

# THE KINETICS AND THERMODYNAMICS OF ADSORPTION OF HEAVY METAL IONS ON TITANIUM- PILLARED AND UN-PILLARED BENTONITE CLAYS

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## ABSTRACT

Titanium-Pillared and Un-Pillared bentonite clays were studied in order to evaluate the thermodynamics and kinetics of heavy metal ion removal from aqueous solutions. The results showed that the maximum sorption of Cu, Cd, Hg and Pb ions occurred within 30 minutes. A pseudo-second order kinetic model was used to characterize the metal ion transport mechanism and the correlation coefficients ( $r^2$ ) were high, confirming the validity of pseudo-second-order. The rate of adsorption was observed to increase with pillaring and does not only depend on the metal ion concentration, but may also involve additional adsorbent –adsorbate interaction processes.. The thermodynamic parameter ( $\Delta G^\circ$ ) was found to be negative at all temperatures studied, which indicate that the adsorption process is spontaneous while  $\Delta S^\circ$  values are positive. The positive values of  $\Delta S^\circ$  showed the increasing randomness of the metal ions at the adsorbent – adsorbate interface. The heat of adsorption (enthalpies,  $\Delta H^\circ$ ) and the activation energies ( $\Delta E_a$ ) were both positive and their values lie within the range associated with physisorption. The results are presented and discussed in terms of the mechanism of ion adsorption on solid Ti-pillared and un-pillared bentonite clay minerals.

**KEYWORDS:** Ti-Pillared, heavy metals, thermodynamics, kinetics, adsorption

## INTRODUCTION

Heavy metals, such as mercury, lead, copper and cadmium are common constituent of industrial and municipal effluents. The effluents containing excess of these toxic metals are subsequently discharged into the soils and rivers, constituting pollution particularly to aquatic lives. The accumulation of these metals in soils may lead to uptake by agronomic plants and leaching to ground and surface waters (Odoemelam, 2005; Adekola *et al.* 2002; Akan *et al.* 2007). It has been reported that movement of these chemicals to plants and water bodies depends on the extent of soil contamination, and may endanger human health through consumption of sea food and vegetable crops, (Kemdrim 1997; Etuk and Mbonu 1999), or directly through skin contact and inhalation of dust particles (Ayodele and Gaya, 2003 ). Vegetables absorb these metals from the ground as well as from deposits and waste dumps within the polluted environment.

Many organic and inorganic compounds can accumulate in plants and result in toxic effects to animals and humans. Therefore, the amount of heavy metals in wastewater as well as industrial runoffs should be minimized to prevent accumulation in the biosphere. The removal of copper from aqueous solution by bentonite clay mineral was recently reported by Ding *et al.* (2009) and Okoye and Obi (2011), and the metal uptake properties was said to be due to large ion exchange and adsorption capacity of bentonite. Therefore, clays are efficient and environmental friendly compounds with proven adsorption properties. However, the application of pillared clays in the field of heavy metal adsorption and removal has not been widely reported.

The pillared clays are two – dimensional zeolite – like, and have been widely used as catalysts or catalyst support in the petroleum industries, due to their molecular sieve properties and enhanced acid sites, (Boou *et al.*1996; Binitha and Sugunan, 2006). The principle behind clay pillaring originates from the insertion of voluminous or oligomeric inorganic metal hydroxycations between the layers of clays in order to keep them apart. On calcination, the metal hydroxycations are decomposed into oxide pillars, which create interlayer and interpillar spaces. The term ‘pillared’ and ‘pillaring’ originated from the work of Vaughan *et al.* (1979). These authors discovered that thermally stable inorganic moieties can be intercalated between the individual clay lamellar sheets. The resulting materials were therefore calcined to give the metal oxide acting as pillars. The pillared materials were demonstrated to have an increased interlamellar distance, an increased pore volume and were accessible by molecules within a specific size range.

The mechanism of metal ion adsorption on clay samples has also not been well studied and reported. However, the pseudo-second-order kinetic model based on the solid adsorbent capacity was recently reported for the kinetic of sorption of divalent metal ions by palm shell powder (Shilpi *et al.* 2008). In this study the thermodynamic and kinetic models were applied to evaluate the mechanism of heavy metal ion removal by both pillared and un-pillared bentonite clays. Attempt was also made to use the pseudo-second-order kinetic equation to model the equilibrium adsorption data.

## EXPERIMENTAL

### CLAY SOURCE AND SAMPLING

Samples of the natural clay were collected from the

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open clay deposit in Ezinachi, Okigwe Local Government Area, Imo State, Nigeria. The clay sample was washed and dried under sunshine for two days.

### Pillaring Procedure

The pillaring agents were prepared following the method described by Lin *et al.* (1993). Titanium chloride ( $\text{TiCl}_4$ ) from Aldrich was mixed with twice the volume of ethanol, and stirred in a solution of glycerol. The total mixture was added drop wise to 2.5g of clay in 250ml of deionised water and allowed to equilibrate under stirring for 4hours at room temperature. The Ti – intercalated clay material was filtered and dried overnight in an oven at 110°C. The intercalated Ti – clay was calcined at 500°C for 4 hours in air to give the Ti-pillared clay (Ti – PILC).

### Equilibrium Adsorption Measurement

The batch adsorption experiments were carried out with 0.5g of clay samples, stirred in solution of each metal ions of interest in a range of 50 to 350mg/l at different temperatures and at different time intervals. In every case the mixture was filtered and the supernatant solution was analyzed for the respective metal ions using atomic absorption spectrophotometer (Bulk Scientific 205A). The metal uptake by the adsorbent at equilibrium was calculated from the following expression:

$$q_e = \frac{(C_o - C_e)V}{M} \quad (1)$$

where  $q_e$  is the amount of metal ion adsorbed in mg/L,  $C_o$  is the initial metal ion concentration in mg/L,  $C_e$  is the concentration after equilibrium in mg/L,  $V$  is the total volume of solution in litre and  $M$  is the mass of clay sample (adsorbent) used in g.

The experimental data were analysed using different kinetic models (first order and second order) as well as Langmuir equations, so as to determine the best fit.

## RESULTS AND DISCUSSION

### Kinetic Studies

The sorption kinetics was studied using a pseudo – second – order model in order to examine the controlling mechanism of adsorption process. The model is used to test experimental data. This sorption kinetics model can be expressed by a pseudo – second- order equation (Lagergren, 1898)

$$dq_t/dt = k_2(q_e - q_t)^2 \quad (2)$$

Where  $q_e$  and  $q_t$  are the amount of each metal ion sorption at equilibrium and at time  $t$ , respectively and given in ( $\text{mgg}^{-1}$ ), while  $k_2$  is the rate constant of the pseudo-second-order ( $\text{g.mg}^{-1}\text{min}^{-1}$ ). Considering the boundary conditions from  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ , and on integrating equation 1 becomes:

$$1/q_e - q_t = 1/q_e + k_2t \quad (3)$$

On rearranging and linearising;

$$t/q_t = 1/k_2q_e^2 + t/q_e \quad (4)$$

It can be assumed that  $h = k_2q_e^2$  where  $h$  can be regarded as the initial sorption rate as  $q_t/t \rightarrow 0$ . Therefore equation (4) can be written as:

$$t/q_t = 1/h + t/q_e \quad (5)$$

The validity of the pseudo-second-order model is tested by a linear plot of  $t/q_t$  as a function of time, (Figure 1 and 2) for Ti-Pillared and un-Pillared samples from which  $k_2$  and  $q_e$  can be determined from the slope and intercept of the plot respectively. Linear plots were obtained in both cases with high correlation coefficients ( $r^2$ ), suggesting that the adsorption mechanism follows the pseudo-second-order model. This observation indicates that the adsorption rate does not only depend on the metal ion concentration, but also show that the rate determining step may in addition, involved other adsorbent – adsorbate interaction phenomena (Musa *et al.* 2008)

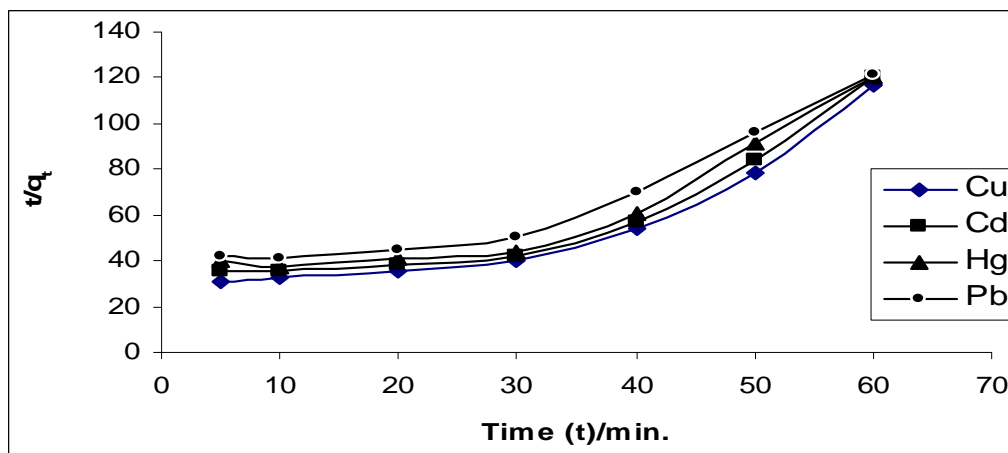
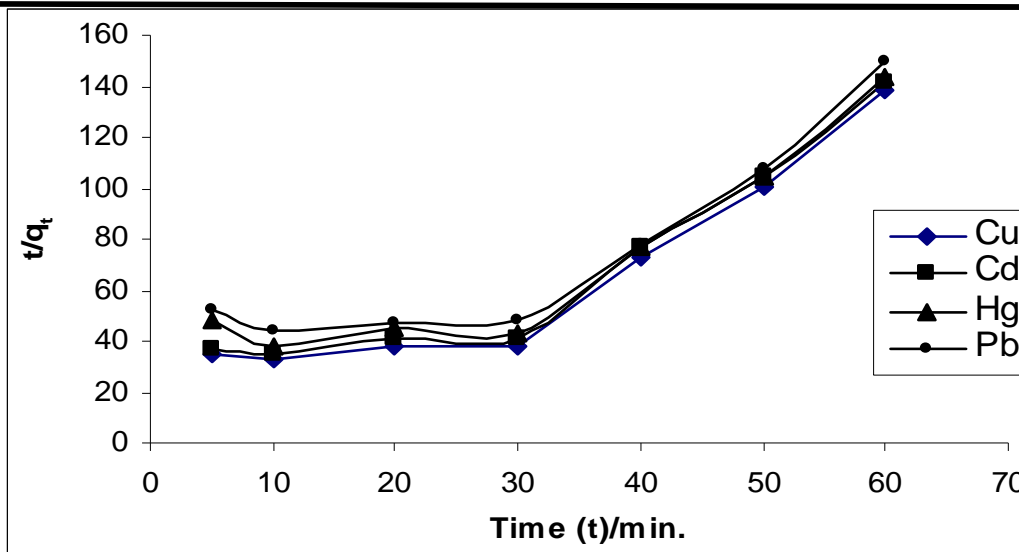


Figure 1: Pseudo-second order kinetic plot for metal ion sorption on Ti-Pillared clay



**Figure 2:** Pseudo-second order kinetic plot for metal ion sorption on an Un-Pillared clay

The pseudo-second-order rate constant  $k_2$ , the initial rate constant  $h$ , the correlation coefficient  $r^2$  and the amount adsorbed at equilibrium  $q_e$  values are given in Table 1. The results presented in Table 1 show that  $k_2$ ,  $h$  and  $q_e$  values increased on pillaring with titanium metal species, and the order of selectivity for the metal ions is given thus: Cu > Cd > Hg > Pb. The rate of sorption of copper on the Ti-Pillared is about three times when compared with the un-pillared sample, while the rate is

twice for both Cd and Hg. The selectivity order reported above is in line with the increasing ionic radii of the metals studied as indicated. These results clearly indicate that both the rate of adsorption as well as the adsorption capacity increased on pillaring, and this is because pillaring props the clay layers apart. In this way, pore sizes were noted to increase, thereby improving the porosity and surface properties of the adsorbents

**Table 1:** Pseudo-second order parameters for the adsorption of heavy metals onTi- pillared clay

Adsorbent	Parameter	Cu	Cd	Hg	Pb
Ti-pillared	$K_2$	1.18	0.60	0.37	0.21
	$h$	0.41	0.21	0.13	0.08
	$q_e$	0.59	0.59	0.59	0.61
	$r^2$	0.998	0.997	0.996	0.995

**Table 2:** Pseudo-second order parameters for the adsorption of heavy metals on an unpillared clay

Adsorbent	Parameter	Cu	Cd	Hg	Pb
Ti-pillared	$K_2$	0.41	0.32	0.18	0.15
	$h$	0.12	0.09	0.06	0.05
	$q_e$	0.54	0.53	0.57	0.58
	$r^2$	0.997	0.996	0.994	0.992
	Ionic radius (Å)	0.65	0.97	1.02	1.19

### Thermodynamic Parameters

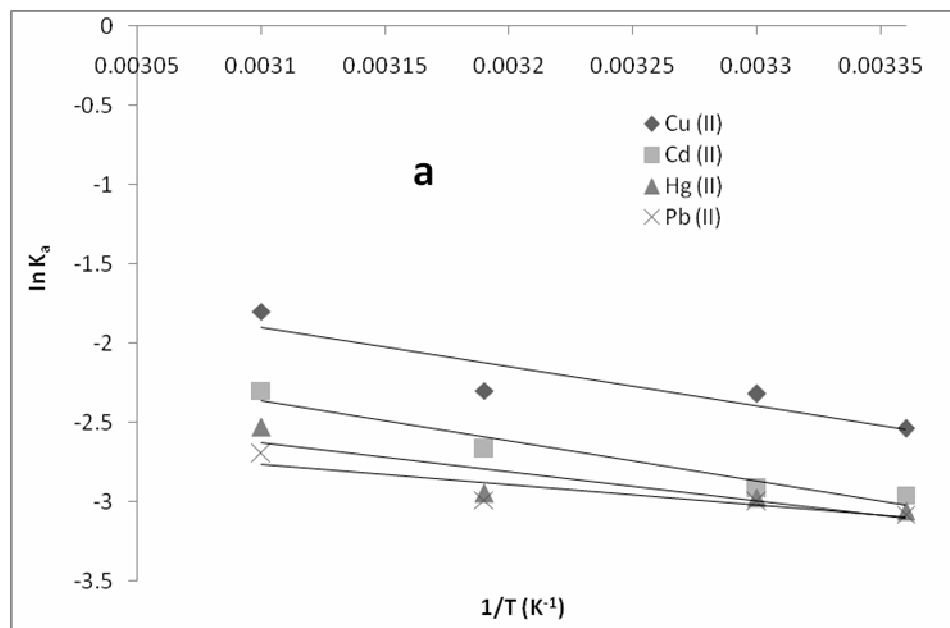
The thermodynamic parameters such as the standard free energy ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) for the adsorption process were calculated using the following equations:

$$\Delta G^\circ = -RT \ln K_a \quad (6)$$

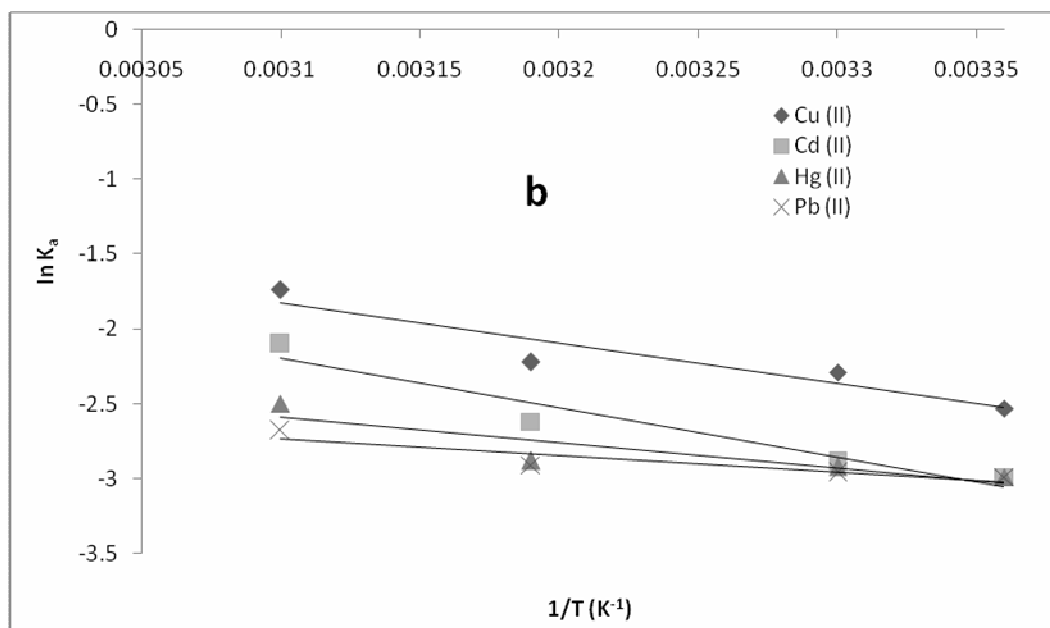
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

$$\ln K_a = \Delta S^\circ/R - \Delta H^\circ/RT \quad (8)$$

Where  $R$  is universal gas constant (8.314kJ/mol),  $T$  is the absolute temperature in Kelvin and  $K_a$  is Langmuir constant. The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were determined from the slope and intercept of the plot of  $\ln K_a$  as a function of  $1/T$  (see Figure 3).



**Figure 3a:** The plot of  $\ln K_a$  versus  $1/T$  for the metal ions adsorbed on Ti-Pillared clay



**Figure 3b:** The plot of  $\ln K_a$  versus  $1/T$  for the metal ions adsorbed on Un-Pillared clay

The values of these parameters are given in Table 3 and 4 for both pillared and un-pillared samples. The free energy values from this study were consistently less than  $-10\text{kJ/mol}$  and increased with increase in temperature. The negative values of  $\Delta G^\circ$  which are consistently lower than  $-10\text{kJ/mol}$  at all temperature, as shown in Table 3 and 4, indicate that the adsorption is spontaneous and involves physical adsorption phenomena (Musa *et al.* 2008). The positive values of

$\Delta H^\circ$  suggest that the adsorption process is endothermic while the positive values of  $\Delta S^\circ$  shows the increasing random movement of the metal ions on the adsorbent surface, which supports the scenario of physical adsorption process (Horsfall and Spiff, 2005). This observation is in good agreement with the work recently reported by Shilpi *et al.* (2008) and Abia *et al.* (2007). These parameters are seen to increase in the following order of metal ions:  $\text{Cu} > \text{Cd} > \text{Hg} > \text{Pb}$ .

**Table 3:** Thermodynamic parameters for the adsorption of heavy metals on Ti- Pillared clay

Metals	$\Delta G^\circ$ (298K)	$\Delta G^\circ$ (303K)	$\Delta G^\circ$ (313K)	$\Delta G^\circ$ (323K)	$\Delta H^\circ$	$\Delta S^\circ$	Ka
Cu (II)	-3.02	-2.85	-2.58	-2.36	+26.18	+10.80	0.18
Cd (II)	-2.92	-2.77	-2.49	-2.26	+28.12	+11.00	0.16
Hg (II)	-2.82	-2.70	-2.34	-2.09	+30.10	+11.82	0.11
Pb (II)	-2.73	-2.60	-2.16	-1.99	+31.20	+12.02	0.10

**Table 4:** Thermodynamic parameters for the adsorption of heavy metals on Un- Pillared clay

Metals	$\Delta G^\circ$ (298K)	$\Delta G^\circ$ (303K)	$\Delta G^\circ$ (313K)	$\Delta G^\circ$ (323K)	$\Delta H^\circ$	$\Delta S^\circ$	Ka
Cu (II)	-2.65	-2.58	-2.21	-1.75	+33.10	+13.42	0.08
Cd (II)	-2.54	-2.43	-2.11	-1.62	+34.15	+14.12	0.05
Hg (II)	-2.46	-2.27	-2.03	-1.55	+36.10	+12.82	0.05
Pb (II)	-2.39	-2.19	-2.01	-1.46	+37.03	+13.27	0.05

The other parameters which can be estimated from the experimental data include activation energy ( $E_a$ ) and sticking probability ( $S^*$ ). These parameters help to give further support for the confirmation of physical adsorption in the present study. The activation energy and sticking probability are calculated using modified Arrhenius type equation, which is related to surface coverage ( $\Theta$ ) as represented below (Amin, 2009; Najim and Yassin, 2009):

$$\ln (1-\Theta) = \ln S^* + E_a/RT \quad (9)$$

The sticking probability  $S^*$ , sometimes described as adsorption probability is a function of the

adsorbate/adsorbent interaction under investigation (Bowker, 1998). The plot of  $\ln (1-\Theta)$  versus  $1/T$ , were used to calculate the values of  $E_a$  and  $S^*$  from slope and intercept respectively. The values of  $E_a$  and  $S^*$  are given in Table 5. The value of  $S^*$  was found to lie in the range of  $0 < S^* < 1$ , while  $E_a$  values were consistent with the values of standard enthalpy ( $\Delta H^\circ$ ), indicating the endothermic nature of the adsorption process and the values lie in the range of physical adsorption. The values of sticking probability as shown in Table 5, indicates that the probability of these metal ions to stick on the surface of un-pillared and Ti-Pillared bentonites are high ( $0 < S^* < 1$ ). These values confirm that the sorption process is physisorption (Najim and Yassin, 2009).

**Table 5:** Sticking probability ( $S^*$ ) and Activation energy ( $E_a$ ) for the adsorption of heavy metal ions onto Un-Pillared and Ti-Pillared clays

Adsorbents	Parameters	Cu (II)	Cd (II)	Hg (II)	Pb (II)
Unpillared clay	$E_a$ ( KJ/mol)	8.98	7.65	6.07	3.82
	$S^*$	0.01	0.02	0.05	0.14
	$r^2$	0.92	0.97	0.98	0.96
Ti-pillared clay	$E_a$ ( KJ/mol)	10.73	10.14	10.10	8.65
	$S^*$	0.01	0.01	0.01	0.01
	$r^2$	0.99	0.99	0.98	0.97

## CONCLUSION

The adsorption characteristics of Ti - Pillared clay follow similar pattern as un-pillared materials. However Ti – Pillared showed higher adsorption rate as well as high capacity for all the metal ions reported in this work, and the order of selectivity are given thus:  $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Hg}^{2+} > \text{Pb}^{2+}$ . This stronger adsorption ability can be attributed to large isomorphous substitution subsequently leading to bigger clay interlayer spacing by  $\text{Ti}^{4+}$ . The standard free energy values ( $\Delta G^\circ$ ) obtained from this study are found to be negative and less than -10kJ/mol at all temperatures, indicating that physisorption rather than chemisorption is predominant in the adsorption mechanism. Positive entropy ( $\Delta S^\circ$ ) found in all cases shows a rapid reversible adsorption – desorption phenomena, indicating physisorption of the metal ions on the adsorbent surface. The results clearly suggest that the adsorption of all the metal ions studied in this work follows a complex process involving both surface adsorption and ion – exchange phenomena. These results therefore demonstrate that pillared bentonite has a great potential to remove cationic heavy metal species from industrial wastes and wastewaters.

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