Journal of Environmental Sustainability, Policy & Systems

MERIDIAN RESEARCH PRESS

Vol 1, Issue 2, 2026

Research Article

TREATMENT OF PRODUCED WATER FROM NIGER DELTA OIL FIELDS USING CHEMICALLY MODIFIED BIO-ADSORBENT

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Abstract

The high concentration of salt, organic contaminants and harmful heavy metals found in Produced Water (PW), which is a significant byproduct of oil and gas extraction, pose serious health and environmental risks. In the Niger Delta, poor PW management has resulted in significant ecosystem degradation and contamination of freshwater resources. Conventional PW treatment methods, like chemical precipitation and membrane filtration processes can often be expensive, demand significant energy, and produce additional waste. This study explores the use of chemically modified bio-adsorbents (cassava peel) as a cost-effective and eco-friendly option for eliminating heavy metals from PW.

The adsorbent was crushed and sieved into 63- and 150-micron size. For 24 hours, each of them received a treatment with diluted nitric acid (500 mL at a concentration of 0.4 mol/L) to remove pigments. After filtering, drying, and rinsing with distilled water, the pH was brought to neutral. It was then soaked in diluted H2SO4 (15ml of H2SO4 to 500ml of distilled water). After filtering, drying, and rinsing with distilled water, the pH was brought to neutral. The bio-adsorbents were applied to the PW samples in a batch process and the filtrate was collected at an interval of 30 minutes for analysis for heavy metals determination using an Atomic Absorption Spectrophotometer.

Co, Ni, Mn, and Mg were the metals that were examined. The concentration of the metals was reduced by the bio-adsorbents to 80%, 80%, 55%, and 30% for Co, Ni, Mn and Mg respectively. The adsorption system was also analysed using Langmuir and Freundlich isotherm models.

It was discovered that the better the adsorption result, the finer the adsorbents. An improved outcome was obtained with 63-micron size than with 150-micron size.

Keywords: Produced water, bio-adsorbents, heavy metals, isotherm models.

Introduction

Background of Study

Managing produced water, a complicated byproduct of oil and gas extraction, is a major environmental and industrial challenge. This is because it contains high levels of salt, organic pollutants, and toxic heavy metals, all of which can harm ecosystems and water quality. In regions like the Niger Delta, where oil exploration is extensive, produced water discharge has been linked to severe environmental degradation, contamination of freshwater resources, and adverse effects on aquatic ecosystems (Ite et al., 2013). Produced water (PW) handling received little to no attention in the early days of subsurface crude oil extraction. In certain cases, it was spilled on ground surface, released to water bodies with little or no form of treatment, or put in underground pits to evaporate or soak into the subsurface. Over time, petroleum engineers came to understand that water injection into the oil reservoirs could improve production (Qun et al., 2019).

Traditional treatment methods, such as membrane filtration, chemical precipitation, and modern oxidation techniques, are often costly, energy-intensive, and prone to secondary waste generation (Gul Zaman et al., 2021). This has driven the need to explore alternative treatment methods that are both cost-effective and environmentally sustainable, such as bio-adsorption.

Bio-adsorption relies on natural or chemically modified biological materials to eliminate contaminants from wastewater through processes such as ion exchange, surface complexation, and physical adsorption (Ziarati et al., 2018). Studies indicate that chemically modified bio-adsorbents exhibit superior adsorption capabilities, especially in eliminating harmful metals that are common in produced water from petroleum activities, such as lead, cadmium, and arsenic (Udeagbara et al., 2021).

The efficacy of chemically modified bio-adsorbents relies on a number of variables, such as the nature of the adsorbent, modification technique, and operational conditions including, temperature, pH and contact time. Recent advancements have concentrated on maximizing adsorption efficiency and regeneration potential by optimizing these parameters, making bio-adsorbent-based treatment a more sustainable alternative to conventional methods (Popoola et al., 2023).

Origin of Produced Water

Large quantities of wastewater are produced by oil and gas companies, which, as part of the oil extraction process, raises it to the surface. The term "produced water" (PW) is commonly used to describe this wastewater (Aguirre Hernandez, 2021). PW is a byproduct of gas and oil extraction. Produced water is water that has been trapped during underground formations and is brought to the surface with oil or gas (Hoek et al., 2021).

Between 1990 and 2015, PW production increased from less than 30,000,000 barrels per day to around 100,000,000 barrels per day (Gul Zaman et al., 2021). Global daily fuel consumption is predicted to increase from 85 million barrels in 2006 to 106.6 million barrels by 2030 (Farhat et al., 2023). PW has been created in large quantities by oil and gas production activities, with oil producing a higher upward flow of PW than gas wells (Liu et al., 2021). 39.5 Mm3/day of PW is thought to be produced by offshore oil and gas fields. PW production is three times more than oil production, with a daily amount of about 200 Mbbl (Baloo et al., 2020).

Additionally, only 2% of the recovered PW is acceptable for the extraction of fossil fuels, with the PW volume in depleted areas potentially reaching up to 98% of the residual content (Gul Zaman et al., 2021). Because of the high concentrations of dangerous toxins, untreated PW discharge into the ecosystem may have catastrophic effects on the environment. The environment, living things, and human body are all negatively impacted by this PW since it contains heavy immiscible oil, organics, heavy metals, salts, suspended particles, and radioactive components (Gogoi et al., 2020). PW must therefore be treated by the oil and gas sectors in order to safeguard both human health and the environment.

Composition of Produced Water

The chemistry of the rocks that PW has come into touch with determines its composition. Some PW can be more than ten times saltier than seawater while others are significantly less salinized than saltwater (Alomar et al., 2022). Additionally, produced water may contain varying amounts of oil residues, sand or mud, naturally occurring radioactive materials, chemicals from fracturing fluids,

bacteria, and dissolved organic components. The treatment, usage, and/or disposal of PW are impacted by compositional differences (Macdonald and Adimie, 2024).

Before the produced water is disposed of or properly reused, it is essential to comprehend the physical and chemical composition of the water in order to suggest a suitable method of bringing the concentration of these dangerous elements down to a level that is acceptable (Emmons et al., 2022).

Adsorbents

It has been discovered that the most efficient method for removing contaminants from water is adsorption (El Messaoudi et al., 2024). The mechanism of adsorption, which is an exothermic process, involves the attachment of solid or gaseous materials to an adsorbent surface (Gul Zaman et al., 2021). According to (Ngene and Tota-Maharaj 2021), adsorbents are materials that, through chemical or physical interactions, attract contaminants to their surface, removing them from liquids or gases. The capacity to regenerate the adsorbent by thermal regeneration or the use of chemical eluents to facilitate the desorption process is another benefit of the adsorption process (Akhtar et al., 2024). Bio-adsorbents are adsorbents gotten from biological sources like agricultural waste to eliminate contaminants from wastewater or PW. They are cost effective and environmentally friendly. Activated carbon (AC) is made from coal or biomass using thermochemical or hydrothermal processes, then undergoes a physical or chemical activation step to enhance its adsorption capabilities. Because of its large surface area and capacity to absorb a variety of organic contaminants, it is frequently utilized (Khan et al., 2023).

Methods of Produced Water Treatment

To improve PW quality or lower the number of harmful pollutants, different treatment processes are required. Desalination, dissolving sand and suspended particles, and de-oiling (removing scattered oil and grease) are the general goals for operators managing produced water.

Reducing soluble organics, the three primary types of primary therapy are hydrocyclone, flocculation, and coagulation. When used to remove oil, the oil goes out the overflow exit, and any remaining particles, including OPW, go out the underflow (Shingote, 2018). If the purpose of the treatment is to remove the solid particles, they leave through the underflow exit, while the treated water leaves through the overflow outlet. During treatment, oil concentrations can decrease from 200–2000 ppm to 20–100 ppm, according to (Raesi and Maddahian 2022). Furthermore, 100% elimination techniques such as activated carbon, membrane, and sand filters can be deployed (Alomar et al., 2022). These processes are the first stages of treatment before more complex purification.

Filtration is particularly useful for removing particulate matter and can be combined with other treatment technologies to improve efficiency (Saravanan et al., 2021). Microfiltration and ultrafiltration are two membrane filtration processes that improve the separation of tiny particles. The removal of finer impurities, such as dissolved salts and heavy metals, is further guaranteed by the use of reverse osmosis and nanofiltration in the final phases of treatment (Gul Zaman et al., 2021).

Coagulation and Flocculation is another method of treatment. While flocculants aggregate fine particles for removal, coagulants, such as ferric chloride and aluminum sulphate, destabilize oil emulsions (Okoro et al., 2025). When it comes to dissolved organic compounds, this approach is less effective than it is for suspended solids. The removal efficiency of oil and fine particulate matter is further improved by the use of flocculants based on polymers (Gul Zaman et al., 2021).

Sedimentation and filtering methods are most effective when used in conjunction with coagulation and flocculation processes. However, secondary contamination and sludge disposal are issues brought up by the usage of chemicals in these procedures (Emmons et al., 2022). Coagulants work by lowering the colloidal system's zeta potential to a point where the particles can come together. This occurred when the proper stirring conditions were met (pez-Maldonado et al., 2014), whereas van der Waals forces cause agglomeration in flocculation.

Secondary Treatment

Approximately 90% of the oil and soluble organic matter that were not removed during primary treatment are removed during secondary treatment, which is utilized to reach a particular level of effluent purity (Motta et al., 2014). Techniques used in the secondary treatment stage include activated sludge, adsorption, and flotation.

(i) Flotation techniques: Flotation uses gas bubbles as a transport medium to extract oil droplets and absorbed particles from PW. To improve oil removal, gas bubbles are injected into the PW in a flotation tank using Dissolved Air Flotation (DAF) and Induced Gas Flotation (IGF) (Udeagbara et al., 2021). As the released air circulates throughout the flotation tank, oil droplets and other suspended submerged particles mix with gas bubbles to create an aerated solution, while skimming eliminates any collected foam on the water's surface (Shen et al., 2022). Large amounts of produced water with a high oil content are handled by this technique in refineries and offshore platforms. It is a very efficient method for the removal of suspended particles and tiny oil droplets. To guarantee peak performance, the procedure demands close observation of variables like air pressure, retention duration, and chemical dosage (Gul Zaman et al., 2021).

(ii) Adsorption: The interaction forces between the dissolved species in the PW to be treated, the solvent, and the adsorbent surface cause the surface phenomena known as adsorption. One of the best technologies for removing heavy metals is adsorption (Renu et al., 2017). Activated carbon and bio-adsorbents, such as agricultural waste materials, are used to remove organic and inorganic pollutants (Alomar et al., 2022). An appropriate adsorbent must guarantee maximum removal of the compounds at a minimal cost and possess a strong affinity for the target chemicals (De Gisi et al., 2016). Bio-adsorbents provide a cost-effective and eco-friendly alternative.

(iii) Activated sludge process: Biological wastewater treatment is the main application for activated sludge processes (ASP) (Ranade and Bhandari, 2014). Bacteria and other organisms present in sludge are mixed with wastewater and agitated to provide adequate oxygenation. After the aeration ends, the mixture is transferred to a secondary clarifier tank where the flocs can settle and the effluent is disposed of. As the sludge returns to the aeration tank, the procedure is repeated (Motta et al., 2014). However, when extremely harmful resistive compounds are present in water, this approach appears to be insufficient (Li et al., 2014).

Tertiary Treatment

Tertiary treatment is used to further lower turbidity and the concentration of ultra-small oil droplets and other contaminants after secondary and primary treatment levels. At this point, organic contaminants like PAHs can be eliminated (Sosa-Fernandez et al., 2018).

(i) Electrodialysis: The primary applications of electrodialysis (ED) in OPW are the removal of heavy metals, dissolved solids (TDS), and inorganic minerals (Baker, 2023). When cation exchange membranes (CEM) and anion exchange membranes (AEM) are present, the separation process occurs. Cation and anion exchange membranes are positioned between the cathode negative electrode and the anode positive electrode to form cells. When an electrical current is supplied to the cell, the positively charged cations in PW are rejected by the AEM as they pass through the CEM and toward the cathode. Furthermore, negative charge anions that go to the anode via the AEM are rejected by the CEM. As a result, solutions between the membranes become both concentrated and diluted.

(ii) Membrane treatment technology: Because a membrane is a microporous semipermeable material, when a driving force is applied through it, substances with varying diameters can be separated. Membranes are categorized according to the size of their pores and the size of the particles they reject (Baker, 2023). Additionally, membranes can be employed as a pre-treatment stage for additional membrane activities. For instance, ultrafiltration (UF) and

nanofiltration (NF) have been used to treat produced water using MF membranes as a pre-treatment step (Olajire, 2020).

(iii) Chemical Oxidation: Organic pollutants are broken down into smaller, less dangerous chemicals by oxidizing agents such as ozone and hydrogen peroxide (Gul Zaman et al., 2021). Although it might be expensive and energy-intensive, this technique aids in the breakdown of hydrocarbons. Advanced oxidation processes (AOPs) like Fenton's reagent and photocatalysis boost efficiency by generating reactive oxygen species that rapidly degrade contaminants (Udeagbara et al., 2021).

(iv) Adsorption Isotherms: Adsorption isotherms are a vital tool for understanding as well as predicting the adsorption behavior of materials and are utilized extensively in a variety of disciplines, such as materials science, chemical engineering, and environmental science. They are graphical representations that show the relationship between the amount of adsorbate (the material being adsorbed) and the pressure or concentration of the adsorbate at a constant temperature (Abin-Bazaine et al., 2022).Langmuir isotherm model and Freundlich isotherm model are typical examples.

Review of Other Peoples' Work

A thorough analysis of the application of photocatalysis as an advanced method for treating produced water was carried out by (Lin et al. 2020). Their research concentrated on the utilization of semiconductors such as TiO_2, ZnO nanorods, and graphene-modified catalysts to break down persistent organic pollutants. The authors demonstrated how well photocatalysis works to remove compounds like phenol, toluene, and naphthalene. In certain situations, up to 99% elimination was achieved. The technique greatly decreased toxicity and enhanced the water's biodegradability, making it viable for additional treatment even if the removal of total organic carbon (TOC) was generally very little. They addressed the advantages of combining photocatalysis with biological treatment and investigated how variables like pH, salinity, and light intensity affect the efficiency of treatment. However, there were clear limitations: synthetic water was frequently used in place of actual samples, excessive salinity and aromatic compounds hindered the production of hydroxyl radicals, and catalyst fouling decreased efficiency. Furthermore, suspended catalysts presented separation difficulties, and some degradation byproducts continued to be hazardous. Notwithstanding these limitations, the study demonstrated photocatalysis's promise as a sustainable produced water pre-treatment method.

Udeagbara et al. (2021) investigated treatment of produced water (PW) from Niger Delta oil fields using a sequential mixing of four locally derived bio-adsorbents: banana peels, orange peels, sponge gourd (Luffa cylindrica), and palm kernel fibres. These materials were placed in an adsorption column in a specific order after being ground and chemically pre-treated. After PW samples from three separate oil fields were passed through these columns, the amount of heavy metals at various intervals was measured using Atomic Absorption Spectroscopy (AAS). The study's removal efficiencies were impressive. After 8 hours of treatment, metals like Pb, Cd, Cu, and Cr were totally (100%) eliminated at 150-micron particle size, while elements like Ni, Fe, and Zn were greatly reduced. Compared to the 300-micron size, the finer particle size offered a greater surface area, which improved adsorption. The effectiveness of sequential adsorption and the validation of the adsorption behavior using Langmuir and Freundlich isotherm models were the study's main strengths. However, there were drawbacks, such as the need to rely solely on room temperature, the lack of attention paid to other operational factors like pH or flow rate, and the presence of metal traces at bigger particle sizes, which suggested partial removal in some circumstances.

(Jiménez et al. 2019) examined the treatment of produced water using a range of advanced oxidation processes (AOPs), including photocatalysis, Fenton, photo-Fenton, sono-Fenton, and ozonation. The study's objective was to identify the most effective method for removing dissolved organic compounds from synthetic produced water, specifically acetic acid, BTEX, phenol, and naphthalene. They assessed the The elimination of TOC, or total organic carbon and the reduction of toxicity using reagents such as TiO_2, hydrogen peroxide, and iron salts under varied settings (pH, temperature, and light intensity). Ozonation with $H2O_2$ at pH 10 demonstrated the highest efficiency of all evaluated techniques, removing 77.8% of the acetic acid and 74% of the TOC. In addition, this method used less energy than other AOPs. Limitations remained, though: Fenton-based and photocatalysis techniques produced hazardous intermediates, had limited TOC removal (<40%), and necessitated strict reagent dosage control to prevent scavenging effects. Performance in the majority of AOPs was also hampered by high salt concentrations. Although full mineralization and scalability are still issues for further investigation, the study did highlight ozonation using H_2O_2 as a possible polishing step in spite of these difficulties.

(Ebrahimi et al. 2009) investigated the use of ceramic membranes in a cross-flow filtering system to handle water produced in oilfields. They concentrated on both pre-treatment with microfiltration (MF) and final treatment with ultrafiltration (UF) and nanofiltration (NF) systems. Under various working conditions, the study investigated how well these membranes could remove oil and total organic hydrocarbons (TOC) while preserving high flux rates. The system obtained early high fluxes with MF starting at 1150 $L/(h \cdot m^2 \cdot bar)$ when feedwater temperatures were maintained at 60°C and cross-flow velocities ranged from 0.6 to 1.3 m/s. However, after 5 hours, this reduced to 200 $L/(h \cdot m^2)$, indicating a considerable flux decline owing to membrane fouling. With up to 99% oil removal and 39% TOC reduction, UF membranes demonstrated remarkable performance and showed great promise for addressing the increasingly demanding water treatment standards. The study did point out certain drawbacks, though, such as flux degradation with time, a lackluster removal of TOC, and the difficulty of maintaining performance in actual produced water conditions—which frequently contain more complicated foulants than model solutions. Notwithstanding these obstacles, the study demonstrated that ceramic membranes are a promising but developing option that requires more development to meet extended operational difficulties and stricter discharge standards.

(Igwe et al. 2013) offered a detailed analysis of treatment methods for offshore produced water, covering both conventional and innovative technology. The study evaluated how oilfield-produced water—laden with hydrocarbons, heavy metals, dissolved solids, and process chemicals—poses environmental concerns and is difficult to clean, especially under the space-limited and regulation-heavy conditions of offshore platforms. The authors examined a number of treatment approaches, such as membrane filtration, air stripping, chemical dosing, gravity separation, UV treatment, and biological procedures. Notably, membrane technologies like reverse osmosis and ultrafiltration were chosen for their small size and great efficacy in removing contaminants. Ion exchange and packed bed adsorption were also covered for improving the quality of effluent. But there were clear drawbacks: a lot of traditional techniques had trouble removing dissolved or emulsified oils, were prone to clogging, or produced additional waste like sludge. Chemical treatments worked well, but they were expensive, required expert operation, and had a corrosion risk. According to the review's findings, there is no one-size-fits-all approach; rather, the best course of action is determined by site-specific elements like as cost, effluent quality, and legal requirements. This highlights the necessity of customized, multi-stage treatment systems in offshore operations.

Materials and Method

Materials used in this research were cassava peel, nitric acid, sulphuric acid, filter paper, produced water samples, glass wares, etc., while equipment were Oven, Milling machine, Sieves, Atomic absorption spectrometry (AAS), PH meter, balance, , etc.

Experimental Procedures

(i) Collection of Materials: Two distinct oil fields, the Nembe oil field in Bayelsa and the Imo River oil field in River State, provided the produced water samples. The cassava peel was gathered at an Ado-Ekiti, Nigeria, local market. From the field to the lab where the studies were carried out, the samples were all stored at room temperature. Chemicals of analytical and standard grade were employed, along with other reagents and additives.



Figure 1: Bio-adsorbent (Cassava peels)



Figure 2: Untreated Produced water samples

(ii) Preparation of Bio-Adsorbent: The adsorbent (Cassava peel) was thoroughly washed with distilled water to get rid of any dirt that might have adhered to it. It was cut into pieces sundried for days and finally dried in an oven at 100°C for 50 minutes. While the primary objective of sun drying is to remove moisture content, oven drying is to remove any kind of adsorbed gas from the surface of the adsorbents. The adsorbents were finally milled and sieved into 63 and 150 micron sizes using a milling machine.

Each of the sieved samples received a 24-hour treatment with 500 mL of 0.4 mol/L HNO3. The samples were then filtered and washed with distilled water until the pH of the filtrate was almost neutral. After this, the samples were sundried and pulverized.

For the purpose of chemical modification of the adsorbent, H2SO4 was employed. A 3% concentration was prepared by diluting 15 mL of concentrated H2SO4 with 500 mL of distilled water. The dried adsorbent was then immersed in the diluted H2SO4 solution for a period of 24 hours to enhance the adsorbent's adsorption sites by introducing additional functional groups and expanding their surface area. This enhances the polarity of the adsorbents and improves their susceptibility to pollutants. The samples were filtered and cleaned with distilled water after the 24-hour interval until the filtrate was nearly neutral. It was sun-dried and ground into a powder.



Figure 3: Modified adsorbent (dried and grinded)

iii. Treatment of produced water and experimental process: The experimental procedure took into account treating produced water batch-wise utilizing modified bioadsorbent. Two 400 ml heat-resistant beakers were used for this treatment procedure. They were cleaned with distilled water and allowed to dry at room temperature. Each of the 400 ml beakers was filled with 400 ml of produced water (sample C). The two beakers were necessary since the modified and sieved adsorbents had different micron sizes. Ten grams of treated adsorbent was added (Cassava peel of 10grams) for the 63-micron size, and 10 grams 150-micron size was measured and poured into the second 400 ml beaker of produced water. The solution was completely mixed and manually swirled for approximately five minutes (5 minutes) until it became uniform, at which point the treatment was permitted to proceed in order to prevent phase separation. About 5 ml of the treated water was filtered into sample bottles using Whatman filter paper every 30 minutes interval for analysis using an atomic absorption spectrophotometer (AAS). Produced water sample D also underwent the same treatment procedure with both particle sizes of the adsorbent.

Parameters Considered for Absorption Process

(i). Effect of contact time: It was examined how contact time affected the adsorption process while controlling the temperature, dosage, initial concentration, and pH. It was observed that the more the contact time, the better the adsorption process as the metals tend towards 100% removal from the produced water.

(ii) Dosage effect: As the adsorption dosage increases, an adsorbent's active adsorption sites grow, improving the elimination of impurities. However, as the adsorption dosage increases, the total adsorption of pollutants (qe) per unit mass of adsorbent may decrease because of the presence of unsaturated sites in the adsorbents during the adsorption process.

(iii) Particle size: As surface area grows and particle size decreases, the number of binding sites for adsorption rises. The surface is one of the most important elements in adsorption. Adsorption is directly correlated with surface area. The surfaces of bio-sorbents may have micro-, meso-, and/or macro-holes. Other crucial components are pore diameter and volume in addition to the surface. The pore volume and pore width determine how much or how much the pollutant molecules diffuse into the pores. The pore diameter and molecular size can be used to compute the pore diffusion. When the pore diameter is greater than the adsorbate molecule's diameter, the adsorbate molecule diffuses farther into the pore.

Results and Discussion

(i) Characterization of Produced water sample: In order to lower heavy metal levels to acceptable levels, this study analyzed and assessed raw produced water samples from two Niger Delta oilfields (Imo River and Nembe oil fields). Before being treated, the raw produced water samples were analyzed. There were a number of pollutants in the produced water samples. Among them were cobalt (Co), Nickel (Ni), Manganese (Mn), Magnesium (Mg) etc, with their concentrations

Table 1: Heavy metal concentration in samples of raw produced water

Heavy metals	Sample C Conc. (mg/L)	Sample D Conc. (mg/L)	Discharge limit (FAO)
Co	0.381	0.253	0.05 - 0.1
Mg	9.848	5.916	5.0
Mn	1.464	0.971	0.2 - 1.0
Ni	0.255	0.195	0.2 – 0.5

The raw samples concentration of heavy metals as indicated in table 2 were treated. Each produced water was treated using the modified bio-adsorbent that had been ground up, treated and sieved. The produced water samples C and D were treated using the batch adsorption process, and the results are displayed in tables 2, 3, 4, 5. The two samples (C and D) treated results were obtained for 63 and 150 µm particle sizes, as shown below.

Table 2: Metal concentrations (ppm) in sample C after treatment with chemically modified adsorbent (cassava peels).

Sample C	**Co**	**Mg**	**Mn**	**Ni**
Initial Concentration (Raw)	0.381	9.848	1.464	0.255
After treatment using 63 µm particle size				
Time (mins)				
30	0.075	6.366	0.571	0.049
60	0.075	6.239	0.517	0.056
90	0.063	5.915	0.502	0.033
120	0.033	5.299	0.450	0.026
150	0.026	4.471	0.415	0.023
After treatment using 150 µm particle size				
Time (mins)				
30	0.096	8.575	0.994	0.115
60	0.094	8.437	0.917	0.084
90	0.086	8.422	0.846	0.071
120	0.089	7.911	0.743	0.048
150	0.083	7.279	0.705	0.036

After produced water sample C was treated, different plots were made from the tables according to the adsorbents and particle sizes that were used. Below were some of the plots.

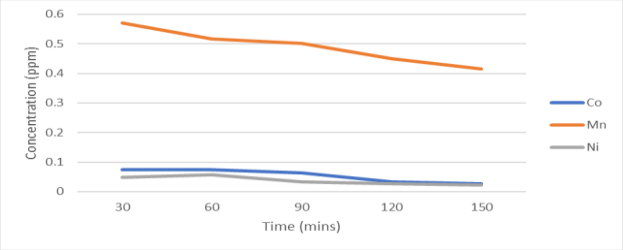


Figure 4: Co, Mn, and Ni concentration against contact time (sample C, 63 µm particle Size)

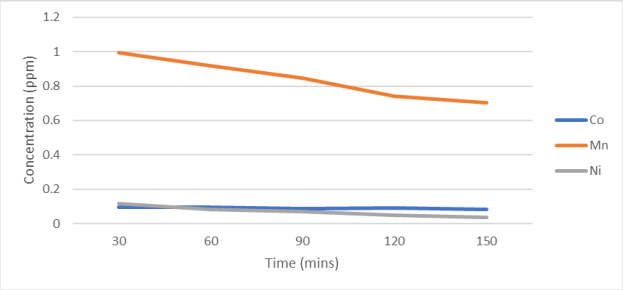


Figure 5: Co, Mn, and Ni concentration against contact time (sample C, 150 µm particle Size)

Table 3: Metal concentrations (ppm) in sample D after treatment with chemically modified adsorbent (cassava peel).

Sample D	Co	Mg	Mn	Ni
Initial Concentration (Raw)	0.253	5.916	0.971	0.195
After treatment using 63 µm particle size				
Time (mins)				
30	0.034	2.992	0.403	0.024
60	0.025	2.908	0.391	0.020
90	0.023	2.272	0.365	0.016
120	0.027	2.507	0.317	0.012
150	0.016	2.458	0.290	0.011
After treatment using 150 µm particle size				
Time (mins)				
30	0.076	4.275	0.414	0.067
60	0.070	3.960	0.442	0.050
90	0.055	3.514	0.479	0.034
120	0.053	3.432	0.515	0.027
150	0.045	3.161	0.554	0.030

Based on the adsorbents and the particle sizes used, different plots were made from table 3 for further explanation of results obtained after produced water (sample D) treatment.

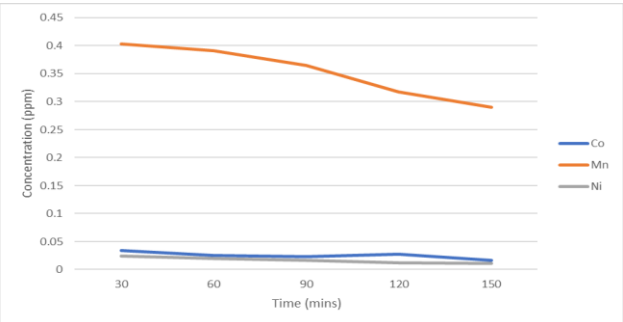


Figure 6: Co, Mn, and Ni concentration against contact time (sample D, 63 µm particle Size)

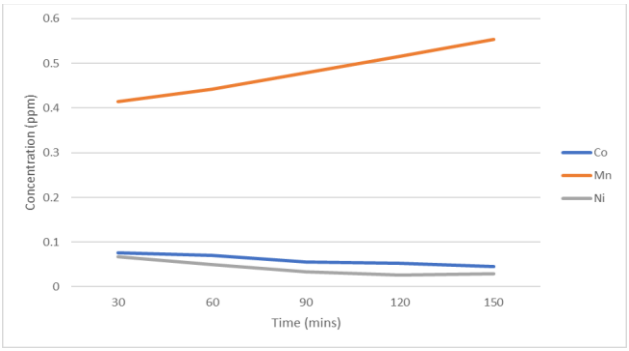


Figure 7: Co, Mn, and Ni concentration against contact time (sample D, 150 µm particle Size)

Figures 4, 5 were drawn from table 2 (Sample C). The plots are linear in shape, and it demonstrates that the longer the contact time, the more effective metals are removed from the produced water sample within 30 minutes to 150 minutes contact time with particle size 63 µm. The concentration of Cobalt (Co), manganese (Mn), nickel (Ni) were drastically reduced after treatment compared to the raw sample. 150 µm particle size also removed the concentration of the metals to a great extent. Magnesium (Mg) ion reduction was the least. Both 63 µm and 150 µm particle sizes did a good job but 63 micron size gave a better result probably because of its large surface area.

The chemically modified bio-adsorbent displayed significant capabilities in treating produced water, with its performance been notably influenced by the particle size. For all analyzed metals, 63 µm particle size performs better. It attains exceptionally high removal efficiency on average, for

Cobalt its 85.72%, Nickel 85.33%, Manganese 66.46%. On the other hand, the average removal of magnesium (Mg) is moderate, 42.55%. This suggests that a higher surface area for adsorption is provided by the smaller particle size, which results in more effective metal ion binding.

Although generally to a lesser degree than the 63 µm size, the 150 µm particle size also exhibited some level of effectiveness. It gave 76.47% for cobalt (Co), 72.24% for nickel (Ni) and Manganese (Mn) 42.55% respectively. However, 17.40% went to magnesium (Mg) which is significantly poor.

Consequently, all the plots for particle size 63 µm, and 150 µm had similar results obtained. The results shows that Co, Mn and Ni were impacted greatly while Mg was the least impacted. As a result, every metal under investigation was drastically lowered below the permissible regulatory limits established by regulatory agencies.

Regardless of the particle size, the bio-adsorbent was quite effective at removing cobalt and nickel, with an average reduction of over 70%. However, 63 µm size has a higher efficiency. For Manganese, it works fairly well, with 63 µm producing better results. Magnesium ion removal was not that good, but 63 µm particle size produced a better result compared with 150 µm particle size.

The plots in figures 6 and 7 were drawn from table 3 (Sample D) are all in linear form. It showed that as the duration of contact between the adsorbent and produced water sample grows, the metal concentrations in the produced water decrease. At contact time of 150 minutes with particle size 63 µm, Cobalt (Co) and Nickel (Ni) were almost removed completely compared to the raw sample concentration of 0.253 and 0.195 respectively. Other metals, however, were not entirely eliminated but were greatly impacted. The effectiveness of the adsorbent affects the removal of metal ions positively. The concentration of metals adsorbed increases as the surface area of the adsorbent increases.

For Mg (63 µm), at 120 and 150 minutes and Mn (150 µm), at 120 and 150 minutes, the concentration increased beyond the initial reduction in concentration at 30, 60 and 90 mins which suggested that desorption must have taken place.

The chemically modified bio-adsorbent performs admirably with 63 µm particle size typically outperforming 150 µm particle size.

For the removal efficiency using 63 µm particle size, Ni (nickel) was 91.49%, Cobalt (Co) 90.12%, manganese 63.62% and Magnesium (Mg) 55.59% respectively. For 150 µm, 78.67% of Nickel (Ni) was removed, 76.36% for cobalt (Co), Manganese (Mn) was 50.53% while magnesium (Mg) got 37.99%.. The efficiencies shows that the finer the particle size, the better the result. 63 micron size performed better than 150 micron size.

The data strongly suggests that using a finer particle size (63 µm) and allowing sufficient contact time are crucial for maximizing the removal efficiency of these metal ions. This information is vital for optimizing the design and operation of the treatment process.

Table 4: Overall treatment efficiency of both samples

	Sample C		Sample D	
Heavy Metals	**(63 µm)**	**(150 µm)**	**(63 µm)**	**(150 µm)**
Co	85.72	76.77	90.12	76.32
Mn	66.46	42.55	63.62	50.53
Mg	42.55	17.40	55.59	37.99
Ni	85.33	72.24	91.49	78.67

(ii)Adsorption Isotherms Analysis: Adsorption isotherms have proven to be crucial for research into adsorption methods and environmental protection and are therefore of paramount importance. The two primary methods for analyzing the data in this study are the Langmuir and the Freundlich isotherm models.

Langmuir isotherm model

The Langmuir isotherm model's linearised form is expressed as follows:

$$C_e/q_e = (1/q_m k) + (1/q_m) \times C_e \quad (1)$$

Freundlich isotherm model

The plot of experimental results can be used to graphically estimate the Freundlich parameters KF and 1/n then utilizing this formulation of the Freundlich equation:

$$lnqe = lnKf + (1/n)\ ln\ Ce \quad (2)$$

In order to examine the outcomes using Langmuir and Freundlich model, the Tables 5 and 6 were computed and necessary graphs were plotted and results analyzed.

Table 5: Metal concentrations in sample C for isothermal analysis

Time (mins)	C_e (mg/L)	q_e (g/L)	C_e/q_e (g/L)	Log C_e (mg/L)	Log q_e (g/L)
30	0.075	12.24	0.0061	1.125	1.09
60	0.075	12.24	0.0061	1.125	1.09
90	0.063	12.72	0.0050	1.200	1.104
120	0.033	13.92	0.0024	1.481	1.144
150	0.026	14.20	0.0018	1.585	1.152

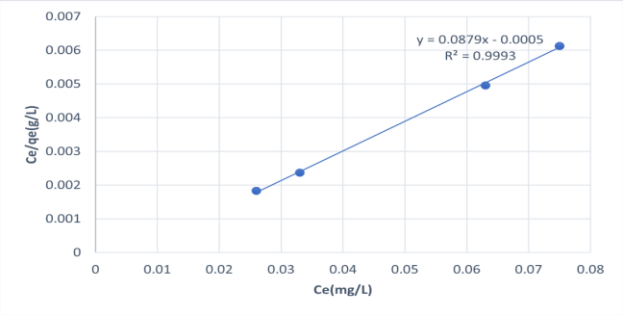


Figure 8: Analysis of (Colbat) Co using Langmuir isotherm for sample C

The plot in figure 8 was extracted from table 5. The adsorption process follows Langmuir model, as seen by the linear relationship between Ce/qe and Ce. The correlation coefficient ($R2$) for Co was found to be 0.9993. The findings demonstrate that the Langmuir sorption isotherm model is a useful tool for studying cobalt (Co) equilibrium. This implies that the adsorbent surface of the metal ion was covered by a single monolayer of the adsorbate. An assessment of the sorption capacity shows that, as expected, the amount of metal ions removed per unit mass of the adsorbent increases with the metal concentration.

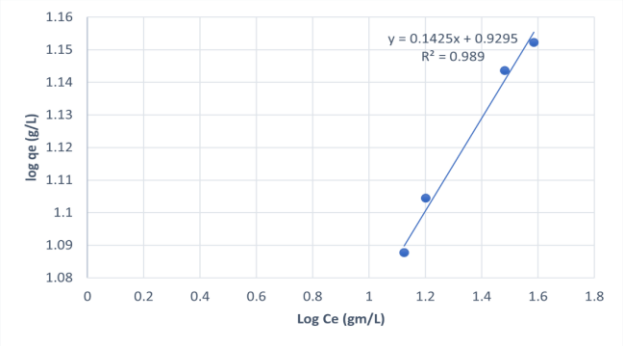


Figure 9: Co analysis for sample C utilizing the Freundlich isotherm

The plot of log qe vs log Ce in figure 9 shows that the Freundlich sorption isotherm is not really suitable for the analysis of the equilibrium study of Co. Langmuir is better. This implies that a heterogeneous layer of the metal ion's adsorbate will cover the adsorbent surface.

Table 6: Metal concentration for sample C for isothermal analysis

Time (mins)	C_e (mg/L)	q_e (g/L)	C_e/q_e (g/L)	Log C_e (mg/L)	Log q_e (g/L)
30	6.366	139.3	0.046	0.80	2.14
60	6.239	144.4	0.043	0.79	2.16
90	5.915	157.3	0.038	0.77	2.20
120	5.299	182.0	0.029	0.72	2.26
150	4.471	215.1	0.021	0.65	2.33

Table 6 was computed to enable plot graphs and make inferences in order to analyze magnesium (Mg) using the Langmuir and Freundlich models.

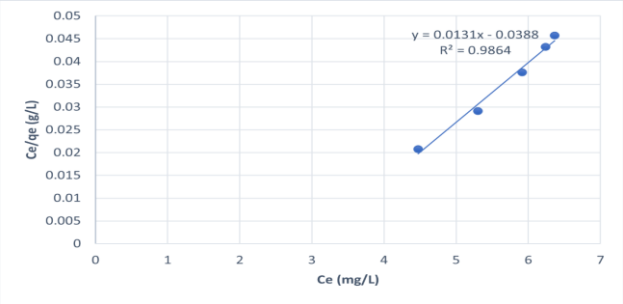


Figure 10: Analysis of magnesium (Mg) using Langmuir isotherm for sample C

Based on the linear plot of Ce/qe vs. Ce, figure 10 shows that the adsorption process adheres to the Langmuir model. The correlation coefficient (R2) for magnesium was found to be 0.9864. The results show that the Langmuir sorption isotherm model is not appropriate for the equilibrium study of magnesium when compared with freundlich model.

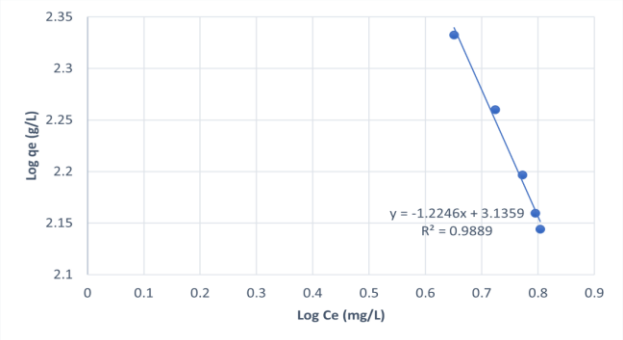


Figure 11: Analysis of Magnesium (Mg) using Freundlich isotherm for sample C

Adsorption follows the Freundlich adsorption model, as seen in Figure 11, according to the plot of log qe vs log Ce, the correlation coefficient (R2) was calculated to be 0.9889. Even though the two values of R2 were high, the highest one is always chosen as been favorable.

Table 7: Metal concentrations in Sample D for isothermal analysis

Time (mins)	C_e (mg/L)	q_e (g/L)	C_e/q_e (g/L)	Log C_e (mg/L)	Log q_e (g/L)
30	0.034	8.76	0.0039	1.47	0.94
60	0.025	9.12	0.0027	1.60	0.96
90	0.023	9.20	0.0025	1.64	0.96
120	0.027	9.04	0.0030	1.57	0.96
150	0.016	9.48	0.0017	1.80	0.98

Table 7 was calculated to plot several graphs and make inferences in order to analyze Cobalt (Co) and magnesium (Mg) using Langmuir and Freundlich models.

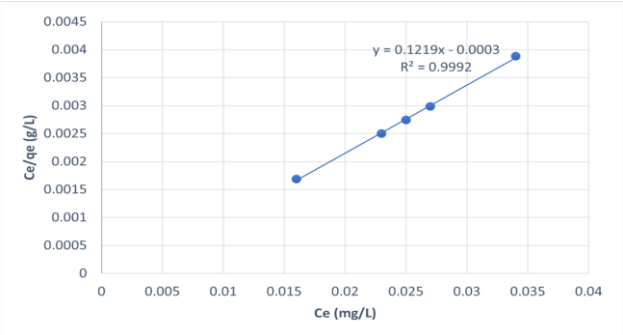


Figure 12: Analysis of Cobalt (Co) using Langmuir isotherm for sample D

Based on the linear plot of Ce/qe vs. Ce, figure 12 showed that the adsorption process adheres to Langmuir isotherm model. The correlation coefficient (R2) for Co was found to be 0.9992. The result showed that Langmuir sorption isotherm model is appropriate for the equilibrium study of Co.

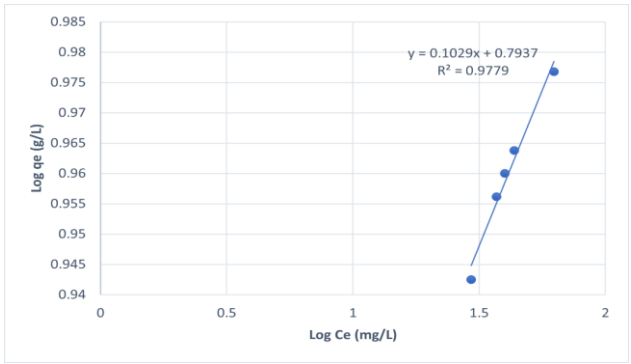


Figure 13: Analysis of Cobalt (Co) using Freundlich isotherm for sample D

As seen in figure 13, according to the plot of log qe vs log Ce, the correlation coefficient (R2) was calculated to be 0.9779. Adsorption process does not agree with this model when compared with Langmuir model.

Table 8: Metal concentrations in Sample D for isothermal analysis

Time (mins)	C_e (mg/L)	q_e (g/L)	C_e/q_e (g/L)	Log C_e (mg/L)	Log q_e (g/L)
30	2.992	117.00	0.026	0.48	2.07
60	2.908	120.36	0.024	0.46	2.08
90	2.272	145.80	0.016	0.36	2.16
120	2.507	136.40	0.019	0.40	2.13
150	2.458	138.36	0.018	0.39	2.14

In order to analyze Magnesium (Mg) with Langmuir and Freundlich models, Table 8 was computed and graphs were plotted and conclusions drawn.

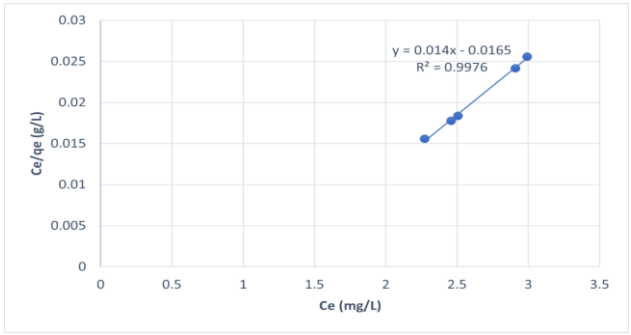


Figure 14: Analysis of Magnesium (Mg) using Langmuir isotherm for sample D

Based on the linear plot of Ce/qe vs. Ce, figure 14 showed that the adsorption process adheres to the Langmuir model. The correlation value (R2) for magnesium was found to be 0.9976. The results show that the Langmuir sorption isotherm model is appropriate for the equilibrium study of magnesium.

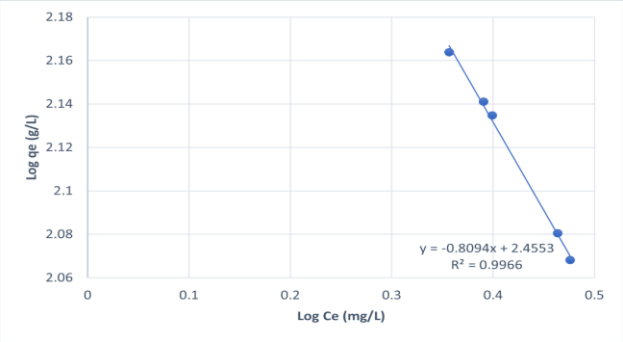


Figure 15: Analysis of Magnesium (Mg) using Freundlich isotherm for sample D

Adsorption does not follow the Freundlich adsorption model, as seen in figure 15, according to the plot of log qe vs log Ce. The correlation coefficient (R2) was calculated to be 0.9966 and Langmuir model was found to be better.

Conclusion

In Nigeria's Niger Delta and globally, heavy metals in produced water are a major hazard to human health and the environment since they are poisonous and carcinogenic. The produced water samples, which came from oil fields in the Niger Delta were discovered to contain metals like Cobalt, Nickel, Manganese, and Magnesium, etc. According to the analysis, the pre-treatment metal concentration was higher than what was anticipated for disposal or reuse as the case may be. After treatment with bio-adsorbent (Cassava peels) using two particle sizes, good results were obtained. The particle sizes used were 63 micron and 150 micron respectively. Both sizes gave good results but 63 micron size performed better due to its large surface area. It was observed that the better the adsorption, the finer the particles.

Nevertheless, the heavy metal concentrations were reduced by the bio adsorbent to 80%, 80%, 57.1%, and 46.8%, for Cobalt, Nickel, Manganese and Magnesium respectively.

Additionally, to validate the results, two models were used for the data analysis. These models were the Langmuir and Freundlich isotherm models. Two metals were used for the test: Cobalt (Co), and Magnesium (Mg). The models showed that the results of the analysis were valid. For this study, only few factors were considered. The concentration of the metals at room temperature was monitored over time while the temperature remained constant. Time was the most crucial factor taken into account. Adsorption is a process that needs time to finish. According to studies on the biological composition of the adsorbent, most agricultural wastes, such as Cassava peels, contain fibrous materials with high concentration of lignocellulose. These materials have strong bonding properties due to their specified components.

Recommendations

I. Consequently, low-cost technologies such as experimented (chemically modified Cassava peels) in this work should be paid attention to especially those involving biodegradable materials (like agricultural biomass) making safe disposal of wastewater possible.
II. Government, policymakers, and industrial experts should lead the conversation away from conventional treatment technologies such as flotation, sedimentation, precipitation, and ultrafiltration which discourage and make almost impossible, and inaccessible through the high cost of setup and operation, and seek ways to promote and make accessible wastewater treatment technologies to both small and medium scale companies through locally produced bio adsorbent as conventional water treatment plants may also not completely remove contaminants.
III. Other Studies should be carried out to explore methods for regenerating the spent chemically modified bio-adsorbent to enhance its reusability, reduce waste, and improve the overall cost-effectiveness of the treatment process.
IV. Efforts should be made to test the commercial viability of these technologies, especially on a large scale. For instance, the effectiveness and efficiency of bio adsorbent dosage application require expanded study and similarly, other key factors affecting the adsorption process.
V. To ensure adherence to environmental discharge regulations and protect public health, regular monitoring and evaluation of treated PW should be mandated.

Acknowledgement

I acknowledge the support of the laboratory staff of the Department of Chemical and Petroleum Engineering, Afe Babalola University Ado-Ekiti, Ekiti State, Nigeria

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