Preparation of Fe$_3$O$_4$@SiO$_2$@ P(AANa-co-AM) Composites and Their Adsorption for Pb(II)

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ABSTRACT: A series of magnetic composites of sodium polyacrylate and polyacrylamide copolymer [Fe$_3$O$_4$@SiO$_2$@P(AANa-co-AM)] were prepared. The investigation showed that the adsorption efficiency of Pb(II) was the best when the acrylamide/acrylic acid (AM/AA) mass ratio of composites was 5:5. Therefore, the composite of this ratio was selected as the adsorbent to systematically absorb Pb(II) in aqueous solution. Static adsorption of Pb(II) to the magnetic composites in aqueous solutions was investigated by varying the solution pH and the concentration of Pb(II). The adsorption kinetics and isotherms model of Pb(II) on the Fe$_3$O$_4$@SiO$_2$@P(AANa-co-AM) composites followed a pseudo-second-order model and the Langmuir isotherm model, respectively. When the temperatures were 298.15, 308.15, and 318.15 K, the maximum adsorption capacities of Fe$_3$O$_4$@SiO$_2$@P(AANa-co-AM) composites were 237.53, 248.14, and 255.10 mg/g, respectively. The thermodynamic study of adsorption showed that the adsorption of Pb(II) on Fe$_3$O$_4$@SiO$_2$@P(AANa-co-AM) composites was a spontaneous endothermic process. The X-ray photoelectron spectroscopy (XPS) analysis showed that the adsorption of Pb(II) was due to the chelation between −COO$^-$ and Pb(II). After four adsorption–desorption cycles, the adsorbent can still maintain a high adsorption capacity.

1. INTRODUCTION

Pb(II) is a common heavy metal that is widely distributed and exists in many forms. It has a high content in wastewater from nonferrous metal smelting, mineral processing, nuclear fuel industry, printing, leather, textile, battery, building materials, electroplating, and alloy manufacturing industries.$^{1,2}$ Pb(II) is highly toxic, non-biodegradable, and often accumulated in organisms, resulting in diseases affecting the human nervous, renal, gastrointestinal, and hematopoietic systems, and is even carcinogenic, posing a serious threat to human health.$^{3,4}$ Therefore, lead-containing wastewater must be treated effectively before discharging. The common methods used in practical application are chemical precipitation, membrane separation, ion exchange, electrodialysis, reverse osmosis, biological treatment, adsorption, and so on.$^{5,6}$ For high-concentration heavy-metal wastewater, reverse osmosis, chemical treatment, or electrochemical treatment can be used to reduce the concentration. However, at lower concentrations, the application cost of these methods is higher. At low concentration, the adsorption method has the advantages of low cost, good adsorption effect, fast adsorption rate, no sludge production, energy-saving, simple operation, and source of a range of materials, such as graphene oxide,$^7$ chitosan,$^8$ activated carbon,$^9$ and silica,$^{10}$ which have been widely used in heavy-metal wastewater treatment. The hydrogels have unique chemical and physical properties such as a cross-linked three-dimensional network structure, obvious hydrophilicity, expansibility, and modifiability. As a new adsorbent, hydrogels have attracted more and more attention to the adsorption properties of dyes and heavy metals.$^{11,12}$ Although a large number of adsorbents have been developed for the treatment of heavy metal wastewater, the preparation of adsorbents with no secondary pollution, high adsorption efficiency, and good reuse performance is still a challenge.$^{13}$ In recent years, magnetic adsorption materials used in water treatment can achieve rapid separation and recovery of adsorbents that reach saturation adsorption, effectively prevent
secondary pollution, and achieve multiple regenerations and reuse of adsorbents.\textsuperscript{13,14} Magnetic adsorbents are usually produced by binding to Fe\textsubscript{3}O\textsubscript{4}. However, the bare magnetic Fe\textsubscript{3}O\textsubscript{4} is prone to agglomeration and easily oxidized in the air. To protect magnetic Fe\textsubscript{3}O\textsubscript{4}, many researchers have further modified magnetic materials.\textsuperscript{15} Zargoosh et al. modified magnetic Fe\textsubscript{3}O\textsubscript{4} with salicyl hydrazide (TSH) and polyacrylic acid (PAA) as adsorbents to absorb Pb(II), the maximum adsorption capacity was 188.7 mg/g.\textsuperscript{16} Ren et al. synthesized Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@poly(acrylate-amin) composites with more carboxylate groups and amino groups on the surface were prepared by solution dispersion polymerization and the performance of Pb(II) adsorption was studied systematically.

The polymers containing polycarboxyl and polyamino groups exhibit excellent adsorption properties for heavy-metal ions.\textsuperscript{18} In this paper, Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@poly(acrylate-acylamide) composites with more carboxylate groups and amino groups on the surface were prepared by solution dispersion polymerization and the performance of Pb(II) adsorption was studied systematically.

2. RESULTS AND DISCUSSION

2.1. Characterization. Figure S1 shows the X-ray diffraction patterns of Fe\textsubscript{3}O\textsubscript{4}, Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}−M, and Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@P(AANa-co-AM) (Figure S1 in the Supporting Information). The six characteristic peaks at 30.4, 35.9, 43.5, 54.0, 57.4, and 63.2° (Figure S1a) were assigned to the (220), (311), (400), (422), (511), and (440) planes of pure Fe\textsubscript{3}O\textsubscript{4}, respectively.\textsuperscript{19} The peak intensity of the Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}−M decreased compared with that of Fe\textsubscript{3}O\textsubscript{4} due to the coating of amorphous SiO\textsubscript{2} layer (Figure S1b). It can be found from Figure S1 that the Fe\textsubscript{3}O\textsubscript{4} characteristic peaks were observed in the XRD map of Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@P(AANa-co-AM), indicating that the crystal structure of Fe\textsubscript{3}O\textsubscript{4} remains unchanged (Figure S1c).

The Fourier transform infrared (FT-IR) spectra of Fe\textsubscript{3}O\textsubscript{4}, Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}−M, Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@P(AANa-co-AM), and Pb−Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@P(AANa-co-AM) magnetic particles are shown in Figure 1. The peak at 576 cm\textsuperscript{−1} was Fe−O vibration, as shown in Figure 1a. The two new peaks appearing at 955 and 1068 cm\textsuperscript{−1} belong to the Si−OH stretching vibration and the Si−O−Si symmetric stretching vibration, respectively (Figure 1b). This indicates that Fe\textsubscript{3}O\textsubscript{4} particles were successfully coated by SiO\textsubscript{2}.\textsuperscript{20,21} As shown in Figure 1, the spectral lines a, b, c, and d show broad and blunt peaks at 3393−2922 cm\textsuperscript{−1}, indicating the presence of association −OH. From Figure 1c, it can be seen that the peaks at 1410 and 1569 cm\textsuperscript{−1} are consistent with the symmetric and antisymmetric telescopic peaks of COO\textsuperscript{−}, and the peaks at 1666 cm\textsuperscript{−1} are consistent with the telescopic vibration of C==O bond in −COO\textsuperscript{−}\textsuperscript{,22} After Pb(II) adsorption by Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@P(AANa-co-AM), due to the strong interaction between −COO\textsuperscript{−} and Pb(II), as shown in Figure 1d, a symmetric telescopic peak and an antisymmetric telescopic peak of the COO\textsuperscript{−} shift from 1569 and 1410 cm\textsuperscript{−1} to 1563 and 1405 cm\textsuperscript{−1}, respectively.

The scanning electron microscopy (SEM) image of Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@P(AANa-co-AM) (Figure 2A) shows that Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@P(AANa-co-AM) has a relatively fluffy plushlike structure, which gives a good platform for the adsorption of heavy metals. Figure 2B is a transmission electron microscopy (TEM) image of Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}−M, and the core−shell structure can be observed. The edge of the gray part was the silica shell, the middle part of the black part was the Fe\textsubscript{3}O\textsubscript{4} core. This indicates that Fe\textsubscript{3}O\textsubscript{4} particles are successfully coated by SiO\textsubscript{2}. When coated with silica, Fe\textsubscript{3}O\textsubscript{4} particles tend to aggregate into larger particles. As the surface of the electrostatic repulsion of silica, the particles have a certain degree of dispersion.

Figure S2 shows the thermogravimetric curve of Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@P(AANa-co-AM) before and after the adsorption of Pb(II). As can be seen from Figure S2, a small weightlessness step appears in the temperature range of 50−215 °C, mainly due to the evaporation of free water contained in the sample. Before adsorption, Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@P(AANa-co-AM) shows obvious weightlessness of about 30 wt % at 215−450 °C, which was mainly due to the oxidative decomposition of oxygen-containing functional groups in Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@P(AANa-co-AM) molecules and the carbonation of polymer chains.\textsuperscript{23} Then, the weight loss was 24.68% at 451−582 °C, which was due to the decomposition and carbonization of the polymer skeleton, while the slow weight loss at 582 °C was attributed to the continued carbonization of the residual substances.\textsuperscript{23,24} After the adsorption, Pb(II) reacted with...
an important parameter that affects the adsorption performance of adsorbents. It not only determines the adsorption capacity of adsorbents but also determines the surface charge of the adsorbents. As shown in Figure 4, the adsorption capacity of Pb(II) by Fe₃O₄@SiO₂@P(AM/AA) composite is lower when the pH value is low and the adsorption capacity qₑ of Pb(II) increased obviously when the pH increases from 2.0 to 3.5. When the pH value is about 4.5, the adsorption capacity reaches the maximum. As the pH value is greater than 4.5, the adsorption capacity decreases gradually. When the pH value is low, too much H⁺ in the solution causes the amino and carboxyl matrix in the Fe₃O₄@SiO₂@P(AM/AA) composite to form −NH₃⁺ and −COOH, which, in turn, weakens its chelating ability with Pb(II). At the same time, H⁺ also competes with Pb(II) for adsorption and occupies more adsorption points. When the pH value increases gradually, the −NH₃⁺ and −COOH protonation on the composite, and a large number of −NH₂ and −COOH chelate with Pb(II), which makes the adsorption capacity of Pb(II) increase greatly. However, when the pH is more than 5, −OH in aqueous solution is easy to hydrolyze with Pb(II) and form Pb(OH)₂ precipitation. Therefore, the following adsorption experiments were carried out under a pH of 4.5.

2.3.3. Influence of Contact Time and Adsorption Kinetics. The influence of contact time on adsorption capacity is shown in Figure 5. The results showed that the adsorbance of Pb(II) decreased gradually. When the pH value is about 4.5, the adsorption capacity of Pb(II) increased greatly when the pH increases from 2.0 to 3.5. When the pH value is about 4.5, the adsorption capacity reaches the maximum. As the pH value is greater than 4.5, the adsorption capacity decreases gradually. When the pH value is low, too much H⁺ in the solution causes the amino and carboxyl matrix in the Fe₃O₄@SiO₂@P(AM/AA) composite to form −NH₃⁺ and −COOH, which, in turn, weakens its chelating ability with Pb(II). At the same time, H⁺ also competes with Pb(II) for adsorption and occupies more adsorption points. When the pH value increases gradually, the −NH₃⁺ and −COOH protonation on the composite, and a large number of −NH₂ and −COOH chelate with Pb(II), which makes the adsorption capacity of Pb(II) increase greatly. However, when the pH is more than 5, −OH in aqueous solution is easy to hydrolyze with Pb(II) and form Pb(OH)₂ precipitation. Therefore, the following adsorption experiments were carried out under a pH of 4.5.

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Table 1. Kinetic Model Parameters of Pb(II) Adsorption on Fe₃O₄@SiO₂@P(AANa-co-AM)

| Cₒ (mg/L) | qₑ (mg/g) | k₁ (min⁻¹) | R² | k₂ (g/(mg·min)) | qₑ (mg/g) | R² |
|-----------|-----------|-------------|----|-----------------|-----------|----|
| 250       | 135.5     | 0.02396     | 0.8033 | 0.0002174 | 266.7 | 0.9952 |

where $q_m$ (mg/g) and $K_L$ (L/mg) are the maximum adsorption capacity and the Langmuir equilibrium constant, respectively.

Freundlich model:

$$\ln qₑ = \ln K_F + \frac{1}{n} \ln Cₑ$$

where $1/n$ and $K_F$ (L/g) are the Freundlich equilibrium constants.

The adsorption equilibrium data obtained from the Langmuir and Freundlich isotherm models are listed in Figure S5A,B and Table 2. The results showed that the $R²$ value of the Langmuir model is larger than that of the Freundlich model and closer to 1. Therefore, the adsorption of Pb(II) by Fe₃O₄@SiO₂@P(AAANa-co-AM) is more in accordance with the Langmuir model, which is monolayer adsorption. According to the Langmuir isotherm equation, the calculated maximum adsorption capacities for Pb(II) by Fe₃O₄@SiO₂@P(AAANa-co-AM) are 237.53, 248.14, and 255.10 mg/g at 298.15, 308.15, and 318.15 K, respectively. The $K_L$ value of the Langmuir model and the $1/n$ value of the Freundlich model between 0 and 1 indicate that the adsorption is easy to proceed. Table 3 summarizes the maximum adsorption capacities of some adsorbents reported in recent years for Pb(II), indicating that the adsorbance of Fe₃O₄@SiO₂@P(AAANa-co-AM) for Pb(II) is comparable or exceeds that of other adsorbents. So, Fe₃O₄@SiO₂@P(AAANa-co-AM) can be used for treating wastewater containing Pb(II).

Table 2. Parameters of Langmuir and Freundlich Isotherm Models

| T (K) | $q_m$ (mg/g) | $K_L$ (L/mg) | $R²$ | $K_F$ (L/g) | $n^{-1}$ | $R²$ |
|-------|--------------|--------------|------|-------------|---------|------|
| 298.15 | 237.53       | 0.3935       | 0.9963 | 84.49       | 0.2677  | 0.8713 |
| 308.15 | 248.14       | 0.5255       | 0.9972 | 94.84       | 0.2671  | 0.8965 |
| 318.15 | 255.10       | 0.8150       | 0.9977 | 109.99      | 0.2570  | 0.8708 |

Langmuir model at three different temperatures was larger than that of the Freundlich model and closer to 1. Therefore, the adsorption of Pb(II) by Fe₃O₄@SiO₂@P(AAANa-co-AM) is more in accordance with the Langmuir model, which is monolayer adsorption. According to the Langmuir isotherm equation, the calculated maximum adsorption capacities for Pb(II) by Fe₃O₄@SiO₂@P(AAANa-co-AM) are 237.53, 248.14, and 255.10 mg/g at 298.15, 308.15, and 318.15 K, respectively. The $K_L$ value of the Langmuir model and the $1/n$ value of the Freundlich model between 0 and 1 indicate that the adsorption is easy to proceed. Table 3 summarizes the maximum adsorption capacities of some adsorbents reported in recent years for Pb(II), indicating that the adsorbance of Fe₃O₄@SiO₂@P(AAANa-co-AM) for Pb(II) is comparable or exceeds that of other adsorbents. So, Fe₃O₄@SiO₂@P(AAANa-co-AM) can be used for treating wastewater containing Pb(II).

Table 3. Maximum Adsorption Capacities ($q_m$) for Pb(II) by Some Adsorbents

| adsorbent | $q_m$ (mg/g) | ref |
|-----------|--------------|-----|
| ECAA      | 219.3        |     |
| AC        | 58.00        | 9   |
| CMC/PAM   | 312.5        | 12  |
| FMMS      | 223.2        | 13  |
| Fe₃O₄/LDH-AM | 266.6 | 14  |
| MNPs      | 188.7        | 16  |
| EDCMS     | 123.5        | 17  |
| Fe₃O₄/P(Cys/HEA) | 38.69 | 19  |
| LLDPE-g-PAA-co-starch/OMMT | 430.0 | 22  |
| M-PAM-HA  | 174.9        | 23  |
| P(AAANa-co-AM)/GO | 452.3 | 25  |
| Fe₃O₄@SiO₂@P(AAANa-co-AM) | 237.53 | this work |

where $q_m$ (mg/g) and $K_L$ (L/mg) are the maximum adsorption capacity and the Langmuir equilibrium constant, respectively.

Freundlich model:

$$\ln qₑ = \ln K_F + \frac{1}{n} \ln Cₑ$$

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To analyze the thermodynamic behavior of adsorption of Pb(II) by Fe$_3$O$_4$@SiO$_2$@P(AANa-co-AM), some thermodynamic parameters can be obtained from the following equations.

$$\Delta G^0 = -RT \ln k^0$$

$$\ln k^0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

where $R$ is the ideal gas constant (8.314 J/(mol·K)), $K^0$ is the adsorption equilibrium constant, $T$ is the absolute temperature, $\Delta G^0$ is the standard Gibbs free energy change, $\Delta H^0$ is the standard enthalpy change (J/mol), and $\Delta S^0$ is the standard entropy change (J/(mol·K)). $K^0$ was obtained from the intercept of plotting $\ln(q_e/C_e)$ versus $C_e$ at three different temperatures by extrapolating $C_e$ to zero according to the Singh and Khan method. $\Delta H^0$ and $\Delta S^0$ were obtained from the slope and intercept in the curve of $\ln K^0$ versus $T^{-1}$. The values of $\ln K^0$, $\Delta H^0$, $\Delta S^0$, and $\Delta G^0$ are listed in Table 4.

Table 4. Thermodynamic Parameters for the Adsorption of Pb(II) on Fe$_3$O$_4$@SiO$_2$@P(AANa-co-AM)

| $T$ (K) | $\ln K^0$ | $\Delta H^0$ (kJ/mol) | $\Delta S^0$ (J/(mol·K)) | $\Delta G^0$ (kJ/mol) |
|---------|------------|------------------------|--------------------------|------------------------|
| 298.15  | 4.148      | 26.09                  | 121.9                    | -10.28                 |
| 308.15  | 4.444      | -                        | -                        | -11.38                 |
| 318.15  | 4.811      | -                      | -                        | -12.72                 |

Normally, when the value of $\Delta H^0$ is between 2.1 and 20.9 kJ/mol, the electrostatic interaction between the adsorption ion and the adsorption site is consistent, which indicates that the adsorption is due to physical adsorption. When the value of $\Delta H^0$ is between 20.9 and 418.4 kJ/mol, the adsorption is transferred from the adsorbent surface to the adsorbing ions to form coordinate bonds or involves charge sharing, which indicates that adsorption is chemical adsorption. The value of $\Delta H^0$ in this work is 26.09 kJ/mol as shown in Table 4, indicating that the adsorption of Pb(II) on Fe$_3$O$_4$@SiO$_2$@P(AANa-co-AM) is chemical adsorption. Meanwhile, the positive value of $\Delta H^0$ indicates that adsorption is a spontaneous endothermic reaction, and increasing the temperature is beneficial to the adsorption process, which is consistent with the discussion on the effect of temperature change. The negative value of $\Delta G^0$ indicates that the adsorption of Pb(II) on Fe$_3$O$_4$@SiO$_2$@P(AANa-co-AM) is a spontaneous process, and the positive value of $\Delta S^0$ indicates that the adsorption process is driven by entropy rather than enthalpy.

2.3.5. X-ray Photoelectron Spectroscopy (XPS) Analysis.

To explore the adsorption mechanism of Fe$_3$O$_4$@SiO$_2$@P(AANa-co-AM) for Pb(II), the samples before and after adsorption were characterized by XPS. The characterization results are given in Figure 7. The characteristic peaks of C 1s, N 1s, O 1s, and Na 1s appeared at 284, 399, 531, and 1071 eV in the full-scale XPS spectra, respectively (Figure 7a). Fe$_3$O$_4$@SiO$_2$@P(AANa-co-AM) of adsorption Pb(II) had strong Pb 4f peaks (Figure 7a), which indicated that Pb(II) was indeed...
adsorbed on the composites. The three group peaks of Fe₃O₄@SiO₂@P(AANa-co-AM) and Fe₃O₄@SiO₂@P(AANa-co-AM)-Pb(II) in Figure 7b belong to the C−C, C−N, and C≡O binding energy of C 1s, respectively.

Clearly, due to the reaction of adjacent N or O atoms with Pb(II), the binding energies of C 1s increases slightly after the adsorption of lead ions. The peaks at 530.67 and 531.27 eV correspond to the C−O and C≡O bond energies in the O 1s high-resolution spectra before adsorption, respectively (Figure 7c). It can be observed that after the adsorption of Pb(II), the bond energy of the C≡O changes less, while the bond energy of the C−O increases significantly from 530.67 to 532.30 eV, which indicates strong chelation between −COO− groups and Pb(II). The peak at 399.60 eV is due to the bond energy of the acylamino N−H in the N 1s high-resolution spectra before the adsorption of the composites (Figure 7d); the bond energy of the N−H remained basically unchanged after adsorption of Pb(II), indicating that the affinity of acylamo to Pb(II) is extremely small due to the weak activity of acylamo. Therefore, the adsorption mechanism of composites for Pb(II) is the chelation of −COO − for Pb(II).

2.3.6. Regeneration Study. In general, in the actual wastewater treatment process, it is necessary to prepare excellent adsorbents with high desorption efficiency and good reusability to reduce the cost. Figure 8 shows the removal rate of Pb(II) in each cycle after desorption with 30 mL of 2% HNO₃ and regeneration with 30 mL of 0.1 mol/L NaOH solution. The results showed that the removal rate of Pb(II) by Fe₃O₄@SiO₂@P(AANa-co-AM) decreased from 99.56 to 93.28% for 100 mg/L of Pb(II) at pH 4.5. This indicates that the Fe₃O₄@SiO₂@P(AANa-co-AM) composite exhibits excellent regeneration performance as an adsorbent for Pb(II).

3. CONCLUSIONS

The adsorption of Pb(II) by magnetic composites is highly dependent on the initial Pb(II) concentration and the solution pH. The adsorption kinetics study of Pb(II) on the magnetic composites can be well described by the pseudo-second-order model. The adsorption isotherm fitted well with the Langmuir model and the calculated maximum adsorption capacities are 237.53, 248.14, and 255.10 mg/g at 298.15, 308.15, and 318.15 K, respectively. Thermodynamic studies show that adsorption is chemical adsorption and a spontaneous endothermic process, which is driven by entropy. The XPS analysis reveals that the mechanism of adsorption of Pb(II) onto the magnetic composites is the chelation of −COO − with Pb(II). Furthermore, the composite exhibits good magnetic responsiveness and reusability, which give it high potential to remove Pb(II) from wastewater.

4. EXPERIMENTAL SECTION

4.1. Materials. Chemical reagents including acrylamide (AM), acrylic acid (AA), tetraethylenesilicate (TEOS), silane coupling agent (3-aminopropyl) triethoxysilane (APTES), K₂S₂O₈, N,N-methylene diphenylamine (MBA), CH₃CH₂OH, ammonium hydroxide (NH₄OH, 25%), NaOH, and HNO₃ were purchased from Chengdu Jinshan Chemical Reagent Co., Ltd, Chengdu, China. FeCl₃·6H₂O, Pb(NO₃)₂, and FeSO₄·7H₂O were purchased from Shanghai Qiangshun Chemical Reagent Co., Ltd, Shanghai, China. The chemical reagents used in the experiment were all analytical grade, and the water used was distilled water.

4.2. Preparation of Magnetic Fe₃O₄ Particles. In this paper, Fe₃O₄ particles were prepared by the co-precipitation method. First, 2.50 g of FeSO₄·7H₂O and 4.86 g of FeCl₃·6H₂O were dissolved in 100 mL of distilled water to form a uniform dark orange solution under magnetic stirring. Then, the aqueous solution of NaOH (5.1 g of NaOH dissolved in 50 mL of distilled water) was injected into the above solution under intense stirring at room temperature for 5 h. Finally, the product was filtered and washed to neutral with distilled water and anhydrous ethanol and dispersed in distilled water by the ultrasonic treatment of 10 min for the next step.

4.3. Preparation of Modified Fe₃O₄@SiO₂. The modified Fe₃O₄@SiO₂ was prepared in two steps. According to previous studies, the core−shell Fe₃O₄/SiO₂ was synthesized by the revised Stöber method. Generally, 20 mL of distilled water, 80 mL of ethanol, 5 g of TEOS, and 5 mL of ammonium hydroxide (25%) were mixed under mechanical stirring in a 313.15 K water bath for hydrolyzing and condensing of TEOS. After 10 min, 100 mL (80 mL ethanol and 20 mL water) of a Fe₃O₄ solution containing about 2 g of Fe₃O₄ was added to this mixed solution. After the reaction was carried out at room temperature for 12 h, the products were collected by a magnet, washed to neutral with distilled water and anhydrous ethanol, and then dispersed again in solutions containing 160 mL anhydrous ethanol, 40 mL of distilled water, and 4 mL of ammonium hydroxide (25%) for further use.

APTES/Fe₃O₄@SiO₂ (Fe₃O₄@SiO₂-M) was prepared by further modification of Fe₃O₄@SiO₂ by silane coupling agent (APTES). The specific experimental methods were as follows: 4 mL of APTES was added to the above-mentioned Fe₃O₄@SiO₂ solution and mechanically stirred for 24 h in a water bath at 333.15 K, and then cooled naturally to room temperature. The resulting product was then collected with a magnet, washed repeatedly with distilled water and ethanol, and dried in a vacuum oven at 333.15 K.

4.4. Preparation of Fe₃O₄@SiO₂@P(AANa-co-AM) Composites. In a water bath of 278.15 K, sodium hydroxide was used to prepare AA with a neutralization degree of 0.8. Typical processes for preparing Fe₃O₄@SiO₂@P(AANa-co-AM) composites with a mass ratio of AM/AA = 5:5 can be described as follows: 2 g of Fe₃O₄@SiO₂-M was ultrasonically dissolved in 50 mL of distilled water for 30 min, then transferred to a 250 mL three-necked flask, 14.8 mL of AANa solution (containing 5.04 g AA), 5.04 g of AM, and 0.1 g of the cross-linking agent were added, and then ventilated with N₂ for 15 min. Under strong mechanical stirring, 10 mL of K₂S₂O₈ solution (containing 0.2 g of K₂S₂O₈) was added to the three-
The obtained Fe₃O₄@SiO₂@P(AANA-co-AM) composites were shredded and soaked in ethanol–water mixture (5:5, v/v) for 24 h to remove unreacted monomers from the sample. Then, the product was dried in a vacuum oven at 338.15 K. The crystal structures of Fe₃O₄, Fe₃O₄@SiO₂-M, and Fe₃O₄@SiO₂@P(AANA-co-AM) magnetic composites with AM:AA mass ratios of 9:1, 7:3, and 3:7 were prepared, respectively. The simple preparation process of the sample is shown in Scheme 1.

### 4.5. Characterization

The crystal structures of Fe₃O₄, Fe₃O₄@SiO₂-M, and Fe₃O₄@SiO₂@P(AANA-co-AM) samples were investigated by X-ray diffraction (XRD, D8 Advance) spectra using Cu Kα radiation (λ = 0.154 nm). The infrared spectra of the composites in the range of 4000–400 cm⁻¹ were measured by Fourier transform infrared (FT-IR, Nicolet iS10) spectroscopy. The morphologies of the samples were observed by scanning electron microscopy (SEM, Spectro Zeiss Evo18) and transmission electron microscopy (TEM, JEOL, JEM-2010). Thermogravimetric analysis (TGA) was performed on a TGA–differential scanning calorimetry (DSC) analyzer (Metter Toledo) under a nitrogen flow with a heating rate of 10 K/min. The functional group changes of Fe₃O₄@SiO₂@P(AANA-co-AM) samples were investigated by X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Al-Kα 1486.6). The sample (0.5 g) was immersed in 500 mL of water to determine the swelling weight of the sample at different contact times and its swelling ratio was calculated until the sample reached a swelling equilibrium. The swelling ratio of the sample can be calculated as SR = (m₁ − m₂)/m₂ where m₁ and m₂ are the masses of the dry sample and the swollen sample, respectively.

### 4.6. Adsorption Experiments

The stock solution of Pb(II) was prepared by dissolving Pb(NO₃)₂ in distilled water and further diluting to the desired concentration. The pH of the solution was adjusted to the desired value with 0.1 M NaOH and 0.1 M HNO₃ solution. Batch experiments were carried out in a water bath thermostat shaker at 120 rpm for 6 h at 298.15 K. In a typical experiment, 50 mL of Pb(II) solutions and 50 mg of adsorbent were mixed in a 100 mL conical flask for adsorption. The influence of the varying initial aqueous pH values was evaluated in the range of 2.0–5.0 with an initial Pb(II) concentration of 200 mg/L at 298.15 K, and the medium with optimum pH value was adopted for all of the following experiments. The influence of the contact time on adsorption was studied by changing the contact time (0–360 min). The adsorption isotherm was obtained by varying the initial Pb(II) concentration from 50 to 300 mg/L at three different temperatures of 298.15, 308.15, and 318.15 K within 6 h, respectively. After filtration, the lead-ion concentration was determined by flame atomic adsorption spectrophotometry (FAAS, Shimadzu AA-6300C). The equilibrium adsorption capacity (qe, mg/g) and the removal rate (R) of Pb(II) were calculated by eqs 7 and 8, respectively

\[
q_e = \frac{(C_0 - C_e)V}{m} 
\]

where \( C_0 \) and \( C_e \) are the initial and the equilibrium concentrations (mg/L), respectively, \( V \) is the volume of the solution (L), and \( m \) is the dry weight of the adsorbent.

\[
R = \frac{C_0 - C_e}{C_0} \times 100\% 
\]

### 4.7. Desorption and Regeneration Studies

The adsorption was carried out in 50 mL of 100 mg/L Pb(II) solution at pH 4.5 with 50 mg of Fe₃O₄@SiO₂@P(AANA-co-AM) at 298.15 K for 6 h. After filtration, the Pb-loaded adsorbent was immersed in 30 mL of 2% (v/v) HNO₃ and shaken at 298.15 K for 2 h. After desorption, the adsorbents were regenerated with 30 mL of 0.1 M NaOH solution and then washed to neutral with distilled water for the next adsorption.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00403.

XRD spectra of Fe₃O₄ (a), Fe₃O₄@SiO₂-M (b), and Fe₃O₄@SiO₂@P(AANA-co-AM) (c). TGA curves of Fe₃O₄@SiO₂@P(AANA-co-AM) before (A) and after (B) adsorbed Pb(II). Pb(II) removal rate and swelling rate bar diagram of Fe₃O₄@SiO₂@P(AANA-co-AM) composites with different AA:AM ratios. Fitting of pseudo-first-order and pseudo-second-order models. Fitting of Langmuir and Freundlich models for Pb(II) adsorption (PDF)
Demo adsorption experiment of adsorbent and magnet (MP4)
Demo adsorption experiment of adsorbent and magnet in solution (MP4)

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Author Contributions
H.L. performed the methodology and writing of the original, draft. F.Z. performed the review and editing. Q.W. managed the resources, formal analysis, and supporting information. All authors read and approved the final manuscript.

Notes
The authors declare no competing financial interest.

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