

Article

Superior adsorption performance of graphitic carbon nitride nanosheets for both cationic and anionic heavy metals from wastewater☆

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ARTICLE INFO

Article history:

Received 16 May 2018

Received in revised form 31 July 2018

Accepted 25 September 2018

Available online 11 October 2018

Keywords:

g-C₃N₄ nanosheets

Nanomaterials

Adsorption

Heavy metals

Wastewater

ABSTRACT

Water pollution caused by highly toxic Cd(II), Pb(II), and Cr(VI) is a serious problem. In the present work, a green and low-cost adsorbent of g-C₃N₄ nanosheets was developed with superior capacity for both cationic and anionic heavy metals. The adsorbent was easily fabricated through one-step calcination of guanidine hydrochloride with thickness less than 1.6 nm and specific surface area of 111.2 m²·g⁻¹. Kinetic and isotherm studies suggest that the adsorption is an endothermic chemisorption process, occurring on the energetically heterogeneous surface based on a hybrid mechanism of multilayer and monolayer adsorption. The tri-s-triazine units and surface N-containing groups of g-C₃N₄ nanosheets are proposed to be responsible for the adsorption process. Further study on pH demonstrates that electrostatic interaction plays an important role. The maximum adsorption capacity of Cd(II), Pb(II), and Cr(VI) on g-C₃N₄ nanosheets is 123.205 mg·g⁻¹, 136.571 mg·g⁻¹, and 684.451 mg·g⁻¹, respectively. The better adsorption performance of the adsorbent than that of the recently reported nanomaterials and low-cost adsorbents proves its great application potential in the removal of heavy metal contaminants from wastewater. The present paper developed a promising adsorbent which will certainly find applications in wastewater treatment and also provides guiding significance in designing adsorption processes.

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1. Introduction

Water pollution has become a serious problem all over the world, especially in the developing countries like China [1]. Among the various pollutants in water, heavy metals, which are mainly discharged by industrial activities such as mining and metallurgy, represent the most hazardous ones because they are highly toxic even at dilute concentration, are non-biodegradable, and will accumulate through the food chain [2,3]. Cd(II), Pb(II), and Cr(VI) are the most commonly existent heavy metals with the highest toxicity in wastewater [4–6]. For protecting the human health, these heavy metals should be removed from wastewater before discharge.

Various methods have been applied for the removal of heavy metals from wastewater, such as chemical precipitation, adsorption, ion-exchange, electrochemical deposition, and membrane separation

[7–9]. Among these methods, adsorption has been recognized to be a promising technology in wastewater treatment and possesses several advantages such as simplicity in operation, low cost, and high efficiency in a wide concentration range [10,11]. A variety of low-cost materials have been adopted as adsorbents for heavy metals, such as activated carbon, clays, biopolymers, and industrial and agricultural wastes [3,12–14]. Other than these traditional adsorbent materials, many nanostructured materials have been developed recently for the adsorption of heavy metals such as nano-sized metals, carbon nanotube, graphene, and various nanocomposites [15–17]. Although they feature larger specific area, higher reactivity and faster kinetics than these traditional adsorbents, the nanostructured adsorbents suffer from high cost and complicated fabrication procedures, which restrict their commercial applications [18,19]. Therefore, novel nanomaterials which are low-cost and easy to be fabricated are still highly required to be developed as adsorbents for the removal of heavy metals from wastewater.

Graphitic carbon nitride (g-C₃N₄) has attracted great attention in recent years in catalysis field, especially in photocatalysis, because of its unique structure and semiconductor properties [20,21]. It is the most stable allotrope of carbon nitride under ambient conditions with stacked layer structures. g-C₃N₄ is only composed of earth-abundant

☆ Supported by the National Natural Science Foundation of China (21525625), the National Basic Research Program (973 Program) of China (2014CB745100), the (863) High Technology Project of China (2013AA020302), the Chinese Universities Scientific Fund (JD1417), China Postdoctoral Science Foundation funded project (2017M610038), and the Fundamental Research Funds for the Central Universities (ZY1712, XK1701).

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carbon and nitrogen elements, and can be easily fabricated through the thermal condensation of several low-cost nitrogen-rich precursors, such as cyanamide, dicyandiamide, melamine, urea, and guanidine hydrochloride [22]. $g\text{-C}_3\text{N}_4$ consists of highly ordered tri-s-triazine units which contains negatively charged functionalities because of the six nitrogen lone-pair electrons [23]. Those functional groups are regarded as suitable sites for capturing metal ions and have been successfully used to synthesize well-dispersed metal nanocatalysts, or even single atom catalysts [24]. Furthermore, the surface amino groups of $g\text{-C}_3\text{N}_4$ are also active in adsorbing various metals [25]. Therefore, $g\text{-C}_3\text{N}_4$ is expected to be a low-cost, environmentally friendly, and efficient adsorbent for metals. However, the application of $g\text{-C}_3\text{N}_4$ for heavy metals adsorption has been rarely reported till now.

In the present paper, $g\text{-C}_3\text{N}_4$ nanosheets were synthesized by simply calcination of guanidine hydrochloride and showed superior adsorption capacity for both cationic and anionic heavy metal contaminants, Cd(II), Pb(II), and Cr(VI). AFM, TEM, N_2 adsorption/desorption analysis, XRD, and FT-IR were employed to characterize the morphology and structure of the as-synthesized $g\text{-C}_3\text{N}_4$ nanosheets. The adsorption kinetics and isotherms for these three heavy metals were studied systematically using several well-established models. The effect of pH value on the adsorption capacities and the reusability of the adsorbent were also investigated.

2. Materials and Methods

2.1. Materials

Guanidine hydrochloride (AR, 99.0%), $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (AR, 99.0%), $\text{Pb}(\text{NO}_3)_2$ (AR, 99.0%), $\text{K}_2\text{Cr}_2\text{O}_7$ (AR, 99.8%), and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (AR, 99.0%) were purchased from Aladdin® (Shanghai, China). HCl (AR, 36.0%–38.0%) and NaOH (AR, 98.0%) were provided by Beijing Chemical Works (China). All the chemicals were used as received. Deionized water was used throughout all the experiments.

2.2. Synthesis and characterization of $g\text{-C}_3\text{N}_4$ nanosheets

A facile one-step calcination of guanidine hydrochloride was adopted to synthesize the $g\text{-C}_3\text{N}_4$ nanosheets [26]. Typically, 5 g of guanidine hydrochloride was put into a 25 ml alumina crucible with a cover, and then heated to 600 °C in a muffle furnace for 4 h at a ramp of 10 °C·min⁻¹ under air. The resultant yellow powder (~0.47 g) was collected as the adsorbent without further treatment.

The surface morphology and roughness of the synthesized $g\text{-C}_3\text{N}_4$ nanosheets were studied using an atomic force microscope (AFM, VEECO Multimode 8, Bruker, Germany), operating in scan mode with a scan rate of 0.977 Hz and sample/line value of 512. Transmission electron microscopy (TEM) was performed on a JEM-2100 microscope (JEOL, Japan) to characterize the morphology and structure of the sample. The nitrogen sorption isotherms of $g\text{-C}_3\text{N}_4$ nanosheets were obtained at 77 K using an Autosorb-1-C chemisorption/physorption analyzer (Quantachrome, USA). Powder X-ray diffraction (XRD) pattern was collected on an Ultima IV diffractometer (Rigaku, Japan) to determine the crystal phases of the sample. Infrared spectrum analysis was performed on KBr discs with a 2 wt% finely ground sample using a Fourier transform infrared (FT-IR) spectrometer (Thermo Nicolet 6700, USA) and the spectrum was recorded in the wavenumber region of 4000–400 cm⁻¹. The Zeta potential measurement was carried out on a SZ-100 dynamic light scattering nanoparticle analyzer (Horiba Scientific, Japan).

2.3. Adsorption experiments

The adsorption properties of the as-synthesized $g\text{-C}_3\text{N}_4$ nanosheets for Cd(II), Pb(II), and Cr(VI) were studied using batch adsorption mode. Typically, 20 mg of the adsorbent was added into conical flasks

containing 20 ml of heavy metal solution with determined concentration. Then the flasks were shaken in a thermostatic shaker at a fixed agitation speed of 200 rpm. After certain times, the solution was collected to analyze the concentration of the heavy metals using an atomic absorption spectrophotometer (Varian SpectraAA55-B, Palo Alto, USA). The adsorption capacity of the heavy metals on the $g\text{-C}_3\text{N}_4$ nanosheets was calculated as:

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

where q_t is the adsorption capacity at a certain time t (mg·g⁻¹), C_0 and C_t are the initial and final concentrations of the heavy metals at a certain time (mg·L⁻¹), respectively, V is the volume of the solution (ml) and M is the weight of the adsorbent (g).

To study the effect of pH, the pH value of the heavy metal solution was adjusted by the addition of HCl or NaOH. The initial concentration of heavy metal ions was 500 mg·L⁻¹ and the adsorption experiments were conducted at 25 °C for 60 min. The reusability of the adsorbent was assessed by 10 successive cycles of adsorption-desorption-regeneration experiments for Cd(II) and Pb(II). For each cycle, Cd(II)/Pb(II) solution with an initial concentration of 500 mg·L⁻¹ was used and the adsorption was conducted at 25 °C for 60 min. For desorption, 20 mg of the adsorbent was added into 20 ml of HCl solution (0.1 mol·L⁻¹) and then stirred at 25 °C for 60 min. After desorption, 20 ml of NaOH solution (0.25 mol·L⁻¹) was mixed with 20 ml of the adsorbent to carry out the regeneration at 25 °C for 60 min. Before the adsorption experiments, the adsorbent was washed with deionized water until pH neutral and dried at 60 °C for 4 h. The adsorption capacities for Cd(II) and Pb(II) were recorded for each cycle. All the adsorption experiments were carried out in triplicate and the average values were reported.

2.4. Adsorption kinetics

The adsorption kinetics study was conducted at 25 °C, 35 °C, and 45 °C for the three heavy metals with the initial concentration of 100 mg·L⁻¹ for different times. The results were analyzed using three kinetic models [27,28]: pseudo-first-order (PFO) model, pseudo-second-order (PSO) model, and Elovich kinetic model, described by the following equations:

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

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

$$q_t = \frac{1}{\beta} \ln(\alpha \beta t) \quad (4)$$

where q_e and q_t are the adsorption capacity at equilibrium and at a certain time t (mg·g⁻¹), respectively, k_1 is the pseudo-first-order rate constant (min⁻¹), k_2 is the pseudo-second order rate constant (g·mg⁻¹·min⁻¹), α is the initial adsorption rate (mg·g⁻¹·min⁻¹), and β is the desorption rate constant (g·mg⁻¹).

2.5. Adsorption isotherms

The adsorption isotherm study was conducted at 25 °C, 35 °C, and 45 °C for the three heavy metals with different initial concentrations for 60 min. The results were analyzed using four isotherm models [27,28]: Langmuir, Freundlich, Redlich–Peterson (R–P), and Khan models, described by the following equations:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

$$q_e = K_f C_e^{1/n} \quad (6)$$

$$q_e = \frac{K_{RP} C_e}{1 + \alpha_{RP} C_e^{\beta_{RP}}} \quad (7)$$

$$q_e = \frac{q_m \beta_K C_e}{(1 + \beta_K C_e)^{\alpha_K}} \quad (8)$$

where q_e and q_m are the adsorption capacity at equilibrium and the theoretically maximum adsorption capacity ($\text{mg} \cdot \text{g}^{-1}$), respectively, C_e is the concentration of heavy metals in aqueous solution at equilibrium ($\text{mg} \cdot \text{L}^{-1}$), K_L is the Langmuir constant ($\text{L} \cdot \text{mg}^{-1}$) related to the energy of adsorption, K_f is the Freundlich constant, which predicts the quantity of the heavy metals per gram of adsorbent at equilibrium ($\text{mg}^{1-1/n} \cdot \text{L}^{1/n} \cdot \text{g}^{-1}$), n is an indicative parameter related to the adsorption effectiveness, K_{RP} ($\text{L} \cdot \text{mg}^{-1}$) and α_{RP} ($\text{L}^{\beta_{RP}} \cdot \text{mg}^{-\beta_{RP}}$) are the Redlich–Peterson model constants, β_{RP} is the Redlich–Peterson model exponent which lies between 0 and 1, β_K ($\text{L} \cdot \text{mg}^{-1}$) is the Khan model constant, and α_K is the Khan model exponent.

2.6. Non-linear regression and error analysis

The non-linear regression method was adopted to solve the isotherm and kinetic models by minimizing the root-mean-square error (RMSE) between the predicted values and the experimental data using MATLAB software [29]. Furthermore, coefficient of determination (R^2) and the non-linear Chi-square (χ^2) were also presented to

quantitatively evaluate the applicability of the above-mentioned isotherm and kinetic models [27–29]. RMSE, R^2 , and χ^2 are defined as:

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^M (q_{i,\text{exp}} - q_{i,\text{cal}})^2}{M-2}} \quad (9)$$

$$R^2 = 1 - \frac{\sum_{i=1}^M (q_{i,\text{exp}} - q_{i,\text{cal}})^2}{\sum_{i=1}^M (q_{i,\text{exp}} - \bar{q}_{\text{exp}})^2} \quad (10)$$

$$\chi^2 = \sum_{i=1}^M \frac{(q_{i,\text{exp}} - q_{i,\text{cal}})^2}{q_{i,\text{exp}}} \quad (11)$$

where $q_{i,\text{exp}}$ and $q_{i,\text{cal}}$ are the experimental data and the calculated results using the above-mentioned models, respectively, M is the number of measurement, and $\bar{q}_{\text{exp}}$ is the mean value of the experimental data.

3. Results and Discussion

3.1. Characterization of g-C₃N₄ nanosheets

The morphology of the as-synthesized g-C₃N₄ nanosheets was studied using AFM and TEM as shown in Fig. 1. AFM image (Fig. 1(a)) reveals that the g-C₃N₄ sample has a rough surface with a height of less than 1.6 nm, indicating the formation of few layered nanosheets [30].

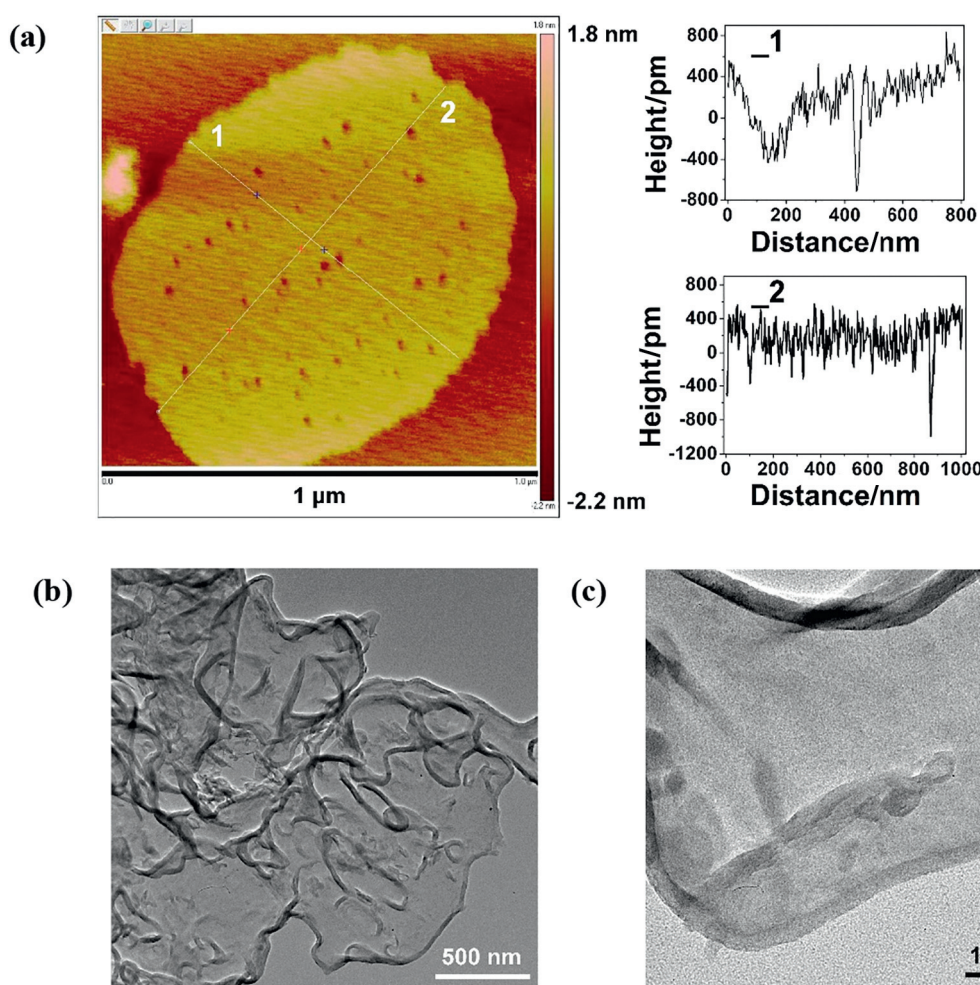


Fig. 1. (a) AFM image of the as-synthesized g-C₃N₄ nanosheets with height profiles; (b–c) TEM images of the as-synthesized g-C₃N₄ nanosheet with different resolutions.

TEM images (Fig. 1(b), (c)) show the layered structures of the g-C₃N₄ nanosheets with bended layer-edges formed to reduce the surface energy and improve their stability [26]. Moreover, the as-synthesized g-C₃N₄ nanosheets are transparent to electron beams as shown in Fig. 1(b), (c) because of their thin nature [31].

Then the specific surface area, phase structure, and chemical structure of the as-synthesized g-C₃N₄ nanosheets were studied by N₂ adsorption/desorption analysis, XRD, and FT-IR, respectively. As shown in Fig. 2(a), the Brunauer–Emmett–Teller (BET) surface area of the g-C₃N₄ nanosheets is determined to be 111.2 m²·g^{−1}. The XRD pattern (Fig. 2(b)) reveals a dominant (002) peak at 27.56° and a minor (100) peak at 12.88°, which are due to the graphitic stacking of the conjugated triazine aromatic units and the intra-planar stacking of the periodic tri-s-triazine motifs [32,33]. Regarding FT-IR, the spectrum (Fig. 2(c)) exhibits several characteristic bands of g-C₃N₄: the characteristic peak terminal cyano groups (C≡N) at 2174.04 cm^{−1}, the band of the typical stretching modes of CN heterocycles in the region of 1650–1200 cm^{−1} with multiple peaks, and the intense band of the out-of-plane bending vibration characteristic of tri-s-triazine rings at 808.81 cm^{−1} [23,33]. Furthermore, a broad band in the range of 3500–3000 cm^{−1} is also observed, which can be attributed to the adsorbed moisture, the stretching vibration modes of uncondensed amino groups, or the surface N—H groups [32]. The above-mentioned characterization results reveal the successful formation of g-C₃N₄ nanosheets through a facile one-step calcination procedure with guanidine hydrochloride as the precursor.

3.2. Adsorption kinetics

The adsorption kinetics describes the uptake rate of the adsorbate on the adsorbent and is an important characteristic which defines the adsorption efficiency and helps to understand the adsorption mechanism [27–29,34]. The adsorption kinetic profiles

of Cd(II), Pb(II), and Cr(VI) on g-C₃N₄ nanosheets at different temperatures are shown in Fig. 3. For all the three heavy metal ions, the adsorption on g-C₃N₄ nanosheets occurred rapidly in the first 20 min. After that, the adsorption capacity increased slightly and reached the equilibrium in about 60 min. This phenomenon is commonly observed in adsorption because the available adsorption sites decrease with increasing the contact time until the equilibrium reaches [35].

In order to evaluate the mechanistic process controlling the adsorption of the heavy metal ions onto g-C₃N₄ nanosheets, three kinetic models containing pseudo-first-order (PFO) model (Eq. (2)), pseudo-second-order (PSO) model (Eq. (3)), and Elovich kinetic model (Eq. (4)) were employed to examine the experimental data as shown in Fig. 3 and the obtained parameters are presented in Table S1. The lower *R*² values and higher RMSE and χ^2 values of the pseudo-first-order model at all circumstances indicate that this model is not suitable for describing the adsorption kinetics of the heavy metal ions on g-C₃N₄ nanosheets. The experimental data exhibits good fitting with the pseudo-second-order model and the Elovich model with *R*² values ranging from 0.770 to 0.963 for the pseudo-second-order model and from 0.750 to 0.989 for the Elovich model, except for Cr(VI) adsorption at 25 °C. The pseudo-second-order model assumes that the adsorption is controlled by the chemisorption process based on valence forces by sharing or exchanging electrons between the adsorbent and the heavy metal ions [35]. The Elovich model has been widely used for describing the activated chemisorption based on the hypothesis that the adsorbent surface is energetically heterogeneous [27,36,37]. So, both mechanisms possibly dominate the chemisorption of heavy metal ions on g-C₃N₄ nanosheets. Furthermore, higher adsorption capacities observed experimentally (Fig. 3) and higher adsorption capacity at equilibrium predicted by the pseudo-second-order model (Table S1) at higher temperature reveal the endothermic nature of the adsorption of heavy metal ions on g-C₃N₄ nanosheets [23].

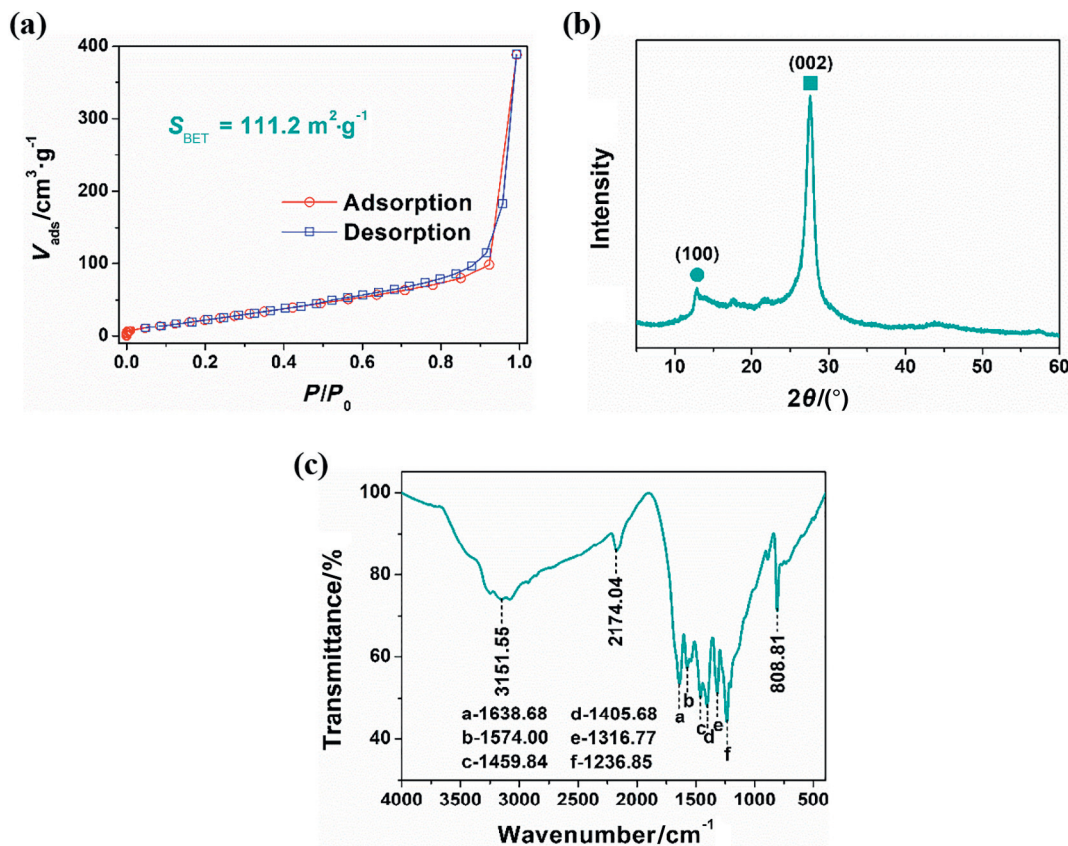


Fig. 2. (a) N₂ adsorption/desorption isotherms, (b) XRD pattern, and (c) FT-IR spectrum of the as-synthesized g-C₃N₄ nanosheets.

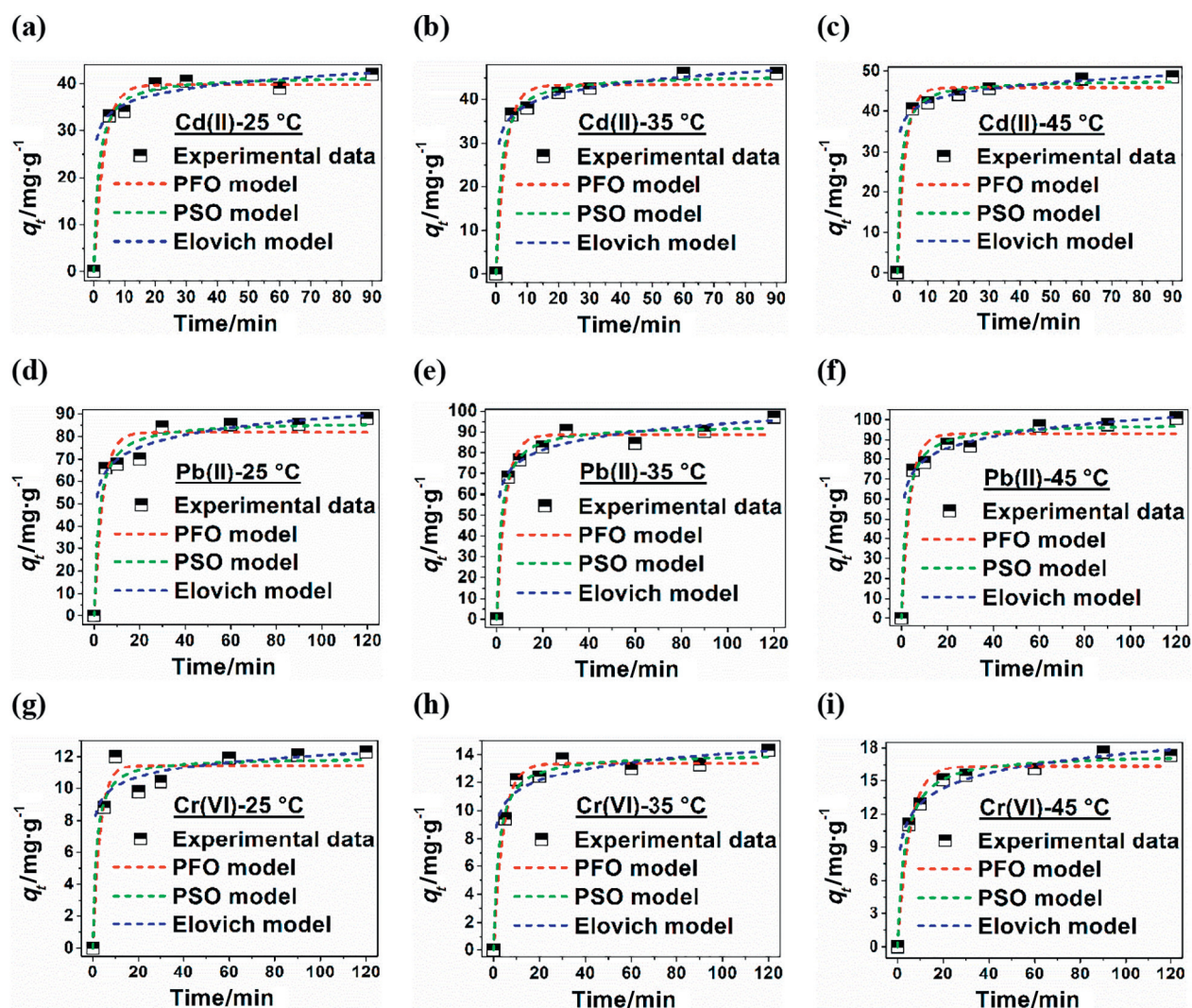


Fig. 3. Adsorption kinetics of Cd(II), Pb(II), and Cr(VI) on g-C₃N₄ nanosheets at different temperatures: (a) Cd(II)-25 °C, (b) Cd(II)-35 °C, (c) Cd(II)-45 °C, (d) Pb(II)-25 °C, (e) Pb(II)-35 °C, (f) Pb(II)-45 °C, (g) Cr(VI)-25 °C, (h) Cr(VI)-35 °C, (i) Cr(VI)-45 °C.

3.3. Adsorption isotherms

The adsorption isotherm describes the equilibrium distribution of the heavy metal ions between the liquid and the solid phase (adsorbent) at given condition [14,38]. It is important to establish an appropriate isotherm model to predict the adsorption efficiency and determine the adsorption mechanism [3,14]. The experimental isotherms were obtained by varying the initial concentration of the heavy metal ions and the results are presented in Fig. 4. Four isotherm models containing Langmuir (Eq. (5)), Freundlich (Eq. (6)), Redlich–Peterson (R–P, Eq. (7)), and Khan models (Eq. (8)), were used to fit the experimental data as shown in Fig. 4, and the obtained parameters are presented in Table S2.

Langmuir isotherm model has been successfully applied for many monolayer adsorption processes which occur at specific homogeneous sites of the adsorbent without any interaction between the adsorbed molecules [39]. For Cd(II) and Pb(II) adsorption, the experimental data exhibits moderate to good fitting with the Langmuir model with R^2 in the range of 0.558–0.791 for Cd(II) and 0.786–0.807 for Pb(II). Higher values of R^2 ranging from 0.931 to 0.983 were obtained for Cr(VI) adsorption illustrating the satisfactory applicability of the Langmuir model. The Freundlich isotherm model is used to model the heterogeneous surface adsorption processes, which assumes that the active sites are not energetically equivalent

[28,29]. As shown in Table S2, the Freundlich model fits the experimental data well with one exception for Pb(II) adsorption at 25 °C where R^2 equals to 0.653. The values of $1/n$ are all below 1, demonstrating the favorability of these heavy metal ions on g-C₃N₄ nanosheets [28]. The two three-parameter isotherm models, Redlich–Peterson and Khan models, incorporate both the Langmuir and Freundlich models, resulting in a hybrid adsorption mechanism, which admits both multilayer and monolayer adsorption [40,41]. The Redlich–Peterson isotherm model is applicable in describing the adsorption equilibrium with a wide concentration range [41]. It approximates to Henry's law at low adsorbate concentrations, and approaches the Freundlich model at high concentrations [28,40]. The Khan isotherm model was proposed as a generalized model for pure solutions [42]. As shown in Fig. 4 and Table S2, the experimental data reveals good fitting with both R–P and Khan models.

For Cd(II) and Pb(II) adsorption, higher values of R^2 and lower values of χ^2 were observed for the two three-parameter isotherm models, illustrating the better fitness and prediction precision. When considering the two three-parameter isotherm models, Freundlich is better than Langmuir in describing the adsorption of Cd(II) and Pb(II) on g-C₃N₄ nanosheets. And for Cr(VI) adsorption, all the four isotherm models are applicable with high values of R^2 and low values of χ^2 . Furthermore, the Freundlich and Redlich–Peterson models cannot be used for predicting the maximum

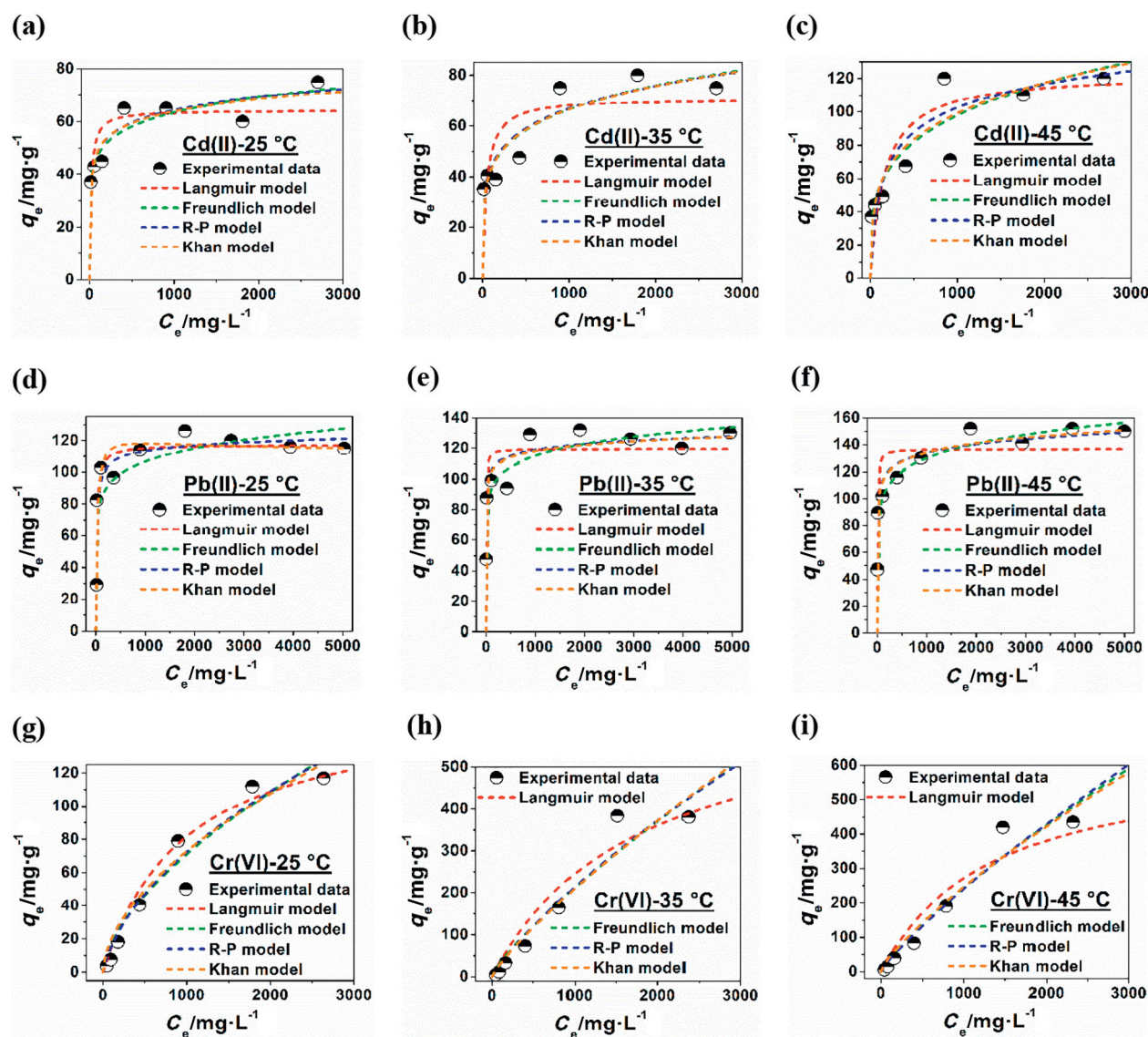


Fig. 4. Adsorption isotherms of Cd(II), Pb(II), and Cr(VI) on g-C₃N₄ nanosheets at different temperatures: (a) Cd(II)-25 °C, (b) Cd(II)-35 °C, (c) Cd(II)-45 °C, (d) Pb(II)-25 °C, (e) Pb(II)-35 °C, (f) Pb(II)-45 °C, (g) Cr(VI)-25 °C, (h) Cr(VI)-35 °C, (i) Cr(VI)-45 °C.

adsorption capacity. The Khan model can be used for predicting the maximum adsorption capacity, but its accuracy is unsatisfactory. Although the Langmuir model cannot fit the experimental data well at some circumstances, it can well predict the maximum adsorption capacity as shown in Fig. 4. Therefore, a hybrid mechanism of multi-layer and monolayer adsorption is responsible for the observed superior adsorption capacity for these three heavy metals, which possibly results from the multiple functional groups presented on g-C₃N₄ nanosheets.

In order to evaluate the adsorption performance of the as-synthesized g-C₃N₄ nanosheets for Cd(II), Pb(II), and Cr(VI), several nanomaterials or low-cost adsorbents reported in recent literatures are referred for comparison on their maximum adsorption capacities. As shown in Table 1, the as-synthesized g-C₃N₄ nanosheets possess better adsorption performance for these three heavy metal ions than many other adsorbents. Although the adsorption performance of g-C₃N₄ nanosheets is not as good as some well-structured nanomaterials, the low-cost and environmentally friendly nature and the convenience in synthesis make g-C₃N₄ nanosheets a promising adsorbent for the treatment of wastewater contaminated by highly toxic heavy metal cations and anions.

3.4. Effect of pH

pH has been recognized to be a key factor influencing the adsorption processes at the water-adsorbent interfaces [23]. The effect of pH on the adsorption capacities for Cd(II), Pb(II), and Cr(VI) on g-C₃N₄ nanosheets was studied at the pH value ranging from 2 to 10. In order to avoid the precipitation of heavy metal ions, the pH value below 8 was applied for Cd(II), and below 6 was applied for Pb(II). As shown in Fig. 5(a)–(b), the adsorption capacities for the cations, Cd(II) and Pb(II), increase obviously with increasing the pH value. While for Cr(VI), which exists as anions, an opposite trend can be seen in Fig. 5c. To further understand the effect of pH value on the adsorption performance, the Zeta-potential values of g-C₃N₄ nanosheets were measured at the pH value ranging from 2 to 10. The results are shown in Fig. 5d, which illustrates that the isoelectric point of the adsorbent is below 2, and the adsorbent is negatively charged at the experimental pH range. The negative charge is due to the Lewis and Brønsted basic sites offered by the nitrogen atoms in different forms [21]. The above-mentioned results demonstrate that electrostatic interaction plays an important role in the adsorption processes. Although electrostatic repulsion exists between the adsorbent and Cr(VI) anions, strong complexation can

Table 1

Comparison of the maximum adsorption capacities of Cd(II), Pb(II), and Cr(VI) on the as-synthesized g-C₃N₄ nanosheets with other nanomaterials or low-cost adsorbents reported recently

Heavy metals	Adsorbents	Dosage/g·L ⁻¹	$q_{\max}^{\text{①}}$ /mg·g ⁻¹	Ref.
Cd(II)	Iron oxide nanoparticles	1	18.32	[43]
	Magnesium oxide–rice husk biochar composite	1	25.880	[44]
	Zeolite NaX	2	38.61	[45]
	Arrowhead plant (<i>Sagittaria trifolia</i> L.) stalk	2	38.2	[46]
	g-C ₃ N ₄ nanosheets	1	123.205	Present work
Pb(II)	EDTA modified β -cyclodextrin/chitosan	0.5	114.8	[47]
	Calixarene-grafted magnetic nanocomposite	0.4	56.82	[48]
	Rodlike ZnO	1	180	[49]
	Arrowhead plant (<i>Sagittaria trifolia</i> L.) stalk	2	97.1	[46]
	g-C ₃ N ₄ nanosheets	1	136.571	Present work
Cr(VI)	Polyethylenimine functionalized halloysite nanotubes	1.1	102.5	[50]
	Modified corn stalks	1.5	227.27	[51]
	Polyethylenimine functionalized Fe ₃ O ₄ /steam-exploded rice straw composite	1	338.98	[52]
	Carbamothiolylimidamide group contained resin	1.67	107.5	[53]
	g-C ₃ N ₄ nanosheets	1	684.451	Present work

^① The values are predicted by Langmuir isotherm model.

form between the surface amino groups and the Cr(VI) anions [25], which is responsible for the observed superior adsorption capacity for Cr(VI).

3.5. Reusability study

Reuse of the adsorbent is of great importance with respect to the practical applications in wastewater treatment. Therefore, the reusability of the as-synthesized g-C₃N₄ nanosheets as adsorbent for heavy metal ions was evaluated. As shown in Fig. 5(e) and (f), the adsorbent can be reused for 10 successive cycles and preserve over 80% of its adsorption ability for both Cd(II) and Pb(II). However, in the case of Cr(VI) adsorption, the desorption of Cr(VI) failed and the adsorbent can be hardly regenerated. This is due to the strong complexation between Cr(VI) anions and the adsorbent other than electrostatic interaction as in the case of cationic Cd(II) and Pb(II) adsorption.

3.6. Adsorption mechanism

In order to study the adsorption mechanism, FT-IR analysis was carried out for the adsorbent loaded with different heavy metals. The FT-IR spectra of all the samples (Fig. 6) display similar absorption bands which can be attributed to the characteristic modes of g-C₃N₄ (Table 2) as discussed in Section 3.1. Obvious shifts are observed for these peaks as shown in Table 2, illustrating that the tri-s-triazine units and terminal N-containing groups are responsible for the adsorption. Furthermore, the broad band ranging from 3500 cm⁻¹ to 3000 cm⁻¹ of the heavy metal loaded adsorbent also changed in its peaks when compared with that of the as-synthesized adsorbent as shown in Fig. 6(a). This result further suggests that surface amino or N—H groups take part in the adsorption of the heavy metals. As shown in Table 1, the maximum adsorption capacity of Cr(VI) is much higher than that of Cd(II) and Pb(II) on g-C₃N₄ nanosheets. One possible

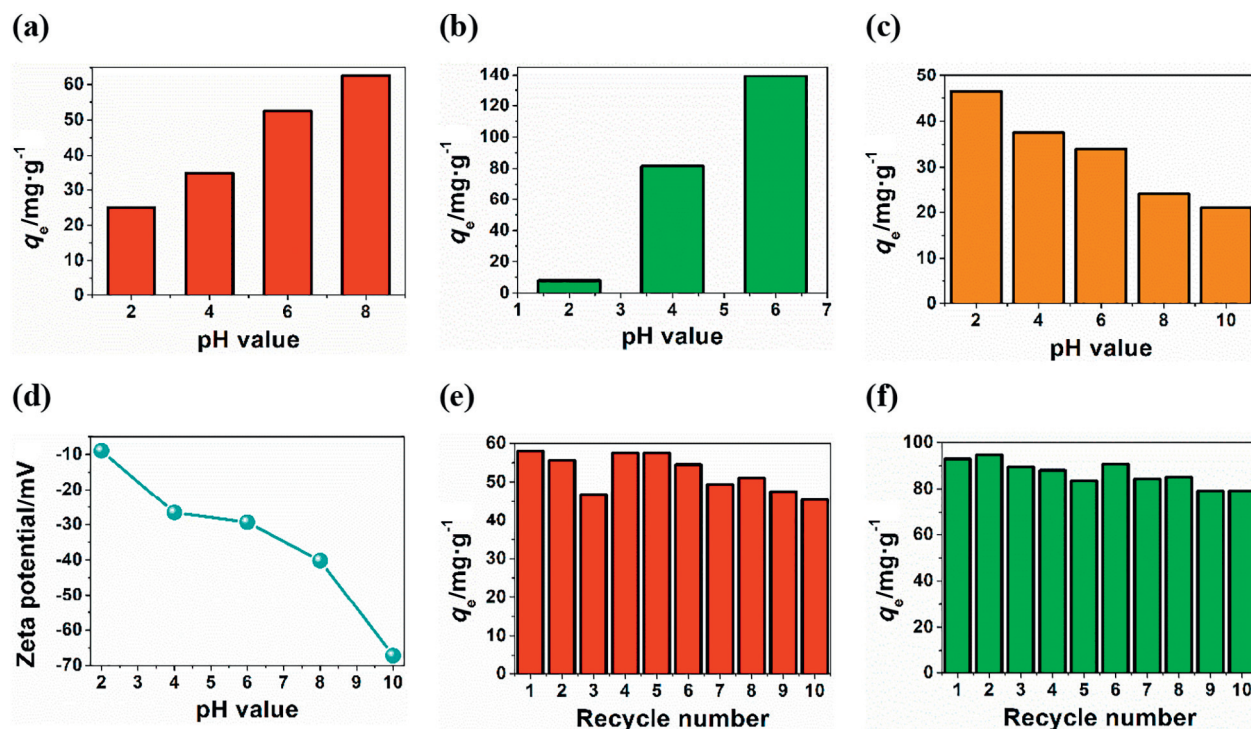


Fig. 5. The dependence of adsorption capacity for Cd(II) (a), Pb(II) (b), and Cr(VI) (c) on pH value; (d) Zeta potentials of the as-synthesized g-C₃N₄ nanosheets at different pH values; adsorption capacities for Cd(II) (e) and Pb(II) (f) during 10 successive adsorption–desorption–regeneration cycles.

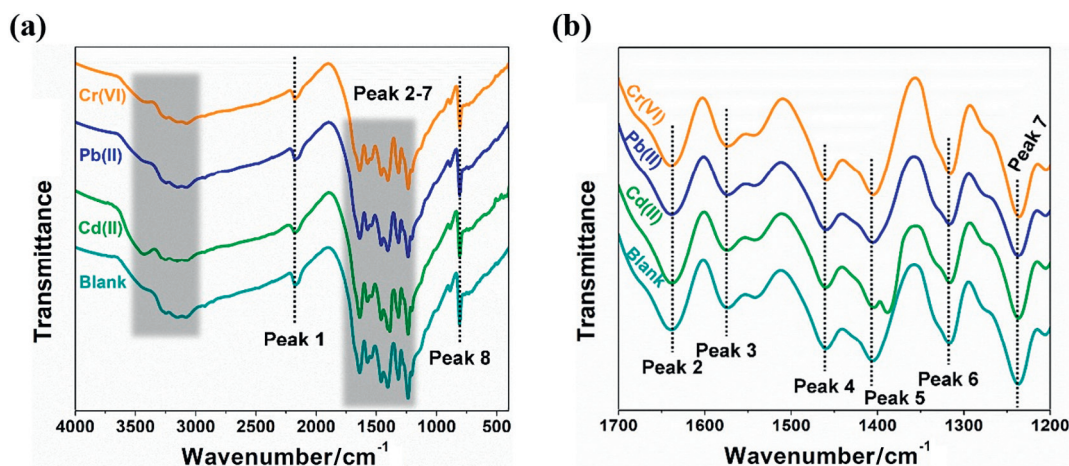


Fig. 6. FT-IR spectra of g-C₃N₄ nanosheets adsorbing different heavy metals, Cd(II), Pb(II), and Cr(VI) with the as-synthesized adsorbent as blank control. (a) Full spectra; (b) spectra in the wavenumber range of 1700–1200 cm⁻¹.

reason is that the adsorption of anionic Cr(VI) mainly occurs on the outer surface of g-C₃N₄ nanosheets while cationic Cd(II) and Pb(II) should firstly penetrate between the g-C₃N₄ layers [19,25]. The adsorption of Cr(VI) is based on the complexation with surface —NH₂ and —NH groups, and the adsorption of Cd(II) and Pb(II) mainly occurs on the tri-s-triazine units through electrostatic interaction [19,25]. Furthermore, the molar maximum adsorption capacity of Cd(II) is 1.096 mmol·g⁻¹, which is higher than that of Pb(II) (0.659 mmol·g⁻¹). This is because Cd(II) cations are smaller than Pb(II) cations and can more easily penetrate between the g-C₃N₄ layers [19]. As discussed above, FT-IR analysis results prove the versatility of the as-synthesized g-C₃N₄ nanosheets in adsorbing both heavy

metal cations and anions with the tri-s-triazine units and surface N-containing groups.

4. Conclusions

In the present work, an environmentally friendly and low-cost adsorbent of g-C₃N₄ nanosheets was developed with superior adsorption capacity for both heavy metal cations and anions when compared with other nanomaterials and low-cost adsorbents reported recently, which is due to the multiple functional groups. The maximum adsorption capacity of Cd(II), Pb(II), and Cr(VI) on g-C₃N₄ nanosheets is 123.205 mg·g⁻¹, 136.571 mg·g⁻¹, and 684.451 mg·g⁻¹, respectively. The adsorbent can be reused for 10 successive cycles with preserving over 80% of its adsorption ability for cationic Cd(II) and Pb(II). The present paper developed a green and low-cost adsorbent of g-C₃N₄ nanosheets which is promising in the removal of heavy metal cations and anions from wastewater and also provided guidelines for designing and studying an adsorption process. To achieve the realistic application in wastewater treatment, finding cheaper raw materials to produce g-C₃N₄ nanomaterials and developing proper reactors should be addressed in the future.

Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2018.09.028>.

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Table 2
The wavenumber and assignment of the FT-IR spectra peaks

Peak number	Heavy metals	Wavenumber/cm ⁻¹	Assignment
1	Blank	2174.04	Terminal cyano groups (C≡N)
	Cd(II)	2176.24	
	Pb(II)	2171.95	
	Cr(VI)	2175.95	
2	Blank	1638.68	Multiple peaks of CN heterocycles stretching modes
	Cd(II)	1638.15	
	Pb(II)	1638.24	
	Cr(VI)	1639.14	
3	Blank	1574.00	
	Cd(II)	1574.29	
	Pb(II)	1573.34	
	Cr(VI)	1573.33	
4	Blank	1459.84	
	Cd(II)	1460.00	
	Pb(II)	1459.54	
	Cr(VI)	1459.31	
5	Blank	1405.68	
	Cd(II)	1388.40	
	Pb(II)	1405.53	
	Cr(VI)	1405.09	
6	Blank	1316.77	
	Cd(II)	1316.22	
	Pb(II)	1316.48	
	Cr(VI)	1315.84	
7	Blank	1236.85	
	Cd(II)	1236.68	
	Pb(II)	1236.89	
	Cr(VI)	1236.00	
8	Blank	808.81	Out-of-plane bending vibration of tri-s-triazine rings
	Cd(II)	807.96	
	Pb(II)	808.17	
	Cr(VI)	807.91	

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