricultural byproducts or food-industry residues that would otherwise be discarded. Their attractiveness lies in their abundance, affordability, and sustainability. Compared with synthetic sorbents or expensive chemical treatments, bio-based alternatives offer an environmentally friendly option for contaminant removal, aligning with principles of the circular economy and waste valorization.

A wide variety of bio-adsorbents have been studied, including fruit peels, nutshells, crop residues, plant fibers, and animal-derived wastes. Among the most widely investigated are eggshells, a byproduct of the poultry and food-processing industries, and sawdust, produced in large quantities by the timber and furniture sectors. While most studies on these materials have focused on the

removal of synthetic dyes and heavy metals from industrial effluents, their potential application to PW containing a complex mixture of metals, salts, and hydrocarbons is receiving increasing attention.

Eggshells are particularly promising as adsorbents due to their chemical and structural properties. They consist primarily of calcium carbonate ($CaCO_3$), which makes up about 90–95% of the shell's dry weight, with the remainder composed of an organic matrix and trace minerals. Their structure exhibits moderate porosity, a feature that facilitates gas and moisture exchange in eggs and provides surface area suitable for adsorption. The carbonate component also supports ion exchange and precipitation reactions, especially with divalent metal cations.

In practical applications, both raw and thermally modified eggshells have been shown to perform effectively as adsorbents. Finely powdered raw shells can remove cationic species through surface interactions and precipitation. When thermally activated, $CaCO_3$ decomposes to calcium oxide (CaO), which is more reactive. Further hydration of CaO yields calcium hydroxide ($Ca(OH)_2$), enhancing pH-mediated precipitation of metals and improving adsorption performance. Several studies have reported successful removal of contaminants such as lead (Pb^{2+}), copper (Cu^{2+}), and arsenic (As^{3+}), often achieving efficiencies greater than 80–90%.

Experimental evidence supports the versatility of eggshell-derived adsorbents for both organic and inorganic pollutants. For example, Zonato *et al*. (2022) examined the use of finely ground eggshell powder to remove two textile dyes, Reactive Blue 198 and Direct Black 22, along with cadmium (Cd^{2+}) and chromium (Cr^{3+}). The material exhibited a relatively high surface area (~435 cm^2/g) and a near-neutral point of zero charge (PZC), consistent with its calcium carbonate composition. In batch adsorption tests, 1.0 g of eggshell powder removed 96–99% of all four contaminants from 50 mL aqueous solutions with initial concentrations of 0.5 mg/L. The authors attributed this

efficiency to a combination of chemisorption, involving complexation at calcium-rich surface sites, and physical adsorption facilitated by the porous structure.

Kinetic analysis in the same study showed that adsorption followed a pseudo-second-order rate law, indicating that chemical bonding rather than physical attraction was the dominant mechanism. Isotherm modeling revealed that dye adsorption fit the Langmuir model, suggesting monolayer coverage on a finite number of homogeneous binding sites. This finding implies that under the tested conditions, eggshells function in a manner comparable to engineered sorbents, providing well-defined sites for pollutant uptake.

Abatan *et al*. (2020) reported similar results when testing eggshell powder for the removal of hexavalent chromium (Cr(VI)) and cadmium (Cd(II)) from water. Their work showed that metal uptake was most effective around pH 6.0 and that increasing the adsorbent dosage and contact time improved performance. As in the study by Zonato *et al*., adsorption kinetics conformed to the pseudo-second-order model, confirming the chemisorptive nature of the process. However, equilibrium data were better represented by the Freundlich isotherm, which assumes adsorption occurs on heterogeneous surfaces and may involve multilayer formation. This suggests that while eggshells provide reactive sites for strong bonding, their surface also supports a range of affinities conducive to multilayer adsorption.

Researchers have also explored ways to enhance the performance of eggshells for removing hydrophobic organic pollutants, such as petroleum hydrocarbons. Surface modification has proven particularly effective. For example, El-Nafaty *et al*. (2012) investigated eggshells functionalized with the cationic surfactant hexadecyltrimethylammonium bromide (HDTMA-Br), producing a modified sorbent (SMES). The treatment imparted both a positive charge and hydrophobic character, improving the material's affinity for nonpolar oil molecules in emulsified wastewater.

In experimental tests, just 1.6 g/L of SMES removed 91.2% of oil within 5 minutes. At a total oil concentration of 194 mg/L, nearly complete removal was achieved within 25 minutes of contact.

Isotherm modeling of the oil adsorption data indicated a better fit with the Freundlich isotherm, consistent with multilayer adsorption on a heterogeneous surface. The adsorption mechanism was attributed mainly to physisorption, involving non-covalent interactions such as van der Waals forces. This was supported by the Freundlich constant (n), which reflects both the favorability and intensity of adsorption. These findings show how surfactant modification can expand the application of eggshells to oil removal and highlight the potential of simple surface chemistry adjustments in improving agricultural waste-derived sorbents.

Beyond synthetic emulsions, eggshells have also been tested on real PW samples. Muhammad *et al*. (2012) conducted biosorption experiments using raw eggshells to remove crude oil from Nigerian PW. Characterization with Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and X-Ray Diffraction (XRD) confirmed the predominance of calcium carbonate ($CaCO_3$) and a porous structure with a calcium content of about 37.4 atomic percent. In batch adsorption trials, the researchers achieved nearly complete oil removal (approaching 100%) from PW containing ~194 mg/L of oil. The optimum dosage for this performance was only 1.8 g/L of eggshell, and adsorption kinetics again followed a pseudo-second-order model, suggesting a chemisorption-dominated mechanism. The estimated uptake capacity of ~100 mg oil per gram of eggshell places this material among the most efficient low-cost sorbents for oil removal.

While eggshells have shown impressive results in removing cationic species and hydrophobic organics, lignocellulosic wastes such as sawdust provide a versatile alternative capable of targeting a broader range of contaminants. Sawdust, the finely divided residue from woodworking, consists

mainly of cellulose, hemicellulose, and lignin. These polymers provide functional groups such as hydroxyl (–OH), carboxyl (–COOH), and methoxyl ($–OCH_3$), which can bind to a variety of pollutants. In its raw form, sawdust is abundant, inexpensive, and moderately porous. With thermal or chemical activation, its surface area and sorption capacity increase significantly, making it a promising precursor for activated carbon production.

Chikri *et al*. (2020) reviewed the use of sawdust for dye removal and noted successful applications for pollutants such as methylene blue, acid red, and Congo red. Adsorption performance was found to depend on particle size, surface chemistry, and solution pH. Smaller particle sizes provided greater surface area, while functionalization with carboxyl and hydroxyl groups increased the number of active binding sites. The pH of the solution influenced both the ionization state of the sorbent and the adsorbate, altering electrostatic interactions and binding efficiency. Raw sawdust primarily removes pollutants through surface complexation within its lignocellulosic structure, whereas chemically treated sawdust, especially when acid or alkali modified shows improved uptake of metals and organics due to higher porosity and enhanced surface chemistry.

Meez *et al*. (2021) focused on heavy metal removal and emphasized sawdust's structural and chemical characteristics. Its fibrous morphology provides a porous framework for diffusion, while functional groups enable binding with ions such as Pb^{2+}, Cd^{2+}, and Cu^{2+}. Adsorption efficiency was reported to depend strongly on contact time and solution pH, with optimal uptake usually occurring in the mildly acidic to neutral range. Kinetic modeling across multiple studies revealed that metal adsorption by sawdust frequently follows a pseudo-second-order model, indicating a chemisorption mechanism involving valence forces through electron sharing or exchange.

Equilibrium data for sawdust-based adsorption systems have generally shown good agreement with both Langmuir and Freundlich models. The Langmuir fit suggests monolayer adsorption on

a uniform surface, while the Freundlich fit indicates multilayer adsorption across heterogeneous sites. This dual behavior reflects the wide range of binding affinities in lignocellulosic materials and highlights sawdust's flexibility in accommodating contaminants with different chemical properties. Meez *et al*. describe sawdust as "a very promising material" for low-cost water treatment, citing its abundance, biodegradability, and effectiveness qualities that make it especially attractive in regions with extensive wood-processing activities.

Although relatively few studies have focused on sawdust for treating PW, the available evidence is encouraging. Alomar *et al*. (2022) discuss an investigation in which chemically modified waste sawdust was applied to PW collected from an Iraqi oilfield. The sample contained roughly 130 mg/L of oil and other organic compounds. Under optimized conditions (pH 3, a dosage of 2 g/L, and a contact time of 90 minutes), the sawdust achieved a maximum adsorption capacity of 23.97 mg/g for organic pollutants, equivalent to approximately 2.4 grams of oil removed per kilogram of sorbent. While this capacity is lower than that reported for many commercial activated carbons, it is still notable considering sawdust's renewability and near-zero cost. The study also emphasized that chemical modification likely involving oxidation or surface functionalization was essential for boosting adsorption capacity. As expected, increasing the dosage of sawdust led to higher overall removal efficiency, demonstrating a scalable relationship between sorbent concentration and contaminant removal. Comparable results have been reported for other agricultural wastes such as nutshells and fruit peels, which, when ground and applied at sufficient dosages, have also shown strong oil adsorption potential.

Taken together, studies on eggshells, sawdust, and related bio-waste materials confirm the viability of low-cost adsorption as a water treatment strategy. These sorbents have consistently achieved high removal efficiencies for a broad spectrum of contaminants, including dyes, phenols, heavy

metals, and hydrocarbons, particularly under optimized batch conditions. Beyond their technical performance, their economic and environmental advantages are clear: materials such as eggshells and sawdust are widely available waste products, and repurposing them as sorbents reduces landfill burden while creating added value. Ongoing research continues to improve their adsorption performance through activation methods such as carbonization, acid or base treatment, and surface functionalization. There is also growing interest in scaling up from batch studies to practical systems such as continuous-flow and packed-bed configurations. In oil-producing regions, where agricultural and wood-processing residues are abundant, the use of these locally sourced sorbents could provide a cost-effective and sustainable option for on-site water treatment.

Table 2.1 Summary of Low-Cost Bio-Adsorbents for Produced Water Treatment

Adsorbent	Source / Composition	Target Pollutants	Treatment Conditions	Removal Efficiency / Capacity	Mechanism	Remarks
Eggshell (Raw)	Poultry industry waste; mainly $CaCO_3$ (~90–95%)	Heavy metals (Cd^{2+}, Cr^{3+}), dyes, oil	pH ~6, ~1.0–1.8 g/L dose, batch contact	~96–100% removal of dyes/oil; ~100 mg oil/g capacity	Ion exchange, chemisorption, precipitation	Porous structure and carbonate sites aid sorption; can be reused after regeneration
Modified Eggshell (with HDTMA-Br)	Eggshell treated with cationic surfactant	Petroleum hydrocarbons (oil emulsions)	1.6 g/L, 5–25 min contact	~91% oil removal in 5 min	Physisorption (multilayer, Freundlich behavior)	Surface chemistry modification greatly enhances hydrophobic compound affinity
Eggshell (on actual PW)	Raw eggshell used on crude-oil-contaminated PW	Oil compounds (~194 mg/L)	1.8 g/L dose, batch test	~100% oil removal	Pseudo-second-order kinetics (chemisorption)	Practical field-like conditions tested; very low cost alternative to synthetic sorbents
Sawdust (Raw / Modified)	Wood processing waste; cellulose, hemicellulose, lignin	Dyes, phenols, metal ions, organics	Variable (pH 3–7), 2 g/L, 60–90 min contact	Up to ~23.97 mg/g for oil in PW	Chemisorption via –OH, –COOH; multilayer adsorption	Activation improves performance; suitable for areas with forestry waste availability
Modified Sawdust (on PW)	Chemically treated sawdust	Oil/organics (~130 mg/L)	2 g/L, pH 3, 90 min	~23.97 mg/g (≈2.4 g oil/kg)	Chemisorption, Freundlich isotherm	Performance improves with chemical treatment; promising for field adaptation

Table 2.2 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 - Homogeneous surface - Identical adsorption sites - No interaction between adsorbed molecules	- Heterogeneous surface - Sites with varying adsorption energies - Multilayer adsorption possible - No saturation limit
Mathematical Expression	$q_e = (Q_{max}\ K\_L\ C_e) / (1 + K\_L\ C_e)$	$q_e = K\_F\ C_e\text{^}(1/n)$
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) - K_L: Langmuir constant (L/mg)	- K_F: Freundlich capacity factor - 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 (e.g., bio-adsorbents)
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 $1/n > 1$: Unfavorable adsorption
Typical Use Cases	Activated carbon, ion-exchange resins, synthetic adsorbents	Bio-adsorbents, natural materials like sawdust, eggshells

In adsorption research, the Langmuir and Freundlich isotherms remain foundational for interpreting equilibrium data. Researchers typically conduct batch experiments where the initial

concentration of a contaminant is varied, and the equilibrium uptake, qe, is measured at a constant temperature. These results are then fitted to isotherm models, with Langmuir and Freundlich usually serving as the starting point. Beyond quantifying performance, the models also provide insight into the mechanisms governing adsorption.

The Langmuir isotherm assumes a homogeneous surface with a finite number of identical sites, leading to monolayer adsorption. A strong fit to this model suggests that each adsorbate molecule occupies a single site without interaction with its neighbors. The Langmuir constant also yields a maximum adsorption capacity, Qmax, which is especially useful for comparing different materials. When the model applies well, it often points to chemisorption involving strong, specific binding forces.

By contrast, the Freundlich isotherm is empirical and better suited for heterogeneous surfaces with a range of binding energies. Unlike Langmuir, it does not predict saturation, making it useful for natural adsorbents such as sawdust, nutshells, and eggshells. A good Freundlich fit suggests multilayer adsorption or physisorption, where weaker forces and surface irregularities dominate.

Comparing the two models has proven valuable across many studies. For example, work on sawdust often shows that adsorption can follow either Langmuir or Freundlich behavior, depending on the contaminant type and any surface treatment applied. El-Nafaty *et al*. (2012) reported that oil adsorption onto surfactant-modified eggshells fit the Freundlich model, indicating multilayer uptake on a heterogeneous surface. In contrast, Zonato *et al*. (2022) found that dye adsorption onto untreated eggshells followed the Langmuir model, consistent with uniform chemisorption. Abatan *et al*. (2020) observed Freundlich behavior for cadmium and chromium adsorption onto eggshell powder, again pointing to surface heterogeneity.

These examples illustrate why isotherm testing is more than a statistical exercise. The model that best fits the data often reveals important details about surface chemistry, adsorbate–adsorbent interactions, and the system's potential scalability. For biosorbents, whether natural or modified, evaluating both models is standard practice, as the outcomes frequently align with known or expected surface characteristics.

While the theoretical basis of Langmuir and Freundlich isotherms has changed little over the past decade, their application has expanded. More complex adsorption systems have prompted the use of hybrid models such as the Langmuir–Freundlich (Sips) isotherm, which accounts for both surface heterogeneity and finite capacity. These newer models combine features of the classical ones, but Langmuir and Freundlich remain the principal benchmarks against which adsorption performance is assessed.

Recent studies continue to show that the Langmuir and Freundlich models remain highly relevant in describing adsorption by low-cost, bio-based adsorbents used for both organic and inorganic contaminants. In most cases, researchers apply either linear or nonlinear regression methods to estimate the characteristic parameters of each model: Q_{max} and KL for Langmuir, and KF and 1/n for Freundlich. These values act as performance indicators. For instance, a higher Q_{max} reflects a greater theoretical adsorption capacity, while a 1/n value less than 1 points to favorable adsorption conditions, particularly on heterogeneous surfaces.

Meez *et al*. (2021) noted that many sawdust-based studies report equilibrium data that align with either Langmuir or Freundlich isotherms, often coupled with pseudo-second-order kinetic behavior that suggests chemisorption. This alignment between isotherm and kinetic modeling strengthens the interpretation of adsorption mechanisms and increases confidence in the derived parameters.

Isotherm modeling also has practical relevance for PW treatment. In field-related work, Udeagbara *et al*. (2021) used local bio-adsorbents in column studies to remove heavy metals from PW in the Niger Delta. Their results, interpreted through both Langmuir and Freundlich models, showed high removal efficiencies, with some metals completely removed under optimized conditions. The isotherm analysis confirmed that removal was achieved through adsorption rather than non-adsorptive processes like precipitation.

Langmuir's century-old model is still valued for its clear description of monolayer adsorption on a surface with uniform sites. Although originally designed for gas–solid systems, it remains useful in aqueous-phase studies, especially with engineered or activated materials that display uniform surface chemistry. Freundlich's empirical model, on the other hand, is better suited for natural or minimally processed biomaterials such as sawdust, nutshells, and eggshells, where surfaces are heterogeneous and adsorption sites vary in energy.

The choice between these two models is usually guided by data. Researchers typically select the model that provides the best statistical fit (often based on R^2) and that makes sense in light of the material's surface properties. For example, Zonato *et al*. (2022) reported Langmuir-type adsorption when textile dyes and metals were adsorbed onto finely ground eggshell, suggesting monolayer coverage and uniform calcium-based sites. In contrast, El-Nafaty *et al*. (2012) found Freundlich-type behavior for oil adsorption on surfactant-modified eggshell, which pointed to a heterogeneous surface and multilayer uptake. Such comparisons are valuable because Langmuir provides a theoretical maximum uptake capacity (Q_{max}) useful for design purposes, while Freundlich captures adsorption behavior at lower concentrations and gives insight into binding intensity.

As systems grow more complex, additional models such as Temkin, Dubinin–Radushkevich, and Sips are often applied to complement the classical ones. These models account for energetic interactions, pore-filling effects, or hybrid adsorption behaviors. Even so, Langmuir and Freundlich remain the starting point in most studies and often suffice for comparing adsorbent performance in screening tests.

Beyond the academic role of model fitting, isotherm parameters carry practical implications. Engineers rely on them to estimate adsorbent requirements, predict column breakthrough times, and judge whether treatment goals can be met under changing influent conditions. For example, a Langmuir Q_{max} of 100 for oil removal by eggshell allows direct calculation of the sorbent mass required to treat a specific volume of PW. Likewise, a Freundlich exponent (1/n) much less than 1 signals that adsorption becomes less efficient at higher concentrations, an important consideration for dynamic treatment systems. In this way, classical isotherm models, though rooted in early 20th-century theory, continue to shape the design and optimization of adsorption technologies, particularly in cost-sensitive applications such as oilfield wastewater treatment.

2.5 Contemporary Trends in Biosorption and Isotherm Modeling for Produced Water Treatment

In recent years, the use of low-cost biosorbents has gained momentum in environmental remediation, especially for wastewater and PW treatment. Materials such as eggshells, sawdust, and other agricultural or industrial byproducts have consistently shown strong potential for removing contaminants like dyes, phenolic compounds, heavy metals, and hydrocarbons. What makes them particularly attractive is their ability to achieve removal efficiencies comparable to commercial activated carbon, while being far more affordable and readily available.

Eggshells are a notable example. They are generated in large volumes by the food industry and are primarily composed of calcium carbonate, with surface functional groups such as hydroxyl and carboxyl that enhance their affinity for cationic pollutants. Zonato *et al*. (2022) showed that unmodified eggshells were capable of removing up to 99% of dyes and metal ions under optimized conditions. Sawdust, another abundant byproduct from wood processing, has also been widely studied for its adsorption potential. Rich in cellulose, hemicellulose, and lignin, it provides a variety of oxygen-containing functional groups that interact with diverse pollutants. Reviews by Chikri *et al*. (2020) and Meez *et al*. (2021) report that both raw and activated sawdust perform well in removing organic dyes and heavy metals, reinforcing its promise as a sustainable water treatment material.

For oilfield applications, these biosorbents have shown encouraging results in treating PW. El-Nafaty *et al*. (2012) reported nearly complete crude oil removal (close to 100%) from PW using raw eggshells. Similarly, Alomar *et al*. (2022) demonstrated that chemically modified sawdust could adsorb about 23.97 mg/g of organic pollutants from real PW samples collected in Iraq. These outcomes highlight the potential of bio-adsorbents as cost-effective, locally sourced, and environmentally friendly treatment options for managing PW in oil-producing regions.

Looking ahead, two parallel trends are emerging in the literature. First, there is a growing interest in integrating biosorbents into hybrid water treatment systems. This could involve using agricultural wastes or biochars as polishing steps following conventional methods such as membrane filtration or flotation, thereby reducing chemical inputs and overall treatment costs. Second, advancements in isotherm modeling are enabling more nuanced interpretations of experimental data. Models such as the Langmuir–Freundlich (Sips), Toth, and Temkin isotherms are being increasingly used to handle complex or mixed adsorption mechanisms. Additionally,

there is a concerted effort to link equilibrium data with dynamic breakthrough experiments in fixed-bed or continuous-flow systems, enhancing the practical applicability of isotherm-derived parameters.

Nevertheless, the Langmuir and Freundlich models remain the foundational tools in this field. Their simplicity, interpretability, and proven relevance make them indispensable for both preliminary studies and full-scale adsorption system design. As recent case studies demonstrate, these models are not just theoretical abstractions, they directly inform real-world decisions such as sizing of treatment beds, predicting breakthrough times, and assessing economic feasibility.

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-adsorbents (eggshell and sawdust); (3) batch adsorption experiments to evaluate heavy metal removal efficiency; and (4) analysis of equilibrium data using adsorption isotherm kinetic 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

PW sample was collected from the skimmer pit of an oil field within the Niger Delta region, Nigeria. The skimmer pit was selected because it serves as the final stage of primary separation, where oil droplets and other hydrocarbons are allowed to rise to the surface while the water phase settles below. 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 collected in clean, airtight plastic containers that were thoroughly rinsed with PW before final sampling to prevent contamination. To preserve the integrity of the sample, the containers were completely filled to minimize headspace and atmospheric oxidation of volatile components.

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, and the concentrations of specific heavy metals: Iron (Fe) and zinc (Zn). These metals were selected due to their prevalence and toxicity in Niger Delta PW, 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 PW represents the complex matrix typical of mature Niger Delta oil fields.

3.2 Preparation and Activation of Bio-Adsorbents

3.2.1 Eggshell Adsorbent

a) Collection and Pre-treatment

Eggshells were obtained from local vendors who prepare boiled eggs for commercial purposes, such as egg roll production. The use of pre-boiled shells facilitated easier removal of the inner membrane, as the membrane becomes more visible and detachable after boiling (Muhammad *et al*., 2012). The collected shells were thoroughly rinsed with clean water to remove any adhering organic matter or dirt. After cleaning, the eggshells were sun-dried for 2–3 days to ensure complete moisture removal. The cleaned eggshells after membrane removal, rinsing and drying are shown in Plate 3.2. The dried shells were then ground using a mechanical grinder to obtain a fine powder. The ground eggshell powder is shown in Plate 3.3.

Plate 3.2 Eggshells after membrane removal, rinsing and sun-drying.

Plate 3.3 Eggshell powder after mechanical grinding.

b) Thermal Activation and Sieving

Thermal activation was performed to enhance the physicochemical and adsorptive properties of the eggshell. A portion of the powdered eggshell was placed in an open ceramic crucible and heated in a muffle furnace at 700 °C for 4 hours. This temperature was selected to improve porosity

and surface area while promoting the partial decomposition of calcium carbonate ($CaCO_3$) to more reactive phases, thereby enhancing ion exchange and precipitation mechanisms (Park *et al*., 2007; Daniel *et al*., 2022). The sample was allowed to cool gradually inside the furnace to prevent thermal shock. The activated eggshell was then sieved using a 60 BSS mesh (250 µm) to ensure consistency in particle size distribution for subsequent adsorption processes. The final activated eggshell powder is shown in Plate 3.4.

Plate 3.4 Thermally activated eggshell powder after calcination at 700°C and sieving.

3.2.2 Sawdust Adsorbent

a) Collection and Pre-treatment

Sawdust was obtained from a sawmill located in Benin City, Nigeria, ensuring the use of a locally abundant waste material as per the research aim. To minimize contamination from dirt, oil, and human traffic, only larger wood fragments were collected directly as they were discharged from

the sawing machine during cutting operations. Finer particles that had accumulated on the floor were deliberately avoided to maintain sample purity. The collected raw wood fragments are shown in Plate 3.5.

Plate 3.5 Raw wood fragments (sawdust) collected directly from the sawmill machine.

b) Comminution

The collected wood fragments were processed using a mechanical grinding machine. The material was ground multiple times to achieve a fine and uniform particle size. This coarsely ground sawdust, depicted in Plate 3.6, was stored in airtight containers before activation.

Plate 3.6 Sawdust after initial mechanical grinding.

c) Thermal Activation

Thermal activation of the sawdust was conducted to enhance its adsorptive capacity by increasing surface area and developing porosity. A measured portion of the prepared sawdust was placed in an open ceramic crucible and heated in a muffle furnace at 300 °C for 1 hour. This partial carbonization step aims to degrade volatile components and initiate pore development (Meez *et al*., 2021). The material was then allowed to cool gradually inside the furnace to prevent thermal shock. The resulting thermally activated sawdust is shown in Plate 3.7.

Plate 3.7 Sawdust after thermal activation at 300°C, before final grinding and sieving.

d) Post-Thermal Grinding, Sieving, and Chemical Activation

Following thermal activation, the material was reground using a mortar and pestle to break down agglomerates and then sieved through a 60 BSS mesh (250 µm) to obtain a fine, uniform powder. This step was crucial to ensure a consistent particle size for the subsequent chemical activation and adsorption experiments.

To further improve surface functionality and remove residual inorganic impurities, the sieved, thermally activated sawdust was subjected to acid treatment. A 2 M hydrochloric acid (HCl) solution was prepared and used at a ratio of 10 g of sawdust to 100 mL of acid solution. The mixture was placed in a shaker water bath at 70 °C and agitated at 120 rpm for 1 hour to facilitate uniform contact between the adsorbent and acid.

After acid treatment, the material was thoroughly washed several times with distilled water until the filtrate reached a neutral pH, and then oven-dried, as shown in Plate 3.8. The final mass of the treated sawdust was 7.2795 g (Plate 3.9), with the reduction from the initial 10 g attributed to the removal of acid-soluble impurities and volatile matter. The final, fully activated sawdust (Plate 3.10) was stored in airtight containers prior to use in adsorption experiments.

Plate 3.8 Chemically activated sawdust undergoing oven drying after washing to neutrality.

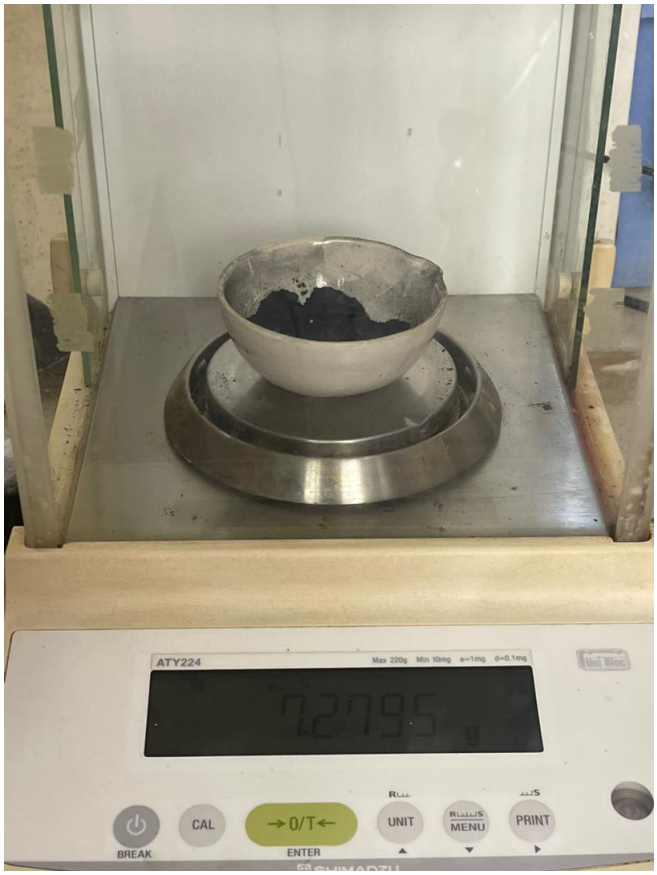

Plate 3.9 Mass measurement of the 10g sawdust sample after the complete acid activation and drying process.

Plate 3.10 Fully activated sawdust adsorbent after the complete thermal and chemical treatment process.

3.3 Batch Adsorption Experiments

Batch adsorption studies were conducted to evaluate the performance of the prepared absorbents in treating PW from oil fields, corresponding to the third research objective. The experiments investigated the effect of a key operational parameter: contact time.

3.3.1 Experimental Procedure

For each experiment, a fixed adsorbent dosage of 2 g was added to 100 mL of the PW in a 250 mL beaker. The samples were agitated on a magnetic stirrer at 150 rpm and maintained at room temperature (≈25 °C). The experiments were carried out at four different contact times: 30 minutes, 1 hour, 1 hour 30 minutes, and 2 hours. This range allows for the observation of adsorption kinetics and the determination of the equilibrium point.

Plate 3.11 Treated produced water samples at different contact times

3.4 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 3.12. The residual concentrations of heavy metals (Fe, Zn) in the digested samples were then determined using Atomic Absorption Spectrophotometry (AAS).

Plate 3.12 Digested produced water samples prepared for analysis via Atomic Absorption Spectrophotometry (AAS)

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3.5 Adsorption Isotherm and Kinetic Modelling

3.5.1 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:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \qquad (3.1)$$

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:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{3.2}$$

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).

3.5.2 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):

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{3.3}$$

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):

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{3.4}$$

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

Linear plots of $\log(q_e - q_t)$ versus t for the PFO model and t/q_t versus t for the PSO 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:

$$q_t = k_{id}\, t^{1/2} + C \tag{3.5}$$

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 Equations 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 (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 (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 Results

This chapter presents the findings from our experiments testing how well the activated sawdust and activated eggshell remove iron (Fe) and zinc (Zn) from real PW from the Niger Delta. We analyze the data to understand the speed of the removal process (kinetics) and the final balance between the water and the material (equilibrium isotherms). This helps us Plate out how the process works. We compare the two materials based on their percentage of metal removed, their holding capacity, and how well the results match known scientific models. The plots showing these trends over time are provided in the Appendix.

Table 4.1 Results of the concentrations (mg/L) of metals for Activated Eggshell and Activated Sawdust

Adsorbent	**Metal**	**C_0 (mg/L)**	**C_e at 30 min (mg/L)**	**C_e at 60 min (mg/L)**	**C_e at 90 min (mg/L)**	**C_e at 120 min (mg/L)**
Sawdust	Iron (Fe)	0.744	0.652	0.461	0.342	0.219
Sawdust	Zinc (Zn)	0.089	0.089	0.066	0.040	0.004
Eggshell	Iron (Fe)	0.744	0.557	0.453	0.340	0.287
Eggshell	Zinc (Zn)	0.089	0.081	0.058	0.032	0.018

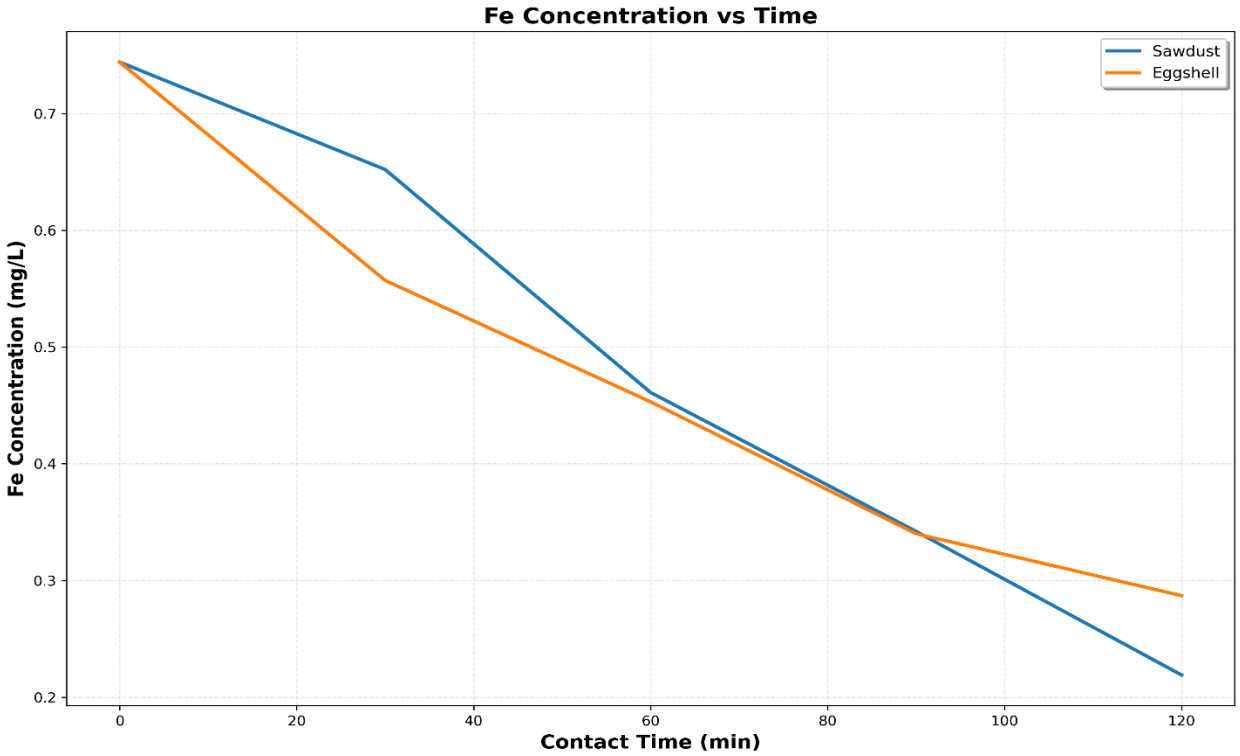

Figure 4.1 Plot of Concentration of Fe versus time for Sawdust and Eggshell

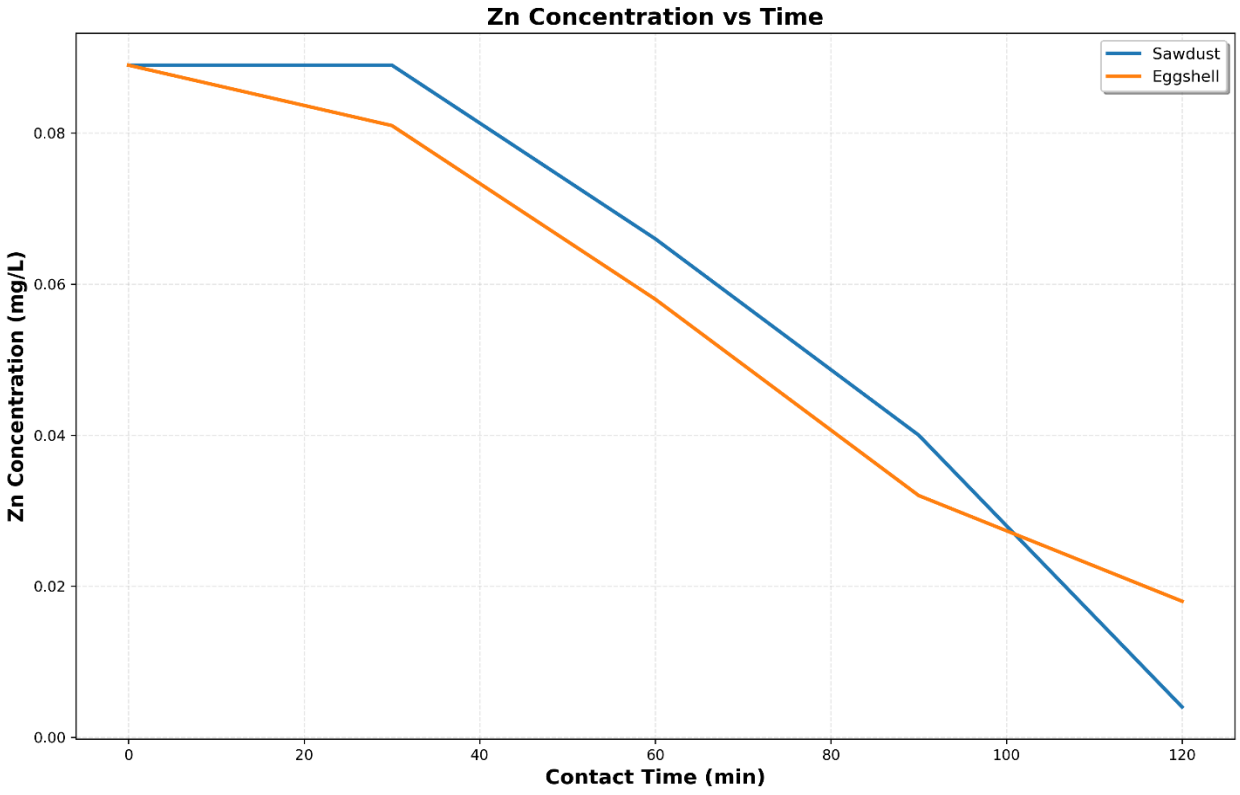

Figure 4.2 Plot of Concentration of Zn versus time for Sawdust and Eggshell

4.2 Adsorption of Heavy Metals using Activated Sawdust

4.2.1 Removal Efficiency and Capacity for Fe and Zn

The treated sawdust effectively removed both iron and zinc from the water over a two-hour period.

For iron, the starting concentration was 0.744 mg/L. After 120 minutes, it was reduced to 0.219 mg/L. This means the sawdust removed 70.6% of the iron. As shown in Table 4.3, the sawdust's capacity to hold iron (q_e) steadily increased over time, ending at 0.02625 mg/g.

For zinc, the removal was even more effective. The starting concentration was 0.089 mg/L, and it was reduced to just 0.004 mg/L. This is a removal efficiency of 95.5%. The final adsorption capacity for zinc was 0.00425 mg/g. The fact that zinc was removed so efficiently, even though there was less of it to start with, suggests that the surface of the sawdust has a particularly strong attraction to zinc ions.

Table 4.2 Removal Efficiency of Activated Sawdust for Fe and Zn over Time

Contact Time (min)	Fe - C_e (mg/L)	Fe - % Removal (%)	Zn - C_e (mg/L)	Zn - % Removal (%)
30	0.652	12.37	0.089	0.00
60	0.461	38.04	0.066	25.84
90	0.342	54.03	0.040	55.06
120	0.219	70.56	0.004	95.51

Table 4.3 Analysis of Activated Sawdust on Iron (Fe) using Adsorption models

Time (min)	C_e (mg/L)	q_e (mg/g)	C_e/q_e (g/L)	Log C_e	Log q_e	q_t (mg/g)	t^0.5	t/q_t	Log(q_e-q_t)
30	0.6520	0.004600	141.7391	-0.1858	-2.3372	0.004600	5.4772	6521.74	-1.6645
60	0.4610	0.014150	32.5795	-0.3363	-1.8492	0.014150	7.7460	4240.28	-1.9172
90	0.3420	0.020100	17.0149	-0.4660	-1.6968	0.020100	9.4868	4477.61	-2.2111
120	0.2190	0.026250	8.3429	-0.6596	-1.5809	0.026250	10.9545	4571.43	N/A

Table 4.4 Analysis of Activated Sawdust on Zinc (Zn) using Adsorption models

Time (min)	C_e (mg/L)	q_e (mg/g)	C_e/q_e (g/L)	Log C_e	Log q_e	q_t (mg/g)	t^0.5	t/q_t	Log(q_e-q_t)
30	0.0890	0.000000	N/A	-1.0506	N/A	0.000000	5.4772	N/A	-2.3716
60	0.0660	0.001150	57.3913	-1.1805	-2.9393	0.001150	7.7460	52173.91	-2.5086
90	0.0400	0.002450	16.3265	-1.3979	-2.6108	0.002450	9.4868	36734.69	-2.7447
120	0.0040	0.004250	0.9412	-2.3979	-2.3716	0.004250	10.9545	28235.29	N/A

Experimental conditions: m = 2 g, V = 0.1 L, C_i(Fe) = 0.744 mg/L, C_i(Zn) = 0.089 mg/L. q_e calculated as $q_e = (C_i - C_e)V / m$.

q_e (equilibrium) for kinetic models is taken as the final value at 120 min.

4.2.2 Adsorption Kinetics of Sawdust

A. Pseudo-First-Order (PFO) Kinetics

For iron, the PFO model fit the data very well, with a high R^2 value of 0.998. The model calculated an equilibrium capacity (q_e,calc) of 0.0413 mg/g, which is close to the experimental value of 0.02625 mg/g. The rate constant (k_1) was 0.0210 per minute. This excellent fit suggests that physical forces (physisorption) play a major role in the rate of iron adsorption.

For zinc, the PFO model also showed a strong fit, with an R^2 of 0.977. The calculated capacity was 0.00678 mg/g (higher than the experimental 0.00425 mg/g), but it still effectively captured the kinetic trend. The rate constant k_1 was 0.0143 per minute.

B. Pseudo-Second-Order (PSO) Kinetics

In contrast, the PSO model did not fit the data well. For iron, the fit was very poor ($R^2 = 0.472$) and it produced a negative calculated capacity of -0.0534 mg/g. For zinc, while the R^2 was higher (0.973), it also gave a negative capacity of -0.00251 mg/g. The failure of this model, especially the impossible negative values, indicates that the chemical bonding (chemisorption) it describes is not the main mechanism controlling the speed of adsorption for sawdust in this case.

C. Intraparticle Diffusion Model

This model showed an extremely strong correlation for both iron ($R^2 = 0.998$) and zinc ($R^2 = 0.960$). The k_{id} value for iron was 0.00391 $mg.g^{-1}.min^{-0.5}$, which is larger than the value for zinc (0.000758 $mg.g^{-1}.min^{-0.5}$). This confirms that iron ions moved into the sawdust pores faster than zinc ions.

However, the constant C had negative values for both metals. This important detail tells us that while pore diffusion is happening, it is not the only thing controlling the speed of adsorption. The process is more complex and is also influenced by the initial movement of ions through the liquid film surrounding each sawdust particle.

Table 4.5 Kinetic Model Parameters for Adsorption of Fe and Zn using Activated Sawdust

Model	Parameter	Fe Value	Zn Value
Pseudo First Order	k_1 (min^{-1})	2.098×10^{-2}	1.432×10^{-2}
	q_e (mg/g)	4.127×10^{-2}	6.784×10^{-3}
	R^2	0.998	0.977
Pseudo Second Order	q_e (mg/g)	-5.344×10^{-2}	-2.506×10^{-3}
	k_2 ($g.mg^{-1}.min^{-1}$)	5.509×10^{-2}	2.124
	R^2	0.471	0.973
Weber Morris	K_{id} ($mg.g^{-1}.min^{-0.5}$)	3.907×10^{-3}	7.580×10^{-4}
	C (mg/g)	-1.661×10^{-2}	-4.417×10^{-3}
	R^2	0.998	0.960

4.2.3 Adsorption Isotherms of Sawdust

A. Langmuir Isotherm

For our sawdust, this model produced unrealistic results, as shown in Table 4.6. The calculated maximum capacities were far too low (0.00324 mg/g for Fe and 0.00114 mg/g for Zn). More critically, the affinity constants (K_L) were negative (-3.89 L/mg for Fe and -118.97 L/mg for Zn), which is impossible as it suggests the metals are repelled by the surface.

Even though the R^2 values seemed acceptable (0.844 for Fe and 0.883 for Zn), the impossible parameters prove that the Langmuir model's assumptions, a perfectly uniform surface and single-layer coverage, are not correct for our real-world water sample. The complex nature of the PW, with many competing ions, creates a messy environment that doesn't fit this ideal model.

B. Freundlich Isotherm

The Freundlich model was a better choice for our data (Table 4.6). It showed a good fit for iron (R^2 = 0.851) and a reasonable fit for zinc (R^2 = 0.814). The K_f value was higher for iron (0.00320) than for zinc (0.000504), confirming that sawdust has a greater capacity for iron, which matches our experimental results.

However, we again saw an unusual result: the n values were negative (-0.65 for Fe and -2.52 for Zn). Normally, a positive 'n' indicates a favorable process. This deviation is likely due to the very low metal concentrations and the competition between different ions in the real PW.

Table 4.6 Isotherm Model Parameters for Adsorption of Fe and Zn using Activated Sawdust

Model	Parameter	Fe Value	Zn Value
Langmuir	q_{max} (mg/g)	3.24×10^{-3}	1.14×10^{-3}
	K_L (L/mg)	-3.89	-118.97
	R^2	0.844	0.883
Freundlich	K_f	3.20×10^{-3}	5.04×10^{-4}
	n	-0.65	-2.52
	R^2	0.851	0.814

While, the Freundlich model was more suitable, the strange parameters from both models highlight a key finding: the adsorption process in real PW is highly complex and is heavily influenced by the mix of contaminants and the non-uniform surface of the sawdust.

The linearized isotherm and kinetic model plots for each Sawdust-metal system are shown in Appendix A and Appendix B respectively.

4.3 Adsorption of Heavy Metals using Thermally Activated Eggshell

4.3.1 Removal Efficiency and Capacity for Fe and Zn

The heat-treated eggshell was also effective at removing both iron and zinc from the PW.

For iron, the starting concentration of 0.744 mg/L was reduced to 0.287 mg/L after 120 minutes. This is a removal efficiency of 61.4%. The eggshell's capacity to hold iron (q_e) increased over time, reaching a final value of 0.02285 mg/g, as detailed in Table 4.3.

For zinc, the performance was more significant. The concentration dropped from 0.089 mg/L to 0.018 mg/L, which is a removal efficiency of 79.8%. The final adsorption capacity for zinc was 0.00355 mg/g.

When we compare the two materials, sawdust achieved a higher removal percentage for both metals under these test conditions. However, the eggshell's performance, especially for zinc, is still very notable. This suggests that eggshell works through a different primary mechanism, most likely involving ion exchange and precipitation, driven by its alkaline, calcium-rich surface.

Table 4.7 Removal Efficiency of Thermally Activated Eggshell for Fe and Zn over Time

Contact Time (min)	Fe - C_e (mg/L)	Fe - % Removal (%)	Zn - C_e (mg/L)	Zn - % Removal (%)
30	0.557	25.13	0.081	8.99
60	0.453	39.11	0.058	34.83
90	0.340	54,30	0.032	64.04
120	0.287	61.42	0.018	79.78

Table 4.8 Analysis of Activated Eggshell on Iron (Fe) using Adsorption models

Time (min)	C_e (mg/L)	q_e (mg/g)	C_e/q_e (g/L)	Log C_e	Log q_e	q_t (mg/g)	t^0.5	t/q_t	Log(q_e-q_t)
30	0.5570	0.009350	59.5722	-0.2541	-2.0292	0.009350	5.4772	3208.56	-1.8697
60	0.4530	0.014550	31.1340	-0.3439	-1.8371	0.014550	7.7460	4123.71	-2.0809
90	0.3400	0.020200	16.8317	-0.4685	-1.6946	0.020200	9.4868	4455.45	-2.5768
120	0.2870	0.022850	12.5602	-0.5421	-1.6411	0.022850	10.9545	5251.64	N/A

Table 4.9 Analysis of Activated Eggshell on Zinc (Zn) using Adsorption models

Time (min)	C_e (mg/L)	q_e (mg/g)	C_e/q_e (g/L)	Log C_e	Log q_e	q_t (mg/g)	t^0.5	t/q_t	Log(q_e-q_t)
30	0.0810	0.000400	202.5000	-1.0915	-3.3979	0.000400	5.4772	75000.00	-2.5017
60	0.0580	0.001550	37.4194	-1.2366	-2.8097	0.001550	7.7460	38709.68	-2.6990
90	0.0320	0.002850	11.2281	-1.4949	-2.5452	0.002850	9.4868	31578.95	-3.1549
120	0.0180	0.003550	5.0704	-1.7447	-2.4498	0.003550	10.9545	33802.82	N/A

Experimental conditions: m = 2 g, V = 0.1 L, C_i(Fe) = 0.744 mg/L, C_i(Zn) = 0.089 mg/L.

q_e (equilibrium) for kinetic models is taken as the final value at 120 min.

4.3.2 Adsorption Kinetics of Eggshell

A. Pseudo-First-Order and Pseudo-Second-Order Kinetics

For iron on eggshell, the PSO model was a much better fit ($R^2 = 0.973$) than the PFO model ($R^2 = 0.949$). Crucially, the PSO model's calculated capacity (0.0464 mg/g) was much closer to the experimental value (0.02285 mg/g) than the PFO's calculation (0.0340 mg/g). This strongly indicates that the rate of iron removal is controlled by chemisorption, such as chemical bonding or precipitation with the calcium carbonate in the eggshell.

In contrast, for zinc, the PFO model was superior ($R^2 = 0.950$) to the PSO model ($R^2 = 0.686$). The PSO model again gave an invalid negative capacity. This shows that zinc removal by eggshell is likely dominated by physisorption or a faster diffusion process.

B. Intraparticle Diffusion Model

The Weber-Morris model showed an excellent fit for both iron ($R^2 = 0.992$) and zinc ($R^2 = 0.993$) on eggshell. The diffusion rate (k_{id}) for iron was 0.00254 $mg.g^{-1}.min^{-0.5}$, which was faster than for zinc (0.000591 $mg.g^{-1}.min^{-0.5}$). The negative C values for both metals confirm, once again, that the process involves multiple steps, including diffusion through the boundary layer and into the particle pores.

Table 4.10 Kinetic Model Parameters for Adsorption of Fe and Zn using Activated Eggshell

Model	Parameter	Fe Value	Zn Value
Pseudo First Order	k_1 (min^{-1})	2.174×10^{-2}	2.507×10^{-2}
	q_e (mg/g)	3.399×10^{-2}	7.379×10^{-3}
	R^2	0.949	0.950
Pseudo Second Order	q_e (mg/g)	4.643×10^{-2}	-2.295×10^{-3}
	k_2 ($g.mg^{-1}.min^{-1}$)	1.754×10^{-1}	2.451
	R^2	0.973	0.686
Weber Morris	K_{id} ($mg.g^{-1}.min^{-0.5}$)	2.543×10^{-3}	5.906×10^{-4}
	C (mg/g)	-4.661×10^{-3}	-2.883×10^{-3}
	R^2	0.992	0.993

4.3.3 Adsorption Isotherms of Eggshell

A. Langmuir Isotherm

Just like with sawdust, the Langmuir model failed for eggshell, producing impossible parameters (Table 4.11). The calculated maximum capacities were too low, and the affinity constants (K_L) were negative (-4.27 L/mg for Fe and -39.13 L/mg for Zn). The high R^2 value for iron (0.946) is

misleading because the model's fundamental assumptions are broken. This confirms that adsorption in this real PW does not form a perfect monolayer.

B. Freundlich Isotherm

The Freundlich model was a good fit for iron adsorption ($R^2 = 0.959$) and a reasonable fit for zinc ($R^2 = 0.805$). The K_f value was much higher for iron (0.00464) than for zinc (0.0000225), showing a greater overall affinity and capacity for iron, which matches the experimental data. However, the model again produced negative n values (-0.75 for both metals), reinforcing that classic models have limited accuracy in this complex wastewater environment.

The linearized isotherm and kinetic model plots for each Eggshell-metal system are shown in Appendix A and Appendix B respectively.

Table 4.11 Isotherm Model Parameters for Adsorption of Fe and Zn using Activated Eggshell

Model	Parameter	Fe Value	Zn Value
Langmuir	q_{max} (mg/g)	5.83×10^{-3}	3.39×10^{-4}
	K_L (L/mg)	-4.27	-39.13
	R^2	0.946	0.781
Freundlich	K_f	4.64×10^{-3}	2.25×10^{-5}
	n	-0.75	-0.75
	R^2	0.959	0.805

A direct comparison of the two adsorbents reveals distinct behaviors and strengths.

In terms of overall efficiency under the tested conditions, activated sawdust was more effective, achieving higher removal percentages for both iron (70.6% vs. 61.4%) and zinc (95.5% vs. 79.8%) compared to thermally activated eggshell.

However, a look at the adsorption capacity provides a more nuanced view. For iron, the eggshell actually demonstrated a slightly higher experimental capacity (0.02625 mg/g) than sawdust (0.02285 mg/g), even though its removal percentage was lower. For zinc, sawdust clearly had a higher capacity (0.00425 mg/g vs. 0.00355 mg/g for eggshell).

The kinetic analysis uncovered a fundamental difference in their removal mechanisms. The adsorption of iron onto sawdust was best described by the PFO model, suggesting a physisorption-driven process. In contrast, iron adsorption onto eggshell followed the PSO model, indicating that chemisorption is the primary mechanism. This is likely due to ion exchange with the calcium carbonate in the eggshell, a strong chemical interaction.

Finally, the isotherm studies yielded a critical shared finding. Both adsorbents deviated significantly from the Langmuir model and produced anomalous parameters with the Freundlich model. This consistent result underscores that the complex, multi-component nature of the real PW itself is a dominant factor, making the adsorption behavior difficult to describe with standard models. Between the two, the Freundlich model was generally the more applicable for describing the equilibrium data.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This research successfully achieved its overarching aim by demonstrating the technical viability of a sustainable treatment strategy for Niger Delta produced water using locally sourced waste materials. The specific objectives of the study were systematically met, yielding conclusive evidence on the efficacy and mechanisms of the adsorption process.

1. The produced water sample collected from the skimmer pit of an oil field within the Niger Delta region was characterized to determine its physicochemical and heavy metal composition. Analysis revealed significant contaminant loading, with iron (Fe) and zinc (Zn) concentrations measured at 0.744 mg/L and 0.089 mg/L, respectively. These findings confirmed the presence of heavy metals, validating the initial hypothesis (H_1) and establishing a baseline for treatment. The characterization also confirmed that the PW exhibited properties typical of oilfield effluents in the Niger Delta, such as high salinity and variable turbidity, reinforcing the necessity for an efficient treatment process.
2. The eggshell and sawdust were successfully processed and activated using distinct methods tailored to their material properties. Eggshells underwent thermal calcination, transforming calcium carbonate into reactive CaO sites, while sawdust was subjected to a combined thermal–chemical activation that enhanced its porosity and introduced oxygen-containing functional groups. These activation methods produced efficient adsorbents with improved surface area and reactivity, meeting the second objective and supporting H_2, which proposed that modification enhances adsorption efficiency.

3. Batch equilibrium experiments showed that both activated sawdust and eggshell were highly effective in reducing metal concentrations. Adsorption efficiency increased with contact time, reaching equilibrium at 120 minutes, confirming H_3. Quantitatively, activated sawdust achieved removal efficiencies of 70.6% (Fe) and 95.5% (Zn), while thermally activated eggshell recorded 61.4% (Fe) and 79.8% (Zn). These results demonstrated the capacity of both adsorbents to significantly improve water quality, validating their potential for low-cost treatment applications.
4. The equilibrium data were analyzed using Langmuir and Freundlich isotherm models, while the kinetics were evaluated using PFO, PSO, and Weber–Morris models. The adsorption data correlated more strongly with the Freundlich isotherm, indicating heterogeneous multilayer adsorption and confirming H_4. Kinetic analysis revealed that sawdust followed the PFO model, implying a physisorption-dominated mechanism, while eggshell fit the PSO model, suggesting chemisorption due to the active calcium oxide sites. The Weber–Morris model further showed that intraparticle diffusion played a secondary but relevant role in the adsorption process.
5. Comparative evaluation showed that sawdust exhibited a broader and stronger affinity for both Fe and Zn, particularly for zinc, due to its high surface area and availability of polar functional groups. Eggshell, on the other hand, showed greater selectivity for iron through surface precipitation and ion exchange mechanisms linked to its CaO content.

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5.2 Recommendations

To build upon this research, the following studies are recommended:

1. **Longer contact times:** It is recommended that future studies extend the contact time beyond 2 hours. Due to power constraints in the laboratory, this study was limited to 120 minutes. A longer contact time is expected to enhance adsorption efficiency and possibly achieve complete removal of metal ions.

2. **Adsorbent Characterization:** Using techniques like SEM and FTIR to analyze the physical and chemical properties of the materials before and after use would help explain *why* they perform as they do, linking their structure to their function.

3. **Higher Activation Temperature:** The eggshell adsorbent was activated at 700 °C, which was the maximum temperature capacity of the available muffle furnace. Future research should explore higher activation temperatures (up to 900 °C) to improve porosity and surface area, thereby enhancing adsorption performance.

4. **Broader Contaminant Range:** Extend adsorption testing to include other heavy metals and oil-in-water components present in PW to assess the full potential of the local adsorbents.

5. **Scale-Up Recommendation:** Based on the promising results from laboratory experiments, pilot-scale testing should be conducted to evaluate the real-field application of these locally sourced materials for PW treatment in the Niger Delta region.

6. **Use of Mixed Adsorbents:** Further studies should investigate the simultaneous use of sawdust and eggshell as a composite or mixed adsorbent to evaluate potential synergistic effects in removing multiple contaminants.

5.3 Contribution to Knowledge

This study contributes significantly to the field of produced water treatment, environmental and waste management.

1. Demonstrating the feasibility of using locally sourced eggshell and sawdust as effective low-cost adsorbents for the removal of heavy metals from produced water.
2. Providing new experimental data on the adsorption behavior of thermally activated eggshell and thermally-chemically activated sawdust for iron (Fe) and zinc (Zn) removal.
3. Promoting sustainable waste-to-resource conversion by transforming agricultural and domestic wastes into valuable environmental remediation materials.
4. Adding to the growing body of knowledge on low-cost, eco-friendly wastewater treatment technologies.

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APPENDICES

Appendix A: Adsorption Isotherm Plots

This appendix contains all linearized Isotherm model plots for each adsorbent-metal system.

A1 Langmuir Isotherm Plots

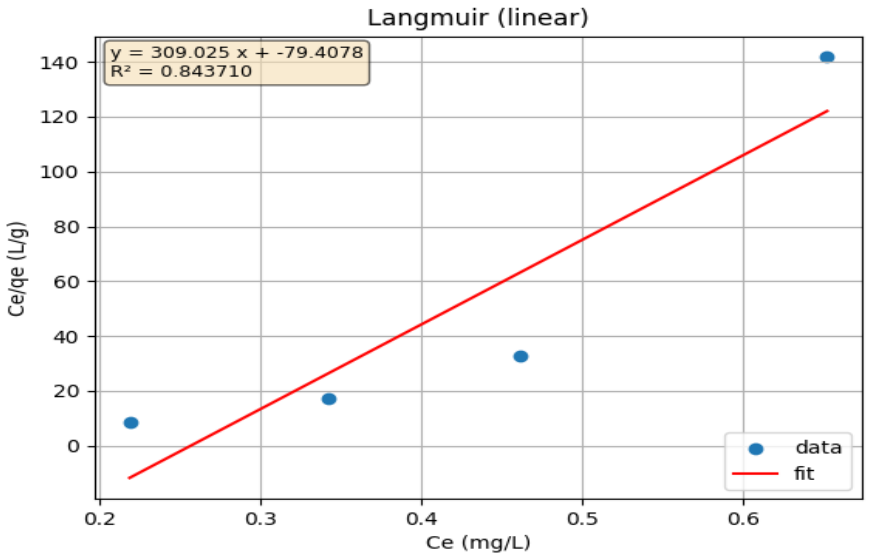

Figure A1 Langmuir plot for Sawdust-Fe

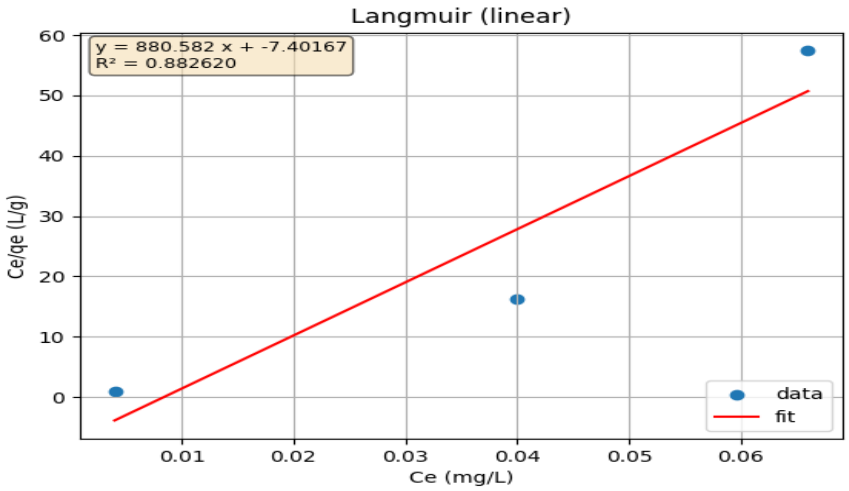

Figure A2 Langmuir plot for Sawdust-Zn

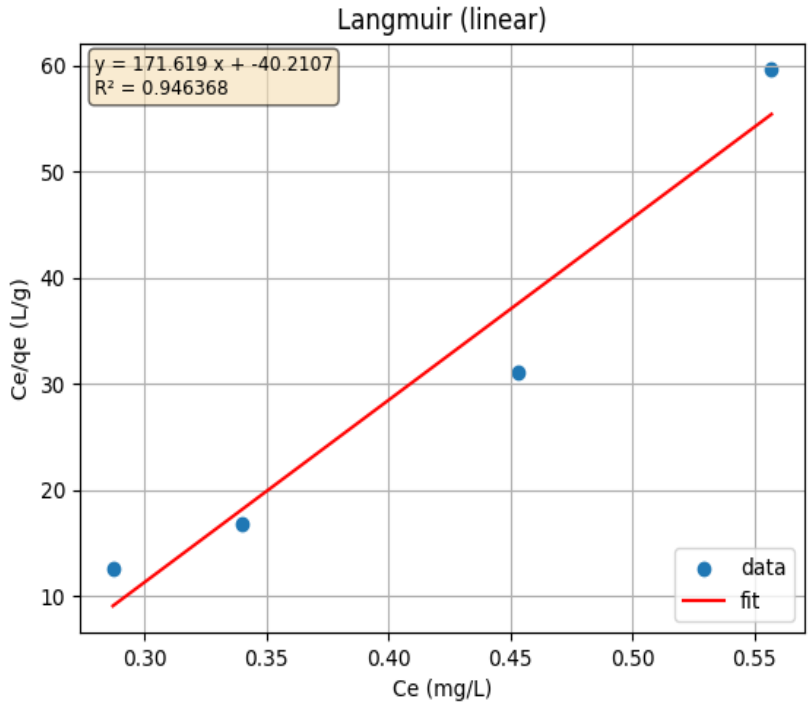

Figure A3 Langmuir plot for Eggshell-Fe

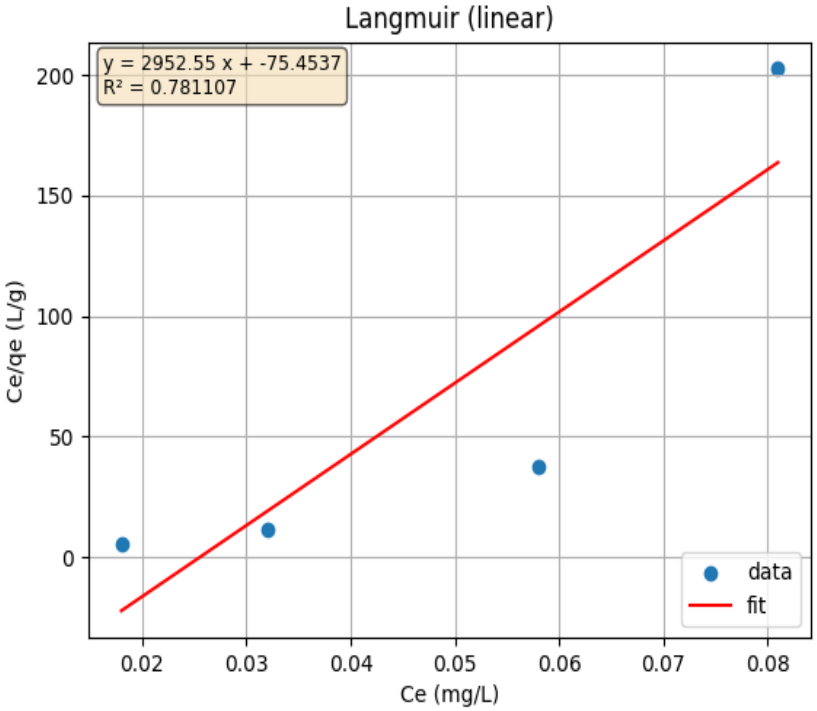

Figure A4 Langmuir plot for Eggshell-Zn

A2 Freundlich Isotherm Plots

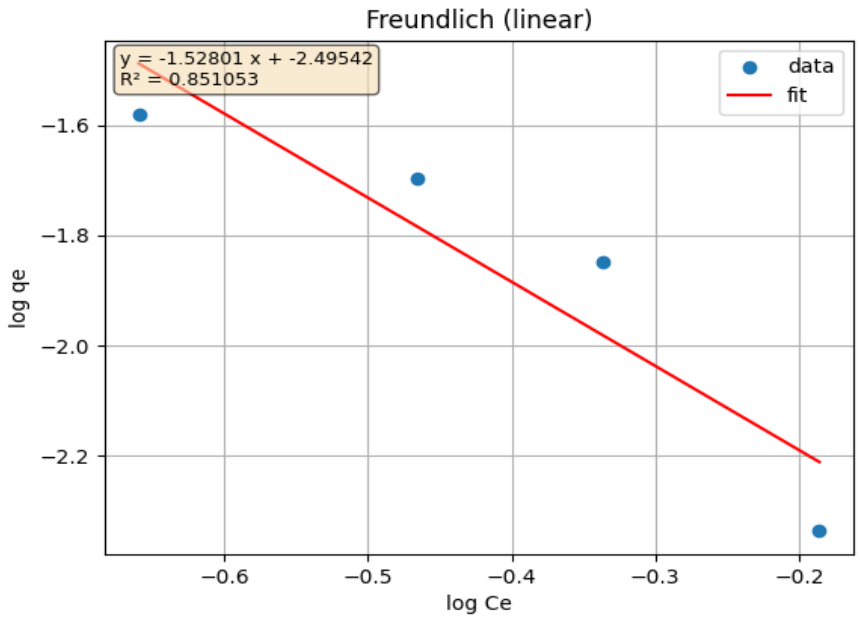

Figure A5 Freundlich plot for Sawdust-Fe

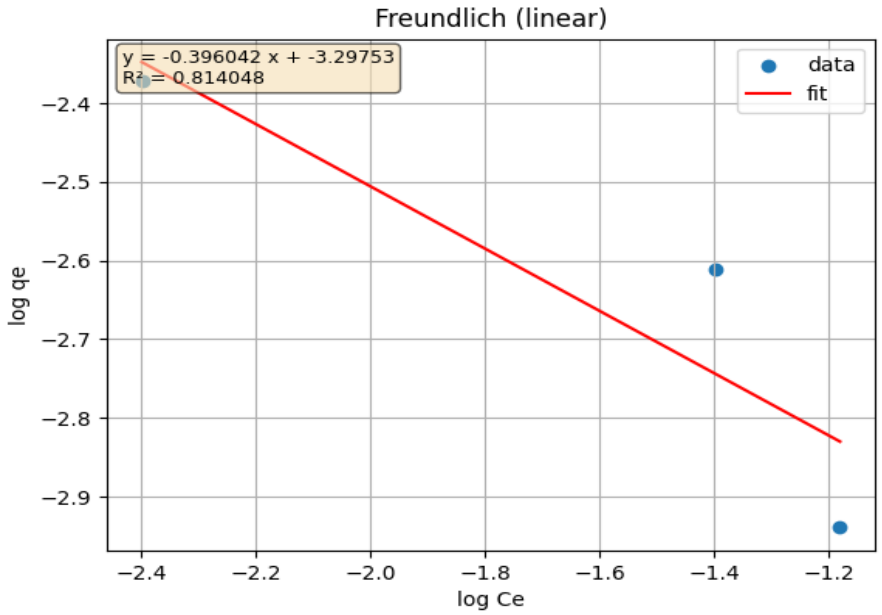

Figure A6 Freundlich plot for Sawdust-Zn

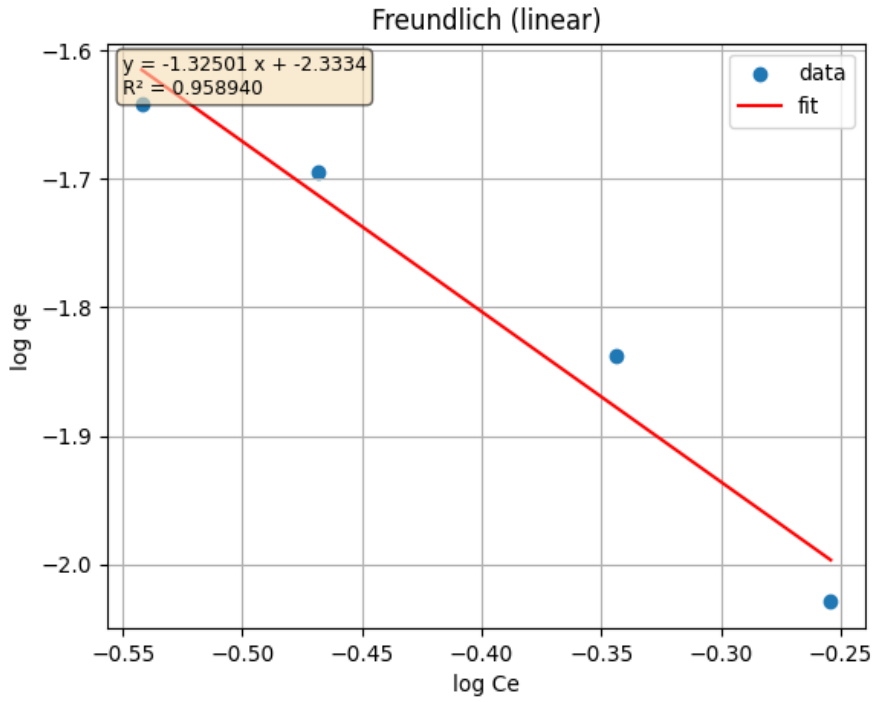

Figure A7 Freundlich plot for Eggshell-Fe

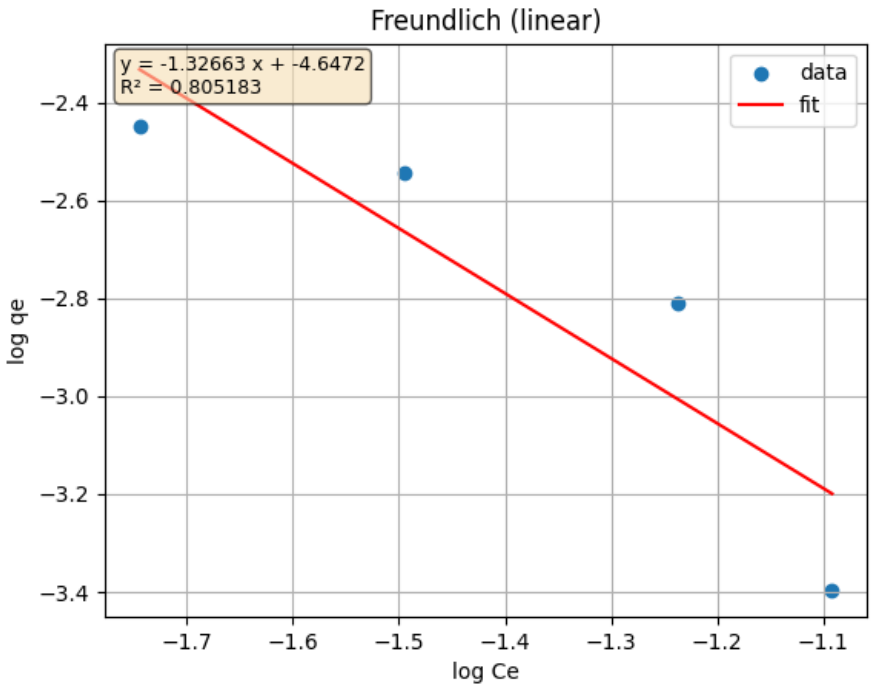

Figure A8 Freundlich plot for Eggshell-Zn

Appendix B: Kinetic Model Plots

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

B1 Pseudo-First-Order (PFO)

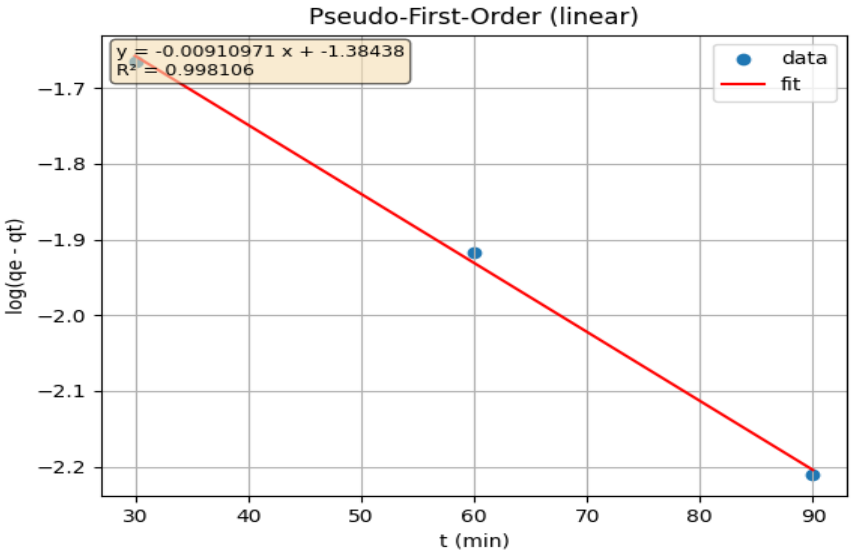

Figure B1 PFO plot for Sawdust-Fe

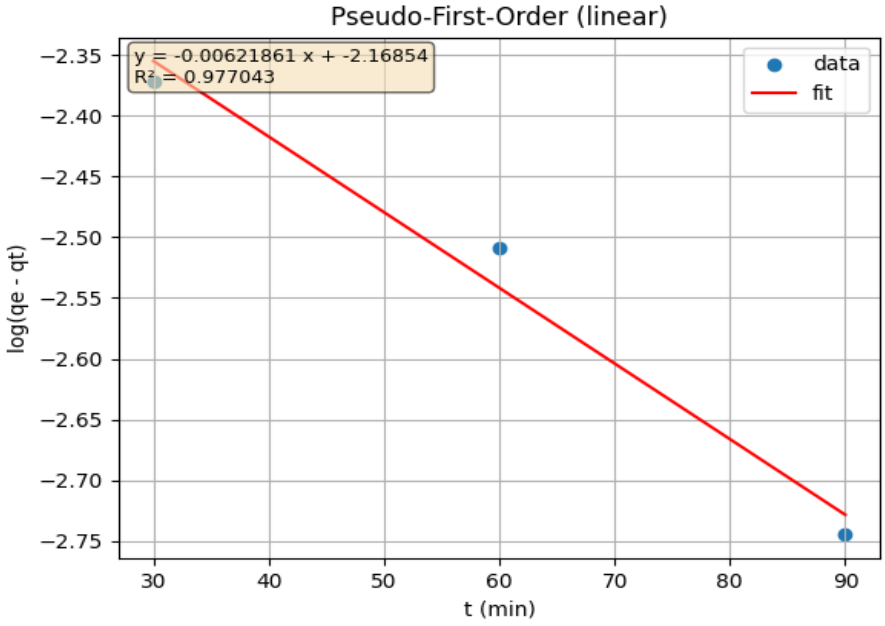

Figure B2 PFO plot for Sawdust-Zn

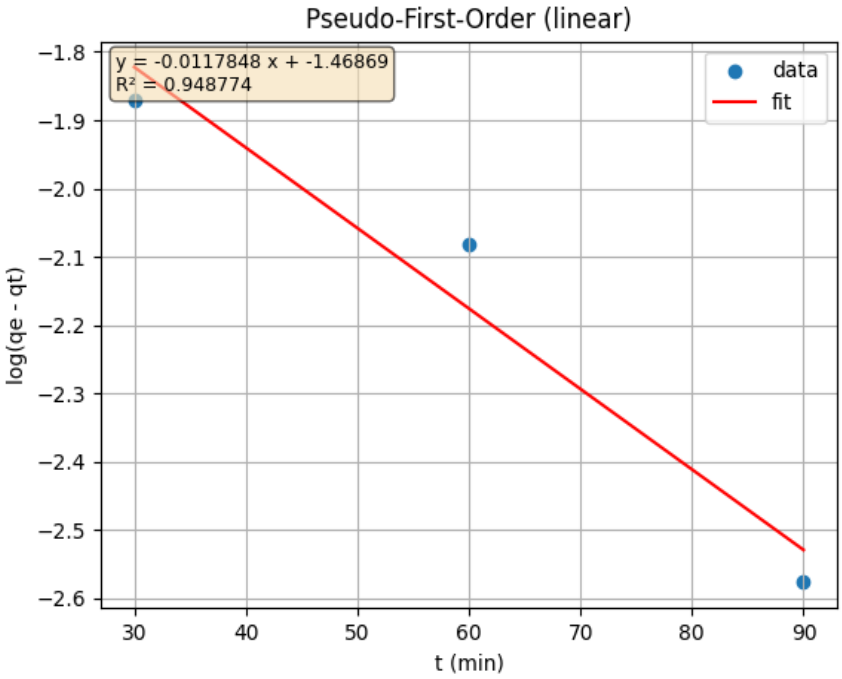

Figure B3 PFO plot for Eggshell-Fe

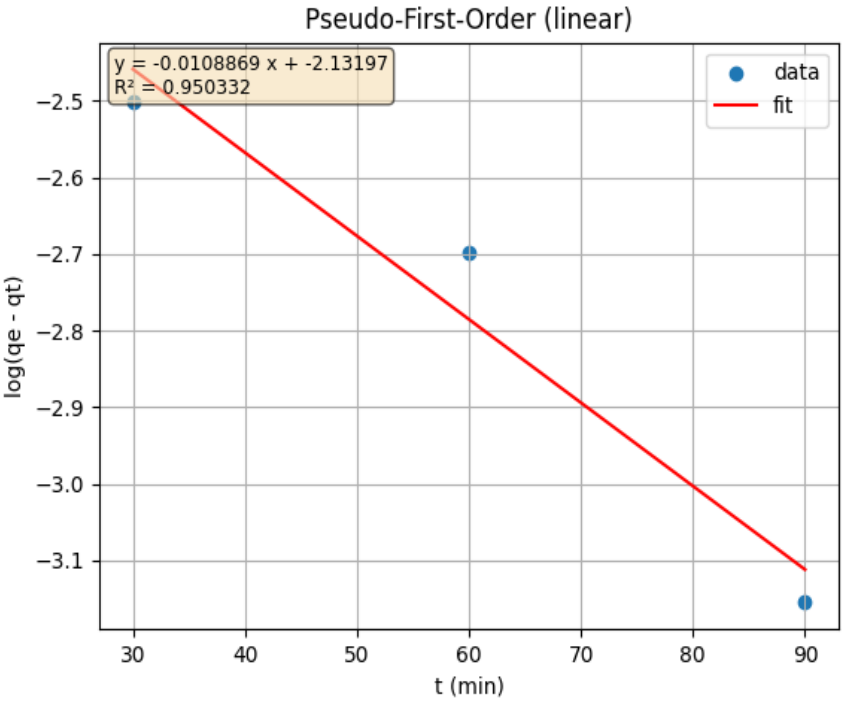

Figure B4 PFO plot for Eggshell-Zn

B2 Pseudo-Second-Order (PSO)

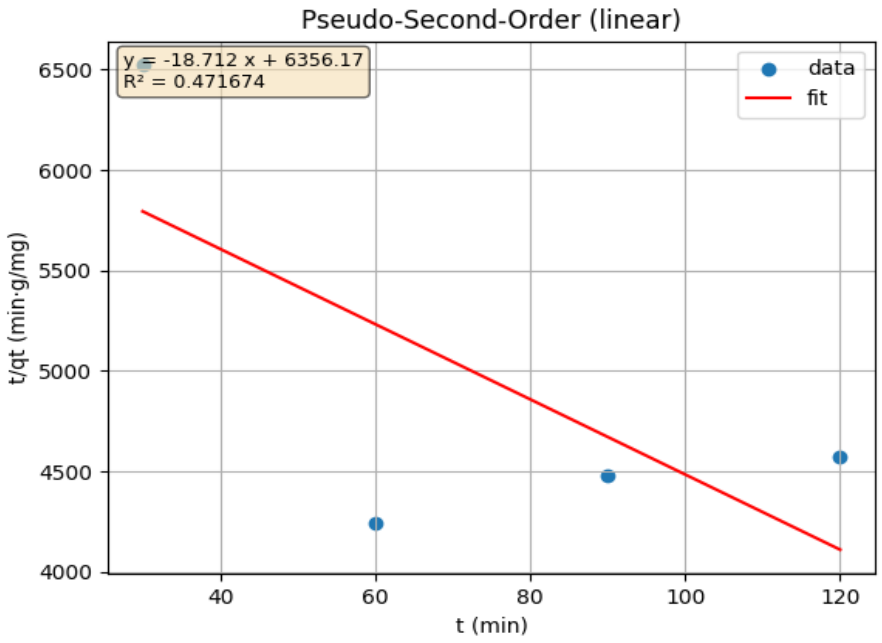

Figure B5 PSO plot for Sawdust-Fe

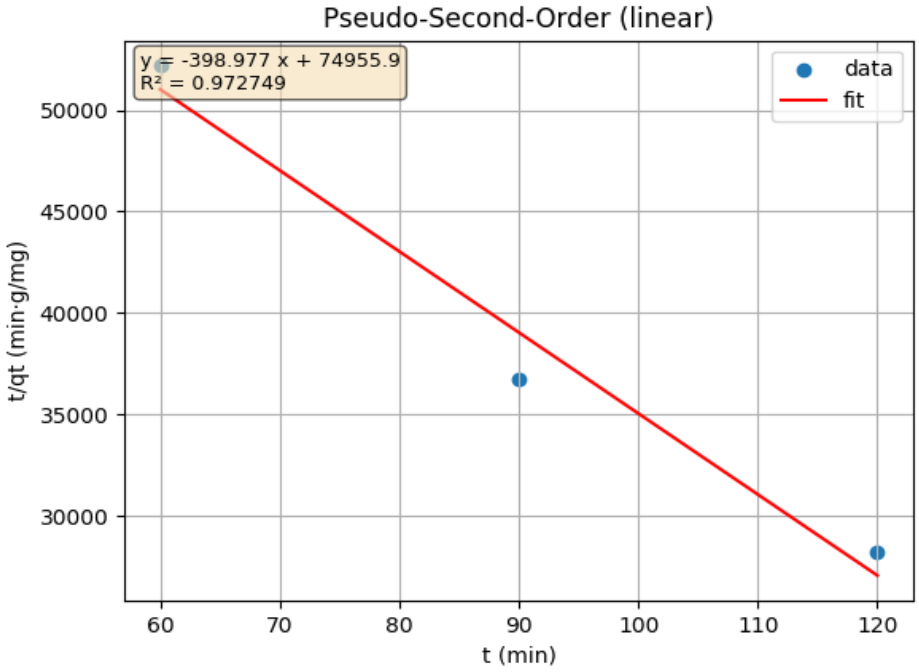

Figure B6 PSO plot for Sawdust-Zn

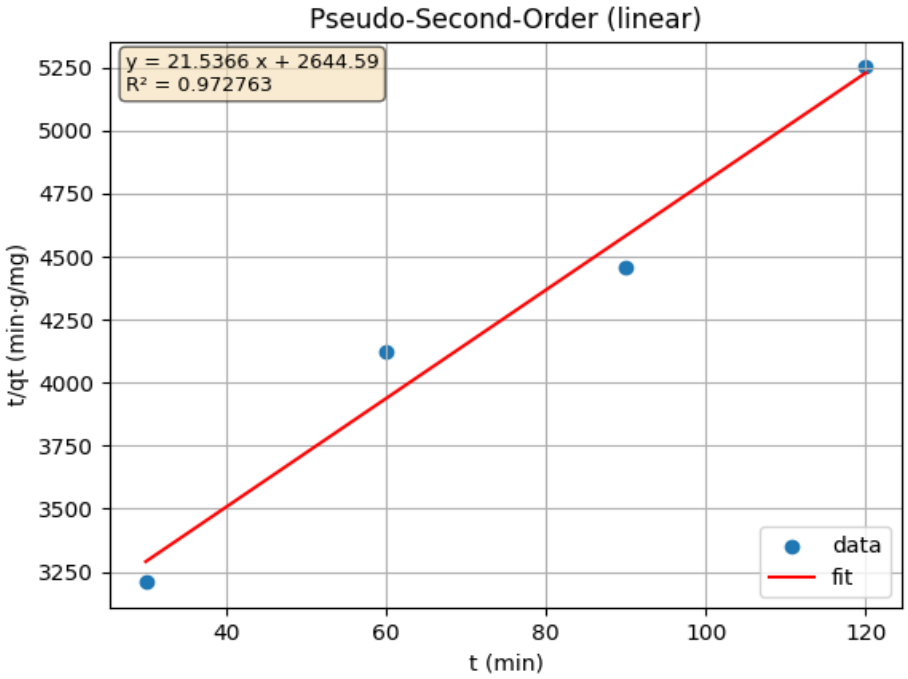

Figure B7 PSO plot for Eggshell-Fe

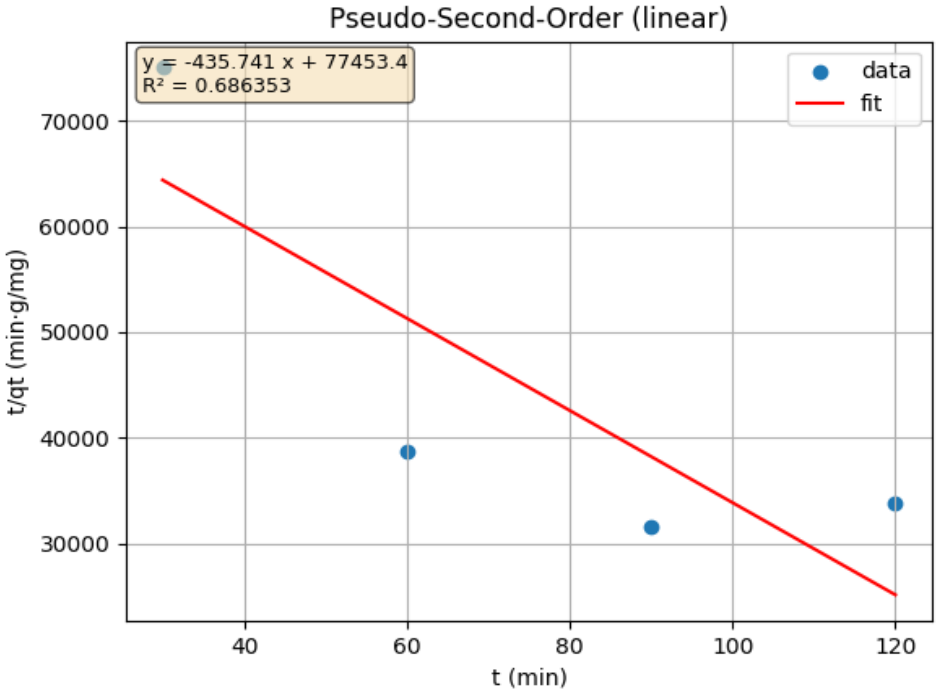

Figure B8 PSO plot for Eggshell-Zn

C3 Weber-Morris Intraparticle Diffusion Plots

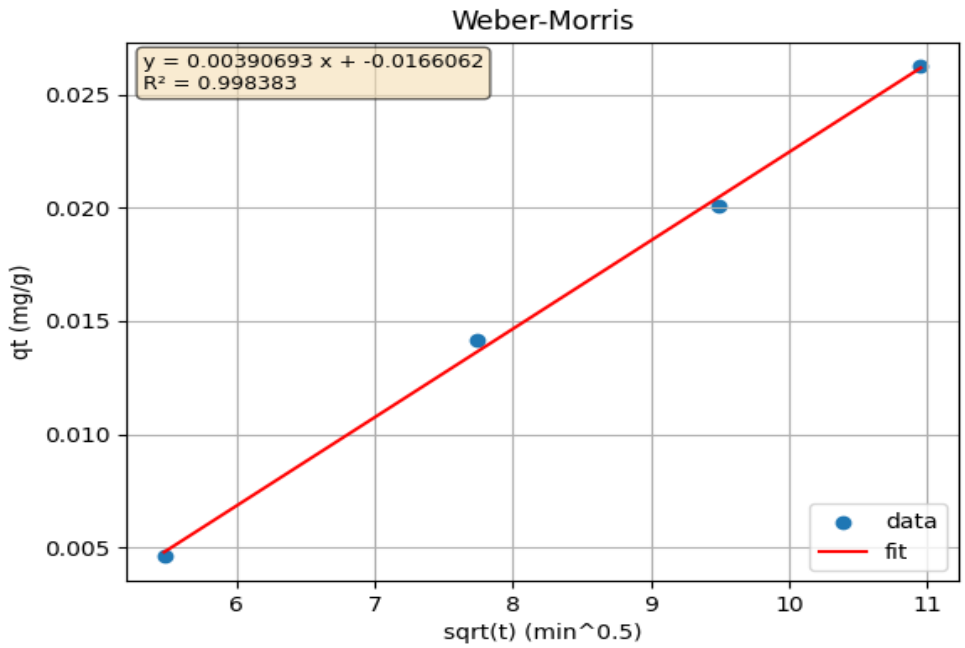

Figure B9 Weber-Morris for Sawdust-Fe

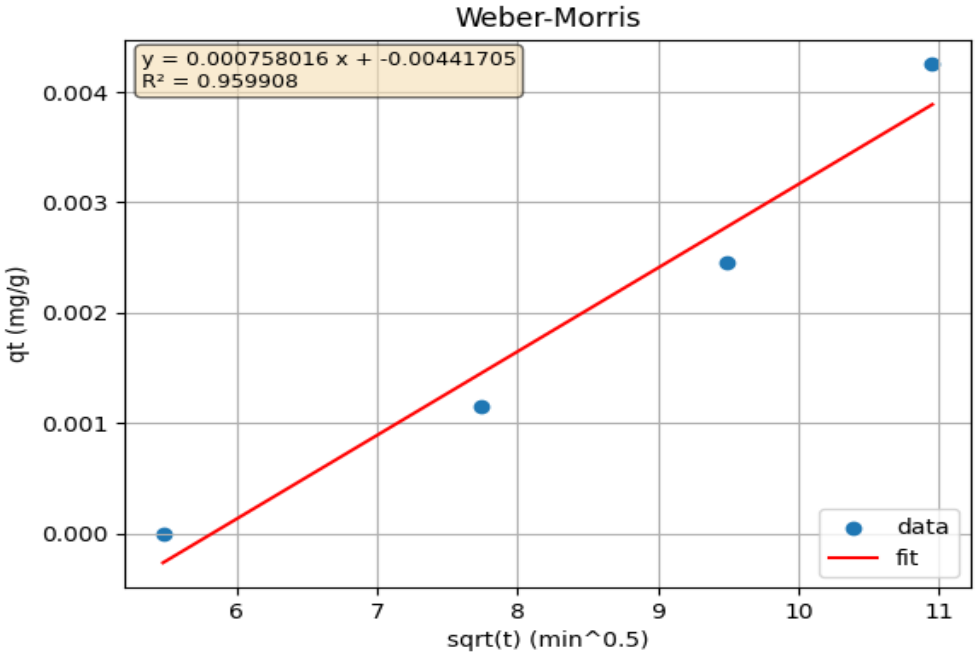

Figure B10 Weber-Morris for Sawdust-Zn

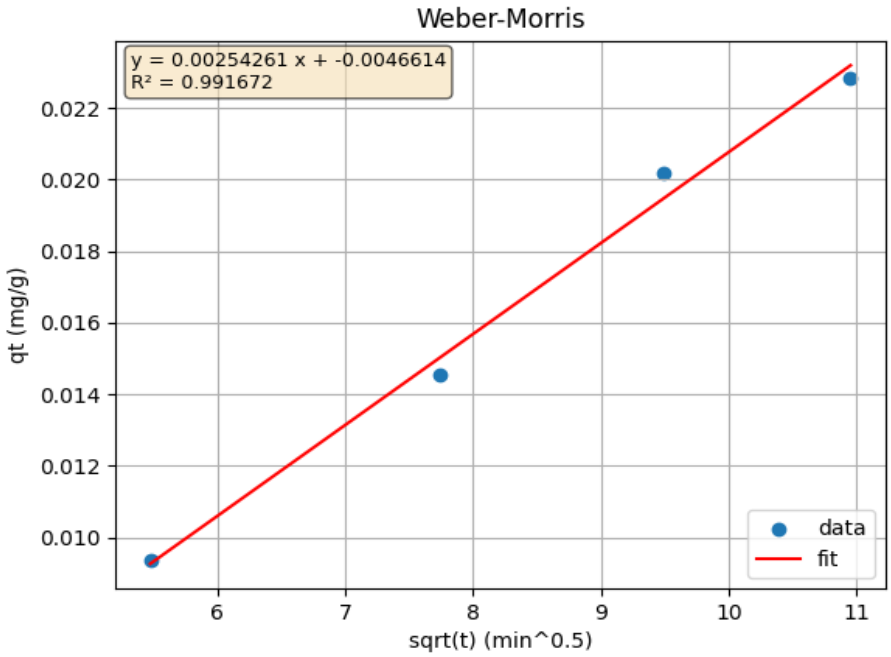

Figure B11 Weber-Morris for Eggshell-Fe

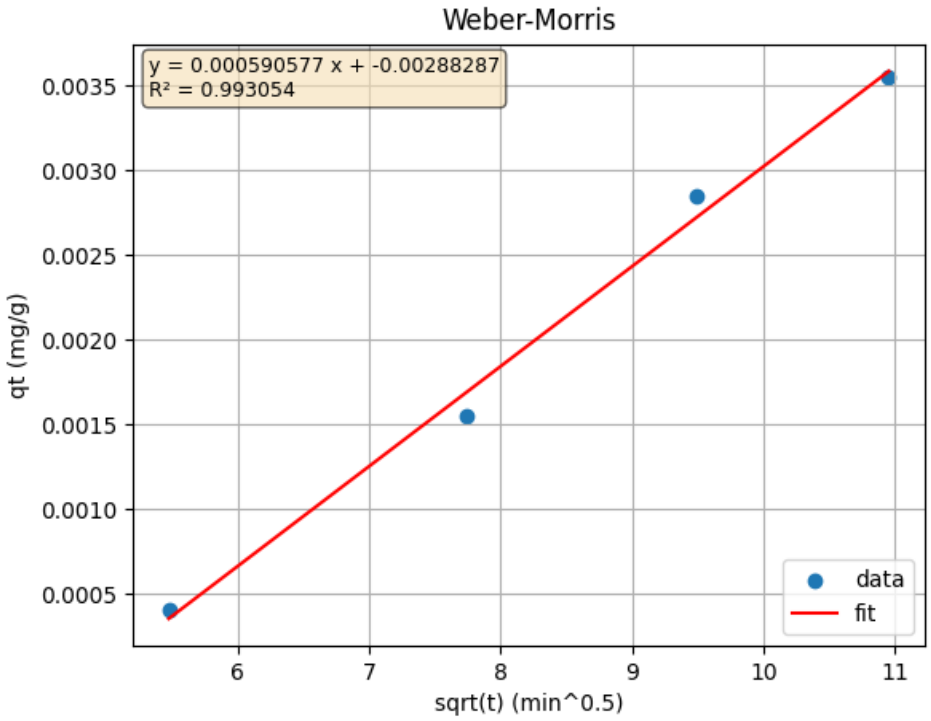

Figure B12 Weber-Morris for Eggshell-Zn