

Research Article

Treatment of Produced Water from Niger Delta Oil Fields Using Selected Bio-Adsorbents

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Abstract

Produced water (PW) is the vast amount of water produced from subsurface during the extraction of oil and gas. PW contains heavy metals which are detrimental to the environment. The majority of PW treatment technologies, which have been in use for many years, have reportedly failed to bring some impurity and metal concentrations down to permissible disposal levels. This study was done to determine how well three locally available materials which are eggshells, groundnut shells, and sugarcane bagasse used in the treatment of PW obtained from Niger Delta oil fields. The adsorbents were ground, and sieved into sizes of 425 and 1180 microns. They were treated individually with diluted nitric acid (400mL of 0.4mol/ LHNO_3) for 24 hours to remove pigments. They were filtered, dried, and rinsed with distilled water until the pH became neutral. PW samples were analysed for heavy metals using an Atomic Absorption Spectrophotometer (AAS). The PW samples were treated with the bio-adsorbents in a batch technique. The metals analysed were As, Cu, Pb and Fe. The bioadsorbents were able to reduce the concentration of the metals to 87%, 91%, 100% and 88% respectively. Langmuir and Freundlich isotherm models were used to analyse the adsorption system. It was observed that the finer the adsorbents the better the adsorption result. 425 microns was able to produce a better result compared with 1180 microns.

Keywords

Produced Water, Bio-Adsorbents, Heavy Metals, Isotherm Models

1. Introduction

Produced water is the term for vast amounts of water that are released as a byproduct of the extraction of oil and gas. Produced water, which is brought to the surface alongside oil or gas, is water that has been trapped during subsurface formations. In recent times, the practice of releasing this generated water into land and aquatic bodies has become a significant environmental problem. There have been instances where it has been dumped into bodies of water with little to no

treatment, spilled on the surface, or dumped into pits below earth where it will evaporate or soak into the ground. In mature or old fields, the quantity of this water generated in oil may be greater than 98% of the material extracted from oil wells depending on a variety of factors [1].

Furthermore, it is the main producer of trash for the oil and gas sector. However, managing produced water was not given much to no attention in the initial stages of subsurface crude

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oil extraction. More so, produced water contains a number of complex mixture of organic and inorganic compounds, dissolved substances, and radioactive substances, as well as particulate matter, inorganic salts, dissolved gases, different minerals, and a significant amount of hydrocarbons like BTEX (benzene, toluene, ethylbenzene, and xylene), PAH (polycyclic aromatic hydrocarbon compounds), etc. Reinjection into a well, direct discharge, or reuse are traditional ways to treat and dispose waste streams. Among these, reinjection of produced water into disposal wells is the most effective method of handling treated water.

Oil and gas produced water (PW), recovered from hydrocarbonaceous formation strata during oil and gas exploration and production, is the largest effluent stream (brine) generated. This mixture of formation water, freshwater and seawater has been preserved for millions of years beneath hydrocarbons in a porous reservoir medium [2]. Tailings treatment chemicals, injection water, small amounts of condensate from gas production, and small amounts of these substances were added to enable successful hydrofracture operations.

In addition, the produced water (PW) from gas fields has been shown to be more acidic than that from oil fields. This might be because gas fields have higher levels of acidic gases such as dissolved CO_2 and H_2S than oil fields [3]. A number of different solvents and chemicals are used in oil and gas fields for exploration and production (E&P) operations [4], with about a third of these chemicals appearing to end up in nearby waterways [5].

It has been shown that the quantity of oil and water produced, or water fraction (the proportion of water produced in relation to the total fluid produced), increases with well age, and although production capacity has been reported to decrease to as much as 50% in a near depleted field could be as low as 98% water [6]. If the energy sector is to be sustainable, the water produced from oil and gas must be treated to a higher standard than regulators require for disposal or reuse. Disposing of unprocessed water from oil and gas production, which contains many toxic substances, can threaten the sustainability of the environment.

The characteristics of the chemical and physical composition of the produced water must be known in order to propose a suitable way to reduce the concentration of these hazardous substances in the produced water to an acceptable level before it is disposed of or appropriately reused. Appropriate management policies must be implemented to ensure the sustainability of the energy sector and to ensure that water from oil and gas production can be safely discharged into the environment and/or reused without endangering the environment. Recent studies [7] have looked at technologies for treating produced water, but lack information on the specific mechanics and process chemistry of the technologies, as well as assessments of their advances by different research groups. A detailed understanding of the mechanistic chemistry of the process is required for information on reaction pathways during treatment and potential environmental impacts of the

resulting by-products.

In order to comply with environmental legislation and to meet standards and requirements for reuse applications, effective pollutant removal treatment is required prior to disposal or any form of reuse of PW. The treatment required depends on the PW composition and the way it is disposed of or recycled. To prevent formation plugging, typically only suspended particles and dispersed hydrocarbons from onshore PW are dumped into deep disposal wells [8]. On the other hand, PW from offshore activities are often released into the ocean and only hydrocarbons are processed in adequate quantities to meet environmental legislation requirements. Reuse in oilfield operations including waterflooding, drilling, and hydraulic fracturing might only need a little amount of PW treatment to meet their requirements. To fulfill more stringent requirements and the requisite quality, reuse in beneficial applications such as agricultural irrigation and industrial operations may necessitate more thorough treatment [9].

2. Uses of Produced Water in Industries

Produced water is used in so many industries. It is reused in oil and gas, used as fracturing water, fire protection, cooling of towers, enhanced oil recovery etc.

2.1. Reuse in Oil and Gas Sector

Many applications such as well drilling, hydraulic fracturing, secondary oil recovery and groundwater pressure maintenance that require vast amounts of water are included in the reuse of produced water at oil and gas operation sites. By treating and reusing produced water resources, the consumption of freshwater resources in these processes can be reduced. Thus, when one compares the cost to the cost of transporting fresh water on-site in the quantities required for these processes, the market for on-site purification of produced water becomes economically viable. Treated water from a produced water collection point in a wellfield is typically closer to most wells than freshwater sources and is a local water supply. Although there are multiple uses on site, two uses, well development by hydraulic fracturing and secondary recovery using improved oil recovery methods, are discussed in more detail below.

2.1.1. Enhanced Oil Recovery

Normal extraction techniques can only extract 20-40% of the total amount of oil on site. Therefore, Enhanced Oil Recovery (EOR) is used to produce additional oil on site from a reservoir. A number of EOR techniques are available as complementary recovery strategies. The oil is displaced towards the production well by injecting water into an aquifer. EOR can recover up to 10% of the remaining oil from depleted oil fields by injecting water and carbon dioxide into the field. Chemical EOR, on the other hand, uses a liquid injec-

tion of chemicals to help hydrocarbons move through the formation to improve hydrocarbon recovery. The amount of water used depends on the reservoir. Water quality considerations for injection include reducing levels of silica and divalent cations to prevent scaling.

2.1.2. Dust Suppression

Dust control on unpaved leasehold roads in oil and gas fields can be accomplished using pumped water. Normally, spraying of the generated dust suppression water is carefully regulated so that the water is not applied outside road boundaries, in buffer zones around creek crossings, or in close proximity to buildings [10].

2.1.3. Fire Protection

The water produced can be used for fighting wildfires or for other purposes. The use of alternative water sources has no negative impact on the drinking water supply, even though drinking water is often used for firefighting. Even the water used in firefighting does not have to meet strict water quality standards. In order for it to be used for fire prevention, the water produced must be readily available, of sufficient volume, and properly treated to prevent corrosion.

2.2. Environmental Impacts of Produced Water

Ever since the first oil and gas wells were drilled and operated in the mid-19th century, there have been reports of the environmental impact of disposing of the extracted water. The degradation of soil, groundwater and the ecosystems it supports are the major environmental problems [11]. Many produced waters contain high concentrations of dissolved ions (salts), hydrocarbons and trace elements which are detrimental to health. Large volumes of water can also adversely affect the environment, such as erosion, large-scale waste disposal basins, and pipeline and road infrastructure. When dealing with produced water there is a risk of unplanned discharges and spills. The size of the receiving body of water is critical to ecosystem degradation because while small streams have little dilution capacity, discharge into the sea results in significant dilution. Temperature, effervescence, low levels of dissolved oxygen, and high and low pH depending on the well type are physical water properties to worry about. Sodium is the most abundant cation in the water produced. High levels of sodium make it difficult for plant roots to absorb calcium, magnesium and potassium; As a result, excess sodium can lead to deficiencies in other cations. In addition, high salinity can lead to poor soil structure and prevent soil water uptake [12, 17].

2.3. Aim and Objective of the Study

The aim of this research work is to reduce the concentration of pollutants in the production water samples. Some of the pollutants it targets; are organic and inorganic salts as well as

certain metals to make the water usable. The objectives of the study are

- 1) Analysis of the heavy metals concentrations in the produced water sample.
- 2) Evaluation of the performance of agro materials (groundnut shell, sugarcane bagasse and eggshell) for produced water treatment in Niger Delta oilfields.
- 3) Assess the quality of treated produced water based on government guidelines [13] and compare whether it is safe to discharge into the environment or reuse for energy sustainability.

2.4. Significance of the Study

When completed, this research work would create a sustainable means of produced water treatment by use of bio-adsorbents that would be environmental friendly and economically cost effective. In same vein, it is also a means of keeping the environment clean unlike the conventional methods that create environmental problems or issues.

3. Methodology

The method used in this research involves several steps ranging from the use of materials and equipment, collection of samples (bioadsorbents and produced water), preparation and treatment of bioadsorbents, determination of heavy metal concentration in the produced water samples and treatment of the produced water using treated adsorbents, the analysis of the treated produced water by atomic absorption spectrometer (AAS) and the interpretation of the results using isotherm models. Therefore, the materials and experimental procedures used to carry out this research are clearly stated.

3.1. Materials and Equipment

In this study, the following materials were used: Produced Water, Sugarcane Bagasse (*Saccharum officinarum*), groundnut Shell (*Arachis hypogaea*) and Eggshell. Others include beakers, distilled water, graduated cylinders, filter paper, chemical reagents, and some laboratory glassware (volumetric flasks, graduated cylinders, funnels, and conical flasks) that have been used in research. The devices used in this study were an oven, a mill, a sieve, an atomic absorption spectrophotometer (AAS), a pH meter, an electronic balance, a refrigerator, etc.

3.1.1. Collection of Samples

The samples utilized in this study were produced water from two different oil fields in the Niger Delta region of southern Nigeria. Sample A was collected from Adanga South oilfield, offshore in Bayelsa State; while sample B was collected from OB/OB oilfield, onshore Rivers State. Both samples were collected from oil fields in the Niger Delta region. The adsorbents; such as sugarcane bagasse (*Sac-*

charum officinarum) and groundnut shell (*Arachis hypogaea*) were bought from popular Opolo market, Yenagoa, Bayelsa State, Nigeria. While, the egg shell were purchased from Aboki who fries Indomie and egg within the neighborhood at Tombia road, Yenagoa, Bayelsa State.

Figure 1 shows the agro materials used to produce bioadsorbents. These are; groundnut shell, sugarcane bagasse and eggshell. Figure 2 shows untreated produced water samples that would be used for the adsorption experiment to determine the quality of the water after treatment.



Figure 1. Agro materials (groundnut shell, sugarcane bagasse and egg shell).



Figure 2. Untreated raw produced water sample A and B.

3.1.2. Preparation and Treatment of Bio-Adsorbents

To prepare the adsorbents, they were thoroughly washed in distilled water to get rid of any dirt or undesired debris that could have stuck to them. For easy handling, they were then divided into pieces and left to dry in the sun for five (5) days. They were then finally dried in an oven at different temperatures and times. However, groundnut shell was oven dried at 40 °C for 30min. while, sugarcane bagasse was oven dried at 80 °C for 1hr and egg shell was oven dried for 40°C for 30min.

After oven drying, the agro materials were milled and sieved in 425 and 1180 micron sizes. Figure 3 shows sieved prepared bio-adsorbents in 425 and 1180 micron sizes.



Figure 3. Shows sieved bio-adsorbents of 425 and 1180 micron sizes.

For further treatment of the bio-adsorbents, the sieved adsorbents (i.e. sugarcane bagasse, groundnut shell and egg shell) were treated separately with dilute nitric acid (400 mL of 0.4 mol/L HNO_3), then covered with aluminum foil and kept for 24hrs. Figure 4 shows the treatment of each bio-adsorbents respectively.



Figure 4. Shows treatment process of bio-adsorbents.

As the pH of the filtrate approached neutrality, the bioadsorbents were then filtered and rinsed with distilled water. Then the treated bio-adsorbents were filtered completely and dried for usage. More so, the figures below shows treated

dried bio-adsorbents ready for use.



Figure 5. Treated and dried groundnut shell.



Figure 6. Treated and dried egg shell.



Figure 7. Treated and dried sugarcane bagasse.

3.1.3. Experimental Procedure and Treatment of Produced Water

The experimental process considered was sequential mixing of treated bioadsorbents with produced water (i.e. treatment of produced water with treated adsorbents in turn) and batchwise. For this treatment process, two heat-resistant beakers with a capacity of 500 ml were rinsed with distilled water and dried at room temperature. Then 300 ml of the produced water (sample A) was measured into each of the 500

ml beakers. The reason for the two beakers was the different micron sizes of the sieved and treated adsorbents. Thereafter, 10 grams of treated adsorbent (groundnut shell) was measured and poured into 300 ml of prepared water. To avoid phase separation, the solution was thoroughly stirred and manually agitated for about five minutes (5 minutes) until it became uniform, then allowed to carry out the treatment. The process was continued for one hour and approximately 5 mL of the treatment solution was filtered into sample bottles with Whatman filter paper. Further, filter out 5 ml from the treatment solution every 1 hour for 5 hours, and the filtrate was collected for analysis with an atomic absorption spectrophotometer (AAS).

Furthermore, the same procedure and treatment process was repeated for the second bioadsorbent (eggshell) and the third bioadsorbent (sugarcane bagasse), and the filtrate was collected into sample bottles every 1 hour for 5 hours, and the filtrate was taken out for analysis with Atomic Absorption Spectrophotometer (AAS). Similarly, the produced water sample B was also treated with treated adsorbents in the same manner, and the filtrate was collected into sample bottles every 1 hour for 5 hours, and the filtrate was taken out for analysis. The treated sample A water using groundnut shell was retreated again using egg shell and the resulting treated water here was retreated again using sugarcane bagasse.

3.2. Parameters Considered For Absorption Process

Several factors were considered while carrying out the absorption process. These factors depends on the absorption method applied, the expected outcome of the experiment and all those factors that will impair on the process. In this research, the parameters considered for the absorption process were:

(a) Dosage: Adsorbent dose is a crucial factor in determining an adsorbent's capacity. In general, as adsorbent dosage is increased, the percentage of heavy metal removal increases [14]. The quantity of adsorbent determines how many surface binding sites are accessible for adsorption. As a result, as adsorbent dosage increases, adsorbate removal % rises. For the maximal removal of adsorbate ions from the solution at a given concentration, there is enough adsorbent present. With an increase in biosorbent dose, it has been found that the sorption capacity of certain biosorbents decreases.

(b) Contact time: The time it takes for the system to reach equilibrium is called the contact time. Various mass transfer processes take place regularly in this heterogeneous solid-liquid system, some of which can be relatively slow. Therefore, to ensure that equilibrium is reached, the contact time must be fixed. A longer contact time can increase the biosorption of heavy metals. This can be explained by the transfer of larger amounts of metal ions from the solution phase to the active centers of the bioadsorbent with increasing contact time [15, 16].

(c) Particle size: The number of binding sites for adsorption increases with increasing surface area and decreasing particle size. One of the crucial components in adsorption is the surface. The surface area is directly related to the adsorption. Micro-, meso- and/or macro-holes can be present on the surfaces of biosorbents. In addition to the surface, pore volume and diameter are other important elements. The amount or the extent of the diffusion of the pollutant molecules into the pores depends on the pore volume and pore diameter. The pore diffusion can be calculated from the pore diameter and the molecular size. The adsorbate molecule diffuses deeper into the pore when the pore diameter is larger than the diameter of the adsorbate molecule.

4. Results and Discussion

But upon analysis of sample A and B produced water, the following heavy metals were observed with a high significant concentration. These are: arsenic (As), copper (Cu), lead (Pb) and iron (Fe). Table 1 shows the concentration of heavy metals that were present in the raw produced water sample.

Table 1. Concentration of heavy metals in raw produced water sample.

Heavy metals	Sample A Conc. mg/L	Sample B Conc. mg/L
AS	6.462	2.888
Cu	4.063	3.231
Pb	6.527	8.767
Fe	2.98	2.637

Therefore, the concentration of heavy metals analyzed from the raw samples as shown in table 1 were treated. A total of three pulverized and sieved pretreated bio-adsorbents were used for each oilfield produced water sample treatment. The

batch adsorption procedure was utilized to treat generated water samples A, and the findings shown in Tables 2, 3, and 4 were obtained from the sequential mixing of the adsorbents used.

The results obtained from sample (A) treatment were for both 425 and 1180 μ particle sizes of the three adsorbents as presented. Specifically, the findings were examined in this way, that is, one by one, because the method was batch-based.

Table 2. The results of the metal concentrations (mg/L) in sample (A) following treatment with sugarcane bagasse (*Saccharum officinarum*).

Sample A	As	Cu	Pb	Fe
Initial Concentration (Raw)	6.462	4.063	6.527	2.980
After treatment with sugarcane bagasse adsorbent using 425 μ particle size				
Time (hr)				
1hr	0.794	0.347	0.000	0.358
2hr	0.162	0.275	0.000	0.268
3hr	0.000	0.132	0.000	0.503
4hr	0.578	0.060	0.000	0.394
5hr	0.325	0.032	0.000	0.394
After treatment with sugarcane bagasse adsorbent using 1180 μ particle size				
Time (hr)				
1hr	0.397	0.448	0.000	0.611
2hr	0.614	0.405	0.091	0.629
3hr	1.101	0.232	0.000	0.575
4hr	0.379	0.118	0.218	0.611
5hr	0.848	0.103	0.000	0.611

Table 3. Langmuir and Freundlich model utilized for the analysis of Arsenic (As) for the sequential mixture of bioadsorbent using sample A.

Time (hrs)	C_e (mg/L)	q_e (g/L)	C_e/q_e (g/L)	$\log C_e$ (mg/L)	$\log q_e$ (g/L)
1	0.8303	168.951	0.0049	0.0808	2.2278
2	0.1986	187.902	0.0011	0.7020	2.2729
3	0.0000	193.860	0.0000	0.0000	2.2875
4	0.6137	175.449	0.0035	0.2120	2.2442
5	0.3610	183.030	0.0020	0.0020	2.2625

Therefore, for the purpose of analyzing Langmuir and Freundlich models, Table 4 were computed to enable plot various graphs and deduce conclusions.

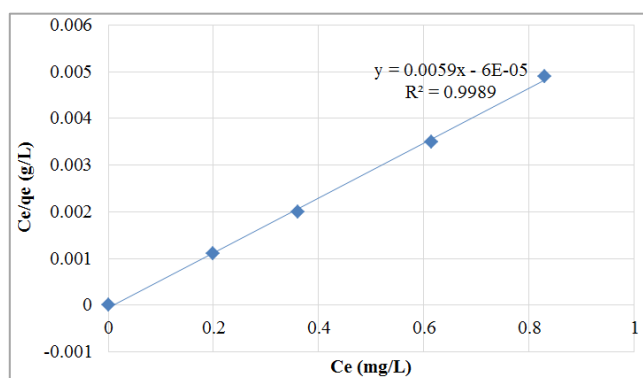


Figure 8. Analysis of As using Langmuir isotherm for sample A.

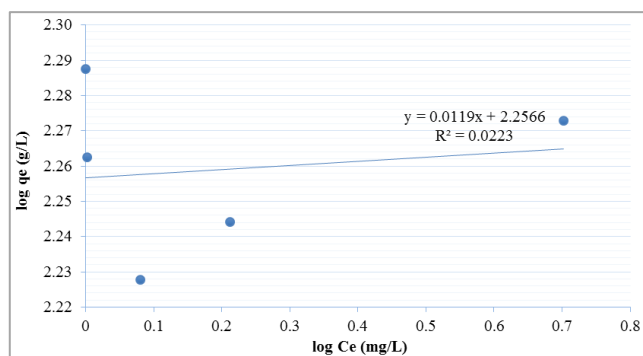


Figure 9. Analysis of As using Freundlich isotherm for sample A.

The plots in Figures 8 and 9 was extracted from Table 3. It shows that the linear plot of C_e/q_e versus C_e indicates that adsorption process follows the Langmuir model. The correlation coefficient (R^2) was found to be 0.9989 for As. The Langmuir sorption isotherm model is effective for studying arsenic (As)'s equilibrium, according to the results. This implies that the adsorbate will cover the adsorbent surface of the metal ion in a single monolayer. The sorption capacity was also evaluated, and it was found that the amount of metal ions

removed per unit mass of the adsorbent increases with the metal concentration as expected.

The Freundlich sorption isotherm model is not suitable for the equilibrium research of As illustrated in Figure 9, as evidenced by the correlation coefficient from the Freundlich isotherm plot of $\log q_e$ vs $\log C_e$.

Table 4. Results of the metal concentrations (mg/L) in sample (B) following treatment with sugarcane bagasse (*Saccharum officinarum*).

Sample B	As	Cu	Pb	Fe
Initial Concentration (Raw)	2.888	3.231	8.767	2.637
After treatment with sugarcane bagasse adsorbent using 425 μ particle size				
Time (hr)				
1hr	0.939	0.390	0.091	0.485
2hr	0.379	0.103	0.155	0.720
3hr	0.289	0.261	0.000	0.738
4hr	0.000	0.204	0.000	0.810
5hr	0.000	0.405	0.407	0.792
After treatment with sugarcane bagasse adsorbent using 1180 μ particle size				
Time (hr)				
1hr	0.433	0.390	0.000	0.774
2hr	0.361	0.204	0.000	0.792
3hr	1.047	0.448	0.000	0.231
4hr	0.975	0.476	0.000	0.304
5hr	0.632	0.577	0.028	0.195

Similarly, the Tables below were computed from results of produced water (sample B) and the relevant graphs were plotted to interpret findings using the Langmuir and Freundlich model.

Table 5. Langmuir and Freundlich model utilized for the analysis of Arsenic (As) for the sequential mixture of bioadsorbent using sample B.

Time hrs	C_e (mg/L)	q_e (g/L)	C_e/q_e (g/L)	$\log C_e$ (mg/L)	$\log q_e$ (g/L)
1	0.2166	80.1420	0.002702703	-0.664341548	1.903860176
2	0.2888	77.9760	0.003703704	-0.539402811	1.891960953
3	0.2527	79.0590	0.003196347	-0.597394758	1.897951317
4	0.5776	69.3120	0.008333333	-0.238372815	1.840808431
5	0.0000	86.6400	0.000000000	0.000000000	1.937718444

Figure 10 was initiated from table 5 in order to analyze Langmuir models of adsorption isotherm.

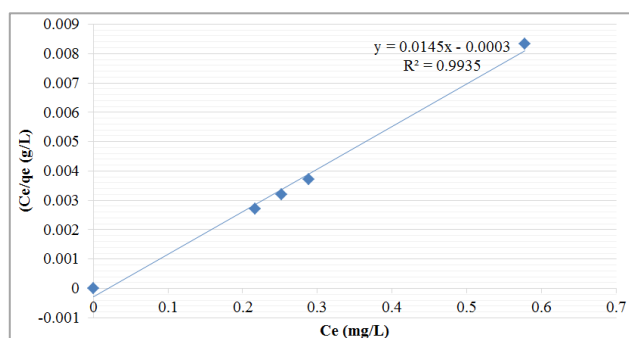


Figure 10. Analysis of arsenic (As) using Langmuir isotherm for sample B.

According to Figure 10, the adsorption process follows the Langmuir model based on the linear plot of C_e/q_e vs C_e for arsenic (As). It was discovered that the correlation coefficient (R^2) was 0.9935.

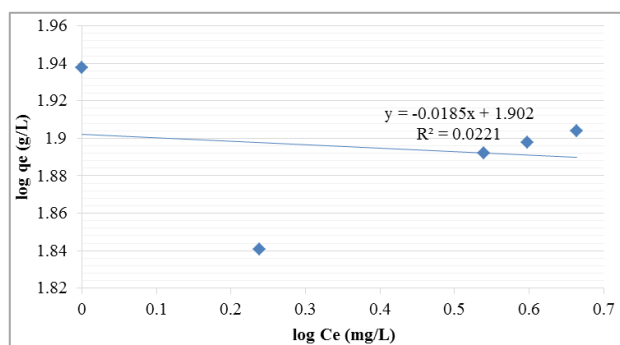


Figure 11. Analysis of arsenic (As) using Freundlich isotherm for sample B.

Freundlich isotherm plot of $\log q_e$ vs $\log c_e$ as depicted in Figure 11 shows that the relationship is not linear. Therefore, Freundlich isotherm sorption model is not appropriate for the equilibrium study of As.

5. Conclusions

In Nigeria's Niger Delta, heavy metal contamination in the produced water presents a major risk to public health and the ecosystem. The produced water samples from the Niger Delta oil field investigated for this study were found to include the following metals: arsenic, copper, lead, and iron. The atomic absorption spectrophotometer (AAS) data showed that the trials were successful. The analysis discovered that the sample's pre-treatment metal content exceeded thresholds anticipated for disposal or reuse. After the metals were treated with bioadsor-

bents (eggshell, groundnut shell, and sugarcane bagasse), their content was reduced to predicted limits established by regulatory bodies. In addition, it is advised that in further research, several materials other than the one employed in this study be used to treat the produced water in the Niger Delta.

Abbreviations

C_e : Equilibrium Concentration

Q_e : Adsorption Capacity

AAS: Atomic Absorption Spectrophotometer

EOR: Enhanced Oil Recovery

BTEX: (Benzene, Toluene, Ethylbenzene, and Xylene)

PAH: Polycyclic Aromatic Hydrocarbon

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Author Contributions

Indighe Macdonald: Conceptualization, Resources, Data curation, Software, Formal Analysis, Investigation, Writing - original draft, Methodology, Visualization, Project administration, Writing - review & editing

Elvis Ogede Adimie: Resources, Data curation, Supervision, Funding acquisition, Validation, Investigation, Project administration

Conflicts of Interest

The authors declare no conflicts of Interest.

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