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Removal of Cd(II) from aqueous solution using cross-linked chitosan–zeolite composite

Feng Zhang[a], Manman Wang[a], Limei Zhou[a], Xiaoyan Ma[b], Yafen Zhou[a,*]

[a]*Chemical Synthesis and Pollution Control Key Laboratory of Sichuan Province, College of Chemistry and Chemical Engineering, China West Normal University, Nanchong 637002, China, Tel. +86 817 2568081; email: cwnuzyf@163.com*
[b]*College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, China*

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ABSTRACT

Cross-linked chitosan–zeolite composite was prepared and characterized by Fourier transform infrared spectroscopy and scanning electron microscope. Adsorption of Cd(II) by the cross-linked chitosan–zeolite composite as a function of solution pH, contact time, initial Cd (II) concentration, and temperature was investigated systematically by batch experiments. The obtained results showed that the removal of Cd(II) was pH dependent and the optimum adsorption was achieved at pH 7.0. The adsorption process could be described by pseudo-second-order kinetic model. Thermodynamic parameters revealed the spontaneous and endothermic nature of the adsorption. The batch adsorption data could be well elucidated by the Langmuir model. The maximum adsorption capacity of Cd(II) on the cross-linked chitosan–zeolite composite at 25℃ determined from the Langmuir model was 102.15 mg/g. The adsorbent was successfully regenerated using EDTA, HNO_3, and HCl solution as desorbent, respectively.

Keywords: Cadmium; Chitosan–zeolite composite; Adsorption; Kinetics; Isotherm

1. Introduction

Heavy metal pollution on soil and water due to the discharge of industrial effluents is a worldwide environmental concern. As heavy metals cannot be degrade biologically and can accumulate in living tissues, their presence in drinking water would endanger to public health and the environment because of their entry into the food chain through waste discharge into bodies of water [1,2]. Cadmium is deemed one of the most toxic heavy metals, often found in wastewaters, especially from metal plating, Cd–Ni batteries, phosphate fertilizers, mining, pigments, stabilizer, and alloy manufacturing [3–5]. The limiting value for cadmium in drinking water is 0.003 mg/L by the World Health Organization [6]. The presence of cadmium in water beyond its permissible limit can adversely damage organs such as kidney, liver, and lung [7], causing acute and chronic disorders such as itai-itai disease, renal damage, emphysema, muscular cramps, hypertension, and testicular atrophy [8].

Several methods have been developed for the removal of cadmium and other heavy metals from wastewater, including chemical precipitation, ion exchange, solvent extraction, reverse osmosis, and membrane filtration [9–13]. However, these methods have some drawbacks such as incomplete metal ion removal, high reagent and energy requirements,

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*Corresponding author.

generation of toxic sludge and long desorption time [7]. Adsorption is considered as an effective and economic method for metal ion removal. In recent years, many studies have focused on developing natural, renewable, and low-cost adsorbents, such as agricultural waste materials and biopolymers [1,14–16], clays [17], and zeolites [18,19]. Among these materials, chitosan and zeolite are relatively cheap and the promising materials to be used as adsorbents. Chitosan is a cationic biopolymer derived from alkaline *N*-deacetylation of chitin, the second most abundant biopolymer in nature [7]. Chitosan has a high potential in metal ion removal because its amine and hydroxyl groups can serve as active sites for metal ions [20]. However, chitosan can be dissolved in acidic medium. To overcome this problem, cross-linking of chitosan with glutaraldehyde [4,21,22], formaldehyde [23,24], epichlorohydrin [7,25,26], epichlorohydrin–triphosphate [27,28], and ethylene glycol diglycidyl ether [29] has been carried out to improve the chemical resistance and mechanical strength of the resulted chitosan. In addition, it has been found that chitosan composites have better adsorption capacity and resistance to acidic environment [20,30,31]. Zeolites are hydrated aluminosilicate with three-dimensional framework structure containing AlO_4 and SiO_4 [32]. They are abundant, readily available, chemically and mechanically stable, and low-cost, making them attractive support materials to form composite with chitosan [28,31–34].

In the present study, glutaraldehyde cross-linked chitosan–zeolite composite was prepared and used to remove Cd(II) ion from aqueous solution by batch adsorption system. The effects of the process parameters such as solution pH, contact time, initial Cd(II) concentration, and temperature were investigated. Data from batch experiments were analyzed using the pseudo-first-order and pseudo-second-order kinetic models for determining the mechanism of adsorption process. The Langmuir and the Freundlich isotherms were used to determine the predicted maximum adsorption capacity. The thermodynamic parameters were also evaluated.

2. Materials and methods

2.1. Materials

Chitosan with a deacetylation degree of 80–95%, cadmium nitrate tetrahydrate, and glutaraldehyde (50 wt.%) was supplied by Sinopharm Chemical Reagent Co. Ltd, China, and used without any further purification. Synthetic zeolite was purchased from Aladdin chemistry Co. Ltd, China, and was crushed and sieved to obtain a particle size smaller than 0.075 mm. Other chemicals were of analytic grade and used as received. Distilled water was used for batch experiments.

2.2. Preparation of the cross-linked chitosan–zeolite composite

The cross-linked chitosan–zeolite composite was prepared as follows. Ten gram of zeolite was dispersed in 30 mL of distilled water by stirring for 30 min. Chitosan solution was prepared by dissolving 1 g of chitosan in 20 mL of 2 wt.% acetic acid solution with continuous stirring. The chitosan solution was then added to the zeolite suspension, and the resulted mixture was continued to be stirred for 30 min and treated in ultrasound bath for 1 h below 50℃. After that, the 5 wt.% glutaraldehyde was slowly dropped into the mixture. The reaction system was stirred for 3 h and frozen for 24 h. Finally, the formed composite gel was washed several times with distilled water and dried at 50℃ overnight for further use.

2.3. Characterization

Surface morphology of samples was determined by scanning electron microscope (SEM) (JSM-6510LV, JEOL, Japan). Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 6700 model FTIR spectrometer (Thermo Nicolet Corporation, USA) using KBr pellets. The BET surface area and average pore diameter were determined by a Micromeritics ASAP 2020 analyzer and by physical adsorption of N_2 at −196℃.

2.4. Batch experiments

Batch adsorption experiments were carried out in an incubator shaker at 150 rpm of orbital stirring using 50-mL Erlenmeyer flasks and performed in duplicate. The initial pH of Cd(II) solution was adjusted to values in the range of 3.0–7.5 by adding either 0.10 mol/L HAc or 0.10 mol/L NaAc solution. In a typical experiment, 20 mg of adsorbent was dispersed to 20 mL of Cd(II) solution with a known initial concentration (40, 50, and 60 mg/L) and pH value and agitated for 2 h at 25℃. After that, the sample was centrifuged and decanted; the residual Cd(II) concentration was analyzed by an atomic absorption spectrophotometer (AAS, WFX-120, Beijing Rayleigh Analytical Instrument Corp., China).

The adsorption capacity of Cd(II) at equilibrium (q_e, mg/g) was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where C_0 (mg/L) and C_e (mg/L) are the concentration of Cd(II) in aqueous solution at initial time and at equilibrium, respectively; V (mL) is the volume of Cd (II) solution; m (mg) is the weight of adsorbent.

2.5. Desorption experiments

For desorption studies, 100 mg of the chitosan–zeolite composite was loaded with 100 mL of 100 mg/L Cd(II) solution at 25℃, pH 7.0, and contact time of 2 h. The agitation rate was fixed at 150 rpm. Cd(II) loaded sorbent was collected and gently washed with distilled water to remove unadsorbed ions. The sorbent was then agitated with 20 mL of 0.10 mol/L EDTA, HNO_3, and HCl solution at 25℃, respectively. The amount of Cd(II) desorbed was determined as mentioned before.

3. Results and discussion

3.1. Characterization

The FTIR spectra of chitosan (a), zeolite (b), the chitosan–zeolite composite (c), and the Cd(II) loaded chitosan–zeolite composite (d) are presented in Fig. 1. As seen in Fig. 1(a), the main bands observed in the FTIR spectrum of chitosan were in accordance with previous reports and were assigned as follows [28,31,35]: 3,426 cm^{-1} (–OH and $–NH_2$ stretching vibrations), 2,927 and 2,875 cm^{-1} (–CH stretching vibration), 1,650 and 1,593 cm^{-1} ($–NH_2$ bending vibration), 1,424 and 1,325 cm^{-1} (C–O stretching vibration), 1,159 cm^{-1} (C–O–C stretching vibration of CH–O–CH), 1,086 and 1,027 cm^{-1} (C–O skeletal vibration). The spectrum of zeolite (Fig. 1(b)) showed several major adsorption bands at 3,442, 1,634, 981, 688, and 471 cm^{-1}. The broad peak at 3,442 cm^{-1} can be assigned to the stretching vibration of hydroxyl in zeolite. The band at 1,634 cm^{-1} can be attributed to the H–O–H bending vibration [28]. The peak at 981 cm^{-1} corresponded to the strong T–O stretching vibration [36], 688 cm^{-1} to the symmetrical T–O stretching [37], and 471 cm^{-1} to the Si–O–Si bending vibration [38], respectively. The spectrum of the cross-linked chitosan–zeolite composite (Fig. 1(c)) showed additional adsorption bands at 2,924 and 2,869 cm^{-1} (–CH stretching vibration) and 1,655 cm^{-1} ($–NH_2$ bending vibration) compared with that of zeolite, indicating that the combination of zeolite with chitosan has occurred [31]. The spectrum of the Cd(II) loaded chitosan–zeolite composite (Fig. 1(d)) was similar to that of the cross-linked chitosan–zeolite composite (Fig. 1(c)). However, it can be observed in Fig. 1(d) that the transmittance in the band at 3,426 cm^{-1} decreased obviously and the band at 1,655 cm^{-1} was shifted to 1,642 cm^{-1} after the adsorption of Cd(II).

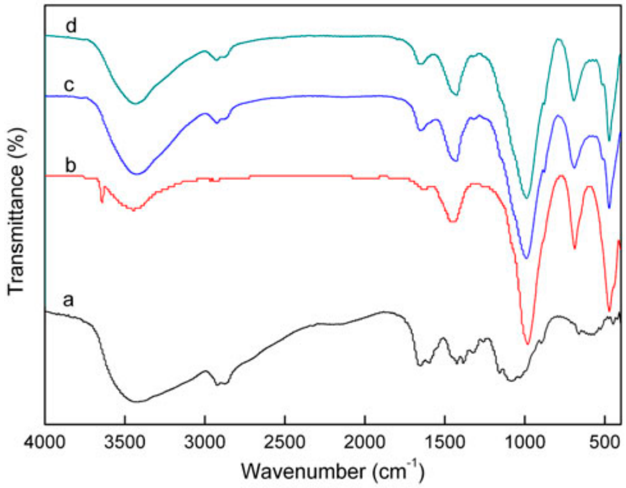

Fig. 1. FTIR spectra of chitosan (a), zeolite (b), the chitosan–zeolite composite (c), and the Cd(II) loaded chitosan–zeolite composite (d).

The SEM images of zeolite (a), the chitosan–zeolite composite (b), and the Cd(II) loaded chitosan–zeolite composite (c) are shown in Fig. 2. The SEM image of zeolite showed a nearly uniform structure with smooth edged lamellar crystals. In comparison with zeolite, the SEM images of the chitosan–zeolite composite and the Cd(II) loaded chitosan–zeolite composite exhibit more rough and irregular surfaces. In addition, the SEM micrograph of the chitosan–zeolite composite loaded with Cd(II) showed a brighter area, which indicates the presence of Cd(II). This is due to better electric conduction properties of cadmium compared to the chitosan–zeolite composite itself, which leads to a brighter image [34].

The values of BET surface area, average pore diameter, and average pore volume for chitosan, zeolite, and the cross-linked chitosan–zeolite composite are presented in Table 1. According to the recommendation by the International Union of Pure and Applied Chemistry, the pores can be divided into three kinds: micropores (diameter < 2 nm), mesopores (2 < diameter < 50 nm), and macropores (diameter > 50 nm) [28]. As seen in Table 1, all the three materials have an average pore diameter between 2 and 50 nm, indicating the presence of mesopores. The average pore diameter of the cross-linked chitosan–zeolite composite is between chitosan and zeolite, which

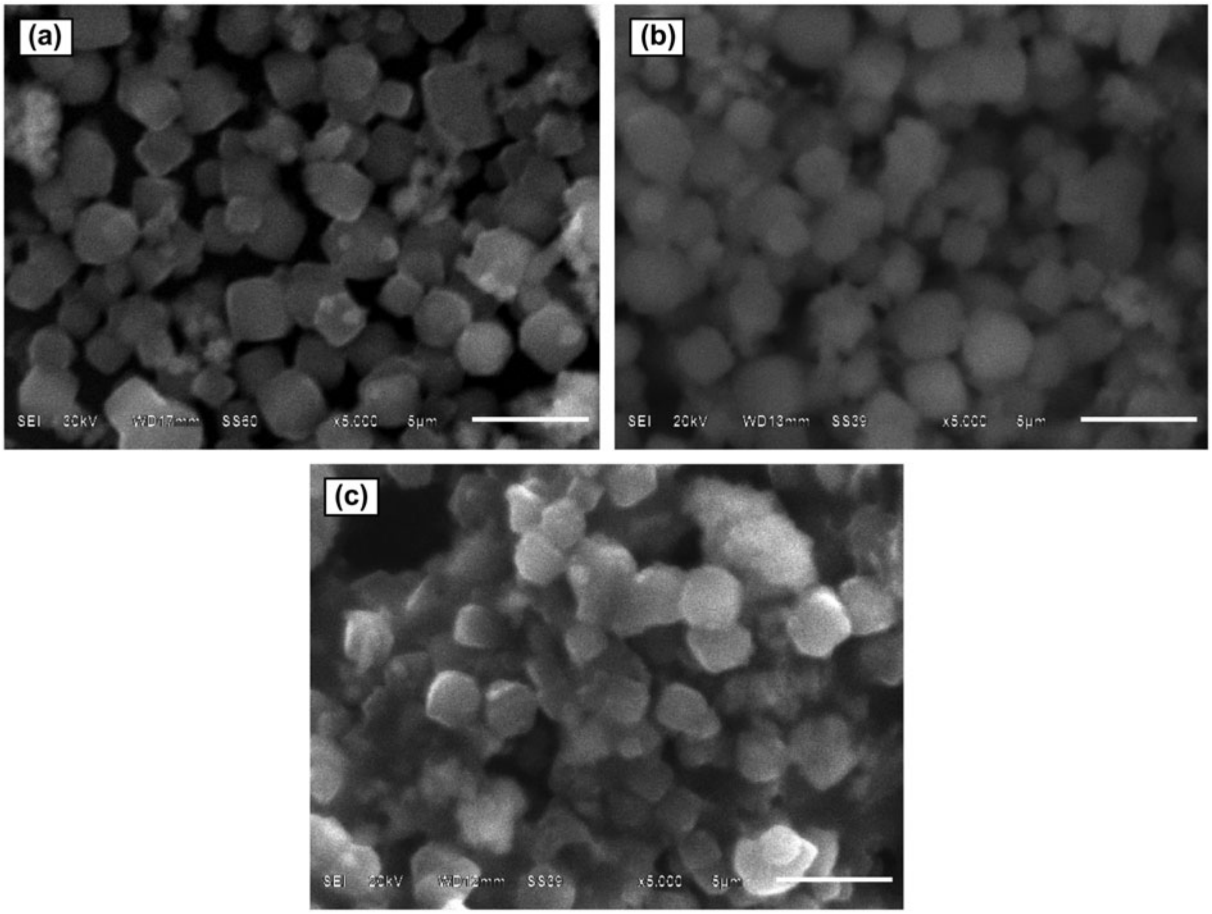

Fig. 2. SEM micrographs of zeolite (a), the chitosan–zeolite composite (b), and the Cd(II) loaded chitosan–zeolite composite (c).

Table 1
BET surface area, average pore diameters, and average pore volume of chitosan, zeolite, and the cross-linked chitosan–zeolite composite

Material	BET surface area (m^2/g)	Average pore diameter (nm)	Average pore volume (m^3/g)
Chitosan	3.57	5.49	0.0029
Zeolite	6.40	10.78	0.013
Cross-linked chitosan–zeolite composite	11.94	10.26	0.031

indicates that cross-linking process has increase the average pore size of the composite. It is observed that chitosan exhibits the least surface area, whereas the cross-linked chitosan–zeolite composite has the largest surface area. In addition, the surface area increases with the increase of pore volume.

3.2. Effect of pH

The pH value of aqueous solution plays an important role in the whole adsorption process [24]. In this study, effect of pH on the adsorption of Cd(II) onto the cross-linked chitosan–zeolite composite was investigated in the pH range of 3.0–7.5 (Fig. 3). As shown in the figure, the Cd(II) adsorption capacity significantly increased when pH of Cd(II) solution increased from 4.0 to 7.0, the optimum adsorption pH being achieved at 7.0. The observed low level of Cd(II) uptake at lower pH may be attributed to the partial protonation of the functional group (–NH) in chitosan–zeolite composite, which would increase the electrostatic repulsion between Cd(II) and the surface of

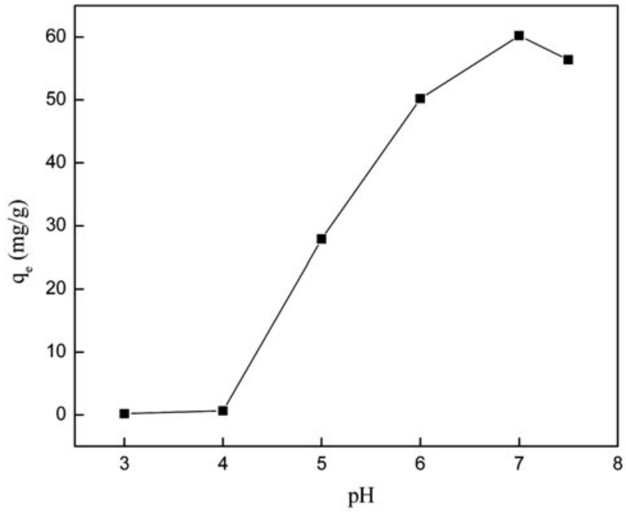

Fig. 3. Effect of pH on the adsorption of Cd(II) onto the cross-linked chitosan–zeolite composite (adsorbent: 20 mg, temperature: 25℃, time: 2 h, initial concentration of Cd(II): 50 mg/L).

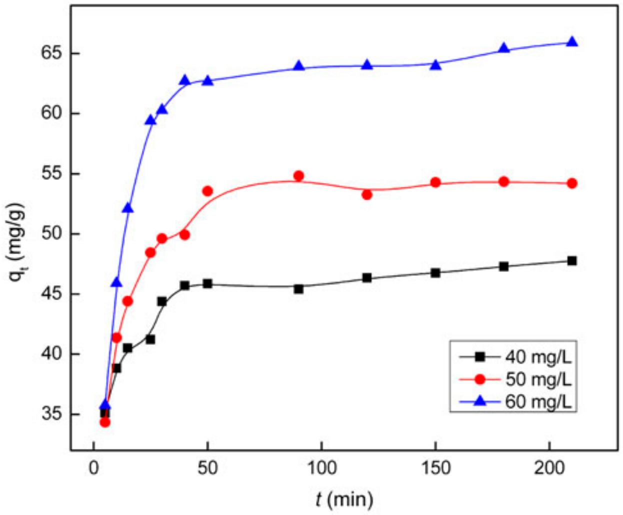

Fig. 4. Effect of contact time on the adsorption capacity of Cd(II) onto the cross-linked chitosan–zeolite composite at different initial concentrations (adsorbent: 20 mg, temperature: 25℃, time: 2 h, pH 7.0).

chitosan–zeolite composite, causing a decrease in the adsorption capacity [16,22,24,34,39]. Another aspect could be attributed to the competition of H^+ ions with Cd(II) ions to same binding sites on the adsorbent [39]. At pH > 7.0, small amount of Cd(II) started to deposit as hydroxides, which also leads to a lower uptake. Similar observations were previously reported in literature [19,22,27]. Therefore, pH 7.0 was selected as the initial pH value of Cd(II) solution for the following adsorption experiments.

3.3. Effect of contact time and initial Cd(II) concentration

Fig. 4 shows the effect of contact time on the adsorption capacity of Cd(II) onto the cross-linked chitosan–zeolite composite at different initial concentrations. As can be seen, the adsorption capacity increased drastically at the beginning of experiment and then increased gradually until the equilibrium was reached at about 120 min. Hence, in the present study, the contact time 2 h was used for further experiments. The phenomenon observed above is attributed to the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the Cd(II) ions in the aqueous solution and those on the adsorbent surface [34]. In addition, the adsorption capacity of Cd(II) onto cross-linked chitosan–zeolite composite at different contact time increased with the increasing of initial concentration (Fig. 4). This is because an increase in initial concentration is helpful to enhance driving force to overcome mass transfer resistance, allowing more Cd(II) ions to pass from the aqueous solution to the adsorbent surface [34].

3.4. Adsorption kinetics

In order to gain insight into the characteristics of the adsorption process, the pseudo-first-order and pseudo-second-order kinetic models were employed to fit experimental data obtained from batch experiments. The pseudo-first-order (Eq. (2)) and pseudo-second-order (Eq. (3)) equations are expressed in linear form as follows [27,32]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where q_e (mg/g) and q_t (mg/g) are the amounts of Cd (II) adsorbed on the cross-linked chitosan–zeolite composite at equilibrium and time t (min), respectively, k_1 (min^{-1}) is the pseudo-first-order rate constant, and k_2 ($\text{g mg}^{-1}\,\text{min}^{-1}$) is the pseudo-second-order rate constant.

The kinetic parameters and correlation coefficients (R^2) for adsorption of Cd(II) onto the cross-linked chitosan–zeolite composite were determined by linear regression (Fig. 5) and were presented in Table 2. As can be seen, the experimental q_e values ($q_{e,\mathrm{exp}}$) are in good agreement with the calculated ones ($q_{e,\mathrm{cal}}$) using the pseudo-second-order kinetic model. In addition, the obtained correlation coefficients (R^2) of the pseudo-second-order kinetic model are much higher than those of the pseudo-first-order kinetic model, implying that the adsorption of Cd(II) is perfectly fitted the pseudo-second-order kinetic model rather than the other one. Several previous studies in literature on the adsorption of Cd(II) onto chitosan or modified chitosan have also shown that the pseudo-second-order kinetic model gave the best fit for the experimental data [16,27,40].

The Weber's intra-particle diffusion model was further applied to identify the diffusion mechanism during the adsorption process, which can be described as the following equation [41].

$$q_t = k_i t^{1/2} \tag{4}$$

where k_i (mg/g min$^{1/2}$) is the intra-particle diffusion rate constant, and q_t has the same meaning as that in Eq. (2). Values of k_i were calculated from plots of q_t vs. $t^{1/2}$ (Fig. 6) and were presented in Table 2. As shown in Fig. 6, the curves are not linear over the whole time period, and the plots exhibit dual nature with initial linear portion followed by plateau, indicating that the adsorption process involves at least two stages. The first sharper portion is a diffusion adsorption stage, which is attributed to the diffusion of Cd (II) through the solution to the external surface of adsorbent. The second portion is a gradual adsorption stage, which is controlled by intra-particle diffusion of Cd(II) through the pores of adsorbent. Also, it can be seen that the initial linear portion of the curves do not pass through the origin and the latter stages of Cd(II) adsorption do not obey Weber equation, which indicates that mechanism of Cd(II) adsorption process is rather complex and the intra-particle diffusion is not the only rate-controlling step.

3.5. Effect of temperature and adsorption thermodynamics

The effect of temperature on the adsorption equilibrium of Cd(II) onto the cross-linked chitosan–zeolite composite was investigated at 25, 35, and 45℃. The equilibrium constant for the adsorption process, K_c, was calculated with Eq. (5):

$$K_c = \frac{C_{\mathrm{ad}}}{C_e} \tag{5}$$

where C_{ad} and C_e are the concentration (mg/L) of Cd (II) adsorbed on the adsorbent and in the solution at equilibrium, respectively.

The standard Gibbs free energy change (ΔG^0) of the adsorption was calculated according to Eq. (6):

$$\Delta G^0 = -RT \ln K_c \tag{6}$$

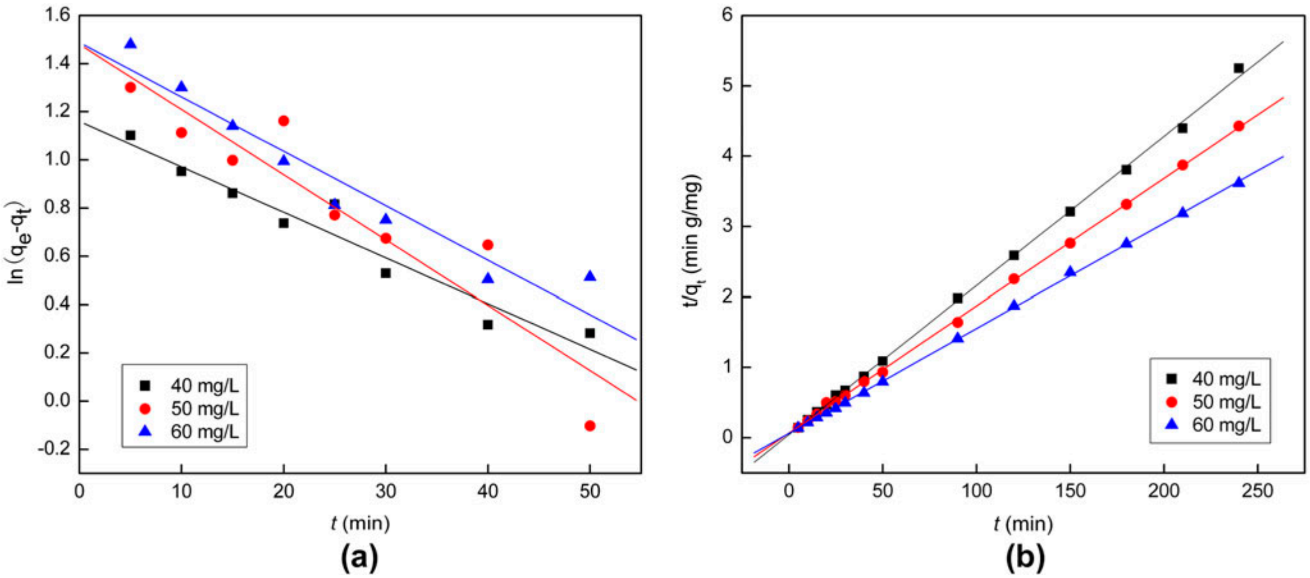

Fig. 5. Pseudo-first-order (a) and pseudo-second-order (b) kinetic models for the adsorption of Cd(II) onto the cross-linked chitosan–zeolite composite (adsorbent: 20 mg, temperature: 25℃, time: 2 h, pH 7.0).

Table 2
Pseudo-first-order, pseudo-second-order kinetic, and intra-particle diffusion model parameters for the adsorption of Cd (II) onto the cross-linked chitosan–zeolite composite

		Pseudo-first order			Pseudo-second order			Intra-particle diffusion model	
C_0 (mg/L)	$q_{e,\mathrm{exp}}$ (mg/g)	$q_{e,\mathrm{cal}}$ (mg/g)	k_1 (1/min)	R^2	$q_{e,\mathrm{cal}}$ (mg/g)	k_2 (g/mg min)	R^2	k_i (mg/g min$^{1/2}$)	R^2
40	46.75	3.19	0.0189	0.9409	47.26	0.0085	0.9990	0.6627	0.8033
50	54.29	4.39	0.0271	0.8670	55.40	0.0041	0.9987	1.006	0.7046
60	65.10	4.43	0.0226	0.9320	66.98	0.0037	0.9998	3.174	0.7229

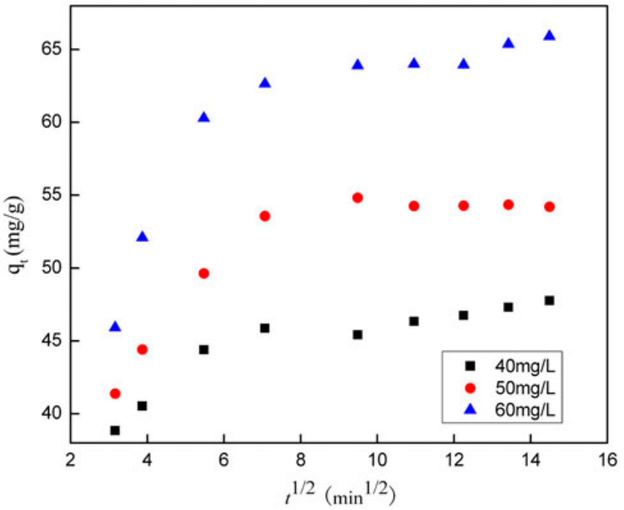

Fig. 6. Intra-particle diffusion plots for the adsorption of Cd(II) onto the cross-linked chitosan–zeolite composite (adsorbent: 20 mg, temperature: 25℃, time: 2 h, pH 7.0).

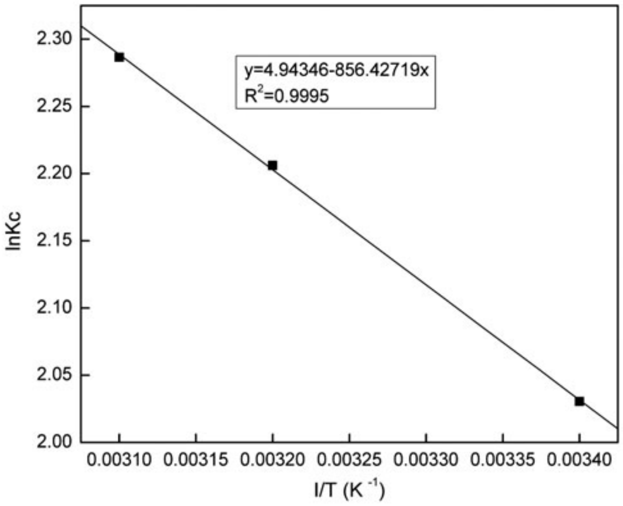

Fig. 7. Plot of $\ln K_c$ vs. $1/T$ for the adsorption of Cd(II) onto the cross-linked chitosan–zeolite composite (adsorbent: 20 mg, time: 2 h, pH 7.0, initial concentration of Cd(II): 50 mg/L).

where R is the universal gas constant (8.314 J/mol/K) and T (K) is the absolute temperature.

The standard enthalpy change (ΔH^0) and entropy change (ΔS^0) of the adsorption were calculated from the slope and intercept, respectively, from the plot of $\ln K_c$ vs. $1/T$ (Fig. 7) according to Eq. (7).

$$\ln\ K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{\mathrm{RT}} \tag{7}$$

The values of thermodynamic parameters are presented in Table 3. It was found that the adsorption of Cd(II) on the cross-linked chitosan–zeolite composite increased with temperature. The negative values of ΔG^0 under all conditions indicate the feasibility and spontaneity of the adsorption process [4,42]. The positive value of ΔH^0 shows that the Cd(II) adsorption on the cross-linked chitosan–zeolite composite is endothermic in nature [4,7]. The positive value of ΔS^0 suggests randomness at the solid–solution interface during adsorption [4].

3.6. Adsorption isotherms

Adsorption isotherm study is important in the design of adsorption systems because it can describe how the adsorbate interacts with adsorbent at equilibrium. The Langmuir and Freundlich isotherms are the most common mathematical models for describing adsorption isotherms in aqueous solution [7,27]. The Langmuir isotherm assumes that the adsorption occurs at a homogeneous surface with all the adsorption sites having equal adsorbate affinity [24]. The Langmuir model can be presented in the linear form as Eq. (8):

Table 3
Thermodynamic parameters for the adsorption of Cd(II) onto the cross-linked chitosan–zeolite composite

Temperature (℃)	K_c	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol/K)
25	7.62	−5.03	7.12	41.10
35	9.08	−5.65		
45	9.84	−6.05		

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

where q_e and C_e are the adsorption capacity (mg/g) and the equilibrium concentration of the adsorbate in solution (mg/L), respectively, while q_m (mg/g) is the maximum adsorption capacity for monolayer formation on adsorbent and b is the Langmuir constant (L/mg) related to the energy of adsorption.

Different from Langmuir model, the Freundlich isotherm model is an empirical equation assuming that the adsorption process takes place on heterogeneous surfaces [24]. The Freundlich model can be expressed as Eq. (9):

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{9}$$

where K_F (mg/g) is the measure of adsorption capacity, and n is the adsorption intensity.

In the present study, the Langmuir and Freundlich models were used to determine the adsorption equilibrium between the chitosan–zeolite composite and Cd(II) ion. The parameters for both models were obtained by linear regression method and presented in Fig. 8 and Table 4. It can be seen that Langmuir isotherm model correlated well ($R^2 = 0.9981$) as compared to Freundlich isotherm ($R^2 = 0.8388$) only, when one group of data was used to represent the entire range of experimental data as shown in Table 4. This indicates that the Langmuir model is more suitable for describing the adsorption equilibrium of Cd(II) onto the chitosan–zeolite composite. It was also found that the maximum adsorption capacity (q_m) determined from the Langmuir model increased with temperature, and which was in the range of the removal capacity for chitosan-based adsorbents reported in the literature (Table 5). Our experimental findings are also in good accordance with the maximum adsorption capacities, predicted by Langmuir model at different temperatures.

The favorability of adsorption can be expressed in terms of a dimensionless separation factor (R_L), which can be calculated from the Langmuir constant according to the following equation [4]:

$$R_L = \frac{1}{1 + bC_0} \tag{10}$$

where b is the Langmuir constant (L/mg) and C_o is the initial concentration of Cd(II) (mg/L). The nature of adsorption can be determined by $R_L > 1$, $0 < R_L < 1$, $R_L = 0$, and $R_L = 1$, which indicates unfavorable, favorable, irreversible, and linear, respectively [34]. In the present study, the values of R_L were in the range of 0.022–0.069 for 50–125 mg/L initial concentration of Cd(II), which lie between 0 and 1, conforming that the adsorption of Cd(II) over the chitosan–zeolite composite is favorable.

3.7. *Adsorption mechanisms*

The FTIR spectroscopic analysis helps to gain insight into the adsorption mechanism. For the cross-linked chitosan–zeolite composite used in this study, it was expected that the nitrogen atoms of amino groups and the oxygen atoms of the hydroxyl groups in chitosan acted as active sites for Cd(II) adsorption [4]. Both nitrogen and oxygen atoms have lone pair of electrons, which makes they can bind the positively charged Cd(II) ion through the electron pair sharing to form metal complex. In addition, the nitrogen atoms have a greater tendency to donate the lone pair of electrons than the oxygen atoms. So, the nitrogen atoms would be the main binding site to form stable metal complex. To understand the nature of Cd(II) adsorption and identify the possible sites of Cd(II) binding to the cross-linked chitosan–zeolite composite, the FTIR spectra of the composite before (Fig. 1(c)) and after (Fig. 1(d)) Cd(II) adsorption were obtained. As seen in Fig. 1(c) and (d), the obvious decrease in transmittance in the band at 3,426 cm^{-1} after Cd(II) adsorption indicated that the bonding of Cd(II) with –NH groups occurred. Thus, the nitrogen atoms of chitosan moiety acted as main adsorption site for Cd (II) adsorption onto the cross-linked chitosan–zeolite composite. Also, it can be observed clearly that the N–H bending vibration at 1,655 cm^{-1} was shifted to 1,642 cm^{-1} after the adsorption of Cd(II), which suggested the attachment of Cd(II) to nitrogen atoms. Similar results were found in previous studies [4,43].

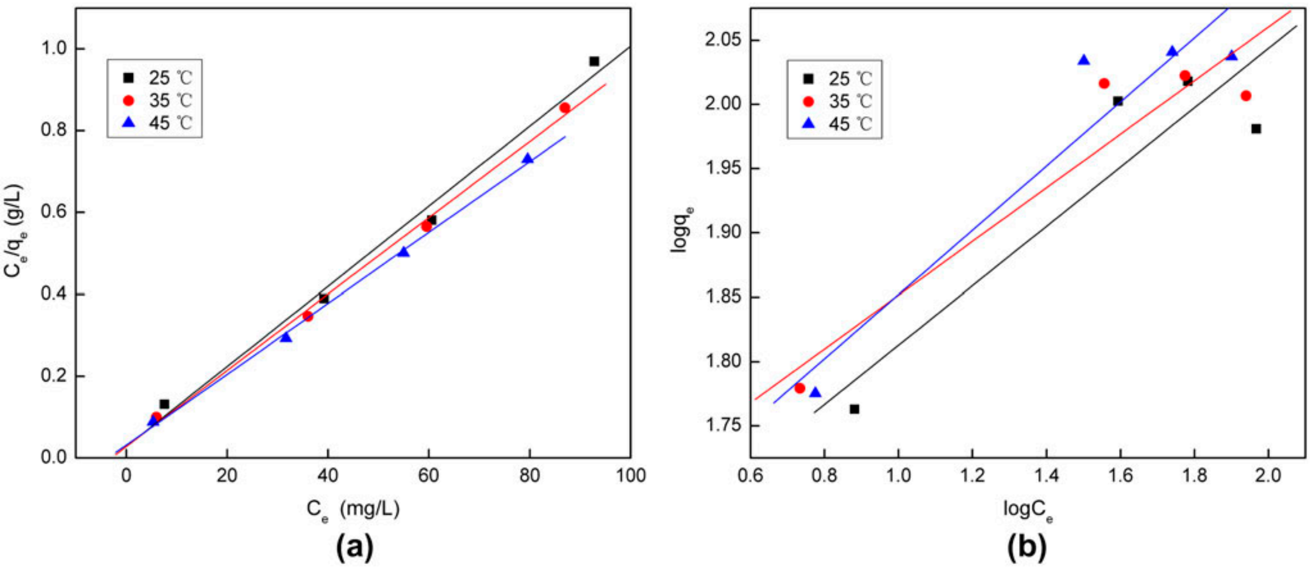

Fig. 8. Langmuir (a) and Freundlich (b) plots for the adsorption of Cd(II) onto the cross-linked chitosan–zeolite composite (adsorbent: 20 mg, solution volume: 20 mL, time: 2 h, pH 7.0).

Table 4
Langmuir and Freundlich isotherm parameters and correlation coefficients for Cd(II) adsorption

Temperature (℃)	Langmuir model		Freundlich model			
	q_m (mg/g)	b (L/mg)	R^2	K_F (mg/g)	n	R^2
25	102.15	0.35	0.9893	38.21	4.33	0.8388
35	107.30	0.33	0.9962	43.94	4.79	0.8953
45	115.47	0.27	0.9981	40.03	4.00	0.8983

Table 5
Cd(II) removal capacity of chitosan-based adsorbents reported in the literature

	Epichlorohydrin cross-linked chitosan-clay	Cross-linked magnetic chitosan-phenylthiourea resin	Chitosan cross-linked with epichlorohydrin-triphosphate	Chitosan/activated carbon composite	Cross-linked chitosan–zeolite composite
Removal capacity (mg/g)	72.31	120 ± 1	83.75	52.63	102.15
Reference	[7]	[24]	[27]	[30]	This study

3.8. Desorption studies

Desorption studies are important to investigate the possibility for the recovery of Cd(II) ions from chitosan–zeolite composite, as well as for the regeneration of the adsorbent for subsequent reuse. Desorption studies were carried out by using HCl, HNO_3, and EDTA solution as eluent. Results showed that the desorption efficiency of Cd(II) attained to 96, 97, and 99% using HCl, HNO_3, and EDTA as desorbent, respectively. EDTA has been widely demonstrated as an efficient desorption agent for metal ions because it can form steady complex with them [7,16,24,27].

4. Conclusions

The present study focused on the removal of Cd (II) from aqueous solution using the cross-linked chitosan–zeolite composite as an efficient adsorbent. The adsorption of Cd(II) was shown to be dependent on the solution pH, and the optimum pH value for the adsorption was 7.0. The kinetics study demonstrated that the kinetic mechanism for the adsorption of Cd(II) followed the pseudo-second-order model, which provided better correlation with the experimental data at different initial Cd(II) concentrations in comparison with the pseudo-first-order kinetic model. Thermodynamic parameters indicated that the adsorption of Cd(II) on the chitosan–zeolite composite was spontaneous and endothermic in nature. The equilibrium adsorption data of Cd(II) on the chitosan–zeolite composite fitted better with the Langmuir isotherm model than the Freundlich isotherm model. Based on the Langmuir isotherm model, the predicted maximum adsorption capacity of Cd(II) at pH 7.0 and 25℃ was found to be 102.15 mg/g. The recovery of Cd(II) ions was achieved by desorption in 0.10 mol/L EDTA, HNO_3, and HCl solution, respectively. Above research findings suggested that the developed chitosan–zeolite composite could be efficiently utilized to remove Cd (II) ions from aqueous solution. Furthermore, chitosan and zeolite are low-cost and non-hazardous materials, and environmentally benign.

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