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Thermodynamic and Kinetic of Cu (II) Removal from Water by Adsorption Using Natural Bentonite

الديناميكية الحرارية وحركية إزالة النحاس الثنائي من الماء بالامتزاز بواسطة البنتونيت الطبيعي

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Abstract: The adsorption kinetics of natural commercial bentonite (NB) with respect to Cu (II) has been studied in order to consider its application to purify metal finishing wastewaters. The batch method has been employed, using metal concentrations in solution ranging from 40 to 2000 mg/l. We have investigated how solution pH, temperature, adsorbent amount, contact time, washing and calcinations of bentonite (the calcinations of bentonite at 700 °C and washed bentonite termed by CB and WB, respectively) affect this process. Results of kinetic experiments showed that Cu (II) adsorption rate was fast, and more than 90% of Cu adsorption occurred within 5 min. Among the kinetic models tested, the adsorption kinetics was best described by the pseudo-second-order equation. The adsorption capacity of Cu (II) ions on NB has increased with increasing pH, adsorbent amount and temperature. The Langmuir adsorption isotherm properly describes the equilibrium adsorption and the maximum adsorption capacities of NB towards Cu (II) were determined to be 24.5, 35.5 and 39.3 mg/g at 293, 313, and 333 K, respectively. Values of Gibbs free Energy ($\Delta G°$) ranging from -17.2, -18.56, and -19.9 kJ/mol suggest that the adsorption process is spontaneous and mainly governed by specific surface interaction mechanism. The values of standard enthalpy ($\Delta H°$) and entropy ($\Delta S°$) were 2.494 kJ/mol and 67.29 J/ (mol K), respectively. The adsorption capacity of washed bentonite sample (WB) was significantly higher than that of Natural bentonite sample (NB) and calcined bentonite sample (CB). Results of this study can be useful for future up-scaling in using this material as a low-cost adsorbent for the removal of Cu (II) from industrial wastewater.

Keywords: *Bentonite clay, Adsorption, Copper, Kinetics, Isotherms, Thermodynamics.*

المستخلص: تمت دراسة حركية امتزاز البنتونيت الطبيعي التجاري للنحاس وذلك من أجل اختبار استخدامه في تنقية مياه الصرف الصحي . تم استخدام طريقة الدفعة الواحدة وذلك باستخدام محاليل تحتوي على مدى من النحاس بين 40 جزء في المليون إلى 2000 جزء من المليون. هذا وقد تمت دراسة تأثير كل من الأس الهيدروجيني، درجة الحرارة ،كمية البنتونيت، زمن الملامسة، كلسنه البنتونيت عند درجة حرارة 700 مْ (CB) وغسل البنتونيت بالماء المقطر (WB) على هذه الدراسة. أظهرت نتائج التجارب الحركية بأن امتزاز النحاس الثنائي كان سريعا وان امتزاز أكثر من 95% من النحاس حدث خلال خمس دقائق. بعد تطبيق النماذج الحركية على حركية الامتزاز تبين أنها تتبع معادلة الرتبة الثانية الوهمية وان مقدره امتزاز ايون

النحاس الثنائي على البنتونيت الطبيعي ازداد بزيادة الأس الهيدروجين وكمية المادة الممتزة ودرجة الحرارة مع توافق نتائج الامتزاز مع معادلة لانجمير حيث كانت أقصى كميات ممتزة للنحاس على البنتونيت الطبيعي 24,5 ملجم/جم و35,5 ملجم/م و39,3 ملجم/جم عند درجة حرارة 313,293 و 333 كلفن على التوالي .تراوحت قيم طاقة جبس الحرة (ΔG°) للامتزاز بين -17,2، -18,56 و -19,9 كيلوجول/مول مما يدل على أن عملية الامتزاز تلقائية وأنها تخضع لتحكم ميكانيكية تفاعلات السطح النوعي .تراوحت قيم الانثالبى القياسية (ΔH°) والانتروبى (ΔS°) كانت 2,494 كيلو جول/مول و67,29 كيلو جول/مول كلفن على التوالي . بينت الدراسة ايضا بأن كفاءة البنتونيت المغسول (WB) أعلى بشكل واضح مقارنة البنتونيت الطبيعي أو البنتونيت المكلسن. لذلك من الممكن اعتبار نتائج هذه الدراسة على البنتونيت الطبيعي، مفيدة كأساس لاستخدام مادة رخيصة الثمن لإزالة النحاس الثنائي من المياه الملوثة الصناعية على المستوى الأكبر.

كلمات مدخليه : *طين منشط، الامتزاز، نحاس، حركية، منحنى ثابت الحرارة، ديناميكا حرارية.*

INTRODUCTION

Heavy-metal pollution occurs in many industrial wastewater such as those produced by metal plating facilities, mining operations, battery manufacturing process, production of paints and pigments, and glass production industry. Due to their accumulation through the food chain and persistent in nature, it is necessary to remove toxic heavy-metals from wastewater. Intake of excessively large doses of copper by man leads to severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal damage and central nervous system irritation followed by depression. Severe gastrointestinal irritation and possible necrotic changes in the liver and kidney could occur (Ajmal, *et al*. 1999).

Conventional technologies for the removal of heavy-metal such as chemical precipitation, electrolysis, ion exchange and reverse osmosis are often neither effective nor economical (Bhattacharya, *et al*. 2006) Among the physio-chemical treatment process, adsorption is highly effective, cheap and easy to adapt (Bhattacharya, *et al*. 2006). Adsorption has been proven to be a successful method for the removal of heavy metals from wastewater. Activated carbon is highly effective in adsorbing heavy metals from wastewater but high cost limits its use (Panday, *et al*. 1985). The abundance of clay minerals and their low cost are a strong candidate as an adsorbent for removal of heavy-metal from wastewater. Because of their high specific surface area and exchange capacity, clay minerals also play a significant role in determining the availability and transport of metal species in soils and water (Sheta, *et al*. 2003).

Bentonite is a natural clay mineral that is found in many places of the world. Any clay of volcanic origin that contains montmorillonite is referred to as bentonite. It belongs to the 2:1 clay family, the basic structural unit of which is composed of two tetrahedrally coordinated sheets of silicon ions surrounding a sandwiched octahedrally coordinated sheet of aluminum ions. The isomorphism substitution of A^{l3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} or Zn^{2+} for A^{l3+} in the octahedral layer results in a net negative surface charge on the clay (Luckham and Rossi, 1999). Compared with other clay types, it has excellent sorption properties and possesses sorption sites available within its interlayer space as well as on the outer surface and edges (Tabak, *et al*. 2007). Adsorption of metal ions onto montmorillonite appears to involve two distinct mechanisms: (1) an ion exchange reaction at permanent charge sites; and (2) formation of complexes with the surface hydroxyl groups (Abollino, *et al*. 2003; Álvarez-Ayuso, *et al*. 2003).

The natural commercial bentonite sample obtained from a local supplier (Bariod Saudi Arabia Limited) in Saudi Arabia. It was chosen for its potential use as an adsorbent for the removal of Cu ions from aqueous solutions (Qunaibit, *et al*. 2005). The present paper reports the results of kinetic and equilibrium adsorption studies of Cu (II) onto NB. Parameters affecting adsorption including, pH, temperature, adsorbent amount, contact time, calcinations and washing of bentonite (the calcinated bentonite at 700°C and washed bentonite are termed CB and WB, respectively) were evaluated. Kinetic and equilibrium isotherm models were used to establish the rate of adsorption, adsorption capacity, and the mechanism for Cu adsorption. Results of this study will be useful for future scale up using this natural material as a low-cost adsorbent for the removal of Cu from wastewater.

MATERIALS AND METHODS

Chemicals

Copper nitrate (Cu $(NO_3)_2 3H_2O$; Extra pure Merck) was used in the adsorption experiments. pH adjustments were carried out using 0.1N hydrochloric acid (HCl) and 0.1N sodium hydroxide (NaOH). All Cu (II) solutions were prepared with ultra-pure water (specific resistivity of 18 MW.Cm) obtained from an E-pure (Barnstead, USA) purifier system. Super purity nitric acid (SpA, 98%) purchased from ROMIL Ltd. (UK) was used for sample preparation. A single element ICP Standard solutions from MV Laboratories INC. (USA) were used for system calibrations.

Adsorbent

NB was characterized by X-ray diffraction (XRD) and chemical analysis. The chemical composition of the tested samples was as follows (in Wt%) :SiO_2 = 40.43, Al_2O_3 = 15.87, CaO = 2.80, K_2O = 0.14, Na_2O = 2.02, Fe_2O_3 = 10.86, MgO = 3.32. Comparative XRD patterns of the natural commercial bentonite clay are shown in Figure (1). It was proved by X-ray analysis on this clay that the dominant component is bentonite (64.9%), kaolinite (10.6%), Geothite (9.5%), Hematite (9.4%) and Boehmite (5.6%).

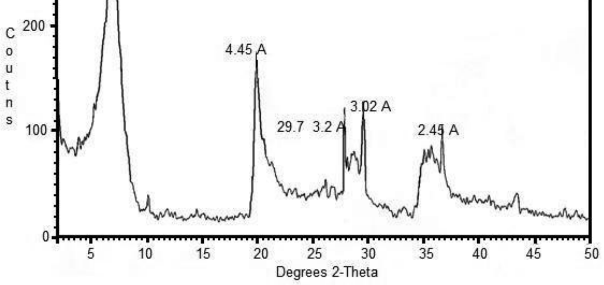

Fig. 1. The XRD patterns of the Natural Bentonite NB.

Characterization of Adsorbent

Commercial natural bentonite, grey in color, with particles size ranging between 0.25-0.0375 mm, was used. Bentonite samples were divided into three parts: the first part used in the adsorption studies as received and labeled by NB; the second part was washed with distilled water several times to remove any dust and other water-soluble impurities. The washed sample was dried in an electric oven at 150–200 °C for several hours before use in the adsorption studies. The washed sample labeled by WB, and the third part was calcined in an oven at 700 °C for 12 hr. The hot sample was cooled down to room temperature over silica gel then grounded and passed through sieves. The calcinated bentonite was labeled by CB and stored in sealed polythene bags. The particles size of WB and CB such as the particles of the received bentonite, NB, ranged between 0.25- 0.0375 mm. The specific surface area of NB was determined by applying the BET (Brunauer, Emmet, and Teller) equation. The resulted surface area of NB, S_{NCB} = 45.9 m^2/g. These values are lower than those expected for montmorillonites (Hillel, 1998), but it may be due to the lack of treatment. In fact, Bourg, *et al*. (1983) and Goldberg (1998) have measured the specific surface area of 23, 9 and 18, 6 $m^2 g^{-1}$ for a montmorillonite without pretreatment; it is possible that N_2 molecules can not penetrate the interlayer regions easily between the layer sheets, involving an underestimation of specific surface areas (Dékány and Nagy, 1991; Sparks, 1995).

Kinetic Experiments

The kinetic experiments were conducted in batch mode on NB. The experimental details were as follows: 0.5 g NB was added to a tube (100 mL) containing 50 mL Cu (II) solution. The corresponding Cu (II) concentration was 200 mg/L. The suspension was shaken for a period between 2 and 60 min with a rotary shaker at a speed of 150 rpm. After being centrifuged, Cu (II) was analyzed by using a Perkin-Elmer Optima 5300 DV ICP optical emission spectrometer coupled with peristaltic pump and AS-93 plus auto sampler unit. All experiments were carried out in duplicate.

Adsorption Isotherms

Adsorption isotherm was studied at 293, 313, and 333 Kelvin (K) by adding 0.5 g NB to a solution containing 50 mL of various concentrations of Cu (II) (ranging from 40 to 2000 mg/L, pH 5.0). The tubes were shaken for 24 hr at 25°c on the rotary shaker at 150 rpm. After being centrifuged, Cu II) was analyzed by Perkin-Elmer Optima 5300 DV ICP optical emission spectrometer atomic. All experiments were carried out in duplicate.

Effect of pH

The effect of initial solution pH on adsorption was determined by mixing 0.5 g of NB with 50 mL of solution containing metal concentration of 500 mg/L at various pH values ranging from 2 to 10. Solution pH was adjusted with 0.5 M, HCl and NaOH solutions. The mixture was shaken for 1 hr and the solution was filtered and analyzed. Also the pH of NB suspension measured before and after Cu (II) adsorption.

Effect of Temperature

The effect of temperature on Cu (II) adsorption on NB was conducted under isothermal conditions at 293, 313, and 333 Kelvin (K) by maintaining the mixtures in a water circulation shaker bath whose temperature varied within ± 0,5 °C. The experimental procedures employed for studying the effect of temperature on the adsorption isotherm were the same as those described in the section above. In order to assume mentaining thermal equilibrium, the bottles were first put into the temperature controlled shaker bath for about 1 hr prior to the experiment.

RESULTS AND DISCUSSION

Kinetics of Adsorption

The adsorption kinetics, yielding the Cu (II) uptake rate, are the most important determinant of the adsorption efficiency of the NB adsorbent, and therefore its potential application. Figure (2) presents the effect of the contact time on the Cu (II) adsorption rate for various concentrations; the Cu (II) adsorption rates increase dramatically during the first 720 minutes (12 hr) at various initial concentrations, reaching equilibrium slowly at 1440 minutes (24 hr).

Two different kinetic models, pseudo-first order and pseudo-second order (Reddad, *et al*. 2002; Gulnaz, *et al*. 2005) were used to fit the experimental data of adsorption rate of Cu(II) onto the NB. The pseudo-first-order kinetic model has been widely used to predict metal adsorption kinetics. It was suggested by Lagergren for the adsorption of solid/liquid systems. The pseudo-first-order model is expressed The pseudo-second-order model is expressed as:

$$1n(q_e - q_t) = 1nq_e - k_1^t \qquad (1)$$

$$\frac{t}{q_1} = \frac{1}{K_2q^2e} + \left(\frac{1}{q_e}\right) t \qquad (2)$$

The second-order rate equation is given as:

$$h = K_2q^2e \qquad (3)$$

where K_1 is the rate constant of pseudo-first-order adsorption (1/min), K_2 (g/mg.min) the rate constant of pseudo-second-order adsorption, h the initial adsorption rate (mg/g.min) and q_e and q_t are the amount of adsorbed Cu(II) on adsorbent (mg /g) at equilibrium and at time t, respectively.

The adsorption kinetic constants and linear regression values are given in Table (1). From the Table, it can be seen that the degree of fit (r^2) for the pseudo-second-order kinetic model ($r^2 = 0.999$) is higher than those of the pseudo-first-order model ($r^2 = 0.77$). Accordingly, the pseudo-second-order kinetic model is applicable, and the plot of t/q_t versus t shows a linear relationship (Figure 3. a-b). Moreover, the calculated values for q_e fit the experimental data. This suggests that the pseudo-second-order adsorption mechanism is predominant and that the overall rate of the Cu (II) adsorption process appears to be controlled by the chemical process (Barbier, *et al*. 2000). The calculated values for q_e for the first-order model do not give reasonable values, which are obviously different from the experimental q_e values. Thus, adsorption of Cu (II) onto NB is not a pseudo-first-order

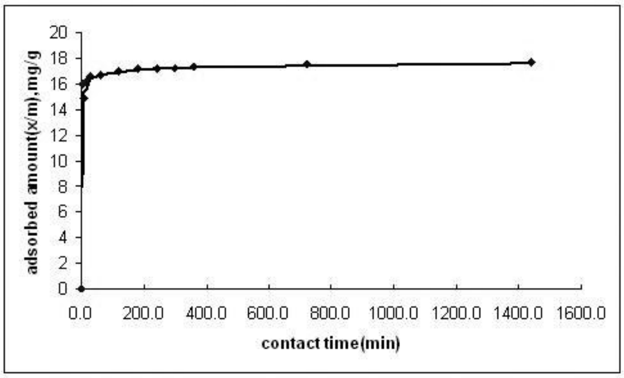

Fig. 2. Effect of contact time on Cu (II) adsorption rate at 200 mg/L.

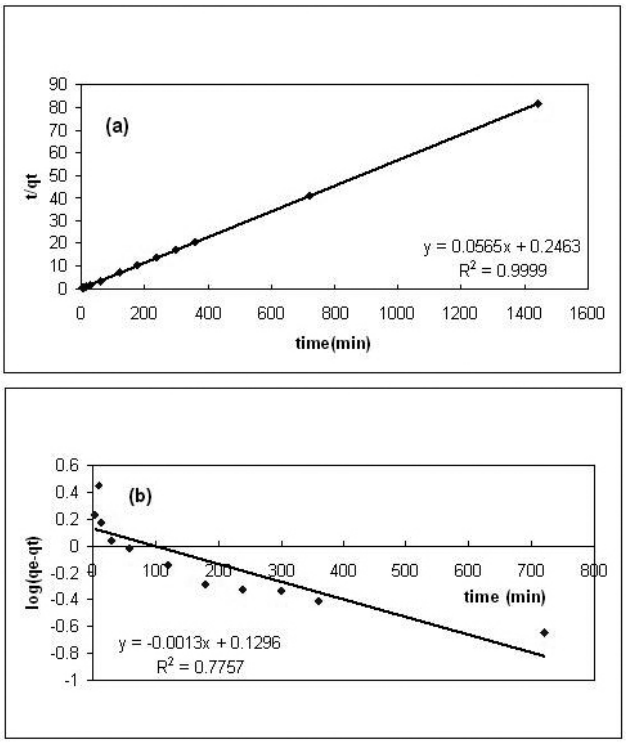

Fig. 3. Test of (a) the first-order Lagergren, and (b) the pseudo-second-order equation for adsorption at 200 mg/L of Cu (II) by NB adsorbent (at 298 ± 1 K).

Table 1. Parameters for adsorption of Cu (II) onto NB derived from the pseudo-first- and second-order kinetic models.

Pseudo-first-order model			pseudo-second-order model			
q_e(mg/g)	K_1(1/min)	r^2	q_e(mg/g)	K_2 (g/mg.min)	h (mg/g.min)	r^2
1.13	0.001	0.77	17.7	0.013	4.1	0.999

Adsorption of Cu (II) by Bentonite Sample (NB)

Effect of Temperature

The effect of temperature on the adsorption of Cu(II) by NB is shown in Figure (4) at 293, 313 and 333 K. It is observed that with increasing temperature, the adsorbed amount of Cu (II) on NB increased. The increase in adsorption with temperature is attributed to the increased rate of diffusion of Cu ions into the NB pores (Fethiye and Pehlivan, 2007). In this study, the adsorption results were analyzed in terms of Freundlich and Langmuir isotherms to establish the relationship between the amounts of Cu(II) adsorbed by the bentonite sample NB. The experimental data conformed to the linear form of Langmuir model expressed in the following equation (Langmuir, 1918):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \left(\frac{1}{K_l q_m}\right) \qquad (4)$$

where C_e is the equilibrium concentration of metal (mg/L), q_e the amount of the metal adsorbed (mg) by per unit of bentonite (g), and qm and KL are the Langmuir constants related to adsorption capacity (mg/g) and the energy of adsorption (L/g), respectively. q_m and K_L constants were evaluated from slope and intercept of the linear plots of C_e/q_e versus C_e, respectively (Figure 5). The Langmuir monolayer adsorption capacity (q_m) gives the amount of Cu (II) required to occupy all the available sites in a unit mass of the bentonite sample (Eren and. Afsin, 2008). The Langmuir monolayer adsorption capacity for NB was found as 31.8, 38.3 and 43.5 mg/g at 293, 313 and 333 K, respectively. The higher adsorption capacity attributed to the adsorption of Cu (II) over these samples could not be modeled by only a cation exchange reaction, but also specific adsorption, which can be described by surface complication model, which define a reaction between functional surface groups and Cu (II) ions (Nir, *et al.* 1994; Weng, *et al.* 2007). The Langmuir constant indicates the capability of clay to retain a solute and also the extent of its movement in a solution phase (Reddy, *et al.* 1986). According to Gomes, *et al.* (2001), K_L is a useful parameter for comparing the adsorption capacities of different clays or materials for any particular ion when measured under the same experimental conditions. From Figure (5) and Table (2) it can be observed that K_L values increase with increasing temperature.

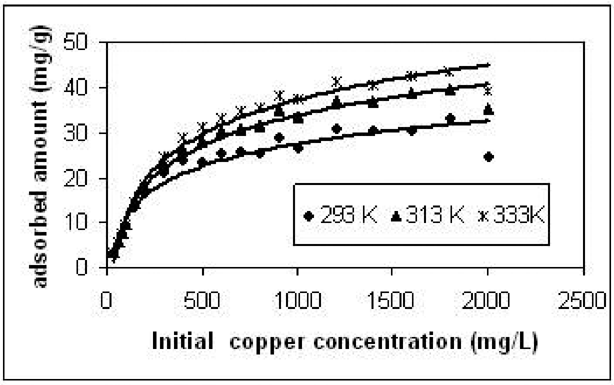

Fig. 4. Adsorption of Cu (II) onto NB as a function of temperatures, 293, 313 and 333 K.

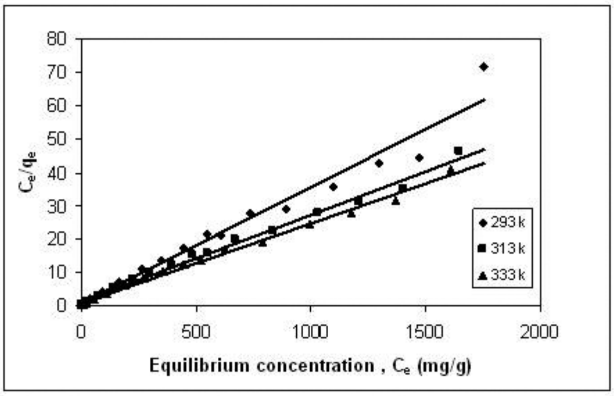

Fig. 5. Linear plots of Langmuir isotherms of Cu (II) adsorption on NB at different temperatures, (a) 293 K, (b) 313 K, and (c) 333 K.

The Freundlich adsorption isotherm is applicable to the adsorption on heterogeneous clay surfaces. The adsorption equilibrium data was applied to the Freundlich model in logarithmic form given as follows (Bai, *et al.* 1998)

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad (5)$$

where K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. K_f and $1/n$ were determined from the intercept and slope of linear plot of log (q_e) versus log (C_e), respectively (Figure 6).

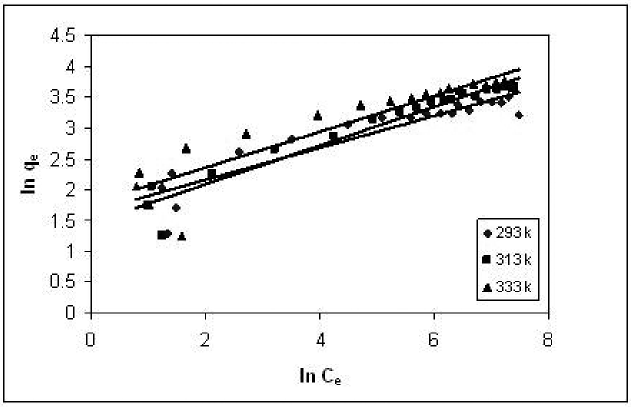

Fig. 6. Linear plots of Freundlich isotherms of Cu(II) adsorption on NB at different temperatures, (a) 293 K, (b) 313 K, and (c) 333 K.

The Freundlich plots did not illustrate good linearity at different temperatures (r^2 = 0.87, 0.85, and 0.83 at 298, 313 and 333 K, respectively). The values of the adsorption coefficients, computed from Freundlich plots are given in Table (2). The adsorption intensity given by the Freundlich coefficient ($1/n$) is smaller than 1 (values at 293, 313 and 333 K are 0.27, 0.28 and 0.29, respectively), indicating that the adsorption of Cu(II) onto bentonite sample under the studied conditions is favorable. The Freundlich adsorption capacity (K_f) is calculated as 4.9, 5.3, and 5.9 at 293, 313 and 333 K, respectively.

Table 2. Parameters of Langmuir and Freundlich adsorption isotherm models for Cu (II) on NB adsorbent at different temperature.

T(K)	Langmuir				Frendlich		
	q_m (mg/g)	K_L(L/mg)	K_L (L/mol)	r^2	K_f	n	r^2
293	31.8	0.0188	1193.8	0.993	4.9	0.27	0.87
313	38.3	0.0217	1237	0.993	5.3	0.28	0.85
333	43.5	0.0258	1470	0.997	5.9	0.29	0.83

Thermodynamic Studies

The thermodynamic parameters of the adsorption, i.e., the standard enthalpy (ΔH°), Gibbs free energy (ΔG°) and entropy (ΔS°) were calculated using the equations (Mohan, *et al.* 2002; Abou-Mesalam, 2003; Weng, *et al.* 2007):

$$\Delta G^\circ = -RT\ 1\text{n}\ K_L \qquad (6)$$

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (7)$$

where R is the ideal gas constant (kJ/mol.K), $K_L = k_{ads}/k_d$ is the Langmuir constant. ΔH° and ΔS° values can be obtained from the slope and intercept of Van't Hoff plots of $\ln(K_L)$ (from the Langmuir isotherm) versus 1/T (Liu and Chiou, 2004). Figure (7) and Table (3) show the results of these thermodynamic calculations. The negative value for the Gibbs free energy for Cu (II) adsorption indicates that the adsorption process is spontaneous and that the degree of spontaneity of the reaction increases with increasing temperature. The overall adsorption process seems to be endothermic (ΔH° = 2.49 kJ/mol). This result also supports the suggestion that the adsorption capacity of NB for Cu (II) increases with increasing temperature. Table (3) also shows that the ΔS° value is positive (67.29J/mol k). This occurs as a result of redistribution of energy between the adsorbate and the adsorbent. Before adsorption occurs, the heavy metal ions near the surface of the adsorbent will be more ordered than in the subsequent adsorbed state, and the ratio of free heavy metal ions to ions interacting with the adsorbent will be higher than in the adsorbed state. As a result, the distribution of rotational and translational energy among a small number of molecules will increase with increasing adsorption by producing a positive value of ΔS° and randomness will increase at the solid–solution interface during the process of adsorption. Adsorption is thus likely to occur spontaneously at normal and high temperatures because ΔH° > 0 and ΔS° > 0. As was suggested by Nunes and Airoldi (1999), the transition metal ions must give up a larger share of their hydration water before they could enter the smaller cavities. Such a release of water from the divalent cations would result in positive values of ΔS°. This mechanism of the adsorption of Cu(II) ions is also supported by the positive values of ΔS°, which show that Cu (II) ions are less hydrated in the bentonite layers than in the aqueous solution. Furthermore, the positive value of ΔS° indicates the increased disorder in the system with changes in the hydration of the adsorbing Cu(II) cations, and suggest that a large amount of heat is consumed to transfer the Cu(II) ions from aqueous into the solid phase.

The typical range of bonding energy for an ion-exchange mechanism is 1.91–3.82 kcal/mol (Ho, *et al*. 2002). It is to be noted that ΔG° values up to 3.82 kcal/mol (20 kJ/mol) are consistent with electrostatic interaction between adsorption sites and the metal ion (physical adsorption), while ΔG° values more negative than 7.62 kcal/mol (40 kJ/mol) involve charge sharing or transfer from the adsorbent surface to the metal ion to form a coordinate bond (Horsfall, *et al*. 2006). The values of ΔG° obtained in this work range from -17.2 to -19.9 kJ/mol, indicating that surface complex reaction may not play a significant role in the adsorption process. It may be suggested that ion-exchange is the major mechanism responsible for the Cu (II) adsorption process. As mentioned previously, the negatively charged groups of SiO^- and AlO^- on the edges of NB surface favor cationic Cu ion adsorption. This type of behavior (i.e., positive values of ΔH° and ΔS° and negative values of ΔG°) has also been observed in some earlier investigations for the adsorption of lead onto kaolinite clay (Orumwense, *et al*. 1996), Cu^{2+}, Pb^{2+}, Ni^{2+} and Cd^{2+} ions on $AlPO_4$ (Naeem, *et al*. 2002), Cu^{2+} (Rauf, *et al*. 1999), Pb^{2+} (Rauf and Tahir 2001), Ni^{2+} (Rauf, *et al*. 2003), Fe^{2+} (Naseem and Tahir 2004) adsorption onto bentonite.

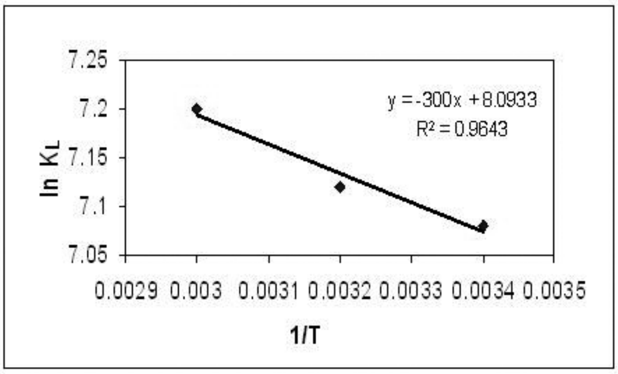

Fig. 7. Plot of the Langmuir isotherm constant ($\ln K_L$) vs. temperature (1/T) (The thermodynamic parameters of adsorption of Cu (II) in Table (3) are determined from this graph).

Table 3. Thermodynamic constants for the adsorption of Cu(II) on commercial natural bentonite (NB) at various temperatures.

T (K)	Ln K_L	ΔG (k/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)	R (kJ/mol.K)
293	7.08	-17.2			
313	7.12	-18.56	2.494	67.29	8.3x 10-3
333	7.29	-19.9			

Effect of clay dosage

The effect of adsorption percentages of Cu (II) on NB was studied at different adsorbent doses (0.1, 0.3, 0.5, 0.7, 1, 2, 3, and 5 g/50 mL, respectively) keeping initial copper concentration (500 and 1000 mg/L), temperature (25 °C) and contact time (24 hr) constant. The results showed that with the increase in the adsorbent dose, the adsorption percentage of Cu (II) increased and the maximum removal was observed with increasing adsorbent dose (Figure 8). Increase in the percentage adsorption with adsorbent dose may be due to the increase in adsorbent surface area and availability of more adsorption sites (Rengaray, *et al.* 2001; Lakatos, *et al.* 2002; Dakiky, *et al.* 2002; Yu, *et al.* 2003; Yabe, *et al.* 2003; Garg, *et al.* 2004). However, unit adsorption (adsorbed amount, mg/g) was decreased with increase in adsorbent dosage (Figure 9). As the adsorbent dose was increased the unit adsorption decreased. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles (Naseem and Tahir 2001).

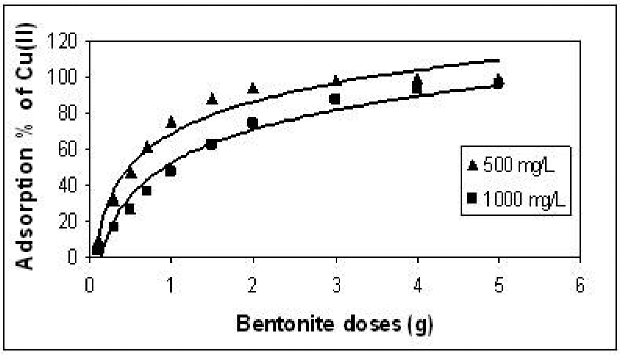

Fig. 8. Removal percentage of Cu(II) as a function of bentonite (NB) doses.

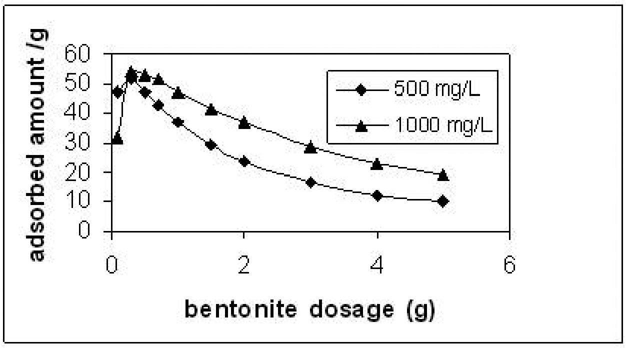

Fig. 9. Adsorbed amount of Cu (II) as a function of bentonite (NB) doses.

Effect of initial pH

Figure (10) shows the adsorbed amount of Cu (II) as a function of equilibrium pH with 10 g/L of NB solution containing of Cu(II). The adsorbed amount of Cu (II) increased abruptly in the pH range from 4.0 to 8.0. Since the copper hydroxide precipitate was found only at pH > 7.0 (Weng, *et al.* 2007), it is confirmed that the removal of Cu (II) by NB at pH < 7.0 was accomplished by adsorption. Marked removal of Cu (II) (>95%) was achieved in the neutral to alkaline regions, which is attributed to concurrent Cu $(OH)_2$ precipitation along with adsorption. It can be seen that the adsorption of Cu (II) on bentonite is markedly pH-dependent. As the surface of bentonite is more protonated at a low pH, it is less able to retain heavy metal ions (Neubauer, *et al.* 2000). The reason for this is that the surface complexation reactions are influenced by the electrostatic attraction between negatively charged groups at the bentonite surface and the ions (Abollino, *et al.* 2003). When adsorption occurs below pH 5.00, the two ions are below the pH of precipitation. In such a system H^+ competes with metal ions, resulting in active sites becoming protonated to the virtual exclusion of metal binding on the bentonite surface (Barbier, *et al.* 2000). This means that at higher H+ concentrations, the bentonite surface becomes more positively charged thus reducing the attraction between surface and metal cations. As the pH increases, more negatively charged surface becomes available thus facilitating greater metal uptake (Bradl, 2004). In return, due to some removal of metals by precipitation above precipitation pH of 5.0, metals were removed by both adsorption and precipitation.

Measuring the values of pH of the NB suspension before and after Cu (II) adsorption can give good conformation for supporting the above comments. Figure (11) shows the pH values of NB suspension before and after Cu (II) adsorption. As can be seen from this figure, there is little increase in the final suspension pH after Cu (II) adsorption compared to pH before Cu (II) adsorption. This result may be attributed to the replacement of alkaline and alkaline earth metals (Na^+, K^+, Ca^{2+} and Mg^{2+}) located in the exchange sites of natural bentonite (NB) with Cu (II) ions existed in the solutions. Furthermore, carbonate, which is present in the natural bentonite structure, may also be dissolved.

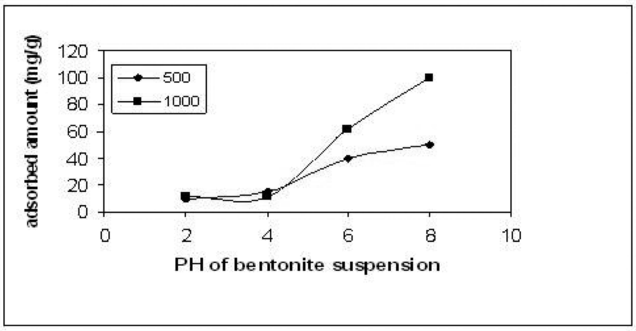

Fig. 10. Effect of pH on Cu (II) adsorption onto NB at two Cu (II) concentration (500 and 1000mg/L.

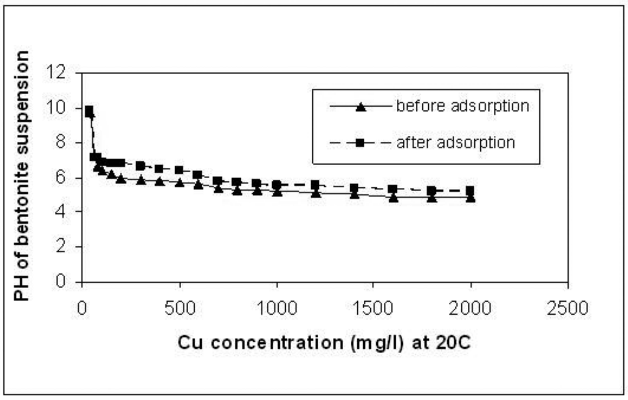

Fig. 11. pH values of bentonite suspension before and after Cu (II) adsorption onto NB surface at 298 K.

Desorption

In metal ion removal process, it is important to study the desorption of the adsorbed metal ions under suitable conditions. In the desorption studies deionized water was used as desorption agent. The NB samples loaded with different adsorbed amount of Cu (II) ions (initial copper concentration = 500, 1000 and 2000 mg/L) were placed in 50 mL deionized water and the amount of Cu (II) ions desorbed within 2 hr measured. Table (4) shows the data of the adsorbed and desorbed amount of Cu (II).ions. The results indicate that there are about 0.056, 0.055 and 0.063% Cu (II) ions desorbed from NB surface loaded by 26.7, 21.7 and 26.6 mg/g, indicating the strong contact between Cu (II) ion and NB surfaces.

Table 4. Adsorbed and desorption % of Cu(II) from NB surfaces.

Initial Cu(II) concentrations (mg/L)	Adsorbed amount (mg/g)	Desorbed (%)
500	26.7	0.056
1000	21.7	0.055
2000	26.6	0.063

Effect of Bentonite Treatment

Figure (12) shows the maximum adsorbed amount of copper ions on NB, WB and CB at initial copper concentrations, 500 and 1000 mg/L. The adsorbed amount of copper ions on WB was significantly higher compared to NB. This result may be due to removal of dissolved and excess salts located in the exchange sites of commercial bentonite (untreated, NB) upon washing. Therefore, the exchange sites on bentonite surfaces increased and consequently become available for more adsorption of copper ions from solution. In addition, it is observed that the adsorbed amount of Cu (II) on CB was lower compared to NB (Figure 12),. Many investigators have indicated that heat treatment of clay leads to dehydration and dehydroxylation of the bentonite, decrease of cation exchange capacity and surface area, and consequently decrease in the adsorption capacity (Bujdak, *et al*. 1997; Suraj, *et al*. 1998; Alkan, *et al*. 2005; Önal, 2007).

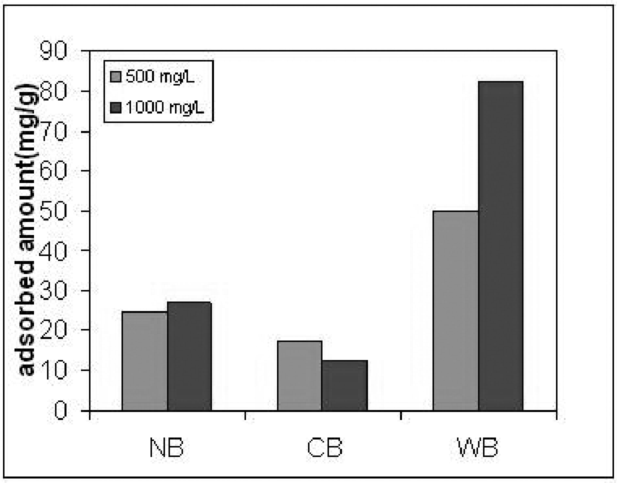

Fig. 12. The adsorbed amount of Cu (III) on NB, calcined bentonite at 700 °C (CB) and washed bentonite (WB) at initial concentration, 500 and 1000 mg/L.

Comparison of Various Low-cost Adsorbents

A comparison of the adsorption affinity KL and the maximum Cu(II) adsorption capacity, Q_m, of natural commercial bentonite (NB) with those of other low-cost adsorbents reported in the literature is given in Table (4). The adsorption capacities of NB and Washed bentonite (WB) are considerably higher when compared with other adsorbent, such as Activated carbon (Machida, *et al.* 2005), Gafted silica (Ciron, *et al.* 2003), Natural zeolites (Machida, *et al.* 2005), Silica (Chiron, *et al.* 2003), Fly ash (Panday, *et al.* 1985) and Aluminas (Rengaraj, *et al.* 2004). Furthermore, although the adsorption capacity of calcined bentonite (CB) is lower compared to NB and WB, it can be seen that it still exhibits a much higher adsorption capacity than the other adsorbent indicated in Table (5).

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Table 5. Adsorption capacity of Cu (II) by various adsorbents.

Adsorbents	Temperature (K)	QM (mg/g)	Sources
Activated carbon	293	3.56	Machida, *et al*. (2005)
Grafted silica	293	16.57	Chiron, *et al*. (2003)
Natural zeolites	303	8.79	Machida, *et al*. (2005)
Silca	293	2.3	Chiron, *et al*. (2003)
Aluminas	298	8.55	Rengaraj, *et al*. (2004)
Natural bentonite	293	24.5	This work
	313	35.5	This work
	333	39.3	This work
Washed bentonite(WB)	298	82.1	This work
Calcined bentonite (CB)	298	17.4	This work

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