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Elimination of Cu (II) and Zn (II) ions in mono-element and the bi-element aqueous solutions by adsorption on natural clay of Bikougou (Gabon)

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This work was undertaken to evaluate the potential of the clay of Bikougou to remove copper (II) and zinc (II) ions (Cu^{2+} and Zn^{2+}) in mono-element and binary aqueous solutions. The experiments were carried out by employing the batch technique through the variations of pH, clay mass, ionic strength, concentration in metal, temperature and contact time. The quantity of ions coppers (II) or zinc (II) adsorbed increases when the pH increases up to pH=5 and beyond, there is precipitation of the metal hydroxides; the quantity of metal ions adsorbed decreases when the clay mass or the ionic force increases. The average adsorption energies of copper (II) and zinc (II) ions are indicative of endothermic reactions. The modeling of the experimental results is better achieved by application of Freundlich adsorption isotherm and Langmuir adsorption isotherm concerning the adsorption of Cu (II) ions with correlation coefficients of 0.98 and 0.93, respectively. The Langmuir adsorption isotherm and Freundlich adsorption isotherm are all applicable for describing the experimental result of isotherm adsorption of Zn (II) ions with correlation coefficient respectively, 0.99 and 0.96. The kinetic which shows more clearly the observed phenomenon is that of the pseudo-second order with the coefficients of correlation close to 0.99. In the binary system copper (II) - zinc (II) the adsorption of copper (II) is favoured compared to that of zinc (II). All these results have shown efficiency as adsorbent of the clay from Bikougou to eliminate Cu^{2+} and zinc (II) ions in mono-element or bi-element aqueous solutions. In the mono-element solution, the adsorption rate varied from 98.59 to 94.41% for the Cu (II) ions and from 86.76 to 53.80% for Zn (II) ions.

Key words: System of bi-element, copper and zinc, adsorption, technique in batch, natural clay mixture.

INTRODUCTION

Some heavy metals ions such as copper (II) and zinc (II) ions (Cu^{2+} and Zn^{2+}) released to the environment from industrial effluents and anthropogenic activities cause pollution of soils and water. Copper is an essential trace element required for proper health in an appropriate limit. Its high uptake may be harmful for human health and causes a number of symptoms for example growth retardation, skin ailments, gastrointestinal disorders among others. It causes a slow dysfunction of the liver and damage to the pancreas on the one hand, and the appearance of the Wilson disease on the other hand (Moore 1991). Zinc is reported as a coenzyme for over 200 enzymes involved in immunity, new cells growth, acid base regulation among others. Data related to Zn

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toxicity are very rare (Barone et al., 1998; Gyorffy and Chan, 1992). Zn toxicity symptoms can be gastric disturbance, cardiac arythmia among others (Salgueiro et al., 2000). The accumulation of Zn (II) ions causes a decrease in the cellular production and disturbance of the growth of the plants while that of Cu(II) ions leads to a delay in growth of plants (Moore,1991). The injection and inhalation of ions Zn (II) and Cu (II) have negative consequences on human health, as previously reported. That is why the World Health Organization has recommended that the concentrations of these ions in drinking water do not overpass 0. 5 mg/l. The same recommendation is applicable to industrial effluents containing these heavy metals before they are release to the environment.

Many physico-chemical methods such as: ions exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis, electroplating and adsorption using the activated carbons or zeolites have been developed. These methods are very costly which limits their generalization. The current research is focused on the development of the cheap adsorbents from the industrial and agricultural wastes compared to that of the active carbon and zeolites found expensive. In the technique of adsorption, considered as materials of low cost, the clays could sometime show an adsorption capacity non-negligible, comparable or even exceeding that of activated carbons in the same conditions of temperature and pH. In fact the porous nature, and the physico-chemical properties of clays: Large mechanical and chemical stability, large specific surface area, acid-base status of Brönsted and Lewis, negative charge on their surface, large cation exchange capacity and their structural variability may be associated to a high adsorption capacity (Ijagbemi et al., 2009).

Several works on heavy metals adsorption from aqueous effluents on the surface of different clay families have been reported: for example Kaolinites (Babel and Kurniawan, 2003), Bentonites (Babel and Kurniawan, 2003; Naseem and Tahir, 2001), Montmorillonites, Smectites, Palygoskites (Babel and Kurniawan, 2003; Gupta and Bhattacharya, 2005, 2008) exist in the literature. The essential results show that the adsorption capacity depends on the nature of the adsorbent and the characteristics of the solution. They are often better described by application of the isotherms of Langmuir (Langmuir, 1918) and/ or Freundlich (Gupta and Bhattacharyya, 2005; Freundlich, 1906) and their kinetic is either of the pseudo-first order (Eba et al, 2010), or that of the pseudo second order (Tien and Huang, 1991; Ho and McKay, 1999a,b; Ho et al., 2001).

The waters of discharges sometimes contain more than a heavy metal (Doula, 2009; Mohan and Singh, 2002); but, few studies are interested in this type of solution. In effect, there is in literature, many references on the adsorption of metals in the mono-element systems as compared to systems with several heavy metals. The main difficulty is the acquisition of adsorption models which describe exactly the experimental data of adsorption related to multi-body dissolved solution. Thus, Huh et al. (2000) and Kwong et al. (1998) proposed a model that allows to evaluate the adsorption capacity of a cation in a multi-element solution by application of the Langmuir extended model.

In a multi-element solution, when the report of the quantity adsorbed of an ion (i) q_e (mix)$_i$ in the mixture is greater than or less than the quantity adsorbed of the same ion (i) in the mono- element solution q_e (mono)$_i$, the two ions compete to attach on the available adsorptions sites on the surface of the adsorbent. The comparison of the report of each ion in multi-element and mono-element solutions allows deducting the species respectively benefiting of preferential and/or decreasing adsorption.

$$\frac{q_e(mix)_i}{q_e(mono)_i} > 1 \text{ and/or } \frac{q_e(mix)_i}{q_e(mono)_i}$$

The present study was undertaken to assess the capacity of the clay from Bikougou (Gabon 11° 37' East and 1 ° 58' North) to attach the Cu (II) and Zn (II) ions in mono and bi-element solutions using as parameters pH of the solutions, mass of adsorbent, ionic strength, initial concentration of the Cu (II) ions and Zn (II) ions, interaction time clay-ions, temperature of the process and initial proportions of ions in the binary solutions.

MATERIALS AND METHODS

Properties of the clay

The natural clay from Bikougou deposit used as adsorbent has been previously characterized. By combining the X-ray powder diffractogram results (Figures 1 and 2) and the whole-rock chemical analyses (Table 1), the modal compositions have been calculated according a constrained multi-linear calculation (Eba et al., 2011). It indicated that the crude clay of Bikougou deposit is constituted mainly of 29.5% of kaolinite, 20% of albite, 16% of montmorillonite and 8% of illite and its other characteristics are presented in Table 2 (Eba et al, 2010).

Ionic solutions

The solutions of Cu (II) ions and Zn (II) ions were prepared by dissolving the appropriate weights of copper chloride (CuCl$_2$; molar mass 170.48 g, purity 99% Prolabo analytical grade) and zinc chloride (ZnCl$_2$: molar mass 136.2 g, purity 98.5 % Prolabo analytical grade) in deionized water. The pH is adjusted by adding drops of solution of HCl or NaOH. The effect of the variation of the ionic strength of the solutions of Cu^{2+} and Zn^{2+} has been achieved by dissolution of potassium chloride (KCl 74.55 g/mol analytical grade) in deionized water.

Adsorption procedure

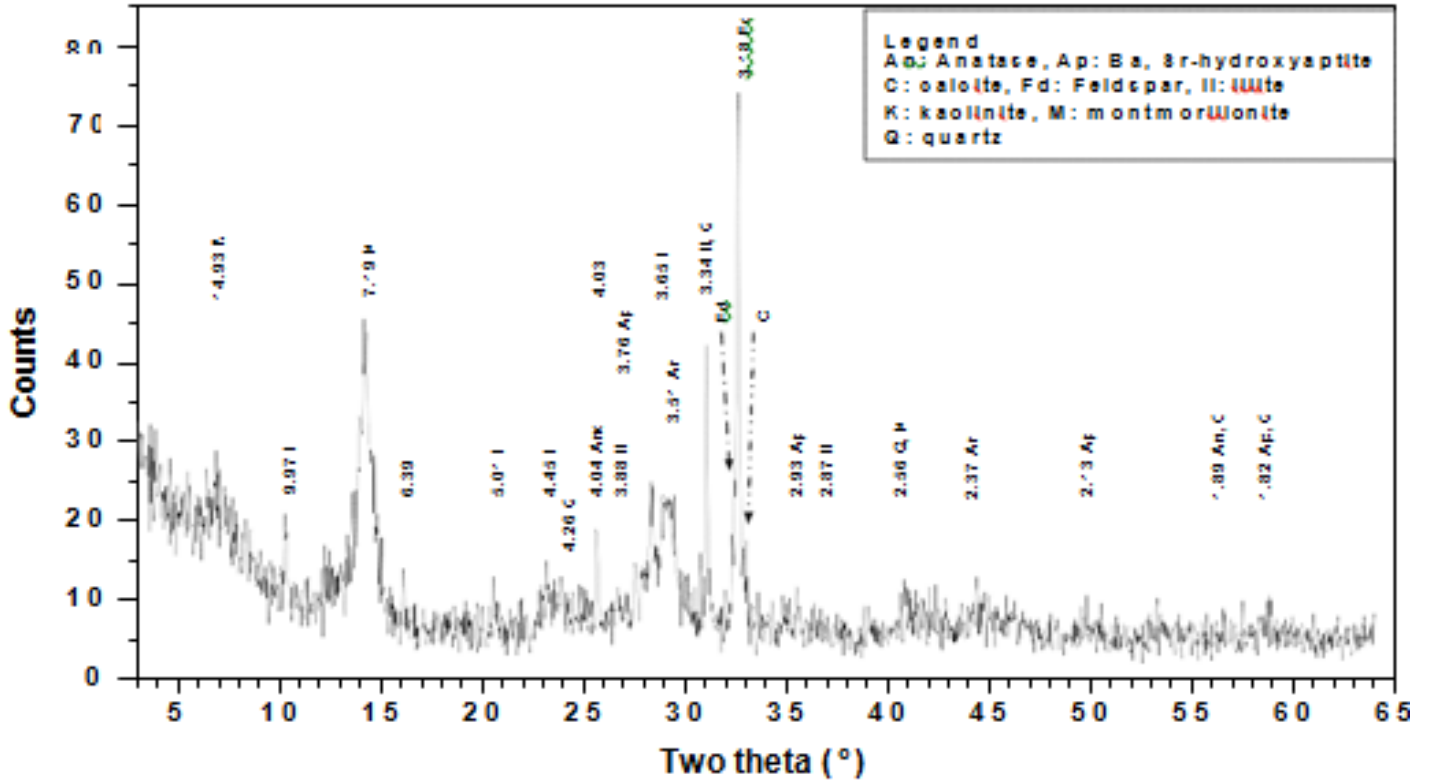The adsorption tests were performed by using batch technique. It

Figure 1. XRD-pattern of crude clay from Bikougou deposit.
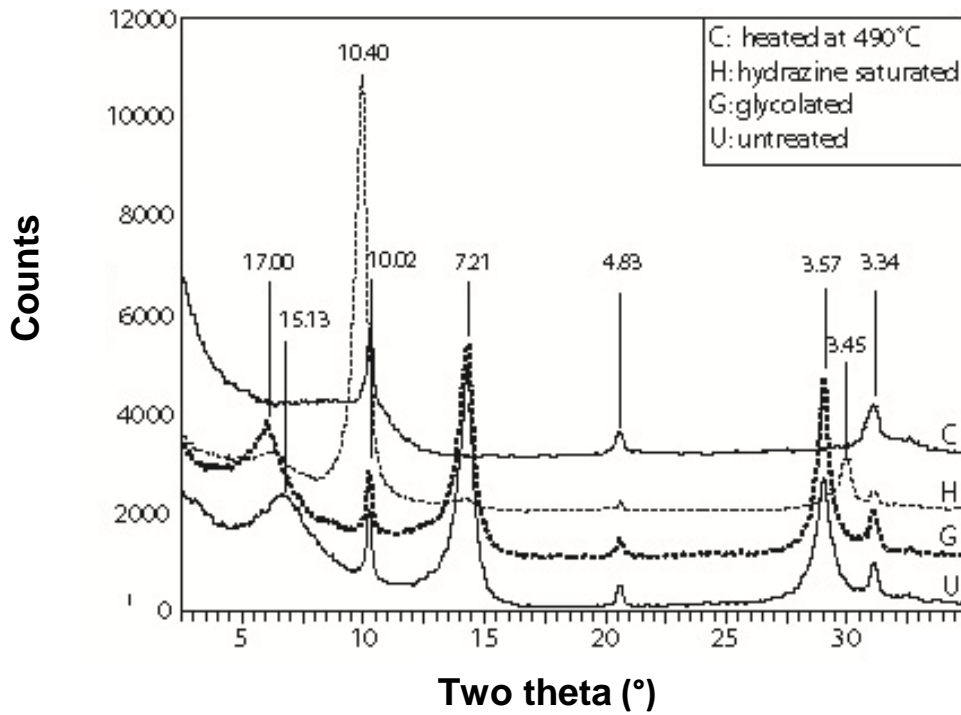

Figure 2. XRD-pattern of clay fraction from Bikougou deposit.

consists of adding an appropriate mass of clay (0.15 g except during the study of the effect of the mass of clay) to a solution (50 ml) containing the ion of the heavy metal (Cu^{2+} and/or Zn^{2+}) in a reactor maintained at constant temperature (except for the study of the influence of temperature) subjected to a constant stirring during a fixed time. After this, the mixture is filtered and the

Table 1. Mineralogical characteristics of clay from Bikougou.

Mineral	Raw clay (%wt)	Clay fraction (% wt)
Kaolinite	29.1	53
Albite	20.3	0.0
Montmorillonite	15.2	40
Illite	10.9	7.0
Quartz	19.1	0.0
Carbonate	3.0	0.0
Maghemite	1.2	0.0
Anatase	0.9	0.0
Ba -Sr hydroxyapite	0.8	0.0
Zircon	Trace	0.0

Table 2. Physio-chemical characteristics of Bikougou clay.

pH_{ZPC}	CEC (meq/100g)	Acidity neutralizations (meq/g)			Surface area (m^2/g)
		NaOH	NaHCO	Na CO	
3	12.87	2.79	0.285	0	170

Table 3. Adsorption models.

Isotherm model	Equation	Linear expression	Plot	Parameters	Reference
Langmuir	$q_e = \dfrac{b \times q_m \times C_e}{1 + b \times C_e}$	$\dfrac{C_e}{q_e} = \dfrac{C_e}{q_m} + \dfrac{1}{bq_m}$ (3)	$\dfrac{C_e}{q_e}$ vs Ce	b and q_m	Langmuir (1918)
Freundlich	$q_e = K_F \times C_e^{1/n}$	$\ln q_e = \dfrac{1}{n}\ln C_e + \ln K_F$ (4)	$\ln q_e$ vs $\ln C_e$	K_F and n	Gupta and Bhattacharyya (2005)

residual concentration in Cu^{2+} and Zn^{2+} in the liquor is measured by ICP-AES.

Calculation

The adsorption capacity: q_e (mg/g) of the metal ion adsorbed is given by the equation:

$$q_e = \left(C_0 - C_e\right) \times \frac{V}{m} \qquad (1)$$

The adsorption rate is given by the equation:

$$\tau\% = \frac{C_0 - C_e}{C_0} \times 100 \qquad (2)$$

Where, C_0 and C_e are respectively the initial and the equilibrium concentrations of the metal ions.

Theoretical basis

Adsorption models

The adsorption models used in this study are presented in Table 3. Where: q_m and b are the Langmuir constants representing respectively, the maximum adsorption capacity and the adsorption equilibrium constant. b value serve to definite the level of strength of the bonding between adsorbat-adsorbent. b high value indicate great the relationship of the bonding adsorbat-adsorbent, probably has resulting tothe chemically controlled process. With b weak value correspond to the low relationship of the bonding adsorbat-adsorbent, certainly as resulting to a physical process (Eba et al., 2011b). K_F and n are the Freundlich constants related respectively, to the maximum adsorption capacity and adsorption intensity. The isotherm adsorption parameters are determined from slopes and intercepts of linear plots related to each model. The Langmuir dimensionless factor (R_L) given by the equation:

Table 4. Kinetic models and adsorption process mechanisms equations.

Kinetic equation	Kinetic equation	Parameter	Reference
Pseudo-first order	$\ln(q_e - q_t) = \ln q_e - k_1 t$ (9)	k_1 and q_e	Achak et al. (2009)
Pseudo-second order	$\dfrac{t}{t} = \dfrac{1}{2_e} + \dfrac{t}{e} \; q \; k$ (10)	k_2 and q_e	Tien and Huang, (1991); Ho et al. (2001)
Intra particular diffusion	$q_t = k_W \times \sqrt{} + C^{ste}$ (11)	k_w et C^{ste}	Weber et al. (1963)
Liquid film diffusion	$LnC_e = -k_x \times t + C^{ste}$ (12)	k_x et C^{ste}	Wan Ngah and Hanafiah (2004)

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

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The Freundlich parameter n serve to appreciate the nature of the adsorption. For $0 < R_L < 1$, the adsorption is favorable, $R_L > 1$ represents the adsorption unfavorable, $R_L = 1$ indicates a linear adsorption and $R_L = 0$ corresponds to an irreversible process (Juang et al., 1997; Kadirvelu and Namasivayam, 2003). The n values higher than unity (n>1) indicate a favorable adsorption process, while the n values weaker than unity (n<1) correspond to unfavorable adsorption (Fifi et al., 2010). The adsorption mean energy (E) given by the equation below is calculated to give how the solute is settled physically (1 kJ/mol ≤ E ≤ 8 kJ/mol) or chemically (E>8kJ/mol) on the available adsorption sites (Eba et al., 2012).

$$E = \frac{1}{(-2\beta)^{0.5}} ($$

6

In a system containing more than one element, it has been proposed the Langmuir extended isotherm equation to calculate the adsorption capacity of the heavy metal present in the mixture q_e (mix) by the expression:

$$q_e(mix) = \frac{q_{m,i} b C_{e,i}}{1 + \sum_{i=1}^{N} b C_{e,i}}$$

7

Where, $C_{e,i}$ is the concentration of the solution to the equilibrium of a solute i in the mixture, b, and $q_{m,i}$ are the parameters determined from the Langmuir model in case of a mono-element solution. The applicability of the previous equation is tested by standard deviation (D. S.), which is defined by the following equation:

$$D.S. = 100 \sqrt{\frac{\sum \left[\left(q_{e,i}^{cal} - q_{e,i}^{exp} \right) / q_{e,i}^{exp} \right]^2}{n-1}}$$

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Inetics studies

Kinetics models used in this study are listed in Table 4. Where,

k_1(min^{-1}), k_2 (g/mg.min), k_w (mg/g. min$^{-0.5}$) and k_x (mg/g.min^{-1}) are respectively, the rate constants related to the pseudo-first order kinetic and pseudo-second order kinetic models, intra-particular diffusion and liquid film diffusion models. The applicability of a kinetic model is attested by the obtainment of its parameters with high correlation coefficient and of a good agreement between experimental and calculated adsorption capacities.

Thermodynamic studies

The equilibrium distribution constant (K_d) of the heavy metal between the solid and liquid phases is given by the equation:

$$K_d = \frac{q_e}{C_e}$$

13

The distribution constant (K_d) serves to calculate Gibbs free energy (ΔG) according to the expression:

$$\Delta G° = -RT \, ln \, K_d$$

14

and the enthalpy and entropy changes of the adsorption process by using the Van't Hoff equation

$$ln \, K_d = -\left(\frac{\Delta H°}{R}\right) \times \frac{1}{T} + \frac{\Delta S°}{R}$$

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RESULTS AND DISCUSSION

The variations of the adsorption capacity of the clay of Bikougou for the Cu^{2+} and Zn^{2+} in the mono-element and binary systems, were measured as function of pH, mass of adsorbent, ionic strength, time of adsorption equilibration, initial concentration of the solute and temperature.

Mono-element system studies

Effect of pH

The impact of pH of adsorption of Cu^{2+} and Zn^{2+} on the
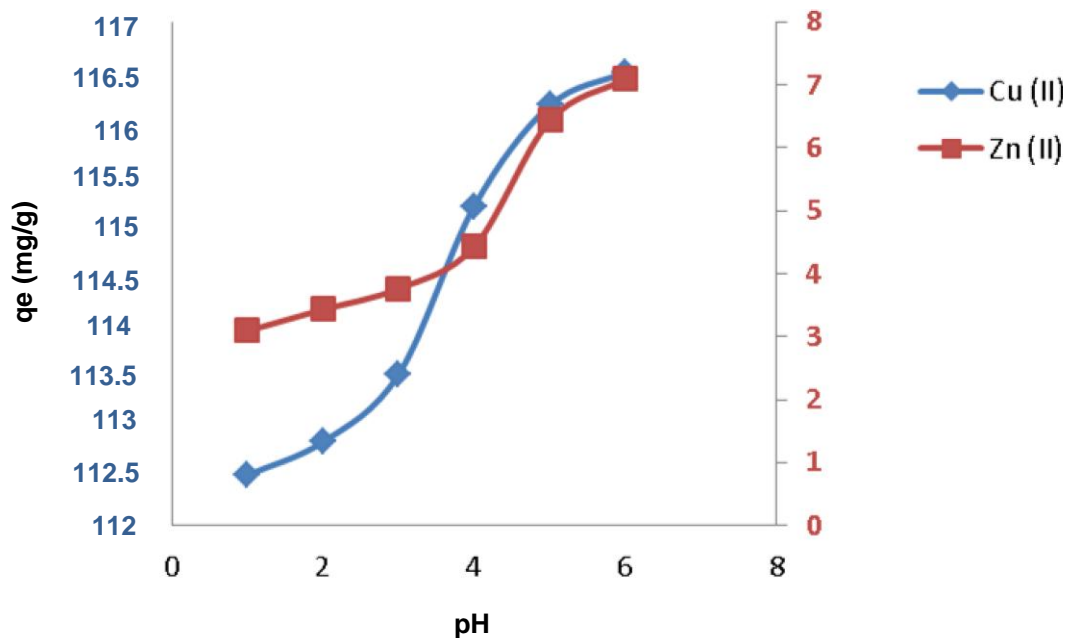
Figure 3. Variations of the amount of copper (II) ions (Co = 377.5 ppm) and zinc (II) ions (Co = 56.25 ppm) adsorbed as a function of pH (temperature= 25°C, mass of clay = 0.15g and contact time = 120min).

surface of the clay from Bikougou has been studied between pH=1 and pH=7, as presented in Figure 3. The quantities of metal ion adsorbed increase nearly linearly from pH=1 to pH=3 for Cu (II) ions and exponentially for pH higher than 3. A hydroxide precipitate appears for pH higher than 6. Similar results are reported in the literature with the adsorption of copper in aqueous solution by bentonite (Youcef and Ashour, 2006). The same behavior is observed for the Zn (II): low linear increase of the adsorption from pH=1 to pH=4 and strong increase beyond pH=4; appearance of a zinc (II) hydroxide to pH greater than 6. Similar results have been obtained by Kaya and Oren (2005) in the case of the adsorption of zinc by bentonite. To explain these results two sides of pH variation should be considered. In the sides of pH ranging from 1 to 3 for the copper (II) and 1 to 4 for the zinc (II), the relative low quantity of metal ions adsorbed is due to the repulsive competition between the metal ions in solution and the hydroniums ions also in the same solution but more mobile and in very large quantity to interact more easily on the adsorption sites (Gupta and Battacharyya, 2008). For the pH higher than 3 (for the copper (II) or 4 (for the zinc (II)), the quantity of hydronium ions is negligible that allows the adsorptions sites to be available for the coppers (II) and zinc (II) ions. When the pH is higher than 6 the precipitation of zinc and copper hydroxides occurs apparently as an increase of the adsorption (Yu et al, 2001; Bayramoglu et al., 2003). Because of the precipitation at pH > 6, adsorption experiments were achieved for pH ≤5 in this study.

### Influence of clay dosage on the adsorption of Cu (II) and Zn (II) ions

The quantities of metal ions adsorbed per unit mass of clay as a function of the mass of clay diminish with the increase in clay mass from 0.05 to 0.5 g (Figure 4). Similar results were observed with the adsorption of copper (II) on the montmorillonite (Lin and Juang, 2002) and the adsorption of the zinc (II) on the bentonite (Youcef, 2006). This can be attributed to two reasons: (I) the decrease in the adsorption capacity observed in the two cases is explained by the fact that the concentration of metal ions in the solution being kept constant contrary of clay mass which grows, liberating more available adsorption sites and for that the amount of metal ions adsorbed per clay unit mass decreases (II) a large amount of adsorbent creates particles aggregates and, consequently, a decrease of the total reactive surface area. That contributes to the decrease of the adsorbed amount per mass unit (Shukla et al., 2002).

The effect of ionic strength on the adsorption of Cu ions (II) and Zn (II)

The results related to the study of the influence of the ionic strength on the evolution of the adsorption capacity of copper (II) or zinc (II) ions on the clay from Bikougou are presented respectively on Figure 5. These results show that the adsorption capacity of
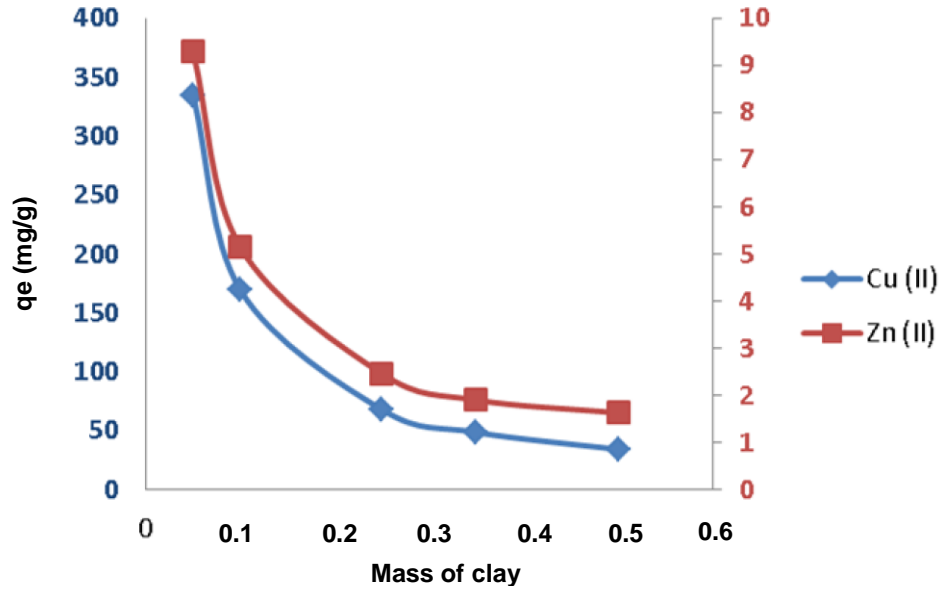
Figure 4. Variations of the adsorbed amounts of copper (II) ions (Co = 377.5 ppm) and zinc (II) ions (Co = 56.25 ppm) as a function of the mass of clay (temperature= 25°C, pH=5 and contact time =120 min).
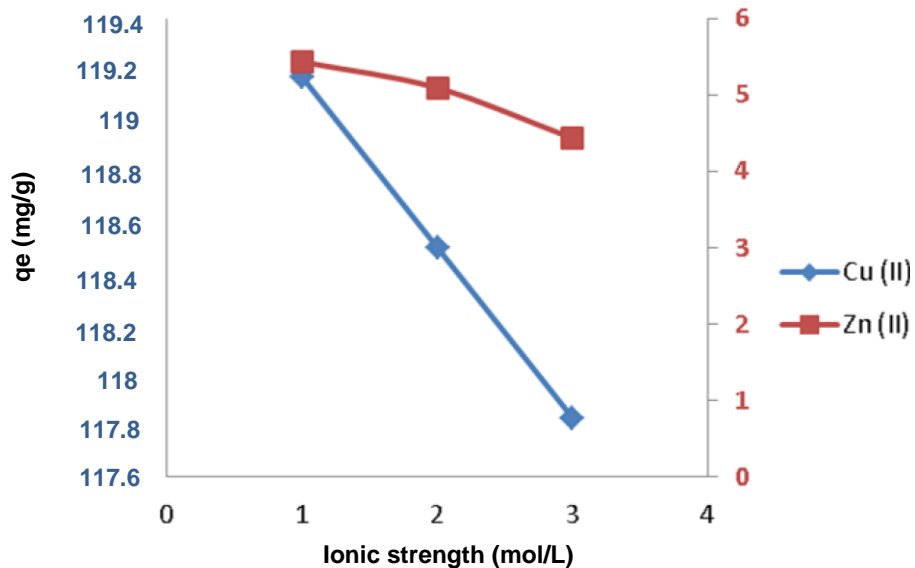

Figure 5. Variations of the amounts of copper (II) ions (Co = 377.5 ppm) and zinc (II) ions (Co =56.25 ppm) adsorbed as a function of the ionic strength (temperature= 25 °C, pH=5, earth clay =0.15 g and contact time =120 min).

both the metal ions decreases when the ionic strength increased from 1 to 3. Similar results were observed with the adsorption of Cu^{2+} on the vermiculite (El-Bayaa et al., 2009) and the adsorption of zinc (II) and Cu^{2+} on earthy sediment (Calvet and Msaky, 1990). These results may be explained by the repulsive competition between potassium ions and copper or zinc ions to attach on the
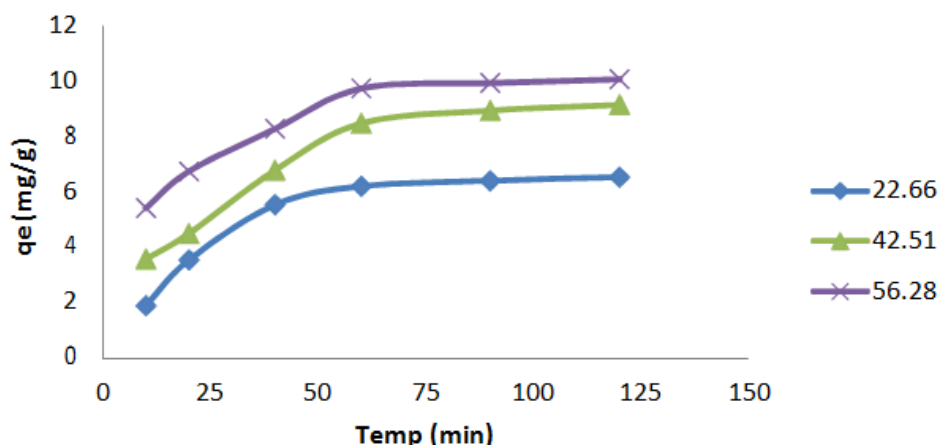
adsorption sites of the clay (Chen and Lin, 2001).

Kinetic studies in the mono-element systems

The results on the evolution of the amounts of copper ions (II) and zinc (II) ions adsorbed per unit mass as a
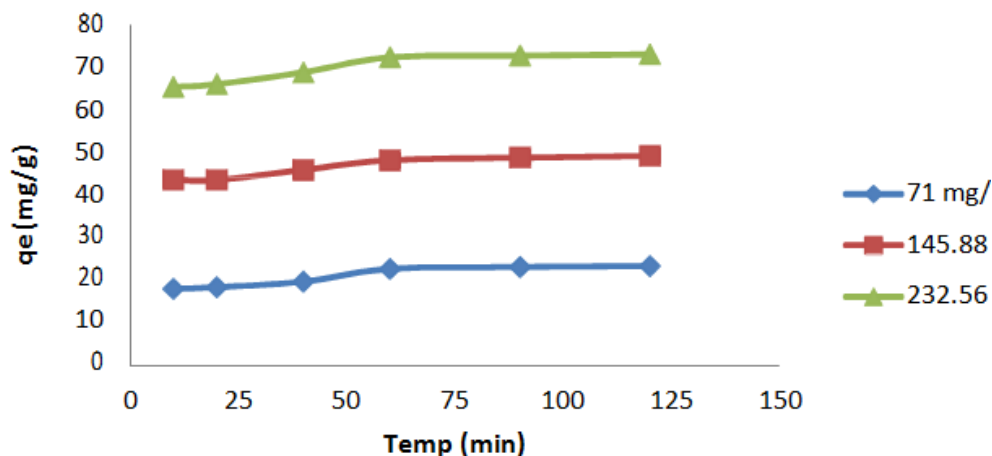
Figure 6a. The amount variations of Cu^{2+} ions adsorbed per unit of mass on the clay of Bikougou as a function of time (temperature= 25°C, pH=5 and mass = 0.15 g).

Figure 6b. The amount variations of Zn^{2+} ions adsorbed per unit of mass on the clay of Bikougou as a function of time (temperature= 25 °C, pH=5 and mass =0.15 g).

function of time are shown in the Figures 6a and 6b, respectively. The adsorption capacity increases rapidly as a function of time to achieve a maximum value of the adsorption equilibrium after 1 h of interaction. These results indicate that the kinetics of fixing copper or zinc ions on the clay surface are fast.

Similar results were observed with the adsorption of copper (II) on a clay of Nigeria (Njoku et al., 2011) and also with the adsorption of the zinc (II) on the bentonite (Mellah and Chegrouch, 1998). The kinetic results were modelized by the use of pseudo first model and pseudo-second order kinetics models.

The plots of pseudo-second order kinetic model for the adsorption of Cu (II) ions and Zn (II) ions on the clay surface are represented in Figures 7a and 7b. The kinetic constants related to the applicability of kinetic models to experimental data are reported in the Tables

5a and 5b for Cu (II) ions and Zn (II) ions, respectively.

The adhesion of the modeling tests to experimental results is better for each of the two ions through the use of the pseudo-second order kinetic model rather than of the pseudo-first order kinetic models. The pseudo-second order rate constant for Cu (II)- clay interaction ranged from $6.82*10^{-3}$ to $5.08*10^{-3}$ g/mg.min and the computed adsorptions capacities remained between 24.39 to 74.63 mg/g have been obtained with high correlation coefficients 0.99 when the initial concentration of Cu (II) solutions increase from 71 to 232.56 mg/L. By applying the pseudo-first order kinetic model, the adsorption rate constant ranged between $4.03*10^{-2}$ to $4.52*10^{-2}$ min^{-1} and calculated adsorption capacities remained between 10.49 and 17.3 mg/g have been obtained with correlation coefficients ranged between 0.708 to 0.824. Comparison between experimental
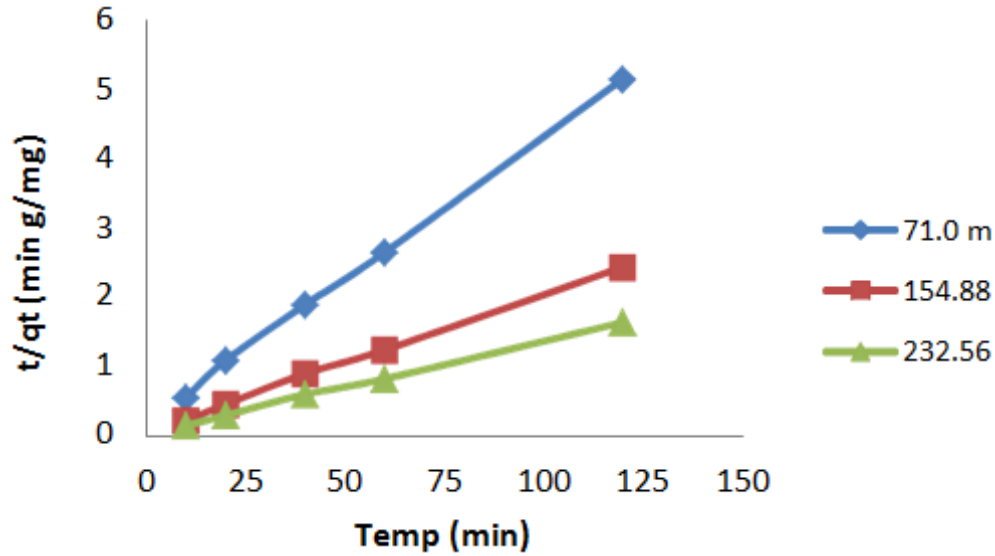
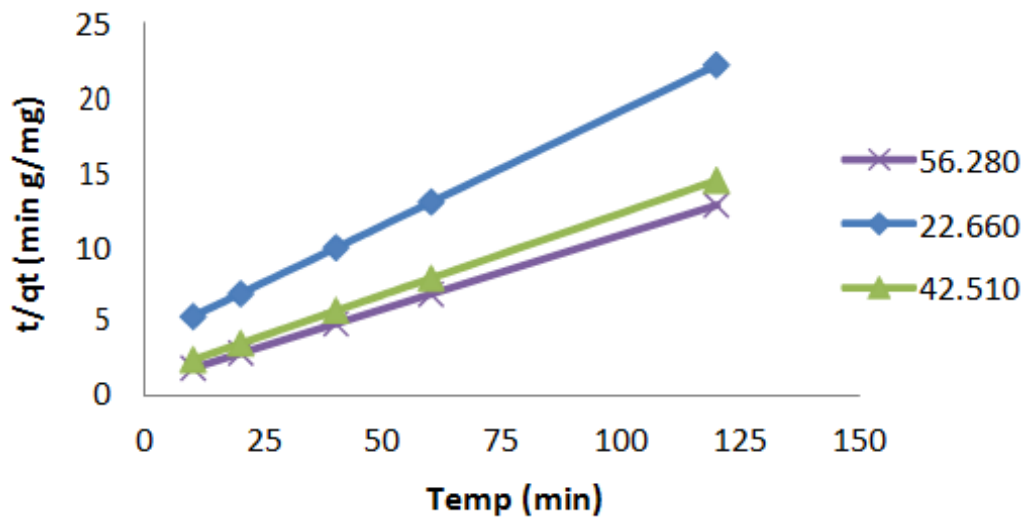**Figure 7a.** Pseudo-second order kinetics plots for the adsorption of Cu^{2+} ions onto clay.

Figure 7b. Pseudo-second order kinetics plots for the adsorption of Zn^{2+} ions onto clay.

adsorption capacities (q_e exp) and modelized adsorption capacities (q_e th) shows that the q_e (th) from pseudo second order model agrees very well with the experimental q_e with a deviation varying from 0.96 to 1.44%. This small difference could be attributed to experimental uncertainties. The application of the pseudo-first order kinetic model gave the q_e values which yield the experimental results with deviation varying from -12.84 to - 55.89%. In the case of zinc (II) ions, kinetic parameters have been obtained with correlation coefficient which are comparable between the kinetic model of the pseudo-second order (R^2 =0.99) and

of the pseudo- first order (R^2 =0.99). In opposite, the adsorption capacities at the equilibrium outcome for the pseudo-first order kinetic model differ significantly from q_e experimental values while those from pseudo-second order kinetic model are comparable to experimental data. The similar results were reported with the adsorption of ions Zn (II) by the montmorillonite (Lin and Juang, 2002).

Studies of reaction mechanisms in the mono-element

The adsorption process mechanisms listed in the Table

Table 5a. Constants and correlation coefficients of kinetic models for the adsorption of copper (II) ions on the clay surface.

Co (mg/l)	Pseudo-first order					Pseudo-second order				Intra-particular diffusion mechanism			Liquid film diffusion mechanism		
	Qe exp (mg/g)	K1 (min^{-1})	Qe théo (mg/g)	Δ	R^2	K2 (g/mg.min)	Qe théo (mg/g)	Δ	R^2	Kw (mg/g.min$^{-0.5}$)	Intercept	R^2	-kfd (mg/g.min^{-1})	Intercept	R^2
71	23.33	4.03E-02	10.49	-12.84	0.824	6.82E-03	24.39	1.06	0.997	0.769	15.374	0.8928	0.0276	3.2189	0.937
145.88	49.29	3.30E-02	10.38	-38.91	0.742	6.50E-03	50.25	0.96	0.998	0.824	40.776	0.9154	0.012	3.2885	0.9187
232.56	73.187	4.52E-02	17.3	-55.89	0.708	5.08E-03	74.63	1.44	0.998	1.099	62.103	0.8946	0.0099	3.6177	0.847

Δ= qe théo- qe exp

Table 5b. Constants and correlation coefficients of kinetic models for the adsorption of zinc (II) ions on the clay surface.

Co (mg/l)	Pseudo-first order					Pseudo-second order				Intra-particular diffusion mechanism			Liquid film diffusion mechanism		
	Qe exp (mg/g)	K1 (min^{-1})	Qe théo (mg/g)	Δ	R^2	K2 (g/mg.min)	Qe théo (mg/g)	Δ	R^2	Kw (mg/g.min$^{-0.5}$)	Intercept	R^2	-kfd (mg/g.min^{-1})	Intercept	R^2
22.66	6.55	2.98E-02	4.64	-1.90	0.998	3.09E-03	6.54	-0.0013	0.999	0.9611	-0.9127	0.9718	0.0293	3.0771	0.9849
42.51	9.17	3.89E-02	5.57	-3.59	0.993	4.43E-03	9.17	0.0043	0.999	0.9884	0.6315	0.9586	0.0118	3.5591	0.9817
56.28	10.09	4.86E-02	5.35	-4.73	0.991	5.78E-03	10.09	0	0.999	0.9288	0.7226	0.9982	0.0077	3.7527	0.9952

Δ= qe théo- qe exp

4 were applied to study mechanism of the adsorption of the Cu (II) and Zn (II) ions onto the clay surface. The plots related to liquid film diffusion model (Figures 8a and 8b) and these for intra-granular diffusion model (Figure 9a and 9b) are linear and their main parameters have been obtained with high correlation coefficients ($R^2 \geq 0.91$ for Cu (II) ions and $R^2 \geq 0.98$ for Zn (II) ions).

For the zinc (II) ions, the low intercept values by applying intra-granular diffusion model and the high intercept values obtained using the liquid film diffusion model suggest that the adsorption in the case of the Zn (II) is not a phenomenon of surface. The intra- granular diffusion played a certain role in the adsorption mechanism beside other factors.

For the copper (II) the high values of the intercept from the intra-granular diffusion model and the related low values of the intercept for the liquid film diffusion model should be due to the fact that adsorption is not controlled by a surface phenomenon or by intra-granular phenol-menon but by other factors of the pseudo-second order kinetics.

Thermodynamic studies in the mono-element systems

The thermodynamic parameters of the adsorption of Cu (II) ions and Zn (II) ions may be linked to the distribution constant (k_d) by the Equation 13. The curves $\ln K_d = f(1/T)$ are linear and were obtained with correlation coefficients of 1 for the copper ion (II) (Figure 10) and 0.999 for the ion zinc (II) (not shown). We deduce from the slopes and intercept of these curves the thermodynamic parameters $\Delta S°$ $\Delta H°$ respectively (Table 6).

The positive values of the enthalpy for the Cu (II) ions on average of 26.694 kJ/mol and for the Zn (II) ions on average of 25.842 kJ/mol indicate that the adsorption of these ions is endothermic. Lin and Juan (2002) obtained the positive enthalpy values for the adsorption on montmorillonite for Zn (II) ions of 7.39 kJ/mol
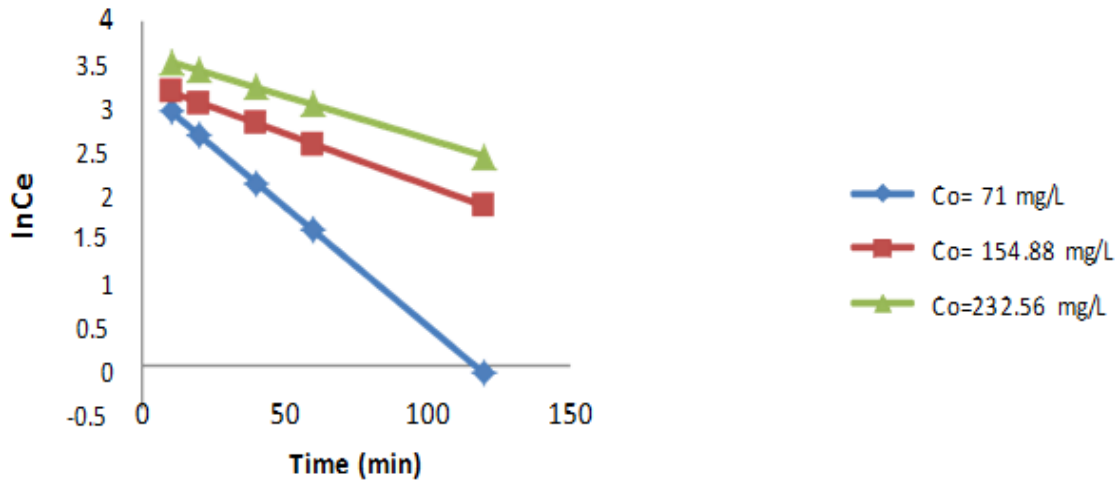
Figure 8a. Plots of liquid film diffusion model for the adsorption of Cu (II) ions onto clay surface.
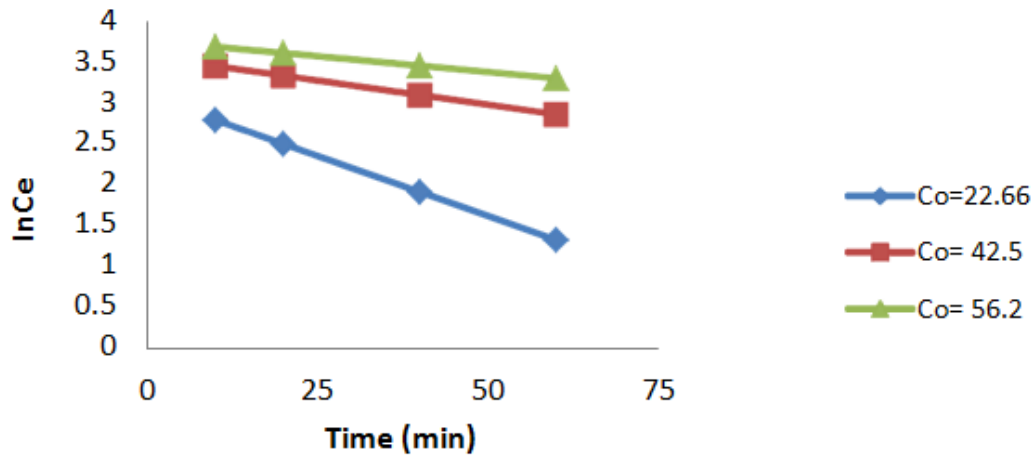

Figure 8b. Plots of liquid film diffusion model for the adsorption Zn (II) ions onto clay surface.
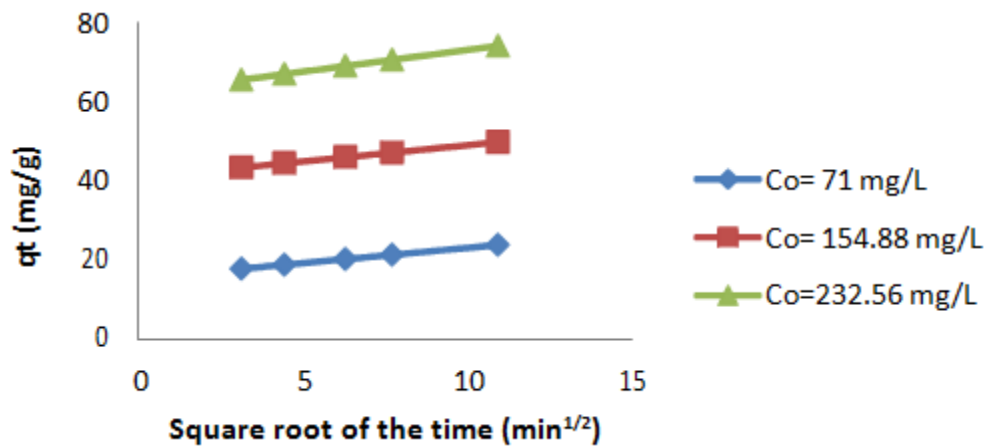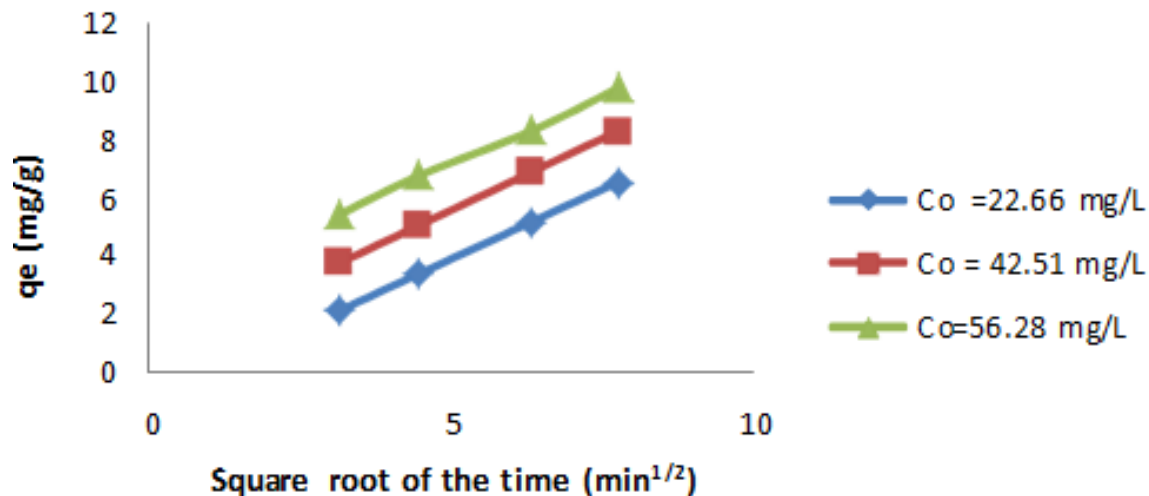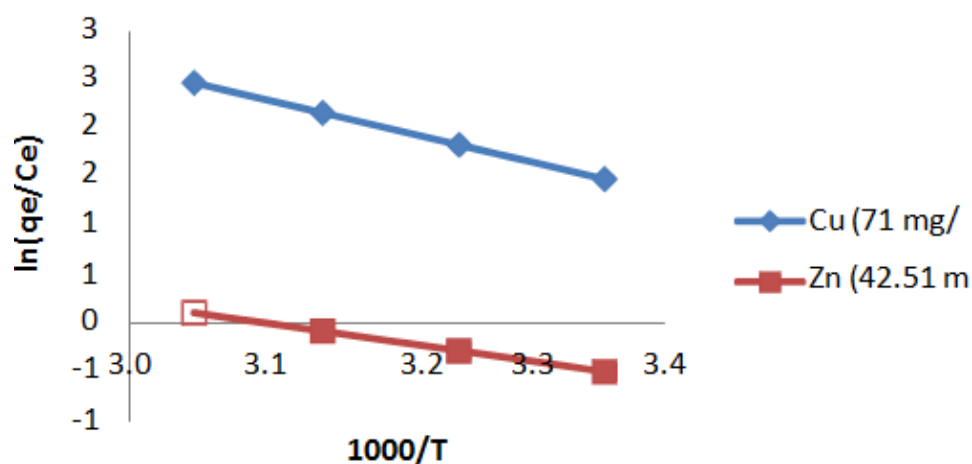

Figure 9a. Plots of change in adsorption capacity (q_e) as a function of the square root of the time for copper (II) ions.

Figure 9b. Plots of change in adsorption capacity (q_e) as a function of the square root of the time for the zinc (II) ions.


Figure 10. Variation of the logarithm of the constant distribution of copper (II) and Zn (II) ions adsorbed as a function of the temperature reverse.

Table 6. Thermodynamic parameters and statistical for the adsorption of Cu (II) and Zn (II) ions on the clay surface.

Ion	Initial concentration (mgl/L)	$\Delta_rG°$ (kJ/mol)				$\Delta_rH°$ (kJ/mol)	$\Delta_rS°$ (J/mol.K)	R^2
		298K	308K	318K	328K			
Cu^{2+}	154.88	-4.854	-5.912	-6.971	-8.029	26.693	105.79	1
	71	-3.668	-4.687	-5.706	-6.725	26.695	101.89	1
Zn^{2+}	42.51	1.217	0.391	-0.435	-1.262	25.842	82.633	0.999
	22.66	-1.094	-1.998	-2.902	-3.805	25.839	90.379	0.999

and for Cu (II) ions of 7.05 kJ/mol. In addition, Amer et   al. (2010) obtained an enthalpy value for adsorption on
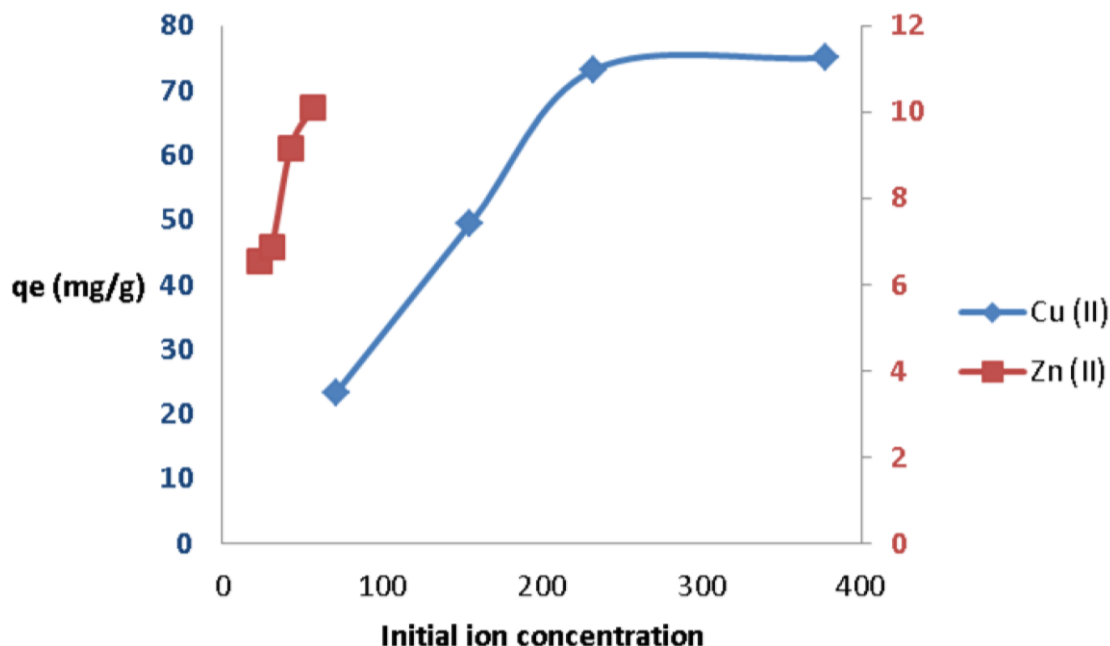
Figure 11. Experimental results of the effects of the ion concentration Cu (II) and Zn (II) on the adsorption by clay of Bikougou.

a kaolinite for Zn (II) of 24.49 kJ/mol, this value is comparable to that obtained in the present study. The positive values of the entropy for the Cu (II) ions of 103.84 J/mol.K and to the Zn (II) ions of 86.506 J/mol.K indicate that the distribution of ions at the surface of the clay is conducted more disorderly than in aqueous solution.

Lin and Juan (2002) have also obtained the values of the positive entropy for adsorption on montmorillonite for Zn (II) of 6.39 J/mol.K and to the Cu (II) of 9.09 J/mol.K. Amer et al. (2010) got a positive value of the entropy of 122.82 J/mol.K for the adsorption of Zn (II) ions on a kaolinite, a value near to that obtained in this study. The negative value of the free enthalpy explains the spontaneous character of the adsorption of each of these ions on the surface of the clay.

Adsorption isotherms studies

Mono-element system (at 25°C)

The experimental variations of the adsorption capacities at the equilibrium of Cu (II) ions and Zn (II) ions as a function of the initial concentration are represented in Figure 11. In each case, the adsorption capacity increases with the initial concentration before reaching the saturation equilibrium.

The adsorption of Cu (II) is that of a type I and that of Zn (II) of type V according to the IUPAC classification (Limousin et al., 2007). Similar results were observed for

the adsorption of Cu (II) and Zn (II) on acidic soils (Arias et al., 2006). The results have been modeled by application of the Langmuir and Freundlich isotherms models. The adsorption isotherm model parameters have been determined from slope and intercept of each linear plot listed in Table 3.

The Langmuir maximum adsorption constant (q_m) 99.909 mg/g for the Cu(II) ions and 11.351 mg/g for Zn (II) ions (Figure 12b) and the energetical Langmuir constant (b) 0.262 L/g for Cu (II) ions and 0.258 L/g for Zn(II) ions have been obtained with correlation coefficients of 0.931 and 0.964, respectively. The separation factor R_L values of 0.010 with Cu (II) ions and 0.064 for Zn (II) ions indicate the favorable nature of the adsorption of these ions onto the clay surface. These b values may be associated to the physically controlled process.

The Freundlich maximum adsorption constant (K_F) of the order of 23.104 and 5.223 L/g and Freundlich intensity factor (n) of 2.392 and 4.950 with correlation coefficients (R^2) of 0.988 and 0.994, respectively, for the copper (II) and zinc (II) ions (Figure 12a). The Freundlich intensity factor (n) higher than unity indicates that the adsorption of copper ions (II) or zinc (II) ions is favorable on the surface of clay from Bikougou as reported by Arias et al. (2006) and Tellan and Owalude (2007).

The experimental adsorption for Cu (II) ions (Table 7a) results are best describe with Freundlich and Langmuir model and for Zn (II) ions (Table 7b) the two models are all applicable. The adsorption isotherm parameters observed in this study are compared with those of
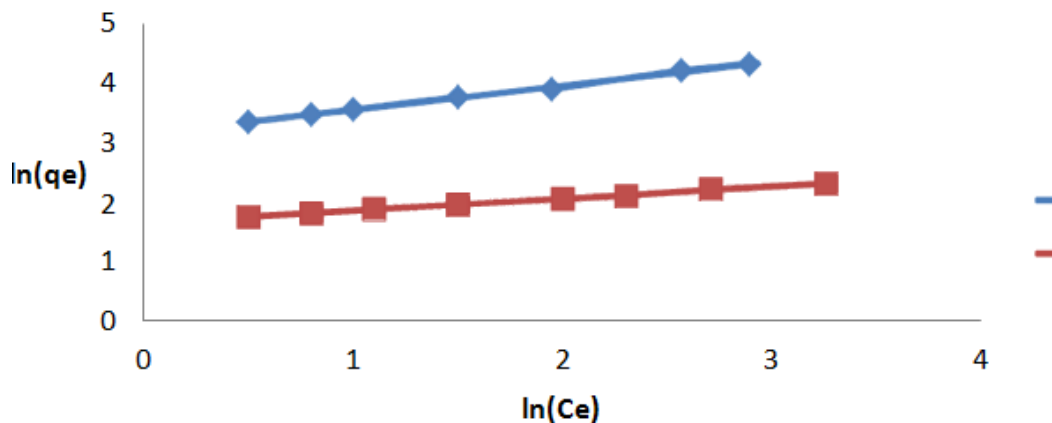
Figure 12a. adsorption isotherms plots of ions Cu^{2+} and Zn^{2+} on the clay obtained using the Freundlich model at pH =5.

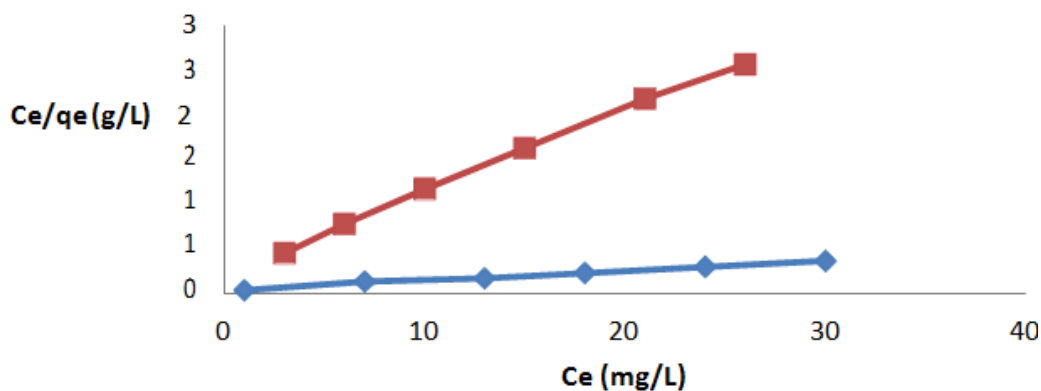**Figure 12b.** Adsorption isotherms plots of ions Cu^{2+} and Zn^{2+} on the clay obtained using the Langmuir model at pH =5.

Table 7a. Langmuir and Freundlich isotherm model parameters and statisticals for the adsorption of Cu (II) ions on the clay surface.

Ions studied (Cu (II)	Langmuir parameter				Freundlich parameter			
	qmax (mg/g)	B (L/mg)	RL	R^2	n	1/n	KF (L/g)	R^2
Cu^{2+} this study	99.909	0.262	0.010	0.931	2.392	0.418	23.104	0.988
Njoku et al. (2011)	15.77	0.032		0.999	2.50	0.4	1.48	0.938
Lin and Juang (2002)	16.147	0.46	0.52	0.975				
Fifi et al. (2010)	0.70	1.81		0.90	1.27	0.78	0.45	0.92
Arias et al. (2006)				0.866-0.949				0.960-0994

Table 7b. Langmuir and Freundlich isotherm model parameters and statisticals for the adsorption Zn (II) ions on the clay surface.

Ion studied (Zn (II))	Langmuir parameter				Freundlich parameter			
	qmax mg/g)	B (L/mg)	RL	R^2	n	1/n	KF (L/g)	R^2
Zn^{2+} this study	11.351	0.258	0.064	0.964	4.950	0.202	5.223	0.994
Lin and Juang (2002)	13.267	0.47	0.52	0.986				
Arias et al. (2006)				0.894-0.961				0.939-0.994
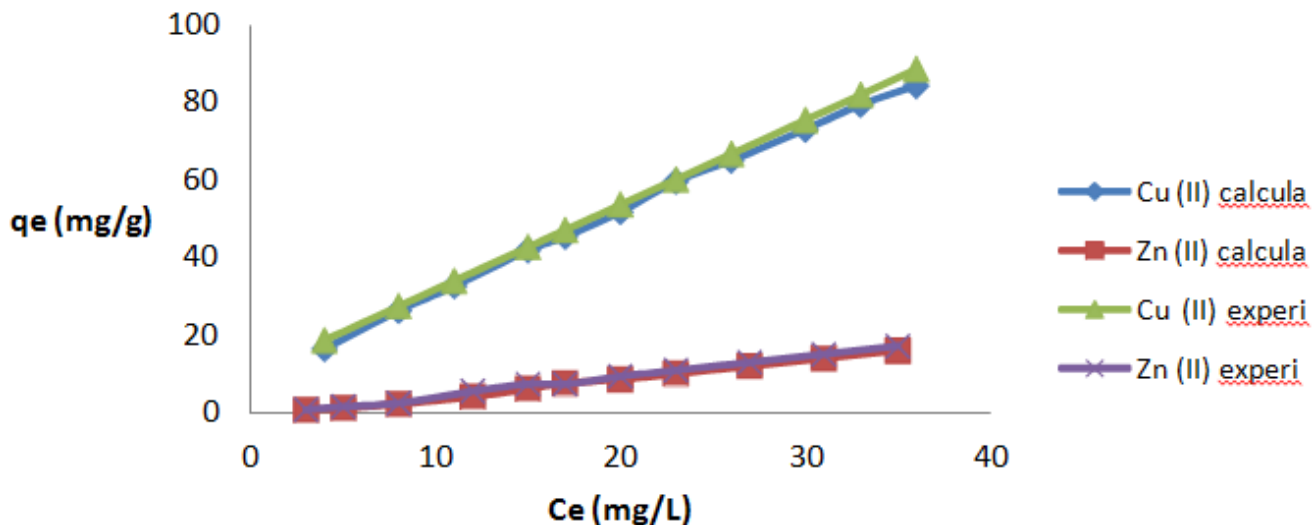
Figure 13. The calculated and experimental adsorption capacities variations of Cu (II) and Zn (II) ions as a function of adsorption equilibrium concentration in binary solutions.

Table 8. Theoretical and calculated adsorption capacities of copper (II) and zinc (II) ions in the mono and bi solutions element.

$\dfrac{[Cu]*100}{[Cu]+[Zn]}$ initial	$\dfrac{[Cu]*100}{[Cu]+[Zn]}$ at equilibrium	qe mix exp Cu	qe mix cal cu	qe mix exp Zn	qe mix cal Zn	qe mono exp Zn	qe mono exp Cu	$\dfrac{q_e mix}{q_e mono}Cu$	$\dfrac{q_e mix}{q_e mono}Zn$
96.40	96.98	0.58	88.67	84.44	0.89	0,766	1.651	70.694	1.25
93.39	94.62	1.23	82.11	79.56	1.6807	1.282	2.659	67.866	1.21
92	93.86	1.86	75.56	73.18	2.56	2.329	3.641	64.586	1.17
90.96	93.25	2.29	66.83	69.47	5.6	4.2	7.397	58.123	1.14
86.09	89.21	3.12	60.28	59.8	7.48	6.216	8.883	52.417	1.15
81.72	85.47	3.75	52.67	60.11	7,45	7.704	7.891	45.8	1.15
79	83.23	4.23	47.17	45.53	9,4687	8.683	9.832	42.119	1.12
74.6	80.62	6.02	42.81	42	11,0263	10.16	11.228	38.989	1.098
70.85	78.26	7.41	34.07	32.77	13,1031	12.13	13.155	31.870	1.069
66.1	74.74	8.64	27.51	26.39	15,1799	14.11	15.134	29.058	0.947
62.64	71.84	9.20	23.83	13.63	17,2567	16.08	16.592	33.005	0.722
60.28	69.84	9.56	18.78	16.63	0,89	0.766	0.7355	30.144	0.623

other authors. The clay from Bikougou is very efficient for Cu (II) ions adsorption has described by the Langmuir isotherm model.

Isotherm binary systems study

The evolution of the adsorption capacity of the ion Cu (II) and Zn (II) in binary solutions has been studied by varying the percentage of initial ions Cu (II) ([Cu] * 100/ [Cu] + [Zn]). Figure 13 shows calculated and experimental adsorption capacities of copper (II) and zinc (II) ions in binary mixtures. Calculated values of adsorption

capacities are close to t experimental values of the two ions. The maximum standard deviation is 5.46 % for the copper (II) and the 5.30% for zinc (II) ions.

Lin and Juan (2002) obtain a standard deviation which is below 9% for the cooper and zinc by sorption in montmorillonite. The application of the Langmuir extended isotherm model makes good account in this study of the experimental results. It is shown in Table 8 that the experimental values of adsorption capacities of Cu (II) ions in the bi- element Cu (II)-Zn (II) solution are greater than those obtained for the same element in mono element Cu (II) solution. In opposite, the experimental adsorption capacities in the bi-solute Cu (II)-Zn (II)

system are less than those of the solution containing only the Zn (II) ions. This indicates the manifestation of a competition between the two ions in a binary solution. Where, Cu (II) ions are selectively fixed on the adsorption available sites in comparison of Zn (II) ions as it is proved by the equilibrium distribution constant of each heavy metal from bi-element and mono-element solutions.

$$\frac{q_e(mix)}{q_e(mono)}$$

This constant is greater than the unity for Cu (II) ions and less than the unity Zn (II) ions adsorbed on the clay surface. When the ions compete to attach on the sites of adsorption on the surface of the adsorbent, the selectivity can be evaluated based on several assumptions: (i) of the standard deviation; (ii) report between initial fraction of a solute mixing and fraction to the surface of the solid.

A gap-positive type of a metal in a multiple system shows that the sorption of this metal is favored in the presence of other metals. If the standard deviation of a metal is equal to zero, the metals had no effect on one another. When the gap-negative type is obtained, the metal concerned is not preferentially adsorbed (Eba et al., 2012).

When the ratio is greater than 1, the ion is preferentially adsorbed and when the report is less than 1, the ion is less adsorbed on the adsorbent. These results show that the copper is selectively adsorbed in relation to the zinc. Table 8 presents the values obtained for the copper ion. A gap-type positive (0.60 to 12.80) and a report

$$\left[\frac{q_e mix}{q_e} \middle/ mono \right]_{Cu} > 1$$

while for Zinc the standard deviation is negative and the report

$$\left[\frac{q_e mix}{q_e} \middle/ mono \right]_{Zn} < 1$$

.

It is concluded therefore that the copper is preferentially adsorbed on the clay of Bikougou compared to the zinc. According to Eba et al. (2012) the essential settings of the selectivity are: the valence, the electronegativity and the hydration enthalpy. If it is considered the electronegativity, the selectivity of an ion plays in favor of ions having a greater electronegativity. The ion with a greater

electronegativity should be fixed more easily than the one that has a more low electronegativity. In this study, the electronegativity of Pauling of zinc (1.65) is lower than that of the copper (II) (Bernard and Busnot, 1996.), so the copper (II) ions would be more selectively adsorbed than zinc (II) ions. Similar results have been obtained in this study. If it is considered the enthalpy of heavy metal hydration reaction

$$M(II) \xrightarrow{H_2O} M(H_2O)_6^{2+}$$
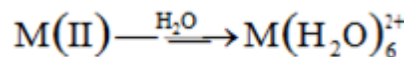
the selectivity plays in favor of an enthalpy of hydration important. A high enthalpy of hydration is the origin of high binding. Copper which has an enthalpy of hydration (-2100kJ/mol) more important than the zinc (-2046 kJ/mol), should be more selectively fixed on the clay than Zn (II) ions as observed in the present study (Bernard and Busnot, 1996). Similar results have been reported by M'leyeh et al. (2002) about the adsorption of copper ions (II) and zinc (II) on clay in Tunisia or it has been proven that the proportion of copper adsorbed is always greater than that of the zinc regardless of its content in the original solution. We have similar results with the adsorption of copper (II) and zinc (II) on a montmorillonite (Lin and Juan, 2002).

Conclusion

The adsorption of Cu (II) and Zn (II) ions on the surface of the clay from Bikougou was made according to the technique in Batch: In the case of mono-element system the amounts of ion Cu (II) ions or Zn (II) ions adsorbed: Increase with the pH and decrease with the increase in ionic strength and in the mass of clay; this adsorption is endothermic for Cu (II) ions as well as for the Zn (II) ions and obeys the kinetics of the pseudo-second order. It is described by the isotherms of Langmuir and Freundlich concerning two ions; the adsorption of each heavy metal on the clay surface is spontaneous. In the binary systems, as this reflects the fact that the competition promotes the adsorption of Cu ions (II) and reduces that of the Zn (II) ions.

$$\left[\frac{q_e mix}{q_e} \middle/ mono \right]_{Cu} > 1 \text{ and } \left[\frac{q_e mix}{q_e} \middle/ mono \right]_{Zn} < 1$$

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