

Thermodynamic and Kinetic Evaluations of Some Heavy Metal Ions on Aluminum-Pillared and Unpillared Bentonite Clays

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ABSTRACT

Aluminium-pillared clay was prepared to evaluate the mechanism of sorption process. The surface area and porosity was determined using Nitrogen (N_2) adsorption-desorption method. The results showed that the maximum sorption of the heavy metals occurred within 30 minutes at pH of 7-10. Pseudo-second order model was observed to fit the sorption process. The thermodynamic parameter (ΔG°) was found to be negative at all temperatures studied, which indicate that the adsorption process is spontaneous. The positive values of ΔS° showed the increasing randomness of the metal ions at the adsorbent-adsorbate interface. The heat of adsorption (enthalpies, ΔH°) and the activation energies (ΔE_a) were both positive and their values lie within the range associated with physisorption. The results are discussed in terms of the mechanism of ion adsorption on solid Al-pillared bentonite.

KEYWORDS: Heavy metal ions, thermodynamics, kinetics, sorption, aluminum-pillared clay.

INTRODUCTION

Industrialization and urbanization in developing countries have seriously and rapidly led to high pollution cases. A great number of health related problems have emanated from the indiscriminate discharge of heavy metal ions into the environment. This is because a large number of these heavy metals are non-degradable and toxic. Heavy metals such as copper, lead, zinc, cadmium, nickel, mercury, chromium, etc, are often found in industrial waste waters, which originate from metal plating, mining activities, ore smelting, battery manufacture, tanneries, petroleum refining, paint industries, pesticides, etc [1, 2, 3]. The concentration of these metals if not controlled in waste water may therefore rise to a lethal level that can be dangerous to mankind, livestock and the aquatic environment.

Several techniques have been applied over the years for the removal of these heavy metals present in industrial waste waters and in polluted soils. Examples of these techniques include chemical precipitation, conventional coagulation, reverse osmosis, ion-exchange and adsorption on activated carbon and zeolites. However, recent studies have shown that adsorption is one of the most cost effective [4] and versatile methodology to combat these pernicious challenges. This technique plays an important role for the removal of toxic metal ions and other inorganic and organic contaminants. It is time saving and easy to manipulate in stagnant and flowing effluents from industries, municipalities and in natural water [5].

Clay minerals are geologic low-cost and readily available materials functioning as excellent cation exchangers, and have often been used in adsorption and in catalysis [6]. Generally clays serve as host in pillaring because of their swelling properties and enlarged structures [7]. The cation exchange capacity (CEC), chemical and pore structures of clay minerals usually, to a greater extent determine their adsorption efficiency [8, 9].

Pillared clays (PILCs) are an interesting class of two-dimensional micro/meso porous materials [10]. Pillaring is designed to improve clay properties: such as high thermal stability, surface area and increased acidity [10, 11].

The objective of the present work is to evaluate the adsorption kinetics and thermodynamics of aluminum-pillared and unpillared bentonites in order to understand the mechanism of heavy metal removal from aqueous solutions.

MATERIALS AND METHODS

Starting Material and Pillarization Process

Natural clay mineral used in this study was obtained from Ezinachi clay deposit in Okigwe, Imo State, Nigeria. The sample was washed with water, dried and sieved to remove other impurities and particles. It was then ground to powder in a mortar and allowed to pass through 106 μ m sieves to get a homogenous powder. The transformation of natural clay mineral into pillared clay was achieved using aluminum (0.1M Al (NO₃)₃.9H₂O) by adding slowly a basic solution of 0.2M NaOH on the aluminum solution under constant stirring. The pillaring solution was now added in drop wise to the clay with constant stirring and aged overnight at room temperature. Afterwards, the intercalated clay suspension was filtered and washed with distilled water. The sample was air-dried at ambient temperature and at 378 K for 4 hours, and then calcined at 473K for 2 hours. The resulting product is aluminum pillared clay mineral (Al-PILC). Nitrogen adsorption-desorption isotherm was determined at - 196°C in an Autosorb - I (Quan-Tachnome). Samples of 0.2302g were out gassed at 180°C under vacuum. The specific surface area (SSA) was determined based on BET model [12]. The specific total pore volume was determined from the adsorption at the relative pressure of 0.95, converted to liquid volume assuming a nitrogen density of 0.808g/ml. The micro pore size distribution was analyzed based on the methods proposed by Horvath and Kawazoe, [13] and by Saito and Foley, [14] were used in considering the oxalic character of the surface.

Equilibrium Adsorption Measurement

The batch adsorption experiments were carried out with 0.5g of clay samples, stirred in 10ml of Cu (II), Cd (II), Hg (II) and Pb (II) solutions of 50mg/l at different temperatures and at different time intervals. The pH of the various metal ions were varied from 2-12. In every case the mixture was filtered and the supernatant solution was analysed for the respective metal ions using Atomic Absorption Spectrophotometer (Bulk Scientific 205A) and Cold Vapor Atomic Adsorption Spectrophotometer (Shimadzu, Model AA-670). The metal uptake by the adsorbent at equilibrium was calculated from the following expression:

$$q_e = (C_o - C_e)V / M \quad (1)$$

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 (second order and Elovich models).

RESULTS AND DISCUSSION

Kinetic Studies

The effect of contact time on adsorption of heavy metal ions onto un-pillared and aluminum-pillared (Al-PILBe) bentonites are represented in Figures 1 and 2. The results revealed that the optimum time for the sorption process was 30 minutes. The adsorption rate was rapid in the first 10 minutes then became a little subdued until equilibrium in the sorbents. Therefore, a 30 minute's shaking time was found to be appropriate and used in all subsequent measurements. Similar observations were reported by Bhattacharyya and Gupta, [15] on the adsorption of Fe (III), Co (II) and Ni (II) onto Kaolinite and montmorillonite.

In order to investigate the adsorption kinetics of the metal ions onto the adsorbents, Lagergren's pseudo-second-order and Elovich models were applied to the experimental data. The linearized form of pseudo-second-order rate equation by Lagergren, [16] is given as:

$$t/q_t = 1/(K_2q_e^2) + (1/q_e)t \quad (2)$$

$$h = K_2q_e^2 \quad (3)$$

Where h (mg.g⁻¹.min⁻¹) can be regarded as the initial sorption rate.

Therefore equation 1 can be re-written as;

$$t/q_t = 1/h + (1/q_e)t \quad (4)$$

Where K_2 (mg.g⁻¹.min⁻¹) is the rate constant of the second order equation, q_t (mg/g) is the amount of metal ions adsorbed at a particular time t (min) and q_e (mg/g) is the amount of metal ions adsorbed at equilibrium.

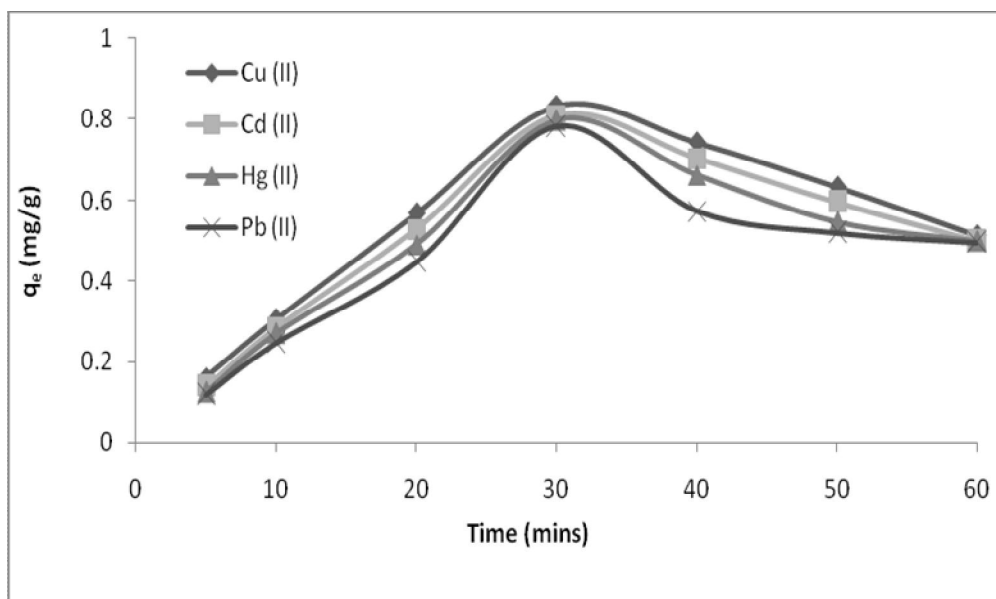


Figure 1. Effect of contact time for adsorption of metal ions onto Unpillared bentonite

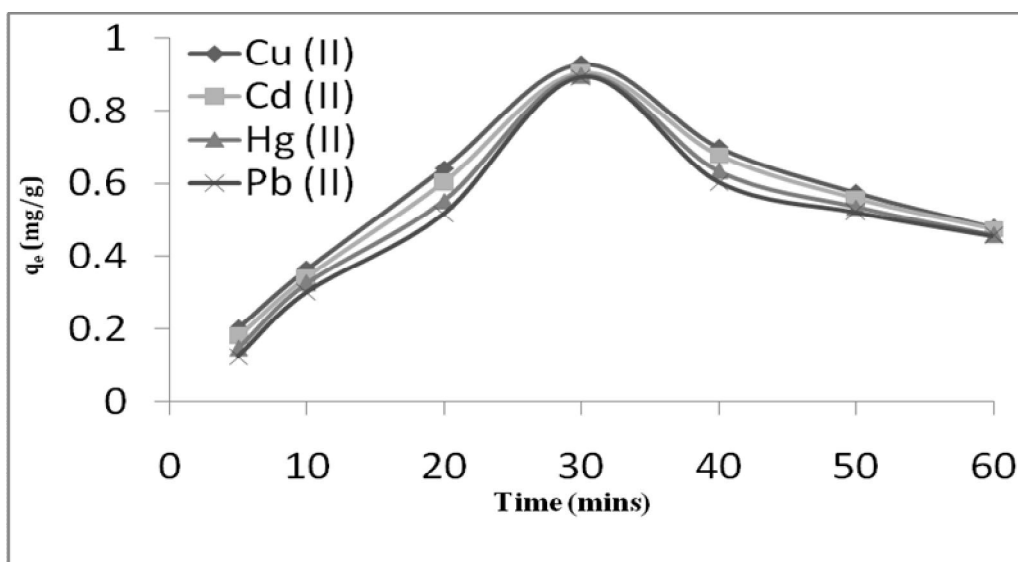


Figure 2. Effect of contact time for adsorption of metal ions onto Al-pillared bentonite

A plot of t/q_t versus t of equation 4 should give a linear relationship, from which q_e , k_2 and h can be obtained from the slope and intercept of the plot respectively. The rate constant (k_2), correlation coefficient (r^2) of the plot together with the amount of metal ions adsorbed at equilibrium (q_e) values are given in Table 1. Pseudo-second-order application is represented in Figures 3 and 4. Linear plots were obtained with high correlation coefficient (r^2), suggesting that the interaction between the adsorbents and the metal ions follow the pseudo-second-order mechanism. The result equally showed that above 30 minutes, the plots begin to deviate a little from linearity. This observation indicates that the rate of sorption does not only depend on metal ion concentration, but equally show that the rate determining step may in addition, involve ion exchange, adsorption and precipitation processes. This is because at lower pH of 2.0 to 6.0, the overall surface charge on the adsorbent would be positive, which will inhibit the approach of positively charged metal cations, consequently reducing metal ions binding on the adsorbent surface as shown in Figures 5 and 6. The $[H^+]$ ions compete effectively with the metal cations thereby causing a decrease in the adsorption capacity. The effect of pH on metal ions adsorption have been studied by many researchers and the results demonstrated that as the initial metal ion concentrations (C_0) increases, the resultant equilibrium final pH decreases for all concentrations and the more the metal ion added, the greater the effect [17]. But with further increase in the pH (10.0 to 14.0), the

formation of anionic hydroxide complexes decrease the concentration of free metal ions; thereby decreasing the adsorption capacity of the metal ions.

The results presented in Table 1 show that k_2 , h , and q_e values increased on pillaring with aluminum metal species, and the order of selectivity for metal ions is given thus: $Cu > Cd > Hg > Pb$. The rate of sorption of copper on the aluminum-pillared is about twice when compared with the unpillared clay. The order of selectivity given above show that the larger the ionic radii, the lower the rate of sorption as indicated in Table 1. These results clearly indicate that both the rate of sorption as well as the sorption capacity increased on pillaring, and this is due to the presence of pillars on the clay interlayer. In this direction, pore sizes were observed to increase, thereby improving the porosity and surface properties of the adsorbents as represented in Table 2 and Figure 7. Similar results were recently reported for the adsorption of heavy metal ions on different adsorbents which have similar chemical structure with that of natural bentonite [18].

Table 1. Parameter obtained from pseudo-second-order model for the adsorption of heavy metal ions on Unpillared and Al-Pillared bentonites, 50mg/L at 298 K

Adsorbents	Parameter	Cu (II)	Cd (II)	Hg (II)	Pb (II)
Unpillared bentonite	K_2 (g.mg ⁻¹ .min ⁻¹)	0.18	0.14	0.12	0.11
	h (mg.g ⁻¹ .min ⁻¹)	0.09	0.07	0.06	0.05
	q_e (mg.g ⁻¹)	0.54	0.53	0.57	0.58
	r^2	0.85	0.86	0.81	0.79
Aluminum-pillared bentonite	K_2 (g.mg ⁻¹ .min ⁻¹)	0.41	0.32	0.18	0.15
	h (mg.g ⁻¹ .min ⁻¹)	0.12	0.09	0.06	0.05
	q_e (mg.g ⁻¹)	0.71	0.71	0.70	0.69
	r^2	0.81	0.80	0.80	0.83
	Ionic radius(Å)	0.65	0.97	1.02	1.19

Table 2. BET surface and micro pore areas, micro pore volume and average diameter of Unpillared and Al-Pillared bentonites.

SAMPLE	BET surface area (m ² /g)	Micro pore volume (cm ³ /g)	Micro pore area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (Å)
Natural bentonite	29.99	0.0011	2.70	0.0010	14.80
Al-Pillared bentonite	49.86	0.0014	3.30	0.013	16.2

On the other hand, the linearized form of Elovich equation applied is given as:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \quad (5)$$

Where α is the initial adsorption rate (mg.g⁻¹) and β is the desorption constant (g.mg⁻¹) related to the extent of surface coverage and activation energy for chemisorptions.

A plot of q_t versus $\ln t$ should give a linear relationship with the constants α and β calculated from the slope and intercept of the plots as represented in Figures 8 and 9. The low correlations of the plot confirm that the Elovich model was not applicable. The kinetic parameters are listed in Table 3 and shows that the rate adsorption increases due to pillarization process. It was observed that the rate of desorption (β) relating to activation energy for chemisorption from the kinetic data was almost constant showing that the mechanism was rather physical.

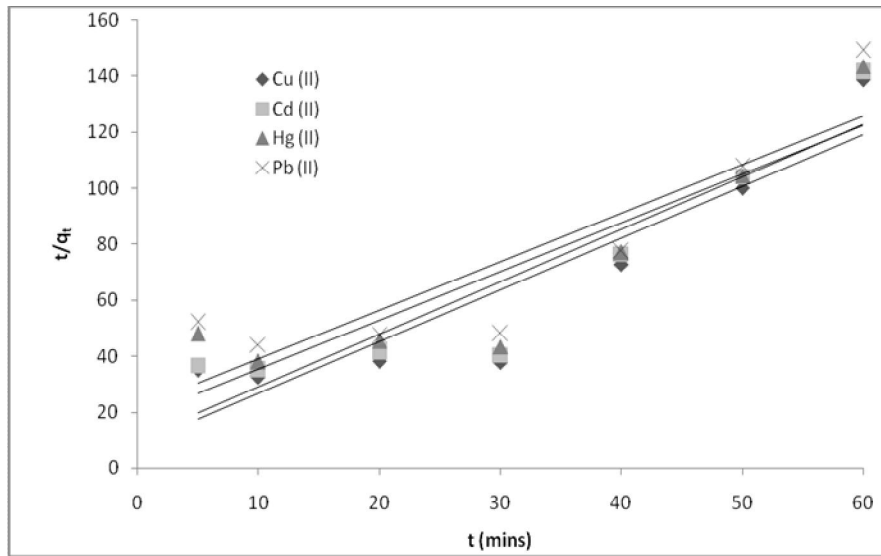


Figure 3. Pseudo-second order kinetics of metal ions onto Unpillared bentonite

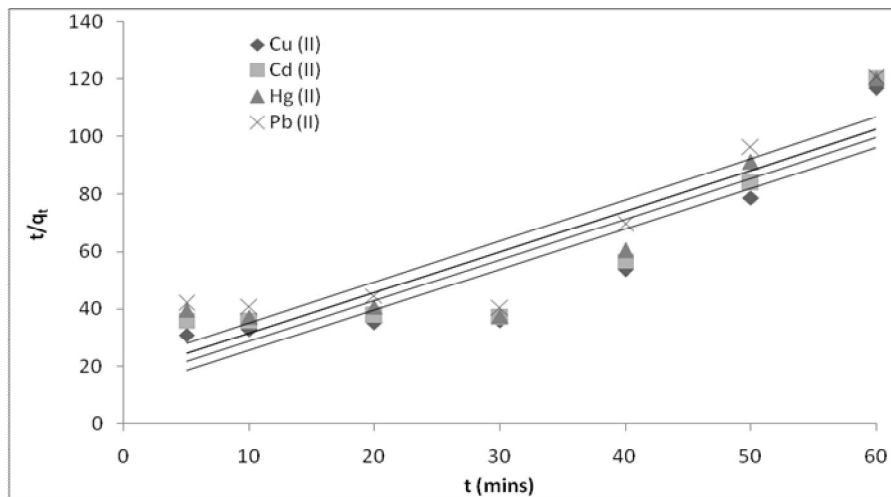


Figure 4. Pseudo-second order kinetics of metal ions onto Al-Pillared bentonite

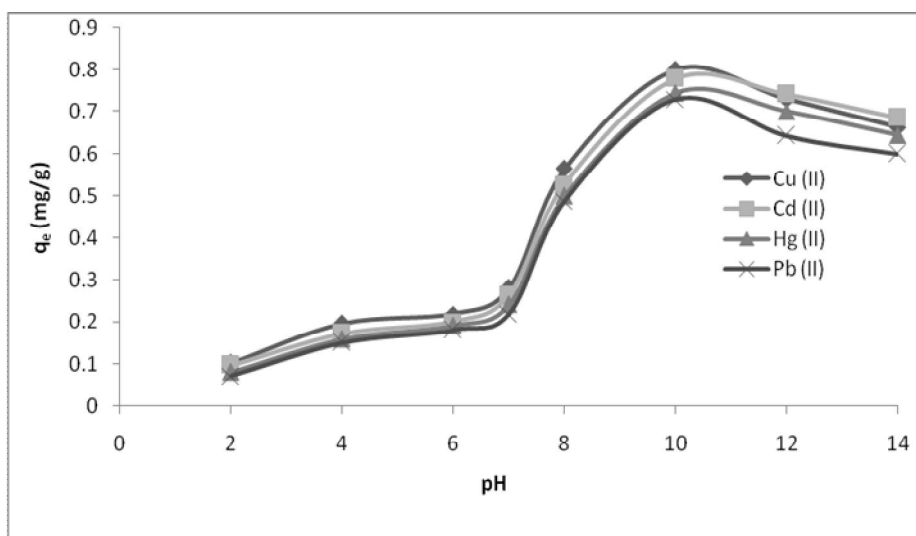


Figure 5. Effect of pH for adsorption of metal ions onto Unpillared bentonite

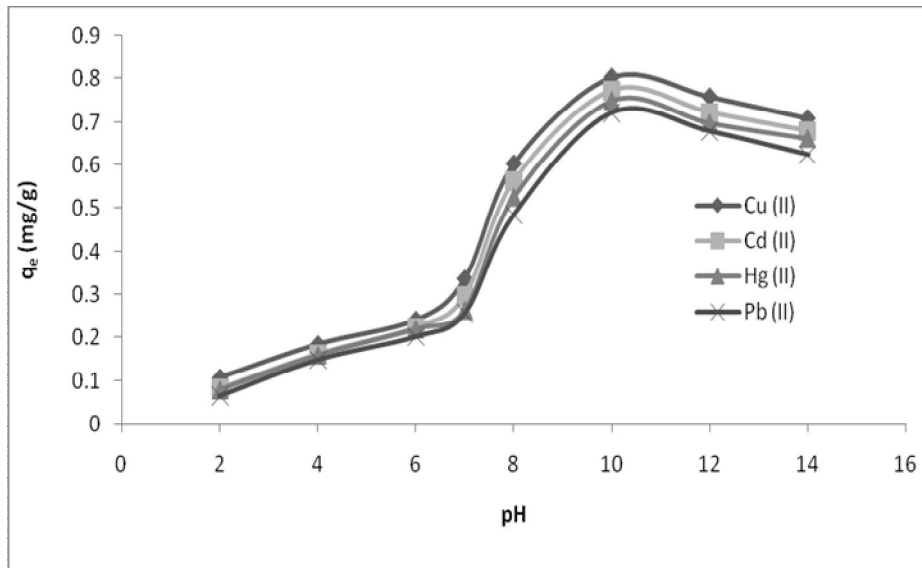


Figure 6. Effect of pH for adsorption of metal ions onto Al-pillared bentonite

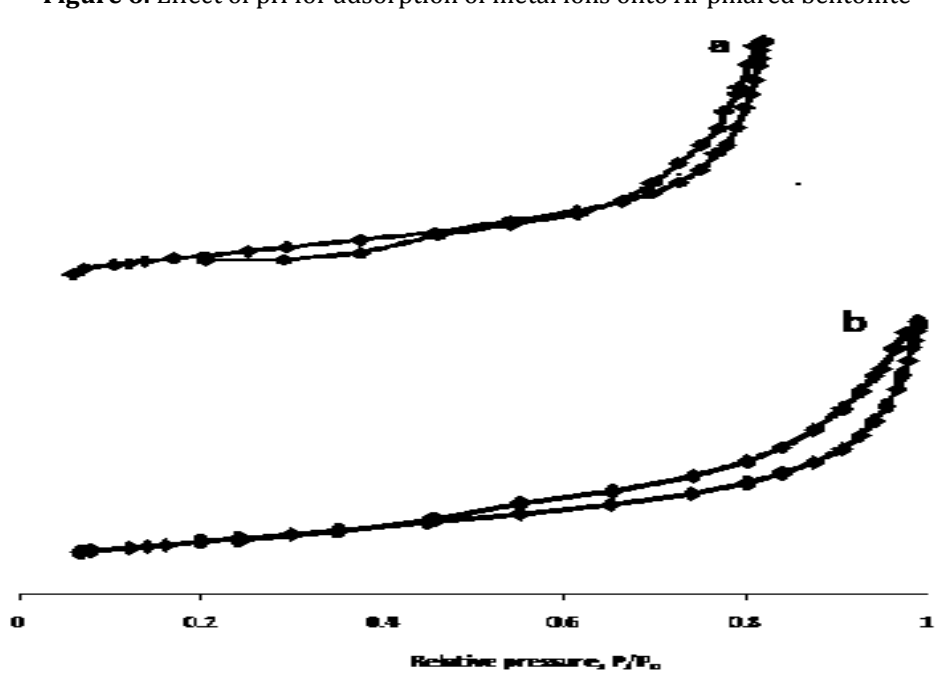


Figure 7. Nitrogen adsorption-desorption isotherm of (a) Unpillared and (b) Al-Pillared bentonites

Table 3. Parameter obtained from Elovich model for the adsorption of metal ions onto Unpillared and Al-pillared bentonites, 50mg/L at 298 K

Adsorbents	Parameter	Cu (II)	Cd (II)	Hg (II)	Pb (II)
Natural bentonite	α (mg.g ⁻¹ .min ⁻¹)	1.28	1.21	1.12	1.02
	β (g.mg ⁻¹)	7.81	8.00	8.00	8.00
	r^2	0.44	0.48	0.56	0.62
Aluminum-pillared bentonite	α (mg.g ⁻¹ .min ⁻¹)	2.79	1.24	1.16	1.04
	β (g.mg ⁻¹)	6.71	6.84	6.89	6.90
	r^2	0.60	0.57	0.57	0.58

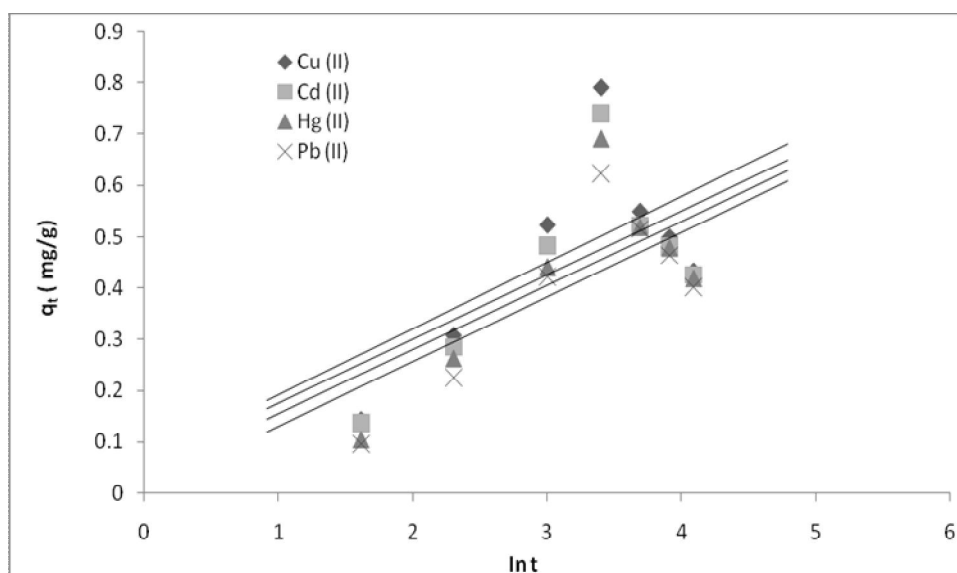


Figure 8. Elovich sorption model for the metal ions onto Unpillared bentonite

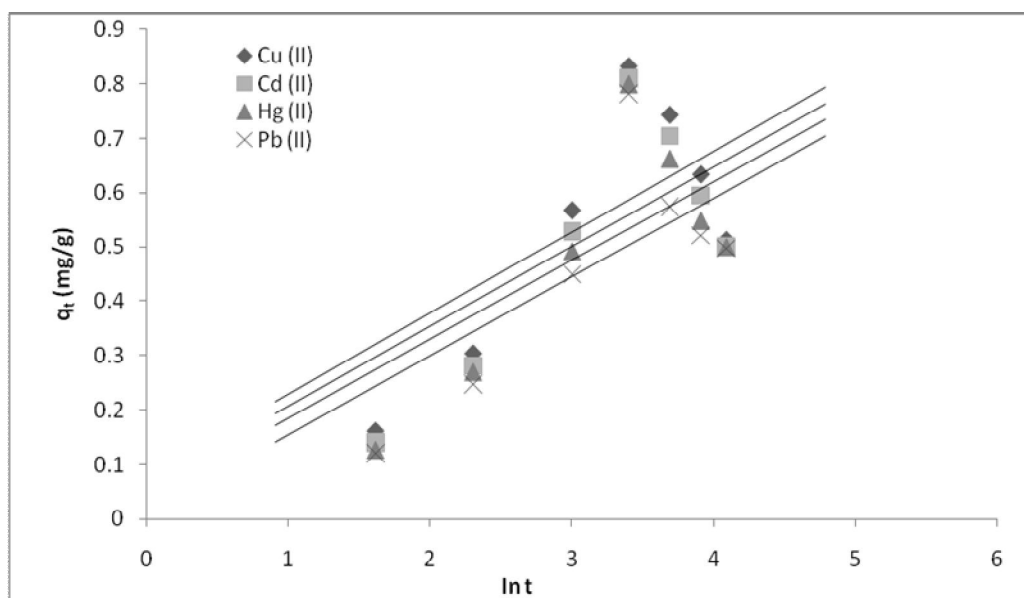


Figure 9. Elovich sorption model for metal ions onto Al-Pillared bentonite

Thermodynamic Studies

The thermodynamic parameters such as ΔG° , ΔH° , and ΔS° , for the adsorption processes are calculated using the following equations:

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

$$\ln K_a = \Delta S^\circ/R - \Delta H^\circ/RT \quad (7)$$

Where R is universal gas constant (8.314 J/mol/K), T is the absolute temperature in Kelvin, K_a is Langmuir constant obtained from Langmuir adsorption model, ΔG° is standard Gibbs free energy change, ΔS° is standard entropy change and ΔH° is standard enthalpy change.

The values of ΔH° and ΔS° were respectively determined from the slope and intercept of the plot of $\ln K_a$ versus reciprocal of temperature (presented in Table 4 and 5). Results indicate that ΔG° values were negative at all temperatures investigated for both the adsorbents. The negative value of ΔG° indicates the spontaneous nature of adsorption of metal ions by the adsorbents. This is in line with other adsorption processes previously reported [18]. It is known that ΔG° up to -20 KJ/mol are consistent with electrostatic interaction between adsorption sites and the metal ion (physisorption) while ΔG° value more than -40 KJ/mol involve charge sharing and transfer from the adsorbent surface to the metal ions to form a coordinate bond (chemisorption). The ΔG° values obtained in this study were consistently less than -10 KJ/mol and increase as temperature increases, indicating that physisorption is the predominant mechanism in the adsorption process.

The positive value of ΔH° for the heavy metal ions on both the adsorbents further confirms that the adsorption process is endothermic. The positive value of ΔS° is an indication of the increasing randomness of the metal ions as well as the existence of some structural changes at the adsorbent-adsorbate interface confirming a physical adsorption ($\Delta G^\circ < -10\text{KJ/mol}$). Similar observations have been reported earlier [19].

Table 4. Thermodynamic parameters for the adsorption of heavy metal ions on Unpillared bentonite

Metals	ΔG° (KJ/mol) (298 K)	ΔG° (KJ/mol)) (303K)	ΔG° (KJ/mol)) (313K)	ΔG° (KJ/mol)) (323K)	ΔH° (J/mol))	ΔS° (J/mol K)	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

Table 5. Thermodynamic parameters for the adsorption of heavy metal ions on Al-Pillared bentonite

Metals	ΔG° (KJ/mol) (298K)	ΔG° (KJ/mol) (303K)	ΔG° (KJ/mol) (313K)	ΔG° (KJ/mol) (323K)	ΔH° (J/mol)	ΔS° (J/mol K)	Ka
Cu (II)	-2.80	-2.67	-2.39	-1.99	+31.80	+12.30	0.03
Cd (II)	-2.70	-2.52	-2.13	-1.88	+32.60	+13.10	0.04
Hg (II)	-2.55	-2.34	-2.08	-1.83	+29.20	+10.00	0.05
Pb (II)	-2.50	-2.22	-2.06	-1.72	+28.03	+10.77	0.06

In order to further support the assertion that physical adsorption is the predominant mechanism, the values of activation energy (E_a) and adsorption probability (S^*) were estimated from the experimental data. They were calculated using a modified Arrhenius type equation related to surface coverage as expressed in equation:

$$\ln(1-\theta) = \ln S^* + E_a/RT \quad (8) \quad [19]$$

The sticking probability S^* , sometimes described as adsorption probability is a function of the adsorbate/adsorbent interaction under investigation. The value of S^* lies in the range $0 < S^* < 1$ (Table 6). The values of activation energy (E_a) and S^* are shown in Table 7. The activation energies calculated were consistent with the values of standard enthalpy (ΔH°) in Tables 4 and 5, both are positive, indicating the endothermic nature of the adsorption process for both the adsorbents and the values lie in the range of physical adsorption. However, the activation energy of the pillared sample was slightly greater than the unpillared clay. This could be attributed to the porosity. The pillared clay has better pore size than the natural. The values of sticking probability are less than 1 for both the adsorbents, indicating that the probability of these metal ions to stick on the surface of the adsorbents is high. These values confirm that the sorption process is physisorption.

Table 6. Sticking probability (S^*) and Activation energy (E_a) for the adsorption of heavy metal ions onto Unpillared and Al-pillared bentonites at different temperatures

Adsorbent	Parameter	Cu (II)	Cd (II)	Hg (II)	Pb (II)
Natural bentonite	E_a (KJ/mol)	8.98	7.65	6.07	3.82
	S^*	0.0162	0.0286	0.0567	0.1430
	r^2	0.92	0.98	0.98	0.96
Al-Pillared bentonite	E_a (kJ/mol)	10.64	9.98	8.73	8.06
	S^*	0.0080	0.0104	0.0173	0.0229
	r^2	0.98	0.98	0.99	0.99

Table 7. The potential adsorption probability relationship between sorbate and sorbent (19)

Values of S^*	Potential sticking probability
$S^* > 1$	Adsorbate unsticking to adsorbent – no sorption
$S^* = 1$	Linear sticking relationship between adsorbate and adsorbent- possible mixture of physisorption and chemisorption mechanism
$S^* = 0$	Indefinite sticking of adsorbate to adsorbent chemisorption mechanism predominant
$0 < S^* < 1$	Favourable sticking of adsorbate to adsorbent- physisorption mechanism predominant

CONCLUSION

The adsorption characteristics of Al-Pillared bentonite clay follow similar pattern as the unpillared sample. The results reveal that both the adsorbents are time and pH dependent. However, Al-pillared showed higher adsorption rate as well as high capacity for all the metal ions reported in this study, 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 larger clay interlayer spacing by Al^{7+} . The standard free energy values (ΔG°) obtained from this study are found to be negative and less than -10KJ/mol , indicating that physisorption rather than chemisorption is predominant in the adsorption mechanism. Positive entropy (ΔS°) found in all cases shows a rapid reversible adsorption – desorption phenomena, indicating physisorption of the metal ions on the adsorbent surfaces. The values of ΔH° and E_a were both positive and lie in the range of physisorption. The results clearly suggest that the adsorption of all the metal ions studied in this work is controlled by 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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