

## Management of Produced Water from Niger-Delta Oil Fields Using a Local Material

Udeagbara SG<sup>1</sup>, Isehunwa SO<sup>1</sup>, Okereke NU<sup>2\*</sup>, Nwanwe O<sup>2</sup>, Oguama I<sup>2</sup>, Kerunwa A<sup>2</sup>

<sup>1</sup>Department of Chemical and Petroleum Engineering, Afe Babalola University, Ado-Ekiti, Nigeria; <sup>2</sup>Department of Petroleum Engineering, Federal University of Technology, Owerri, Nigeria

### ABSTRACT

Produced Water (PW) from petroleum reservoirs often contains heavy metals and other contaminants that are harmful to the environment. Most of the commonly used treatment techniques have been reported to be ineffective in reducing some of the contaminants' concentrations to recommended disposal levels. This study was designed to evaluate the effectiveness of bio-adsorbent (orange peel) for treating PW from Niger Delta oil field.

A 2.0 m steel adsorption column (0.4 m internal diameter) having four treatment compartments was designed and constructed using standard procedures. Orange peel was washed thoroughly with distilled water, sun-dried (4 days during harmattan period) and oven-dried at 105±5°C for 3 hours. It was ground into powder, sieved (150 and 300 microns), and then washed with 0.4mol/L HNO<sub>3</sub>, filtered and rinsed with distilled water to remove any pigment that might interfere with the result. Sample of PW was obtained from field R in the Niger Delta and analysed for heavy metals using an Atomic Absorption Spectrophotometer (AAS). Sample was treated in adsorption column over 3 hours using 150 micron size of adsorbent. Treatment was repeated with 300 micron size. Treated sample was analysed with AAS and characterized. Adsorptions of heavy metals were evaluated using Langmuir and Freundlich models. Data were analysed using regression and ANOVA at  $\alpha=0.05$ .

Concentrations of lead, nickel, cadmium, copper and Barium in PW from field R reduced by 96.2, 47.2, 78.6, 96.1 and 42.1 percent, respectively after four hours of treatment with 150 micron size, and for 300 micron size, the concentrations of the same metals reduced by 3.0, 88.8, 57.1, 11.8 and 18.4 percent respectively. The concentrations of other metals were equally reduced to an acceptable limit. The finer adsorbent was more effective. Langmuir model best described the adsorption of lead with isotherm R<sup>2</sup> of 0.97, while Freundlich isotherm described the adsorption of nickel and iron, with isotherms R<sup>2</sup> of 0.84 and 0.93 respectively.

Produced water from Niger Delta oil field was effectively treated of contaminants using orange peel with 150 micron size gave the best result

**Keywords:** Oilfield water treatment; Heavy metals adsorption; adsorption isotherms; Bio

### INTRODUCTION

Water is important for drilling, well stimulation, and for tertiary recovery purposes. Water needed for these operations can come from groundwater or surface sources as well as from municipal water supplies, or at times water recycled or re-used from some other source. Some of the water sent to the subsurface for

drilling and other well completion activities comes back to the surface and should be treated as a waste stream [1]. The waste stream also involves water emanating from subsurface geologic formations as a result of drilling, stimulating as well as completion activities [2].

\*Correspondence to: Okereke NU, Department of Petroleum Engineering, Federal University of Technology, Owerri, Nigeria, Tel No: 08035364239; E-mail: udeagbarasg@abuad.edu.ng

Received Date: August 03, 2021; Accepted Date: October 08, 2021; Published Date: October 18, 2021

Citation: Udeagbara SG, Isehunwa SO, Okereke NU, Nwanwe O, Oguama I, Kerunwa A (2021) Management of Produced Water from Niger-Delta Oil Fields Using a Local Material. J Petrol Env Biotech 10:p351.

Copyright: © 2021 Udeagbara SG, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Produced water is a waste stream that returns to the surface from the subsurface during production of oil or gas, and comprises formation water, and water injected into the formation during well stimulation process or during enhanced oil recovery processes [3]. Produced water is usually generated throughout the life of a well, and according to Clark and Veil, about 21 billion barrels of produced water is generated annually in the United States. Another important produced water category is called flow back water generated when some of the water flows back after water injected at high pressure into a formation during a well stimulation process like hydraulic fracturing is completed. Produced water generated by flow back water usually contains chemical constituents and dissolved salts, which are more than the original fracturing fluid (Clark and Veil) [4].

Produced water could as well be referred to as a waste stream emanating from the hydrocarbon bearing reservoir during the process of oil and gas production from the reservoir. Water is usually discovered along with oil and gas in the subsurface reservoir, with water found to settle beneath the other components within the reservoir because of its higher density. This naturally occurring water in the reservoir is referred to as formation water or connate water. Water production can occur during oil and gas well operations after production has taken place for a long time, depending on the reservoir drive mechanism controlling the well. Production of reservoir fluids (oil and gas) from the reservoirs is always accompanied by water (brine). This extracted water is called 'produced water'. Volume of oil and gas produces decreases, while that for produced water increases with time such that it exceeds the volume of oil and gas extracted before the reservoir goes below economic limit. The profitability of oil and gas field development is negatively affected by excess water production because more cost is incurred in managing the produced water which is in excess of oil and gas production volumes. These produced waters have many components, with negative impacts on the environment. Among the components are heavy metals [5-8].

The physiochemical properties of produced water vary based on the location and the geologic nature of the field, the characteristics of the geologic formation from which the water was extracted, and the nature of hydrocarbon extracted from the field. For fields where water injection is carried out, the properties and volumes of the extracted water may vary due to the introduction of additional water into the well to enhance hydrocarbon extraction. John Veil presented the main components of produced water and will be the focus of this work [9].

- Salt content of water which includes: salinity, conductivity, or total dissolved solids.
- Oil and grease which is not a single chemical; it comprises of various organic compounds associated with hydrocarbons in the formation.
- Organic as well as inorganic compounds introduced as chemical additives to enhance drilling and production activities.
- Radioactive materials that occur naturally and found its way into the produced water from certain formations.

## LITERATURE REVIEW

### Conventional Methods of Produced Water Treatment

Numerous produced water treatment methods such as removal of heavy metals and other contaminants have been existence for the past few decades and are documented in the literature. These methods can be grouped into chemical, biological and physical processes with physical and chemical methods being common in the treatment of produced water [10]. According to Gunatilake, chemical precipitation was the most widely used conventional method for removing heavy metals and other contaminants based on its effectiveness in treating inorganic waste streams based on acidity management in a basic solution. However, the demerits of chemical precipitation are numerous; the discharge of large volume of sludge extracted would need additional treatment, reduction in metal precipitation, improper settling, the sludge of metal precipitates and the environmental effect thereafter on the sludge management.

Coagulation-flocculation may also be used to manage waste water with toxic and other heavy metals by introducing a coagulant during the process but this treatment may not stabilize any colloidal particle and may lead to sedimentation. Despite these methods being very expensive, they also cause disposal issues and are even practicable for the management of water contaminated with toxic and other heavy metals. The problems that do arise during the conventional treatment which includes much intake of reagent and power, low selectivity issue, much operational cost and generation of more pollutants. Apart from these issues, there is a need to search for alternative treatments to substitute the conventional technologies of removing heavy metals from polluted water sources. Among these conventional methods are, (Gunatilake) [11-13].

**Membrane filtration:** Membrane filtration is a good method of effluent management that can yield high quality effluent, in a wide range of conditions without encountering much problems along the line. Membrane eliminate solids, dissolved salts and other impurities from wastewater by channeling them through a semi-permeable membrane, concentrated waste is captured on the membrane surface [14].

**Flotation and basic filtration:** Flotation is used to remove grease, oil and some suspended solids from wastewater. Basic filtration is mostly used in removing large solids materials from wastewater. This treatment is used to ensure effluent meets the regulatory limits before disposed or re-use as the case may be.

**Biological Processes:** Biological processes make use of bacteria to remove organic matter in produced/wastewater generally. They also remove ammonia from wastewater by nitrification and denitrification processes.

**Membrane bioreactor:** Membrane bioreactors (MBR) are an advanced wastewater management technology. MBR process involves combining the activated sludge process with membrane filtration either (MF or UF) in a single tank. MBR is very suitable when the aim is to reuse the treated wastewater. MBR is mostly used in food processing industry, treatment of

wastewater in the cities, as well as industrial handling of wastewater.

**Ion exchange:** Ion exchange is mostly used to remove traces of contaminants in water for high-level applications such as boiler feed water, ultra-pure water for the semi-conductor and pharmaceutical industries. Ion exchange removes undesired ions dissolved in wastewater and replaces them with desirable ions that are held in an ion exchanger which is introduced into process. A resin is mostly used as the ion exchanger.

**Disinfection:** Disinfection is mostly used to kill pathogens where there is a risk of close contact between human beings and the treated wastewater. It is mainly used as a secondary treatment method. Disinfection processes are: chlorination, ultra violet light, and ozone, etc

## Produced Water Management

This research provides information on how the produced water is handled when it gets to the surface from the reservoir. Oil, gas and water flow into the separator and water is separated from the oil and gas. Nearly all produced water is managed in the following ways, but not without some environmental effect:

- Injection of water into a hydrocarbon-bearing formation to enhance hydrocarbon recovery
- Disposal of produced water into a non-hydrocarbon-bearing formation (depleted wells) through water injection wells
- Discharge to surface water bodies after treatment
- Evaporation
- Paying a commercial disposal service to take the water and manage it
- Reuse for oil and gas operations (drilling fluids, fracture fluids)
- Reuse for other purposes

## Options available for Managing Produced Water

Arthur presented various options for managing produced water during oil and gas well production operations. The options include:

- Use of down hole separators which aids in separating water from oil and gas and re-injecting it into a suitable formation. This prevents or minimizes production of water to surface lines. Polymer gels can also be used to block fissures that contribute to produce water extraction. Produced water is managed through this option and it is an attractive method, though it is not always possible.
- Re-injection of produced water into the same formation or other suitable formations. Prior to produced water re-injection, the water is first treated to reduce fouling, scaling agents, and bacteria. The treated water is conveyed from the production site to the injection site.
- Discharge of produced water onshore and offshore such that discharge limits are met. Although, some locations may not require treatment before discharge.
- Re-use of wastewater for oil and gas operations – involves managing the produced water to meet the quality required for injecting it back for drilling and work-over activities.

- Used to enhance other multi-purpose activities – in some instances, significant treatment of produced water is an important requirement to ensure the quality needed for important benefits such as irrigation, cattle and animal consumption, and drinking water for human consumption, etc.

## Summary of Research works on produced water

Aquatic plants such as duckweeds, water hyacinth, and green algae (*Chlorella vulgaris*) were used by El-Din in determining their viability for produced water purification. The plants were prepared and treated before use for produced water treatment. Parameters such as chemical oxygen demand (COD), biological oxygen demand (BOD) were considered in this work. According to their result, COD and BOD were reduced in the produced water by 43% and 42% respectively by duckweed, 28% and 33% respectively by water hyacinth and 33% and 38% by green algae. From the results, duckweeds showed efficiency in the removal of pollutants in comparison with other plants.

Phytoremediation method (treatment of wastewater using plants) was used by Kingdom and Ezeilo in improving the treatment of produced water in Niger delta region. Phytoremediation deals with de-polluting waste water, soil or air with plants which are able to contain, degrade or extract metals, pesticides, solvents as well as crude oil and its derivatives and some other pollutants from the sample. In their work, the effectiveness of water hyacinth in the treatment of produced water was compared with that of a conventional method. Their comparison was based on assessing the quality of the discharged treated effluent and its impact on health and environment when discharged to the environment. The outcome of their research revealed that the effluent quality showed an improvement in the absorption of nutrients from produced water, which is a clear indication of the efficiency of water hyacinth in produced water treatment. Most significant reductions were observed in the BOD which showed 5% efficiency and sulphate ( $\text{SO}_4^{2-}$ ) with about 50% removal. This indicated a reduction in the organic waste and an improvement in the taste and odour Isehunwa and Onovae, worked on the evaluation of produced water discharged in the Niger Delta region of Nigeria. Their work was aimed at investigating if oil companies observed environmental rules and regulations before discharging produced water. The produced water samples were obtained from two oil terminals and three flow stations. The parameters analyzed were pH, resistivity, oil/grease content, copper, cadmium, iron, nickel, barium, manganese, lead, zinc, magnesium, chloride, sulphate, carbonate, bicarbonate, total dissolve solids, total suspended solids, biochemical oxygen demand (BOD) and discharge temperature etc, Their research showed that some parameters like chlorides, total dissolved solids, total suspended solids, iron and oil/grease content were above the standard limits as established by the regulatory bodies whereas the rest were within the limits [15].

## MATERIALS AND METHOD

Produced water, distilled water, beakers, measuring, cylinders, Filter paper, reagents and some other laboratory glass wares were



used in the research. Among the equipment used during this research were Atomic Absorption Spectrophotometer (AAS), fabricated adsorption column, sieving machine (mechanical shaker), Milling Machine, oven, etc.

The metals considered in this research were Manganese (Mn), Barium (Ba), nickel (Ni), magnesium (Mg), chromium (Cr), zinc (Zn), calcium (Ca), Boron (B), Tin (Sn), copper (Cu), iron (Fe), arsenic (As), lead (Pb), cadmium (Cd), and some other impurities contained in the produced water sample.

## COLLECTION OF SAMPLE AND MATERIALS

The sample (Produced water) was collected from Imo River oil field in Rivers State, Niger Delta. The adsorbent (Orange peels) was collected from ABUAD farm in Ado-Ekiti, Ekiti State. All the chemical reagents and other materials used in this research are of analytical grade.



Figure 1.0: Raw orange peels.



Figure 1.1: Sample of produced water and filtrates from the adsorption column.

## PREPARATION OF ORANGE PEELS AND EXPERIMENTAL PROCEDURE

The adsorbent (orange peels) was thoroughly washed with distilled water in order to remove unwanted particles (dirt) that may interfere with the result. It was cut into pieces, sun dried for four (4) days, and oven dried for three (3) hours at 105°C. It was milled and sieved into 150 and 300 micron size, washed with dilute nitric acid to remove any pigment and subsequently dried for use [16].



Figure 1.2: Adsorption Chamber.

## USE OF THE ADSORBENT FOR THE TREATMENT IN THE ADSORPTION COLUMN

20-gram (150 micron size) of orange peels was measured and transferred into the first column of the adsorption chamber. This was followed by measuring 250 ml of the sample (produced water) collected from Imo River oil field. The sample was allowed to flow through the adsorption column containing the adsorbent to enable adsorption take place. The filtrate emanated from the bottom of the chamber was collected at an interval of an hour and analyzed for the metal concentrations. The particle size of 150 micron was replaced with 300 micron of the same orange peels and the experiment was repeated, the filtrate was analyzed and the result recorded [17].

## RESULTS AND DISCUSSION

The result shown on table 1.0 was obtained from the experiment performed in the adsorption chamber. The result from the sample was for 150 and 300 micron particle sizes.

Figure 1.3 is a plot of some of the metal concentrations against time as shown on table 1.0 after 4 hours of treatment. The metal concentrations plotted against time are Pb, Ni, Cd, Cu and Ba. The table also shows some other metal concentrations that were not captured on the plot. The adsorbent used for this treatment was orange peels with 150 micron particle size.

The plot revealed that the more the time for the adsorption to take place, the more the metal concentrations on the sample reduces. The plot was a linear relationship. After 4 hours of treatment, the concentration of Pb, Ni, Cd, Cu and Ba were able to reduce from 0.132, 0.036, 0.014, 0.076, 0.038 (mg/l) to

0.005, 0.019, 0.003, 0.003 and 0.022 (mg/l) respectively. Notable reductions in the concentration of other metals were as well achieved as presented on table 1.0. The result shows that orange peels are good adsorbent in the treatment of produced water as it was found to contain fibrous materials and other necessary functional groups responsible for the adsorption. The result obtained was also commendable as it was found to be within the discharge limits as set by the regulatory bodies.

Figure 1.4 is also a plot of some metals concentration against time shown on table 1.0 as well. The same produced water (sample R) was used here as well as the same orange peels, but with particle size of 300 micron. The metals concentration plotted against time on the figure were Pb, Ni, Cr, Zn and Ba. Their concentrations were found to reduce from 0.132, 0.036, 0.071, 0.125, and 0.038 to 0.128, 0.004, 0.064, 0.008, and 0.031 respectively after 4 hours of treatment in the chamber. The plot is linear showing that the more the time taken for the adsorption process, the more the concentration of the toxic metals are reduced from the produced water. The table also shows some other metals concentration not plotted on the figure. The metals are Cd, Cu, Fe, Mg, Mn, Ca, Ar, B, and Sn. Unlike the plotted ones, their concentrations were as well reduced to acceptable limits [18].

Comparing the results from the two particle sizes (150 microns and 300 microns) as shown on the table and on the plots, one can confidently say that both particle sizes did a good job as they were able to bring down the concentration of the metals to allowable limits. The result obtained from 150 micron particle size was better than that of 300 micron particle size. The good result was as a result of the effect of surface area of the particles. From literature, it was stated that the smaller the particles, the larger the surface area and the better the adsorption process. The result obtained from the analysis conformed to the literature as it could be seen that 150 micron particle size with large surface area gave a better result than 300 micron particle size with smaller surface area.

For an efficient and effective adsorption process using some of these low cost agricultural wastes, the particle size should be made as smaller as possible so as to ensure larger surface area. The large surface area of the particles exposes very well the adsorption sites and the necessary functional groups responsible for the adsorption. For the 150 micron size, the percentage reductions for the metals concentration (Pb, Ni, Cd, Cu, Fe, Mg, Cr, Zn, Mn, Ca, Ar, B, Sn, Ba) were found to be 92.21%, 47.22%, 78.57%, 96.05%, 55.79%, 25.28%, 64.79%, 93.60%, 19.35%, 98.42%, 20.43%, 24.79%, 71.61%, 42.11% respectively.

## RESULTS ANALYSIS BASED ON ADSORPTION ISOTHERMS

### The Langmuir Model

This isotherm model explains the relationship between the quantity of materials extracted and its equilibrium concentration within bulk solutions. Langmuir isotherm model is suitable for monolayer adsorption on a surface that contains a

certain fixed number of similar sites. Langmuir sorption model assumes a uniform adsorption on the surface and transmigration in the surface plane. Langmuir isotherm model could be defined as:

$$q_e = \frac{K_L C_e}{1 + b C_e}$$

Where  $q_e$  is the adsorption capacity at equilibrium in (mg/g),  $C_e$ , the equilibrium concentration (mg/l) and  $K_L$  is the Langmuir constant in (ml/mg).

### The Freundlich Model

The Freundlich model is a unique model which considers the occurrence of the adsorption process on heterogeneous surfaces; and the model also highlights that capacity of adsorption is related to the concentration of the adsorbent. The Freundlich isotherm model could be expression as:

$$q_e = K_F C_e^{1/n}$$

Note  $K_F$  is the Freundlich constant and  $1/n$  is a constant showing the intensity of reaction. These Freundlich parameters  $K_F$  and  $1/n$  can be graphically estimated from the plot of experimental values and then applying the Freundlich equation in this form:

$$\ln q_e = \ln k_f + (1/n) \ln c_e$$

Considering the treatment of sample R with orange peel, the linear plot of  $q_e / c_e$  vs  $c_e$  indicates that adsorption of Pb ion obeys the Langmuir adsorption model (figure 1.5). Values of  $Q$ ,  $b$ ,  $k_L$ , and  $RL$  determined from the plot are indicated on (table 1.4). The coefficient of correlation ( $R^2$ ) shown on the plot was 0.9761 for Langmuir model and 0.8123 for Freundlich model (figure 1.6). The results showed that the Langmuir sorption model is favourable for study on the equilibrium of Pb, and this indicates the formation of monolayer coverage of the adsorbate on the adsorbent surface for the metal ion. The amount of metal ion extracted per unit mass of the adsorbent rises with the metal concentration as expected. The equilibrium separation factor  $RL$ , of 0.809 (table 1.4) indicated that the sorption of Pb ion on the adsorbent surface (orange peel) was found to be a favorable process [19].

Considering Ni ion adsorption on the adsorbent surface, the linear plot of  $\log q_e$  vs  $\log c_e$  indicates that adsorption obeys the Freundlich model (figure 1.8). The correlation coefficient ( $R^2$ ) was found to be 0.8462 which is more favorable than Langmuir with 0.778 (figure 1.7). This shows that the Freundlich sorption isotherm is favourable for equilibrium study for Ni, and this indicates the formation of heterogeneous layer coverage of the adsorbate on the adsorbent surface for the metal ion. The values of  $k_f$  and  $n$  were determined from the plot as shown on (table 1.4). These values indicate that the adsorption process was a

favorable one. Hence forth, the Freundlich model best describe the adsorption of Ni on the adsorbent surface.

For Fe (iron) adsorption on the adsorbent surface, Freundlich isotherm model gives a better result when compared with Langmuir model. The linear plot of logqe vs logce indicates that adsorption obeys the Freundlich adsorption isotherm (figure 2.0). The correlation coefficient (R2) shown on the plot was found to be 0.9341. This shows that the Freundlich sorption model is favourable for equilibrium study for Fe compared with R2 of 0.8594 on the Langmuir plot (figure 1.9). This indicates that the formation of heterogeneous layer coverage of the adsorbate on the adsorbent surface for the metal ion. The values of kf and n as calculated from the plot are shown on (table 1.4). These values indicate that the sorption of Fe on the surface of the adsorbent is a favorable process. Therefore, Freundlich model best describes the adsorption of Fe on the adsorbent surface [20-21].

**Table1.0:** Result of the concentrations (mg/l) of the metals treated with orange peel (Sample R -Imo River sample).

Sample	Pb	Ni	Cd	Cu	Fe	Mg	Cr	Zn	Mn	Ca	Ar	B	Sn	Ba
Ra	0.1	0.	0.	0.	0.	3.	0.	0.1	0.	43	4.	1.5	0.1	0.
w	32	03	01	07	55	69	07	25	06	0	65	9	55	03
	6	4	6	2	9	1		2					8	
POST TREATMENT WITH ADSORBENTS USING 150 MICRON PARTICLES SIZE														
1h	0.1	0.	0.	0.	0.	3.	0.	0.1	0.	39	4.	1.4	0.1	0.
rs	11	03	01	07	48	55	06	23	05	7	43	9	28	03
	4	3	4		5	6		9					7	
2h	0.	0.	0.	0.	0.	3.	0.	0.1	0.	16	4.	1.4	0.	0.
rs	02	02	01	07	42	35	06	13	05	5	38	53	09	03
	7	8	2		2	3		7					8	4
3h	0.	0.	0.	0.	0.	3.1	0.	0.	0.	59	3.	1.3	0.	0.
rs	01	02	00	00	32	2	03	06	05		92	7	06	02
	4	8	8	3		2	8	2					9	6
4h	0.	0.	0.	0.	0.	2.	0.	0.	0.	6.	3.	1.1	0.	0.
rs	00	01	00	00	24	76	02	00	05	8	7	8	04	02
	5	9	3	3	4	4	5	8					4	2
POST TREATMENT WITH ADSORBENTS USING 300 MICRON PARTICLE SIZE														
1h	0.1	0.	0.	0.	0.	3.	0.	0.1	0.	37	4.	1.5	0.1	0.
rs	32	03	01	07	48	65	07	23	05	7	63	9	54	03
	5	4	4	1	8	1		9					7	
2h	0.1	0.	0.	0.	0.	3.	0.	0.1	0.	30	4.	1.5	0.1	0.
rs	3	03	01	07	45	57	06	22	05	3	6	75	52	03
	4	2	3	2	7	9		7					6	
3h	0.1	0.	0.	0.	0.	3.	0.	0.1	0.	65	4.	1.5	0.1	0.
rs	31	00	01	07	34	33	06	1	05		57	72	4	03
	6	1	1	4	5	6		4					4	

4h	0.1	0.	0.	0.	0.	2.	0.	0.	0.	10	4.	1.5	0.1	0.
rs	28	00	00	06	31	71	06	01	04		52	71	36	03
		4	6	7	5		4	4	2					1

**Table1.1:** Assessment of Pb (lead) using Langmuir and freundlich isotherm models for sample R with orange peel.

t (hrs)	Ce (mg/l)	qe (g/l)	Ce/qe (g/l)	Log Ce (mg/l)	Log qe (g/l)
1	0.111	0.000656	169.21	-0.9547	-3.1831
2	0.027	0.00328	8.232	-1.5686	-2.4841
3	0.01	0.00381	2.63	-2	-2.419
4	0.005	0.00397	1.26	-2.301	-2.4012

**Table1.2:** Assessment of Ni (nickel) using Langmuir and freundlich isotherm models for sample R with orange peel.

t (hrs)	Ce (mg/l)	qe (g/l)	Ce/qe (g/l)	Log Ce (mg/l)	Log qe (g/l)
1	0.034	6.25E-05	544	-1.4685	-4.2041
2	0.028	0.00025	112	-1.5528	-3.6021
3	0.024	0.000375	64	-1.6198	-3.4259
4	0.019	0.000531	35.78	-1.7212	-3.301

**Table1.3:** Assessment of Fe (iron) using Langmuir and freundlich isotherm models for sample R with orange peel.

t (hrs)	Ce (mg/l)	qe (g/l)	Ce/qe (g/l)	Log Ce (mg/l)	Log qe (g/l)
1	0.48	0.00225	213.33	-0.3188	-2.6478
2	0.42	0.00413	101.69	-0.3768	-2.384
3	0.323	0.00716	45.11	-0.5228	-2.1451
4	0.244	0.00963	25.34	-0.6126	-2.0457

**Table1.4:** A comparism of coefficient of determination and other parameters for treatment with orange peel with sample R using the two models.

Metal	Langmuir model	Freundlich model						
	R2	b	KL	RL	Qo	R2	n	KF
Pb	0.98	1.79	0.00558	0.809	0.00312	0.81	8.83	1.2

Ni	0.78	11.29	0.001	0,711	0.000	0.85	0.56	1.39
			33		118			
Fe	0.86	1.44	0.003	0.557	0.002	0.93	0.699	1.1
			33		31			

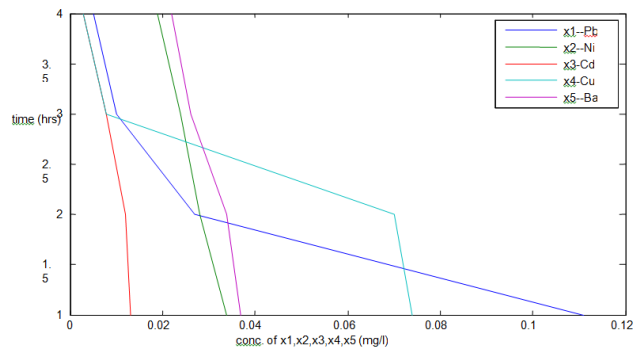


Figure 1.3: plot of conc. of Pb, Ni, Cd, Cu Ba vs time (Sample R, 150 micron size).

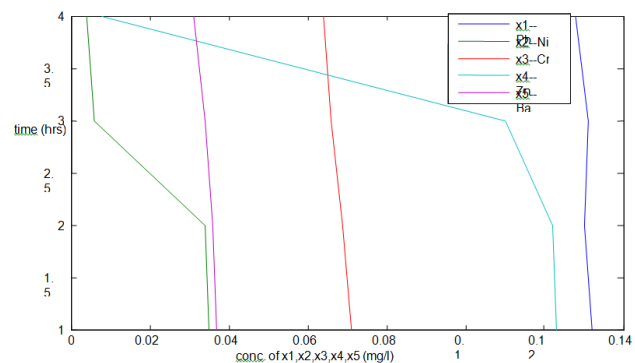


Figure 1.4: plot of conc. of Pb, Ni, Cr, Zn and Ba vs time (Sample R, 300 micron size).

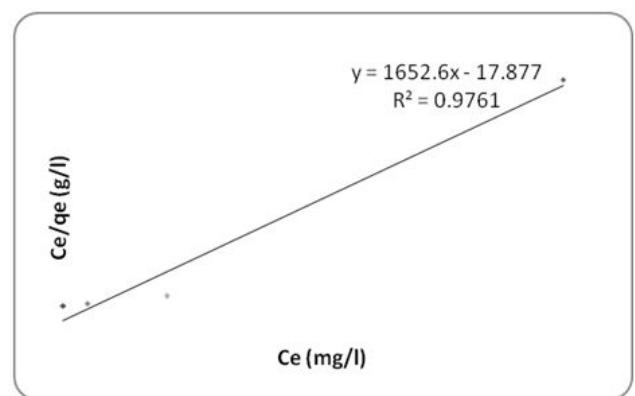


Figure 1.5: Assessment of Pb using Langmuir isotherm for sample R.

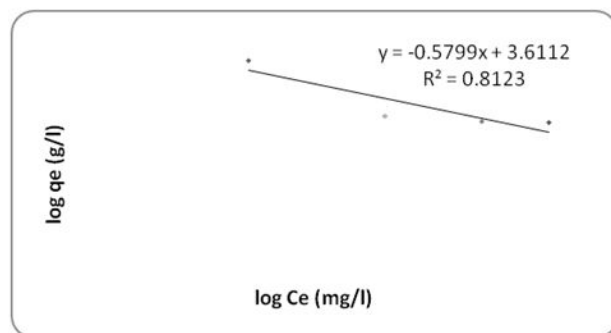


Figure 1.6: Assessment of Pb using Freundlich isotherm for sample R.

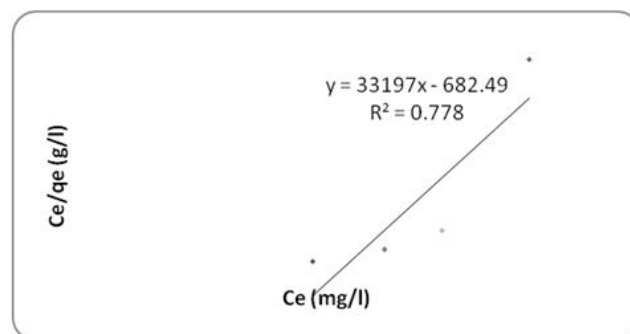


Figure 1.7: Assessment of Ni using Langmuir isotherm for sample R.

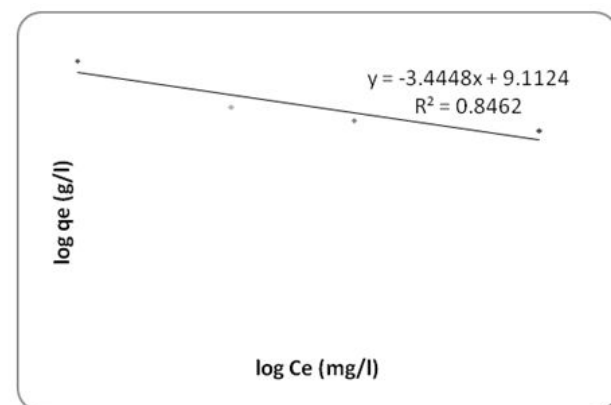
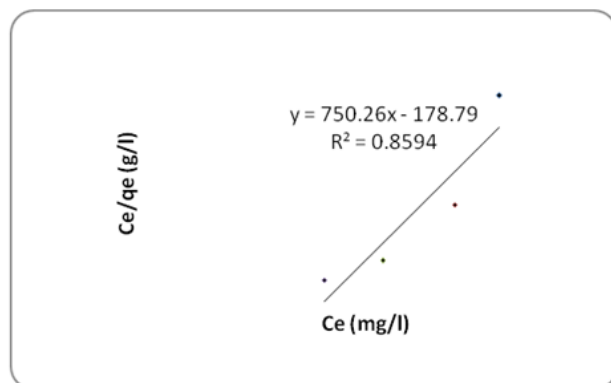
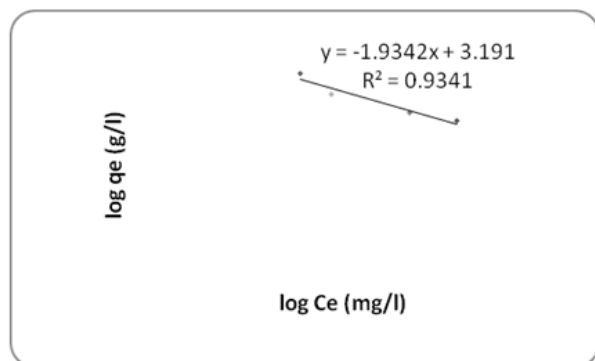


Figure 1.8: Assessment of Ni using Freundlich isotherm for sample R.





**Figure1.9:** Assessment of Fe using Langmuir isotherm for sample R.



**Figure2.0:** Assessment of Fe using Freundlich isotherm for sample R.

## CONCLUSION

The produced water from Niger Delta region of Nigeria analyzed in this research was discovered to contain traces of heavy metals. The experimental procedures used in the analysis of these metals were done with standard solution of each metal prepared at room temperature in the laboratory. The experiments were successful; the metal concentrations before and after treatment with the adsorbent were analyzed with the help of an Atomic Absorption Spectrophotometer

Before the treatment, the analysis showed that the concentration of the metals in the sample was in excess of what is expected before discharge or re-use as the case may be. After the treatment using the adsorbent (orange peels), the concentration of most of the metals were reduced to expected limits as set by the regulatory bodies. 150 micron size of the adsorbent produced a good result compared with 300 micron size. It was noted that the finer the particles, the better the adsorption.

Two models were used to validate the result obtained from the analysis. These models were Langmuir and freundlich isotherm models. The three metals selected for the test were lead (Pb), Nickel (Ni) and Iron (Fe). The models proved that the results obtained from the analysis were valid.

## ACKNOWLEDGEMENT

The support of the laboratory staff of the Department of Petroleum Engineering, Afe Babalola University Ado-Ekiti, Ekiti state is acknowledged.

## REFERENCES

1. Aclione A, Thyara CN, Mauricio I, Ramon L. Produced Water from oil - A Review of the Main Treatment Technologies. *J Environ Chem.* 2018; 2:1 23-27.
2. Aharoni C, Ungarish M. Kinetics of Activated Chemisorptions, Part 2 Theoretical Model. *J Chem Soc., Faraday Trans 1.*1977; 73: 456.
3. Ahmet S, and Erdal O. The Accumulation of Arsenic, Uranium, and Boron in Lemna gibba L, Exposed to Secondary Effluents. *J Ecosyst Restor.* 2009;35.
4. Al-Anber ZA, and Matouq MAD. Batch Adsorption of Cadmium ions from Aqueous Solution by Means of Olive cake. *J Hazard Mater.*2008; 151: 194-201.
5. Allen JS, and Brown PA. Isotherm Analyses for Single Component and Multi-component Metal Sorption onto Lignite. *J Chem Technol Biotechnol.* 2004; 62: 17-24.
6. Altundogen HS, Bahar N, Mujide B, and Tumen F. The use of Sulphuric acid - Carbonization Products of Sugar beet pulp in Cr(VI) Removal. *J Hazard Mater.* 2007; 144: 255-264.
7. Ahmed A, Taleb HI, Abdul SG, Mustafa IK, Hussain A. Produced Water Treatment using Naturally Abundant Pomegranate Peel. *J Desalination Water Treat.*2016; 57: 6693-6701.
8. Anandh B, Deepthi P, Lavanya S, Sivaku D. Treatment of Dairy Wastewater using Eucalyptus wood Saw Dust activated Carbon Powder. *J Chem Pharma Sci.* 2015; 8: 4729-4733.
9. Annadural RS, Juang and Lee JD. Adsorption of Heavy Metals from Wastewater Using Banana and Orange Peels. *Water Sci Technol.* 2002; 1:185-190.
10. Annadural RS, and Lee JD. Adsorption of Heavy Metals from Wastewater using Banana and Orange peels. *Water Sci Technol.* 2012; 1: 185-190.
11. Arthur JD, Bruce PE, Langhus G, Chirag Patel, CPG. Technical Summary of Oil & Gas Produced Water Treatment Technologies. ALL Consulting, LLC, United States Environmental Protection Agency;2005.
12. Badr E, Said M, Reda A. Potential uses of Aquatic Plants for Wastewater Treatment. *J Microbiol Biotechnol.* 2018;2:7-39.
13. Bulut Y, Gozubenli N, Aydin H. Equilibrium and Kinetics Studies for Adsorption of Direct blue 71 from Aqueous Solution heat Shells. *J Hazard Mater.* 2007; 144: 300-306.
14. Casaday AL. Advances in Floatation Unit Design for Produced Water Treatment. *Soc Pet Eng.* 1993; SPE #25472.
15. Clark CE, and Veil JA. Produced Water Volumes and Management Practices in the United States, States (ANL/EVS/R-09/1) U.S. Department of Energy - National Energy technology Laboratory; 2009.
16. El-Din R, Said MB, Abdel-Aziz. Potential use of aquatic plant for produced water Purification. Agricultural Microbiology Department, Agricultural and Biological Research Division, National Research Centre, Dokki, Cairo, Egypt; 2018.
17. Gregory KB, Vidic RD & Dzombak DA. Water management challenges associated with the production of shale gas by hydraulic fracturing Elements. 2011; 7(3), 181-186.
18. Gunatilake SK. Methods of Removing Heavy Metals from Industrial Wastewater. *J Multidiscip Eng Sci Stud. (JMESS).* 2015;1(1).
19. Isehunwa SO & Onovae S. Evaluation of produced water discharge in the Niger-Delta; 2011.
20. Igunnu ET & Chen G Z(2014). Produced water treatment technologies. *Int J Low Carbon Technol.* 2014; 9(3), 157-177.
21. John V. U.S. Produced Water Volumes and Management Practices. Kingdom KD and Ezeilo FE. Secondary Treatment of Produced Water from an Oilfield in Niger Delta Using Phytoremediation Technique. *Pet Technol Dev J.* 2012; Vol.1.