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# Highly effective sequestration of Cd(II) from aqueous solution using marine diatom biomass: Adsorption performances and mechanism

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Highly efficient, economic feasible and environmentally friendly adsorbents have been a research hotspot for Cd(II) sequestration. In this study, various nonliving marine diatom biomass were prepared for Cd(II) removal. The Cd(II) adsorption properties of the diatom biomass was unveiled by adsorption kinetic, isotherm and thermodynamic analysis, and the adsorption mechanism was revealed using spectrometric identification methods. Results suggested that nonliving marine diatom biomass (*Chaetoceros*, *Nitzschia*, and *Thalassiosira* sp.) could efficiently remove Cd(II) from aqueous solution, with nonliving *Nitzschia* possessing the highest adsorption capacity. The adsorption capacity of nonliving *Nitzschia* was 289–430 mg g<sup>-1</sup> (288–308 K) in the absence of ionic competition and under low turbidity conditions, which was much higher than that of most of adsorbents of great concern. The kinetic, isotherm and thermodynamic analysis suggested the adsorption of Cd(II) was a spontaneous, endothermic and chemisorption involved process. Moreover, inorganic salts and turbidity showed negative effects on Cd(II) adsorption, whereas humic acid showed a positive effect. Adsorption mechanism analysis demonstrated that amine and pyrrolic nitrogen groups were responsible for Cd(II) adsorption. It is also worth noting that organics leaching during adsorption would also affect chemical bonds distribution on the biomass, which should be taken into account when elucidating the heavy metal adsorption mechanism of bio-adsorbents.

## KEYWORDS

heavy metal, cadmium ions, adsorption, microalgae, marine diatom

## 1 Introduction

Cadmium, one of the toxic and commonly used heavy metals, is released into the environment through a number of anthropogenic activities, including the manufacturing of batteries, pigments, screens, and the combustion of fossil fuels. (Ozer and Pirinççi, 2006). Cadmium ions are not only present in aquatic solutions but can also get concentrated through food chains (e.g., rice). Drinking water or eating food containing cadmium can cause a series of health problems (Dinesh and Singh, 2002).

Due to the toxic implications of cadmium ions, the removal of cadmium from aqueous environments is a focus of many ongoing research studies. Among the techniques,

adsorption has been proven to be one of the most efficient, popular, and cost-effective methods for cadmium ion removal from an aqueous solution (Burakov et al., 2018). With increasing emphasis on sustainable development, economically feasible and environmentally friendly adsorbents have become a research hotspot (Zhou et al., 2018). Bio-adsorbents have been widely reported as efficient and eco-friendly adsorbents for heavy-metal sequestration, which includes algae, bacteria, fungi, natural organic matters, and agroforestry wastes (Bilal et al., 2013; He and Chen, 2014; Zeraatkar et al., 2016). Among these adsorbents, algae biomass is a great alternative bio-adsorbent for heavy metal removal because algae can use carbon dioxide as a carbon source *via* photosynthesis, which makes it more eco-friendly and sustainable than other microorganism adsorbents (Shang et al., 2015).

The algae species used for cadmium adsorption mainly include living and non-living green, red, and brown algae (Sheng et al., 2004; He and Chen, 2014; Suresh et al., 2015). There is more inclination to use marine algae than freshwater algae to treat heavy-metal wastewater because freshwater shortage has become a worldwide issue. Marine macroalgae, including green algae, red algae, and brown algae, were widely reported as effective adsorbents for Cd(II) sequestration from aqueous solution (Davis et al., 2003; Ibrahim, 2011; He and Chen, 2014). However, very few studies concerning heavy-metal removal by marine microalgae, which are very widespread in the ocean, were conducted. Diatom, which is a common microalgae species in the ocean and accounts for over 40% of marine primary production, contributes considerable biomass to the marine ecosystem (Armburst, 2009; Ma et al., 2018). The cell wall of a diatom mainly consists of C, O, N, Si, S, and P elements and possesses abundant chemical bonds, including -OH, -COOH, -COOM, -NH<sub>2</sub>, -R<sub>2</sub>NH, -SO-, -PO-, -HC=O, R<sub>2</sub>C=O, -NO-, -CH<sub>3</sub>, and -CH<sub>2</sub>- (Ma et al., 2018). Moreover, a silicon skeleton with an abundant microporous structure consisting of the cell wall of a diatom would make the diatom provide more adsorption sites than other algae species. From these aspects, it is likely that marine diatoms possess great potential to be an efficient and economic bio-adsorbent for heavy-metal ion removal. At present, only a few studies focus on the physiological and biochemical responses of freshwater diatom to metal ions, which reveals that some living diatom species can uptake and tolerate some heavy metal ions (Morin et al., 2008; Guo et al., 2010; Ding et al., 2012; Ma et al., 2018).

Therefore, in the present study, the potentials of three non-living marine diatom species (*Chaetoceros* sp., *Nitzschia* sp., and *Thalassiosira* sp.) have been examined for sequestration of Cd(II) from aqueous solution. The adsorption process was analyzed using various kinetic, isothermal, and thermodynamic models. Meanwhile, influences of environmental substances, including inorganics, turbidity, and humic acids, on the adsorption were also investigated. Moreover, the mechanisms of Cd(II) adsorption of dry inactivated biomass of marine diatom were fully studied. This is among the first studies to unveil the potential of various kinds of non-living marine diatom biomass species to adsorb Cd(II) from an aqueous solution.

## 2 Materials and methods

### 2.1 Preparation of bio-adsorbent

The three pure marine diatom strains, which belong to *Chaetoceros* sp., *Nitzschia* sp., and *Thalassiosira* sp., respectively, were isolated from Dapeng Bay of Shenzhen City, China. The cultivations of pure marine diatom were carried out in f/2 media (Guillard et al., 1975) under aeration conditions and harvested at the end of the stationary phase. The harvested diatom solution was centrifuged at 4,000 r/min for 10 min (Hettich UNIVERSAL 5810R, Germany). The collected biomass was re-suspended in deionized water and centrifuged under the same condition three times to remove the impurities in the culture. Then, the diatom biomass was freeze-dried in a refrigerated compressed air dryer (Labconco FreeZone 2.5, United States). The obtained dry biomass samples were maintained in a drying basin for the preparation experiments.

### 2.2 Batch Cd(II) adsorption experiments

Batch adsorption experiments were carried out in plastic centrifuge tubes containing 50 mL metal ion solution with known initial concentrations varying from 10 to 700 mg/L. The adsorbent dose was set to 1 g/L, and the pH of the metal ion solution was 6.4. The tubes were agitated in a shaker at 100 rpm and subjected to a temperature of 25°C for 24 h to ensure the adsorption reached equilibrium. The sample was taken from each tube at various intervals (5, 10, 15, 20, 30, 60, 120, 360, 720, and 1440 min). The samples were then centrifuged at 4,000 rpm for 10 min, and the supernatants were filtered (0.22 μm). The resulting solution was diluted with distilled water and then used for heavy-metal concentration measurement (ICP, Shimadzu ICPE-9000, Japan), and each measurement has three parallel samples in order to reduce the random errors. All experiments were performed twice. In order to investigate the influences of co-existing substances in natural water on Cd(II) adsorption by the biomass, the adsorption assays under different levels of common cations in water (Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>), turbidity, and humic acid were also conducted, respectively.

### 2.3 Characterization of bio-adsorbent

The surface morphology of adsorbents was examined using a scanning electron microscope equipped with an energy-dispersive X-ray analyzer (Hitachi, S4800, Japan). The surface chemical groups of the adsorbents were identified using Fourier-transform infrared (FTIR) spectroscopy (KBr pellets; IR Prestige-21 FTIR spectrometer, Shimadzu, Japan) in the range 400–4,000 cm<sup>-1</sup>. The Brunauer–Emmett–Teller (BET) surface areas and pore size distributions of the adsorbents were determined using a TriStar II 3020 series surface area and porosity analyzer (Micromeritics Instrument Corporation, United States). The chemical states of atoms on the surface of the adsorbents before and after Cd(II) adsorption were analyzed using X-ray photoelectron spectroscopy (XPS; PH 1800, Japan).

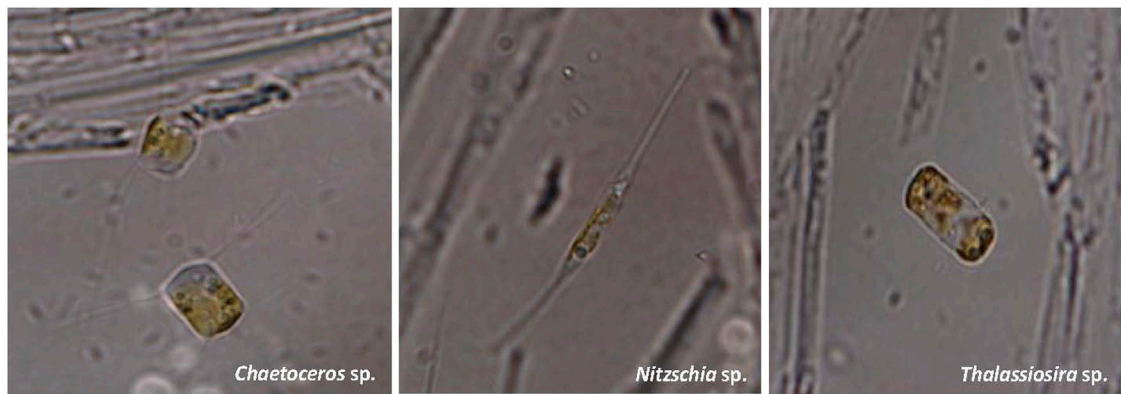


FIGURE 1  
Fluorescence microscope images of *Chaetoceros* sp., *Nitzschia* sp., and *Thalassiosira* sp.

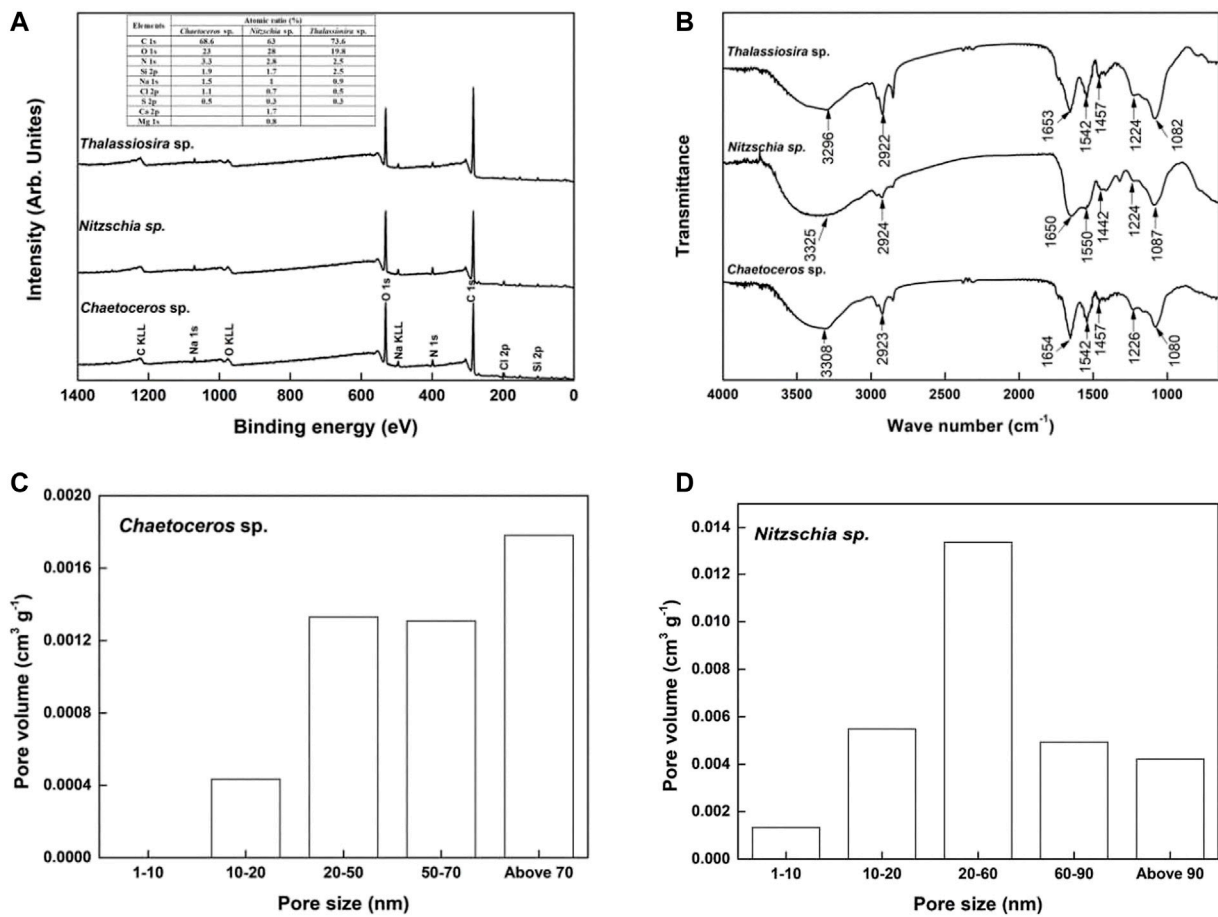
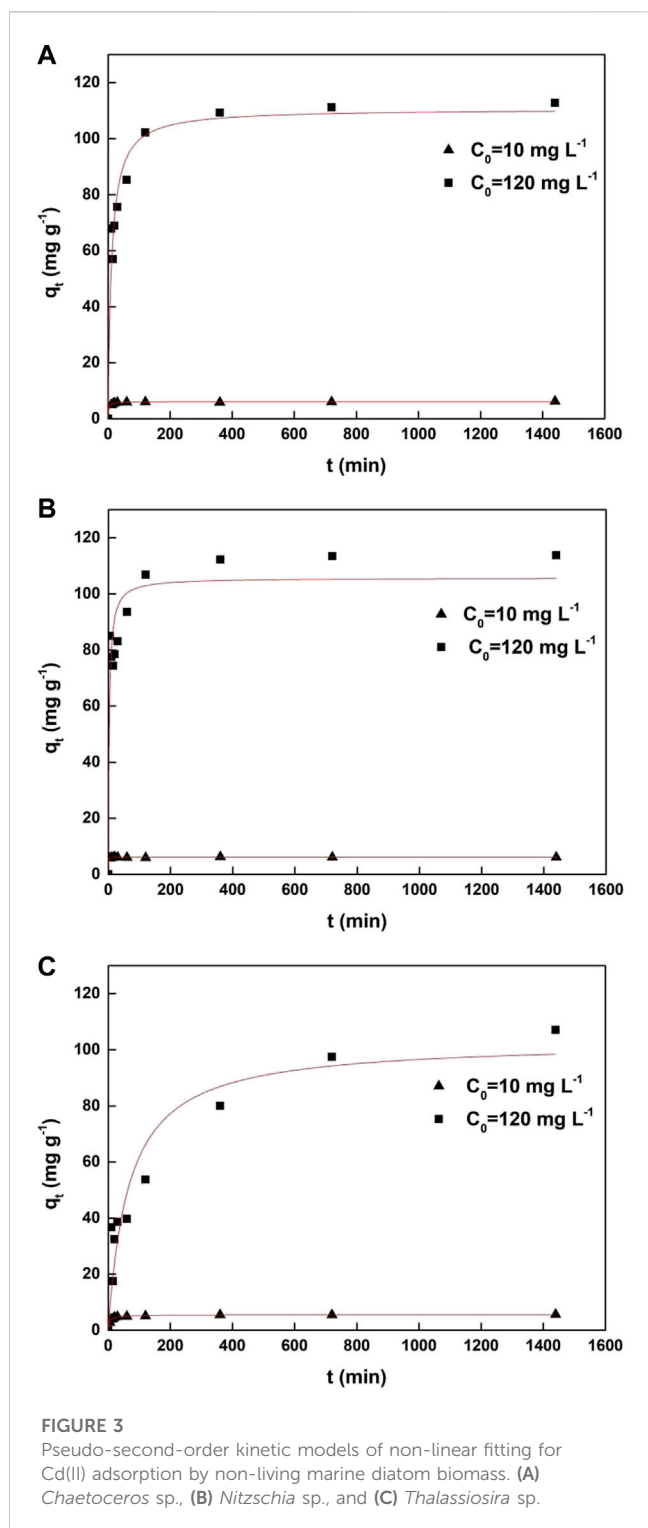


FIGURE 2  
Properties of non-living diatom biomass. (A) XPS spectrum, (B) FTIR spectrum, and (C–D) Pore size distribution.



## 2.4 Analysis

### 2.4.1 Adsorption amount of Cd(II)

The adsorption amount of Cd(II) per unit mass of the diatom biomass at equilibrium ( $q_e$ ,  $\text{mg g}^{-1}$ ) and the adsorption amount of Cd(II) per unit mass of adsorbent at time  $t$  ( $q_t$ ,  $\text{mg g}^{-1}$ ) were determined as follows:

$$q_t = \frac{(C_0 - C_t)V}{W}, \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{W}, \quad (2)$$

where  $C_0$  ( $\text{mg L}^{-1}$ ),  $C_t$  ( $\text{mg L}^{-1}$ ), and  $C_e$  ( $\text{mg L}^{-1}$ ) are the heavy-metal concentrations at time zero, time  $t$ , and at equilibrium, respectively;  $V$  is the volume of the solution (L); and  $W$  is the mass of dry adsorbent used (g).

### 2.4.2 Kinetic study

Pseudo-second-order model is widely used for bio-adsorbent to predict the adsorption kinetics. The non-linear form of the pseudo-second-order equation is given by

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

where  $q_e$  and  $q_t$  are the amounts of solute adsorbed ( $\text{mg g}^{-1}$ ) at equilibrium and at any time  $t$  (min), respectively.  $k_2$  is the rate constant for pseudo-second-order reaction ( $\text{g mg}^{-1} \text{min}^{-1}$ ). The straight line plots of  $1/q_t$  versus  $1/t$  are used to obtain the constants for the pseudo-second-order reaction.

### 2.4.3 Adsorption isotherms

The most common adsorption isotherm models, Langmuir and Freundlich, were applied to predict the equilibrium parameters of the Cd(II) adsorption process on the diatom biomass.

The non-linear form of the Langmuir isotherm model can be expressed as

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}, \quad (4)$$

where  $q_e$  is the amount of Cd(II) adsorbed at equilibrium ( $\text{mg g}^{-1}$ ),  $q_m$  is the maximum adsorption capacity ( $\text{mg g}^{-1}$ ),  $C_e$  is the equilibrium concentration of metal ions in solution ( $\text{mg L}^{-1}$ ), and  $K_L$  is the Langmuir constant that is related to the free energy of adsorption ( $\text{L mg}^{-1}$ ).

The non-linear form of the Freundlich isotherm model is given as

$$q_e = K_F C_e^{1/n}, \quad (5)$$

where  $q_e$  is the amount of Cd(II) adsorbed at equilibrium ( $\text{mg g}^{-1}$ ),  $C_e$  is the equilibrium concentration of metal ions in solution ( $\text{mg L}^{-1}$ ),  $K_F$  is the Freundlich constant ( $\text{mg L}^{-1}$ ) that is related to the adsorption capacity of the sorbent, and  $n$  is the Freundlich constant related to the adsorption intensity (dimensionless) of adsorbent.

### 2.4.4 Adsorption thermodynamics

The sorption isotherms of Cd(II) on diatom biomass at 288 K, 298 K, and 308 K were obtained to determine the thermodynamic parameters. The standard Gibbs free energy change ( $\Delta G$ ), standard enthalpy change ( $\Delta H$ ), and standard entropy change ( $\Delta S$ ) were determined from  $K_L$  and  $T$  by the following equations:

$$\Delta G = -RT \ln K_0, \quad (6)$$

$$\ln K_0 = \frac{\Delta S}{R} - \frac{\Delta H}{RT}, \quad (7)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T}, \quad (8)$$

TABLE 1 Kinetic parameters for Cd(II) adsorption onto various non-living marine diatom biomass.

Adsorbent	Initial concentration of Cd <sup>2+</sup>		Pseudo-second-order		
	C <sub>0</sub> (mg L <sup>-1</sup> )	Experiment	q <sub>e</sub> (mg g <sup>-1</sup> )	k <sub>2</sub> (g mg <sup>-1</sup> min <sup>-1</sup> )	R <sup>2</sup>
<i>Chaetoceros</i> sp.	10	6.25	6.14	7.26 × 10 <sup>-2</sup>	0.995
	120	113	111	8.09 × 10 <sup>-4</sup>	0.957
<i>Nitzschia</i> sp.	10	6.15	6.14	7.29 × 10 <sup>-1</sup>	0.997
	120	114	106	2.94 × 10 <sup>-3</sup>	0.876
<i>Thalassiosira</i> sp.	10	5.69	5.53	3.99 × 10 <sup>-2</sup>	0.991
	120	107	103	1.46 × 10 <sup>-4</sup>	0.891

where  $R$  is the universal gas constant ( $8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$ ), and  $T$  is the absolute temperature (K).  $K_0$  is the thermodynamic equilibrium constant. Values of  $K_0$  are obtained by plotting  $\ln(q_e/C_e)$  versus  $q_e$ . The intercept of the fitting line with the vertical axis gives the values of  $K_0$  (Niwas et al., 2000).  $\Delta H$  was obtained from the slope of the linear plot of  $\ln K_L$  against  $1/T$ , and  $\Delta S$  was obtained from Eq. 8.

## 3 Results and discussion

### 3.1 Characteristics of non-living marine diatom biomass

#### 3.1.1 Cell morphology and composition of the biomass

The cell morphology of *Chaetoceros* sp., *Nitzschia* sp., and *Thalassiosira* sp. strains were measured using a fluorescent microscope. It can be seen from Figure 1 that the cell of *Chaetoceros* sp. was almost round or cylinder-shaped with several strip-shaped matters attached to the cell. In comparison, the cells of *Nitzschia* sp. and *Thalassiosira* sp. were rhombus- and cylinder-shaped, respectively.

As shown in Figure 2A, both the non-living biomass of *Chaetoceros* sp. and *Thalassiosira* sp. consisted of C, O, N, Si, Na, Cl, and S, with a little difference in the atomic ratio of these elements. In comparison, the non-living biomass of *Nitzschia* sp. contained Ca and Mg elements except for C, O, N, Si, Na, Cl, and S, which suggested that the chemical composition on the surface of *Nitzschia* sp. was significantly different from that of *Chaetoceros* sp. and *Thalassiosira* sp.

#### 3.1.2 Functional groups of the biomass

FTIR spectra of the non-living diatom biomass were visualized to obtain information about the chemical bonds presented on the surface of the biomass. The chemical bond information corresponding to each FTIR peak was obtained mainly according to published references (Zhu, 2005; Robert et al., 2007). As shown in Figure 2B, the shapes of FTIR spectra for non-living *Chaetoceros* sp. and *Nitzschia* sp., and *Thalassiosira* sp. biomass were similar, which implies that these three diatom biomasses possess similar chemical groups on the surface. A broad and strong peak ( $3,308 \text{ cm}^{-1}$  for *Chaetoceros* sp.,  $3,325 \text{ cm}^{-1}$  for *Nitzschia* sp., and  $3,296 \text{ cm}^{-1}$

for *Thalassiosira* sp.) assigned to the overlapping of  $-\text{OH}$  and  $-\text{NH}$  stretching bands of polymeric compounds. The peaks at around  $2,923 \text{ cm}^{-1}$  represented the stretching vibration of  $-\text{CH}_3$ . The peaks at around  $1,653 \text{ cm}^{-1}$  were due to the overlapping of  $\text{C}=\text{O}$  stretching vibration and  $\text{C}=\text{C}$  bonds, respectively. The peaks at around  $1,550$  and  $1,450 \text{ cm}^{-1}$  could be assigned to the stretching vibration of  $\text{N}-\text{H}$  and variable angle vibration of  $-\text{CH}_2-$ , respectively. The peak at around  $1,080 \text{ cm}^{-1}$  represented the overlapping of  $\text{C}-\text{O}$  vibration in the alcoholic hydroxyl group and  $\text{Si}-\text{O}-\text{Si}$  stretching vibration. These results indicated that the non-living biomass of *Chaetoceros* sp., *Nitzschia* sp., and *Thalassiosira* sp. contained diverse chemical groups, such as carbonyl, hydroxyl, and amine groups, on its surface, which were potential binding sites for the heavy-metal ion (González et al., 2011; He and Chen, 2014).

#### 3.1.3 Surface area and porous distribution of the biomass

The BET surface area of non-living *Chaetoceros* and *Nitzschia* were  $0.7$  and  $4.6 \text{ m}^2 \text{ g}^{-1}$ , respectively, while the BET surface area of non-living *Thalassiosira* was not detected under the same weight condition as the other two species. This result suggested that *Nitzschia* possesses the highest surface area, followed by *Chaetoceros*, and *Thalassiosira* possesses the lowest. The cumulative pore volume of non-living *Chaetoceros* and *Nitzschia* were  $0.0048$  and  $0.0293 \text{ cm}^3 \text{ g}^{-1}$ , respectively. Moreover, it is clear from Figure 2D that mesopores took up the majority of pore volume on the surface of non-living *Nitzschia*, followed by macropores, and micropores took up the least. In comparison, the surface of non-living *Chaetoceros* was occupied by macropores, followed by mesopores, with no micropores on it (Figure 2C). These results indicated that non-living *Nitzschia* biomass possesses a more abundant pores structure than the other two diatom species.

### 3.2 Adsorption behavior of Cd(II) on non-living marine diatom biomass

#### 3.2.1 Adsorption kinetics

As shown in Figure 3 and Table 1, the results show that Cd(II) adsorption by all the diatom biomass fit the pseudo-second-order model very well, with a correlation coefficient  $R^2 > 0.88$ . For initial Cd(II) concentration of  $10$  and  $120 \text{ mg L}^{-1}$ , the equilibrium



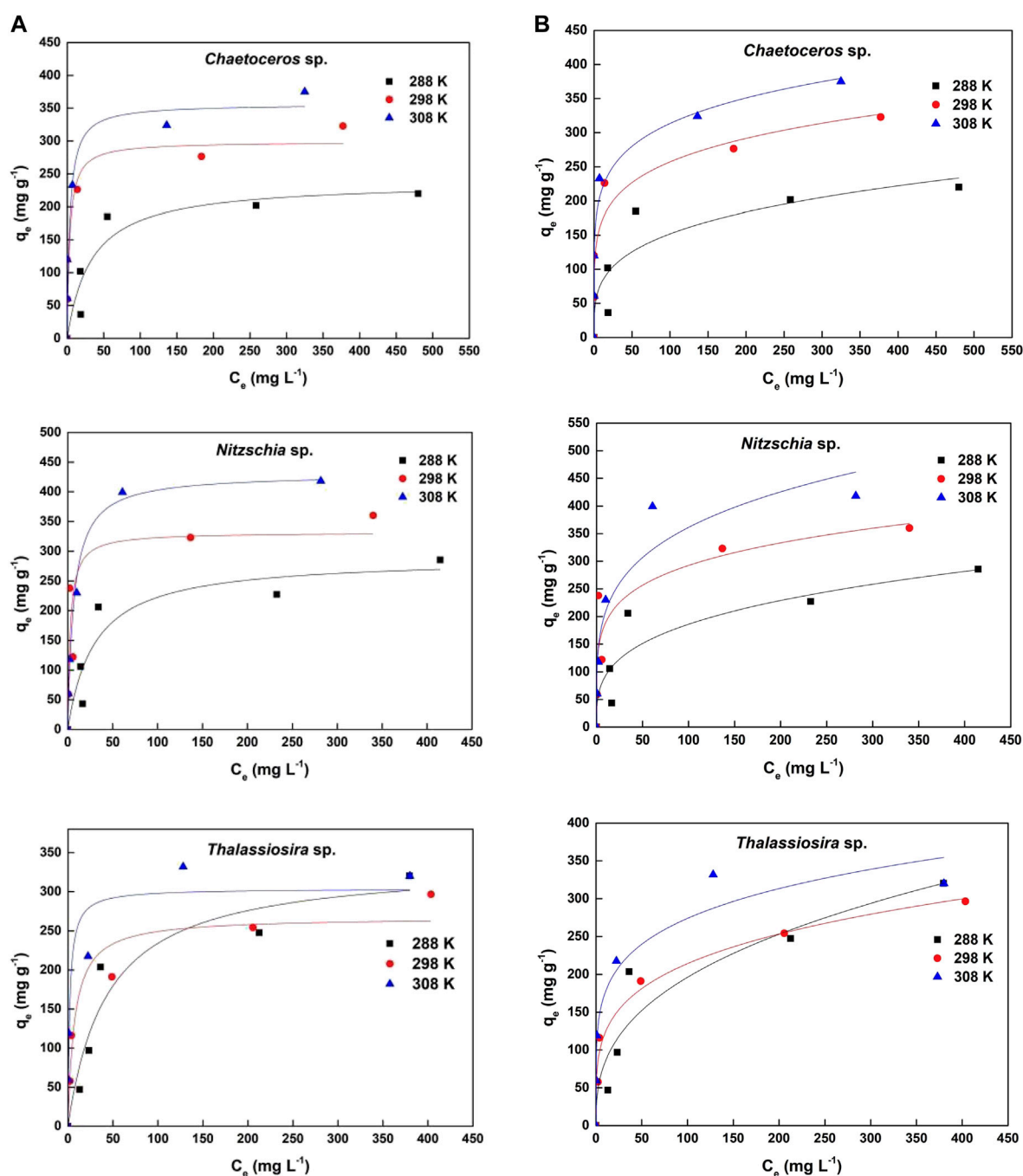


FIGURE 4

(A) Langmuir isotherm and (B) Freundlich isotherm non-linear fittings for Cd(II) adsorption by three kinds of non-living marine diatom biomass.

adsorption amount of Cd(II) by *Chaetoceros* sp., *Nitzschia* sp., and *Thalassiosira* sp. were calculated to be 6.14, 6.14, and 5.53 mg g<sup>-1</sup> and 111, 106, and 103 mg g<sup>-1</sup>, respectively, which were in good agreement with the experimental capacities of 6.25, 6.15, and 5.69 mg g<sup>-1</sup> and 113, 114, and 107 mg g<sup>-1</sup>, respectively. The suitability of the pseudo-second-order model indicates that chemical interaction is the rate-controlling step in the whole adsorption process, and the adsorption behavior involves valence forces through sharing of electrons between metal ions and the

diatom biomass. Furthermore, the tendency of the adsorption rate constant ( $k_2$ ) was calculated according to the model as follows: *Nitzschia* sp. > *Chaetoceros* sp. > *Thalassiosira* sp., suggesting that Cd(II) was adsorbed fastest by non-living *Nitzschia*, followed by non-living *Chaetoceros*, and the slowest by non-living *Thalassiosira*.

### 3.2.2 Adsorption isotherms

The Cd(II) equilibrium adsorption data were fit to the non-linear Langmuir and Freundlich adsorption isotherm models

**TABLE 2** Non-linear fit parameters of Langmuir and Freundlich models and thermodynamic parameters for Cd(II) adsorption onto various non-living marine diatom biomass.

Adsorbent	Temperature	Langmuir model			Freundlich model			Adsorption thermodynamics		
	(K)	$Q_m$ (mg g <sup>-1</sup> )	$K_L$ (L mg <sup>-1</sup> )	$R^2$	$K_F$ (mg L <sup>-1</sup> )	$n$	$R^2$	$\Delta G$ (kJ mol <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )
<i>Chaetoceros</i> sp.	288	238	0.0303	0.877	42.9	3.64	0.795	-1.60	57.7	206
	298	299	0.296	0.752	111	5.51	0.712	-3.66		
	308	356	0.271	0.790	148	6.14	0.820	-5.72		
<i>Nitzschia</i> sp.	288	289	0.0336	0.853	47.0	3.35	0.813	-1.50	42.1	151
	298	332	0.359	0.764	123	5.30	0.825	-3.02		
	308	430	0.147	0.986	122	4.23	0.905	-4.53		
<i>Thalassiosira</i> sp.	288	336	0.0229	0.915	36.1	2.72	0.883	-1.76	44.4	160
	298	267	0.137	0.934	70.3	4.13	0.976	-3.36		
	308	304	0.492	0.929	113	5.19	0.937	-4.96		

(Figure 4). The calculated parameters corresponding to the two models were summarized in Table 2. For all temperature conditions (T = 288, 298, and 308 K), based on the values of correlation coefficient ( $R^2$ ), the adsorption data of Cd(II) by three diatom biomass fit both the Langmuir and Freundlich models well. Furthermore, for every non-living diatom biomass, the Langmuir constant ( $K_L$ ) generally increased with temperature, which indicates that the adsorption of Cd(II) by the diatom biomass was an endothermic reaction process and higher temperature within some range favors the adsorption. The generally higher values of Freundlich constants ( $K_F$  and  $n$ ) under higher temperatures also indicated that the adsorption processes of the three diatom biomass can be promoted by temperature.

As shown in Table 2, for the temperature ranging from 288 K to 308 K, the theoretical  $q_{max}$  of *Chaetoceros* sp., *Nitzschia* sp., and *Thalassiosira* sp. were 238–356 mg g<sup>-1</sup>, 289–430 mg g<sup>-1</sup>, and 267–336 mg g<sup>-1</sup>, respectively, which indicates that *Nitzschia* sp. possesses better Cd(II) adsorption capacity than *Chaetoceros* sp. and *Thalassiosira* sp. The higher BET surface of non-living *Nitzschia* was probably one of the reasons for its higher adsorption capacity compared with the other two algae species. The highly efficient and newest adsorbents reported elsewhere were selected to compare with the non-living diatom biomass in the present study. As shown in Table 3, in the absence of competitive cations and under low turbidity conditions, the non-living marine diatom biomass in the present study possess much higher Cd(II) adsorption capacity than all the other reported algae species, and also most of the other kinds of bio-adsorbents. In comparison with other adsorbents except for bio-adsorbents, the dry marine diatom biomass still shows better Cd(II) adsorption capacity. Although some reported adsorbents, such as some clay-based materials, nanoscale particles, modified bio-adsorbents, and polymeric substances, showed higher Cd(II) adsorption capacity than the diatom biomass, there is still a long way to go to use these adsorbents in heavy-metal wastewater treatment in future because of complicated modification/preparation processes applied for those adsorbents (Uddin, 2017;

Chen et al., 2018). In addition, nano-materials always face difficult separation and potential biological safety risk problems, which make it hard to apply in wastewater treatment. In comparison, marine diatom biomass was not only highly efficient in adsorbing cadmium ions from an aqueous solution, but it is also easy to obtain and eco-friendly. From these aspects, the dry marine diatom biomass would be a competitive adsorbent used for cadmium wastewater in the future.

### 3.2.3 Adsorption thermodynamics

The thermodynamics parameters, the enthalpy change ( $\Delta H$ ) and entropy ( $\Delta S$ ), were calculated from the linear plot of  $\ln K_0$  versus  $1/T$  and are given in Table 2. The values of  $\Delta H$  were positive for all adsorption cases, which indicates that the adsorption process was endothermic and Cd(II) ions were adsorbed more efficiently on the diatom biomass under higher temperatures. The value of  $\Delta H$  can be used to differentiate chemisorption and physisorption. It was reported by Wang et al. (2012) and Sun et al. (2015) that the adsorption process was mainly physisorptive when  $\Delta H < 20$  kJ mol<sup>-1</sup> and was mainly chemisorptive when  $80 < \Delta H < 400$  kJ mol<sup>-1</sup> or  $40 < \Delta H < 120$  kJ mol<sup>-1</sup>. Therefore, it can be inferred from the  $\Delta H$  values for the three diatom biomass that the Cd(II) adsorption processes of non-living *Chaetoceros* sp., *Nitzschia* sp., and *Thalassiosira* sp. were dominated by chemisorption.

The positive value of  $\Delta S$  indicates that there is an increase in the randomness in the system solid/solution interface during the adsorption process (Xie et al., 2011). The positive entropy change was possibly stemming from the changes taking place in the structure of the adsorbent and dispersing of water molecules from Cd(II) ions surrounded by water molecules during the adsorption process (Ozer and Pirinççi, 2006). Negative values of  $\Delta G$  for three non-living diatom biomass indicated the spontaneous nature of the reaction between Cd(II) and the biomass. The values of  $\Delta G$  became more negative with temperature, which meant that the adsorption process was more favorable at high temperatures.

TABLE 3 Comparisons of Cd adsorption capacities between non-living marine diatom biomass and highly efficient adsorbents reported elsewhere.

Adsorbent		Adsorption capacity (mg g <sup>-1</sup> )	References
Active carbon	Modified AC	46.95	Ge and Wang (2017)
	Mesoporous AC	239.45	González and Pliego-Cuervo (2014)
Clay-based materials	Bentonite methylene bis-acrylamide	416.61	Uddin (2017)
	Hydroxyapatite	142.85	
	Ionic liquid-modified clay	90.5	Naderi et al. (2018)
	Sodium polyacrylate grafted montmorillonite nanocomposite	63.49	Zeng et al. (2023)
Nano-materials	Graphene oxide/SiO <sub>2</sub> /Fe <sub>3</sub> O <sub>4</sub>	166.7	Burakov et al. (2018)
	Graphene oxide/PAMAMs	253.81	Wang et al. (2018)
	Hydroxyapatite NPs	235.7	Dubey et al. (2017)
Metal-organic frameworks	EDTA/chitosan/TiO <sub>2</sub>	209.2	Alizadeh et al. (2018)
	Thiosemicarbazide-modified chitosan	257.2	Li et al. (2016)
	Inorganic sulfur-containing transition metal compound-based MOF	833.3	Yazdi et al. (2021)
Chitosan-based materials	Chitosan-based nanocomposite	341.62	Maity and Ray (2018)
Biochar-based materials	Iminodiacetic acid-modified magnetic biochar	180	Zhou et al. (2018)
	N-doping biochar	211.2	Yu et al. (2018)
	CaCl <sub>2</sub> -modified biochar	92.73	Gao et al. (2023)
Bio-adsorbents	Succinate bonded pullulan	476.2	Dai et al. (2018)
	Sesame	84.74	
	J-g-P (AM-co-AANa) prepared from jute cellulose	344.8	Li et al. (2018)
	LaFe@CS beads	31.5	Lan et al. (2022)
	Brown algae ( <i>Sargassum filipendula</i> )	132	He and Chen (2014)
	Red algae ( <i>Galaxanura oblongata</i> )	85	
	Green algae ( <i>Tetraselmis chuii</i> )	210.54	Kumar et al. (2015)
	Marine diatom ( <i>Chaetoceros</i> sp.)	238–356	This study
	Marine diatom ( <i>Nitzschia</i> sp.)	289–430	This study
	Marine diatom ( <i>Thalassiosira</i> sp.)	267–336	This study

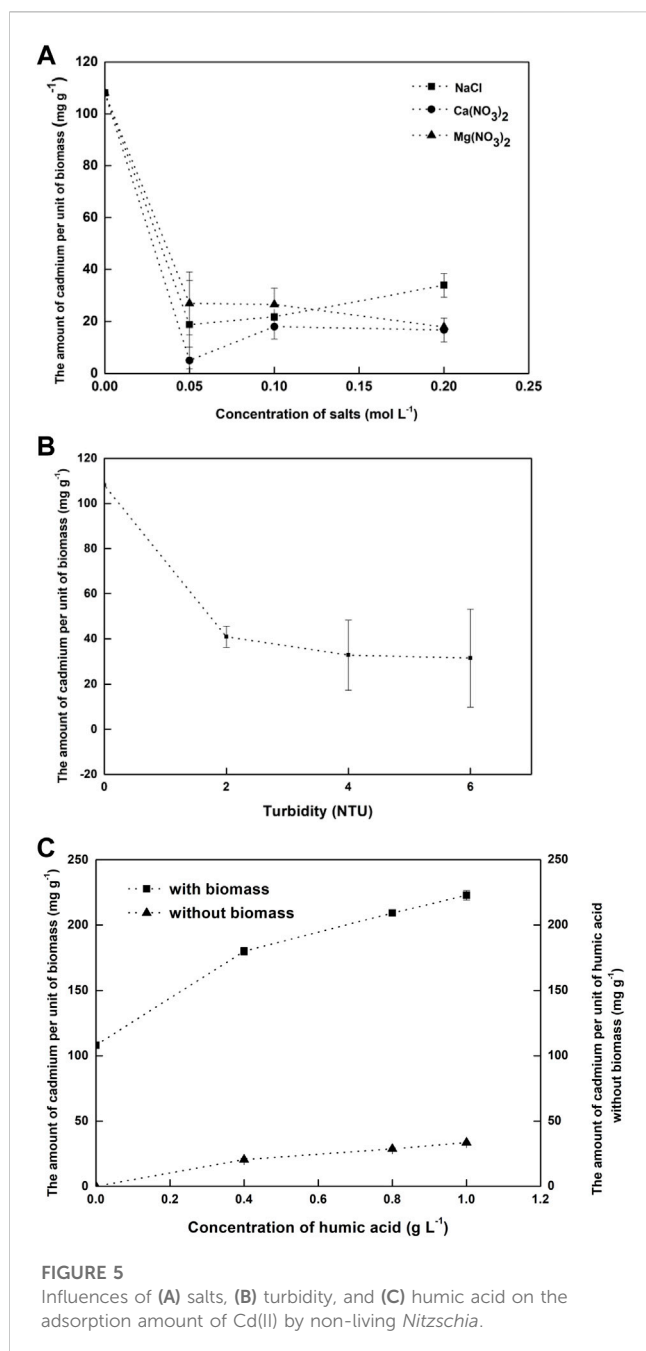
### 3.3 Influences of co-existing substances in natural water on adsorption capacity of Cd(II) by non-living diatom biomass

#### 3.3.1 Inorganic salts

Investigation of the influences of Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> on Cd(II) removal is of great importance due to their general existence in natural water and wastewater. As shown in Figure 5A, the amount of Cd(II) adsorbed by non-living *Nitzschia* decreased sharply from 108.1 mg g<sup>-1</sup> to below 30 mg g<sup>-1</sup> when Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> at 0.05 mol L<sup>-1</sup> were, respectively, added into the adsorption system. As the concentration of Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> increases to 0.05–0.2 mol L<sup>-1</sup>, the amount of Cd(II) adsorbed by non-living *Nitzschia* decreased by 68.7%–88.95%, 83.3%–95.3%, and 75.1%–92.2%, respectively. According to the significance analysis results by

SPSS software, the decreased extent of the amount of Cd(II) adsorbed by the biomass shows no significant correlation to the type of foreign ions ( $p > 0.05$ ), suggesting similar influences of Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> in the range from 0.05 to 0.2 mol L<sup>-1</sup> on the amount of Cd(II) adsorbed by non-living *Nitzschia*. The effects of foreign ions (Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>) on the adsorption of cadmium ions are mainly ascribed to 1) foreign ions competing with Cd(II) for the limited reactive sites on the surface of non-living *Nitzschia*, which reduces the adsorption amount of the adsorbates; 2) ionic strength of Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> impacting non-living *Nitzschia* particles aggregation by influencing electrostatic interactions; and 3) ionic strength affecting the activity coefficient of Cd(II) and thus limiting the cadmium ions transfer from the solution to the surface of adsorbent (Peng et al., 2017). Another explanation for the negative effects of Ca<sup>2+</sup>





and  $Mg^{2+}$  on the adsorption capacity of adsorbents was that both  $Ca^{2+}$  and  $Mg^{2+}$  in high concentration ( $>400\text{ mg L}^{-1}$ ) can form hydrates with water " $Ca^{2+}/Mg^{2+} \cdot (H_2O)_n$ ", and these complexes could cover the surface of the adsorbents, making it less available to adsorbates, and resulting in a decreased number of heavy-metal ions adsorbed (Cheng et al., 2014). It is also noted from the results that the decreased extent of the amount of Cd(II) adsorbed by non-living *Nitzschia* shows no significant correlation to the concentration of foreign ions from 0.05 to 0.2 mol L<sup>-1</sup> ( $p > 0.05$ ). This would be explained by the possibility that the minimum concentration of the foreign ions (0.05 mol L<sup>-1</sup>) was high enough to make the adsorption capacity decrease to the lowest level.

Although  $Ca^{2+}$  and  $Mg^{2+}$  showed negative effects on the amount of Cd(II) adsorbed by the diatom biomass, the concentration of  $Ca^{2+}$  and  $Mg^{2+}$  is detected in the range of 10–80 mg L<sup>-1</sup> ( $Ca^{2+}$ : 0.00025–0.0020 mol L<sup>-1</sup>,  $Mg^{2+}$ : 0.0004–0.0033 mol L<sup>-1</sup>) in the surface freshwater (Cheng et al., 2014), which was far lower than the concentration set in this study. Therefore, it is likely that the adsorption of Cd(II) would be far less affected than the extent shown in the present study when using non-living *Nitzschia* for Cd(II) treatment in surface freshwater.

### 3.3.2 Turbidity

Figure 5B shows the effect of turbidity on the amount of Cd(II) adsorbed by non-living *Nitzschia*. The amount of Cd(II) per unit mass of non-living *Nitzschia* sharply decreased by 62.2% when the turbidity increased to 2 NTU and tended to be stable afterward. The suspended particles might have blocked the micro-pores on the surface of non-living *Nitzschia* and occupied the active sites for Cd(II) adsorption, therefore resulting in the decreased adsorption amount of Cd(II).

### 3.3.3 Humic acid

Humic acid is a widespread organic macromolecule in the natural environment. It is usually applied in agricultural feed, the petrochemical industry, battery production, etc. It has been reported that humic acid can combine with cations through ionic bonding force or coordination interactions (Kinniburgh et al., 1999). As shown in Figure 5C, the amount of Cd(II) adsorbed by non-living *Nitzschia* increased evidently with the concentration of additive humic acids. A similar result was reported by Zeng et al. that the adsorption capacity of Cd(II) by the bentonite could be enhanced by humic acids (Zeng, 2008). Meanwhile, it can be seen from Figure 5C that humic acid was capable of adsorbing Cd(II) to some extent (around 25 mg g<sup>-1</sup>) in the absence of an adsorbent, which was similar to the results reported elsewhere. However, the significantly increased amount of Cd(II) adsorbed by non-living *Nitzschia* when humic acid was introduced cannot be fully explained by the small adsorption amount of Cd(II) by humic acid itself. As the surface of non-living *Nitzschia* contains various cations, such as  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $Cu^{2+}$ , it can be inferred that the interactions between humic acid and those cations probably simultaneously occurred during the Cd(II) adsorption process. Therefore, the positive effect of humic acid for Cd(II) adsorption by non-living *Nitzschia* might be ascribed to 1) humic acid combining with some other cations (e.g.,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , etc.) on the surface of non-living *Nitzschia* or in the solution, which makes more active sites available for Cd(II) adsorption. 2) Cd(II) was directly complexed by humic acid to form organic bonds with cadmium; 3) humic acid was first adsorbed onto the surface of non-living *Nitzschia*, and then complexation or ion exchange of Cd(II) with abundant functional groups of humic acids (amines, carboxylic acid, and carbonyl) took place.

## 3.4 Adsorption mechanism

Non-living *Nitzschia*, which possessed the highest Cd(II) adsorption capacity among the three diatom species, was used for adsorption mechanism analysis. Organics leaching was a common phenomenon for non-living bio-adsorbents during the adsorption

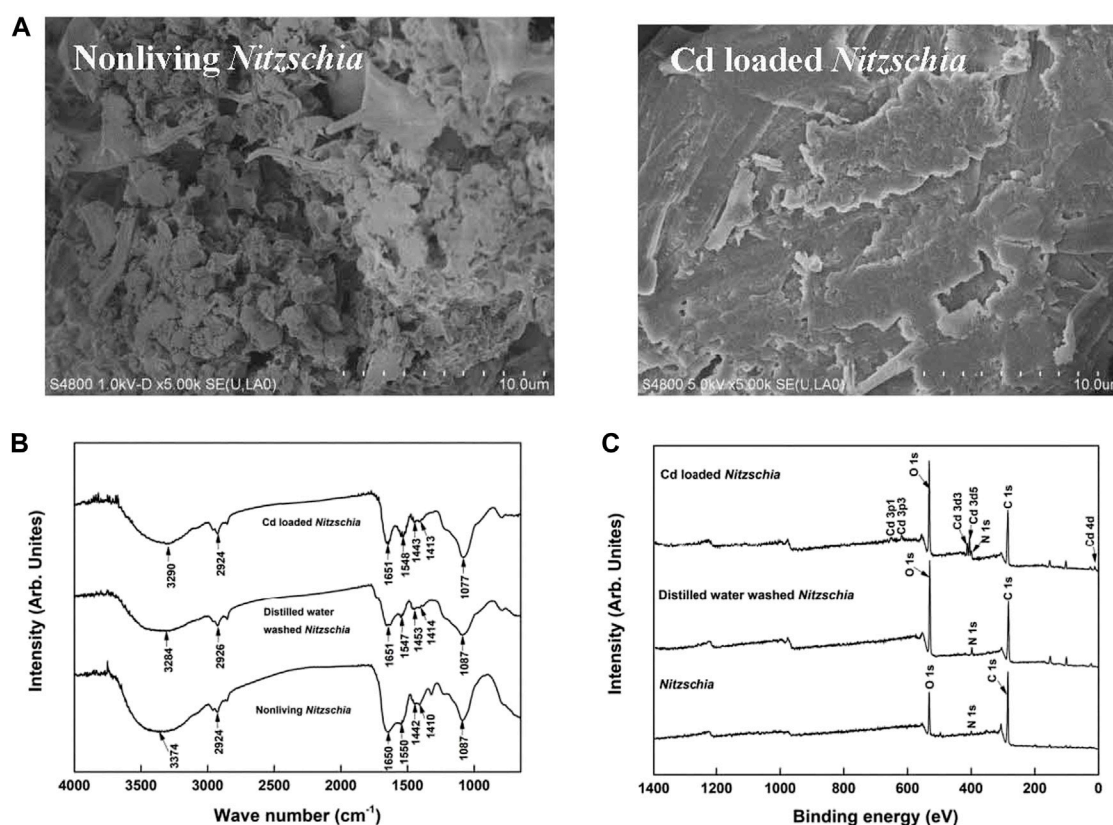


FIGURE 6

Characteristics of non-living, distilled water-washed, and Cd-loaded *Nitzschia* biomass. (A) SEM images, (B) FTIR spectra, and (C) XPS spectra.

process (Chen and Yang, 2005; Yang et al., 2011), which would possibly affect the distribution of chemical bonds on the bio-adsorbents. Therefore, in order to reveal the influence of organics leaching on the chemical bonds on the surface of non-living *Nitzschia*, FTIR and XPS analyses for distilled water-washed *Nitzschia* under the same conditions as the adsorption process were also conducted.

### 3.4.1 SEM

The surface morphologies of non-living *Nitzschia* biomass before and after Cd(II) adsorption were examined by SEM (Figure 6A). The non-living *Nitzschia* biomass shows an unconsolidated and flocky surface texture. After Cd(II) adsorption, the loose surface becomes caked and lumpish, which might be due to the complexation of cadmium ions with the functional chemical groups on the surface of non-living *Nitzschia*.

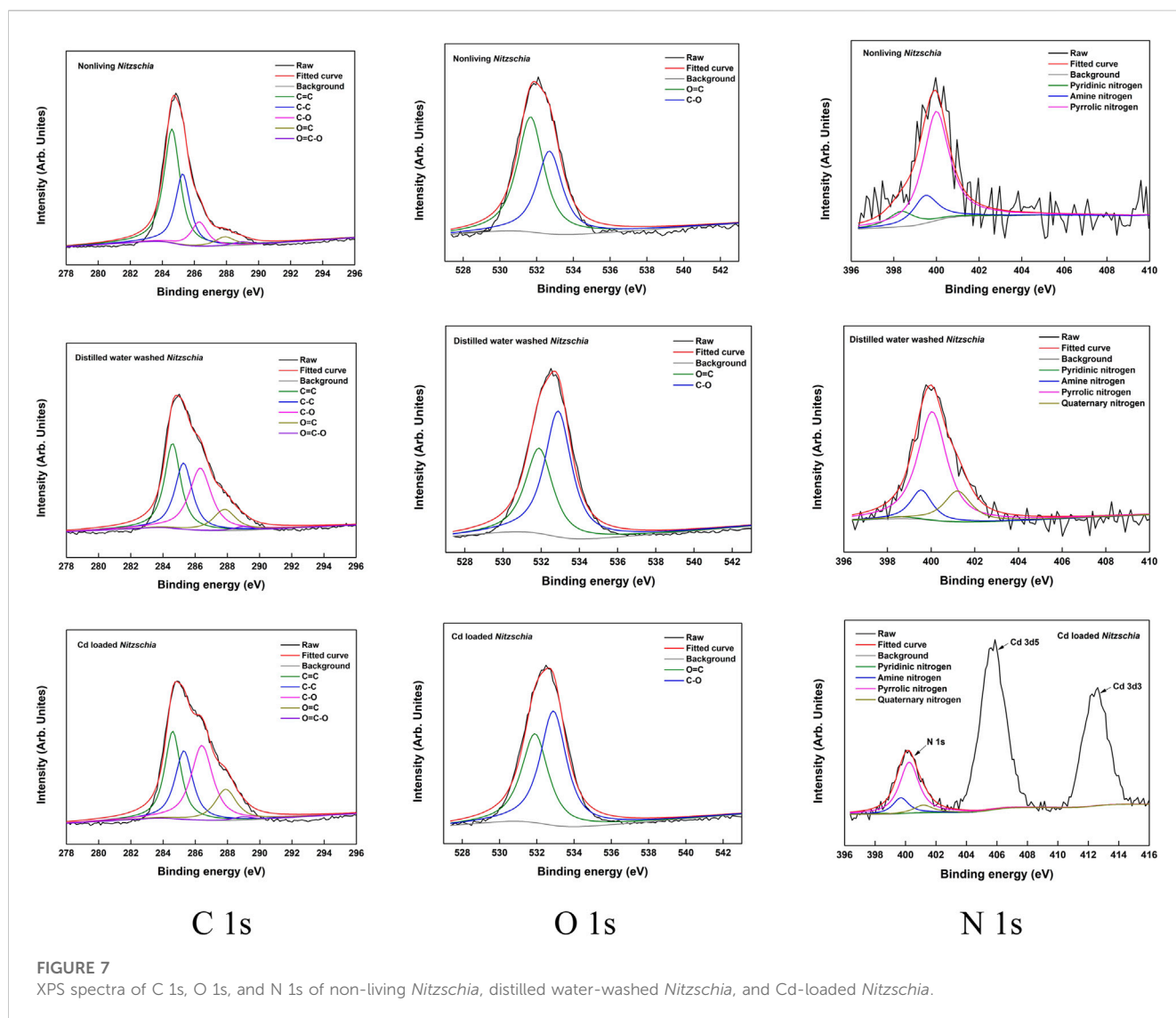
### 3.4.2 FTIR

As shown in Figure 6B, after being washed with distilled water, the overall FTIR spectrum of *Nitzschia* biomass was similar to raw non-living *Nitzschia*, with an evident shift of the peak assigned to the overlapping of -OH and -NH stretching bands of polymeric compounds. The peak representing the overlap of C=C/C=O became a little narrow. These results suggested that the distribution of chemical groups such as -OH, -NH, C=C/C=O could also be affected by water washing, which was hardly

mentioned in most of the reported studies (Yang et al., 2011; Zheng et al., 2011). In comparison, after Cd adsorption, an evident shift of the peak assigned to the overlapping of -OH and -NH stretching bands of polymeric compounds was observed, which was similar to the biomass sample being washed by distilled water. In contrast, the intensity of the peak assigned to -NH (1548 cm<sup>-1</sup>) became much stronger after Cd adsorption. This result implied that -NH bonds might be involved in the interaction with Cd(II) on the surface of the non-living *Nitzschia*.

### 3.4.3 XPS analysis

A comparison of XPS spectra survey scans among non-living *Nitzschia*, distilled water-washed *Nitzschia*, and Cd(II)-loaded *Nitzschia* is illustrated in Figure 6C. It can clearly be seen from the figure that the peaks representing the Cd chemical state occurred only in the XPS spectra of Cd(II)-loaded *Nitzschia*, which demonstrated that Cd(II) was adsorbed onto the surface of non-living *Nitzschia*. Additionally, it is also noted that the atomic ratio of C 1s on the surface of the non-living *Nitzschia* decreased from 76.5% to 56.5% after being washed by distilled water, indicating that the organic leaching happened when non-living *Nitzschia* mixed with water. A similar decrease of C 1s in Cd-loaded *Nitzschia* was also observed. In order to further understand the functional bonds responsible for Cd ion adsorption, binding energy (BE) profiles of carbon (C 1s), oxygen (O 1s), and nitrogen (N 1s) atoms on non-living *Nitzschia*, distilled water-washed, and Cd(II)-loaded *Nitzschia*



are shown, respectively, in Figure 7, and the ratio of various C 1s, O 1s, and N 1s bonds which were calculated by peak area is shown in Table 4.

The C 1s spectra of the non-living *Nitzschia* comprised five peaks with differentiated BE values (284.6, 285.3, 286.3, 287.9, and 289 eV) *via* deconvolution. These peaks can be assigned to C=C, C-C, C-O, O=C, and O=C-O bonds, respectively (Beamson and Briggs, 1992; Yang et al., 2011; Deng et al., 2017). After Cd(II) adsorption, the ratio of C=C and C-C decreased, whereas the ratio of C-O and O=C increased, with no notable shifts of binding energy for the five carbon bonds. Meanwhile, after being mixed with distilled water, the changing trend of the carbon bonds was found to be very similar to the diatom sample after Cd(II) adsorption. Consequently, taking organics leaching into account, the decreases of C-C and C=C bonds after adsorption were due to organics leaching. In comparison, the decrease of C-C/C=C was also found for some bio-adsorbents after heavy-metal adsorption (Yang et al., 2011; Zheng et al., 2011). However, the decrease in the C-C/C=C

ratio was attributed to partial breakage of the C-C/C=C bonds oxidized by heavy-metal ions (Zheng et al., 2011) or confirming the functional carbon bonds directly based on the change of C 1s after adsorption (Yang et al., 2011), without unveiling the effects of organics leaching on the chemical bonds of the adsorbent surface.

The O 1s spectra of the non-living comprised two peaks with differentiated BE values *via* deconvolution, which were assigned to O=C and C-O, respectively, with a higher ratio of O=C and a lower ratio of C-O bonds. After being washed with distilled water, the ratio of O=C was found to decrease by 18%, whereas the ratio of C-O increased correspondingly by 18%. Moreover, the binding energy (BE) value of O=C and C-O shifted to a higher level by 0.2 eV. This result suggested that organics leaching could also affect the ratio of oxygen bonds and induce BE shifts of oxygen bonds on *Nitzschia*. In previous studies, the complexation between O=C and heavy metal ions was usually confirmed by the results that O=C bonds on the bio-adsorbent decreased and C-O bonds increased after heavy-metal adsorption, in which the

TABLE 4 Summary of binding energy and area ratios of C 1s, O 1s, and N 1s on non-living, distilled water-washed, and Cd-loaded *Nitzschia* biomass.

Chemical bond		Binding energy (eV)			Ratio (%)		
		Non-living <i>Nitzschia</i>	Distilled water-washed <i>Nitzschia</i>	Cd-loaded <i>Nitzschia</i>	Non-living <i>Nitzschia</i>	Distilled water-washed <i>Nitzschia</i>	Cd-loaded <i>Nitzschia</i>
C 1s	C=C	284.6	284.6	284.6	52.3	30.9	27.9
	C-C	285.3	285.3	285.3	29.9	26.1	24.5
	C-O	286.3	286.3	286.4	11.2	31.0	33.0
	O=C/O-C-O	287.9	287.8	287.9	4.9	10.6	13.5
	O=C-O	289.0	289.0	289.0	1.7	1.4	1.2
O 1s	O=C	531.7	531.9	531.9	58.9	40.9	44.1
	C-O	532.7	532.9	532.9	41.1	59.1	55.9
N 1s	Pyridinic nitrogen	398.4	398.6	398.5	10.5	1.2	1.3
	Amine nitrogen	399.5	399.5	399.7	17.3	13.5	17.9
	Pyrrolic nitrogen	400.0	400.0	400.2	72.2	67.4	70.7
	Quaternary nitrogen	—	401.2	401.2	—	18.0	10.1

formation of O-heavy-metal bonds was not observed, and the effect of organics leaching on oxygen bonds was hardly mentioned (Chen and Yang, 2006; Yang et al., 2011; Li et al., 2012). Based on the present results, the involvement of O=C in heavy-metal complexation became ambiguous in those previous studies because organics leaching could also lead to the decrease of O=C and increase of C-O bonds. After Cd(II) adsorption, a decrease of O=C and an increase of C-O bonds were found compared with raw non-living *Nitzschia* with no new peak representing metallic oxygen observed, which was similar to the result of distilled-water-washed *Nitzschia*. Moreover, the binding energy (BE) value of O=C and C-O also shifted to a higher level by 0.2 eV compared with raw non-living *Nitzschia*. Therefore, it can be inferred that the change of oxygen bond distribution on *Nitzschia* after Cd(II) adsorption was due to organic leaching rather than the complexation of C=O with Cd(II).

The N 1s spectra of the non-living *Nitzschia* comprised three peaks with differentiated BE values *via* deconvolution, which can be assigned to pyridinic nitrogen, amine nitrogen, and pyrrolic nitrogen, respectively (Wang et al., 2017; Ji et al., 2018). After being washed with distilled water, the quantities of pyridinic nitrogen, amine nitrogen, and pyrrolic nitrogen decreased by 9.3, 3.8, and 4.8, respectively, and a new peak representing quaternary nitrogen of 18.0% occurred. This result indicated that some of the pyridinic nitrogen, amine nitrogen, and pyrrolic nitrogen were protonated in distilled water. In comparison, after Cd(II) adsorption, the ratio of pyridinic nitrogen decreased by 9.2%, which was similar to the sample after being washed with distilled water. However, different from the sample after being washed with distilled water, the ratio of amine and pyrrolic nitrogen groups after

Cd(II) adsorption showed no notable change compared with raw non-living *Nitzschia*. These results implied that Cd(II) ions interacted with both amine and pyrrolic nitrogen during adsorption, which inhibited the protonation of these two nitrogen bonds. Moreover, the binding energy of amine nitrogen and pyrrolic nitrogen increased from 399.5 and 400.0 to 399.7 and 400.2, respectively, after Cd(II) adsorption (Table 4), which further confirmed the coordination of amine nitrogen and pyrrolic nitrogen with cadmium ions. The increased BE value of the nitrogen atom was because the nitrogen atom donates electrons to cadmium ions, and thus, the electron density around the nitrogen atom decreases (Yang et al., 2011). The greater affinities of amine and pyrrolic nitrogen to Cd ions than pyridinic nitrogen might be explained by the hard and soft acids and bases theory (HSAB) that the soft acid (Cd<sup>2+</sup>) interacts preferentially with the soft base (pyrrolic nitrogen and amine) than the hard base (pyridinic nitrogen) and the soft acid interacts with the soft base, usually *via* coordination. Similarly, Ji et al. reported a higher affinity of pyrrolic nitrogen to Pb<sup>2+</sup> than pyridinic nitrogen (Ji et al., 2018).

## Conclusion

Non-living marine diatom biomass (*Chaetoceros*, *Nitzschia*, and *Thalassiosira* sp.) could efficiently remove Cd(II) from aqueous solution in the absence of ionic competition and under low turbidity conditions, with non-living *Nitzschia* possessing the highest adsorption capacity. The adsorption process was a spontaneous, endothermic, and chemisorption-involved process. The adsorption of Cd(II) was inhibited by inorganic salts and turbidity but was promoted by humic acid.



The adsorption mechanism analysis demonstrated that amine and pyrrolic nitrogen showed good affinities to Cd(II), whereas pyridinic nitrogen did not. The results of the present study indicated that diatom biomass was a great alternative for Cd(II) sequestration from an aqueous solution. Further studies, such as immobilization and recycling, should be conducted to promote its application in real heavy-metal wastewater treatment.

## Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding author.

## Author contributions

XW contributed to the conception and design of the study, conducted part of experiments, analyzed the data, and wrote the manuscript. JW and SZ conducted parts of the experiments. All authors contributed to manuscript revision, read, and approved the submitted version.

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## Conflict of interest

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