



# Journal of Applied Sciences

ISSN 1812-5654

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## Treatment of Aqueous Solution of Lead Content by using Natural Mixture of Kaolinite-Albite-Montmorillonite-Illite Clay

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**Abstract:** The possible use of clay from Bikougou (Gabon), as an adsorbent, for the removal of lead from wastewater was investigated. The experiments were conducted using batch technique at 308 K and pH 4. The adsorption of Pb (II) ions in aqueous solution on clay has been studied as function of pH, concentration, time and temperature. Its efficiency increased with increasing of pH (from 2 to 8), Pb (II) ions in aqueous solution (pH higher 3), contact time of equilibration and temperature. The experimental data follow the Langmuir isotherm with correlation coefficient higher than 0.99 and maximum adsorption capacities varying between 24.12 to 25.64 mg g<sup>-1</sup> at pH 4 and temperatures ranged between 308 and 318 K. Adsorptions kinetics obeys to a pseudo-second-order model with linear correlation coefficient higher than 0.96. Calculated and experimental amounts of Pb (II) ions adsorbed are in the same order. The negative Gibbs free energy value corresponds to a simultaneous process. The great capability of Bikougou clay to remove Pb (II) ions from aqueous solution demonstrated its potential as a low cost effective way to remediate Pb-contaminated water.

**Key words:** Clay, low cost adsorbent, lead removal, isotherm, spontaneous process

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### INTRODUCTION

Lead is a heavy metal widely disseminated in the nature, particularly in the human environment. Gas from fuel combustion, paint, battery, glass and mining industries release lead in their effluents (Gueu *et al.*, 2007; Zhu *et al.*, 2008). Now, lead is not biodegradable and also found presenting adverse metabolic effects such as poisoning of red blood cells, nervous system attack and kidneys damage (Wang *et al.*, 2007; Garcia and Corredor, 2004; Frisbie *et al.*, 2002). Then, the removal of lead from industrial effluents is becoming a great concern for scientific community. Taking into account all the above, a number of technologies for the removal metal ions from aqueous solutions have been developed over the years. The most important of them, include chemical precipitation, ultrafiltration, electrochemical deposition, ion exchange and reverse osmosis (Ahmad *et al.*, 2009). But these technologies do not seem to be economically generalizable because of their high costs and that developing countries may not afford such technologies. In the last few years, adsorption has been shown to be an

alternative method for removing dissolved metal ions from wastewaters (Bayat, 2002). The adsorption process is a phenomenon known since the 17th century when, it was discovered that porous materials have the property to adsorbing gas and subsequently, the same behaviour is observed for solutions (Brunauer, 2007). Inactivated charcoals and activated carbons were firstly used as adsorbents but their high cost has limited their use. In order to minimise processing costs, several investigations have focused on the search of low-cost adsorbents of agricultural and biological origin (Babel and Kurniawan, 2003). Among them, clays and clays materials considered as low-cost materials have proved their efficiency as adsorbent in a treatment of aqueous solution of metal ions content (Eba *et al.*, 2010). For instance, using a review of lead adsorption results by low-cost adsorbents, from contaminated water. Babel and Kurniawan (2003) reported that montmorillonite, kaolinite, illite and bentonite may remove respectively, 0.68, 0.12, 1.41, 4.29 and 0.68 mg g<sup>-1</sup> of lead as given by Langmuir model. Gupta and Bhattacharyya (2008) showed that kaolinite and montmorillonite allow to uptake respectively 11.5 and

31.1 mg g<sup>-1</sup>. Gupta and Bhattacharyya (2005) have also found that kaolinite and montmorillonite modified clays are able to absorb respectively 5.44 and 31.44 mg g<sup>-1</sup> of lead at 303 K. This study is undertaken to study the potential of clay from Bikougou (Gabon) to adsorb lead (II) ions from aqueous solution. The effect of the solution pH, contact-time and temperature on the removal of Pb (II) ions was investigated. The adsorption isotherm and probable mechanism was explained. The thermodynamic parameters for the adsorption Pb (II) ions have been also computed and discussed.

**MATERIALS AND METHODS**

**Adsorbent characterization:** The clay material taken from Bikougou deposit (Gabon 11°37'E and 1°58'N) was used as adsorbent in this work. It was characterized for its clay minerals content (X-rays) (Fig. 1, 2), composition in major (as oxides) and traces elements (Table 1). Clay values of Surface Specific Area (SSA) were performed using the method of methylene blue (Hang and Brindley, 1970). Its Cation Exchange Capacity (CEC) was determined using the ammonium acetate method at pH 7 (Remi and Orsini, 1976). The acidity of surface was evaluated by means of Boehm titration method (Mukana and Kifuani, 2000). The point of zero charge was given by the use of potentiometric titrations (Ijagbemi *et al.*, 2009) (Table 2).

The X-ray powder diffractograms of the crude clay (Fig. 1) shows the presence of four clayey minerals with some impurities: (i) Kaolinite, identified by its ray at 7.19 Å in crude clay (ii) Montmorillonite recognized for its typical rays at 14.93 Å (iii) Illite known for the displaying a dool at 9.92 Å ; other illite rays are at 5.04, 4.45, 3.38, 3.65, 3.34, 2.87 and 2.54 Å in Fig. 1. (iv) Feldspars are revealed by reflections at 3.18, 3.21, 4.04 Å. The pattern is typical of andesine or albite. The other mineral species identified are (Fig. 1): Quartz (rays at 3.34, 3.18 and 2.56 Å); carbonates calcite mineral (rays at 3.05, 2.93 Å) and as gaylussite (rays at 3.205, 6.39 and 2.63 Å); anatase (rays at 3.51, 2.37

and 1.89 Å); maghemite (rays at 2.93, 2.56 Å); Ba, Sr-hydroxyapatite (rays at 4.45, 3.76, 1.82, 2.13 and 2.93 Å).

The X-ray diffractogram of the crude material is completed by the diffractogram of the clay fraction from which three minerals are identified. (i) Kaolinite identified by its ray at 7.21 Å in untreated fraction (curve U) which is shifted at 10.40 Å by hydrazine saturation from clay fraction (curve H). (ii) Montmorillonite recognized for its typical ray at 15.13 Å. (curve U) which is shifted at 17 Å (curve G) with the ethylene-glycol treatment or reduced to 9.80 Å (curve C) on heating at 490°C. (iii) Illite known for the displaying a dool at 10.02 Å (curve U) which is not affected by the above mentioned treatments (Fig. 2).

Many constituents present in the crude clay such as albite, carbonate, maghemite, anatase, quartz and Ba, Sr-hydroxyapatite have been not found in the clay fraction. The clay fraction was extracted with Robinson pipette, according to Stokes law, from whole-rock aqueous suspension, after oxidation of organic matter using H<sub>2</sub>O<sub>2</sub> and destruction of acid soluble minerals using HNO<sub>3</sub> (5%).

**Adsorbate and aqueous solution:** Pb (II) ions used in this study have been obtained from Pb (NO<sub>3</sub>)<sub>2</sub> (Prolabo Analytical grade), it was used without further purification. Aqueous solutions of Pb (II) were prepared by dissolving an accurately weighed amount of Pb (NO<sub>3</sub>)<sub>2</sub> in deo-ionised water to achieve concentration of Pb (II) (ranged from 19 to 120 mg L<sup>-1</sup>).

**Adsorption procedure:** The adsorption of Pb (II) ions on to clay was studied by means of batch technique. A known weight (0.25 g) of clay was equilibrated with 50 mL of the spiked lead solution of known concentration, in a stopped propylene flask, at a fixed temperature and in a thermostatic shaker for known period time. After the equilibration using a constant stirring speed, the suspension was filtered out and analyzed for its lead concentration, using an atomic adsorption spectrometer (Analyst 100 Perkin Elmer, Varian AA 20). The effects of

Table 1: Chemical composition of clay material from Bikougou

Major elements	Wt (%)	Trace elements	Concentration (ppm)	Trace elements	Concentration (ppm)	Trace elements	Concentration (ppm)	Trace elements	Concentration (ppm)
SiO <sub>2</sub>	54.32	As	< L.D.	Eu	115.00	Ni	29.26	U	0.40
Al <sub>2</sub> O <sub>3</sub>	24.64	Ba	357.80	Ga	27.45	Pb	7.06	V	97.89
Fe <sub>2</sub> O <sub>3</sub>	3.87	Be	1.06	Gd	2.62	Pr	4.13	W	37.17
MnO	0.02	Bi	< L.D.	Ge	1.06	Rb	15.93	Y	9.02
MgO	0.60	Cd	< L.D.	Hf	2.21	Sb	< L.D.	Yb	0.75
CaO	2.53	Ce	36.67	Ho	0.32	Sm	3.29	Zn	56.69
Na <sub>2</sub> O	3.09	Co	17.51	In	< L.D.	Sn	1.14	Zr	82.77
K <sub>2</sub> O	0.89	Cr	61.45	La	19.86	Sr	505.60		
TiO <sub>2</sub>	0.90	Cs	0.51	Lu	0.11	Ta	0.40		
P <sub>2</sub> O <sub>5</sub>	0.05	Cu	38.43	Mo	< L.D.	Tb	0.35		
LOI	8.35	Dy	1.87	Nb	6.42	Th	1.81		
Total	99.26	Er	0.83	Nd	17.25	Tm	0.12		

Major elements expressed in weight percentage; Trace elements in ppm; L.D: Limit of detection; LOI: Loss of ignition

Table 2: Characteristics of Bikougou clay deposit

pH of point zero charge (PZC)	CEC (meq 100 g <sup>-1</sup> )	Acidity neutralizations (meq g <sup>-1</sup> )			Surface area (m <sup>2</sup> g <sup>-1</sup> )
		NaOH	NaHCO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	
3	12.87	2.79	0.285	0.0	170

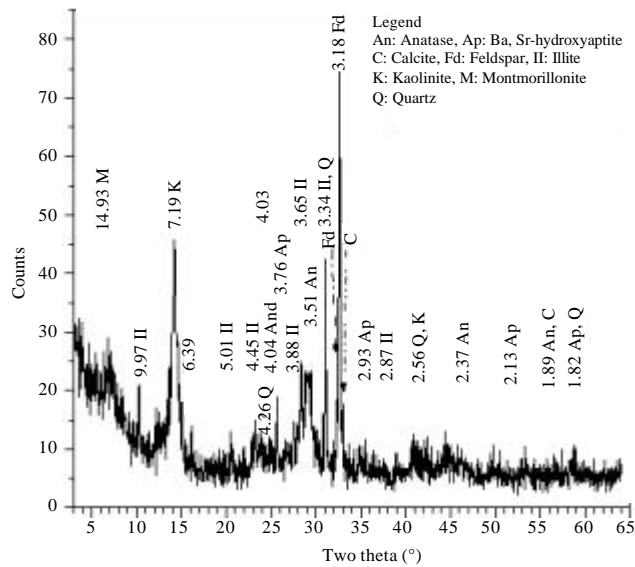


Fig. 1: XRD patterns of crude clay from Bikougou deposit

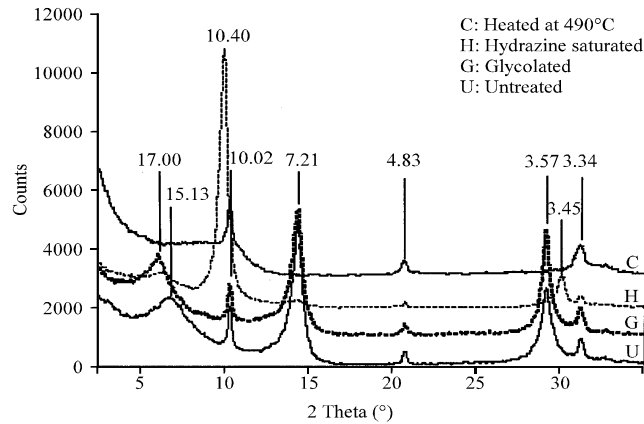


Fig. 2: XRD patterns of clay fraction from Bikougou deposit

several parameters such as pH, contact-time, initial concentration of lead solutions and temperature on the adsorption were studied.

**Calculation:** The amount of lead (II) ions adsorbed per unit mass of adsorbent and percentage of Pb (II) ions adsorbed (% ads) were calculated by using respectively the Eq. 1 and 2:

$$q_t(\text{mg L}^{-1}) = (C_0 - C_t) \times \frac{V}{m} \quad (1)$$

$$\text{ads (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

where, C<sub>0</sub> and C<sub>t</sub> are the initial concentration and concentration after any time of interaction adsorbate-

adsorbent of lead in aqueous solutions, V is the volume of lead solution and m is the mass of clay.

**Adsorption results models:** The adsorption process is normally described in this study by the use of Langmuir and Dubinin-Kaganer-Radushkevich (DKR) isotherms (Langmuir, 1918; Gupta and Bhattacharyya, 2005; Karapinar and Donat, 2009). These adsorption isotherm models serve to characterize the interaction of Pb (II) with the clay from Bikougou. Each of them, provides a relationship between the Pb (II) concentration in the solution and the uptake of Pb (II) adsorbed onto the solid phase when the two phases are at equilibrium. The adsorption experimental data obtained for equilibrium condition are analyzed by using the linear forms of Langmuir and DKR adsorption isotherms.

Langmuir isotherm is applicable if the monolayer coverages of adsorbent by adsorbate takes place on an homogeneous adsorbent surface. The Langmuir coefficients b and  $q_m$  representing respectively the adsorption equilibrium constant and the monolayer maximum adsorption capacity are determined from the intercepts and the slopes of the plots  $C_e/q_e$  vs  $C_e$ . A further analysis of Langmuir equation can be made on the basis of a dimensionless separation constant  $R_L$  (Juang *et al.*, 1997). For favourable adsorption  $0 < R_L < 1$  and  $R_L > 1$  represents unfavourable adsorption,  $R_L = 1$  linear adsorption and  $R_L = 0$  corresponds to an irreversible process (Kadirvelu and Namasivayama, 2003).

The DKR equation is used to explain the energetic heterogeneity of solid at low coverages as monolayer region in micropores. The DKR parameters  $X_m$  and  $\beta$  representing respectively, the maximum adsorption capacity and the coefficient of mean energy may be obtained from the intercepts and slopes of plots  $\ln q_e$  vs  $e^2$ .

When the kinetics of the adsorption follows the pseudo-second-order kinetics (Tien and Huang, 1991; Ho and McKay, 1999c; Ho *et al.*, 2001) the plot  $t/q_e$  vs. t gives a linear relationship which allows computation of the amount of Pb (II) ions adsorbed per unit mass of clay at equilibrium ( $q_e$ ) and the second order rate constant ( $k_2$ ).

Thermodynamic parameters such as enthalpy and entropy changes are estimated using the Langmuir constant b at plotting  $\ln b$  vs  $1/T$  (K) (Eba *et al.*, 2010). The Gibbs free energy of the reaction is then computed as  $\Delta G^0 = \Delta H^0 - T\Delta S^0$ .

## RESULTS AND DISCUSSION

**Properties of the used clay:** Table 1 shows the mineral composition of the clay used. The main constituent of the crude clay is  $SiO_2$  (54.32 w.t. %),  $Al_2O_3$  is the next main

constituent (24.64 w.t. %) followed by notable amounts of  $Fe_2O_3$  (3.87 w.t. %),  $Na_2O$  (3.09 w.t. %) and  $CaO$  (2.53 w.t. %). Among the analyzed 43 trace elements, prevailing elements are Sr (506 ppm), Ba (558 ppm). Other elements contents are <100 ppm. The constrained multilinear calculation realized by combining X-rays results and whole-rock chemical analyses was used to quantify the percentage of each mineral in the crude clay (Njopwouo, 1984; Yvon *et al.*, 1990).

The results presented in the Table 3 show the mineralogical composition of the crude clay material. The whole rock comprises kaolinite (29.1%), albite (20.3%), montmorillonite (15.2%) and illite (10.9%).

The data reported in the Table 2 show the surface properties of clay. The CEC value (12.87 meq/100 g) which is similar to that of pure illite (10-15 meq/100 g) (Baeyens and Bradbury, 2004), is higher than those for standard technical kaolinites (5 meq/100 g) (Ma and Eggleton, 1999) and lower than that of pure montmorillonite (40-100 meq/100 g) (Maes *et al.*, 1979). A simulation accounting for the estimated modal compositions yielded a CEC value of 12.45 meq/100 g; implying that the CEC of the present material is the balance sum of the CECs of its contrasted constitutive clay minerals. The SSA value ( $170 \text{ m}^2 \text{ g}^{-1}$ ), is higher than those for illite (Oswego illite  $78 \text{ m}^2 \text{ g}^{-1}$ ) or of kaolinite (Florida kaolinite  $35 \text{ m}^2 \text{ g}^{-1}$ ) and lower than that of montmorillonite ( $700\text{-}410 \text{ m}^2 \text{ g}^{-1}$ ) (Santamarina *et al.*, 2002). It is to be noted that specific surface area cannot represent a general characteristics of a particular type of material, because its value depends of particle size, particle shape, number distribution of cracks and pores in the material (Gupta and Bhattacharyya, 2008). The PZC value (3) is higher than for kaolinite (2.8) (Appel *et al.*, 2003) and lower than for montmorillonite (3.5) (Ijagbemi *et al.*, 2009). The Acidity Neutralization (AN) values are higher than that for kaolinite (Florida kaolinite  $0.1 \text{ meq g}^{-1}$ ) (Baker *et al.*, 1985).

**Table 3: Mineralogical composition of clay from Bikougou**

Mineral	Untreated clay	
	(whole-rock) wt (%)	Clay fraction (%)
Kaolinite	29.1	53.0
Albite	20.3	0.0
Montmorillonite	15.2	40.0
Illite	10.9	7.0
Quartz	19.1	0.0
Carbonates	3.0	0.0
Maghemite	1.2	0.0
Anatase	0.9	0.0
Ba-Sr hydroxyapatite	0.8	0.0
Zircon	Trace	0.0

Composition of untreated clay material and its fraction (wt %). The composition of untreated clay is determined by combining qualitative X-ray data and chemical analysis while the composition of clay fraction is determined from X-ray pattern intensities measurements without absorption correction

Table 4: Amounts ( $q_e$  (mg g<sup>-1</sup>)) and percentage (ads (%)) of Pb (II) ions adsorbed as function of pH and salt initial concentration

Initial concentration (mg L <sup>-1</sup> )	pH							
	2		4		6		8	
	$q_e$ (mg g <sup>-1</sup> )	ads (%)	$q_e$ (mg g <sup>-1</sup> )	ads (%)	$q_e$ (mg g <sup>-1</sup> )	ads (%)	$q_e$ (mg g <sup>-1</sup> )	ads (%)
25	2.39	47.8	5	100	4.986	99.73	4.95	99.09
30	2.57	42.94	6	100	5.97	99.51	5.76	95.86
35	2.55	36.4	6.895	98.51	6.739	96.28	6.94	99.19
40	2.08	26.0	7.626	95.33	7.99	99.88	7.92	99.02

where:  $q_e$ , in mg g<sup>-1</sup>, is the equilibrium amount of Pb (II) adsorbed per specified amount of adsorbent; ads is the percentage of Pb (II) adsorbed

The neutralization of the acids on the surface with NaOH, NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> translated the presence of functional group, such -OH<sup>-</sup>, -C = O and -COOH (Boehm, 1994). Clay characteristics from this study, are not in agreement with those of single clay species, because those for clay from Bikougou are the balance sum of characteristics, of its constitutive clay minerals. All these parameters allow to assess the potential of clay as adsorbent.

**Effect of pH:** The experiments for the effect of pH on adsorption capacities of clay for Pb (II) ions were performed using different initial concentrations varying from 20 to 40 mg L<sup>-1</sup> of lead content and 250 mg of clay, at various pH between 2 and 8 during 90 min. Table 4 reports the pH influence of Pb (II) ions adsorption onto clay surface. It is observed that the adsorption capacity of clay increases greatly with the increase in pH from 2 to 4 and the adsorption high level obtained from a pH of 4 increases weakly as far as pH 8. When initial concentrations are below 25 mg L<sup>-1</sup>, all the Pb (II) ions are adsorbed on clay assuming that the number of sites adsorbing is higher than the amount of Pb (II) ions to be adsorbed, this gives the impression that the adsorption is constant from pH 4 to 8. In agreement with this work (for high concentration than 25 mg L<sup>-1</sup>), a continuous increase of adsorption amounts of lead (II) ions with the increase in pH has been reported by Wang *et al.* (2007) using MnO<sub>2</sub>/CNTS as adsorbent, Potgieter *et al.* (2006) with palygorskite as adsorbent, Zhu *et al.* (2008) using bentonite as adsorbent and Gupta and Bhattacharyya (2005) with kaolinite and montmorillonite as adsorbents. The observed changes in lead uptake as function of pH could be explained from the hypothesis of a competition between H<sub>3</sub>O<sup>+</sup> and Pb (II) ions for the approach of available adsorption sites on adsorbent surface (Gueu *et al.*, 2006). At low pH than that of Point of Zero Charge (PZC), there is a large excess of H<sub>3</sub>O<sup>+</sup> ions which compete repulsively with Pb (II) ions for the attainment of adsorption available sites on adsorbent surface. The number of Pb (II) ions reaching adsorption sites is weak. The result is now a weak level of Pb (II) ions uptake. When pH is higher than that of PZC, the amount of H<sub>3</sub>O<sup>+</sup> ions is negligible and more Pb (II) ions could

reach available adsorption sites on clay surface. The level of Pb (II) ions adsorbed increases then, considerably. The literature reports similar views about the effect of pH on Pb (II) adsorption by silicate minerals (Zhu *et al.*, 2008; Ayari *et al.*, 2007). The maximum sorption efficiency in the pH range 4-8 may be due also to the combination between adsorption process and lead hydroxide precipitation. Gupta and Bhattacharyya (2008) and Jain and Ram (1997) observed this behavior of continuous increase of adsorption capacity of Pb (II) ions on kaolinite and on montmorillonite with the increase in pH from 2 to 6 and appearance from pH 6 of the lowly soluble Pb (II) hydroxide. Instead that, experiments in this work were realized at pH 4.

**Adsorption isotherms studies:** The adsorption isotherms for Pb (II) removal were studied using initial concentration of Pb (II) ions such as 67.978, 74.202, 78.03 and 80.186 mg L<sup>-1</sup> and adsorbent mass of 0.1 g at 308, 313 and 318±1K. Amounts of Pb (II) ions adsorbed per unit mass of clay increased gradually with increasing concentration of lead (Table 5). Similar results have been reported by Ayari *et al.* (2007) and Gupta and Bhattacharyya (2008) for the Pb (II) adsorption from aqueous solution onto bentonite and montmorillonite, respectively. These results are related to number of Pb (II) ions capable to react with available numerous adsorption sites on the adsorbent surface, this number of Pb (II) ions is growing with the increase of concentration of Pb(II) ions solution.

The data obtained are used to trace the Langmuir plots isotherms:  $C_e/q_e$  as function of  $C_e$  (Fig. 3) and DKR (Erdem *et al.*, 2004) plots isotherms:  $\ln q_e$  as function of  $e^2$  (Fig. 4). From these plots (Fig. 3, 4), the corresponding parameters of the two models and their linear correlation coefficients ( $R^2$ ) are determined and conclusion could be drawn about the adherence of each isotherm model to adsorption experimental data. The results are presented in the Table 6.

The adsorption data follow the Langmuir isotherm model, because, its correlation coefficients from 308 K to 318 K are higher than 0.99. The equilibrium constant, b, varies from 3.196 at 308 K to 7 at 318 K. The large values of constant, b are an indication of the high strength of

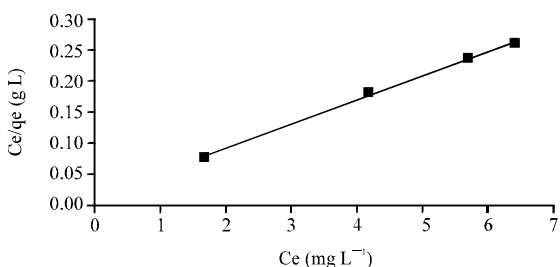


Fig. 3: Plot of variations of the ratio of the equilibrium concentration ( $C_e$ ,  $\text{mg L}^{-1}$ ) on amount adsorbed specified amount of adsorbent ( $q_e$ ,  $\text{mg g}^{-1}$ ) as a function of equilibrium concentration for Pb (II) ions adsorption on clay at 308K (initial concentration 67.94, 74.20, 78.03 and 80.19  $\text{mg L}^{-1}$ , pH 4)

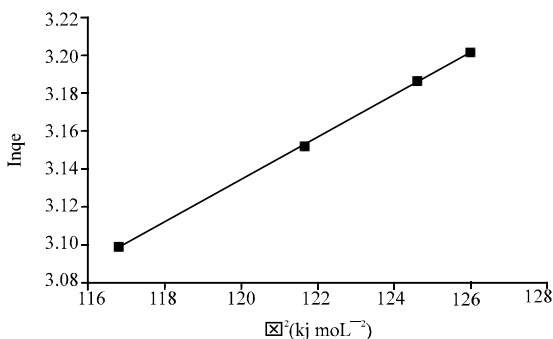


Fig. 4: Plot of variations of the logarithm of amount adsorbed per specified amount of adsorbent ( $q_e$ ,  $\text{mg g}^{-1}$ ) as a function of the square of Polanyi potential ( $\epsilon^2$  ( $\text{kJ/mol}^2$ )) for Pb (II) ions adsorption on clay at 308K (initial concentration 67.94, 74.20, 78.03 and 80.19  $\text{mg L}^{-1}$ , pH 4)

Table 5: Amount of Pb(II) ions adsorbed per unit mass of clay at different temperature

Initial concentration of Pb (II) solution ( $\text{mg L}^{-1}$ )	Experimental amount of Pb (II) adsorbed per unit mass of clay $q_e$ , ( $\text{mg g}^{-1}$ )		
	308 K	313 K	318 K
67.98	22.13	21.80	22.00
74.20	23.36	23.68	24.02
78.02	24.16	23.95	24.12
80.19	24.58	23.65	24.16

the interactions adsorbent- adsorbate, most probably chemisorptions. The adsorption capacity,  $q_m$ , is found appreciably large with values of 25.64  $\text{mg g}^{-1}$  (308 K) to 24.63  $\text{mg g}^{-1}$  (318 K). The separation factor,  $R_L$ , with its values remained between 0.0046-0.0039 (308 K) and 0.00178-0.0021 (318 K) corresponds to the case of favourable adsorption of Pb (II) ions on the clay

adsorbent (Juang *et al.*, 1997) in conformity with the requirement  $R_L < 1$  (Lin and Juang, 2002). The large values of Langmuir parameters from 308 to 318 K, imply that the adsorption of Pb (II) ions is limited to monolayer coverage and also that adsorbent surface is energetically homogeneous.

The Dubinin-Kaganer-Radushkevich (DKR) equation, has been found to describe the sorption of Pb (II) ions on clay. The linear correlation coefficients remained between 0.8401 and 0.9998 (in the ranges 308-318 K of temperature), correspond to the level of monolayer coverage of microspores on the adsorbent surface. Values of  $X_m$  (DKR monolayer capacity) are ranged from 5.92  $\text{mg g}^{-1}$  to 8.57  $\text{mg g}^{-1}$  with the increase in temperature from 308 to 318 K. These high values of  $X_m$  indicate the nature favourable of the adsorption of Pb (II) on clay. The adsorption energy E reveals the nature of adsorption. If the E value is ranged between -1 and -8  $\text{kJ mol}^{-1}$ , adsorption process is physical and if the E value is ranged between -9 and -16  $\text{kJ mol}^{-1}$ , it is chemically controlled adsorption. The E values for the present study, decrease from, -9.407  $\text{kJ/mol}$  at 308 K, to -10.425  $\text{kJ mol}^{-1}$  at 313 K and to -10.20  $\text{kJ mol}^{-1}$  at 318 K. That corresponds to an ion-exchange mechanism (Hellferich, 1962; Kwon *et al.*, 1998). This sorption chemically controlled process was also reported by Saeed *et al.* (2003).

Other workers have reported values of the adsorption parameters in similar ranges. Gupta and Bhattacharyya (2008) from studies of adsorption of Pb (II), Cd (II) and Ni (II) on kaolinite and montmorillonite, found Langmuir adsorption capacity,  $q_m$ , between 11.5 to 31.1  $\text{mg g}^{-1}$  at 303 K and pH 5.7,  $R_L$  ranged between 0.0021 to 0.0003 and  $R^2$  remained from 0.98 to 0.99 for Pb (II) adsorption. Lin and Juang (2002) have reported DKR Adsorption capacity,  $X_m$ , of 5.27 and of 2.09  $\text{mg g}^{-1}$ , adsorption energy E of: -13.8 and -12.6  $\text{kJ mol}^{-1}$  and correlation coefficients  $R^2$  of 0.962 and of 0.978 for Cu (II) and Zn (II), respectively from the adsorption studies of these ions on surfactant-modified montmorillonite.

**Thermodynamics studies:** In order to determine the thermodynamic feasibility and the thermal effects accompanying the adsorption process, the amounts of Pb (II) ions adsorbed ( $q_e$  ( $\text{mg g}^{-1}$ )) and equilibrium concentration ( $C_e$  ( $\text{mg L}^{-1}$ )) of Pb (II) ions in aqueous solution were determined at 308, 313 and 318 K. Pb (II) adsorption on the clay increases with the increase in temperature. The interaction is endothermic. Similar results have been reported by Gupta and Bhattacharyya (2008) for adsorption of Pb (II) on montmorillonite and/or kaolinite.

Table 6: Langmuir and DKR isotherm fitted parameters for the adsorption of Pb (II) onto clay from Bikougou (pH 4, initial concentrations 67.98, 74.202, 78.2 and 80.18 mg L<sup>-1</sup> clay 2 g L<sup>-1</sup>)

T(K)	Langmuir				DKR			
	q <sub>m</sub> (mg g <sup>-1</sup> )	b (L mg <sup>-1</sup> )	10 <sup>3</sup> R <sub>L</sub>	R <sup>2</sup>	X <sub>m</sub> (mg g <sup>-1</sup> )	β (mol kJ) <sup>2</sup> *10 <sup>4</sup>	E (kJ mol <sup>-1</sup> )	R <sup>2</sup>
308	25.64	3.196	3.9-4.6	0.9989	5.92	113	-9.407	0.9998
313	24.21	6.88	1.8-2.13	0.9984	7.32	92	-10.425	0.7942
318	24.63	7	1.78-2.10	0.9993	6.75	96	-10.20	0.8401

Where: T is the temperature in Kelvin; q<sub>m</sub> is the Langmuir monolayer maximum capacity; b is the Langmuir equilibrium constant; R<sub>L</sub> is the Langmuir dimensionless factor; R<sup>2</sup> is the correlation coefficient; X<sub>m</sub> is the DKR maximum adsorption capacity; β is the activity coefficient related to the mean energy; E is the adsorption mean energy

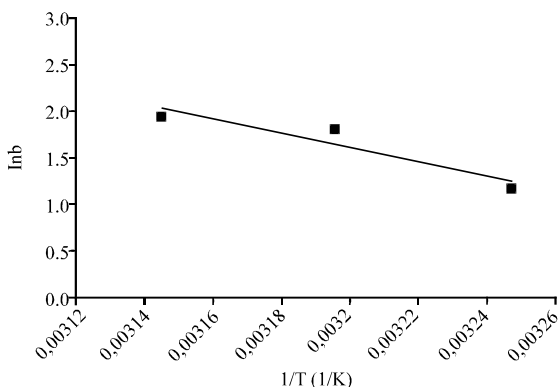


Fig. 5: Plot related to the variations of Langmuir equilibrium constant (b, L/g) as a function of the temperature reverse (1/T, K<sup>-1</sup>) for Pb (II) ions adsorption on clay at pH 4

The plot of ln b versus 1/T (Fig. 5) gives effectively, a linear relationship with regression coefficient of equal to 0.86.

The Gibbs free energy values decrease from -3.205 kJ mol<sup>-1</sup> at 308 K, to -4.290 kJ mol<sup>-1</sup> at 313 K and to -5.375 kJ mol<sup>-1</sup> at 318 K indicating that the process is spontaneously more feasible with the increase in temperature. The positive value of enthalpy changes (63.655 kJ mol<sup>-1</sup>) corresponds to endothermic interactions Pb (II)-clay. The considerably high values of ΔH<sup>0</sup> suggest strong interactions corresponding to a controlled chemical process, between Pb (II) ions and the clay. In the other hand, the positive value of ΔS<sup>0</sup> (0.217078 kJ/mol/K) indicates that Pb (II) ions in aqueous solution are in a much more ordered state compared to the chaotic distribution when adsorbed on clay. Thermodynamic data on Pb (II) adsorption have been obtained through other works. In agreement with the results of the present work, for the adsorption of Pb (II) on peat and on activated carbons from coconut and seed hull of palm tree respectively, Ho and McKay (1999a, b) and Gueu *et al.* (2007) found a positive value of the adsorption enthalpy. Wang *et al.* (2007) have reported that ΔH<sup>0</sup>, ΔS<sup>0</sup>, ΔG<sup>0</sup> for sorption of Pb (II) on manganese dioxide coated carbon nanotubes have values of 0.35301, 0.02297 and

-6.496 kJ mol<sup>-1</sup>. Ahmad *et al.* (2009) have obtained the values of enthalpy, entropy and Gibbs free energy changes, respectively of 120.02, 0.13 and -20.99 kJ mol<sup>-1</sup> at 303 K for adsorption of Pb (II) on sawdust of Meranti wood. In opposite case, exothermic adsorption of Pb (II) of -58.9 and -31.5 kJ mol<sup>-1</sup>, negative values of the entropy change of -209.7 and -116.3 J/mol/K and Gibbs free energy value of -64.6 and -35.8 kJ mol<sup>-1</sup>, respectively have been obtained on kaolinite and also on montmorillonite by Gupta and Bhattacharyya (2008). The convergence is linked to thermodynamic behavior with respect to the adsorption of Pb (II) ions and not to the values obtained on the thermodynamic parameters because of not identity of adsorbents used.

**Kinetic studies:** Assuming a pseudo-second-order kinetic model, the experimental data were subjected to the integrated form of law of pseudo-second-order model (Ho and McKay, 1999c). One can immediately observe the fast increase in Pb (II) uptake in just five minutes. This fast reaction implies the strong electrostatic interaction between the negatively charged clay surface and Pb (II) ions. The removal equilibrium of lead by clay is attained at about of twenty-thirty minutes (Jain and Ram, 1997). The linear plots in the system of coordinates t/q<sub>e</sub> versus t presented in Fig. 6, illustrate the fit of the pseudo-second-order kinetic model to experimental data.

The pseudo-second-order kinetics parameters k<sub>2</sub>, q<sub>e</sub> and R<sup>2</sup> are reported in the Table 7.

The correlation coefficients for the linear plots are greater than 0.999 at 308K and than 0.96 at 313 and 318 K, in conformity with the requirement (R<sup>2</sup> = 1) of the validity of a kinetics model (Al-Futaisi *et al.*, 2007).

The kinetic constants k<sub>2</sub> (g mg<sup>-1</sup>\*min) vary in a random way with the initial concentration of Pb (II) solution, decreasing with the increase in initial concentration at 308 and 313 K and no known rule at 318 K. An examination of the temperature effect (Table 7) shows that the values of constant rate decrease with the increase in temperature from 308 to 313K. The great level of rate constants (0.6 g/(mg×min) ≤ k<sub>2</sub> ≤ 4.038 g/(mg×min) is an evidence of strong interaction between Pb (II) ions and adsorption sites on the adsorbent. This is a



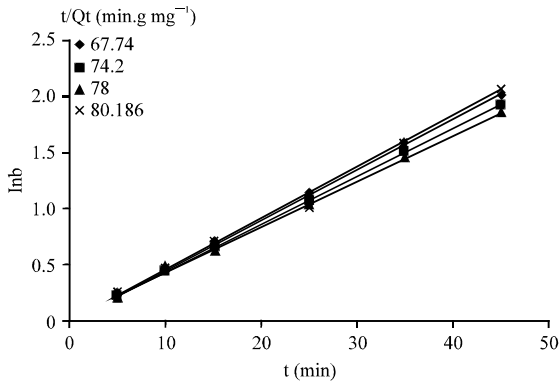


Fig. 6: Plots related to variations of the ratio between adsorbent-adsorbate contact time ( $t$ , min) on the amount adsorbed per specified amount of adsorbent ( $q_e$ ,  $\text{mg g}^{-1}$ ) as a function of time for Pb (II) ions adsorption on clay at 308 K for different initial concentration (67.74, 74.2, 78 and  $80.186 \text{ mg L}^{-1}$ ) at pH 4

Table 7: Pseudo-second-order kinetic parameters for the adsorption of Pb (II) on clay (pH 4)

T (K)	$k_2$ (g/mg.min)	$q_e$ (mg $\text{g}^{-1}$ )	$q_{ex}$ (mg $\text{g}^{-1}$ )	$R^2$
308	2.942	22.220	22.101	1
	1.986	23.474	23.362	1
	1.190	24.509	24.160	0.9993
	1.628	22.442	24.590	0.9993
313	2.006	21.786	21.798	0.9985
	1.668	23.640	23.680	0.9996
	0.973	23.529	24.111	0.9634
	0.600	17.513	23.640	0.9625
318	1.929	21.320	22.000	0.9995
	2.655	23.640	24.031	0.9940
	4.038	23.585	24.130	0.9988
	0.772	26.738	24.160	0.9622

Where: T is the temperature in Kelvin;  $q_e$  in mg/g, is the equilibrium amount of Pb (II) adsorbed per specified amount of adsorbent obtained by calculation from the second order kinetics model;  $q_{ex}$  is the experimental equilibrium amount of Pb (II) adsorbed per specified amount of adsorbent;  $R_L$  is the Langmuir dimensionless factor;  $R^2$  is the correlation coefficient;  $k_2$  is rate constant

characteristic of a chemical reaction also called irreversible process. The good agreement between calculated  $q_e$  and experimental  $q_{ex}$  (amounts of Pb (II) ions adsorbed), demonstrates that the adsorption kinetics of Pb (II) onto clay follows very accurately the pseudo second order model according to Ho and McKay (2000). Other researchers have found results in agreement with those obtained in the present work. Pseudo-second-order kinetic model was applied during the adsorption of lead (II) ions on bentonite clay and parameters values such as: rate constant, amount of metal ions adsorbed and correlation coefficient have been obtained and equal respectively to  $0.0297 \text{ g/mg/min}$ ,  $36.71 \text{ mg g}^{-1}$  and 0.99

(Zhu *et al.*, 2008). Gupta and Bhattacharyya (2008) found Pb (II) ions adsorption kinetics on kaolinite and montmorillonite, to follow the pseudo-second-order with rate constant varying between 0.035 and  $0.0804 \text{ g/mg/min}$ , amount of metal ions adsorbed ranged from 6.4 to  $22.3 \text{ mg g}^{-1}$  and correlation coefficient equal to 0.99. It is to be noted that although the adsorption of ions Pb (II) ions on bentonite, kaolinite, montmorillonite and clay from Bikougou follows the kinetics of the pseudo-second order kinetic parameter values are not identical because of differences in the nature, structure and composition between the clay adsorbents.

## CONCLUSION

This study shows that clay from Bikougou has a great potential as adsorbent usable for the removal of Pb (II) ions from aqueous solutions. The amount of Pb (II) ions adsorbed on clay is pH, initial concentration of Pb (II) ions solution and temperature dependent. Langmuir and DKR models describe the adsorption isotherm but the best fit ( $R^2 = 0.99$ ) of experimental data is obtained with Langmuir isotherm. The adsorption process is spontaneous because of negative Gibbs free energy values given. It is accompanied by an endothermic interaction and a positive value of  $\Delta S^0$  change. The adsorption obeys to kinetics of pseudo-second-order model and is controlled by a chemical mechanism.

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