Mechanism of Cd(II) and Cu(II) Adsorption onto Few-Layered Magnetic Graphene Oxide as an Efficient Adsorbent

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ABSTRACT: Heavy metal contamination caused by industrial discharge is a challenging environmental issue. Herein, an efficient adsorbent based on few-layered magnetic graphene oxide (FLMGO) was fabricated, characterized, and utilized to remove aqueous Cd(II) and Cu(II). Results present that the two components graphene oxide (GO) and Fe₃O₄ of FLMGO promote mutually, enabling FLMGO to outperform either GO or Fe₃O₄. Specifically, FLMGO adsorbs Cd(II) and Cu(II) with adsorption quantities of 401.14 and 1114.22 mg·g⁻¹ in 5 and 7 min, respectively. Moreover, FLMGO can be readily recovered via magnetic separation using a hand-held magnet. Adsorptions are spontaneous, endothermic, and entropy increasing, which are the best described by the Freundlich and pseudo-second-order model.

1. INTRODUCTION

The water environment is being contaminated continuously due to the booming growth of the global population and ever-intensifying human activities such as urbanization and industrialization. Among the knotty environmental issues, heavy metal pollution mainly caused by industrial effluents is a significant one. Various heavy metals including cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb), chromium (Cr), arsenic (As), and so forth are being discharged into the water environment. Heavy metals are chemically stable and non-biodegradable and thus can be persistently accumulated in the environment. Either long time or high level exposure to toxic heavy metals can induce a series of severe health problems including neurological damage, anemia, bone defect, cancer, and so forth. Therefore, developing efficient techniques to harness heavy metal pollution is urgently needed.

Common techniques for heavy metal removal include membrane extraction, ion exchange, electrochemical separation, catalytic reduction, adsorption, and so forth. Among these techniques, the adsorption technique is preferred owing to its superiorities such as low cost, high efficiency, and easy operation. Various adsorbents were employed for wastewater remediation, including activated carbon, chitosan, biochar, zeolite, polymer, carbon nanotube, metal–organic frameworks (MOFs), carbon quantum dots (CQDs), and graphene. Recently, graphene-based materials have garnered enormous attention as high-efficiency adsorbents for scavenging heavy metals from water. As an important graphene derivative, graphene oxide (GO) is the fabrication platform of many graphene-based materials. Generally, GO can be fabricated via exfoliating natural graphite under an oxidative condition based on the well-known Hummers method. During GO fabrication, various oxygenous groups including carbonyl, carboxyl, hydroxyl, and epoxy are introduced onto the aromatic ring, making GO highly hydrophilic, consequently form stably dispersed hydrosol.

The abundant oxygenous groups and the conjugated π electrons enable GO to interact with either inorganic or organic contaminants via π−π interaction, hydrogen bonding, and electrostatic attraction. However, the well dispersion of GO has both its pros and cons. On the one hand, well dispersion makes the adsorption sites of GO sufficiently exposed toward contaminants to make the most advantage of the adsorption potential. On the other hand, however, well dispersion makes GO recovery be cumbersome, leading to inferior recycling efficiency and secondary contamination. To overcome this drawback, magnetic particles were introduced to obtain recovery convenience. Among magnetic phases, Fe₃O₄ attracted particular interests because of its easy fabrication, good biocompatibility, and low cost. In the GO/Fe₃O₄ architecture, Fe₃O₄ provides four functions.
Provides separation and recovery convenience. (2) Provides steric hindrance against the restack and aggregation of the graphene sheets due to the strong π–π interaction. (3) Provides adsorption capacity. (4) Attachment onto graphene sheets inhibits the agglomeration of Fe3O4 itself.

In view of the benefits brought by Fe3O4 introduction, a number of studies were carried out regarding the adsorption performance of GO/Fe3O4 for various aqueous contaminants, accordingly, remarkable progress was achieved.20−22,31−34 However, further research efforts are needed to fill two gaps: (1) the adsorption efficiency of GO/Fe3O4 is yet to be improved in terms of either enhancing the adsorption capacity or shortening the adsorption time. (2) Deep and clear understanding of the interaction mechanism of GO/Fe3O4 with aqueous contaminants at the atomic level.

The two objectives of this work are as follows: (1) fabricate a highly efficient adsorbent based on the GO/Fe3O4 architecture with high adsorption capacity and short adsorption time for aqueous heavy metals. (2) Clarify the GO/Fe3O4 heavy metal interaction mechanism at an atomic level. Accordingly, efforts were made in three levels: (1) fabrication level. The reaction conditions were elaborately designed and controlled to obtain a few-layered magnetic graphene oxide (FLMGO) based on the GO/Fe3O4 architecture with high adsorption efficiency. (2) Characterization level. The as-fabricated FLMGO was intensively characterized to reveal its morphological, chemical, and physical features which are responsible for its high adsorption efficiency. (3) Mechanism level. The adsorbent–adsorbate interaction mechanism was deeply elucidated based on a comprehensive analysis via incorporating the batch adsorption tests, adsorption fittings, and spectroscopic features of FLMGO before and after adsorption.

Two major aqueous contaminants, Cd(II) and Cu(II), were selected as models to examine the adsorption efficiency of FLMGO. The findings of this work may impel the GO/Fe3O4 architecture as a potential adsorbent toward practical application.

2. ADSORPTION FITTING AND INTERACTION MECHANISM

The adsorption isotherms were investigated via fittings based on the Langmuir, Freundlich, Temkin, and D-R models. The adsorption kinetics were analyzed via fittings based on the pseudo-first-order (PFO), pseudo-second-order (PSO), intra-particle diffusion (IPD), liquid film diffusion (LFD), and Bangham models. The thermodynamic parameters were determined via the fitting based on the van’t Hoff equation. The adsorption type and mechanism were clarified based on the overall consideration of the adsorption experiments, adsorption fittings, and the XPS spectra of the samples before and after adsorption.

3. Quantitative Evolution of Aqueous Cd(II) and Cu(II) Species with pH. The following reaction was analyzed in terms of equilibrium thermodynamics to investigate the quantitative evolution of aqueous Cd(II) and Cu(II) species with pH

\[ \text{M}^{2+} + \text{iOH}^- \rightleftharpoons \text{M(OH)}^{2-i}_i \]

\[ \beta_i = \frac{C_{\text{M(OH)}^{2-i}_i}}{C_{\text{M}^{2+}}C_{\text{OH}^-}} \]  

where M denotes Cd or Cu, \( \beta_i \) is the stability constant of the i-grade complex \( \text{M(OH)}^{2-i}_i \), undoubtedly, \( \beta_0 = 1 \). \( \text{COH}_i \) and \( C_{\text{M(OH)}^{2-i}_i} \) denotes the molar concentrations of \( \text{OH}^- \), \( \text{M(OH)}^{2-i}_i \).

Equation 2 gives eq 3, which is used to determine \( C_\text{a} \) the total concentration of the entire M(II) species

\[ C_i = C_{\text{M}^{2+}} \sum_{i=0}^{n} \beta_i \left( \frac{C_{\text{OH}^-}}{C_{\text{M}^{2+}}C_{\text{OH}^-}} \right)^i \]  

Equation 3 gives eq 4, which is used to determine \( X_i \) the molar fraction of i-grade species \( \text{M(OH)}^{2-i}_i \)

\[ X_i = \frac{C_{\text{M(OH)}^{2-i}_i}}{C_i} = \frac{\beta_i \left( \frac{C_{\text{OH}^-}}{C_{\text{M}^{2+}}C_{\text{OH}^-}} \right)^i}{\sum_{i=0}^{n} \beta_i \left( \frac{C_{\text{OH}^-}}{C_{\text{M}^{2+}}C_{\text{OH}^-}} \right)^i} \]  

where 0 ≤ \( X_i \) ≤ 1, \( \sum_{i=0}^{n} X_i = 1 \).

In view of \( C_{\text{OH}^-} = 10^{pH-14} \), eq 4 becomes

\[ X_i = \frac{\beta_i 10^{pH-14}}{\sum_{i=0}^{n} \beta_i 10^{pH-14}} \]  

\( X_i \) at varying pH is determined by eq 5 to plot Figure S1 (in Supporting Information), which illustrates the quantitative evolution of aqueous Cd(II) and Cu(II) species with pH, specifically:

(1) Cd(II): when pH < 8, the dominant Cd(II) species is \( \text{Cd}^{2+} \); when 8 < pH < 10, the dominant Cd(II) species are \( \text{Cd}^{2+} \) and \( \text{Cd(OH)}^+ \); when 10 < pH < 12, the dominant Cd(II) species is \( \text{Cd(OH)}_2^+ \) and when pH > 12, the dominant Cd(II) species is \( \text{Cd(OH)}_3^- \) or even \( \text{Cd(OH)}_4^- \).

(2) Cu(II): when pH < 7, the dominant Cu(II) species is \( \text{Cu}^{2+} \); when 7 < pH < 8, the dominant Cu(II) species are \( \text{Cu(OH)}^+ \) and \( \text{Cu(OH)}_2^- \); when 8 < pH < 11, the dominant Cu(II) species is \( \text{Cu(OH)}_2^- \) and when pH > 11, the dominant Cu(II) species is \( \text{Cu(OH)}_3^- \) or even \( \text{Cu(OH)}_4^- \).

4. RESULTS AND DISCUSSIONS

4.1. Characterization. Figure 1 shows the XRD patterns of Fe3O4, GO, and FLMGO. For GO, the peak at 2θ = 12.9° is the typical (001) reflection of GO.23 For Fe3O4 and FLMGO, the peaks at 2θ = 21.3, 30.3, 35.6, 43.1, 53.6, 57.2, and 62.7° are assigned to the (002), (220), (311), (400), (442), (511), and (440) reflections of magnetite, respectively,22 which can be indexed as the face-centered cubic structure with the space group of \( Fd\bar{3}m \), in well accordance with JCPDS NO. 19-7029.
This identification confirms the in situ formation of Fe$_3$O$_4$ on the graphene sheets. However, no clear graphene peak was detected in the XRD pattern of FLMGO, possibly due to the strong crystallinity of Fe$_3$O$_4$ which made GO diffraction weak.

Figure 2 displays the FESEM images of GO and FLMGO, as well as the EDX elemental spectrum of FLMGO. In the GO image, typical laminar morphology was observed. The folded and interlaced graphene sheets were clearly viewable. In the FLMGO image, the laminar morphology of graphene sheets were still apparent. Besides, spherical Fe$_3$O$_4$ particles with a diameter of around 150 nm were wrapped in the graphene interlayer. The two components GO and Fe$_3$O$_4$ of FLMGO bring beneficial effects for each other. For GO, Fe$_3$O$_4$ particles provide steric hindrance against the restack and aggregation of the graphene sheets. For Fe$_3$O$_4$, GO serves as a matrix to prevent Fe$_3$O$_4$ from agglomerating; meanwhile, it serves as a shield to protect Fe$_3$O$_4$ from being dissolved by corrosive media.36 The elemental signals detected in the EDS elemental spectrum confirmed the existence of C, O, and Fe in FLMGO.

Figure S2 (in Supporting Information) shows the FTIR spectra of Fe$_3$O$_4$, GO, and FLMGO. The peaks at 3420, 3425, and 3431 cm$^{-1}$ are due to the stretching vibration of O$-$H. The peaks at 1632 and 1637 cm$^{-1}$ come from the stretching vibration of aromatic C$\equiv$C, confirming the existence of graphene rings in GO and FLMGO.24 The peaks at 1403 and 1404 cm$^{-1}$ correspond to the stretching vibration of C$-$OH, and the peaks at 1110 and 1085 cm$^{-1}$ are ascribed to the stretching vibration of C$-$O. These oxygenous groups in GO and FLMGO were those introduced via oxidative exfoliation of graphite during GO preparation. Finally, the peaks at 582 and 611 cm$^{-1}$ in the FTIR spectrum of Fe$_3$O$_4$ and FLMGO are assigned to the stretching vibration of Fe$-$O,22 indicating the presence of Fe$_3$O$_4$ in FLMGO. Careful observation reveals two main differences. (1) The difference between FLMGO and GO. The peak intensities decreased noticeably, and peak positions shifted slightly as the former is compared with the latter regarding the oxygenous groups. (2) The difference between FLMGO and Fe$_3$O$_4$. The peak intensity decreased remarkably, and the peak position shifted noticeably as the former is compared with the latter regarding Fe$-$O. These two differences yield two implications. (1) GO was reduced during FLMGO fabrication. (2) Considerably strong chemical interaction exists between Fe$_3$O$_4$ and GO in FLMGO.

Figure S3 (in Supporting Information) demonstrates the TG-DTA curves of FLMGO. The thermal process comprised four consecutive stages as manifested by different background colors. In the first stage, $T < 100 \, ^{\circ} C$, the slight weight loss of 1.55% is due to the evaporation of the surface moisture. In the second stage, $100 \, ^{\circ} C < T < 350 \, ^{\circ} C$, weight loss 8.51% and notable DTA value correspond to the removal of relatively labile oxygenous groups.18 In the third stage, $350 \, ^{\circ} C < T < 800 \, ^{\circ} C$, weight loss 8.54% and the considerable DTA value correspond to the removal of relatively stable oxygenous groups and pyrolysis of the carbon skeleton.18 In the fourth
stage, $T > 800 \, ^\circ C$, the weight loss corresponds to the pyrolysis of the residue carbon skeleton. Finally, the weight percent was stabilized at 53.85%. Based on the abovementioned analyses, the weight percent of the oxygenous groups and Fe$_3$O$_4$ in FLMGO were determined as approximately 17 and 54%, respectively.

The specific surface area is a crucial parameter which directly correlated with the adsorption efficiency of a potential adsorbent. Figure S4 (in Supporting Information) presents the $N_2$ adsorption–desorption isotherms and pore size distribution curve of FLMGO. The adsorption isotherm and hysteresis loop refer to type V and H3, respectively, as proposed by the IUPAC standards. These types are indicative of the mesoporous material which commonly appears in either flaky or layered materials. The pore size was centered at 3.8 nm, verifying the mesoporous feature. Distribution of Fe$_3$O$_4$ particles along the graphene sheets gives rise to these slit-shaped mesopores. The BET surface area and BJH pore volume were 224.10 m$^2$·g$^{-1}$ and 0.3114 cm$^3$·g$^{-1}$, respectively. The high specific area is capable of accommodating abundant adsorption sites whereby exhibiting high adsorption capacity.

Fe$_3$O$_4$ brings FLMGO with magnetic properties. Accordingly, the magnetization curve of FLMGO was measured at room temperature to investigate the origin of magnetic separation. As Figure S5 (in Supporting Information) depicts, FLMGO has saturation magnetization, remanence, and coercivity as 9.0891, 0.5233 emu·g$^{-1}$, and 0.2500 kG, respectively. Owing to this sufficient saturation magnetization and low remanence, FLMGO can be readily magnetized or demagnetized when an outer magnetic field generated using a hand-held magnet is present or absent. Resultantly, magnetic separation is completed in 15 s, as illustrated by the inset at the lower right corner. The convenient separation is essential for realizing high adsorption efficiency.

The pH$_{pzc}$ (point of zero charge) is a crucial indicator reflecting the surface charge and determining the electrophoretic motion of the collosol particles. When pH reaches pH$_{pzc}$, the net total surface charge and thus the zeta potential become zero. Figure S6 (in Supporting Information) indicates that the zeta potential of FLMGO hydrosol decreased as pH increases, thereby reaching zero at pH = 5, indicating that pH$_{pzc}$ of FLMGO is 5. Accordingly, when pH < 5, the surface charge of FLMGO is positive, and when pH > 5, the surface charge of FLMGO is negative, respectively.

4.2. Adsorption Performance. 4.2.1. Performance Control for Fe$_3$O$_4$, GO, and FLMGO. Adsorption performance of each single component and composite was compared and analyzed via a control experiment, in which all conditions were set identical for Fe$_3$O$_4$, GO, and FLMGO. Figure 3 shows that the adsorption efficiencies for both Cd(II) and Cu(II) were in the order FLMGO > GO > Fe$_3$O$_4$. Regarding GO as the benchmark, the outperformance of FLMGO over GO is caused by two reasons: (1) Fe$_3$O$_4$ particles hinder the aggregation of graphene sheets. (2) Fe$_3$O$_4$ itself adds to the adsorption capacity. Regarding Fe$_3$O$_4$ as the benchmark, the outperformance of FLMGO over Fe$_3$O$_4$ is caused by three reasons: (1) GO acts as a matrix to prevent Fe$_3$O$_4$ from agglomerating. (2) GO acts as a shield to protect Fe$_3$O$_4$ from being dissolved by corrosive media. (3) GO itself adds to the adsorption capacity. In conclusion, the mutual promotion between GO and Fe$_3$O$_4$ render a synergistic effect, which made FLMGO outperform either GO or Fe$_3$O$_4$.

Figure 4. Effect of pH on the adsorptions of Cd(II) and Cu(II) by FLMGO. Cd(II) adsorption: pH = 3–13, $t =10$ min, $D = 500$ mg·L$^{-1}$, $C_0 = 200$ mg·L$^{-1}$, and $T = 25$ °C. Cu(II) adsorption: pH = 3–13, $t =10$ min, $D = 500$ mg·L$^{-1}$, $C_0 = 600$ mg·L$^{-1}$, and $T = 25$ °C.

4.2.2. Effect of pH. pH is a crucial influential factor which impacts adsorption via influencing the adsorbate, adsorbent, and adsorption media (usually water): (1) pH influences the species distribution of the adsorbate. (2) pH influences the surface charge of the adsorbent. (3) pH influences the ionization of water. Figure 4 shows that as pH increased, Cd(II) adsorption increased to reach its peak at pH = 7, followed by small fluctuation, whereas Cu(II) adsorption increased to reach its peak at pH = 8 and then decreased. These curves can be interpreted based on Figure S1 and S6 (in the Supporting Information). When pH < 5, FLMGO has a positive charge, while the dominant species of Cd(II) and Cu(II) are Cd$^{2+}$ and Cu$^{2+}$, respectively. Besides, the water ionization is biased toward H$^+$. The electrostatic repulsion between FLMGO and Cd$^{2+}$ (or Cu$^{2+}$) and the competitive adsorption of H$^+$ with Cd$^{2+}$ (or Cu$^{2+}$) lead to low adsorption efficiency. When pH exceeds 5, the FLMGO is negatively charged, while Cd$^{2+}$, Cd(OH)$^+$, Cu(OH)$^+$, or Cu(OH)$_2$ is the dominant Cd(II) or Cu(II) species. Thereby, the electrostatic attraction between negative FLMGO and positive Cd(II) (or Cu(II)) enhances adsorption. However, Cd(II) and Cu(II) adsorption decreased by different extents with the further increase in pH, and the decrease in the latter was more remarkable than the former. These are due to the formation of hydroxide precipitates. Moreover, Cu(OH)$_2$ emerges as dominant species under a lower pH than Cd(OH)$_2$ does (Figure S1).

4.2.3. Effect of the Contact Time. Contact time is one of the critical adsorption parameters, as short contact time means high adsorption efficiency. Figure S7 (in Supporting Information) illustrates the adsorption isotherm and pore size distribution curve of FLMGO. The adsorption isotherm and hysteresis loop refer to type V and H3, respectively, as proposed by the IUPAC standards. These types are indicative of the mesoporous material which commonly appears in either flaky or layered materials. The pore size was centered at 3.8 nm, verifying the mesoporous feature. Distribution of Fe$_3$O$_4$ particles along the graphene sheets gives rise to these slit-shaped mesopores. The BET surface area and BJH pore volume were 224.10 m$^2$·g$^{-1}$ and 0.3114 cm$^3$·g$^{-1}$, respectively. Owing to this sufficient saturation magnetization and low remanence, FLMGO can be readily magnetized or demagnetized when an outer magnetic field generated using a hand-held magnet is present or absent. Resultantly, magnetic separation is completed in 15 s, as illustrated by the inset at the lower right corner. The convenient separation is essential for realizing high adsorption efficiency.

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Figure 3. Performance control of Fe$_3$O$_4$, GO, and FLMGO on Cd(II) and Cu(II). Cd(II) adsorption: pH = 7, $t = 10$ min, $D = 500$ mg·L$^{-1}$, $C_0 = 200$ mg·L$^{-1}$, and $T = 25$ °C. Cu(II) adsorption: pH = 8, $t = 10$ min, $D = 500$ mg·L$^{-1}$, $C_0 = 200$ mg·L$^{-1}$, and $T = 25$ °C.
4.2.5. Effect of the Adsorbate Initial Concentration. Batch adsorption was implemented on heavy metals with an initial concentration of 100–1000 mg L\(^{-1}\) to assess the capability of FLMGO treating target contaminants with different concentrations. Figure S9 (in Supporting Information) shows that as metal concentration increases, the adsorption percent decreased, while adsorption quantity increased. Likewise, these tendencies can be explained from two perspectives. (1) Adsorbate perspective. On the one hand, adsorbates exceed the adsorbent capacity due to high initial concentration and make the adsorption percent decrease thermodynamically. On the other hand, high adsorbate concentration gives rise to a high concentration gradient and sufficient collision frequency with the adsorbent, thereby making adsorption quantity increase kinetically. (2) Adsorbent perspective. On the one hand, with the increase in adsorbate concentration, few vacant adsorption sites are left available to uptake adsorbates, making the adsorption percent decrease thermodynamically. On the other hand, with the increase in adsorbate concentration, adsorption sites are subject to more collisions by adsorbates, making the adsorption quantity increase kinetically. Figure S9 displays that FLMGO maintained an adsorption percent of >95% on Cd(II) and > 89% on Cu(II) with a concentration of 100–1000 mg L\(^{-1}\), indicating superior adaptability to concentration fluctuation.

4.2.6. Effect of Coexisting Substances. Electrolytes and organic substances are commonly present in wastewater, which may interfere with the adsorption of the target metal onto the adsorbent. Therefore, investigating the effect of coexisting substances is necessary. In this work, NaCl and humic acid (HA) were used to represent the coexisting electrolyte and organic substance, respectively. Accordingly, adsorption efficiency was evaluated under the presence of NaCl and HA with different concentrations. The electrolyte impacts adsorption efficiency either favorably or unfavorably via affecting all the three elements of the adsorption system as follows. (1) Impact on the adsorbate. First, the electrolyte competes particularly with ionic adsorbates for adsorption sites. Second, the electrolyte induces adsorbates to salt out. Third, some electrolytic ions such as F\(^-\) and Cl\(^-\) may complex metal ions to change its aqueous species. (2) Impact on the adsorbent. Electrolytic ions adsorbed onto the adsorbent surface to change its thickness of the electric double layer and surface charge via electrical neutralization. These changes make adsorbent particles be squeezed and poorly dispersed. (3) Impact on adsorption media (generally water). Electrolyte addition enhances the electric conductivity of a solution, whereby facilitating the mobility of ionic adsorbates to influence the adsorption kinetics.

HA is a category of widespread organic substances coming from the degradation and conversion of the remains of animals and plants. Similar to the electrolyte, HA may impact adsorption efficiency either favorably or unfavorably. HA is water-soluble and highly hydrophilic. The aromatic rings and various functional groups including carboxyl, hydroxyl, carbonyl, and quinonyl in its molecule can bind various water contaminants. On the one hand, heavy metal-complexed HA may disperse stably in solution due to its high hydrophilicity, thereby decreasing adsorption efficiency. On the other hand, heavy metal-complexed HA may be attached onto graphene via π–π interaction, subsequently separated along with graphene after adsorption, thereby increasing adsorption efficiency.

Figure S10 (in Supporting Information) shows that adsorption efficiency of both Cd(II) and Cu(II) fluctuates slightly as NaCl concentration varies in the range 0–35 mmol L\(^{-1}\), which yields two implications. (1) The favorable and unfavorable impacts on adsorption brought by NaCl balance each other. (2) An inner sphere complex with a compact and stable structure may be formed\(^{38,39}\) between FLMGO and Cd(II) or Cu(II) via chemical interaction, thereby making adsorption insensitive to the electrolyte.

Figure S11 (in Supporting Information) exhibits that Cd(II) adsorption decreased notably, while Cu(II) adsorption decreased slightly as HA concentration increased in the range of 0–350 mg L\(^{-1}\). These results provide indications with respect to the impacts brought by HA on adsorption: for Cd(II), the unfavorable one prevailed over the favorable one; while for Cu(II), the favorable and unfavorable ones balanced each other. In all, the impact of HA on Cu(II) adsorption was slighter than that on Cd(II), implying that FLMGO may have a stronger interaction with Cu(II) than with Cd(II).

4.2.7. Effect of Temperature. The temperature effect on adsorption efficiency was also inspected. Figure S12 (in Supporting Information) shows that when temperature increased from 10 to 35 °C, adsorption efficiency of both Cd(II) and Cu(II) increased by a certain extent. Accordingly, endothermic adsorptions are suggested. These results can be understood from the perspectives of both thermodynamics and...
kinetics. (1) Thermodynamic perspective. Elevating temperature enhances the ionization of the functional groups to form more binding sites for heavy metals. (2) Kinetic perspective. Elevating temperature intensifies Brownian motion to facilitate the diffusion of adsorbates toward the adsorbent.

4.2.8. Cyclic Adsorption Efficiency. Recycling efficiency of the adsorbent is an important factor that needs special attention. In this work, five consecutive cycles were implemented with the following procedure. The Cd(II)- or Cu(II)-adsorbed FLMGO was put into 20 mL of deionized water, and the pH was adjusted to 3. Then, the suspension was shaken for 30 min. Finally, the regenerated FLMGO was collected for the next cycle of adsorption.

Figure 5 shows that even after five consecutive cycles, the decay of Cd(II) adsorption efficiency was very slight. However, the adsorption efficiency of Cu(II) was 100% after one cycle and then decayed more in the subsequent cycles.

decay of Cu(II) adsorption efficiency was more noticeable. Generally, decay of recycling efficiency is mainly caused by two losses: adsorbents not recovered (matter loss) and adsorption sites not regenerated (energy loss). Specifically, the difference of the regeneration efficiency regarding Cd(II) and Cu(II) was ascribed to the difference of the regeneration degree of Cd(II)- and Cu(II)-adsorbed FLMGO. As Figure 5 displays, the adsorption efficiency of Cd(II) is noticeably inferior to that of Cu(II) under a pH of 3. This implies that Cd(II)-adsorbed FLMGO is regenerated more completely than Cu(II)-adsorbed FLMGO under a pH of 3. Therefore, FLMGO exhibited a better recycling efficiency for Cd(II) than for Cu(II).

4.3. Adsorption Fitting. 4.3.1. Adsorption Isotherms. The Langmuir model \( Q_e = Q_{\text{max}} \frac{Q_0}{1 + K_L C_0} \) is expressed as

\[
Q_e = \frac{Q_{\text{max}} C_e}{1 + K_L C_e}
\]

Where \( Q_{\text{max}} \) (mg·g\(^{-1}\)) stands for the monolayer adsorption capacity, \( K_L \) (L·mg\(^{-1}\)) is the constant related to the adsorption energy. The adsorption feature is predicted based on the equilibrium factor \( R_L \) which is defined as \( R_L = 1/(1 + C_0 K_L) \). Specifically, \( 0 < R_L < 1 \) represents favorable adsorption, \( R_L > 1 \) represents unfavorable adsorption, \( R_L = 0 \) represents irreversible adsorption, and \( R_L = 1 \) represents linear adsorption.

The Freundlich model \( Q_e = K_F C_e^{1/n} \) is expressed as

where \( K_F \) and \( n \) are constants associated with the adsorption capacity and intensity, respectively. The value of \( n \) discloses whether the adsorption is chemical \( (n < 1) \) or physical \( (n > 1) \). The Temkin model \( Q_e = (RT/A_T)(\ln B_T + \ln C_e) \) is expressed as

\[
Q_e = \frac{(RT/A_T)(\ln B_T + \ln C_e)}{1 + \ln C_e}
\]

where \( R \) (8.314 J·mol\(^{-1}\)·K\(^{-1}\)) is the gas constant, \( T \) (K) is the thermodynamic temperature, and \( A_T \) (J·mol\(^{-1}\)) and \( B_T \) (L·g\(^{-1}\)) are constants associated with the adsorption heat and the maximum binding energy, respectively. The D-R model \( Q_e = \frac{C_e}{k_D^d + C_e} \) is expressed as

\[
Q_e = \frac{C_e}{k_D^d + C_e}
\]

where \( Q_{\text{max}} \) is the maximum adsorption capacity, \( \beta \) is the Polanyi potential, and \( \epsilon \) is a constant related with \( E \) (k·mol\(^{-1}\)), the mean free energy of adsorption.

The fitting curves of the isotherm models are illustrated in Figure S13 (in Supporting Information), and the corresponding fitting results are listed in Tables S1 and S2 (in Supporting Information). Among the four isotherm models, the Freundlich model renders the best fitting, as the linear correlation coefficient \( R^2 \) is 0.9947 and 0.9992 for Cd(II) and Cu(II) adsorption, respectively. However, the Langmuir fitting is also quite satisfactory, whose \( R^2 \) is 0.9586 and 0.9839 for Cd(II) and Cu(II) adsorption, respectively. More importantly, the Langmuir and Freundlich parameters \( R_L \) and \( n \) indicative of the adsorption type are all <1. These results suggest that (1) the adsorbent surface is heterogeneous with respect to adsorption affinity. Clearly, this heterogeneity arises from both phase and functional group diversity in FLMGO. (2) Both Cd(II) and Cu(II) adsorptions are favorable chemical processes. However, neither Temkin nor D-R fittings were satisfactory.

4.3.2. Adsorption Kinetics. The PFO model \( Q_t = \frac{k_1 t}{1 + (k_2 Q_e)^{1/2}} \) is expressed as

\[
Q_t = \frac{k_1 t}{1 + (k_2 Q_e)^{1/2}}
\]

where \( k_1 \) (min\(^{-1}\)) is the PFO rate constant. The PSO model \( Q_t = \frac{k_1 t^{1/n}}{1 + k_2 t^{1/n}} \) is expressed as

\[
Q_t = \frac{k_1 t^{1/n}}{1 + k_2 t^{1/n}}
\]

where \( k_2 \) (g·mg\(^{-1}\)·min\(^{-0.5}\)) is the PSO rate constant. The IPD model \( Q_t = k_d t^{0.5} + C \) is expressed as

\[
Q_t = k_d t^{0.5} + C
\]

where \( k_d \) (g·mg\(^{-1}\)·min\(^{-0.5}\)) is the IPD rate constant and \( C \) (mg·g\(^{-1}\)) is a constant about the boundary layer thickness.

The LFD model \( Q_t = \frac{1}{k_l \ln(t)} \) is expressed as

\[
Q_t = \frac{1}{k_l \ln(t)}
\]

where \( k_l \) is the LFD rate constant. The Bangham model \( Q_t = k D t + C \) is expressed as

\[
Q_t = k D t + C
\]

where \( k_D \) is the Bangham rate constant and \( C \) (mg·g\(^{-1}\)) is a constant about the boundary layer thickness.

The fitting curves of the kinetic models are illustrated in Figure S14 (in Supporting Information), and the correspond-
ing fitting results are listed in Tables S1 and S2 (in Supporting Information). Among the five kinetic models, the PSO model renders the best fitting, as the linear correlation coefficient R² is 0.9999 and 0.9998 for Cd(II) and Cu(II) adsorption, respectively. More importantly, adsorption capacity for Cd(II) and Cu(II) as determined via PSO fitting are 403.23 and 1146.91 mg·g⁻¹, respectively, which are in good accordance with the batch adsorption results 401.14 and 1114.22 mg·g⁻¹, respectively (Figure S7 in Supporting Information). These fitting results indicate that the adsorption rate is controlled by chemical interaction.45 The IPD fitting is also quite satisfactory. Particularly, IPD fitting curves of both Cd(II) and Cu(II) adsorptions display three consecutive stages as highlighted by red, dark green, and violet backgrounds (Figure S14e in Supporting Information). These three stages correspond to film diffusion, pore diffusion, and surface reaction, respectively, which are characteristic of chemical adsorption.49 Moreover, the surface reaction stage manifest the lowest slope, indicating that surface reaction or the chemical interaction between the adsorbate and adsorbent controls the adsorption rate, supporting the conclusion of PSO fitting. Finally, the PFO, LFD, and Bangham fittings are far from being satisfactory, suggesting that neither LFD nor pore diffusion controls the adsorption rate. In conclusion, Cd(II) and Cu(II) adsorption rates are simultaneously controlled by IPD and chemical interaction.

4.3.3. Adsorption Thermodynamics. The parameters of the adsorption thermodynamics are calculated using the van’t Hoff equation

\[ \ln K^\theta = \frac{-\Delta G}{RT} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \]

where \( K^\theta \) (L·g⁻¹) is the equilibrium constant, \( \Delta G \) (kJ·mol⁻¹) is the free energy change, \( \Delta H \) (kJ·mol⁻¹) is the enthalpy change, and \( \Delta S \) (J·K⁻¹·mol⁻¹) is the entropy change. The fitting curves are shown in Figure S15 (in Supporting Information), and thermodynamic parameters are listed in Tables S1 and S2 (in Supporting Information).

Tables S1 and S2 list \( \Delta G < 0, \Delta H > 0, \) and \( \Delta S > 0 \), accordingly, spontaneous, endothermic, and entropy increasing features are inferred. Furthermore, as the temperature increases, \( \Delta G \) becomes more negative, meaning that adsorption becomes more spontaneous, which is in accordance with the endothermic feature and the efficiency enhancement owing to increasing temperature (Figure S12 in Supporting Information). Finally, \( \Delta S > 0 \) suggests that the randomness of the adsorption system increases as adsorption proceeds.

4.4. Interaction Mechanism. The XPS spectra of the adsorbent before (FLMGO) and after (FLMGO-Cd and FLMGO-Cu) adsorption were scrutinized to clarify the adsorbent–adsorbate interaction mechanism. Figure 6 compares the survey spectra of GO, FLMGO, FLMGO-Cd, and FLMGO-Cu. The O 1s and C 1s peaks signify oxygen and carbon, the intrinsic elements of GO. The intensity ratios of O 1s/C 1s for GO and FLMGO were 1.86 and 1.36, respectively. (2) The difference in peak position. The O 1s peak of FLMGO displays a single peak, while that of both FLMGO-Cd and FLMGO-Cu displays two sub-peaks. (2) The difference in the peak position. The O 1s peak of FLMGO-Cd is at 530.7 and 531.9, and that of FLMGO-Cu is at 530.7 and 531.9 and 530.3 and 531.7 eV, respectively. (3) The difference in peak intensity. The overall O 1s peak intensity of FLMGO-Cd and FLMGO-Cu is noticeably lower than that of FLMGO. These differences suggest that the oxygen atoms in FLMGO participated in Cd(II) and Cu(II) uptake. Figure 7 compares the Cd 3d spectrum of FLMGO-Cd and Cu 2p spectrum of FLMGO-Cu. Three important differences were discovered, which are summarized as follows. (1) The difference in peak shape. The O 1s spectrum of FLMGO displays a single peak, while that of both FLMGO-Cd and FLMGO-Cu displays two sub-peaks. (2) The difference in the peak position. The O 1s peak of FLMGO-Cd is at 531.6 eV, while that of FLMGO-Cu is at 530.7 and 531.9 and 530.3 and 531.7 eV, respectively. (3) The difference in peak intensity. The overall O 1s peak intensity of FLMGO-Cd and FLMGO-Cu is noticeably lower than that of FLMGO. These differences suggest that the oxygen atoms in FLMGO participated in Cd(II) and Cu(II) uptake.
coordinated toward Cd(II) and Cu(II). (3) Difference in peak intensity. The overall C 1s peak intensity of FLMGO-Cd and FLMGO-Cu is relatively higher than that of FLMGO, which implies that the oxygen atoms bonded to carbon atoms participated in Cd(II) and Cu(II) uptake. In conclusion, the interaction mechanism of FLMGO with Cd(II) or Cu(II) is proposed as follows: the lone pair electrons in C=O, C−O−related groups were coordinated toward Cd(II) and Cu(II) to induce chemical interaction. This conclusion is consistent with those of both isotherm and kinetic fittings. The adsorption of Cd(II) and Cu(II) by FLMGO and the proposed adsorption mechanism are graphically represented in Scheme S2 (in Supporting Information).

4.5. Performance Evaluation. The removal performance of FLMGO on the target contaminants was further assessed via comparing with some reported adsorbents,21,22,26−29,51−55 which are summarized in Table 1. Clearly, FLMGO has some advantages as high adsorption capacity and fast adsorption kinetics. These advantages endow FLMGO with encouraging application potential in heavy metal remediation.

5. CONCLUSIONS

A highly efficient adsorbent based on FLMGO was fabricated. Batch adsorption indicates that FLMGO adsorbs Cd(II) and Cu(II) with adsorption quantities of 401.14 mg·g−1, 92.77%, and 1114.22 mg·g−1 in 5 and 7 min, respectively, exhibiting superior adsorption efficiency. Moreover, FLMGO can be easily recovered via magnetic separation for recycling. The coordination of the lone-pair electrons in C=O- and C−O−related groups toward Cd(II) and Cu(II) is the main interaction mechanism. Based on its high adsorption efficiency, FLMGO has promising application in heavy metal remediation.

6. EXPERIMENTAL SECTION

6.1. Material Preparation. All reagents were analytically graded without further purification. Deionized water was used throughout the whole experiments. GO colloidal was prepared by oxidative exfoliation of natural flake graphite using the modified Hummers method.35 In a typical process of FLMGO fabrication, GO colloidal (0.2 mg·mL−1, 500 mL) was ultrasonicated for 30 min; then, a 30 mL solution containing...
0.5448 g of FeCl₃·6H₂O, 0.2004 g of FeCl₂·4H₂O, and 0.2160 g of EtONa·3H₂O was added into the GO colloidal. The mixture was then electrically stirred for 30 min to form a homogeneous suspension. The suspension was heated up to 80 °C. Afterward, 25 wt % NH₄H₂O solution was intermittently dropped into the suspension to maintain pH = 10–11. Finally, the as-obtained sample was washed with deionized water and EtOH repeatedly and vacuum-dried to obtain FLMGO. Single Fe₃O₄ was fabricated based on the same process as FLMGO with the absence of GO.

6.2. Characterization Methods. The XRD patterns of the samples were collected by X-ray diffraction (XRD; PANalytical X’Pert PRO, Netherlands). Morphology of the samples was scanned by field-emission scanning electron microscopy (JSM-6701F; JEOL, Japan). The elemental spectrum of FLMGO was taken by energy-dispersive X-ray spectroscopy (EDX 2768; Bruker, Germany). The functional groups of the samples were identified by Fourier transformation infrared spectroscopy (FTIR; Bruker IFS66E, Germany). The surface elements of the samples were analyzed using X-ray photoelectron spectra (XPS; Kratos Axis Supra, England). The mass content of the functional groups and Fe₃O₄ in FLMGO was determined by thermogravimetry-differential thermal analysis (TG-DTA; NETZSCH, STA449C, Germany). The pore size distribution and the specific surface area of FLMGO were characterized by the N₂ adsorption–desorption instrument (Micromeritics, ASAP 2020 V3.04 G, USA). The magnetic property of FLMGO was evaluated using a vibrating sample magnetometer (VSM; LakeShore 8607, USA). The acidity of adsorbate solution and adsorbent hydrosol was supervised using a pH meter (pH; Shanghai precision instrument Co. Ltd PHS-3B, China). The zeta potential of FLMGO hydrosol was measured using a microelectrophoresis meter (zeta potential; Shanghai Zhongchen Co. Ltd JS94H, China).

6.3. Batch Adsorptions. Aqueous solutions with the desired Cd(II) or Cu(II) concentration were prepared by dissolving the exact amount of Cd(NO₃)₂·4H₂O or Cu(NO₃)₂·3H₂O in deionized water. For batch adsorptions, 20 mL of heavy metal solution was fetched and transferred into a conical flask. The solution pH was adjusted using 0.1 mol·L⁻¹ HCl or NaOH solution. FLMGO was added; then, the flask was shook in a thermostatic oscillator. After a certain duration, FLMGO was immediately recovered via magnetic separation using a NdFeB magnet, leaving a clear solution. Post adsorption samples were rinsed for XPS analysis. The residual concentration of the heavy metal in the post adsorption solution was evaluated using an atomic absorption spectrophotometer (PerkinElmer A800, USA).

The adsorbent dosage D (mg·L⁻¹), adsorption percent Rᵢ (%), and adsorption quantity Qᵢ (mg·g⁻¹) were determined using eqs 6–8:

\[ D = \frac{m}{V} \]  \hspace{1cm} (6)

\[ Rᵢ = \frac{C₀ − Cᵢ}{C₀} \times 100\% \]  \hspace{1cm} (7)

\[ Qᵢ = \frac{(Cᵢ − C₀)V}{m} \]  \hspace{1cm} (8)

The subscript i has three possible values: i = 0, e, and t, which indicate the start, equilibrium, and t moment of adsorption, respectively. Cᵢ (mg·L⁻¹) and V (mL) denote the concentration and volume of heavy metal solution, respectively, and m (g) denotes the adsorbent mass. All Q, and Cᵢ in this work have the same meanings as eqs 7 and 8. All adsorptions were conducted in duplicate, and the mean values were presented. The FLMGO fabrication process is graphically represented in Scheme S1 in Supporting Information.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c01770. Schematic illustration of FLMGO fabrication; schematic illustration of Cd(II) and Cu(II) adsorption by FLMGO and the proposed adsorption mechanism; quantitative evolution of aqueous heavy metal species with pH, Cd(II) and Cu(II); FTIR spectra of Fe₃O₄, GO, and FLMGO; TG-DTA curves of FLMGO; N₂ adsorption–desorption isotherms of FLMGO and pore size distribution of FLMGO; magnetization curve of FLMGO (inset at the upper left corner: magnification of the hysteresis loop and at the lower right corner: a display of the magnetic separation of FLMGO from water under an external magnetic field); dependence of zeta potential of FLMGO hydrosol on pH; effect of the contact time on the adsorption of Cd(II) and Cu(II) by FLMGO; effect of FLMGO dosage on the adsorption of Cd(II) and Cu(II); effect of Cd(II) and Cu(II) initial concentrations on their adsorption by FLMGO; effect of the electrolyte on the adsorptions of Cd(II) and Cu(II); effect of Cd(II) and Cu(II) initial concentrations on their adsorption by FLMGO; effect of HA on the adsorptions of Cd(II) and Cu(II) by FLMGO; effect of temperature on the adsorptions of Cd(II) and Cu(II) by FLMGO; fitting curves of the adsorptions of Cd(II) and Cu(II) by FLMGO based on various isotherm models, Langmuir, Freundlich, Temkin, and D-R; fitting curves of the adsorptions of Cd(II) and Cu(II) by FLMGO based on various kinetic models, PFO, PSO, LFD, Bangham, and IPD of Cd(II) and Cu(II) (external diffusion, internal diffusion, and surface reaction); fitting curve of Cd(II) and Cu(II) by FLMGO based on the van’t Hoff equation; fitting and calculation results of Cd(II) adsorption by FLMGO; and fitting and calculation results of Cu(II) adsorption by FLMGO (PDF)

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Notes
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ABBREVIATIONS
GO, graphene oxide; FLMGO, few-layered magnetic graphene oxide; HA, humic acid; PFO, pseudo-first-order; PSO, pseudo-second-order; IPD, intraparticle diffusion; LFD, liquid film diffusion

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