



Article Preparation of Graphene Oxide Hydrogels and Their Adsorption Applications toward Various Heavy Metal Ions in Aqueous Media

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Abstract: Graphene oxide is a two-dimensional material that has been extensively studied in various fields due to its good mechanical properties, water dispersibility, and a large number of oxygencontaining functionalities on its surface. In this study, graphene oxide powder was prepared using graphite powder to take advantage of its large specific surface area and abundance of oxygencontaining functional groups. The graphene oxide powder was cross-linked with acrylic acid and acrylamide and polymerized to produce graphene oxide hydrogels, which were used to adsorb four metal ions including Cu(II), Pb(II), Zn(II), and Cd(II) from aqueous solutions. The adsorption performance of the graphene oxide hydrogels was investigated at different pHs, temperatures, initial metal ion concentrations, and competition principles, as well as their adsorption and desorption after three repeated adsorption-desorption experiments. It was found that the graphene oxide hydrogels exhibited good adsorption performance for all four metal ions under different conditions. The graphene oxide hydrogels for the adsorption of Cu(II), Pb(II), Zn(II), and Cd(II) ions were best fitted using the Langmuir monolayer adsorption model and the quasi-secondary reaction kinetic model. Good adsorption was achieved for all four metal ions under different competing adsorption principles. After three adsorption-desorption cycles, the adsorption capacity of the graphene oxide hydrogels for all four metal ions remained at 88% and above. These results indicate that graphene oxide hydrogels are a stable, efficient, low-cost, and reusable adsorbent material for the treatment of metal ions in solution.

Keywords: metal contamination; adsorption mechanism; graphene oxide; adsorption capacity; hydrogel

1. Introduction

With evolving times, economic development has been accompanied by the rapid growth and development of both industry and agriculture around the world [1]. As the scale and production of industry and agriculture continue to increase, the amount of wastewater generated increases along with the amount of water used [1]. Therefore, the recycling and reuse of wastewater have been key issues in addressing water stress [2]. Wastewater is characterized by a complex variety of pollutants, some of which can be recycled. Among the various pollutants in wastewater, heavy metals are of interest because of their special characteristics [3]. Heavy metals have irreversible properties and deposition characteristics [3]. If left untreated, they can accumulate in the environment, become toxic to organisms, damage ecosystems, and pose a threat to human health through amplification in the biological chain [4,5]. Through the research and practical exploration by a large number of scholars at home and abroad, a variety of treatment methods for heavy metals



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). in wastewater have emerged at this stage; however, simply having a good wastewater treatment method implemented is no longer the center of research for researchers at home and abroad [6,7]. The treatment of heavy metals in wastewater needs to increase efficiency while reducing costs, including economic and time costs, as environmentally friendly practices and recycling and other multi-dimensional advantages have become the current direction of research at home and abroad.

There are many different metal ions in wastewater, among which Cu(II), Pb(II), Zn(II), and Cd(II) ions are often found together, which makes it more difficult to treat wastewater [8]. Compared with the common treatment methods for metal ions in wastewater, i.e., chemical addition, biofilm treatment, photodegradation, and other treatment methods, the adsorption method is the center of this experiment because of its short treatment cycle, low treatment cost, recyclability of adsorbent, and its environmental friendliness [9]. The adsorption effect can be improved by increasing the number of adsorbents [10]. To improve the adsorption effect, increasing the adsorption capacity of the adsorbent is a certain size and directly affects the adsorption capacity of the adsorbent, increasing the active site of the adsorbent can effectively improve the adsorbent and study an adsorbent with high-adsorption efficiency for the treatment of metal ions in wastewater [13].

Graphene is a popular porous material used in research and is described as a twodimensional carbon nanomaterial [14]. Graphene is a high-strength, high-toughness, and high-optical-absorption material widely investigated for battery applications, as well as for the thermal properties of graphene thin films. In addition to these advantages, graphene has a huge specific surface area ($\sim 2600 \text{ m}^2 \cdot \text{g}^{-1}$) and a rich pore structure that is of wide interest for the adsorption of pollutants [15]. Graphene oxide, a derivative of graphene, is not only electrically conductive, but also has a series of oxygen-containing functional groups, such as hydroxyl, carboxyl, and epoxy groups, attached to the lamellar structure of graphene that can effectively combine with other ions [16]. The use of graphene powder enables the preparation of graphene with a large number of carboxyl groups. Graphene oxide powders with a large number of carboxyl groups can be prepared using graphite powder [17]. Moreover, graphene oxide can also be combined with other materials, such as gold nanomaterials, to form complexes, and has been used to adsorb dyes from wastewater, showing that graphene oxide–gold nanomaterials can adsorb two dyes, methylene blue and methyl orange, within a short period [18]. Graphene oxide, Fe_3O_4 , and chitosan have been prepared as ternary composites in which the epoxy, carboxyl, aromatic ring, and trivalent irons interacted with each other; these ternary composites were shown to have some adsorption effect on the Ni(II), Cu(II), and Pb(II) cations [19].

Acrylic acid can be polymerized alone or together with other materials under certain conditions to form polyacrylic acid hydrogels, which are cross-linked polymers with a three-dimensional network structure containing a large number of hydrophilic groups inside the network structure, with water absorption and high water retention properties, and can be modified by other materials due to the ease of cross-linking with other materials. Polyacrylic acid can be polymerized together with saprolite to form a hydrogel, which can adsorb silver nanoparticles, allowing them to be uniformly dispersed on the surface of the hydrogel [20]. The reaction of acrylic acid with acrylamide is a free radical reaction. The free radical polymerization of acrylic acid with acrylamide leads to the formation of polyacrylic acid–polyacrylamide hydrogels, which can also adsorb silver nanoparticles, allowing them to be uniformly dispersed [21]. This hydrogel also adsorbs nano-silver ions, which allows for their uniform dispersion. Hydrogels with hydrogen bonding, amide groups, and electrostatic interaction were prepared from a high-performance montmorillonite with acrylic acid and acrylamide and used for the adsorption of dyes, which were shown to be very effective for the adsorption of methylene blue at 200 mg \cdot L⁻¹ due to the presence of electronegative particles and reaction sites on the surface of the hydrogel [22]. Hydrogels are simple to make and do not consume a lot of resources and energy. Hydrogels formed

using graphene oxide and ascorbic acid have good adsorption properties for Pd and Cd, and the adsorption performance can still reach 80% after six reuses. Therefore, hydrogels are often used as an adsorbent material and have the advantage of being reusable [23].

In this paper, graphene oxide-modified acrylic hydrogels were used to increase the specific surface area of the hydrogels and the number of oxygen-containing functional groups on the surface of the hydrogels, which improved the adsorption capacity for heavy metals. The crystal structure, functional groups, and adsorption properties of the synthesized products were studied using various characterization methods. The adsorption capacity of graphene oxide hydrogels for Cu(II), Pb(II), Zn(II), and Cd(II) metal ions was compared. The effects of pH, temperature, initial metal concentration, contact time, competitive adsorption between various ions, and interfering ions on the adsorption of heavy metals by GO/P(AA-co-AM) were investigated. The Langmuir monolayer adsorption model and the quasi-secondary reaction kinetic model were used to fit the correlation study results.

2. Materials and Methods

2.1. Chemicals and Materials

Sulphuric acid, phosphoric acid, hydrogen peroxide, hydrochloric acid, potassium persulphate, potassium permanganate, and sodium hydroxide were supplied by Sinopharm Reagent Co. (Shanghai, China). Acrylamide was provided by MACKLIN Corporation Biochemical Co, Ltd. (Shanghai, China). All reagents used in the experiment were analytically pure. The water used for the experiments was deionized water whose conductivity was less than $3 \ \mu S \cdot m^{-1}$.

2.2. Preparation of Graphene Oxide Hydrogels

2.2.1. Preparation of Graphene Oxide

Graphene oxide was prepared using a modified Hummer's method by dispersing 5 g of graphite powder in a 1000 mL conical flask containing 27 mL of a mixture of sulphuric acid (95–97%) and 3 mL of phosphoric acid and stirring for 30 min at 1000–2000 rmp·min⁻¹ in an ice bath (0–10 °C). After stirring, 15 g of potassium permanganate was added to the mixture. The mixture was then raised to 50 °C and stirred for 12 h. The oxidized mixture was cooled to room temperature, 30% hydrogen peroxide solution was added, and the golden yellow mixture was left to stand without color change. The graphene oxide powder was obtained by washing with 1 mol·L⁻¹ hydrochloric acid solution and deionized water several times to obtain a dark brown precipitate, which was dried to a constant weight at 50 °C and ground and sieved through 100 mesh to obtain graphene oxide powder [24]. The graphene oxide powder was obtained by grinding and passing through 100 mesh sieves.

2.2.2. Synthesis of Graphene Oxide Hydrogels

A mixture of graphene oxide powder and deionized water was prepared in an amount of 0.5 g·L⁻¹. Amounts of 7.2 g of acrylic acid, 2.2 g of propionamide, 2.4 g of sodium hydroxide, and 16 mg of N'N-methylenebisacrylamide were added to a 100 mL beaker and the solid was shaken to dissolve and 80 mg of potassium persulphate was added. The beaker was placed in a water bath at 45 °C and the polymerization reaction took place at 45–50 °C for 6 h. The polymer surface was washed with deionized water and dried to a constant weight at 50 °C. Then, the polymer was ground and sieved through 100 mesh to obtain a graphene oxide hydrogel powder.

2.3. Material Characterization

The phase structures of the graphene oxide and graphene oxide hydrogels were characterized using D-Max 2550 Rigaku X-ray powder diffraction (XRD) with Cu K α radiation. The functional group information of the graphene oxide and graphene oxide hydrogels was studied using a Fourier-transform infrared (FTIR) spectrophotometer (IFS 66v/S) in the wave-number range of 500–4000 cm⁻¹.

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2.4. Removal of Cu(II), Pb(II), Zn(II), and Cd(II) Using GO/P (AA-co-AM)

The treatment effects of GO/P(AA-co-AM) on the removal of Cu(II), Pb(II), Zn(II), and Cd(II) ions from aqueous solutions were systematically investigated here. In this paper, the removal of Cu(II), Pb(II), Zn(II), and Cd(II) ions from aqueous solutions using GO/P (AA-co-AM) was systematically investigated. The procedure was performed using the following conditions: (1) pH = 2-7; Cu(II), Pb(II), Zn(II), and Cd(II) ion concentrations of 1000 mg·L⁻¹; temperature of 25 °C; (2) the range of the temperature was from 25 to 45 °C, Cu(II), Pb(II), Zn(II), and Cd(II) ion concentrations of 1000 mg·L⁻¹; (3) Cu(II), Pb(II), Zn(II), and Cd(II) ion concentrations ranging from 5 to 2000 mg·L⁻¹ at 25 °C, with a contact time ranging from 5 to 60 min; and (4) the competitive adsorption principle for Cu(II), Pb(II), Zn(II), and Cd(II), where the concentration of each metal ion in the solution was 1000 mg·L⁻¹ at 25 °C, and the principles of competitive adsorption were Cu(II), Pb(II), Zn(II) and Cd(II); Cu(II), Pb(II) and Zn(II); Cu(II) and Pb(II); Cu(II) and Zn(II); Pb(II) and Zn(II); Pb(II) and Cd(II); Zn(II) and Cd(II); Cu(II) and Cd(II). The used GO/P (AA-co-AM) particles were collected, dried to a constant weight, dissolved and desorbed with 0.1 M HCl solution, and then read. The mixture of graphene oxide hydrogel and heavy metals was stirred in a constant temperature shaking incubator at 200 rmp \cdot min⁻¹ for 60 min. The mixture was left to stand, 1 mL of the supernatant was taken for solid-liquid separation, and the concentration of metal ions in the adsorbed solution was determined using atomic absorption. The experiment was repeated three times and the average of the three replicates was taken with an experimental error of 5%.

The adsorption of heavy metal ions by GO/P(AA-co-AM) was calculated using Equation (1):

$$Q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where Q_e is the metal absorption concentration at equilibrium (mg·g⁻¹), C_0 is the initial concentration of the metal ion (mg·L⁻¹), C_e is the equilibrium concentration of the metal ion (mg·L⁻¹), V is the volume of the solution (L), and m is the mass of GO/P(AA-co-AM) in the solution (g).

2.5. Adsorption Kinetics Experiments

In this experiment, the widely used adsorption kinetic models, quasi-primary reaction kinetics and quasi-secondary reaction kinetics are used to investigate the adsorption rates of Cu(II), Pb(II), Zn(II), and Cd(II) metal ions by the GO/P(AA-co-AM) hydrogels and the mode of adsorption. The quasi-primary reaction kinetic equation is expressed as follows:

$$\ln\left(Q_e - Q_t\right) = -k_1 + \ln Q_e \tag{2}$$

The quasi-secondary reaction kinetic equation is expressed as follows:

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2 Q_e^2} \tag{3}$$

where *t* is the adsorption time (min); Q_e is the number of metal ions adsorbed by the GO/P(AA-co-AM) hydrogel at adsorption equilibrium (mg·g⁻¹); Q_t is the number of metal ions adsorbed by the hydrogel at *t* (mg·g⁻¹); and k_1 and k_2 are the quasi-primary and quasi-secondary adsorption rate constants, respectively.

2.6. Intraparticle Diffusion Model

To further analyze the adsorption behavior of metal ions adsorbed by the GO/P(AAco-AM) hydrogels, an intraparticle diffusion model was used to determine the limiting effect of the diffusion state of metal ions within the hydrogel on the overall adsorption process. The results for the adsorption of four metal ions by the GO/P(AA-co-AM) hydrogels were therefore fitted using an intraparticle diffusion model with the following equation expressions:

$$Q_t = K_p \cdot t^{1/2} + C \tag{4}$$

where Q_t is the amount of the GO/P(AA-co-AM) hydrogels adsorbed for metal ions at t (mg·g⁻¹), K_p is the intraparticle diffusion rate constant (mg·g⁻¹·t^{1/2}), t is the adsorption time (min), and *C* is the intensity of the boundary layer.

2.7. Adsorption Isotherms

The adsorption behavior of metal ion adsorption on the GO/P(AA-co-AM) hydrogels was analyzed using the Freundlich isotherm and Langmuir isotherm, which are commonly used for adsorption behavior, where the equation expression for the Langmuir isotherm is

$$C_e/Q_e = \frac{1}{(K_L \cdot Q_m)} + \frac{C_e}{Q_m}$$
(5)

The equation expression for the Freundlich isotherm is given by

$$\ln Q_e = \ln K_F + \frac{1}{n(\ln C_e)} \tag{6}$$

where C_e is the concentration of metal ions at adsorption equilibrium (mg·L⁻¹), Q_e is the number of metal ions adsorbed by the GO/P(AA-co-AM) hydrogels at adsorption equilibrium (mg·g⁻¹), Q_m is the theoretical saturation amount of metal ions adsorbed by the GO/P(AA-co-AM) hydrogels, K_L and K_F are the equilibrium constants of the Langmuir isotherm and Freundlich isotherm, respectively, and n is the concentration index.

3. Results and Discussion

3.1. FTIR, XRD, and XPS Characterization

The FTIR spectra of P(AA-co-AM) (a), GO (b), and GO/P(AA-co-AM) (c) were analyzed using an IFS 66v/S FTIR spectrometer, and the results are shown in Figure 1a–c. From the FTIR spectrum of P(AA-co-AM) (Figure 1a), it can be seen that the strong absorption bands of the amide group are present at 3462 and 3354 cm^{-1} , where the -NH₂ stretching vibration peak of acrylamide (AM) is present when acrylic acid (AA) is cross-linked with acrylamide (AM) to form P(AA-co-AM) [25]. The stretching vibration peak of C-H in the alkyl group is at 2984 cm⁻¹. The absorption peaks at 1650 and 1575 cm⁻¹ are the peaks of the C=O stretching vibration in the amide group (-CONH₂) of acrylamide (AM) and the C=O stretching vibration in the carboxylate anion (-COO-) of acrylic acid (AA) when cross-linking with acrylamide (AM) to form P(AA-co-AM) [13,26,27]. Therefore, the results indicate that the P(AA-co-AM) hydrogel was successfully synthesized by the polymerization of acrylic acid (AA) with acrylamide (AM). The FTIR spectrum of GO in Figure 1b shows a strong hydroxyl (-OH) stretching vibration peak at 3461 cm^{-1} , which is the formation of intermolecular hydrogen bonds after the oxidation of graphite. At 1621 cm^{-1} , the stretching vibration peak of carbonyl C=O in the carboxyl group (-COOH) or the stretching vibration peak of the olefin group (C=C) formed after the oxidation of graphite is shown [28]. The presence of the monosubstituted olefin group (=CH-) at 997 cm^{-1} in the infrared spectrum is not the only evidence of the presence of C=C in GO [29]. This result indicates that the graphite has been successfully oxidized to produce graphene oxide with inter-analytical hydrogen bonds and olefin groups. The FTIR spectrum of GO/P(AA-co-AM) in Figure 1c shows that the strong obtuse peak at 3440 cm⁻¹ is the stretching vibration peak of the hydroxyl-OH in the carboxylic acid group (-COO-) or the hydroxyl-OH in the graphene oxide are intermolecular hydrogen bonds, and at 1615 cm^{-1} the stretching vibration peak of the carbonyl-C=O in the carboxylate anion (-COO-) in the acrylic acid (AA) at 1650 cm^{-1} can be observed [13,26,27]. The stretching vibration peak moved to this point, thus indicating that graphene oxide (GO) was successfully crosslinked on the P(AA-co-AM) hydrogel to synthesize the GO/P(AA-co-AM) hydrogel, and a



large number of intermolecular hydrogen bonds, including hydroxyl radicals and carboxyl radicals, were formed on the surface of the GO/P(AA-co-AM) hydrogel.

Figure 1. FTIR spectra of (**a**) P(AA-co-AM), (**b**) GO, and (**c**) GO/P(AA-co-AM). XRD patterns of (**d**) GO and (**e**) GO/P(AA-co-AM).

The macroscopic XPS spectra of GO/P(AA-co-AM) and P(AA-co-AM) were analyzed using electronic energy spectroscopy, respectively, and the macroscopic XPS spectra are shown in Figure 2. Both GO/P(AA-co-AM) and P(AA-co-AM) detected C 1s (284.74 eV), N 1s (400.59 eV), O 1s (532.42 eV), and Na 1s (1071.54 eV) characteristic peaks. Since XPS analysis can be performed semi-quantitatively, the fractional heights and ratios of the characteristic peaks of C 1s and O 1s show that the carbon–oxygen ratio decreases significantly after cross-linking graphene oxide, and the content of oxygen-containing functional groups in the polymer increases significantly.



Figure 2. XPS spectra of (a) GO/P(AA-co-AM) and (b) P(AA-co-AM).

From the XRD pattern of GO in Figure 1d, it can be determined that the characteristic peaks of the crystalline form of the oxides formed after the oxidation of graphite are similar to the characteristic peaks of organic substances that are polycarbonate and have hydroxyl and carboxyl groups, which indicates that graphite was successfully oxidized to graphene oxide. As shown in Figure 1e, a broad peak with an acute angle appears on the left side for the GO/P(AA-co-AM) sample, which indicates that graphene oxide was successfully cross-linked with acrylic acid and acrylamide to form the targeted graphene oxide hydrogel.

Figure 3 shows the FTIR spectra of the GO/P(AA-co-AM) hydrogels after the adsorption of Cu(II), Pb(II), Zn(II), and Cd(II) ions. It can be seen from the figure that the -OH absorption band located around \sim 3400 cm⁻¹ on GO/P(AA-co-AM) before adsorption of metal ions has shifted to the right after adsorption, and the strong stretching vibration peak before adsorption has become smoother, which indicates that the adsorption of the GO/P(AA-co-AM) hydrogel is directly related to -OH. The absorption peak at 1668 cm⁻¹ is the absorption peak of the carbonyl C=O stretching vibration in the amide group (-CONH₂) in acrylamide (AM) when acrylic acid (AA) and acrylamide (AM) are cross-linked to form a hydrogel. The absorption peak at 1535 cm^{-1} is the carbonyl C=O stretching vibration peak in the carboxylate anion (-COO-) in acrylic acid (AA), or the carbonyl C=O stretching vibration peak in the carboxylate group (-COOH) formed after the oxidation of graphite, or the stretching vibration peak of the olefin group (C=C). The vibrational peak at 1050 cm^{-1} is the result of the rightward shift of the olefin group (=C-H-) after monosubstitution before adsorption. The changes in the stretching and vibrational peaks of the functional groups on the surface of the GO/P(AA-co-AM) hydrogels after the adsorption of metal ions indicate that the oxygen-containing functional groups on the surface of the GO/P(AA-co-AM) hydrogels play an important role in the adsorption mechanism of the four metal ions. The oxygen-containing functional groups on the surface of the hydrogel play a role.



Figure 3. FTIR spectra after adsorption of GO/P(AA-co-AM)-Cu, GO/P(AA-co-AM)-Pb, GO/P(AA-co-AM)-Zn, and GO/P(AA-co-AM)-Cd.

3.2. Exposure to Metal Ions

Figure 4 shows the adsorption of Cu(II), Pb(II), Zn(II), and Cd(II) ions by the GO/P(AAco-AM) hydrogels for different initial metal concentrations. While investigating whether the GO/P(AA-co-AM) hydrogels have the theoretical adsorption capacity, an attempt was made to investigate the limits of adsorption of the GO/P(AA-co-AM) hydrogels for the four metals. The graphs show the adsorption limits of GO/P(AA-co-AM) for the removal of Cu(II), Pb(II), Zn(II), and Cd(II) at initial concentrations of 0–2000 mg·L⁻¹. The amount of GO/P(AA-co-AM) hydrogel used was 1.0 g·L⁻¹, the adsorption conditions were 200 r·min⁻¹, and the adsorption time was 60 min. It can be seen from Figure 4 that the adsorption of the GO/P(AA-co-AM) hydrogel for the four metals varied, but in the initial concentration range of 0–300 mg L^{-1} of metal ions, the adsorption of the four metals on the GO/P(AA-co-AM) hydrogels was positively correlated at initial concentrations of $0-300 \text{ mg} \cdot \text{L}^{-1}$. Increasing the initial concentrations of the metal ions resulted in different deviations from the positive correlation line. This may be because the GO/P(AA-co-AM) hydrogel has a large number of folds and adsorption sites on the surface, and when the ion concentration is in a certain range, the metal ions can be adsorbed on the hydrogel surface without ion exchange or other forms of exchange. However, when the initial concentration of the metal continues to increase, the original adsorption site is close to being occupied, and then ion exchange or other forms of exchange are required to enable the metal ions

to be adsorbed into the hydrogel. The adsorption obtained by this exchange is limited by many objective conditions and the competitive ability of different metal ions is different; thus, different adsorption effects can be produced.



Figure 4. Adsorption of Cu(II), Pb(II), Zn(II), and Cd(II) ions removed by GO/P(AA-co-AM) at initial concentrations of 0–2000 mg·L⁻¹ (mGO/P(AA-co-AM) = 1 g·L⁻¹, stirring speed = 200 r·min⁻¹, t = 60 min).

Among the different adsorption effects of the four metal ions shown in Figure 4, the best metal ion adsorbed by the GO/P(AA-co-AM) hydrogel was Pb(II), and the GO/P(AAco-AM) hydrogel could still maintain a good adsorption effect when the initial concentration amount of Pb(II) ion in the solution was 2000 mg·L⁻¹. The adsorption amount of Pb(II) adsorbed by the GO/P(AA-co-AM) hydrogel with an initial concentration of 2000 mg·L⁻¹ was 1658.5 mg·g⁻¹, and the adsorption rate could reach 82.93% and did not reach the adsorption limit. Continuing to increase the initial concentration of metal ions, the adsorption amount of the GO/P(AA-co-AM) hydrogels for Pb(II) would continue to increase, but the adsorption rate would decrease. This is because as the initial concentration increases, the active sites on the surface of the hydrogel decrease as the metal ions are bound; however, the middle of the hydrogel is also free of some metal ions and hydrogen ions (H^+) and free hydrogen bonds (-H) that are combined with the active sites, and as the concentration of hydrogen ions and hydrogen bonds increases and the concentration of metal ions in the solution decreases, the free metal ions in the solution are prevented from adsorbing. As the concentration of hydrogen ions and hydrogen bonds increases and the concentration of metal ions in solution decreases, the free metal ions in solution are prevented from binding to the active sites on the GO/P(AA-co-AM) hydrogels. Compared with the adsorption capacity of the GO/P(AA-co-AM) hydrogel for Pb(II), the adsorption capacity of the GO/P(AA-co-AM) hydrogels for Cu(II) was relatively weak. The adsorption capacity of the GO/P(AA-co-AM) hydrogel for Cu(II) with an initial concentration of 2000 mg·L⁻¹ was 1341.87 mg·g⁻¹ and the adsorption rate could reach 67.09%. However, the adsorption capacity of the GO/P(AA-co-AM) hydrogel for Zn(II) and Cd(II) metal ions was relatively weak; after the initial concentration of metal ions exceeded 300 mg· L^{-1} , the adsorption capacity of the GO/P(AA-co-AM) hydrogel for Zn(II) and Cd(II) continued to increase with the initial concentration of metal ions. There were different cases of weakening, with the adsorption rate decreasing significantly with increasing initial concentrations of metal ions. Although the adsorption capacity of the hydrogel for both metal ions increased, when the concentration of the metal itself was increased to 1000 mg·L⁻¹, the adsorption capacity of the hydrogel for both metal ions did not increase significantly when the initial concentration of the metal ions was increased. When the initial concentration of metal ions in the solution was 1000 mg \cdot L⁻¹, the adsorption of the GO/P(AA-co-AM) hydrogels for Zn(II) and Cd(II) was 723 mg \cdot g⁻¹ and 635 mg \cdot g⁻¹ with 53.87% and 54.83% adsorption, respectively.

The effect of pH on the adsorption of metal ions by the GO/P(AA-co-AM) hydrogels is shown in Figure 5a. With the gradual increase in pH, the adsorption of the GO/P(AAco-AM) hydrogel for Cu(II), Pb(II), and Zn(II) metal ions showed an increasing trend, which should be due to the high content of hydrogen ions in the solution at lower pHs. The high content of hydrogen ions may compete with metal ions for limited adsorption sites, thus leading to a decrease in the adsorption capacity of the hydrogel for metal ions or the hydrogen ions combined with the carboxyl group (-COO-) on the surface of the GO/P(AA-co-AM) hydrogel. This makes the negative charge on the surface of the hydrogel unable to attract the positive charge of the metal ions, which weakens the electrostatic adsorption between the hydrogel and the metal ions. The adsorption of all four metal ions on the GO/P(AA-co-AM) hydrogel at the lowest pH was greater than 550 mg·g⁻¹, indicating that the adsorption of metal ions by the GO/P(AA-co-AM) hydrogels is not only electrostatic. However, when the pH is increased to a certain level, the metal ions combine with other anions in the solution, such as hydroxide, and precipitate metal compounds at higher pHs, which is why the adsorption effect of the GO/P(AA-co-AM) hydrogel on Cd(II) decreases with the increasing pH. The turnaround at pH = 4 and Pb(II) and Zn(II) metal ions are close to the maximum value of adsorption. There is an objective fact that the actual industrial wastewater generated has a generally low pH. Therefore, the solution at pH = 4 was chosen to analyze the adsorption mode of the four metal ions adsorbed by the GO/P(AA-co-AM) hydrogels.



Figure 5. (a) Adsorption capacity of Cu(II), Pb(II), Zn(II), and Cd(II) ions removed by GO/P(AA-co-AM) at pH 2–6, respectively ($C_0 = 1000 \text{ mg} \cdot \text{L}^{-1}$, $C_m = 1 \text{ g} \cdot \text{L}^{-1}$, t = 60 min). (b) Adsorption capacity of Cu(II), Pb(II), Zn(II), and Cd(II) ions removed by GO/P(AA-co-AM) at different temperatures ($C_0 = 1000 \text{ mg} \cdot \text{L}^{-1}$, $C_m = 1 \text{ g} \cdot \text{L}^{-1}$, t = 60 min).

The effect of temperature on the adsorption of Cu(II), Pb(II), Zn(II), and Cd(II) by the GO/P(AA-co-AM) hydrogels is shown in Figure 5b. In the graph, the adsorption of all four metal ions by the hydrogel increased to varying degrees with increasing temperature. This is because the increase in temperature improves the swelling properties of the hydrogel and the migration rate of metal ions in solution also accelerates at the same time, enhancing the exchange between the hydrogel and metal ions. It is concluded that the increase in temperature contributes to the adsorption reaction and indicates that the adsorption of metal ions by the GO/P(AA-co-AM) hydrogels is a heat absorption reaction.

3.3. Discussion of Adsorption Mechanisms

3.3.1. Adsorption Kinetic Model

The fitted kinetic curves for the quasi-primary and quasi-secondary reactions of the GO/P(AA-co-AM) hydrogels for the adsorption of four metal ions are shown in Figure 6, and the correlation coefficients for the fitted kinetic curves for the quasi-primary and quasi-secondary reactions in Table 1 are shown. The slope and intercept of the fitted curves can be obtained by fitting the results to the kinetic quasi-level kinetic and quasi-secondary reaction kinetic models. The slope and intercept of the fitted curves can be used to calculate the Q_e and the k₁ and k₂ corresponding to the two reaction kinetic models. The results of the fitting

of the two reaction kinetic response curves compared with the fitted results of the quasisecondary reaction kinetic model are closer to the actual equilibrium adsorption amount Q_e obtained. The correlation coefficient was better than that of the quasi-secondary reaction kinetics ($\mathbb{R}^2 > 0.997$). Based on the above results, it can be determined that the interaction of the GO/P(AA-co-AM) hydrogels with the four metal ions includes ion exchange, sharing, and interaction, thus indicating that the main adsorption mode is chemisorption, i.e., the oxygen-containing functional groups on the surface of the GO/P(AA-co-AM) hydrogels combine with the metal ions. By comparing the adsorption rate constants of the quasi-secondary reaction kinetics, k_2 , the rate at which the adsorption of the four metal ions reaches adsorption equilibrium is known. Therefore, the adsorption rates of the GO/P(AA-co-AM) hydrogels for the four metal ions can be obtained as Zn(II) > Cd(II) > Pb(II) > Cu(II), with Zn(II) reaching adsorption equilibrium the fastest. Compared with the other three metal ions, Cu(II) is the last to reach adsorption equilibrium.



Figure 6. Kinetic model for quasi-mono and quasi-directional reactions of (**a**) Cu(II), (**b**) Pb(II), (**c**) Zn(II), and (**d**) Cd(II) ions adsorbed by GO/P(AA-co-AM) ($C_0 = 1000 \text{ mg} \cdot \text{g}^{-1}$, pH = 4, T = 25 °C).

Table 1. Model coefficients for the reaction kinetics of GO/P(AA-co-AM) for the adsorption of Cu(II), Pb(II), Zn(II), and Cd(II) ions.

Ions	$Q_e/{ m mg} \cdot { m g}^{-1}$	Ps	eudo-First Orde	er	Pseudo-Second Order			
		$Q_e/{ m mg} \cdot { m g}^{-1}$	k_1	R ₁	$Q_e/{ m mg} \cdot { m g}^{-1}$	k_2	R ₂	
Cu ²⁺	785.72	661.41	0.03073	0.907	787.4	0.000661	0.997	
Pb ²⁺	970.03	950.24	0.06489	0.876	990.09	0.000843	0.999	
Zn ²⁺	764.96	695.31	0.03993	0.960	763.36	0.001361	0.999	
Cd ²⁺	729.89	687.83	0.04752	0.667	729.93	0.000885	0.998	

3.3.2. Particle Diffusion Model

A particle diffusion model was used to fit the diffusion patterns of the four metal ions adsorbed by the GO/P(AA-co-AM) hydrogels shown in Figure 7. For the intraparticle diffusion model, if the C value of the fitted curve is 0 and the fitted curve passes through the origin, then intraparticle diffusion is the only limiting factor for the adsorption of the

GO/P(AA-co-AM) hydrogels. Conversely, if it does not pass through the origin, then there are other adsorption mechanisms working together in the adsorption process of the hydrogels, and the larger the C value, the more pronounced the boundary layer effect, which means that the adsorption effect of the boundary layer of the adsorbent is more important for the overall adsorption process. The larger the C value, the more pronounced the boundary layer effect, and the greater the role of the adsorber boundary layer in the overall adsorption process.



Figure 7. Diffusion model of Cu(II), Pb(II), Zn(II), and Cd(II) ions adsorbed by GO/P(AA-co-AM) ($C_0 = 1000 \text{ mg} \cdot \text{g}^{-1}$, pH = 4, T = 25 °C).

As shown in the figure, the fitted curves of the intraparticle diffusion model for the adsorption of the four metal ions by the GO/P(AA-co-AM) hydrogels do not pass the origin, which indicates that the adsorption mechanism of the hydrogels for the four metal ions is not only the intraparticle diffusion mechanism, but also other mechanisms acting together between the hydrogels and the metal ions. From the fitted results, it can be seen that the boundary effect C values are relatively large, indicating that the surface adsorption of the GO/P(AA-co-AM) hydrogels is very important for the whole adsorption process, which is consistent with the results from the quasi-secondary kinetic model, and chemisorption is also an important mechanism in the adsorption of metal ions by the GO/P(AA-co-AM) hydrogels.

3.3.3. Adsorption Isotherms

Two common adsorption isotherm models were fitted for the adsorption of four metal ions with the GO/P(AA-co-AM) hydrogels to investigate the mode of the GO/P(AA-co-AM) hydrogels for the adsorption of four metal ions. The Langmuir isotherm is based on relatively homogeneous and intermolecular force-free single-molecule layer adsorption, while the Freundlich isotherm is based on a non-uniform adsorption system where the adsorbent is a multi-molecular layer. The results of the adsorption of the four metal ions on the GO/P(AA-co-AM) hydrogels were fitted using the two adsorption isotherms and the fitted adsorption isotherms are shown in Figure 8. The fitted equations for the adsorption of the four metal ions by the GO/P(AA-co-AM) hydrogels can be obtained from the fitted results, where the R² obtained from the Langmuir isotherm for the four metal ions is greater than the R^2 obtained from the Freundlich isotherm for the four metal ions, which indicates that the GO/P(AA-co-AM) hydrogels exhibit a high adsorption capacity. The adsorption mode of the four metal ions tends to be a relatively homogeneous, intermolecular forcefree single-molecule layer adsorption, with a fixed number of active adsorption sites on the surface of the adsorbent, each with the same adsorption energy, and no combination with other adsorbates after the desired sites are occupied. The saturation amounts of the GO/P(AA-co-AM) hydrogels for the adsorption of Cu(II), Pb(II), Zn(II), and Cd(II) ions are $1268.65 \text{ mg} \cdot \text{g}^{-1}$, 2026.87 mg $\cdot \text{g}^{-1}$, 704.24 mg $\cdot \text{g}^{-1}$, and 632.91 mg $\cdot \text{g}^{-1}$, respectively, which

are consistent with the actual experimental saturation amounts of the GO/P(AA-co-AM) hydrogels. The results were similar to those obtained from the actual GO/P(AA-co-AM) hydrogels for the adsorption of the four metal ions. The experimental results indicate that the hydrogels have good adsorption properties for all four metal ions.



Figure 8. (a) Langmuir isotherm model and (b) Freundlich isotherm model of GO/P(AA-co-AM) adsorption of Cu(II), Pb(II), Zn(II), and Cd(II) ions (pH = 4, T = $25 \degree C$, $t = 60 \mod C$.

The adsorption of GO/P(AA-AM) hydrogels and other hydrogels in the literature for metal ions were compared as shown in Table 2.

	$Q_m/\mathrm{mg}\cdot\mathrm{g}^{-1}$						
Adsorbent –	Cu ²⁺	Pb ²⁺	Zn ²⁺	Cd ²⁺	– Keport		
GO/P(AA-AM)	787.4	990.09	763.36	729.93			
P(AA-AM)	185.73	587.99	208.42	402.86	[30]		
P(AA/AM)	69.81	-	-	-	[31]		
P(AA/MMA)	153.8	216.1	-	-	[32]		
ATP/P(AA/AM)	156.3	84.03	-	-	[33]		
FA/P(AA/AM)	-	103.8	-	-	[34]		

Table 2. Maximum adsorption of heavy metal ions on the GO/P(AA-AM) hydrogels in comparison with other literature.

3.4. Competitive Adsorption of Four Metal Ions

The results of the competitive adsorption of four metal ions by the GO/P(AA-co-AM) hydrogels under eight different competitive adsorption principles were investigated, as shown in Figure 9. To determine the strength of the competitive ability of the hydrogel adsorption for different metal ions, the affinity between metal ions and the GO/P(AA-co-AM) hydrogels was shown by the competitive partition coefficient K_d and the selection coefficient α . The equations used to determine the competitive partition coefficient K_d and the selection coefficient α are expressed as follows:

$$K_d = \left(Q_i / C_{01} + Q_2 / C_{02} + \dots + Q_j / C_{0j}\right) \tag{7}$$

$$\alpha = K_d(T) / K_d(I) \tag{8}$$

where K_d is the competitive partition coefficient, Q_i is the amount of component I adsorbed (mg·g⁻¹), C_{0i} is the initial concentration of competing metal ions (mg·L⁻¹), and α is the selectivity coefficient. K_d (T) and K_d (I) are the K_d for strongly and weakly adsorbed ions, respectively.

The equation provides the sum of the partition coefficients, K_d , for all different adsorbents within the same system as 1. On this basis, the larger the value of K_d , the more competitive the adsorbent is for the active site of the adsorbent within this system relative to other adsorbents, and the stronger the affinity of this adsorbent with the adsorbent than

other adsorbents. For the selection coefficient α , when the value of α is larger, it means that for two different metal ions in the same adsorption system, the adsorbent is more selective for the strong adsorbent ions.



Figure 9. Results of competitive adsorption of GO/P(AA-co-AM) on Cu(II), Pb(II), Zn(II), and Cd(II) ions ($C_i = 1000 \text{ mg} \cdot \text{L}^{-1}$, $C_m = 1 \text{ g} \cdot \text{L}^{-1}$, t = 60 min).

The results of the competitive adsorption of the GO/P(AA-co-AM) hydrogels for the adsorption of four metal ions for eight different competitive adsorption principles are shown in Figure 9. The partition coefficients K_d and the selection coefficients α for competitive adsorption are shown in Table 3. It can be seen from the figure that when the four metal ions are no longer present in the solution alone, the adsorption of the GO/P(AAco-AM) hydrogel for all four metal ions decreases to varying degrees, and it can be seen that the most significant decrease in the adsorption of the hydrogel for the four metal ions is for Pb. Moreover, in the presence of other metal ions, the adsorption of the hydrogels for Pb decreases by about 50% compared with the adsorption of Pb by the hydrogel alone. The adsorption capacity of Pb decreased by about 50% from 950.4 mg \cdot g⁻¹ to about 480 mg \cdot g⁻¹. As shown in Table 3, the competitive nature of the Cu, Pb, and Cd metal ions is relatively similar, and the selection coefficients, α , for the three metal ions are all around 1 for the four different competitive adsorption principles. When the four metal ions are in the same system, the partition coefficients for the Cu, Pb, and Cd metal ions can be Cu > Cd > Pb. In contrast, the partition coefficients of Cu, Pb, and Cd ions in the other three adsorption principles were $Pb \ge Cu > Cd$, while Zn was significantly less competitive than the other three metal ions, and the partition coefficients of competitive adsorption in the eight different competitive adsorption principles were smaller than the other three metal ions. The size of the affinity between the hydrogel and the metal ion is related to three aspects: (1) the smaller the water and radius of the metal ion, the stronger the affinity between the metal ion and the hydrogel; (2) the more electronegative the metal ion is, the stronger the ability to bind to the hydrogel and the stronger the affinity will be; and (3) the stronger the affinity of the metal ions that form covalent bonds that are more likely to bind to active adsorption sites on the surface of the hydrogel, the stronger the affinity for the hydrogel. The sizes of the hydration radii of four of the Cu(II), Pb(II), Zn(II), and Cd(II) metal ions are Pb < Cd < Zn < Cu [35]. However, the electronegativities of these Cu(II), Pb(II), Zn(II), and Cd(II) metal ions are 1.90, 2.33, 1.65, and 1.69, respectively [36]. The electronegativity of Cu is greater than that of Cd and Zn, and the electronegativity of the four metal ions is ranked as Pb > Cu > Cd > Zn, which is consistent with the fact that the partition coefficients of the four metal ions are ranked as $Pb \ge Cu > Cd > Zn$ in practice, indicating that the competitive ability of the GO/P(AA-co-AM) hydrogels when adsorbing metal ions is more related to the electronegativity of the metal ions.

Table 3. Partition coefficients and selective washout for competitive adsorption of metal ions on the GO/P(AA-co-AM) hydrogels.

Ions	Cu ²⁺	K Pb ²⁺	d Zn ²⁺	Cd ²⁺	Pb ²⁺ /Cu ²⁺	Pb ²⁺ /Zn ²⁺	Pb ²⁺ /Cd ²⁺	α Cu ²⁺ /Zn ²⁺	Cu ²⁺ /Cd ²⁺	Zn ²⁺ /Cd ²⁺	Cd^{2+}/Zn^{2+}
$Cu^{2+} + Pb^{2+} + Zn^{2+} + Cd^{2+}$	0.275	0.270	0.178	0.277	0.982	1.517	0.975	1.545	0.993	0.643	1.555
$Cu^{2+} + Pb^{2+} + Zn^{2+}$	0.376	0.378	0.245	-	1.005	1.543	-	1.535	-	-	-
$Cu^{2+} + Zn^{2+}$	0.610	-	0.390	-	-	-	-	1.564	-	-	-
$Pb^{2+} + Zn^{2+}$	-	0.610	0.390	-	-	1.564	-	-	-	0.669	-
$Zn^{2+} + Cd^{2+}$	-	-	0.401	0.599	-	-	-	-	-	-	1.494
$Cu^{2+} + Pb^{2+}$	0.500	0.500	-	-	1.000	-	-	-	-	-	-
$Pb^{2+} + Cd^{2+}$	-	0.506	-	0.494	-	-	1.024	-	-	-	-
$Cu^{2+} + Cd^{2+}$	0.513	-	-	0.487	-	-	-	-	1.530	-	-

3.5. Cyclic Stability

To test the reusability of the GO/P (AA-co-AM) hydrogels, the four metal ions were adsorbed using the hydrogels, and the adsorbed hydrogels were desorbed using $0.1 \text{ mol} \cdot L^{-1}$ of HCl solution. The adsorption–desorption experiment was repeated three times. The adsorption capacities of the desorbed hydrogels were obtained, as shown in Figure 10. From Figure 10, it can be determined that the adsorption capacity of the GO/P(AA-co-AM)hydrogels for the four metal ions decreases to different degrees with the increase in the number of repeated adsorption-desorption cycles. This is because the individual metal ions are more strongly bound to the GO/P(AA-co-AM) hydrogel during the adsorptiondesorption process, and this active site is occupied and not resolved during the desorption process. Therefore, when the metal ions adsorbed with the GO/P(AA-co-AM) hydrogel are reused, the previously occupied active site cannot absorb the metal ions again. Therefore, the adsorption capacity of the GO/P(AA-co-AM) hydrogels was reduced. In addition, the GO/P(AA-co-AM) hydrogels were filtered and dried in repeated adsorption-resolution experiments, so the graphene oxide hydrogels were always in the swollen and dried states. The frequent switching of these two states caused a certain degree of damage to the threedimensional mesh structure inside the hydrogel, which also led to the degradation of the adsorption performance of the graphene oxide hydrogel. After three repeated adsorptionresolution experiments, the adsorption capacities of the GO/P(AA-co-AM) hydrogels for the adsorption of Cu(II), Pb(II), Zn(II), and Cd(II) ions were reduced to 90.12%, 94.34%, 96.54%, and 88.91% of the original adsorption capacities, respectively.



Figure 10. Adsorption capacities of Cu(II), Pb(II), Zn(II), and Cd(II) ions removed by GO/P(AA-co-AM) when the hydrogel was repeated three times ($C_0 = 2500 \text{ mg} \cdot \text{L}^{-1}$, $C_m = 1 \text{ g} \cdot \text{L}^{-1}$, t = 60 min).

The internal structure mechanism of GO/P(AA-AM) hydrogel is shown in Figure 11. By cross-linking acrylamide hydrogels and doping graphene oxide in the hydrogels, the monosubstituted olefins of graphene oxide can form rings with acrylic acid and acrylamide, thus achieving a three-dimensional mesh structure, while graphene oxide can be successfully cross-linked in the hydrogels. The free water in the hydrogel can adsorb metal ions during the hydrogel swelling process. The carboxylic acid functional group and hydroxyl functional group on graphene oxide can adsorb metal ions through ion exchange.



Figure 11. Mechanistic diagram of the internal structure of GO/P(AA-AM) hydrogels.

4. Conclusions

It was found that the graphene oxide could cross-link with acrylic acid and acrylamide, increasing the oxygen-containing functional groups and olefin double bonds on the hydrogel surface. The adsorption behavior of the GO/P(AA-co-AM) hydrogel for the adsorption of Cu(II), Pb(II), Zn(II), and Cd(II) ions can be fitted using the quasi-secondary reaction kinetic model and the Langmuir isotherm model. The maximum adsorption capacities of the GO/P(AA-co-AM) hydrogels for the adsorption of Cu(II), Pb(II), Zn(II), and Cd(II) were 1268.65 mg·g⁻¹, 2026.87 mg·g⁻¹, 704.24 mg·g⁻¹, and 632.91 mg·g⁻¹, respectively. It was shown that under different adsorption principles, the adsorption effect of the GO/P(AA-co-AM) hydrogels for the four metal ions was more balanced and stable, and the GO/P(AA-co-AM) hydrogels were suitable for the adsorption of multiple metal ions under coexistence conditions. The GO/P(AA-co-AM) hydrogel has a certain adsorption capacity even after three times of reuse. The present work shows that the GO/P(AA-co-AM) hydrogels can be used as an efficient and stable composite that can adsorb a wide range of metal ions.

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