Korean J. Chem. Eng., 33(5), 1629-1639 (2016)
DOI: 10.1007/s11814-015-0299-0

pISSN: 0256-1115
eISSN: 1975-7220

Kinetic, thermodynamic and equilibrium studies on the removal of copper ions from aqueous solutions by natural and modified clinoptilolites

Mehdi Irannajad†, Hossein Kamran Haghighi, and Eshagh Safarzadeh

Department of Mining and Metallurgical Engineering, Amirkabir University of Technology, Tehran, Iran

(*Received 5 July 2015 • accepted 30 December 2015*)

Abstract−This paper presents the adsorption of Cu(II) ions from aqueous solution on Na and Fe-modified clinoptilolite. The copper adsorption experiments were performed in a batch system considering an optimum contact time of 24 h. Changes in the surfaces and structure were characterized by SEM data. According to the SEM results, it was anticipated that the removal efficiency of Fe-modified clinoptilolite was the highest compared with the natural and Na-modified clinoptilolites. Adsorption of Cu(II) ions by modified clinoptilolites was investigated as a function of the initial Cu(II) concentration, solution pH, and temperature. According to the results, the maximum adsorbed Cu amount onto Fe-modified was 19.40 mg/*l* at the optimum operating condition with a pH value of 5.5 and temperature of 60 °C. According to the thermodynamic evaluations, positive ΔS and negative ΔG were found for the adsorption process showing that the adsorption reaction is a spontaneous process and more favorable at high temperatures. Sorption data have been interpreted in terms of Langmuir and Freundlich, Temkin and Dubinin-Radushkevich. The adsorption equilibrium was best described by the Langmuir adsorption isotherm. In addition, according to the Sips model, the sorption of Cu(II) ions on the Fe-modified clinoptilolite was found to be heterogeneous. The kinetic study showed that the Fe-modified clinoptilolite followed the pseudo-second order model. The results indicated that the clinoptilolite-rich tuff in its iron oxide form could be efficiently used for the removal of copper from aqueous solutions.

Keywords: Copper, Adsorption, Clinoptilolite, Kinetic, Thermodynamic, Isotherm

INTRODUCTION

Wastewaters containing heavy metals are being continuously produced and pollute the environment by various activities. Heavy metals are toxic or dangerous, endangering human health [1]. Copper is one of the most important hazardous metals in industrial wastewaters [1], and a high concentration of it can cause grievous health problems. Zeolites are crystalline hydrated aluminosilicates of alkaline earth cations with an open-framework of tetrahedral $(Si,Al)O_4$ components. Among these minerals, clinoptilolite is the most common natural zeolite categorized in the heulandite group, the structure of which is characterized by large crossing open channels. The specific physico-chemical characterization of this mineral such as high crystallinity, regular sub-nanometric cavities, and highly selective ion-exchange capacity, makes it applicable in heavy metal sorbents [2]. Clinoptilolite is the most well-known and abundant natural zeolite. It has large sedimentary mines with high purity in the world [3,4]. The negative charge of the clinoptilolite framework is counterbalanced with cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) which come from tetrahedral coordinated aluminum [5].

The main methods to remove heavy metals from wastewaters include coagulation, carbon adsorption, ion exchange, precipitation, reverse osmosis, etc. [6]. The adsorption technique is usual for the removal of heavy metals from waste water and has advantages over other removal techniques like being economical and readily accessible [7,8]. Zeolite usage for environmental remediation is a well-known technique [9-12]. The capability of clinoptilolite for removal of various ions makes it applicable for environmental remediation. With respect to the type of treatment, clinoptilolites are classified into two groups: natural and modified. Pretreatment operation on natural clinoptilolite is usually carried out to change its characteristics. There are many pretreatment methods to improve the characteristics of clinoptilolite. It is chemically pretreated to eliminate cations and locate removable ones more readily before its usage [13]. One of these pretreatments is performed by various tetrachloride salts. For instance, the kinetic study on the uptake of heavy metals by Bulgarian natural zeolite showed that among these elements, Pb was immobilized by natural zeolite and the rate of elemental immobilization was enhanced by zeolite pretreated with NaCl [14]. The modification of clinoptilolite with HCl enhances the acidity and the effective diameter of the channels and pores [15]. The specific surface area for the zeolite treated by sodium salts was more than that for the untreated zeolite. Investigation of the sorption characteristics of a Mexican clinoptilolite-rich tuff for iron, manganese, and iron-manganese systems indicated that sodium treated zeolite removed more Mn and Fe from a solution. Elimination of arsenic from drinking water was examined using pretreated clinoptilolite with NaCl and $FeCl_3$ [16]. The results showed that at a lower initial arsenate concentration, the adsorption rate and concentration of arsenate were increased when the treated clinoptilolite was used. Recently, clinoptilolite treated with HCl was used as an adsorbent for the removal of Cu^{2+} [17]. The results of this study showed that the adsorption of copper using the treated clinoptilolite is dependent on the pH of the adsorbent, contact

---

†To whom correspondence should be addressed.
E-mail: iranajad@aut.ac.ir

time, temperature, mass of adsorbent, and the initial concentration of the metal in the synthetic wastewater [17].

The other chemical substance used for pretreatment of natural clinoptilolite is iron. Fe-treated zeolites have been described to be capable of adsorbing high concentrations of heavy metals in solutions, which mainly depend on the pH, temperature and metal concentration [18-24]. The sorbent characteristic of the iron oxides improves the characteristics of natural clinoptilolites. Natural clinoptilolite can be treated and modified by adding it to an iron solution. Doula [24] synthesized natural clinoptilolite by adding it to an iron nitrate solution under strong alkaline conditions [24]. In this research, the treated system adsorbed larger Cu concentrations than natural clinoptilolite. Dimirkou and Doula [25] applied the clinoptilolite-iron oxide system (Clin-Fe system) for the elimination of Mn^{2+} and Zn^{2+} ions from drinking water [25]. Dimirkou and Doula applied the aforementioned system for the elimination of Cu^{2+} and Zn^{2+} from contaminated drinking water [18,19]. Similar results were obtained for copper and zinc ions adsorption using the Clin-Fe system. At the experimental conditions of this research, the maximum adsorbed Mn amount for the natural and Fe-modified clinoptilolite was found to be 7.69 mg/g and 27.1 mg/g, respectively. Such enhancement also occurred for the uptake of Zn. Some researchers investigated lead elimination from solutions using the natural and iron-treated zeolite [26]. Furthermore, Doula [27] showed that the simultaneous elimination of Cu, Mn and Zn by amorphous Fe-oxide clinoptilolite was enhanced in comparison with unmodified clinoptilolite. There are some works carried out on the removal of copper single-ion by using various sorbents such as chitosan, kaolinite, montmorillonite, their modified derivatives, sawdust, lignin and clinoptilolite [17,28-31]. However, the lack of research on the adsorption modeling of copper single-ion by untreated, sodium and iron-treated clinoptilolites is seen. Thus, in this study, the development of kinetic and isothermal models and thermodynamic evaluations has been carried out for the first time.

The main aim of this study was to examine the capability of using Na-, Fe-modified and natural clinoptilolite for the maximum removal of Cu(II) ions from aqueous solutions. In this study, an economical, readily available and successful adsorbent material, clinoptilolite, was identified as an attractive alternative adsorbent for Cu(II) removal from polluted aqueous solutions after being modified with iron oxides. Adsorption of Cu(II) ions by Fe-modified clinoptilolites was investigated as a function of the initial Cu(II) concentration, solution pH, and temperature. Finally, the kinetic and isothermal models and thermodynamic evaluations for the copper adsorption using Fe-modified clinoptilolite have been investigated.

MATERIAL AND METHODS

1. Clinoptilolite

Samples of natural zeolite were taken from Abegarm mine (Semnan, Iran) with a particle size range of 0.5-0.7 mm. With respect to the XRD analysis of the natural sample, the major phase composition of the natural zeolite used in this work was clinoptilolite, whereas the minor phases were quartz and gypsum. To justify XRD analysis, the results obtained by the optical microscopy are illustrated in Fig. 1. The exchange cations were Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}. The chemical composition of the sample is presented in Table 1. As can be seen, the natural clinoptilolite contained SiO_2 (61.0%) and Al_2O_3 (9.55%), while the content of other metal oxides was less than 10%. Thus, the Si/Al ratio of the natural clinoptilolite of this study is 5.27, which is close to some natural clinoptilolites [16,32].

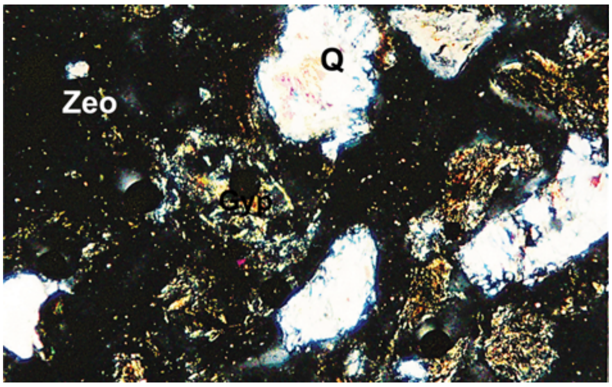

Fig. 1. Optical microscopy analysis for natural clinoptilolite (Zeo: Zeolite; Q: Quartz; Gyp: Gypsum).

The modified and natural clinoptilolites were first heated at 65 °C for 13 h before BET analysis. The surface areas of these clinoptilolites were evaluated with respect to the Brunauer Emmett-Teller method (BET) by nitrogen adsorption using a NOVA 2200e surface area & pore size analyzer.

2. Fe-modified Clinoptilolite

The aim of chemical treatment is not only to remove certain cations from the structure of the clinoptilolite but also to substitute more easily replaceable ions [33]. The Fe-modified clinoptilolite was prepared by the following method: the sample was prepared by mixing 30 g of clinoptilolite, 100 mL of 1 M $Fe(NO_3)_3$ solution prepared from its salt with the grade of >99% from Merck, and 180 mL of 5 M KOH solution obtained from its powder with the grade of 90% from flake. The suspension was diluted to 2,000 mL with water kept at 70 °C for 60 h and then washed with distilled water followed by drying for a day.

3. Na-modified Clinoptilolite

The Na-modified clinoptilolite was prepared by contacting 1 M NaCl solution with natural clinoptilolite for 24 h. The NaCl solution was prepared from its salt with the grade of ≥99%, purchased from Merck. The treated clinoptilolite was then washed with deionized water until no presence of chloride ions was observed. Finally, the sample was dried at 90 °C for 24 h.

4. Cation Exchange Capacity

The composition of the natural clinoptilolite illustrated in Table 1

Table 1. Chemical composition of natural clinoptilolite sample (wt%)

Composition	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	LOI	Si/Al
%	61.3	0.33	9.55	1.40	3.68	0.78	3.68	2.68	2.80	13.90	5.23

was used to evaluate the cation exchange capacity (CEC). According to the literature, the hypothetical CEC was readily obtained by the sum of mmol of Al and Fe per gram of clinoptilolite [34]. In this study, this value was found to be 2.05 mequiv/g.

To find the experimental value of CEC, 1 g of the natural clinoptilolite was added to 100 mL of 1 M NaCl solution. Then, the amount of cations released from the zeolite during the Na exchange was analyzed and found to be 1.81 mequiv/g. Thus, the value of 1.81 mequiv/g was approved as CEC. It was supposed that the other cations such as K, Ca and Mg would not contribute to the cation exchange.

5. Stock Copper Solutions

A stock solution of copper was prepared in various concentrations using metal salts dissolved in deionized water. These solutions for the batch study were made by using $CuSO_4\cdot 6H_2O$ (purchased from Merck) and pH values were adjusted by adding NaOH and HCl solutions (purchased from Merck).

6. Experiments

All sorption experiments were conducted by mixing 2 g of natural or modified clinoptilolites with 40 mL of synthetic solutions having various concentrations of copper ions, and temperatures. The mixture was equilibrated for various times and then filtered. The final concentration of the heavy metal ions in the aqueous phase was then determined using an atomic absorption spectrophotometer (AAS). Removal or sorption efficiency of the system ($\%S_{eff.}$) is obtained from the removed metal ion to the initial amount ratio as in Eq. (1):

$$\%\ S_{eff.}=((C_i-C_e)/C_i)\times 100 \quad (1)$$

where C_i and C_e are the initial and final concentrations of metal ions in the solution (mg/*l*), respectively.

6-1. Effect of the Initial pH

To determine the effect of an initial pH on adsorption, 40 mL of the synthetic solution containing 1,000 mg/L of copper ions was contacted with 2 g of Fe-modified clinoptilolite under the condition being the pH range of 2.5 to 5.5, the temperature of 20 °C and time of 24 h. The pH values were adjusted by adding HCl and NaOH solutions.

6-2. Effect of the Initial Copper Concentration

The effect of various metal concentrations in the range of 200 to 1,000 mg/*l* on the removal efficiency was investigated at the optimum pH of 5.5 and clinoptilolite dosage of 2 g per 40 mL for 24 h.

6-3. Effect of Temperature on Cu^{2+} Removal

The effect of temperatures (20, 40, and 60) °C on the metal removal was determined while keeping all other parameters constant. 40 mL of Cu^{2+} solutions with different initial concentrations in sealed containers were contacted with 2 g of Fe-modified clinoptilolite for 24 h at a pH of 5.5 and different temperatures.

6-4. Adsorption Isotherms

The investigation of the isotherm data is vital to evaluate an equation, which could be used for design purposes. As mentioned, one of the innovations of this study is to derive adsorption isotherms for copper ion removal by clinoptilolites in terms of Langmuir and Freundlich, Sips, Tempkin, and Dubinin-Radushkevich. All experiments to construct the adsorption isotherms were conducted at the condition being the temperature of 60 °C, pH of 5.5, the adsorbent dosage of 2 g, the solution volume of 40 mL and time of 24 h.

The following parameters were used in the adsorption studies: sorption capacity of the substrate (q_e) expressed in terms of metal amount absorbed on the unitary natural sorbent mass (S: mg/g) and C_i and C_e are the initial and final (equilibrium) concentration of Cu(II) solution (mg/*l*). The q_e parameter has been calculated as indicated in Eq. (2):

$$q_e=(C_i-C_e)/S \quad (2)$$

where C_i and C_e are the initial and final concentrations of metal ions in the solution (mg/*l*), respectively, and S is the concentration of adsorbent in the mixture (g/*l*).

6-5. Kinetic Evaluation

The following adsorption kinetic models were used to deduce the experimental data and evaluate the controlling mechanism of copper adsorption:

Lagergren's first-order rate expression, namely pseudo-first-order rate equation, has been widely used to image adsorption processes [35]. The integrated form of this equation is given in Eq. (3):

$$\log(q_e-q_t)=\log q_e-\frac{k_1 t}{2.203} \quad (3)$$

where q_e represents the adsorption capacity at an equilibrium state and q_t (mg g^{-1}) is the amount of ion adsorbed per unit of adsorbent at any time of t. Furthermore, k_1 (min^{-1}) indicates the pseudo-first order constant. The k_1 constant was obtained from the plot of log (q_e-q_t) against t.

The pseudo-second-order-rate model is another well-known model used in adsorption studies [35,36]. The integrated form of this model is defined as follows (Eq. (4)):

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

In this equation, k_2 (g m/g min) indicates the rate constant of the pseudo-second-order and the other parameters are similar to the parameters introduced in Eq. (3). The k_1 constant and q_e were obtained by the linear plot of t/q_t against t.

RESULTS AND DISCUSSION

1. Structural Comparison of Clinoptilolites

SEM analysis was applied to compare the three various types of clinoptilolites mentioned in this study. The SEM images of various types of clinoptilolites, shown in Fig. 2, show that the morphology of the crystals of clinoptilolites modified by NaCl and $FeNO_3$ is similar. In addition, the XRD results of Na-modified and natural clinoptilolites show no significant changes in the positions and intensities of the diffraction peaks. The XRD result of Fe-modified clinoptilolite indicates no new diffraction peaks. However, the intensity of reflections indicates the presence of Fe in the Fe-modified clinoptilolite structure. According to Fig. 2, the number of pores in the clinoptilolite surface is increased due to washing of impurities and formation of pores over the material in the surface. These pores are the most for Fe-modified in comparison with natural and Na-modified clinoptilolite. Therefore, it is antici-

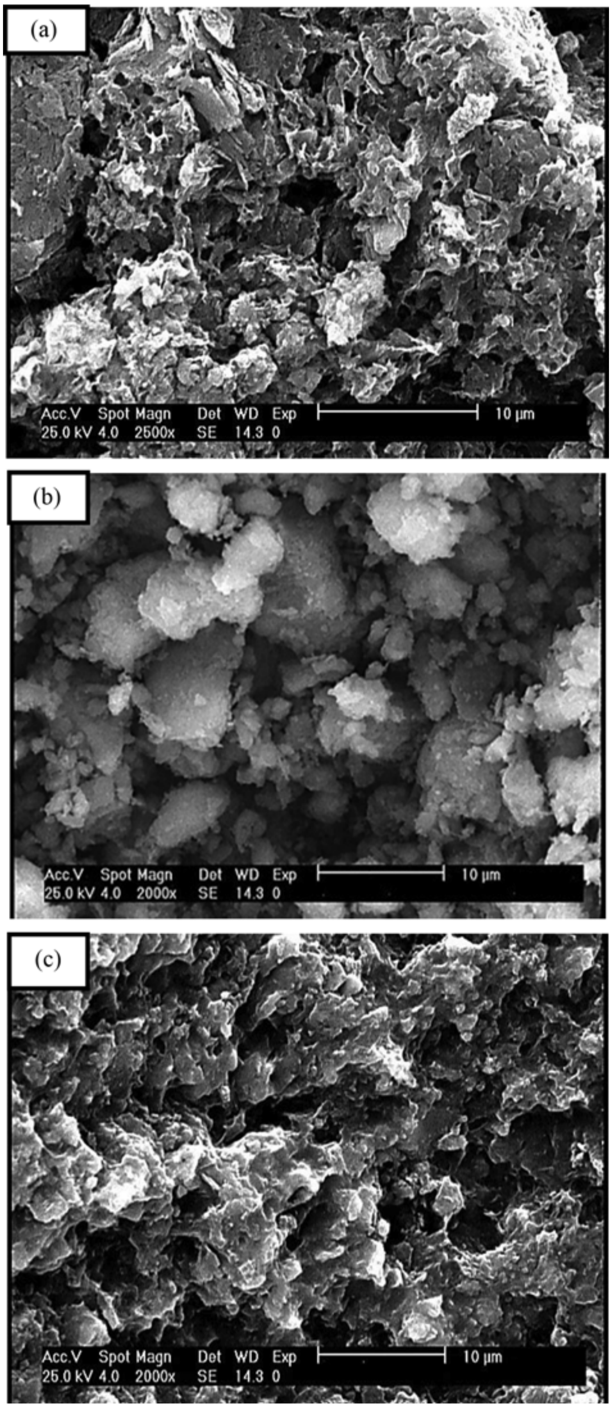

Fig. 2. **Scanning electron microscopy analysis for (a) natural, (b) Fe-modified and (c) Na-modified clinoptilolites.**

pated that the removal efficiency of Fe-modified clinoptilolite was the highest compared with the other two. Accordingly, the following experiments were conducted using Fe-modified clinoptilolite as an efficient adsorbent for the removal of copper ions from the solutions.

2. Effect of Solution pH

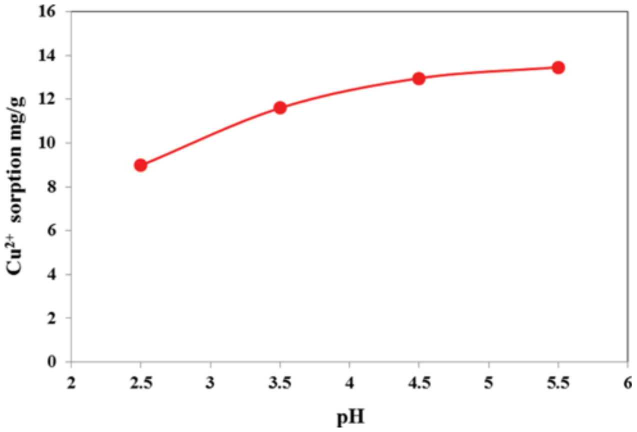

Fig. 3. **Effect of initial pH on metal sorption using natural clinoptilolite (concentration=1,000 mg/L, T=20 °C, pH=2.5-5.5, adsorbent dosage of 2 g, and solution volume of 40 mL).**

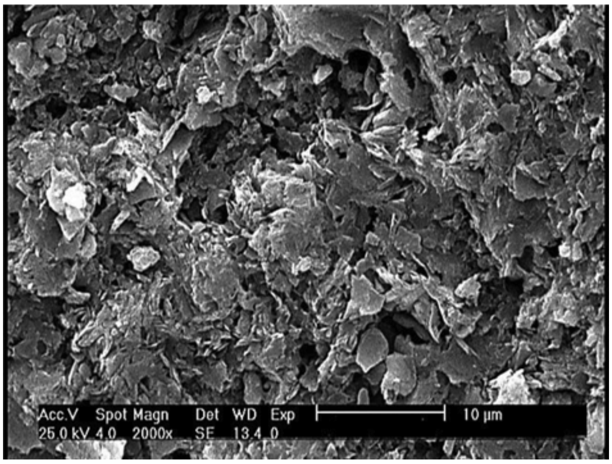

Fig. 4. **SEM images of copper adsorption in the lower pH using natural clinoptilolite (concentration=1,000 mg/L, T=20 °C, pH=3, time=120 h).**

The pH of the aqueous solution is a significant controlling parameter in the adsorption, and metal removal is usually enhanced with increasing pH values [13]. The number of copper ions adsorbed from the solution using natural clinoptilolite increases with an increase in initial solution pH as shown in Fig. 3. According to the literature, zeolites are not only influenced by solution pH, but also they change the pH of the solution. They tend to have a higher pH. Furthermore, the removal efficiency of metal ions generally increased when the initial pH of the solution was increased [13,25,37-39]. This is due to the high selectivity of clinoptilolites for H_3O^+ ions when the H_3O^+ ions concentration is high. Thus, at acidic pHs, the ions compete with H^+ in order to exchange the sites of clinoptilolite [13,40-42]. On the other hand, at higher pHs, the H^+ concentration is lower, giving way to more heavy metals being adsorbed from the solution as specified by enhancements in q_e [42]. The result of SEM illustrated in Fig. 4 confirms this. The reduction of the copper adsorption on natural clinoptilolite is seen in this figure.

In addition, a slight precipitate was detected in some of the adsorption reactions, indicating that the removal of heavy metal ions from liquid solution was due to not only ion exchange but

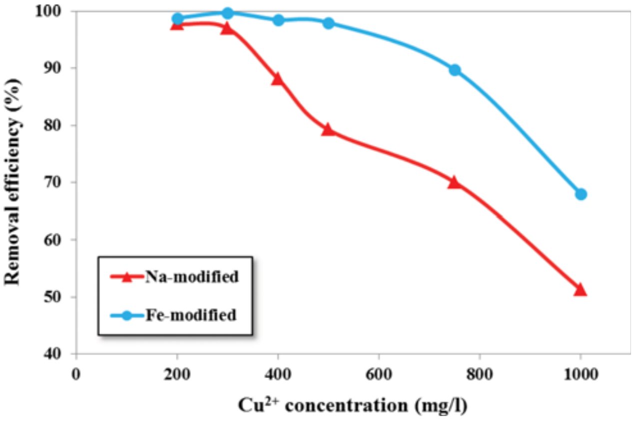

Fig. 5. Effects of metal concentration on removal efficiency of metal (T=20 °C, pH=5.5, adsorbent dosage of 2 g, and solution volume of 40 mL).

also settling in channels and the surface of the clinoptilolite [13].

3. The Effect of Metal Ions Concentration onto Modified Clinoptilolites

In the adsorption process, due to ion exchange reactions, exchangeable cations (Na, K, Ca, Mg) from the clinoptilolite lattice transferred to the solution, and copper cation ions from the solution bound to the clinoptilolite. Fig. 5 illustrates the effects of metal concentration on metal sorption (under the condition being as T=20 °C, pH=5.5, adsorbent dosage of 2 g, solution volume of 40 mL, and Cu concentration of 1,000 mg/L) for Fe-modified clinoptilolite. As shown in Fig. 5, the removal efficiency of metal decreased with an increase in initial Cu^{2+} concentrations for both samples. The decrease in metal removal with an increase in initial metal concentration refers to decreasing appropriate exchange sites for Cu^{2+} on the samples and proposes that the main mechanism for metal removal can be a cation exchange process [43,44].

It seems that the Fe-modified clinoptilolite retains almost the entire Cu^{2+} concentration from the solutions when the initial metal concentration is lower than 400 mg/L. Due to the presence of non-crystalline Fe formations located in the cationic positions in the zeolite channels, as well as amorphous iron oxides (goethite) located at the surface of the zeolite crystal, the adsorption capacity of Fe-modified clinoptilolite is higher than that of Na-modified clinoptilolite. This high adsorption capacity for the Fe-modified clinoptilolite belongs to the negative surface charge [45]. Fig. 6 shows that copper is adsorbed on the surface and is diffused in the Fe-modified clinoptilolite cavities. Furthermore, the experimental sorption capacity of Cu(II) for the Fe-modified clinoptilolite from a solution with the concentration of 1,000 mg/L was found to be 13.46 mg per one gram of adsorbent.

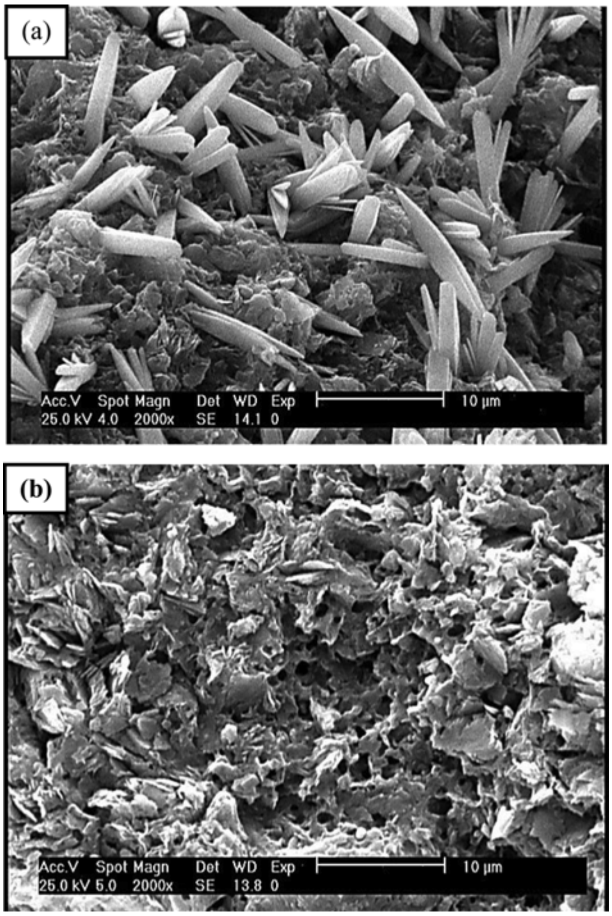

Fig. 6. SEM images of (a) copper adsorption on the surface of Fe-modified clinoptilolite and (b) diffusion of that in the clinoptilolite cavities (T=20 °C, pH=5.5, adsorbent dosage of 2 g, and solution volume of 40 mL).

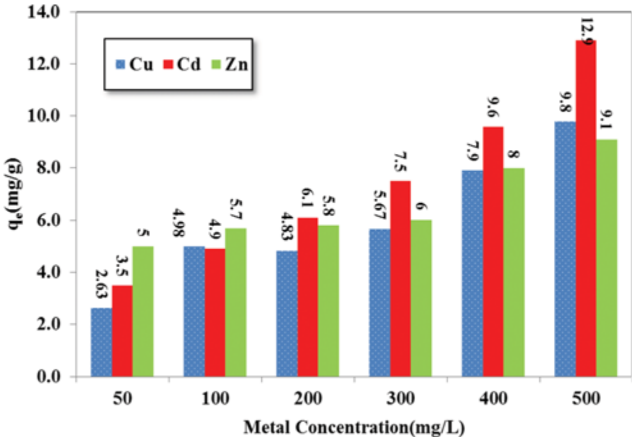

Fig. 7. Effect of interference ions on copper adsorption by Fe-modified clinoptilolite (T=20 °C, t=30 min, adsorbent dosage of 2 g, solution volume of 40 mL, and pH=5.5).

Fig. 7 shows the adsorption of copper in the presence of various concentrations of interference ions (zinc and cadmium). According to the results, the q_e of copper adsorption in the absence of impurities for the initial copper concentrations of 50, 100, 200, 300, 400 and 500 mg/L were 2.60, 4.02, 4.00, 5.98, 7.97, and 9.98, respectively. At lower concentrations of zinc and cadmium, the amount of copper adsorption in the absence of the impurities is lower than that of the condition in which impurities exist. Furthermore, the copper adsorption decreased with an increase of interference ions. According to this figure, the effect of zinc concentration on copper adsorption is less than that of cadmium. Some

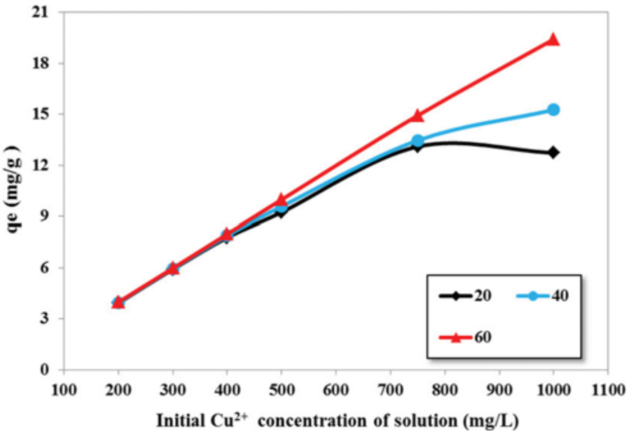

Fig. 8. Effect of temperature and copper concentration of solution on Cu^{2+} sorption using Fe-modified clinoptilolite (T=20, 40, 60 °C, pH=5.5, adsorbent dosage of 2 g, and solution volume of 40 mL).

researchers proposed that this behavior depends on the hydration energies [46,47]. The ions with the highest free energy of hydration should therefore favor staying in the solution phase. According to hydration energies, the selectivity adsorption for ions is as follows: Cd>Zn>Cu [46].

4. Effect of Temperature on Cu^{2+} Removal

The influence of temperatures at three levels of 20, 40, and 60 °C on the metal removal regarding the variations of initial copper concentration was investigated while keeping all other parameters constant. The results are illustrated in Fig. 8. Removal efficiencies for the Fe-modified clinoptilolite at three temperature levels of 20, 40, and 60 °C and constant concentration of Cu 1,000 mg/L were found to be 12.72, 15.26 and 19.40, respectively. In this research, we did a thermodynamic study to calculate changes in free energy (ΔG) at various temperatures, enthalpy (ΔH) and entropy (ΔS), respectively. According to the results, ΔG values for 20 °C (293 K), 40 °C (313 K), and 60 °C (323 K) were found to be −2535.54, −2709.07 and −2882.6 J/mol, respectively. Furthermore, the values corresponding to ΔH and ΔS were 6.66 J/mol and 8.68 J/mol·K, respectively. Positive ΔH values indicate the endothermic behavior of copper adsorption on the Fe-modified clinoptilolite. This indicates that adsorption enhances with an increase in temperature. Furthermore, positive ΔS and negative ΔG show that the adsorption reaction is a spontaneous process and more favorable at high temperatures. Obviously, since the temperature was being raised, the adsorption was increased and this enhancement probably occurred due to the exchange capability of the alkaline metals such as potassium and sodium (i.e., existing in the composition of clinoptilolite) that increased at high temperatures [13,48-50]. Some researchers also showed a direct correlation between the amount of heavy metal adsorbed in the Fe-modified zeolite and those of released calcium and sodium [26]. This enhancement was principally ascribed to the exchange of potassium and calcium cations and will simplify the heavy metal exchange in the solutions [48,51].

5. Adsorption Isotherms

Several equilibrium models have been developed to describe adsorption isotherm relationships. The two main isotherm models used in this work are the Langmuir and Freundlich models. The Langmuir isotherm is applied for describing monolayer homogeneous adsorption processes with Eq. (5) [52]:

$$C_e/q_e=C_e/q_m+1/K_Lq_m \tag{5}$$

where C_e is equilibrium concentration of Cu(II) ions (mg/L) and q_e is the amount of the Cu(II) ions adsorbed (mg) per unit of clinoptilolite (g); q_m and K_L are the Langmuir constants related to the monolayer capacity (mg/g) and the equilibrium constant (mg/L), respectively. By plotting C_e/q_e vs. C_e and determining the slope of the linear ($1/q_m$) and its intercept ($1/K_Lq_m$), the values of q_m and K_L were found.

The Freundlich isotherm is used for explaining the adsorption on heterogeneous surfaces as in Eq. (6) [53]:

$$\text{Log } q_e=\log K_F+(1/n)\log C_e \tag{6}$$

where K_F (mg/g) and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. In this isotherm, by plotting log(q_e) vs. log(C_e) and determining the slope (1/n) and the intercept of the linear (log K_F), the values of n and K_F were found.

With respect to the experimental and procedure sections, the Langmuir and Freundlich isotherms for copper ion removal by

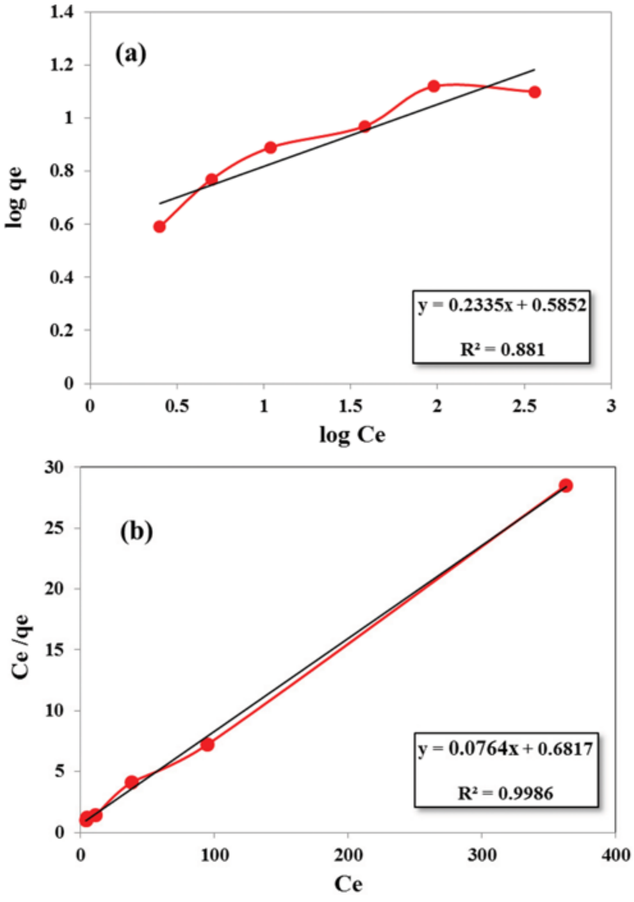

Fig. 9. Linearized (a) Freundlich and (b) Langmuir isotherms for Fe-modified clinoptilolite (T=60 °C, pH=5.5, adsorbent dosage of 2 g, and solution volume of 40 mL).

Table 2. The calculated parameters for Langmuir, Freundlich and Temkin Dubinin-Radushkevich isotherms

Isotherm parameters							
Langmuir		Freundlich		Temkin		Dubinin-Radushkevich	
q_m (*l*/g)	13.09	K_F (mg/g)	3.85	A_T (L/g)	1.18	q_s (mg/g)	33.61
K_L (*l*/mg)	0.11	n (g/*l*)	4.28	B (J/mol)	94.12	E (kJ/mol)	2.24
R^2	0.998	R^2	0.881	R^2	0.966	R^2	0.900

Fe-modified clinoptilolite were developed. As shown in Fig. 9, the experimental data fits well with the linearized Langmuir and Freundlich isotherms. The values of K_L, b, K_F and n obtained from both models are presented in Table 2. Generally, the Langmuir isotherm provided a better correlation for Fe-modified clinoptilolite with a regression coefficient of 0.99. Regarding this figure, the following Langmuir expressions were developed for copper adsorption: $C_e/q_e=0.6817+0.0764C_e$. Some researchers have also reported that, for all cases, the Langmuir model denotes a better fit to the data than the Freundlich model [13,37,48]. As seen in the isotherm results, a similar result was repeated in the present study.

Freundlich parameters (K_F and n) specify whether the nature of sorption is either favorable or unfavorable [54]. The intercept and the slope refer to sorption capacity and sorption intensity, respectively. According to the literature, slopes of <<1 show that "sorption intensity is favorable to the entire range of concentrations studied," whereas a harsh slope (>1) shows that the amount of sorption is favorable at high concentrations in comparison with lower concentrations" [54,55]. "*A high value of the intercepts, K_B is indicative of a high sorption capacity*" [55]. For our sorption study, n value is closer to unity, which indicates that sorption intensity is favorable for the entire concentrations.

The use of two isotherm models for Cu(II) adsorption suggests that in the monolayer sorption or the heterogeneous surface, both conditions exist under the experimental conditions. To exactly determine which type of sorption occurred on the surface, the Sips model was used. The Sips model (shown in Eq. (7)) is a combination of Langmuir and Freundlich equations applied for evaluating the heterogeneous/homogenous adsorption:

$$q_e=\frac{k_sC_e^n}{1+a_sC_e^n} \tag{7}$$

where, k_s represents the Sips model isotherm constant (L/g), α_s is the other Sips model constant (L/mg) and n is the model exponent. Fig. 10 shows the Sips model curve plotted for the Fe-modified clinoptilolite. According to the results, the R-squared value of 97% showed that the model well fitted the data. With respect to this model, the isotherm constants (k_s and α_s) and the exponent value were found to be 1.78, 1.72, and 0.29, respectively. According to the literature, the n value for homogeneous materials is 1, while for heterogeneous materials it is less than one [56]. Thus, with respect to the n value of this study (n<1), the sorption of Cu(II) ions on the Fe-modified clinoptilolite is assumed heterogeneous.

The Temkin isotherm model includes a factor that clearly considers the interactions between the adsorbent-adsorbate [57]. The heat of molecular adsorption in the layer would decrease due to these interactions. The adsorption is identified by a distribution of binding energies [58]. Eq. (8) shows the expression of Temkin model [57]:

$$q_e=\frac{RT}{b_T}\text{Ln}A_TC_e \tag{8}$$

In this equation $B=(RT/b_T)$ indicates the Temkin constant corresponding to heat of adsorption, A_T (L/g) is equilibrium binding constant related to maximum binding energy, C_e (mg/L) is the equilibrium concentration, T (K) is the absolute solution temperature and R (8.314 J/mol K) is the universal gas constant. According to the results shown in Fig. 11, the values of A_T and B were 1.18 L/g

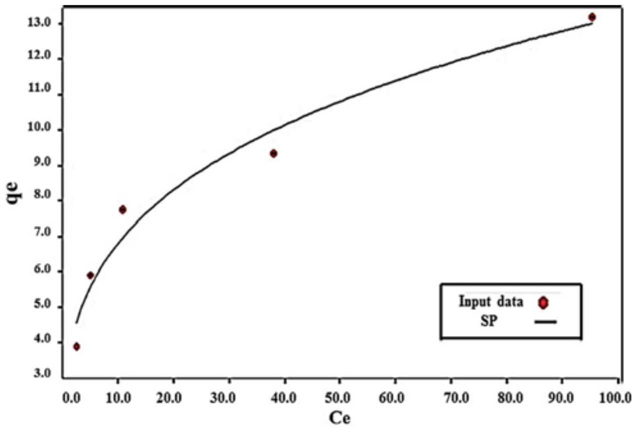

Fig. 10. Sips isotherm for Fe-modified clinoptilolite (T=60 °C, pH=5.5, adsorbent dosage of 2 g, and solution volume of 40 mL).

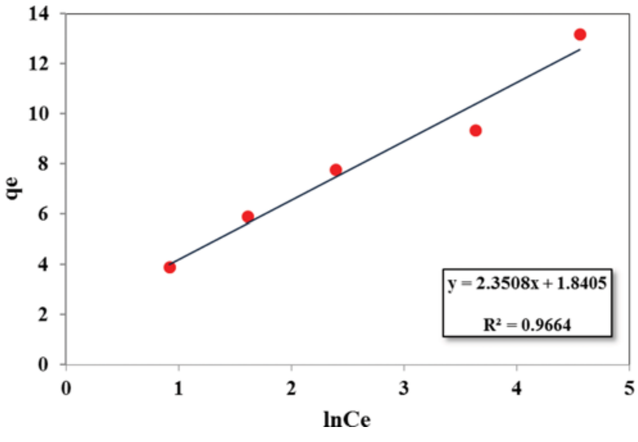

Fig. 11. Linear form of Temkin isotherm for Fe-modified clinoptilolite (T=60 °C, pH=5.5, adsorbent dosage of 2 g, and solution volume of 40 mL).

and 94.12 J/mol, respectively. According to Table 2, the R^2 of the model (0.966) shows a good fit for the Temkin model.

The Dubinin-Radushkevich isotherm has been commonly used to show the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [59,60]. With respect to the Sips model of this study, showing the heterogeneous sorption of Cu(II) ions on the clinoptilolite, the Dubinin-Radushkevich model can help to express the adsorption mechanism. This model is based on assuming energetically ionic species binding followed by multilayer adsorption [61]. Eqs. (9) and (10) are used to express the linear form of the Dubinin-Radushkevich isotherm:

$$\ln(q_e) = \ln(q_s) - K_{ad}\varepsilon^2 \tag{9}$$

$$\varepsilon = RT\ln\left[1+\frac{1}{C_e}\right] \tag{10}$$

In this equation, q_s is isotherm saturation capacity (mg/g), K_{ad} is Dubinin-Radushkevich isotherm constant (mol^2/kJ^2) and is Dubinin-Radushkevich isotherm. The approach was usually applied to discriminate the physical and chemical adsorption [62]. For calculating the energy used to remove a molecule from the surface, a parameter, namely E, can be examined using Eq. (11) [63,64]:

$$E = \left[\frac{1}{\sqrt{2K_{ad}}}\right] \tag{11}$$

According to the results obtained from Fig. 12, values of q_s, and E were 33.61 mg/g and 2.24 kJ/mol, respectively. These values represent the physical adsorption of ions. With respect to Table 2, the R^2 (0.900) represents a good fit for this model. Finally, according to Table 2, among the models discussed above, the Langmuir model has the highest correlation coefficient (0.998), indicating good expression of the adsorption process.

5. Effect of Time and Kinetic Study

The effect of contact time on the adsorption of Cu on Fe-modified clinoptilolite was investigated by varying time (5-25 h) in the initial ion concentration of 1,000 mg/L. Fig. 13 shows the results. The adsorption efficiency of copper increases with prolonging time. The rate of adsorption is initially rapid, but it slowly reduces with prolonging time until equilibrium state after 24 h. Therefore, the adsorption time of 24 h was selected as the best time for the adsorption of Cu^{2+} from aqueous solution when using Fe-modified

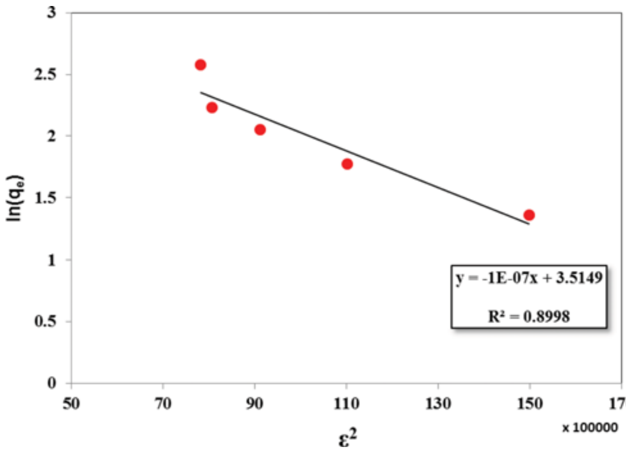

Fig. 12. Linear form of Dubinin-Radushkevich isotherm for Fe-modified clinoptilolite (T=60 °C, pH=5.5, adsorbent dosage of 2 g, and solution volume of 40 mL).

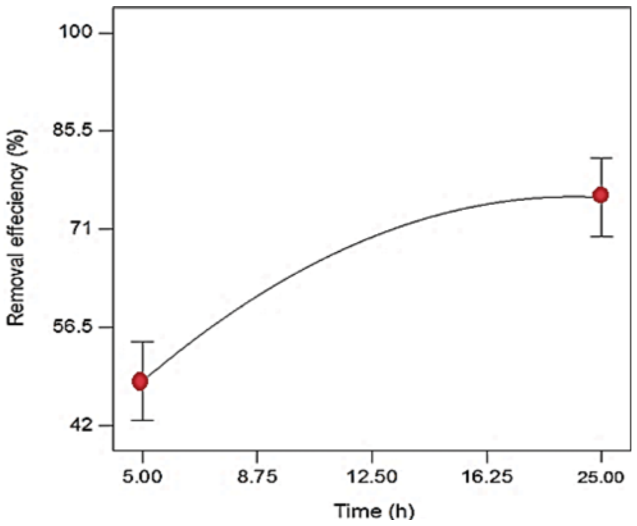

Fig. 13. Effect of contact time on the adsorption of Cu sorption (T=60 °C, pH=5.5, adsorbent dosage of 2 g, solution volume of 40 mL and Cu concentration of 1,000 mg/L).

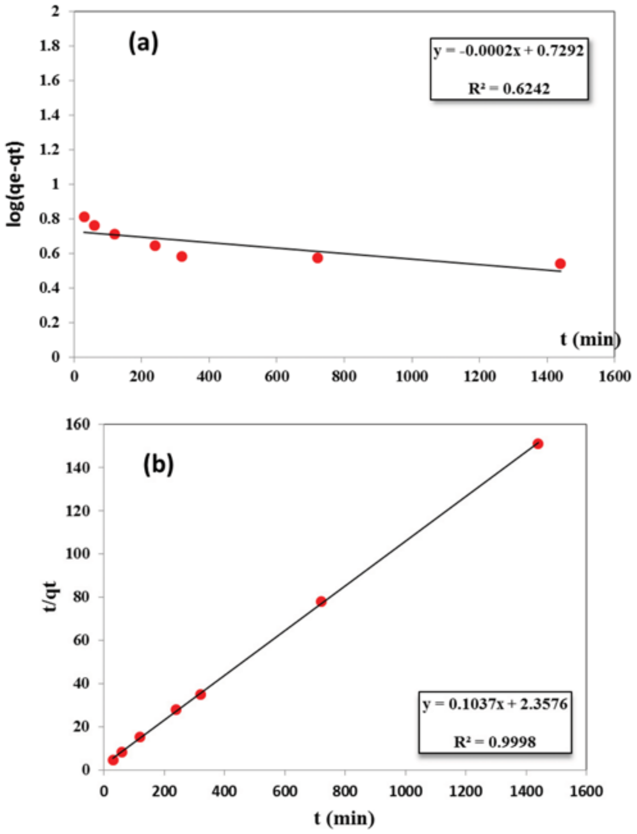

Fig. 14. (a) The pseudo first order model and (b) pseudo second order model for copper adsorption using Fe-modified clinoptilolite (T=60 °C, pH=5.5, adsorbent dosage of 2 g, solution volume of 40 mL, and Cu concentration of 1,000 mg/L).

Table 3. Comparison of zinc and cadmium adsorption using various adsorbents

Adsorbents	q_m (mg/g)	Ref.
Rice husk modified with tartaric acid	31.58	[69]
Sawdust (Poplar tree) modified with sulfuric acid	13.95	[70]
Sawdust (Poplar tree) modified with sodium hydroxide	6.92	[71]
Sawdust modified with Reactive Orange 13	8.07	[72]
Peanut husk modified with sulfuric acid	10.15	[73]
Cassava tuber bark waste modified with Thioglycollic acid	90.9	[74]
Jute fibres	8.40	[75]
Cork powder modified with Sodium chloride	19.5	[76]
Carrot residues modified with hydrochloric acid	45.09	[77]
Sugarbeet pulp modified with hydrochloric acid	0.15	[78]
Nipah palm shoot biomass modified with mercaptoacetic acid	66.71	[79]
Coirpith modified with Sulfuric acid and ammonium persulphate	39.7	[80]
Fe-modified zeolite in this study	13.46	

clinoptilolite as the adsorbent.

The kinetics of adsorption is a significant factor in the controlling process. To study the adsorption of copper using clinoptilolite, pseudo-first-order and pseudo-second-order kinetic models were applied to evaluate the adsorption process. Fig. 14 shows plots of the aforementioned kinetic models. Fig. 14(a) shows the first order kinetic curve. As seen, the correlation coefficient of copper adsorption is 0.626, which means that the modified clinoptilolite does not follow the pseudo-first order model. However, Fig. 14(b) shows the curve of t/q_e versus t belonging to the copper adsorption. The correlation coefficient for the pseudo-second order model (>.99) shows good agreement of the copper adsorption process with this model. This good agreement with the pseudo-second order kinetic model shows that the mechanism of adsorption belongs to the adsorbate and adsorbent [65,66]. This agrees with some studies performed on copper sorption using zeolites [67,68]. The values k_2 and q_e of this model were found to be 00.5 and 9.46, respectively.

6. Comparative Study

Table 3 shows a comparison of copper adsorption using various adsorbents. The copper sorption capacity of Fe-modified clinoptilolite is higher than that of some adsorbents such as sawdust (Poplar tree) modified with sodium hydroxide, sawdust modified with Reactive Orange, peanut husk modified with sulfuric acid, jute fibers and sugar beet pulp modified with hydrochloric acid. However, the other adsorbents such as cassava tuber bark waste, carrot residues, Nipah palm shoot biomass and coir pith have higher capacity in comparison with the adsorbent used in the present study.

7. Stability of Clinoptilolite

The stability of Fe-modified clinoptilolite was investigated in packed-column experiments. Stability experiments were performed in the pH range from 1 to 6 to evaluate the leaching of ions from Fe-modified clinoptilolite. With respect to the acidic treatment at a pH of 1, the clinoptilolite released insignificant quantities of Al, Fe, Na cations. According to the XRD patterns, Fe-modified clinoptilolite treated at pH 1-6 for 150 h had similar diffraction patterns with negligible variation in crystallinity. Elemental analysis by XRF confirmed that the Al composition of the Fe-modified and unmodified clinoptilolite at various pHs was similar. Similar results were obtained for Na and natural clinoptilolite.

CONCLUSION

This research describes the possibility of using clinoptilolite to remove Cu^{2+} ions from aqueous solutions. The samples were prepared in three different forms, which include one untreated and two treated. The results of SEM analysis showed that the number of pores in the clinoptilolite surface was increased, as the pores of Fe-modified clinoptilolite were more than natural and Na-modified clinoptilolite. The adsorption of Cu(II) ions by clinoptilolite samples was studied on the Fe-modified type as an effect of pH, initial concentration, and temperature. The optimum pH for the adsorption of Cu^{2+} is 5.5, and at lower pH the quantity of H^+ ions in the solution may compete for the sorption sites from the clinoptilolite network. Furthermore, according to the results, the removal efficiency of metal decreased with increasing initial Cu^{2+} concentrations for the modified clinoptilolite. In addition, with respect to the thermodynamic studies, the values corresponding to ΔH and ΔS were found to be 2.66 J/mol and 8.68 J/mol·K, respectively. Thus, positive ΔS and negative ΔG showed that the adsorption reaction was a spontaneous process. Sorption data have been interpreted in terms of Langmuir and Freundlich, Tempkin and Dubinin-Radushkevich. As a result, the adsorption equilibrium was best described by the Langmuir adsorption isotherm. In addition, according to the Sips model, the sorption of Cu(II) ions on the clinoptilolite was found to be heterogeneous. The kinetic study showed that the Fe-modified clinoptilolite follows the pseudo-second order model. According to the results, this adsorbent was appropriate for copper removal from aqueous media.

REFERENCES

1. F. Fu and Q. Wang, *J. Environ. Manage.*, **92**, 407 (2011).
2. K. Elaiopoulos, T. Perraki and E. Grigoropoulou, *Micropor. Mesopor. Mater.*, **112**, 441 (2008).
3. G. Gottardi and E. Galli, *Natural Zeolites*, Berlin, Springer-Verlag (1985).

4. F. A. Mumpton, *Natural Zeolites Occurrence Properties and Use*, New York, Pergamon (1976).
5. K. Koyama and Y. Takéuchi, *J. Crystallogr.*, **145**, 216 (1977).
6. W. W. Eckenfelder, *Industrial Water Pollution Control*, New York, McGraw-Hill (1989).
7. Ö. Yavuza, Y. Altunkaynakb and F. Güzel, *Water Res.*, **37**, 948 (2003).
8. H. Cui, L. Y. Li and J. R. Grace, *Water Res.*, **40**, 3359 (2006).
9. K. Payne and T. Abdel-Fattah, *J. Environ. Sci. Health*, **Part A A39**, 2275 (2004).
10. T. M. Abdel-Fattah, L. K. Isaacs and K. Payne, *Federal Facilities Environ. J.*, **14**, 113 (2003).
11. S. Babel and T. A. Kurniawan, *J. Hazard. Mater.*, **97**, 219 (2003).
12. K. Payne and T. M. Abdel-Fattah, *J. Environ. Sci. Health*, **40**, 723 (2005).
13. S. Çoruh, *Desalination*, **225**, 41 (2008).
14. M. Panayotova and B. Velikov, *J. Environ. Sci. Health A.*, **37**, 139 (2002).
15. A. Arcoya, J. Gonzalez, N. Travieso and X. Seoane, *Clay Minerals*, **29**, 123 (1994).
16. M. Bilici Baskan and A. Pala, *Desalination*, **281**, 396 (2011).
17. S. A. Abdulkareem, E. Muzenda, A. S. Afolabi and J. Kabuba, *Arabian J. Sci. Eng.*, **38**, 2263 (2013).
18. A. Dimirkou, *Water Res.*, **41**, 2763 (2007).
19. M. K. Doula and A. Dimirkou, *J. Hazard. Mater.*, **151**, 738 (2008).
20. A. Dimirkou, A. Ioannou and M. Doula, *Adv. Colloid Interface Sci.*, **97**, 37 (2002).
21. Z. Li, J.-S. Jean, W.-T. Jiang, P.-H. Chang, C.-J. Chen and L. Liao, *J. Hazard. Mater.*, **187**, 318 (2011).
22. E. Erdal, *J. Hazard. Mater.*, **165**, 63 (2009).
23. D. K. Maria, *Water Res.*, **40**, 3167 (2006).
24. M. K. Doula, *Chemosphere*, **67**, 731 (2007).
25. A. Dimirkou and M. K. Doula, *Desalination*, **224**, 280 (2008).
26. M. Kragović, A. Daković, Ž. Sekulić, M. Trgo, M. Ugrina, J. Perić and G. D. Gatta, *Appl. Surface Sci.*, **258**, 3667 (2012).
27. M. K. Doula, *Water Res.*, **43**, 3659 (2009).
28. W. S. Wan Ngah, C. S. Endud and R. Mayanar, *React. Funct. Polym.*, **50**, 181 (2002).
29. K. G. Bhattacharyya and S. S. Gupta, *Sep. Purif. Technol.*, **50**, 388 (2006).
30. B. Acemioğlu, A. Samil, M. H. Alma and R. Gundogan, *J. Appl. Polym. Sci.*, **89**, 1537 (2003).
31. S. Larous, A. H. Meniai and M. B. Lehocine, *Desalination*, **185**, 483 (2005).
32. B. Concepción-Rosabal, G. Rodríguez-Fuentes, N. Bogdanchikova, P. Bosch, M. Avalos and V. H. Lara, *Micropor. Mesopor. Mater.*, **86**, 249 (2005).
33. R. Petrus and J. WarchoÅ, *Micropor. Mesopor. Mater.*, **61**, 137 (2003).
34. N. Lihareva, L. Dimova, O. Petrov and Y. Tzvetanova, *Micropor. Mesopor. Mater.*, **130**, 32 (2010).
35. H. Yuh-Shan, *Scientometrics*, **59**, 171 (2004).
36. S. Kocaoba, Y. Orhan and T. Akyuz, *Desalination*, **214**, 1 (2007).
37. K. S. Hui, C. Y. H. Chao and S. C. Kot, *J. Hazard. Mater.*, **127**, 89 (2005).
38. M. Sprynskyy, B. Buszewski, A. P. Terzyk and J. Namiesnik, *J. Colloid Interface Sci.*, **304**, 21 (2006).
39. V. J. Inglezakis, M. D. Loizidou and H. P. Grigoropoulou, *J. Colloid Interface Sci.*, **261**, 49 (2003).
40. E. Álvarez-Ayuso, A. García-Sánchez and X. Querol, *Water Res.*, **37**, 4855 (2003).
41. A. H. Ören and A. Kaya, *J. Hazard. Mater.*, **131**, 59 (2006).
42. N. Moreno, X. Querol and C. Ayora, *Environ. Sci. Technol.*, **35**, 3526 (2001).
43. K. Gedik and I. Imamoglu, *J. Hazard. Mater.*, **155**, 385 (2008).
44. V. J. Inglezakis, M. D. Loizidou and H. P. Grigoropoulou, *Desalination*, **214**, 1 (2007).
45. M. K. Doula, *Water Res.*, **40**, 3167 (2006).
46. S. K. Ouki and M. Kavannagh, *Waste Manage. Res.*, **15**, 383 (1997).
47. G. Eisenman, *Biophysical J.*, **2**, 259 (1962).
48. U. Wingenfelder, B. Nowack, G. Furrer and R. Schulin, *Water Res.*, **39**, 3287 (2005).
49. L. Ćurković, Š. Cerjan-Stefanović and T. Filipan, *Water Res.*, **31**, 1379 (1997).
50. V. J. Inglezakis, K. J. Hadjiandreou, M. D. Loizidou and H. P. Grigoropoulou, *Water Res.*, **35**, 2161 (2001).
51. S. CerjanStefanovic, L. Ćurkovic and T. Filipan, *Croat. Chem.*, **Acta**, 281 (1996).
52. I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
53. H. Freundlich, *Z. Phys. Chem.*, **57**, 385 (1906).
54. F. H. Frimmel and L. Huber, *Environ. Int.*, **22**, 507 (1996).
55. G. McKay, M. S. Otterburn and A. G. Sweeney, *Water Res.*, **14**, 21 (1980).
56. E. Gutiérrez-Segura, M. Solache-Ríos, A. Colín-Cruz and C. Fall, *J. Environ. Manage.*, **97**, 6 (2012).
57. M. I. Tempkin and V. Pyzhev, *Acta Phys. Chim.*, **12**, 327 (1940).
58. A. Dada, A. Olalekan, A. Olatunya and O. Dada, *J. Appl. Chem.*, **3**, 38 (2012).
59. A. Günay, E. Arslankaya and İ. Tosun, *J. Hazard. Mater.*, **146**, 362 (2007).
60. A. Dąbrowski, *Adv. Colloid Interface Sci.*, **93**, 135 (2001).
61. J. Perić, M. Trgo and N. Vukojević Medvidović, *Water Res.*, **38**, 1893 (2004).
62. J. Rouquerol, F. Rouquerol, P. Llewellyn, G. Maurin and K. S. Sing, *Adsorption by powders and porous solids: principles, methodology and applications*, Academic Press (2013).
63. M. M. Dubinin, *Chem. Rev.*, **60**, 235 (1960).
64. J. P. Hobson, *The J. Phys. Chem.*, **73**, 2720 (1969).
65. F. A. Pavan, S. L. P. Dias, E. C. Lima and E. V. Benvenutti, *Dyes Pigm.*, **76**, 64 (2008).
66. V. Vimonses, S. Lei, B. Jin, C. W. K. Chow and C. Saint, *Chem. Eng. J.*, **148**, 354 (2009).
67. D. Georgiev, B. Bogdanov, Y. Hristov and I. Markovska, *World Academy of Sci., Eng. Technol.*, **6**, 1098 (2012).
68. R. Han, W. Zou, Z. Zhang, J. Shi and J. Yang, *J. Hazard. Mater.*, **137**, 384 (2006).
69. K. K. Wong, C. K. Lee, K. S. Low and M. J. Haron, *Process Biochemistry*, **39**, 437 (2003).
70. F. N. Acar and Z. Eren, *J. Hazard. Mater.*, **137**, 909 (2006).
71. M. Sciban, M. Klasnja and B. Skrbic, *Wood Sci. Technol.*, **40**, 217 (2006).
72. S. Shukla and R. S. Pai, *Sep. Purif. Technol.*, **43**, 1 (2005).
73. Q. Li, J. Zhai, W. Zhang, M. Wang and J. Zhou, *J. Hazard. Mater.*, **141**, 163 (2007).

74. M. Horsfall Jr., A. A. Abia and A. I. Spiff, *Bioresour. Technol.*, **97**, 283 (2006).
75. S. Shukla and R. S. Pai, *Bioresour. Technol.*, **96**, 1430 (2005).
76. N. Chubar, J. R. Carvalho and M. J. N. Correia, *Colloids Surf., A: Physicochem. Eng. Aspects.*, **238**, 51 (2004).
77. B. Nasernejad, T. E. Zadeh, B. B. Pour, M. E. Bygi and A. Zamani, *Process Biochem.*, **40**, 1319 (2005).
78. E. Pehlivan, S. Cetin and B. Yanık, *J. Hazard. Mater.*, **135**, 193 (2006).
79. D. Wankasi, M. Horsfall Jnr and A. Ibuteme Spiff, *Electronic J Biotechnol.*, **9**, 587 (2006).
80. C. Namasivayam and K. Kadirvelu, *Chemosphere*, **34**, 377 (1997).