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TREATMENT OF PRODUCED WATER FROM NIGER DELTA OIL FIELDS USING SEQUENTIAL MIXTURE OF BIO-ADSORBENTS

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ABSTRACT

Produced water (PW) is extracted from the reservoir alongside oil, and it often contains heavy metals and other impurities that are harmful to man and the environment at large. Most of the treatment technologies that have been in use for years have been reported to be ineffective in reducing some of the impurities and metal concentrations to allowable disposal levels. This study was designed to evaluate the effectiveness of four selected local materials 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 $105\pm 5^{\circ}\text{C}$ (3 hours, I and II), 150°C (30 minutes, III) and 80°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 analyzed for heavy metals using an Atomic Absorption Spectrophotometer (AAS).

The produced water Samples were treated in adsorption column over 7 hours using the bio-adsorbents sequentially. Treated samples were analyzed with AAS and characterized. Adsorption of metals was evaluated using Langmuir and Freundlich models and Data were analyzed using regression and other statistical methods

For the 150 micron size on sample R, lead (Pb), cadmium (Cd), copper (Cu), and chromium (Cr) were completely (100%) adsorbed from the produced water after 8 hours of treatment while other metals (Ni, Fe, Mg, Zn, Mn, Ca, Ar, B, Sn, Ba) were found to be 86.11%, 90.76%, 39.25%, 94.40%, 43.55%, 99.26%, 54.62%, 44.53%, 84.52%, and 47.37% respectively. while the reduction in 300 micron size were 23.48% for Pb, 80.20% for Ni, 71.42% for Cd, 19.73%, for Cu. 43.65% for Fe, 34.79% for Mg, 12.67% for Cr, 88.8% for Zn, 35.48% for Mn, 98.95% for Ca, 23.01% for Ar, 44.52% for B, 14.83% for Sn and 23.68% for Ba respectively. The finer adsorbent with large surface area was more effective. Similar results were obtained for Produced water samples from the other fields.

Sequential mixture of the selected bio-adsorbents proved worthwhile in the treatment of contaminants in Produced water from Niger Delta oil fields.

Key Words: Produced water, Toxic metals, adsorption column, adsorption isotherms, Bio- adsorbents

Background of the Study

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).

Produced water Composition

The composition of produced waters varies. This could be as a result of different formation characteristics, reservoir compositions, and other activities engaged by industries as a result of well maintenance and development. Produced water constituents are made up of two groups (organic and inorganic compounds). Inorganic constituents in produced water are either insoluble (examples are precipitates, grit, inorganic scales and others) and soluble. Soluble salts are divided into anions and cations. Examples of cations in produced water are monovalent cations of sodium and potassium and the multivalent cations of calcium, iron, and magnesium. Major anions are sulphate, chlorides, carbonate as well as bicarbonate. Non-charged soluble inorganic species can as well be found; examples of these include silicate (H_4SiO_2) and Borate (H_3BO_3), etc.

Organic compounds in produced water are either separable with gravimetric and de-oiling methods (oils and greases are grouped into this category), or they are soluble, requiring more complex processing for removal. Soluble organic constituents could be grouped into compounds that are dissociable into ionic form with phenol, mono-carboxylic acids and di-carboxylic acids as examples and into compounds that are not dissociable such as non-ionic soluble oils and glycols.

Generally, most produced waters have pH values between 6 and 8 (Kulthanan, 2013). Buffering is usually made available through the presence of bicarbonate. Normally the pH value of produced water would remain neutral unless caustics soda or acidic solution is added in the course of treatment.

Treatment is required in most cases in order to ensure conformance with beneficial effluent use standards; in most of the applications, the major pressing wastewater treatment needs includes one or more of the following:

- (i) Removal of oil and grease.
- (ii) Reduction of TDS in produced water.
- (iii) Reduction in concentration of Benzene.
- (iv) Reduction in concentration of biological oxygen demand emanating from soluble organics.
- (v) Suspended solids control
- (vi) Decrease in volumes of brine required in disposal.
- (vii) Regulation of total and fecal coliforms in final wastewater stream.
- (viii) Elimination of some special constituents, such as boron, that prevents an end use (such as irrigation).
- (ix) Moderation of the sodium absorption ratio parameter (SAR) to prevent clayey soil damage in land application (irrigation, infiltration, groundwater recharge, etc.).

In the handling and treatment of produced water generated onshore and offshore in the past years, the main four items in the list above have been of highest priority as objectives in produced water treatment. As focus is channeled towards development of produced water as a source for beneficial use of water supplies, the last four items in this list will continue to gain importance (Abdullah, *et al*, 2009).

Sources of Heavy Metals and Toxicity in produced water

Heavy metals occur naturally on earth and possess commonly known properties such as having persistence, high toxicity and also functioning as non-biodegradable pollutants when they aggregate in the ecosystem. Based on previous studies, heavy metals are applied to a group of metals and metalloids having atomic density greater than 4g/cm^3 or 5 times or more and are greater than water. The classification of heavy metals can be grouped into three different types including toxic metals (such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn, etc), precious metals (such as Pd, Pt, Ag, Au, Ru, etc), and radionuclides (such as U, Th, Ra, Am etc), (Tchounwou, 2012).

Heavy metals in produced water could come from formation water, aquifer as well as from crude oil if the oil is saturated with water. Heavy metals sources that penetrate into the water system can derive from both natural and anthropogenic sources. The major source of heavy metal contamination includes urban industrial aerosols, solid waste from animals, mining activities, as well as industrial and agricultural chemicals. Sometimes various industrial waste water containing heavy metals are known to contaminate the water system. Acid rain as well breaks down the soils and the rocks, releasing heavy metals into water bodies.

Heavy metals present in the environment results to an increasing number of environmental issues such as deterioration of our ecosystems due to its rising accumulation. For example, Nickel is one of the carcinogenic which cause serious lung and kidney issues, aside from gastrointestinal distress, pulmonary fibrosis and skin dermatitis if exceeding its critical level. Instead of nickel, lead might also cause damage to the kidney, liver and reproductive system. The toxic symptoms of nickel are anemia, insomnia, headache, dizziness irritability, muscles weakness, hallucination and renal problems. Heavy metals emanating from mining operations into the environment will pollute the surface and also the underground water sources. This gives rise to soil pollution and the increasing rate of pollution when mined ores and other materials are dumped on the ground surface as a means of disposal. When soils are polluted, these toxic metals are taken up by plants and eventually accumulate in their tissues. Animals that feed on such polluted plants and drink from dirty waters, as well as marine lives that thrive in heavy metal contaminated waters also accumulate such metals in their tissues and milk, which can cause adverse effect (Tchounwou, 2012).

Dehydration/treating Processes of Crude Oil.

The method of treating “wet” crude oil for the separation of water associated with it varies according to the form(s) in which water is found with the crude. Free-water removal comes first in the treating process, followed by the separation of “combined” or emulsified water along with any foreign matter such as sand and other sediments. The basic approaches of handling “wet” crude oils are illustrated in Figure 1.7.

Again, from an economic point of view, removal of free water at the beginning will reduce the size of the treating system, hence its cost. The same applies for the separation of associated natural gas from oil in the gas–oil separator plant (GOSP). A dehydration system in general comprises various types of equipment. Most common are the following:

- (i) Free-water knockout vessel
- (ii) Wash tank
- (iii) Gun barrel
- (iv) Flow treater (heater/treater)
- (v) Chemical/Injector
- (vi) Electrostatic dehydrator

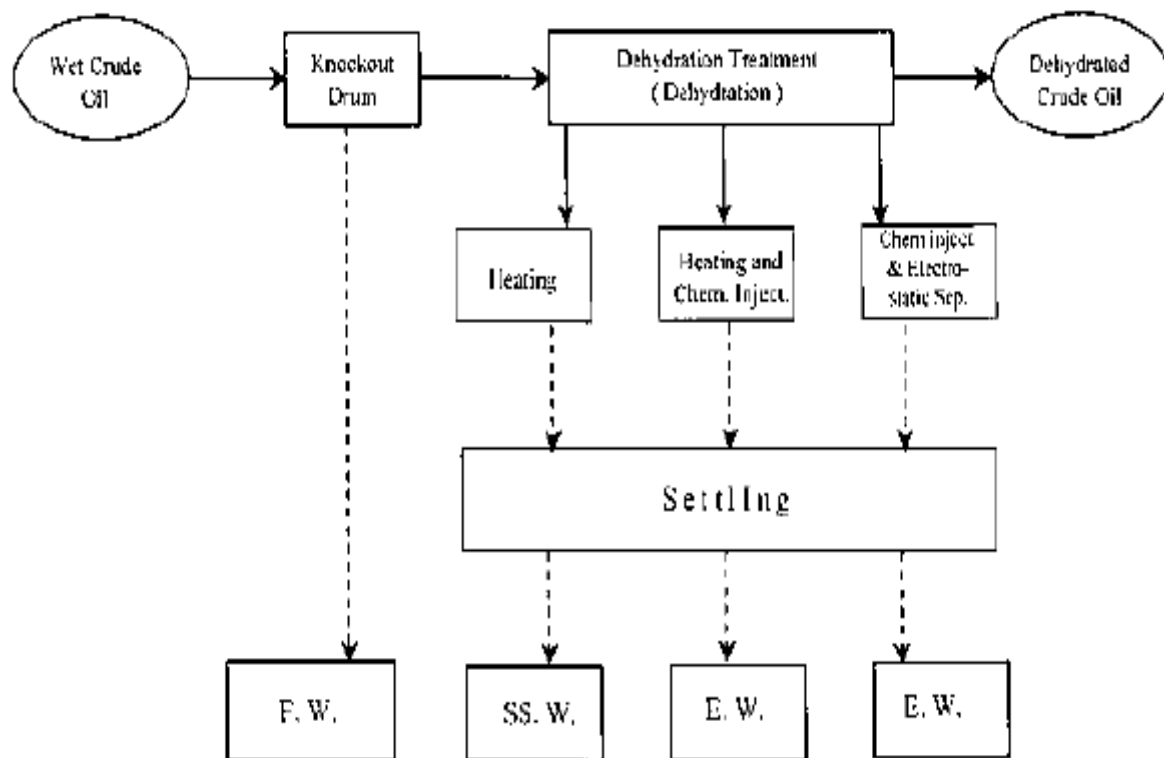


Figure 1.0: Basic approach of handling wet crude oil. (F.W. = fresh water, SS.W. = suspended water, E.W. = emulsified water.), (Abdel-Aal, *et al*, 2003).

Resolution of Emulsified Oil

This is the heart of the dehydration process, which consists of three consecutive steps:

- (i) Breaking the emulsion: This requires weakening and rupturing the stabilizing film surrounding the dispersed water droplets. This is a destabilization process and is affected by using what is called an “aid,” such chemicals and heat.
- (ii). Coalescence: This involves the combination of water particles that became free after breaking the emulsion, forming larger drops. Coalescence is a strong function of time and is enhanced by applying an electrostatic field, impingement on a solid surface area, and water washing.
- (iii). Gravitational settling and separation of water drops: The larger water droplets resulting from the coalescence step will settle out of the oil by gravity and be collected and removed (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

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 three 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 1.1 *Luffa cylindrica* and palm kernel fiber



Figure 1.2: Banana peels and raw orange peels



Figure 1.3 Produced water samples and filtrates from adsorption process



Figure 1.4 Atomic Absorption Spectrophotometer (AAS)

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; sun-dried (24 hours during summer 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

Sequential Mixture of the Adsorbents in the Adsorption Column

The adsorption chamber is made up of four columns where the adsorbents were packed individually. The next stage of the experiment was carried out by packing 8-gram (150 microns) each on the four columns with banana peels, orange peels, palm kernel fiber and luffa cylindrica in that order, and 250 ml of sample R (produced water) was flown through the first column to the last column, and the filtrate was collected at the last column at an interval of two hours and was subjected to analysis using the Atomic Absorption Spectrometer. The same procedure was repeated for sample X, Y respectively and the filtrates were analyzed as well. The columns were replaced with 300 microns of each of the adsorbents and the process was repeated for the three samples and the filtrates obtained at two hours intervals were analyzed as well.

Results and Discussion

Figure 1.5 is a plot of the concentration of Pb, Ni, Cd, and Cu (mg/l) against time (hrs) for particles size of 150 micron. The plots are linear with negative slopes. From the result (table 1.0) and plots, it shows that the concentration of the metals decreased with increase in time. After 8 hours of treatment, it was observed that there were no traces of lead (Pb), cadmium (Cd), Copper (Cu) and chromium (Cr). This shows that the adsorbents were good in the treatment as they were able to remove entirely the traces of the four metals mentioned above from the produced water. Other metals (Fe, Mg, Cr, Zn, Mn, Ca, Ar, B, Sn, Ba) were also removed to the expected levels by the adsorbents. Fe, Mg, Zn, Mn, Ca, Ar, B, Sn, Ba were reduced from 0.552, 3.699, 0.125, 0.062, 430, 4.65, 1.59, 0.155 and 0.038 (mg/l) to 0.051, 2.247, 0.007, 0.035, 3.20, 2.110, 0.882, 0.024 and 0.020 (mg/l) respectively. The reduction in concentration of other metals is given in table 1.0. The result reviewed that the arrangement of the adsorbents in the adsorption plant as described above gives a good result with a particle size of 150 micron.

Figure 1.6 is a plot of the concentration of Cr, Zn, Mn, Sn and Ba against time with a particle size of 300 micron from the same sample R using same adsorbents arrangement in the plant as described above. The same nature of plots as in figure 1.5 was obtained. It was linear plots with negative slopes showing that there is a strong relationship among the dependent and the independent variables. The plots reviewed that the concentrations of the metals decrease with increasing time. The metal concentrations Pb, Ni, Cd, Cu, Fe, Mg, Cr, Zn, Mn, Ca, Ar, B, Sn and Ba (from table 1.0, both the plotted and none plotted on the graph) decreased from 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 and 0.038 (mg/l) to 0.101, 0.071, 0.004, 0.061, 0.311, 2.412, 0.062, 0.014, 0.040, 4.5, 3.58, 1.371, 0.132 and 0.029 (mg/l) respectively. The reductions from 300 micron particle size reviewed that the adsorbents did a good job in the management of produced water as the adsorbents were able to reduce the concentration of the metals to an appreciable limit. The 150 micron particle size as described above gives a better result when compared with that of 300 micron particle size; this is because of the large surface area of the 150 micron size.

Figure 1.7 is a plot of the concentration of Pb, Ni, Cd, Cu and Cr (mg/l) against time (hrs) for particle size of 150 micron. The plot follows the trend of the previous ones plotted in the sense that it's linear with negative slopes. From the result (table 1.1) and the plots, it shows that the concentration of the metals decreased with increase in time. After 8 hours of treatment, it was observed that there were no traces of lead (Pb) and Copper (Cu). This shows that the adsorbents with particle size of 150 microns were good especially for lead and copper as they were able to remove the two metals completely from the produced water sample. The concentration of other metals were as well positively affected as shown, Ni, Cd, Fe, Mg, Cr, Zn, Mn, Ca, Ar, B, Sn and Ba (table 1,1) decrease from 0.026, 0.007, 0.783, 5.106, 0.121, 0.163, 0.071, 390, 5.544, 2.151, 0.144 and 0.045 (mg/l) to 0.014, 0.003, 0.003, 3.200, 0.077, 0.047, 0.028, 4.2, 3.202, 1.120, 0.030 and 0.020 (mg/l) respectively.

Figure 1.8 is also a plot of some of the metal concentrations against time. The metals are Pb, Ni, Cd, Cu, Cr, and Zn, with a particle size of 300 micron for the same sample X using same adsorbents arrangement on the plant as described above. The same nature of plot as in figure 1.7 was obtained. It was a linear plot with negative slopes showing that there is a strong relationship between the dependent and the independent variable. The plot showed that the metal concentrations decrease as time increases. Unfortunately, with a particle size of 300 micron as can be seen on the result (table 1.1), Pb and Cu could not be completely removed from the produced water sample unlike the particle size of 150 microns. It goes to show that particle size matters a lot when using the adsorbents. The smaller the particle size, the larger the surface area and, the better the result. The concentration of the metals (Pb, Ni, Cd, Cu, Fe, Mg, Cr, Zn, Mn, Ca, Ar, B, Sn and Ba (table 1.1) decreased from 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 and 0.045 (mg/l) to 0.031, 0.017, 0.004, 0.031, 0.014, 1.601, 0.083, 0.087, 0.031, 2.5, 3.923, 1.894, 0.121 and 0.031 (mg/l) respectively

Figure 1.9 and 1.10 are the plots of some of the metals analyzed against time. Figure 1.9 is a plot of the concentration of Pb, Ni, Cu, Cr, Mn and Ba (mg/l) against time (hrs) for particle size of 150 micron from sample Y obtained from Kolo creek oil field in Rivers/Bayelsa state in Niger Delta region. Figure 1.10 is a plot of concentration of Pb, Ni, Cu, Cr, Zn and Ba against time for particle size of 300 micron from the same sample Y. Both plots are linear with negative slopes. From the result (table 1.2) and the plots, it shows that the concentration of the metals decreased with increase in time.

Analysis reviewed that there was no trace of Cadmium (Cd) in the sample obtained from Kolo creek oil field. This could be as a result of none Cadmium existence within the geological location. It was observed that after 8 hours of treatment using 150 micron particle size, there was no trace of Copper (Cu) left in the sample. This shows that the adsorbents with particle size of 150 microns were good especially for copper as they were able to remove the metal completely from the sample

From figure 1.10 with particle size of 300 micron, it was observed that after same 8 hours of treatment, some traces of copper (Cu) (0.015 ppm) was still present. This could be as a result of the particle size with smaller surface area when compared with that of 150 micron particle size. Another notable thing in figure 1.10 was the absence of calcium (Ca) from the produced water after 8 hours of treatment which was not obtained under 150 micron particle sizes. The results obtained with both particle sizes (150 and 300 micron) were all encouraging. This shows there is a great potential in using some of these low cost agricultural waste in the management of produced water and waste waters in general. Table 1. 2 gives a more detail of the results and the extent to which the concentration of the toxic metals in the produced water sample was greatly reduced. Averagely, 150 micron particle sizes produced a better result when compared with 300 micron particle sizes.

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:

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

In the sequential mixture of the adsorbents, the linear plot of c_e/q_e vs c_e indicates that adsorption of Pb ion is in line with the Langmuir adsorption isotherm (figure 1.11). The values of Q and b as obtained from the plot are given on (table 1.6). The coefficient of correlation (R^2) was 0.9981 for Langmuir model and 0.4119 for same Pb for freundlich model (figure 1.12). The results indicate that the Langmuir sorption isotherm 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 amount of metal ion extracted per unit mass of the adsorbent rises with the metal concentration as expected and the sorption capacity is stated on (table 1.6). The value of the equilibrium separation factor R_L , of 0.119 (table 1.6) revealed that the sorption of Pb ion on the sequential mixture of the adsorbent surface was found to be a favorable process. The correlation coefficient from freundlich isotherm plot of $\log q_e$ vs $\log c_e$ could not give a better result, showing that freundlich sorption isotherm is not favorable for equilibrium study of Pb.

For the Ni ion adsorption on the adsorbent surface, the linear plot of c_e/q_e vs c_e indicates that adsorption obeys the Langmuir adsorption isotherm model (figure 1.13). The correlation coefficient (R^2) was found to be 0.973. This shows that the Langmuir sorption isotherm model is favorable for equilibrium study for Ni, and this suggests the formation of monolayer coverage of the adsorbate on the adsorbent surface for the metal ion. Q_o , R_L and b values were calculated from the plot as shown in (table 1.6). The R_L value of 0.473 indicates the adsorption process was a favorable one. Freundlich isotherm model result which produced a correlation coefficient value of 0.943 (figure 1.14) for Ni adsorption was not that good when compared with the Langmuir model. Therefore, the Langmuir isotherm model best describe the adsorption of Ni on the adsorbent surface. When it comes to Fe (iron) adsorption on the sequential mixture of the adsorbent surface, Langmuir isotherm model gives a better result when compared with Freundlich isotherm model. The linear plot of c_e/q_e vs c_e indicates that adsorption obeys the Langmuir adsorption model (figure 1.15). The values of Q_o , R_L and b as obtained from the plot are indicated on (table 1.6). The coefficient of correlation (R^2) as shown on the plot was found to be 0.8326. This shows that the Langmuir sorption model is favorable for equilibrium study for Fe compared with the value of R^2 of 0.7954 on the Freundlich plot (figure 1.16). This suggests the formation of monolayer coverage of the adsorbate on the adsorbent surface for the metal ion. The separation factor (R_L) with a value of 0.575 (table 1.6) indicates that the adsorption of Fe on the sorbent surface is a favorable process.

Table 1.0: Result of the sequential mixture of the adsorbents (sample R- Imo River, 150 micron)

metals	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
2hrs	0.017	0.024	0.013	0.050	0.432	3.11	0.07	0.120	0.052	350	3.98	1.490	0.125	0.035
4hrs	0.011	0.021	0.011	0.046	0.333	2.883	0.052	0.110	0.055	150	3.42	1.352	0.085	0.029
6hrs	0.006	0.008	0.007	0.005	0.226	2.521	0.034	0.048	0.042	45	2.82	1.301	0.057	0.023
8hrs	ND	0.005	ND	ND	0.051	2.247	ND	0.007	0.035	3.20	2.110	0.882	0.024	0.020

AFTER TREATMENT WITH ADSORBENTS USING 300 MICRON PARTICLE SIZE														
2hrs	0.129	0.031	0.014	0.074	0.388	3.650	0.071	0.122	0.061	361	4.56	1.570	0.154	0.036
4hrs	0.125	0.027	0.011	0.070	0.372	3.520	0.068	0.121	0.052	207	4.32	1.552	0.152	0.035
6hrs	0.121	0.015	0.007	0.067	0.342	3.212	0.066	0.113	0.051	49	4.27	1.431	0.136	0.032
8hrs	0.101	0.071	0.004	0.061	0.311	2.412	0.062	0.014	0.040	4.5	3.58	1.371	0.132	0.029

Table 1.1: Result of the sequential mixture of the adsorbents (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.														
2hrs	0.058	0.023	0.006	0.057	0.521	4.625	0.099	0.160	0.059	190	5.412	2.007	0.136	0.043
4hrs	0.029	0.020	0.004	0.004	0.223	4.212	0.092	0.146	0.055	110	5.110	1.655	0.121	0.032
6hrs	0.005	0.018	0.004	0.001	0.005	3.345	0.090	0.081	0.042	33	4.228	1.364	0.059	0.029
8hrs	ND	0.014	0.003	ND	0.003	3.200	0.077	0.047	0.028	4.2	3.202	1.120	0.030	0.020

AFTER TREATMENT WITH ADSORBENTS USING 300 MICRON PARTICLE SIZE														
2hrs	0.074	0.026	0.007	0.068	0.642	4.720	0.121	0.162	0.066	250	5.512	2.151	0.140	0.043
4hrs	0.055	0.022	0.007	0.054	0.048	3.622	0.098	0.094	0.053	129	5.433	2.100	0.128	0.041
6hrs	0.038	0.021	0.005	0.047	0.023	2.301	0.092	0.090	0.050	66	4.534	2.002	0.123	0.038
8hrs	0.031	0.017	0.004	0.031	0.014	1.601	0.083	0.087	0.031	2.5	3.923	1.894	0.121	0.031

Table 1.2: Result of the sequential mixture of the adsorbents (Sample Y -- Kolo creek)

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	0.186	0.183	ND	0.035	0.622	4.851	0.279	0.168	0.076	300	3.112	1.802	1.511	0.081

4 hrs	0.183	0.158	ND	0.031	0.462	3.454	0.181	0.161	0.060	158	2.822	1.541	1.424	0.068
6 hrs	0.170	0.134	ND	0.025	0.230	2.282	0.145	0.142	0.023	53.10	2.432	1.231	1.342	0.056
8 hrs	0.168	0.119	ND	ND	0.122	0.324	0.098	0.112	0.020	1.38	1.712	1.122	1.133	0.047

AFTER TREATMENT WITH ADSORBENTS USING 300 MICRON PARTICLE SIZE

2 hrs	0.190	0.192	ND	0.038	0.788	5.550	0.390	0.172	0.075	320	4.233	1.801	1.692	0.079
4 hrs	0.086	0.185	ND	0.034	0.611	4.322	0.386	0.160	0.074	171	4.134	1.722	1.642	0.072
6 hrs	0.053	0.157	ND	0.026	0.399	3.101	0.352	0.125	0.057	35	3.401	1.667	1.457	0.033
8 hrs	0.007	0.110	ND	0.015	0.212	0.338	0.299	0.008	0.007	ND	3.199	1.363	1.244	0.007

Table 1.3: Analysis of Pb (lead) using Langmuir and freundlich models isotherm for sample R

t (hrs)	Ce (mg/l)	qe (g/l)	Ce/qe (g/l)	Log Ce (mg/l)	Log qe (g/l)
2	0.017	0.00359	4.735	-1.7696	-2.4449
4	0.011	0.00378	2.910	-1.9586	-2.4225
6	0.006	0.00394	1.523	-2.2218	-2.4045
8	0.000	0.00413	0.000	0.000	-2.3840

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

t (hrs)	Ce (mg/l)	qe (g/l)	Ce/qe (g/l)	Log Ce (mg/l)	Log qe (g/l)
2	0.024	0.000375	64	-1.6198	-3.4260
4	0.021	0.000469	44.77	-1.6778	-3.3010
6	0.008	0.000875	9.14	-2.0969	-3.0457
8	0.005	0.000969	5.16	-2.3010	-3.0000

Table 1.5: Analysis of Fe (iron) using Langmuir and freundlich models for sample R

t (hrs)	Ce (mg/l)	qe (g/l)	Ce/qe (g/l)	Log Ce (mg/l)	Log qe (g/l)
2	0.432	0.00375	115.20	-0.3645	-2.4259
4	0.333	0.00684	48.68	-0.4776	-2.1649
6	0.226	0.01019	22.17	-0.6459	-1.9918
8	0.051	0.0157	3.25	-1.2924	-1.8041

Table 1.6.: A comparison of correlation coefficient and other parameters for 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	0.99	56	0.192	0.119	0.00342	0.41	11.20	0.867
Ni	0.97	30.96	0.013	0.473	0.000404	0.94	2.07	0
Fe	0.83	1.34	0.0083	0.575	0.00621	0.80	2.26	0.875

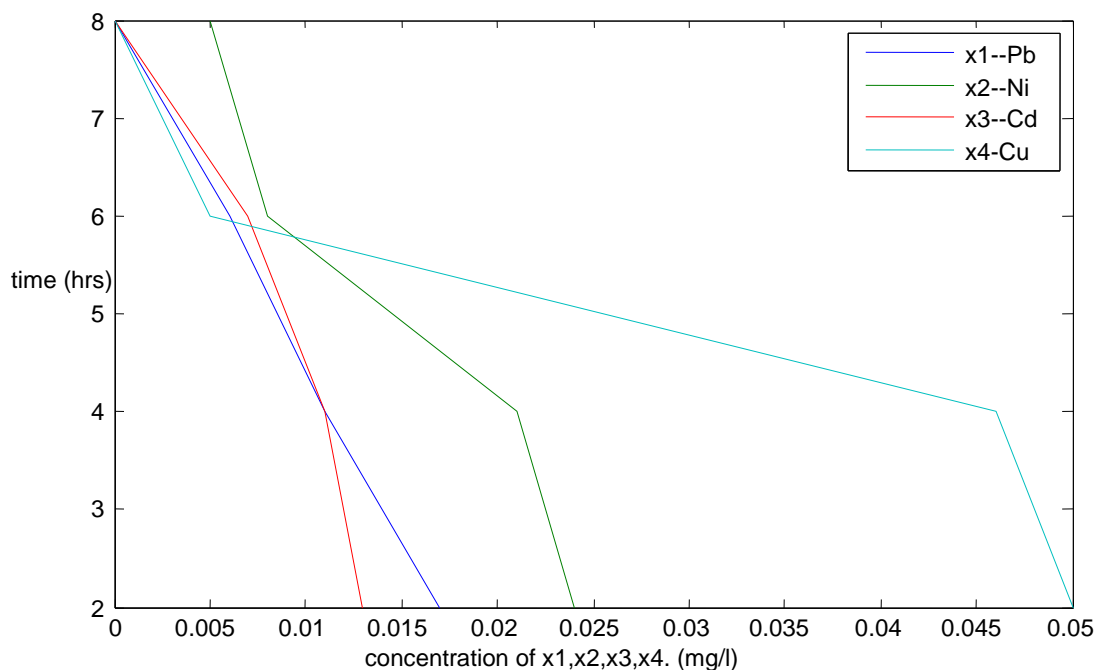


Figure 1.5:: plot of concentration of Pb, Ni, Cd, Cu vs time. (Sample R, 150 micron size):

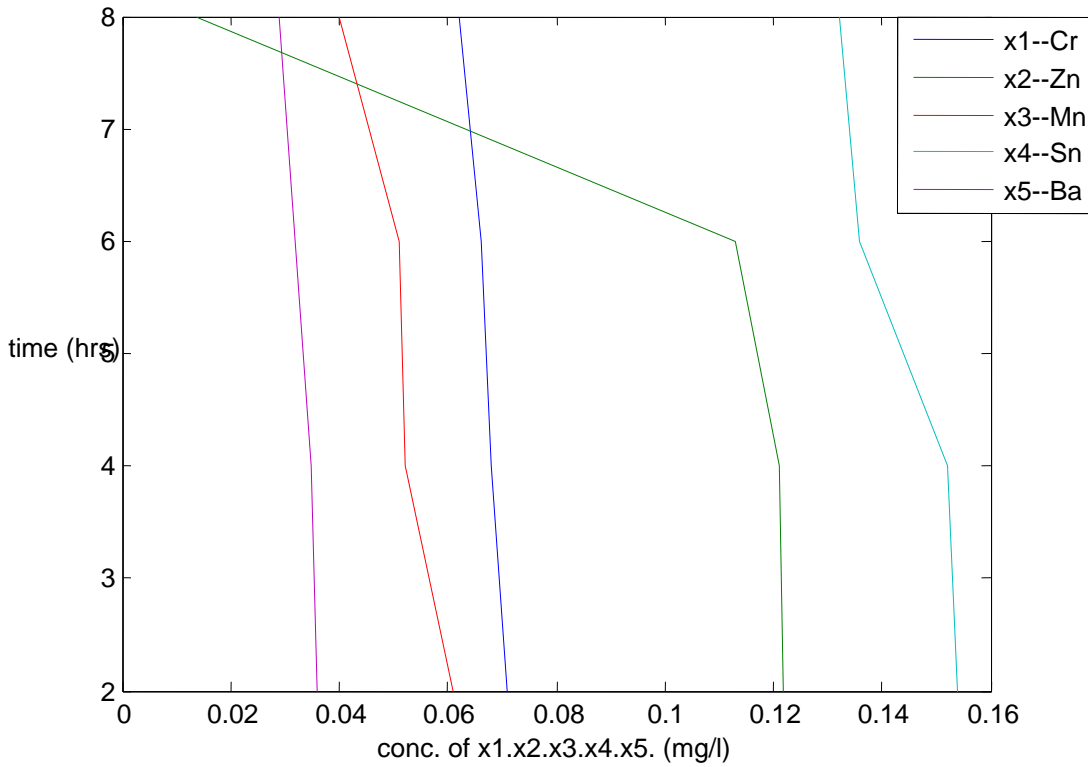


Figure 1.6: plot of concentration of Cr,Zn,Mn,Sn,Ba vs time (Sample R, 300 micron size)

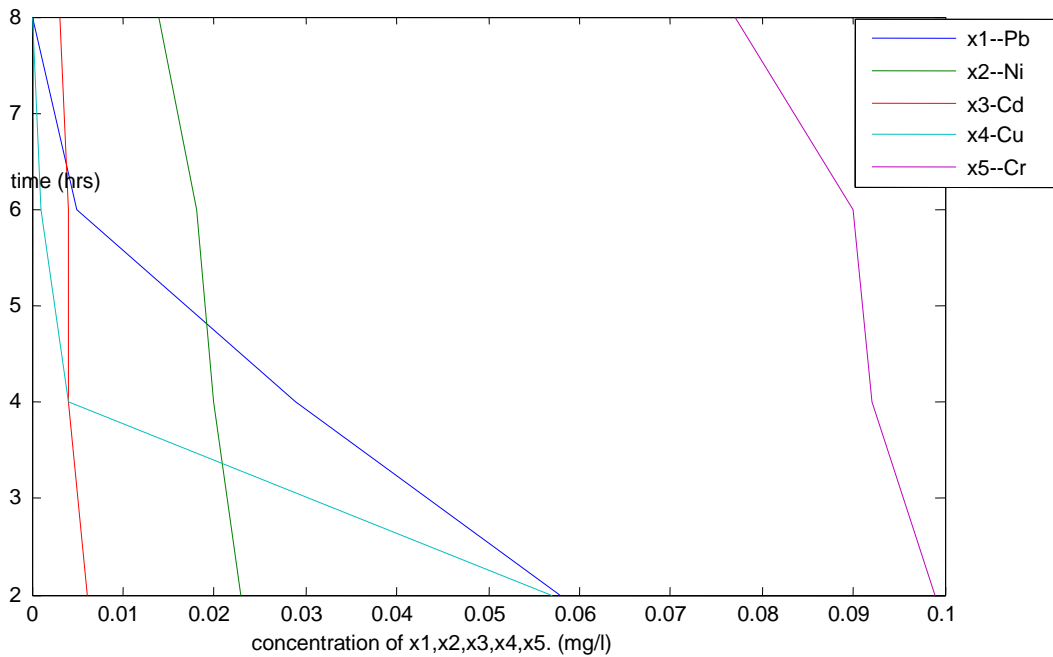


Figure 1.7:: Plot of conc. of Pb, Ni, Cd, Cu, Cr vs time. (Sample X, 150 micron size)

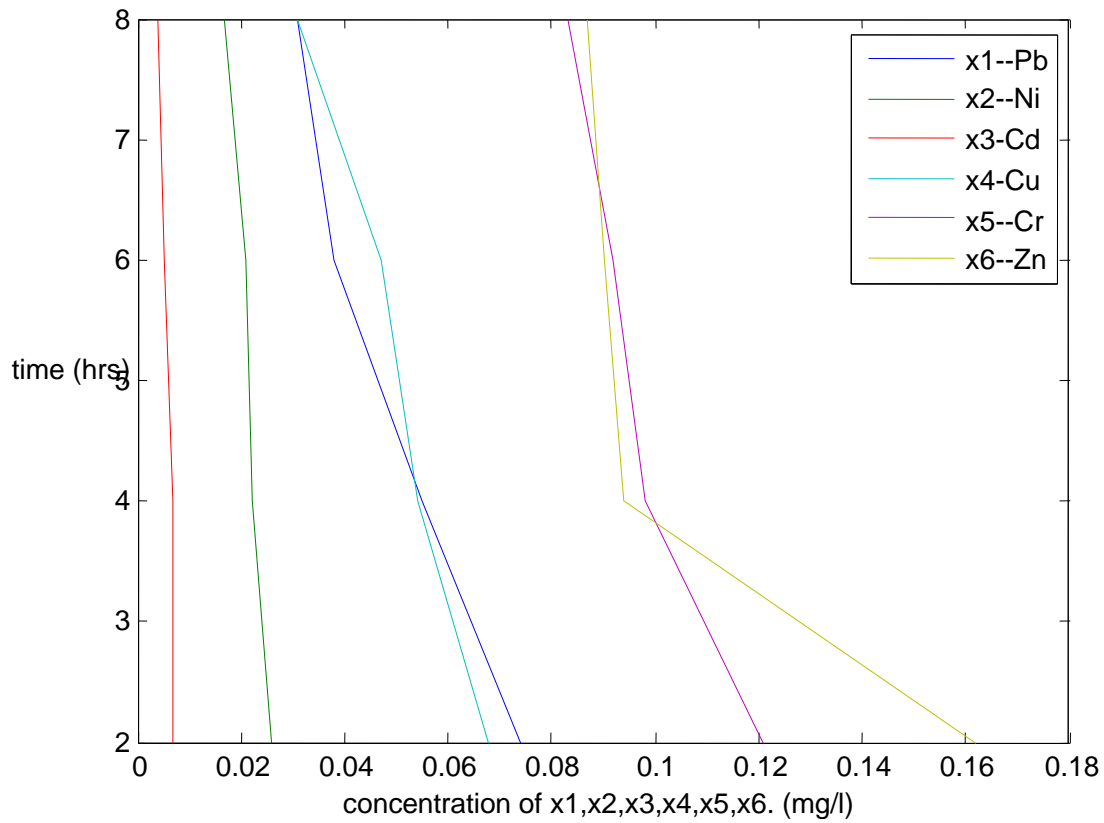


Figure 1.8: plot of conc. of Pb,Ni,Cd,Cu,Cr,Zn vs time. (Sample X, 300 micron size)

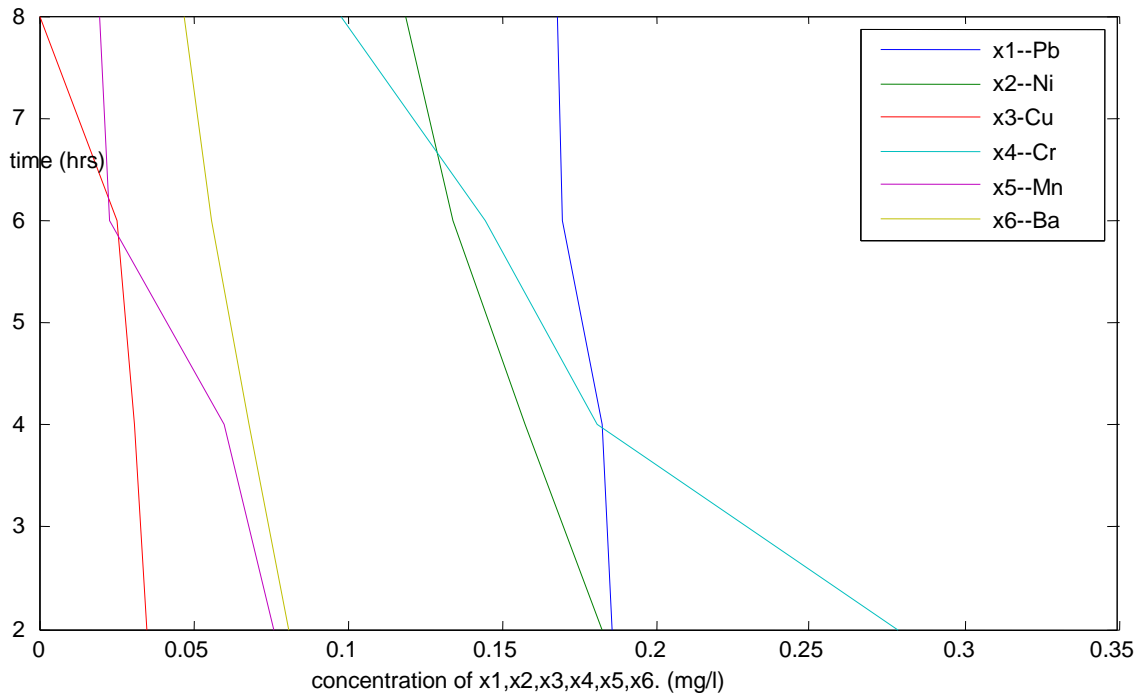


Figure 1.9: plot of conc. of Pb,Ni,Cu,Cr,Mn,Ba vs time. (Sample Y, 150 micron size)

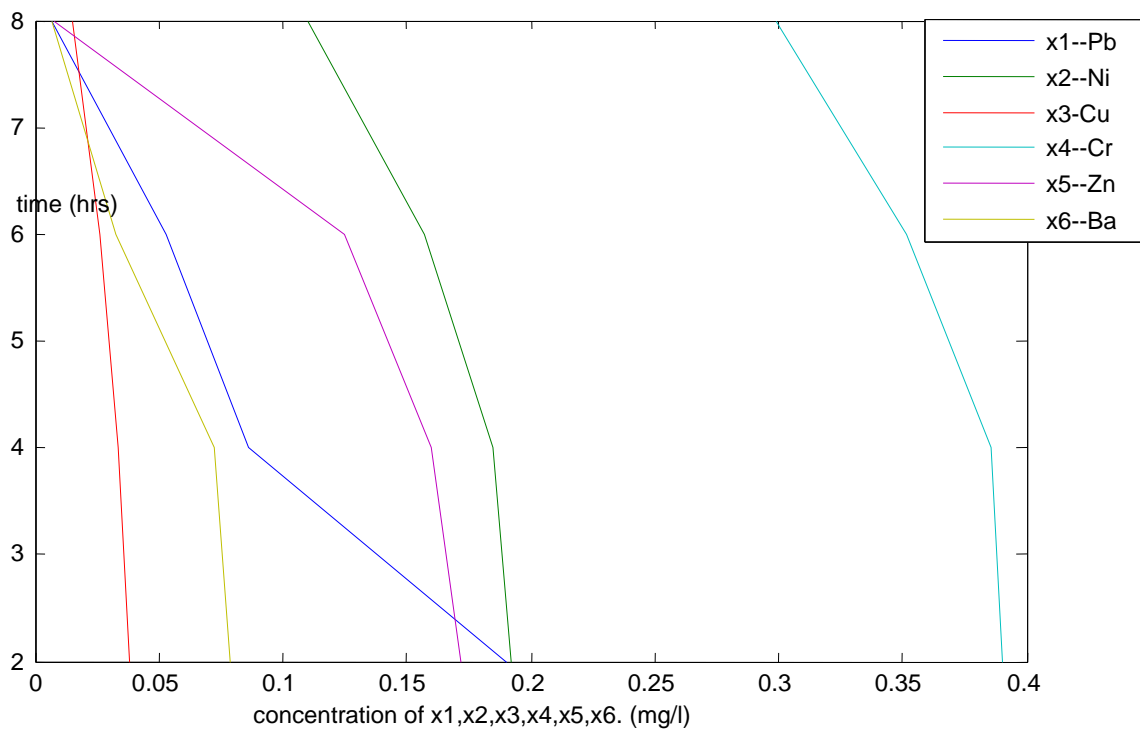


Figure 1.10: plot of conc. of Pb,Ni,Cu,Cr,Zn,Ba vs time. (Sample Y, 300 micron size).

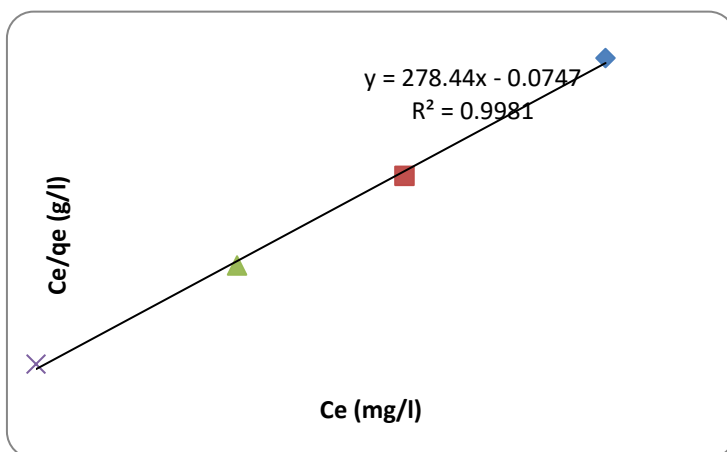


Figure 1.11 : Analysis of Pb using Langmuir isotherm for sample R

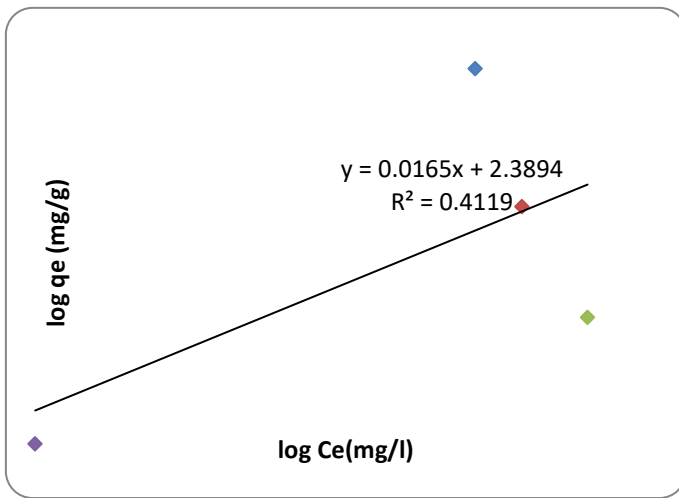
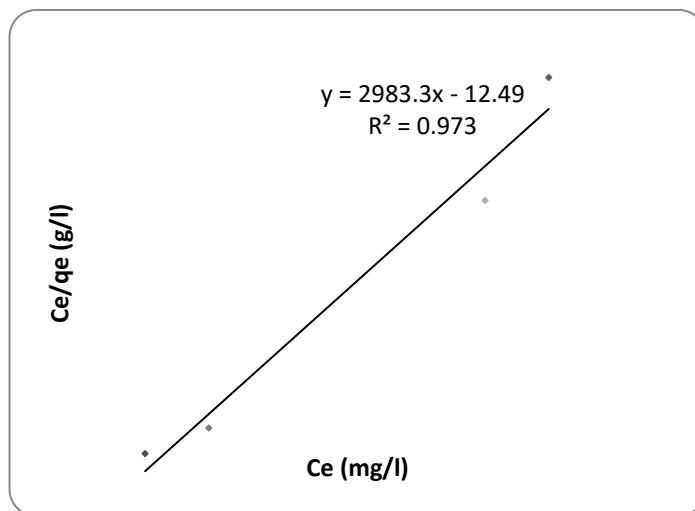
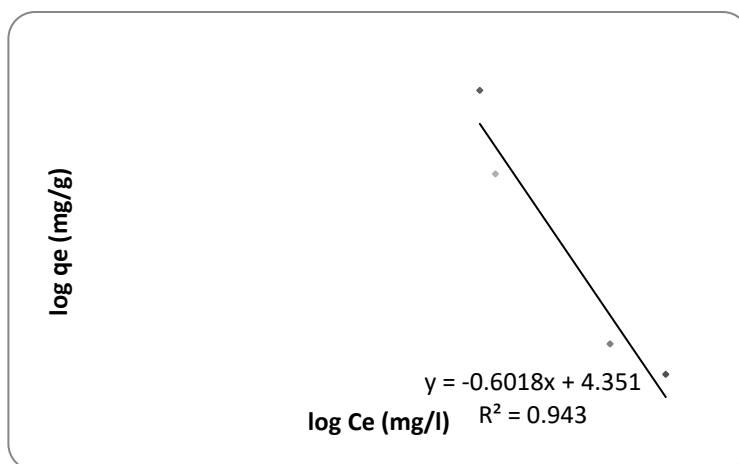


Figure 1.12 : Analysis of Pb using freudlich isotherm for sample R



Freundlich isotherm for sample R



Freundlich isotherm for sample R

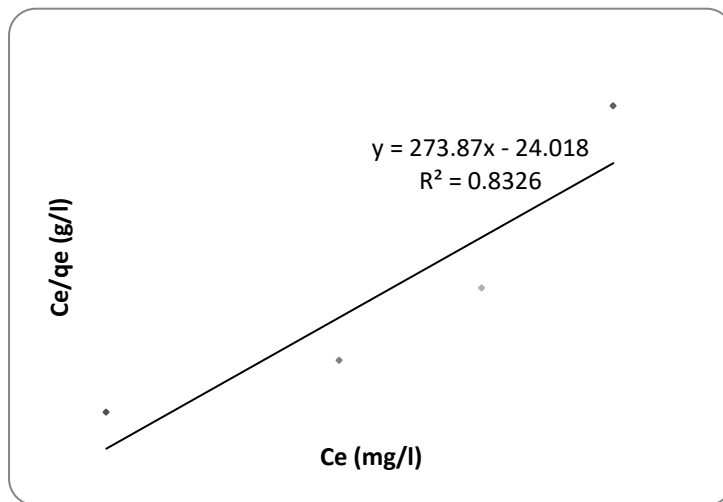


Figure 1.15: Analysis of Fe using langmuir isotherm for sample R

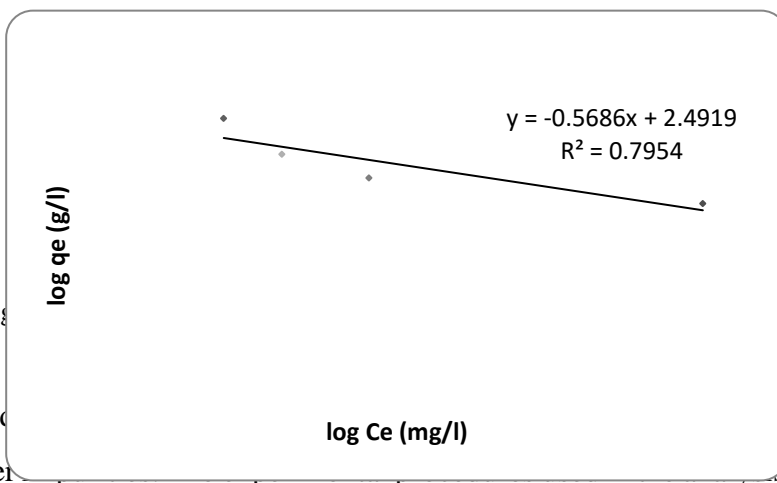


Fig
The proc
and other

vered to contain traces of heavy metals
of these metals were done with standard

solutions of each metal prepared in the laboratory at room temperature. The experiments were successful; the metal concentrations before and after treatment with the bioadsorbents 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 sequentially, the concentrations of most of the metals were reduced to the expected level as can be seen

from the results. Sequential 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 are *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.

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