Enhanced adsorptive performance of tetracycline antibiotics on lanthanum modified diatomite

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Abstract−A natural mineral diatomite was modified with lanthanum species using an ion exchange process to improve its adsorption performance for tetracycline removal. The prepared lanthanum-modified diatomite was characterized by scanning electron microscopy, X-ray diffractometry and Fourier transform infrared spectroscopy. The results showed that lanthanum was successfully immobilized onto diatomite, with a content of lanthanum element of about 1.5% (atomic ratio). The prepared adsorbent was evaluated for the adsorptive removal of tetracycline, and the adsorption isotherm, kinetics and mechanism were investigated. The adsorbent exhibited higher adsorption capacity than other adsorbents reported in literature, reaching 1056.9 mmol/kg. Langmuir model better fitted the experimental data than did other models. The removal of tetracycline was favorable at near neutral pH conditions. The tetracycline adsorption well followed pseudo-second-order kinetics model, and most of tetracycline was adsorbed within the initial 15 min. The increase in ionic strength reduced the tetracycline adsorptive removal, indicating that tetracycline adsorption on La-modified diatomite may be attributed to the formation of out-sphere surface complexes.

Keywords: Tetracycline, Diatomite, Lanthanum, Adsorption, Isotherm

INTRODUCTION

Antibiotics widely applied in pharmaceutical and personal care products (PPCPs) have caused increasing concern over the past decades. Most of the antimicrobial chemicals eventually enter into rivers, lakes and other water bodies. Consequently, antibiotics have been detected in potable water in many countries [1]. The transfer and spread of antibiotic-resistant genes among microorganisms potentially threaten ecosystem functions and human health [2,3]. Exposure even to low-level antibiotics could lead to significant toxic consequences. The increasing emergence of antibiotic resistance in human pathogens has already been identified as a special concern by the World Health Organization regarding treating infectious disease and other pathologies [4].

Tetracyclines, the second most widely used antimicrobial chemicals in the world, are widely applied in human therapy and livestock industry [5]. As tetracycline molecules are usually neutral or negatively charged in environmental water, conventional techniques such as sand filtration, sedimentation, flocculation and coagulation are not efficient for tetracycline removal as expected [6]. Recently, a number of oxidation processes such as photodegradation [7], ozonation [8], photo-Fenton process [9], photoelectrocatalytic degradation [10] have been tested for the removal of tetracyclines. However, the complete mineralization of these organic pollutants seems not practical economically. In addition, these oxidation processes may generate more toxic intermediates than their parent pollutants [11]. By contrast, adsorption process can transfer the pollutants from one phase to another efficiently, and no toxic intermediates are generated. A variety of adsorbents such as montmorillonite [12], rectorite [13], graphene oxide [14], Fe/OMC-100 [15], Fe-Mn binary oxide [16], carbon nanotubes [2], and $MnFe_2O_4$/activated carbon magnetic composites [17] have been reported for the removal of tetracyclines. These results proved that adsorption is a highly effective approach for the removal of tetracyclines.

Natural minerals, as the cheapest adsorbent, are the best choice in most developing countries. As a siliceous and low cost material, diatomite has the potential for practical water and wastewater treatment due to its unique physical and chemical properties including high porosity, high permeability, large surface area and chemical inertness [18]. However, compared with carbonaceous materials (e.g., carbon nanotubes or activated carbon), natural minerals have much lower adsorption capacities of tetracyclines removal. Lanthanum, a rare earth element, has been introduced into some adsorbents to enhance the phosphate removal performance [19,20]. The introduction of Lanthanum into natural diatomite may improve its adsorption performance. Moreover, it has been scarcely reported on the enhanced adsorptive removal of organic pollutants by La-based sorbents.

In this research, lanthanum was incorporated into natural mineral diatomite using a simple ion exchange process. The prepared La-modified diatomite was then used for the adsorptive removal of tetracycline and the performance including adsorption kinetics,

isotherm and mechanism were systematically studied.

MATERIALS AND METHODS

1. Materials and Apparatus

Tetracycline (TC) was purchased from Hefei Bomei Biological Science and Technology Co., Ltd. (Anhui Province, China) and used without further purification. Diatomite was provided by Linjiang Meston Powdery Materials Co., Ltd. (Jilin Province, China). All the chemicals used were of analytical grade. Deionized (DI) water was used to prepare all solutions.

2. Preparation of Lanthanum Modified Diatomite

First, 10 g of diatomite was soaked in 100 ml of 0.5 M lanthanum chloride (LaCl$_3$) solution for 24 h. Then the treated diatomite was collected by filtration and dried at 100 ^{o}C overnight. The prepared sorbent was stored in desiccators before use. The prepared lanthanum modified diatomite is denoted as La-modified diatomite.

3. Characterization of La-modified Diatomite

The prepared La-modified diatomite was characterized by a Philips Quanta-2000 scanning electron microscope (SEM) coupled with an energy dispersive X-ray (EDX) spectrometer. X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-3B X-diffrac-

tometer. FTIR spectra (KBr pellets) were recorded on a Nicolet NEXUS 470 FTIR spectrophotometer from 400 to 4,000 cm^{-1}.

A zeta potential analyzer (Zetasizer 2000, Malvern Co., UK) was used to analyze the zeta potential of raw diatomite and La-modified diatomite. The content of the sorbent in the solution was about 200 mg/L. NaNO$_3$ was used as a background electrolyte to maintain an appropriately constant ionic strength of 0.01 M. After being mixed for 48 h, 20 mL of suspension was transferred to a sample tube. The zeta potential was then measured by electrokinetic analysis.

4. Batch Adsorption of TC on La-modified Diatomite

A stock TC solution of 500 mg/L was prepared by dissolving TC in DI water. It was stored in a refrigerator at 277 K and used within three days. The stock solution was diluted with DI water to prepare desired TC solutions for the subsequent batch experiments.

Adsorptive removal of TC was determined by batch experiments in conical flasks. In the tests of adsorption isotherm, ionic strength effect, pH effect, and coexisting ions effect, 10 mg of La-modified diatomite was added into 50 mL TC solution of 15 mg/L. For the kinetics study, 200 mg of La-modified diatomite was added into 1,000 mL TC solution of 15 mg/L. These mixtures were shaken at 145 rpm for 24 h. The temperature was kept constant at 298 K. All the solution pH values were maintained at neutral pH except for
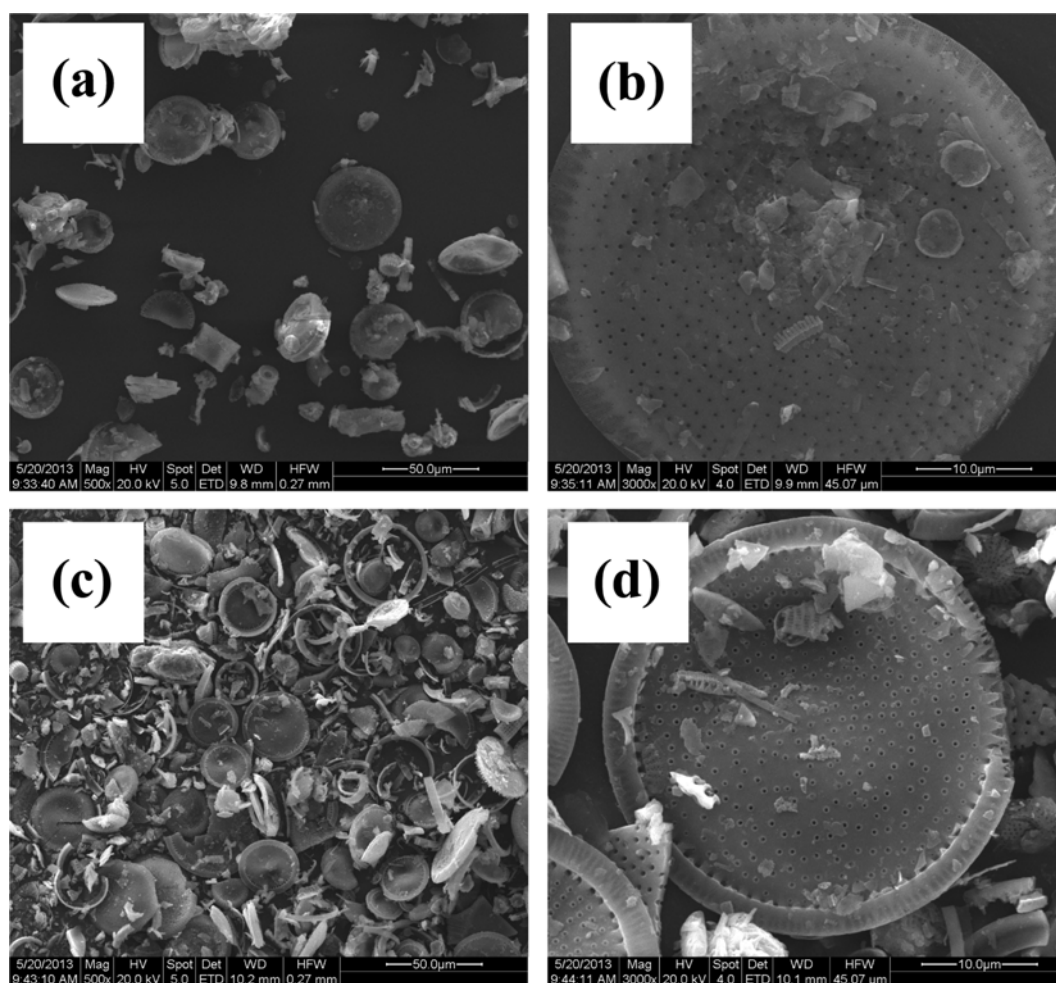

Fig. 1. SEM micrographs of raw diatomite (a), (b) and La-modified diatomite (c), (d).

the pH effect study. The solution pH was adjusted by adding HNO_3 or NaOH solution.

5. Analyses

Samples were collected and filtered through a 0.45 μm membrane before analysis. The TC concentration of the samples was determined by measuring the absorbance at a fixed wavelength (360 nm) [21] by an UVmini-1240 spectrophotometer (Shimadzu).

RESULTS AND DISCUSSION

1. Characterization of La-modified Diatomite

1-1. Morphologies of La-modified Diatomite

As illustrated in Fig. 1, the raw diatomite used in this study is comprised of the discoid plates like lotus head and fragments of these plates. The discoid plates are highly porous with an approximate size 50 μm. The porous structure of the diatomite is expected to improve its adsorption performance. For the La-modified diatomite, there is no significant change in the morphologies after the modification. The content of lanthanum element is found to be about 1.5% (atomic ratio), as presented in Fig. 2. Meanwhile, the EDX analysis shows the atomic ratios of Si and C are 21.7% and 12.3%, respectively, for the La-modified diatomite. After TC adsorption, the atomic ratios of Si and C become 18.2% and 22.3%, respectively. This indicates that a considerable amount of TC was adsorbed onto the La-modified diatomite.

1-2. XRD Patterns of Raw Diatomite and Used La-modified Diatomite

The XRD patterns of raw diatomite and used La-modified diatomite after adsorption were examined and presented in Fig. 3. Two common peaks at $2\theta=21.8°$ and $26.6°$ were observed for both samples. The strong and broad peak at $2\theta=21.8°$ is related to the diffraction peak of cristobalite (JCPDS NO. 39-1425), while the weak peak at $2\theta=26.6°$ is attributed to quartz (JCPDS NO. 46-1045). The two peaks are the major characteristic peaks of diatomite. Apparently, the XRD patterns of the used La-modified diatomite are almost identical to those of raw diatomite except for an insignificant broadening of the peak, which might indicate the intercalation of lantha-
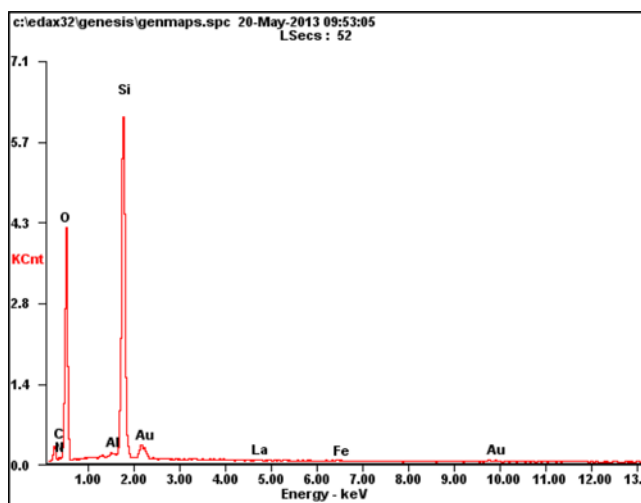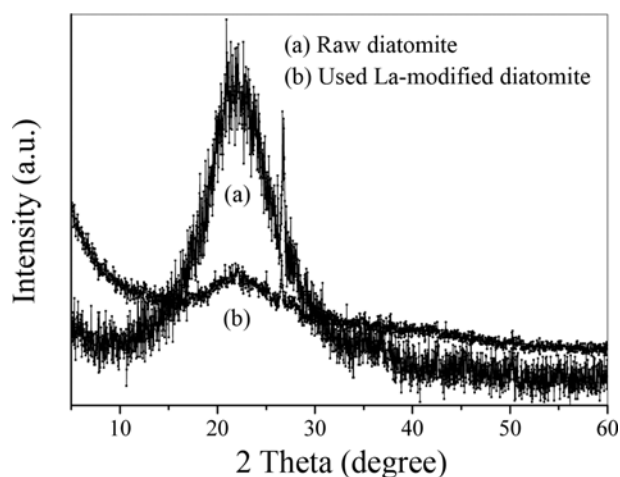

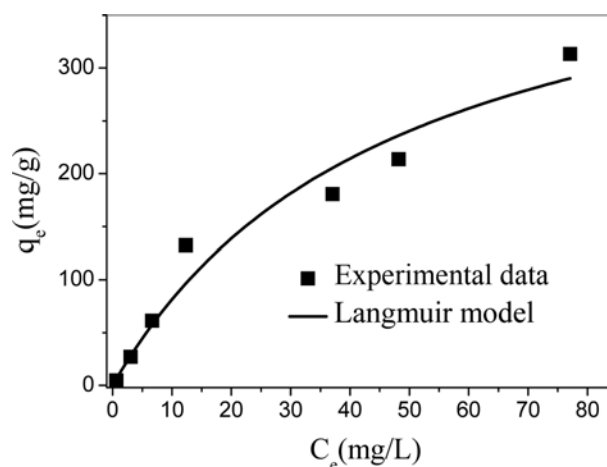Fig. 3. XRD patterns of raw diatomite (a) and used La-modified diatomite (b).

Fig. 4. Langmuir adsorption isotherm of TC onto La-modified diatomite.

num. This demonstrates that the structure of diatomite was not significantly changed after modification and adsorption process, indicating the uptake of TC occurred on the external surface of the adsorbent [22].

2. Adsorption Isotherm

Sorption isotherm of TC on La-modified diatomite is plotted in Fig. 4. The experimental data are well fitted by Langmuir isotherm model [23]. The Langmuir equation is represented as:
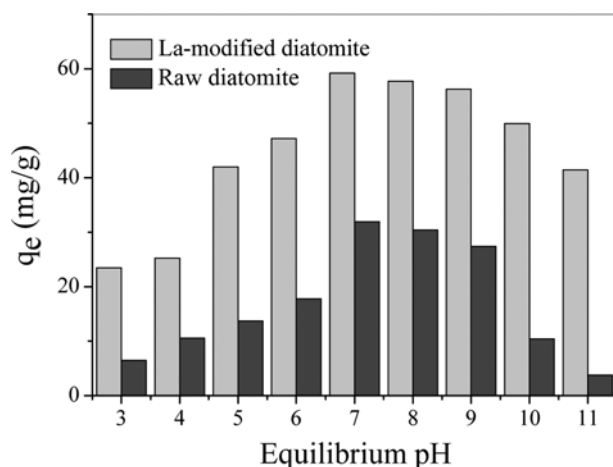
$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \tag{1}$$

where q_e is the amount of tetracycline adsorbed onto La-modified diatomite (mg/g), C_e is the equilibrium concentration (mg/L), q_m is the maximum adsorption capacity of the sorbent (mg/g) and k_L is the equilibrium adsorption constant related to the affinity of binding sites (L/mg).

As illustrated in Fig. 4, the correlation coefficient of Langmuir model is 0.952 and the experimental data are fitted well by Langmuir model. For the La-modified diatomite, the maximal adsorp-

Fig. 2. EDX graph of La-modified diatomite.

Table 1. Comparison of TC adsorption capacities on various adsorbents

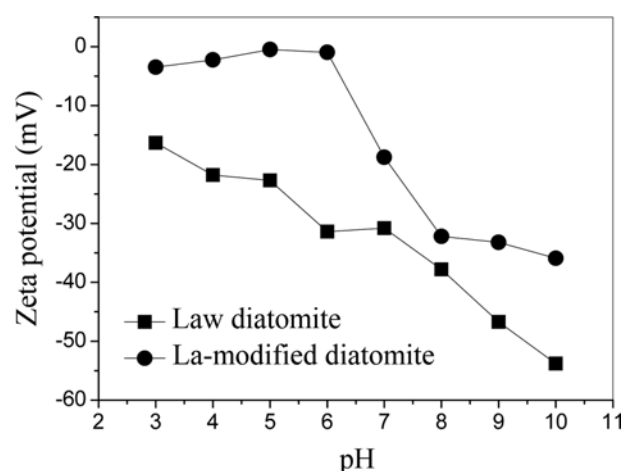| Sorbents q$_m$ (mmol kg^{-1})		References
La-modified diatomite	1056.9	This study
MnFe$_2$O$_4$/activated carbon	590.5	[17]
Fe/OMC-100	433	[15]
Palygorskite	210	[22]
Rectorite	290	[13]
Marine sediments	35-69	[24]
Chitosan	93.04	[25]
Benzyldimethylhexacylammonium	10[a]	[6]
Clays	1.66	[21]
Single-walled carbon nanotubes	800-900[a]	[2]
Multi-walled carbon nanotubes	90-100[a]	[2]
Graphite	70-8.0[a]	[2]
Activated carbon	30[a]	[2]

[a]The estimated values according to the isotherms of the literatures

Fig. 5. Effect of solution pH on TC adsorption.

tion capacity of the Langmuir model is 469.7 mg/g, which equals to 1056.9 mmol/kg. Table 1 summarizes the maximal adsorption capacities of other adsorbents reported in the literature. Note the La-modified diatomite exhibited the much higher maximal adsorption capacity for TC than other adsorbents.

3. Effect of Solution pH on TC Adsorption

Batch adsorption experiments were carried out to evaluate the effect of pH on TC adsorption by the La-modified diatomite and raw diatomite from pH 3.0 to 11.0, as presented in Fig. 5. It demonstrates that TC adsorption was strongly pH dependent for both adsorbents. The change in the adsorption capacity of the two adsorbents under different equilibrium pH conditions followed the similar trend as well. Under acidic conditions, the adsorption of TC increased dramatically with an increase in solution pH, while the TC uptake decreased gradually with increasing pH under alkaline conditions. The maximum TC uptake was observed at pH 7.0, and the adsorption capacity achieved 59.2 and 31.9 mg/g for La-modified diatomite and raw diatomite, respectively. This indicates that lanthanum species immobilized on diatomite enhanced TC uptake

Fig. 6. Zeta-potential of raw diatomite and La-modified diatomite. Adsorbent dose=200 mg/L, ionic strength 0.01 M NaNO$_3$, equilibrium time 48 h.

significantly. From this point of view, the La-modified diatomite has the great potential for practical water treatment considering its excellent adsorptive performance at neutral pH which is the environmental conditions of natural waters.

For both La-modified diatomite and raw diatomite, their surface functional groups result in an increase in the negative charge density with the increasing solution pH, which is confirmed by their zeta potentials as a function of solution pH presented in Fig. 6. Meanwhile, from pH 6.0 to 9.0, a dramatic decrease of zeta potentials was observed for both adsorbents. It was reported that the pH$_{zpc}$ of diatomite was typically below pH 3.0 because of a permanent structural negative charge caused by Si-OH [26]. In contrast, all the zeta potentials detected from pH 3.0 to 11.0 for both adsorbents were below zero, while those of La-modified diatomite were obviously higher than those of raw diatomite. On the other hand, TC (H$_2$L) is an amphoteric compound with pK$_a$ values at 3.3, 7.7 and 9.7 [16]. Its predominant species are expected to be cation (H$_2$L$^+$) at pH< 3.3, zwitterions (H$_2$L^0) at 3.3<pH<7.7, and negatively charged anions (HL$^-$, L^{2-}) at pH>7.7. Under basic conditions, both TC and La-modified diatomite are negatively charged and the repulsive force between them are expected to increase with increasing pH, which results in the decrease in the TC removal. Similarly, both TC and La-modified diatomite are more negatively charged and the increased repulsive force would decrease TC uptake. By contrast, at near neutral pH conditions, TC molecules are zwitterions and their negative charge density increases gradually with the increasing pH. For La-modified diatomite, its negative charge density is enhanced more sharply from pH 6.0 to 8.0 compared with those under acidic conditions. Their repulsive force might be the weakest so that the highest TC uptake was achieved.

4. Adsorption Kinetics of TC on Lanthanum Modified Diatomite

Adsorption kinetics is often used to evaluate the performance of an adsorbent. The kinetics of TC adsorption is plotted in Fig. 7. It can be observed that most of TC was quickly adsorbed within the initial 15 min and the adsorption equilibrium was achieved within 24 h. Similar TC adsorption kinetics was also observed on a low
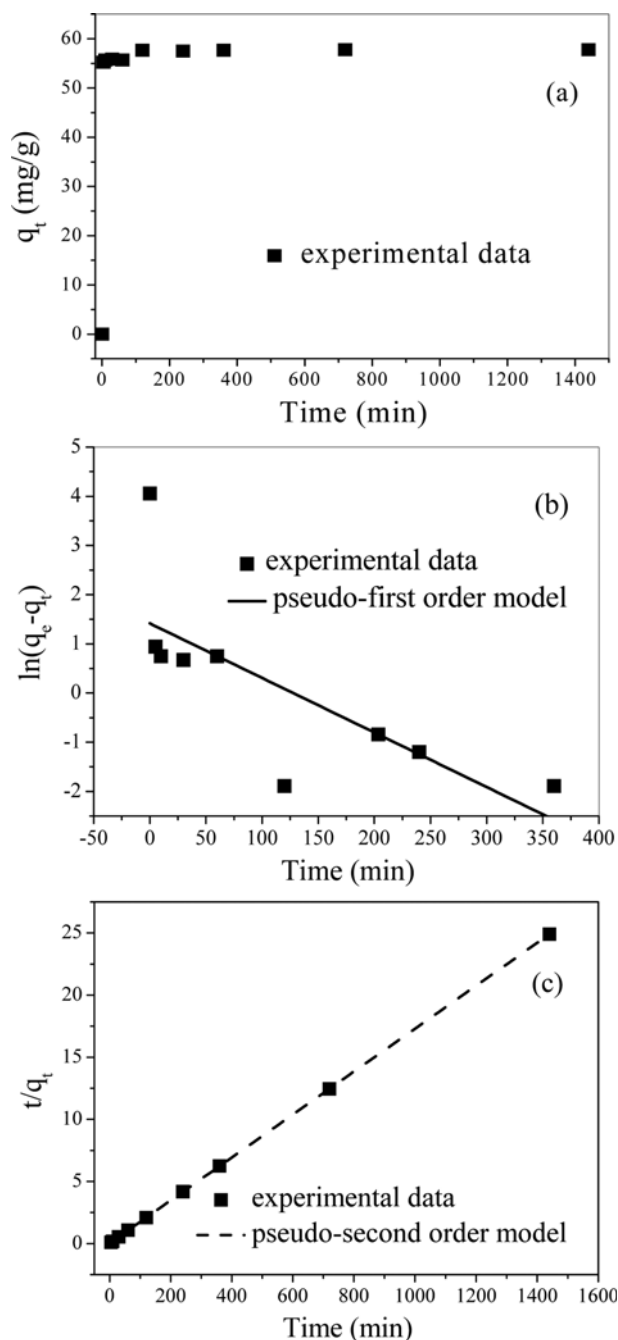
Fig. 7. Adsorption kinetics (a) and linear adsorption kinetics simulation (b), (c) of TC onto La-modified diatomite.

charge Na-montmorillonite SAZ-1 [27]. As a result, an adsorption time of 24 h was used in the following tests. Pseudo-first-order and

pseudo-second-order kinetics models were used to fit the experimental data. Usually, pseudo-second-order kinetics model is used to describe chemisorption of pollutants from aqueous solution onto sorbent.

The nonlinear pseudo-first-order model can be expressed as [28]:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{2}$$

The nonlinear pseudo-second-order model can be expressed as [29]:

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

The mathematical representations of the linear models of pseudo-first-order and pseudo-second-order kinetics are given in the following equations [30]:

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where q_e and q_t are the adsorption capacities (mg/g) of the adsorbent at equilibrium and at time t (min), respectively; and k_1 (min^{-1}) and k_2 (g/(mg min)) are the related adsorption rate constants for pseudo-first-order and pseudo-second-order model, respectively.

Note that the non-linear kinetic models of both pseudo-first-order and pseudo-second-order models well fit the experimental data. Their correlation coefficients (R^2) are both above 0.996 as shown in Table 2. The q_e values derived from the pseudo-first-order and pseudo-second-order kinetics are 56.8 and 57.3 mg/g, respectively, which are very close to the experimental value. By contrast, the correlation coefficients of the linear pseudo-first-order and pseudo-second-order kinetics were of 0.479 and 0.999, respectively. The related q_e values from pseudo-first-order and pseudo-second-order kinetics are of 4.12 and 57.9 mg/g. Apparently, the experimental data are well fitted only by linear pseudo-second-order kinetics model. The linear pseudo-first-order kinetics fails to fit the data. Given both linear and non-linear pseudo-second-order kinetics model can fit the experimental data, the TC adsorption might be chemisorption to some extent. However, it failed to discern which non-linear kinetics better fit the experimental adsorption data in this research.

5. Effect of Ionic Strength

To better understand the adsorption mechanism of TC onto La-modified diatomite, the effect of ionic strength of solution on the adsorptive removal of TC was studied under different pH conditions, as presented in Fig. 8. It can be seen that solution pH has a significant influence on the adsorption capacity at different ionic strength in the pH range from 3.0 to 11.0, which is consistent with the aforementioned pH effect result. The increasing the ionic strength

Table 2. The non-linear and linear kinetic model parameters for the adsorption of TC on La-modified diatomite

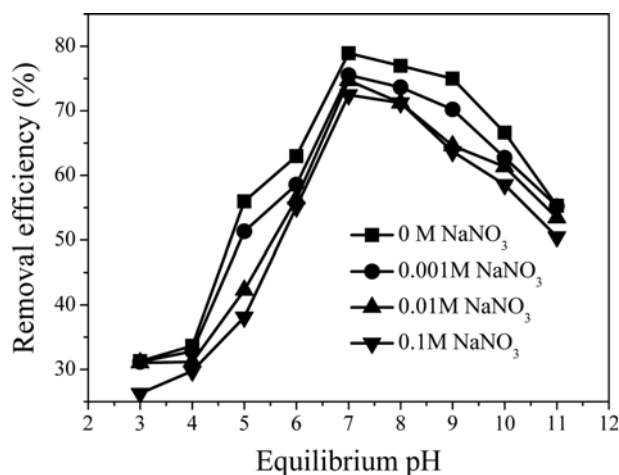| Model	Pseudo-first-order model			Pseudo-second-order model		
	k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 (g/(mg·min))	q_e (mg/g)	R^2
Non-linear linear	118.77	56.8	0.996	0.0777	57.3	0.998
Linear	0.0110	4.12	0.479	0.0285	57.9	0.999

Fig. 8. Effect of ionic strength on TC adsorption under different pH conditions.

from 0.001 M to 0.1 M NaNO$_3$ did not change the position of the pH edge in the pH range from 3.0 to 11.0.

It is well known that anions adsorbed by outer-sphere association are strongly sensitive to ionic strength. As weakly adsorbing anions such as NO$_3^-$ can also form outer-sphere complexes through electrostatic forces, the adsorption of anions is suppressed by the competition. By contrast, anions adsorbed by inner-sphere association either show little sensitivity to ionic strength or respond to higher ionic strength with greater adsorption [31,32]. Hence, the experimental results suggest that TC adsorption on La-modified diatomite may form out-sphere surface complexes. Meanwhile, the screening effect, i.e., placing Na$^+$ and NO$_3^-$ between TC and La-modified diatomite, was observed with increasing ionic strength, indicating the TC adsorption on La-modified diatomite was dominantly attributed by electrostatic interaction. Actually, the hydrolysis of La(III) in aqueous media could produce a number of Lanthanum hydroxides with abundant OH groups, which are deduced to

form out-sphere surface complexes with TC molecules during adsorption.

6. FTIR Analysis

The FTIR spectra of the La-modified diatomite before and after TC adsorption are recorded in Fig. 9. The bands at 471, 806, 1,090 and 1,200 cm^{-1} are ascribed the vibrations of Si-O. Due to the low content of TC on the used sorbent, no apparent difference is observed between the backbone vibration of the silicate structure of the diatomite before and after TC adsorption, indicating that the TC adsorbed does not alter the sorbent structure [22]. However, a weak increase of the intensity of bands at 2,852 and 2,925 cm^{-1} is observed after TC adsorption. The two bands may be attributed to the vibration of C-H stretching of CH$_3$ and CH$_2$ in aromatic molecules [33]. The frequency at 1,629 cm^{-1} ascribed to C-O stretching became broader while the band at 1,382 cm^{-1} ascribed to C=C skeleton stretching became stronger [34]. These provide further evidence that TC molecules have been adsorbed onto the La-modified diatomite.

CONCLUSION

Natural mineral diatomite was successfully modified by lanthanum species by an ion exchange process to enhance its adsorption performance for tetracycline removal. Though the content of lanthanum was very low (1.5%, atomic ratio), the prepared adsorbent exhibited a maximal adsorption capacity as high as 1056.9 mmol/kg, higher than all other carbonaceous and non-carbonaceous adsorbents reported in the literature. Neutral pH conditions were favorable for the adsorptive removal of tetracycline, which is beneficial for practical application. A high adsorption rate was observed, while most of tetracycline molecules were quickly adsorbed within the initial 15 min. Pseudo-second-order kinetic model better fit the kinetic data than pseudo-first-order kinetic model. The increasing ionic strength suppressed the adsorption, indicating that the tetracycline molecules were adsorbed on the external surface of prepared adsorbent via out-sphere surface associations. The results show that the above demonstrates that La-modified diatomite is a prospective adsorbent for organic pollutant removal.

ACKNOWLEDGEMENTS

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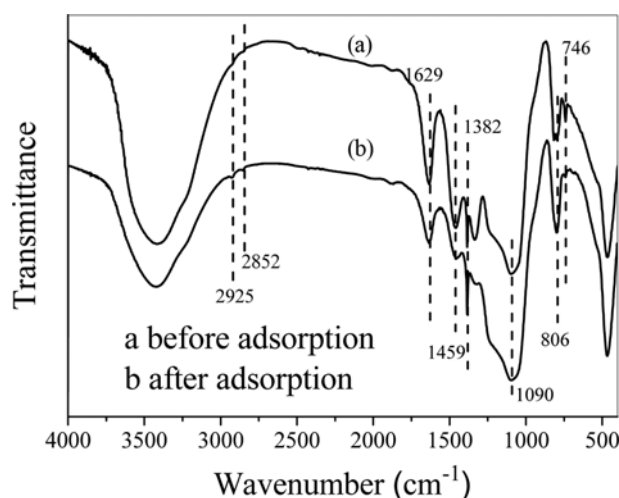

Fig. 9. FTIR spectra of La-modified diatomite before (a) and after TC adsorption (b).

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