Research Article

Management of Produced Water from Niger Delta Oilfield with Modified Agricultural Waste

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Abstract
Hydrocarbon reservoirs contain produced water as one of its constituents. Produced water most times contains toxic materials and other impurities that affect the ecosystem. Most of the available treatment techniques have not been very effective in reducing some of the contaminants to an acceptable disposal limits.Banana peels was washed with clean water, dried under the sun for three days, and oven-dried at 105 ± 5^oC for 3 hours. It was milled, sieved (150 and 300 microns,), and then treated with 0.4mol/L HNO_3, rinsed with clean water to remove any pigment that might interfere with the result. Sample (produced water) was treated in adsorption chamber for 4 hours using 150 micron size of adsorbent. Treatment was repeated with 300 micron size. Treated sample was analyzed and characterized.

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 87.18%, 23.08%, 42.86%, 100%, 80.12%, 34.33%, 28.93%, 45.40%, 47.89%, 97.18%, 33.06%, 43.24%, 62.50%, and 44.44% respectively. Similar reductions in same metals with 300 micron size were equally obtained. The finer adsorbent was more effective. Langmuir model best described the adsorption of lead with isotherm R^2 of 0.98, while Freundlich described the adsorption of nickel and iron, with isotherms R^2 of 0.85 and 0.93 respectively.

Produced water from Niger Delta oil field was effectively treated of contaminants using banana peels with 150 micron size produced the best result.

Keywords: Adsorption chamber, Adsorption, produced water, Heavy/toxic metals

Introduction
Study background
Oil reservoirs contain naturally occurring water called formation water, which is heavier (denser) and lie beneath the oil. Also, to ensure more oil recovery, additional water is often injected into the the hydrocarbon zone to improve the energy needed to force the oil from the reservoir to the surface. Formation and injected water are mainly the constituents of produced water, with some level of contaminants which include organic matters, toxic/heavy metals, minerals, solid materials, and production chemicals which are introduced at some point in the separation and production line [1].

When produced water is not managed properly, it has serious adverse effects on the ecosystem and it can also damage the reputation of the company involve. It has been observed that every aspect of oil activities, in different levels, poses negative impacts on the environment and that the environmental consequences impose economic effects on the indigenes of that area [1].Flowback water is another necessary category of water. Water is actually needed in well stimulation, hydraulic fracturing in particular. Water is mixed with some other components like propping agent and injected into the formation to open up the pores to improve the flow of oil. A large portion of this water after weeks of well treatment finds its way back to the surface. This water is called flow back water. It

typically contains certain levels of chemical constituents, which are dissolved salts, more than the original fluid [2].Produced water can as well be refers to as the water brought from the subsurface to the surface during the production of oil and gas from the reservoir. Oil and gas usually exists alongside water in the subsurface, with the water been heavier than the oil and gas and settles under the hydrocarbons in the reservoir. This water which occurs naturally in the reservoir is refers to as formation water, sometimes, connate water. After production has taken place for a long period of time in a well, it can start producing water, which depends on the energy drive mechanism governing the production.

Extraction of oil and gas from reservoirs is often accompanied by water (brine). The extracted water is called 'produced water'. As the reservoir depletes the volume of produced water increases and is compelled to exceed the volume of the oil/gas produced before the reservoir is depleted beyond economic gain. Produced waters most times have negative impacts on the development of an oilfield economically, because to the cost incurred in producing waters over the possible period of extraction. Most components of produced waters have negative impact on the environment. Such components are the heavy metals, organic matters, oil and grease, solids materials, etc [3].

Research works on seeking for better ways for produced water management is on the increase due to some strict regulations on produced water discharge by the regulatory agencies. However, more efforts are being put towards finding a cost-effective method for produced water re-use since it is a water source which can be used for irrigation, water source for industrial activities, agriculture, and reinjection into a well to boast oil recovery. If the water is to be reuse, it is important to bring down the level of contaminants by picking a proper treatment technique that would ensure that the requirements of water quality are met. In addition, there are two main objectives in produced water management: removal of undesired constituents such as excessive hardness, dissolved solids, organisms, light hydrocarbon, etc and effluent adjustment especially when it is going to be re-used in areas like irrigation and other agricultural activities [4].

Produced water Composition
The composition of produced waters differs, and this is attributed to different formation characteristics, reservoir compositions, and other activities engaged by industries as a result of work over maintenance and development. Produced water constituents comprises of two groups which are inorganic compound and organic compound. Inorganic compounds in produced water can be classified as insoluble and soluble salts. Precipitates, grit, etc are examples of insoluble inorganic compounds while monovalent cations of sodium and potassium and the multivalent cations of calcium, manganese, iron, and magnesium, as well as anions like carbonate, chloride, sulphate, and bicarbonate are examples of soluble compounds. Soluble organic components are classified into compounds that can dissociate into ionic state with di-carboxylic acids and phenol as examples and into compounds that cannot dissociate with non-ionic soluble oils and glycols as examples [5].

Generally speaking, most produced waters have pH in the range of

6 and 8 (Kulthanan, 2013). Buffering is normally carried out with bicarbonate. Normally, pH of produced water would remain neutral except if sodium carbonate or acidic solution is introduced during treatment. Most times, treatment is required in most cases in order to ensure conformance with beneficial effluent use standards; in most of the applications, the aim of the treatment is to get rid of the following from the produced water:
i.   Removal of oil and grease.
ii. Reduction of total dissolved solids (TDS) in produced water.
iii. Reduction in concentration of Benzene.
iv. Reduction in concentration of biological oxygen demand (BOD) emanating from soluble organics, toxic metals, etc.

Literature Review
Conventional Methods of Treatment
Numerous methods of heavy metal and other contaminants removal from wastewater have been in existence for many years and these can be grouped into biological, chemical, and physical processes. However, in most treatment, physical and chemical processes are more practiced. Among these conventional methods of metal and contaminant removal from produced water and other wastewater, chemical precipitation is the most commonly applied in treating inorganic effluents based on acidity management in a basic solution, [6].

Despite this method been very capital intensive, they create disposal issues and are even been used for the management of water contaminated with toxic and other heavy metals. The problems may come up during the conventional treatment includes much intake of reagent and power, selectivity issue usually low, much operational expenses and creation of more pollutants. Apart from these issues outlined above, it is very pertinent to search for an alternative route to substitute the conventional technologies of removing heavy metals and other contaminant from polluted water sources. Among these conventional methods are [6].

i.   Flotation and basic filtration: This method is used to eliminate grease, oil and some other suspended solids from wastewater. Basic filtration is employed in handling large solid materials from wastewater. These treatments may be used so that effluent meets the discharge limits set by the regulatory bodies before it is been disposed or re-use along the line..
ii. Biological Processes: This method of treatment uses bacteria to eliminate organic matter in produced water and other wastewater in general. They as well remove ammonia from wastewater by nitrification and denitrification processes.
iii. Disinfection: Disinfection is deployed to destroy pathogens especially where the treated water is expected to get in contact with human. Disinfection is usually carried out as secondary method of treatment. Chlorination, ozone, and ultra violet light are some of secondary methods of wastewater treatment. available.

Produced Water management options in practice
In produced water management, most oil and gas industries make use of some options which include [7].
i.   Prevent the production of water unto surface facility – use of separators at the subsurface which separate water from gas

and oil stream and re-inject it into suitable formation. Also, polymer gels can be used to block fissures and fractures that contribute towards produced water. Produced water is eliminated via this option and it is an attractive method, though it is not always possible.

ii. Injection of produced water – this involves re-injection of produced water into the same formation in the subsurface or other suitable formation; it also involves the conveyance of the produced water from the production site to the injection site. Treatment of the produced water to be injected is necessary to ensure the reduction of concentration of contaminants contained in the water. Although waste water is generated in this option, the waste is replaced back into the reservoir.

iii. Discharge of produced water– this entails management of produced water to meet-up with the discharge limits for onshore and offshore operations set by the regulatory bodies. Sometimes some locations may not necessarily need treatment before discharge.

Summary of Research works on produced water

conducted a research on "Removal of heavy metals from produced water obtained from Niger Delta oilfield using biosorption techniques". The sample (produced water) was characterized for heavy metals and other contaminants. They investigated the uptake of metal ions by batch process using sawdust as adsorbent (raw and pre-hasted). They used sawdust in two different forms which were the raw sawdust and hydrolyzed sawdust (sawdust that was completely soaked in water and heated for about 30mins). Both materials were thoroughly rinsed with clean water, dried under the sun and were finally oven dried at 800c for 3 hours. The two sawdust adsorbents were screened to obtain a uniform particle size (mesh size 0.2-0.8mm) and were preserved at 360C for use. They carried out all experiments in batch mode using the different adsorbents under the same temperature conditions and constant volume with designated weight[8].

The results showed that the capacity of sawdust to successfully reduce the concentration of heavy metals and other contaminants from wastewater is considered a-cost effective and a good alternative to much expensive conventional methods of treatment [9].carried out a research work on the improved treatment of produced water from Niger delta region by the method of phytoremediation. phytoremediation means treatment of wastewater using plants. Phytoremediation deals with the de-polluting waste water, soil, etc with the help of certain plants which can extract impurities, solvents as well as crude oil and its derivatives and some other pollutants from the sample. Their study was aimed at determining the effectiveness of water hyacinth plants in treating produced water and then to compare the quality of discharged treated effluent with that of discharge from conventional treatment method with a view to ascertaining the impacts on environment. The outcome of their research revealed high effluent quality with marked improvement which is due to the effectiveness of the plant (water hyacinth). The plant recorded 5% reduction in BOD, and 50% reduction in sulphate (SO42). These results showed a decrease in the organic waste, a good odour and a better taste of the sample.

worked on the evaluation of produced water discharged in the Niger Delta region of Nigeria. Their work was aimed at investigating if oil companies actually observed environmental rules and regulations before discharging produced water [5]. Samples were obtained from two (2) oil terminals and three (3) flow stations. The parameters analyzed were cadmium, barium, manganese, lead, pH, zinc, sulphate, total dissolve solids, total suspended solids, biochemical oxygen demand (BOD) and discharge temperature, chloride, etc, Their research showed that some parameters like chlorides, total dissolved solids, total suspended solids, iron and oil/grease content were above the discharge limits whereas the rest were within the limits.

Materials and method

The following materials were used in this work: Distilled water, Sample of produced water (X), Banana peels, Reagents, Laboratory glass wares and some other materials..

The following equipment were used: Sieve apparatus, Oven, Atomic Absorption Spectrophotometer, Milling Machine, Adsorption chamber, Balance, pH meter, etc.

The heavy metals analyzed were lead (pb), nickel (Ni), cadmium (Cd), copper (Cu), iron (Fe), magnesium (Mg), chromium (Cr), zinc (Zn), calcium (ca), Boron (B), Tin (Sn), arsenic (As), Manganese (Mn), Barium (Ba) as well as other contaminants in the produced water.

Collection of Sample and Materials

Produced water sample (X) was collected from number oil field in Rivers State, Niger Delta. The adsorbent (Banana peels) was purchased from a local market in Ado-Ekiti, Nigeria.. All the chemicals and other reagents used were of analytical and standard grade.

Figure 1.0: Raw Banana peels

Figure 1.1: Produced water sample and filtrates from adsorption process

Preparation of Banana Peels and the Experimental Procedure

The adsorbent (banana peels) was washed with clean water to remove any adhering dirt.. It was slice into pieces; dried under the sun for 24 hours during hammer time, and oven dried for 3 hours at 105°C. The peels were milled and sieved into particle sizes of 150 and 300 micron. They were washed with 0.4ml nitric acid to remove any pigment that may interfere with the result. The particles were finally modified with 0.4mol hydrochloride acid and dried before use. The modification was done by washing the particles with 0.4ml hydrochloric acid until the filtrate was near neutral. Modification was done to expose very well the adsorption sites of the adsorbent.

Figure 1.2: Adsorption Chamber

Use of the Adsorbent for the treatment in the Adsorption Column
The next stage of the experiment was carried out by packing 20-gram (150 micron size) of banana peels in the first column of the adsorption chamber. 250 ml of produced water obtained from Nembe oil field was allowed to flow across the column packed

with the adsorbent in the adsorption chamber to enable adsorption occur. The filtrate emanating from the bottom of the chamber was collected at an interval of 1 hour and analyzed for the metal concentrations. The particle size of 150 micron was replaced with 300 micron of the same banana peels and the experiment was repeated, the filtrate was analyzed and the result was recorded.

Results and Discussion
The result presented on table 1.0 is obtained from the experiment carried out in the adsorption chamber. The result presented is for 150 and 300 micron sizes as indicated on the table. Figures 1.3 and 1.4 are the plots of some metal concentrations against time from table 1.0. Figure 1.3 is for 150 micron particle size while figure 1.4 is for 300 micron particle size. Both particle sizes were used for the treatment of the produced water sample from Nembe oil field in Bayelsa state,

Niger Delta part of Nigeria.

Figure 1.3 is a plot of concentration (mg/l) of Cd, Cu, Cr, Mn and Sn against time (hrs) after four hours of treatment with Banana peels; and the particle size used here was 150 micron. From the table and the plot compared with the raw (untreated) data; it was observed that the concentration of the metals, Cd, Cu, Cr, Mn and Sn reduced from 0.007, 0.07, 0.121, 0.071, 0.144 to 0.004, 0.000, 0.086, 0.037 and 0.054 respectively after four hours of treatment. This goes to show that banana peel is a good adsorbent for treating produced water from Nembe oil field. The plot also revealed that after four hours of treatment, cu ion concentration was completely eliminated from the produced water sample; this makes Banana peels one of the best adsorbent for removing Cu ion from produced water samples and other waste water in general. The concentration of other metals (Pb, Ni, Fe, Mg, Zn, Ca, Ar, B, Ba) on the table as treated with 150 micron particle size were as well reduced to an appreciable level as recommended by the regulatory bodies.

Figure 1.4 is a plot of concentration (mg/l) of Cd, Cu, Cr, Mn and Sn against time (hrs) after four hours of treatment with Banana peels; and the particle size used here was 300 micron. From the table and the plot compared with the raw (untreated) data; it was observed that the concentration of the metals, Cd, Cu, Cr, Mn and Sn reduced from 0.007, 0.07, 0.121, 0.071, 0.144 to 0.005, 0.033, 0.092, 0.043 and 0.129 respectively after four hours of treatment. Other metals on the table (Pb, Ni, Fe, Mg, Zn, Ca, Ar, B, Ba) not shown on the plot were as well positively affected by the adsorbent in terms of reduction in their concentrations.

Generally speaking, both plots (figures 1.3, 1.4) are linear in nature showing that there is a strong relationship existing between the dependent variable and the independent variable; in other words, the level of metal concentration reduction depends on the effectiveness of the adsorbent. The banana peels have proved to be very effective in this adsorption process. Both particle sizes proved to be very efficient, but a better result was obtained with the particle size of 150 micron. This was considered to be because of finer surface area exhibited by150 micron particle size compared to 300 micron size. For the 150 micron size, the concentration reduction (percentage) of the metals (Pb, Ni, Cd, Cu, Fe, Mg, Cr, Zn, Mn, Ca, Ar, B, Sn, Ba) were 87.18%, 23.08%, 42.86%,

100%, 80.12%, 34.33%, 28.93%, 45.40%, 47.89%, 97.18%, 33.06%, 43.24%, 62.50%, 44.44% respectively. Similar reduction in percentage level was obtained with 300 micron particle size, though 150 micron size proved to the best size for the treatment as earlier stated.

Analysis of the result using Adsorption Isotherms
The Langmuir Model

This isotherm model is used to express the relationship that exists between the amount of material obtained from the solution and the bulk of the solution equilibrium concentration. Monolayer adsorption site is the only condition where Langmuir sorption model is valid. That means the adsorption sites must be similar and uniform. This model could be can written as:

$$q_e = (K_L C_e) / (1+bC_e)\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where KL = Langmuir constant in (ml/mg),. q_e = equilibrium capacity in (mg/g), C_e, = concentration at equilibrium (mg/l).

The Freundlich sorption isotherm
This sorption isotherm model assumes adsorption takes place in none uniform or heterogeneous surfaces.. This sorption model can be written as:

$$q_e = K_F C_e^{1/n}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where K_F = the sorption constant, $1/n$ = reaction intensity (constant). The constants K_F, $1/n$ could be calculated from an experimental plot when this model equation is presented as:

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

For the treatment of sample X with banana peels, plot of ce/qe vs ce revealed that adsorption of Pb ion follows the Langmuir adsorption model (figure 1.5). Values of Q, b, kL, and RL determined from the plot are indicated on (table 1.4). The coefficient of correlation (R^2) shown on the plot was 0.98 for Langmuir model and 0.81 for Freundlich sorption model (figure 1.6). The results revealed that the Langmuir sorption model is more favourable for equilibrium study for Pb, and this suggests the formation of monolayer coverage of the adsorbate on the adsorbent surface area. Amount of ion obtained per mass of the adsorbent rises with the metal concentration. The value of the equilibrium separation factor R_L, of 0.809 (table 1.4) showed that the sorption of Pb ion on the adsorbent surface (banana peels) was found to be a favorable process.

However, for Ni ion adsorption, plot of log q_e vs log c_e indicates the process follows Freundlich sorption model (figure 1.8). The correlation coefficient (R^2) was found to be 0.85 more favorable than Langmuir with 0.78 (figure 1.7), indicating that the Freundlich model is favouable for the study of nickel, which entails the formation of non-uniform (heterogeneous) coverage of the adsorbate for the metal ion. K_f and n were determined from the plot as shown on (table 1.4). The values showed that the process was a favorable one. Hence, the Freundlich sorption model best describe the adsorption of Ni on the adsorbent surface.

When it comes to Fe (iron) adsorption, Freundlich sorption model gives a better result compared with Langmuir model. The linear plot of $log q_e$ vs $log c_e$ shows that adsorption follows the Freundlich adsorption isotherm (figure 2.0). The correlation coefficient (R^2) on the plot was 0.93. This indicates that the Freundlich model is more favourable for study of Fe. This shows formation of non-uniform (heterogeneous) coverage of the adsorbate on the surface of the adsoebent for the metal ion under investigation. K_f, n as estimated from the plot are presented on (table 1.4). The values showed that adsorption of Fe on the adsorbent surface are favorable.Therefore, Freundlich model best describes the adsorption of Fe on the adsorbent surface.

Table 1.0: Concentrations (mg/l) of the metals treated with banana peels (Sample X -Nembe)

Sample X	pb	Ni	Cd	Cu	Fe	Mg	Cr	Zn	Mn	Ca	Ar	B	Sn	Ba
Raw	0.078	0.026	0.007	0.07	0.783	5.106	0.121	0.163	0.071	390	5.544	2.151	0.144	0.045
AFTER TREATMENT WITH ADSORBENTS USING 150 MICRON PARTICLES SIZE.														
1hrs	0.073	0.024	0.006	0.068	0.621	4.820	0.099	0.160	0.068	211	5.395	2.012	0.142	0.043
2hrs	0.057	0.023	0.005	0.005	0.413	4.581	0.095	0.153	0.056	135	5.122	1.812	0.129	0.038
3hrs	0.034	0.021	0.004	0.003	0.237	3.844	0.092	0.122	0.039	63	4.488	1.522	0.078	0.034
4hrs	0.010	0.020	0.004	ND	0.151	3.353	0.086	0.089	0.037	11	3.711	1.221	0.054	0.025

AFTER TREATMENT WITH ADSORBENTS USING 300 MICRON PARTICLE SIZE													
1hrs	0.076	0.026	0.007	0.070	0.654	4.986	0.121	0.161	0.069	259	5.543	2.151	0.144	0.043
2hrs	0.059	0.025	0.007	0.062	0.338	4.623	0.099	0.098	0.058	141	5.464	2.111	0.140	0.043
3hrs	0.043	0.023	0.006	0.044	0.123	4.202	0.095	0.097	0.055	80.4	4.732	2.007	0.134	0.041
4hrs	0.033	0.023	0.005	0.033	0.062	3.377	0.092	0.096	0.043	15	3.866	1.998	0.129	0.038

Table 1.1: Analysis of Pb with Langmuir and freundlich isotherm models for sample X.

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	0.010	0.00381	2.63	-2.0000	-2.4190
4	0.005	0.00397	1.26	-2.3010	-2.4012

Table 1.2: Analysis of Ni with Langmuir and freundlich isotherm models for sample X

t (hrs)	Ce (mg/l)	qe (g/l)	Ce/qe (g/l)	Log Ce (mg/l)	Log qe (g/l)
1	0.034	0.0000625	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	-3.3010

Table 1.3: Analysis of Fe with Langmuir and freundlich models for sample X

t (hrs)	Ce (mg/l)	qe (g/l)	Ce/qe (g/l)	Log Ce (mg/l)	Log qe (g/l)
1	0.480	0.00225	213.33	-0.3188	-2.6478
2	0.420	0.00413	101.69	-0.3768	-2.3840
3	0.323	0.00716	45.11	-0.5228	-2.1451
4	0.244	0.00963	25.34	-0.6126	-2.0457

Table 1.4: A comparism of coefficient of determination and other parameters for treatment with banana peel with sample X using the two models

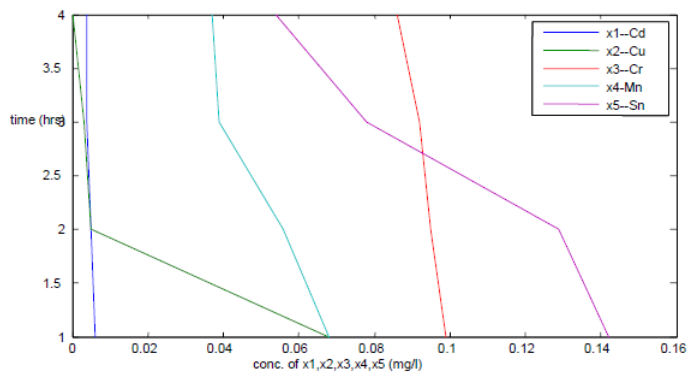| Meta l	Langmuir model					Freundlich model		
	R^2	b	K_L	R_L	Qo	R^2	n	K_F
Pb	0.98	1.79	0.00558	0.809	0.00312	0.81	8.83	1.2
Ni	0.78	11.29	0.00133	0,711	0.000118	0.85	0.56	1.39
Fe	0.86	1.44	0.00333	0.557	0.00231	0.93	0.699	1.10

Figure 1.3: plot of conc. of Cd, Cu, Cr, Mn, Sn vs time (Sample X, 150 micron size)
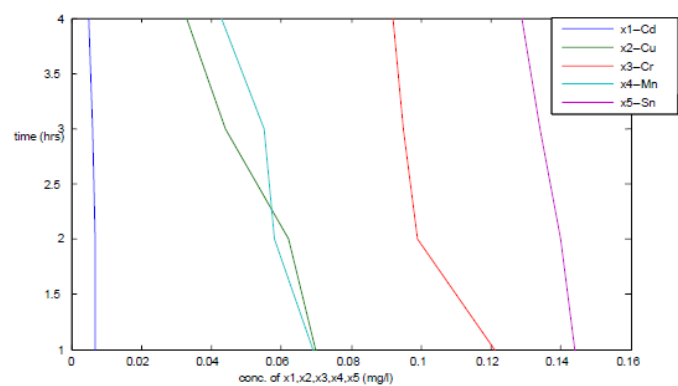

Figure 1.6: Analysis of Pb with freundlich model for sample X

Figure 1.4: plot of conc. of Cd, Cu, Cr, Mn, Sn vs time (Sample X, 300 micron size)

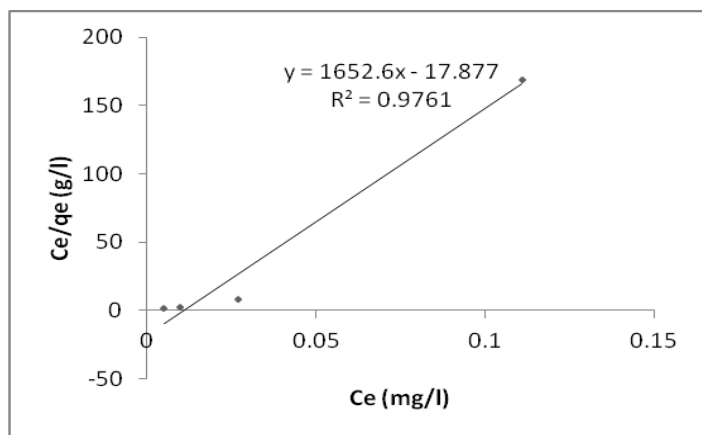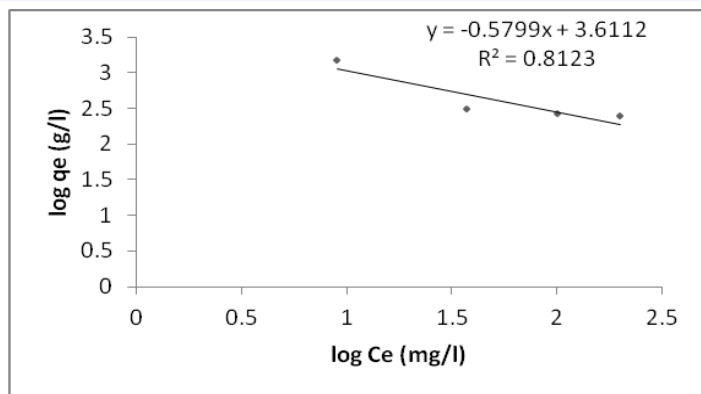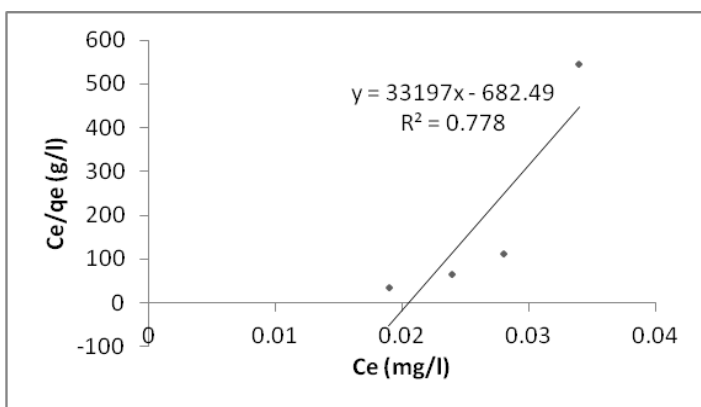**Figure 1.7:** Analysis of Ni with Langmuir model for sample X.

Figure 1.5: Analysis of Pb with Langmuir model for sample X
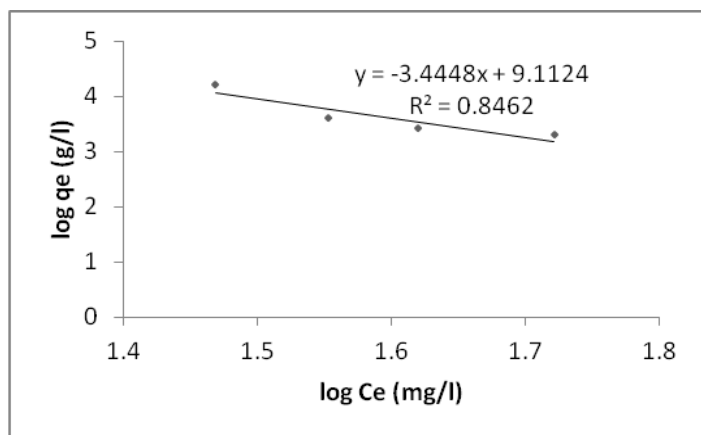
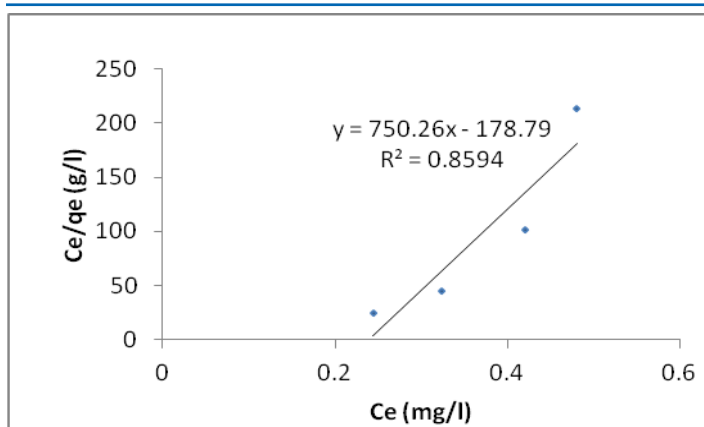**Figure 1.8:** Analysis of Ni with freundlich model for sample X

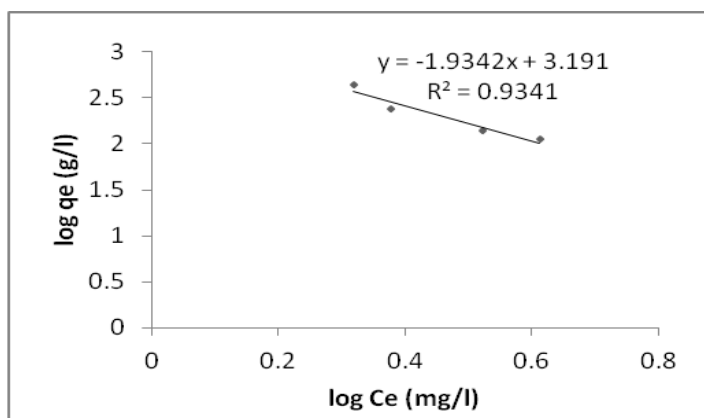**Figure 1.9:** Analysis of Fe with Langmuir model for sample X

Figure 2.0: Analysis of Fe with Freundlich models for sample X

Conclusion

Produced water obtained from Niger Delta region of Nigeria analyzed in this research was discovered to cotain traces of toxic and heavy metals as well as other impurities. The experimental procedures employed during the analysis of the metals were done with standard solution of each metal prepared at room temperature in the laboratory. The experiments were done successfully. The metal concentrations before and after treatment were analyzed with Atomic Absorption Spectrophotometer (AAS).

The result obtained from the raw sample (produced water) showed that the concentration of the metals in the sample were in excess of what is required before discharge or re-use as the case may be. On completion of the treatment using the adsorbent (banana peels), the concentration of most of the metals were reduced to acceptable limits. 150 micron size of the adsorbent produced an excellent result compared with 300 micron size. It was observed that the finer the particles, the larger the surface area, and the better the adsorption.

Two models were applied to validate the result obtained from the analysis. The models were Langmuir and freundlich isotherm models. The 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.

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