Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.905972

54 (2015) 2868–2882
May

Taylor & Francis
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Adsorption of copper from aqueous solution onto natural sepiolite: equilibrium, kinetics, thermodynamics, and regeneration studies

Merve Dönmez[a], Selva Camcı[a], Feryal Akbal[a,*], Mehtap Yağan[b]

[a]*Engineering Faculty, Environmental Engineering Department, Ondokuz Mayıs University, Samsun, Turkey, Tel. +90 362 3121919; Fax: +90 362 4576094; email: feryal.akbal@gmail.com*
[b]*Arts and Science Faculty, Chemistry Department, Ondokuz Mayıs University, 55139 Kurupelit, Samsun, Turkey*

Received 7 May 2013; Accepted 6 March 2014

ABSTRACT

The adsorptive properties of natural sepiolite in the removal of copper (Cu^{2+}) from aqueous solution were investigated. The results show that the amount of adsorption of copper ion increases with initial copper concentration, contact time, and solution pH. The pseudo-first-order, pseudo-second-order, and Elovich models were used to describe the kinetic data and the rate constants were evaluated. The adsorption of the copper onto natural sepiolite at different operating conditions followed the pseudo-second-order model. The equilibrium data were analyzed using the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R) isotherm models. The equilibrium adsorption results are fitted better with Langmuir isotherm compared to the other models. The Langmuir monolayer adsorption capacity of sepiolite was estimated as 9.64 mg/g at pH 6.0 and temperature of 20˚C. An increase in temperature was found to induce a positive effect on the sorption process. Sorption of Cu^{2+} onto sepiolite was spontaneous and endothermic. The values of the enthalpy (ΔH) and entropy of activation (ΔS) were 14.892 kJ/mol and 96.342 J/mol K, respectively, at pH 5.0.

Keywords: Adsorption; Sepiolite; Kinetics; Isotherms; Thermodynamics; Regeneration

1. Introduction

The discharge of toxic metals into watercourses is a serious pollution problem which may affect the quality of water supply. Increasing concentrations of these metals in the water constitute a severe health hazard mainly due to their non-degradability and toxicity [1]. Copper has been known as one of the most common toxic metals, which finds its way to the water stream from industries like electroplating, mining, electrical and electronics, iron and steel production, the non-ferrous metal industry, the printing and photographic industries, and metalworking and finishing processes. According to the US Environmental Protection Agency standards, the permissible limit of copper for industrial effluents to be discharged to surface water is 0.25 mg/L [2].

Conventional methods that have been used to remove heavy metal ions from various industrial effluents usually include chemical precipitation, membrane separation, ion exchange, evaporation, electrolysis, etc. and are often costly or ineffective, especially in removing heavy metal ions from dilute solutions [3,4]. Adsorption using sorbents is one of the most popular and effective processes for the removal of heavy metals from wastewater. The adsorption process offers

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*Corresponding author.

flexibility in design and operation and in many cases produces treated effluents suitable for re-use. In addition, because adsorption is sometimes reversible, the regeneration of the adsorbent with resultant economy of operation may be possible [5,6].

Sepiolite is a natural hydrated magnesium silicate clay mineral, $(Si_{12})(Mg_8)O_{30}(OH)_6(OH_2)_4{\cdot}8H_2O$ [7]. Structurally it is formed by blocks and channels extending in the fiber direction. Sepiolite has several adsorption applications due to its channel structure. The presence and concentration of surface functional groups play an important role in the adsorption capacity and the removal mechanism of the adsorbates [8]. The ability of sepiolite to adsorb heavy metal ions from water is significant for the removal of these toxic pollutants from the environment. Owing to the crystal-chemical features of sepiolite, heavy metal retention by the mineral can occur by adsorption and/or cation-exchange reaction. Adsorption can be seen as taking place on the oxygen ions of the tetrahedral sheets, on the water molecules at the edges of the octahedral sheet and on Si–OH groups along the direction of the fibers, whereas exchange occurs by substituting the solvated cations inside the channels and/or inside the octahedral at the edges of the channels [9].

The present study deals with the adsorption abilities of sepiolite for removal of copper from aqueous solutions. The influence of several parameters such as initial copper ion concentration, solution pH, particle size of adsorbent, stirring rate, and temperature on adsorption under kinetic and equilibrium conditions was explored. Regeneration was tried for several cycles with a view to recover the adsorbed Cu^{2+} and also to restore sepiolite to its original state.

2. Materials and methods

2.1. Chemicals

A stock solution containing 1,000 mg of Cu (II) per liter was prepared by dissolving $Cu(SO_4)_2{\cdot}5H_2O$ in double distilled water and was used to prepare the adsorbate solution by appropriate dilution.

2.2. Adsorbent Characterization

The sepiolite used was obtained from the Eskisehir region, in Turkey. The chemical composition of natural sepiolite determined by X-ray Fluorescence analysis given in Table 1 indicates the presence of silica and magnesium oxides as major constituents along with traces of aluminum, potassium, sodium, iron, and titanium oxides in the form of impurities. Specific surface area and pore volume of sepiolite were determined using the BET analysis (Quantachrome Instruments, Nova 4000E). The specific surface area, pore volume, and average pore diameter of sepiolite are 327 m^2/g, 0.55 cc/g, and 0.001 μ, respectively.

Table 1
Chemical composition of sepiolite

Components	%
Al_2O_3	1.834
CaO	0.219
Cr_2O_3	0.004
F	1.392
CuO	0.002
Fe_2O3	0.716
K_2O	0.320
MgO	33.591
MnO_2	0.007
MoO_3	0.005
NiO	0.003
Rb	0.03
SO_3	0.048
SiO_2	61.731
SrO	0.005
TiO^2	0.089
V_2O_5	0.024
Y_2O_3	0.001
ZnO	0.002
ZrO_2	0.003

FTIR spectra of sepiolite were measured on a Bruker Vertex 80 V spectrometer. The sepiolite sample was mixed with KBr and pressed to a plate for measurement. The XRD analyses of sepiolite samples were completed using a Rigaku miniflex diffractometer with Cu X-ray ($\lambda = 1.5405$ Å) in the range of 2θ between 2 and 70°, scanning speed 2° θ/min, 40 kV, 30 mA, and phase analysis of powdered fragments from XRD pattern were found out using Shimadzu XRD-6000. The XRD pattern of sepiolite is shown in Fig. 1. The

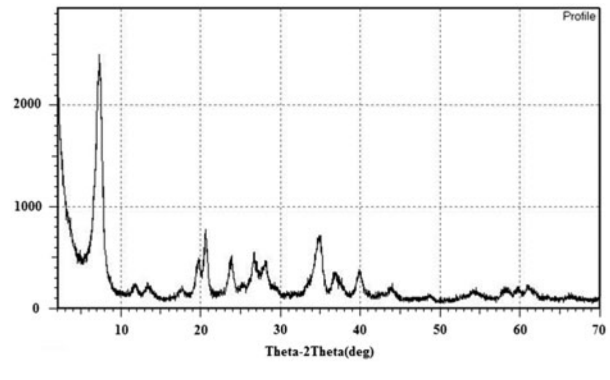

Fig. 1. XRD spectrum of sepiolite.

sepiolite was characterized by strong reflection at about 7° 2θ, and weak reflections at about 20°, 25°, 28°, and 35° 2θ. XRD spectrum of the sepiolite sample showed weak peaks at 40° 2θ due to the dolomite impurity. Scanning electron micrograph (SEM) photographs of sepiolite are presented in Fig. 2. These SEM images indicate that sepiolite has a fibrous structure.

2.3. Adsorption experiments

2.3.1. Kinetic studies

Kinetic studies were conducted in a temperature-controlled shaker using 25 mL of copper solution of 100 mg/L and a fixed adsorbent dosage of 25 mg at a temperature of 20°C. The pH of the solutions was initially adjusted by the addition of either 0.1 N HCl or 0.1 N NaOH solutions.

At the end of the adsorption period, the samples were centrifuged at 5,000 rpm for 5 min and the residual concentration of copper in solution was measured with atomic absorption spectrophotometer (Unicam 929) at a wavelength of 324.7 nm using direct air-acethylene flame method.

The experiments were carried out by varying initial copper concentration (50–150 mg/L), particle size (35–65 mesh), solution pH (4.0–6.0), and agitation rate (100–250 rpm). The Cu^{2+} concentration retained in the adsorbent phase, q_t (mg/g) was calculated according to the following relation:

$$q_t = \frac{(C_0 - C_t).V}{m} \tag{1}$$

where C_0 (mg/L) and C_t (mg/L) are the concentrations in the solution at time $t = 0$ and at time t, V is the volume of solution (L), and m is the amount of adsorbent (g) added.

2.3.2. Equilibrium studies

Adsorption of Cu^{2+} was carried out by a batch technique to obtain equilibrium data. For isotherm studies, adsorption experiments were carried out by shaking 25 mg of the sepiolite sample with 25 mL of copper solution of varying concentrations (50–175 mg/L) in a series of 100 mL conical flasks. The initial pH of the adsorbate solution was adjusted to the desired pH using 1 N HCl or 1 N NaOH aqueous solutions. The flasks were agitated in a temperature-controlled orbital shaker. The equilibrium was found to have been attained in 6 h contact time. The suspensions were centrifuged at 5,000 rpm for 5 min at the end of the adsorption process and then the supernatant liquid was analyzed for the residual concentration of metal ions.

Batch sorption studies were performed at different pH values, particle sizes, temperatures, and agitation rates to obtain equilibrium isotherms. The effect of pH was observed by studying the adsorption of copper over a pH range of 4–6. The sorption studies were also carried out at different temperatures, i.e. 20, 40, and 60°C, to determine the effect of temperature and to evaluate the sorption thermodynamic parameters. The equilibrium adsorption uptake in the solid phase, q_e (mg/g), was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e).V}{m} \tag{2}$$

where q_e is the equilibrium concentration of Cu^{2+} on the adsorbent (mg/g), C_0 the initial concentration of the Cu^{2+} solution (mg/L), C_e the equilibrium concentration of the Cu^{2+} solution (mg/L), m the mass of adsorbent (g), and V the volume of the Cu^{2+} solution (L).

2.3.3. Regeneration studies

The feasibility of sepiolite reuse was assessed using desorption and regeneration processes. Desorption

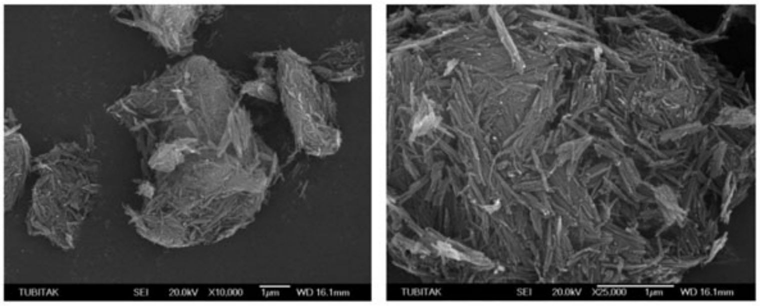

Fig. 2. SEM photograph of sepiolite.

experiments were performed using 0.1 M HCl in a batch experimental study. The Cu^{2+} loaded sepiolite was washed with deionized water to remove any unadsorbed Cu^{2+}. The spent sepiolite was then re-suspended in 50 mL of 0.1 M HCl following the same equilibrium condition for the adsorption process. The solution mixture was filtered and the adsorbent was washed several times with distilled water in order to remove excess acid. It was then treated with 50 mL of Cu^{2+} solution and the above procedure was repeated for three cycles. Desorption experiments are carried out with different initial concentrations of Cu^{2+} ranging from 50 to 150 mg/L, while maintaining the adsorbent amount of 10 g/L and an initial pH value of 5.0 at 20˚C.

3. Theory

3.1. Kinetics of adsorption

Kinetics is the study of the rates of chemical processes to understand the factors that influence the rates. Study of chemical kinetics includes careful monitoring of the experimental conditions which influence the speed of a chemical reaction and hence, help attain equilibrium in a reasonable length of time. Such studies yield information about the possible mechanism of adsorption and the different transition states on the way to the formation of the final adsorbate–adsorbent complex and help develop appropriate mathematical models to describe the interactions. Once the reaction rates and the dependent factors are unambiguously known, the same can be utilized to develop adsorbent materials for industrial application and will be useful in understanding the complex dynamics of the adsorption process [10].

3.1.1. Pseudo-first-order equation

The Lagergren's equation is probably the earliest known example describing the rate of adsorption in the liquid-phase systems. This equation has been one of the most used equations particularly for pseudo-first-order kinetics [10]. The Lagergren's first-order reaction model is expressed as follows:

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{3}$$

where k_1(min^{-1}) is the pseudo-first-order adsorption rate coefficient. The integrated form of the Eq. (3) for the boundary conditions of $t = 0$, $q_t = 0$ and $t = t$, $q_t = q_t$,

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

where q_e and q_t are the values of amount adsorbed per unit mass at equilibrium and at any time t. The values of k_1 can be obtained from the slope of the linear plot of log $(q_e - q_t)$ vs. t. If the pseudo-first-order kinetics does not properly account for the kinetics of the adsorption process, two important discrepancies are usually noticed: (1) k_1 $(q_e - q_t)$ does not represent the number of available sites and (2) ln q_e is not equal to the intercept of the plot of ln $(q_e - q_t)$ against t.

3.1.2. Pseudo-second-order equation

The second-order kinetics may be tested on the basis of the equation [10].

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

where k_2 is the second-order rate coefficient. Separation of the variables followed by integration and application of the boundary conditions ($q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$) yields a linear expression of the form.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

The initial adsorption rate, h, of a second-order process is defined as:

$$h = k_2 . q_e^2 \tag{7}$$

The initial adsorption rate, h, adsorption capacity, q_e, and the pseudo-second-order rate coefficient, k_2, can be determined experimentally from the slope and intercept of a plot of t/q_t against t.

3.1.3. Elovich kinetic equation

Elovich equation is a rate equation based on the adsorption capacity commonly expressed as the following Eq. (8).

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{8}$$

where α is the initial adsorption rate (mg/g/min) and β the desorption constant (g/mg) related to the extent of surface coverage and activation energy for chemisorption. Eq. (8) is simplified by assuming $\alpha\beta >> 1$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, which becomes [11].

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \tag{9}$$

3.2. Adsorption isotherms

The equilibrium isotherm equations were used to obtain the relation between the equilibrium concentrations of the adsorbate in the liquid phase and in the solid phase. These isotherms are as follows.

3.2.1. Freundlich isotherm

Freundlich isotherm describes that the ratio of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of solute in the solution is not constant at different concentrations. For many systems, the heat of adsorption decreases in magnitude with increase in the extent of adsorption.

$$q_e = K_f C_e^{1/n} \tag{10}$$

where C_e is the concentration of Cu^{2+} at equilibrium in the liquid phase and q_e is the corresponding concentration of the Cu^{2+} in the solid phase, K_f ($mg^{1-1/n}\ L^{1/n}/g$) is the Freundlich constant, which indicates the relative adsorption capacity of the adsorbent related to the bonding energy, and n is the heterogeneity factor representing the deviation from linearity of adsorption and is also known as Freundlich coefficient [12].

3.2.2. Langmuir isotherm

The Langmuir model suggests that an uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate [13].

$$C_e/q_e = C_e/q_m + 1/K_L.q_m \tag{11}$$

where C_e is equilibrium concentration of Cu^{2+} (mg/L) and q_e is the amount of the Cu^{2+} adsorbed by per unit of sepiolite (mg/g). q_m and K_L are the Langmuir constants related to the adsorption capacity (mg/g) and the equilibrium constant (L/mg), respectively.

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter R_L which is determined as follows:

$$R_L = 1/(1 + K_L.C_0) \tag{12}$$

where K_L is a Langmuir constant and C_0 is the initial Cu^{2+} concentration. The nature of the adsorption process is either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) [14].

3.2.3. Temkin isotherm

Temkin isotherm model considered the effects of indirect adsorbate–adsorbate interaction isotherms which explained that the heat of adsorption of all the molecules on the adsorbent surface layer would decrease linearly with coverage due to adsorbate–adsorbate interactions. Therefore, the adsorption potentials of the adsorbent for adsorbates can be evaluated using the Temkin adsorption isotherm model, which assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation.

$$q_e = \frac{RT}{b}\ln(A_T C_e) \tag{13}$$

$$B_T = \frac{RT}{b} \tag{14}$$

$$q_e = B_T \ln A_T + B_T \ln C_e \tag{15}$$

where B_T and A_T (L/g) are the Temkin constants and can be determined by a plot of q_e vs. ln C_e. Also, T is the absolute temperature (K) and R is the universal gas constant (8.314 J/mol K). The constant b (J/mol) is related to the heat of adsorption [15].

3.2.4. D–R isotherm

Dubinin and Radushkevich have proposed another isotherm which can be used to analyze the equilibrium data. It is not based on the assumption of homogeneous surface or constant adsorption potential, but it is applied to estimate the mean free energy of adsorption (E). If the value of E is between 1 and 16 kJ/mol, then physical adsorption prevails, and if the value is more than 16 kJ/mol, then chemisorption prevails. The non-linear form of D–R equation:

$$q_e = Q_m \exp\left(-K\varepsilon^2\right) \tag{16}$$

Eq. (15) is represented in a linear form as given by Eq. (16):

$$\ln q_e = \ln Q_m - K\varepsilon^2 \tag{17}$$

where K (mol^2/kJ^2) is a constant which relates to the adsorption energy; Q_m (mg/g) is the maximum adsorption capacity; and ε can be calculated from Eq. (17).

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{18}$$

The D–R isotherm constants, K (mol^2/kJ^2) and Q_m (mg/g), are estimated from the slope and intercept of the plot between ln q_e and ε^2 [12].

The mean free energy of adsorption (E), defined as the free energy change when 1 mol of ion is transferred from infinity in solution to the surface of the solid, was calculated from the K value using the following relation Eq. (18) [11].

$$E = \frac{1}{\sqrt{(2K)}} \tag{19}$$

3.2.5. Generalized isotherm:

A generalized isotherm equation was tested for correlation of the equilibrium data. Linear form of the generalized isotherm is given by:

$$\log\left[\frac{Q_m}{q_e} - 1\right] = \log K_G - N_b \log C_e \tag{20}$$

where K_G is the saturation constant (mg/L), N_b the cooperative binding constant, Q_m the maximum adsorption capacity of the adsorbent (mg/g) (obtained from Langmuir isotherm model), and q_e (mg/g) and C_e (mg/L) are the equilibrium copper concentrations in the solid and liquid phases, respectively. From the plot of log [(Q_m/q_e)−1] vs. log C_e; the intercept gave log K_G and the slope gave N_b constants [13].

3.3. Thermodynamic parameters

The Gibbs free energy change of the adsorption process is related to the equilibrium constant (K_D) by the classical Van't Hoff equation:

$$\Delta G = -RT \ln K_D \tag{21}$$

$$K_D = \frac{q_e}{C_e} \tag{22}$$

The Gibbs free energy change is also related to the entropy change and heat of adsorption at constant temperature according to the following equation:

$$\Delta G = \Delta H - T\Delta S \tag{23}$$

Combining the above two equations, one gets:

$$\ln K_D = \frac{-\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{R}\frac{1}{T} \tag{24}$$

where ΔG is the free energy change (kJ/mol), ΔH the change in enthalpy (kJ/mol), ΔS the entropy change (kJ/molK), T the absolute temperature (K), and R the universal gas constant (8.314×10^{-3} kJ/molK). The values of ΔH and ΔS were determined from the slopes and intercepts of the plots of ln K_D vs. $1/T$ [16].

4. Results and discussion

4.1 Effect of adsorbent amount

The effect of the amount of sepiolite on the adsorption of Cu^{2+} is shown in Fig. 3. The adsorption capacity decreased from 7.01 to 2.0 mg/g by increasing the adsorbent amount from 10 to 50 g/L. Adsorption capacity is defined as the mass of Cu^{2+} adsorbed per unit mass of adsorbent. If the adsorbent amount is increased by keeping the Cu^{2+} concentration constant, the amount of Cu^{2+} adsorbed per unit mass of adsorbent decreases due to the availability of less number

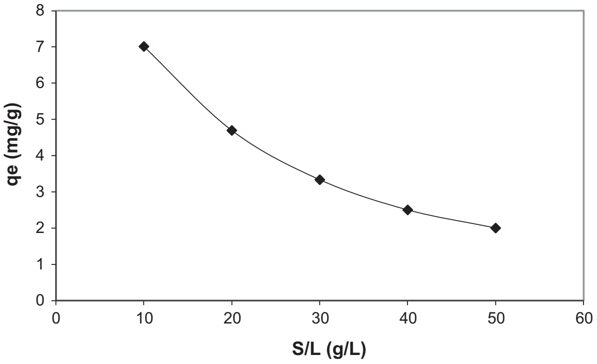

Fig. 3. Effect of solid/liquid ratio on the adsorption of Cu^{2+} onto sepiolite (Cu^{2+} concentration: 100 mg/L; pH 5; particle size: 45 mesh; and temperature: 20˚C).

of Cu^{2+} ions. This indicates that increasing the adsorbent amount results in unsaturated adsorbent sites during adsorption process because of which adsorption capacity decreases [12]. The percentage removal of Cu^{2+} increases from 70 to 99.9% by increasing the adsorbent amount from 10 to 50 g/L. The increase in Cu^{2+} removal with an increase in the sepiolite amount is due to the increase in surface area and adsorption sites available for the adsorption of Cu^{2+}.

4.2. Adsorption kinetics

The kinetics of the adsorption process was studied by carrying out a set of adsorption experiments at constant temperature and monitoring the amount adsorbed with time. The adsorption kinetics normally includes two phases: a rapid removal stage followed by a much slower stage before the equilibrium is established. In order to investigate the mechanism of adsorption, adsorption process was analyzed using the pseudo-first-order, pseudo-second-order, and Elovich models.

The influence of initial concentration on adsorption of copper onto sepiolite was investigated in the concentration range 50–150 mg/l at pH 5.0, temperature of 20˚C, and adsorbent dosage of 10 g/L. Fig. 4 represents the plots of the amount of copper adsorbed (mg/g) vs. contact time for different initial metal concentrations. From these plots, it was found that the amount of adsorption i.e. mg of adsorbate per gram of adsorbent increased with an increase in the contact time at all initial metal ion concentrations and equilibrium was attained within 360 min. Further, it was observed that the amount of metal ion uptake, q_t (mg/g), increased with an increase in initial metal ion concentration. When initial concentration increased from 50 to 150 mg/L, the amount of copper adsorbed increased from 4.99 to 7.76 mg/g. The increase in the adsorption capacity with an increase in the initial Cu^{2+} concentration may be due to the higher adsorption rate and the utilization of all the active sites available for adsorption at higher concentrations. At higher initial metal concentrations, the driving force to overcome the mass transfer resistance for the migration of the metals from the bulk solution to the mineral surface increases. However, each unit mass of adsorbent is subjected to a larger number of metal cations, which gradually fill up the sites until saturation is reached. In such a case, further increase of metal concentrations is not accompanied with an increase in the amount of metal adsorbed per unit mass of adsorbent [17]. The increase in the initial metal concentration results in a decrease in the overall removal efficiency. The removal percent of Cu^{2+} for initial concentrations of 50, 100, and 150 mg/L were 99, 70, and 52%, respectively.

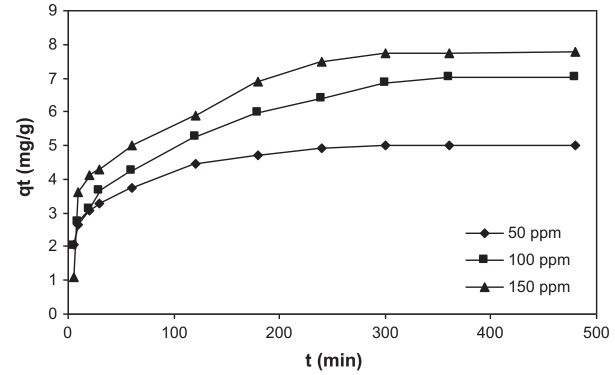

Fig. 4. Effect of contact time on the adsorption of Cu^{2+} onto sepiolite for different initial concentrations (adsorbent dose: 1 g/L; pH 5.0; particle size: 45 mesh; temperature: 20˚C; and agitation rate: 200 rpm).

The effect of particle size on adsorption of copper was investigated with different particle sizes in the range 35–65 mesh at temperature of 20˚C, pH 5.0, and initial copper concentration of 100 mg/L (Fig. 5). As can be seen, the plots of kinetics obtained have an identical shape, and that the capacity of copper sorption at the equilibrium increases with the decrease of particle size. It can be seen from the figure that the amount of copper adsorbed increased from 5.90 to 7.66 mg/g, while decreasing in the particle size from 35 to 65 mesh. The percentage removals of copper were 59, 70, and 77% for 35, 45, and 65 mesh of the particle size, respectively.

The pH of the aqueous solution is an important controlling parameter in the adsorption process. In

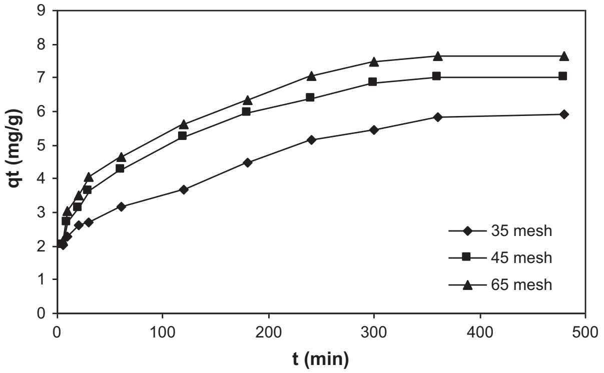

Fig. 5. Effect of contact time on the adsorption of Cu^{2+} onto sepiolite for different particle sizes (Cu^{2+} concentration: 100 mg/L; adsorbent dose: 1 g/L; pH 5.0; temperature: 20˚C; and agitation rate: 200 rpm).

the present work, adsorption of Cu^{2+} onto sepiolite was investigated over the pH range of 4.0–6.0 for a constant sepiolite amount of 10 g/L and Cu^{2+} concentration of 100 mg/L at temperature of 20˚C. Fig. 6 represents the plots of the amount of copper adsorbed (mg/g) vs. contact time for different initial pH values of 4.0, 5.0, and 6.0, respectively. When initial solution pH increased from 4.0 to 6.0, the amount of copper adsorbed increased from 6.52 to 7.90 mg/g and the percentage removal of copper increased from 65 to 79%. Because of the protonation and deprotonation of the acidic and basic groups of the adsorbents, its adsorption behavior for metal ions is influenced by the pH value, which affects the surface structure of sorbents, the formation of metal hydroxides, and the interaction between sorbents and metal ions. The increase in the metal removal as the pH increases (i.e. as the solution becomes more basic) can be explained on the basis of a decrease in competition between proton and metal species for the surface sites, and by the decrease in positive surface charge, which results in a lower columbic repulsion of the sorbing metal [18].

The change in solution pH with time at an initial Cu^{2+} concentration of 100 mg/L and the sepiolite amount of 10 g/L is shown in Fig. 7. It was found that, the solution pH was increased with an increase in the adsorption of Cu^{2+} on sepiolite. The pH values increased from 4.01 to 5.72, 5.00 to 5.99, and from 6.00 to 6.10 with an increase in adsorption time from 5 to 480 min, for initial pH values of 4.00, 5.00, and 6.00, respectively. It can be seen that there is no significant change in the final value of solution pH at pH 6.00, but in acidic medium after the adsorption of Cu^{2+} the pH values were increased.

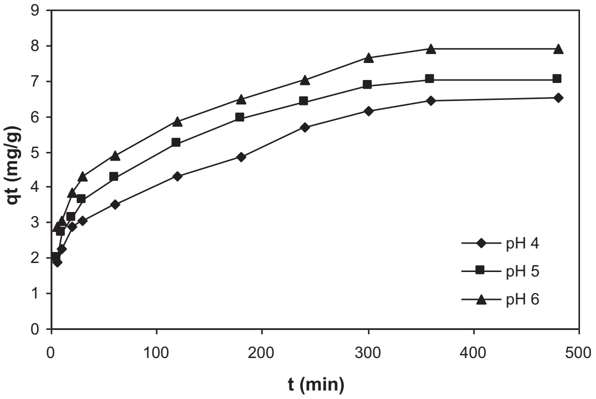

Fig. 6. Effect of contact time on the adsorption of Cu^{2+} onto sepiolite for different initial pH values (Cu^{2+} concentration: 100 mg/L; adsorbent dose: 1 g/L; particle size: 45 mesh; temperature: 20˚C; and agitation rate: 200 rpm).

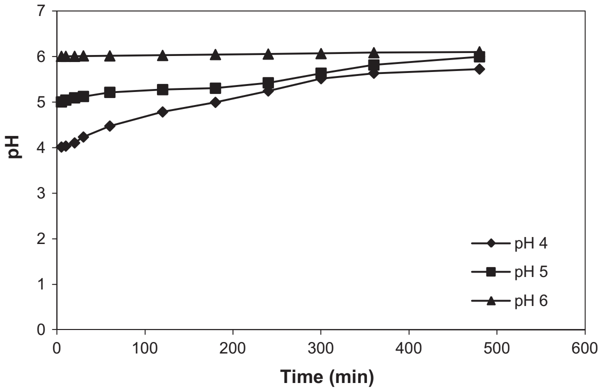

Fig. 7. Variations of pH values during the adsorption of Cu^{2+} onto sepiolite (Cu^{2+} concentration: 100 mg/L; adsorbent dose: 10 g/L; particle size: 45 mesh; and temperature: 20˚C).

In order to assess the effect of the agitation rate on adsorption of copper on sepiolite, three different agitation rates have been chosen as shown in Fig. 8, where it can be noted that the retention of copper increases progressively with the agitation rate as time increases. Therefore, it can be concluded that the agitation rate encourages a better transfer of species between the adsorbent and adsorbate. For agitation rates of 100, 150, and 250 rpm, the adsorption capacities were found to be 6.60, 7.02, and 7.97 mg/g and percentage removal rates were found to be 66, 70, and 80%, respectively.

Table 2 lists the rate constants for different initial copper concentrations, initial pH values, particle sizes, and agitation rates by the pseudo-first-order, pseudo-second-order, and Elovich models. It can be seen that the correlation coefficients of pseudo-second-order kinetic are higher than that of the pseudo-first-order and Elovich kinetic models. This finding shows that kinetics of the Cu adsorption by the sepiolite is better described by pseudo-second-order kinetic model rather than pseudo-first-order and Elovich models. Uptake of Cu (II) on kaolinite, montmorillonite, ZrO-kaolinite, ZrO-montmorillonite, TBA-kaolinite, TBA-montmorillonite, acid-activated kaolinite, and acid-activated montmorillonite has been found to be in conformity with second-order kinetics [10]. Also from Table 2, the experimental and the calculated equilibrium adsorption capacity increases with an increase in the initial metal ion concentration, in initial solution pH, in agitation rate, and decrease in particle size.

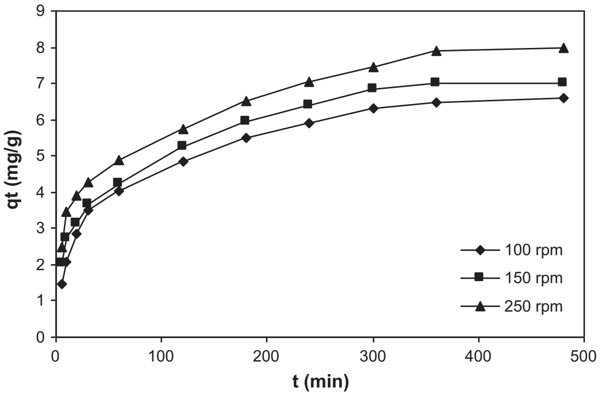

Fig. 8. Effect of contact time on the adsorption of Cu^{2+} onto sepiolite for different agitation rates (Cu^{2+} concentration: 100 mg/L; adsorbent dose: 10 g/L; pH 5.0; particle size: 45 mesh; and temperature: 20℃).

4.3. Adsorption isotherms

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose [19].

Sorption isotherms of copper ions at various particle sizes of sepiolite are shown in Fig. 9. The amount of copper ion adsorbed increased under the condition that the particle size of the sorbent decreased. This may be attributed to the larger external surface available with smaller particles at a constant total mass of sepiolite in the system.

The effect of pH on the adsorption of Cu^{2+} onto sepiolite was examined in the range 4.0–6.0. Fig. 10 show the adsorption isotherms of copper at different pH values. The change in the adsorption amount with pH can be explained by the concentration and activity of hydrogen ions and ion-exchange mechanism. The increase of the suspension pH results in an increase in the negative charge of sepiolite. This can be ascribed to either the adsorption of OH ions onto the positive charge centers of sepiolite or the deprotonation of surface hydroxyl groups. As a result, the removal of Cu^{2+} ions increases since interaction of Cu^{2+} ions with sepiolite surface occurs more easily. At low pH values, hydrogen ions at active sites on the sepiolite surface compete with Cu^{2+} ions for adsorbing each other. In this case, hydrogen ions can adsorb at active sites on sepiolite.

Table 2
Kinetic parameters for pseudo-first-order, pseudo-second-order kinetic, and Elovich models for the adsorption of Cu^{2+} onto sepiolite

		Pseudo-first-order kinetic			Pseudo-second-order kinetic				Elovich		
Parameter	q_e, exp (mg/g)	$k_1 \times 10^3$/ (min)	q_e, cal (mg/g)	R^2	$k_2 \times 10^3$ (g/mg min)	q_e, cal (mg/g)	h	R^2	α (mg/g min)	β (mg/g)	R^2
Metal concentration (ppm)											
50	4.997	26.0	5.228	0.7924	16.2	5.128	0.427	0.9987	2.982	1.453	0.987
100	7.015	16.3	7.583	0.8122	5.39	7.299	0.287	0.9926	1.013	0.847	0.983
150	7.765	15.8	7.139	0.9954	5.10	8.149	0.339	0.9943	1.066	0.727	0.962
Particle size (mesh)											
35	5.900	9.3	4.943	0.9112	4.94	6.083	0.183	0.9788	0.892	1.095	0.921
45	7.015	16.3	7.583	0.8122	5.39	7.299	0.287	0.9926	1.013	0.847	0.983
65	7.665	13.5	7.143	0.9005	4.88	7.968	0.310	0.9915	1.129	0.781	0.982
Solution pH											
4.0	6.520	9.9	5.671	0.9181	4.47	6.752	0.204	0.9812	0.795	0.931	0.949
5.0	7.015	16.3	7.583	0.8122	5.39	7.299	0.287	0.9926	1.013	0.847	0.983
6.0	7.900	7.0	5.042	0.8067	5.07	8.143	0.336	0.9910	1.641	0.823	0.972
Agitation rate											
100	6.600	9.8	5.255	0.9743	5.31	6.835	0.248	0.9929	2.982	1.453	0.987
150	7.015	16.3	7.583	0.8122	5.39	7.299	0.287	0.9926	1.013	0.847	0.983
250	7.975	9.8	6.167	0.9124	4.95	8.149	0.329	0.9904	1.066	0.727	0.962

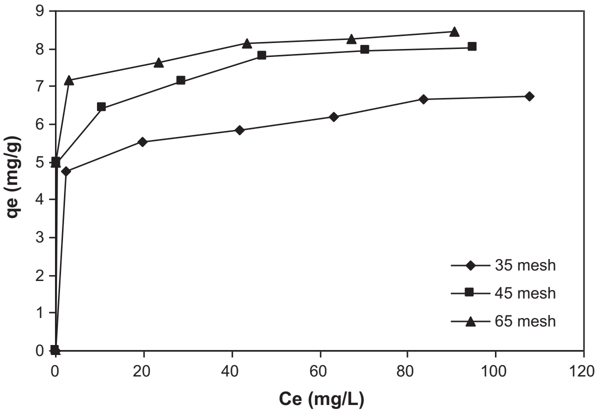

Fig. 9. Adsorption isotherms of Cu^{2+} onto sepiolite for different particle sizes (adsorbent dose: 1 g/L; pH 5.0; equilibrium time: 360 min; temperature: 20℃; and agitation rate: 200 rpm).

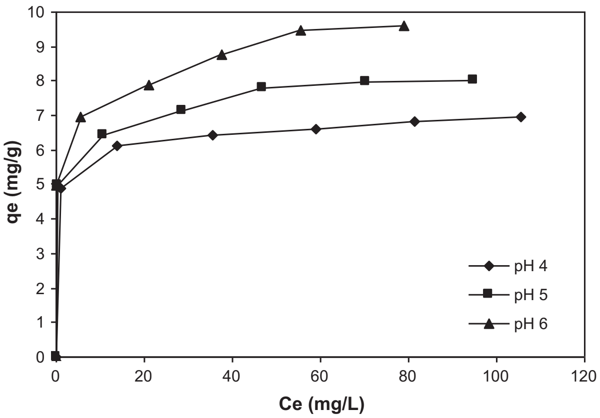

Fig. 10. Adsorption isotherms of Cu^{2+} onto sepiolite for different pH values (adsorbent dose: 1 g/L; particle size: 45 mesh; equilibrium time: 360 min; temperature: 20℃; and agitation rate: 200 rpm).

Again, at high hydrogen concentrations, negative charge density will decrease at active sites on sepiolite, and therefore, the adsorbed amount will decrease [20].

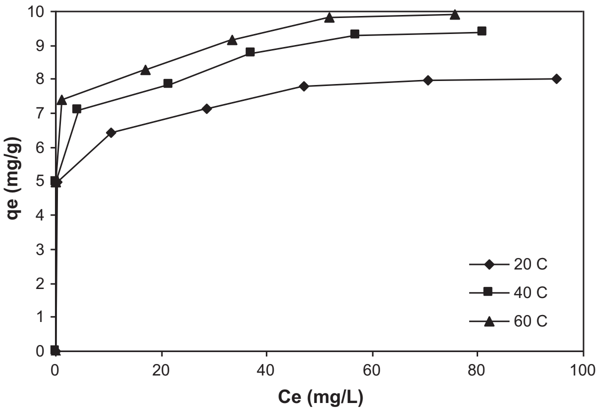

Fig. 11. Adsorption isotherms of Cu^{2+} onto sepiolite for different temperatures (adsorbent dose: 1 g/L; pH 5.0; particle size: 45 mesh; equilibrium time: 360 min; and agitation rate: 200 rpm).

The effect of temperature on the adsorption isotherm was studied by carrying out a series of isotherms at temperatures of 20, 40, and 60℃, as shown in Fig. 11. The adsorption capacity increased from 7.76 to 9.92 mg/g at Cu^{2+} concentration of 100 mg/L when temperature of the solution was increased from 20 to 60℃. This may be a result of increase in the mobility of the copper ion with increasing temperature. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface [19]. The temperature has two major effects on the adsorption process. Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. In addition, changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate.

Fig. 12 shows the experimental results obtained from a series of experiments performed using different agitation rates, ranging from 100 to 250 rpm. The uptake of copper increases with an increase in the agitation rate. Increasing agitation rate reduced the film boundary layer surrounding sepiolite particles thus increasing the external film transfer coefficient and hence the rate of uptake. The highest copper removal capacity of sepiolite was obtained at the agitation rate of 250 rpm [21].

The experimental equilibrium adsorption data have been tested using Freundlich, Langmuir, Temkin, Dubinin–Radushkevich, and generalized isotherm equations. Parameters related to each isotherm were determined using linear regression analysis and the square of the correlation coefficients (R^2) have been calculated. A list of the parameters obtained together with R^2 values is given in Table 3.

From Table 3, the Langmuir isotherm model yielded the best fit with the highest R^2 value (0.99) compared to the other models. The fact that the Langmuir isotherm fits the experimental data very well indicates that almost complete monolayer coverage of the adsorbent particles. The values of R_L (Table 3), for adsorption of Cu^{2+} on the sepiolite, were found to be within 0 and 1 which indicates a highly favorable adsorption. Langmuir constants i.e. adsorption

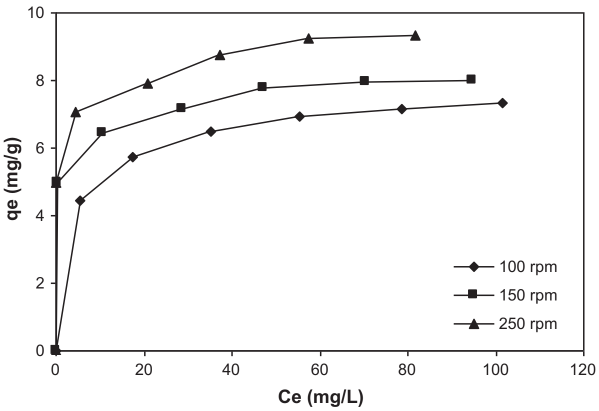

Fig. 12. Adsorption isotherms of Cu^{2+} onto sepiolite for different agitation rates (adsorbent dose: 1 g/L; pH 5.0; particle size: 45 mesh; equilibrium time: 360 min; and temperature: 20°C).

capacity, Q_m and rate of adsorption, K_L, ranged from 6.770–9.930 mg/g and 0.289–1.350 L/mg, respectively. Comparison of sepiolite and other natural adsorbents for Cu^{2+} removal is given in Table 4.

The equilibrium data also fitted to Freundlich equation. K_F is the Freundlich constant indicative of the relative adsorption capacity of the adsorbent related to the bonding energy and can be defined as the adsorption or distribution coefficient. It represents the quantity of Cu^{2+} adsorbed onto adsorbent for unit equilibrium concentration. The constant n is the heterogeneity factor which represents the deviation from linearity of adsorption as follows: if the value of $n = 1$, the adsorption is linear; $n < 1$, the adsorption process is chemical; if $n > 1$, the adsorption is a favorable physical process [11,27]. The n values (5.814–18.518) were higher than 1.0, indicating that adsorption of Cu^{2+} onto sepiolite is a favorable physical process. Moreover, the magnitude of K_F ranged between 3.415 and 7.464, which indicates high adsorptive capacity and easy uptake of Cu^{2+} from aqueous solution by sepiolite.

The value of coefficient of determination ($R^2 =$ 0.673–0.911) indicates that the D–R isotherm model does not fit well with the equilibrium experimental data when compared with the other models considered. The maximum adsorption capacity, q_m, obtained using D–R isotherm model ranged 6.183–8.879 mg/g for the adsorption of Cu^{2+} by sepiolite which is less than the value of q_m obtained using the Langmuir isotherm model. The mean free energy of adsorption, E, ranged between 0.433 and 15.811 kJ/mol.

The constant b, obtained for Temkin isotherm model was 1,595–7,315 J/mol. The correlation coefficients obtained were $R^2 \geq 0.925$, which indicates that the Temkin isotherm fit well with the equilibrium data obtained for the adsorption of Cu^{2+} onto sepiolite. But Temkin isotherm model is not as good as Langmuir isotherm model. Apparently, the generalized adsorption isotherm represents the equilibrium data reasonably well. The binding constant N_b and saturation constant K_G were calculated between 0.053–0.172 and 1.300–2.192 mg/L, respectively.

4.4. FTIR spectra of sepiolite

The FTIR spectra of sepiolite samples before and after copper adsorption are shown in Fig. 13. The band in the FTIR spectra of sepiolite was observed at 3,568/cm corresponding to the vibrations of the coordinated water, the intensity of this band was decreased after adsorption. A band at 1,664/cm was detected due to the vibration of zeolitic water; the band was maintained after adsorption, although its intensity was decreased. The Si–O–Si band at 1,020/cm is observed as a result of the Si–O vibrations. The small band observed at 781/cm is the OH bending vibration of Mg–Fe–OH. The peak at 684/cm is due to the bending vibration of Mg–OH. The peak at 477/cm is attributed to the Si–O–Si bending vibration. Dolomite impurities give rise to the 1,440/cm band.

4.5. Thermodynamic studies

In order to observe the effect of temperature on the adsorption capacity, experiments were carried out in three different temperatures of 20, 40, and 60°C for a fixed initial metal ion concentration of 100 mg/L. The values of Gibbs free energy (ΔG) have been calculated by knowing the value of enthalpy of adsorption (ΔH) and the entropy of adsorption (ΔS) which are obtained from slope and intercept of a plot of ln K_D vs. 1/T shown in Fig. 14.

Table 5 presents the values of thermodynamic parameters. A positive value of the standard enthalpy change indicates that the adsorption is endothermic and also its magnitude gives information on the type of adsorption, which can be either physical or chemical. The enthalpy of adsorption, ranging from 2.1 to 20.9 kJ/mol corresponds to a physical sorption [28]. The adsorption enthalpy of Cu^{2+} ions on sepiolite is in range of physisorption. The Gibbs free energy change (ΔG) is negative as expected for a spontaneous process under the conditions applied. The value of ΔG becomes more negative with the increase of temperature, indicating more efficient adsorption at high temperature. At high temperature, cations are

Table 3
Isotherm constants and regression coefficients for the adsorption of Cu^{2+} onto sepiolite

	Langmuir				Freundlich			Temkin			Dubinin–Radushkevic				Generalized		
	Q_m	K_L	R_L	R^2	$1/n$	K_f	R^2	A_T	B_T	R^2	q_m	K	E	R^2	K_G	N_b	R^2
Particle size (mesh)																	
35	6.770	0.353	0.028	0.995	0.089	4.329	0.951	3,846	0.507	0.926	6.183	0.352	1.192	0.673	1.300	0.053	0.951
45	7.812	1.000	0.009	0.999	0.054	6.006	0.972	92.9×10^6	0.333	0.949	7.980	0.030	4.016	0.799	1.432	0.085	0.984
65	8.417	1.350	0.007	0.999	0.053	6.635	0.995	391×10^6	0.343	0.992	7.928	0.003	12.910	0.911	1.268	0.053	0.995
Solution pH																	
4.0	6.944	0.942	0.010	0.999	0.077	4.883	0.989	1.137	1.527	0.925	6.595	0.129	1.961	0.886	1.422	0.077	0.989
5.0	7.812	1.000	0.009	0.999	0.054	6.006	0.972	92.9×10^6	0.333	0.949	7.980	0.030	4.016	0.799	1.432	0.085	0.984
6.0	9.643	0.580	0.007	0.996	0.065	6.847	0.934	135	0.930	0.985	8.470	0.003	12.910	0.762	1.408	0.065	0.935
Temperature °C																	
20	7.812	1.000	0.010	0.999	0.054	6.006	0.972	92.9×10^6	0.333	0.949	7.980	0.030	4.016	0.799	1.432	0.085	0.984
40	9.443	0.718	0.009	0.997	0.073	6.652	0.972	897×10^3	0.501	0.970	8.436	0.004	11.180	0.798	1.419	0.073	0.972
60	9.930	0.990	0.017	0.997	0.059	7.464	0.980	85×10^6	0.423	0.988	8.879	0.002	15.811	0.823	1.330	0.059	0.981
Agitation rate (rpm)																	
100	7.485	0.289	0.009	0.998	0.172	3.415	0.978	987×10^3	0.496	0.941	6.827	2.668	0.433	0.859	2.192	0.172	0.978
150	7.812	1.000	0.014	0.999	0.054	6.006	0.972	92.9×10^6	0.333	0.949	7.980	0.030	4.016	0.799	1.432	0.085	0.984
250	9.372	0.764	0.010	0.998	0.072	6.637	0.975	16.598	1.004	0.993	8.412	0.005	10.000	0.802	1.412	0.072	0.975

Table 4
Comparison of adsorption capacity of sepiolite with other adsorbents for Cu^{2+} removal

Adsorbent	pH	Temperature (℃)	Model used to calculate adsorption capacity	Adsorption capacity (mg/g)	Reference
Sepiolite	5	30	Langmuir	48.62	[20]
Zeolite	5	30	Langmuir	23.3	[22]
Perlite	5	Room temp.	Langmuir	8.62	[23]
Kaolinite	5.7	30	Langmuir	4.3	[24]
Montmorillonite	5.7	30	Langmuir	25.5	[24]
Kaolinite	7	30	Langmuir	1.22	[25]
Bentonite	4.8	20	Langmuir	6.13	[26]
Sepiolite	6	Room temp.	Langmuir	9.64	This study

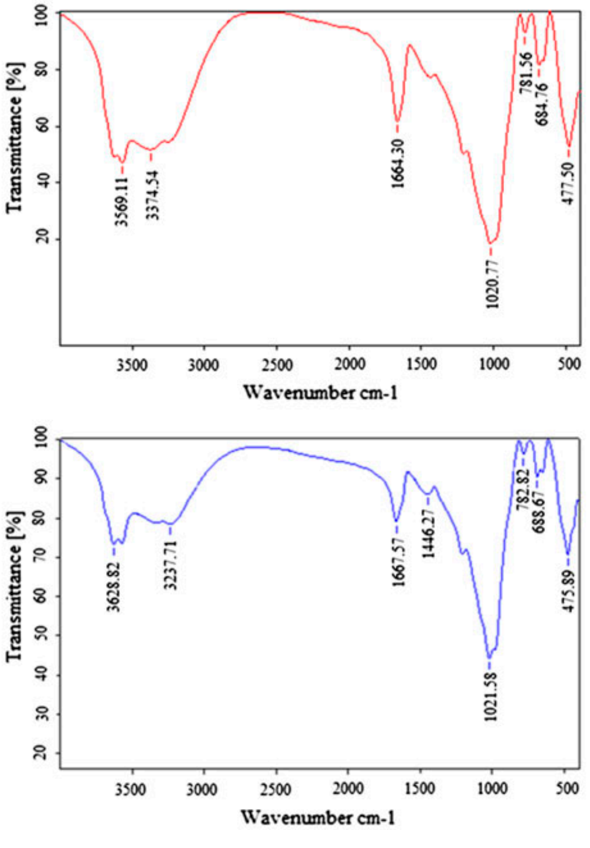

Fig. 13. FTIR spectrum of sepiolite before and after adsorption of copper.

readily desolvated and hence its adsorption becomes more favorable. The positive value of entropy change (ΔS) suggests the affinity of sepiolite towards Cu^{2+} ions in aqueous solutions and may suggest some structure changes on the adsorbents [26].

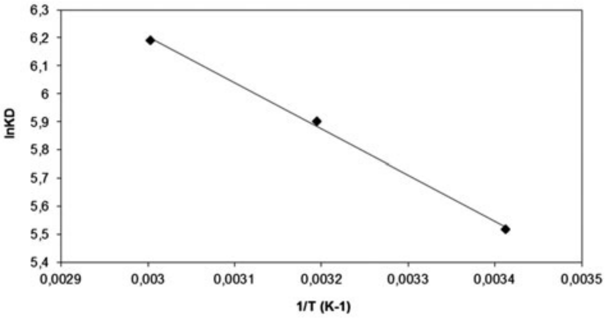

Fig. 14. Plots of ln K_D vs. 1/T for Cu^{2+} adsorption onto sepiolite.

4.6. Regeneration studies

The repeated availability of sepiolite for Cu^{2+} adsorption through many cycles of adsorption/desorption is quite crucial for the application of sepiolite in the removal of Cu^{2+} from real wastewater. Therefore, the recycling of sepiolite in the removal of Cu^{2+} was investigated. The regenerated sepiolite samples were used for the removal of Cu^{2+} at different initial concentrations in the range of 50–150 mg/L. Table 6 shows the adsorption capacities of sepiolite for Cu^{2+} ions after reusing for three times. After three cycles, the sorption capacity of the sepiolite decreased from 7.95 to 5.95 mg/g at 150 ppm Cu^{2+} concentration and pH 5.0. The percentage removal of Cu was found to decrease from 99.42 to 55.34% for Cu concentration of 50 mg/L and 53.03 to 39.67% for Cu concentration of 150 mg/L. These results show that adsorption capacity of sepiolite for Cu^{2+} ions is well after reusing for three times, which indicates that the sepiolite has a good reusability.

Table 5
Termodynamic parameters for the sorption of Cu^{2+} onto sepiolite

Temperature (°K)	K_D (mL/g)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol°K)
293	249.04	−13.440	14.892	96.342
313	365.12	−15.354		
333	488.23	−17.139		

Table 6
Adsorption–desorption of Cu^{2+} using 0.1 M HCl as a desorbing reagent

	1st Cycle		2nd Cycle		3rd Cycle	
Cu concentration (mg/L)	Adsorption (mg/g)	Desorption (mg/g)	Adsorption (mg/g)	Desorption (mg/g)	Adsorption (mg/g)	Desorption (mg/g)
50	4.971	1.946	3.522	2.579	2.767	2.067
75	6.441	2.616	4.677	2.506	2.742	2.110
100	7.135	2.881	6.797	2.851	3.494	2.194
125	7.794	3.852	6.902	2.643	4.423	2.542
150	7.955	4.273	6.591	2.662	5.951	2.498

5. Conclusion

Based on the results of the experiments, the following conclusion can be achieved: (1) Adsorption of Cu^{2+} is strongly dependent on solution pH, initial metal ion concentration, particle size of adsorbent, and temperature; (2) the kinetics of the adsorption of Cu^{2+} onto the sepiolite was best described by the pseudo-second-order model; (3) the Langmuir isotherm is most applicable to describe the adsorption of copper on sepiolite; (4) the adsorption capacity at higher temperature is higher than that of lower temperature. An increase in raising temperature of the adsorption capacity of sepiolite implies that the enthalpy change (ΔH) has positive values, indicating that the adsorption process of copper on sepiolite was endothermic; and (5) natural sepiolite is a suitable material for adsorption and immobilization of Cu^{2+} from wastewater.

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