

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

Removal of Copper (II) Ions from Aqueous Solutions using Na-mordenite

Xue-Song Wang^a; Hai-Qiong Hu^a; Cheng Sun^b

^a Department of Chemical Engineering, Huaihai Institute of Technology, Lianyungang, Jiangsu, P. R. China ^b School of the Environment, Nanjing University, Jiangsu, P. R. China

To cite this Article Wang, Xue-Song , Hu, Hai-Qiong and Sun, Cheng(2007) 'Removal of Copper (II) Ions from Aqueous Solutions using Na-mordenite', *Separation Science and Technology*, 42: 6, 1215 — 1230

To link to this Article: DOI: 10.1080/01496390701241956

URL: <http://dx.doi.org/10.1080/01496390701241956>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Removal of Copper (II) Ions from Aqueous Solutions using Na-mordenite

Xue-Song Wang and Hai-Qiong Hu

Department of Chemical Engineering, Huaihai Institute of Technology,
Lianyungang, Jiangsu, P. R. China

Cheng Sun

School of the Environment, Nanjing University, Jiangsu, P. R. China

Abstract: The potential to remove copper (II) ions from aqueous solutions using Na-mordenite, a common zeolite mineral, was thoroughly investigated. The effects of relevant parameters solution pH, adsorbent dose, ionic strength, and temperature on copper (II) adsorption capacity were examined. The sorption data followed the Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherms. The maximum sorption capacity was found to be 10.69 mg/g at pH 6, initial concentration of 40 mg/dm³, and temperature of 40°C. Different thermodynamic parameters viz., changes in standard free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) have also been evaluated and the results show that the sorption process was spontaneous and endothermic in nature. The dynamics of the sorption process were studied and the values of rate constant of adsorption, rate constant of intraparticle diffusion were calculated. The activation energy (E_a) was found to be 11.25 kJ/mol in the present study, indicating a chemical sorption process involving weak interactions between sorbent and sorbate. The interaction between copper (II) ions and Na-mordenite is mainly attributable to ion exchange. The sorption capacity increased with the increase of solution pH and the decrease of ionic strength and adsorbent dose. The Na-mordenite can be used to separate copper (II) ions from aqueous solutions.

Keywords: Adsorption, copper (II), Na-mordenite, sorption mechanism, wastewater treatment

Received 8 May 2006, Accepted January 2007

Address correspondence to Xue-Song Wang, Department of Chemical Engineering, Huaihai Institute of Technology, Lianyungang, Jiangsu 222005, P. R. China. Tel.: +86-518-5890786; E-mail: snowpine1969@yahoo.com.cn

INTRODUCTION

Copper (Cu), which is widely used, is one of the principal heavy metals responsible for causing hemolysis, liver, and kidney damage, irritation of the upper respiratory tract, gastrointestinal disturbance, diarrhea (1). The main anthropogenic pathway through which Cu (II) enters the water bodies is via wastes from industrial processes such as dyeing, paper, petroleum, copper/brass-plating, and copper-ammonium rayon. In the copper-cleaning, copper plating, and metal-processing industries, Cu (II) concentrations approach 100–200 mg/dm³; this value is very high with respect to water quality standards and Cu (II) concentration of wastewaters should be reduced to a value of 1.0–1.5 mg/dm³ (2).

Conventional methods for removing copper ions from aqueous solutions include chemical precipitation, chemical oxidation and reduction, ion-exchange, and activated-carbon adsorption (3). However, these processes have significant disadvantages such as incomplete metal removal, particularly at low concentrations and high operational costs (4). In recent years, zeolites have gained popularity in liquid-phase adsorption processes due to their low costs, high abundance, easy manipulation, and harmlessness to the environment (5). Because zeolites exchange cations easily, a lot of researchers have mainly focused on their use in removal of heavy metals from contaminated water sources (6–7). In this work, we show the application of Na-mordenite (a common zeolite mineral) in the removal of copper (II) ions from aqueous solutions.

MATERIALS AND METHODS

Naturally occurring mordenite was provided for study by China University of Mining and Technology. The mordenite was lightly ground and sieved. Fine particles with a diameter < 150 µm were used to prepare the Na-mordenite. To prepare homoionic Na-mordenite, 30 g of mordenite was mixed with 500 cm³ of 1 M NaCl. After 24 h end-over-end shaking, the mordenite suspension was centrifuged at 3000 rpm and the supernatant was replaced with fresh 1 M NaCl solution. This procedure was repeated three times, followed by a three-fold washing with 500 cm³ de-ionized water. The Na-mordenite was dried at 60°C overnight and stored in polyethylene flask for further experiments.

The stock solutions of Cu²⁺ (2000 mg/dm³) were prepared in de-ionized water using copper sulfate (CuSO₄ · 5H₂O) (analytical grade reagent). All working solutions were prepared by diluting the stock solution with de-ionized water.

Batch adsorption experiments were carried out by shaking 0.25 g of sorbent with 50 cm³ aqueous solution of the desired concentration in a temperature-controlled water-bath shaker. The pH of solutions was adjusted to constant values. Continuous mixing was provided during the experiments

with a constant agitation speed of 200 rpm. Kinetic studies were carried out at constant pH 6 with initial concentration (40 mg/dm^3) and adsorbent dose of 2 g/dm^3 at various temperatures ($20, 30, 40^\circ\text{C}$). After shaking, the samples were withdrawn at suitable time intervals, filtered through a $0.45 \mu\text{m}$ membrane filter, and then analyzed for Cu^{2+} concentrations with an atomic absorption spectrophotometer (AAS). For the isotherm studies, 0.25 g of Na-mordenite was put into 50 cm^3 solutions of various concentrations of Cu^{2+} (20 to 100 mg/dm^3). The flasks were shaken for 30 min to reach equilibrium. A known volume of the solution was removed and filtered for Cu^{2+} analysis. The effect of pH on the adsorption of Cu^{2+} was studied by varying the pH from 2.0 to 6.0 . The effect of temperature on adsorption equilibrium was studied by varying temperatures from 20 to 40°C . The effect of the sorbent dose on the uptake of Cu^{2+} was investigated by varying the range of Na-mordenite doses from 1.0 to 5.0 g/dm^3 with an initial concentration 40 mg/dm^3 and agitation speed of 200 rpm . 0.1 and 0.01 M NaNO_3 were employed as background electrolyte to investigate the effect of ion strength on uptake of Cu^{2+} .

The amount of Cu^{2+} sorbed by Na-mordenite (q) in the sorption system was calculated using the mass balance:

$$q = \frac{V(C_i - C_e)}{M} \quad (1)$$

where V is the solution volume (dm^3), M the amount of sorbent (g), and C_i and C_e (mg/dm^3) the initial and equilibrium metal concentrations, respectively.

XRD measurement was done with Analytical X-ray spectrometer (D/Max-3B) using $\text{Cu K}\alpha$ radiations. Sears's method was chosen to estimate the surface area of the Na-mordenite and the copper bisethylenediamine complex method was used to determine the cation exchange capacity (CEC) of the Na-mordenite. The detailed procedures for the determinations of the surface area and cation exchange capacity are referred to by (8). The particle sizes of Na-mordenite sample were analyzed using Coulter Laser equipment. Samples were stirred and ultrasound used to facilitate particle dispersion.

RESULTS AND DISCUSSION

Adsorbent Characterization

The XRD spectrum of the Na-mordenite is given in Fig. 1. The result indicates that the adsorbent used in this study consists mainly of mordenite. The surface area of a porous material is one of the most useful micro-structural parameters for defining its properties. It is the total internal boundary between the solid phase and the pore system (8). The specific surface area of Na-mordenite was $7.0 \text{ m}^2/\text{g}$. The CEC is the number of equivalents of exchangeable charge per mass of adsorbent. In this work, the value of Na-mordenite CEC

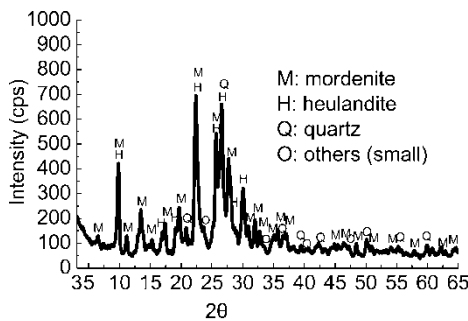


Figure 1. XRD pattern for Na-mordenite.

was found to 14.2 meq/100 g. These values (specific surface area and CEC) are comparable to those of kaolinite with the similar determination methods (8). The mean diameter of the sample used in these experiments is 107.2 μm.

Effect of Agitation Time

The distribution of the sorbate between sorbent and solution is influenced by agitation time. The effect of shaking time on the sorption at various temperatures was studied between 1 and 30 minutes. The results are presented in Fig. 2. In general, a two-stage kinetic behavior is observed: very rapid initial sorption in a contact time of 2 minutes, followed by a second stage with a much lower sorption rate. In process application, this rapid sorption phenomenon is very advantageous. According to these results, the 30 min agitation time was considered to be sufficient for the sorption of Cu (II) onto Na-mordenite and was used for all the rest of the batch

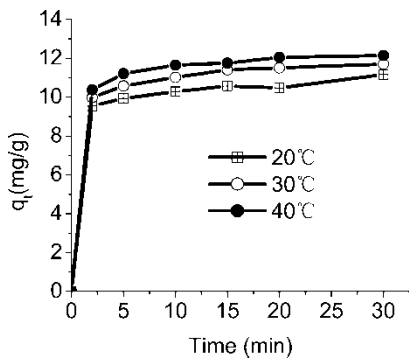


Figure 2. Variation of Cu (II) sorption capacity against time at various temperatures (adsorption dose: 2 g/dm³; initial concentration: 40 mg/dm³, pH 6).

experiments. Figure 2 also shows that the amount of Cu (II) uptake per unit weight of Na-mordenite increases with increasing temperature.

Kinetic Modeling

The investigation of the kinetics of sorption is critical to understanding the influence of variables on sorption. The sorption rate is particularly important, mainly in applications as in the industrial wastewater treatment. Different models were used in this study to determine the sorption kinetics of Cu (II), the Lagergren first-order rate model [equation 2] (9), the pseudo-second-order model [equation 3] (10), the intraparticle diffusion model [equation 4] (11).

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_{\max}^2} + \frac{1}{q_{\max}} t \quad (3)$$

$$q_t = k_p t^{0.5} \quad (4)$$

where q_e and q_t are the amounts of copper ions adsorbed onto the sorbent (mg/g) at equilibrium and at any given time t (min), respectively; k_1 the rate constant of first-order (min^{-1}); q_{\max} the maximum adsorption capacity (mg/g), k_2 [g/(mg min)] the rate constant of the pseudo-second-order model; k_p [mg/(g min^{0.5})] the intraparticle diffusion rate constant of the Morris-Webber model.

The values of k_1 , k_2 and the correlation coefficients R_1 and R_2 calculated for the adsorption of Cu (II) at various temperatures from the linear plots are listed in Table 1. The first-order equation of Lagergren did not apply well the entire range of contact times, which can be seen in Fig. 3(a). The sorption system does not therefore follow a first-order reaction. The insufficiency of the first-order model to fit the kinetic data could possibly be due to a boundary layer controlling the beginning of the sorption process (12).

The pseudo-second order model is based on the assumption that the rate limiting step may be a chemical sorption involving valence forces through sharing or exchange of electrons between the sorbent and the sorbate (4). The correlation coefficients at various temperatures are considerably lower

Table 1. Kinetic parameters for the adsorption of Cu (II) onto Na-mordenite (adsorbent dose: 2 g/dm³; initial concentration: 40 mg/dm³; initial pH 6)

Temperature (°C)	k_1 (min ⁻¹)	R_1	k_2 [g/(mg min)]	R_2	K_p [mg/(g min ^{0.5})]	R_p
20	0.052	0.920	0.1200	0.9990	0.365	0.975
30	0.123	0.970	0.1422	0.9999	0.425	0.970
40	0.144	0.994	0.1612	0.9999	0.413	0.939

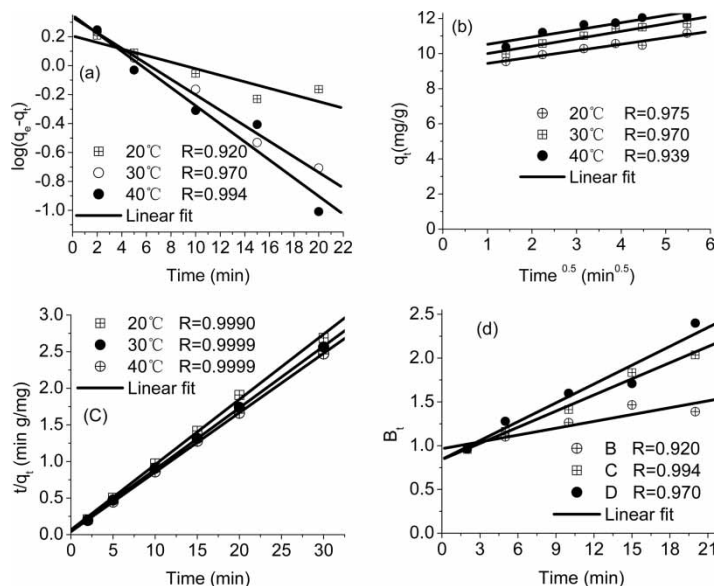


Figure 3. Kinetic models: (a) Lagergren model, (b) Morris-Webber model, (c) pseudo-second order model, (d) Reichenberg model for the adsorption of Cu (II) onto Na-mordenite at various temperatures (adsorbent dose: 2 g/dm³; initial concentration: 40 mg/dm³; initial pH 6).

for intraparticle diffusion compared to those of the pseudo-second order where the coefficients are all in excess of 0.99 (Fig. 3(c) and Table 1). The nature of the rate-limiting step in a batch system can be assessed from the properties of the solute and sorbent (13).

According to McKay (14), there are four stages in the adsorption process of which any one or more may control the rate at which the solute is adsorbed and the amount of solute that is adsorbed onto the solid particles. The four steps are described as:

- (i) solute transfer from the bulk solution to the boundary film,
- (ii) solute transport from boundary film to the surface of the sorbent (external diffusion),
- (iii) transfer of the solute from the surface of the sorbent to the intraparticle active sites (intraparticle diffusion),
- (iv) uptake of the solute on the active sites.

The first and fourth steps are considered as non-limiting as the agitation provided is sufficient to avoid a concentration gradient in the solution, whereas the sorption is seen as a quasi instantaneous mechanism. So, the external mass transfer resistance and the intraparticle mass transfer resistance are the major controlling stages.

According to equation (4) for intraparticle diffusion by Webber and Morris, the plot for q_t against $t^{0.5}$ should be linear. From Table 1 and Fig. 3 (b), it is evident that intraparticle diffusion is not the sole rate-determining step and that Cu (II) sorption onto Na-mordenite is best represented by a pseudo-second order rate model.

The Reichenberg equation was also applied to check that sorption proceeds via external diffusion or intraparticle diffusion mechanism (15). The Reichenberg equation can be expressed in the following form:

$$X = \left(1 - \frac{6}{\pi^2}\right) e^{-B_t} \quad (5)$$

where $X = q_t/q_e$ and B_t is a mathematical function of X which can be calculated from each value of X as:

$$B_t = -0.4977 \ln(1 - X) \quad (6)$$

Plots of B_t versus t are also shown in Fig. 3(d), which are straight lines. Figure 2(d) shows that intraparticle diffusion is the rate controlling step with a small fraction of the sorption that occurs through external diffusion (film diffusion) because the plots do not pass through the origin.

Table 1 also indicates that the values of k_2 increase with increase in temperature. The increase in the rate of adsorption with increasing temperature is described by the Arrhenius equation:

$$\ln k_2 = \ln A_0 - \frac{E_a}{RT} \quad (7)$$

where A_0 is the temperature independent factor called "frequency factor," E_a the activation energy (kJ/mol), R is the gas law constant (8.314 J/mol K), and T is the absolute temperature (K).

A linear relationship was obtained between $\ln k_2$ and $1/T$ (Fig. 4). The values of A_0 and E_a were calculated from the intercept and slope of the $\ln k_2$ versus $1/T$ plot and were found to be 12.18 g/mg min and 11.25 kJ/mol, respectively. The value of 11.25 kJ/mol in the present study indicates a chemical sorption process involving weak interactions between the sorbent and the sorbate (16). The relatively low E_a value suggests that the adsorption has a low potential energy barrier.

Adsorption Isotherm

In the present investigation, the data from the equilibrium batch sorption experiments were applied to the Langmuir isotherm (17). The basic assumption of the Langmuir adsorption isotherm is based on monolayer coverage of

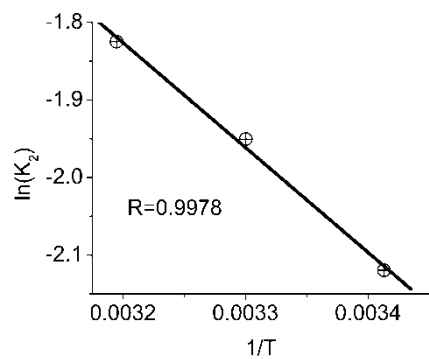


Figure 4. Plot of $\ln K_2$ against $1/T$.

the sorbate on the surface of adsorbent. The linearized form of the Langmuir equation is

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_a} \tag{8}$$

where C_e (mg/dm³) is the equilibrium concentration of the adsorbate, q_e (mg/g) the amount of the adsorbate adsorbed at equilibrium, q_m (mg/g) and K_a (dm³/g) Langmuir's constants related to the capacity and energy of the adsorption, respectively. The linear nature of the curve was found by plotting C_e/q_e versus C_e at different temperatures (Fig. 5), suggesting the applicability of the Langmuir isotherm for the present system. The values of q_e and K_a at various temperatures were determined from the slopes and intercepts of the respective plots and are presented in Table 2. From these results it was clear that the values of the maximum adsorption capacity (q_m) increased with the rise of temperature. Further, it confirmed the fact that an endothermic process took place in this adsorption system. The Langmuir isotherm constant (K_a) can be used to

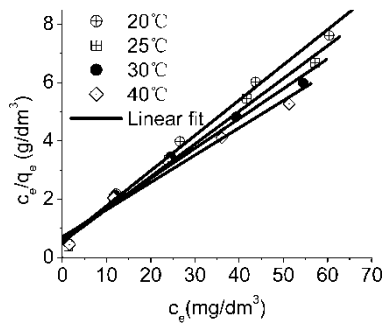


Figure 5. Langmuir isotherm plots for the adsorption of Cu (II) onto Na-mordenite at various temperatures.

Table 2. Langmuir and Freundlich isotherms constants and correlation coefficients

Temperature (°C)	Langmuir			Freundlich		
	q _m (mg/g)	K _a (dm ³ /mg)	R	K _F	n	R
20	8.267	0.2170	0.9962	3.268	4.46	0.9995
25	8.916	0.2122	0.9940	3.427	4.51	0.9956
30	9.778	0.1517	0.9902	3.153	3.85	0.9947
40	10.692	0.1328	0.9846	3.079	3.55	0.9897

indicate the affinity of Na-mordenite towards copper (II) ion. It is seen from Table 2 that the values of K_a decreased with the rise of temperature.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, R_L, which is defined as:

$$R_L = \frac{1}{1 + K_a C_i} \quad (9)$$

where K_a is the Langmuir constant and C_i is the initial concentration of copper (II) ions. The value of R_L indicates the shape of the isotherm as follows:

R _L value	Type of isotherm
R _L > 1	Unfavorable
R _L = 1	Linear
0 < R _L < 1	Favorable
R _L = 0	Irreversible

According to Singh et al. (18), R_L values between 0 and 1 indicate a favorable adsorption process.

In the present investigation, the values of the separation factor, R_L, indicated that the sorption process was very favorable and the adsorbent employed exhibited an optimum potential (Fig. 6).

The Freundlich isotherm is another widely used sorption model. The Freundlich equation proposes a monolayer sorption with a heterogeneous energetic distribution of active sites and with interactions between sorbed molecules (19). The linearized form of the Freundlich isotherm is

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (10)$$

where C_e is the equilibrium concentration (mg/dm³), q_e the amount adsorbed at equilibrium (mg/g) and K_F and n constants incorporating all factors affecting the adsorption process, such as the adsorption capacity and intensity, respectively. Values of K_F and n were obtained from the intercepts and slopes of the plots of log q_e versus log C_e and are shown in Table 2.

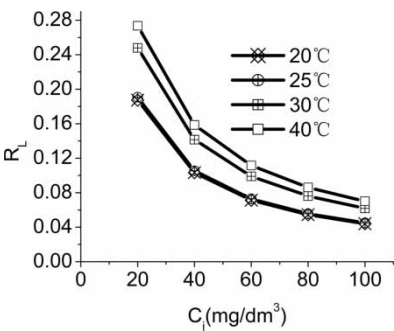


Figure 6. Plots of R_L versus initial concentration (C_i) at various temperatures.

Figure 7 shows that the Freundlich isotherm fits the experimental data very well. According to Kadirvelu and Namasivayam (20), n values between 1 and 10 represent beneficial adsorption.

Thermodynamic parameters including the standard enthalpy change (ΔH^0), the Gibbs free energy change (ΔG^0), and the entropy change (ΔS^0) for the adsorption of Cu (II) onto Na-mordenite have also been calculated using the following equation (11), (12) and (13) (21):

$$\Delta G^0 = -nRT \tag{11}$$

$$\ln C_e = -\ln K_0 + \frac{\Delta H^0}{RT} \tag{12}$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \tag{13}$$

where n represents the Freundlich constant, R is the gas law constant [J/mol K], and T is the absolute temperature (K). C_e is the Cu (II) concentration at

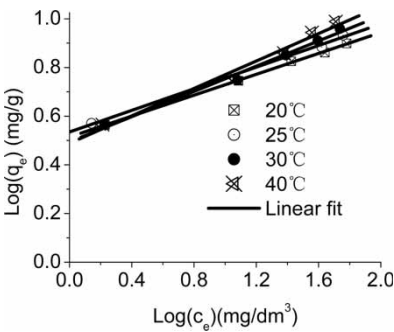


Figure 7. Freundlich isotherm plots for the adsorption of copper (II) ion onto Na-mordenite at various temperatures.

Table 3. Thermodynamic parameters at various temperatures

Temperature (°C)	ΔG ⁰ (kJ/mol)	ΔS ⁰ (J/mol)	ΔH ⁰ (kJ/mol)
20	−10.86	58.07	6.15
25	−11.17	58.13	
30	−9.69	52.31	
40	−9.23	49.16	

equilibrium (mg/dm³), and K₀ a constant. The values of these parameters were calculated and are presented in Table 3. It is obvious from this table that the negative values of free energy change (ΔG⁰) were an indication of the spontaneous nature of the adsorption process. The positive value of standard enthalpy change (ΔH⁰) indicated the endothermic nature of the adsorption process and the positive values of ΔS⁰ suggested the increasing randomness at the solid/solution interface at various temperatures.

The data were also fitted to the Dubinin-Radushkevich (D-R) isotherm (21) to evaluate the nature of sorption. This model envisages about the heterogeneity of the surface energies and can be written in the following linear form (15):

ln q_e = ln X_m − βF² (14)

F = RT ln(1 + 1/C_e) (15)

where q_e is the amount of sorbate sorbed by the Na-mordenite (mol/g), X_m is the maximum sorption capacity of sorbent (mol/g) under investigation, β is a constant (kJ²/mol²) related to energy, F is polar potential, R is the gas law constant [J/mol K], T is the absolute temperature (K), and C_e is the concentrations at equilibrium (mol/dm³).

The plots of ln (q_e) against F² are linear with high correlation coefficients at various temperatures (Fig. 8 and Table 4). This shows that the D-R sorption isotherm is applicable and reliable for this adsorption system studied. The constant (β) was obtained from the slope of the plot of ln (q_e) versus F² and the values are given in Table 4.

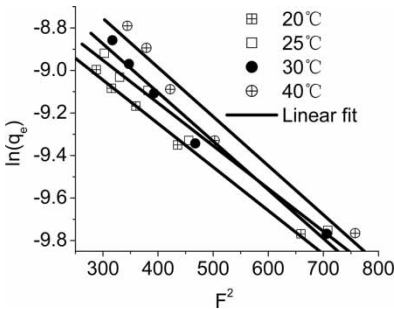


Figure 8. D-R sorption isotherms of Cu (II) onto Na-mordenite

Table 4. Constants of D-R sorption isotherm and sorption energy (E_s)

Temperature (°C)	R	β (kJ ² /mol ²)	E_s (kJ/mol)
20	0.9979	−0.00205	15.62
25	0.9920	−0.00201	15.77
30	0.9881	−0.00229	14.77
40	0.9813	−0.00231	14.71

The values of sorption energy (E_s) (kJ/mol) can be correlated to β by using the following relationship (15):

$$E_s = 1/\sqrt{-2\beta} \tag{16}$$

If the magnitude of E_s is between 8 and 16 kJ/mol, the adsorption process proceeds by ion exchange, while for values of $E_s < 8$ kJ/mol, the adsorption process is of a physical nature (5). The values of sorption energy are presented in Table 4 and the results show that the interaction between copper (II) ions and the Na-mordenite proceeded by ion exchange. These results are in agreement with those obtained in the study of interaction between copper (II) ions and HEU-type zeolites, which are defined as the zeolite mineral series having the distinctive framework topology of heulandite and the ratio Si/Al > 4 (22).

Effect of Solution pH

The experimental results obtained for copper ions uptake by Na-mordenite under different initial pH conditions are shown in Fig. 9. The copper (II) ions uptake was sensitive to pH variation over the examined range of 2 to 6. At low pH values, the surface of the sorbent would be also surrounded by H^+ ions, which decrease the copper interaction with binding sites of the

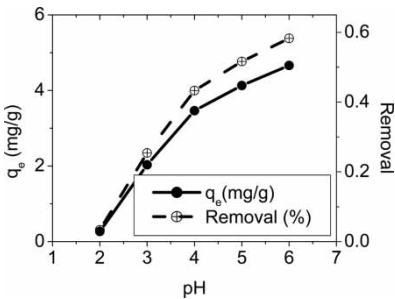


Figure 9. Effect of solution pH on uptake of copper ions on Na-mordenite (sorbent dose: 2 g/dm³; initial concentration: 40 mg/dm³; agitation speed: 200 rpm)

Na-mordenite by greater repulsive forces. As the pH increased, the overall surface on the Na-mordenite became negative and adsorption increased.

The percentage removal of copper (II) ion was obtained by calculation using the following equation:

$$\text{Removal (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (17)$$

where C_i and C_e (mg/dm³) represent the initial concentration and equilibrium concentration, respectively. The copper ion removal against pH of solution is also shown in Fig. 8. At pH 2, the maximum Cu (II) removal efficiency was only 3.34%, whereas at pH 6 the removal efficiency increased to 58.26%. Further increase in pH was not attempted because of the possibility of precipitation of the copper ions at pH > 6.

Effect of Sorbent Dose

The effects of the adsorbent dose on the uptake and removal of copper (II) ions are illustrated in Fig. 10. As the sorbent dose was increased from 1.0 to 5.0 g/dm³, the equilibrium sorption capacity, q_e , decreased from 23.89 to 6.03 mg/g. However, the copper ion removal efficiency, increased from 59.73 to 75.42% with an increase in the sorbent dose of from 1.0 to 5.0 g/dm³. Evidently, the equilibrium sorption capacity and removal are sensitive to the variation of sorbent dose.

Effect of Ionic Strength

Ionic strength has a key impact on the uptake of the copper (II) ion uptake onto Na-mordenite (Fig. 11). In the presence of 0.01 and 0.1 M NaNO₃, the maximum uptake capacities (q_m) of the copper ion were decreased with the

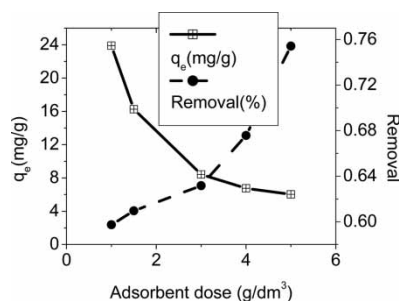


Figure 10. Effect of sorbent dose on uptake of copper ions on Na-mordenite (initial solution pH 6; initial concentration: 40 mg/dm³; agitation speed: 200 rpm)

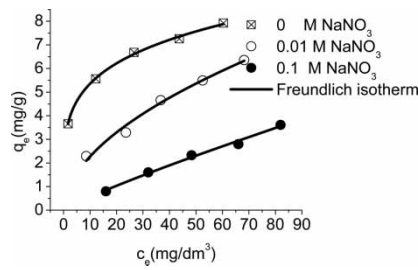


Figure 11. Effect of ion strength on copper ion uptake (20°C, initial concentration 40 mg/dm³; sorbent dose 2 g/dm³).

increase in the ionic strength. This can be explained in terms of two aspects. Firstly, the competition of Na⁺ ions with the copper (II) ions for sorption sites of Na-mordenite resulted in the observed decrease in the maximum uptake capacities with increasing electrolyte NaNO₃ concentration. Secondly, adsorption is sensitive to the change in ionic strength if electrostatic attraction is a significant mechanism. Thus the results show electrostatic attraction plays an important role in the adsorption of copper (II) ions onto Na-mordenite (23). At high ionic strength, the increased amount of NaNO₃ can help to swamp the surface of the sorbent, which decrease the copper ion's access to the surface sites. When a solid adsorbent is in contact with sorbate species in solution, they are bound to be surrounded by an electrical diffused double layer, the thickness of which is significantly expanded by the presence of the electrolyte. Such expansion inhibits the sorbent particles and copper ions

Table 5. Uptake capacities for Cu (II) of various adsorbents reported in the literature

Adsorbent	q _m (mg/g)	References
Baggase fly ash	2.26	(24)
Clinoptilolite	3.8	(8)
Groundnut shell	4.48	(26)
Chabazite	5.1	(8)
Sawdust	5.12	(25)
Lignite	6.4	(26)
<i>C. rangiformis</i>	7.68	(2)
Wheat shell	8.32	(27)
Pine bark	9.47	(28)
Tree fern	10.6	(29)
Na-mordenite	10.69	This study
Cotton boll	11.4	(1)
Activated carbon (Filtrisorb 200)	24.1	(30)

from approaching each other more closely and, through the decreased electrostatic attraction, results in the decreased uptake of copper ions (16).

Comparison with other Adsorbents

In order to justify the validity of Na-mordenite as an adsorbent for adsorption, its adsorption potential must be compared with various other adsorbents used for this purpose. The values of maximum sorption capacity reported in the literature are given in Table 5. It shows that Na-mordenite has good adsorption capacity when compared with other adsorbents. The adsorption capacity differences of copper (II) ion uptake are ascribed to the properties of different adsorbent such as structure, functional groups and surface areas (1).

CONCLUSIONS

Na-mordenite was found to be an effective sorbent for the removal of copper (II) ions from wastewater. It was noted that an increase in the temperature and decrease with the sorbent dose and ionic strength resulted in a higher copper loading per unit weight of the sorbent. The sorption of copper ions onto Na-mordenite was found to be pH dependent. The sorption of copper (II) ions onto Na-mordenite is due to its spontaneous and endothermic nature. Adsorption data indicate the applicability of pseudo-second order kinetics. These results show that Na-mordenite can be used for the removal of copper (II) ions from aqueous solutions.

REFERENCES

1. Ozsoy, H.D. and Kumbur, H. (2006) Adsorption of Cu (II) ions on cotton boll. *J. Hazar. Mater.*, In print, doi: 10.1016/j.jhazmat.2006.01.035.
2. Ekmekyapar, F., Aslan, A., Bayhan, Y.K., and Cakici, A. (2006) Biosorption of copper (II) by nonliving lichen biomass of *Cladonia rangiformis* hoffm. *J. Hazar. Mater.*, In print, doi: 10.1016/j.jhazmat.2006.02.003.
3. Wang, X.S. and Qin, Y. (2005) Equilibrium sorption isotherms for Cu^{2+} on rice bran. *Process Biochem.*, 40: 677–680.
4. Cochrane, E.L., Lu, S., Gibb, S.W., and Villaescusa, I. (2006) A comparison of low-cost biosorbents and commercial sorbents for the removal of copper from aqueous media. *J. Hazar. Mater.*, In print, doi: 10.1016/j.jhazmat.2006.01.054.
5. Onyango, M.S., Kojima, Y., Kumar, A., and Kuchar, D. (2006) Uptake of fluoride by Al^{3+} pretreated low-silica synthetic zeolites: adsorption equilibrium and rate studies. *Sep. Sci. Technol.*, 41: 683–704.
6. Garcia-Sanchez, A., Alastuey, A., and Querol, X. (1999) Heavy metal adsorption by different minerals: application to the remediation of polluted soils. *Sci. Total Environ.*, 242: 179–188.
7. Ouki, S.K. and Kavannagh, M. (1999) Treatment of metals-contaminated wastewaters by use of natural zeolites. *Wat. Sci. Tech.*, 39: 115–122.
8. Bhattacharyya, K.G. and Gupta, S.S. (2006) Kaolinite, Montmorillonite, and their modified derivatives as adsorbents for removal of Cu (II) from aqueous solution. *Sep. Purif. Technol.*, In print doi: 10.1016/j.seppur.2005.12.014.

9. Lagergren, S. (1889) Theorie der sogennanten adsorption geloster stoffe. *K. Seveska Veterskapad Handle*, 24: 1–39.
10. Ho, Y.S. (2003) Removal of copper ions from aqueous solution by tree fern. *Wat. Res.*, 37: 2323–2330.
11. Morris, W.J. and Weber, J.C. (1963) Kinetics of adsorption on carbon from solution. *J. Saint, Eng. Div., ASCE.*, 89: 31–59.
12. Ho, Y.S., Ng, J.C.Y., and McKay, G. (2000) Biosorption of copper from wastewaters: a review. *Sep. Purif. Methods*, 29: 189–232.
13. Ho, Y.S. and McKay, G. (2003) Sorption of dyes and copper onto biosorbents. *Process Biochem.*, 38: 1047–1046.
14. McKay, G. (1984) The sorption of basic dye onto silica from aqueous solution-solid diffusion model. *Chem. Eng. Sci.*, 39: 129–138.
15. Ahmad, R. (2005) Sawdust: cost effective scavenger for the removal of chromium (III) ions from aqueous solutions. *Water, Air, and Soil Pollution*, 163: 169–183.
16. Krishnan, K.A. and Anirudhan, T.S. (2003) Removal of cadmium (II) from aqueous solutions by steam-activated sulphurised carbon prepared from sugarcane bagasse pith: kinetics and equilibrium studies. *Water S.A.*, 29: 147–156.
17. Langmuir, I. (1916) The constitution and fundamental properties of solids and liquids. *J. Am. Chem. Soc.*, 38: 2221–2295.
18. Singh, K.K., Singh, A.K., and Hasan, S.H. (2006) Low cost bio-sorbent “wheat bran” for the removal of cadmium from wastewater: kinetic and equilibrium studies. *Bioresource Technology*, 97: 994–1001.
19. Freundlich, H.M.F. (1906) Uber die adsorption in lasungen. *Z. Phys. Chem*, 57: 385–470.
20. Kadirvelu, K. and Namasivayam, C. (2003) Activated carbon from coconut coirpith as metal adsorbent: adsorption of Cd (II) from aqueous solution. *Adv. Environ. Res.*, 7: 471–478.
21. Dubinin, M. and Radushkevich, L.V. (1974) The equation of the characteristic curve of activated charcoal. *Proc. Acad. Sci. USSR, Phys. Chem. Sect.*, 55: 327.
22. Godelitsas, A. and Armbruster, T. (2003) HEU-type zeolites modified by transition elements and lead. *Micropor. Mesopor. Mater.*, 61: 3–24.
23. Das, N.C. and Bandyopadhyay, M. (1991) Removal of lead by vermiculate medium. *Appl. Clay Sci.*, 6: 221–231.
24. Gupta, V.K. and Ali, I. (2000) Utilization of bagasse fly ash (a sugar industry waste) for the removal of copper and zinc from wastewater. *Sep. Purif. Technol.*, 18: 131–140.
25. Shukla, S.R. and Pai, R.S. (2005) Adsorption of Cu (II), Ni (II), and Zn (II) on dye loaded groundnut shells and sawdust. *Sep. Purif. Technol.*, 43: 1–8.
26. Kaewsarn, P. (2002) Biosorption of copper (II) from aqueous solutions by pre-treated biomass of marine algae. *Padina sp. Chemosphere*, 47: 1081–1085.
27. Basci, N., Kocadagistan, E., and Kocadagistan, B. (2004) Biosorption of copper (II) from aqueous solutions by wheat shell. *Desalination*, 164: 125–140.
28. Al-Asheh, S., Banat, F., Al-Omari, R., and Duvnjak, Z. (2000) Prediction of binary sorption isotherms for the sorption of heavy metals by pine bark using single isotherm data. *Chemosphere*, 41: 659–663.
29. Ho, Y.S., Huang, C.T., and Huang, H.W. (2002) Equilibrium sorption isotherm from metal ions on tree fern. *Process Biochem.*, 37: 1421–1430.
30. Chen, J.P. and Wu, S. (2004) Simultaneous adsorption of copper ions and humic acid onto an activated carbon. *J. Colloid Interf. Sci.*, 280: 334–342.