



Investigation of Kinetic and Thermodynamic Behaviour of Adsorption of Lead (II) ions onto Functionalized Nigerian Ahoko Kaolin

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ABSTRACT

This paper focus on the investigation of kinetic and thermodynamic characteristic of adsorption of Pb^{2+} ions unto functionalized Nigerian Ahoko Kaolin. The adsorption rate of Pb^{2+} onto the TPP-functionalized and the un-functionalized kaolin was found to increase from 0.479 to 1.915 and 0.340 to 1.894 ($mgg^{-1}min^{-1}$) in the first 10 min while increasing the initial Pb^{2+} concentration from 250-1000 mg/L. There was decrease in adsorption thereafter attaining equilibrium after 70 min. Increase in temperature from 298 to 323 K increase both the pseudo-second order reaction rate constant K_2 and the initial sorption rate h on both the functionalized and un-functionalized kaolin. The values of K_2 increase from 0.365 to 0.426 ($mgg^{-1}min^{-1}$) and 0.217 to 0.296 ($mgg^{-1}min^{-1}$). The values of enthalpy obtained suggest that the adsorption process is endothermic in both material used with the functionalized kaolin showing higher endothermic behavior. The values for entropy and enthalpy are 106.40 and 33318.82 ($kJmol^{-1}$) for functionalized kaolin and 109.78 and 34624.73 ($kJmol^{-1}$) for the un-functionalized kaolin. The adsorption process follows a pseudo-second order reaction path.

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Introduction

There is no doubt that lead is extremely toxic and dangerous to human being. Lead is pollutant that is present in both water and air. In air, it is derived from lead emission from automobiles while processing industries such as metal plating, acid battery, metal clean up services are the major mean of lead pollution into the water bodies (Acharya, J. *et al*, 2009). Lead has detrimental effect on the human body and its function affect the metabolism, blood and kidney. Lead also accumulate in the body more rapidly than it is excreted. It retard haemoglobin production, the major cause of anemia, therefore it is imperative that regulation of safe limit and removal of excess lead from the environment be taken very seriously. There is permissible limit of lead in wastewater and other medium by relevant agency. For example, the environmental protection agency (EPA) has a limit of 0.05 mg/L while Indian's bureau of standard (BIS) has standard of 0.1 mg/L (Goel J., *et al* 2005).

There are several technologies are in use for the heavy metals from the location in the environment. Some of these technologies include precipitation where as metal are precipitated from contaminated water by the process of conversion of soluble heavy metal into insoluble salt that will precipitate, thereafter the precipitate can be removed by physical method such as clarification or filtration. Another technique is removal heavy metal include solid/liquid separation and biological process. While solid/ liquid separation involve the use of precipitation, ion exchange, and co-precipitation to transfer the contaminant from dissolved state to solid phase by separation by gravity settling or sedimentation, biological processes involves the use of bacteria in catalyzing many of the cleaning involving heavy metals removal. For example Moringa Oleifera has been used as a biological material for metal removal (Jamal *et al* 2008). In all of these techniques, the removal of heavy metal at low concentration are difficult to use,

hence the process of adsorption is one of the few alternative method available for heavy metal at such condition (Bong *et al* 2004). Quite a number of adsorbent materials have been studied for their capacity to remove heavy metal, these materials are mainly natural or biological materials such as activated carbon, Chitosan lignite, zeolites and kaolin. Several studies have shown that kaolin can be an effective material for the removal of heavy metal ion from wastewaters. Kaolin is regarded as a good adsorbent for the removal of heavy metal such as As, Cd, Co, Cu, Fe, Mn, Ni, Zn, and Pb in their ionic form (Salem A. and Akbari R.S., 2011) Several factors influence the adsorption capacity of kaolin particularly pH and the presence of hydroxyl groups on the edge of the kaolinite framework and further modification of kaolin can as well increase the adsorption capacity. Few studies carried out on the modification of kaolin before adsorption process indicate that the capacity of such modified kaolin increases especially for the removal of heavy metal such as Pb (Salem A. and Akbari R.S., 2011). Therefore kaolin both in it natural and functionalized form is regarded as low cost adsorbent material for the removal of Pb from wastewater, however to our knowledge Nigerian Ahoko Kaolin adsorption properties and capacity has not being investigated since it is know fact that the adsorption capacity of kaolin depend on chemical and mineralogical composition of such material. This is a first part of our work on Nigerian Ahoko Kaolin as an adsorbent with focus on the kinetic and thermodynamic behaviour of the material in the adsorption of Pb ion.

Material and Method

The materials used in this research are kaolin sample obtained from Ahoko Kogi state Nigeria, chemicals such as tripolyphosphate (VI) solution, hydrogen peroxide, Sodium hydroxide, distilled and deionised water.

Kaolin Collection and Pre-treatment

The Kaolin used in this research work was obtained from Ahoko, Kogi State, Nigeria. After collection, some solid, metallic and other hefty materials were eliminated from the kaolin sample. The sample was also sieved using a 250 μm Sieve in order to eliminate particles which are not clay from the kaolin sample and 500 g of the kaolin sample was suspended into distilled water in a 1000ml beaker for 8.0 hours. The raw kaolin sample was purified by treating the samples with minute quantity of 30% hydrogen peroxide solution until all effervescence stopped. This method of treatment was performed in order to remove any organic particles left in the clay. The treated sample was left for 24 hours and then there was decantation of the supernatant, and deionised water was used to thoroughly wash the kaolin sample left, in order to remove any traces of hydrogen peroxide left in the kaolin clay. The sludge suspended kaolin was dried using an electric oven at a temperature of 363 K to obtain the kaolin clay sample used. The kaolin sample's mineralogical phase were identified with an X-ray diffraction (XRD machine model X'pert Pro by Philips. The beam was focused using a 1/8" and 1/4" divergence slit, The scan step used was 65.1352s while the scan step size was 0.0170° (2 theta) and the generator setting was fixed at 30 mA and 40 kV). The image of the starting was also recorded by Scanning Electronic Microscope (SEM) (FEI Quanta 200 environmental SEM model).

Modification of the Kaolin

100g of the kaolin clay sample were bring into an equilibrium state with 2 liters of 200 mg/liters (0.40L of 0.10 mol/L) of Potassium Dihydrogen Phosphate (KH_2PO_4) using a magnetic stirrer at a revolution of 250rpm for 5.0 hours and centrifuged at 2000rpm for 10.0 minutes, to ensure thorough equilibration. The kaolin samples were then washed thoroughly with 1000 mL of distilled water to remove excess H_2PO_4^- ions, until the phosphate test is found to be negative. The electric oven was then used to dry the modified kaolin clay at a temperature of 363 K

Kinetics of Lead (II) Ion Adsorption

1.0 g/liter each of stock solution of a standard lead (II) was prepared from its nitrate salt with distilled water. The solutions with metal ion of concentration of 250, 500, and 1000 mg/L were prepared and the pH adjusted to 6.0 ± 0.2 with 0.10 mol/liter sodium hydroxide. Kinetic experimental studies were performed on the batch adsorption method at a temperature of 25°C on a water bath shaker at 250rpm using 120 milliliters capped polyethylene bottles containing 100 mL of 250, 500, and 1000 mg/liter of lead (II) solutions and 5.0 g of both tripolyphosphate-modified and unmodified kaolin samples. 10.0 mL of the aliquots/suspensions were withdrawn from the water bath shaker at different time interval. The suspensions were then centrifuged at 4000rpm for 10.0 minutes and the Atomic Absorption Spectrometer was used to analyze the supernatants for the metal ions. The above procedure was repeated at temperatures of 298, 308, and 323 K using 1000 mg/L concentration of the stock lead (II) ion solution with the modified and unmodified kaolin clay samples, in order to study the effect of temperature on the kinetic of the adsorption of lead (II) ion.

Blank samples containing lead (II) without the kaolin adsorbent are used in this research study were also analyzed.

The amount of lead (II) adsorbed by the kaolin clay adsorbents were calculated using:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

Where: q_e concentration of metal ion adsorbed by the kaolin at equilibrium (mg/L)

C_0 is initial metal ion concentration (mg/L)

C_e is the equilibrium concentration of the metal ion (mg/L)

V is the volume of adsorbate (L)

W is the weight of the adsorbents used (g)

The experimental readings were obtained using an Atomic Absorption Spectrometer (AAS). The air-acetylene flame was used and absorption lines used is 283.3nm

Result and Discussion of Results

Material specifications

Figure 1 and 2 present both the XRD and SEM analysis of the Nigerian Ahoko Kaolin used in the adsorption studies. The XRD pattern of the refined sample reveals a sharp and narrow peak with a basal reflection at $2\theta = 12.37^\circ$ ($d = 7.15 \text{ \AA}$). This is similar to the peak position in a typical kaolin sample. There are confirm presence of secondary phase identified as quartz. The surface morphology of the Kaolin sample was studied by SEM to further confirm the material is indeed kaolin-like. The SEM image of the refined kaolin clearly reveal kaolinite particles with varying sizes. These come with a low aspect (crystal-width to thickness) ratio. Apart from the usual pseudo-hexagonal platelet which is still visible, rough edge are also observed in most of the particles, however the observed platelets show thinness of kaolinite flakes indicating finesse of the kaolin surface. The SEM reveal highly ordered and crystalline particles.

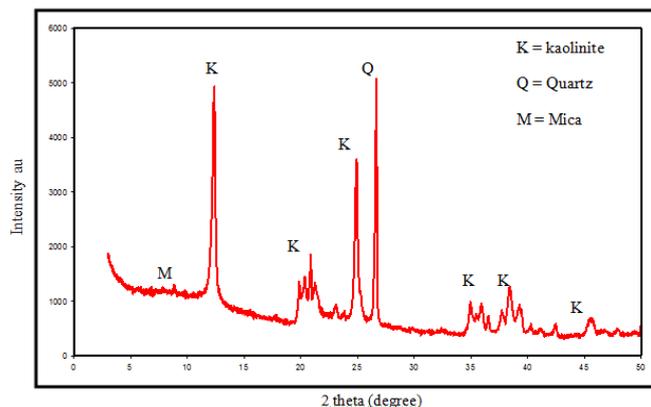


Figure 1: XRD pattern of Nigerian Ahoko Kaolin

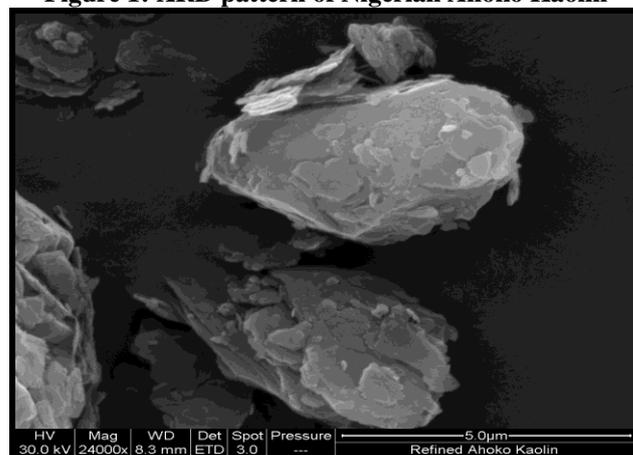


Figure 2: SEM image of Nigerian Ahoko Kaolin

Kinetic Study

Effects of Initial Lead Concentration on Kinetics

Fig. 3 and 4 presents the adsorption capacity of both TPP-modified and the unmodified kaolin as a function of lead (II) ion initial concentration and of time

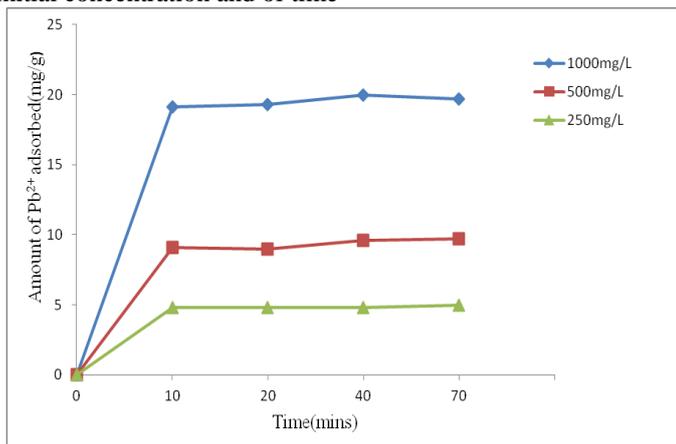


Figure 3: Effect of varying concentration of Pb^{2+} on modified kaolinite clay at various contact time

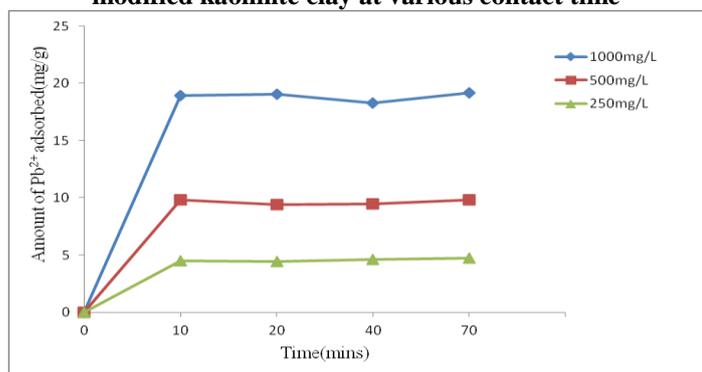


Figure 4: Effect of varying concentration of Pb^{2+} on unmodified kaolinite clay at various contact time

The figures shows the amount of lead (II) uptake q_t (mg/g) and the adsorbed quantity of lead (II) ion per unit time to have increased with time of contact between the adsorbate and adsorbent at all initial lead (II) ion concentration (Unuabonah *et al.*, 2007, and Teoh *et al.*, 2013), also from Fig. 3 and 4, the rate of adsorption was obtained from the slope. The rate of adsorption of lead (II) ion on TPP-modified and unmodified kaolin for the first 10 minutes was observed to increase from 0.479 to 1.915 and 0.340 to 1.894 ($mg\ g^{-1}\ min^{-1}$) for the TPP-functionalized and unmodified kaolin adsorbents respectively with increase in the initial lead (II) ion concentration from 250 to 1000 mg/L. At time interval of 10 to 70 minutes, the adsorption rate of lead (II) ion decreases to 0.071, 0.120, 0.281 and 0.0675, 0.140, 0.274 ($mg\ g^{-1}\ min^{-1}$) for the TPP-functionalized and unmodified kaolin respectively for 250, 500, and 1000 (mg/L) respectively of the initial lead(II) concentration. Above contact time 70 minutes, there was further decrease in the rate of adsorption of lead (II) ion.

The initial steep adsorption curve in Fig.3 and 4 suggested that the adsorption occurs rapidly on the surface of both TPP-functionalized and the unmodified adsorbent for the first 10 minutes and later became slower until it attains equilibrium. The large initial sorption rate is due to an increased number of empty adsorption spot existing at the early phase of the process of adsorption. The results obtained were examined and studied using both the pseudo-first-order and pseudo-second-order models. The pseudo-first-order model show a very poor fit after

the first 10 minutes of reaction with time but the pseudo-second-order produce a very appropriate fit for all reaction time as shown in Fig. 5 and 6 for both TPP-functionalized and the unmodified respectively

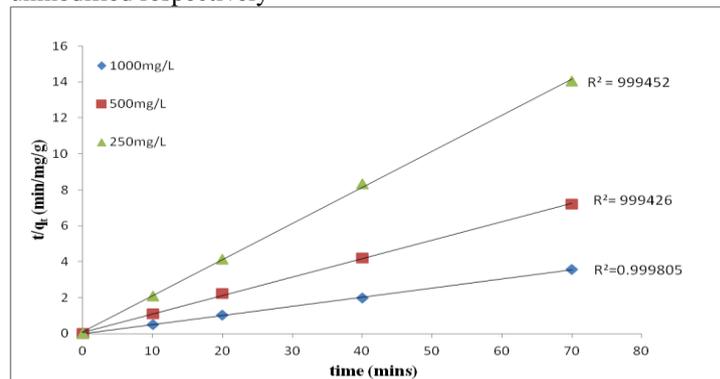


Figure 5: Pseudo-second order plots for adsorption of Pb ions on TPP-Modified sorbent at 298 K

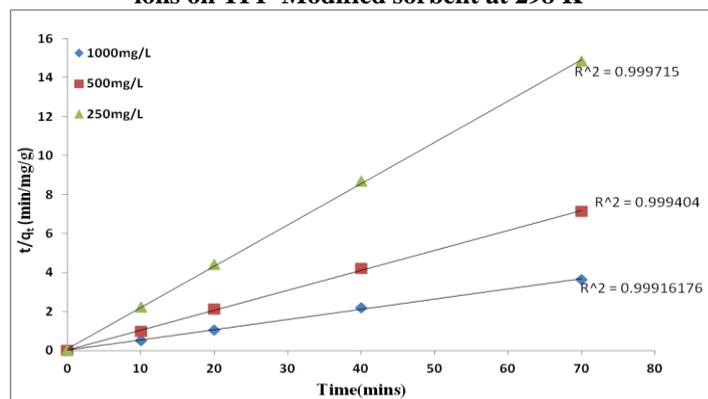


Figure 6: Pseudo-second order plots for adsorption of Pb ions on unmodified sorbent at 298 K

Fig. 5 and 6 presents a linear relationship between the t/q_t and time for both TPP-modified and unmodified kaolin adsorbent at different lead (II) ion concentration. The initial sorption rate h , pseudo-second-order rate constant k and the quantity of lead (II) ion adsorbed at equilibrium q_e were found from the pseudo-second-order model as given in table 1 and 2.

Table 1: Pseudo-Second Order Kinetics Modified kaolin

Time (mins)	t/q_t 1000 (mg/g)	t/q_t 500 (mg/g)	t/q_t 250 (mg/g)
0	0	0	0
10	0.522	1.1	2.09
20	1.037	2.225	4.152
40	2	4.197	8.333
70	3.56	7.2	14.029
Pseudo-second order rate for the adsorption of varying concentration of Pb^{2+} ions			
R^2	0.99980523	0.999426	0.999452
SLOPE	0.05059351	0.102326	0.200772
INTERCEPT	0.00718182	0.079273	0.099182
q_e (mg/g)	19.7653823	9.77269	4.980772
K (g/mg/min)	0.356	0.381	0.406
h (mg/g/min)	139.07	36.39	10.07

Increasing lead (II) ion concentration increases the initial sorption rate h , from 10.07 to 139.07 and 9.434 to 78.57 ($mg\ g^{-1}\ min^{-1}$) for TPP-modified and unmodified kaolin respectively as the concentration of lead(II) increases from 250 to 1000 (mg/L).

The quantity of lead (II) ion adsorbed at equilibrium q_e was obtained from the slope of the plot of t/q_t versus t in Fig. 5 and 6 which follow same trend showing an increase from 4.981 to 19.765 and 4.727 to 19.029 ($mg\ g^{-1}$) for TPP-modified and

unmodified kaolin but a decrease in the pseudo-second-order constant K_2 as shown in table 3 and 4. TPP-modification of kaolin increased the initial sorption rate h , specifically at a very high concentration. The linearity of the pseudo-second-order model in Fig. 5 and 6 suggests a chemical reaction rather than a physical adsorption reaction (Unuabonah *et al.*, 2007 and Xiao *et al.*, 2010). The corresponding linear plots of k , h , and q_e of the adsorption process are often expressed as a function of C_o for the adsorption of lead (II) ion onto TPP-modified and unmodified kaolin.

Table 2: Pseudo-Second Order Kinetics Unmodified kaolin

TIME(mins)	t/q_t 1000 mg/L	t/q_t 500 mg/L	t/q_t 250 mg/L
0	0	0	0
10	0.528	1.002	2.22
20	1.05	2.125	4.417
40	2.188	4.222	8.685
70	3.655	7.133	14.8255

Pseudo-second order rate for the adsorption of varying concentration of Pb^{2+} ions			
R^2	0.99916176	0.999404	0.999715
SLOPE	0.0525526	0.102342	0.211557
INTERCEPT	0.01272727	0.030818	0.105909
q_e (mg/g)	19.0285552	9.77114	4.726863
K (g/mg/min)	0.217	0.338	0.422
h (mg/g/min)	78.57	32.26	9.434

For the TPP-modified kaolin, the following correlation from figure 7 was obtained.

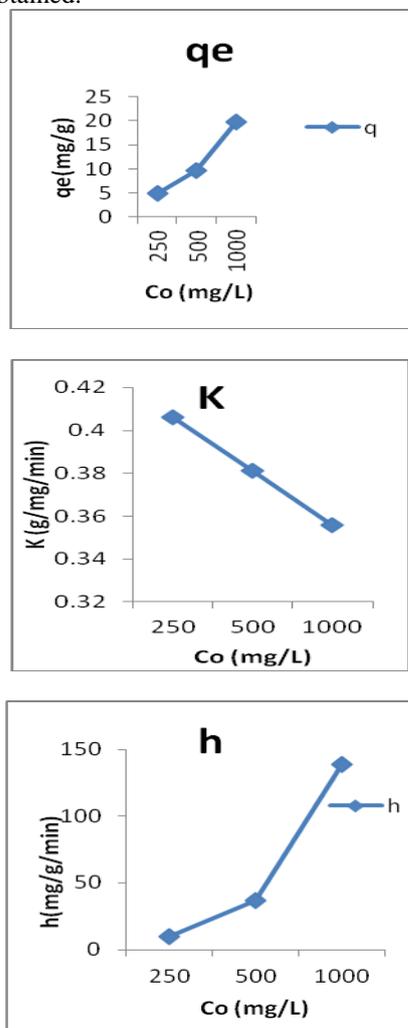


Figure 7: Corresponding linear plots of K , h and q_e as a function of C_o adsorption of Pb^{2+} onto TPP-functionalized kaolin

For unmodified kaolin, the following correlation from fig 8 was also obtained:

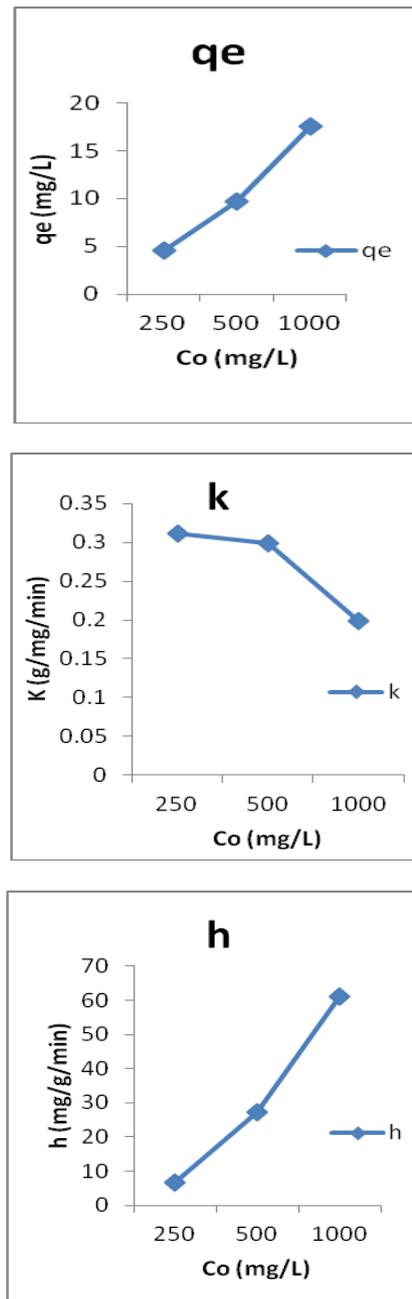


Figure 8: Corresponding linear plots of K , h and q_e as a function of C_o adsorption of Pb^{2+} onto unmodified kaolin

$$q_e = 0.01899C_o - 0.098155 \quad R^2 = 0.999531$$

$$K = 0.4825 - 0.00027C_o \quad R^2 = 0.992572$$

$$h = 0.092244C_o - 13.721 \quad R^2 = 0.999987539$$

The validity of the order of adsorption process is based on two criteria, namely regression coefficient and calculated q_e (Xiao *et al.*, 2010) as obtained from the regression correlation coefficients and slopes of Fig. 5 and 6. However the correlation coefficients and q_e for the second order model were very high

The Effects of Temperature on Kinetic Lead Ion Adsorption

Fig. 9 and 10, is a plot of the linearize type of the second order model for the adsorption of 1000 (mg/L) at varying temperatures.

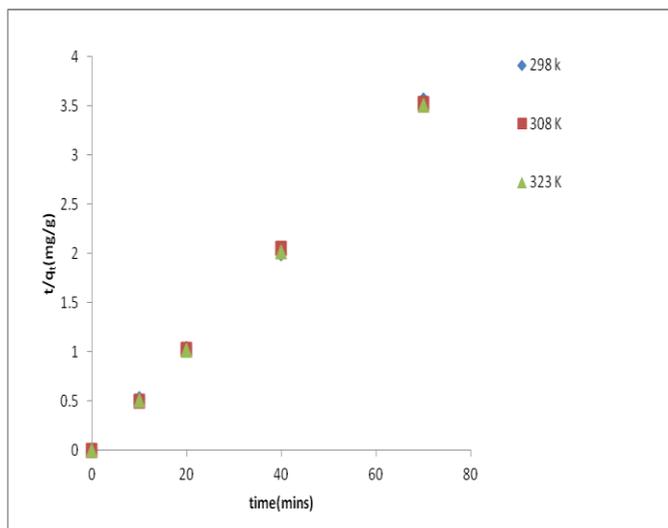


Figure 9: Pseudo-second plots for adsorption of 1000mg/L of Pb ions on modified adsorbent at varying temperatures

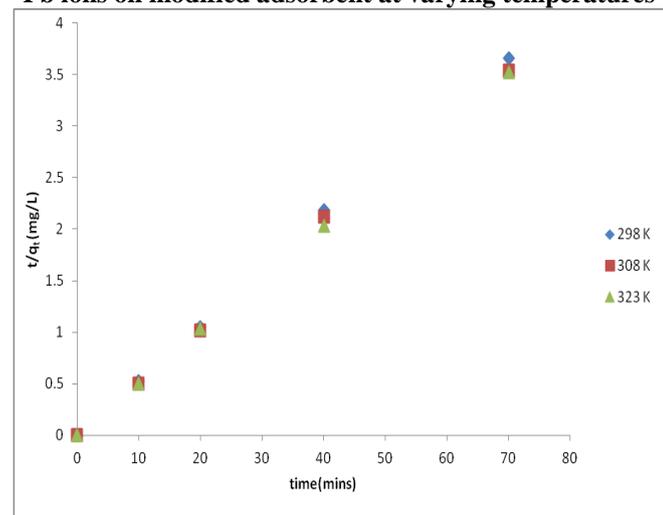


Figure 10: Pseudo-second plots for adsorption of 1000mg/L of Pb ions on unmodified adsorbent at varying temperature

Differences in the temperature influences the time needed for the lead (II) ion adsorption to attain equilibrium. Table 3 and 4 shows that increase in temperature from 298 to 323 K also increases both pseudo-second-order rate constant K_2 and the initial sorption rate h , on both the TPP-modified and the unmodified adsorbents.

Table 3: Effect of Temperature on Kinetics Lead Ion Adsorption functionalized kaolin

TIME(mins)	298 K	308 K	323 K
0	0	0	0
10	0.522	0.498	0.507
20	1.037	1.025	1.013
40	2	2.058	2.016
70	3.56	3.525	3.509
Pseudo-second order rate for the adsorption of 1000 (mg/L) of Pb ²⁺ ions at varying temperature			
R ²	0.999805227	0.999801767	0.999985458
SLOPE	0.050593506	0.050513636	0.05011039
INTERCEPT	0.007181818	0.006818182	0.005909091
q _e (mg/g)	19.76538234	19.79663457	19.95594143
K (g/mg/min)	0.365	0.375	0.426
h (mg/g/min)	139.07	146.97	169.6

Table 4 Effect of Temperature on Kinetics Lead Ion Adsorption unmodified kaolin

Time (mins)	298 K	308 K	323 K
0	0	0	0
10	0.528	0.502	0.505
20	1.05	1.021	1.03
40	2.188	2.119	2.032
70	3.655	3.534	3.524
Pseudo-second order rate for the adsorption of 1000 (mg/L) of Pb ²⁺ ions at varying temperature			
R ²	0.99916176	0.999086704	0.99993562
SLOPE	0.052552597	0.050861039	0.050344805
INTERCEPT	0.012727273	0.011090909	0.008545455
q _e (mg/g)	19.02855519	19.66141511	19.86302253
K (g/mg/min)	0.217	0.235	0.296
h (mg/g/min)	78.57	90.84	116.78

The values of the pseudo-second-order rate constant K_2 were observed to slightly increase from 0.365 to 0.426 ($\text{mgg}^{-1}\text{min}^{-1}$) and 0.217 to 0.296 ($\text{mgg}^{-1}\text{min}^{-1}$) with increase in temperature from 298 to 323 K for TPP-modified and unmodified adsorbent respectively as shown in table 8 and 9. This indicates that increasing temperature will increase the energetic force of lead (II) ion onto the adsorbent (Hafne *et al.*, 2008).

Also the relationship between pseudo-second-order rate constant K_2 and temperature is used in determining the activation energy and this is described with equation as shown below:

$$K_2 = K_0 \exp\left(\frac{-E}{RT}\right) \quad (2)$$

Where K is the rate constant of adsorption of pseudo-second-order ($\text{mgg}^{-1}\text{min}^{-1}$), K_0 is the temperature-independent factor ($\text{mgg}^{-1}\text{min}^{-1}$), E is the adsorption activation energy (KJmol^{-1}), R is the gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$) and T is the absolute Temperature (K).

Figure 11 presents a plot of $\ln K$ against $1/T$, which produce a straight line with $\frac{-E}{RT}$ as the slope of the graph.

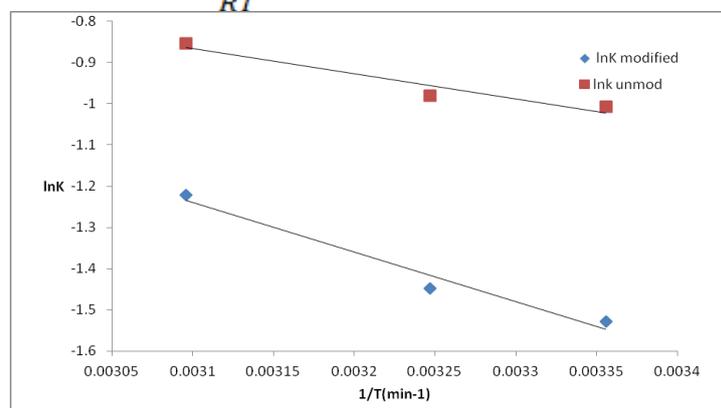


Figure 11: Relationship between T and K for TPP-modified and unmodified kaolinite clay (Pb²⁺ =1000(mg/L))

The size of the activation energy provides an insight on the adsorption type, which can either be physical or chemical. In physical the activation energy is often small, and it is a reversible reaction while in chemical, the activation energy is high. The values activation energy E obtained are 9993.43 and 5075.714 KJmol^{-1} for TPP-modified and unmodified kaolin respectively for 1000 (mg/L) concentration of lead (II) ion

Thermodynamic Study

The thermodynamic parameter such as change in enthalpy ΔH° , change in entropy ΔS° and change Gibb free energy

ΔG° of the sorption onto TPP-modified and unmodified kaolin are useful in defining whether the sorption reaction is endothermic or exothermic, spontaneity and feasibility of the sorption process (Xiao *et al.*, 2010). The thermodynamic parameters can also be related to distribution coefficient of solute between the solid-liquid phases by the below:

$$\log \frac{q_e}{C_e} = \frac{\Delta S^{\circ}}{2.303R} - \left(\frac{\Delta H^{\circ}}{2.303R} \right) \frac{1}{T} \quad (3)$$

$$\Delta G^{\circ} = -RT \ln K_c \quad (4)$$

Where ΔS° and ΔH° are the standard entropy and enthalpy for the adsorption process, q_e is the capacity of adsorption (mg g^{-1}), $K_c = \frac{C_{ad}}{C_e}$, C_{ad} is the quantity of lead (II)

ion adsorbed and C_e is the quantity of lead (II) ion in the solution at equilibrium (Aksu, 2002). Fig. 13 is the plot of $\log \frac{q_e}{C_e}$ against $\frac{1}{T}$ for 1000 (mg/L) initial concentration of lead

(II) ion. The change entropy ΔS° and the change in enthalpy ΔH° was found from the intercept and slope respectively. The values for entropy and enthalpy are 106.40 and 33318.82 (KJ mol^{-1}) for TPP-modified and 109.78 and 34624.73 (KJ mol^{-1}) for unmodified kaolin. The values of change in enthalpy calculated from the plot suggest that the adsorption is endothermic with onto TPP-modified having much of the endothermic nature. The positive values of change in entropy also suggest increasing randomness at the liquid-solid interphase. The change in Gibb's free energy of the adsorption process were as shown in table 5 for TPP-modified and unmodified kaolin.

Table 5: Gibb's free Energy of the Adsorption Process

MODIFIED				
Temperature (K)	$\log(q_e/C_e)$	T (K)	1/T (1/K)	Gibbs energy ΔG (KJ/mol)
298 K	-0.278	298	0.003356	-8116.526
308 K	-0.097	308	0.003247	-9446.467
323 K	0.173	323	0.003096	-11090.793
slope(H/2.303R)	-1739.78	ΔH	33318.82	
Intercept(S/2.30R)	5.557036	ΔS	106.40	
UNMODIFIED				
298 K	-0.397	298	0.003356	-7427.761
308 K	-0.03	308	0.003247	-9686.984
323 K	0.09	323	0.003096	-9417.775
slope(H/2.303R)	-1808.35	ΔH (KJ.K/mol)	34624.73	
Intercept(S/2.303R)	5.73371	ΔS (KJ.K/mol)	109.78	

The values obtained via the above equation (4) are -8116.526, -9446.467, -11090.793 (KJ mol^{-1}) and -7427.761, -9686.98, -9417.775 (KJ mol^{-1}) for TPP-modified and unmodified kaolin at 298, 308 and 323 K respectively. The negative values denoted a spontaneous and a feasible process. The results obtained for both the kinetics and the thermodynamic study of adsorption of metal ions were follows similar trend as that obtained by Unuabonah *et al.*, 2007, Hafne *et al.*, 2008, Xiao *et al.*, 2010, Igbokwe *et al.*, 2012, Teoh *et al.*, 2013.

Intra-particle Diffusion

The intraparticle diffusion rate was obtained from the plot q_t versus $T^{0.5}$ (Figure 12 and 13) for both TPP-modified and unmodified kaolin and the intraparticle diffusion coefficient were also obtained for both adsorbents.

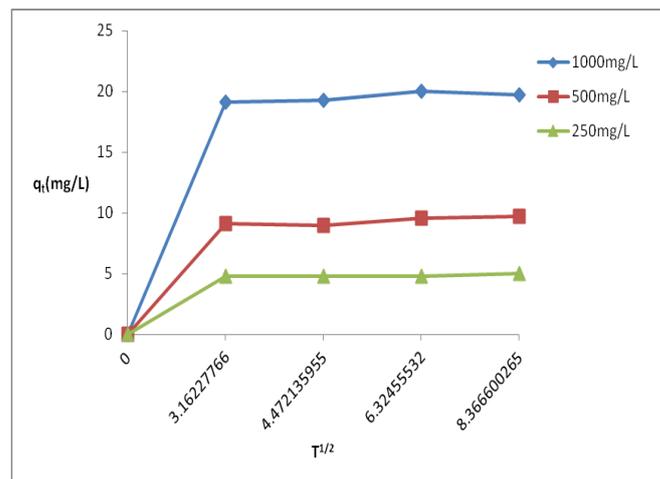


Figure 12 diffusion plot for adsorption of Pb²⁺ onto TPP-Modified kaolinite clay

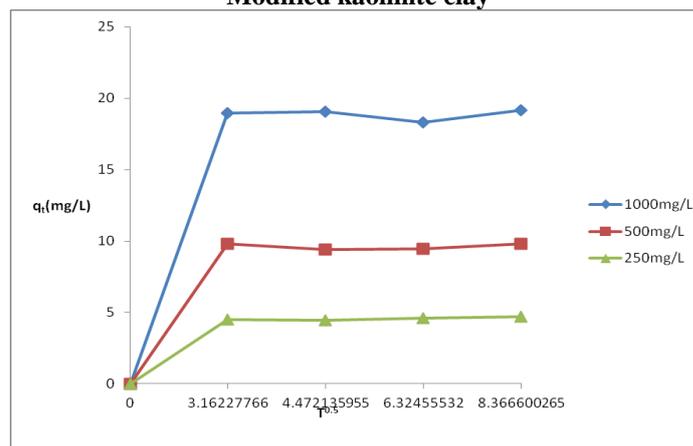


Figure 13: Intra-particle diffusion plot for adsorption of Pb²⁺ onto unmodified kaolinite clay

The intercept of the plot suggest the boundary effect hence the larger the intercept, the greater the contribution of the surface adsorption in the rate limiting step.

Conclusions

From the research studied, it can be concluded that modification of kaolin with TPP-modified increases the rate of adsorption of lead (II) ion onto the kaolin. There is often an increase in both the amount of lead (II) ion adsorbed and initial sorption rates but with a decrease in the overall rate of adsorption of lead (II) ion onto both adsorbents with an increasing concentration of lead (II) ion in aqueous solution

The adsorption process is observed to be endothermic feasible and spontaneous, with the TPP-modified kaolin being more endothermic. The negative value of ΔG° indicate feasibility and spontaneity while the positive values of change in entropy and change in enthalpy suggests the endothermic nature of adsorption and affinity of both adsorbent toward lead (II) ion. This also indicates that an increase in temperature increases the initial sorption rate as well as amount of lead (II) ion adsorbed from aqueous solution by both TPP-modified and unmodified kaolin.

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