Research Article

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Amino-functionalized graphene oxide for Cr(VI), Cu(II), Pb(II) and Cd(II) removal from industrial wastewater

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Abstract: Amino-functionalized graphene oxide (GO-NH₂) was synthesized by grafting (3-aminopropyl) triethoxysilane on the graphene oxide (GO) surface. The GO-NH₂ with high surface area and numerous active sites can efficiently adsorb Cr(VI), Cu(II), Pb(II) and Cd(II) ions. The maximum adsorption capacities of GO-NH₂ for Cr(VI), Cu(II), Pb(II) and Cd(II) were 280.11, 26.25, 71.89 and 10.04 mg g⁻¹, respectively. The pseudo-first-order and pseudo-second-order kinetic models were employed to describe the kinetic processes. The experimental data agreed well with the pseudo-second-order kinetic equation, and the adsorption of heavy metals onto GO-NH₂ occurs via chemical adsorption. The characteristics of Cr(VI), Cu(II), Pb(II) and Cd(II) in the GO-NH₂ adsorption processes were analyzed using the Langmuir and Freundlich isotherm models. The adsorption processes of Pb(II) and Cd(II) on GO-NH₂ were fit by the Langmuir model. The Freundlich isotherm model was well correlated to Cr(VI) and Cu(II). The GO-NH₂ is a promising material for the removal of heavy metal ions from industrial wastewater. This study provides an effective pathway to process industrial wastewater, and the GO-NH₂ has a good adsorption effect for the treatment of heavy metals in industrial wastewater.

Keywords: Heavy metal; Adsorption; Kinetic adsorption; Isotherm; industrial wastewater.

1 Introduction

With the rapid industrialization and anthropogenic mishandling, the quantity of toxic heavy metal ions globally emitted into the surroundings has increased, especially in freshwater systems [1]. Heavy metals are released from various industries, especially electroplating, metal smelting and mining industries [2]. Heavy metals, including hexavalent chromium (Cr), divalent copper (Cu), divalent lead (Pb) and divalent cadmium (Cd), can cause many detrimental effects to the ecological environment and pose a serious threat to human health. Toxic heavy metals have attracted great attention in the environmental arena because they can be easily stored, accumulated and transferred throughout the environment and amongst living organisms. Undoubtedly, the removal of heavy metal ions in polluted water has become an extremely urgent environmental issue to be solved. Various conventional methods for heavy metal removal from an aqueous system have been developed, such as chemical precipitation, reverse osmosis, ion exchange, membrane filtration and adsorption [3]. Adsorption is now regarded as one of the most promising technologies owing to its low operational cost and its environmentally friendly properties in the process of removing trace levels of heavy metal ions [4]. Although various adsorbents have been applied for heavy metal ion removal from aqueous solutions [5-7], more effort should be devoted to explore these excellent adsorption materials. Nowadays, various novel adsorbents were developed to remove heavy metal ions in wastewater [8].

Nanostructured materials have a large surface area and numerous surface active sites. The effectiveness of various nanostructured adsorbents for the adsorption of heavy metal ions from contaminated water has been demonstrated [9-12]. Graphene has a high specific surface area, which makes it a great prospect for potential adsorbent applications [13]. Graphene is difficult to be modified directly owing to

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the inactive surface. Graphene oxide (GO) can be easily functionalized and used to explore for sorbents [1,14]. GO contains plenty of oxygen-containing functional groups (such as hydroxyl, epoxy, carbonyl and carboxyl groups), and it also exhibits hydrophilic properties. However, the direct application of GO to remove heavy metal ions has several disadvantages [14]. GO tends to aggregate with layered structures owing to its strong inter-planar interactions, which leads to reduced adsorption capacity and adsorption efficiency. Furthermore, the limited functional groups on GO are not enough to effectively remove heavy metal ions [15]. To achieve a high adsorption efficiency and selectivity, GO has been modified with various functional groups to remove heavy metal ions in contaminated water. Dong et al. synthesized polydopamine-mediated surface-functionalized GO composites by utilizing polyethylenimine to provide abundant amino groups, and its adsorption capacities for Cu^{2+} , Cd^{2+} , Pb^{2+} and Hg^{2+} were 87, 106, 197 and 110 mg g^{-1} , respectively [16]. Nitrogen-containing functional groups can exhibit a strong coordination ability with heavy metal ions [15].

Amino-functionalized graphene oxide (GO-NH_2) was synthesized by a hydrothermal method using GO and (3-aminopropyl) triethoxysilane (APTES) for Cr(VI), Cu(II), Pb(II) and Cd(II) removal. We investigated the adsorption process in water solutions with different pH values, different contact times and various heavy metal ion concentrations. The pseudo-first-order and pseudo-second-order kinetic models were used to describe the kinetic processes. Moreover, the adsorption isotherms for heavy metal ions were analyzed using Langmuir and Freundlich isotherms. GO-NH_2 exhibited a high adsorption capacity for heavy metal ion removal from real industrial wastewater.

2 Experimental

2.1 Materials

Graphite powder, APTES and standard heavy metals (1 000 mg L^{-1} of $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Cu}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2$) were purchased from Sigma-Aldrich (USA). Potassium permanganate, hydrogen peroxide (30%), potassium nitrate, sulfuric acid, sodium hydroxide and hydrochloric acid were purchased from Aladdin (Shanghai, China). Deionized water was obtained from a Millipore unit (Bedford, MA, USA).

2.2 Graphene oxide preparation

GO was prepared following the reported method [17]. Briefly, one gram of graphite powder and 1 g of potassium nitrate were mixed into a flask, and 50 mL sulfuric acid was added to the mixture in an ice bath. Potassium permanganate (6 g) was then added and stirred for 1 h at room temperature, and then 200 mL water was gradually added and stirred for 20 min at room temperature. Subsequently, 10 mL of a H_2O_2 (30%) aqueous solution was added, and the color of the mixture changed from dark brown to yellow. The mixture was centrifuged at 11 000 rpm for 20 min and then washed with 5% HCl solution and water until the pH value reached 7.0. Finally, the residual was dried in a vacuum oven at 100°C to obtain the GO powder.

2.3 Synthesis of GO-NH_2

The GO-NH_2 was synthesized by grafting APTES onto the GO surface. GO (1 g) was dispersed in ethanol (300 mL) through ultrasonication for 1 h. Then, APTES (10 mL) was added into a round-bottom flask under 70°C water bath. The mixture was vigorously stirred and refluxed for 4 h. After the reaction, the suspension was centrifuged at 11 000 rpm for 20 min. Following centrifugation and ultrasonication, the solid phase was washed with ethanol and water to remove the residual APTES. Finally, the GO-NH_2 was dried at 100°C under vacuum for further use.

2.4 Characterization

Scanning electron microscopy (SEM) was determined by using a Sigma 300 microscope (ZEISS, Germany). Transmission electron microscopy (TEM) was conducted on a Tecnai F30G2 microscope (FEI, Netherlands). X-ray diffraction (XRD) patterns were recorded with D8 ADVAHCL (Bruker, Germany) using Cu K radiation. The Fourier transform infrared (FTIR) spectroscopy was performed on a Fourier transform infrared Nicolet 5700 spectrophotometer (USA) in KBr pellets at room temperature. The zeta potentials at different pH values were measured by a NanoZS90 Zetasizer (Malvern, UK). The pH values of the heavy metal ion solutions were measured with a PHSJ-4A pH meter (Shanghai Precision Science Equipment Co. Ltd., China). The concentrations of heavy metals were monitored by a 6300 series inductively coupled plasma (ICP) spectrometer (ThermoFisher, USA). The elemental composition of GO and GO-NH_2 was analyzed with an Elemental Analyzer (Elementar, German).

2.5 Batch adsorption Experiments

Cr(VI), Cu(II), Pb(II) and Cd(II) were employed to evaluate the adsorption performance of GO-NH₂. The batch adsorption experiments were carried out by mixing GO-NH₂ (20 mg) with different concentrations of heavy metals in solution (20 mL). The adsorption process of heavy metal ions for an adsorbent is highly dependent on the initial pH of the solution. To study the effects of the pH, the initial pH values of heavy metal solutions were adjusted with 1 mol L⁻¹ HCl or NaOH solution. The initial concentration of heavy metal ions (100 mg L⁻¹) were prepared by diluting standard stock solutions with deionized water. All the adsorption experiments took place in test tubes under constant stirring (400 rpm) at 2°C. To investigate the adsorption equilibrium, different concentrations (10 ~ 300 mg L⁻¹) of heavy metal ions were used in the adsorption experiments.

After adsorption, the supernatant was separated from the suspensions by centrifugation at 10 000 rpm for 20 min, and the heavy metal ions of the aqueous phase were analyzed by the ICP spectrometer. The amount of metal ions adsorbed per unit mass of GO-NH₂ was calculated according to the following equation (1):

$$Q_t = \frac{(C_0 - C_t) \times V}{w} \quad (1)$$

where Q_t (mg g⁻¹) is the amount of heavy metal ions adsorbed onto unit amount of GO-NH₂ at time t (min), C_0 (mg L⁻¹) is the initial concentration of heavy metal ions in the solution, C_t (mg L⁻¹) represents the adsorption concentration at time t , V (mL) is the volume of the metal solution, and w (mg) represents the weight of the adsorbent used.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

3.1 Characterization

APTES was used to functionalize GO to increase its sorption efficiencies of heavy metal ions. The Si-OCH₂CH₃ group in the APTES modifier reacts with the hydroxyl groups in GO [18]. The morphologies and structures of GO and GO-NH₂ were observed by SEM and TEM, respectively. The SEM image of GO (Figure 1A) shows that the GO agglomerated

into a two-dimensional multilayered structure with a smooth surface and lateral sizes of several nanometers, which demonstrates the large specific surface area of GO. The diverse layers can overlap and interweave with each other to form the bright and shaded areas on the GO surface. A much rougher surface and more wrinkled structure are found in the GO-NH₂ SEM image (Figure 1B), and yet, the image was very similar to the GO SEM image. The TEM image of GO (Figure 1C) shows that few-layered structures were formed with lateral dimensions of several micrometers and that the GO had a smooth surface with many wrinkles. From Figure 1D, the GO-NH₂ TEM image shows that the GO-NH₂ retained multilayered structures similar to those of GO. The wrinkled surface of the GO-NH₂ film formed due to the crumpling and scrolling of GO-NH₂ sheets to maintain a high surface area and the nanostructure.

The FTIR spectrums of GO and GO-NH₂ are shown in Figure 2A. The characteristic peaks of GO-NH₂ at 3 243 cm⁻¹ and 1 537 cm⁻¹ can be attributed to the N-H stretching and asymmetric bending vibration, respectively [19]. Compared with GO, a new peak appeared at 901 cm⁻¹ for GO-NH₂, corresponding to the symmetric Si-O stretching vibration [20]. The FTIR spectral difference for GO-NH₂ indicates that APTES was grafted onto the GO surface through chemical bonding.

Figure 2B illustrates the XRD patterns of the GO and GO-NH₂ powders. An obvious characteristic diffraction peak appeared at 10.58°, which is attributed to the major oxygen-containing groups in GO. The results are consistent with the typical loose-layer-like structure of GO, corresponding to an interlayer spacing of 0.84 nm [21]. The small peak at 42.37° indicates a trace amount of graphite in GO [22]. The peak at 21° of GO-NH₂ might correspond to the existence of -NH₂ [23].

An elemental analysis of the nitrogen, carbon and hydrogen contents in GO, APTES and GO-NH₂ was performed, and the data are given in Table 1. The results show 0, 6.33 and 5.34 atomic % of nitrogen in GO, APTES and GO-NH₂, respectively. There is a significant increase in the nitrogen content of GO from 0 to 5.34%, after grafting APTES onto the GO surface. The carbon and hydrogen contents of GO-NH₂ are slightly different from those of GO. The results clearly demonstrate that APTES has been grafted onto the GO surface.

The pH zero point of charge (pH_{zpc}) is an important parameter to evaluate the adsorption property of an adsorbent [24]. The pH_{zpc} is the pH value when the net surface charge of the adsorbent equals zero. The GO-NH₂ charge is related to the pH, and the relationship was investigated by zeta potential measurements. As the

Figure 1: SEM images of (A) GO and (B) GO-NH₂; TEM images of (C) GO and (D) GO-NH₂.

Figure 2: (A) FTIR spectra of GO and GO-NH₂; (B) XRD patterns of GO and GO-NH₂.

Figure 3: (A) Zeta potentials of GO-NH₂ under various pH conditions; (B) Dependence of the GO-NH₂ adsorption capacity of Cr(VI), Cu(II), Pb(II) and Cd(II) ions on the pH of the solution. [conditions: C₀=100 mg L⁻¹; adsorbent dose=20 mg; temperature: 25°C; stirring: 400 rpm; adsorption time: 4 h].

Table 1: Elemental analysis of GO and GO-NH₂.

Sample	N%	C%	H%
GO	0	49.76	2.39
APTES	6.33	48.83	10.47
GO-NH ₂	5.34	49.5	3.53

pH increases, oxygen-containing functional groups are deprotonated, resulting in an increase in the negative charge on the GO-NH₂ surface. Figure 3A demonstrates that the zeta potential of GO-NH₂ increased first and then decreased gradually to -40 mV as the pH increased. The pH value varied in the range of 2.0 ~ 7.0, and the pH_{zpc} of GO-NH₂ is 3.8. The GO-NH₂ surface is negatively charged when the pH value is higher than 3.8. The hydroxyl and carboxylic functional groups on the GO-NH₂ edges develop negative charges due to deprotonation.

3.2 Effects of pH

The solution pH plays an important factor in the adsorption process owing to its remarkable effect on the speciation of metal ions, the surface charge and the protonation degree of the adsorbent. Various optimum pH values for adsorption experiments have been observed for different metals. The adsorption capacity through protonation and deprotonation of the functional material surface can be affected by the pH value [25]. The effects of the solution pH on the adsorption process was also investigated. For Cr(VI), Cu(II), Pb(II) and Cd(II), a series

of batch equilibrium adsorption experiments with GO-NH₂ under different pH conditions are shown in Figure 3B. The adsorption capacities of Cu(II), Pb(II) and Cd(II) increase as the pH value of the solution increases. For acidic solutions, the transformation of -NH₂ into NH₃⁺ causes a few -NH₂ sites on the GO-NH₂ surface to be available to react with heavy metal ions [26]. There are the weak electrostatic interactions between the GO-NH₂ and the metal ions because the low pH can inhibit the deprotonation of the functional groups on the GO-NH₂ surface [27]. Moreover, the H⁺ and H₃O⁺ in solution will compete for available adsorption sites on the GO-NH₂ surface. When the pH value increases, the protonation of amino groups is reduced, and the GO-NH₂ surface has more -NH₂ groups. Thus, more binding sites are available to coordinate with heavy metal ions, and the adsorption capacities of Cu(II), Pb(II) and Cd(II) increase. The amino groups on the GO-NH₂ surface adsorbed the hydroxyl ions with increasing the pH value, and more electrostatic adsorption replaces the coordination complexes [28]:

The maximum sorption capacity is observed at different pH values for Cr(VI), Cu(II), Pb(II) and Cd(II) ions. The adsorption capacity of Cr(VI) decreases with increasing pH values. Potassium dichromate can be dissolved in different ionic forms at different pH values. At an acidic pH value, the predominant Cr(VI) species consisted of H₂CrO₄⁰, HCrO₄⁻,

Figure 4: (A) Effects of contact time on the removal of Cr(VI), Cu(II), Pb(II) and Cd(II) by GO-NH₂; (B) The simulated pseudo-first-order kinetics and (C) the simulated pseudo-second-order kinetics for Cr(VI), Cu(II), Pb(II) and Cd(II) sorption onto GO-NH₂. [conditions: $C_0=100$ mg L⁻¹ (Cr(VI), Cu(II), Pb(II) and Cd(II)); pH=2.0 Cr(VI), 4.0 Cu(II), 5.0 Pb(II), 5.0 Cd(II); adsorbent dose=20 mg; temperature: 25°C; stirring: 400 rpm; adsorption time: 4 h].

CrO₄²⁻ and Cr₂O₇²⁻ [29]. The high adsorption efficiency of Cr(VI) at low pH is attributed to the electrostatic attraction to the highly protonated and positively charged GO-NH₂ [30]. The functional groups on the GO-NH₂ surface can change from protonated to deprotonated as the solution pH value increases. Negatively charged HCrO₄⁻ and Cr₂O₇²⁻ can be easily adsorbed to positively charged GO-NH₂ because

of electrostatic attraction. The surface charge of GO-NH₂ is positive when the pH value is less than 3.8. Negatively charged HCrO₄⁻ and Cr₂O₇²⁻ can be easily captured by the GO-NH₂. The predominant species of Cr(VI) is HCrO₄⁻ at a pH of 2.0 [31]. The adsorption capacity of Cr(VI) is highly dependent on the pH, and the maximum sorption capacity is observed at a pH of 2.0. Consequently, 2.0 was chosen as the optimal pH value for Cr(VI) adsorption.

3.3 Kinetics of metal ions on GO-NH₂

To investigate the adsorption capacity of GO-NH₂, adsorption experiments with Cr(VI), Cu(II), Pb(II) and Cd(II) were carried out at pH values of 2.0, 4.0, 5.0 and 5.0, respectively. The effect of contact time on the adsorption of heavy metal ions is shown in Figure 4A. The adsorption capacities of the heavy metals increased rapidly within the first 10 min and reached equilibrium at approximately 300 min. The GO-NH₂ sorbent had an excellent performance during the initial adsorption period because a large number of reaction sites were available for the adsorption of heavy metal ions. The adsorption capacities of Cr(VI), Cu(II), Pb(II) and Cd(II) are 96.02, 14.13, 38.43 and 14.01 mg g⁻¹, respectively.

Adsorption kinetics provide important information about the metal ion adsorption mechanisms of GO-NH₂. The pseudo-first-order kinetics and pseudo-second-order kinetics models were used to determine the rate constant and controlling mechanism of the adsorption process. The pseudo-first-order kinetic model is generally expressed as follows:

$$-\ln\left(1 - \frac{Q_t}{Q_e}\right) = k_1 t + C, \quad F = Q_t/Q_e \quad (2)$$

where Q_e (mg g⁻¹) is the amount of heavy metal ions adsorbed at equilibrium, Q_t (mg g⁻¹) is the amount of adsorption at any time t , and k_1 is the pseudo-first-order rate constant (min⁻¹). The plots of $-\ln(1-F)$ versus t are depicted in Figure 4B. The expression of the pseudo-second-order kinetics model is given as:

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \quad (3)$$

The linear form of the model obtained by the integral can be expressed as:

Table 2: Parameters of two kinetic models for Cr(VI), Cu(II), Pb(II) and Cd(II) adsorption onto GO-NH₂.

metal	first-order rate constants			second-order rate constants		
	Q _e (mg/g)	K ₁ (1/min)	R ²	K ₂ (g/mg·min)	Q _e (mg/g)	R ²
Cr(VI)	88.9	0.0056	0.9635	0.0035	90.4	0.9996
Cu(II)	14.1	-0.0001	-0.1331	0.1812	11.6	0.9058
Pb(II)	49.4	0.0025	0.7034	0.0011	53.9	0.9527
Cd(II)	9.1	0.0004	0.2007	0.0223	10.6	0.9564

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \left(\frac{1}{Q_e}\right) t \quad (4)$$

where k_2 (g mg⁻¹ min⁻¹) is the pseudo-second-order rate constant. The slope and intercept of a linear plot versus t yield the values of Q_e and k_2 , respectively, and the plot of versus t is shown in Figure 4C. The correlation coefficients were calculated from the pseudo-first-order and pseudo-second-order models, and the kinetic parameters were obtained for the adsorption of heavy metal ions on the GO-NH₂ at 25°C. The results are summarized in Table 2. The Q_e values obtained by the pseudo-second-order equation are 90.4, 11.6, 53.9 and 10.6 mg g⁻¹ for Cr(VI), Cu(II), Pb(II) and Cd(II), respectively. The correlation coefficient values of the pseudo-second-order model for Cr(VI), Cu(II), Pb(II) and Cd(II) ions are 0.9996, 0.9058, 0.9527 and 0.9564, respectively. The pseudo-second-order kinetic model fits the adsorption data for heavy metal adsorption on the GO-NH₂ better than the pseudo-first-order kinetic model. The pseudo-second-order kinetic model is predominant for the entire adsorption process. This phenomenon suggests that adsorption is the rate-controlling mechanism for heavy metal ion adsorption on the GO-NH₂. However, the correlation coefficient (0.9635) of the pseudo-first-order model is also higher for Cr(VI), suggesting that the adsorption process is also determined by the diffusion of Cr(VI) on the adsorbent.

3.4 Adsorption isotherms

Adsorption isotherms can describe the interaction between the adsorption capacity and the concentration of heavy metal ions at equilibrium. The effects of the initial metal ion concentrations on the adsorption capacity of the GO-NH₂ are shown in Figure 5A. The adsorption capacities of the heavy metals increased as the initial concentration increased from 10 to 200 mg L⁻¹. The maximum adsorption capacities are

Figure 5: (A) Adsorption isotherms of GO-NH₂ for metal ions; (B) Langmuir isotherm model for Cr(VI), Cu(II), Pb(II) and Cd(II) sorption onto GO-NH₂; (C) Linear fitting curves with the Freundlich model for Cr(VI), Cu(II), Pb(II) and Cd(II) sorption onto GO-NH₂. [conditions: $C_0=100$ mg L⁻¹ (Cr(VI), Cu(II), Pb(II) and Cd(II)); pH=2.0 Cr(VI), 4.0 Cu(II), 5.0 Pb(II), 5.0 Cd(II); adsorbent dose=20 mg; temperature: 25°C; stirring: 400 rpm; adsorption time: 4 h].

280.11, 26.25, 71.89 and 10.04 mg g⁻¹ for Cr(VI), Cu(II), Pb(II) and Cd(II), respectively. Obviously, the adsorption ability of GO-NH₂ toward Cr(VI) and Pb(II) is much higher than that for Cd(II) and Cu(II). These results reveal that GO-NH₂ has a stronger adsorption ability and a higher affinity for Cr(VI) and Pb(II). Moreover, the experimental data were analyzed using Langmuir and Freundlich isotherms. The Langmuir isotherm treats the adsorbent as a homogeneous adsorption surface with equivalent adsorption sites and energy, whereas the Freundlich isotherm assumes it is a heterogeneous surface [32]. The Langmuir adsorption model is described as follows:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \quad (5)$$

The Freundlich isotherm model is expressed as follows:

$$\ln Q_e = \ln k + \frac{1}{n} \ln C_e \quad (6)$$

where C_e (mg L⁻¹) is the equilibrium concentration of the adsorbate, Q_e (mg g⁻¹) is the amount adsorbed per unit mass of the adsorbent at equilibrium, Q_m (mg g⁻¹) is the maximum adsorption capacity corresponding to the Langmuir model, and b (L mg⁻¹) represents the equilibrium constant of the adsorption reaction. The values of Q_m and b can be calculated from the slope and intercept of a linear plot of C_e/Q_e versus C_e , and k and n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively.

The Langmuir and Freundlich isotherm parameters were calculated by means of linear fitting, as shown in Table 3. The adsorption isotherms of Cd(II) and Pb(II) are better fitted with the Langmuir model than the Freundlich model, implying that Cd(II) and Pb(II) adsorption onto GO-NH₂ is homogeneous [19,33]. The Freundlich model is more appropriate for Cr(VI) ($R^2=0.9957$) and Cu(II) ($R^2=0.8191$) adsorption, suggesting that the active sites on the GO-NH₂ surface are heterogeneous for Cr(VI) and Cu(II) sorption [11]. The Q_m values calculated from the Langmuir model are 280.11, 26.25, 71.89 and 10.04 mg g⁻¹ for Cr(VI), Cu(II), Pb(II) and Cd(II), respectively.

3.5 Adsorption mechanism

The adsorption process of heavy metal ions on the GO-NH₂ surface mainly includes three sorption mechanisms:

Table 3: Related constants and linear regression coefficients of Langmuir and Freundlich fitting for Cr(VI), Cu(II), Pb(II) and Cd(II) adsorption onto GO-NH₂.

Metal ions	Langmuir			Freundlich		
	Q_m (mg/g)	b (L/mg)	R^2	n	K (mg/g)	R^2
Cr(VI)	280.11	0.0207	0.9108	1.3626	493.86	0.9957
Cu(II)	26.25	0.0134	0.6930	2.6659	15.22	0.8191
Pb(II)	71.89	-0.1085	0.9289	3.3025	89.10	0.8968
Cd(II)	10.04	-0.1353	0.8595	3.8466	12.44	0.5489

(a) ion exchange, (b) surface complexation, and (c) electrostatic attraction [34]. For GO-NH₂, large amounts of -NH₂ can spread over the layered structure of GO to produce additional bare sorption sites for potential sorption, and NH₂ always forms chelates with heavy metals [23]. The GO-NH₂ can adsorb heavy metals via electrostatic interactions because it has various kinds of oxygen-containing active functional groups, such as hydroxyl, carbonyl and epoxy groups.

An ion exchange reaction between heavy metal ions and protons on -COOH or -OH groups is one adsorption mechanism. Metals are predominately adsorbed by a combination of ion exchange with carboxyl functional groups, and the possible relevant reactions between the oxygenous functional groups on the GO-NH₂ surface and the heavy metal ions may be represented as follows [14, 35]:

Surface complexation between heavy metal ions and various functional groups plays a significant role in the adsorption of metal ions. After APTES supplied -NH₂ to GO, the adsorption capacity increases owing to complexation between the amino groups and heavy metals [4]. Amino groups can chelate heavy metal ions, and heavy metal ions are strongly bound to amino groups [23]. The relevant reaction might be expressed as follows:

Heavy metal ion adsorption might also involve electrostatic attraction. The epoxy, carboxyl and hydroxyl groups on

Figure 6: Removal of heavy metals from industrial wastewater by the GO-NH₂. [conditions: initial concentrations of Cr(VI), Cu(II), Pb(II) and Cd(II) were 15.47, 11.01, 7.59 and 3.88 mg L⁻¹, respectively].

the GO-NH₂ surface can adsorb metal ions via electrostatic attractions [23]. The electrostatic attraction between positively charged heavy metal ions and the negatively charged surface of GO-NH₂ provides a driving force for the adsorption process. The carboxyl and hydroxyl groups on the GO-NH₂ surface can remove metal ions via electrostatic attraction, and the relevant reaction can be expressed as [14]:

The amino groups on the GO-NH₂ surface can be protonated to form -NH₃⁺ at low pH, and the -NH₃⁺ groups can adsorb anionic hexavalent Cr (HCrO₄⁻ and Cr₂O₇²⁻) owing to electrostatic attraction. The reactions can be expressed by the following equations [4]:

3.6 Adsorption of heavy metal from industrial wastewater

Generally, the adsorption of adsorbents in simulated heavy metal wastewater in the laboratory has been tested repeatedly [3,36], while few cases have investigated heavy metals in industrial wastewater with adsorbents. The high adsorption capacity of GO-NH₂ for Cr(VI), Cu(II), Pb(II) and Cd(II) indicates that it has great potential for treating heavy metals in industrial wastewater. Consequently, the

application of the GO-NH₂ sorbent was investigated with an industrial wastewater sample from a metal smelting plant in northwest China. The initial concentrations of Cr(VI), Cu(II), Pb(II) and Cd(II) were 15.47, 11.01, 7.59 and 3.88 mg L⁻¹, respectively. The suspended solids were removed by filtration, and the pH value of the industrial effluent was adjusted to 5.0 with HCl. The adsorption experiments were carried out by adding GO-NH₂ (20 mg) into the industrial effluent (20 mL) under constant stirring (400 rpm) at 25°C for 1 h. Figure 6 shows the results of adsorption on GO-NH₂ for Cr(VI), Cu(II), Pb(II) and Cd(II) in the industrial wastewater sample. The removal efficiencies of Cr(VI), Cu(II), Pb(II) and Cd(II) are 79.19%, 7.25%, 93.41% and 20.10%, respectively.

4 Conclusion

In this study, amino-functionalized GO was synthesized by a solvothermal method to investigate its adsorptive properties for Cr(VI), Cu(II), Pb(II) and Cd(II). The maximum adsorption capacities of Cr(VI), Cu(II), Pb(II) and Cd(II) are 280.11, 26.25, 71.89 and 10.04 mg g⁻¹ at optimal pH values of 2.0, 4.0, 5.0 and 5.0, respectively. The sorption kinetics of all the ions agreed well with the pseudo-second-order kinetic model, which indicates that the adsorption process is chemical sorption. The sorption isotherms of Pb(II) and Cd(II) agreed with the Langmuir model, whereas the Freundlich model isotherms fit the Cr(VI) and Cu(II). Removal experiments for Cr(VI), Cu(II), Pb(II) and Cd(II) in industrial wastewater by GO-NH₂ were carried out, and the maximum removal efficiency of the heavy metals is for Pb(II) (93.41%). All the above results indicate that GO-NH₂ can be considered as an effective sorbent for heavy metal removal.

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