Mesoporous Layered Graphene Oxide/Fe₃O₄/C₃N₃S₃ Polymer Hybrids for Rapid Removal of Pb²⁺ and Cd²⁺ from Water

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Supporting Information

ABSTRACT: Mesoporous layered magnetic hybrid GFP2 composed of C₃N₃S₃ polymers, Fe₃O₄ nanoparticles (Fe₃O₄ NPs), and graphene oxide with a mesoporous layered “sandwich”-like structure was successfully explored by in situ simple polymerization tactic for rapid removal of Pb²⁺ and Cd²⁺ from water. It shows good selectivity and high adsorption capacity (277.78 and 49.75 mg/g) for Pb²⁺ and Cd²⁺, respectively. It exhibits the fast adsorption kinetics (>80% elimination efficiency in less than 30 min). The Langmuir isotherm model based on typical monomolecular layer adsorption fits better with the data of adsorption than the Freundlich isotherm model. The adsorption process of GFP2 for Pb²⁺ and Cd²⁺ can be explained well with the pseudo-second-order kinetics model. GFP2 is a kind of recyclable solid absorbent, which is an excellent candidate in the heavy metal wastewater treatment. More importantly, GFP2 was set with Fe₃O₄ NPs which makes it easily separable from wastewater with an extra magnet.

INTRODUCTION

With the rapid development of urbanization and industrialization, lots of toxic pollutants (organic waste and heavy metal ions) release into the environment.¹ Unlike organic waste, heavy metal ions once released into the environment cannot be biodegraded. They usually enter water from air or soil in a variety of ways because of their solubility.² The heavy metal pollution of water not only affects millions of people worldwide and is a leading global risk factor for illness and death but also affects organisms and plants living in rivers, lakes, oceans, and ground water.³–⁵ Inorganic lead and cadmium are among the most highly toxic water pollutants, which originate from metal smelting, plating, tanneries, battery manufacturing, pigment manufacturing, petroleum refining, etc.⁶–¹⁰ Lead (Pb) is harmful to the human organ system most notably the nervous, renal, and reproductive systems, and, more importantly, children are particularly sensitive to lead exposure as it causes mental retardation at lower lead levels.¹¹,¹² Cadmium (Cd) is a well-known toxic heavy metal with a destructive impact on most organ systems in the aquatic environment. It can cause liver damage, renal dysfunction, lung insufficiency, bone degeneration, and hypertension in humans.¹³,¹⁴ Therefore, a lot of researchers have devoted enormous contribution for the removal of lead and cadmium from polluted water. Traditional sewage treatment technology which includes solvent extraction, aggregation, ion exchange, and membrane separation cannot separate the dissolved heavy metal ions completely from contaminated water.¹⁵,¹⁶ Artificial adsorbents offer a promising way to overcome current difficulties and show outstanding performances on lead and cadmium separation from contaminated water, especially nanomaterial-based adsorbents. Up to now, a lot of artificial nanoadsorbents for the elimination of lead and cadmium have been developed. Such as, nanometal oxide,¹⁷ silicon-based nanomaterials,¹⁸ titanosilicate zeolites,¹⁹,²⁰ polymers,²¹,²² nanocarbon materials,²³–²⁵ biochar,²⁶,²⁷ and others.²⁸–³⁰ However, most of these adsorbents are either complicated to produce or too costly for large-scale industrial production. Thus, the development of new nanoadsorbents and evaluating their adsorption properties are key factors for applying artificial adsorbent technology.

Trimercapto-triazine-trisodium salt (Na₃C₃N₃S₃, TMT-15), which is a widely used homogeneous aqueous solution adsorbent in the wastewater treatment, has excellent chelation ability with almost all of the heavy metal ions.³¹,³² However, TMT-15 is used in the form of aqueous solution so it is difficult to regenerate and recycle. Graphene oxide (GO), which has a large theoretical surface area and rich oxygen functional groups, is an ideal candidate to develop a new promising nanoadsorbent for heavy metal removal.³³,³⁴ In particular, magnetic GO-based nanoadsorbents have attracted much attention because of their high adsorption capacities and
simple magnetic separation. Thus, anchoring Fe\textsubscript{3}O\textsubscript{4} nanoparticles (Fe\textsubscript{3}O\textsubscript{4} NPs) onto the large surface area of GO and in situ polymerization with Na\textsubscript{3}C\textsubscript{3}N\textsubscript{3}S\textsubscript{3} might be a promising method to overcome the above difficulties.

In this paper, mesoporous layered GO/C\textsubscript{3}N\textsubscript{3}S\textsubscript{3} polymer hybrids (GP) and GO/Fe\textsubscript{3}O\textsubscript{4}/C\textsubscript{3}N\textsubscript{3}S\textsubscript{3} polymer hybrids (GFP) are first prepared for highly efficient and rapid removal of Pb\textsuperscript{2+} and Cd\textsuperscript{2+} from contaminated water through in situ polymerization and interface-induced co-assembly methods. GFP nanocomposites were prepared by anchoring Fe\textsubscript{3}O\textsubscript{4} NPs onto the surface of GO and in situ polymerization with Na\textsubscript{3}C\textsubscript{3}N\textsubscript{3}S\textsubscript{3}. In comparison with that, GP nanocomposites were prepared in a similar way except without Fe\textsubscript{3}O\textsubscript{4} NPs. The physical and chemical characterization of the prepared adsorbents was conducted to analyze their composition and structure, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Brunauer–Emmett–Teller (BET) and thermogravimetric analysis (TGA). Moreover, a series of small batch experiments are carried out to investigate the adsorption property.

■ RESULTS AND DISCUSSION

Characterization of GP and GFP. The structure and morphology of the as-obtained adsorbents were first characterized by SEM. Figures 1 and S1 are typical SEM photos of the P, GP, and GFP, respectively. Figure S1 displays many granules of irregular shape (200 nm to 10 \textmu m), which are made up of a mass of nanoparticles. The pure polymer P particles accumulate in a random way, whereas the GP and GFP hybrids pack in a “sandwich”-like layered way (Figure 1). The layered structure formed by the ordered stacking of the C\textsubscript{3}N\textsubscript{3}S\textsubscript{3} polymer and GO is clearly discernible for the six hybrids. In Figure 2, TEM images of GP and GFP hybrids show the porous network morphology. For GFP, it was observed that magnetite Fe\textsubscript{3}O\textsubscript{4}NPs sized about 8–12 nm and a part of their clusters were dispersed and embedded in the backbone of the GFP network. The morphology of GO was also investigated by TEM. As seen from Figure 2, the copper grid substrates are covered with a lot of thin films with many wrinkles, indicating the existence of GO.

The XRD patterns of P, GP, and GFP are shown in Figure 3. No obvious sharp diffraction peaks were observed for P and GP except for a steamed bread peak, which could be assigned to the (220), (311), (400), (422), (511), (440), and (533) planes of the cubic spinel crystal structure of Fe\textsubscript{3}O\textsubscript{4} with the cell constant \(a = 8.39\) Å (JCPDS card no. 19-0629).\textsuperscript{38,39} The characteristic peak of GO at 10.4° might be covered up by the amorphous polymer matrices.

XPS was used to further study the detailed elemental composition information of P, GP, and GFP (Figures 4 and 5). Figure 4a shows that the spectrum of P and GP had five peaks (S 2p, S 2s, C 1s, N 1s, and O 1s) while GFP had six sharp peaks (S 2p, S 2s, C 1s, N 1s, O 1s, and Fe 2p) in the survey scan spectrum. Higher-resolution XPS spectra were also determined to further study the electronic states of S, C, N, and Fe. Peaks located at 724.3 and 711.3 eV appeared in the Fe 2p spectrum (Figure 4b), consistent with Fe 2p\textsubscript{1/2} and Fe 2p\textsubscript{3/2} indicating the appearance of Fe\textsubscript{3}O\textsubscript{4} NPs in hybrid GFP.\textsuperscript{41} The relative integral ratio of the Fe element for GFP evidently became bigger from GFP1 to GFP3, which are corresponding to content of Fe\textsubscript{3}O\textsubscript{4} NPs. In the S 2p spectrum (Figure 5), peaks for S 2p\textsubscript{3/2} and S 2p\textsubscript{1/2} were observed at 168.9, 165.8, 165.0, and 164.3 eV, respectively, which are higher than those in the precursor H\textsubscript{3}C\textsubscript{3}N\textsubscript{3}S\textsubscript{3}.\textsuperscript{42} It showed that C\textsubscript{3}N\textsubscript{3}S\textsubscript{3} has been successfully grafted on GO. Four different peaks centered at 284.7, 285.4, 287.9, and 290.4 eV were evidently became bigger from GFP1 to GFP3, which are corresponding to content of Fe\textsubscript{3}O\textsubscript{4} NPs. In the S 2p spectrum (Figure 5), peaks for S 2p\textsubscript{3/2} and S 2p\textsubscript{1/2} were observed at 168.9, 165.8, 165.0, and 164.3 eV, respectively, which are higher than those in the precursor H\textsubscript{3}C\textsubscript{3}N\textsubscript{3}S\textsubscript{3}.\textsuperscript{42} It showed that C\textsubscript{3}N\textsubscript{3}S\textsubscript{3} has been successfully grafted on GO. Four different peaks centered at 284.7, 285.4, 287.9, and 290.4 eV were observed in the C 1s deconvolution spectrum of GP and GFP, corresponding to C≡C/C≡C/C≡H in aromatic rings, C–O, C=O, and O–C=O groups, respectively, signifying the existence of GO in the composites.\textsuperscript{34} In Figure 5, the results of high-resolution of N 1s scan were fitted with three components at 399.4, 400.2, and 404.0 eV, signifying the formation of nitrogen-containing aromatic polymers in the composites.\textsuperscript{33} From the XPS spectra, we can conclude that GP and GFP were successfully obtained.

FTIR, a useful technique for identifying the detailed structure of the matter at a molecular scale, was used to certify the formation of the GP and GFP hybrids. As is shown in Figure 6, four different strong bands displayed at 1723, 1476, 1233, and 824 cm\textsuperscript{-1}, which are assigned to the stretching vibration of the C≡N bond, the six-membered ring of symmetrical triazines, the C–N group, and the out-of-plane

Figure 1. SEM images of (a) P, (b) GP1, (c) GP2, (d) GP3, (e) GFP1, (f) GFP2, and (g) GFP3.
bending vibration of symmetrical triazines, which indicates the formation of polymerization.\textsuperscript{44} The absorption bands near 1636 and 1124 cm\textsuperscript{−1} are assigned to the stretching vibration of C−N and C=S bonds, corresponding to the formation of thione, which is one kind of terminal group in the polymerization (C\textsubscript{3}N\textsubscript{3}S\textsubscript{3}) chain.\textsuperscript{32} FTIR analysis showed the characteristic peaks of O−H (3382 cm\textsuperscript{−1}), C=O (1733 cm\textsuperscript{−1}), C=C (1615 cm\textsuperscript{−1}), and C−O (1274 and 1052 cm\textsuperscript{−1}) for GO.\textsuperscript{35} Obviously, most of the characteristic peaks appeared in GP and GFP hybrids, while some of them overlapped with other peaks. The broad and weak band at 565 cm\textsuperscript{−1} corresponds to the Fe−O bond, which certifies the existence of Fe\textsubscript{3}O\textsubscript{4} NPs in the GFP hybrids.\textsuperscript{45} Moreover, the absorption bands near 1637 and 3440 cm\textsuperscript{−1} referred to the H−O−H bending mode and O−H stretching mode, respectively, showing the existence of interstitial water in the hybrids.

As is shown in Figure S2, further information for the preparation of GFP is provided by the TGA curves in the oxygen atmosphere. From 200 to 600 °C, GP and GFP both showed an obvious mass loss, which corresponded to the combustion of GO and P. It was certain that Fe\textsubscript{3}O\textsubscript{4} was oxidized to Fe\textsubscript{2}O\textsubscript{3} during the whole process. So, with the degradation of Fe\textsubscript{3}O\textsubscript{4}NP content, the last hybrid weight degraded.

In order to research the adsorption process and the specific surface area of the magnetic adsorbent GFP, the pore size distribution and BET specific surface area of the GFP samples (Figure S3) were determined by the N\textsubscript{2} adsorption and desorption experiments. From the N\textsubscript{2} sorption isotherm at 77.3 K, we found that GFP1, GFP2, and GFP3 all showed classic IUPAC-IV adsorption behavior with a BET specific surface area of 133.3, 123.8, and 103.3 m\textsuperscript{2}/g, individually. The Barrett–Joyner–Halenda sorption average pore width (4V/A) are 12.3 nm (GFP1), 11.6 nm (GFP2), and 10.3 nm (GFP3), respectively. The aperture distribution of hybrids showed that all kinds of particles have a narrow dimensional range (2−50 nm). It can be declared that the adsorbents we prepared are all mesoporous materials.

**Effects of pH and Adsorption Isotherms.** During the simple adsorption experiment, the adsorbent GFP1 showed so weak magnetic force that it became difficult to separate from water by an extra magnet after adsorption. It also indicated that their removal capacity to Pb\textsuperscript{2+} (or Cd\textsuperscript{2+}) are as follow: GFP1 > GFP2 > GFP3. Thus, we use GFP2 to do further experiment research. The pH value is one of the most important parameters affecting the adsorption capacity of the adsorbent to the heavy metal ions. In order to study the dependences of the adsorption capacity for Pb\textsuperscript{2+} (or Cd\textsuperscript{2+}) on the pH value (2.0−7.0) over GFP2. In Figure 7, it showed the mass of Pb\textsuperscript{2+} (or Cd\textsuperscript{2+}) adsorbed per unit mass of GFP2 (q\textsubscript{e}, mg/g) at different pH. Obviously, the q\textsubscript{e} increased when the pH values changed from 2.0 to 6.0, and it reduced obviously as the pH further increased. Notably, the adsorption maximal value

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**Figure 2.** TEM images of (a) GP1, (b) GP2, (c) GP3, (d) GFP1, (e) GFP2, and (f) GFP3.

**Figure 3.** XRD patterns of P, GP, and GFP.

**Figure 4.** XPS spectra of P, GP, and GFP: (a) survey scan, (b) Fe 2p spectra.
appeared at pH = 6.0. It is consistent with the zeta potential value of bulk C₃N₃S₃ polymer (−33.5 mV at pH = 6.7) in the literature.⁴⁶

The adsorption equilibrium isotherms provide rich information about surface properties, adsorption mechanisms, and the affinity of the adsorbent to the adsorbate.⁴⁷ It dictates the quantity of adsorbents needed when they are used in heavy metal pollution of water. In the paper, the adsorption of Pb²⁺ (or Cd²⁺) with different initial concentrations (25, 50, 100, 150, 200, 250, 300, 400, and 500 mg/L) was researched for 24 h at room temperature and pH = 6.0. To determine the mechanistic parameters associated with Pb²⁺ (or Cd²⁺) adsorption, we analyzed the experimental data using the commonly applied Langmuir and Freundlich isotherm models (Figures 8 and S4).⁴⁸,⁴⁹ The Langmuir and Freundlich equations are given as

\[
\frac{C_e}{q_e} = \frac{C_e}{Q_{\text{max}}} + \frac{1}{Q_{\text{max}} b}
\]

(1)

\[
\ln q_e = \ln K_c + \frac{1}{n} \ln C_e
\]

(2)
where \( C_e \) is the final equilibrium concentration of adsorbate solution (mg/L), \( q_e \) is the mass of the adsorbate which are adsorbed by per unit heft of the adsorbent (mg/g), \( Q_{\text{max}} \) is the maximum theoretical monolayer adsorption capacity (mg/g), \( b \) (L/mg) and \( K_F \) are the Langmuir and Freundlich constant, and \( n \) is the indicators of the adsorption intensity. Fitting of the isotherm data and the Pb\(^{2+}\) and Cd\(^{2+}\) sorption constants obtained with the Langmuir and Freundlich models for GFP2 are showed in Table 1. The data indicate that the correlation coefficients \( R^2 \) of Langmuir is much bigger than those of Freundlich. It demonstrates that the Langmuir model is well in agreement with the observation data, showing that the nanoadsorbent surface is the monolayer occupied by Pb\(^{2+}\)/(Cd\(^{2+}\)). However, the \( R^2 \) of Freundlich was 0.954 (Pb\(^{2+}\)) and 0.947 (Cd\(^{2+}\)) onto GFP2 also appeared during the adsorption process. The \( Q_{\text{max}} \) value from the adsorption of GFP2 for Pb\(^{2+}\) and Cd\(^{2+}\) are 277.78 and 49.75 mg/g, respectively, at 298 K. Table 2 presents the adsorption capacities for Pb\(^{2+}\) and Cd\(^{2+}\) in water on various solid adsorbents. The maximum adsorption capacity to Pb\(^{2+}\) is much smaller than the high-efficiency Pb\(^{2+}\) adsorbents (e.g., flowerlike MgO nanostructures and PTMT exhibiting capacities of 1980.0 and 375.9 mg/g),\(^{17,32}\) and is much higher than a lot of reported adsorbents (e.g., TMU-5, modified cellulose, and Fe\(_2\)O\(_3@\)AlO(OH) exhibiting capacities of 29.6–251.0 mg/g).\(^{30–32}\) The maximum adsorption capacity to Cd\(^{2+}\) is much smaller than the high-efficiency Cd\(^{2+}\) adsorbents (e.g., flowerlike MgO nanostructures and PEI-grafted gelatin sponge exhibiting capacities of 1500.0 and 65.0 mg/g),\(^{17,53}\) and is more than those of the gelatin sponge (9.35 mg/g).\(^{53}\) The \( n \) value is small which indicates that the chemical adsorption strength between them are high, which was in accordance with \( K_F \) and shows that Pb\(^{2+}\) is easier to be fixed on to GFP2 than Cd\(^{2+}\).

### Adsorption Process and Adsorption Kinetics

In order to estimate the equilibrium time and determine the adsorption rate, dependence of the amount adsorbed for Pb\(^{2+}\) (Cd\(^{2+}\)) on the contact time is shown in Figure 9. We set the initial concentration of Pb\(^{2+}\) (Cd\(^{2+}\)) at 100 mg/L, and conducted the experiments at pH = 6 and room temperature. The large BET surface area and the mesoporous structure in GFP2 are specially reflected in the fast kinetics of Pb\(^{2+}\) (Cd\(^{2+}\)) adsorption by GFP2, which showed that >80% elimination efficiency

| adsorbent                           | metal ions | adsorption capacity, mg/g | reference |
|-------------------------------------|------------|---------------------------|-----------|
| flowerlike MgO nanostructures       | Pb\(^{2+}\) | 1980.0                    | 17        |
| PTMT                                | Pb\(^{2+}\) | 375.9                     | 32        |
| TMU-5                               | Pb\(^{2+}\) | 251.0                     | 56        |
| modified cellulose                  | Pb\(^{2+}\) | 192.0                     | 55        |
| Fe\(_2\)O\(_3@\)AlO(OH)            | Pb\(^{2+}\) | 29.6                      | 54        |
| PEI-grafted gelatin sponge          | Pb\(^{2+}\) | 66.0                      | 57        |
| GFP2                                | Pb\(^{2+}\) | 277.8                     | this work |
| flowerlike MgO nanostructures       | Cd\(^{2+}\) | 1500.0                    | 17        |
| PEI-grafted gelatin sponge          | Cd\(^{2+}\) | 65.0                      | 57        |
| gelatin sponge                      | Cd\(^{2+}\) | 9.4                       | 57        |
| GFP2                                | Cd\(^{2+}\) | 49.8                      | this work |

Table 1. Fitting Plot of the Adsorption Data and the Pb\(^{2+}\) and Cd\(^{2+}\) Adsorption Constants Obtained by the Langmuir, Freundlich Isotherm Models

| Isotherm model | Pb\(^{2+}\) | Cd\(^{2+}\) |
|---------------|-------------|-------------|
| Q\(_{\text{max}}\) (mg/g) | 277.78      | 49.75       |
| b (L/mg)      | 0.182       | 0.01        |
| R\(^2\)       | 0.998       | 0.996       |
| K\(_F\)       | 70.778      | 1.82        |
| n             | 3.446       | 1.866       |
| R\(^2\)       | 0.954       | 0.947       |

Table 2. Adsorption Capacities for Pb\(^{2+}\) and Cd\(^{2+}\) in Water on Various Solid Adsorbents
from the following equation

\[ q_e \equiv \frac{M}{W} \]

where \( q_e \) is the quantity of the adsorbate adsorbed per unit weight of the adsorbent (mg/g) when adsorption is up to equilibrium. 

In order to better understand the adsorption process, the adsorption kinetic plots were analyzed using a pseudo-second-order kinetics model\(^{47}\) based on the assumption that chemisorption is the rate-determining step. The equation is given below

\[ \frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e} \]  

where \( q_t \) is the quantity of the adsorbate adsorbed per unit mass of the adsorbent (mg/g) at given time \( t \) (min), \( q_e \) is the amount of the adsorbate adsorbed per unit weight of the adsorbent (mg/g) when adsorption is up to equilibrium, \( k_2 \) (g/(mg-min)) is the rate constant of the pseudo-second-order kinetic model, \( k_2 \) and \( q_e \) can be obtained by the intercept and slope of the linear equation of \( t/q_t \) versus \( t \). Moreover, the beginning sorption rate \( V_0 \) (mg/(g-min)) can be calculated from the following equation

\[ V_0 = k_2q_e^2 \]  

Figure 10 displays the kinetic plots of \( t/q_t \) versus \( t \), and Table 3 shows the correlation coefficients and rate constants of the pseudo-second-order kinetic. From the experimental results, we can find that the linear plot fits well with the relation of \( t/q_t \).

\[ q_e \equiv \frac{M}{W} \]

### Table 3. Correlation Coefficients and Rate Constants of the Pseudo-Second-Order Kinetic Model

|          | \( q_e \) (mg/g) | \( k_2 \) (g/(mg-min)) | \( V_0 \) (mg/(g-min)) | \( R^2 \) |
|----------|-----------------|-----------------------|------------------------|----------|
| Pb\(^{2+}\) | 97.09 (mg/g)    | 0.0014                | 12.771                 | 0.999    |
| Cd\(^{2+}\) | 46.08 (mg/g)    | 1.1524                | 2.447                  | 0.998    |

In order to further understand the adsorption process, the second-order kinetics model, 47 based on the assumption that chemisorption is the rate-determining step. The equation is given below

\[ \frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e} \]  

where \( q_t \) is the quantity of the adsorbate adsorbed per unit mass of the adsorbent (mg/g) at given time \( t \) (min), \( q_e \) is the amount of the adsorbate adsorbed per unit weight of the adsorbent (mg/g) when adsorption is up to equilibrium, \( k_2 \) (g/(mg-min)) is the rate constant of the pseudo-second-order kinetic model, \( k_2 \) and \( q_e \) can be obtained by the intercept and slope of the linear equation of \( t/q_t \) versus \( t \). Moreover, the beginning sorption rate \( V_0 \) (mg/(g-min)) can be calculated from the following equation

\[ V_0 = k_2q_e^2 \]  

Figure 10 displays the kinetic plots of \( t/q_t \) versus \( t \), and Table 3 shows the correlation coefficients and rate constants of the pseudo-second-order kinetic. From the experimental results, we can find that the linear plot fits well with the relation of \( t/q_t \).

\[ q_e \equiv \frac{M}{W} \]

### Table 3. Correlation Coefficients and Rate Constants of the Pseudo-Second-Order Kinetic Model

|          | \( q_e \) (mg/g) | \( k_2 \) (g/(mg-min)) | \( V_0 \) (mg/(g-min)) | \( R^2 \) |
|----------|-----------------|-----------------------|------------------------|----------|
| Pb\(^{2+}\) | 97.09 (mg/g)    | 0.0014                | 12.771                 | 0.999    |
| Cd\(^{2+}\) | 46.08 (mg/g)    | 1.1524                | 2.447                  | 0.998    |

show that the \( K_4 \) is high, which changed from 2.551 \times 10^4 to 2.582 \times 10^4 for Pb\(^{2+}\), while from 4.362 \times 10^4 to 6.842 \times 10^4 for Cd\(^{2+}\). The results show that the strong affinity existing between Pb\(^{2+}\) (Cd\(^{2+}\)) and GFP2 indicates that usual cations (e.g. K\(^+\), Ca\(^{2+}\), Na\(^+\), and Mg\(^{2+}\)) do not affect the binding of Pb\(^{2+}\) (Cd\(^{2+}\)) onto the adsorbent of GFP2. It also shows us that the \( K_4 \) for Cd\(^{2+}\) is a little higher than the \( K_4 \) for Pb\(^{2+}\). The high adsorption capacity for Pb\(^{2+}\) (Cd\(^{2+}\)) in GFP2 might be reasonably related to the high concentration of thiol groups in the adsorbent, which is very useful for the coordination between the thiols and Pb\(^{2+}\) (Cd\(^{2+}\)) in the framework of the material.\(^{56}\) According to the theory of hard and soft acids and bases (HSAB principle), Cd\(^{2+}\) is classified as a soft acid which tends to have strongest affinity to S, N, and O functional groups in GFP2, and Pb\(^{2+}\) as an intermediate acid has medium affinity. In contrast, alkali and alkaline earth metal ions (e.g. K\(^+\), Na\(^+\), Ca\(^{2+}\), and Mg\(^{2+}\)) identify as hard acids and have the weakest affinity to GFP2. Thus, the experimental results agreed well with the HSAB principle.

The secondary pollution resulting from the leakage of adsorbent constituents is a common problem during the pollution treatment process. After each adsorption experiment,
the iron concentration measured in solution is less than 0.001 mmol L$^{-1}$, which means that the Fe$_3$O$_4$ nanoparticles do not come off from GFP2 during the adsorption process. Therefore, GFP2 is stabilized under the given environment.

After each sorption experiment, iron concentration measured in solution is lower than 0.001 mmol L$^{-1}$, which means that no dissolution of the nanoparticles occurs during the immersion of these microbeads in solution. Overall, GFP2 can be directly used for the treatment of natural waters polluted by Pb$^{2+}$ (Cd$^{2+}$).

**Desorption and Recycling Research studies.** Recycling performance of the adsorbent, which could make the price of environmental remediation, is a key factor for their large-scale application. To research Pb$^{2+}$ (Cd$^{2+}$) recycling usage and desorption of GFP2, EDTA (2.0 mol/L) is used for the elution of adsorbed Pb$^{2+}$ (Cd$^{2+}$) onto GFP2 in the experiment. The adsorption-desorption cycle data are displayed in Figure S5. It shows that the adsorption capacities for Pb$^{2+}$ and Cd$^{2+}$ after five cycles decreased by approximately 6.4 and 11.6%, respectively, which may be attributed to the deactivation of adsorption centers during the desorption process. Overall, the experimental results indicate that GFP2 is an excellent candidate in heavy metal-contaminated water remediation.

## CONCLUSIONS

In the text, mesoporous layered magnetic hybrid GFP2 composed of GO, Fe$_3$O$_4$ nanoparticles (Fe$_3$O$_4$ NPs), and C$_3$N$_3$S$_3$ polymers with a mesoporous layered “sandwich” structure were successfully explored by an in situ simple polymerization strategy for rapid removal of Pb$^{2+}$ and Cd$^{2+}$ from water. The adsorbent (GFP2) shows high adsorption capacity (277.78 and 49.75 mg/g) and good selectivity for Pb$^{2+}$ and Cd$^{2+}$, respectively. Owing to its large BET surface area (123.8 m$^2$/g) and mesoporous structure, it exhibits the fast adsorption kinetics (>80% elimination efficiency within only 30 min). The Langmuir isotherm model based on typical monomolecular layer adsorption fits well with the adsorption data. The adsorption process of GFP2 for Pb$^{2+}$ and Cd$^{2+}$ can be explained well with the pseudo-second-order kinetics model. The adsorption capacities for Pb$^{2+}$ and Cd$^{2+}$ after five cycles decreased by approximately only 6.4 and 11.6%, respectively, indicating that GFP2 is a kind of recyclable solid absorbent, which is an excellent candidate in the heavy-metal wastewater treatment. More importantly, GFP2 was set with Fe$_3$O$_4$ NPs and it can be simply separated from wastewater using an extra magnet (Figure S6). Obviously, GFP2 with a simple preparation method, excellent recyclability, good selectivity for capturing Pb$^{2+}$ and Cd$^{2+}$, and stability has a good opportunity to be applied in the heavy metal wastewater treatment in the future.

## EXPERIMENTAL SECTION

**Preparation of GP.** Graphite oxide was prepared by chemical exfoliation of graphite powder based on a modified Hummer’s method.$^{57}$ The specific procedure for the preparation of GP were as follows: first, a certain amount of GO was dispersed in 300 mL of water by ultrasound, named suspension A. Second, 0.04 mol NaOH was dissolved in 50 mL of water and 0.02 mol Na$_3$C$_3$N$_3$S$_3$ monomer was dissolved in alkaline solution by stirring to get a bright yellow solution B. Then A and B were mixed together and stirred vigorously for 0.5 h, named suspension C. Third, 0.03 mol iodine in a concentrated aqueous solution of KI was dropped slowly into suspension C at 0 °C under stirring and continued to stir for 12 h at room temperature. The mixture color progressively changed from brown to blue-gray, and then the precipitate was separated by centrifugation. Next, the precipitate was washed with water for five times and dried at 50 °C. The same method was used to prepare composites P, GP1, GP2, and GP3 with GO using 0, 0.25, 0.5, and 1.0 g, respectively.

**Preparation of GFP (Scheme 1).** A modified Massart method$^{58}$ was used to prepare magnetite Fe$_3$O$_4$ NPs (8–12 nm). The process is as follows: first, 0.5 g of GO was dispersed in 300 mL of water by ultrasound, named suspension A. Second, 0.04 mol NaOH was dissolved in 50 mL of water and 0.02 mol Na$_3$C$_3$N$_3$S$_3$ monomer was dissolved in alkaline solution by stirring to get a bright yellow solution B. Then A and B were mixed together and stirred vigorously for 0.5 h, named suspension C. Third, a certain amount of Fe$_3$O$_4$ NPs were dispersed in 150 mL of 0.01 mol/L nitric acid solution by using an ultrasonic cleaner, and recover them by a magnetic field. Subsequently, the Fe$_3$O$_4$ NPs were redispersed in 150 mL
of water, named suspension D. Fourth, suspension D was added into suspension C slowly under mechanical stirring, then counted stirring for 0.5 h. Finally, 0.03 mol iodine in a concentrated aqueous solution of KI was dropped slowly into the above suspension at 0° C under stirring, and continued to stir for 12 h at room temperature. The mixture color progressively changed from brown to black, and then the precipitate was separated by a magnet. Then the precipitate was washed with water several times and was dried at 50° C. The same method was used to prepare composites GFP1, GFP2, and GFP3 with Fe3O4NPs using 0.25, 0.5, and 1.0 g, respectively (Scheme 1).

Adsorption Experiments. In the adsorption experiments, Pb(NO3)2 and Cd(NO3)2·4H2O were used to research the adsorption properties. The adsorption isotherm experiment for the GP (GP1, GP2, and GP3) and GFP (GFP1, GFP2, and GFP3) adsorbents is carried out in a typical process: the adsorbents (0.03 g) were added into 30 mL of heavy metal salt solution (in range of 25–500 mg/L) in a plastic tube. Then they were vibrated at 200 rpm for 12 h on a constant temperature shaking bed. The residual Pb2+ (Cd2+) concentration in adsorption liquid was determined with inductively coupled plasma–optical emission spectrometry (Optima8000, PerkinElmer). Three replicates were set for each sample, and the mean values were used to measure the absorption characteristics. The adsorption capacity (qe) and elimination efficiency (E (%)) of Pb2+ (or Cd2+) were determined using formulas 6 and 7, respectively.

$$q_e = \frac{V(C_0 - C_e)}{m}$$  \hspace{1cm} (6)  

$$E(\%) = \frac{C_0 - C_e}{C_0} \times 100$$  \hspace{1cm} (7)  

where C e and C0 are the equilibrium and initial concentrations of Pb2+ (or Cd2+) (mg/L) in the aqueous solution, individually; m is the dry-weight of the adsorbent (g), q e is the weight of the adsorbate adsorbed per unit dry mass of the adsorbent (mg/g) and V is the solution volume (L). The experiments of adsorption kinetics and environmental effect factors were carried out using 30 mg of adsorbent in 30 mL of Pb2+ (or Cd2+) solution (100 mg L−1).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02347.

Materials of experimental, preparation of Fe3O4 NPs, characterization of materials, SEM images of (a) GP2 and (b) GFP2, TGA curves of P, GP, and GFP, the N2 characterization of materials, SEM images of (a) GP2, (d) GFP2, and (f) GFP3, Freundlich isotherms of (a) GP2 (Pb2+) and (b) GFP2 (Cd2+), adsorption–regeneration cycles of Pb2+ (Cd2+) onto GFP2, and magnetic separation of GFP2 (PDF).

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Notes

The authors declare no competing financial interest.

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