Adsorption of cadmium on activated zeolite, characterization, mechanism in micro-polluted water

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ABSTRACT

High-efficiency, inexpensive, and simple preparation methods are the main features of future adsorption materials. To improve the adsorption efficiency of cadmium in micro-polluted water, natural zeolite was modified by high-temperature treatment combined with HCl-acidified to obtain activated zeolite. The structural characterizations were performed by X-ray powder diffractometer, scanning electron microscopy, Fourier-transform infrared spectroscopy, and Brunauer–Emmett–Teller surface area analysis. The characterization results confirmed that the internal structure of activated zeolite was dispersed and loose, the specific surface area, average pore diameter, and total pore volume increased, and the adsorption capacity was improved. Furthermore, adsorption isotherm, kinetics, and thermodynamics studies were further conducted to study the adsorption mechanisms. The kinetic studies demonstrated that the pseudo-second-order (R^2 = 0.983) model described the adsorption of cadmium onto activated zeolite better than the pseudo-first-order (R^2 = 0.934) and intra-particle diffusion model (R^2 = 0.950), suggesting an equilibrium time of 180 min at 25°C. The Langmuir model, the Freundlich model, Temkin, and Redlich–Peterson adsorption isotherm equations were used to fit active zeolite adsorption Cd(II). The result showed that cadmium adsorption can be better described using the Langmuir model (R^2 = 0.966), indicating that the process was single-molecular-layer adsorption. Thermodynamic analysis indicated that the adsorption process was spontaneous and endothermic, and was driven by the increase of entropy. Hence, this study demonstrated the adsorption capacity of activated zeolite was improved and activated zeolite was a promising adsorbent for the effective removal of cadmium from micro-polluted water.

Keywords: Activated zeolite; Adsorption; Modification; Cadmium; Micro-polluted water

1. Introduction

Cadmium is one of the most toxic and common heavy metals that affect humans, animals, and plants. It was the first of 12 harmful substances with global presence and impact proposed by the United Nations Environment Programme in 1984 [1]. All cadmium compounds have been classified as human carcinogens [2]. Along with the rapid population growth, industrialization, and economic development, cadmium was widely released into the environment. Cadmium pollution at different levels had been a common environmental issue in many river systems in the world [3], and it had a trend of gradual expansion. The irrigation area of micro-polluted water was large in China. Long-term irrigation had caused heavy metal pollution in some farmland, especially cadmium pollution [4]. According to the National Soil Pollution Survey Bulletin released in 2014, the point over-standard rate of cadmium reached 7.0% [5].

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Cadmium has strong chemical activity in the soil environment and is easy to enter the farmland ecosystem through micro-polluted irrigation water and other ways. It also has relatively high mobility in plants and is easy to migrate to seeds and accumulate in agricultural products through root absorption. Its impact on the ecological environment is much higher than that of other heavy metals. It is the most widely polluted farmland soil and the most prominent heavy metal element exceeding the standard in agricultural products in China [6]. Cadmium is easily accumulated in animal and human organs through the food chain, such as the brain, kidney, and liver, which is harmful to the human body [7].

According to previous literature, the commonly used existing methods for heavy metal pollution in wastewater include electric remediation [8], adsorption, chemical precipitation [9,10], plant extraction remediation [11], and combined remediation technology [12]. Among these methods, adsorption is now recognized as a traditional and popular treatment method due to its high efficiency, low cost, reliability, and variety of adsorbents [13]. Adsorbent plays a key role in an adsorption process and its performance determines the removal efficiency and cost [14]. A large number of different types of adsorbents have been studied, such as manganese iron oxide-biochar composites [15] with biochar as the carrier, black humic acid [16] prepared from Shanxi lignite, ceramsite [17] prepared from waste red mud, silica gel adsorbent [18], and aspartic acid modified magnetic chitosan [19]. However, because graphene, biochar, and other materials are expensive, it is necessary to find low-cost, efficient, and fast adsorption materials. Clay is a water-bearing aluminosilicate consisting of a mixture of fine-grained clay minerals, other mineral crystals, and metal oxides. Based on these properties, clays can be classified into different categories, zeolites being one of them [20]. Zeolites are aluminosilicate minerals containing water and alkali, which have micropores and multi-channel framework structures [21]. Zeolites have been studied and applied for the removal of organic pollutants, iron and manganese, and ammonia nitrogen pollution in water [22–25]. However, there is an open framework in natural zeolite, and a large number of impurities and water molecules are distributed in the internal pores of natural zeolite, which affect the adsorption capacity to a certain extent [26]. The adsorption capacity of heavy metals and other pollutants is also limited [27]. The adsorption capacity of zeolite can be greatly improved by modification in different ways. The modification of natural zeolite mainly includes heating modification, acid-base modification, surfactant modification, and metal and metal oxide modification [28]. In this paper, a simple activated zeolite with a short reaction time and high removal efficiency was prepared by heating modification. Most research has focused on the adsorption mechanisms by investigating adsorption isotherms, kinetics, and thermodynamic analysis, coupled with the effects of experiment conditions such as pH, temperature, and time on adsorption behaviors.

2. Materials and methods

2.1. Experimental materials

The activated zeolites used in this experiment were purchased from Yusong Water Supply and Drainage Equipment Factory in Gongyi City. They are clinoptilolite with a variety of colors that include light gray, milky white, and pale red. The particle size range from 0.5 to 1.5 mm.

2.1.1. Modification method

The activated zeolites were made of high-quality zeolite ore, crushed and granulated, soaked in 5% dilute hydrochloric acid for more than 2 h, then controlled at about 350°C in a high-temperature furnace and roasted at high temperature for about 1 h. The main physical and chemical performance measures of activated zeolite included specific gravity (SG), 2.23 g/cm^3, porosity ≥ 56%, water ≤ 2.0%, SiO_2, 68%~70%, AL_2O_3, 13%~14%, and Fe_2O_3, 1%~1.8%.

2.1.2. Pretreatment of activated zeolite

The activated zeolite was crushed by a pulverizer and screened by 40~60 mesh to obtain activated zeolite particles with a particle size of 0.3~0.45 mm. Then the crushed activated zeolite is washed with tap water until it is not turbid, and then washed with distilled water. Finally, the zeolite is soaked in deionized water for 24 h to dissolve impurities and reduce its pH. After that, the zeolite is placed at 105°C in a digital display electric heating and constant temperature drying oven for 24 h, dried, cooled to room temperature and sealed into sample bags for storage.

2.2. Adsorption experiment

2.2.1. Static adsorption experiment

A certain amount of activated zeolite was weighed and placed in a conical flask, and 100 mL of simulated wastewater containing a certain concentration of Cd(II) was added. At a certain temperature and a rotational speed of 180 rpm, the activated zeolite was taken out after a period of constant temperature oscillation, and the supernatant at 1 cm below the liquid level was taken for 3 min. The concentration of Cd(II) in the adsorbed wastewater was measured by graphite furnace atomic absorption spectrophotometer.

The single factors were as follows: The dosages of adsorbent were 0.01, 0.05, 0.1, 0.2, 0.4, 0.6, and 0.8 g. The values of pH were 2, 3, 4, 5, 6, 7, 8, 9 and 10. Temperatures were 25°C, 30°C, 35°C, 40°C, 45°C, and 65°C. Adsorption times were 10, 20, 30, 45, 60, 90, 120, 150, 180, and 210 min. The initial Cd(II) concentrations were 20, 40, 60, 80, and 100 μg/L.

2.2.2. Dynamic adsorption experiment

Activated zeolite has good adsorption performance. The adsorption process was further simulated by a dynamic adsorption experiment. Therefore, activated zeolite is used as an adsorption medium for adsorption column experiments. Operating parameters are mass, 50 g; filter media height, 800 mm; filtration speed, 4 m/h; peristaltic pump speed, 80 rpm; and the flow rate, 46.67 mL/min. The dynamic adsorption system operates intermittently, injecting a contaminated liquid containing 100 μg/L of Cd(II), and taking the adsorption filter column every 30 min to filter the water and detect the concentration of Cd(II). After each consecutive run for 12 h, stop for 12 h, and continue running. The adsorption filter column runs for a total of 26 h.

2.3. Adsorption efficiency

2.3.1. Removal rate of cadmium by activated zeolite

The expression is as follows:

$$\text{Removal rate} = \frac{C_0 - C_e}{C_0} \times 100\% \tag{1}$$

where C_0 and C_e are the initial Cd(II) concentrations (μg/L) and the concentration at which adsorption equilibrium is reached (μg/L), respectively.

2.3.2. Calculation of cadmium adsorption capacity

The adsorption capacity of the adsorbent can be calculated according to Eq. (2):

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

where q_e is the equilibrium adsorption capacity of adsorbent per unit mass (μg/g), C_0 is the initial concentration of cadmium (μg/L), C_e is the equilibrium concentration of cadmium corresponding to q_e (μg/L), V is the concentration of the liquid (L), m is the amount of adsorbent (g).

2.4. Adsorption model

2.4.1. Isothermal adsorption model

The isotherm of Cd(II) adsorption was fitted to both the Langmuir and Freundlich adsorption models. The Langmuir adsorption model hypothesized that the sorption is a monolayer sorption, and the Freundlich adsorption model is an empirical formula used to study multilayer adsorption models.

The linear form of Langmuir [29] isothermal equation is as follows:

$$\frac{C_e}{Q_e} = \frac{1}{kQ_m} + \frac{C_e}{Q_m} \tag{3}$$

where Q_e (μg/g) is the monolayer adsorption capacity, C_e (μg/L) is the equilibrium concentration of cadmium corresponding to Q_e, Q_m (μg/g) is the saturated adsorption capacity of the monomolecular layer, k is the adsorption constant.

The linear form of Freundlich [30] isothermal equation is as follows:

$$\ln Q_e = \ln k + \frac{1}{n} \ln C_e \tag{4}$$

where Q_e (μg/g) is monolayer adsorption capacity, C_e (μg/L) is the equilibrium concentration of cadmium corresponding to Q_e, k is the adsorption constant, n is a characteristic constant related to adsorption intensity or adsorption degree, and n usually is greater than 1.

The linear form of Temkin [31] isothermal equation is as follows:

$$Q_e = B \ln A_T + B \ln C_e \tag{5}$$

where A_T (L/mol) and B are equilibrium binding energy and heat of the adsorption obtained from the intercept and slope of the graph between Q_e vs. $\ln C_e$.

The Redlich–Peterson [32] isotherm equation is as follows:

$$Q_e = \frac{AC}{1 + BC_e^g} \tag{6}$$

where Q_e (μg/g) is monolayer adsorption capacity, C_e (μg/L) is the equilibrium concentration of cadmium corresponding to Q_e, A, B, and g are Redlich–Peterson parameters, and g is between 0 and 1.

2.4.2. Adsorption thermodynamics model

The thermodynamic description of the adsorption process consists of three parameters: Gibbs free energy (ΔG, kJ/mol), enthalpy change (ΔH, kJ/mol), and entropy change (ΔS, J/mol·K). The relationship between the three is as follows:

$$\Delta G = \Delta H - T\Delta S \tag{7}$$

Further derivation of the above formula can be expressed as:

$$\Delta G = -RT \ln K_c \tag{8}$$

where R is the ideal gas constant, the value is 8.314 J/(mol·K); T is the adsorption temperature, the unit is K, and K_c is the equilibrium constant. The calculation formula is as follows:

$$K_c = \frac{C_{Ae}}{C_e} \tag{9}$$

where C_{Ae} (μg/L) is the concentration of cadmium ions on the adsorbent at equilibrium, C_e (μg/L) is the concentration of cadmium ions remaining in the solution at equilibrium.

The summary formula is as follows:

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{10}$$

A linear function can be obtained by plotting $\ln K_c$ vs. T^{-1}. The values of ΔH and ΔS can be calculated from the slope and intercept of the fitted line.

2.4.3. Adsorption kinetic models

Adsorption kinetics can be used to determine the adsorption rate. Using the quasi-first-order kinetic model, the quasi-second-order kinetic model, and the internal diffusion equation to linearly fit the experimental data. The

pseudo-first-order reaction kinetics equation [33] is as follows:

$$\ln\left(q_1 - q_t\right) = \ln q_1 - \frac{k_1}{2.303}t \tag{11}$$

where q_t (μg/g) is the adsorption capacity at time t, q_1 (μg/g) is the adsorption capacity at equilibrium, t (min) is the reaction time, k_1 (min^{-1}) is the pseudo-first-order kinetic adsorption rate constant.

The pseudo-second-order kinetic equation [34] is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{t}{q_2} \tag{12}$$

where q_t (μg/g) is the adsorption capacity at time t, q_2 (μg/g) is the adsorption capacity at equilibrium, t (min) is the reaction time, k_2 (g/(μg·min)) is the pseudo-second-order kinetic adsorption rate constant.

The internal diffusion equation [35] is given by the following formula.

$$q = k_3 t^{1/2} + C \tag{13}$$

where k_3 (μg/(g·s$^{1/2}$)) is the rate constant of intraparticle diffusion adsorption, and C is the constant.

3. Results and discussion

3.1. Adsorbent characterization

3.1.1. Scanning electron microscopic analysis

The scanning electron microscopy (SEM) images of natural zeolite and activated zeolite are shown in Fig. 1. The magnifications of SEM images are ×2,000. Fig. 1a shows that the surface of natural zeolite was smooth, irregular lamellar structure with some holes, and the internal structure was relatively flat and dense. Fig. 1b showed that the surface of activated zeolite was uneven with obvious holes, and the internal structure was relatively dispersed and loose. Water was discharged from the pores of natural zeolite by heating it at a high temperature, which increased the internal channels and made the internal structure loose. The results were further corroborated by SEM.

3.1.2. X-ray diffraction analysis

X-ray diffraction (XRD) of the zeolites before and after modification are shown in Fig. 1c. The diffraction absorption peak of activated zeolite was higher at the same XRD angle
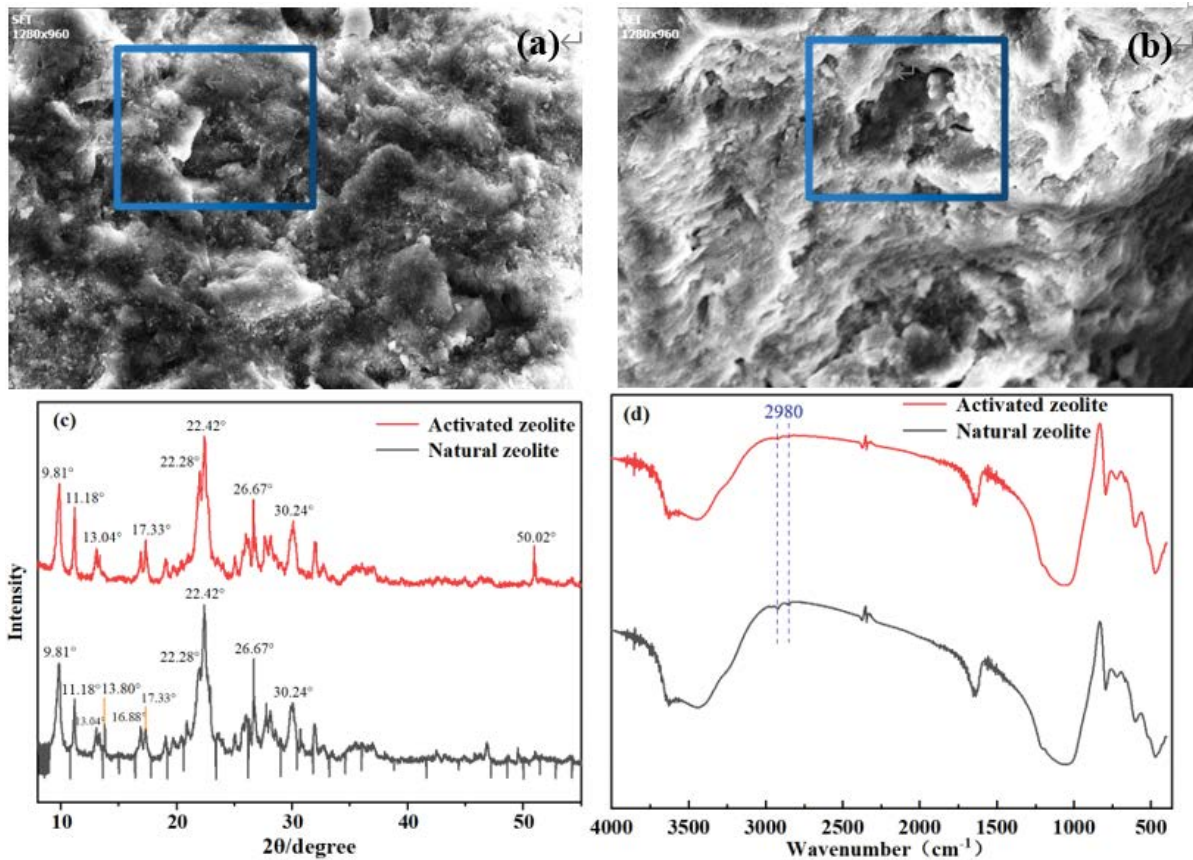

Fig. 1. Scanning electron microscopy (SEM) of zeolite modification before (a), SEM of zeolite modification after (b), X-ray diffraction (XRD) patterns before and after zeolite modification (c), and Fourier-transform infrared spectroscopy (FTIR) analysis of zeolite modification before and after (d).

compared with the XRD spectrum of natural zeolite. A weak diffraction absorption peak of activated zeolite appeared at the XRD angle 2θ of 50.02°. This indicated that after acidification and high-temperature heating modification, water in the natural zeolite was evaporated, and some impurities in the natural zeolite were washed. The purity of the natural zeolite increased, which made the characteristic structure of the activated zeolite more obvious. The diffraction absorption peaks of some impurities did not change the crystal phases or structure of the natural zeolite.

3.1.3. Fourier-transform infrared spectroscopy analysis

The Fourier-transform infrared spectroscopy (FTIR) analysis of zeolite before and after modification is shown in Fig. 1d. The infrared absorption peak position of zeolite before and after modification did not move significantly. The peak area of natural zeolite and activated zeolite did not change significantly, which indicated that the basic structure of activated zeolite was consistent with natural zeolite. However, near 2,980 cm⁻¹, the vibration band related to H_2O was reduced in the infrared spectrum of activated zeolite, and these subtle changes in the infrared absorption peaks of activated zeolite and natural zeolite indicated that the water in natural zeolite was evaporated after high-temperature heating, thereby achieving the purpose of modification.

3.2. Influence of various factors on adsorption of Cd(II)

3.2.1. Influence of activated zeolite dosage on the adsorption of cadmium

In order to investigate the influence of different adsorbent dosages on the adsorption of Cd(II) by activated zeolite, different doses of activated zeolite (0.01, 0.05, 0.1, 0.2, 0.4, 0.6, and 0.8 g) were used to adsorb Cd(II). The Cd(II) adsorption experiments were carried out at pH = 6 with an initial Cd(II) concentration of 100 μg/L, adsorption temperature of 25°C, and adsorption time of 3 h. As shown in Fig. 2a, with the increase of adsorbent dosage of activated zeolite, the adsorption capacity decreased, while the removal rate of Cd(II) increased first and then stabilized. At low doses, the removal rates were low due to insufficient adsorption sites, and as the adsorption dose increased, the adsorption sites increased and the removal rate increased. When the dosage of activated zeolite increased from 4 to 6 g/L, the removal rate of Cd(II) increased significantly, the removal rate reached 90.48%, and the adsorption capacity was 150.8 μg/g. When the dosage of activated zeolite increased to 8 g/L, the removal rate of Cd(II) was 91.26%, and there was no obvious increase. The removal rate of Cd(II) increased because the adsorption capacity of activated zeolite was high at the initial stage. When the dosage of activated zeolite increased to more than 6 g/L, the removal rate of Cd Cd(II) did not increase significantly. The reason may be that the adsorption of cadmium by activated zeolite was about to reach saturation. Considering the economic and environmental issues, an adsorbent amount of 6 g/L was chosen as the optimal dosage.

3.2.2. Influence of pH on the adsorption of cadmium

The Cd(II) adsorption experiments were carried out in the pH range of 2.0~10.0 with the dosage of activated zeolite 6 g/L, initial Cd(II) concentration of 100 μg/L, adsorption temperature of 25°C, and adsorption time of 3 h. The influence of pH on the adsorption of Cd(II) is shown in Fig. 2b.When pH was in the range of 2~6, the removal rate of Cd(II) increased with the increase of pH value. The removal rate of Cd(II) decreased slightly as the pH increased from 6 to 7. When the pH value increased from 7 to 9, the removal rate of Cd(II) increased again, and the adsorption capacity of Cd(II) increased rapidly. It increased from 145.32 to 157.68 μg/g. When the pH value increased above 9, the removal rate and adsorption capacity of Cd(II) decreased. The aqueous solution presented an alkaline environment, Cd(II) reacted with OH– in water, and cadmium hydroxide precipitated, affecting the test's adsorption effect. The best adsorption was observed at pH 6.0, when the adsorption capacity of Cd(II) was 159.67 μg/g and removal reached 95.8%. According to the experimental data, pH = 6 was chosen as the optimum pH value for the following experiments.

3.2.3. Influence of temperature on the adsorption of cadmium

A series of temperatures (25°C~65°C) were used to evaluate the effect of temperature on removal by activated zeolite. The Cd(II) adsorption experiments were carried out at pH = 6 with an adsorption dose of 6 g/L, initial Cd(II) concentration of 100 μg/L, and adsorption time of 3 h. As shown in Fig. 2c, the removal rate of Cd(II) increased with the increase in temperature. The increase in temperature was conducive to the adsorption of Cd(II) in water by activated zeolite, which also indicated that the increase in temperature promoted the adsorption of Cd(II) by activated zeolite. The results indicated that the whole adsorption process was an endothermic reaction process.

3.2.4. Influence of adsorption time on the adsorption of cadmium

Adsorption time was set as 10, 20, 30, 45, 60, 90, 120, 150, 180, and 210 min. The Cd(II) adsorption experiments were carried out at pH = 6 with an adsorption dose of 6 g/L, initial Cd(II) concentration of 100 μg/L, and adsorption temperature of 25°C. The influence of adsorption time on Cd(II) removal is shown in Fig. 2d. The removal rate of Cd(II) increased rapidly at the start of adsorption, but as adsorption time increased, the removal rate gradually tended to be 95%. The adsorption equilibrium time of activated zeolite was 180 min. The adsorption equilibrium capacity of activated zeolite for Cd(II) increased with time.

3.2.5. Influence of initial concentration on the adsorption of cadmium

A series of solutions with different initial Cd(II) concentrations (20~100 μg/L) were used to evaluate the effect of initial Cd(II) concentration on effective adsorption/removal by activated zeolite with the temperature at 25°C, pH = 6, and the dosage of activated zeolite 6 g/L, and adsorption time of 3 h. As shown in Fig. 2e, with the increase of initial Cd(II) concentration, the adsorption removal rate of Cd(II) by activated zeolite decreased gradually, and the adsorption capacity of activated zeolite decreased gradually. The
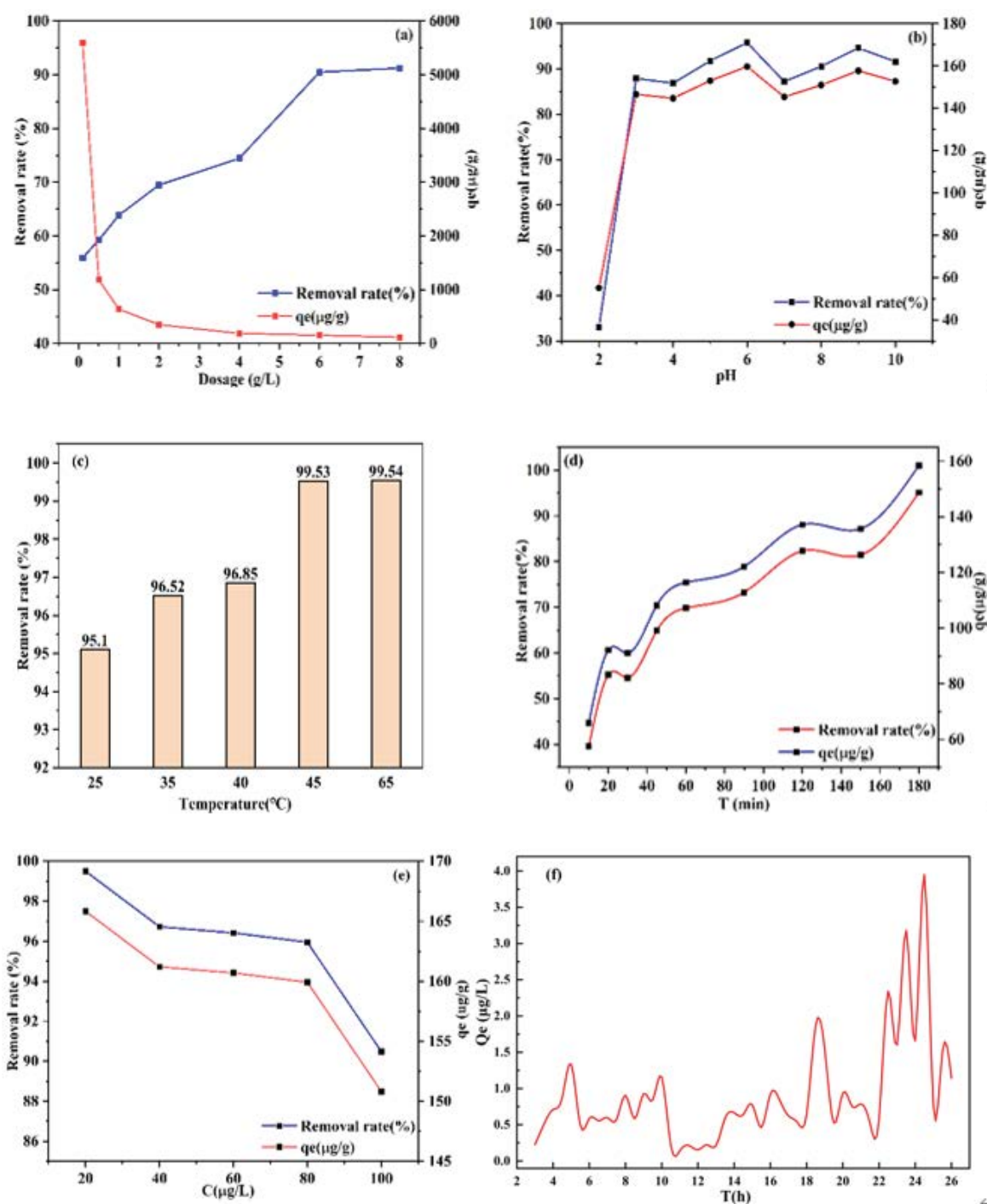
Fig. 2. Effects of different activated zeolite adsorbent dosage on adsorption of Cd(II) by activated zeolite (a), effects of different pH on adsorption of Cd(II) by activated zeolite(b), effects of reaction temperature on Cd(II) removal by activated zeolite (c), effects of reaction time on adsorption of Cd(II) (d), effects of initial Cd(II) concentration on adsorption of Cd(II) by activated zeolite (e), and dynamic adsorption curve under activated zeolite media (f) (Experiments on the effects of various factors on Cd(II) adsorption were carried out at room temperature).

main reason was that the amount of adsorbent was certain, and the adsorption capacity was limited. The adsorption capacity increased with increasing solution concentration, causing the adsorption rate of activated zeolite for Cd(II) to decrease.

3.2.6. Analysis of the dynamic adsorption effect of modified zeolite on cadmium ions

The dynamic adsorption effect of the adsorption filter column on Cd(II) is shown in Fig. 2f. It can be seen from Fig. 2f that the activated zeolite adsorption filter column

has not reached adsorption saturation, and the concentration of Cd(II) in the adsorption water is much lower than the 0.01 mg/L. The average Cd(II) removal rate of activated zeolite in water was 90.98%.

3.3. Adsorption mechanism

3.3.1. Adsorption isotherm analysis

Fig. 3a–d shows the curves of Langmuir, Freundlich, Temkin, and Redlich–Peterson adsorption isotherm equations fitted by active zeolite adsorption Cd (II). The Langmuir model was plotted on a line of C_e/Q_e vs. C_e, and the simulated linear correlation coefficient $R^2 = 0.9965$, the other relevant parameters of Langmuir models were calculated according to formula (3), $K = -3.72$ g/μg, $Q_m = 149.25$ μg/g. The Freundlich model was plotted on the line of $\ln Q_e$ vs. $\ln C_e$, and the simulated linear correlation coefficient $R^2 = 0.8734$, $\ln k$ was the line intercept, and k was calculated 1.932, and $1/n$ was the slope, 0.5339. The Temkin model was plotted on the line of Q_e vs. $\ln C_e$, and the simulated linear correlation coefficient $R^2 = 0.925$. The Redlich–Peterson adsorption isotherm model was plotted on the line of Q_e vs. C_e, and the simulated linear correlation coefficient $R^2 = 0.896$. The linear correlation coefficient of the Langmuir model was better, indicating

that the adsorption of Cd(II) by activated zeolite was more in line with the Langmuir model, and the theoretical maximum adsorption amount Q_m of activated zeolite can reach 149.25 μg/g. It is consistent with Na-P zeolite adsorption Cd, which is more in line with the Langmuir model [36].

3.3.2. Adsorption kinetics analysis

Fig. 4a–c shows the first- and second-order kinetic fits and the intraparticle diffusion kinetics fit of adsorption of Cd(II) by activated zeolite, respectively. The first-order kinetic equation was obtained by plotting $\ln(q_e-q_t)$ vs. t, and k_1 was the slope, $k_1 = 0.0101$ min⁻¹, $q_1 = 86.46$ μg/g. The second-order kinetic equation was obtained by plotting t/q_t vs. t, and k_2 could be calculated by the intercept, $k_2 = 0.0003$ g/(μg·min), $q_2 = 163.93$ μg/g. The intraparticle diffusion kinetics equation was obtained by plotting q_t vs. $t^{1/2}$, and k_3 was the slope, $k_3 = 7.7312$ μg/(g·s$^{1/2}$), C was the intercept, $C = 50.829$. As shown in Fig. 3c and d, the R^2 of the quasi-first-order kinetics was 0.9339, while the quasi-second-order kinetic model had a R^2 of 0.9 826 indicating a better linear relationship. Therefore, the adsorption of Cd(II) by activated zeolite fits the pseudo-second-order kinetic model better. Moreover, comparing the theoretical
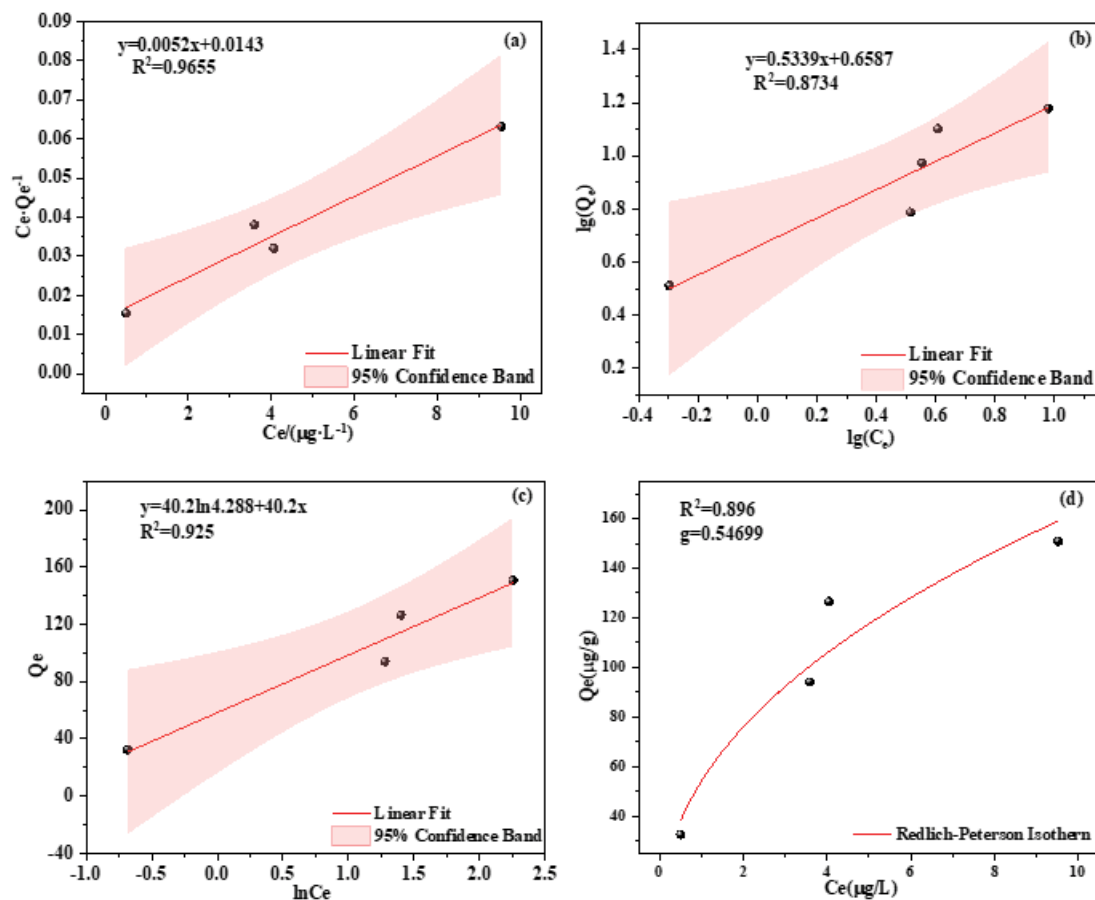

Fig. 3. Langmuir isotherm curve fitting of activated zeolite adsorption Cd(II) (a), Freundlich isotherm curve fitting of activated zeolite adsorption Cd(II) (b), Temkin isotherm curve fitting of activated zeolite adsorption Cd(II) (c), and Redlich–Peterson isotherm curve fitting of activated zeolite adsorption Cd(II) (d).
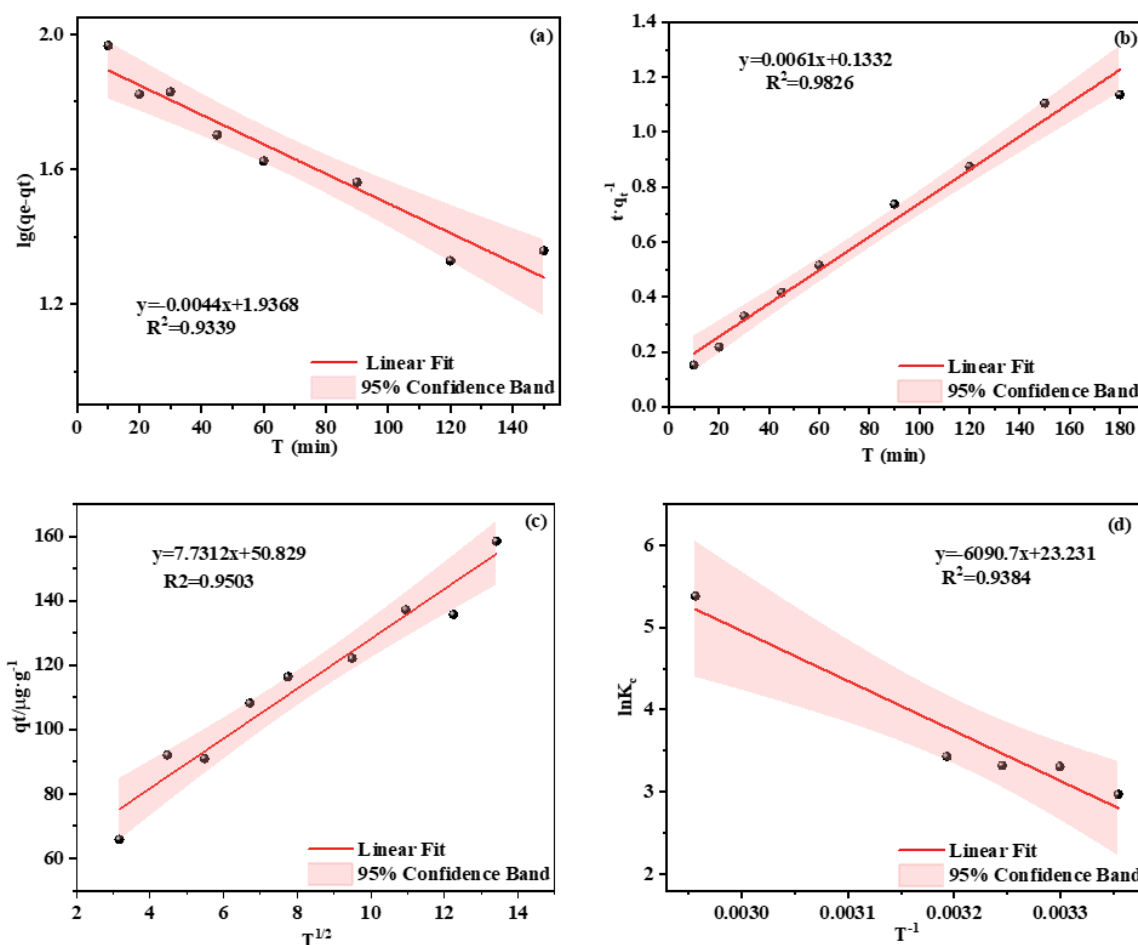
Fig. 4. Quasi-first-order kinetic model of activated zeolite adsorption Cd(II) (a), and quasi-secondary kinetic model of activated zeolite adsorption Cd(II) (b), intraparticle diffusion kinetics model of activated zeolite adsorption Cd(II) (c), and thermodynamic fit of activated zeolite adsorption Cd(II) (d).

equilibrium adsorption amount ($q_{e,cal}$) calculated by the theoretical equation and the experimentally obtained adsorption amount (q_e = 158.50 µg/g, exp), their values in the quasi-second-order kinetic model were more similar. In conclusion, the pseudo-second-order kinetic adsorption mechanism played a major role in the adsorption process of activated zeolite for Cd(II). The results were consistent with the kinetic model of zeolite powder adsorption of Cd(II) [37]. It can be seen from Fig. 4c that after the linear fitting of the internal diffusion dynamic model, the straight line did not pass through the origin. Therefore, it can be inferred that the internal diffusion of particles was not the only adsorption rate control step in the adsorption process of activated zeolite for Cd(II). Overall, the adsorption process of Cd(II) on activated zeolite may be controlled by surface active site adsorption and internal diffusion adsorption.

3.3.3. Thermodynamic analysis of adsorption

The adsorption experimental data in the different temperatures were analyzed, as shown in Fig. 4d. In the experiment, a linear fit was performed by $\ln K_c$ to $1/T$, and the equation $\ln K_c = -6090.7 (1/T) + 23.231$ was obtained, and the

Table 1
Thermodynamic fitting parameters of activated zeolite adsorption Cd(II).

T (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol·K)
298.15	–7.36		
303.15	–8.34		
308.15	–8.51		
313.15	–8.93	50.64	0.19
318.15	–14.18		
338.15	–15.13		

relevant thermodynamic values in Table 1 were obtained through the fitting curves. As seen from the data in Table 1, ΔG was all negative, which was less than zero, so the adsorption process was spontaneous. At the same time, the absolute values of ΔG increased with the temperature, indicating that an increasing temperature was conducive to the adsorption reaction. According to the literature, the adsorption process of ΔG between –20 and 0 kJ/mol is physical adsorption, while ΔG between – 400 and – 80 kJ/mol is chemical adsorption

Table 2
Comparison between the adsorption capacity of different adsorption materials

Adsorbent	C_0	Adsorption capacity	References
5A zeolite	20 mg/L	176.367 mg/g	[41]
Struvite zeolite	50 mg/L	249.35 mg/g	[42]
Artificial zeolite	29.5 µg/L	14.4 µg/g	[43]
Montmorillonite-chitosan	96 mg/L	20.61 mg/g	[44]
Polyaspartate-montmorillonite	30 mg/L	67.57 mg/g	[45]
Activated zeolite	100 µg/L	149.25 µg/g	This paper

process [38]. In Table 1, ΔG value was calculated according to the thermodynamic experimental data –7.36 kJ/mol (298 K), –8.34 kJ/mol (303 K), –8.51 kJ/mol (308 K), –8.93 kJ/mol (313 K), – 14.18 kJ/mol (318 K), –15.13 kJ/mol (338 K), Therefore, the adsorption of Cd(II) by activated zeolite belonged to physical adsorption. In the adsorption process, the absolute values of the adsorption heat caused by various adsorption forces were~10 kJ/mol for van der Waals force, 5 kJ/mol for hydrophobic interaction force, 2~40 kJ/mol for hydrogen bond interaction force, and greater than 60 kJ/mol for chemisorption interaction force [39,40]. The thermodynamic enthalpy (ΔH = 50.64 kJ/mol) obtained from the experiment indicated that the adsorption of activated zeolite on Cd(II) had chemical adsorption characteristics. In addition, ΔH was positive, indicating that when activated zeolite adsorbs Cd(II), the increase of temperature was conducive to the adsorption process. The adsorption reaction was an endothermic process. The entropy value ΔS was 0.19 kJ/mol K and positive, indicating that the entropy value of activated zeolite increased in the adsorption process of Cd(II) and the adsorption process of activated zeolite on Cd(II) was a process that increased the chaos of the solution system.

3.3.4. Comparison between adsorption performance of different adsorbents

Scholars have used various types of zeolites and different modification methods to adsorb Cd(II) in recent years, and the adsorption performance is compared in Table 2. From the comparison in Table 2, it can be seen that the activation prepared in this paper can adsorb lower concentrations of Cd(II) solution and has a high adsorption capacity, which indicates that activated zeolite is a good adsorbent material and has broad application prospects in micro-polluted water containing a low concentration of Cd(II).

4. Conclusions

- The natural zeolite was modified by high-temperature treatment combined with HCl-acidified to obtain activated zeolite. The adsorption performance of activated zeolite was improved. The activated zeolite was used as an adsorbent for Cd(II) in micro-polluted water and exhibited excellent adsorption properties.
- At 25°C, 6 g/L of adsorbent was used for 100 mL of a 100 µg/L Cd(II) solution, in which adsorption equilibrium was achieved after 180 min, with an adsorption rate of more than 90%.

- The adsorption mechanism of activated zeolite was found to be consistent with the quasi-secondary kinetic model. The isothermal adsorption model was accorded with the Langmuir model, and the maximum theoretical adsorption capacity of activated zeolite was up to 149.25 µg/g. The thermodynamic model study found that the Gibbs free energy ΔG of activated zeolite adsorption Cd(II) was less than 0, the thermodynamic enthalpy ΔH was greater than 0, and the thermodynamic entropy ΔS was greater than 0, indicating that the whole adsorption process was a spontaneous endothermic process with increased entropy. By studying the values of thermodynamic entropy change ΔG and thermodynamic enthalpy change ΔH, it was found that there were physical adsorption and chemical adsorption in the adsorption process. Moreover, the activated zeolite was quite stable under the conditions studied. Absorption of Cd(II) by activated zeolite is feasible and efficient.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contributions

Y.S: designed the research; S.T.Z, X.W and C.P.F, operation of specific experiments, Y.S and S.T.Z wrote and revised the paper; X.W and S.T.Z analyzed the data.

Consent to publish

All authors have read and agreed to the published version of the manuscript.

Availability of data and materials

We confirm that neither the entire paper nor any part of its content has been published or is being considered elsewhere. All text and figures were originally written by the authors and the language was proofed by Language Service.

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