International Journal of

Chemical

Technology

Isothermal and Kinetic Studies of Simultaneous Removal of Mn (II) and Pb (II) Ions in Aqueous Solution by Adsorption onto Clay from Bikougou Deposit (Gabon)

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ABSTRACT

This work aimed to evaluate the potential of the clay from Bikougou to adsorb simultaneously Mn (II) and Pb (II) from binary aqueous solutions. The experiments were realized by using batch technique at the temperature of 308 K and pH 4 with adsorption isotherms and the interaction of adsorbent-adsorbate time as parameters. Adsorption isotherm models of Freundlich, Langmuir and Dubinin-Kaganer-Radushkevich are all appropriate to describe the experimental adsorption results with their correlation coefficients above 0.95. The maximum amount of Mn (II) and Pb (II) ions adsorbed simultaneously is 85.379 mg g^{-1} and was obtained by applying the model of Dubinin-Kaganer-Radushkevich. The Mn (II) ions are preferentially adsorbed at multilayer available Freundlich surface sites and Pb (II) ions on the available adsorption sites on monolayer Langmuir homogeneous surface. The Pb (II) and Mn (II) mean adsorption energies are indicative of chemical and physical processes. In the bi-solute of Mn(II)-Pb(II) system, Pb(II) adsorption is promoted during its competition with Mn(II) for the adsorption sites. Mn(II) and Pb(II) ions compete for the attainment of adsorption sites following the kinetics of pseudo-second order with correlation coefficients greater than 0.99. All these results have shown the efficiency of clay adsorbent for the simultaneous removal of Pb (II) and Mn (II) from aqueous solution.

Key words: Bi-component system, lead and manganese, adsorption, batch technique, natural mixture clay

INTRODUCTION

Heavy metals as Mn and Pb released to environment through industrial effluents have been found toxic and responsible of serious pollution. The accumulation of Mn and Pb through ingestion and inhalation has shown adverse effects against human health including: kidneys damage, nervous and reproductive systems attack as reported by Lin and Juang (2002) and Eba *et al.* (2007). It is necessary that heavy metal must be removed before the industrial effluents transferred to the environment. Several methods are used for treatment of heavy metal aqueous solutions, such as ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis, electrochemical deposition, adsorption using activated carbons (Gueu *et al.*, 2007) or zeolites (Erdem *et al.*, 2004). Because of the high cost of above processes, recourse of low-cost adsorbents has been appeared to be an alternative opportunity in adsorption technology and interest towards these materials is growing (Babel and Kurniawan, 2003; Unlu and Ersoz, 2006).

A non-exhaustic list of low-cost adsorbent includes wood sawdust, clays, clay materials and other materials of agricultural and industrial wastes origin (Ahmad *et al.*, 2009; Larous *et al.*, 2005; Shukla *et al.*, 2002; Gueu *et al.*, 2006).

Clays are widely used in many fields of technology and science such as paints, paper, cosmetics, plastics, rubbers, refractory materials, pharmaceuticals, pesticides, food industries, ceramics, lubricants, hazards prevention (Al-Jlil *et al.*, 2009; Ekosse, 2000; Carretero, 2002; Yvon *et al.*, 2002; Bizi *et al.*, 2003; Petit *et al.*, 2004; Martin *et al.*, 2004; Clerc *et al.*, 2005; Denac *et al.*, 2005a, b; Yao *et al.*, 2005). In adsorption technology, considered as low-cost adsorbents, clays have already been showed to have high adsorption capacity which may even exceed that of activated carbon under the same conditions of temperature and pH. Clays are characterized by many properties which are useful in adsorption technology such as: high specific surface area, mechanical and chemical stability, high cation exchange capacity, Brönsted and Lewis acidities, negative surface charge and structural variability (Ijagbemi *et al.*, 2009).

Several studies on the adsorption in aqueous solution of lead and manganese were conducted. Without being exhaustive, we mention Babel and Kurniawan, 2003 who reported that the montmorillonite, kaolinite, illite and bentonite adsorb respectively 0.68, 0.12, 1.41, 4.29 and 0.68 mg g^{-1} of Pb (II) as given by applying the Langmuir isotherm.

Similarly Gupta and Bhattacharyya (2005, 2008) have obtained with pure kaolinite and montmorillonite and modified stared respectively 11.5 and 31.1 mg g^{-1} respectively and 5.44 and 31.44 mg g^{-1} of Pb (II) at their surface.

The lead adsorption was also obtained with other families of clays such as bentonite (Naseem and Tahir, 2001; Inglezakis *et al.*, 2007; Ayari *et al.*, 2007; Zhu *et al.*, 2008), kaolinite (Jiang *et al.*, 2009; Unuabonah *et al.*, 2009; Bosco, 2009), montmorillonite, smectite, palygorskite (Erdem *et al.*, 2004; Da-Fonseca *et al.*, 2006; Potgieter *et al.*, 2006; Eloussaief and Benzina, 2010). Experiments on adsorption of manganese by clay (Da-Fonseca *et al.*, 2006; Eba *et al.*, 2010), as clinoptilolite (Doula, 2009) and kaolinite (Bosco, 2009) have been reported. The results of these most previous studies are best described by applying the Langmuir isotherm and kinetics is generally either first order or second order.

Wastewaters contain generally more than one heavy metal (Doula, 2009; Mohan and Singh, 2002). The protection of the environment requires more studies on multi-solute system solutions. It is to be noted the large number of references related to literature concerning single sorption of heavy metal ions studies in comparison of the few studies of multi-component systems. The main difficulty is the obtainment of adsorption models which describe accurately the experimental adsorption data from multi-solute solutions. At the purpose to make the problem tractable, in spite the system complexity, some simplified modeling approaches have been introduced. Machida *et al.* (2005), Lin and Juang (2002), Bedelean *et al.* (2009), Amer *et al.* (2010) and Ho and McKay (1999b) used competitive Langmuir model to compute simultaneous adsorption respectively of Cu (II) and Pb (II) onto activated carbon, Cu (II) and Zn (II) on surfactant – modified montmorillonite and on sphagnum peat moss. In the binary solution of Pb (II) and Zn (II) and Pb (II) and Cd (II) (Minceva *et al.*, 2007), Pb (II) is quantitatively better fixed than Cd (II) and Zn (II) on natural zeolite. These results were interpreted based on the isotherms of Langmuir and Freundlich. In addition, for binary and ternary solutions of Cd, Pb, and Zn (Stefan *et al.*, 2008), montmorillonite fixed with greater affinity Pb and the adsorption followed the sequence Zn<Cd<Pb. Chotpantarat *et al.* (2011) studied competitive sorption of Pb^{2+}, Ni^{2+}, Zn^{2+} and Mn^{2+} on the lateritic soil where they found Pb^{2+} preferably settled on the sorbent surface than Ni^{2+}, Zn^{2+} and Mn^{2+}. In

these previous works, batch and column techniques were used to investigate the mutual effects of metals in multi-metals system by measuring the ratio of the sorption capacity of one metal in multi-metals systems, q_i (mix),to the sorption capacity of given metal in single-metal system, q_i(o). If q_i(mix)/q_i(o)>1, sorption of metal, i, is enhanced by the other metals ions. If q_i(mix)/ q_i (o) = 1, metals had no effects on each other. If q_i(mix)/qi(o)<1, metals i competed with other metals for sorption sites of the adsorbent . These works require the knowledge of the adsorption amount of a metal in the multi-solute system and in single system. Similar demand concerns the applicability of the extended forms of Langmuir, Freundlich and D.K.R. models. That takes more time to reach the end of a study.

In the purpose to minimize the duration of multi-metals system studies, the mutual effects of metal in multi-metals system should be evaluated by measuring the ratio of each metal in multi-metals solution before and after sorption process. In the practice, only the percentage of each solute might be measured in aqueous effluents polluted by more than one metal. An isotherm equation model correlating the variations of each metal ratio in multi- component system and its concentration to equilibrium should be inquired.

The present work aimed to determine the potential of clay from Bikougou (Gabon 11°37'E and 1°58'N) using batch technique (El-Said, 2010), for the simultaneous removal of Mn (II) and Pb (II) ions from aqueous solution, without a preceding single adsorption isotherm study of each heavy metal. The research of an isotherm model connecting the ratio of the sorption capacity of each heavy metal and its equilibrium concentration in multi-component solution is tested.

MATERIALS AND METHODS

Adsorbent characterization: Clay (in whole-rock material) from Bikougou deposit, used as adsorbent, was previously characterized (Eba *et al.*, 2010). The X-ray powder diffractograms of the natural sample and of its clay fraction (Fig. 1, 2) indicate that whole-rock is constituted with four clayey minerals:

* Kaolinite, identified by its ray at 7.19Å in crude clay (Fig. 1), which is shifted at 10.40 Å by hydrazine saturation from clay fraction pattern (Fig. 2 curve h)
* Montmorillonite recognized for its typical ray at 14.93 Å (Fig. 1) or at 15.13 Å (Fig. 2, curve U) which is shifted at 17 Å (Fig. 2, curve G) with the ethylene-glycol treatment or reduced to 9.80 Å (Figure 2, curve C) on heating at 490°C
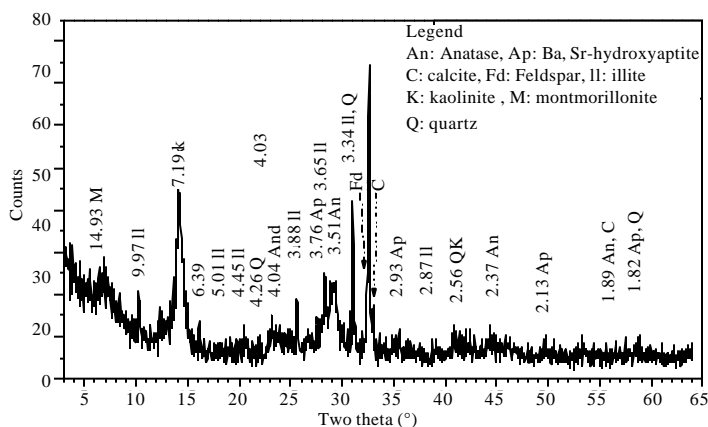

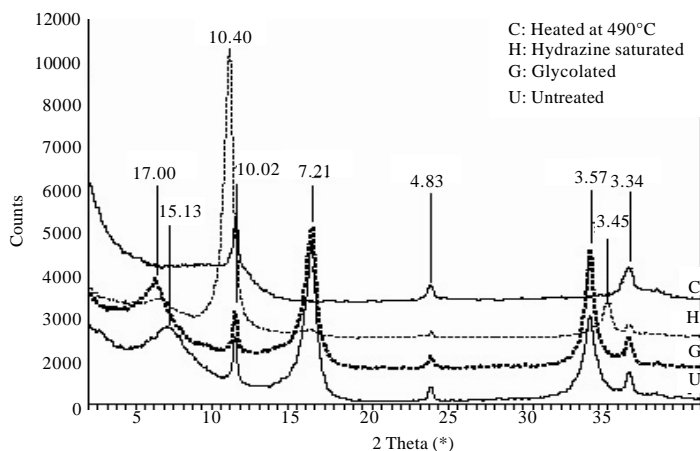Fig. 1: XRD patterns of crude clay from Bikougou deposit

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

- Illite known for the displaying a dool at 9.92 Å (Fig. 1) or at 10.02 Å (Figure 2, curve U) which is not affected by the above mentioned treatments (Fig. 2). Other illite rays are at 5.04 Å, 4.45 Å, 3.38 Å, 3.65 Å, 3.34 Å, 2.87 Å, 2.54 Å in Fig. 1
- Feldspars are revealed by reflections at 3.18, 3.21, 4.04 Å. The pattern is typical of andesine or albite. Quartz (rays at 3.34 Å, 3.18 Å and 2.56 Å), carbonates as calcite mineral (rays at 3.05 Å, 2.93 Å) and as gaylussite (rays at 3.205 Å, 6.39 Å, 2.63 Å), anatase (rays at 3.51 Å, 2.37 Å and 1.89 Å), maghemite (rays at 2.93 Å, 2.56 Å) and Ba, Sr-hydroxyapatite (rays at 4.45 Å, 3.76 Å, 1.82 Å, 2.13 Å and 2.93 Å) are the other mineral species identified in Fig. 1

After X Rays, complementary experiments have been realized. These experiments are related to determination of Specific Surface Area (SSA) (Santamarina *et al.*, 2002), according to methylene blue method (Hang and Brindley, 1970), cation exchange capacity by using ammonium acetate methods at pH7 (Remi and Orsini, 1976), acid surface functional groups (Khan *et al.*, 2009) by means of Boehm titration (Rockstraw, 2000) and point of zero charge with the employment of potentiometric titration (Ijagbemi *et al.*, 2009).

Adsorbate and aqueous solution: Mn (II) ($MnCl_2$, $4H_2O$, MW: 197.90g.mol^{-1}) and Pb (II) ($Pb(NO_3)_2$, MW: 325g.mol^{-1}) were used as simultaneous adsorbate in this work. Obtained from Prolabo (analytical grade), they were utilized without further purification. Simultaneous solutions of Mn (II) and Pb (II) were prepared by dissolution weighed amounts of $MnCl_2$, $4H_2O$ and $Pb(NO_3)_2$ in de-ionised water to achieve concentration of Mn (II) and Pb (II) wanted.

Adsorption procedure: Weighed amounts (0.15 g) of the adsorbent were introduced into bottles containing 50 mL of Mn (II) and Pb (II) solution kept at pH 4. The bottles were shaken at room temperature (303 K) at constant stirring speed using a thermostatic shaker for various times to attain equilibrium. The dispersions were then filtered out and solutions were analyzed for their Mn and Pb concentration, by using an atomic adsorption spectrometer (Analyst 100 Perkin Elmer).

Calculation: The amounts of Mn (II) and Pb (II) ions adsorbed per unit of mass: q_t (mg g^{-1}) were calculated by using the equation:

$$q_t = \frac{C_0 - C_t}{m} \times V \tag{1}$$

where, C_o and C_t are the initial Mn (II) or Pb (II) concentrations and concentrations of the same cations after any time of interaction adsorbent-adsorbate, V is the volume of adsorbate solution and m the mass of clay.

Theoretical basis: The adsorption process is generally described by the Freundlich (Gupta and Bhattacharyya, 2005; Freundlich, 1906), Langmuir (Langmuir, 1918) and Dubinin-Kaganer-Radushkevich (DKR) (Karapinar and Donat, 2009) isotherms. Freundlich isotherm could be expressed by the linearized equation:

$$\ln q_t = \frac{1}{n} \ln C_t + \ln K_F \tag{2}$$

Langmuir isotherm in its linearized form is expressed by the equation:

$$\frac{C_t}{q_t} = \frac{C_t}{q_m} + \frac{1}{bq_m} \tag{3}$$

And the DKR isotherm is given by the equation:

$$\ln q_t = \ln X_M - \beta \varepsilon^2 \tag{4}$$

where, q_t is the amount adsorbed per unit mass of the adsorbent. C_t is the equilibrium concentration of the adsorbate after any time of adsorbate-adsorbent interaction time. K_F and n correspond to Freundlich maximum adsorption capacity and adsorption intensity. q_m and b represent respectively the Langmuir maximum adsorption capacity and adsorption equilibrium constant and X_M, β, ε are respectively the DKR maximum adsorption capacity, activity coefficient related to mean adsorption energy and Polanyi potential.

If the isotherm model fits accurately experimental data, then, linear Freundlich, Langmuir or DKR plots could be obtained by plotting (1) $\ln q_t$ vs ln C_t, (2) C_t/q_t vs Ct or (3) $\ln q_t$ vs ε^2 respectively. Adsorption parameters are computed from these plots. A further analysis of Langmuir equation can be made on the basis of a dimensionless equilibrium constant R_L given by:

$$R_L = \frac{1}{(bC_o + 1)} \tag{5}$$

where, b is the Langmuir equilibrium constant and Co any adsorptive concentration at which the adsorption is carried out. For favorable adsorption $0 < R_L < 1$ and $R_L > 1$ represents unfavorable adsorption, $R_L = 1$ linear adsorption and $R_L = 0$ corresponds to an irreversible process (Juang *et al.*, 1997; Kadirvelu and Namasivayam, 2003). An isotherm is found to be suitable if its correlation coefficient is equal to unity.

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 equation might be assumed:

$$\frac{t}{q_t} = \frac{1}{k_2 q^2_e} + \frac{t}{q_e}$$

(6)

where, k_2 is the second-order rate constant and q_e amount of heavy metal ions adsorbed. Then, the plot t/q_t vs. t gives a linear relationship which allows computation of q_e and k_2.

The competitive adsorption isotherm model, proposed in the present study, is a Langmuir, Freundlich or D.K.R. equation type in which the amount adsorbed per unit mass: q_t of each metal is replaced by its ratio.

RESULTS AND DISCUSSION

Adsorbent characterization: The chemical composition of the whole-rock is reported in Table 1. By combining the X-ray results and the whole-rock chemical analyses, the modal compositions of untreated clay can be estimated according to a constrained multi-linear calculation as reported by Yvon *et al.* (2002). The other clay characteristics such as specific surface area, cation exchange capacity, acid surface functional groups and point of zero charge are reported in Table 2 (Eba *et al.*, 2011).

Table 1: Chemical composition of clay material from bikougou

Major elements	Weight % of major elements	Trace elements (I)	Concentration of trace elements (I) (ppm)	Trace elements (II)	Concentration of trace elements (II) (ppm)	Trace elements (III)	Concentration of trace elements (III) (ppm)	Trace elements (IV)	Concentration of trace elements (IV) (ppm)
SiO_2	54.32	As	<L.D.	Eu	115.00	Ni	29.26	U	0.40
$Al2O_3$	24.64	Ba	357.80	Ga	27.45	Pb	7.06	V	97.89
$Fe2O_3$	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_2O	3.09	Co	17.51	In	<L.D.	Sn	1.14	Zr	82.77
K_2O	0.89	Cr	61.45	La	19.86	Sr	505.60		
TiO_2	0.90	Cs	0.51	Lu	0.11	Ta	0.40		
$P2O_5$	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 percentages of oxides and trace elements expressed in parts per millon (ppm)); L.O.I. (loss on ignition); <L.D. (below detection limit)

Table 2: Characteristics of bikougou clay deposit

pH of point zero charge (PZC)	CEC (meq/100 g)	Acidity neutralizations (meq/g)			Surface area ($m^2 g^{-1}$)
		NaOH	$NaHCO_3$	Na_2CO_3	
3	12.87	2.79	0.285	0	170

Adsorption isotherms studies: The adsorption isotherm for the simultaneous removal of Mn (II) and Pb (II) from aqueous solution of pH 4 was realized at 303K using 0.15 g of adsorbent and 50 mL of bi-solute solutions of 146.1446 mg L^{-1} and 180.933 mg L^{-1} which contained respectively 51.19% and 68.78% of Mn. The amounts of Mn (II) and Pb (II) simultaneously adsorbed increased with the increase in initial concentration of the two heavy metals in solution (Table 3). This may be attributed to the presence in relatively large concentration of the two heavy metals ions in the same solution. It is to be noted that, generally, when heavy metal concentration increases, number of ions to be adsorbed increases, consequently adsorption increases, indicating that the number of ions to be adsorbed is lower sometime to that of available adsorption sites on adsorbent surface. Similar results are reported in the literature (Ayari *et al.*, 2007; Gupta and Bhattacharyya, 2008).

The data obtained were tested to the well known isotherms of Langmuir, Freundlich and DKR. The plots C_t/q_t vs t (Fig. 3), $\ln q_t$ vs $\ln C_t$, (Fig. 4) and $\ln q_t$ vs ε^2 (Fig. 5), illustrate the adherence of each model to the experimental data. Satisfactory agreement between experimental data and the model predicted values are expressed by the correlation coefficient (R^2). The parameters for Langmuir, Freundlich and DKR isotherm models are reported in Table 4. The three models are applicable to describe the simultaneous adsorption of Mn (II) and Pb (II) ions on the adsorbent surface.

The Langmuir model effectively described the adsorption data with all correlation coefficients (R^2) ranged between 0.9812 and 0.9982 for Mn (II) and from 0.9992 to 0.9998 for Pb (II) (Table 4). This was confirmed by the variations of the dimensionless parameter R_L remained

Table 3: Amounts of Mn (II) and Pb (II) ions adsorbed at equilibrium at 303K (pH 4, contact time 45 min clay 3 g L^{-1})

Initial ratio of Mn in solution (%)	q(Mn) (mg g^{-1})	q(Pb) (mg g^{-1})	(q(Mn)+q(Pb)) (mg g^{-1})
51.19	16.05	21.367	37.417
68.78	24.508	18.627	43.135

Where: q(Mn) and q(Pb) in mg g^{-1}, are the equilibrium amount of Mn (II) and Pb(II) adsorbed per specified amount of adsorbent respectively; q(Mn) + q(Pb) is the equilibrium amount of Mn (II) and Pb(II) adsorbed simultaneously per specified amount of adsorbent
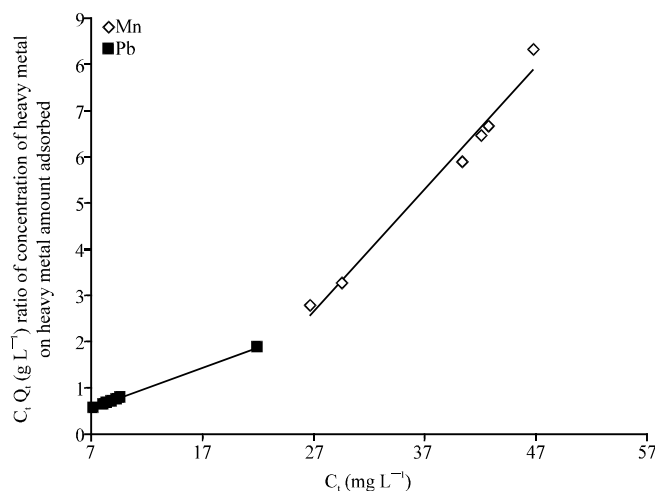

Fig. 3: Plots of variations of the ratio of the equilibrium concentration (C_t, mg L^{-1}) on amount adsorbed specified amount of adsorbent (q_t, mg/g)as a function of equilibrium concentration for Pb (II) and Mn(II) ions adsorption for simultaneous removal of Mn and Pb with Mn percentage of 51.19% (303K, pH4 clay 3 g L^{-1} and contact time 45 min)
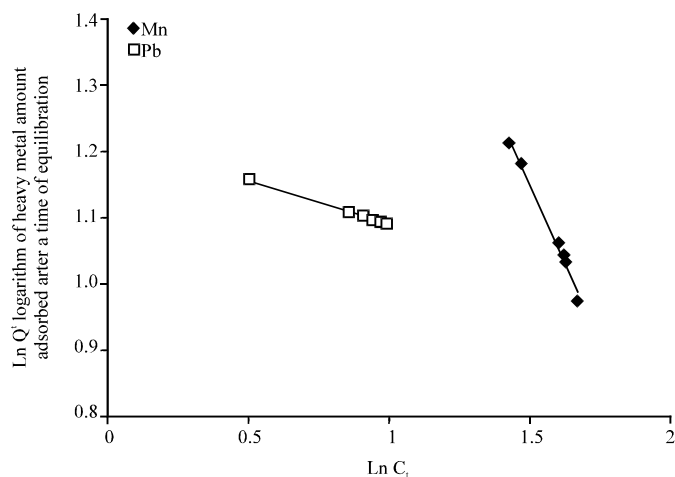
Fig. 4: Plots of variations of the logarithm of amount adsorbed per specified amount of adsorbent (q_e, mg g^{-1}) as a function of the logarithm of equilibrium concentration of binary solution of Mn(II) and Pb (II) (with Mn (II) percentage of 51.19%; 303K, pH4 clay 3 g L^{-1} and contact time 45 min)
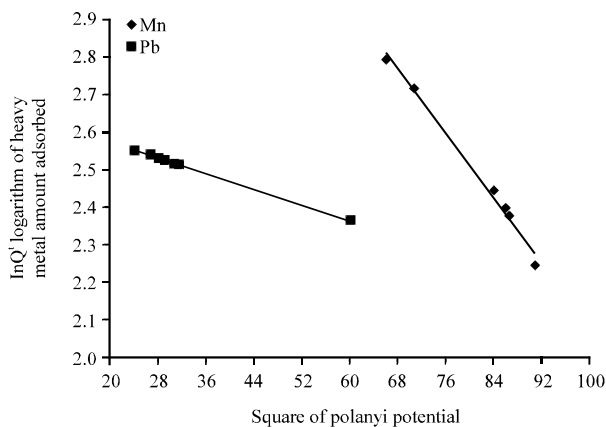

Fig. 5: Plots of variations of the logarithm of amount adsorbed per specified amount of adsorbent (q_t, mg g^{-1}) as a function of the square of Polanyi potential (ε^2, (Kj/mol)^2) for simultaneous removal of Mn(II) and Pb(II) (with Mn percentage of 51.19% (303K, pH 4 clay 3g L^{-1}, contact time 45 min)

Table 4: Langmuir, Freundlich and DKR parameters and statisticals for simultaneous adsorption of Mn (II) and Pb (II) ions at 303K, pH4 and contact time 45 min

Percentage of Mn in solution		Langmuir isotherm				Freundlich isotherm			DKR isotherm		
		q_m (mg g^{-1})	b (L g^{-1})	R_L	R^2	K_F (mg g^{-1})	1/n	R^2	X_m (mg g^{-1})	E (kJ moL^{-1})	R^2
51.19	Mn	3.80	0.0589	0.19	0.9812	12.91	0.938	0.9867	68.854	-4.180	0.9905
	Pb	11.07	1	0.013	0.9998	3.397	0.1337	0.9978	14.525	-9.805	0.998
68.78	Mn	7.79	0.0415	0.16	0.9982	12.317	0.7866	0.9975	23.547	-5.913	0.9997
	Pb	10.14	10.06	0.00176	0.9992	2.833	0.0374	0.9308	11.216	-9.535	0.9877

Where: qm is the Langmuir monolayer maximum capacity; b is the Langmuir equilibrium constant; R_L is the Langmuir dimensionless factor; R^2 is the correlation coefficient; K_F is the Freundlich maximum adsorption capacity; n is the adsorption intensity; Xm is the DKR maximum adsorption capacity; E is the adsorption mean energy

between 0.16 and 0.19 for Mn (II), and between 0.013 and 0.00176 for Pb (II). The monolayer capacity, q_m, for Pb (II) is appreciably high with values of 11.07 and 10.14 mg g^{-1} compared to that of Mn (II) with values of 3.8 and 7.79 mg g^{-1}. The high b values for Pb more than unity, corresponded to a strong bonding, probably chemically controlled sorption. In the opposite, the weak b values for Mn, were an indication of physical interaction.

The Freundlich linear correlation coefficients were found $R^2 > 0.93$ both for Mn (II) and Pb (II) (Table 4). Values of Freundlich maximum multilayer capacity (K_F) decreased for Mn (II) when Mn (II) concentrations increase while K_F for Pb (II) decreased when Pb (II) ions concentration de creased. That is an illustration of competitive adsorption between Mn (II) and Pb (II) on sorption sites. The values of Freundlich intensity; n, remained were found higher than unity in conformity with the requirement of favourable adsorption. The fact that Pb n values were found more high than those of Mn implied that, Pb (II) ions followed a chemical sorption process contrary to Mn (II) ions adsorption which was physical (Ijagbemi *et al.*, 2009).

Parameters of D.K.R isotherm indicated that this model fitted also the adsorption experimental data, with its all correlation coefficients $R^2 > 0.98$ (Table 4). The saturation limit, X_m, representing the total specific micropore volume of the clay, diminished for Mn (II) from 68.854 to 23.543 mg g^{-1} when the Mn percentage rised from 51.1 to 68.78%, (Mn initial concentration increased from 74.814 to 124.44 mg L^{-1}) and for Pb (II) from 14.525 to 11.213 mg g^{-1} when Pb initial concentration decreased from 71.329 to 56.448 mg L^{-1}. The sorption energy E worked out by using the following relationship was determined:

$$E = -\frac{1}{\sqrt{(-2\beta)}} \tag{7}$$

For Mn (II) and Pb (II), the sorpti on energy (E) varied respectively from -4.18 to -5.913 kJ mol^{-1} and -9.805 to -9.533 kJ mol^{-1}. This is an indication that Mn^{2+} and Pb^{2+} sorption reactions are respectively physically and chemically controlled (Saeed *et al.*, 2003).

Values of adsorption parameters found were in good agreement with those reported by other workers. Taty-Costodes *et al.* (2003), found Langmuir adsorption capacity, q_m, from studies of adsorption of Pb (II) and Cd (II) on sawdust, between 8.45 and 22.22 mg/g in the pH range 7-4 ($R^2 = 0.91$-0.99) for Pb (II) adsorption. Gupta and Bhattacharyya, 2008 have reported Freundlich adsorption capacity, K_F, as 0.4-7.5 mg g^{-1} for adsorption of Pb (II) on kaolinite and on montmorillonite respectively ($R^2 = 0.99$, n = 0.7). Eba *et al.* (2010) studied the adsorption of Mn (II) on clay from Bikougou in single system. Their results showed the decrease of Mn (II) monolayer capacity, great increase of multilayer capacities and weak adsorption mean energy of Mn (II) in bi-solute system of Mn (II)-Pb (II). This is a consequence of mutual effect observed when numerous cations compete in multi-component system to adsorption sites. In this case, some metals ions are preferably adsorbed in comparison to other metals ions.

In a multi-element system of heavy metals in which previous experiments concerning sorption of single metal ions are not realized, the comparison of percentages for each metal, in initial solution and on solid surface at the equilibrium could help, using the sign of deviation, to appreciate the selectivity of clay surface for a given metal. The ratio in initial solution should be found equal to that on the adsorbent surface. A positive value of deviation indicates a promoted adsorption of this ion metal compared to the other ions metal. Table 5 presents comparison of percentages of Mn (II)

Table 5: Comparison between initial percentages of Mn (II) and Pb (II) in aqueous solution and percentages of amount adsorbed of Mn (II) and Pb (II) on clay. pH 4; 0.15 g of clay; temperature 308 K; interaction time 45 min

Initial percentage of each heavy metal solute aqueous system			Percentages of amount of each heavy metal adsorbed on clay in bi-component system at equilibrium		
$\dfrac{Mn}{(Mn+Pb)} \times 100$	$\dfrac{Pb}{(Mn+Pb)} \times 100$	$\dfrac{Mn}{(Mn+Pb)} \times 100$ (experimental)	Deviation×100	$\dfrac{Pb}{(Mn+Pb)} \times 100$ (experimental)	Deviation×100
51.19	48.81	42.8949	-18.00	57.1051	14.52
68.79	31.21	56.83	-17.39	43.17	38.32

and Pb (II) in initial solution and on adsorbent surface. When the initial percentage values of Mn (II) increased from 51.19 to 68.79%, those of its amounts adsorbed increase from 42.89% with a deviation of -18 %, to 56.83 % with a deviation of -17.39%. Pb (II) initial percentage values in aqueous solution decrease from 48.81, to 31.21% with the corresponding ratio of amounts adsorbed decreasing relatively from 57.1051% with a deviation of 14.52, to 43.17% with a deviation of 38.32%. It is demonstrated the promoted adsorption of Pb (II) as compared to that decreasing of Mn (II) in a binary: Pb(II)-Mn (II) solution According to our results, in which Pb (II) ions are selectively adsorbed than Mn (II) ions, the selectivity in adsorption ions on adsorbent surface has been reported by other workers. Thus, in binary systems (Cd (II) / Zn (II), Zn (II) / Pb (II) and Cd (II) / Pb (II)) natural zeolite as adsorbent, selectively binds these ions according to the sequence Pb (II)>Cd (II)>Zn (II) (Minceva *et al.*, 2007). The same selectivity is obtained on the binary and ternary systems involving the same ions adsorption on montmorillonite (Stefan *et al.*, 2008). However, selectivity was not observed during the adsorption of lead and manganese on kaolinite by Kamel *et al.* (2004), indicating that both Mn (II) and Pb (II) were determined quantitatively at the same level. In opposite, Chotpantarat *et al.* (2011) found in a multi-system of Pb (II), Ni (II), Mn (II) and Zn (II) that Pb (II) is more adsorbed on a lateritic soil than Mn (II).

These results show the importance of to keep account of the percentages of each metal ion, in initial solution and at equilibrium on adsorbent surface and also that of the resulted deviation, to establish the selectivity of a clay surface for some metal ions in a multi-element system. A positive deviation of a metal, i, in multi-system, proves that the sorption of this metal is promoted by the presence of the other metals. If deviation of a metal, i, is equal to zero, metals had no effect on each other. When the negative deviation is obtained, metal, i, competes with the other metals for available sorption sites of adsorbent. It is obtained that, in a binary Mn (II)-Pb (II) solution, the adsorption of Pb (II) is enhanced by Mn (II),while Mn (II) ions compete with those of Pb (II) to sorption sites on the clay surface.

The selectivity of heavy metal ions on adsorbent surface depends on the metal ions characteristics and of accessibility to adsorption and/or exchange sites of clay.

Metal ion with higher electronegativity would be fixed more readily than that possessing low electro negativity. According to the electro negativity, Pb (II) (2.33) might be more adsorbed on negatively charged clay surface than Mn (II) (1.56) (Bernard and Busnot, 1996) in conformity with our results where Pb (II) ions were more selectively adsorbed than Mn (II) ions.

Adsorption and exchange process might depend of size of hydrated metal ions. The metal ions with larger ionic hydrated radius have lower charge density and lower electrostatic attraction, which limits the interaction of these metal ions with the adsorption sites. In this case, Pb (II) with smaller hydrated radius such 0.187nm would be more adsorbed on the adsorbent sites than Mn (II)

Table 6: Parameters of Langmuir, Freundlich and DKR equation types

Metal ions	Initial ratio (P_o)	Equilibrium ratio (P_{exp})	Langmuir equation type				Freundlich equation type			DKR equation type		
			P_L	b	R_L	R^2	P_F	n	R^2	P_{DR}	E (kJ mol^{-1})	R^2
Mn^{2+}	51.19	42.8949	23.81	0.076	0.466	0.9868	176.79	0.782	0.9657	102.83	-6.225	0.9722
Pb^{2+}	48.81	57.1051	64.1	0.934	0.466	0.0688	37.93	1.838	0.11	49.28	-7.58	0.11
Mn^{2+}	68.79	56.83	45.25	0.0089	0.61	0.9461	164.79	3.76	0.44	74.113	-7.715	0.4325
Pb^{2+}	31.21	43.17	42.55	26.11	0.61	0.998	43.93	53.47	0.43	44.04	-15.43	0.2697

Where: P_0 is the ratio of metal ions in initial bi-solute solution; P_{exp} is the ratio of metal ions on solid surface; P_L is a maximum ratio of a metal ions on solid surface as given by Langmuir equation type; b is energetic constant of Langmuir equation type; R_L is a separation factor of Langmuir equation type; R^2 is a correlation coefficients; P_F is a maximum ratio of a metal ions adsorbed as given by Freundlich equation type; n is adsorption intensity constant as given by Freundlich equation type; P_{DR} is a maximum ratio of concentration surface of metal ions as given by DKR equation type and e is mean energy of the adsorption process

which shows higher hydrated radius of 0.235 nm (Chotpantarat *et al.*, 2011).This is in good agreement with our results indicating the preferable adsorption of Pb (II) in the bi-solute Mn (II)-Pb (II) system. Because of the absence of data on single metal adsorption on the clay, competitive adsorption equations have been tested by substituting the amount of metal adsorbed per unit weight by the metal ratio adsorbed in the classic Langmuir, Freundlich and D.K.R isotherm equations. The results are presented in Table 6. The Langmuir equation type gives a best fit of experimental data according to the requirement of favorable adsorption. Freundlich and D.K.R equations types give very weak correlation coefficients and so that, these models fit wrongly the experimental data. For the Mn (II) experimental ratio of 42.89 and 56.83% obtained at equilibrium on the adsorbent surface correspond, according to Langmuir equation type, Mn (II) maximum ratio of monolayer adsorption of 23.81% (R^2 = 0.9868) and 45.25 % (R^2 = 0.9461) respectively. The rest is assigned to multilayer adsorption. It is demonstrated that, when in initial solution, the ratio of Mn (II) increases, the part of Mn (II) ions adsorbed on monolayer than on multilayer sites rises. As observed with classic isotherms, when the Mn (II) and Pb (II) ions compete for the attainment of adsorption sites, Pb (II) preferably fixed on adsorption monolayer sites and Mn (II) on adsorption multilayer sites is also described well by using the Langmuir equation type.

Kinetics studies: Assuming a pseudo second order kinetic model (Ho and McKay, 1999a; Hanafiah *et al.*, 2006). The plots t/q_t vs t (Fig. 6) was linear and indicated the best applicability of this model to experimental results. All the linear correlation coefficients (R^2) were found greater than 0.99 in conformity with the requirement (R^2 = 1) of the validity of a kinetic model (Al-Futaisi *et al.*, 2007). As summarized in Table 7, the kinetic rate constants k_2 (g/min.g) decreased for Mn (II) from 10.157 to 0.917 when its percentages in bi-solute solution increased from 51.19 to 68.79%. In the same conditions, adsorption rate constants of Pb (II) ions increased from 4.208 to 13.697 g/min.g. This demonstrates that, the adsorption rate constant value increases with the diminution of metal ion adsorbed as reported by Eba *et al.* (2010). The high values of the kinetic rate constant show that the adsorption reaction is fast on the surface of this clay .The adsorption equilibrium is established after thirty minutes. The comparison of amounts adsorbed of heavy metals, q_e (mg g^{-1}) (obtained from the slope of the second-order plot) 16.155 and 24.62 mg g^{-1} for Mn (II) and 21.365 and 18.66 for Pb (II), and experimental (q_{exp}) 16.0511 and 24.508 mg g^{-1} for Mn (II), and 21.367 and 627 mg g^{-1} for Pb (II) respectively, shows that the simultaneous adsorption process of Mn (II) and Pb (II) in aqueous solution followed very accurately the pseudo
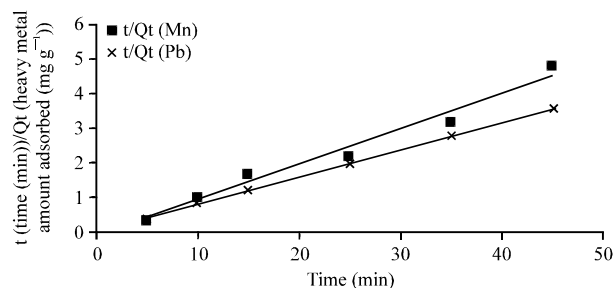
Fig. 6: Plots related to variations of the ratio between adsorbent-adsorbat contact time (t, min) on the amount adsorbed per specified amount of adsorbent (Q_t, mg g^{-1}) as a function of time for simultaneous removal of Mn (II) and Pb (II) (with Mn percentage of 51.19%; pH 4, 303 K and clay 3 g L^{-1})

Table 7: The pseudo second order kinetic parameters for the simultaneous adsorption of the simultaneous adsorption of Mn (II) and Pb (II) ions at 303K (pH 4, clay 3 g L^{-1})

Percentage of Mn in solution		qexp (mg g^{-1})	qe (mg g^{-1})	% deviation	k2 (g mg^{-1} mg.min)	R2
51.19	Mn	16.051	16.155	0.956	10.157	1
	Pb	21.367	21.365	0.0	4.208	0.9999
68.78	Mn	24.508	24.62	8.8	0.917	0.9924
	Pb	18.627	18.66	4.5	13.697	1

Where: q_{ex} is the experimental equilibrium amount of Mn (II) Pb (II) adsorbed per specified amount of adsorbent; qe in mg g^{-1}, is the equilibrium amount of Pb (II) adsorbed per specified amount of adsorbent obtained by calculation from the second order kinetics model; k_2 is rate constant; R_2 is the correlation coefficient

second order kinetic model, because deviation is lower than 1% in the solution of 51.19% of Mn (II) content. The deviation still existing (between 4.5 and 7.5% in solution of 68.78% of Mn (II) content) might be due to the uncertainty inherent in obtaining the experimental q_{ex} values.

CONCLUSION

This study showed that the natural clay originated from Bikougou deposit is a mixture of kaolinite-albite-montmorillonite-illite clayey minerals and has a great potential as adsorbent exploited here in simultaneous removal of Mn (II) and Pb (II) ions from aqueous solutions. The adsorptions isotherms have revealed that Langmuir, Freundlich and DKR adsorption isotherm models fitted well the experimental results. Pb seemed more adsorbed on monolayer surface and Mn is preferentially adsorbed on multilayer heterogeneous surface. Experimental data have proved every time,that the equilibrium ratio of Pb(II) on solid surface is higher than that in initial bi-metal ions solution. That is a consequence of the promoted adsorption of Pb(II) .Contrary results have been obtained with Mn(II).

The theoretical maximum amounts of simultaneous Mn (II) and Pb (II) ions adsorbed are obtained by using D.K.R model. The values of adsorption mean energy are referring for Mn (II) to a physical process and for Pb (II) to a chemically controlled interaction. The simultaneous removal of Mn (II) and Pb (II) ions on the surface of the clay followed a pseudo second order kinetic model. The adsorption rate constants for Mn (II) decreased and those of Pb (II) increased when the percentage of Mn in the bi-metal solution of Mn (II) and Pb (II) increased.

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