Preparation of Humic Acid/L-Cysteine-Codecorated Magnetic Fe₃O₄ Nanoparticles for Selective and Highly Efficient Adsorption of Mercury

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ABSTRACT: Humic acid and l-cysteine-codecorated magnetic Fe₃O₄ nanoparticles (HA/LC-MNPs) were synthesized using a coprecipitation method. Humic acid fractions abundant with carboxyl and hydroxyl groups can be selectively coated on the surface of MNPs during synthesis. HA/LC-MNPs with abundant heteroatoms (N, S, and O) show excellent removal capacity, great selectivity, and also fast trapping of Hg²⁺ in a wide pH range. The adsorption capacity of HA/LC-MNPs for Hg²⁺ can reach 206.5 mg/g, and the chemisorption was attributed to the major adsorption form. In competitive adsorption, HA/LC-MNPs preferentially adsorbed Hg²⁺ with an affinity order of Hg²⁺ >> Pb²⁺ > Cu²⁺ ≫ Zn²⁺ > Cd²⁺. In total, 93.91% of Hg²⁺ can be quickly captured in the presence of a 6000 times higher concentration of competing metal ions (Pb²⁺, Cu²⁺, Cd²⁺, and Zn²⁺) within 30 min. The adsorption mechanism was analyzed using X-ray photoelectron spectroscopy (XPS). It suggested that the HA/LC-MNPs enhanced the adsorption capacity of Hg²⁺ because of the complexing abilities of the multiple thiol, amino, and carboxyl groups in sorbents with Hg²⁺, the ion exchange ability of the carboxyl group, and the negative charge surface. All in all, HA/LC-MNPs are a potentially useful and economic material for the selective removal of Hg²⁺ from polluted water.

1. INTRODUCTION

Nowadays, the world is facing severe water crisis, and water shortage has become a direct threat to the development and even survival of human beings. One important reason for this crisis is water pollution by human activities.1 A large amount of metal-contaminated wastewater bearing hazardous heavy metals (e.g., Hg²⁺, Pb²⁺, Cu²⁺, and Cd²⁺) produced from the industrial production (e.g., mining, metallurgy, and pesticide synthesis) are discharged into the environment, leading to their accumulation in the vital organs of humans through the food chain and further causing diseases and disorders.2 In these metals, mercury is a notorious heavy metal, which can produce a great harmful effect on the nervous, kidney and immune systems, posing a severe risk for human beings.3 The World Health Organization has announced the maximum acceptable concentration of Hg²⁺ in drinking water as low as 1 ppb.4 Therefore, the removal of hazardous heavy metals from wastewater is a crucial issue. Compared with many other wastewater treatment methods, adsorption is considered an efficient technique for the removal of a low concentration of toxic heavy metals from the aqueous medium, which is important to achieve the purification of water. In this context, several efficient functionalized sorbents have been developed such as sPAN fiber,6 chitosan/sulfhydryl-functionalized graphene oxide composite,7 and functionalized layered double hydroxide.8

Over the past few years, magnetic Fe₃O₄ nanoparticles (MNPs) and their hybrids such as porous Fe₃O₄/poly-(C3N3S3),9 nanomagnetic cellulose,4 and chitosan−graft−polyacrylamide magnetic composite microspheres7 have generated increasing interest as sorbents for the removal of heavy metals from water because of their fast kinetics, ease of magnetic separation, high removal efficiency, and environmental friendliness.10 As a low-cost sorbent extracted from low-rank coal, humic acids containing large amounts of oxygen-containing functional groups have been used to decorate the MNPs (HA-MNPs).11 The application of HA-MNPs in the separation of metals from water has been extensively reported, which covered the removal of inorganic arsenic species,12 the rapid extraction of uranium from seawater,13 and even the reduction of Cr(VI) to Cr(III) via a coupled reduction–complexation mechanism, owing to the phenol and quinone groups existing in HA.14 There is no doubt that HA-MNPs are a promising material for metal cations. However, because of the properties of the hard Lewis
base of oxygen-containing functional groups, HA-MNPs are hard to be used for the effective removal of some hazardous metals (e.g., Hg^{2+} and Ag^{+}), which are a part of soft Lewis acids. HA-MNP materials are suffering from low selectivity and weak affinity for these metals.

In general, thiol-functionalized sorbents show remarkable binding affinity for soft heavy metals. Grafting modification is the most regular way to obtain thiol-functionalized sorbents using small molecules with thiols as reactants. Chitosan/sulphydryl-functionalized graphene oxide composite^7^ and thiol-functionalized graphene^5^ were reported for selective and efficient removal of mercury. Although the adsorption performance may be excellent, the relevant grafting synthesis process of these sorbents always involved in a complicated or dangerous chemical reaction. Also, because chemical grafting modification is on the basis of original activity sites (e.g., −COO− and −OH), which may produce a block reaction and result in the inactivation of adsorption sites, the increase of the adsorption sites in sorbents for metals is limited. Meanwhile, for HA-MNP materials, the HA with abundant −OH and −COO− can affect the surface charge status and aggregation potential of MNPs by inducing a shift in the zero point of charge (ZPC) of MNPs in water.10 Therefore, the inactivation of original functional groups as a result of thiol grafting modification will affect the stability of adsorption for HA-MNPs. For these reasons, complicated chemical grafting modification is a good but not better option for improving the adsorption properties of HA-MNPs.

Herein, L-cysteine with −SH and −NH2 was inserted in the HA-MNPs through a simple coprecipitation method to improve its binding affinity for mercury. The final sorbent was magnetic Fe3O4 nanoparticles (HA/LC-MNPs) codecorated with multifunctional groups. The multifunctional groups in HA/LC-MNPs can exhibit synergistic adsorption for hazardous mercury.

All in all, the goal of this work is to prepare the HA/LC-MNPs with multifunctional groups by an easy synthesis procedure using completely green materials to improve the selectivity and adsorption capacity of HA-MNPs for mercury. Also, the multifunctional binding chemistry on HA/LC-MNPs for the adsorption of mercury will be investigated.

2. RESULTS AND DISCUSSION

2.1. Preparation and Characterization of the HA/LC-MNPs. The weight loss of bare MNPs, HA-MNPs, and HA/LC-MNPs was measured by thermogravimetric analysis (TGA) (Figure 1). The color of bare MNPs was changed from black to brown and the magnetism was disappeared after thermal treatment above 1000 °C. There was 5.20% of weight loss for bare MNPs when they were heated to 600 °C. After subtracting the weight loss of bare MNPs, the TGA showed that HA-MNPs and HA/LC-MNPs contained 14.31 and 19.52% of organic components (HA or HA/LC), respectively. Thus, the content of organic components coated on HA/LC-MNPs is larger than 11.40% reported by Liu et al.11 The sulfur content in HA/LC-MNPs measured by a sulfur analyzer was 1.60%. Because the organic component accounted for 19.52% of the weight of HA/LC-MNPs, the concentration of the sulfur element in the organic component was about 8.20%. Meanwhile, most of the sulfur was in the form of the thiol group of LC, and thus it can be calculated that the surface of HA/LC-MNPs contained about 31% of LC and 69% of HA.

The chemical bonds of HA/LC-MNPs were measured by Fourier transform infrared (FT-IR) (Figure 2). The FT-IR spectra of MNPs and HA/LC-MNPs centered at around 600 cm\(^{-1}\) were attributed to the stretching vibration of the Fe−O bond.15 Two peaks at the wavelengths of 1600 and 1400 cm\(^{-1}\) were observed for HA/LC-MNPs, representing the symmetric and asymmetric stretching of the C=O vibration of the carboxyl groups\(^16^\) from HA and LC. The absorption bands at 2924 and 2853 cm\(^{-1}\) were the stretching vibration of aliphatic C−H in CH\(_2\) and/or CH\(_3\).\(^17^\) Compared with HA, HA/LC-MNPs had a weaker absorption band of C−H and two stronger absorption bands of C=O and O−H (3425 cm\(^{-1}\)Ad14).
sugest that the HA fractions abundant with −COO− and −OH can be selectively coated on the surface of MNPs during the synthesis. There were no apparent FT-IR peaks pointing to −SH in the spectra because of the low sulfur content of HA/LC-MNPs and the rather weak absorb signal of −SH groups in the IR.18 Besides, abundant −OH in HA/LC-MNPs resulted in a strong overlapping effect on the amino peak.

The structure and size of the sorbent were measured by transmission electron microscopy (TEM), as shown in Figure 3a,b. The HA/LC-MNPs consisted of spherical particles with a typical diameter below 10 nm, but the entire HA/LC-MNP particles contained aggregates with no uniform size and fractal feature. From the TEM images, it was noted that the light gray shells with no fixed shape were covered on the surface of the dark core, which may be Fe3O4. It formed a relaxed organic-inorganic nanomaterial with a core−shell structure. Figure 3c shows the distributions of carbon (C), oxygen (O), and sulfur (S) in sorbents measured by the scanning transmission electron microscopy energy-dispersive spectrometry (STEM EDS) mapping method. The sorbents with abundant C, O, and S elements on their surfaces confirmed the successful synthesis of HA/LC-MNPs.

2.2. Heavy Metal Removal Using HA/LC-MNPs. The batch adsorption of Cu2+, Pb2+, Cd2+, Zn2+, and Hg2+ by HA/LC-MNPs from the solution was conducted. The adsorption capacity (q0, mg/g) and distribution coefficient (Kd, mL/g) were used to evaluate the affinity of HA/LC-MNPs for metal ions. A metal ion concentration of around 100 ppm was used to assess q0 and the results are listed in Table S1. It indicated that HA/LC-MNPs provide a higher adsorption capacity for Hg2+ (156.52 mg/g) than for the other metals, and the order of the adsorption capacity of HA/LC-MNPs for metal ions was Hg2+ ≫ Pb2+ > Zn2+ > Cu2+ > Cd2+. Meanwhile, Table 1 summarizes the removal of metal ions in a lower initial concentration of 10 ppm, whose adsorption results can be used to calculate Kd. As shown in Table 1, the concentrations of Hg2+ decreased from the initial concentration of 10 ppm to 1.11 ppm after adsorption, with 88.90% removal achieved. Also, the Kd value of HA/LC-MNPs for Hg2+ even reached 1.21×104 mL/g, and in general, the adsorption material with a Kd value above 104 mL/g is considered an exceptional sorbent. Thus, the selectivity and adsorption ability of HA/LC-MNPs toward Hg2+ are much higher than those for other metals, and the selectivity order for the five heavy metals is Hg2+ ≫ Pb2+ > Cu2+ > Cd2+ > Zn2+.

To further study the selectivity of the sorbent for mercury, 30 mL of a solution containing a mixture of all of the five metals with an initial concentration of 10 ppm for Pb2+, Cu2+, Cd2+, Zn2+, and Cd2+ and an extremely low initial concentration of 6.10 ppb for Hg2+ was used for the adsorption experiments, and the obtained results are shown in Table 2. It can be seen that the removal of Hg2+ reached 93.91% and its Kd was 3.11 × 104, which was far higher than those of the other metals. A selectivity order of Hg2+ ≫ Pb2+ > Cu2+ > Zn2+ > Cd2+ was summarized, which was generally in agreement with those seen in single adsorption experiments in Table 1. It

| Table 1. Adsorption Results of HA/LC-MNPs toward Individual Metal Ions |
|-----------------|---------|---------|---------|
| Metal Ions      | q0 (ppm)| Kd (mL/g) |
| Cu              | 10.50   | 22.57   | 4.37 × 10^2 |
| Pb              | 9.03    | 46.07   | 1.28 × 10^3 |
| Cd              | 11.60   | 21.72   | 4.16 × 10^2 |
| Zn              | 11.50   | 14.96   | 2.63 × 10^2 |
| Hg              | 10.00   | 88.90   | 1.21 × 10^4 |
| Hg2+            | 11.05   | 63.58   | 2.50 × 10^3 |
| Cu              | 10.50   | 38.28   | 9.31 × 10^2 |
| Pb              | 10.27   | 63.58   | 2.50 × 10^3 |
| Cd              | 9.83    | 7.63    | 1.18 × 10^2 |
| Zn              | 10.00   | 9.00    | 1.48 × 10^2 |
| Hg              | 6.10a   | 93.91   | 3.11 × 10^4 |
| Hg2+            | 6.04a   | 93.91   | 3.11 × 10^4 |

*Standard deviations.

| Table 2. Adsorption Results of HA/LC-MNPs toward Mixed Metal Ions |
|-----------------|---------|---------|---------|
| Metal Ions      | q0 (ppm)| Kd (mL/g) |
| Cu              | 11.05   | 38.28   | 9.31 × 10^2 |
| Pb              | 10.27   | 63.58   | 2.50 × 10^3 |
| Cd              | 9.83    | 7.63    | 1.18 × 10^2 |
| Zn              | 10.00   | 9.00    | 1.48 × 10^2 |
| Hg              | 6.10a   | 93.91   | 3.11 × 10^4 |

*ppb.
means that HA/LC-MNPs still show high selectivity toward Hg^{2+} in the presence of a 6000 times higher concentration of competing metal ions (Pb^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+}).

2.3. Relative Selectivity for Hg^{2+}, Pb^{2+}, and Cu^{2+} as a Function of pH. 2.3.1. pH Effects on the Removal of Single Hg^{2+}. The pH of a solution can greatly affect the adsorption behavior of the sorbent for metal ions by the protonation/deprotonation process of functional groups. In this work, the influence of the solution pH toward Hg^{2+} removal by HA/LC-MNPs was investigated over a pH range from 2 to 6 (Figure 4) with other parameters kept constant. As expected, with the increasing pH, higher removal efficiency of Hg^{2+} was observed. The Hg^{2+} removal increased from 59.99% at pH 2.0 to 94.95% at pH 6.0, and HA/LC-MNPs showed greatly increasing removal efficiency for Hg^{2+} when the pH was above 3.0. Meanwhile, the ZPC of HA/LC-MNPs was 4.28 (Figure 4), obtained by finding a point where the initial pH is equal to the final pH after adsorption.

Based on the above results, the pH effects for the adsorption of single Hg^{2+} can be explained as follows. Because the dissociation of carboxyl groups of HA generally starts at pH 3.0, which is greatly lower than those of the other functional groups, at pH < 3, the surface of the sorbent was surrounded by positive charges as a result of the presence of large amounts of H^+, which caused the competitive adsorption with Hg^{2+}. When the initial solution pH increased, the dissociation of carboxyl groups gradually generated negative charges on the sorbent surface. Finally, the whole surface of the sorbent was abundant with negative charges at pH 4.28. Thus, both the electrostatic interaction and more empty active sites for metal ions caused by the deprotonation of acidic groups improved the removal efficiency of Hg^{2+} with pH. In this process, the decreasing pH of the solution after Hg^{2+} adsorption should be attributed to the substitution of H^+ by Hg^{2+} by ion exchange. Meanwhile, 59.99% of Hg^{2+} removal at pH 2.0 illustrates that there was a stronger chemical interaction between HA/LC-
MNs and Hg²⁺, which also played a major role in Hg²⁺ adsorption.

2.3.2. pH Effects on the Removal of Hg²⁺ in a Ternary Metal Solution. According to Tables 1 and 2, HA/LC-MNPs showed great affinity toward Hg²⁺, Pb²⁺, and Cu²⁺. Hence, the competitive adsorption behavior of three metals was further studied to assess the potential to separate Hg²⁺ from a ternary metal solution. The adsorption of Hg²⁺ from a solution containing a mixture of Hg²⁺/Pb²⁺/Cu²⁺ with an initial concentration of 10 ppm was performed using 20 mg of HA/LC-MNPs over a pH range from 2 to 6, and the obtained results are shown in Figure 5. The removal of all heavy metals increased with increasing pH. About 85.17% of Hg²⁺ was adsorbed at pH 6.0, and 47.81% of Hg²⁺ was removed at pH 2.0. Compare to a single-ion solution (in Table 1), the removal rate of Hg²⁺ only decreased by 6.92% at pH 5.0 when it coexisted with both Pb²⁺ and Cu²⁺. The change of the separation factor of HA/LC-MNPs for Hg²⁺ in the presence of coexisting Pb²⁺ and Cu²⁺ with pH is shown in Figure 5. SF_Hg and SF_Pb were varied in the range of 7.07–16.64 and 2.31–4.20, respectively. Because the separation factor, which was greater than 1, means that Hg²⁺ preferentially absorbed by the sorbent, the above results indicated the good selectivity of HA/LC-MNPs for Hg²⁺ in a mixed Hg²⁺/Pb²⁺/Cu²⁺ solution in a wide pH range. Besides, SF_Hg increased first and then decreased with the increasing pH, and the maximum value was at pH 3.0. It means that the adsorption ability of HA/LC-MNPs for Pb²⁺ was improved at pH > 3.0, which may be attributed to the good affinity of carboxyl groups in the sorbent toward Pb²⁺.⁴,²²,²³

2.4. Adsorption Kinetics. The time dependence of Hg²⁺ adsorption on HA/LC-MNPs is shown in Figure S1. It can be seen that the rate of Hg²⁺ uptake was initially high and more than 82% of total Hg²⁺ was removed in the first 5 min. There was a gradual reduction in the rate of removal afterward, but the adsorption equilibrium can be reached within 30 min. The high adsorption rate can be attributed to the good dispersity of MNPs, which provided a more effective contact area for ions. The adsorption kinetics of HA/LC-MNPs was fitted using the conventional pseudo-first-order and pseudo-second-order kinetic models. The results are shown in Figure 6.

Because of the higher linear correlation coefficient, R² value (0.9999), the pseudo-second-order kinetic model can well represent the adsorption data. The pseudo-second-order kinetic model assumes a chemisorption process involving covalent forces and ion exchange, which is always widely used to explain the removal of heavy metals from water.¹⁷

2.5. Adsorption Isotherms. The adsorption isotherm of HA/LC-MNPs for Hg²⁺ is shown in Figure 7. To analyze the adsorption behavior of HA/LC-MNPs, the adsorption data were fitted using the Langmuir and Freundlich isotherm models.²⁴,²⁵ According to the linear correlation coefficient, R² value, the Langmuir isotherm model was better to describe the adsorption performance of HA/LC-MNPs for Hg²⁺. The calculated maximum adsorption capacity of HA/LC-MNPs for Hg²⁺ in this work was 206.5 mg/g at pH 5.0. The comparisons of the adsorption capacity of different adsorbents for Hg²⁺ are shown in Table 3. The HA/LC-MNPs showed good adsorption ability for Hg²⁺ in aqueous solution.

![Figure 7. Adsorption performance of HA/LC-MNPs at different Hg²⁺ concentrations fitted with equilibrium models. Condition: pH = 5.0.](image)

Table 3. Adsorption Capacity of Different Adsorbents for Hg²⁺

| adsorbents                        | adsorption capacity, mg/g | ref |
|----------------------------------|----------------------------|-----|
| HA/LC-MNPs                       | 206.5                      | this work |
| HA-MNPs                          | 97.0                       | 11  |
| sulfonic and carboxylic acid group-modified MNPs | 83.1                      | 26  |
| chitosan magnetic composite microsphere | 88.5                      | 9   |
| dimercaptosuccinic acid-modified MNPs | 227                      | 27  |
| polyacrylamide-grafted chitosan and silica-coated MNPs | 263.9                     | 9   |
| thiol-modified Fe₃O₄@SiO₂         | 148.8                      | 28  |

2.6. Adsorption Mechanism. Heteroatoms (N, S, and O) have been considered to play a key role in the performance of the sorbent for Hg²⁺ adsorption.²⁹,³⁰ Therefore, for HA/LC-MNPs, thiol, amino, carboxyl, and other oxygen-containing functional groups would be the major adsorption sites. The X-ray photoelectron spectroscopy (XPS) spectra of the sorbent before and after Hg²⁺ adsorption are shown in Figure 8. Two new Hg 4f peaks deconvoluted into the 4f₇/₂ peak at 101.1 eV and the 4f₅/₂ peak at 105.2 eV appeared in the survey spectrum of the sorbent after adsorption (Figure 8a,b),
verifying the presence of mercury capping on the surface of HA/LC-MNPs.

The high-resolution C 1s spectra of HA/LC-MNPs shown in Figure 8c,d can be deconvoluted into three subpeaks with binding energies (BEs) of 284.80, 286.33 (286.35), and 288.52 (288.48) eV before (after) adsorption, which were assigned to C−C, C−O (C−N and C−S), and O−C−O, respectively. Their relative contents are given in Table 4 based on the area percentage of the subpeak. The relative contents of C−O (C−N and C−S) and O−C−O decreased at different extents after Hg2+ adsorption. Similar results were observed in the O 1s spectrum in Figure 8e,f. The relative contents of O−C at 532.12 eV (532.41 eV) and O−C−O at 533.40 eV (533.61 eV) also decreased obviously after adsorption. The increasing BE of O−C and O−C−O at the O 1s spectrum after Hg2+ adsorption is likely to be caused by the binding of Hg2+ onto the oxygen atoms in the form of Hg:O coordinate bonds, thus reducing its electron density. Meanwhile, the solution trended to become acids after adsorption at pH 5.0 (Figure 4), and the solution pH decreased from 5.0 to 4.5. Therefore, both the acidification of the solution and the greatly decreasing relative content of O−C−O in the O 1s spectrum indicate that the ion exchange existed between Hg2+ and the carboxyl group in adsorption.

The N 1s spectra of HA/LC-MNPs before and after adsorption of mercury are shown in Figure 9a,b. Before adsorption, the N 1s spectrum can be fitted to two subpeaks. One is centered at 399.73 eV, assigned to the N atom in the −NH2 groups. The other one is located at 401.72 eV, attributed to the protonated species (−NH3+)34,39 However, after Hg2+ adsorption, the subpeak of −NH3+ in the N 1s spectrum disappeared. It indicates that Hg2+ is adsorbed into the sorbent surface through the N atom in the form of chemical interaction. Meanwhile, a new subpeak with higher BE appeared at 406.12 eV. It should be attributed to the fact that the lone pair of electrons on the N atom was donated to the shared bond between N and Hg2+ when a new kind of coordination bond formed between Hg2+ and the N atom in the −NH2 groups. Similar results were reported by Li et al.40 in the adsorption of Ni2+ using the amino-functionalized

![Figure 8. XPS survey spectrum of HA/LC-MNPs and HA/LC-MNPs-Hg (a), high-resolution Hg 4f spectra of HA/LC-MNPs-Hg (b), C 1s spectra of HA/LC-MNPs (c) and HA/LC-MNPs-Hg (d), and O 1s spectra of HA/LC-MNPs (e) and HA/LC-MNPs-Hg (f). Condition: pH 5.0.](https://dxxdoi.org/10.1021/acsomega.1c00583)
cellulose. Therefore, the N 1s spectrum verified that the complexation between $-\text{NH}_2$ and $\text{Hg}^{2+}$ was one of the adsorption mechanisms.

The deconvolution of the S 2p spectrum is shown in Figure 9c,d. Generally, thiols often display two subpeaks, namely, the S 2p$_{3/2}$ peak at around 163.77 eV and the S 2p$_{1/2}$ peak at about 164.97 eV. As the major form of sulfur in HA/LC-MNPs, thiols also presented these two peaks at 163.56 and 164.66 eV before mercury adsorption (Figure 9c). In the peak fitting process, the full width at half-maximum of the S 2p peaks was set at 1.40 eV. The S 2p$_{1/2}$ and S 2p$_{3/2}$ peaks were separated by 1.10–1.20 eV. Meanwhile, the S 2p$_{1/2}$ subpeak area was constrained to half the area of the S 2p$_{3/2}$ subpeak. It would be hard to oxidize $-\text{SH}$ to $-\text{S}^{-}$ by the air exposure in a limited time during experiments. Therefore, the subpeak at 168.30 eV was likely to be the S–Fe bond and/or the sulfur atom in a more positive environment.

After mercury adsorption, four subpeaks were observed in the BE region of 160–166 eV. The energy peaks at 165.28 and 163.33 eV should be matched with the free thiol group as described in the spectrum before adsorption. Meanwhile, two new peaks at BEs of 162.23 and 164.08 eV appeared in the S 2p spectrum, which should be assigned to S 2p$_{3/2}$ and S 2p$_{1/2}$ respectively, corresponding to the complex R–S/Hg. Similar results were observed in the form of R–S/Cu. Thus, the coordination of $\text{Hg}^{2+}$ with the S atom of thiol groups in the sorbent should be another adsorption mechanism.

### 2.7. Reusability

An ethylenediaminetetraacetic acid (EDTA) solution (0.1 mol/L) was used for the desorption of $\text{Hg}^{2+}$ capping on the surface of HA/LC-MNPs. It was shown that the desorption efficiency of $\text{Hg}^{2+}$ was 89.29% after four recycles. Good reproducibility was displayed.

### 3. CONCLUSIONS

L-cysteine with $-\text{SH}$ and $-\text{NH}_2$ was inserted in the HA-MNPs through a simple coprecipitation method to improve its binding affinity for mercury. The adsorption capacity of HA/LC-MNPs for mercury was significantly improved. A maximum adsorption capacity of 206.5 mg/g was achieved, which was higher than that of HA-MNPs. More importantly, HA/LC-MNPs show excellent selectivity toward $\text{Hg}^{2+}$ in the presence of competing metal ions with high concentrations, and a selectivity order of $\text{Hg}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$ was summarized. It was observed that 59.99% of $\text{Hg}^{2+}$ removal at pH 2.0 suggested that chemisorption was the major adsorption form of HA/LC-MNPs for $\text{Hg}^{2+}$, corresponding to the fitting results of the Langmuir isothermal model. Besides, the rate of $\text{Hg}^{2+}$ uptake was initially high and more than 82% of total $\text{Hg}^{2+}$ ions were removed in the first 5 min, and the final adsorption equilibrium can be reached within 30 min. The XPS results indicate that the adsorption mechanism mainly occurs through the complexion of the HA/LC-MNPs with $\text{Hg}^{2+}$ through the $-\text{NH}_2$, $-\text{SH}$, and $-\text{C}–\text{O}$–groups. Ion exchange of carboxyl groups and electrostatic adsorption also played an important role in mercury adsorption. All in all, HA/LC-MNPs are a potentially useful and economic material for the selective removal of mercury ions from polluted water.
4. MATERIALS AND METHODS

4.1. Synthesis and Characterization of HA/LC-MNPs. At first, 0.5 g of HA and 0.2 g of l-cysteine were dissolved in 50 mL of water with pH values of 4.0–6.0. Then, 6.0 g of FeCl₃·6H₂O and 3.0 g of FeCl₄·4H₂O were dissolved in 100 mL of water and heated to 90 °C. At this temperature, two solutions, 10 mL of 25% ammonium hydroxide and the prepared 50 mL of a HA and l-cysteine mixed solution were added simultaneously. The mixture was stirred at 90 °C for additional 30 min and then cooled to room temperature. The black precipitate was washed with water several times to separate the nanoparticles from free iron, HA, and l-cysteine. Finally, the black precipitate was dried at 90 °C under a vacuum condition for additional 4 h. The desired sorbents were then obtained. The structure of the prepared sorbents was characterized by FT-IR, TEM, TGA, and XPS.

4.2. Typical Sorption Study in the Solution with a Single Metal Ion/Mixed Metal Ions. The adsorption experiments of HA/LC-MNPs for heavy metals were conducted using a batch method. A certain amount of the sorbent was added into 30 mL of the solution containing different concentrations of Cu²⁺, Zn²⁺, Pb²⁺, Cd²⁺, and Hg²⁺. The initial pH of the solution was set as 5.0 to avoid the precipitation of Pb²⁺ at a higher pH. For further distinguishing the high precipitation of Pb²⁺ at a higher pH, 0.1 M HNO₃ was used to indicate the selectivity of the HA/LC-MNPs for the metal ions.

To determine the selectivity of the sorbent to Hg²⁺, some experiments containing Cu²⁺, Zn²⁺, Pb²⁺, Cd²⁺, and Hg²⁺ all together were carried out. For further distinguishing the high selective ions of Cu²⁺, Hg²⁺, and Pb²⁺, an experiment containing only Cu²⁺, Hg²⁺, and Pb²⁺ in the solution was also carried out. The separation factor for A and B (SFₐ) was used to indicate the selectivity of the HA/LC-MNPs for the metal ions.

The effects of the initial solution pH on the adsorption of mixed heavy metals by HA/LC-MNPs were observed. The range of the initial solution pH was adjusted by 0.1 M HNO₃ and NaOH aqueous solutions to pH 2.0–6.0. Approximately 20 mg of the dried sorbent was dispersed in 30 mL of a 10 ppm metal ion solution at various initial pH values under continuous stirring for 30 min to achieve adsorption equilibrium.

4.3. Adsorption Kinetics and Adsorption Isotherms of HA/LC-MNPs for Mercury. Adsorption experiments of HA/LC-MNPs for Hg²⁺ with various adsorption times (0–60 min) were conducted. Thirty milligrams of the sorbent was added to 30 mL of the aqueous solution containing 10 ppm Hg²⁺. To maintain the liquid-to-solid ratio constant, several parallel adsorption experiments were performed simultaneously. At specified time intervals, one of the adsorption experiments was ended. The residual solution was then diluted and measured by AFS.

Adsorption capacities of HA/LC-MNPs for Hg²⁺ with different initial concentrations of the solution were also performed. Ten milligrams of the sorbent was injected into 30 mL of the solution. To avoid the large experimental error as a result of dilution of the residual solution to meet the detection limit of AFS, the maximum initial concentration of Hg²⁺ in the solution was set as 100 ppm.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00583.

Extraction method of humic acid from lignite; description of adsorption parameters and models, adsorption capacity of HA/LC-MNPs toward individual metal ions; removal of Hg²⁺ with various times; and atomic percentage of C/N/O/S on the surface of HA/LC-MNPs (PDF)

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### Notes

The authors declare no competing financial interest.

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