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TREATMENT OF PRODUCED WATER FROM NIGER DELTA OIL FIELDS USING SIMULTANEOUS MIXTURE OF ADSORBENTS

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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 four selected bio-adsorbents combined for treating PW from Niger Delta oil fields.

Orange peels (I), banana peels (II), sponge gourd (*Luffa cylindrica)* (III) and palm kernel fibers (IV) were washed with distilled water, sun-dried (24 hours) and oven-dried at $105\pm5^{o}C$ (3 hours, I and II), $150^{o}C$ (30 minutes, III) and $80^{o}C$ (3 hours, IV). They were ground into powder, sieved (150 microns, Group A) and (300 microns, Group B), washed with 0.4mol/L HNO_3, filtered and rinsed with distilled water. Samples of PW were obtained from fields R, X, and Y in the Niger Delta and analysed for heavy metals using an Atomic Absorption Spectrophotometer (AAS).

Samples were treated in adsorption column over 6 hours using the adsorbents simultaneously. Treated samples were analysed with AAS and characterised. Adsorption of heavy metals were evaluated using Langmuir and Freundlich models. Data were analysed using regression and other statistical methods.

For the 150 micron size of sample R, the percentage reductions for the metal concentrations (Pb, Ni, Cd, Cu, Fe, Mg, Cr, Zn, Mn, Ca, Ar, B, Sn, Ba) were found to be 100%, 52.7%, 100%, 100%, 85.87%, 19.48%, 100%, 92.8%, 17.74%, 98.86%, 22.32%, 29.56%, 78.06%, and 44.74% respectively, while the reduction in 300 micron size were 1.52%, 97.2%, 71.4%, 17.1%, 43.8%, 45.6%, 7.04%, 89.6%, 35.4%, 99.6%, 0.0001%, 1.19%, 14.19% and 0.002% respectively. The finer adsorbents were more effective. Similar results were obtained for PW samples from the other fields

Produced water from Niger Delta oil fields was effectively treated of contaminants using four selected bio-adsorbents mixed simultaneously.

Key Words: **Produced water, Heavy metals adsorption, adsorption isotherms, Bio-adsorbents**

Background of the Study

Produced water constitutes the largest waste stream from petroleum operations. Global production is estimated at over 60 million barrels per day. The volume produced from each petroleum reservoir depends on factors such as geological structure, petrophysics, reservoir drive mechanism, depletion stage, well completion method and production practices (Isehunwa and Onovae, 2011).

The management of produced water has become very important because of the volume involved, cost of treatment and environmental impact of entrapped chemicals. Many oil producing countries have therefore made laws and guidelines on the quality of produced water to be discharged.

In the early days of crude oil extraction from the subsurface, little or no effort was made in handling produced water. In some situations it was discharged to water bodies with little or no form of treatment, spilled on ground surface, or placed in underground pits to evaporate or soak into the subsurface. As time went on, petroleum engineers realized that water injection into the oil reservoirs could enhance production (Jerry, 2002).

Produced water during oil and gas production operations constitutes the most prominent waste in the industry. The water varies greatly in quality as well as quantity. At times, the water can be a useful by-product or even a marketable commodity. Produced water is sometimes considered a waste, but the industry is beginning to know that this waste water is a potential profit stream. Considering produced water as either a waste or commodity has its cost implication, which needs to be managed in-accordance with the specific objectives of each production project and also depending on the region. If this is not well addressed, the life of the well could be adversely affected, thereby leading to substantial recoverable reserves being left in the ground. Industry practice on handling produced water must also protect the environment or the operator could be fined by regulatory authorities. The methodology for handling produced water depends on the composition of the produced water, the location of the asset in consideration, the volume of reserves and the facilities available in the asset (Jerry, 2002).

Crude Oil Processing

Crude oil–gas–water mixtures produced from wells are generally directed, through flow lines and manifold system, to a central processing and treatment facility normally called the gas–oil separation plant. The first step in processing of the produced stream is the separation of the phases (oil, gas, and water) into separate streams. This takes place in mechanical devices known as two-phase gas–oil separators when the produced stream contains no water or three-phase separators when the produced stream contains water. Gas–oil

separation carried out in these separators is recognized as the backbone process in a train of field processing units of oil and gas operations. The separators are used to relieve the excess pressure due to the gas associated with the produced crude and, consequently, separating it from the oil. When water exists in the produced stream, separators are also used to separate the free water from the oil. Once separation is done, each stream undergoes the proper processing for further field treatment, as shown in figure 1.0.

Oil leaving the separator does not generally meet the purchaser's specifications. Oil may still contain between 10% and 15% water that exists mostly as emulsified water. The presence of this salt water presents serious corrosion and scaling problems in transportation and refinery operations. Water remaining in the oil is known as the basic sediments and water (BS&W). A maximum of 1% BS&W and in some cases less than 0.5% BS&W is acceptable. The limit on the salt content of the remnant water in oils is usually in the range of 10 to 15 PTB (pounds of salt per thousand barrels of oil). If these specifications are not met, then further treatment of the oil leaving the separator will be needed. Such treatment involves emulsion treatment/dehydration and desalting processes. After oil treating, there may be a need to stabilize the crude oil to optimize the oil recovery and reduce its volatility. Some produced crude oils contain hydrogen sulfide and other sulfur products. When it contains more than 400 ppm of H_2S gas, the oil is classified as sour crude. Sour crude oils present serious safety and corrosion problems. In such cases, another treatment known as the sweetening process is needed to remove hydrogen sulfide or reduce its content to acceptable limits (Abdel-Aal, *et al*, 2003).
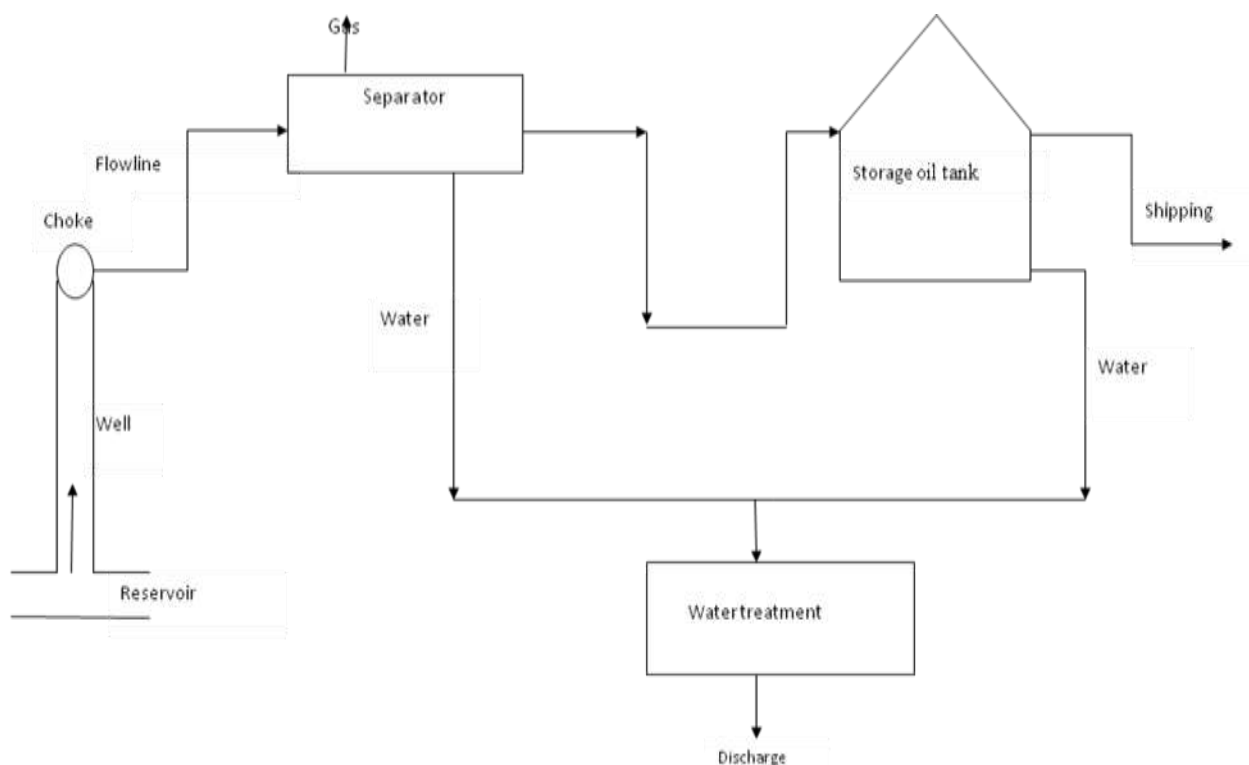

Figure 1.0: An outline of the processing surface field operations

Three-Phase Oil–Water–Gas Separation

Generally, water produced with the oil exists partly as free water and partly as water-in-oil emulsion. In some cases, however, when the water– oil ratio is very high, oil-in-water rather than water-in-oil emulsion will form. Free water produced with the oil is defined as the water that will

settle and separate from the oil by gravity. To separate the emulsified water, however, heat treatment, chemical treatment, electrostatic treatment, or a combination of these treatments would be necessary in addition to gravity settling.

Along with the water and oil, gas will always be present and, therefore, must be separated from the liquid. The volume of gas depends largely on the producing and separation conditions. When the volume of gas is relatively small compared to the volume of liquid, the method used to separate free water, oil and gas is called a free-water knockout. In such a case, the separation of the water from oil will govern the design of the vessel. When there is a large volume of gas to be separated from the liquid (oil and water), the vessel is called a three-phase separator and either the gas capacity requirements or the water–oil separation constraints may govern the vessel design. Figure 1.1 is a typical three- phase separator.
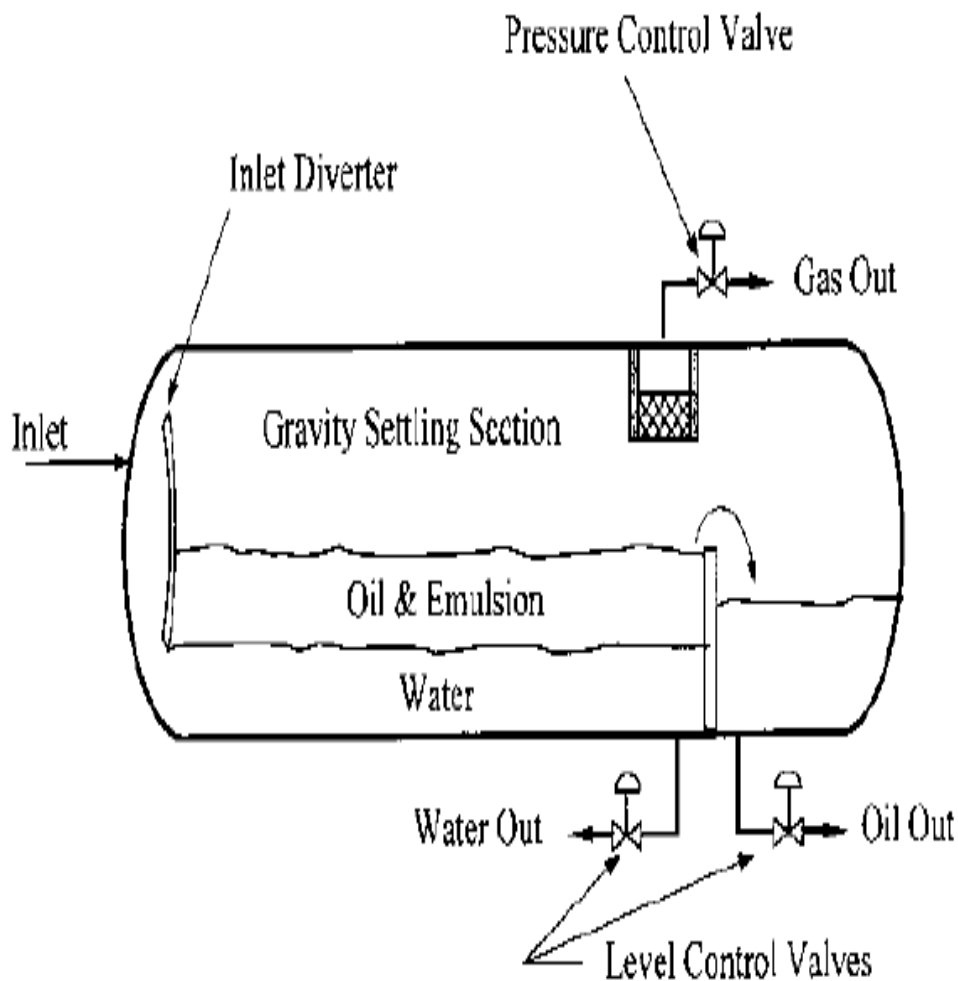
Figure 1.1: Horizontal three-phase separator (Abdel-Aal,*et al*. 2003)

Emulsion Treatment and Dehydration of Crude Oil

The fluid produced at the wellhead consists usually of gas, oil, free water, and emulsified water (water–oil emulsion). Before oil treatment begins, we must first remove the gas and free water from the well stream. This is essential in order to reduce the size of the oil–treating equipment.

The objective of this treatment is first to remove free water and then break the oil emulsions to reduce the remaining emulsified water in the oil. Depending on the original water content of the oil as well as its salinity and the process of dehydration used, oil-field treatment can produce oil with a remnant water content of between 0.2 and 0.5 of 1%. The remnant water is normally called the bottom sediments and water (B.S.&W.). The treatment process and facilities should be carefully selected and designed to meet the contract requirement for B.S &W. Care should be taken not to exceed the target oil dryness. Removal of more remnant water than allowed by contract costs more money while generating less income because the volume of oil sold will be based on the contract value of the B.S.&W (Khaled, *et al*, 2015).

The basic principles for the treating process are as follows:

(i). Breaking the emulsion, which could be achieved by either any, or a combination of the addition of heat, the addition of chemicals, and the application of electrostatic field

(ii). Coalescence of smaller water droplets into larger droplets

(iii). Settling, by gravity, and removal of free water.

Oil Emulsions

Rarely does oil production takes place without water accompanying the oil. Salt water is thus produced with oil in different forms as illustrated in Figure 1.2. Apart from free water, emulsified water (water-in-oil emulsion) is the one form that poses all of the concerns in the dehydration of crude oil.

Oil emulsions are mixtures of oil and water. In general, an emulsion can be defined as a mixture of two immiscible liquids, one of which is dispersed as droplets in the other (the continuous phase), and is stabilized by an emulsifying agent. In the oil field, crude oil and water are encountered as the two immiscible phases together. They normally form water-in-oil emulsion (W/O emulsion), in which water is dispersed as fine droplets in the bulk of oil. This is identified as type C in Figure 1.3. However, as the water cut increases, the possibility of forming reverse emulsions (oil-in-water, or O/W emulsion) increases. This is type B in Figure 1.3.
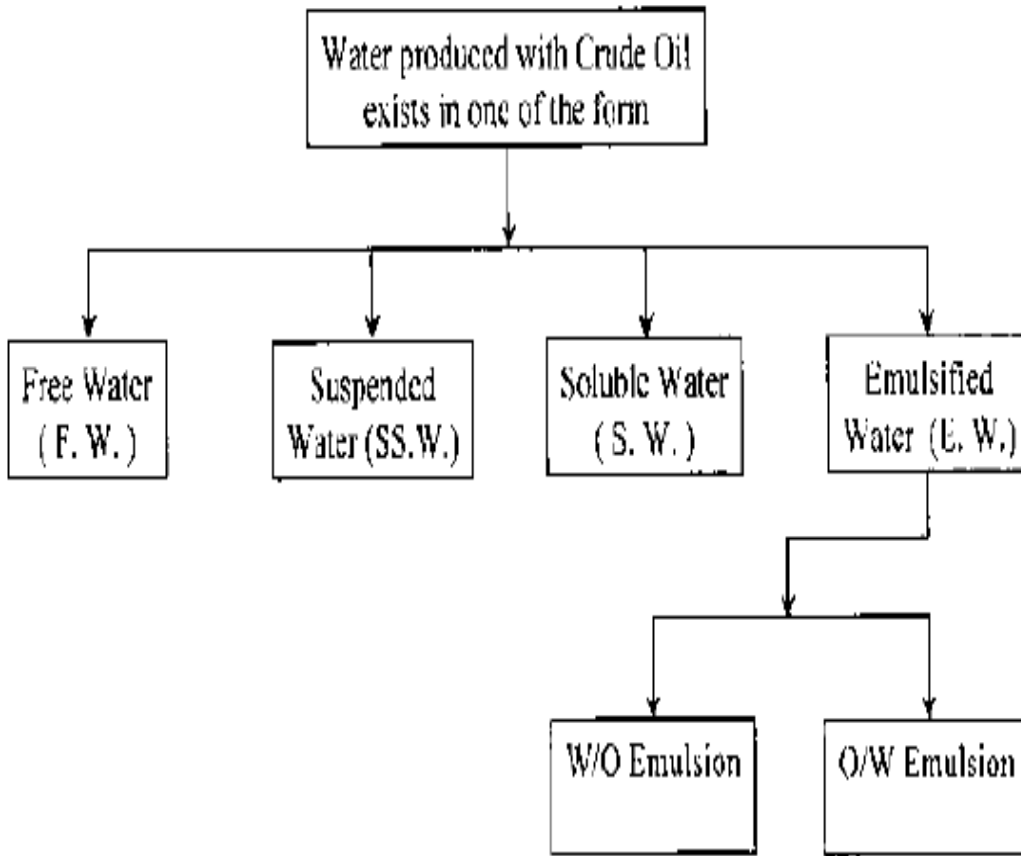
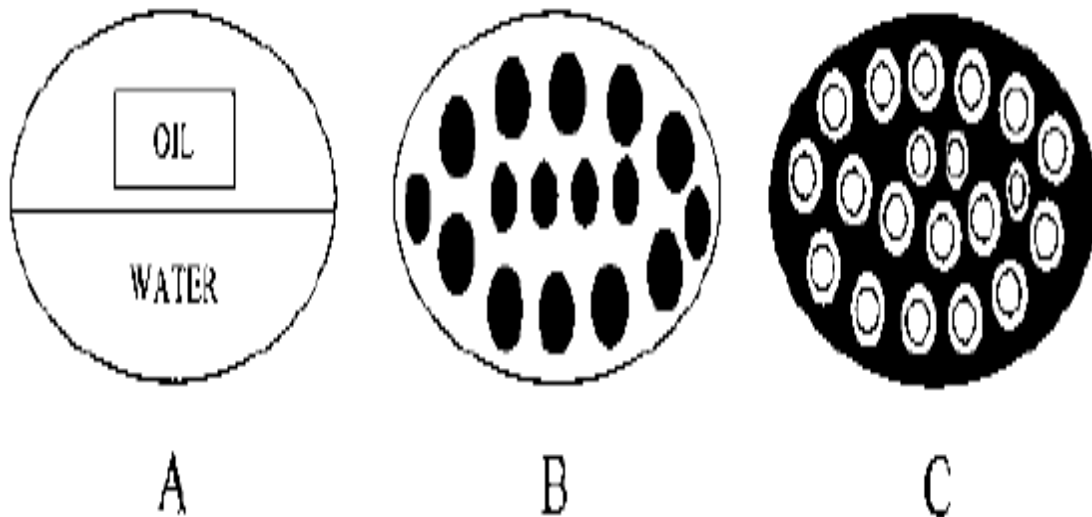Figure 1.2: Forms of saline water produced with crude oil (Abdel-Aal, *et al*, 2003).

Fig 1.3: Schematic representation of (A) a non-dispersed system, (B) an O/W emulsion, and (C) a W/O emulsion.

(Abdel-Aal, *et al*, 2003).

Options available for Managing Produced Water

In managing produced water, some of the options available to the oil and gas operators include (Arthur, 2005):

(i)   Prevent the production of water unto surface facility – using separators downhole which separate water from gas and oil stream and re-inject it into suitable formation. Also, polymer gels can be used to block fissures that contribute towards produced water. Waste water is eliminated via this option and it is an attractive strategy, however it is not always possible.

(ii)   Injection of produced water – involving re-injection of produced water into the same formation or other suitable formation; involves the conveyance of the produced water from the production to the injection site. Treatment of the produced water to be injected, thereby reducing fouling and scaling agents and bacteria might be possible. Although waste water is generated in this option, the waste is replaced back into the reservoir.

(iii)   Produced water discharge – involves treatment of produced water to meet onshore or offshore discharge regulations. Although, some locations do not require treatment before discharge.

(iv)   Re-use of wastewater for oil and gas operations – involving the treating of produced water to meet the quality required for using it for drilling and work-over operations.

(v)   Used to support other multi-purpose benefits – in some instances, significant treatment of produced water is a crucial requirement in order to meet the quality required for important benefits such as irrigation, restoration of arable land, cattle and animal consumption, and drinking water for human consumption

Materials and method

The materials used in this research work were: Produced water samples from Niger delta oil fields, Luffa cylindrica (*Sponge gourds*)**,** Banana peels, Orange peels, Palm kernel fiber, Chemical reagents, Filter paper, Glass wares, etc.

The equipment used were: Milling Machine**,** Adsorption column**,** Mechanical Shaker**,** Oven**,** Atomic Absorption Spectrophotometer (AAS)**,** Weighing balance**,** pH meter**,** Refrigerator**,** Sieves, 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) as well as Barium (Ba) and some other contaminants in the produced water samples.

Collection of Samples and Materials

Produced water samples were collected from four different oil fields in the Niger Delta area. Sample R was collected from Imo River oil field in Rivers State; Sample X was collected from Nembe oil field in Bayelsa State, sample Y was from Kolo creek oil field in Rivers/Bayelsa State. The adsorbents (Banana peels, Orange peels, Luffa cylindrica) were purchased from a local market in Ado-Ekiti, Nigeria, and the palm-kernel fiber was collected from ABUAD farm in Ado-Ekiti, Ekiti state. All the chemicals and other reagents used were of analytical and standard grade

Figure 1.4 Luffa cylindrica and palm kernel fiber

Figure 1.5: Banana peels and raw orange peels

Figure 3.7 Produced water samples and filtrates from adsorption process

Preparation of Banana Peels, Orange Peels, Luffa Cylindrica, Palm Kernel Fiber and the Experimental Procedure

The adsorbents were prepared by washing them thoroughly with distilled water to remove any dirt that may be stuck on it. They were then cut into pieces; suns dried (24 hours during hammer time period), and were

finally dried in an oven at 105°C for 3 hours for banana and orange peels, 150°C for 30 minutes for luffa cylindrica, and 80°C for 3 hours for palm kernel fiber

Simultaneous mixture of the Adsorbents in the Adsorption Column

After drying, the adsorbents were crushed using the milling machine and were sieved with the mechanical shaker using mesh size of 150 and 300 microns. The sieved samples were treated separately with 200ml of 0.4mol L^{-1} HNO_3 for 24 hours. After which they were filtered and rinsed with distilled water until the filtrate was near neutral. 2-gram of the residue (adsorbents-150 microns) each (8-gram in total) was mixed simultaneously and was packed in one of the adsorption column. 250 ml of sample R (produced water) was flown through the adsorption column containing the adsorbents to allow adsorption to take place. The filtrate was collected at an interval of two hours and was subjected to analysis using AAS to determine the concentration of the heavy metals listed above. The mixture of the adsorbents on the column was replaced with a fresh one and sample X, and Y was flown in that order through the adsorption column and the filtrate of each was collected at an interval of two hours as well and analyzed. The process was repeated all over again using a particle size of 300 micron.

Results and Discussion

The results presented in table 1.0 to 1.3 were obtained from the simultaneous mixture of the adsorbents used for the treatment of produced water samples (R, X, Y) in the adsorption column. The results from each sample were for both 150 and 300 micron particle size.

The plots in figure 1.6 extracted from table 1.0 were more of linear form showing that the more the contact time, the more the produced water sample loses its toxic metals. At 8 hours with 150 micron particles size, lead (Pb), cadmium (Cd), cupper (cu), and chromium (Cr) were all completely removed from the produced water sample. This means that Pb, Cd, Cu and Cr were reduced to zero from their raw values of 0.132, 0.014, 0.076 and 0.071mg/l to 0.00 mg/l each. Other metals (nickel, iron, magnesium zinc, manganese, calcium, arsenic, boron, tin barium etc) were as well reduced to the barest minimum beyond the regulatory limits as set by the regulatory bodies

The result obtained with the 300 micron particle size (fig.1.7) were equally good as the metals were all affected positively in terms of the reduction of their concentrations on the produced water. The metals were all reduced to allowable limits though none of them could be removed completely as can be seen when compared with 150 micron particle size. This goes to show that in the adsorption process, contact time and particle size matter a lot as they are among the determining factors for effective and efficient adsorption process. The more the surface area of the adsorbents and the more the contact time, the better the adsorption process.

The plots (fig. 1.8 from table 1.1) are all linear with negative slopes; it shows that the more the contact time between the adsorbents and the produced water sample, the more the metal concentrations in the produced water go down. Lead (pb) and cupper (cu) were completely adsorbed from the sample after eight hours (8hrs)

of treatment while other metals were positively affected but not completely removed. The metals removal depends on the activeness of the adsorbents. The more the availability of the adsorption sites, the more the metals is adsorbed.

From the plots (fig.1.9) for 300 micron size, very good results were also obtained just like that of 150 micron particle size. The concentration of almost all the metals investigated were reduced to the barest minimum as required by the regulatory body though better results were obtained with 150 micron size because of larger surface area.

The plots (fig.2.0) extracted from table table1.2 were all linear with negative slopes; it shows that the more the contact time between the adsorbents and the produced water sample, the more the metal concentrations in the produced water drop. Cupper (Cu) was found to be completely removed from the sample after eight (8) hours of treatment.. It was observed that the produced water sample from Kolo creek oil field does not contain Cadmium at all. This could be as a result of the location of the field.

Figure 2.1 is a plot of Pb, Ni, Cu, Fe (mg/l) against time (hrs) for 300 micron particle size. The plots are linear with same negative slopes as the previous one of 150 micron size. From the plots, cupper (Cu) was completely removed from the sample after eight (8) hours of treatment. Zn, Mn, Ca and Ba were also completely eliminated from the sample after 8 hours of treatment according to table 1.2

In summary it was observed that adsorption process is more favorable when the surface area of an adsorbent is large. The larger the surface areas, the smaller the particles and the more the adsorption sites for effective adsorption process. From the research, better results were obtained with 150 micron size because of its large surface area compared with 300 micron size. Simultaneous mixture of the adsorbents has proved worthwhile in the treatment of produced water from Niger Delta oil field. The results obtained were in accordance with the discharge limits as stated by the regulatory bodies.

Analysis of the results using Adsorption Isotherms

The Langmuir Model

This isotherm model is used to express the relationship that exists between the quantity of extracted material and its equilibrium concentration in bulk of solutions. Langmuir isotherm is only acceptable (valid) for monolayer adsorption on a surface containing finite number of similar sites. Langmuir isotherm model assumes a uniform adsorption on the surface and transmigration in the plane of the surface. Langmuir isotherm can be expressed as:.

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

where q_e is capacity of adsorption 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 isotherm model is a model that considers adsorption process to occur on heterogeneous surfaces; and the model further states that adsorption capacity is related to the concentration of the adsorbent in question. The freundlich model can 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 reaction intensity. These freundlich parameters K_F and $1/n$ can be estimated graphically from the plot of experimental values and then applying the freundlich equation in this form:

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

The linear plot of c_e / q_e vs c_e indicates that adsorption process follows the Langmuir model (figure 2.2). The values of Q and b were obtained from the slope and intercept of the plotted data (table 1.5). The correlation coefficient (R^2) was found to be 0.9676 for Pb and 0.0038 for same Pb (figure 2.3). The results revealed that the Langmuir sorption isotherm model is good for equilibrium study for Pb. This suggests the formation of monolayer coverage of the adsorbate on the adsorbent surface for the metal ion.

The quantity of metal ion extracted per unit mass of the adsorbent rises with the metal concentration as expected and the sorption capacity was also determined. The value of the equilibrium separation factor $R_{L,}$ of 0.812 (table 1.5) revealed that the sorption of Pb ion on the simultaneous mixture of the adsorbents was found to be a favorable process. The correlation coefficient from freundlich isotherm plot of $log\ q_e$ vs $log\ c_e$ (figure 2.3) could not give a better result, showing that freundlich sorption isotherm model is not suitable for equilibrium study of Pb.

For the Ni adsorption, the linear plot of $log q_e$ vs $log c_e$ indicates that adsorption obeys the freundlich sorption model (figure 2.5). The values of k_f and n were determined from the slope and intercept of the plot respectively (table 1.5). The correlation coefficient (R^2) was estimated to be 0.9835. This shows that the freundlich sorption isotherm is good for equilibrium study of Ni. This suggests the formation of heterogeneous layer coverage of the adsorbate on the adsorbent surface for the metal ion. The values of k_f and n (table 1.5) indicate the adsorption process is favorable. Langmuir isotherm model result for Ni adsorption (fig 2.4) was not that bad when looked into critically, but fortunately Freundlich model gave a better result when it comes to Ni adsorption on the adsorbent surface.

For Fe (iron) adsorption on the simultaneous mixture of the adsorbents, Freundlich-type isotherm model gives a better result than Langmuir isotherm model. The plot of $log q_e$ vs $log c_e$ indicates that adsorption obeys the freundlich adsorption model (figure 2.7). The values of k_f and n were calculated from the slope and intercept of the plotted data (table 1.5). The correlation coefficient (R^2) was estimated as 0.8723. This shows that the freundlich sorption isotherm model is suitable for equilibrium study for Fe, when compared with the value of R^2 (0.7484) on the Langmuir plot (figure 2.6). This suggests the formation of heterogeneous layer coverage

of the adsorbate on the adsorbent surface for the metal ion. The values of k_f and n as indicated on (table 1.5) indicate that the sorption of Fe on the adsorbent surface is a favorable process

Table 1.0: Results of the concentrations (mg/l) of metals in sample R (Imo River sample) for simultaeneous mixture

Sapmle R	pb	Ni	Cd	Cu	Fe	Mg	Cr	Zn	Mn	Ca	Ar	B	Sn	Ba
Raw	0.132	0.036	0.014	0.076	0.552	3.699	0.071	0.125	0.062	430	4.65	1.59	0.155	0.038
AFTER TREATMENT WITH ADSORBENTS USING 150 MICRON PARTICLES SIZE.														
2hrs	0.112	0.025	0.013	0.07	0.488	3.455	0.07	0.122	0.058	390	4.43	1.48	0.124	0.037
4hrs	0.027	0.023	0.01	0.067	0.355	3.256	0.067	0.112	0.055	155	4.32	1.352	0.088	0.032
6hrs	0.011	0.02	0.008	0.005	0.244	3.122	0.032	0.068	0.051	55	3.82	1.322	0.067	0.024
8hrs	ND	0.017	ND	ND	0.078	2.965	ND	0.009	0.051	4.9	3.612	1.12	0.034	0.021

AFTER TREATMENT WITH ADSORBENTS USING 300 MICRON PARTICLE SIZE														
2hrs	0.132	0.034	0.013	0.076	0.451	3.655	0.071	0.122	0.061	360	4.62	1.577	0.154	0.036
4hrs	0.131	0.034	0.011	0.073	0.422	3.522	0.068	0.122	0.055	211	4.61	1.572	0.152	0.036
6hrs	0.131	0.003	0.01	0.071	0.312	3.234	0.066	0.111	0.053	44	4.61	1.571	0.139	0.032
8hrs	0.13	0.001	0.004	0.063	0.311	2.011	0.066	0.013	0.04	1.3	4.58	1.571	0.133	0.031

Table 1.1: Results of the concentrations (mg/l) of metals in sample X (Nembe sample) for simultaneous mixture

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.														
2hrs	0.068	0.024	0.006	0.058	0.422	4.722	0.099	0.161	0.067	200	5.297	2.011	0.141	0.042
4hrs	0.054	0.023	0.005	0.003	0.233	4.281	0.097	0.143	0.055	120	5.024	1.722	0.122	0.035
6hrs	0.007	0.022	0.005	0.001	0.007	3.445	0.092	0.089	0.049	44	4.188	1.323	0.077	0.031
8hrs	ND	0.022	0.004	ND	0.005	3.256	0.082	0.059	0.036	4.8	3.612	1.121	0.034	0.021

AFTER TREATMENT WITH ADSORBENTS USING 300 MICRON PARTICLE SIZE													
2hrs	0.074	0.026	0.007	0.068	0.544	4.721	0.121	0.161	0.069	250	5.542	2.151	0.142	0.043
4hrs	0.058	0.024	0.006	0.052	0.038	3.223	0.098	0.098	0.057	120	5.412	2.101	0.133	0.043
6hrs	0.033	0.023	0.006	0.041	0.023	2.101	0.094	0.095	0.053	70.52	4.231	2.005	0.127	0.041
8hrs	0.023	0.023	0.005	0.024	0.016	1.401	0.091	0.095	0.039	1.41	3.822	1.994	0.127	0.035

Table 1.2: Results of the concentrations (mg/l) of the metals in sample Y (Kolo creek sample) for simultaneous mixture

Sample Y	pb	Ni	Cd	Cu	Fe	Mg	Cr	Zn	Mn	Ca	Ar	B	Sn	Ba
Raw	0.192	0.231	ND	0.038	0.805	5.578	0.397	0.174	0.081	505	4.522	1.921	1.74	0.091
AFTER TREATMENT WITH ADSORBENTS USING 150 MICRON PARTICLES SIZE.														
2 hrs	0.188	0.189	ND	0.035	0.651	4.981	0.281	0.172	0.074	308	3.221	1.722	1.505	0.072
4 hrs	0.185	0.164	ND	0.033	0.362	3.554	0.179	0.158	0.058	150	2.792	1.441	1.449	0.058
6 hrs	0.171	0.124	ND	0.021	0.244	2.482	0.155	0.132	0.023	55.88	2.204	1.202	1.322	0.051
8 hrs	0.171	0.118	ND	ND	0.172	1.326	ND	0.112	0.019	1.11	1.678	1.142	1.228	0.045

AFTER TREATMENT WITH ADSORBENTS USING 300 MICRON PARTICLE SIZE														
2 hrs	0.184	0.231	ND	0.037	0.755	5.499	0.395	0.173	0.075	300	4.442	1.898	1.722	0.085
4 hrs	0.066	0.188	ND	0.035	0.621	5.355	0.382	0.165	0.071	160	4.311	1.852	1.667	0.065
6 hrs	0.043	0.094	ND	0.031	0.433	3.221	0.341	0.122	0.055	40	3.311	1.733	1.552	0.032
8 hrs	0.008	0.028	ND	ND	0.291	0.244	0.332	ND	ND	ND	3.201	1.733	1.499	ND

Table 1.3: Analysis of Pb (lead) using Langmuir and freundlich models for simultaneous mixture of the adsorbents using sample R

t (hrs)	Ce (mg/l)	qe (g/l)	Ce/qe (g/l)	Log Ce (mg/l)	Log qe (g/l)
2	0.112	0.000625	179.200	-0.9508	-3.2041
4	0.027	0.00328	8.231	-1.5686	-2.4841
6	0.011	0.00378	2.910	-1.9586	-2.4225
8	0.000	0.00413	0.000	0.000	-2.3840

Table 1.4: Analysis of Ni (nickel) using Langmuir and freundlich models for simultaneous mixture of the adsorbents using sample R

t (hrs)	Ce (mg/l)	qe (g/l)	Ce/qe (g/l)	Log Ce (mg/l)	Log qe (g/l)

2	0.025	0.000344	72.67	-1.6020	-3.4634
4	0.023	0.000406	56.65	-1.6383	-3.3915
6	0.020	0.000501	40.00	-1.6989	-3.3010
8	0.017	0.000594	28.62	-1.7696	-3.2262

Table 1.5: A comparism of Correlation coefficient and other parameters for the simultenous mixture of the adsorbents with sample R using the two models

metal	Langmuir model					Freundlich model		
	R^2	b	K_L	R_L	Q_o	R^2	n	K_F
Pb	0.97	1.75	0.00525	0.812	0.003	0.038	6.33	0.9932
Ni	0.97	47.6	0.0099	0.369	0.00021	0.98	0.794	1.39
Fe	0.74	15.5	0.00399	0.105	0.000258	0.87	2.64	0.993
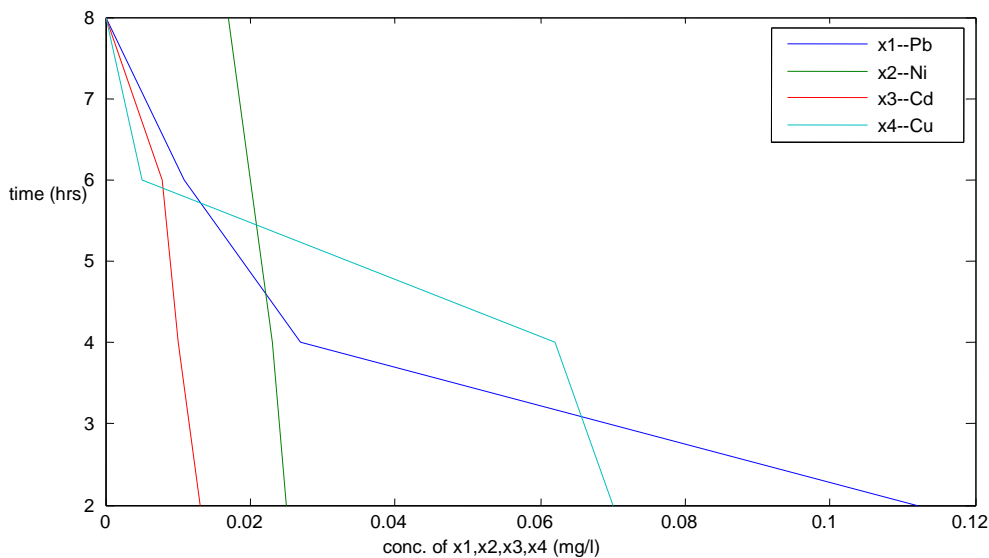
Figure 1.6: plot of conc. of Pb,Ni,Cd,Cu vs time. [Sample R, 150 micron size)
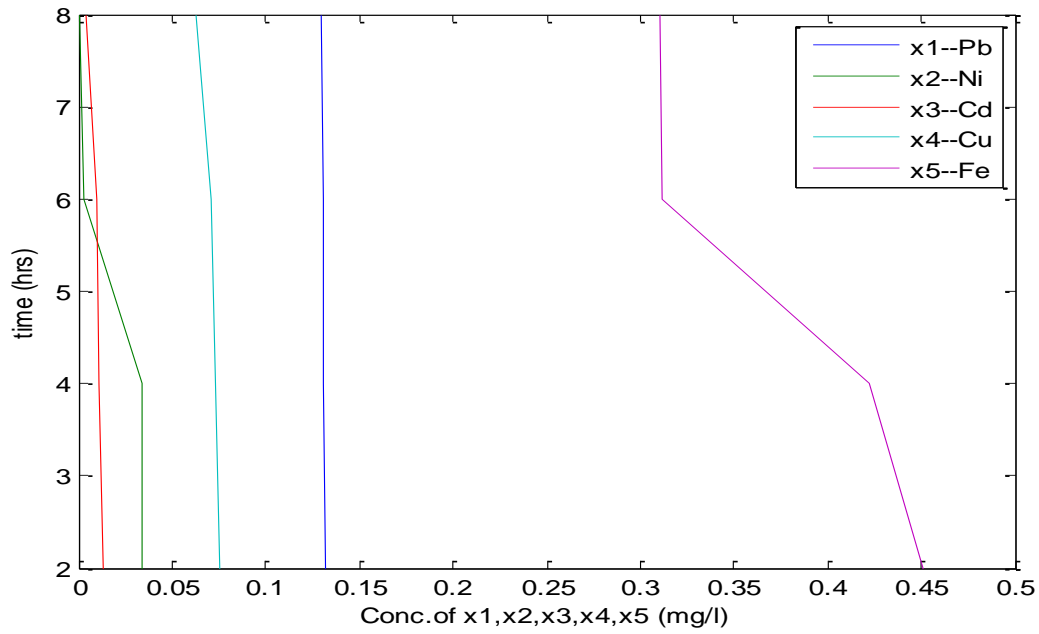
Figure 1.7: plot of conc. of Pb,Ni,Cd,Cu vs time. (Sample R, 300 micron size)
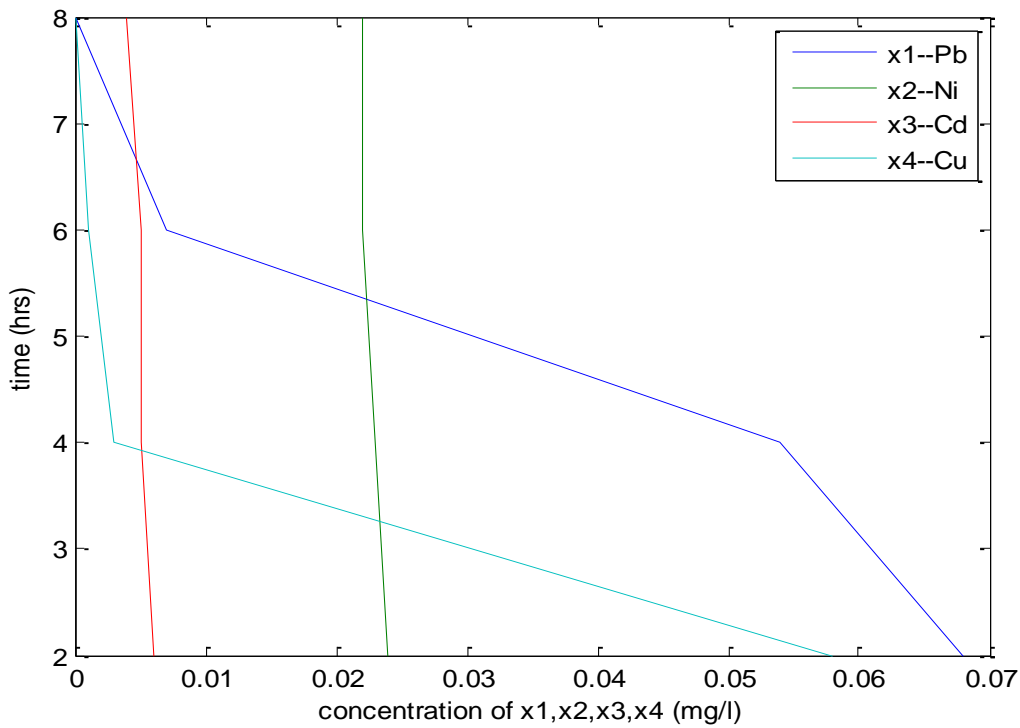
Figure.1.8: plot of conc. of Pb,Ni,Cd,Cu vs time. (Sample X, 150 micron size)
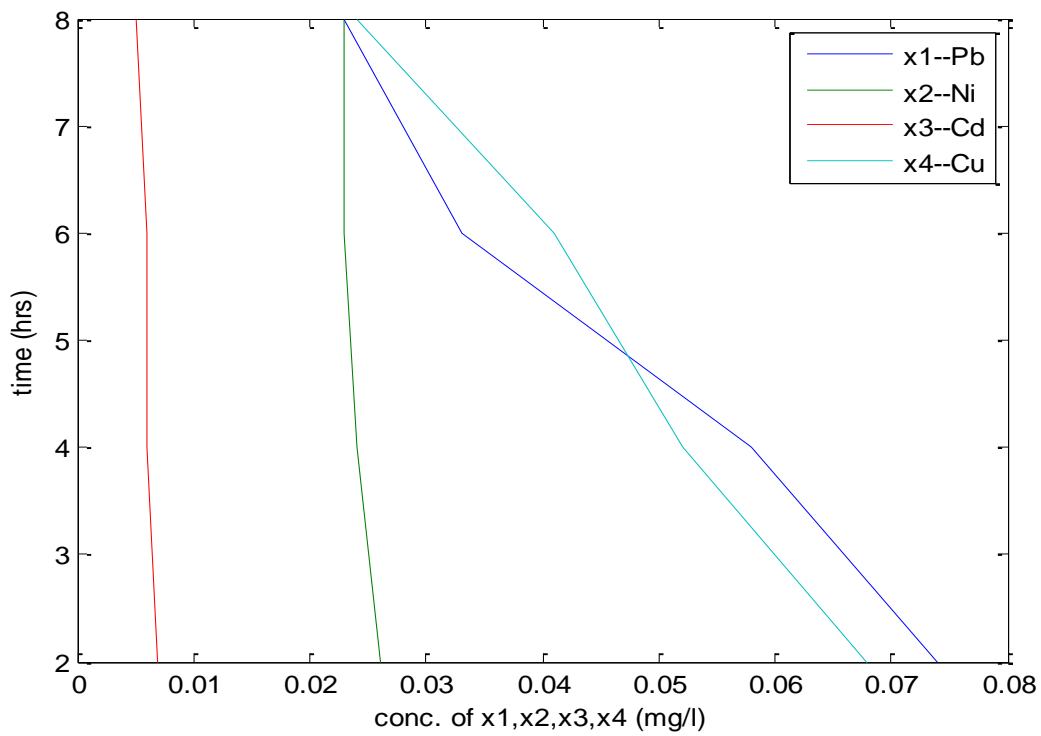
Figure 1.9: Plot of conc. of Pb,Ni,Cd,Cu vs time {Sammple X, 300 micron size)
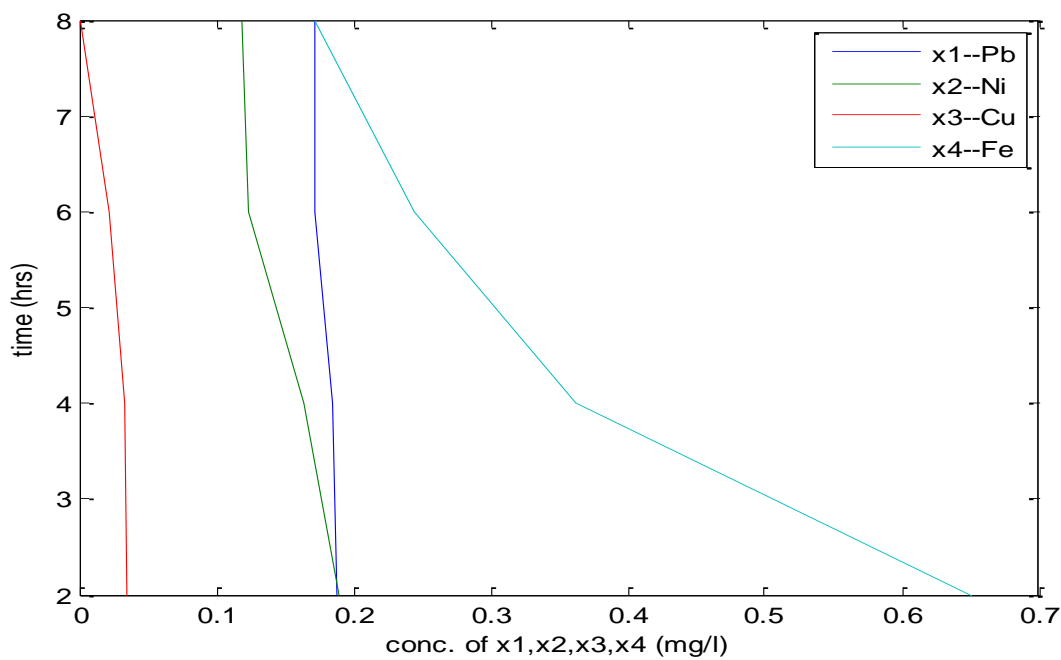
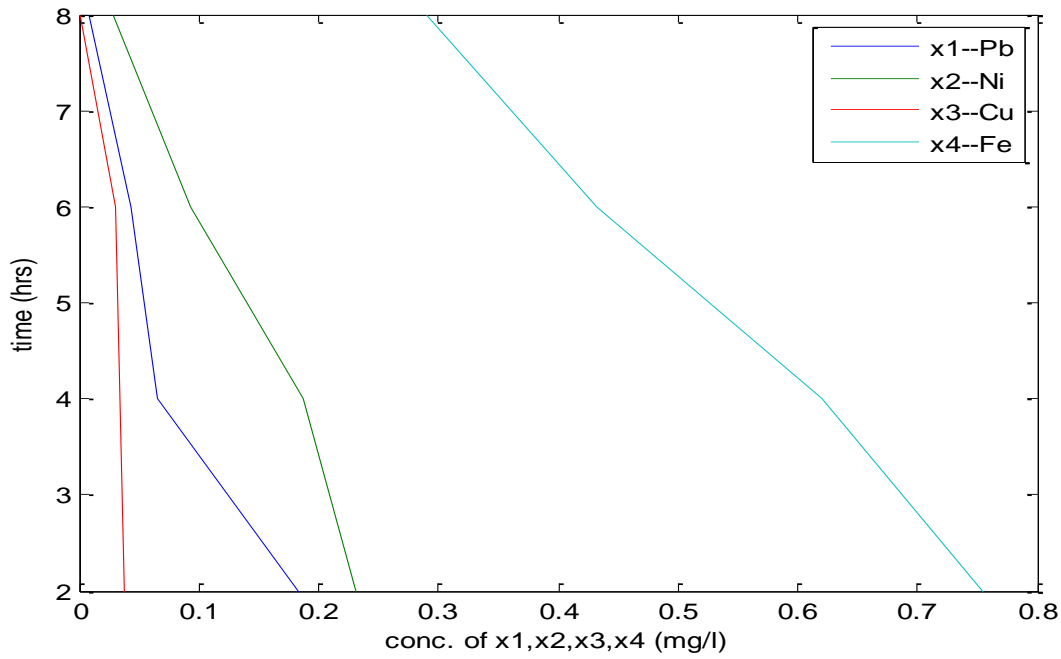Figure 2.0: plot of conc. of Pb, Ni, Cu, Fe vs time (Sample Y, 150 micron size)

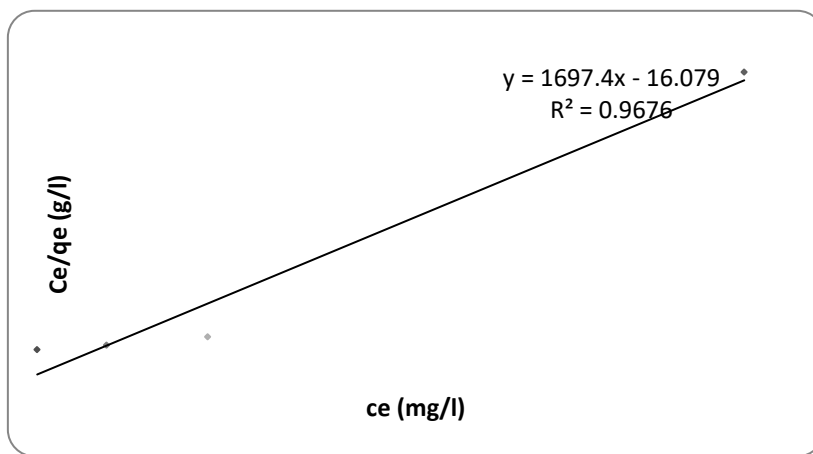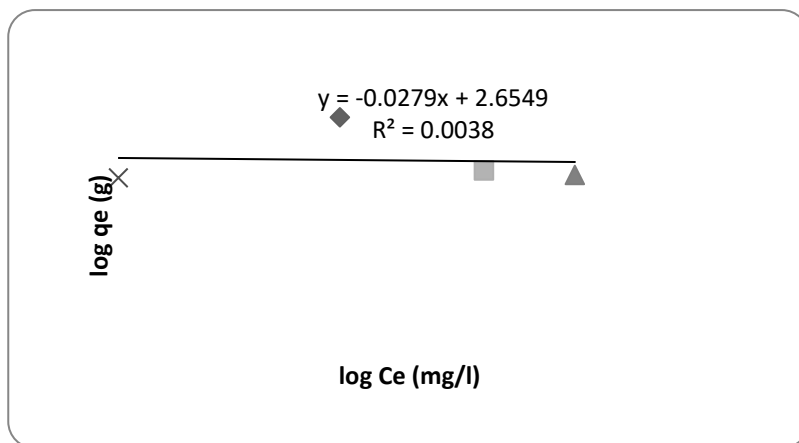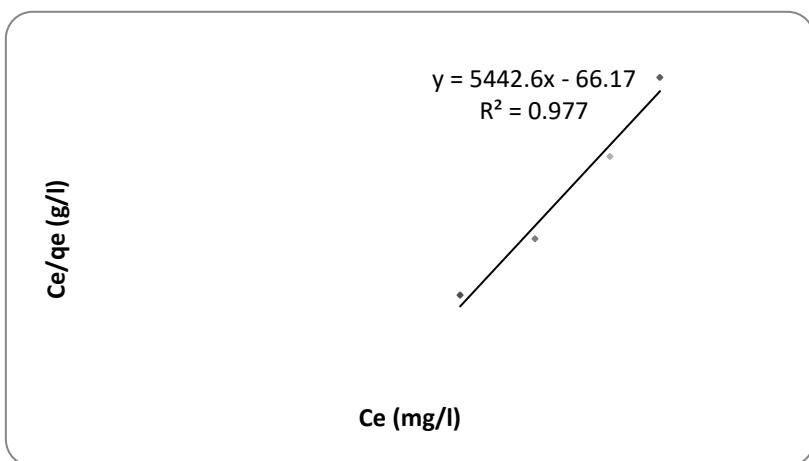Figure 2.1: plot of conc of Pb, Ni, Cu, Fe vs time. (Sample Y, 300 micron particle size)
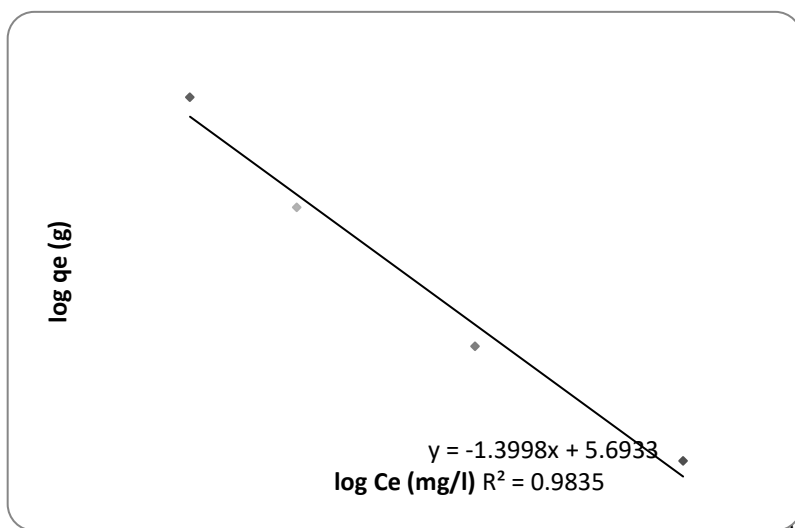

$y = 1697.4x - 16.079$
$R^2 = 0.9676$
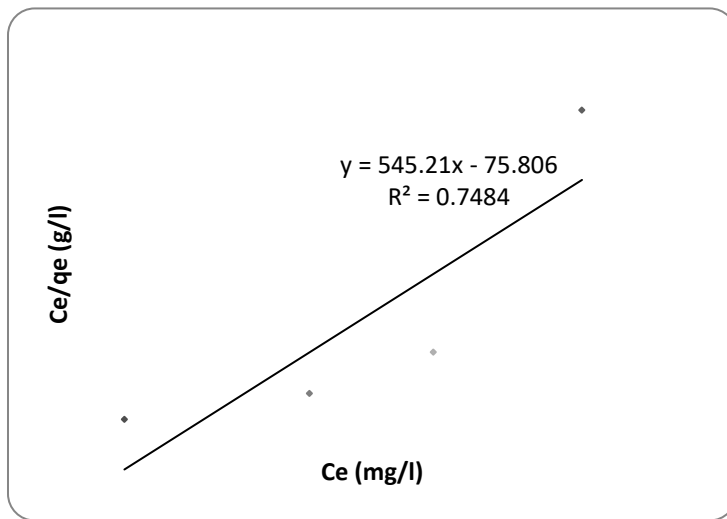
Figure 2.2 : Analysis of Pb using langmuir isotherm for sample R

$y = -0.0279x + 2.6549$
$R^2 = 0.0038$

...ndlich isotherm for sample R

y = 5442.6x - 66.17
R² = 0.977

Ce/qe (g/l)

Ce (mg/l)

nuir isotherm for sample R

log qe (g)

y = -1.3998x + 5.6933
log Ce (mg/l) R² = 0.9835

dlich isotherm for sample R

$y = 545.21x - 75.806$
$R^2 = 0.7484$

Ce/qe (g/l)

Ce (mg/l)

Langmuir isotherm for sample R

$y = -0.8564x + 2.6813$
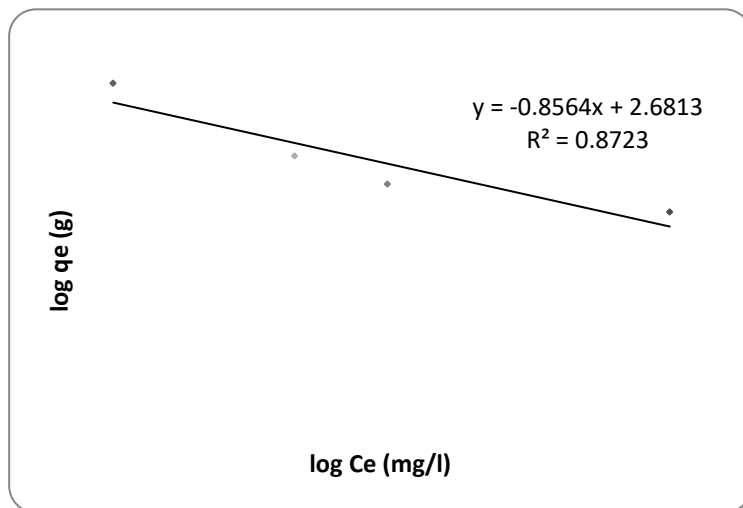$R^2 = 0.8723$

log qe (g)

log Ce (mg/l)

Figure 2.7 : Analysis of Fe using Freundlich isotherm for sample R

Conclusion

The produced water samples investigated in this research were discovered to contain traces of toxic and heavy metals. The experimental procedures used in the analysis of these metals were done with standard solutions of each metal prepared at room temperature. The experiments were successful; the metal concentrations before and after treatment with the bioadsorbnts were analyzed with Atomic Absorption Spectrophotometer

Before the treatment, the analysis showed that the concentrations of the metals in the samples were in excess of what is expected before discharge or re-use as the case may be. After the treatment using the adsorbents mixed simultaneously, the concentrations of most of the metals were reduced to the expected level as can be seen from the results. Simultaneous mixture of the adsorbents produced a good result when compared with individual use of the adsorbents.

Two models were employed in this research to validate the results obtained from these analyses. These models were simply the ***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

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