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Equilibrium, Thermodynamic and Kinetic Studies on the Adsorption of lead(II) from Solution by "Agbani Clay"

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Abstract

This paper describes the adsorption of Lead(II) ions from solution by Agbani clay obtained from Nkanu west local government area, Enugu state, Nigeria. The aim of this study was to investigate the potential of Agbani clay as a low-cost adsorbent for Lead(II) ions from industrial wastewaters. The adsorption experiment was performed using batch technique to investigate the effect of pH, initial metal ion concentration, temperature and time. All these parameters proved to be useful in the description of the adsorption process. An optimum pH of adsorption was achieved at 6.0. Equilibrium isotherm models showed the Freundlich isotherm with the best fit as indicated by the regression coefficient R^2 value of 0.9891, this was followed by the Temkin isotherm, (0.9121) and the least the Langmuir isotherm (0.8687). Kinetic studies revealed the Pseudo-second order with the best fit of 0.9982, although a good fit was also obtained (0.9924) by the Pseudo-first order model. Thermodynamic analysis showed a spontaneous adsorption process as negative values of ΔG^0 were obtained at all temperatures. The positive enthalpy change ΔH^0, (14.37KJ/mol) indicated an endothermic process and an increase in adsorption with increase in temperature was observed. A highly disordered process was indicated by the positive entropy change ΔS^0 (62.75J/molK). The results showed the applicability of Agbani clay as a low cost adsorbent for lead(II) ions from aqueous solution.

Keywords: Agbani clay, equilibrium, isotherm, kinetic, lead(II), thermodynamic.

Introduction

The problem of pollution of the environment with toxic metal substances such as heavy metals have become a major problem of great environmental concern. The reason is simply due to their high toxicity and harmful effect to plants, animals and humans[1]. Lead is widely used in many industries such as battery, metal plating, smelting, painting and mining industries. The wastewaters generated by these industries are usually contaminated with lead, which spreads into the environment thereby accumulating in the food chain since they are non-biodegradable and subsequently results in serious environmental health problems. A lot of research have been performed on the removal of lead from effluents because this metal is highly toxic to most living things and also have no known biological use[2]. Lead is a general metabolic poison and enzyme inhibitor. When present in high concentrations can cause serious damages to the central nervous system and affect the functioning of the blood, liver, kidney and brains of humans[3,4].

The permissible level of lead in drinking water is 0.05mg/l, the concentration in most industrial wastewaters is approximately in the range 200-500mg/l, according to water quality standard, this value is extremely high. It is therefore necessary that the concentration should be reduced to acceptable levels which satisfies environmental regulations[5].

The methods which have been used to remove lead and other heavy metals from industrial effluents include solvent extraction, membrane filtration, ion exchange, chemical precipitation, electrochemical deposition, chemical oxidation and reduction, reverse osmosis and adsorption. Among these techniques exploited, adsorption have been found to be the most successful to its relative low maintenance cost, high efficiency and ease of operation[6]. Most studies on the removal of heavy metals and organic substances from solution by adsorption have been performed using activated carbon[7,8,9]. In situations where commercial activated carbons are not used, other low cost materials have often been used to prepare activated carbon[10,11,12]. However, whether commercial activated carbon or the activated carbon prepared from other materials are used, this method is quite expensive. Therefore the need for cheaper or low cost adsorbents have become the focus of many scientist. Various low cost materials have been utilized and they include drumstick[13], cocoa shell[14], solid agricultural waste[15], clay[16] and marine algae[17].

In the present study, Agbani clay which was obtained from Agbani in Nkanu west local government area, Enugu state, Nigeria was used as an adsorbent for lead for lead removal from solution. The aim of this experiment was to investigate the feasibility of the clay as a low-cost adsorbent. The effect of pH, initial lead(II) ion concentration, contact time and temperature on the adsorption process were determined. Thermodynamics, equilibrium and kinetic parameters were also determined.

Methodology

Adsorbent and Adsorbate Preparation: The sample of Agbani clay was collected from Agbani in Nkanu west local government area, Enugu, Nigeria. The clay was immersed in excess distilled water in a plastic container and stirred to ensure uniform dissolution. The mixture was filtered in order to remove unwanted plant materials and suspended particles, after which the filtrate was kept for 24hrs to settle. Excess water was decanted from the top while the clay material at the bottom was sundried for several days. It was then oven dried at a temperature of 105^0C for 2hrs, pulverized and then passed through a100µm mesh sieve. The clay sample was used as an adsorbent.

The adsorbate lead(II) ions were prepared by dissolving appropriate quantity of analytical grade of $Pb(NO_3)_2$ in de-ionized water in order to obtain a stock solution of concentration 1000mg/l. Several standard solutions of concentrations 20, 40, 60, 80 and 100mg/l were then prepared from the stock solution by serial dilution. The pH of each solution was adjusted to the required value by drop wise addition of 0.1M NaOH or 0.1M HNO_3 using a pH meter. Freshly prepared solution was used for each experiment.

The chemical characterization of the clay was obtained by the use of classical method with the Atomic Absorption Spectrophotometer (AAS) (Buck scientific model 210VGP).

Sorption Experiment: The effect of pH, initial metal ion concentration, time and temperature on the adsorption of lead(II) by Agbani clay was performed using batch technique. This was done at pH values, (1-8), initial metal ion concentration (20-100mg/l), contact time, (10-120 min) and temperature (27-45^0C). The experiment was performed by contacting 2g of the adsorbent with 20mls of a given concentration of lead(II) solution in a thermostat water bath for temperature regulation. For a particular study, a parameter was varied while the others were kept constant at the end of the given contact time, the solution was filtered and the filtrate was analyzed for the concentration of lead(II) ions remaining in solution using the AAS. Each experiment was done in duplicate and the mean value was calculated to ensure quality assurance. The amount of lead(II) ions adsorbed by the clay was calculated from a mass balance equation given in (1).

$$qe = v[Co-Ce]/m \quad (1)$$

The percentage adsorbed by the clay was calculated from (2).

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

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

Results and Discussion

Chemical Composition of Agbani Clay: The result for the chemical characterization of Agbani clay as determined by classical method is shown in table 1. it is expected that lead(II) ions in solution should be removed mainly by alumina and silica since the clay consist mainly of a large percentage of SiO_2 and Al_2O_3. However, other elements are present in smaller compositions and may have some effect on the adsorption capacity of the clay mineral.

Effect of Initial Lead(II) ion Concentration: The adsorption of metal ions by an adsorbent is strongly dependent on the initial concentration of metal ions in solution. This makes it an important parameter to be determined in adsorption studies. The result on the effect of initial lead(II) ion concentration on its adsorption by Agbani clay is shown in figure 1. It is seen that an increase in adsorption capacity with increase in metal ion concentration was obtained. This is simply due to the presence of more lead(II) ions in solution available for binding to the active sites of the clay with increase in concentration. This increase in concentration acts as a driving force which overcomes to mass transfer between lead ions and the active sites on the adsorbent[18].

Adsorption Dependence on pH: The initial pH of a solution is also a very important factor to be considered in adsorption studies as it has been observed to play a major role in the adsorption of metal ions by various adsorbents[19]. The result illustrating the dependence of pH on adsorption of lead by Agbani clay mineral is presented in figure 2. It was observed that minimal adsorption uptake were recorded at lower pH values, and increased with increase in pH. Maximum adsorption was obtained in the pH range of 4 to 8 with optimum adsorption at 6.0. This can be explained that at low pH values the solution is highly acidic. This led to the competition between lead ions and protons for the active sites on the clay resulting in a low adsorption capacity. Subsequently, as the pH of the solution increased, the number of protons decreased which reduced the competition between lead ions and protons for the active sites, hence more lead ions were adsorbed from solution[20].

Temperature Effect on Adsorption: The result on the dependence of temperature on the adsorption of lead(II) ions unto Agbani clay is presented in figure 3. An increase in adsorption uptake capacity with increase in temperature from 27-45^0C was observed. This increase in adsorption with temperature increase indicated an endothermic adsorption process. It also suggested that the mechanism involved in the removal of lead(II) ions by Agbani clay is a chemical adsorption. However, this mechanism is restricted to just one layer of adsorbed metal ions but may be accompanied by additional layers of physically adsorbed metal ions unto the existing chemically adsorbed layer[21]. Such trend of increase in adsorption with increase in temperature has been reported[22].

Table-1
Chemical characterization of Agbani Clay

Composition	SiO_2	Al_2O_3	CaO	MgO	Na_2O	Fe_2O_3	K_2O	TiO_2	MnO	LOI
Weight %	50.3	26.09	1.93	1.77	1.35	2.31	1.01	0.56	0.81	13.87

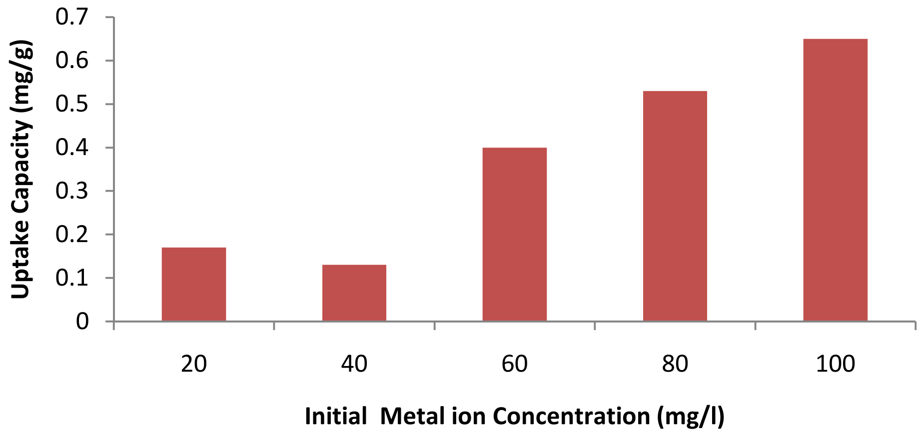

Figure-1
Effect of initial metal ion concentration on adsorption of Lead(II) by Agbani Clay (pH, 6.0, time, 2hrs, Temp, 300K)

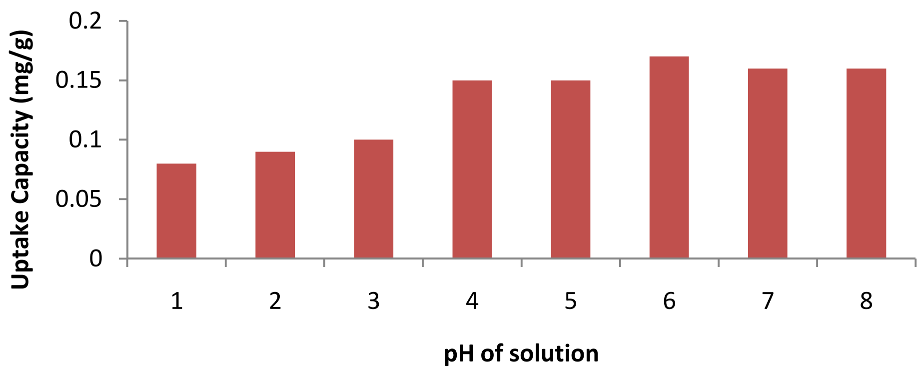

Figure-2
Effect of pH on the adsorption of Lead(II) by Agbani Clay (Conc, 20mg/l, Time, 2hrs, temp, 300K)

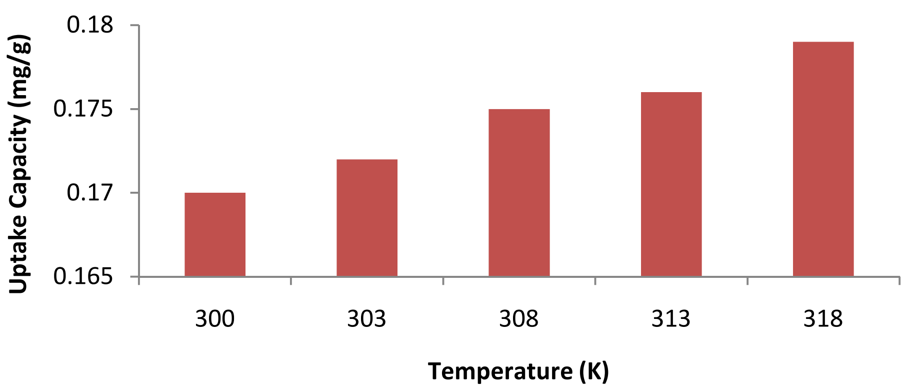

Figure-3
Effect of Temperature on the adsorption of Lead(II) by Agbani Clay (pH 6.0, Conc, 20mg/l, Time, 2hrs)

Effect of Time on Adsorption: The effect of contact time is a very important factor to be considered in adsorption studies as it helps establish the rate of adsorption and the attainment of equilibrium for a particular process. Figure 4 shows a representation of the effect of contact time on lead adsorption by Agbani clay. As observed, a fast initial uptake was obtained in the initial stage with equilibrium adsorption attained within 50 minutes. The fast metal uptake observed at the initial stage is due to the availability of abundant active sites on the clay surface which became saturated with time. The fast initial uptake observed initially and the subsequent gradual uptake may be due to two different types of adsorption mechanism namely ion exchange and chemisorptions respectively[23].

Isotherm Modeling: Equilibrium adsorption isotherms helps provide important information on the adsorption mechanisms, the surface properties and affinities of the adsorbent. The Langmuir, Freundlich and Temkin isotherm equations were applied in this study. The linear regression is frequently used to determine the best-fitting isotherm and the applicability of isotherm equations is compared by judging the correlation coefficients.

Langmuir Isotherm: The Langmuir isotherm is valid for a monolayer adsorption unto a surface containing a finite number of identical sites[24]. The linear form of the Langmuir equation is given in (3).

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

Where qe (mg/g) is the adsorption capacity at equilibrium, qm (mg/g) is the maximum adsorption capacity, Ce (mg/l) is the concentration of lead(II) ions in solution at equilibrium and b (L/mg) is the Langmuir isotherm constant. the plot of Ce/qe against Ce is shown in figure 5 and the constants qm and b were obtained from the slope and intercept respectively. Table 2 shows the parameters obtained from the Langmuir isotherm.

Temkin Isotherm: The Temkin isotherm considers the effect of the heat of adsorption of all molecules and assumes that this heat decreases linearly with coverage due to adsorbate and adsorbent interactions[25]. The linear form of the Temkins isotherm equation is given in (4).

$$qe = [RT/b]lnA + [RT/b]lnCe \quad (4)$$

Where $RT/b = B$ (J/mol) which is Temkin constants related to the heat of sorption, A(L/g) is the equilibrium binding constants corresponding to the maximum binding energy, R is the universal gas constant (8.314J/mol/K) and T(K) is the absolute temperature. The plot of qe against $lnCe$ is shown in figure 6 and the Temkins isotherm parameters are recorded in table 2.

Freundlich Isotherm: This isotherm is applicable to non-ideal adsorption on heterogeneous surfaces[26] and the linear form of the Freundlich isotherm equation is given in (5)

$$lnqe = lnKf + 1/nlnCe \quad (5)$$

Where n and Kf (L/g) are Freundlich constants representing the adsorption intensity and adsorption capacity respectively. Kf and n can be determined from the intercept and slope of the linear plot of $lnqe$ against $lnCe$ shown in figure 7. It is seen from Table 2 that Freundlich isotherm gave a better fit to the experimental data than the Temkins and Langmuir isotherms judging by their R^2 values. Also the value of n showed a favorable adsorption between the adsorbent and adsorbate species[27].

Table-2
Equilibrium Isotherm Model Parameters

Langmuir Isotherm			Freundlich Isotherm				Temkin Isotherm		
qm	b	R^2	1/n	n	Kf	R^2	A	B	R^2
0.828	0.061	0.8687	0.533	1.88	0.09	0.989	0.671	0.1836	0.9121

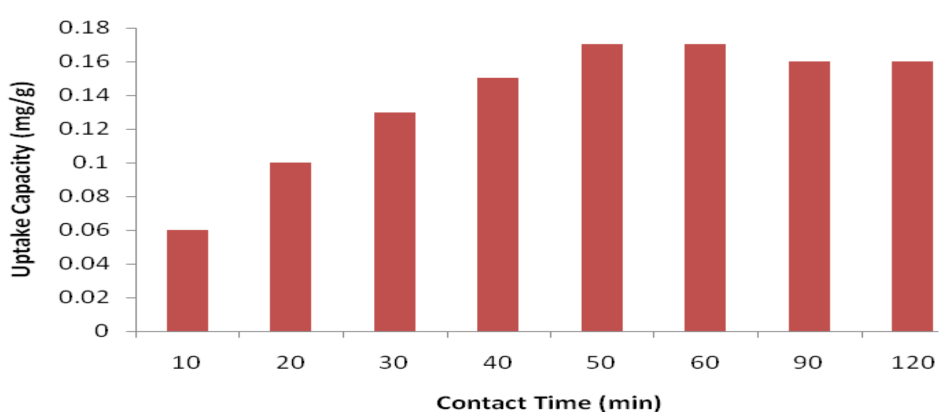

Figure-4
Effect of Contact time on the adsorption of Lead(II) by Agbani Clay (pH, 6.0, Conc, 20mg/l, temp, 300K)

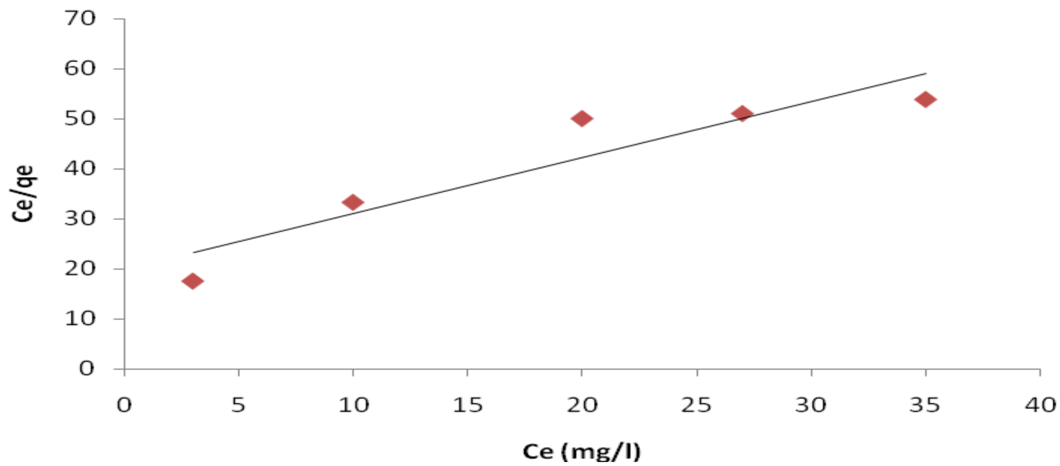

Figure-5
Langmuir Isotherm model on the adsorption of Lead(II) by Agbani Clay (pH, 6.0, time, 2hrs, Temp, 300K)

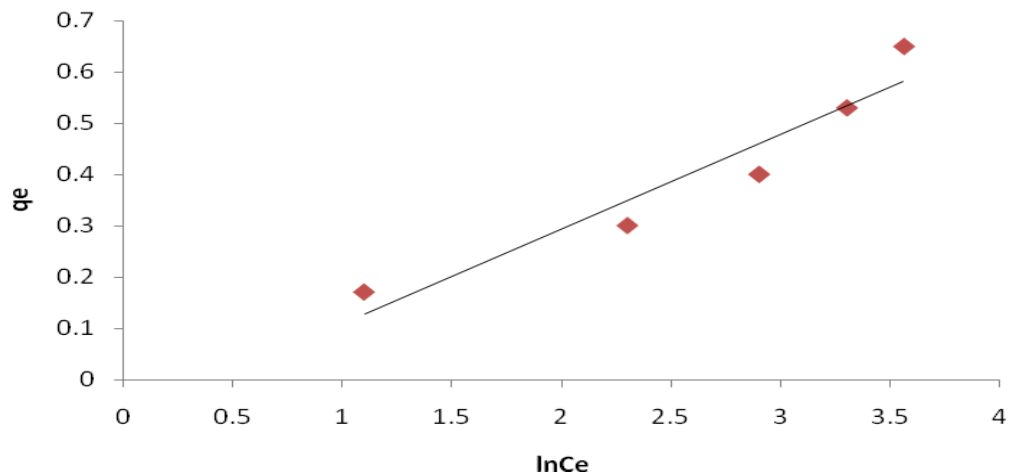

Figure-6
Temkin Isotherm model on the adsorption of Lead(II) by Agbani Clay (pH, 6.0, time, 2hrs, Temp, 300K)

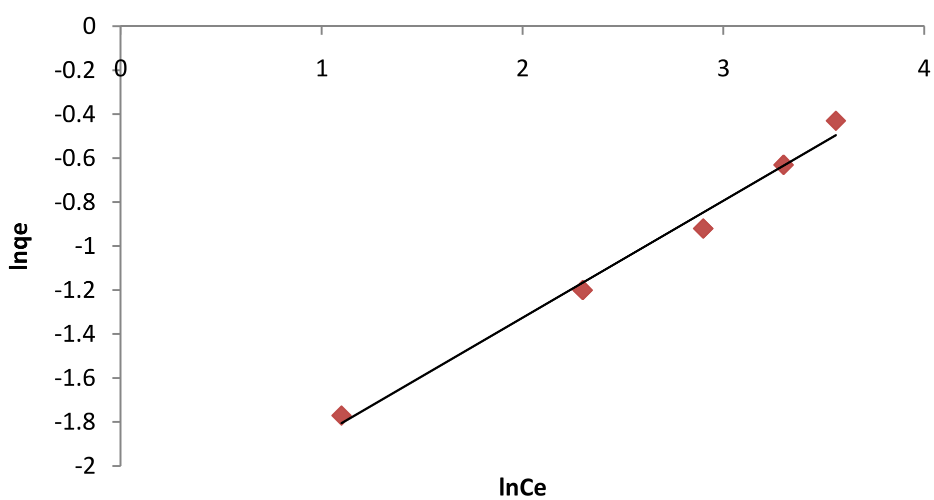

Figure-7
Freundlich Isotherm model on the adsorption of Lead(II) by Agbani Clay (pH, 6.0, time, 2hrs, Temp, 300K)

Kinetic Modeling: In order to investigate the rate mechanism of the adsorption process, the Pseudo-first order and Pseudo-second order models were applied to the kinetic data.

Pseudo First-Order: The Lagergren first order model[28] was applied to the data deduced from the effect of time on adsorption, the linear form of the equation is given in (6).

$$ln[qe-qt] = lnqe- Kit \quad (6)$$

Where *qe* and *qt* are the amounts of lead(II) adsorbed (mg/g) at equilibrium and time *t* respectively, *Ki* (min^{-1}) is the Pseudo first order rate constant of adsorption. The value of *qe* and *Ki* were calculated from the intercept and slope of the plot of *ln(qe-qt)* against *t*, shown in figure 8. The respective values and the regression coefficient (R^2) obtained are given in table 3.

Pseudo Second Order: The Pseudo second order equation is based on the assumption that chemisorptions is the rate-determining step[29] and is given in (7)

$$t/qt = 1/K_2qe^2 + t/qe \quad (7)$$

where K_2 (g/mg/min) is the rate constant of Pseudo-second order adsorption. Values of *qe* and K_2 were calculated from the slope and intercept of the plot of *t/qt* against *t* and is shown in figure 9. The pseudo-second order kinetic parameters are given in table 3. Looking at the values of the regression coefficient presented in table 3, it is seen that the pseudo-second order model gave a better fit to the adsorption data than the First order model, although, the value obtained in the Pseudo-first order is still appropriate in describing the kinetics of sorption involved in this experiment. This shows that surface processes involving chemisorptions and physisorption participate in the adsorption of lead(II) ions by Agbani clay.

Thermodynamics: The thermodynamic parameters for the adsorption of lead(II) by Agbani clay was deduced from the data obtained on the effect of temperature. The thermodynamic parameters include changes in Gibbs free energy ΔG^0, enthalpy change ΔH^0 and entropy change ΔS^0, these parameters were determined from (8)-(10).

$$Kc = Cad/Ce \quad (8)$$

$$\Delta G^0 = -RTlnKc \quad (9)$$

$$\Delta G^0 = -\Delta S^0(T) + \Delta H^0 \quad (10)$$

Where Kc is the equilibrium constant obtained at different initial concentrations, *Cad* (mg/l) is the concentration of lead(II) ion adsorbed while *Ce* (mg/l) is the equilibrium concentration, *R* is the universal gas constant and *T*(K) is the absolute temperature. The profile for the change in free energy with temperature is shown in figure 10 and thermodynamic parameters are recorded in table 4. The R^2 value obtained showed a good fit to the data. Negative values of the Gibbs free energy obtained at all temperatures showed that the adsorption process is spontaneous and the degree of spontaneity increases with increasing temperature. The adsorption process was also found to be endothermic as indicated by the positive enthalpy change, ΔH^0 of 14.37KJ/mol., this supports our result obtained on the increase in adsorption with increase in temperature. The positive value of entropy change ΔS^0 suggested an increase in entropy with adsorption. This occurred as a result of redistribution of energy between the adsorbate and adsorbent. Before adsorption, the metal ions near the surface of the adsorbent will be more ordered than in the subsequent adsorbed state and the ratio of free metal ions to ions interacting with the adsorbent will be higher than in the adsorbed state. Therefore the distribution of rotational and translational energy among molecules will increase with increase in adsorption, by producing a positive value of ΔS^0 and an increase in randomness at the solid-solution interface during adsorption[30].

Table-3
Kinetic Parameters

Pseudo-First Order			Pseudo-Second-Order		
qe	**Ki**	**R^2**	**qe**	**K_2**	**R^2**
0.2	0.056	0.9924	0.31	0.077	0.9982

Table-4
Thermodynamic Parameters

Temperature (K)	ΔG^0 (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (J/mol/K)
300	-4.34	14.37	62.75
303	-4.56		
308	-4.98		
313	-5.17		
318	-5.66		

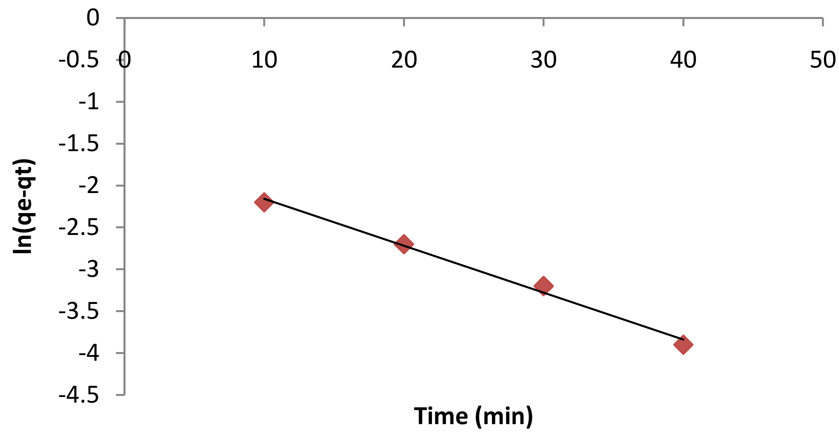

Figure-8
Pseudo First-Order Model on the adsorption of Lead(II) by Agbani Clay (pH, 6.0, Conc, 20mg/l, temp, 300K)

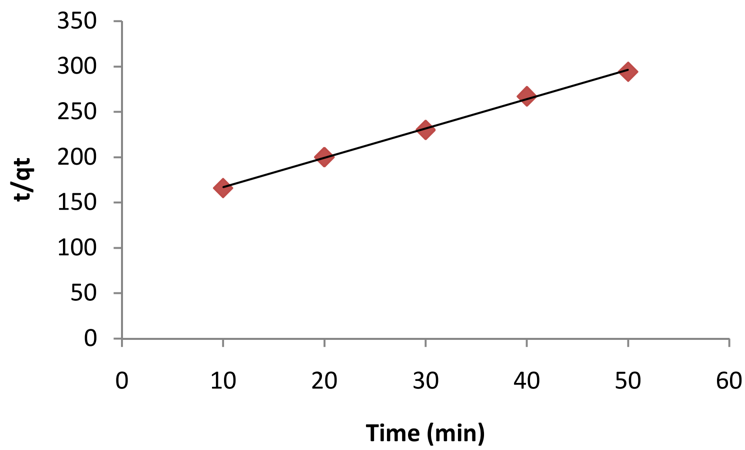

Figure-9
Pseudo Second-Order Model on the adsorption of Lead(II) by Agbani Clay (pH, 6.0, Conc, 20mg/l, temp, 300K)

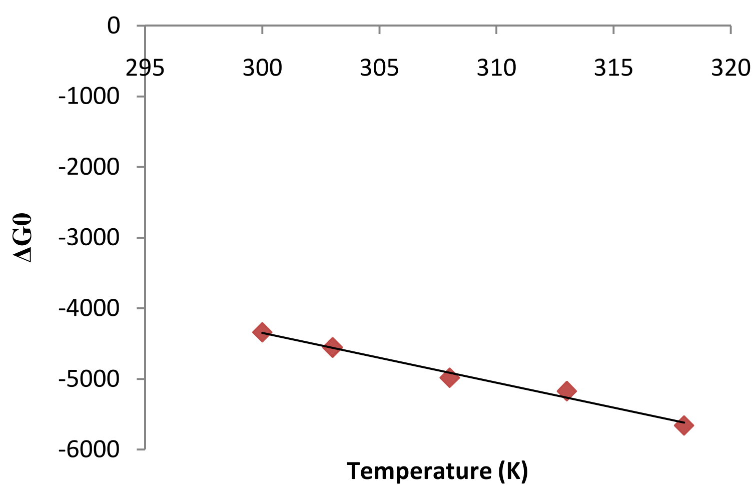

Figure-10
Thermodynamic plot on the adsorption of Lead(II) by Agbani Clay (pH 6.0, Conc, 20mg/l, Time, 2hrs)

Conclusion

The results of this experiment showed that Agbani clay can be used as a low-cost adsorbent for the removal of Lead(II) ions from aqueous solution. Hence, most small scale industries in Nigeria and developing nations can make use of this material, in order to overcome the problem of high cost involved in treating industrial wastewaters.

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