

Adsorption of oxytetracycline from aquaculture wastewater by modified zeolites: kinetics, isotherm, and thermodynamics

Xiaocai Yu*, Runqiang Yu, Bining Xue, Jiaqi Liao, Wanting Zhu, Siyao Tian

College of Ocean Technique and Environment department, Dalian Ocean University, Dalian 116000, China, emails: yuxiaocai321@126.com (X. Yu), 850212309@qq.com (R. Yu), 704092330@qq.com (B. Xue), 1073089762@qq.com (J. Liao), 837215775@qq.com (W. Zhu), 452550472@qq.com (S. Tian)

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ABSTRACT

In this study, lanthanum modified zeolite (La-Z) was used as an adsorbent to adsorb oxytetracycline (OTC) from aquaculture wastewater. La-Z was characterized by scanning electron microscopy, transmission electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction, Fourier transform infrared spectroscopy, and Brunauer–Emmett–Teller. The effects of modification concentration of lanthanum on zeolites (0–0.06 mol/L), the dosage of La-Z (0.02–0.12 g), initial concentration of OTC (5–30 mg/L), solution pH (5–10) and reaction time (10–60 min) on the adsorption of OTC by La-Z were investigated. Orthogonal experiments were used to find the optimal adsorption conditions. The kinetics were studied by a quasi-first-order model, quasi-second-order model, Weber–Morris, Ritchie-second-order model, and Boyd models, and the isotherms were analyzed by Langmuir and Freundlich models. When the modified concentration of lanthanum was 0.02 mol/L, the dosage of adsorbent was 0.1 g, the initial concentration of OTC was 5 mg/L, the adsorption time was 40 min, pH was 7, and the removal rate was 99.18%. The initial concentration of OTC has maximum influence on the adsorption process. The kinetic results have shown that there was a significant linear correlation between the experimental results and the quasi-second-order kinetic model. By the internal diffusion model, it is found that the La-Z adsorption rate was controlled both internal diffusion and external diffusion in common, which was a multi-step process. The adsorption isotherm conforms to the Langmuir model, and the maximum adsorption quantity was 36.38 mg/g. The thermodynamic showed that the adsorption process was an endothermic process in which entropy was increased making it a spontaneous process.

Keywords: Adsorption; Antibiotics pollutants; Aquaculture wastewater; Kinetics

1. Introduction

With the widespread use of antibiotics in veterinary drugs and aquaculture for disease control and growth, the release of antibiotics into the environment has become one of the major and global public health issues that require urgent action. According to global estimates, the annual use of antibiotics was between 100,000 and 200,000 tons [1]. Chlortetracycline (CTC), oxytetracycline (OTC), and tetracycline (TC) were the most commonly used antibiotics. At

present, a variety of antibiotics and their metabolites have been detected in seawater [2]. These findings have raised concerns about the content of antibiotics in seawater and the possible effects on human health caused by the transfer and spread of antibiotic resistance genes between microorganisms [3]. However, there were few studies on the practical application of antibiotics in aquaculture wastewater. Therefore, effective measures need to be taken to remove antibiotics from contaminated water. At present, ion exchange [4], adsorption [5–8], oxidation [9,10], complexation [11], and photocatalysis [12] have been used for the removal of

* Corresponding author.

tetracyclines from wastewater. Among the removal methods, adsorption was the most efficient and cost-effective.

Natural zeolites have properties such as abundant availability, porosity, screening, ion exchange characteristics, acid resistance, and strong binding of water capabilities. Thus, natural zeolites found their use as a promising low-cost material in adsorption processes. Lanthanum is a rare earth element, non-toxic in nature and relatively abundantly available in the earth's crust. Thus, lanthanum is considered to be environmentally friendly, and more and more attention has been made for the use of it toward environmental protection research.

Therefore, lanthanum modified zeolite (La-Z) was used as an adsorbent to remove OTC from aquaculture wastewater. The effects of various factors such as pH, interference ions on the adsorption were investigated, and the adsorption kinetics and adsorption isotherms were studied experimentally. The surface and structure of La-Z were analyzed by characterization methods. Finally, the regeneration of adsorption materials was studied in order to find a cheap, efficient, and reusable adsorbent to be used in water pollution purification and other fields.

2. Materials and methods

2.1. Materials

The zeolites used in the experiment were Bao Jia Tun, Faku County, Shenyang, Liaoning Province, China natural clinoptilolite. After crushing and screening, the particle size was measured to be 100 mesh. The experimental reagents include OTC, lanthanum nitrate hexahydrate (AR, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), ammonium sulfate (AR, $(\text{NH}_4)_2\text{SO}_4$), sodium nitrate (AR, NaNO_3), sodium nitrite (AR, NaNO_2), potassium dihydrogen phosphate (AR, KH_2PO_4), hydrochloric acid (AR, HCl), and sodium hydroxide (AR, NaOH) were used in pH regulation. Stock solution of OTC was configured using seawater for aquaculture area.

Various analytical techniques were used to observe the surface characteristics of the raw and modified adsorbents. The specific surface area of the adsorbent was measured by Brunauer–Emmett–Teller (BET) analyzer (Quantachrome 3.0) is Boynton Beach, Florida (Quantachrome Instruments Corporate Headquarters), the surface of the adsorbent before and after modification was observed by electron microscope scanner (SU1510), internal changes of adsorbents before and after modification by transmission electron microscopy (TEM, JEM-2100), and the elemental composition of the adsorbent was measured by energy-dispersive X-ray spectroscopy (EDS) analyzer (Model 550i). Infrared scanner (FT-IR650) was used to determine the surface groups of adsorbents before and after modification. X-ray diffractometer (D/MAX-2500) was used for observing the composition of adsorbents and TEM (JEM-2100 (UHR)) was used for observing the internal structure of adsorbents JEOL Ltd., (Japan).

2.2. Methods

2.2.1. Preparation

Before the experiment, 5 g natural zeolites were weighed in a conical bottle, and $\text{La}(\text{NO}_3)_3$ solutions with concentrations of 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 mol/L were

prepared in a shaking table for 1 h, maintaining the temperature at 60°C. The modified zeolite La-Z was prepared by washing it with anhydrous ethanol and deionized water for six times, and then drying and grinding at 85°C.

2.2.2. Determination of OTC

Fifty milliliters of prepared OTC polluted wastewater and a certain amount of adsorbent La-Z were added to 250 mL conical bottle, and the shaking table was placed to control the temperature at 25°C and the rotating speed was maintained at 150 rpm for 1 h. At the end of the experiment, the 5 mL suspensions were taken out and centrifuge to determine the adsorbance of OTC. The specific experimental conditions are shown in Table 1.

After adsorption equilibrium, the concentration of OTC in solution was determined, and the equilibrium adsorption quantity (q_e , mg/g) was calculated according to Eq. (1).

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 stands for the initial concentration of OTC (mg/L), C_e stands for the residual concentration of OTC (mg/L), V stands for the volume of OTC solution (L), and W stands for the dosage of La-Z (g).

Under the optimized experimental conditions, simulated OTC polluted culture wastewater with ion concentrations of 100 mg/L Na^+ , NO_2^- , NO_3^- , PO_4^{3-} , NH_4^+ was prepared, and the effect of coexisting interference ions on the adsorption of OTC by La-Z was studied.

3. Results and discussion

3.1. Characterization of materials

3.1.1. SEM and TEM analysis

From the scanning electron microscopy (SEM) diagram, it can be seen that the surface of the unmodified zeolite was rough and fluffy (Fig. 1a), while the surface of La-Z was smooth (Fig. 1b). This showed that in the process of modification, the surface impurities of unmodified zeolites can be removed and the dispersion of La-Z was stronger. Larger specific surface area and more adsorption sites were obtained, which was beneficial to adsorption. Through the TEM analysis of Fig. 2a, it was found that the surface of natural zeolite was relatively smooth. Black spots were found to be uniformly distributed on the surface of zeolite and some black spots were also distributed in the interior of La-Z. As a result, some of the lanthanum entered into the pore of zeolite in the process of modification, which was also confirmed by pore size analysis.

3.1.2. EDS and XRD analysis

From the EDS energy spectrum analysis in Fig. 3a, it can be seen that elements such as C, O, Al, Si, and La were presented in the modified zeolite, in which the mass fractions of C, O, Al, and Si were 13.583%, 58.204%, 2.92%, and 25.191%, respectively. The content of La was 0.102%, indicated that lanthanum had been successfully compounded into natural

Table 1
Experimental conditions

	Experimental conditions	Modified concentration (mol/L)	Dose of zeolite(g)	Concentration of OTC (mg/L)	Reaction time (min)	pH	Temperature (K)
1	Modified concentration	0–0.06	0.1	10	20	7	298
2	Dose of zeolite	0.02	0.02–0.12	10	20	7	298
3	Concentration of OTC	0.02	0.1	5–30	20	7	298
4	Reaction time	0.02	0.1	10	10–60	7	298
5	pH	0.02	0.1	10	20	5–10	298
6	Interfering ions	0.02	0.1	10	20	7	298

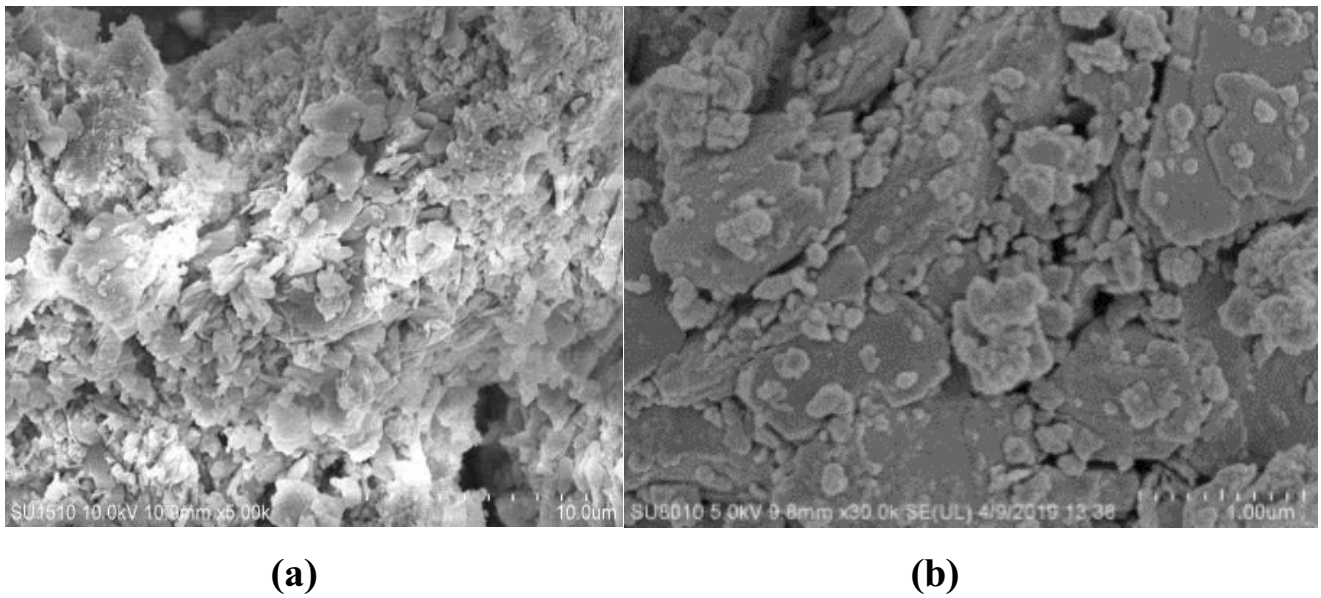


Fig. 1. SEM images of natural zeolites (a) and La-Z (b).

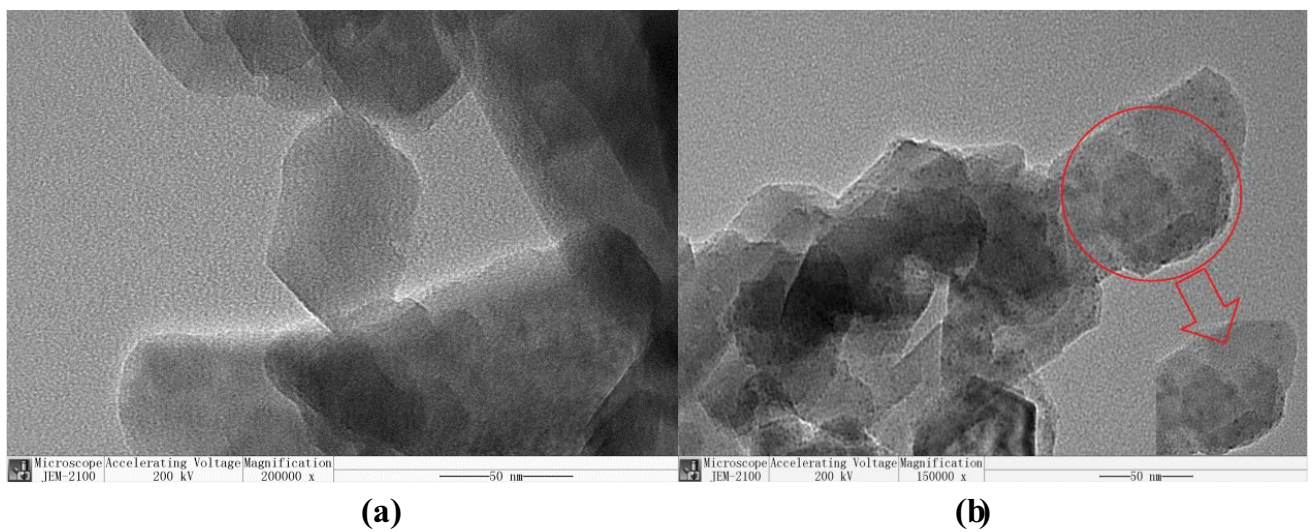


Fig. 2. TEM images of natural zeolites (a) and La-Z (b).

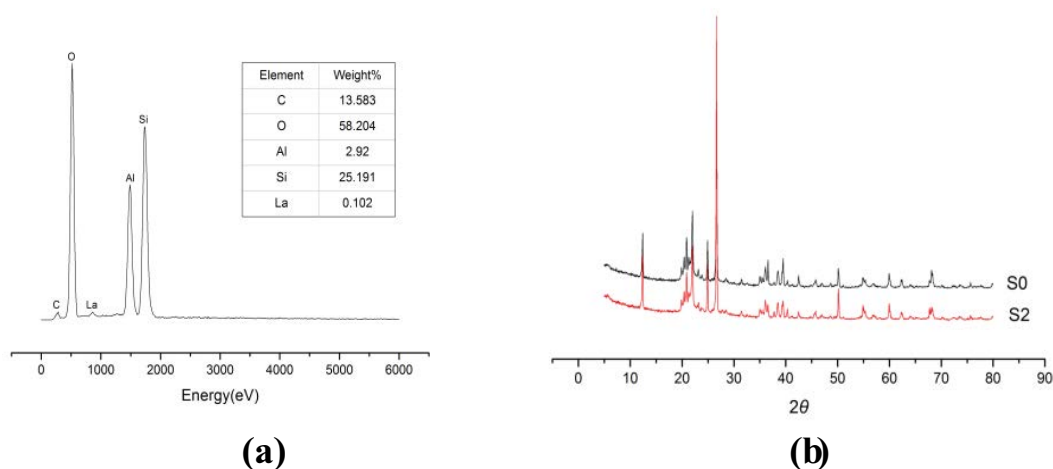


Fig. 3. EDS analyses (a) and XRD patterns (b) of natural zeolite (S0) and La-Z (S2).

zeolite. From the X-ray diffraction (XRD) analysis (Fig. 3b), it was found that the unmodified zeolite (S2) and La-Z (S0) exhibited strong peaks at $2\theta = 12.376^\circ$, 20.381° , 21.239° , 26.64° , and 50.134° . Based on comparison with the JCPDS card number, these characteristic peaks can be attributed to zeolites and the corresponding substances aluminum silicate hydroxide ($\text{Al}_4(\text{OH})_8(\text{Si}_4\text{O}_{10})$ and $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$), silicon oxide (SiO_2), and sodium aluminum silicate ($\text{NaAlSi}_3\text{O}_8$). In La-Z (S0), it was found that peaks at $2\theta = 27.973^\circ$, 31.642° , 39.478° , and 44.856° were different from those observed for natural zeolite (S2). Based on the comparison with the JCPDS card number, it can be seen that the aforementioned peaks correspond to the characteristic peaks of $\text{La}(\text{OH})_3$, indicated that $\text{La}(\text{OH})_3$ was loaded onto zeolite in the form of $\text{La}(\text{OH})_3$ and that the modification was successful. Compared with the unmodified zeolite, the characteristic La-Z peak was not sharp, which indicated that the particle size of the modified material was smaller and accounts for a smaller surface area of La-Z, which led to more adsorption sites on La-Z, which was conducive to adsorption.

3.1.3. FT-IR analysis

The Fourier transform infrared spectroscopy (FT-IR) results of unmodified zeolite (S0) and La-Z (S2) are shown in Fig. 4. The intensity of the characteristic peaks changed before and after the modification of zeolite, while the functional groups detected did not change. There was an obvious absorption peak observed near 1630 cm^{-1} due to the bending vibration of H–O–H [13]. The intensity of the absorption peak at 3434 cm^{-1} increased obviously, which may be due to the stretching vibration of the –OH group changed by the hydrolysis of La^{3+} during the modification process, which led to the change of $\text{La}(\text{OH})_3$.

3.1.4. N_2 adsorption and desorption isotherm and pore size analysis

Figs. 5a and b report the nitrogen adsorption isotherm and pore size distribution of La-Z and unmodified zeolite. According to the BDDT classification, the N_2 adsorption

isotherms of La-Z and unmodified zeolites belonged to BDDT type IV classification. Results showed that the adsorption of La-Z was mainly in a porous sublayer. The N_2 adsorption quantity of La-Z was larger than that of unmodified zeolites. In addition, as shown in Fig. 5b, the pore diameters of both La-Z and unmodified zeolites are mesoporous, although as shown in Table 2, the pore size of modified zeolite was larger than that of unmodified zeolite and the specific surface area increased, while the pore volume became smaller. This may be due to the fact that in the process of zeolite modification, Lanthanum was incorporated into the pores of zeolites, while the lanthanum surface area was superimposed with the surface area of zeolite micropores, resulting in an increase of the pore size of La-Z.

3.2. Single-factor experiment

3.2.1. Effect of modification concentration of La-Z

Fig. 6a reports the effect of modification concentration of La-Z on adsorption. The results showed that the removal

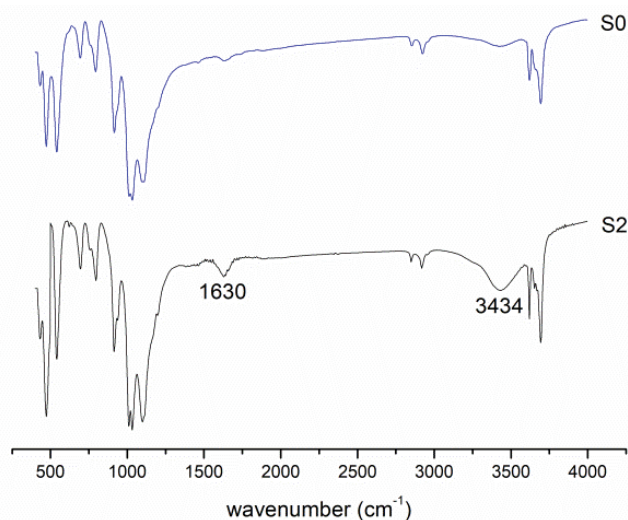


Fig. 4. FT-IR spectra of natural zeolite (S0) and La-Z (S2).

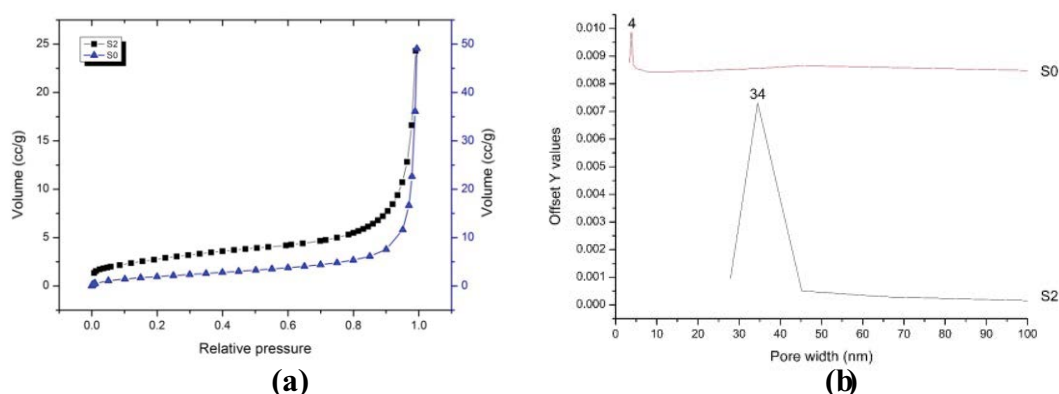


Fig. 5. N_2 adsorption and desorption isotherm (a) and pore size analysis (b) of natural zeolite (S0) and La-Z (S2).

Table 2
BET parameters of zeolites

Sample	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
Natural zeolite S0	7.956	0.072	3.057
Modified zeolite S2	10.267	0.038	6.482

rate of OTC by (i) the removal rate of OTC by unmodified zeolite was only 31.26%. The adsorption performance of zeolite for OTC was improved by lanthanum modification, as modification broadens the pores on the surface of zeolite and improves the adsorption quantity, (ii) when the modified concentration reached 0.02 mol/L, the maximum OTC removal rates and unit adsorption quantity were 79% and 7.9 mg/g, respectively, (iii) when the modified concentration exceeded 0.03 mol/L, the removal rate of OTC and the unit of adsorption quantity of La-Z decreased obviously, tended to become stable gradually. The reason for this phenomenon may be that when the modified concentration reached 0.03 mol/L, $La(OH)_3$ was supersaturated on the zeolite surface, which reduced the active adsorption point on the La-Z surface and weakened adsorption.

3.2.2. Effect of La-Z dosage

Fig. 6b reports the effect of La-Z dosage on OTC removal rate and unit adsorption quantity was studied. The results showed: (i) the unit adsorption quantity reached the peak, 14.51 mg/g, when the dosage was 0.02 g, and the unit adsorption quantity decreased gradually with the increase of dosage; (ii) The removal rate increased with the increase of dosage and reached the peak, 81.76%, when the dosage was 0.12 g. This behavior was attributed to the availability of more number of vacant surface sites and large surface areas with the increased dosage, which resulted in the increase in the removal rate of OTC.

3.2.3. Effect of initial concentration OTC

Fig. 6c reports the removal effect of OTC when the initial concentration was 5–30 mg/L. Results showed that, when the initial concentration was 5 mg/L, the removal

rate was the highest, which was 92.30%. The removal rate decreased with the increase of the initial concentration, but the unit adsorption quantity increased. Due to the increased concentration of antibiotics, the competitive adsorption of pollutants to the limited active surface led to the decrease of antibiotic removal rate. However, with the continuous increase of antibiotic concentration, the strong driving force increased the probability of collision between antibiotic molecules and modified zeolites, and the number of effective collisions increased, so the unit adsorption quantity increased.

3.2.4. Effect of reaction time

Fig. 7a reports that with the increase of reaction time, the removal rate and unit adsorption quantity gradually increased and reached a stable state consequently with the increase of reaction time. Within 20 min of reaction, the removal rate of OTC was faster, and the unit adsorption quantity increased significantly. This is due to the fact that there are many adsorption active sites on the surface of La-Z at the initial stage of the reaction, which increases the adsorption efficiency. However, with the progress of the reaction, there is a repulsion between the antibiotic molecules adsorbed on the La-Z surface and the antibiotic molecules in the solution, which makes the remaining sites on the surface difficult to occupy. At this time, the increase of unit adsorption quantity tends to be flat, reaching adsorption saturation. Therefore, the reaction time of 20 min was selected as the follow-up reaction condition.

3.2.5. Effect of pH

Figs. 7b and d report the effect of pH on solution adsorption and different pH values had a significant effect on the

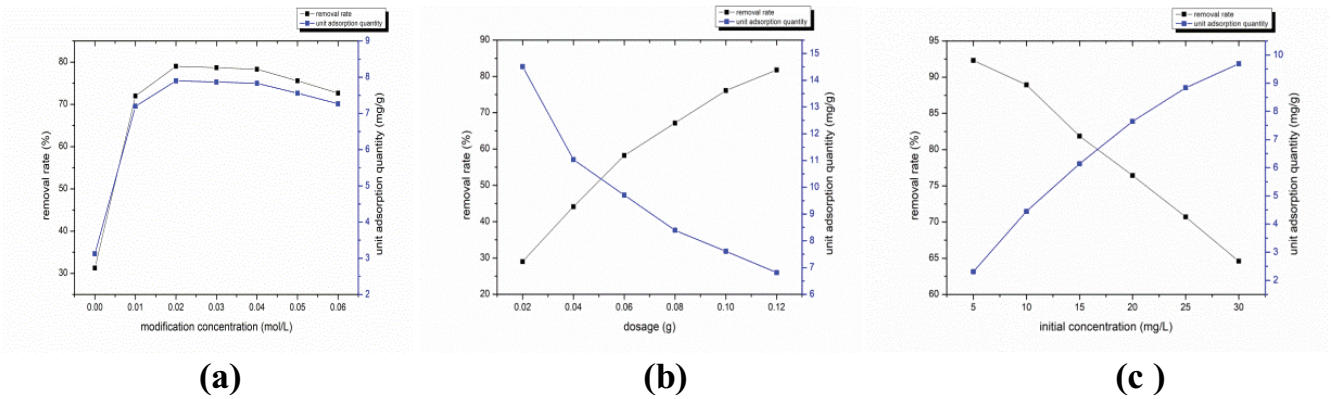


Fig. 6. Effects of different factors on the adsorption of OTC (modified concentration (a), dosage of La-Z (b), and initial concentration of oxytetracycline (c)).

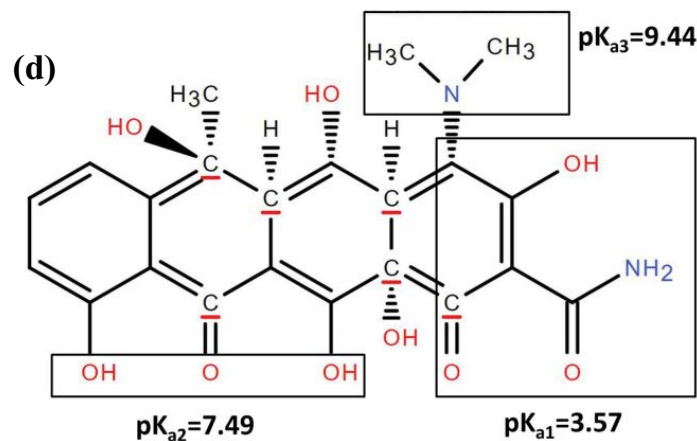
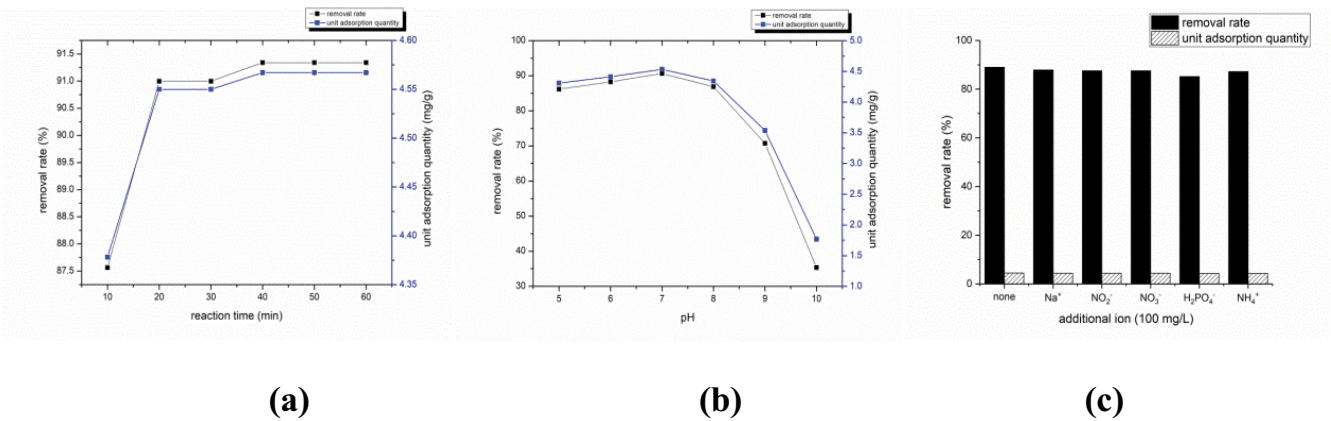


Fig. 7. Effects of different factors on the adsorption of OTC (adsorption time (a), pH (b), interference ions (c), and OTC molecular plane structural formula (d)).

La-Z adsorption quantity. When the pH was 7, the highest unit adsorption quantity (4.53 mg/g) and the removal rate (90.66%) were observed. The ionization equilibrium constants pK_{a1} , pK_{a2} , and pK_{a3} of OTC were 3.57, 7.49, and 9.44, respectively, indicated that OTC existed in the form of cations, zwitterions, and anions under different pH conditions. In addition, many studies had shown that La-Z may

have a positive charge. When the solution pH was 5–7, the removal rate and unit adsorption quantity were not high, due to the competitive adsorption of positively charged OTC cations and H⁺ in solution, which weakened the adsorption effect. Under alkaline conditions, competitive adsorption occurred between OH⁻ and OTC anions [14]. Under high pH conditions (pH > 8), the dissociated OTC molecules

were transformed into anions. Therefore, the weak interaction between the adsorbent surface and negatively charged OTC molecules, as well as the competition between OH⁻ and OTC anions for the limited active surface sites, once again led to a poor adsorption performance.

3.2.6. Effect of interfering ions

Fig. 7c reports the effect of interfering ions on adsorption. The interference ions used in this study were common interference ions in aquaculture. Including Na⁺, NO₂⁻, NO₃⁻, H₂PO₄⁻, and NH₄⁺ (concentration of 100 mg/L). The results showed that under the interference of Na⁺, NO₂⁻, NO₃⁻, and NH₄⁺, the effect on the adsorption of OTC by La-Z was not obvious. However, in the presence of H₂PO₄⁻, the removal of La-Z will be affected to a certain extent, mainly due to the ligand exchange between lanthanum and H₂PO₄⁻ to form insoluble phosphate [15–17]. In practice, the solution of OTC was configured by the seawater in which many extra ions exist; therefore, the overall effects of interfering ions are neglected.

3.3. Orthogonal experiments

Through the orthogonal experiment, the best conditions for the adsorption of OTC by La-Z and the conditions that can best affect the adsorption behavior under the condition of synthesizing all kinds of single factors were obtained.

It can be seen from Table 3, that the best conditions for OTC removal: the modified concentration was 0.02 mol/L, the dosage was 0.1 g, the initial concentration of OTC was 5 mg/L, the adsorption time was 40 min, pH was 7, the removal rate was 99.18% and the unit adsorption quantity was 2.48 mg/g. The ranked order of the influence of the degree of each independent factor in adsorption was as follows: initial concentration of OTC > modified concentration > pH > dosage of La-Z > reaction time. The initial concentration of OTC was the biggest factor affecting the adsorption of OTC by La-Z.

3.4. Adsorption kinetics of modified zeolite

3.4.1. Quasi-first-order kinetic model and quasi-second-order model

The adsorption kinetic analysis was studied to analyses the adsorption mechanism, including the adsorption rate and possible rate-limiting steps of the reaction process.

The equation of quasi-first-order kinetics and quasi-second-order kinetic models is given as [18,19]:

$$Q_t = Q_e \left(1 - \exp \left(-\frac{k_1}{2.303} t \right) \right) \quad (2)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (3)$$

Table 3
Orthogonal experiment

Orthogonal experiment	Modified concentration (mol/L)	Dose of zeolite (g)	Concentration of OTC (mg/L)	Reaction time (min)	pH	Removal rate (%)	Unit adsorption quantity (mg/g)
1	0.02	0.06	5	10	5	96.43	4.018
2	0.02	0.08	10	20	6	94.09	5.88
3	0.02	0.1	15	30	7	87.13	6.53
4	0.02	0.12	20	40	8	70.76	5.90
5	0.03	0.06	10	30	8	75.54	6.29
6	0.03	0.08	5	40	7	92.30	2.88
7	0.03	0.1	20	10	6	63.03	6.30
8	0.03	0.12	15	20	5	73.84	4.62
9	0.04	0.06	15	40	6	77.28	9.66
10	0.04	0.08	20	30	5	65.10	8.14
11	0.04	0.1	5	20	8	93.68	2.34
12	0.04	0.12	10	10	7	87.56	3.65
13	0.05	0.06	20	20	7	67.67	11.28
14	0.05	0.08	15	10	8	77.51	7.27
15	0.05	0.1	10	40	5	90.31	4.52
16	0.05	0.12	5	30	6	95.74	1.99
k_1	348.41	316.92	378.15	324.53	325.68		
k_2	304.72	329.00	347.51	329.29	330.15		
k_3	323.62	334.15	315.76	323.50	334.67		
k_4	331.23	327.91	266.57	330.66	317.49		
R	43.69	17.23	111.58	7.16	17.18		
Verification						99.18	2.48

where Q_t represented the adsorption amount at t (mg/g), Q_e represented the equilibrium adsorption quantity of quasi-first-order model (mg/g), k_1 was a quasi-first-order adsorption rate constant (1/min); and k_2 was quasi-second-order adsorption rate constant (g/mg/min). In Eq. (3), the quasi-second-order kinetic parameters can be used to calculate the initial adsorption rate ($h:h = k_2 Q_e^2$).

From the adsorption kinetic fitting diagram (Figs. 8a and b) and the model fitting data (Table 4), it can be seen that: (i) the highest correlation coefficient for quasi-first-order kinetics was 0.861, while the correlation coefficient for quasi-second-order kinetics was significantly higher at 0.999 and (ii) the quasi-second-order dynamic linear fitting was obviously better than that of quasi-first-order dynamics. Therefore, it can be concluded that OTC adsorption kinetics by different concentrations of La-Z exhibited a better fit to the quasi-second-order kinetic model.

3.4.2. Weber–Morris model

In order to determine the importance of diffusion in the adsorption process, the Weber–Morris kinetic model is used for further analysis, and its expression can be expressed as Eq. (4) [20]:

$$Q_t = k_{ip} t^{1/2} + C \quad (4)$$

where k_{ip} was the intra-particle diffusion rate constant (mg/g/min^{0.5}), C was constant. If intra-particle diffusion was involved in the adsorption process, the curves of Q_t and $t^{1/2}$ in the fitting graph should be linear, and if these lines pass through the origin, intra-particle diffusion was a rate control step [21]. Otherwise, intra-particle diffusion was not the only rate control step, and there was a certain degree of boundary layer diffusion or external mass transfer in the adsorption process.

The Weber–Morris model fitting curve is shown in Fig. 9, with the corresponding dynamic parameters listed

in Table 5. As shown from the linear regression data, the fitting curve was composed of two different regions. The first part included the adsorption period of 3–15 min, which represented the external mass transfer. In this adsorption process, it can be seen that the slope of the fitting curve was larger, due to the fact that in the initial stage of adsorption, there were many adsorption sites on the zeolite surface and the adsorption of antibiotics mainly occurred on the zeolite surface, which made the adsorption reaction easy. In addition, the concentration gradient of antibiotics on the zeolite surface and in the solution produced a strong driving force to accelerate the adsorption rate. The second linear part included the adsorption period of 25–65 min, which represented the diffusion in the particles. The fitting curve did not pass through the origin, which indicated that the adsorption rate of La-Z in the OTC solution was not limited to the control of intra-particle diffusion. In the process of adsorption, the internal, and external diffusion of particles are simultaneously controlled in a multi-step process. When the adsorption reaction enters the second stage, the surface adsorption site tends to be saturated and the resistance of antibiotics to adsorption into the zeolite pores increases, resulting in a slow adsorption rate and a decrease in the slope of the fitting curve.

3.4.3. Ritchie-second-order model and Bangham diffusion model

Ritchie-second-order model is given as [22]:

$$\frac{1}{q_t} = \frac{1}{q_e} + \frac{1}{k_R q_e} t \quad (5)$$

where k_R (min⁻¹) is the Ritchie-second-order rate constant, t (min) is the time, q_e (mg/g) represented the amount of antibiotic adsorbed at equilibrium and q_t (mg/g) represents the amount of antibiotic at time, “ t .”

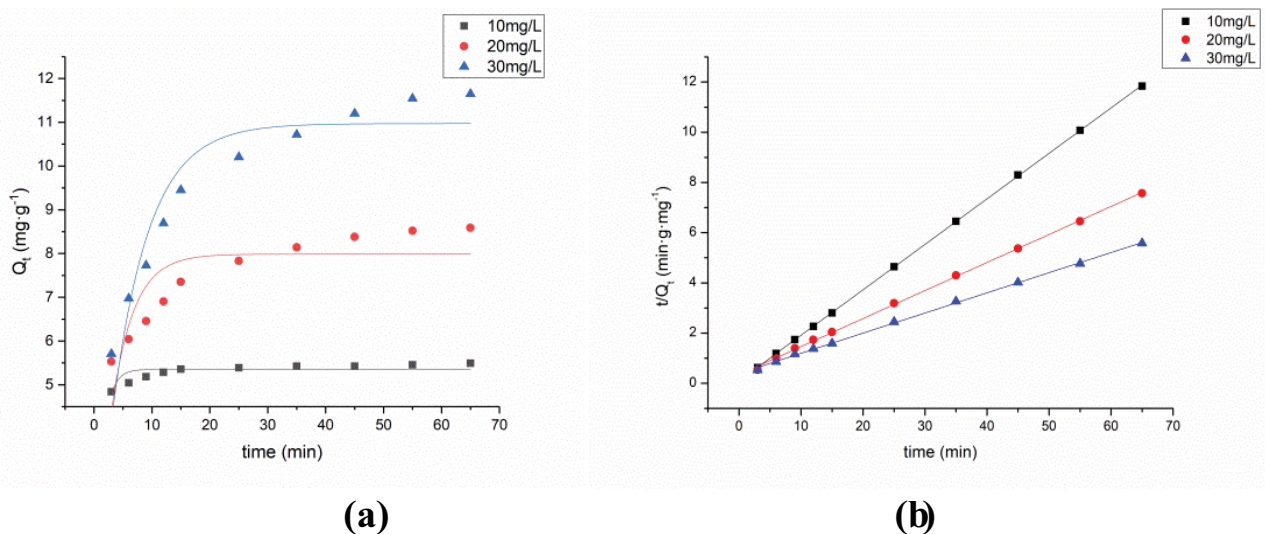


Fig. 8. Quasi-first-order kinetic model (a) and quasi-second-order kinetic model (b).

Table 4
Quasi-first-order and quasi-second-order fitting data

Concentration of OTC (mg/L)	Quasi-first-order kinetic			Quasi-second-order kinetic		
	q_e (mg/g)	K (1/min)	R^2	q_e (mg/g)	K (g/mg/min)	R^2
10	5.354	1.716	0.608	5.518	0.335	0.999
20	7.987	0.610	0.616	8.954	0.036	0.999
30	10.971	0.365	0.861	12.456	0.016	0.999

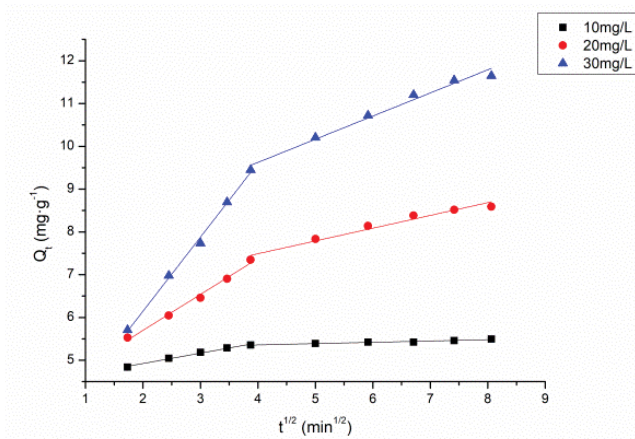


Fig. 9. Weber–Morris internal diffusion model fitting.

Bangham diffusion model was given as [23]:

$$\log \log \left(\frac{C_0}{C_0 - q_t m} \right) = \log \left(\frac{k_0 m}{2.303 V} \right) + a \log t \quad (6)$$

where C_0 (mg/L) is the initial concentration of OTC in solution, V (mL) is the volume of solution, m (g/L) is the weight of adsorbent per liter of solution, q_t represented the adsorption amount at t (mg/g), and a (<1) and k_0 (mL/g/L) are Bangham constants.

Ritchie-second-order model is shown in Fig. 10 and Table 6. The curve in Fig. 10 was fitted with a straight line (i.e., linear fitting) and found that $R^2 < 0.99$ which revealed that the interaction between OTC and La-Z surface was not the only factor controlling the adsorption rate. Experimental adsorption data were analyzed based on Bangham model and reported in Fig. 11 and Table 7. The fitting coefficient $R^2 < 0.99$, indicated that pore diffusion was not the only factor

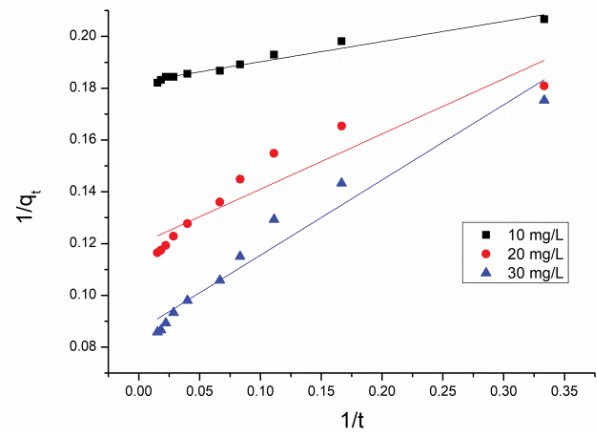


Fig. 10. Ritchie-second-order model.

controlling the rate of adsorption. The results of the above two models confirming the results obtained in the Weber–Morris kinetic model. The process of OTC adsorption by La-Z was controlled by intra-particle diffusion and the interaction between the adsorbent surface and pollutants. It was a multi-step process.

3.4.4. Isotherm of adsorption

Adsorption isotherms describe how solutes interact with adsorbents. In this study, Langmuir and Freundlich isotherms were used to analyze the interaction between solutes and adsorbents. Langmuir isotherm for the adsorption process is given in Eq. (7) [24,25]:

$$\frac{c_e}{q_e} = \frac{1}{(k_1 \times q_m)} + \frac{c_e}{q_m} \quad (7)$$

where q_m is the maximum adsorption quantity (mg/g), c_e is the residual concentration of antibiotics in the solution

Table 5
Weber–Morris internal diffusion fitting data

Concentration of OTC (mg/L)	Weber–Morris internal diffusion model					
	k_1 (mg/g/min ^{0.5})	C	R_1^2	k_2 (mg/g/min ^{0.5})	C	R_2^2
10	0.243	4.438	0.989	0.031	5.236	0.951
20	0.841	4.015	0.988	0.299	6.295	0.957
30	1.732	2.681	0.996	0.541	7.459	0.978

Table 6
Ritchie-second-order model fitting data

Concentration of OTC (mg/L)	Ritchie-second-order model		
	q_e	k_R	R^2
10	5.482	12.832	0.963
20	8.354	4.692	0.873
30	11.563	3.444	0.951

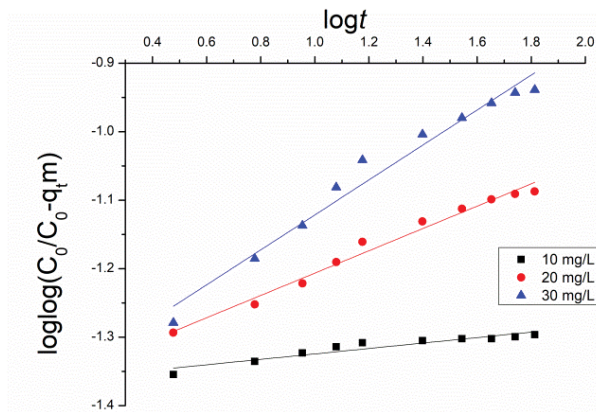


Fig. 11. Bangham diffusion model fitting.

Table 7
Bangham diffusion model fitting data

Concentration of OTC (mg/L)	Bangham diffusion model		
	a	k_0 (mL/g/L)	R^2
10	0.040	99.592	0.889
20	0.163	98.400	0.981
30	0.255	96.760	0.969

(mol/L), and k_1 is the adsorption constant of Langmuir. Langmuir isotherm parameters were calculated from the intercept and slope of the graph obtained from Eq. (7).

Freundlich isotherm for the adsorption process is given in Eq. (8) [26]:

$$Q_e = k_f C_e^{1/n} \quad (8)$$

where K_f is the Freundlich adsorption constant, n is the non-uniform coefficient.

Langmuir and Freundlich adsorption isotherm models are widely used to describe the adsorption process and explore the adsorption mechanism. The La-Z adsorption data at different initial concentrations and temperatures were fitted by Langmuir equation and Freundlich equation, respectively. The results are presented in Figs. 12 and 13 and Table 8. It can be seen from Fig. 12 that the linear fitting of the Langmuir isotherm with $R^2 > 0.9$ was a better fit than the nonlinear fitting of the Freundlich isotherm. This clearly indicated that the adsorption process of La-Z to OTC was

more consistent with the Langmuir isotherm. The Langmuir adsorption constant K was less than 0.5, which indicated that the adsorption process of La-Z to OTC belonged to preferential adsorption. The maximum adsorption capacity of La-Z to OTC at 318 K was calculated to be 36.377 mg/g.

3.4.5. Thermodynamics of adsorption

The thermodynamics parameters include Gibbs free energy (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°), the relationship between them is according to Eqs. (9)–(11) [27]:

$$\Delta G^\circ = -RT \ln K \quad (9)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (10)$$

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (11)$$

where T is the temperature (K), K is the distribution coefficient (L/g), R is the ideal gas constant (8.314 J/mol/K). From Eq. (11), it is evident that by plotting $1/T$ vs. $\ln K$, ΔS° and ΔH° were obtained from the intercept and slope, respectively, of the linear fitting line. ΔG° was then calculated using Eq. (10) using ΔS° and ΔH° .

It can be seen from Table 8 that ΔG° decreases gradually with the increase of temperature, indicating that a higher temperature was beneficial to the adsorption of OTC into La-Z adsorbent. $\Delta G^\circ < 0$ indicates that the adsorption process was spontaneous. A positive value of ΔS° was indicating that the degree of disorder-ness of solid-liquid interface increases in the process of adsorption. A positive value of ΔH° was indicating that the adsorption process being an endothermic process (Table 9).

4. La-Z adsorption regeneration experiment

In this study, the adsorbed saturated La-Z was immersed in a 1.6 mol/L NaCl solution. After shaking at 150 rpm for 1 h, the mixture was removed, washed with deionized water, and dried in the oven at 100°C. The regenerated adsorbent was reused three times and the removal rate was calculated, with the adsorption performance of the regenerated adsorbent established in comparison to the pristine La-Z. The removal rate of regenerated adsorbents was shown in Fig. 14. Results showed that after three cycles of regeneration, the removal rate of OTC by La-Z was higher than 60%, indicated that the adsorbent maintained a good adsorption performance after process (Table 10).

5. Comparison with other adsorbents

Table 10 compares the adsorption quantity of different adsorbents for OTC. Table 10 shows that the q_m of the obtained La-Z was not very high compared with the Al-MOF/GO [28] adsorbent. This was due to the fact that the configuration solution of OTC in this study was derived from aquaculture wastewater, in which there were many interfering ions and the pH value was close to 8. Based on previously reported study outcomes, it is known that pH and some

Table 8
Isotherm fitting data at different temperatures

T/K	Langmuir				Freundlich	
	K	q_m (mg/g)	R^2	1/n	K_f	R^2
298	0.039	28.902	0.984	1.65496	1.09×10^{-7}	-2.363
308	0.039	32.216	0.984	10.13723	1.440×10^{-26}	0.508
318	0.040	36.377	0.984	-7.47223	1.881×10^{-6}	-2.030

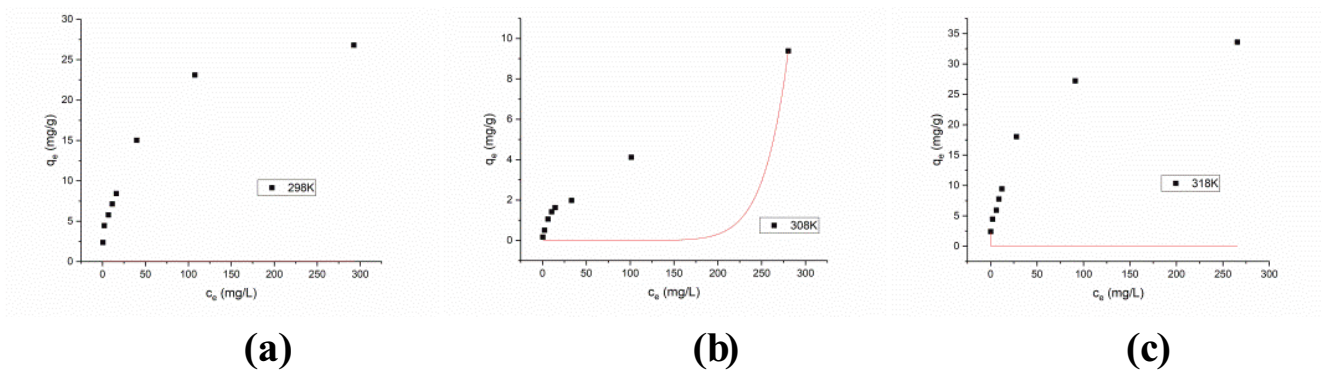


Fig. 12. Freundlich model fitting at different temperatures (298, 308, and 318 K).

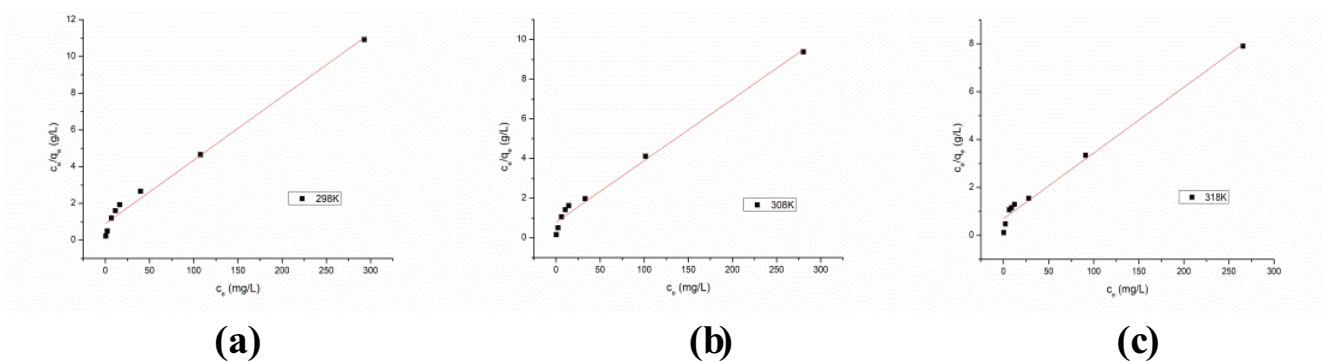


Fig. 13. Langmuir model fitting at different temperatures (298, 308, and 318 K).

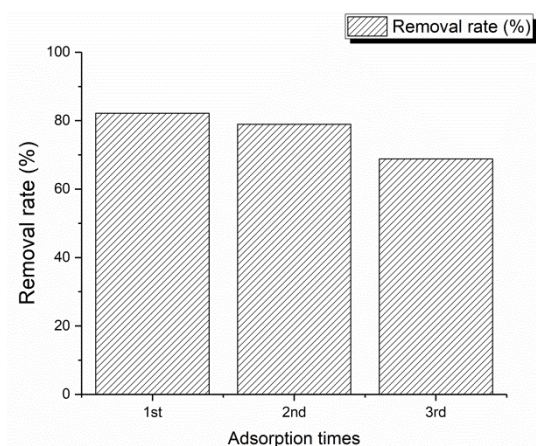


Fig. 14. Adsorption regeneration of La-Z using NaCl.

Table 9
Thermodynamics fitting data

T/K	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/mol)
298	-44.991	-	-
308	-63.793	25.314	108.96
318	-91.256	-	-

interfering ions have a very negative effect on the adsorption of OTC. In addition, Al-MOF/GO, nanobiochar, and magnetic graphene oxide [7,29] had a higher specific surface area ($>140 \text{ m}^2/\text{g}$) than La-Z, resulting in a higher adsorption quantity. However, Al-MOF/GO, nanobiochar, and magnetic graphene oxide had a higher economic cost than La-Z in practical use. Therefore, in terms of cost and efficiency, La-Z

Table 10
Maximum adsorption quantity (q_m) of various adsorbents for oxytetracycline

Adsorbent	q_m (mg/g)	Reference
La-Z	36.38	This study
Illite	9.75	[8]
Kaolinite	6.25	[8]
Al-MOF/GO	240.13	[28]
Nanobiochar	520	[29]
Magnetic graphene oxide	86.28	[7]

was a promising and economical adsorbent for the removal of OTC from aquaculture wastewater.

6. Conclusions

The surface functional groups and surface structure of natural zeolites changed after lanthanum modification. The characterization results of TEM, EDS, XRD, and FT-IR showed that lanthanum was effectively loaded onto natural zeolites. The specific surface area was increased from 7.956 to 10.267 m²/g. Single-factor and orthogonal experiments were performed to assess the factors affecting the adsorption of OTC by lanthanum modified zeolite (La-Z). The results showed that the initial concentration of OTC was an important factor affecting the removal of OTC by La-Z adsorbent. The best conditions for OTC removal by La-Z were as follows: the modified concentration was 0.02 mol/L, the dosage of La-Z was 0.1 g, the initial concentration of OTC was 5 mg/L, the adsorption time was 40 min, pH was 7, the removal rate was 99.18% and the unit adsorption quantity was 2.48 mg/g. The factors affecting the rate of adsorption of OTC using La-Z adsorbent were found to be in the following order: initial concentration of OTC > modified concentration > pH > dosage of La-Z > reaction time. Kinetic analysis showed that the kinetic process of OTC adsorption by La-Z well can be described by quasi-second-order kinetic model. Using Weber–Morris model, Ritchie-second-order model, and Bangham diffusion model, it was found that the adsorption of OTC by La-Z adsorbent was found to be a multi-component process controlled by both internal and external diffusion. The study of adsorption isotherm showed that the adsorption process of OTC by La-Z was in agreement with the Langmuir model, and the maximum adsorption quantity was 36.38 mg/g. The thermodynamic analysis of adsorption revealed that the adsorption process of OTC was a spontaneous entropy-increasing endothermic physical adsorption process. Through regeneration experiments, it was found that regenerated La-Z maintained good adsorption properties, with a simple method of obtaining and regenerating the regenerated material being effective, with a short regeneration time for the adsorbent. The utility model has the advantages of low economic costs and strong practicability. La-Z is a practical and economical adsorbent for OTC in aquaculture wastewater.

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