



Study on removal and stabilization of heavy metals in contaminated sediment using modified clinoptilolite

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ABSTRACT

The effectiveness and mechanism of modified clinoptilolite in removing Cd²⁺ and Zn²⁺ from aqueous solutions and stabilizing Cd and Zn from contaminated sediment were investigated. It was found that the calcination-NaOH modified clinoptilolite with the particle sizes of 2–4 mm had the best effect on removing Cd²⁺ and Zn²⁺ from the aqueous solution. According to the Langmuir isotherm model, the maximum adsorption capacities of Cd²⁺ and Zn²⁺ would be 25.26 and 21.16 mg/g at 25°C, respectively. The Dubinin–Radushkevich adsorption model and the pseudo-second-order model indicated that the type of adsorption of Cd²⁺ and Zn²⁺ by modified clinoptilolite could be recognized as chemisorption. Toxicity characteristic leaching procedure showed that modified clinoptilolite could effectively reduce the leaching of Cd and Zn from the sediment. It was also observed that modified clinoptilolite could effectively lower the bioavailability and mobility of Cd and Zn in sediment using BCR sequential extraction. The results in this study showed that modified clinoptilolite could effectively remove Cd²⁺ and Zn²⁺ from water and stabilize Cd and Zn in the sediment.

Keywords: Modified clinoptilolite; Sediment; Stabilization; Heavy metal; Adsorption

1. Introduction

Industrial activities, such as metallurgy, mining, printing and dyeing, usually release heavy metals into the natural environment, including rivers and sediment [1]. The heavy metals in rivers and sediment adversely affect ecosystems and human health as non-degradable toxic pollutants [2]. For example, Cd accumulated in kidneys can cause urinary system diseases, and Cd in bones replaces calcium and softens the bones [3,4]. Uptake of excessive Zn can lead to nausea, vomiting, drowsiness, lethargy, anemia, and dizziness [5]. Therefore, the treatment of heavy metals in water and sediment has become one of the principal topics for environmental protection. Compared with other water

treatment technologies such as electrochemical degradation, membrane separation, ion exchange, and precipitation, adsorption is more simple, economical, and efficient [6]. Dairy manure-derived biochar was used for the effective removal of Cu²⁺, Zn²⁺ and Cd²⁺ from aqueous solutions [7]. Li et al. used the multi-carboxyl-functionalized silica gel to remove aqueous Cu²⁺, Cd²⁺, Ni²⁺, and Zn²⁺ ions [8]. Wang et al. [9] reported that graphene oxide synthesized via modified Hummers' method could effectively remove aqueous Cu²⁺, Cd²⁺, Ni²⁺, and Zn²⁺. Stabilization technology is widely used in the treatment of heavy metal-contaminated sediment, which minimizes adverse effects on ecosystems by reducing the mobility of heavy metals [10]. Zhang et al. [11] found that biochar could effectively reduce the bioavailability and

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leachability of heavy metal in soil. Li et al. [12] treated heavy metals-contaminated sediments by sulfate-reducing bacteria, and the results indicated lower leaching potential of Cu, Zn, Pb, and Cd. Wan et al. [13] found that nano-chlorapatite synthesized by sodium dodecyl sulfate could stabilize Pb in the sediment.

Zeolite is widely used in chemical and environmental fields as sorbent [14], which is a porous mineral composed of aluminosilicate, exchangeable cations, and zeolitic water [15]. Zeolite has four-connected tetrahedral frameworks which consist of silicon-oxygen and aluminum-oxygen tetrahedrons [16], with the silicon and aluminum atoms situated at the center and connected to the four oxygen atoms around them through oxygen bridge bonds [17]. The structure grants zeolite hydrothermal stability to avoid destroying when desorption or adsorption of crystalline water [18]. The specific surface of zeolite is large to adsorb molecules smaller than the pore size [19]. Because zeolite has negatively charged lattices to adsorb cations in the surrounding environment, it is commonly used to remove aqueous pollutants [20]. Clinoptilolite is the most abundant natural zeolite with an open reticular structure, which allows the access of tiny particles in the surrounding environment into the internal structure [21]. While, there are few studies using clinoptilolite to stabilize heavy metals in sediment.

The aim of this work was to investigate the adsorption characteristics of aqueous Cd^{2+} and Zn^{2+} by the modified clinoptilolite. The clinoptilolite was calcined at different temperatures and steps, then modified by NaOH, NaCl, LaCl_3 , ZrOCl_2 , and $\text{Ce}(\text{NO}_3)_3$. Furthermore, the stabilization on Cd- and Zn-contaminated sediment by modified clinoptilolite was also studied. The BET specific surface area, Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD) were used to characterize the modified clinoptilolite, and the adsorption mechanism was analyzed. Toxicity characteristic leaching procedure (TCLP) and sequential extraction BCR procedure were used to evaluate the stabilization effect on heavy metals-contaminated sediment.

2. Materials and methods

2.1. Materials

The natural clinoptilolite was purchased from Jinan (Shandong Province, China). The heavy metal-contaminated sediment used in the experiment was collected from Xiaofu River in Zibo (Shandong province, China), where the upper 0–20 cm sediment samples in depth were randomly collected from the river, saved in sealable bags, and then transported to the laboratory. After air drying and grinding, all the samples were screened through a 100-mesh sieve for future use. The properties of the sediment are shown in Table 1.

2.2. Screening of modifiers and particle size

Natural clinoptilolite was washed with deionized water and dried, then divided into the following four particle ranges in diameter: 0.25–0.45 mm, 0.5–1.0 mm, 1.0–2.0 mm, and 2.0–4.0 mm. NaOH, NaCl, LaCl_3 , ZrOCl_2 , and $\text{Ce}(\text{NO}_3)_3$ were used to modify natural clinoptilolite in different diameters.

Table 1
Properties of the contaminated sediment in Xiaofu River

pH	8.38
TP (mg/kg)	1.95
Cu (mg/kg)	335.70
Zn (mg/kg)	517.24
Cd (mg/kg)	4.35
Organic (%)	13.50

HCl, NaOH, or NaCl as modifier: 15.0 g of natural clinoptilolite was put into a conical flask containing 250 mL of HCl, NaOH, or NaCl solution at a concentration of 2 mol/L. Then, the conical flask was shaken in a water bath at 95°C for 3 h. The liquid supernatant was decanted and the treated clinoptilolite was washed with deionized water for several times and then dried in a muffle furnace at 105°C for 2 h [22].

LaCl_3 , ZrOCl_2 , or $\text{Ce}(\text{NO}_3)_3$ as modifier: 15.0 g of natural clinoptilolite was put into a conical flask containing 250 mL of LaCl_3 , ZrOCl_2 , or $\text{Ce}(\text{NO}_3)_3$ solution at a concentration of 2 mol/L, separately. The conical flask was stirred for 3 h with a magnetic stirrer, and the pH was adjusted to 10 with 2.0 mol/L NaOH solution. The liquid supernatant was decanted and the treated clinoptilolite was washed with deionized water for several times and then dried in a muffle furnace at 105°C for 2 h.

2.3. Calcinating of the natural clinoptilolite

Based on the screening of modifiers and clinoptilolite particle size, two processes were used to investigate the adsorption effect of the modified clinoptilolite. One was calcinating the clinoptilolite before the modification mentioned above; the other one was calcinating the clinoptilolite after the modification mentioned above. For the calcination process, five 10 g of clinoptilolite samples were treated in a muffle furnace and calcined at 200°C, 300°C, 400°C, 500°C, and 600°C for 2 h, respectively.

All the modified clinoptilolite experiments were performed by a batch method. The modified clinoptilolite was put into a conical flask with the solid/liquid ratio of 1.0 g clinoptilolite/100 mL of Cd^{2+} or Zn^{2+} solution and sealed. The flask was shaken for 12 h in an incubator shaker at isothermal condition (25°C) at a constant speed of 120 rpm until equilibrium was reached. Thereafter, the treated solution was centrifuged for 15 min at a speed of 3,000 rpm. The supernatant was subjected to filtration using a 0.45 μm filter. Then, the Cd^{2+} or Zn^{2+} concentration was measured by the atomic absorption spectrophotometer (AAS, TAS-990, Beijing Puxi Company, China). Based on the test results, the optimized modifying process and particle sizes for removing Cd^{2+} and Zn^{2+} from the aquatic solutions by clinoptilolite could be determined.

2.4. Adsorption isotherms

At 25°C, 1.0 g of the screened modified clinoptilolite was put into 100 mL Cd^{2+} or Zn^{2+} solution to make a series

of clinoptilolite concentrations of 10, 20, 40, 80, 100, 150, 200, 300, 400 mg/L, respectively. The mixture was shaken at 120 rpm continuously for 12 h. The remaining Cd^{2+} or Zn^{2+} was measured by AAS. Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm equations were used to fit and analyze the experimental data.

The Langmuir equation is an adsorption isotherm that can be utilized in monolayer adsorption processes [23]. It assumes that the adsorption positions are evenly distributed on the surface of the solid. The Langmuir adsorption isotherm can be expressed as Eq. (1):

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{(bq_{\max})} \quad (1)$$

where C_e is the concentration of Cd^{2+} or Zn^{2+} in solution (mg/L), q_e is the adsorption capacity (mg/g), q_{\max} is the theoretical maximum adsorption amount (mg/g), and b is the Langmuir adsorption constant.

Freundlich isotherm model is an empirical model and it assumes the existence of heterogeneous adsorption centers on the surface of the adsorbent. The adsorption isotherm equation can be expressed as Eq. (2) [24].

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

where K_F is the Freundlich reaction constant, which is related to adsorption interaction and adsorption amount, and the constant n reflects the intensity of adsorption.

Temkin isotherm model contains a factor relating to the adsorbent–adsorbate interaction. This model assumes that the adsorption heat of all molecules in the adsorbed layer decreases linearly with the increase of the coverage and the binding energy is uniformly distributed [25]. Temkin adsorption isotherm is expressed as Eq. (3) [23]:

$$q_e = B \ln K_i + B \ln C_e \quad (3)$$

where $B = RT/b$, K_i is the equilibrium binding constant (L/mg) related to maximum binding energy, and B is related to the heat of adsorption.

Dubinin–Radushkevich isotherm model does not hypothesize a homogeneous surface or constant adsorption potential [23]. It is usually used to determine whether the adsorption process is chemisorption or physisorption [26]. The Dubinin–Radushkevich adsorption isotherm can be expressed as Eq. (4):

$$\ln q_e = \ln q_s - K\varepsilon^2 \quad (4)$$

where q_e is the equilibrium concentration of Cd^{2+} and Zn^{2+} on adsorbents (mol/g), q_s is the adsorption capacity (mol/g), K is the isotherm constant, and ε is the Polanyi potential, which can be calculated as Eq. (5):

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_0} \right) \quad (5)$$

where R is the gas constant (8.314 J/(mol K)), T is the absolute temperature (K), and C_e is the equilibrium concentration of Cd^{2+} and Zn^{2+} in solution (mol/L). The mean free energy of sorption can be computed using Eq. (6):

$$E = \frac{1}{\sqrt{2K}} \quad (6)$$

The adsorption process is chemisorption if the value of E is between 8 and 16 kJ/mol. When the adsorption energy is lower than 8 kJ/mol, the adsorption can be considered as physical adsorption [27].

2.5. Adsorption kinetics

At 25°C, 1.0 g of modified clinoptilolite with the best adsorption effect on Cd^{2+} and Zn^{2+} was dispersed into 100 mL water containing 100 mg/L of Cd^{2+} or Zn^{2+} , followed by shaking at 120 rpm. Partial samples were taken out after 0.25, 0.5, 1, 2, 4, 6, 8, 10, and 12 h, respectively, and the remaining concentration of Cd^{2+} or Zn^{2+} was measured. Pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were used to fit and analyze the experimental data.

The commonly used adsorption kinetic models include pseudo-first-order and pseudo-second-order kinetic models [28]. The pseudo-first-order and pseudo-second-order dynamic equation can be expressed as Eqs. (7) and (8), respectively.

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2) + \frac{t}{q_e}} \quad (8)$$

where q_e is the adsorption capacity (mg/g) of the modified clinoptilolite at the equilibrium of adsorption, q_t is the adsorption capacity (mg/g) of the modified clinoptilolite at time t , k_1 is the pseudo-first-order adsorption constant (h^{-1}), k_2 is the pseudo-second-order adsorption constant (h^{-1}), and t is adsorption time (h).

The intraparticle diffusion model is expressed as Eq. (9) [29]:

$$q_t = k_d t^{1/2} + C \quad (9)$$

where k_d ($\text{mg g}^{-1} \text{h}^{1/2}$) is the intraparticle diffusion rate constant and C is associated to the boundary layer thickness.

2.6. Regeneration of modified clinoptilolite

At 25°C, 1.0 g of the modified clinoptilolite was put into 100 mL Cd^{2+} or Zn^{2+} solution to make a concentration of 400 mg/L. The mixture was shaken at 120 rpm continuously for 12 h. The remaining Cd^{2+} and Zn^{2+} were measured by AAS. After the adsorption experiment, the heavy metal-loaded clinoptilolite was added to 100 mL of 0.1 M HCl solution

and stirred for 5 h. Then, the clinoptilolite was washed, dried, and used for another adsorption cycle. The adsorption–desorption cycles were repeated several times.

2.7. Selectivity of modified clinoptilolite

1.0 g modified clinoptilolite was added to 100 mL solution contained Cd^{2+} and Zn^{2+} , wherein the concentration of Cd^{2+} and Zn^{2+} was 400 mg/L, respectively. The mixture was shaken at 120 rpm continuously for 12 h. The remaining Cd^{2+} and Zn^{2+} were measured by AAS.

2.8. Stabilization of heavy metals in sediment

The screened modified clinoptilolite with the best adsorption effect on Cd^{2+} and Zn^{2+} was mixed with the sediment. The dosage percentage of clinoptilolite is 2.5%, 5%, 10%, and 15% of the sediment mass, respectively. The mixtures were stirred for 1 h, and added with deionized water every day to keep the sediment moisture of 70% in the next 1 week. Then, the mixture was kept in a cool place to dry naturally. The tests of BCR and TCLP were carried out for the sediment before and after the stabilization test [30].

2.9. Characterization of clinoptilolite

The characteristics of natural clinoptilolite and the modified clinoptilolite with the best adsorption effect on Cd^{2+} and Zn^{2+} were analyzed. Chemical compositions of clinoptilolite were analyzed with an X-ray fluorescence spectrometer (XRF, AXIOS, PANalytical, the Netherlands) and an inductively coupled plasma optical emission spectrometer (ICP-OES, iCAP 7600, Thermo Fisher, United States). Surface morphology was observed by scanning electron microscopy (SEM, SUPRA55, Carl Zeiss AG, Germany). The specific surface area and pore size distribution were measured on a Brunauer–Emmett–Teller surface area analyzer (BET, V-Sorb 2800P, Gold APP, China). The crystal structure and mineral composition were determined by X-ray diffractometer (D8 Advance, Bruker, Germany). FTIR spectra of clinoptilolite were investigated by an FTIR.

3. Results and discussion

3.1. Screening of modifiers and particle size of clinoptilolite

The influence of different modifiers and particle sizes on the adsorption of Cd^{2+} and Zn^{2+} by clinoptilolite is shown in Fig. 1. The adsorption capacity of Cd^{2+} and Zn^{2+} by clinoptilolite was not significantly improved after the modification by NaCl, ZrOCl_2 , and LaCl_3 and $\text{Ce}(\text{NO}_3)_3$, except for NaOH. The particle size had an effect on the removal efficiency of Cd^{2+} and Zn^{2+} , and the removals by the clinoptilolite with particle sizes of 2.0–4.0 mm are higher than those less than 2.0 mm. It is observed that the modified clinoptilolite by NaOH with particle sizes of 2.0–4.0 mm removed the most Cd^{2+} and Zn^{2+} , 90.1% and 74.5%, respectively. The reason probably is that NaOH caused the partial exchange between Na^+ and larger particles on the surface of clinoptilolite [22]. Therefore, a part of Na^+ in the clinoptilolite existed as exchangeable cations to exchange with the metal cations.

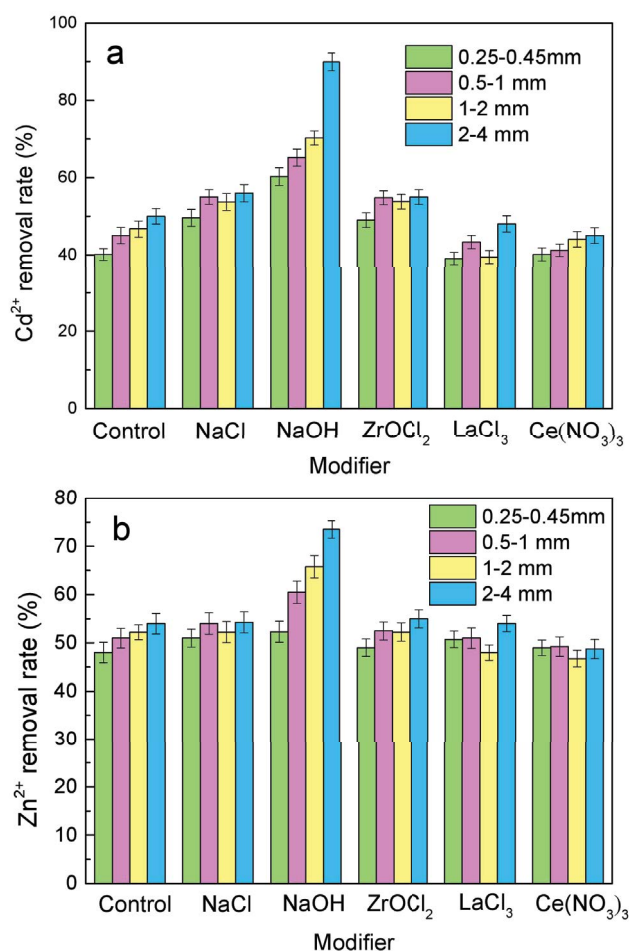


Fig. 1. Cd^{2+} and Zn^{2+} removal under different modifiers and particle sizes of clinoptilolite. (a) Cd^{2+} ; (b) Zn^{2+} .

3.2. Influence of calcination temperature of clinoptilolite on Cd^{2+} and Zn^{2+} adsorption

The influence of calcination temperature and modification on the adsorption effect of Cd^{2+} and Zn^{2+} by clinoptilolite is shown in Fig. 2. The screened modifier of NaOH and the clinoptilolite particle size of 2.0–4.0 mm were used in the tests. In the modified scheme of calcination-NaOH, the removal rate of Cd^{2+} and Zn^{2+} increased with rising temperature and reached the highest of 95% and 79% at 600°C, respectively. This phenomenon can be attributed to the evaporation of the attaching water in the internal channel of clinoptilolite, which increased the internal space and hence enhanced the adsorption capacity of clinoptilolite [31]. The best modification scheme was calcination-NaOH with the calcination temperature of 600°C.

3.3. Adsorption isotherm

The experimental data were fitted by various adsorption isotherms, such as Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich models. The fitting curves are shown in Fig. 3, and the fitted parameters are presented in Table 2. The R^2 values of Langmuir adsorption model ($R^2_{\text{Cd}} = 0.996$,

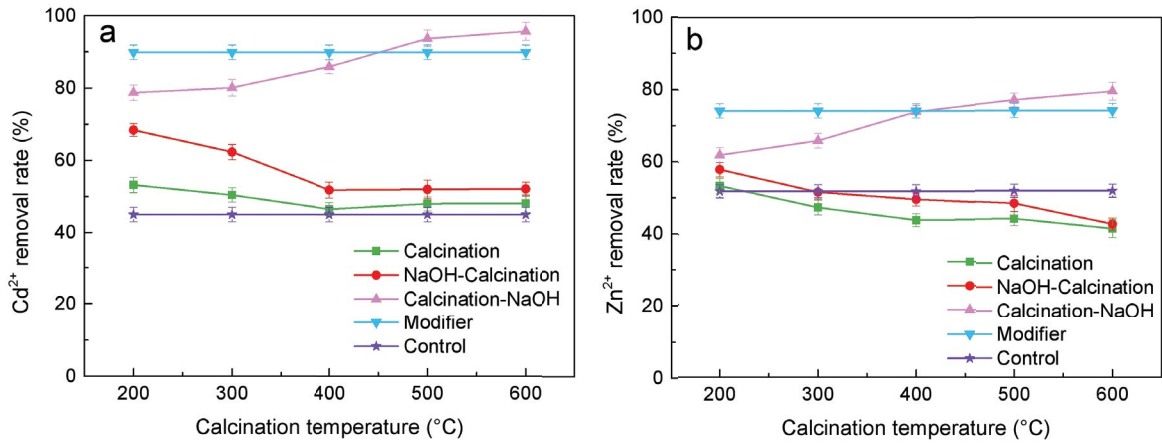


Fig. 2. Influence of calcination temperature and modification order on the adsorption effect of Cd²⁺ and Zn²⁺ by clinoptilolite. (a) Cd²⁺; (b) Zn²⁺.

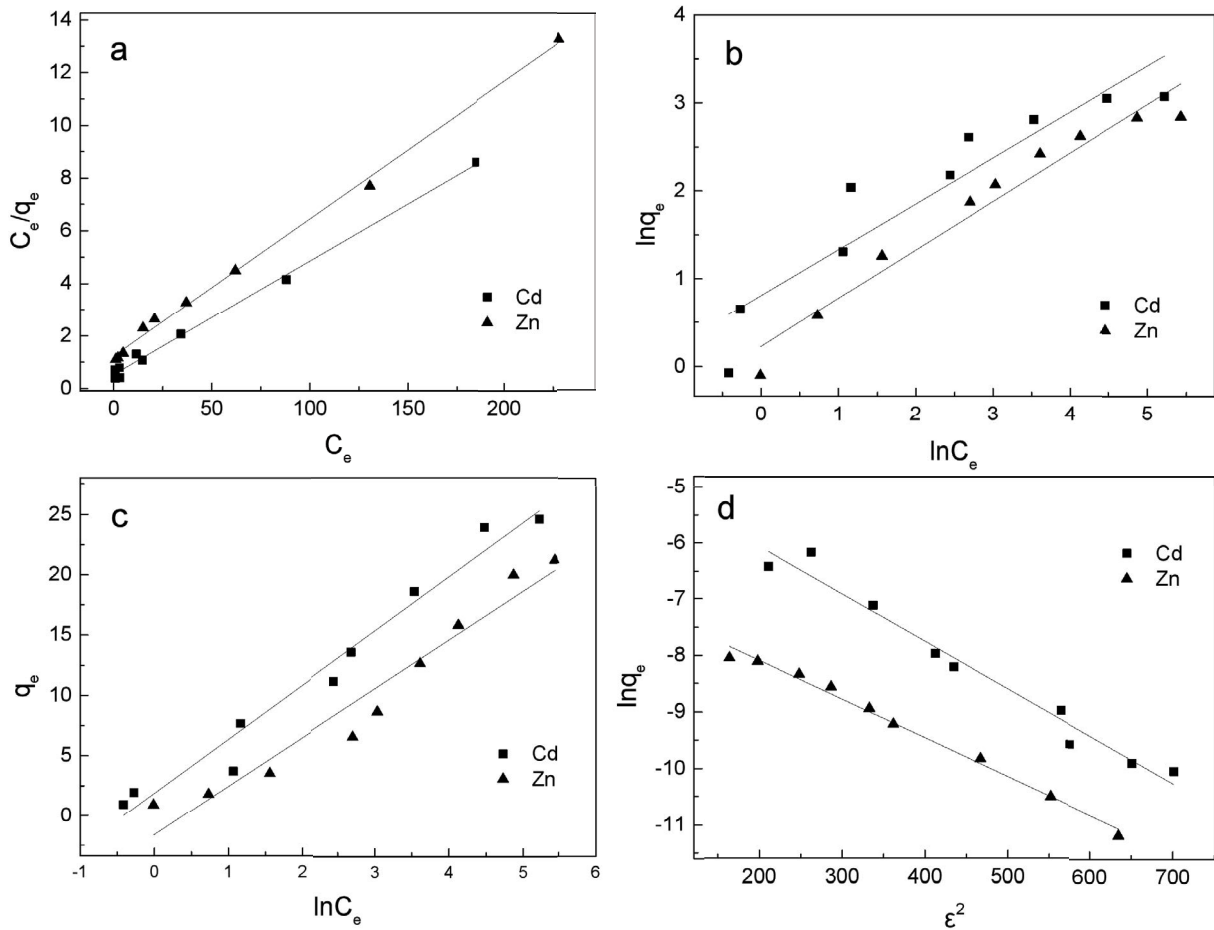


Fig. 3. Linearized isotherms of Cd²⁺ and Zn²⁺ adsorption onto modified clinoptilolite. (a) Langmuir isotherm; (b) Freundlich isotherm; (c) Temkin isotherm; (d) Dubinin–Radushkevich isotherm.

$R_{Zn}^2 = 0.997$) are higher than the values of Freundlich, Temkin, and Dubinin–Radushkevich adsorption models. It indicates that the adsorption of Cd²⁺ and Zn²⁺ on the modified clinoptilolite surface was generally monolayer adsorption processes and adsorption sites distribute uniformly

[32]. Based on the Langmuir adsorption isotherm equation, the maximum adsorption capacity of Cd²⁺ and Zn²⁺ was 25.26 and 22.16 mg/g at 25°C, respectively. The adsorption capacities of modified clinoptilolite for Cd²⁺ and Zn²⁺ from aqueous solutions are compared with other clinoptilolite in

Table 2

Parameters for adsorption of Cd²⁺ and Zn²⁺ based on Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isothermal equations

Adsorption isotherm model	Parameter	Cd ²⁺	Zn ²⁺
Langmuir isotherm	q_{\max} (mg/g)	25.256	22.157
	B (L/mg)	0.086	0.996
	R^2	0.040	0.997
Freundlich isotherm	K_F	2.246	1.256
	$1/n$	0.521	0.874
	R^2	0.551	0.954
Temkin isotherm	B	4.486	4.039
	K_t	1.513	0.674
	R^2	0.966	0.939
Dubinin–Radushkevich isotherm	q_s (mol/g)	0.2576×10^{-3}	0.3538×10^{-3}
	E	8.103	8.512
	R^2	0.966	0.973

Table 3 [33–40]. It can be seen that the maximum adsorption capacity of modified clinoptilolite in this experiment was higher than that of other clinoptilolite. The parameter n of Freundlich adsorption model reflects the degree of deviation from the linearity of adsorption. If the value of $n = 1$, the adsorption follows a linear function; for values $n < 1$, the adsorption is unfavorable, and if $n > 1$, the adsorption is favored [41]. In our study, the values of n were higher than 1. Therefore, the adsorption was favored. It also implies that the adsorption affinity for Cd²⁺ and Zn²⁺ on clinoptilolite was high. In Dubinin–Radushkevich adsorption model, the magnitude of E was between 8 and 16 kJ/mol, which indicates the adsorption to be chemisorption [42]. According to the Temkin isotherm model, the binding energy on the surface of clinoptilolite was evenly distributed [36].

3.4. Adsorption kinetics

The pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were used to fit and analyze the experimental data. The fitting curves and parameters are presented in Figs. 4 and 5, and Table 4, respectively. It can be observed in Fig. 4 that the metal ions were rapidly combined at the adsorption sites on the surface of the clinoptilolite in the initial reaction. More than 50% of Cd²⁺ and Zn²⁺ were adsorbed from aqueous solutions in the first 2 h. As the reaction goes on, the adsorption capacity increased gradually and the adsorption rate reduced. The adsorption rate was equal to the desorption rate when the reaction reached the adsorption equilibrium. According to the fitting curve, the adsorption by modified clinoptilolite followed the pseudo-second-order model ($R_{\text{Cd}}^2 = 0.998$, $R_{\text{Zn}}^2 = 0.999$) rather than the pseudo-first-order model ($R_{\text{Cd}}^2 = 0.861$, $R_{\text{Zn}}^2 = 0.866$) or the intraparticle diffusion model ($R_{\text{Cd}}^2 = 0.900$, $R_{\text{Zn}}^2 = 0.837$). The formation of chemical bonds is the main factor affecting the pseudo-second-order kinetic adsorption, indicating that the process was dominated by chemical adsorption [43].

Table 3

Maximum adsorption capacity of modified clinoptilolite and other clinoptilolite

Adsorbents	Adsorption capacity (mg/g)		Ref.
	Cd ²⁺	Zn ²⁺	
Bentonite-zeolite	–	12.72	[34]
Natural zeolite	10.30	9.00	[35]
Natural clinoptilolite	10.08	–	[36]
Zeolite	20.58	–	[37]
Acid-clinoptilolite	0.36	0.18	[38]
Na-clinoptilolite	14.05	8.17	[39]
Natural clinoptilolite	2.10	2.70	[40]
Natural zeolite	–	1.16	[41]
Modified clinoptilolite	25.26	22.16	This study

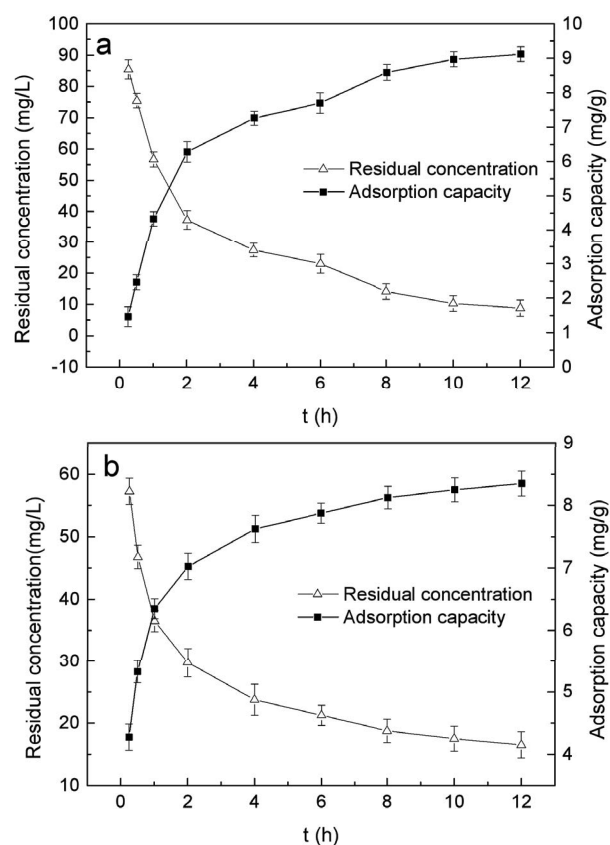


Fig. 4. Kinetic test of Cd²⁺ and Zn²⁺ adsorption onto modified clinoptilolite. (a) Cd²⁺; (b) Zn²⁺.

3.5. Stabilization of heavy metals in sediment by modified clinoptilolite

3.5.1. TCLP

The TCLP can evaluate the leachability of heavy metals in the sediment in the acid condition, which estimates the stabilization effect of heavy metals in the dredged sediment.

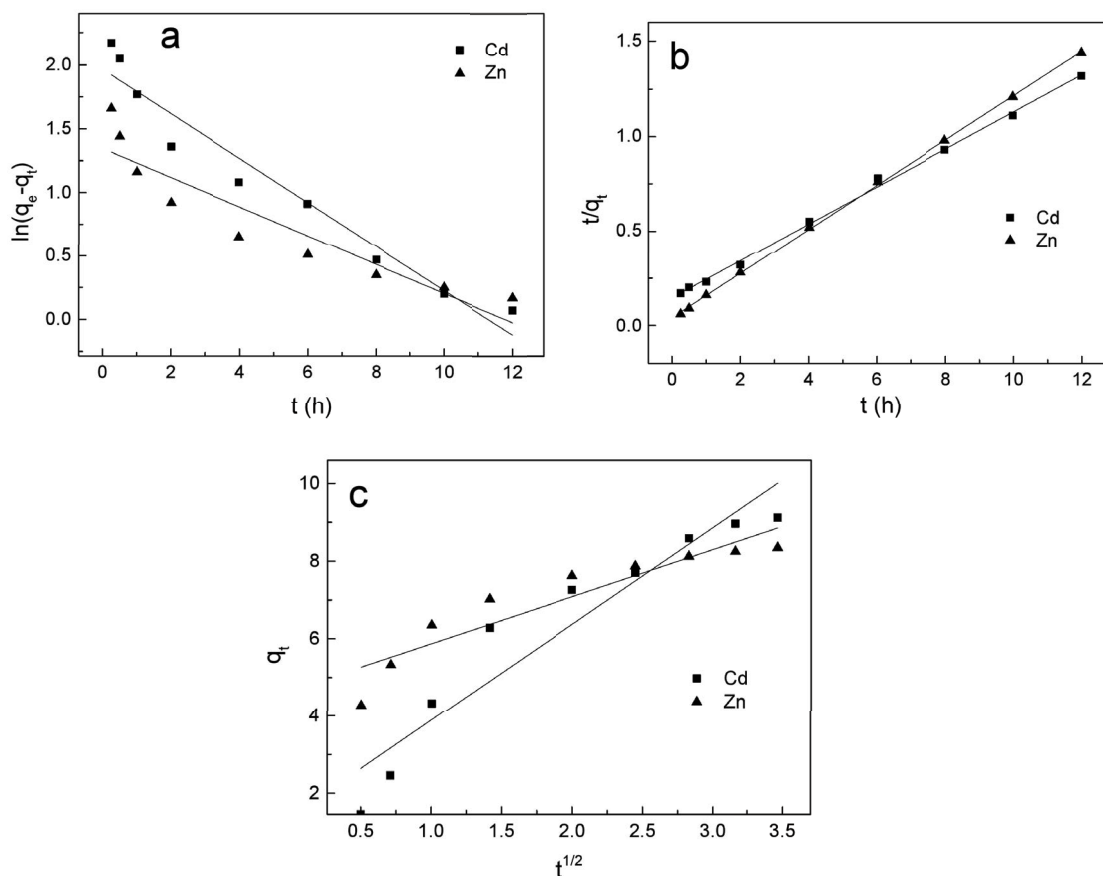


Fig. 5. Adsorption kinetics plots for Cd^{2+} and Zn^{2+} adsorption onto modified clinoptilolite. (a) pseudo-first-order model; (b) pseudo-second-order model; (c) intraparticle diffusion model.

Table 4

Parameters for adsorption of Cd^{2+} and Zn^{2+} based on pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetic equations

Adsorption kinetic model	Parameter	Cd^{2+}	Zn^{2+}
Pseudo-first-order kinetics	q_e (mg/g)	7.128	3.838
	k_1	0.173	0.114
	R^2	0.861	0.866
Pseudo-second-order kinetics	q_e (mg/g)	10.193	8.851
	k_2	0.066	0.320
	R^2	0.998	0.999
Intraparticle diffusion kinetics	k_d	2.490	1.212
	C	1.395	4.662
	R^2	0.900	0.837

As shown in Fig. 6, the leaching amounts of Cd^{2+} and Zn^{2+} in the control sediment (without modified clinoptilolite) were 0.12 and 25.00 mg/kg, respectively. It can be seen that the leaching amounts of Cd and Zn decreased with the increase of modified clinoptilolite when the dosage was less than 10%. When the dosage was more than 10%, the leaching amounts did not change significantly. When the dosage was 10%, the leaching amount of Cd^{2+} and Zn^{2+} was 0.05 and

11.56 mg/kg, respectively. The optimum dosage of modified clinoptilolite was found to be 10% in the stabilization of Cd and Zn in the sediment.

3.5.2. BCR continuous extraction test

Based on BCR extraction, the heavy metal species are divided into four forms: the acid extractable fraction, the reducible fraction, the oxidizable fraction, and the residual fraction according to the decrease of mobility and bioavailability [44]. Heavy metals with high mobility and bioavailability can cause serious negative impact on the environment [45].

The change of heavy metals fractionation after the stabilization test is shown in Fig. 7.

In the control group, about 59% of Cd existed in the extractable and reducible fraction with higher toxicity. After the stabilization of the modified clinoptilolite, this ratio was lower than 40%. The oxidizable fraction decreased from 21.7% to 9.6% and the residual fraction increased from 17.0% to 63.5%. Most Zn in the control group was found in the exchangeable fraction (47.1%), which meant that it had high bioavailability and mobility. After the stabilization of the modified clinoptilolite, the oxidizable Zn decreased from 47.1% to 28.6% and the residual Zn increased from 20.3% to 35.5%. It can be seen that the acid extractable and reducible

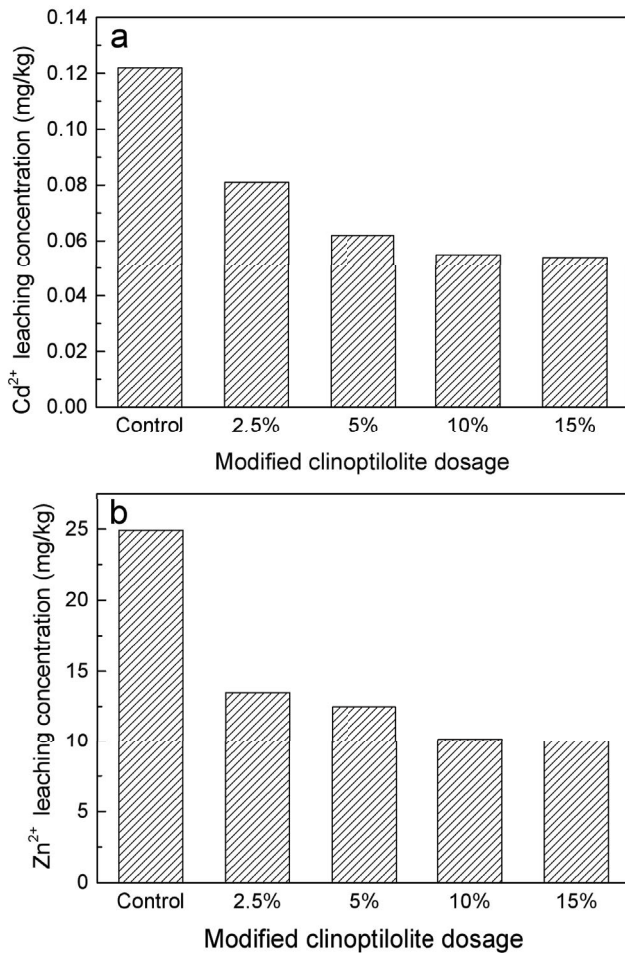


Fig. 6. Leaching amount of Cd and Zn in sediment with different dosage of modified clinoptilolite. (a) Cd²⁺; (b) Zn²⁺.

fractions of Cd and Zn in the sediment were converted into more stable oxidizable and residual fraction by the stabilization treatment. Therefore, the ecological toxicity of Cd and Zn contaminated sediment could be reduced through the amendments of modified clinoptilolite. The optimum dosage of modified clinoptilolite was 10%.

3.6. Regeneration of modified clinoptilolite

The adsorption capacity of regenerated clinoptilolite is shown in Fig. 8. It can be seen that the adsorption capacity did not decrease significantly after the first four recycles; the adsorption capacity of modified clinoptilolite for Cd²⁺ and Zn²⁺ decreased by 10.6% and 14.2%, respectively. This phenomenon indicates that the modified clinoptilolite was an economical material which can be reused at least four times by regeneration. After the fifth cycle, the adsorption capacity of modified clinoptilolite for Cd²⁺ and Zn²⁺ decreased by 38.1% and 42.3%, respectively. It is estimated that the structure of the modified clinoptilolite was damaged or inactivated, and the adsorption and removal ability of heavy metal ions was drastically reduced.

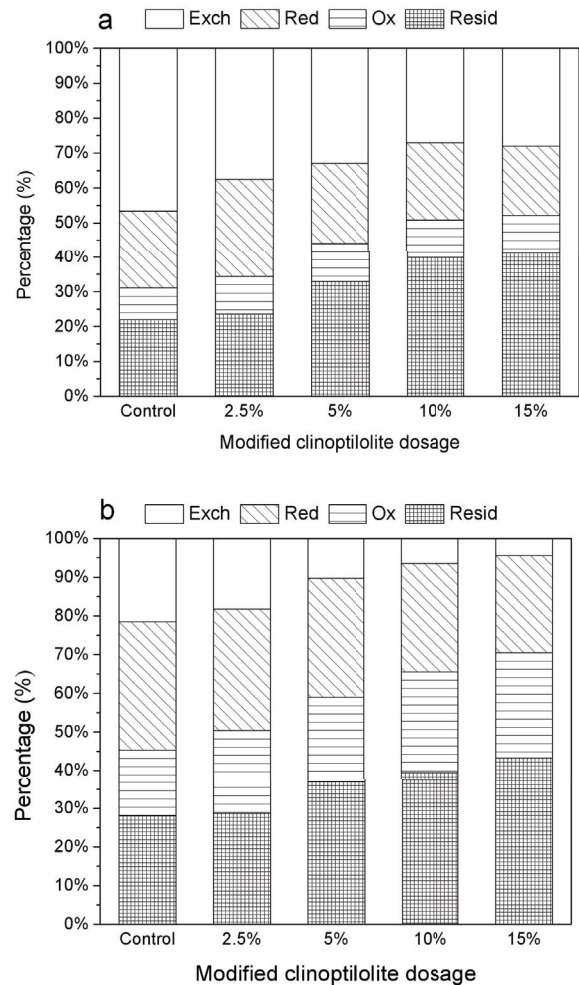


Fig. 7. Metal fractionation in contaminated sediment (a) Cd, (b) Zn. (Exch: acid extractable fraction, Red: reducible fraction, Ox: oxidizable fraction, Resid: residual fraction).

3.7. Selectivity of modified clinoptilolite

Table 5 shows that the adsorption capacity for Cd²⁺ and Zn²⁺ from multi-component solution is lower than the corresponding value from single-component. In the single-component solution, the adsorption capacity for Cd²⁺ and Zn²⁺ was 25.26 and 22.16 mg g⁻¹, respectively. In the multi-component solution, the adsorption capacity for Cd²⁺ and Zn²⁺ was 16.12 and 6.35 mg/g, respectively. The data indicate that the adsorption sites of clinoptilolite were limited, and Cd²⁺ was more competitive than Zn²⁺, which may be affected by radius of hydrated ion and hydration energy [35].

3.8. Characterization of the modified clinoptilolite

3.8.1. Main components

The main components of natural clinoptilolite before and after modification are shown in Table 6. The data show that the content of Na⁺ was significantly increased, indicating a part of Ca²⁺, Fe²⁺, K⁺, and Mg²⁺ in the pore channels of clinoptilolite had been replaced by Na⁺. It was been

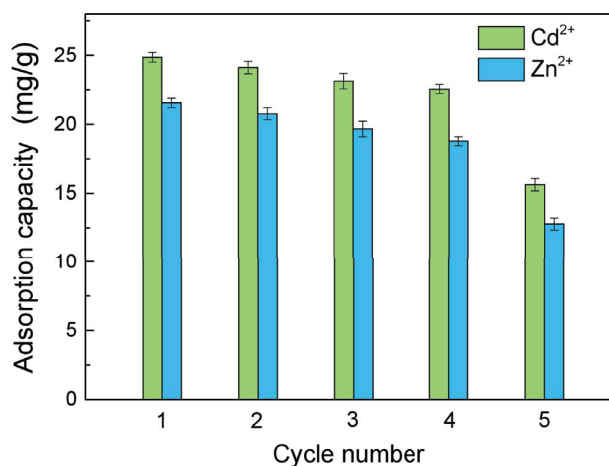


Fig. 8. Adsorption capacity of the regenerated modified clinoptilolite.

Table 5

Adsorption capacity of modified clinoptilolite for Cd²⁺ and Zn²⁺ from single-component and multi-component solution

	Single-component solution		Multi-component solution	
	Cd ²⁺	Zn ²⁺	Cd ²⁺	Zn ²⁺
Adsorption capacity (mg/g)	25.26	22.16	16.12	6.35

Table 6

Main components of natural and modified clinoptilolite

Components (%)	Natural clinoptilolite	Modified clinoptilolite
SiO ₂	76.01	75.86
Al ₂ O ₃	13.25	13.50
Na ₂ O	3.20	5.31
CaO	2.58	2.03
Fe ₂ O ₃	2.02	1.53
K ₂ O	1.96	1.11
MgO	0.98	0.66

studied that Ca²⁺, Fe²⁺, K⁺, and Mg²⁺ could combine with the clinoptilolite stably, and not easily be exchanged by other heavy metal cations [46]. Na⁺ had a better mobility than other cations, making modified clinoptilolite more likely to exchange with heavy metal cations [47–49].

3.8.2. XRD analysis

The XRD spectra of natural clinoptilolite before and after modification are shown in Fig. 9. The SiO₂ diffraction peaks of natural clinoptilolite show that the SiO₂ had different crystal forms, of which 81% was quartz [50]. The spectra of the modified clinoptilolite showed similar pattern

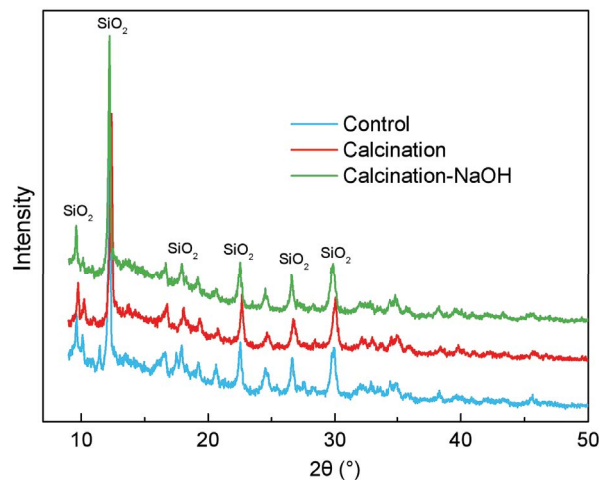


Fig. 9. XRD image of the natural and modified clinoptilolite (particle sizes for both of the clinoptilolite are 2.0–4.0 μm).

to those of the natural clinoptilolite, indicating that modification did not alter the original crystal structure of the clinoptilolite.

3.8.3. Pore size and surface area

The specific surface area and pore size of the clinoptilolite before and after the modification were analyzed. The results are shown in Fig. 10 and Table 7. The proportion of larger holes increased obviously after modification. The holes with radius less than 2 nm disappeared, and the proportion of the pores with radius between 5 and 20 nm was also greatly increased. The specific surface area and total porous volume of clinoptilolite increased significantly after calcination due to the effect of the evaporation of water molecules and the volatilization of organic matter in the pores [51]. The average pore size of the natural clinoptilolite increased from 15.90 to 24.54 nm after calcination and NaOH modification. The specific surface area, total porous

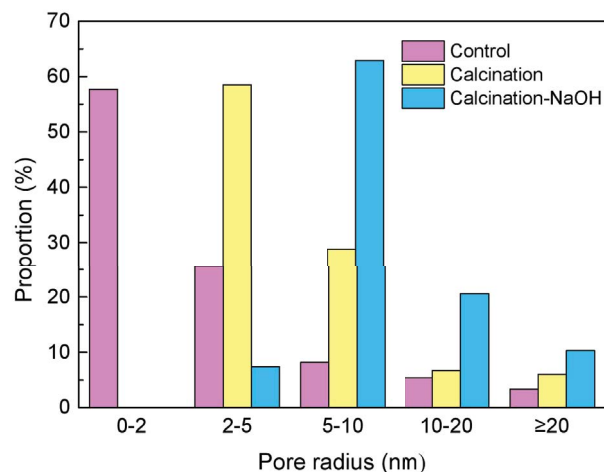


Fig. 10. Pore size distribution of clinoptilolite.

Table 7
Specific surface area, total porous volume and average pore size of clinoptilolite

	Specific surface area (m ² /g)	Total porous volume (cm ³ /g)	Average pore size(nm)
Natural clinoptilolite	2.3951	0.0107	15.90
Natural clinoptilolite after calcination	3.2082	0.0154	20.62
Clinoptilolite modified by calcination-NaOH	3.2005	0.0152	24.54

volume, and average pore size were effectively improved by the modification, which could result from the substitution of Na⁺ for larger molecules in clinoptilolite. It was more conducive to the entry of heavy metal ions into the structure of clinoptilolite [52].

3.8.4. FTIR analysis

The FTIR spectra of clinoptilolite are shown in Fig. 11. According to the FTIR analysis before and after modification, it was found that strong absorption bands occurred in 1,030–1,100 cm⁻¹, which associated with the antisymmetric stretching vibration of Si–O–Si skeleton. The symmetric stretching vibration of Si–O or Al–O near 800 cm⁻¹ and the flexural vibration of Si–O or Al–O of 470–500 cm⁻¹ was caused by the internal vibration of silicon oxygen tetrahedrons or aluminum oxygen tetrahedrons [53]. It showed that the modification did not destroy the basic structure of the clinoptilolite. After modification, the O–H stretching vibration peaks at 3,621 and 3,694 cm⁻¹ were weakened, which probably indicated that some O–H bonds broke off and formed new chemical bonds with Na⁺. The bending vibration peak of Si–O or Al–O related to clinoptilolite binding water at 3,448 cm⁻¹ shifted to low wavelength, which may be due to the evaporation of water.

3.8.5. SEM analysis

The SEM image for the clinoptilolite (Fig. 12) shows the typical cubic structure of zeolite, which indicates that modification had not changed the basic structure of the clinoptilolite [54]. The inter-granular cavitation with clearly formed cavities evident on the grain surface of clinoptilolite was observed after calcination [55]. The pore size of the modified clinoptilolite increased, which was more conducive for the entry and adsorption of macromolecules. This is in accordance with the conclusions obtained from the above BET analysis [56].

3.9. Cost analysis

Zeolite is an effective, readily available, and low-cost adsorbent. In this study, a preliminary cost analysis of the adsorption of clinoptilolite on Cd²⁺ and Zn²⁺ was carried out according to the maximum sorption capacity and material price. Activated carbon is one of the most used adsorbents with maximum adsorption capacity for Cd²⁺ and Zn²⁺ from 9.43 to 11.72 mg/g [57,58]. The commercial price of activated carbon is about 1.20–2.00 \$/kg, and the adsorption cost for Cd²⁺ and Zn²⁺ on activated carbon is about 0.102–0.212 \$/g. Montmorillonite is a low-cost natural material

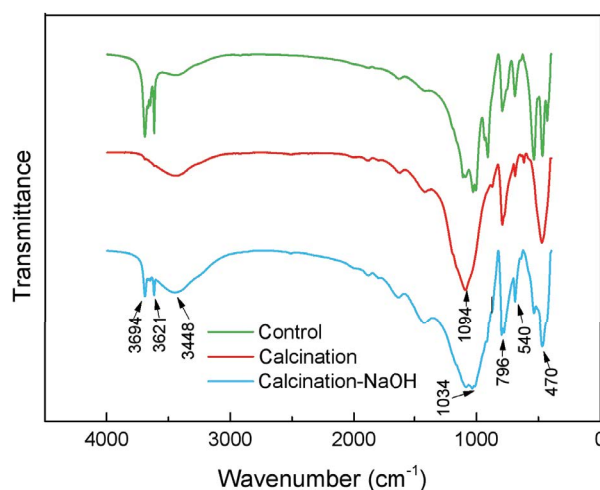


Fig. 11. FTIR spectra of clinoptilolite.

with a maximum adsorption capacity for Cd²⁺ and Zn²⁺ of 7.42–17.80 mg/g and adsorption cost of about 0.011–0.027 \$/g [59,60]. The maximum adsorption capacities of modified clinoptilolite for Cd²⁺ and Zn²⁺ in this study were 25.26 and 22.16 mg/g, respectively. The production cost of the modified clinoptilolite is about 0.15 \$/kg based on our study, resulting in the adsorption cost of 0.006 \$/g, which is much lower than activated carbon or montmorillonite. Therefore, modified clinoptilolite can be used as an inexpensive and effective adsorbent for the treatment of heavy metal contaminated wastewater.

The modified clinoptilolite can also be used in the solidification/stabilization of dredged heavy metal contaminated sediment. The treated sediment can be utilized as a fertilizer for plants growing on river banks [61]. When the amount of clinoptilolite additive is 10% of the dry weight of the sediment, the cost is about 15 \$ per ton of sediment, which is less than 40 \$ per ton of sediment of the chelator and humic acid mixture [62].

4. Conclusions

The natural clinoptilolite was modified by various methods. It was found that the calcination-NaOH modified clinoptilolite with the particle size of 2–4 mm had the best effect on the removal of Cd²⁺ and Zn²⁺ in the aqueous solution, and the optimum calcination temperature was 600°C. The adsorption process matched the Langmuir isotherm model and the pseudo-second-order model, indicating that the adsorption of Cd²⁺ and Zn²⁺ by clinoptilolite was monolayer adsorption and dominated by chemical reaction.

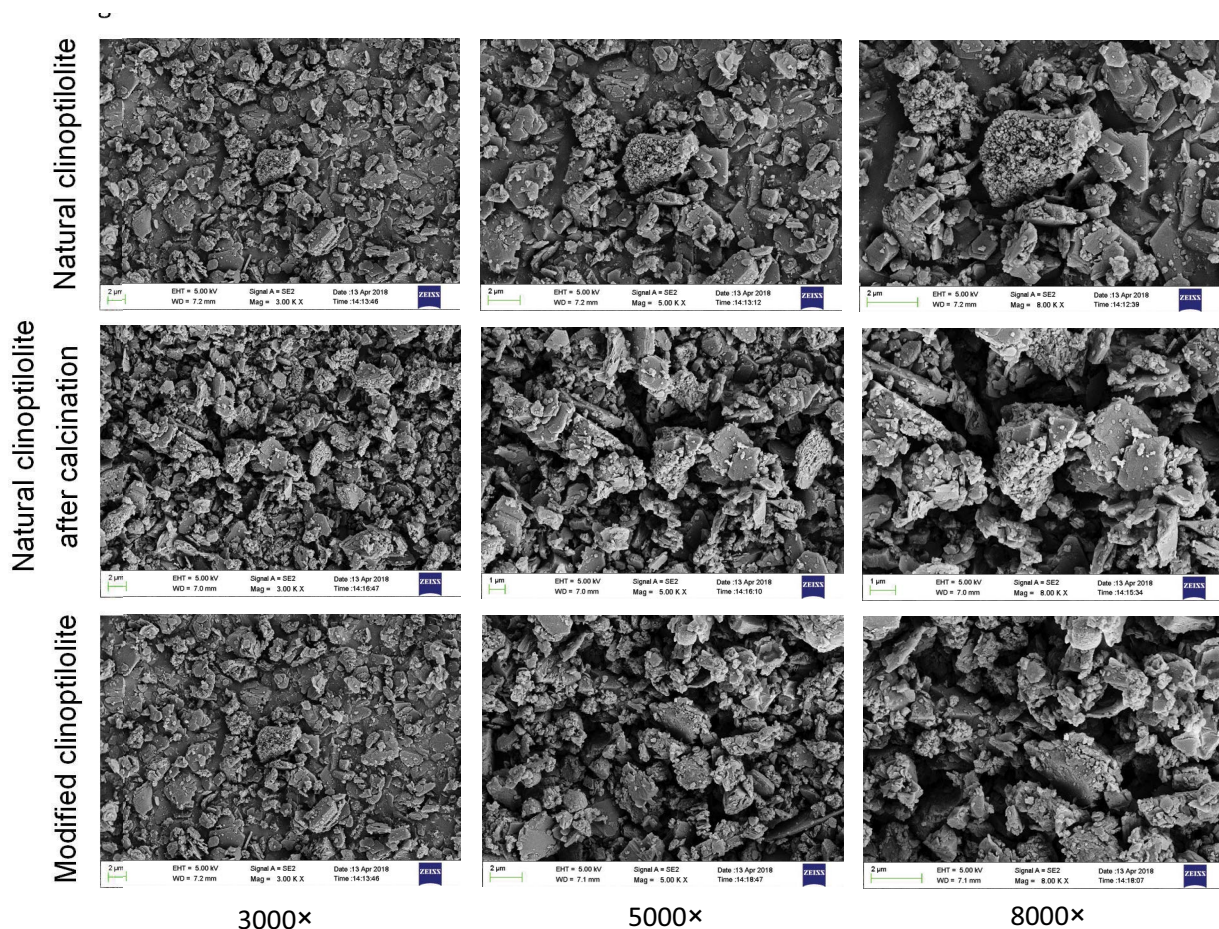


Fig. 12. SEM morphologies of the clinoptilolite.

The modified clinoptilolite was used to stabilize heavy metals in contaminated sediment, and the results showed that the leaching amount of Cd and Zn in the sediment decreased under acidic conditions. Parts of the acid extractable and reducible fraction of Cd and Zn in the sediment were converted into more stable oxidizable and residual fraction by the stabilization treatment using the modified clinoptilolite. The modified clinoptilolite was characterized by XRD, BET, FTIR, and SEM. It was found that the modification process did not destroy the basic framework of clinoptilolite. The calcination process resulted in the separation of bound water from the clinoptilolite structure. The specific surface area, total porous volume, and average pore size of the clinoptilolite were effectively improved by the modification. It was more conducive for the entry of heavy metal ions to the structure of clinoptilolite, resulting in better the adsorption effect. Therefore, modified clinoptilolite could be applied as an effective sorbent in the Cd and Zn removal from water or a stabilizer in the Cd- and Zn-contaminated sediment.

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