Adsorption behavior of isocyanate/ethylenediamine tetraacetic acid-functionalized graphene oxides for Cu$^{2+}$ removal

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ABSTRACT

A special adsorption of Cu$^{2+}$ removal is demonstrated using specifically functionalized graphene oxide (GO)/isocyanate (MDI) composites, on which ethylenediamine tetraacetic acid (EDTA) is grafted via amidation and carbamate reaction. The structure and morphology of GO and functionalized composites (EDTA/MDI/GO) were characterized by scanning electron microscope (SEM), Fourier transform infrared spectra (FT-IR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Thermogravimetric analysis (TGA). This study investigated the adsorption and desorption behaviors of heavy metal cations and the effects of solution conditions such as pH on Cu$^{2+}$ removal. The experimental results illustrated that after introducing EDTA and MDI into the GO, the maximum adsorption capacity reached 254.2 ± 10.4 mg/g within 180 min, obviously higher than the GO prepared without these additions (136.5 ± 7.2 mg/g). The EDTA/MDI/GO adsorption kinetics and equilibrium adsorption isotherm fitted the pseudo-second-order kinetic model ($R^2 = 0.995$) and Langmuir isotherm model ($R^2 = 0.986$) well, respectively. Furthermore, EDTA/MDI/GO also displayed good reusability for the efficient removal of Cu$^{2+}$ after being washed with HCl, suggesting potential application in Cu$^{2+}$ cleanup.

Key words | adsorption, Cu$^{2+}$, ethylenediamine tetraacetic acid, graphene oxide, isocyanate

INTRODUCTION

Water pollution caused by the indiscriminate disposal of metal ions and organic contaminants has been a rising worldwide environmental concern. Copper ions are toxic heavy metal cations discharged by various sources including paper industries, electroplating, wastes from plastics and printed circuit boards. Up to date, a variety of contaminant remediation technologies have been developed for elimination of heavy metal ions from wastewater, such as electrodialysis (Huang et al. 2018), chemical reduction (Li et al. 2016), ultrafiltration (Huang et al. 2016), membrane separation (Gonte & Balasubramanian 2016), ion exchange (Liu et al. 2017), adsorption and so forth. Adsorption is one of the promising and effective methods, due to the high efficiency, stability and simple operational conditions.

Graphene oxide (GO), an oxidized derivative of graphene, presents excellent adsorbent performance for heavy metals, dyes and pharmaceutical antibiotics because of the abundant oxygen-containing functional groups on the large two-dimensional (2D) surface, such as hydroxyl, carboxyl and epoxy groups (Ai et al. 2018). These oxygen-containing functional groups not only can remove the pollutants in wastewater, but also provide reactive sites of chemical reactions for functionalizing graphene oxide (Guo et al. 2018). Thus, a large number of molecules, especially some small functional organic molecules, can be grafted onto the surface of graphene oxide by chemical reaction.

Ethylenediamine tetraacetic acid (EDTA) is an excellent metal ion chelating agent, which contains four reactive carboxyl groups and six coordination atoms that can form stable complexes with most metal ions, including alkali metals, rare earth, transitional metals and so on (Chen et al. 2018). However, the complexes formed by EDTA and metal ions are water soluble, which is rarely used in wastewater treatment directly. As a result, immobilization...
of EDTA on different supporting materials for adsorption purpose has received widespread attention. For example, EDTA modified β-cyclodextrin/chitosan (CDCS-EDTA) prepared by Wu et al. (2018) showed Pb$^{2+}$ and anionic dye acid red 73 (AR) adsorption capacity up to 114.8 mg/g and 754.6 mg/g, respectively. New quaternized cellulose derivative based on EDTA and hydroxyethyl cellulose (HEC) was successfully prepared by Jalal et al. (2018) and the adsorption capacity for Pb$^{2+}$ and Cu$^{2+}$ was 109.65 and 77.10 mg/g, respectively. Nevertheless, most of the modification work for using EDTA as a waste water treatment adsorbent is limited to reduce the water solubility of the EDTA complex. However, an efficient method of reducing the water solubility of the EDTA complex and simultaneously enhancing the ability to complex metal ions is rarely reported.

As a popular emerging material in recent years, graphene oxide is an excellent adsorbent for heavy metal waste water treatment, and the study of modifying graphene oxides to enhance the adsorption capacity is highly common (Wang et al. 2018). In typical examples, the graphene oxide was modified by organic molecules as active agents, such as carboxyl compounds (Zhao et al. 2017), amine compounds (Pan et al. 2017), alkyl lithium reagents and organic isocyanates (Xu et al. 2016). Among these molecules, the highly active –NCO groups of isocyanate are easy to react with –OH, –COOH on the surface of GO, forming the urethane bond and the amide bond. This approach not only improves the dispersing ability of GO in the organic solvents, but also provides the possibility of grafting other molecules with certain specific functions onto the graphene oxide surface. Soleimani et al. (2018) have grafted organic isocyanates onto the surface of graphene oxide to synthesise Slide ring hydrogels, which showed a hydrogel adsorption capacity up to 92.3 mg/g. Kim et al. (2012) found that isocyanates modified graphene oxide could be uniformly and stably dispersed in a variety of polar aprotic solvents. Thus, diisocyanate-modified graphene oxide can be used as an intermediate, in which one of the –NCO in the MDI is grafted onto the GO and the other –NCO reacts with the active –COOH groups on the EDTA.

The purpose of this work is to investigate the grafting of EDTA and MDI on the surface of GO and study its chelating ability in adsorption for removal of Cu$^{2+}$. Batch adsorption tests of Cu$^{2+}$ by EDTA/MDI/GO and GO were carried out to study the adsorption kinetics, adsorption isotherms and desorption performance. The results indicated a promising material of EDTA/MDI/GO in the removal of Cu$^{2+}$ from aqueous solutions rapidly and efficiently.

### EXPERIMENTAL

#### Materials

Graphite from Alfa Aesar reagent company was used to prepare GO. All the reagents were analytical grade without further treatment. Copper sulfate (CuSO$_4$5H$_2$O) was purchased from Fucheng chemical reagent factory (Tianjian). Isocyanate (MDI) and ethylenediamine tetraacetic acid (EDTA) were purchased from Shanghai Huntsman Polyurethanes Co. Ltd, and Tianjin Chemical Reagent Manufacturing Co. Ltd, respectively. Distilled water was used for preparation, dilution, and analytical purposes in all the experiments.

#### Synthesis

#### Preparation of GO

GO was prepared from expandable graphite using a modified Hummers’ method. First of all, K$_2$S$_2$O$_8$ (2 g), P$_2$O$_5$ (2 g), expandable graphite (2 g) and concentrated H$_2$SO$_4$ (25 mL) were put into a 250 mL round-bottomed flask. The mixture was transferred to an 80 °C water bath followed by strong stirring for 8 h. Subsequently, the mixture was filtered and washed several times with distilled water, followed by drying in a vacuum oven at 40 °C for 12 h. Secondly, the preoxidation graphite (2 g), NaNO$_3$ (1.5 g) and concentrated H$_2$SO$_4$ (50 mL) were added into a 250 mL round-bottomed flask in an ice bath with stirring. Meanwhile, KMnO$_4$ was added gradually and the mixture was reacted in an ice-water bath for 2 h, then the reaction was carried out at 50 °C for two days. Subsequently, 200 mL of distilled water and 10 mL 30% H$_2$O$_2$ were added dropwise to the reactor with continuous stirring to reduce the residual KMnO$_4$ until no bubbles appeared. The color of the mixture was changed to brilliant yellow, and then filtered and washed with 5% HCl and plenty of distilled water until the pH was 7. The product was dried in the freeze-drying machine.

#### Synthesis of EDTA/MDI/GO

The EDTA/MDI/GO composite was prepared by the following process. GO (0.1 g) was dispersed into 50 mL anhydrous dimethylformamide (DMF) and ultrasonicated for 1 h at room temperature to form a homogeneous suspension. Then, 5 mL MDI was dissolved into the suspension under
stirring and the reaction was carried out at 70 °C for 4 h. After being filtered and washed several times with anhydrous DMF, the sample was dried in a vacuum drying oven at 50 °C and the primary product, MDI/GO, was achieved. Subsequently, the MDI/GO was mixed with EDTA (4 g) followed by ball-milling for 3 h. After that, the composite was washed several times with alkali and deionized water to remove excess EDTA, followed by filtering and lyophilizing to obtain EDTA/MDI/GO. The absorbent characterization technique is shown in the supplementary material (SM 1), available with the online version of this paper.

Adsorption experiment

The adsorption capacity of the GO and EDTA/MDI/GO samples for the removal of Cu²⁺ metal ions was studied. Detail of the adsorption experiment is discussed in supplementary material (SM 2), available online. The adsorption capacity (q, mg/g) of Cu²⁺ adsorbed onto EDTA/MDI/GO and GO is calculated from Equation (1):

\[ \text{Qe} = \frac{(C_0 - C_e)V}{W} \]

where \( C_0 \) and \( C_e \) are the initial and equilibrium concentration of Cu²⁺ (mg/L), respectively; \( V \) is the volume of Cu²⁺ solution (L), and \( W \) is the dry mass of EDTA/MDI/GO or GO adsorbent (g).

Data processing

Each set of data was performed in parallel three times, and each factor was repeated five times in total, then the standard deviation of the five sets of data was calculated. The equations are represented as follows:

\[ Q_i = \frac{q_1 + q_2 + q_3 + q_4 + q_5}{5} \]

\[ \bar{Q} = \frac{Q_1 + Q_2 + Q_3 + Q_4 + Q_5}{5} \]

\[ SD = \left( \frac{\sum (Q_i - \bar{Q})^2}{5 - 1} \right)^{1/2} \]

where \( Q_i \) is the average of three parallel experiments; \( \bar{Q} \) is the average of five sets of data; \( SD \) is the standard deviation of five sets of data.

RESULTS AND DISCUSSION

Adsorbent characterization

Surface morphology and structure of the produced composites were investigated by scanning electron microscopy (SEM). SEM images of GO and EDTA/MDI/GO are shown in Figure 1(a) and 1(b). It can be observed in Figure 1(a) that the GO structure resembles waves in crumpled with a wrinkled surface. On the contrary, in Figure 1(b), the particles on the surface of EDTA/MDI/GO had congregated into a larger size. It can be seen that the introduction of MDI and EDTA can effectively improve the surface area of GO sheets to some degree.

The Fourier transform infrared (FT-IR) spectra of GO, MDI/GO and EDTA/MDI/GO are shown in Figure 1(c). Two characteristic peaks located at 3,392 cm⁻¹ and 1,738 cm⁻¹ are observed in the GO, corresponding to the stretching vibration of O-H and C = O stretching frequencies of the -COOH groups on the GO surface (Rattana et al. 2012), respectively. The peaks at 1,620 cm⁻¹ and 1,056 cm⁻¹ are attributed to the C-C bond and C-O bond (Motamedi et al. 2014), respectively. The absorption peak at 2,335 cm⁻¹ of MDI/GO represents -NCO, and the C = O stretching vibration at 1,738 cm⁻¹ becomes not obvious due to the appearance of a stronger absorption at 1,651 cm⁻¹ that can be attributed to the carbonyl stretching vibration, indicating that MDI is grafted onto the surface of GO. In the EDTA/MDI/GO spectrum, two characteristic peaks at 1,598 cm⁻¹ and 1,411 cm⁻¹ are ascribed to the stretching of benzene. In addition, the peak located at 3,331 cm⁻¹ results from N-H or O-H stretching vibrations. The two absorption peaks at 1537 cm⁻¹ and 1309 cm⁻¹ illustrate the presence of interactions between the carbonyl functional group of EDTA with -NCO of MDI/GO.

XRD was applied to investigate the structure of GO and EDTA/MDI/GO, as shown in Figure 1(d). According to the characteristic analysis of XRD patterns, a unique intense diffraction peak at 2θ = 11.32° is assigned to the diffraction peak of the (001) plane in the pure GO (Zhang et al. 2016). For the EDTA/MDI/GO composites, there is a wide diffuse scattering peak located at 2θ = 7.18°. The interlayer spacing is calculated as 12.29 Å, which is larger than that of the GO layer. These results suggest that EDTA and MDI participate into the GO grafting reaction.

The functional group compositions of the GO and EDTA/MDI/GO samples were revealed by XPS spectra. Figure 2 shows the XPS survey and C 1s spectra of GO and EDTA/MDI/GO. The C 1s spectrum of GO
(Figure 2(b)) usually consists of four types of carbon bonds, namely C = C (285.0 eV), C - C (285.2 eV), C - O (287.1 eV) and C = O (288.5 eV) (Sun et al. 2013). The prominent peaks in the GO spectrum (Figure 3(a)) can be observed at 285.3 eV and 532.6 eV, corresponding to the C 1 s and O 1 s, respectively. Compared with GO, the XPS spectrum of the EDTA/MDI/GO (Figure 2(c)) presents a relatively high N 1 s peak, which suggests the presence of N-atoms in this sample. In Figure 2(d), two additional peaks can be observed at 287.1 eV and 291.1 eV, which can be ascribed to the formed C-N and N-C = O groups (Lai et al. 2011), respectively.

To study the weight loss features of the GO and EDTA/MDI/GO, TGA curves of both samples were analyzed, as shown in Figure 3. As exhibited in Figure 3(a), the weight loss of GO in the temperature range of 71 °C to 210 °C is approximately 34%, mainly due to the removal of physically adsorbed water and the pyrolysis of the surface oxygen functional groups. It is obvious that the weight loss of MDI modified GO has two steps. In Figure 4(b), the initial 10.73% weight loss at 165 °C is attributed to the degradation of the surface oxygen functional groups. The weight loss of GO in the corresponding range is approximately 15%, which indicates that the oxygen functional groups of GO are reduced during the process of modification with MDI. The subsequent 29.31% weight loss at 300 °C can be ascribed to the degradation of the functional groups of MDI grafted onto GO. However, it can be found in Figure 4(c) that the loss of EDTA/MDI/GO is 5.1% in the initial stage, which can be linked to the dehydration process. The major weight loss occurred at 159–200 °C, which could be related to the complete decomposition of oxygen-containing functional groups of EDTA. The above results indicate that the thermal stability of the complex is increased in comparison with GO, and the variation of TGA curves also attests to the existence of MDI and EDTA on the surface of GO.
Adsorption kinetics

The results shown in Figure 4(a) imply that the adsorption capacity of the adsorbents increases sharply in the first 20 min due to the existence of plenty of binding sites for Cu$^{2+}$, and the Cu$^{2+}$ ions absorbed on EDTA/MDI/GO sorbents reach their maximum capacities at 180 min. This rapid adsorption is directly owed to the 2D structure of EDTA/MDI/GO, because this 2D structure enables the adsorbents to be ready for accessibility of the chelating EDTA, making it easy for metal chelation to take place.

To evaluate the kinetic mechanism that controls the adsorption process, the pseudo-first-order and the pseudo-second-order models were used to fit the data in Figure 4(b) and 4(c). The pseudo-first-order, pseudo-second-order equations (Xu et al. 2015) and Weber-Morris model (Gan et al. 2015) were represented as follows:

\[
\log\left(\frac{Q_e}{Q_t}\right) = \log \frac{Q_e}{Q_0} - \frac{k_1 \cdot t}{2.303}
\]

\[
\frac{t}{Q_t} = \frac{1}{k_2 \cdot Q_e} + \frac{t}{Q_e}
\]

\[
Q_t = k_3 \cdot t^{1/2} + C
\]
where \( t \) is the contact time, \( Q_t \) is the amount of metal ions adsorbed at time \( t \), \( k_1 \) and \( k_2 \) are the pseudo-first-order rate constant and the pseudo-second-order rate constant, respectively, \( k_t \) is the intra-particle diffusion rate constant and \( C \) is a constant related to the thickness of the boundary. The pseudo-first-order and the pseudo-second-order kinetic parameters of \( Cu^{2+} \) adsorbed by GO and EDTA/MDI/GO are given in Table 1. The results show that the pseudo-second-order kinetic model provides better correlation of the experimental data, which suggested the adsorption is controlled by chemical adsorption.

The Weber-Morris model is presented as Figure 4(d). The experimental data are related by two straight lines, which indicates that the adsorption of \( Cu(II) \) on the surface of the adsorbent has two stages, namely external diffusion and intra-particle diffusion. The related parameters are summarized in Table 1. The first stage is the surface diffusion process: there are enough adsorption sites on the surface of the adsorbent to bind with \( Cu^{2+} \), so the adsorption speed is faster; the second stage is the slow diffusion phase of the particle; the active site on the surface of the adsorbent is gradually occupied, \( Cu^{2+} \) gradually diffuses into the internal

<table>
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<th>Kinetic models</th>
<th>Parameters</th>
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<td></td>
<td>( C )</td>
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</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.975</td>
<td>0.98</td>
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</table>

Figure 4: Effect of contact time on the adsorption uptake of \( Cu^{2+} \) (a); pseudo-first-order adsorption kinetics (b); pseudo-second-order adsorption kinetics (c) and Weber-Morris model adsorption kinetics (d).
pores, resulting in a slower adsorption rate and a slow increase in the adsorption amount. Furthermore, the second stage line does not pass through the origin, indicating the adsorption process was controlled by the two stages of surface diffusion and internal diffusion of particles.

**Adsorption isotherms**

Figure 5(a) shows the adsorption isotherms of Cu\(^{2+}\) at its initial concentration range of 10–70 mg/L. Cu\(^{2+}\) ions are more favorably adsorbed on EDTA/MDI/GO and the adsorption capacity of Cu\(^{2+}\) attained 254.2 ± 10.4 mg/g, while the adsorption capacity for Cu\(^{2+}\) on GO is 136.5 ± 7.2 mg/g.

In order to obtain the adsorption capacity of adsorbents and explore the microscopic mechanism between Cu\(^{2+}\) and adsorbents, adsorption isotherms have been investigated based on the general Langmuir and Freundlich isotherm models (Ding et al. 2014). The Langmuir isotherm model is expressed as follows:

\[
\frac{C_e}{Q_e} = \frac{C_e}{Q_{\text{max}}} + \frac{1}{K_L Q_{\text{max}}} \tag{8}
\]

The Freundlich isotherm represents multilayer adsorption on a heterogeneous surface, and the Freundlich adsorption equation is given as:

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{9}
\]

where \(C_e\) is the equilibrium concentration of the metal ion in the solution (mg/L); \(q_e\) is the amount of metal ion adsorbed.

![Figure 5](https://iwaponline.com/wst/article-pdf/78/12/2459/525377/wst078122459.pdf)  
**Figure 5** | Adsorption isotherms at pH 5.5 (a), Langmuir absorption isotherm (b), Freundlich absorption isotherm (c) of Cu\(^{2+}\) absorption for GO and EDTA/MDI/GO.
by adsorbent at an equilibrium concentration (mg/g); $Q_{\text{max}}$ (mg/g) represents the theoretical maximum adsorption capacity (mg/g); $K_L$ is the Langmuir equilibrium adsorption constant; $n$ and $K_F$ are the Freundlich model adsorption constants, representing the adsorption intensity of the adsorbent and the adsorption capacity, respectively.

Langmuir and Freundlich isotherms for GO and EDTA/MDI/GO were presented in Figure 5(b) and 5(c), and the coefficients were evaluated by fitting experimental equilibrium data. It can be seen from Table 2 that the Langmuir model shows a good agreement with the experimental data, with a correlation coefficient of 0.986 at pH 5.5. Our investigation demonstrates that the Freundlich model fits the results with a correlation coefficient of 0.849. Thus, adsorption may be assumed to occur at homogeneous binding sites on the surface of the adsorbents up to monolayer coverage. The maximum adsorption capacities of Cu$^{2+}$ on EDTA/MDI/GO and GO from testing five times are 254.2 ± 10.4 mg/g and 136.5 ± 7.2 mg/g, respectively.

In addition, $R_L$ expressed the separation factor, which can also be used to estimate the type of the adsorption as unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$), and is indicated as follows:

$$R_L = \frac{1}{1 + K_L C_0}$$

where $C_0$ (mg/L) is the highest initial Cu$^{2+}$ concentration. The value of $R_L$ were calculated and can be seen in Table 2, and a favorable adsorption was suggested as $0 < R_L < 1$.

**Effect of pH**

The pH of aqueous solutions is an important factor that may influence the adsorbent. The results are shown in Figure 6(a), suggesting that the uptake of Cu$^{2+}$ increases when the pH is elevated from 2.0 to 5.5. When the pH value was settled in the range of 2–3, the adsorption capacity of metal ions in GO is slightly greater than that in EDTA/MDI/GO. However, the adsorption of Cu$^{2+}$ in EDTA/MDI/GO is higher than that in GO when increasing the pH from 3 to 5.5.

In this system, Cu$^{2+}$ can be adsorbed onto EDTA/MDI/GO surface by reacting Cu$^{2+}$ with EDTA chelating groups, -COOH and -OH groups, respectively. One explanation could be attributed to the formation of Cu$^{2+}$-EDTA chelates on the EDTA/MDI/GO surface, such as Cu$^{2+}$-HEDTA and Cu$^{2+}$-H$_2$EDTA. Besides this reason, other effects of pH on the adsorbents are surface charge, degree of ionization and speciation. In an acidic solution, the species of surface groups are -COOH and -OH, respectively. The pH decrease leads to neutralization of the surface charge, and thus the
adsorption of cations should decrease. In addition, there is some competition on -COO⁻ and -O⁻ sites between proton and metal cations in an acidic condition, which will result in a lower adsorption capacity. The increase in the pH values of the solution will convert more groups to -COO⁻ and -O⁻, and provide electrostatic interactions that are favorable for adsorbing Cu²⁺ and other cationic species. These results are also confirmed by the zeta potential results of GO and EDTA/MDI/GO. Figure 6(b) shows that the zeta potential of GO and EDTA/MDI/GO decreases when pH increases from 2 to 6. It is obvious that the zeta potential of GO is higher than that of EDTA/MDI/GO. This can be attributed to the fact that the active ingredient EDTA of EDTA/MDI/GO is more difficult to dissociate under acidic conditions compared to GO, which generates an electrostatic repulsion to Cu²⁺. With the increase of solution pH value, the zeta potential of EDTA/MDI/GO is more negative than that of GO, which indicates that the amounts of -COOH and -OH of EDTA/MDI/GO are higher than that of GO. Thus, the functional groups of GO and EDTA/MDI/GO can be ionized to make adsorbent electronegative anions in the solution and provide strong electrostatic attraction between metal ions and adsorbents.

However, it is worth noting that the precipitation of Cu²⁺ hydroxide may occur at high pH of beyond 5.5. The test of the precipitation of Cu²⁺ at different pH values was performed by mixing 25 mL of 20 mg/L standard Cu²⁺ solution with a series of pH buffer solutions. The pH values are 4, 4.5, 5, 5.5, 6, 6.5 and 7, respectively. It is found that when the pH is higher than 6, precipitation of Cu²⁺ occurs. Thus, a pH of 5.5 was selected as the optimum pH for Cu²⁺ adsorption.

Regeneration of the adsorbent

Generally, the recycle capability is one of the most important factors in evaluating a sorbent. A typical recycle process was carried out by treating EDTA/MDI/GO powders preloaded with Cu²⁺ in an HCl solution (0.1 mol/L). Figure 7 demonstrates the reusability of EDTA/MDI/GO toward the removal of Cu²⁺. It can be found that EDTA/MDI/GO exhibits better performance than GO after 10 wash recycles. After eight cycles, 78% of the initial adsorption capacity of EDTA/MDI/GO remained.

CONCLUSIONS

The introduce of EDTA and MDI to the GO surface via amidation and carbamate reaction can significantly increase the adsorption capacity of GO for Cu²⁺ removal. The adsorption behavior of Cu²⁺ on the EDTA/MDI/GO well fits the Langmuir equation and pseudo-second-order equation. The maximum adsorption capacity varies with pH of the solution, and the maximum adsorption capacity of EDTA/MDI/GO composites for Cu²⁺ can reach 254.2 ± 10.4 mg/g, which is two times higher than that of GO. On the other hand, 78% adsorption capacity is retained after eight times in circulation, proving that the sorbents can be reused after being treated with HCl solution. These results indicate that the EDTA/MDI/GO composites can be an effective adsorbent for toxic heavy removal.

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