Batch Sorption of Lead(II) From Aqueous Stream by "Ekulu" Clay-Equilibrium, Kinetic and Thermodynamic Studies

Dawodu F. A[1], Akpomie G. K[2], and Abuh M. A[2]

[1]Department of Chemistry (Industrial), University of Ibadan, Oyo State, Nigeria

[2]Projects Development Institute (PRODA), Emene Industrial Layout, Enugu, Nigeria

fadawodu@yahoo.com

***Abstract*– Ekulu clay obtained from Ekulu in Enugu state Nigeria was utilized as a low-cost adsorbent for Lead(II) ions from solution. Batch adsorption technique was used to investigate the effect of pH, initial metal ion concentration, contact time and temperature on the adsorption process. Optimum pH of adsorption was obtained at a pH of 5.0 and equilibrium adsorption was achieved within 60 minutes. The Freundlich isotherm model gave a better fit to the adsorption data than the Langmuir isotherm. Kinetic studies revealed both the pseudo-first order and pseudo-second order as appropriate mechanism in the explanation of the sorption process. However, the pseudo-first order model with R^2 value of 0.994 was better than that of the pseudo-second order, 0.9833 obtained. Thermodynamics studies showed negative values of ΔG^0 at all temperatures. An entropy change, ΔS^0 of 32.93J/mol/K and enthalpy change ΔH^0 of 7.108kJ/mol were recorded. The result of this study indicated that the adsorption of lead(II) ions unto Ekulu clay is spontaneous, highly disordered and endothermic in nature.**

***Keywords*–** Sorption, Ekulu Clay, Heavy Metals, Lead(II), Equilibrium, Kinetic and Thermodynamics

I. INTRODUCTION

The major cause of industrial pollution in our world today is the release of industrial wastewaters containing heavy metals. These metals can have negative effects on plants, animals and human health, especially when present in high concentrations. Apart from the health effect they are non-renewable in nature. This implies that effective recovery of these metals is as important as their removal from effluents. The problem of industrial wastewater disposal has been of major environmental concern [1]. The pollutants contained in these effluents are so toxic that wastewaters have to be treated before disposal to water bodies. Heavy metals are also present in high concentrations which are non-biodegradable, hence their concentrations have to be reduced to acceptable standards before disposal into the environment [2]. If the concentration is not reduced it will have an adverse effect on public health and the quality of portable waters. Metals found to be of great environmental concern by the World Health Organization (WHO) are lead, mercury, chromium, zinc and iron [3]. Lead is one of the most toxic among these metals. The assimilation of relatively small amount of lead over a long period of time in humans can cause malfunctioning of the organs and central nervous system, high concentration of lead can damage the brain, liver and kidney [4]. As a result of this, maximum permissible limits for lead and other heavy metals in treated wastewaters are been enforced in many developing developed nations.

A lot of techniques have been used for the removal of heavy metals from wastewaters which include biological process, chemical reaction, coagulation, electrolytic method, solvent extraction, chemical precipitation, ion exchange, sedimentation, filtration, membrane process, reverse osmosis and adsorption [5]-[7]. Although, these techniques are useful, they are expensive, complex and ineffective at certain concentrations of heavy metals. The adsorption technique has been found to be the most effective and economical. Most adsorption studies have been performed using activated carbon as the adsorbent which still have the disadvantage of high cost, making it seldom applicable to developing nations [8]-[11]. Due to the high cost involved in the use of activated carbon, the removal of heavy metals using low cost adsorbent materials have been carried out by many research workers , which includes the use of clay [12], tree fern [13], bentonite [14], montmorillonite [15] and biomass materials [16]-[20]. However, most studies on the use of low cost materials for adsorption of heavy metals made use of chemical modification or the preparation of activated carbon from these materials thereby increasing the capital cost for application of such techniques.

In this study, Ekulu clay obtained from Ekulu, Enugu state, Nigeria was used as a low-cost adsorbent for the removal of lead(II) ions from solution. The clay was used without chemical modification or treatment in order to maintain the aim of a low-cost adsorbent. The effect of various experimental parameters such as pH, initial metal ion concentration, contact time and temperature were investigated. Equilibrium, kinetic and thermodynamic parameters were determined.

II. MATERIALS AND METHOD

A. Adsorbent Preparation

All the reagents used were of analytical grade and distilled de-ionized water was used in preparation of all solutions.

1000mg/l stock solution of lead(II) ions was prepared by dissolving known amount of $Pb(NO_3)_2$ in distilled de-ionized water. The pH of each solution was adjusted to the required value using a pH meter by the drop wise addition of 0.1M NaOH or 0.1M HNO_3 when required. Freshly prepared solution was used for each experiment.

B. Adsorbent Preparation and Characterization

Ekulu clay was obtained from Ekulu, Enugu, Nigeria. The collected clay was soaked in excess distilled deionized water in a pre-treated plastic container. The mixture was stirred until the clay was completely dissolved and then filtered in order to get rid of suspended particles and plant materials. The filtrate collected was allowed to settle for 24hrs. After the clay had settled at the bottom of the container, excess water was decanted from the top of the mixture. The clay obtained was sundried for several days, the oven dried at 105^0C for 2hrs. After drying the clay was grinded and then passed through a 100µm mesh sieve after which the clay was kept for use as the adsorbent.

The chemical characterization of the clay was performed using classical methods and the use of the Atomic Absorption Spectrophotometer (AAS) (Buck scientific model 210VGP).

C. Batch Adsorption Method

The effect of pH, initial metal ion concentration, contact time and temperature on the adsorption of lead(II) by Ekulu clay was determined using batch method. This was performed for different pH (1-8), metal concentration, (20-100mg/l), contact time, (10-120min) and temperature, (27-45^0C). Each adsorption study was performed by adding 2g of the adsorbent to 20mls of a given concentration of the adsorbate in a thermostat water bath (Haake wia model) for temperature regulation. At the end of the given contact time the solution was filtered. The amount of lead(II) ions remaining in the filtrate was determined using the AAS. Each experiment was repeated and the mean value was calculated in order to minimize errors. The uptake capacity of the clay for lead(II) ions was calculated from the mass balance equation given in eq. (1).

$$qe = v[Co\text{-}Ce]/m \qquad (1)$$

The percentage of lead(II) ions adsorbed was calculated from eq. (2).

$$\%\ Adsorbed = [Co\text{-}Ce]/Co \times 100 \qquad (2)$$

Where *qe* is the uptake capacity (mg/g), *Co* is the initial lead ion concentration (mg/l), *Ce* is the concentration of lead ion remaining in solution at equilibrium (mg/l), *v* is the volume of lead(II) ion solution used (litres) and *m* is the mass of clay used in (g).

III. RESULTS AND DISCUSSION

A. Chemical Composition of Clay Mineral

The chemical composition of Ekulu clay as obtained by classical method is shown in Table 1, it is observed that silica and alumina are the major constituents, other elements are present in trace amounts. Thus Pb(II) ions in solution should be predominantly removed by alumina and silica present in the clay.

TABLE 1: CLAY COMPOSITION

Composition	% by weight
Al_2O_3	27.9
SiO_2	48.21
CaO	1.98
MgO	2.03
Na_2O	1.97
Fe_2O_3	2.67
K_2O	1.32
TiO_2	0.84
MnO	1.01
LOI	12.07

B. Effect of Solution pH

The result on the effect of pH on the adsorption of lead(II) ions by Ekulu clay is shown in fig.1. It was observed that their was an increase in adsorption uptake capacity of the clay with increase in solution pH. Maximum lead(II) adsorption was obtained at pH 5.0. This optimum pH obtained of 5.0 was used in all subsequent adsorption studies. It is observed from the figure that the initial pH of a solution played a major role in lead adsorption. Under high acidic conditions (low pH values) the adsorption of lead(II) ions is not significant since the metal binding sites on the clay surface were closely associated with H_3O+ which restricted the approach of the positive Pb(II) ions due to repulsive forces. However the adsorption uptake capacity increase as pH increased since more metal binding sites were exposed with negative charges which attracted the positive Pb(II) ions unto the surface of the adsorbent[21],[22].

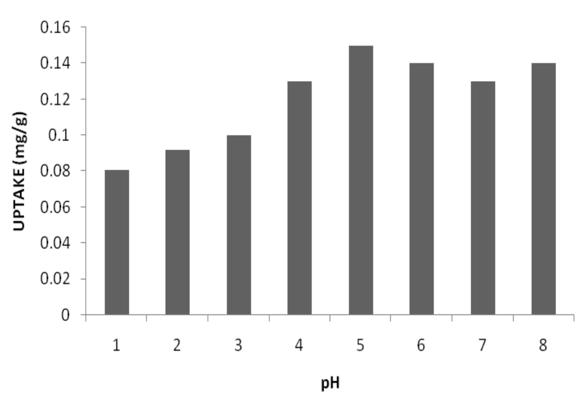

Fig. 1: Effect of pH on the adsorption of Lead(II) ions (conc,20mg/l, time, 2hrs, temp, 300K)

C. Effect of Initial metal ion concentration

The initial metal ion concentration is an important factor to be considered in adsorption studies, since the rate of adsorption of an adsorbent for a metal ion is dependent on the initial concentration of metal ion present in solution. The effect of initial lead(II) ion concentration on adsorption by Ekulu clay is presented in Fig.2. it is seen that the uptake capacity of the clay for this metal ion increased with increase in initial concentration of lead(II) ions. This increase is simply due to the presence of more metal ions in solution available for sorption. This increase in concentration increased the driving force overcoming resistances to mass transfer between the adsorbent and adsorbate species which led to the increase in adsorption observed [23].

D. Effect of Time on Adsorption

At a fixed pH, initial metal ion concentration and temperature, the result on the effect of varying the sorption time is presented in Fig. 3. The adsorption rate was seen to increase rapidly at the initial stage and optimum adsorption was attained within 40minutes. However, the equilibrium (maximum) adsorption was obtained in 60 minutes. The fast initial uptake is due to the availability of abundant active sites for sorption which became saturated with time. Furthermore, after the equilibrium time, further increase in contact time showed a slight reduction in the uptake capacity. This is probably due to the saturation of the clay surface with Pb(II) ions followed by adsorption and desorption processes occurring [24].

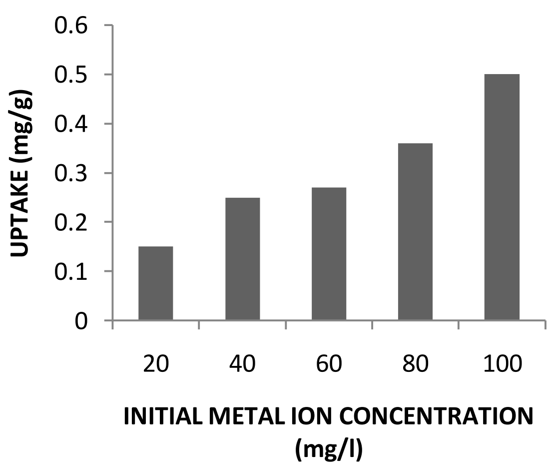

Fig. 2: Effect of initial metal ion concentration. (pH,5.0, time, 2hrs, temp, 300K)

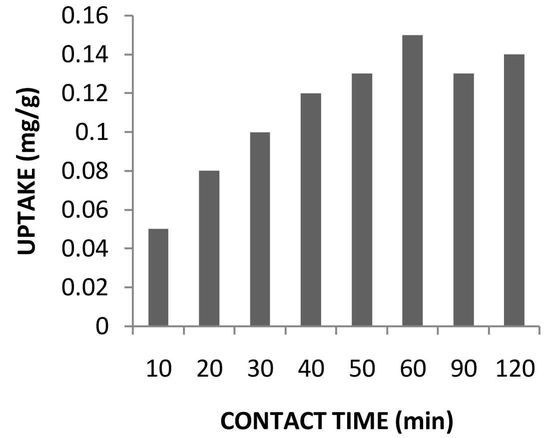

Fig. 3: Effect of contact time on the adsorption of Lead(II) ions. (pH, 5.0, conc, 20mg/l, temp, 300K)

F. Effect of Solution Temperature.

The effect of solution temperature on the adsorption of lead(II) ions unto Ekulu clay is shown in Fig.4. An increase in adsorption uptake capacity with temperature increase was observed. This suggested that the adsorption process is more likely an endothermic one. It also suggests chemical interactions between Ekulu clay and lead ions in solution. This increase is probably due to increase in the energy of the solution with increasing temperature which stimulated the diffusion of lead ions unto the clay surface. Studies on the effect of temperature on adsorption is quite complex, in the sense that it presents different types of behaviours in different experiments. However, the trend of increase in adsorption with temperature has been reported [25].

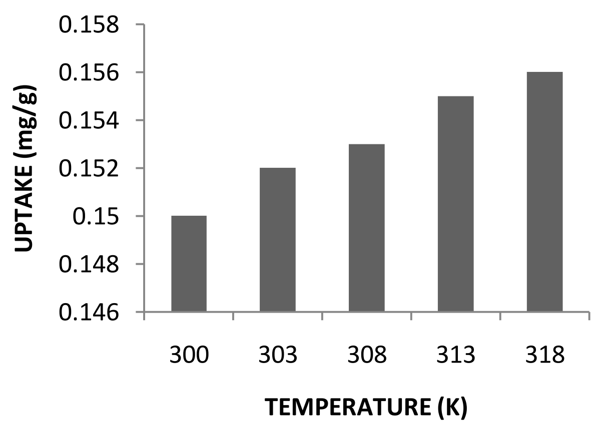

Fig. 4: Effect of Temperature on the adsorption of lead(II) ions (pH, 5.0, conc, 20mg/l, time, 2hrs)

G. Equilibrium Isotherms

The Langmuir and Freundlich adsorption isotherms were applied to the data obtained on the effect of initial metal ion concentration. Each isotherm was assessed based on the closeness of the value of the regression coefficient (R^2) to one. The closer the R^2 value to 1 the more appropriate the isotherm.

TABLE 2: EQUILIBRIUM PARAMETERS

Langmuir Isotherm			
qm	**b**	**R^2**	
0.557	0.052	0.7491	
Freundlich Isotherm			
1/n	**n**	**Kf**	**R^2**
0.436	2.29	0.074	0.8708

H. Langmuir Isotherm

This isotherm assumes that metal uptake occurs on a homogenous surface by monolayer adsorption without interactions between the active sites on the adsorbent or adsorbed metal ions [26]. The linearized form of the Langmuir isotherm is given in eq. (3).

$$Ce/qe = Ce/qm + 1/qmb \quad (3)$$

Where *Ce*(mg/l) is the concentration of lead(II) ions in equilibrium, *qe*(mg/g) is the equilibrium uptake capacity, *qm*(mg/g) is the maximum adsorption capacity corresponding to a complete monolayer coverage and *b*(L/mg) is the Langmuir isotherm constant which quantitatively reflects the affinity between the adsorbent and the adsorbate. A linear plot of *Ce/qe* against *Ce* confirms the isotherm and is shown in Fig.5. The constants *qm* and *b* were calculated from the slope and intercept respectively. The Langmuir isotherm parameters are given in Table 2. A low value of *b* indicates a favourable adsorption process [27]. The value of *b* obtained is low which implies that the sorption of lead(II) ions unto Ekulu clay is a favourable one.

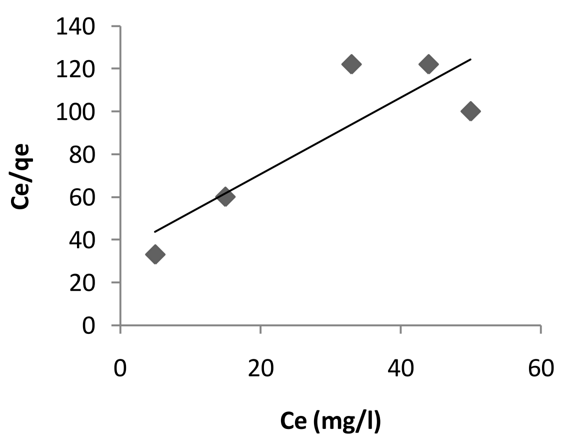

Fig. 5: Langmuir isotherm model on the adsorption of lead(II) ions

I. Freundlich Isotherm

The freundlich isotherm unlike the Langmuir isotherm assumes that adsorption takes place on a heterogeneous surface which involves a multilayer adsorption of metal ions [28]. The linear form of the freundlich equation is given in eq. (4).

$$lnqe = lnKf + [1/n]lnCe \quad (4)$$

where *n* is a dimensionless constant describing the adsorption intensity and *Kf* (L/g) is the freundlich isotherm constant describing the adsorption capacity of the adsorbent. This isotherm was confirmed by the plot of *lnqe* against *lnCe* shown in fig.6. The constants *n* and Kf were obtained from the slope and intercept respectively. The freundlich isotherm parameters are presented in Table 2. As seen in Table 2, the value of the regression coefficient (R^2) of this model is closer to 1 than that obtained for the Langmuir isotherm. This shows a greater applicability of the freundlich isotherm in the description of the adsorption data. A value of *n* above unity indicates a favourable adsorption [28]. Again a favourable adsorption was obtained between lead(II) ions and Ekulu clay.

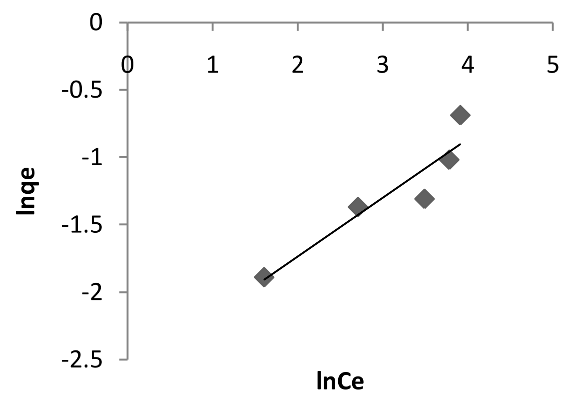

Fig. 6: Freundlich Isotherm model on the adsorption of lead(II) ions

J. Kinetic Studies

The pseudo-first order and pseudo-second order model equations were applied to the data deduced on the effect of contact time in order to evaluate kinetic parameters. These models were also assessed based on the closeness of their regression coefficient to one.

TABLE 3: KINETIC PARAMETERS

Pseudo-first order		
qe	**Ki**	**R^2**
0.157	0.0407	0.994
Pseudo-second order		
qe	**K_2**	**R^2**
0.243	0.101	0.9833

K. Pseudo-first Order Model

The lagergren first order kinetic model equation [29] is given in eq. (5).

$$ln[qe-qt] = lnqe-Kit \quad (5)$$

where *qe*(mg/g) is the amount of lead(II) ions adsorbed at equilibrium, *qt*(mg/g) is the amount adsorbed after a given time *t*, *Ki* (min-1) is the pseudo first order rate constant and *t* is the contact time (min). This model was applied by a linear plot of *ln(qe-qt)* against *t* as shown in fig.7. The constants *qe* and *Ki* were obtained from the intercept and slope respectively. The pseudo-first order kinetic parameters are given in Table 3.

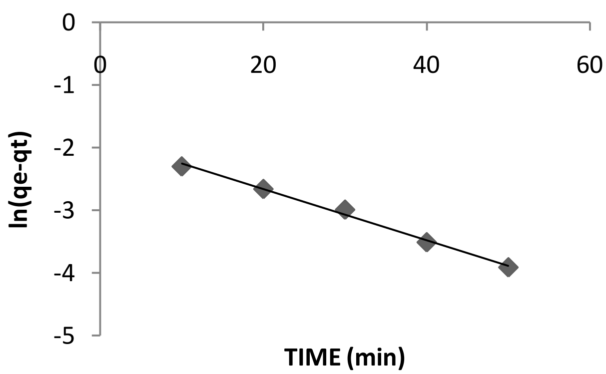

Fig. 7: Pseudo-first order model on the adsorption of Lead(II) ions

L . Pseudo-Second Order Model

The pseudo-second order model assumes that the rate of occupation of active sites is proportional to the square of the number of unoccupied sites. It also assumes that most adsorption systems follow a second order mechanism [13]. The linear form of the pseudo-second order equation is given in eq. (6).

$$t/qt = 1/K_2qe^2 + t/qe \quad (6)$$

Where *qe* (mg/g) is the maximum adsorption capacity for the pseudo-second order adsorption, K_2 (g/mg/min) is the equilibrium rate constant for pseudo-second order adsorption. The constants *qe* and K_2 were calculated from the slope and intercept of the plot *t/qt* against *t* shown in fig.8. The pseudo-second order parameters are given in Table 3. Looking at the R^2 values, it is observed that both models gave good fits to the experimental results. However the Pseudo-first other model was better than the pseudo second order model.

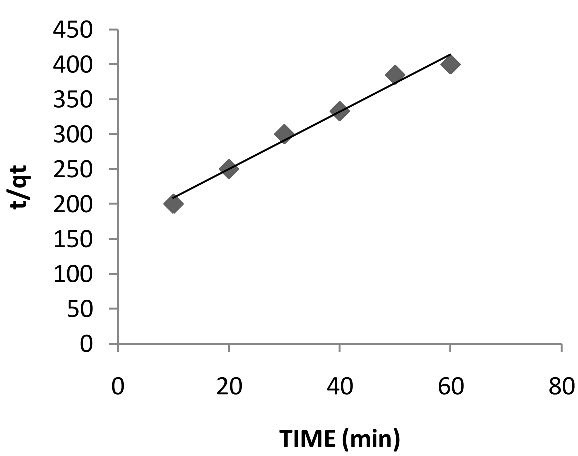

Fig. 8: Pseudo-Second order model on the adsorption of lead(II) ions

TABLE 4: THERMODYNAMIC PARAMETERS

T(K)	ΔG^0 (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (J/mol/K)
300	-2.74	7.108	32.93
303	-2.91		
308	-3.03		
313	-3.22		
318	-3.35		

M. Thermodynamics of sorption

Thermodynamic analysis was applied to the data obtained on the effect of temperature on adsorption. The equilibrium constant *Kc* at different initial concentration was calculated from eq. (7).

$$Kc = Cad/Ce \quad (7)$$

Where *Cad* (mg/l) is the concentration of lead(II) adsorbed by the clay at equilibrium and *Ce* (mg/l) is the concentration of lead(II) remaining in solution at equilibrium. The change in Gibbs free energy was calculated from eq. (8).

$$\Delta G^0 = RTlnKc \quad (8)$$

Where *R* is the ideal gas constant (8.314J/mol/K), *T* is the absolute temperature (K). the changes in entropy ΔS^0 and enthalpy ΔG^0 were obtained from (9).

$$\Delta G^0 = -\Delta S^0(T) + \Delta H^0 \quad (9)$$

A linear plot of ΔG^0 against *T*(K) confirms the model and is shown in fig.9. The constants ΔS^0 and ΔH^0 were obtained from slope and intercept respectively, thermodynamic parameters obtained are presented in Table 4. The value of R^2 obtained showed a good agreement between the entropy change and temperature. Negative values of ΔG^0 obtained at all temperatures indicated a spontaneous process. A highly disordered process was also indicated by the positive value of ΔS^0. Similarly, the positive enthalpy change showed an endothermic adsorption process, which implies an increase in adsorption capacity with temperature increase.

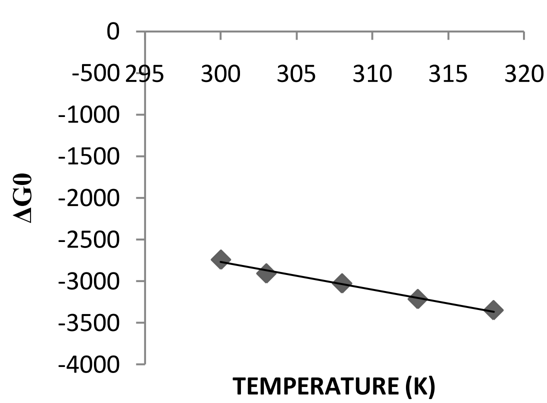

Fig. 9: Thermodynamic plot for the adsorption of lead(II) ions

IV. CONCLUSION

The batch adsorption of Lead(II) ions unto Ekulu clay showed that the clay can be used as a cheap alternative adsorbent for removal of lead ions. Adsorption parameters such as pH, initial metal ion concentration, contact time and temperature were useful in the description of the adsorption process. Langmuir and freundlich isotherms showed a favourable adsorption process. Both the pseudo-first and pseudo-second order models were applicable in kinetics analysis. Thermodynamics studies indicated a highly disordered, spontaneous and endothermic sorption process between Lead(II) ions and Ekulu clay.

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