Larhyss Journal, ISSN 1112-3680, n° 12, Janvier 2013, pp. 37-54
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THE REMOVAL OF HEAVY METAL IONS (COPPER, ZINC, NICKEL AND COBALT) BY NATURAL BENTONITE

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ABSTRACT

The removal of Copper (Cu^{2+}), Zinc (Zn^{2+}), Nickel (Ni^{2+}) and Cobalt (Co^{2+}) from aqueous solutions by adsorption onto natural bentonite was investigated. Experiments were carried out as a function of shaking time, temperature of solution and thermal treatment of bentonite. The kinetic processes of metal ions adsorption on bentonite were described by applying pseudo-first order and pseudo-second order rate equations. The pseudo-second order reaction rate model was found to describe best the kinetic data. The thermodynamic parameters (ΔH, ΔS and ΔG) for Copper (Cu^{2+}), Zinc (Zn^{2+}), Nickel (Ni^{2+}) and Cobalt (Co^{2+}) adsorption onto bentonite were also determined from the temperature dependence. The adsorption was endothermic reactions for Copper (Cu^{2+}) and Zinc (Zn^{2+}), and exothermic for Nickel (Ni^{2+}) and Cobalt (Co^{2+}). The results suggested that natural bentonite is suitable as an adsorbent material for adsorption of metal ions from aqueous solutions.
Keywords: natural Bentonite, Copper (Cu^{2+}), Zinc (Zn^{2+}), Nickel (Ni^{2+}) and Cobalt (Co^{2+}), adsorption, thermodynamic parameters.

RESUME

L'élimination du cuivre (Cu^{2+}), Zinc (Zn^{2+}), Nickel (Ni^{2+}) et du cobalt (Co^{2+}) à partir des solutions aqueuses par adsorption sur la bentonite naturelle a été étudiée. Les différentes études sont réalisées en fonction du temps d'agitation, la température de la solution et le traitement thermique de la bentonite. La cinétique d'adsorption des différents ions métalliques est décrite en appliquant l'équation de pseudo-premier ordre et pseudo-deuxièmes ordre. Le modèle pseudo-deuxième ordre a été sélectionné pour mieux décrire les données cinétiques. Les paramètres thermodynamiques (AH, AS et ΔG) du cuivre

(Cu^{2+}), Zinc (Zn^{2+}), Nickel (Ni^{2+}) et le cobalt (Co^{2+}) ont été également déterminée à partir de la dépendance en température. L'adsorption est endothermique pour le cuivre (Cu^{2+}) et le zinc (Zn^{2+}), et exothermique pour le nickel (Ni^{2+}) et le cobalt (Co^{2+}). Les résultats suggèrent que la bentonite naturelle est appropriée comme un matériau adsorbant pour l'adsorption des ions métalliques à partir de solutions aqueuses.

Mots clés: Bentonite naturelle, Cuivre (Cu^{2+}), Zinc (Zn^{2+}), Nickel (Ni^{2+}) et Cobalt (Co^{2+}), adsorption, paramètres thermodynamiques.

INTRODUCTION

The presence of heavy metals in the environment can be detrimental to a variety of species. Therefore, the elimination of heavy metals from waters and wastewaters is important to protect public health (Mellah and al., 1997). The most important characteristic of these metals is that they are not biodegradable and therefore persistent (Namasivayam and al., 1995). Furthermore, most of the metal ions are toxic to living organisms (Benjamin and al., 1982). The heavy metal levels in wastewater, drinking water, and water used for agriculture must be reduced to the maximum permissible concentration.

Numerous processes exist for removing dissolved heavy metals, including ion exchange, precipitation, solvent extraction, phytoextraction, ultrafiltration, reverse osmosis, electrodialysis and adsorption onto activated carbon are the conventional methods for removal of heavy metal ions from aqueous solutions (Kahashi and al., 1983; Huang and al., 1984; Applegate and al., 1984; Sengupta and al., 1986; Gonzales-Davila and al., 1990; Geselbarcht and al., 1996).

In the recent years the adsorption of heavy metals by a variety of substances has been the subject of many studies.

One of the powerful treatment processes for the removal of metal ions from water with a low cost is adsorption. Various substances, such as activated carbon, natural and synthetic zeolites, aluminosilicate (clay minerals) and ion exchange resins have been used as adsorbents for the removal of heavy metals from water and wastewater.

On account of higher surface area, cation exchange capacity and adsorption affinity for organic and inorganic ions, bentonite (mainly montmorillonite) is the most promising candidates for use in decontamination and disposal of high-level heavy metal wastes (Takahashi and al., 1987; Zhixiong and al., 1989). Bentonite is a 2:1 mineral with one octahedral sheet and two silica sheets, which forms a layer (Mitchell and al., 1993).

In this research, adsorption ability of natural bentonite was investigated for removal of Cu^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+} ions from aqueous solution. The effect of shaking time, temperature of solution, and effect of thermal treatment on the adsorption capacity of the natural bentonite, amount of this sample was treated in furnace at different temperatures (500, 700 and 1000 °C) were examined.

MATERIALS AND METHODS

Bentonite source

The clay samples used in this study were collected from the east of Morocco, it was obtained in powdered form (average particle size 5 μm). The bentonite samples in this study were used in their natural state without any treatment, without saturation with any cation.
It was proved by previous X-ray analysis on this clay that the dominant component is montmorillonite ($(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot (H_2O)_n$), with the characteristic features at d_{001} = 15,15 *Å* and d_{101} = 4,50 *Å*. The remaining components are quartz, feldspar, calcite and dolomite. Its chemical, mineralogical and physico-chemical characteristics are summarized in tables 1, 2 and Fig. 1.

Table 1 : Chemical composition of Bentonite sample, wt (%)

Constituent	Weight (%)
SiO_2	53,06
Al_2O_3	10,43
CaO	8,05
MgO	5,32
Fe_2O_3	1,67
Na_2O	2,47
K_2O	0,54
TiO_2	0.08
MnO	0.07
LOI[a]	18,02

[a] Loss on ignition.

Table 2 : Physico-chemical properties of Bentonite

Parameters	Value
pH	9,3
Conductivity ($mscm^{-1}$)	2,67
BET surface area (m^2g^{-1})	60
Average particle size (µm)	5
Zeta potential (mv) at pH 4;7and 11	-37,0; -16,2; -44,2
Pore volume (cm^3g^{-1})	100

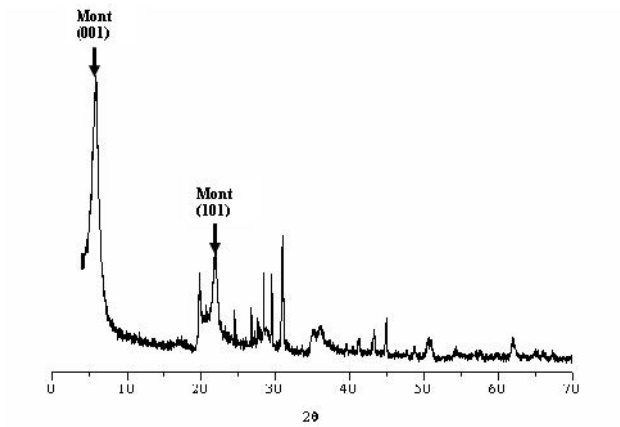


Figure 1: The X-ray patterns of the natural Bentonite

Reagents

All the reagents used were analytical grade chemicals. The metal ions studies were Cu^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+}. We prepared a stock solution of copper, zinc, nickel and cobalt using their nitrate salts: $CuSO_4$, $5H_2O$; $C_4H_6O_4Zn$, $2H_2O$; $NiCl_2$, $6H_2O$ and $CoCl_2$, $6H_2O$, respectively, in distilled water. The table 3 regroups the different characteristics of these heavy metals. The distilled water that we used during our tests is characterized by a pH varies of 6.40 and 6.80 and a conductivity of 16.0 *µS/cm.*
Each stock solution of heavy metal was diluted to prepare working solutions. The buffer solutions (pH 4 and 7) were used to calibrate the pH meter. The pH of each test solution was adjusted to the required value with diluted HCl solution at the start of the experiment.

Table 3 : Different characteristics of salts of heavy metals.

	Copper sulphate	**Cobalt chloride**	**Nickel chloride**	**Zinc acetate**
Molecular formula	$CuSO_4$, $5H_2O$	$CoCl_2$, $6H_2O$	$NiCl_2$, $6H_2O$	$C_4H_6O_4Zn$, $2H_2O$
Purity of salt (%)	99	98	97	99
pH	5.10 ± 0.01	5.40 ± 0.01	5,19 ± 0.01	6.49 ± 0.01
conductivity (µs.cm^{-1})	1618	1782	1756	1022

Batch adsorption studies

The ion exchange of heavy metals on natural bentonite was carried out using the batch method. Batch adsorption experiments were conducted using 1 *g* of adsorbent with 50 *ml* of solutions containing heavy metal ions of desired concentrations at constant temperatures. The mixture was shaken for different intervals of time. The solutions were then filtered through 0,22 μm filter membranes and the concentration of heavy metal was measured by Activia ICP-Optical Emission Spectrometer.
Adsorption capacity of heavy metal q_t *(mg/g)* was calculated using the equations:

$$q_t = (C_0 - C_t)V/m \quad (1)$$

Where *V* (l) is the solution volume, *m* is the weight of the adsorbent (g), *Co* and *Ct* are the concentration of the metal ion in initial and final solution *(mg/l)*, respectively.

RESULTS AND DISCUSSION

Effect of shaking time

The effect of shaking contact time was studied using a constant concentration of metal ions solution (500 *mg/l*) at ambient temperature (20 °*C*). The adsorption of Cu^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+} onto natural bentonite as a function of time in the range 15-360 min. Fig.2 shows the variation of amount adsorbed with shaking time for metal ions.
Amount adsorbed for metal ion (Cu^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+}) increases with increasing contact time, and remained nearly constant after equilibrium as shown in Fig. 2. Equilibrium was attained within 60 min of shaking time for Cu^{2+}, while more than 150 min is required to approach equilibrium for other metal ions.
The order of adsorption of metals on bentonite under the same conditions is: $Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+}$. Amount adsorbed of Cu^{2+} at the optimum adsorption conditions was found as 28.88 *mg/g*, Zn^{2+} 20.5 *mg/g*, Ni^{2+} 17.05 *mg/l* and Co^{2+} 13.85 *mg/g*.
The difference in amount removal of different heavy metal ions at the same initial metal ions concentration, adsorbent dose and contact time may be attributed to the difference in their chemical affinity and ion exchange capacity with respect to the chemical functional group on the surface of the adsorbent (Ajay Kumar Meena and al., 2005).

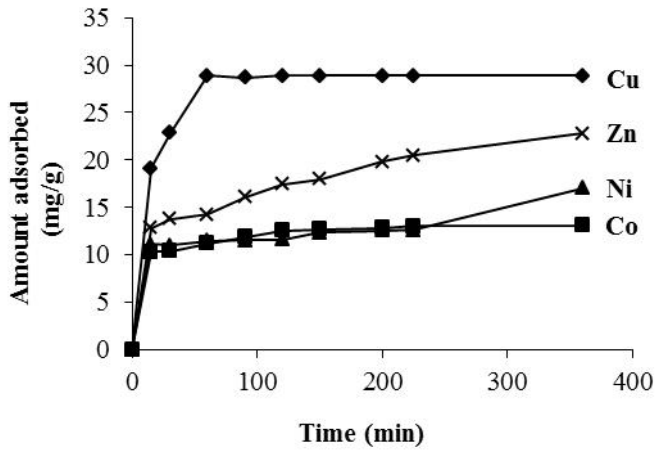


Figure 2: Variation in amount adsorbed of metal ions onto Bentonite as a function of shaking time.

Effect of pH

The effect of pH on the metal adsorption by the Bentonite was studied in the pH region between 2 and the pH of solution (5 and 6), where the material exhibits chemical stability. The pH was limited to values less or equal to 6 because of precipitation at higher pH (Mohan and al., 2002).

As seen in Fig. 3, the adsorption efficiency of copper ion increased from 13.4 to 25.73; 11.6 to 19.1; 11.8 to 15.35 and 12.8 to 15.2 *mg/g* with increase in pH of the solution and remains almost constant. At low pH, the number of available hydrogen ions is high and Cu^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+} ions have to compete with them for adsorption sites on the adsorbents surface. The weak efficiency adsorption of metal ions, under acid conditions, probably reflects a reduction in the quantity of negative surface changes on Bentonite surface.

The high sorption levels for the Bentonite between pH 3 and 5 indicate that a high affinity for metal ions predominant in this pH region.

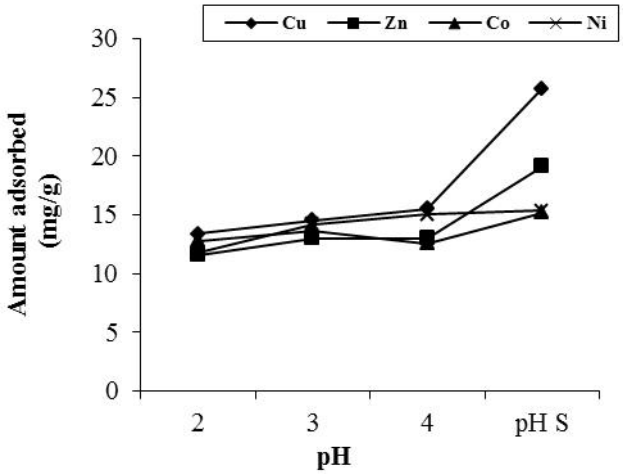


Figure 3: Effect of pH on amount adsorbed per unit mass of Bentonite

Effect of temperature of solution

The adsorption of metal ions has been found to increase with an increase in temperature from 15 to 40 °*C* as shown in Fig. 4. The increase in adsorption capacity of bentonite with temperature indicates an endothermic process. The increase in adsorption with temperature may be attributed to either increase in the number of active surface sites available for adsorption on the adsorbent or the desolvation of the adsorbing species and the decrease in the thickness of the boundary layer surrounding the adsorbent with temperature, so that the mass transfer resistance of adsorbate in the boundary layer decreases (Ajay Kumar Meena and al., 2005). Since diffusion is an endothermic process, greater adsorption will be observed at higher temperature. Thus, the diffusion rate of ions in the external mass transport process increases with temperature.

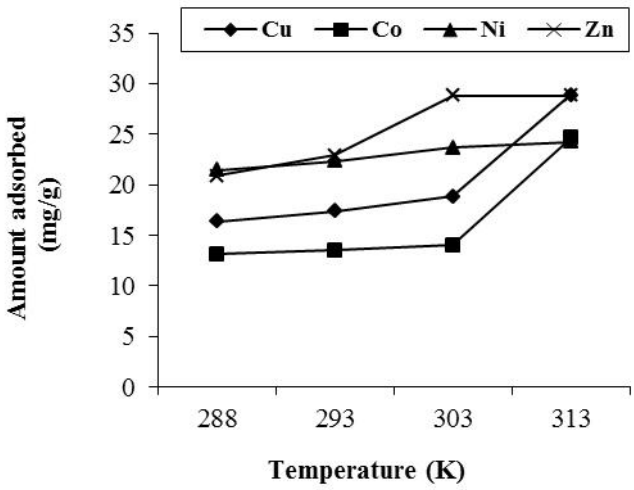


Figure 4: Effect of temperature on adsorption of Cu^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+}

Effect of thermal treatment

Fig. 5 shows the variation of the amount of metal ions on bentonite treated at different temperature (500, 700 and 1000 °*C*). It was observed that adsorption capacity of metal ions increase with increasing temperature to 700 °*C*. It believed that at temperature higher than 700 °*C* not only dehydratation and dehydroxylation occur but also a total/partial structural collapse of the montmorillonite eventually occurs. This would explain the reported low adsorption capacity.

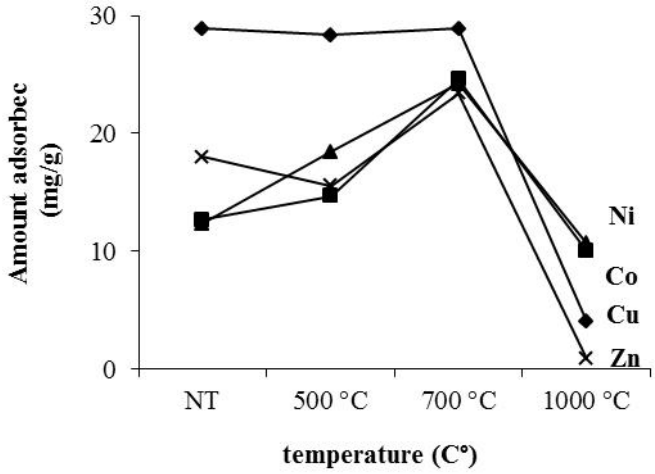


Figure 5: Effect of thermal treatment on the Cu^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+} adsorption by Bentonite

Kinetic studies

The kinetics of adsorption describes the rate of metal ions uptake on natural Bentonite and this rate controls the equilibrium time. The kinetics of adsorbate uptake is required for selecting optimum operating conditions for the full-scale batch process (Gupta and al., 1997).
The kinetic parameter, witch is helpful for the prediction of adsorption rate, gives important information for designing and modelling the processes. The kinetics of the adsorption data was analyzed using different kinetic models such as pseudo-first-order and pseudo-second-order models.

Pseudo-first-order model

The kinetic data were treated with the Lagergren first-order model (Lagergren and al., 1898) :

$$dq/dt = k_1 (qe-q) \quad (2)$$

Integrating equation (2) with respect to integration conditions $q = 0$ to $q = qt$ at $t = 0$ to $t = t$, the kinetic rate expression becomes:

$$Ln (q_e - q_t) = Ln\, q_e - k_1 t/2.303 \quad (3)$$

The first-order rate constant *k1* (*min -1*) can be obtained from the slope of the

plot of *Ln (qe – qt)* against time *t*, as shown in Fig. 6. The adsorption first-order rate constants were found to be 0.11, 0.07, 0.05 and 0.02 *min-1* for metal ions Cu^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+}, respectively.
If the adsorption process can be described by pseudo-first order equation, there should be good linear relationship between *Ln (qe – qt) and t*.
In the present study, the plot of *Ln (qe – qt)* versus time *t* was not linear over the entire time range (Fig. 6), indicating that more than one mechanism involved in adsorption. This confirms that it is not appropriate to use the Lagergren kinetic model to predict the adsorption kinetics for metal ion.

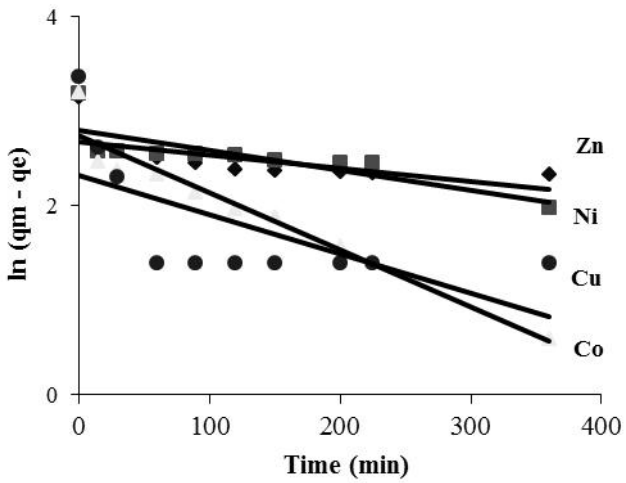


Figure 6: Pseudo-first-order kinetics for Cu^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+} adsorption by Bentonite.

Pseudo-second-order model

Adsorption kinetics was explained by the pseudo-second-order model given by Ho and McKay (Ho and al., 1998) as follows:

$$dq/dt = k_2 (qe-q)^2 \quad (4)$$

Integrating equation (4) for the boundary conditions $q = 0$ to $q = qt$ at $t = 0$ to $t = t$ is simplified as:

$$t/q_t = 1/k_2q_e^2 + t/q_e \quad (5)$$

Where k_2 *(g mg-1 min-1)* is the second-order rate constant determined from the plot of *t/qt* against *t*, as shown in Fig. 7.
The correlation coefficients of the pseudo-second-order kinetic model were higher than 0.9491. The pseudo-second-order adsorption mechanism was predominant for adsorption of metal ions by natural bentonite. The plot of *t/qt* against *t* present multi linearity for different metal ions. The adsorption second-order rate constants were found to be 0.0034, 0.0033, 0.0074 and 0.0587 *min-1* for metal ions Cu^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+}, respectively.
The pseudo second order reaction rate model was found to describe best the kinetic data. The applicability of this model showed that sorption process is complex and involves more than one mechanism. The rate constant k_2, the correlation coefficient R^2 and removal capacity at equilibrium state (qe) were calculated and presented in table 4.

Table 4 : Comparison of the pseudo-first-order and pseudo-second-order adsorption rate constants for different metal ions

Metal ions	Pseudo-first-order kinetics			Pseudo-second-order kinetics		
	q_e (mg g-1)	k_1 (min-1)	R^2	k_2 (g mg-1 min-1)	R^2	q_e (mg g-1)
Cu^{2+}	28.88	0.11	0.4273	0.0034	0.9992	28.88
Zn^{2+}	20.5	0.07	0.4304	0.0033	0.9996	20.5
Ni^{2+}	17.05	0.05	0.6583	0.0074	0.9491	17.05
Co^{2+}	13.85	0.02	0.9352	0.0587	0.9843	13.85

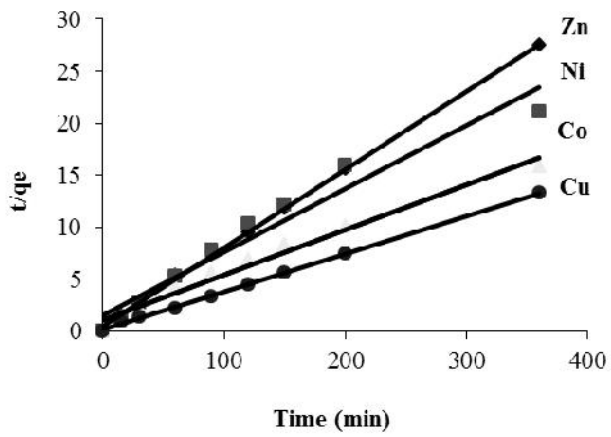


Figure 7: Pseudo-second-order kinetics for Cu^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+} adsorption by Bentonite.

Adsorption isotherm

Adsorption alters the distribution of a solute in the constituent phases and the interfaces between them [W. J. Weber Jr and al, 1991]. The adsorption studies were conducted at fixed initial adsorbent dose by varying concentration of heavy metal.
The equilibrium data obtained were described by the following two widely used isotherms. Langmuir isotherm is:

$$Ce/qe = 1/bqm + (1/qm)\ Ce \quad (6)$$

Freundlich isotherm is:

$$qe = kf\ Ce^{1/n} \quad (7)$$

Where b is Langmuir equilibrium coefficient (*L/mg*), qm is the maximum capacity of the adsorbent (*mg/g*), Ce (*mg/L*) the equilibrium concentration, k_f and n Freundlich coefficient.
A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L (known as the separation factor), which is considered as a more reliable indicator of adsorptions.
This parameter is given by:

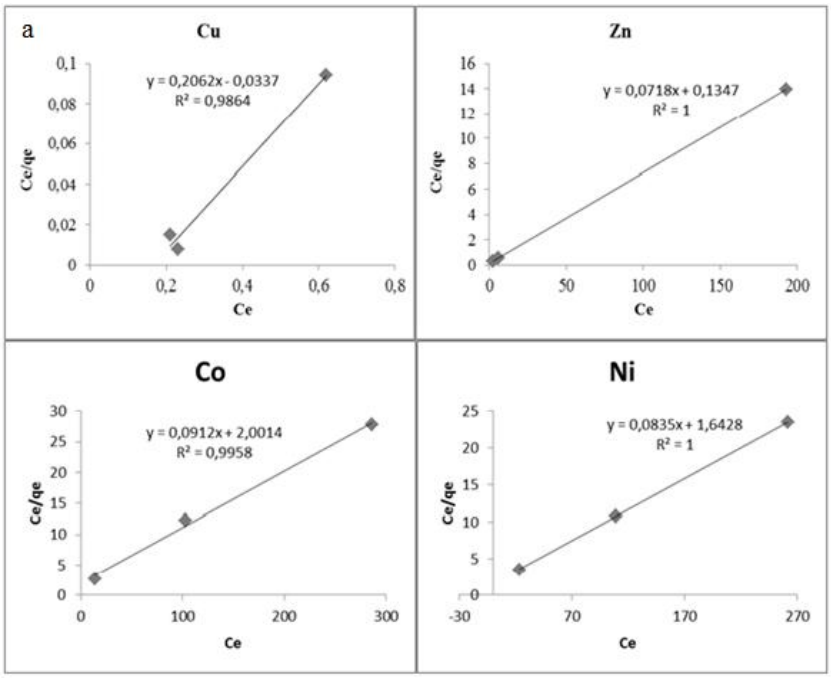
$$R_L = 1/(1 + bCi) \quad (8)$$

Where Ci is the initial concentration metal ion (mg/L).

For favorable adsorption $0 < R_L < 1$, while $R_L > 1$ represents unfavorable adsorption, and $R_L = 1$ indicates linear adsorption. If $R_L = 0$, the adsorption process is irreversible (Hall and al., 1966).
Fig. 8a and 8b dis play linear plots of Ce/qe versus Ce and Lnqe versus LnCe at 293 K.
For Langmuir isotherm in Fig. 8a, the values of qm, b and R_L were determined from experimental data by linear regression. According to Freundlich isotherm (Fig. 8b), the values of K_f and n were obtained similarly.
The data in table 5 present the results, along with associated correlation coefficients R^2. Since R_L values lie between 0 and 1 for all metal ions studies, it is seen that the adsorption of heavy metal ions is favourable (Mckay and al., 1982).
The data reveal that the Langmuir model yields better fit than the Freundlich model.

Table 5: Different parameters derived from Langmuir and Freundlich adsorption equations

Isotherm Model	Parameter				R^2
		qm	B	R_L	
Langmuir	Cu^{2+}	28,85	0,207	0,008	0,98
	Zn^{2+}	23,45	0,146	0,014	1
	Co^{2+}	24,60	0,013	0,141	0,99
	Ni^{2+}	24,25	0,016	0,114	1
Freundlich		k_f	N		
	Cu^{2+}	26,821	7,818		0,61
	Zn^{2+}	12,131	3,82		0,86
	Co^{2+}	19,53	4,02		0,99
	Ni^{2+}	14,31	3,48		0,96



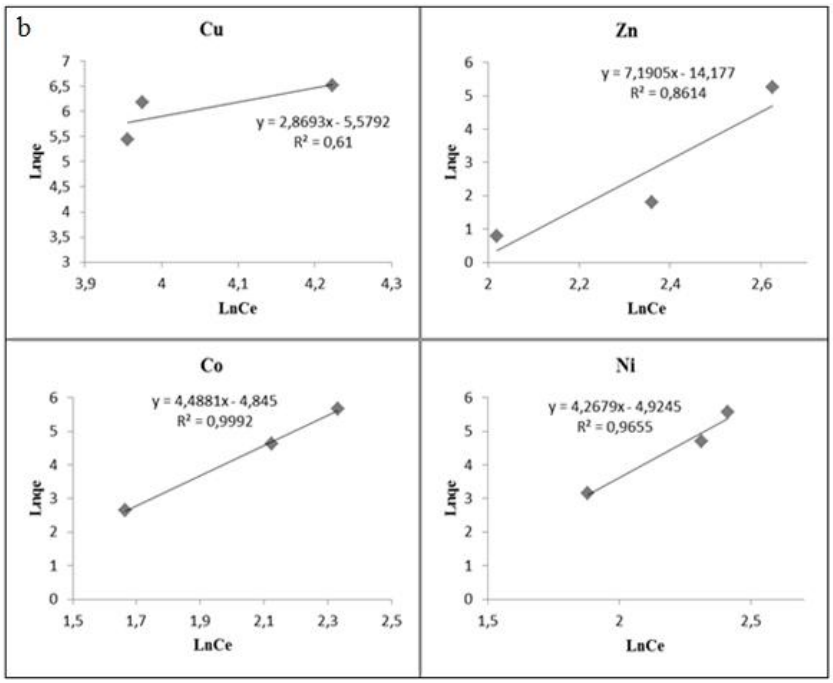


Figure 8: Fitting lines of (a) Langmuir and (b) Freundlich isotherms of Cu(II) ion onto Bentonite

Thermodynamic studies

The amounts of adsorption of heavy meal by natural bentonite are measured in temperature 288-313 *K*. Analysis of thermodynamics of equilibrium adsorption data can give more important information on adsorption process. In the present study, thermodynamic parameters *ΔH*, *ΔS* and *ΔG* were calculated by using the equation (Khan and al., 1995; Abou-Mesalam, 2003; Akil and al., 1998):

$$\text{Ln } k_d = \Delta S/R - \Delta H/RT \quad (9)$$

Where k_d is the distribution coefficient (ml/g^{-1}), *ΔH*, *ΔS* and *T* are the enthalpy, entropy, and temperature in Kelvin, respectively, and *R* is the gas constant. The plot of *lnkd* against *1/T* for metal ions is shown in Fig. 9. The values of enthalpy (*ΔH*) and entropy (*ΔS*) were obtained from the slope and intercept of *lnkd* against *1/T* plots. Gibbs free energy (*ΔG*) was calculated using the well-known equation:

$$\Delta G = \Delta H - T\Delta S \quad (10)$$

The values of the thermodynamic parameters for the adsorption of metal ions on bentonite are given in Table 6.

Table 6 : Thermodynamic parameters for the adsorption of metal ions on Bentonite

Metal	**ΔH (kJ/mol)**	**ΔS (J/mol)**	**ΔG (KJ/mol) 288 K**	**293 K**	**303 K**	**313 K**
Cu^{2+}	46.37	221.6	-17.45	-18.55	-20.77	-22.99
Zn^{2+}	65.74	243.1	-4.27	-5.49	-7.92	-10.35
Ni^{2+}	-3.58	6.1	5.34	5.37	5.43	5.49
Co^{2+}	-1.36	14.4	5.51	5.58	5.72	5.87

For Cu^{2+} and Zn^{2+} the positive value of enthalpy change ΔH shows that the adsorption of metal ions is endothermic. The numerical value of ΔG decreases with increased temperature as shown in Table 6, indicating that the reaction is spontaneous and more favourable at higher temperature. One possible explanation of endothermicity of heats of adsorption is that the metal ions are well solvated. In order for the metal ions to be adsorbed, they have to lose part of their hydration sheath. This dehydratation process of the ions requires energy. This energy of dehydratation supersedes the exothermicity of the ions getting attach to the surface (Naseem and al., 2001). It can be inferred that both adsorption and ion exchange take place at low temperature, while only ion exchange occurs with increasing temperature (Chegrouche and al., 1997).
For Ni^{2+} and Co^{2+}, the negative value of enthalpy change ΔH indicating that the adsorption of metal ions is exothermic. The positive values of ΔG at various temperatures indicate the no spontaneous nature of the adsorption process.
The positive value of ΔS indicated that the adsorption process was irreversible. In addition, the positive value of ΔS suggested some structural change of bentonite and favours complexion and stability of adsorption.

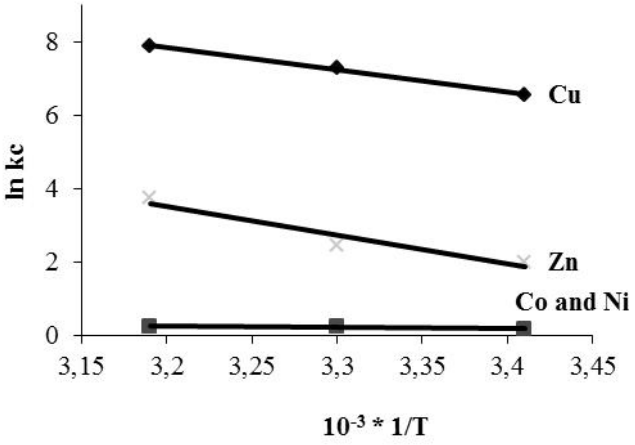


Figure 9 : Plot of Ln kc against 10^{-3}*1/t for heavy metals on natural Bentonite

Comparison with other adsorbents (synthetic zeolithe)

The percent adsorption (%) is calculated using the equation:

$$\% \text{ adsorption} = ((C_i - C_f)/ C_f) * 100 \quad (11)$$

Where C_i and C_f are the concentration of the metal ions in initial and final solution, respectively.
Fig. 10 shows the variation of the amount adsorbed of metal ions on Bentonite and on synthetic zeolithe. The order of adsorption of metals ions on natural bentonite and synthetic zeolithe under the same conditions is: $Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+}$.
These results show that natural bentonite and synthetic zeolithe can be used effectively for the removal of metal ions from aqueous solutions. The bentonite presents an affinity important of adsorption of heavy metal with a low cost than the zeolithe.

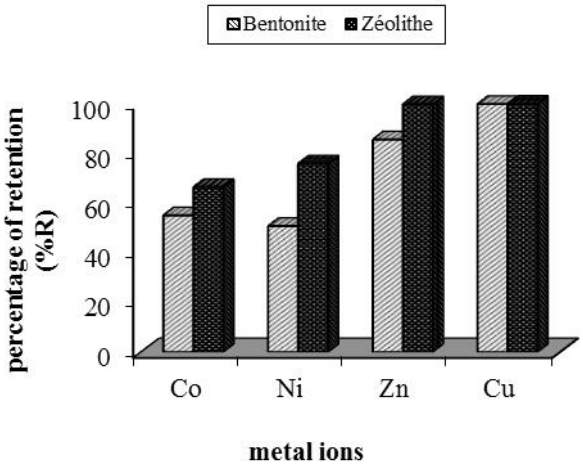


Figure 10: Comparison of adsorption by the Bentonite and the zeolithe

CONCLUSION

The results of this study indicate that bentonite can be successfully used for the Cu^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+} ions removal from aqueous solutions. Natural clays present a major advantage of giving low cost recovery processes making them suitable for use in water purification.

Taking into account the results, we have considered it of great interest to assess the ability of locally available bentonite for the adsorption of metal ions from aqueous solutions in the batch technique and optimization of conditions for its adsorption.

The kinetic studies indicated that equilibrium for metal ions adsorption on bentonite is established in 60 *min*. The pseudo second order reaction rate model was found to describe best the kinetic data.

The temperature variations have been used to evaluate the values of ΔH, ΔS and ΔG. The positive value of ΔH for Cu^{2+} and Zn^{2+} indicates that the adsorption of metal on bentonite is an endothermic process, and the negative values for Ni^{2+} and Co^{2+} indicates that the adsorption of metal is an exothermic process. The negative value of ΔG for Cu^{2+} and Zn^{2+} showed spontaneous nature of adsorption, and the positive values of ΔG for Ni^{2+} and Co^{2+} at various temperatures indicate the no spontaneous nature of the adsorption process. The positive values of ΔS show the existence of some structural changes at the solid-liquid interface. Also, the positive ΔS favor complexation and stability of adsorption.

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