



Sequestering of Fe and Pb ions from Wastewater by *Canarium schweinfurthii* after carbonization and chemical treatment: Isothermal and Kinetic Modeling

*¹BASSEY UWEM, EDJERE OGHENEKOHWIRORO, OTOLO SOLOMON EBIYE

Department of Environmental Science, Federal University of Petroleum Resources, Effurun, Delta State Nigeria
Corresponding author Email : bassey.uwem@fupre.edu.ng

ABSTRACT: In this paper agricultural waste; *Canarium schweinfurthii* was explored for the sequestering of Fe and Pb ions from wastewater solution after carbonization and chemical treatment at 400°C. Optimum time of 30 and 150 min with percentage removal of 95 and 98% at optimum pH of 2 and 6 was obtained for Fe and Pb ions. Kinetics model followed pseudo-first order as sum of absolute error (E_{ABS}) between Q_e and Q_c greater than that of pseudo second order. Parameters evaluated from isothermal equation (Freundlich and Langmuir) showed that K_L and Q_0 for Fe > Pb and R^2 for Langmuir > Freundlich. The study reveals the suitability of the adsorbent for sequestering of Fe and Pb ions from industrial wastewater.

©JASEM

<http://dx.doi.org/10.4314/jasem.v20i1.18>

KEYWORDS: Adsorbent; Pb; Fe; Kinetics and Isotherm

Introduction

Man's activities in the environment have greatly led to an increase in concentration levels of heavy metals. These have generated a lot of interest in pollution studies. Heavy toxic metals entered into the environment through wastewater from metal plating industries and industries of lead, cadmium and nickel batteries, phosphate fertilizer, mining, pigments electroplating, Corrosion, and other industrial waste (Ahalya *et al.*, 2005). Natural sources of these metals include; rock-weathering, releases from terrestrial and submarine sediments, some of these metals are often found in crude oils in small quantities and discharged into the environment during the refining process (Cutler, 2007). The discharge of heavy metals into the environment has become a matter of concern and seems to threaten the survival of living things (Zupanc *et al.*, 2002).

Conventional methods of removing heavy metal pollutant from wastewater can be expensive, prohibitive for developing economy and most times do not effectively remove polluting metals. Thus, it becomes imperative to search for cheap and alternative means and bio-sorbents lately have become of considerable interest (Bassey *et al.*, 2015). Adsorption by activated carbon, by far, has become a method of choice to offset this problem. Adsorption becomes a preferred choice than other physicochemical techniques of heavy metal remediation due to its simplicity, cheap, easy to scale-up and most importantly able to remove low concentration substance even at part per million

levels with high efficiency. Activated carbon has been widely used in water treatments because of its high specific surface area, chemical stability and durability. Its utilization for heavy metals adsorption greatly relies upon surface acidity and special surface functionality (Sato *et al.*, 2007) and coordination to functional groups (Jia *et al.*, 2002). The quality of activated carbon is dependent upon the extent of its surface area, number of pores as well as its surface functional groups. Structurally, carbon is made up of tiny graphite-like platelets with a wall of open cavities that form the pore system. The presence of tiny pores on their internal and external surfaces has been attributed to be responsible for adsorption of organic materials, non-polar compounds and metals from gaseous and liquid media (Ekpete *et al.*, 2010). Generally Activated carbons are generated using materials such as; coal, wood, coconut shell, after some form of activation process (Lartey and Acqual, 1999). Recent, agricultural waste material has been adopted for production of activated carbons at temperature range of 450-700°C (Okieimen and Wuana, 2007; Tarawou and Horsfall, 2007). The common process involved during the production of activated carbon is based on carbonizing and activating the carbonaceous at certain furnace temperature. This can be achieved physically; a process involving carbonization of the precursor material or chemically; a process of adding a chemical agent and then subjecting it to temperature (Dilek and Ozgur, 2008). Metal uptake by biosorption is reported to occur through interactions with functional groups native to the biomass cell wall

(Goksungur *et al.*, 2005; Krishnakuman *et al.*, 2007). It is metabolism-independent and proceeds rapidly within some minutes by any one or combination of the following metal binding mechanisms; coordination, complexation, ion exchange, physical adsorption (e.g. electrostatic) or inorganic microprecipitation

Carbonaceous surfaces, typically in the form of soot particles, play an important role in the chemistry of adsorption. These carbons are characterized by a high degree of chemical and morphological heterogeneity that affects their function. These characteristics affect their interactions with molecular adsorbates and, hence, the adsorption capacity (or efficiency) and catalytic activity. According to Osu and Odoemelam (2010), modification of the adsorbent (*Crasstrorea gasar*) by esterifying the carboxylic group present in the cell wall with ethanol in the presence of HCl did not improve the adsorptive capacity of the adsorbent used. Jameel (2011) reported that the presence of -OH, -CH₂-, -CHO, -C=C- and -C-O- at 3412.01, 2926.11, 2856.67, 1660.77 and 1095.60 cm⁻¹ in duckweed enhanced binding the metals of metal ions onto the adsorbent. Therefore this work is aimed at optimizing the function and usefulness of evaluating the isothermal and kinetic model of treating Fe and Pb ions in waste water using carbonization and chemical treatment of *Canarium schweinfurthii*

MATERIALS AND METHODS

Air dried endocarps of *Canarium schweinfurthii* were milled and passed through 250 micron mesh screen. The sieves were kept for carbonization.

Carbonization of adsorbent: The sieved biomass was activated by placing it in an electric furnace at 300°C and heated for one hour. After which it was allowed to cool in an ice bath.

Chemical activation of carbonized adsorbent : 10 g of carbonized endocarp of *Canarium Schweinfurthii* was transferred into a beaker containing 50 cm³ of 0.5 molar trioxonitrate (V) acid. The beaker contents were thoroughly homogenized until a paste was formed. The homogenized samples was then transferred to crucible and placed at the centre of a Gallenkamp electric muffle furnace and heated at 400°C for 10 minutes. The chemically activated sample were cooled in an ice bath and washed with distilled water to a pH range of 6-7, and was further oven dried at a temperature of 105°C for 20 minutes, product obtained was screened through a 250 µm mesh size sieve. This process was repeated till sustainable quantity was obtained.

Preparation of simulated wastewater: Aqueous solution containing the respective selected metals: Pb and Fe was prepared from analytical grade Pb(NO₃)₂, FeSO₄·7H₂O. 1000 mg/L stock solutions of each of the metal salts were prepared. The solution was introduced for each metal according to the method of continuous dilution from the sample.

Preparation of reagents and standard solutions: 1000 mg/L Pb: 1.60 g of Pb (II) from Pb(NO₃)₂ was dissolved in 1000 cm³ volumetric flask before being made to mark with distilled water. The solution was shaken to ensure thorough mixing. Other concentrations (10, 25, 50, 75, 100 and 150 mg/L) were prepared from the stock solution by serial dilution from a formulae C₁V₁= C₂V₂; 1000 mg/L Fe: 4.96 g of Fe (II) from FeSO₄·7H₂O was dissolved in 1000 cm³ standard thorough mixing. Other concentrations (10, 25, 50, 75, 100 and 150 mg/L) were obtained from this solution by serial dilution.

Sorption experiment was carried out at pH of 2, 4, 6, 8, 9 and contact time of 30, 60, 90, 120 and 150 min for their optimization. Residual metal ion concentration was determined using atomic absorption spectrophotometer AA-6300 Shimadzu and Accufys 211 model.

Desorption studies: Recovery of the metal ion adsorbed from the adsorbent was done using different concentrations of hydrochloric acid (0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) mol/dm³. The desired volume of 40 cm³ of 5 mg/L of metal solution was poured into designated Pyrex conical flask for each concentration of desorbing agent. Solutions of metal ions were contacted using adsorbent dosage of 0.5 g for the optimum pH, contact time, stirring speed after which they were filtered. The filtrate was kept for analysis and the spent biomass contacted with the appropriate concentration of the desorbing agent for the optimum contact time, at the end of which the contents were filtered. Filtrates were analyzed for metal ion concentration using atomic absorption spectrophotometer AA-6300 Shimadzu and Accufys 211 model.

Characterization of activated carbon: Moisture content was determined by oven drying 5 g of the biomass at constant temperature of 105°C for five hours. Desiccators were used to preserve the sample from uptake of moisture. Percentage moisture content was determined according to the expression below.

$$\text{Percentage moisture content} = \frac{W_2 - W_3}{W_2 - W_1} \times 100 \quad (1)$$

W_1 = Weight of crucible

W_2 = Initial weight of crucible with sample

W_3 = Final weight of crucible with sample

Bulk density was determined by using 2 g of granular activated carbon of 10-30 mesh size carbon placed in a 25 cm³ cylinder and tapping it for at least one to two minutes after which the volume of carbon in (g/m³) signifying bulk density was derived as

Weight of dry sample (g) - volume of packed dry sample (g)

Conductivity (μS/cm) was determined by suspending one gram of activated carbon in distilled water for twenty minutes and conductivity measured as micro siemen (μS/cm).

Determination of ash content was carried out by measuring 2 g of powdered carbon of 325 μm into a crucible and heating the content to 115°C in an oven for 6 hours. The carbon was then heated in the centre of Gallenkamp muffle furnace at 950°C for 1.5 hours, the crucible was removed and placed in desiccators in order to prevent moisture uptake. Ash was derived as

$$\text{Ash (\%)} = \frac{\text{Final solid weight}}{\text{Initial carbon weight (g)}} \times 100 \quad (2)$$

Hardness of the sample was measured using wet attrition method reported by Toles *et al.* (2007) Into a 100 cm³ acetate buffer made of 0.07 M sodium acetate and 0.03 M acetic acid of pH 4.8 in a 150 cm³

beaker 1 g of the sample was added. To allow proper agitation, the solution was stirred for twenty four hours. The filtered sample was then well washed and dried in an oven for four hours at 90°C.

Percentage hardness was derived as

$$\text{Hardness (\%)} = \frac{\text{Initial weight (g)} - \text{final weight (g)}}{\text{Initial weight}} \times 100 \quad (3)$$

Yield (%) was measured by weighing the weight of raw sample before and after carbonization and calculated as

$$\text{Yield (\%)} = \frac{\text{weight of raw sample (g)} - \text{weight of carbonized sample (g)}}{\text{weight of carbonized sample (g)}} \times 100 \dots (4)$$

RESULT AND DISCUSSION

Table 1: Characterization of Activated carbon

Parameter	Value
Ash content (%)	3.97±0.036
Moisture content (%)	2.72±0.072.
Hardness (%)	7.23±0.225
Electrical conductivity (μS/cm)	205.837±3.814
% Yield	81.267±1.124
Bulk density (g/m ³)	0.83±0.036

Values are mean ±standard deviation

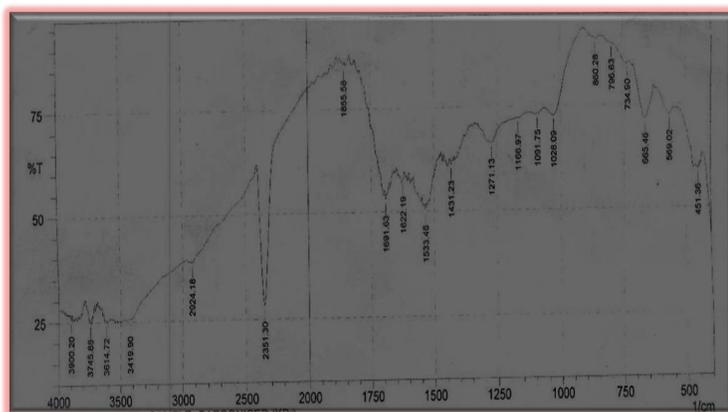


Fig 1 FTIR spectra *Canarium* recorded from 4000 to 500 cm⁻¹.

Table 2. Functional groups present in the adsorbent

Wave number (cm ⁻¹)	Bond	Functional group	Strength
3419.90	N-H	Primary, secondary amine and amide	M
1271.13, 1166.97, 1028.09	C-O	Alcohols, Carboxylic acids and esters	M
2924.18	-CH ₂		W

Strong signal at 2351.30 cm⁻¹ is due to overlap between stretching and bending vibration of molecules

*¹BASSEY UWEM, EDJERE, OGHENEKOHWIRORO OTOLO, SOLOMON EBIYE

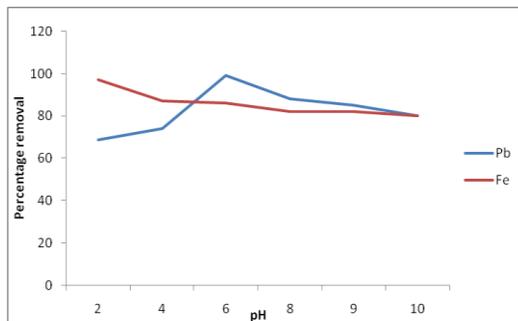


Fig 2: Variation of pH

Effect of pH: Fig 2 show optimum pH of 2 and 6 for Fe and Pb. Percentage removal for both metal ions reduced at alkaline medium. This is due to the fact that at higher pH metal ions combines with OH⁻ radicals present in the adsorbent and in solution forming metal hydroxide precipitate, which affect the adsorption of metal ions by the adsorbent (Bailey *et al.*, 1999). There is high possibility of increase in repulsive forces between OH⁻ ions with radicals such as NO₃⁻ and SO₄²⁻ generated from Pb(NO₃)₂ and FeSO₄·7H₂O used for the preparation of simulated solution which would negatively affect the adsorption

of these ions. Quek *et al.*(1998) in their study on the application of sago waste for the adsorption of Pb (II) and Cu (II). The sorption process was examined in terms of its isotherm and kinetics for Pb (II) and Cu (II). Optimum pH range was found to be 4 to 5.5 for both metals this was because at such pH range hydrogen ions influents the surface charges of the adsorbent positively. Wong *et al.*(2003) using rice husk modified with tartaric acid as adsorbent for the removal of Pb (II) ions and reported that reported that as pH increased from 2 to 4 and gradually increased above 5.

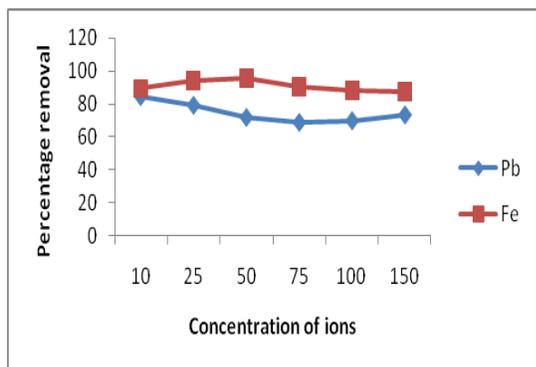


Fig 3: Variation of metal concentration

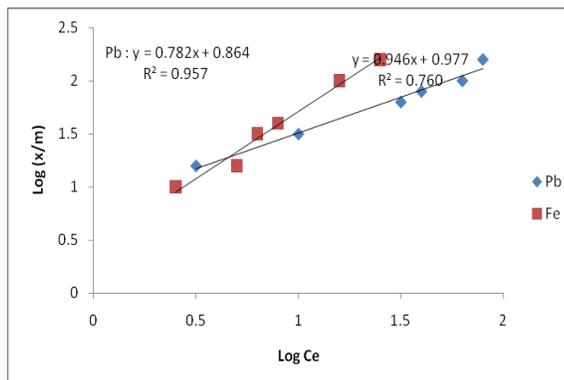
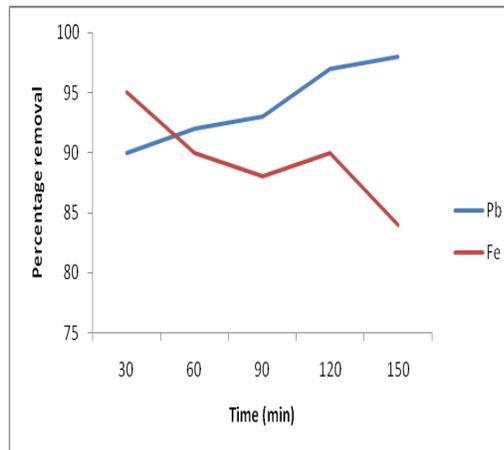
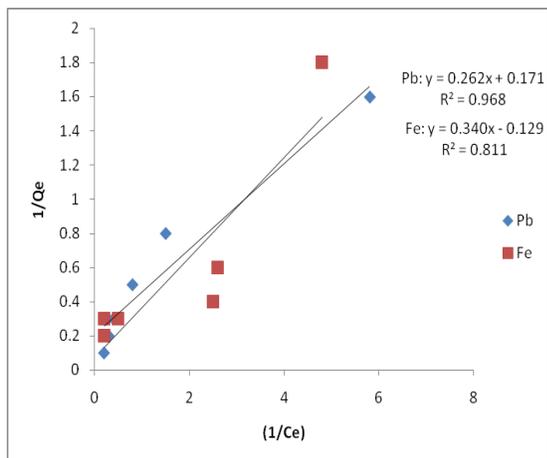


Fig 4: Freundlich plot for Pb and Fe



*¹BASSEY UWEM, EDJERE, OGHENEKOHWIRORO OTOLO, SOLOMON EBIYE

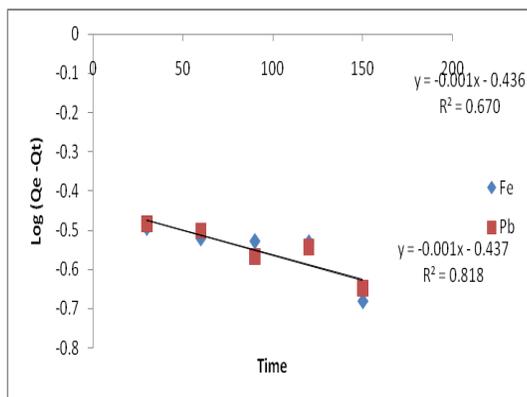
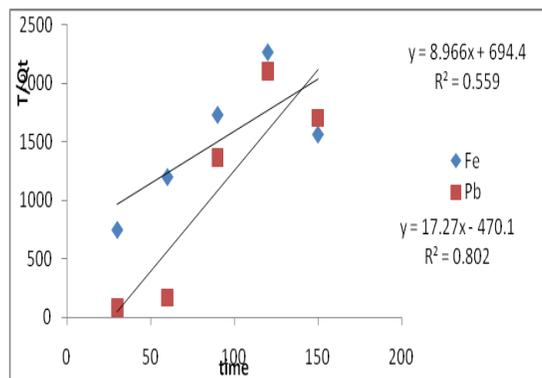
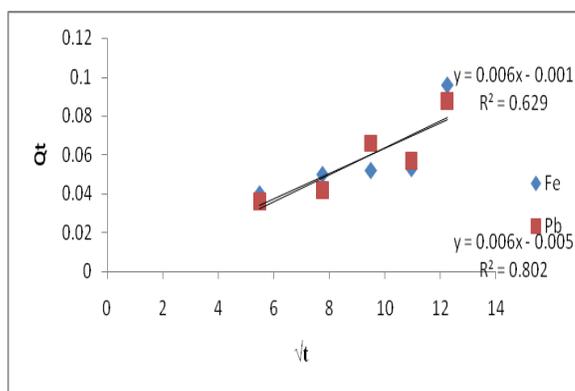
Fig5: Langmuir plot for Pb and Fe**Fig 7:** Pseudo-first order plot for Fe and Pb**Fig 6:** Contact time**Fig 8:** Pseudo-second order plot for Fe and Pb**Fig 9:** Intra particle diffusion plot for Fe and Pb

Fig 6 shows the effect of contact time on adsorption of Fe and Pb. Optimum time of 30 and 150 minutes was obtained for Fe and Pb. Longer optimum time obtained for Pb ions is due to its large ionic size of 1.20 Å compared to Fe having 0.78 Å. The fast adsorption rate in stage before optimum time for both metal ions may be due to availability of uncovered surface area of the adsorbent which becomes exhausted. An increase in optimum time for the uptake of Pb ions was not surprising as plot obtained for intra particle diffusion gave high boundary layer of 0.005 for Pb compared to that of Fe having 0.001 as shown in table 3 and 2. Kannan and Sundaram (2001) reported that In adsorption process, the metal ions from the bulk solution travels to the thin film surrounding the adsorbent, during the process is either the thin film in the liquid generates a impermeable membrane (boundary layer) for the metal ions to pass through or the impermeable membrane may be negligible, if the former occurs the time profile of the metal ions uptake by the adsorbent may eventually increase. Simulated Pb ion solution repelled the travel of the ion to the surface of the

adsorbent. Boundary effect is an important parameter that comes into to play during metal ion adsorption. Metal ions travels across the boundary layer of the adsorbent before diffusing onto the adsorbent surface, followed by movement into the porous surface of the adsorbent. According to Kannan and Sundaram (2001) they reported that the larger the boundary layer, the more difficult for metal ions to diffuse onto the surface of the adsorbent. This explain the fact that adsorption under the same experimental condition depends upon the substrate and the metal ions. Enthalpies of hydration for studied metal ions are -1946 kJ/mol for Fe (II), -1480kJ/mol for Pb (II). This pattern shows that less negative enthalpy of hydration leads to better adsorption (Ayuba and Khuzaifa, 2014). It was observed that the trend in percentage removal of metal ion was of the order Pb (98%) > Fe (95%) > at various optimum time. Ademiluyi and Ujile (2013) studied on adsorption of Fe (II) from simulated aqueous solution. Bamboo biomass was carbonized and modified with trioxonitrate (V) acid. It was reported that there was significant increase in the adsorption of Fe (II) ions from the aqueous

solution as carbon dosage increased within contact time of 30 minutes.

Table 3. Kinetic parameters for Fe

Kinetics Equation	Q_c (mg/g)	Q_c (mg/g)	K_1 (1/min)	K_2 (g/mg.min)	h (mg/g.min)	C	R^2	Error (E_{ABS})
Pseudo first order	0.360	0.366	0.00203	NA	NA	NA	0.670	0.006
Pseudo second order	0.360	0.112	NA	0.114	1.4×10^{-3}	NA	0.559	0.108
Intra particle diffusion	NA	NA	NA	NA	NA	0.001	0.629	NA

NA: not applicable
 R^2 : Correlation coefficient
 C : boundary layer

Table 4: Kinetic parameters for Pb

Kinetics Equation	Q_c (mg/g)	Q_c (mg/g)	K_1 (1/min)	K_2 (g/mg.min)	h (mg/g.min)	C	R^2	Error (E_{ABS})
Pseudo first order	0.364	0.366	0.002	NA	NA	NA	0.818	0.002
Pseudo second order	0.364	0.058	NA	0.6323	2.1×10^{-3}	NA	0.802	0.306
Intra particle Diffusion	NA	NA	NA	NA	NA	0.005	0.802	NA

K_2 Pseudo-second order rate constant
 h initial reaction rate

Pseudo-First order equation and Pseudo-second order equation: Tables 3 and 4 give parameters for pseudo-first and pseudo-second order kinetics of Fe and Pb adsorption. The slopes and intercepts of plots of $\log(Q_c - Q_t)$ versus t were used to determine the first-order rate constant K_1 and equilibrium adsorption capacity (theoretical adsorption capacity) Q_c . values obtained showed the closeness of experimental adsorption capacity of value 0.360mg/g for Fe and 0.364 mg/g for Pb to theoretical adsorption capacity. Q_c of values 0.360mg/g for both metals. Intercept from the plot of t/Q_t versus t is use for estimating the value of h (initial reaction rate). A comparison of the results, showed high correlation coefficients for pseudo first order kinetics, hence it applied as a kinetic model for the order of the reaction.

Intra-particle diffusion: Tables 3 and 4 give parameters for intra-particle diffusion of metal ions. It is observed that there was an interference of boundary layer for both metal ions. Itodo *et al.* (2009) reported that deviation of the plot of q_t against $t^{0.5}$ shows that intra-particle transport is not the only rate limiting step, possibly adsorption occurred on the surface of the adsorbent or there was movement of metal ions through the particle-sample interface onto

the pores of the adsorbent. Similar results were reported by Badmus *et al.*(2007).

Intra-particle diffusion kinetics gives an idea of the penetrating capacity and movement of metal ions into the microspores structure of the adsorbent. The process involves series of stages. The first stage signifies movement of ions to the external surface of the adsorbent. The second involves rapid flow of ions into the microspores structure of the adsorbent. The last stage the microspores structure of the adsorbent becomes exhausted, making diffusion of metal ions to remain constant.

According to Hameed *et al.* (2006) irrespective of large value of regression coefficient, for intra-particle diffusion kinetic model to predict the kinetics of adsorption, the following parameters must be accomplished. A linear plot for intra-particle diffusion passing through the origin must be obtained. Boundary effect should be zero as this increases the rate of diffusion($C \leq 0$)

- High regression coefficient value to ascertain applicability

Table 5: Isothermal parameters for Fe sequestering

Isotherm	K _F	K _L	Q ₀	N	1/n	R ²
Freundlich	9.484	NA	NA	1.057	0.946	0.760
Langmuir	NA	0.374	7.752	NA	NA	0.811

Table 6: Isothermal parameters for Pb sequestering

Isotherm	K _F	K _L	Q ₀	N	1/n	R ²
Freundlich	7.311	NA	NA	1.279	0.782	0.957
Langmuir	NA	0.653	5.848	NA	NA	0.968

Freundlich isotherm model: $\text{Log} \frac{x}{m} = \frac{1}{n} \text{log} C_e + \text{Log} K_F \dots\dots\dots (5)$

Where $\frac{1}{n}$ and K_F represent the Freundlich constant, related to the adsorption intensity and adsorption capacity.

Freundlich equation is used in investigating the nature of the adsorbent surface. 1/n represents the adsorption intensity, used for predicting the effect of metal ions concentration on the surface of the adsorbent, and it is also a measure of the adsorbent strength (Hamidi *et al.*, 2013) From Tables 5 and 6 the values of 1/n for Fe (0.946) > Pb (0.782) indicating normal adsorption as 1/n > implies cooperative processes. Chilton *et al.*(2002) and Goldberg (2005) reported that large values for 1/n indicates changes in adsorbent surface over different metal ion concentration and that when 1/n>1 the amount of metal ions in the adsorbent is more than that in the solution. They also reported that as 1/n tends to zero, surface of adsorbent becomes more heterogeneous the influence of the ions on the surface of the adsorbent, making it more heterogeneous. Values of n obtained for all metal Arivoli *et al.* (2005) reported that adsorption intensity (n) > 1 indicates the prevalence of chemisorptions over physical adsorption. K_F value obtained for Fe (9.484 mg/g) for is greater than that of Pb (7.311mg/g). K_F is a measure of the capacity of the adsorbent for the metal ion of interest and gives the concentration of the metal ions per unit mass of the adsorbent.

K_L = Langmuir isotherm constant in L/mg
 The equation represents the equilibrium distribution of metal ions between the solid and liquid phases. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of metal ions in the plane of the surface. From Table 5 and 6 Q₀ obtained for Fe (7.7519mg/g) is higher than that of Pb (5.8480mg/g).

Parameters obtained from Langmuir plot based on the equation

$$\frac{1}{Q_e} = \frac{1}{Q_0} + \frac{1}{Q_e K_L C_e} \dots\dots\dots (6)$$

where
 C_e = Equilibrium concentration of adsorbate in mg/g
 Q_e = amount of metal ion adsorbed per gram of the adsorbent at equilibrium

The adsorptive capacity of metal ions per unit adsorbent (mg/g) was determined the expression:

$$Q_e = \frac{(C_i - C_e)}{M} \times V \dots\dots\dots (7)$$

Q₀ = Maximum monolayer coverage capacity in mg/g

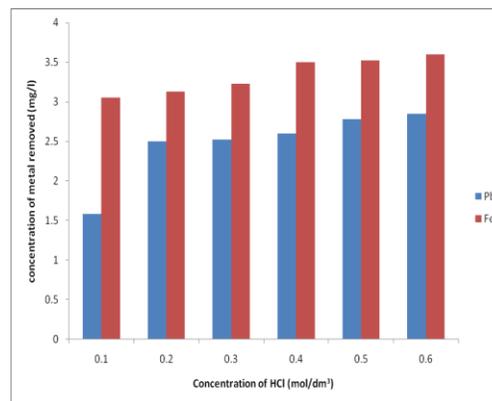


Fig 10

Fig 10 shows the concentration of metal ions recovered from both adsorbents using hydrochloric acid of different concentration. It could be seen that as the concentration of eluent increases, recovery of metal ions also increases. Matheikal *et al.* (1991) reported that higher concentrations of acids, increases proton availability, thereby dislodging metal ions that are bonded to the adsorbent by making adsorbent-adsorbate bond weak, due to changes in bond orientation. This is not surprising as large numbers of protons are made available for protonating hydroxyl or carbonyl groups present in the adsorbent, thereby preventing attractive force between H⁺ and carbonyl or hydroxyl groups (Horsfall and Spiff, 2003). The

*¹BASSEY UWEM, EDJERE, OGHENEKOHWIRORO OTOLO, SOLOMON EBIYE

order of metal ions recovery was Fe > Pb. The results obtain reveals the existence of both physical and chemical bond binding adsorbent-adsorbate in the simulated solution. Economy application of adsorbents depends on the extent of regeneration after a particular cycle of usage. The ability and ease of recovery of metal ions from adsorbent is vital if adsorption process is to be viable. Acids have the potential to elute metal ions from biosorbents, thereby important for detoxification process (Cortoras, 1992). According to Gadd (1990) adsorbent tends to deteriorate when there is prolonged exposure to higher concentration of acids. The metal ions recovered can be concentrated into purer form. Chaney *et al.* (2007) proposed burning of plant biomass to further concentrate the bio-ore. These authors showed that the value of the metal recovered in the biomass was shown to offset the cost of the technology. Furthermore, Watanabe (1997) reported that Zn and Cd recovered from a typically contaminated site could have a resale value of \$1,060/hectare.

Conclusion: The results show that the sequestration was favored in 30 and 150min with percentage removal of 95 and 98% for Fe and Pb. This effect is as a result of uptake of metal ions due to availability of adsorption sites. Kinetics models of the metal ions followed the pseudo first order with correlation coefficient of 0.670 and 0.818 for Fe and Pb. Prevalence of chemisorptions over physisorption is an indication of interaction between functional group on the adsorbent surface and the studied metal ions.

Acknowledgments: Authors are grateful to the management of Port Harcourt Refining Company a subsidiary of Nigerian National Petroleum Cooperation for permission granted in making use of their quality control Laboratory and also to the Federal Government of Nigeria for her financial support for this research.

REFERENCES

- Ahalya, N., Kanamadi, R. D. and Ramachandra, T. V. (2005). Biosorption of Chromium (VI) from aqueous solutions by the husk of Bengal gram (*Cicer avientinum*). *Electron. Journal of Biotechnology*. 8(3): 257-264.
- Cutler, J. C. (2007) "Hydrocarbon Chemistry: In: Encyclopedia of Earth. Eds. (Washington, D. C. Environmental Information Coalition, National Council for Science and the Environment.
- Zupanc, C. A. Hornung, O. Hinrichsen and M. Muhler. (2002). The Interaction of Hydrogen with Ru/MgO Catalysts. *Journal of Catalysis*. 209, 501-514.
- Bassey, U. Suleiman, M. A. T. Ochigbo, S. S. Ndamitso, M. M. Daniel, E. D. Otolu, S. E. and Chukwudi, A. (2015). Adsorption Isotherm, Kinetics and Thermodynamics Study of Cr (VI) ions onto Modified Activated Carbon from endocarp of *Canarium schweinfurthii*. *International Research Journal of Pure and Applied Chemistry*. 6(1): 46-55.
- Sato, S., Yoshihara, K., Moriyama, K., Machida, M., and Tatsumoto, H. (2007) Influence of activated carbon surface acidity on adsorption of heavy metal ions and aromatics from aqueous solution, *Appl. Surf. Sci.* 253: 8554–8559
- Jia, Y.F., Xiao, B., and Thomas, K.M. (2002). Adsorption of metal ions on nitrogen surface functional groups in activated carbons, *Langmuir*. 18 : 470–478
- Ekpete, O.A., Sor, E.N., Ogiga, E and Amadi, J.N. (2010). Adsorption of Pb²⁺ and Cu²⁺ ions from Aqueous Solutions by Mango Tree (*Mangifera indica*) Sawdust, *International Journal of Biological and Chemistry Science*. 4: 1410- 1416.
- Lartey, R.B. and Acqual, F. (1999). Developing National Capability for Manufacture of Activated Carbon from Agricultural Wastes. *Bioresource Technology*. 12: 120-135.
- Okieimen, F.E. and Wuana, R.A. (2007). Preparation and Characterization of Activated Carbon from Rice Husks. *Journal of Chemical Society*, 32: 126-136.
- Tarawou, T., Horsfall, M., Jnr. and Jose, V. (2007). Adsorption of Methyl Red by Water hyacinth (*Eichornia crassipes*), *Biomass Chemistry and biodiversity*. 4, 2236-2245
- Dilek, C. and Oznur, U. (2008) Production and Characterization of Activated Carbon from Bituminous Coal by Chemical Activation. *African Journal of Biotechnology*. 7: 3703-3710.
- Goksungur, Yekta, Uren, Sibel and Guvenc, Ulgar. (2005). Biosorption of Cadmium and Lead ions

- by ethanol treated waste baker's yeast biomass. *Bioresource Technol.* 96(1): 103-109
- Krishnakuman Parvathi, Ramachandramurthy Nagendran and Redhakrishnan Nreshkumar.(2007). Lead biosorption onto waste beer yeast by product a means to decontaminate effluent generated from artery manufacturing industry. *Electron. Journal. of Biotechnol.* 10: 92-104
- Osu Charles . I. and S.A. Odoemelam.(2010). Studies on Adsorbent Dosage, Particle Sizes and pH Constraints on Biosorption of Pb(II) and Cd(II) Ions from Aqueous Solution Using Modified and Unmodified *Crasostrea Gasar* (Bivalve). *International Archive of applied sciences and technology.* 1(1): 62-68
- Jameel .M. Dhabab. (2011). Removal of some heavy metal ions from their aqueous Solutions by duckweed. *Journal of Toxicology and Environmental Health Sciences.* 3(6):164-170,
- Toles, C.A., Marshall, W.E., Johns, M.M., Wartelle, L.H. and Mcaloon, A. (2007). Acid Activated Carbons from Almond Shells Physical Chemical and Adsorptive Properties and External Cost of Production. *Bioresources Technology.* 71: 27-87.
- Bailey, S.E., Olin, T.J., Bricka, R.M. and Adrian, D.D.(1999). A Review of Potentially LowCost Sorbents For Heavy Metals. *Water Research.* 33(11):2469-2479.
- Quek, S.Y, Wase, D.A.J. and Forster, C.F. (1998). The use of Sago Waste for the Sorption of Lead and Copper. *Water Resources.* 24(3):251-256.
- Wong, K.K., Lee, C.K., Low, K.S. and Haron, M.J. (2003). Removal of Cu and Pb by Tartaricacid Modified Rice Husk from Aqueous Solution. *Chemosphere.* 50: 23-28.
- Kannan, N. and Sundaram , M. (2001). Kinetics and mechanism of removal of methylene blue by adsorption on various carbons- a comparative study, *Dyes and Pigments,* 51: 25-40.
- Ayuba, A.M. and Khuzaifa, Y.M.(2014). *The Effect of Halides on the Adsorption of Cd (II)Onto Groundnut Shell (Arachis hypogeal)- a Thermodynamic Study.* Book of Proceeding of the 37th Annual Chemical Society of Nigeria Conference. 2: 262-270.
- Ademiluli, F.T. and Ujile, A.A.(2013). Kinetics of Batch Adsorption of Iron II ions fromAqueous Solution Using Activated Carbon from Nigerian Bamboo. *International Journal of Engineering and Technology.* 3(6): 623-629.
- Itodo, A.U., Abdulrahman, F.W., Hassan, L.G., Maigandi, S.A. and Happiness, U.O. (2009). Thermodynamic Equilibrium, Kinetics and Adsorption Mechanism of Industrial Dye Removal by Chemically Modified Poultry Droppings Activated Carbon. *Nigerian Journal of Basic and Applied Science.* 17(1):38-43.
- Badmus, M.A, Audu T.O. and Anyata B.U.(2007). Removal of Pb (++) ion from Industrial Wastewater. *Turkish Journal of Engineering and Environmental Science.* 31 (1) :437.
- Hameed, B.H., Din, A.M. and Ahmad, A.L. (2006). Adsorption of Methylene Blue ontoBamboo Based Activated Carbon: Kinetics and Equilibrium Studies. *Hazardous Materials.* 137(3): 695- 699
- Hamidi, A.A., Mohd, S.Y., Mohd, N. A., Nurul, H .A. and S.A. (2013). Physico-chemical Removal of Iron from Semi-aerobic Landfill Leachate by Limestone Filter:*Adsorption Science Technology.* 2(3): 53-64
- Chilton, N., Jack, N., Losso, N., Wayne, E. and Marshall, R. (2002). Freundlich AdsorptionIsotherm of Agricultural by Product Based Powered Activated Carbon in GeosminWater System. *Bioresource Technology.* 85 (2) :131-135.
- Goldberg, S. (2005). *Equations and Models Describing Adsorption Processes in Soils*⁴. Soil Science Society of America. 677 S. Segoe Road, Madison, WI 53711, USA. *Chemical Processes in Soils.*
- Arivoli, S., Hema, M., Karuppalah, M. and Saravanan, S. (2005). Adsorption of Chromium ion by Acid Activated Low Cost Carbon-Kinetic, Mechanistic, Thermodynamic and Equilibrium Studies. *European Journal of Chemistry.* 17: 70-78.
- Matheikal, J.T., Iyengar L. and Venkobacter C. (1991). Sorption and Desorption of Cu (II)

*¹BASSEY UWEM, EDJERE, OGHENEKOHWIRORO OTOLO, SOLOMON EBIYE

- by *Ganoderma lucidum*. *Water Pollution Resource Journal*. 26:181-200.
- Horsfall, M. and Spiff, A.I. (2003). Removal of Cu^{2+} and Zn^{2+} from Wastewater by Cassava (*Manihot esculentus*) Waste Biomass. *African Journal of Biotechnology*. 2 :969-976
- Cortas, D., Millar, M., Viedma, P., Pimentel, J. and Mestre, (1992). A. Biosorption of Metalions by *Azobacter vinelandii*. *World Journal of Microbiology and Biotechnolog*. 8:319-323.
- Gadd, G.M.(1990). Adsorption of Fe (II) from Wastewater. *Biosorption Chemistry*. 2: 421-426.
- Chaney, R., Angle, J., Broadhurst, C., Peters, C., Tappero, R. and Sparks, D.(2007). Improved Understanding of Hyperaccumulation Yields Commercial Phytoextraction and Phytomining Technologies. *Journal of Environmental Quality*. 36: 1429–1444.
- Watanabe, M. (1997). Phytoremediation on the Brink of Commercialization. *Environmental Science Technology*. 31:182–186