Journal of Hazardous Materials 159 (2008) 427–434

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Phosphoric acid modified-Y zeolites: A novel, efficient and versatile ion exchanger

P. Panneerselvam[a], N. Thinakaran[a], K.V. Thiruvenkataravi[a], M. Palanichamy[b], S. Sivanesan[a,*]

[a] Environmental Management Laboratory, Department of Chemical Engineering, A.C. College of Technology, Anna University, Guindy, Chennai 600025, Tamil Nadu, India
[b] Department of Chemistry, Anna University, Guindy, Chennai 600025, Tamil Nadu, India

ARTICLE INFO

Article history:
Received 6 December 2007
Received in revised form 12 February 2008
Accepted 13 February 2008
Available online 17 February 2008

Keywords:
Copper removal
Isotherms
Kinetics
Thermodynamics

ABSTRACT

Large pore HY zeolite was modified with phosphoric acid by wet method. The modified zeolite was converted to Na^+ form using aqueous $NaHCO_3$ solution. The Na^+ form of modified zeolite, represented as PNa_2Y, was characterized by XRD, BET surface area, SEM, and AAS techniques. The XRD analysis showed diffraction patterns same as that of parent HY zeolite, as a result there has been no structural degradation during modification. It was then tested for sorption of Cu^{2+} ions from aqueous solution. The Cu^{2+} content of the solution was analyzed by AAS. PNa_2-Y shows higher sorption capacity (≈40%) than the parent Na-Y (≈23%) zeolite, which is attributed to the double of amount Na^+ content in PNa_2-Y compared to the Na-Y zeolite. Equilibrium modeling data were found to fit more to the linear Langmuir model than the Freundlich model. The thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), were also calculated. These parameters confirmed that the sorption of Cu^{2+} is feasible, spontaneous and endothermic.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Heavy metals are toxic substances and therefore their removal from wastewater is required prior to their discharge into receiving waters. Among the several methods available, sorption by ion exchange is an attractive one; its application is relatively simple and safe, as it requires only mild operating conditions. Ion exchange is the exchange of ions between a liquid phase and a porous solid, which may be synthetic or natural (resins or zeolites). Using low cost exchanger e.g., zeolite, the method can be made cost-effective [1]. Zeolites are naturally occurring hydrated alumino silicate minerals. They belong to the class of minerals known as "tectosilicates". The structures of zeolites consist of three dimensional frameworks of SiO_4 and AlO_4 tetrahedra. The aluminum ion is small enough to occupy the position in the centre of the tetrahedron of four oxygen atoms, while the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice. The negative charge is balanced by cations (Na^+, K^+, or Ca^{2+}). These cations are exchangeable with certain cations in solutions, such as lead, cadmium, copper, zinc, and manganese [2]. The cations and water molecules occupy the non-framework positions such as the voids and channels, formed by different combination of Si- or Al-tetrahedra in the framework.

They are represented by the empirical formula

$$M_{2/n}O, Al_2O_3, xSiO_2, yH_2O$$

where M^{n+} is the exchangeable cation of valency n. Generally, this ion is Na^+, K^+, Ca^{2+}, Mg^{2+} or some organic ion present during the synthesis. By exchanging these ions with other ions such as Ag^+, La^{3+}, Ce^{3+}, catalytic and sorbent properties can be induced [3,4]. The main applications of natural zeolites include environmental pollution control and remediation, energy conservation, agriculture and aquaculture, odor control, and mining and metallurgy [5]. Mining waste and copper mine drainage contribute significant quantities of dissolved copper to effluent streams. Other sources are fertilizer manufacturing, petroleum refining, paints and pigments, steel works, foundries, electroplating and electrical equipments, brass, etc. Although copper is an essential element, acute doses cause metabolic disorders. Inhalation of copper produces dermatitis. Chronic copper poisoning causes hemolytic anemia, neurological abnormalities and corneal opacity [6]. Metal ion solution absorbed by aquatic plants and animals prove very toxic, if the concentration is sufficiently high. Intake of copper from drinking water can be around 1.4 mg per day from soft water and 0.05 mg per day from hard water. The maximum acceptable limit of copper ion concentration in drinking water is <3000 μg dm^{-3}. Copper, along with

* Corresponding author. Tel.: +91 44 22203525; fax: +91 44 22203525.
E-mail address: sivanesh@yahoo.com (S. Sivanesan).

0304-3894/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2008.02.033

Table 1
Adsorption capacities Q^o (mg/g) for some zeolite materials

Adsorbent	Adsorption capacity Cu (II)	Reference
Clinoptilolite	0.011	[9]
Natural zeolite	0.21	[10]
Kaolinite	0.76	[11]
Ball clay	1.60	[11]
Kaolinite	1.9	[12]
Na-montmorillonite	3.04	[13]
Kaolinite	4.47	[14]
Kaolinite-HA	4.8	[12]
Diatomite	5.54	[14]
Vermiculite	8.60	[15]
SDS modified clay	16.13	[16]
Bentonite	18.16	[14]
Natural zeolite	25.04	[17]
Modified-Na-Y zeolite	27.16	Present study
Phosphoric acid modified-Y zeolite	36.88	Present study

arsenic and mercury is recognized as exhibiting the highest relative mammalian toxicities such as liver damage, Wilson disease, insomnia, etc. The permissible limit of copper effluent discharge is 0.25 mg/l, as per the Environmental protection Agency (EPA) USA, 0.05–0.1 mg/l by Environmental protection Department (EPD) Hong Kong and 2 mg/l by Pollution control Department (PCD) Thailand [7,8]. Recently there have been many reports on the sorption of Cu^{2+} with different adsorbents and the results are presented in Table 1. Comparison of the data illustrates that the sorption capacity of phosphoric acid modified-Y zeolite is better than all other adsorbents. Presence of double the amount of exchangeable Na^+ compared to the parent might be the cause for it. But hitherto, only unmodified zeolites have been examined for ion exchange capacity, in which 1 mol of sodium ion is exchanged for every mole of Al^{3+} presents in the frame work of zeolite. There have been reports of modification of zeolite with H_3PO_4, for catalytic application [18,19]. In the present study, Y zeolite has been modified with phosphoric acid. Each mole of phosphoric acid introduced into the zeolite provides two moles of exchangeable protons which can be replaced by Na^+ ions using a mild base like $NaHCO_3$. Such a modified zeolite has been tested for sorption of Cu^{2+} ions from aqueous solution.

2. Experimental

2.1. Materials and methods

HY zeolite was purchased from Sud-Chemie India Ltd., Mumbai, India. Copper sulphate was obtained from Qualigens Fine Chemicals Ltd., Mumbai, India. All other chemicals used were of analytical reagent grade procured from Rankem Fine Chemicals Ltd., New Delhi, India.

2.2. Preparation of modified zeolite

About 2 g of HY zeolite in 40 ml of double distilled water was mixed with 0.262 g of phosphoric acid. The mixture was kept under vigorous stirring at 60 °C for 3 h and then evaporated to dryness in an air oven at 120 °C. 30 ml of aqueous $NaHCO_3$ solution was added to the result zeolite and kept under vigorous stirring at 60 °C for 3 h to obtain the sodium form. It was then filtered and the residue washed with water and dried in air oven at 120 °C overnight before use. The reaction scheme Fig. 1 illustrates the sequence of steps in the above treatment.

2.3. Sorption of Cu^{2+} ions

Sorption of Cu^{2+} ions the modified PNa_2-Y and Na-Y zeolites were used for sorption of Cu^{2+} by batch method. The batch experiments were carried out with 20 ml of 50 mmol Cu^{2+} solution. About 50 mg of zeolite was added and the uptake of Cu^{2+} ions by the zeolite was determined. The pH of the solution was measured using a pH meter (Elico Model LI-120, Hyderabad, India). Adjustments of pH were made with 0.1 M HCl and 0.1 M NaOH solutions. The screw cap bottle containing the adsorbate and adsorbent was placed in

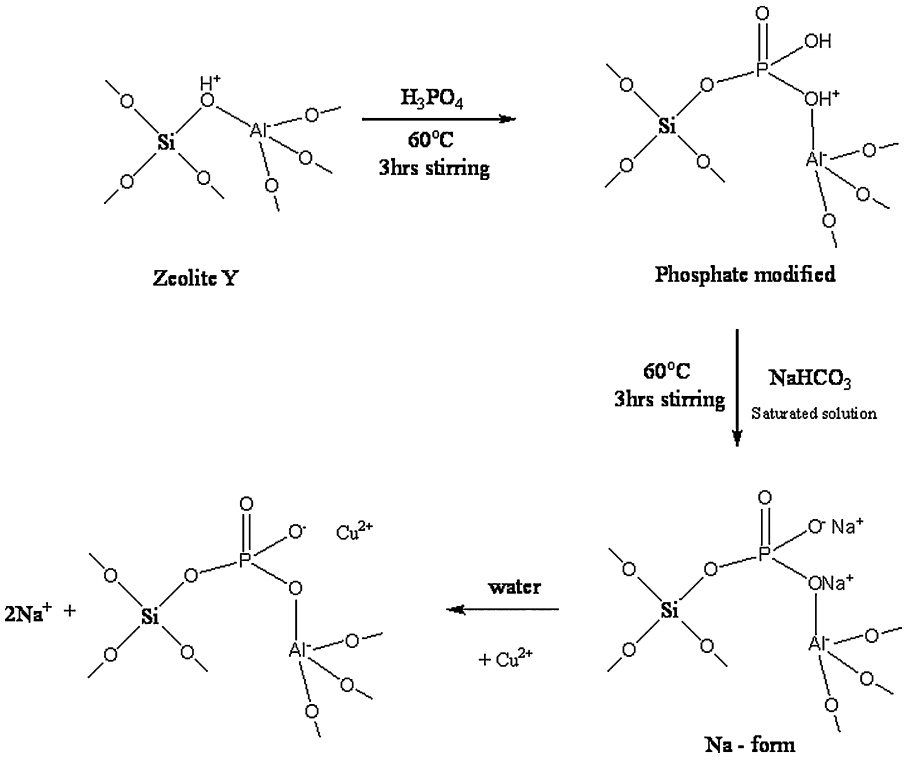

Fig. 1. Reaction schemes illustrating modification of PNa_2-Y zeolite.

the thermostatic orbital shaker (Neolab, Mumbai, India) and shaken at a constant speed of 200 rpm. The temperature was varied from 303 to 323 K. After equilibrium, the samples were centrifuged and the filtrates were analyzed. The kinetic studies were carried out using magnetic stirrer. The samples were withdrawn from the stirrer at regular time intervals and then centrifuged. The absorbance of supernatant solution was measured using Atomic absorption spectrophotometer (SHIMADZU, AA-6300). The sorption of by the modified zeolites was computed using the following equations.

$$\text{Removal efficiency}\,(\%) = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \quad (1)$$

$$q_e = \frac{(C_o - C_e)V}{m} \quad (2)$$

where q_e is the amount of sorbed Cu^{2+} ions (mmol/g), C_o and C_e are the initial and equilibrium concentration of Cu^{2+} ion in solution (mmol/l), respectively, V is the solution volume and m is mass of the adsorbent (g).

3. Results and discussion

3.1. Characterization of modified zeolite

The BET surface areas of both modified PNa_2-Y and Na-Y zeolites were measured using Smart Sorbs 92 Surface area analyzer where N_2 gas was used as adsorbate. The surface areas of modified Na-Y and PNa_2-Y zeolites were 562.17 and 581.89 m^2/g, respectively. The XRD analysis of the modified Na-Y and PNa_2-Y zeolites was measured using D-Max/111-VC Model with nickel filtered and Cu Kα radiation (λ = 1.5406 Å). The spectra are shown in Fig. 2. Both the spectra show nearly similar patterns illustrating absence of structural degradation during modification. Scanning electron microscope (SEM) images were taken using a Joel Jsm-6360 scanning electron microscope. The images were taken to study the surface morphology of zeolite particles. The SEM pictures of the parent H-Y, Na-Y and PNa_2-Y zeolites are shown in Fig. 3. The picture shows that the aggregates of the particles and the morphology of particles in all the three pictures appear the same (Fig. 3a and b).

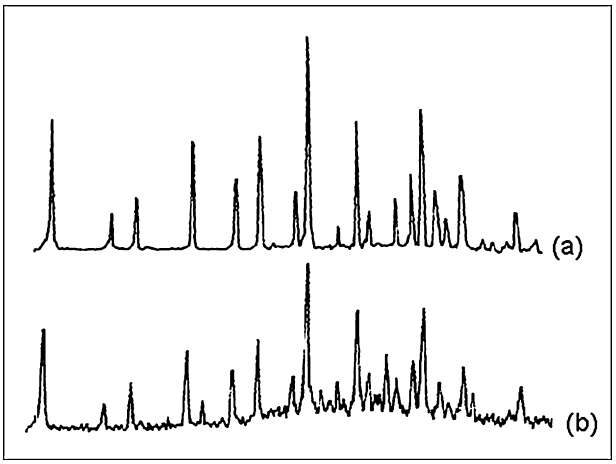

Fig. 2. X-ray powder diffraction patterns of (a) Na-Y; (b) PNa_2-Y zeolites.

Hence, the modification of PNa_2-Y zeolite might not have resulted in structural degradation of the parent zeolite.

3.2. Effect of pH

The effect of pH of the suspending medium on copper removal was studied by performing equilibrium sorption experiments at different pH values. The results are illustrated in Fig. 4. The effect of pH on Cu^{2+} sorption is examined in the pH range 2–6. For the PNa_2-Y zeolite the uptake efficiency gradually increases as the pH increases from 2 to 3.5 close to pH 2 some amount of Na^+ ions of $=P^+(ONa)_2$ is replaced by protons. As a result the sorption capacity becomes less, with increase in pH, such exchange is suppressed, and therefore Cu^{2+} ions could be better adsorbed. Hence, there is a gradual increase in sorption with the increase in pH from 2 to 3.5. But above pH 3.5, a sudden rise in the Cu^{2+}uptake was observed which could be attributed to precipitation of Cu^{2+} as $Cu(OH)_2$. The Na-Y zeolite also exhibited similar behavior. But PNa_2-Y zeolite shows higher

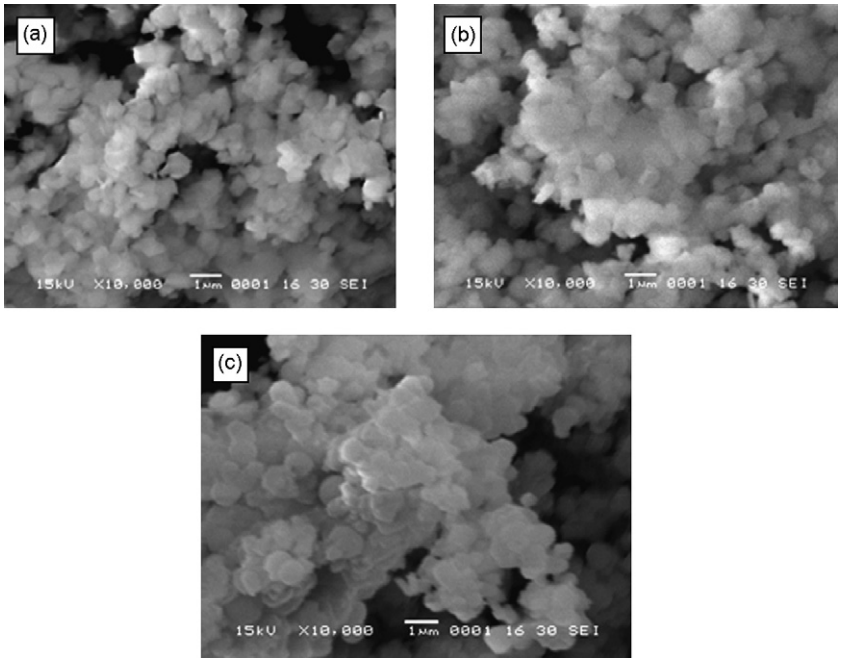

Fig. 3. SEM image of (a) parent H-Y, (b) Na-Y and (c) PNa_2-Y zeolites.

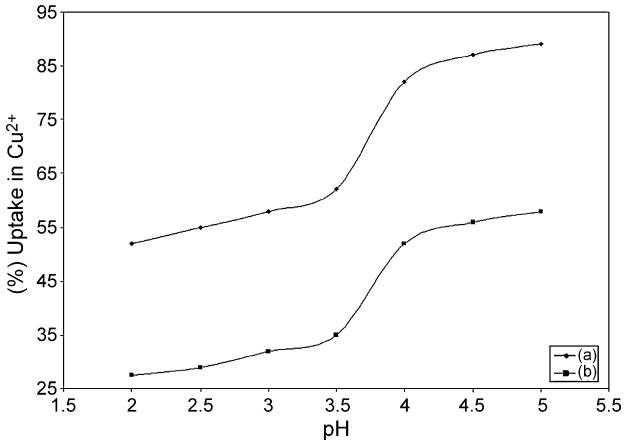

Fig. 4. Effect of pH in Cu^{2+} ions from aqueous solutions onto (a) Na-Y; (b) PNa_2-Y zeolites.

sorption capacity than the parent Na-Y zeolite. Hence, optimum pH range for the removal of Cu^{2+} was found to be 2–3.5.

3.3. Kinetic studies

Preliminary investigations on the rate of sorption of Cu^{2+} ions by Na-Y and PNa_2-Y indicated that the processes were quite rapid and typically 40–55% sorption occurred within the first 20 min of contact. The initial rapid sorptions subsequently give way to a slow approach to equilibrium, and saturation is reached in about 45 min. The amount of copper ions sorbed after each interval time, for a fixed concentration of 50 mmol/l at different temperatures, are plotted in Fig. 5. The amount of Cu^{2+} sorbed at equilibrium increases with the increase in temperature indicating an endothermic nature of the process and the time required to reach saturation remained practically unaffected. It is well recognized that the characteristics of sorbent surface are critical factors that affect the sorption rate parameters and the diffusion resistance plays an important role in the overall transport of the solute to describe the change. The rate constant for the metal ion removal from the solution was determined using pseudo-first-order and pseudo-second-order rate models. The Lagergren first-order rate expression [20] is written as:

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

where q_e and q_t are the amount of metal ion (mmol/g) sorbed by Na-Y and PNa_2-Y zeolites at equilibrium and time t (mmol/g), respectively, and k_1 is the rate constant of the first-order adsorption (min^{-1}). The slope and intercept of the linear plots of $\log(q_e - q_t)$ versus t, are shown in Fig. 6. It was observed that the sorption followed the Lagergren equation over the entire range of shaking time explored and the values of the first-order rate constants did not

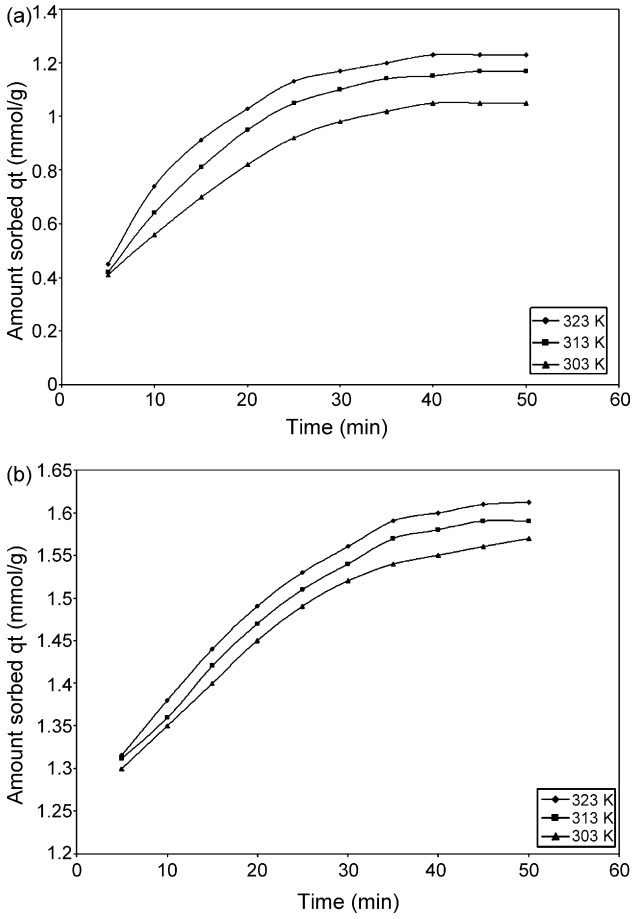

Fig. 5. Effect of contact time on the sorption of Cu^{2+} ions from aqueous solutions onto (a) Na-Y; (b) PNa_2-Y zeolites.

change with temperature as shown in Table 2. In many cases, the first-order equation of Lagergren does not fit well with the whole range of contact time and is generally applicable over the initial stage of the sorption processes [21].

The pseudo-second-order rate model [22] is expressed as:

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

where k_2 (g/mmol min) is the rate constant of pseudo-second-order kinetic model.

The kinetic plot of t/q_t versus t for Cu^{2+} removal at different temperatures is presented in Fig. 7. The relationship is linear, and the correlations between the parameters also explain that the process of sorption of each ion follows pseudo-second-order kinetics. The product $k_2 q_e^2$ is the initial sorption rate represented as $h = k_2 q_e^2$. From Table 2 it can be shown that the values of the initial sorption

Table 2
The calculated parameters of the pseudo-first-order and pseudo-second-order kinetic models of Cu^{2+} ions from (a) Na-Y; (b) PNa_2-Y zeolites

Temperature (K)	Pseudo-first-order			Pseudo-second-order			
	k_1 (min^{-1})	q_e (mmol/g)	R_1^2	q_e (mmol/g)	h (mmol/g)	k_2 (g/mmol min)	R_2^2
Na-Y							
303	0.023	0.527	0.951	1.40	0.422	0.431	0.981
313	0.027	0.721	0.949	1.65	0.971	0.714	0.987
323	0.032	1.021	0.983	1.94	1.847	0.982	0.979
PNa_2-Y							
303	0.025	0.991	0.923	1.98	1.498	0.761	0.991
313	0.033	1.205	0.951	2.21	3.117	1.271	0.986
323	0.039	1.631	0.960	2.86	6.890	1.689	0.972

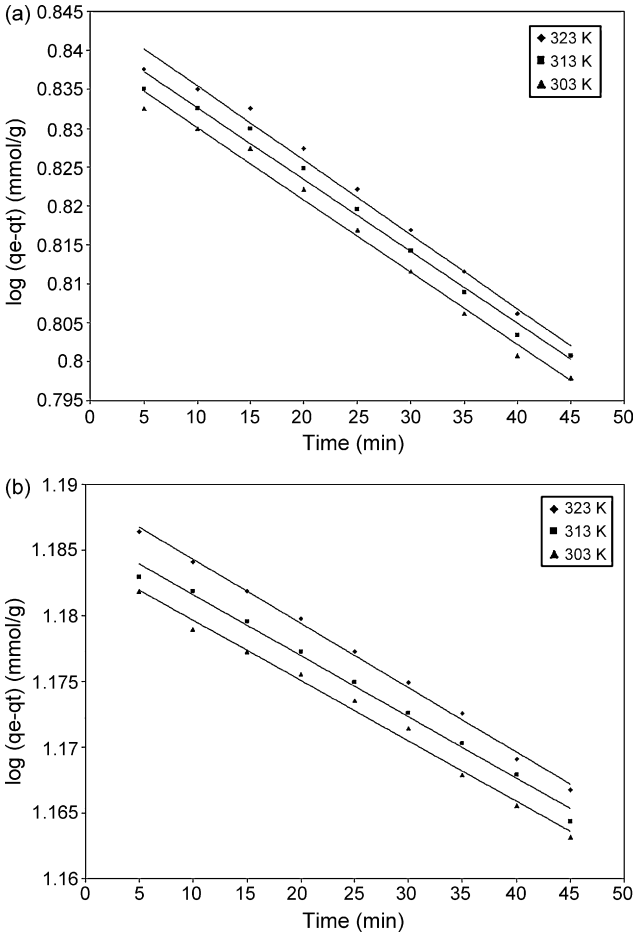

Fig. 6. Pseudo-first-order kinetics plots for the sorption of Cu^{2+} ions from aqueous solutions onto (a) Na-Y; (b) PNa_2-Y zeolites.

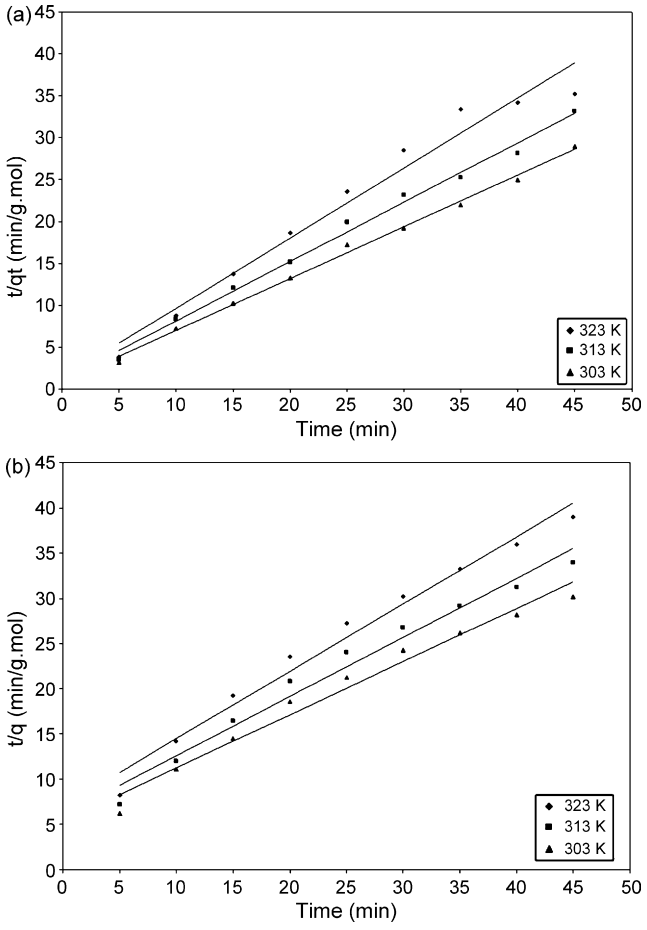

Fig. 7. Pseudo-second-order kinetics plots for the sorption of Cu^{2+} ions from aqueous solutions onto (a) Na-Y and (b) PNa_2-Y zeolites.

rate 'h' and rate constant 'k_2' increase with increase in temperature. The correlation coefficient R^2 has an extremely high value, and its calculated equilibrium sorption capacity 'q_e' is consistent with the experimental data .The results suggest that the pseudo-second-order sorption mechanism is predominant and that the over all rate constant of each ion appears to be controlled by the chemisorption process [21,22]. Other simplified models were also tested since the above two equations did not give definite mechanism. It is also known that at an intensive stirring of the sorptive system, the intraparticle diffusion of solute from the solution into the sorbent pores could be a limiting step. The Morris–Weber equation [23] is written as;

$$q_t = K_{ad} t^{1/2} \tag{5}$$

where K_{ad} is the rate constant of the intraparticle transport (mmol/g $min^{1/2}$). According to this model, if straight line passing through the origin is obtained by plotting a graphic of q_t versus $t^{1/2}$, it can be assumed that the involved mechanism is diffusion based. In that case the slope of the linear plot is the rate constant of the intraparticle transport as can be seen in Fig. 8. The Morris–Weber relationship holds good and the values of K_{ad} were calculated, from the slope of the linear plots obtained, and are presented in Table 3.

3.4. Sorption isotherms

The sorption isotherms for the removal of Cu^{2+} at three different temperatures were studied. The isotherms are regular positive, and concave to the concentration axis. These results reflect the efficiency of modified-Y zeolite for the Cu^{2+} ion removal from aqueous solution in a wide range of concentrations. The uptake of ions increase with the increase in temperature thus indicating that the process is to be endothermic. The sorption studies were carried out at 303, 313 and 323 K to determine the sorption isotherms. The isotherm parameters were evaluated using Langmuir and Freundlich models. The Langmuir isotherm equation could be written [24] as:

$$\frac{C_e}{q_e} = \frac{1}{Q^o b} + \frac{C_e}{Q^o} \tag{6}$$

where q_e is the amount of solute sorbed per unit weight of adsorbent (mmol/g), C_e the equilibrium concentration of the solute (mmol/l), Q^o the monolayer adsorption capacity (mmol/g) and b the constant related to the free energy of adsorption ($b\alpha\, e^{-\Delta G/RT}$).

Table 3
Intraparticle diffusion rate constant for the sorption of Cu^{2+} onto (a) Na-Y; (b) PNa_2-Y zeolite

Temperature (K)	K_{ad} (mmol/g $min^{1/2}$)	R^2
Na-Y		
303	0.621	0.966
313	0.699	0.972
323	0.764	0.980
PNa_2-Y		
303	0.792	0.992
313	0.821	0.995
323	0.855	0.982

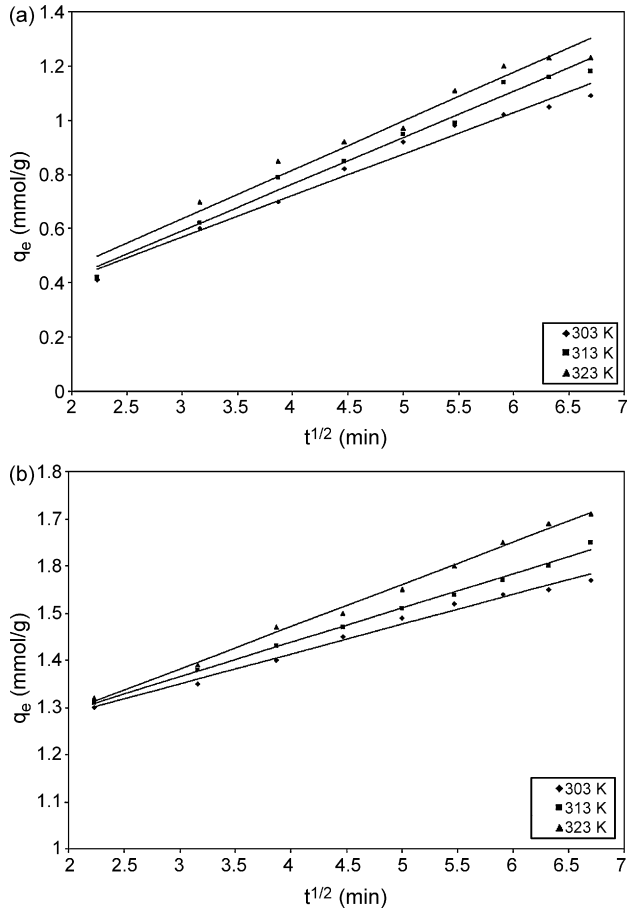

Fig. 8. Morris–Weber kinetics plots for the sorption of Cu^{2+} ions from aqueous solutions onto (a) Na-Y and (b) PNa_2-Y zeolites.

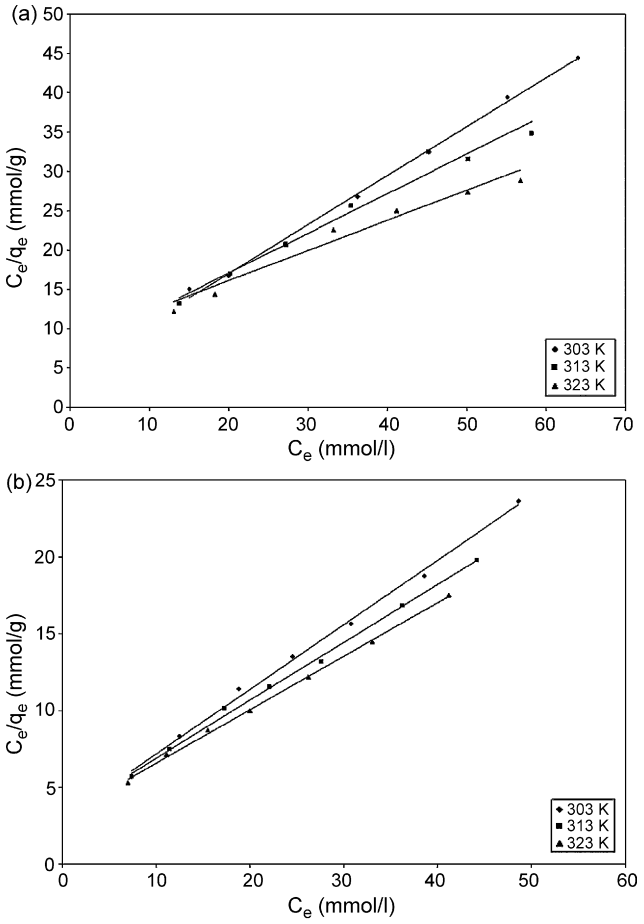

Fig. 9. Langmuir isotherm plots for the sorption of Cu^{2+} ions from aqueous solutions onto (a) Na-Y; (b) PNa_2-Y zeolites.

The logarithmic form of Freundlich equation may be written [25] as:

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \quad (7)$$

where K_F is a constant indicative of the relative adsorption capacity of the adsorbent (mmol/g) and $1/n$ the constant indicative of the intensity of the sorption process. The Langmuir and Freundlich isotherms for the sorption of the Cu^{2+} ion on the modified zeolite are shown in Figs. 9 and 10. The straight lines obtained for the two sorption isotherms indicate that the sorption of both ions fit with the investigated isotherm models. The corresponding Langmuir and Freundlich parameters along with correlation coefficient are given in Table 4. The slope of the Freundlich isotherm for all cases is less than one, indicating a concentration dependent sorption of Cu^{2+} ions onto modified zeolites PNa_2-Y and Na-Y. Also, the monolayer sorption capacity (Q^o) for copper ion was found to be higher for PNa_2-Y than the Na-Y zeolite. The Langmuir constants, Q^o and b increase with the increase in temperature showing that the sorption capacity and intensity of the sorption are enhanced at higher temperatures. Hence, the active surfaces available for sorption might have increased with increase in temperature. Another reason is the change in pore size by which enhanced rate of intraparticle diffusion of the solute [26].

Although the Freundlich and Langmuir Constants, K_F and Q^o, respectively have different meanings they lead to the same conclusion about the correlation of the experimental data with the sorption model. The basic difference between K_F and Q^o is that Langmuir isotherm assumes sorption free energy independent of both surface coverage and the formation of monolayer, and the solid surface reaches saturation while the Freundlich isotherm does not

Table 4
Langmuir isotherm plots for the sorption of Cu^{2+} ions from aqueous solutions onto (a) Na-Y; (b) PNa_2-Y zeolites

Temperature (K)	Langmuir isotherm			Freundlich isotherm		
	Q_o (mmol/g)	b (l/mmol)	R_L^2	$1/n$	K_F (mmol/g)	R_F^2
Na-Y						
303	1.42	0.122	0.990	0.33	0.69	0.983
313	1.65	0.138	0.996	0.30	0.71	0.978
323	1.93	0.167	0.991	0.26	0.79	0.979
PNa_2-Y						
303	2.37	0.142	0.993	0.29	0.42	0.964
313	2.69	0.157	0.995	0.27	0.47	0.948
323	2.99	0.182	0.998	0.24	0.49	0.938

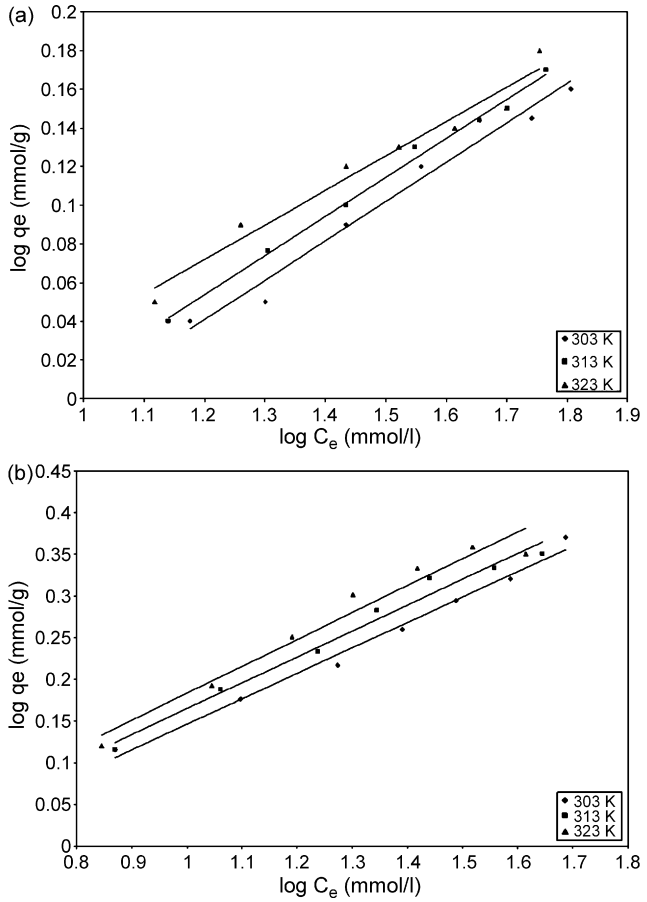

Fig. 10. Freundlich isotherm plots for the sorption of Cu^{2+} ions from aqueous solutions onto (a) Na-Y; (b) PNa_2-Y zeolites.

predict saturation of the solid surface by the sorbate, and therefore, the surface coverage being mathematically unlimited. In conclusion, Q^o is the monolayer sorption capacity while K_F is the relative sorption capacity or sorption power [26].

3.5. Determination of thermodynamic parameters

Thermodynamic parameters such as enthalpy change (ΔH°), free energy change (ΔG°) and entropy change (ΔS°) can be estimated using equilibrium constants. The free energy change of the sorption reaction is given by the following equation.

$$K_D = \frac{\text{Amount of metal in adsorbent}}{\text{Amount of metal in solution}} = \frac{V}{W} \quad (8)$$

$$\Delta G^\circ = -RT \ln K_D \quad (9)$$

where ΔG° is the standard free energy change (J) and R is the universal gas constant, 8.314 $mol^{-1}\,K^{-1}$. The distribution coefficient (K_D) increased with the increase of temperature, indicating the endothermic nature of adsorption. A plot of ΔG° versus temperature T (K), was found to be linear .The value of ΔH° and ΔS° were determined from the slope and intercept of the plots and the values are shown in Table 5. The negative values of ΔG° at various temperatures indicate the spontaneous nature of the adsorption processes. The positive value of ΔS° indicates an increase in the randomness from solid to solution interface during the adsorption process. In addition, the positive value of ΔH° indicates that the adsorption is endothermic.

Table 5
Thermodynamic parameters for the sorption of Cu^{2+} ions from aqueous solutions onto (a) Na-Y; (b) PNa_2-Y zeolites

Temperature (K)	$-\Delta G^\circ$ (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
Na-Y			
303	0.019	1.357	0.0104
313	0.029		
323	0.060		
PNa_2-Y			
303	0.110	2.413	0.0195
313	0.163		
323	0.199		

4. Conclusions

From this study it is concluded that phosphoric acid modified-Y zeolite can be a better adsorbent than the parent zeolite. The modification can also be extended to other zeolites for enhanced sorption properties. The modified zeolites can be employed for the removal of all types of heavy metal ions .The adsorption isotherm data fit well with Langmuir isotherm while the kinetic data were represented by Pseudo-second-order kinetic model. The removal efficiency increases with the increase in temperature and hence sorption process is endothermic in nature. This study forecasts that treatment of wastewater, particularly heavy metal ion removal and softening of hardwater, could be better carried out with the phosphoric acid modified zeolite than the parent NaY zeolite. It is suggested that the modification with phosphoric acid could also be extended to all other zeolites for such treatments. The results of this study cleary envisage that such modified zeolites can very well be recommended for wastewater treatment and control of environmental pollution.

References

[1] V.J. Inglezakis, M.M. Loizidou, Ion exchange studies on natural and modified zeolites and the concept of exchange site accessibility, J. Colloid Interface Sci. 275 (2004) 570–576.
[2] M.A. Stylianou, V.J. Inglezakis, K.G. Moustakas, Removal of Cu (II) in fixed and batch reactors using natural zeolite and exfoliated vermiculite as adsorbents, Desalination 215 (2007) 133–142.
[3] D.W. Breck, Zeolite Molecular Sieves, Structure Chemistry and Use, Wiley, New York, 1974.
[4] A. Dyer, Introduction to Zeolite Molecular sieves, John Wiley & Sons, Chichester, 1988.
[5] M.S. Berber-Mendoza, R. Leyva-Ramos, P. Alonso-Davila, Comparison of isotherms for the ion exchange of Pb (II) from aqueous solution onto homoionic clinoptilolite, J. Colloid Interface Sci. 301 (2006) 40–45.
[6] D. Mohan, C.U. Pittman Jr., P.H. Steele, Single, binary and multi-component adsorption of copper and cadmium from aqueous solutions on Kraft lignin—a biosorbent, J. Colloid Interface Sci. 297 (2006) 489–504.
[7] M.A. Keane, The removal of copper and nickel from aqueous solution using Y zeolite ion exchangers, J. Colloid Interface Sci. 297 (2006) 489–504.
[8] A.H. Englert, J. Rubio, Characterization and environmental application of a Chilean natural zeolite, Int. J. Miner. Process. 75 (2005) 21–29.
[9] V.J. Inglezakis, M.D. Loizidou, H.P. Grigoropoulou, Equilibrium and kinetic ion exchange studies of Pb^{2+}, Cr^{3+}, Fe^{3+}, and Cu^{2+} on natural clinoptilolite, Water Res. 36 (2002) 2784–2792.
[10] S. Kocaoba, Y. Orhan, T. Akyuz, Kinetic and equilibrium studies of heavy metal ions removal by use of natural zeolite, Desalination 214 (2007) 1–10.
[11] V. Chantawong, N.W. Harvey, V.N. Bashkin, Comparision of heavy metal adsorptions by Thai kaolin and ballclay, Water Air Soil Pollut. 148 (2003) 111–125.
[12] M. Arias, M.T. Barral, J.C. Majuto, Enhancement of copper and cadmium adsorption on kaolin by the presence of humic acid, Chemosphere 48 (2002) 1081–1088.
[13] O. Abollino, M. Aceto, M. Maiandrino, Adsorption of heavy metals on Na-montmorillonite: effect of pH and organic substances, Water Res. 37 (2003) 1619–1627.
[14] T.A. Kurniawan, G.Y.S. Chan, Comparisons of low-coast adsorbents for treating wastewaters laden with heavy metals, Sci. Total Environ. 366 (2006) 409–426.
[15] E.A. Ayuso, A. Garcia-Sanchez, Removal of heavy metals from wastewater by vermiculites, Environ. Technol. 24 (2003) 615–625.
[16] S.H. Lin, R.S. Juang, Heavy metal removal from water by sorption using surfactant-modified montmorrilonite, J. Hazard. Mater. B92 (2002) 315–326.

[17] J. Peric, M. Trgo, N.V. Medvidovic, Removal of zinc, copper, and lead by natural zeolite—a comparison of adsorption isotherms, Water Res. 38 (7) (2004) 1893–1899.
[18] J. Zhuang, D. Ma, G. Yang, Solid-state MAS NMR studies on the hydrothermal stability of the zeolite catalysts for residual oil selective catalytic cracking, J. Catal. 228 (2004) 234–242.
[19] Y. Yoshimura, N. Kijima, T. Hayakawa, Catalytic cracking of naphtha to light olefins, Catal. Surv. Jpn. 4 (2) (2000).
[20] A.K. Singh, D.P. Singh, K.K. Pandey, V.N. Singh, Wollastonite as adsorbent for removal Fe (II) from water, J. Chem. Technol. Biotechnol. 42 (1988) 39–47.
[21] G. McKay, Y.S. Ho, The sorption of lead (II) on peat, Water Res. 33 (1999) 585–587.
[22] G. McKay, Y.S. Ho, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–460.
[23] W.J. Weber, J.M. Morris, Kinetics of adsorption on carbon from solutions, J. Sanit. Eng. Div. Am. Soc. Eng. 89 (1963) 31–39.
[24] I. Langmuir, The adsorption pf gases on plane surfaces glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.
[25] H.M.F. Freundlich, Uber die adsorption in losungen, Zeitschrift fur physcikalische Chemie (Leipzig) 57A (1906) 385–470.
[26] D. Mohan, K.P. Sing, Single and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse an agricultural waste, Water Res. 36 (2002) 2304–2318.