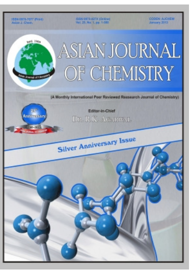
Asian Journal of Chemistry; Vol. 25, No. 6 (2013), 3161-3166

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13566



Adsorption Characteristics of Cu^{2+} on Natural Zeolite from Baiyin, China

BAOWEI ZHAO*, LI ZHANG, OBEMAH D. NARTY and RUIRUI LI

School of Environmental and Municipal Engineering, Lanzhou Jiaotong University, Lanzhou 730070, P.R. China

*Corresponding author: Fax: +86 931 4956017; Tel: +86 931 4938017; E-mail: baoweizhao@mail.lzjtu.cn

(*Received*: 7 February 2012; *Accepted*: 14 December 2012) AJC-12540

Heavy metal pollution of soils in Baiyin, China has become a more serious environmental problem. This paper attempts to present adsorption characteristics of Cu^{2+} on natural zeolite from Baiyin. The results showed that the adsorption depends on lower pH values (pH < 3) is explained by the dissolution of crystal structure and the competitive reaction between copper ions and H^+. The results also showed that the reduction in grain size leads to increase in the adsorption capacity of zeolite, in that an increase of zeolite dose results in an increase in the adsorption efficiency. Different electrolytes have different effect on adsorption of Cu^{2+}. The electrolytes employed exhibited the adsorption efficiencies in the order $NaNO_3 > KNO_3 > Mg(NO_3)_2 > Ca(NO_3)_2$. When the concentration of the electrolyte ($NaNO_3$) is between 0.0001 and 1 mol/L, adsorption capacity decreases initially, which will be attributed with increase in ionic concentration. The adsorption capacity of Cu^{2+} at 35 ºC was about 9 % more than at 15 ºC. The results also showed that the adsorption capacity increases with an increase in initial concentration of Cu^{2+}. This paper also discusses the kinetics and adsorption isotherms of Cu^{2+} on zeolite. The pseudo-second order model was found to be appropriate for kinetic analysis of the adsorption of Cu^{2+}, whiles the Langmuir isotherm was well fitted with the experimental data rather than Freundlich isotherm. Experimental data showed that zeolite has the immense potential of immobilizing heavy metals in the study area.

Key Words: Cu^{2+}, Adsorption, Zeolite, Baiyin.

INTRODUCTION

Baiyin is one of the most important industrial cities in China known for the processing non-ferrous metals. It is located in the central part of the Gansu Province. Heavy metal pollution of the soil in this area is an increasing environmental problem that requires an urgent attention. This results mainly from water used for irrigation from industrial wastewater, fertilizers and agrochemicals as well as sewage from inhabited area. This may be due to less precipitation in this area[1,2]. It has been reported that the amount of heavy metals such as Cu, Cr, Pb, Zn, Cd, As, Hg, *etc*., in the field soil from sewage and irrigation areas, have significantly exceeded the levels that are generally classified as environmentally acceptable. This effect has also resulted in a reduction of agricultural output even at some point in time the farmers recorded less or no harvest. This trend in farm outputs tends to increase year by year[3]. Excessive concentrations of heavy metals in soils pose serious and long-term threat to animals, human health and ecological systems because these contaminants are non-biodegradable by natural process and persistent in soils. They can accumulate and enter the food chain and eventually can get into animals and humans, causing various diseases. According to the present pollution situation, the soil remediation is essential and imminent for Baiyin and its environs.

There are three major technologies for remediating metal-contaminated soils. They include agricultural, physicochemical and biological treatment[4-6]. Agricultural methods comprise of earth swap and deep plowing, which show certain amount of risk. The earth swap as the most direct improved method is extremely expensive while the deep plowing method destroys the field and can also cause contamination of groundwater in the future. It is time-consuming and fails to prevent pollution expansion for the bio-treatment method. Physico-chemical technique includes extraction, stabilization and solidification which prevent effectively the transport of heavy metals into deeper soil layers and groundwater[7]. *In situ* metal inactivation (immobilization) belongs to a category of physicochemical method which is a technique that leads to amendments. This method uses clay minerals, lime, zeolite, peat and compost that are incorporated and mixed with the contaminated soil. Amendments basically interact with metals and change the speciation of metals, reducing their mobility, leaching and bioavailability in the soil[8,9]. Zeolite may be more suitable for remediation of contaminated soils by heavy metal than any other amendments, because it favourably adjusts soil pH value, improves soil granular structure and does not import new pollutants[10].

The use of natural zeolite as an amendment technique has gained interest among researchers, due to its particular structure, high ion exchange capacity and superior sorption property[11]. As nontoxic, ecologically advantageous and affordable materials, these natural zeolites have also been used successfully in the remediation strategies especially to immobilize heavy metals in soils. Zeolites are hydrated and crystallized aluminosilicates with a three-dimensional framework structure consisting of SiO_4 and AlO_4 that are tetrahedrally connected by all their oxygen at the vertices forming interconnected cavities and channels where H_2O molecules and exchangeable cations (Na^+, K^+, Ca^{2+} or Mg^{2+}) balance the negative charge generated from the isomorphous replacement of Si by Al[12-14]. These innocuous cations are easily exchangeable with certain cations in soils such as copper, cadmium, zinc and lead. The natural zeolite of the clinoptilolite type is one of the world's most abundantly occurring and most abundantly used zeolitic minerals[15]. The reserve of natural zeolite minerals reaches more than 170 thousand tons of which the high-grade clinoptilolite minerals occupy 41-52 % in Pingchuan area of Baiyin City, China.

Considering other technologies for remediation of metal-contaminated soils will not only be expensive in terms of costs but also influence agriculture production in Baiyin and its environs which is relatively poor. From an economic point of view, the use of natural zeolite is most suitable in Baiyin for soil amendment due to its low costs and availability. However, studies on efficiency of heavy metals-removal by employing zeolite from Baiyin are limited in literature. The use of zeolite from Baiyin and its environs for remediation of metal-contaminated soils, will probably provides an effective way to control contaminated environment and also benefits synthetic usage of local zeolite. Furthermore, loess soils topographically cover the vast land expanding from central Asia to north China and are common in Baiyin. Studies on the use of zeolite for soil remediation can offer important theoretical basis and technological support to the aspects of remediation of heavy metal-contaminated soils in the northwestern part of China without any doubt.

The aim of this study is to investigate the adsorption properties of the natural zeolite with respect to copper as undesired metal ion from aqueous solutions. The kinetics of the process and the adsorption capacity of zeolite are determined in relation to the effects of various factors on the adsorption characteristics. The parameters that will be of interest in this study include contact time, grain size, initial solution pH, zeolite dose, types of electrolyte, ionic strength, temperature and initial metal ion concentration. This partial study in solid and solution system will provide relevant experimental data for further analysis.

EXPERIMENTAL

The natural zeolite consists mainly of clinoptilolite was provided by Original Zeolite Company in Baiyin of Gansu Province, China. They first were crushed into smaller pieces from their initial rock like forms, sieved (between 20 and 40 mesh) and washed using distilled water to pH 7. They were then dried in an oven at 100 ± 5 ºC for 2 h. Subsequently, they were grounded in a mortar, sieved (100 mesh) and stored in glass bottle. Copper nitrate solution was used in the batch experiments. Distilled water was used in all the experimental work.

Batch adsorption experiments: Batch adsorption experiments were carried out in 50 mL Erlenmeyer flasks and were done by subjecting a given dose of adsorbent for a period of shaking with 20 mL of copper solutions containing background electrolyte on a rotary shaker (CHA-S Shaker, Jintan Danyang Instrumental Company, China) (150 rpm) at a certain temperature. There are eight factors to be considered as mentioned earlier in the study objects. They include contact time (4 h), grain size (> 100 mesh), pH (5.0-7.0), zeolite dose (0.2 g), type of electrolyte ($NaNO_3$), ionic strength (0.01 mol/L), temperature (25 ºC) and initial metal concentration (50 mg/L). The studies were performed by varying one of the factors and keeping other conditions constant (as the data shown between brackets). The adsorbent and adsorbate were separated by centrifugation (Model 752, Shanghai Spectrum Instrumental Company, China) (3500 rpm) over 0.5 h. Metal concentrations in the supernatant were determined by using flame atomic absorption spectrophotometer (Spectr AA220FS, USA). All assays were carried out in duplicate and mean values were recorded accordingly.

Data analysis: The amount of Cu^{2+} adsorbed onto the zeolite can be determined using the equation below:

$$q = \frac{(C_1 - C_2)V}{1000m} \quad (1)$$

where q represents the mass of copper adsorbed per unit weight of zeolite (mg/g); C_1 is initial concentration of copper (mg/L); C_2 is final concentration of copper (mg/L); V represents the volume of the reacting solution (mL); m represents the amount of zeolite used (g). Removal efficiency of Cu^{2+} by zeolite can be expressed in percentage as:

$$\text{Removal}\,(\%) = \frac{(C_1 - C_2)}{C_1} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

Effect of contact time: The kinetic experiments were performed by using 0.2 g of zeolite at 25 ºC for different equilibration times. Fig. 1 showed that there was a growing tendency of increase in adsorption capacity of Cu^{2+} with contact time until at 4 h where it attained its equilibrium and then the per cent removal becomes constant. The percentage removal of Cu^{2+} always reached 91.3 % within 2 h. However, the removal of Cu^{2+} was 95.3 % and adsorption capacity was also 4.77 mg/g at 4 h after attaining the pseudo- equilibrium state. Consequently, 4 h was chosen as the reaction equilibration time for further adsorption experiments. In order to investigate the rate law describing adsorption of Cu^{2+}, the kinetic data obtained from the batch experiments were analyzed using two kinetic equations, namely, the pseudo-first order[16] and the pseudo-second order equations[17]. They can be expressed as follows:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \quad (3)$$

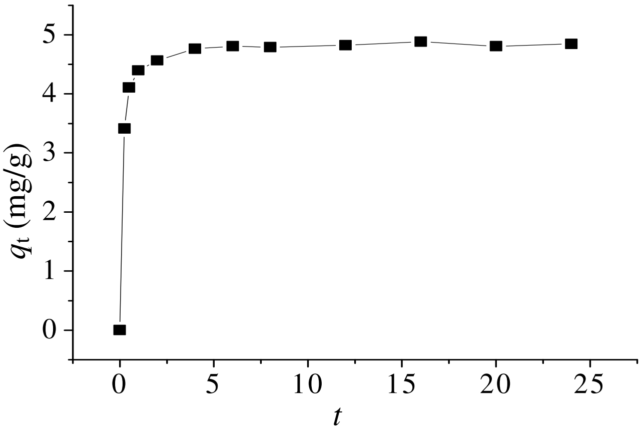


Fig. 1. Effect of contact time on adsorption of Cu^{2+} by natural zeolite

and $$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where q_t is the amount of Cu^{2+} adsorbed (mg/g) at time t (h); q_e is the amount of Cu^{2+} adsorbed (mg/g) at equilibrium; k_1 and k_2 are rate constants for pseudo-first and pseudo-second order, respectively. Based on the plot of log (q_e - q_t) *vs.* t, the values of q_e, k_1 and R^2 for pseudo-first order equation were calculated as 4.774, 1.260 and 0.9754. And based on the plot of t/q_t *vs.* t, the values of q_e, k_2 and R^2 for pseudo-second order equation were calculated as 4.861, 2.126 and 0.9999, respectively. It was also found that pseudo-second order reaction model was more appropriate for describing the adsorption of Cu^{2+} by the zeolite duo to higher R^2. The study also indicated that the adsorption was a heterogeneous progress with an initial rapid adsorption step followed by a slower step. The rapid step was thought to be due to the abundant availability of active sites on external surface of natural zeolite. However, slower adsorption may be due to slower diffusion of cations into the interior channels of natural zeolite.

Effect of grain size: Table-1 indicates that decrease in grain size of natural zeolite causes a notable increase in adsorption capacity of Cu^{2+}, which is in agreement with the results of Oren and Kaya[18]. When the mesh size was greater than 100, adsorption capacity of Cu^{2+} reached 4.705 mg/g, which increased by 12.5 % compared to 20-40 mesh, whiles the removal rate was 94.1 %. Table-1 shows that the smaller the grain size of natural zeolite, the higher its adsorption and removal capacity of heavy metal. This may be attributed to decrease grain size that leads to increase of specific surface area of zeolite thereby increasing a higher contact area with solution. Moreover, due to thinning liquid membrane on the surface of zeolite, there exist vibrations which make it favourable for adsorbate to be easily attached onto the surface of zeolite. Considering the difficulty of the process and separating the liquid and solid phase, adsorbent of grain sizes more than 100 mesh was chosen for the remaining aspects of the batch adsorption experiment.

Effect of pH values of solution: The pH of aqueous solutions is classified as one of the most important controlling parameters in the adsorption process. The pH may affect the degree of ionization of the adsorbate and the surface property of the adsorbent, for example, solubility and speciation of metal ions in solution and the overall charge of zeolite. Speciation of the metal has a significant impact on the removal efficiency of the zeolites. The pH of solution was adjusted by addition of NaOH or HNO_3 when is needed. Adsorption of Cu^{2+} generally increases as the pH increase as shown in Fig. 2. At pH 2, adsorption capacity was 0.24 mg/g that was found to be the lowest in the studied range and removal efficiency was less than 5 %. A rapid increase in initial pH from 2 to 3 resulted in an increase in the removal rate of *ca.* 76 % for Cu^{2+}. At pH values higher than 3, the per cent of adsorbed Cu^{2+} eventually exceeded 95 % and the adsorption performance onto zeolite pose a slight increase and then remained almost unchanged. Therefore, the efficiency of metal adsorption depends on different pH values of the test solution. The removal of Cu^{2+} from solution was not only due to ion exchange but also adsorption of other ions through precipitation.

TABLE-1
EFFECT OF GRAIN SIZE ON ADSORPTION
OF Cu^{2+} BY NATURAL ZEOLITE

Size (mesh)	q_e (mg/g)	Increase in adsorption (%)	Removal (%)
20-40	4.182	–	83.6
40-60	4.365	4.39	87.3
60-80	4.420	5.70	88.4
80-100	4.435	6.06	88.7
> 100	4.705	12.5	94.1

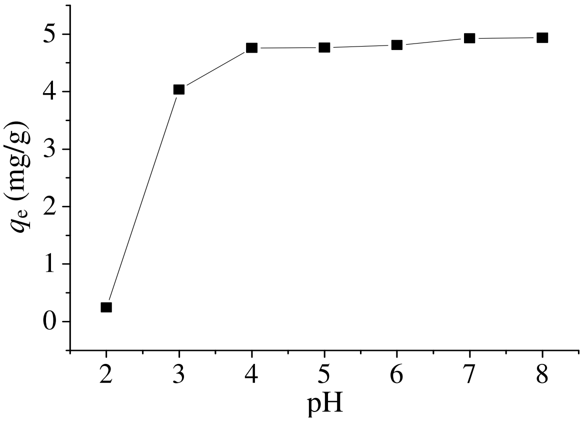


Fig. 2. Effect of initial pH of solution on adsorption of Cu^{2+} by natural zeolite

At lower pH values, Cu^{2+} removal was inhibited possibly as a result of a competition between H^+ and Cu^{2+} on surface exchangeable sites with an apparent preponderance of H^+. Moreover, zeolite surface was found to be positively charged when the pH of the solution was lower. The reduction in removal metal ions as pH decreases can be ascribed to this increase in positive charge on zeolite surface. In addition, a maximum number of reactive H^+ can react with the hydroxyl on surface of zeolite, which may possibly render the surface of zeolite dissolve partially and thus reduce the rate of adsorption. The abrupt and rapid increase of adsorption at pH 3 can be attributed to the replacement of exchangeable cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) present at the exchangeable sites. As the pH continue to increase from 4 to 8, the negative charge density on the surface of zeolite increases due to deprotonation of the metal binding sites (Si-OH and Al-OH) and thus the Cu^{2+} adsorption increase[19,20].

In addition to the ion exchange factor, the formation of copper species with OH^- plays an important role in the increase of Cu^{2+} removal above pH 7. Above this pH the resultant solution turns blue forming precipitation. Depending on the pH and metal concentration, copper may form complexes with OH^-. The examples of such complexes include $Cu(OH)_2$, $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$, at higher pH values (pH > 7). As a result, copper hydroxyl species may be involved in the adsorption and also be deposited onto the zeolite structure. Besides, zeolites are not only influenced by pH but in turn are capable of affecting the solution pH. The zeolite surfaces may again be affected by the ambient pH which is not equal to the external solution pH value. Natural zeolites are generally weakly acidic in nature and sodium-form exchangers are selective for hydrogen. This leads to high pH values when the sample is equilibrated with relatively dilute electrolyte solutions making metal feasible for hydroxide precipitation within the boundaries of zeolite and at the surface of zeolite[21].

Effect of zeolite dose: Fig. 3 illustrates the effect of zeolite dose on removal of Cu^{2+} from the aqueous solutions. As zeolite dose increase from 0.1 to 1 g, the amount of Cu^{2+} adsorbed onto the zeolite decreases while the removal rate of Cu^{2+} increases from 74.5 to 98.1 %. The removal rate of Cu^{2+} reaches a higher value of 95.0 % using 0.2 g of zeolite. According to the water supply regulations, the concentration of Cu^{2+} in any drinking water should not exeed 2 mg/L[22]. When the initial concentration of Cu^{2+} was 50 mg/L in the prepared solution, using 0.3 g of natural zeolite drastically reduces the concentration of Cu^{2+} below the accepted requirement and again attains equilibrium with adsorption rate of 97.6 %. It was obvious that the equilibrium concentration of the test substance in solution will decrease with increasing amount of zeolite for a given initial metals concentration, since the fraction of metal removed increases when the amount of adsorbent was increased in the batch flasks with a fixed initial concentration. With the increase of dosage of zeolite, there is an introduction of additional adsorption sites (or surface area) which can adsorb more Cu^{2+} from the solution.

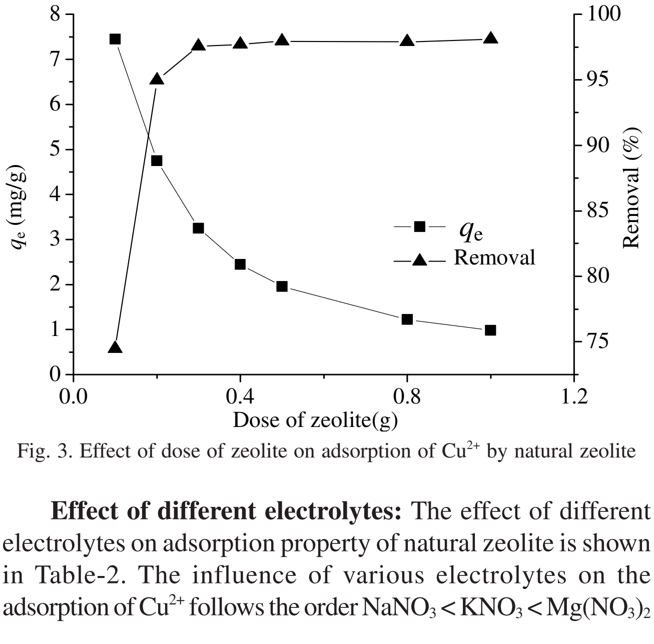


Fig. 3. Effect of dose of zeolite on adsorption of Cu^{2+} by natural zeolite

Effect of different electrolytes: The effect of different electrolytes on adsorption property of natural zeolite is shown in Table-2. The influence of various electrolytes on the adsorption of Cu^{2+} follows the order $NaNO_3 < KNO_3 < Mg(NO_3)_2 < Ca(NO_3)_2$. Han *et al.*[23] reported the removal of uranium by manganese oxide coated with zeolite. The results of electrolyte effects was identical with those in this study. The adsorption capacity for Cu^{2+} was 4.779 mg/g and the removal rate was 95.6 % by using sodium nitrate as the electrolyte. This value was the highest compared with other electrolytes. When using $Ca(NO_3)_2$ as an electrolyte, the adsorption capacity decreases by 18.6 % than using $NaNO_3$. It is apparent that the removal rate of Cu^{2+} using the electrolytes containing divalent cations is lower than using electrolytes containing monovalent cations when electrolyte concentrations are equal (0.01 M). This is attributed to the strong competition between divalent cations and Cu^{2+} for available adsorption sites. Moreover, the removal rate of Cu^{2+} using the electrolyte containing K^+ and Ca^{2+} is, respectively lower than using the electrolyte containing Na^+ and Mg^{2+} because the ionic radius of potassium and calcium are, respectively greater than those of sodium and magnesium, causing relative difficulty in the penetration into the zeolite channel.

TABLE-2
EFFECT OF DIFFERENT ELECTROLYTES ON ADSORPTION OF Cu^{2+} BY NATURAL ZEOLITE

Electrolyte	q_e (mg/g)	Decrease in adsorption (%)	Removal (%)
$NaNO_3$	4.779	–	95.6
KNO_3	4.469	6.49	89.4
$Mg(NO_3)_2$	4.306	9.90	86.1
$Ca(NO_3)_2$	3.889	18.6	77.8

Effect of electrolyte concentration: The result relating to the effect of ionic strength on the adsorption capacity of natural zeolite is shown in Fig. 4. It includes two stages. Firstly, a decrease in adsorption of Cu^{2+} was produced when electrolyte concentration was increased from 0.0001 to 0.1 M. The reduction trend showed that the binding efficiency decreases when cations increase in the solution, which can be attributed to the competitive effect between Cu^{2+} and Na^+. Another factor that can be considered is the increase of the electrolyte concentration which results in increase in ionic strength of Na^+, so the effective concentration (or activity) of Cu^{2+} in solution will eventually decrease. Secondly, the adsorption capacity gradually increases with the increase in electrolyte concentration continuously from 0.1 to 1 M and finally was almost the same with equal initial ionic strength (0.0001 M). The adsorption capacity for Cu^{2+} decreases *ca.* 7 % when electrolyte concentration was 0.1 M compared with 0.0001 M.

Effect of temperature: As can be seen from Fig. 5, the adsorption capacity for Cu^{2+} at 35 ºC was more than at 15 ºC. The 9 % proportional increase in Cu^{2+} removal rate with increased temperature demonstrates that the adsorption of Cu^{2+} onto the natural zeolite occurred by chemisorption and is thermodynamically favourable as proposed by Poots *et al.*[24] and Yang *et al.*[25]. The increase of temperature enforces cation exchange capacity in certain range.

Effect of initial metal concentration: Fig. 6 represents the change of adsorption capacity under different metal ion concentrations. Increasing the metal ion concentration leads to an increase of the adsorption capacity of Cu^{2+} by the natural zeolite. This is attributed to the concentration differences.

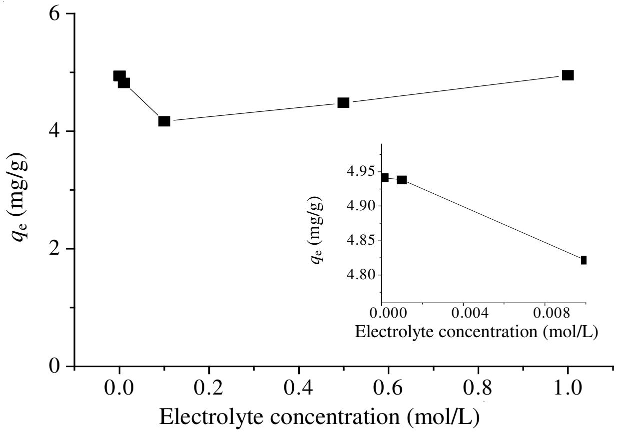


Fig. 4. Effect of electrolyte concentration on adsorption of Cu^{2+} by natural zeolite

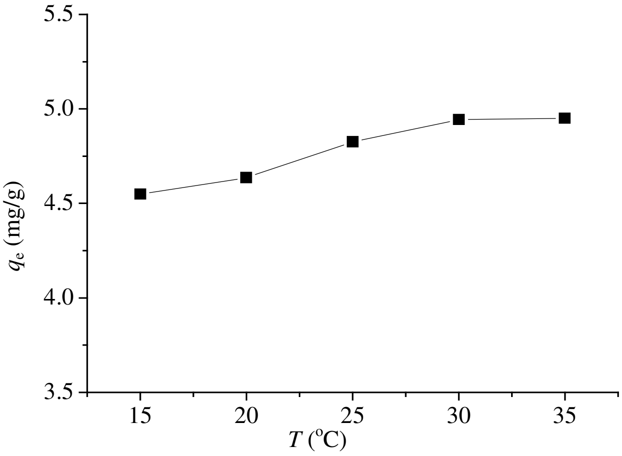


Fig. 5. Effect of temperature on adsorption of Cu^{2+} by natural zeolite

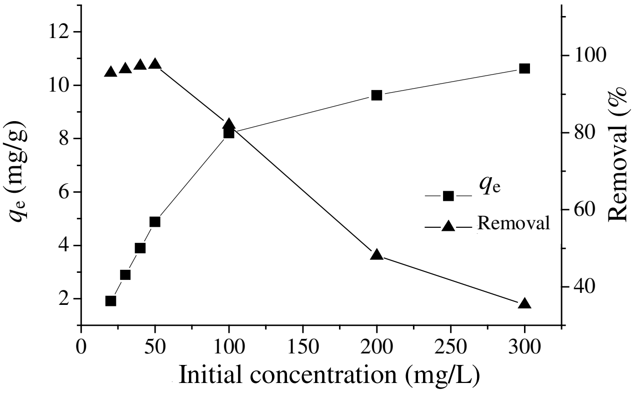


Fig. 6. Effect of initial metal concentration on adsorption of Cu^{2+} by natural zeolite

Several equilibrium models have been developed to describe adsorption isotherm relationships. The two main isotherm models used in this work are the nonlinear forms of Langmuir[26] and Freundlich[27] models:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{5}$$

$$q_e = K_F C_e^{1/n} \tag{6}$$

where K_L and K_F are the Langmuir constant and Freundlich constant, respectively; q_e (mg/g) is the amount of Cu^{2+} adsorbed at equilibrium; q_{max} is the maximum adsorption capacity (mg/g); C_e is the equilibrium concentration (mg/L) and n is the Freundlich constant related to the adsorption affinity of the adsorbent. The equilibrium data for the concentrations of Cu^{2+} adsorbed ranged from 20-300 mg/L well fitted with Langmuir model (q_{max} = 10.87, K_L = 0.433, R^2 = 0.9195) and Freundlich one (K_F = 3.65, n = 4.75, R^2 = 0.8817). Data analyses were performed by employing Origin 8.0 software. The maximum adsorption capacity of natural zeolite was determined to be 10.87 mg/g when the Langmuir model was used. The correlation coefficient values determined indicated that the Langmuir model was better over the Freundlich model. The Langmuir constant K_L is related to the Gibb's free energy change of adsorption (kJ/mol) according to the formula below[28]:

$$\Delta G = -RT \ln(1000K_L) \tag{7}$$

where R is the gas constant 8.314 J/mol K) and T is the temperature (K). The calculated Gibbs free energy -15.0 kJ/mol indicates the degree of spontaneity of the adsorption process. The negative values reflect a more energetically favourable adsorption process.

Conclusion

The adsorption of Cu^{2+} by zeolite from the study of effect of contact time follows the pseudo-second order model. Adsorption capacity of zeolite was slightly increased with the decrease of grain size. Weakly acidic condition was found to be suitable for the removal of heavy metals when taking natural zeolite as the adsorbent in practical adsorption process. With an increase in the dose of zeolite, adsorption capacity of Cu^{2+} decreased. Different electrolytes were found to have different effects on adsorption of Cu^{2+}. Between 0.0001 and 1 M, the adsorption capacity decreased firstly and then increased with the increase of the ionic concentration. The effect of temperature was found to have little effect on the adsorption of Cu^{2+} in the range from 15-35 ºC. The experimental data obtained from the batch studies gave a good fit by employing the non-linear forms of Langmuir and Freundlich isotherm models. The maximum adsorption capacity of the natural zeolite was found to be 10.87 mg/g calculated by the Langmuir's equation. From this present study it is concluded that, it is a good prospect that using the local zeolite from Baiyin will be the best remedies for soil contaminated locally by heavy metals.

ACKNOWLEDGEMENTS

This study was financially supported by the Program for Changjiang Scholars and Innovative Research Team in University (IRT0966), the National Natural Science Foundation of China (21167007) and the Natural Science Foundation of Gansu Province (1010RJZA070).

REFERENCES

1. S.Y. Chen and T. Han, *J. Gansu Sci.*, **20**, 69 (2008).
2. Z.R. Nan and J.J. Li, *Arid Zone Res.*, **17**, 39 (2000).
3. G.L. Wang, C.Z. Liu and Z.Y. Lu, *J. Gansu Agri. Univ.*, **41**, 79 (2006).
4. A.A. Mahabadi, M.A. Hajabbasi, H. Khademi and H. Kazemian, *Geoderma*, **137**, 388 (2007).
5. C.F. Lin, S.S. Lo, H.Y. Lin and Y.C. Lee, *J. Hazard. Mater.*, **60**, 217 (1998).
6. Y. Uysal and F. Taner, *Asian J. Chem.*, **24**, 1217 (2012).

7. X. Querol, A. Alastuey, N. Moreno, A.A. Esther, G.S. Antonio, J. Cama, C. Ayora and M. Simon, *Chemosphere*, **62**, 171 (2006).
8. R. Herwijnen, T.R. Hutchings, A.A. Tabbaa, A.J. Moffat, M.L. Johns and S.K. Ouki, *Environ. Pollut*., **150**, 347 (2007).
9. W. Hartley, R. Edwards and N.W. Lepp, *Environ. Pollut*., **131**, 495 (2004).
10. W.Y. Shi, H.B. Shao, H. Li, M.A. Shao and S. Du, *J. Hazard. Mater*., **170**, 1 (2009).
11. R.S. Bowman, *Micro. Meso. Mater*., **61**, 43 (2003).
12. E. Erdem, N. Karapinar and R. Donat, *J. Colloid Interf. Sci*., **280**, 309 (2004).
13. Y.S. Ok, J.E. Yang, Y.S. Zhang, S.J. Kim and D.Y. Chung, *J. Hazard. Mater*., **147**, 91 (2007).
14. P. Castaldi, L. Santona, S. Enzo and P. Melis, *J. Hazard. Mater*., **156**, 428 (2008).
15. M. Rehakova, S. Cuvanova, M. Dzivak, J. Rimar and Z. Gavalova, *Curr. Opin. Solid State Mater. Sci*., **8**, 397 (2004).
16. S. Lagergren and B.R. Svenska, *Veternskapsakad Handlinger*, **24**, 1 (1898).
17. Y.S. Ho, W.T. Chiu, C.S. Hsu and C.T. Huang, *Hydrometallurgy*, **73**, 55 (2004).
18. A.H. Oren and A. Kaya, *J. Hazard. Mater*., **131**, 59 (2006).
19. K.S. Hui, C.Y.H. Chao and S.C. Kot, *J. Hazard. Mater*., **127**, 89 (2005).
20. M.R. Panuccio, A. Sorgona, M. Rizzo and G. Cacco, *J. Environ. Manage*., **90**, 364 (2009).
21. H. Leinonen and J. Lehto, *Waste Manage. Res*., **19**, 45 (2001).
22. T. Motsi, N.A. Rowson and M.J.H. Simmons, *Int. J. Mineral Processing*, **92**, 42 (2009).
23. R. Han, W. Zou, Y. Wang and L. Zhu, *J. Environ. Radio*., **93**, 127 (2007).
24. V.J.P. Poots, G. Mckay and J.J. Healy, *Water Res*., **10**, 1061 (1976).
25. J.E. Yang, E.O. Skogley, S.J. Georgitis, B.E. Schaff and A.H. Ferguson, *Soil Sci. Soc. Am*., **55**, 1358 (1991).
26. I.J. Langmuir, *J. Am. Chem. Soc*., **40**, 1361 (1918).
27. H. Freundlich and W. Heller, *J. Am. Chem. Soc*., **61**, 2228 (1939).
28. V.K. Jha, M. Matsuda and M. Miyake, *J. Hazard. Mater*., **160**, 148 (2008).