Adsorption and Removal of Mercury(II) by a Crosslinked Hyperbranched Polymer Modified via Sulfhydryl

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1. INTRODUCTION

Mercury is one of the most representative toxic ions in heavy metals. It is mainly released into the environment by burning fossil fuels such as coal and incomplete incineration of mercury-containing wastes. Then, it accumulates in the body through the food chain, causing serious damage to the kidney, lungs, and immune and nervous systems.1 Therefore, the World Health Organization has set strict drinking water standards for the content of Hg(II) ions, which is less than 6 μg/L.2 In general, the complete restoration of mercury-containing sewage is considered an urgent problem, especially for massively contaminated groundwater because Hg(II) can be converted to the more toxic methyl mercury (the organic form) through microorganisms such as sulfate-reducing bacteria.3 Traditional methods such as membrane separation, electrochemistry, reverse osmosis, catalysis, ion exchange, and so forth may not well achieve high removal efficiency for Hg(II).4 Therefore, effective and economical methods for Hg(II) removal must be developed. Meanwhile, adsorption technology has the characteristics of multifunction, low cost, specificity, and high efficiency. It is one of the most widely used and rapidly developing technologies in the chemical process and attracts much attention. Of course, it has been reported that many types of adsorbents, such as nanoporous composites,5,6 silicon matrix composites,7 organic composite membranes,8 and so forth, can be used to remove mercury ions from aqueous solutions. However, some of the adsorbents still have the disadvantages of poor adsorption performance, high price, and complex preparation process. Therefore, it is necessary to consider a new adsorption material with maximum removal efficiency of Hg(II) ions.

In recent years, hyperbranched polyamide-amines (H-PAMAMs) have appeared in many applications where a perfect structure is not required. Researchers tend to use the H-PAMAM spikes instead of polyamide-amine (PAMAM) spikes to prepare adsorbent materials.9 H-PAMAMs have the advantages of a low production cost and a short production cycle, making them economically suitable for large industrial applications.10 However, there is a non-negligible problem that they are soluble and difficult to separate when they are used directly as adsorption materials.11,12 Therefore, researchers often fix them on various substrates to remove heavy metal ions from wastewater.13 Some studies have confirmed that appropriate surface chemical modification is an effective strategy to improve the interaction between adsorbents and related adsorbates. The existing literature reports that the...
adsorption of Hg(II) can be significantly increased by the modification of sulfur-containing substances (e.g., mercaptans, sulfide, and sulfonated substances) or the presence of sulfur on the surface of the adsorbents. Therefore, many studies have been carried out to improve the adsorption capacity of the adsorbents by soaking their surface with sulfur-containing substances such as sodium sulfide (Na₂S), potassium sulfide (K₂S), carbon disulfide (CS₂), cysteamine hydrochloride, and so forth. Furthermore, to our knowledge, there is no relevant literature on the modification of H-PAMAMs with thiourea. However, there was no obvious stretching vibration of S–H observed in the range of 570–600 cm⁻¹ due to the fact that a large number of sulfhydryl groups were slightly shifted after Hg(II) adsorption, indicating that both N and O atoms were involved in Hg(II) adsorption, in which the C–N, N–H, O–H, and C=O groups transferred single pairs of electrons to a Hg(II) empty orbit. Based on the analysis of Fourier transform infrared spectroscopy (FT-IR) spectra, it was shown that the related groups of N, O, S atoms on CHAP-SH were synergistically involved in the adsorption of Hg(II).

2. RESULTS AND DISCUSSION

2.1. Characterization of CHAP-SH. 2.1.1. FT-IR Analysis. In order to explore the possible adsorption mechanisms and potential adsorption sites of Hg(II) on CHAP-SH, the infrared spectrograms of the samples before and after adsorption were compared and analyzed, and the results are shown in Figure 1.

![Figure 1](https://doi.org/10.1021/acsomega.2c00622)

**Figure 1.** FT-IR spectra of H-PAMAMs (a), CHAP-SH (b), and CHAP-SH–Hg (c).

First, two broad and blunt peaks on H-PAMAMs appeared at 3421 and 3158 cm⁻¹, which meant that the tensile vibration corresponded to O–H and N–H, respectively, which also confirms the effective crosslinking process of H-PAMAMs. In addition, C=O (1633 cm⁻¹) and C–N (1508 cm⁻¹) bands were detected on CHAP-SH. Moreover, after sulfur doping, sulfur was embedded by combining with C or O elements on the surface of the adsorbents, and the C–S bond peak was observed in the range of 570–1300 cm⁻¹, which also confirmed the successful modification of H-PAMAMs by thiourea. However, there was no obvious stretching vibration peak of −SH in the range of 2500–2600 cm⁻¹, which might be due to the fact that a large number of sulphhydryl groups were grafted in the CHAP-SH channel, and the infrared absorption of −SH was weak, leading to the reduction of infrared spectral sensitivity. Meanwhile, it can be observed in Figure 1c that the stretching vibration of C–S groups (680 cm⁻¹) disappeared, mainly because C–S was formed by C–S in the acidic medium and combined with Hg(II) to form Hg–S–Hg. Furthermore, the broad bands of 3300–3500 cm⁻¹ (O–H and N–H), 1646 cm⁻¹ (C=O), and 1540 cm⁻¹ (C–N) were slightly shifted after Hg(II) adsorption, indicating that both N and O atoms were involved in Hg(II) adsorption, in which the C–N, N–H, O–H, and C=O groups transferred single pairs of electrons to a Hg(II) empty orbit. Based on the analysis of Fourier transform infrared spectroscopy (FT-IR) spectra, it was shown that the related groups of N, O, S atoms on CHAP-SH were synergistically involved in the adsorption of Hg(II).

2.1.2. SEM and EDS Analyses. The surface morphologies of CHAP-SH before and after adsorption were examined using the scanning electron microscopy (SEM)—energy-dispersive spectroscopy (EDS) procedure. As shown in Figure 2a, CHAP-SH was characterized by a honeycombed surface morphology, which provided favorable conditions for the adsorption of metal ions. CHAP-SH presented uniformly doped sulfur on the surface (Figure 2c), indicating that sulfur had been successfully dispersed and impregnated on CHAP-SH. The CHAP-SH–Hg images (Figure 2b) and EDS maps (Figure 2d) indicated that the pore structure in CHAP-SH was filled and Hg(II) was adsorbed on the surface of the adsorbents, which means that the location of mercury and sulfur in CHAP-SH–Hg matched well and Hg(II) bound to the sulfur on CHAP-SH. In addition, we also performed the Brunauer–Emmett–Teller (BET) analysis on the samples. The experimental data showed that the surface area of CHAP-SH was relatively small with a value of 1.942 m²/g, and the total pore volume was 0.0092 cm³/g (the relevant figure is not given because of the small surface area).

2.1.3. Thermogravimetric Analysis. The thermal stability of CHAP-SH before and after adsorption was explored in the range of 30–800 °C. The thermogravimetric analysis (TGA) curves (Figure 3a) showed that the weight loss of CHAP-SH occurred in two steps. The first mass loss (30–150 °C) was attributed to the loss of weakly bound water. The second weight loss (180–400 °C) was attributed to two factors: (1) thermal decomposition of functional groups and (2) the exfoliation and decomposition of sulfide formed on the surface of CHAP-SH. Comparing the TGA curves of CHAP-SH–Hg (Figure 3b) and CHAP-SH, the difference in weight loss between CHAP-SH–Hg and CHAP-SH was about 7.06%, which could be attributed to the decomposition of mercuric sulfide, the volatilization of mercury complexes, and the generation of mercury complexes during adsorption. The factors listed above have a slight effect on the thermal stability of CHAP-SH. The above investigation was consistent with the work of Rumayor et al.

2.2. Investigation of CHAP-SH Adsorptive Properties. 2.2.1. Selective Adsorption and the Influence of Coexisting Ions on Adsorption. When multiple metal ions coexist, the adsorption performance of each metal ion [Hg(II), Cu(II), Pb(II), Cd(II), and Zn(II)] in a multicomponent system by CHAP-SH was studied. Figure 4a shows that the adsorption capacity of CHAP-SH on Hg(II) (83.30 mg/g) was greater than that of Cu(II) (55.49 mg/g), Pb(II) (55.21 mg/g), Cd(II) (43.99 mg/g), and Zn(II) (28.74 mg/g). These results
showed that CHAP-SH had good adsorption selectivity for Hg(II). It could also be seen from Figure 4a that the removal rate of Hg(II) in multimetal solution was lower than that in single mercury ion solution, which was due to the poor availability of binding sites.32 In multimetal solutions, different metal ions competed for the same adsorption sites of the adsorbents, and the metal with strong affinity would replace the metal with weak affinity.33 Also, the influence of coexisting ions on the adsorption of Hg(II) by the adsorbent is described in Figure S1; the research showed that the introduction of common coexisting ions made it difficult to inhibit the adsorption of Hg(II) by CHAP-SH, which indicated that the adsorbent had a good specificity for Hg(II) ions.

2.2.2. Influence of the pH Value of Solution on Adsorption. The pH value of a solution is one of the indispensable factors in the study of adsorption process because it has a great influence on the state of metal ions and adsorbent functional groups.34 Figure 4b shows that the adsorption capacity of CHAP-SH for Hg(II) was unchanged significantly at different pH values. The adsorption capacity of CHAP-SH remained above 84.3 mg/g with pH ranging from 3.0 to 5.5 and reached the maximum at pH 4.5. However, the amino groups on the surface of CHAP-SH were positively charged under protonation and the large repulsion between the protonated amino groups and Hg(II) ions prevented the adsorption, resulting in a low adsorption capacity at lower pH values. In addition, there was a large number of H+ in the solution that might compete with Hg(II) for adsorption.35 As pH increased from 3.0 to 4.5, the deprotonation of the amino

Figure 2. SEM images of (a) CHAP-SH and (b) CHAP-SH after Hg(II) adsorption and EDS map scanning images of (c) CHAP-SH and (d) CHAP-SH−Hg.

Figure 3. TGA curves of (a) CHAP-SH and (b) CHAP-SH−Hg.

Figure 4. (a) Selective adsorption of multimetal ions by CHAP-SH and (b) effect of pH on Qe for Hg (II) (m/V = 1.0 g/L, C0 = 100 mg/L, T = 298 K).
groups on the adsorbents can effectively coordinate with Hg(II) to increase the adsorption capacity. There was a small decrease in the adsorption capacity above pH 4.5; the reason for this phenomenon may be explained by the formation of the hydroxyl species of mercury, such as soluble Hg (OH)+

The kinetic models applied to Hg(II) adsorption by CHAP-SH (pH = 4.5, m/V = 1.0 g/L). Therefore, we measured 3 h as the optimal contact time.

To further elucidate the adsorption behavior of CHAP-SH, the nonlinear fitting of experimental data was carried out by using pseudo-first-order and pseudo-second-order kinetic models, and the formulas are shown in eqs 1 and 2, respectively.

\[
Q_t = Q_{e,1}(1 - e^{-k_1t})
\]  

(1)

\[
Q_t = \frac{k_2Q_{e,2}t}{1 + k_2Q_{e,2}t}
\]  

(2)

where \(Q_{e,1/2}\) and \(Q_e\) (mg/g) stand for the adsorption capacity at equilibrium and \(t\) (min), respectively. \(k_1\) (1/min) and \(k_2\) (g/(mg·min)) represent the rate constants of the pseudo-first-order and pseudo-second-order kinetic models, respectively. Moreover, the parameters of the two kinetic models were obtained from relevant experimental data and are shown in Table 1.

Table 1. Kinetic Parameters of Hg(II) Adsorption on CHAP-SH

| \(C_0\) (mg/L) | \(Q_{e,1}\) (mg/g) | \(k_1\) (1/min) | \(R^2\) | \(k_2\) (g/(mg·min)) | \(Q_{e,2}\) (mg/g) | \(R^2\) |
|--------------|-----------------|----------------|--------|-----------------|-----------------|--------|
| 300          | 230.044         | 0.4926         | 0.8888 | 0.00495         | 237.023         | 0.9614 |

Figure 5. (a) Effect of initial ion concentration on the adsorption of Hg(II) by CHAP-SH and H-PAMAMs and (b) nonlinear fitted curve with two kinetic models applied to Hg(II) adsorption by CHAP-SH (pH = 4.5, \(T = 298\) K, m/V = 1.0 g/L).
The formal equations of the four isothermal models are expressed as follows: 41,42

(i) Langmuir isotherm

\[ Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \]  

where \( Q_m \) (mg/g) is the maximum adsorption capacity and \( K_L \) (L/mg) is the Langmuir isotherm constant.

(ii) Freundlich isotherm

\[ Q_e = K_F C_e^{1/n} \]  

where \( K_F \) is the Freundlich isotherm constant and \( n \) is the exponent of the adsorption process.

(iii) Redlich–Peterson isotherm

\[ Q_e = \frac{K_R C_e}{1 + \alpha_R C_e^g} \]  

where \( K_R \) (L/g) is the Redlich–Peterson isotherm constant, \( \alpha_R \) (1/mg) is also a constant, and \( g \) is an index between 0 and 1.

(iv) Sips isotherm

\[ Q_e = \frac{Q_s K_s C_e^{1/n}}{1 + K_s C_e^{1/n}} \]  

where \( Q_s \) (mg/g) is the Sips maximum adsorption capacity and \( K_s \) and \( 1/n \) represent the equilibrium constant and the exponent of Sips isotherm, respectively, and the other parameters are defined above.

The adsorption isotherms are shown in Figure 6; the results showed that the adsorption capacity increased rapidly with the increase of Hg(II) concentration and then tended to be stable. In addition, the equilibrium adsorption capacity raised slightly with the increase of temperature. Subsequently, the experimental data were fitted with four isotherm models, and the fitting diagram is shown in Figure 6(a–c). Furthermore, the calculated parameters of the corresponding adsorption isotherm models are shown in Table 2. In the two-parameter isothermal model, the \( R^2 \) value of the Langmuir isotherm model (0.9877–0.9987) was higher than that of the Freundlich isothermal model (0.9422–0.9787), indicating that the Langmuir isothermal model could better describe the adsorption behavior. Moreover, the values of \( 1/n \) in the Freundlich isotherm model were less than 1, indicating that the adsorbents had desirable adsorption. 83 Meanwhile, the \( R^2 \) values and parameter data listed in Table 2 showed that among the four kinds of isothermal models, Langmuir and Redlich–Peterson isotherms had better correlation with the experimental data. In addition, the \( n \) values of Sips isotherms in Table 2 were 0.874, 0.885, and 0.898, respectively, which were all close to 1, indicating that the CHAP-SH adsorption of...
Hg(II) was more inclined to monolayer adsorption at these three temperatures. All the above results indicated that the adsorption was an approximate monolayer process and a dynamic equilibrium adsorption process.\textsuperscript{44}–\textsuperscript{45} Moreover, the negative values of adsorption of Hg(II) was an endothermic reaction with \( \Delta H^0 \), and the Gibbs free energy \( \Delta G^0 \) were obtained by fitting a plot based on the van’t Hoff thermodynamic equation.\textsuperscript{46} The related equations are represented by the following eqs \( 7-9 \), respectively:\textsuperscript{46}

\[
\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}
\]

\[
\Delta G^0 = -RT \ln K_d
\]

\[
K_d = \frac{C_0 - C}{V \times mC}
\]

(7)

(8)

(9)

where \( K_d \) (L/g) and \( T \) (K) represent the solid–liquid distribution coefficient and the absolute temperature, respectively. \( R \) is the universal gas constant with a value of 8.314 J/(mol·K). \( \Delta S^0 \) and \( \Delta H^0 \) were obtained from the intercept and the slope of the \( \ln K_d \) versus \( T^{-1} \) plot, respectively. \( \Delta G^0 \) can be obtained from the above formula, and the other parameters are defined above. Meanwhile, the thermodynamic parameters at different temperatures are listed in Table 3.

| T (K) | \( \ln K_d \) | \( \Delta G^0 \) (kJ/mol) | \( \Delta H^0 \) (kJ/mol) | \( \Delta S^0 \) (J/(mol·K)) |
|-------|---------------|-----------------|-----------------|----------------|
| 298   | 2.07          | -7.19           | 23.06           | 102.02        |
| 308   | 2.29          | -8.69           | 23.06           | 102.02        |
| 318   | 2.42          | -9.21           | 23.06           | 102.02        |

As shown in Table 3, \( \Delta H^0 \) (23.06 kJ/mol) and \( \Delta S^0 \) [102.02 J/(mol·K)] values were both positive, indicating that the adsorption of Hg(II) was an endothermic reaction with random increase.\textsuperscript{49} Moreover, the negative values of \( \Delta G^0 \) elucidated the facility and spontaneity of the adsorption process, and the enhancement of negative \( \Delta G^0 \) accompanied by temperature rising revealed that the adsorption process was more efficient at higher temperatures.\textsuperscript{48} Generally, the \( \Delta H^0 \) values of physical adsorption and chemical adsorption were in the range of 2.1–20.9 and 20.9–418.4 kJ/mol, respectively,\textsuperscript{49} and the \( \Delta H^0 \) value of this adsorption process was 23.6 kJ/mol. Therefore, the adsorption of Hg(II) by CHAP-SH was chemisorption.

2.2.5. Regeneration and Desorption Studies. The regeneration of CHAP-SH was successfully achieved by desorbing five times with 0.1 M HCl. After regeneration, CHAP-SH was used to repeatedly remove the target contaminant Hg(II). Figure 7 shows that CHAP-SH expressed good regenerative performance, and the removal rate of Hg(II) decreased from 98.41 to 84.96% after five cycles. In conclusion, CHAP-SH had a high removal rate, good adsorption capacity, and good regeneration properties for Hg(II), which was suitable for water treatment. The change in the Hg(II) concentration after CHAP-SH desorption at different temperatures was investigated, as shown in Figure S2. Under the condition of the same desorption time, the desorption speed increased with the increase in temperature, which means that a higher temperature is beneficial for the desorption of Hg(II) ions. Also, Table 4 summarizes the maximum adsorption capacities of some adsorption materials for Hg(II) ions reported in recent years. It was found that CHAP-SH had a relatively high adsorption capacity for Hg(II) ions compared with other adsorbents. Although its adsorption capacity was slightly lower than previously reported CHS@Cu₃(BTC)₃-DMTZ and CGPET, the preparation process of CHAP-SH shows energy-saving and ecological advantages and requires neither high-temperature activation nor a complex preparation process. Therefore, CHAP-SH is a good adsorbent for the treatment of aqueous solutions containing Hg(II) ions.

2.3. Adsorption Mechanism. 2.3.1. XPS Analysis. Based on the above work, we further analyzed the wide-resolution and high-resolution X-ray photoelectron spectroscopy (XPS) spectra of CHAP-SH before and after adsorption, as shown in Figure 8. In the full spectrum (Figure 8a), compared with that of H-PAMAMs, a new S 2p peak (163.43 eV) appeared in CHAP-SH, indicating that thiourea had been successfully modified to the surface of CHAP-SH.\textsuperscript{50} Compared with CHAP-SH binding energies, new binding bands such as Hg 4f, Hg 4d5, Hg 4d3, and Hg 4p3 were found in the CHAP-SH–Hg(II) full spectrum, which further confirmed the adsorption of Hg(II) on CHAP-SH.\textsuperscript{51} The deconvolution of C 1s spectrum for CHAP-SH (Figure 8b) showed peaks at 284.82, 287.14, and 289.08 eV corresponding to the C–C, C–S, and O–C=O bonds, respectively.\textsuperscript{52} Moreover, the C–S and O–C=O bonds on CHAP-SH were transferred to lower binding energies (286.01 and 288.27 eV, respectively) after the adsorption of Hg(II), confirming the interaction with Hg(II). Moreover, it should be noted that the strength of the C–S bond on CHAP-SH–Hg was slightly increased and overlapped with the binding energy of the C–S bond due to the formation of the C=O–Hg bond.\textsuperscript{53} In the high-resolution spectra of O 1s (Figure 8c), the O=O, –OH, and O=C=O bonds were found at 530.78, 531.85, and 534.8 eV, respectively.\textsuperscript{54} After adsorption, these three peaks shifted slightly, indicating that CHAP-SH formed different bonds with Hg(II). The deconvolution of N 1s spectrum of CHAP-SH showed that two major peaks at 398.93 and 399.71 eV in Figure 8d.
belonged to $-\text{NH}_2$ and $-\text{NH}$, respectively, and the binding energies of $-\text{NH}$ and $-\text{NH}_2$ moved to higher values (398.93–399.56 and 399.71–401.27 eV, respectively). The results showed that $-\text{NH}$ or $-\text{NH}_2$ groups were involved in this process, which also confirmed the results of FT-IR analysis. In addition, a new peak appeared at 406.28 eV after adsorption, which was the $\text{N}^-\text{Hg}$ bond formed by the ion exchange between $-\text{NH}_2$ and Hg(II). In order to further determine the role of the sulfur-containing groups, the S 2p spectrum was investigated on CHAP-SH and CHAP-SH–Hg(II)-adsorbed samples (Figure 8e). It could be seen that some energy shifts (0.57 and 0.72 eV) had taken place compared with the energy of CHAP-SH [162.85 eV ($S\text{p}_{2/3}$) and 164.13 eV ($S\text{p}_{1/2}$)], which was due to the excellent affinity between C–S groups and Hg(II) ions. The peak at 167.78 eV was considered to correspond to sulfide impurities.

Together, the XPS and FT-IR results indicated that the adsorption mechanism of the interaction between Hg(II) and the functional groups associated with O, N, or S atoms on CHAP-SH might occur in the manner of $-\text{O}^-\text{Hg}$, $-\text{N}^-\text{Hg}$, or $-\text{S}^-\text{Hg}$.

### 3. CONCLUSIONS

A postsynthetic modification strategy was explored where the crosslinked H-PAMAMs were modified by thiourea to achieve the functionalization of H-PAMAMs. Following that, a new type of adsorbent containing sulfhydryl groups (CHAP-SH) was constructed to realize the efficient and rapid removal of Hg(II). Through systematic experimental research, the results showed that the saturated adsorption capacity of CHAP-SH for Hg(II) can reach 282.74 mg/g at 318 K and pH = 4.5. According to the analysis of isothermal models and kinetic models, the whole adsorption process was an approximate monolayer chemisorption. In addition, the removal rate of Hg(II) still remained at a good level after five reuse cycles, and it presented high selectivity for Hg(II) in the actual treatment.

Table 4. Maximum Adsorption Capacities ($Q_m$) for Hg(II) of Some Adsorbents

| adsorbents       | $Q_m$ (mg/g) | experimental conditions | refs |
|------------------|-------------|-------------------------|------|
| Fe$_3$O$_4$@PPy | 232.56      | $C_0 = 5–50$ mg/L, pH = 6, $T = 318$ K | 36   |
| MFC-S            | 282         | $C_0 = 50–500$ mg/L, pH = 3, room temperature | 34   |
| CGPET            | 322.51      | $C_0 = 150$ mg/L, pH = 5, $T = 318$ K | 14   |
| MWCNT-AA         | 101.35      | $C_0 = 100–500$ mg/L, pH = 6, room temperature | 35   |
| CHS$@$Cu$_3$(BTC)$_2$–DMTZ | 627.6 | $C_0 = 125–1000$ mg/L, pH = 3, $T = 298$ K | 40   |
| MPTMS–VER       | 0.286       | $C_0 = 10–400$ mg/L, pH = 5.0–6.0, $T = 303$ K | 26   |
| PSAC-S           | 136.5       | $C_0 = 20–200$ mg/L, pH = 6, $T = 298$ K | 1    |
| MCP              | 247.51      | $C_0 = 100–350$ mg/L, pH = 5, $T = 293$ K | 44   |
| CHAP-SH          | 282.74      | $C_0 = 100–300$ mg/L, pH = 4.5, $T = 318$ K | this work |

“Note: PSAC-S, sulfur-anchored palm-shell-waste-activated carbon powder; CGPET, glutaraldehyde-crosslinked chitosan microparticles modified by epichlorohydrin and aminothiourea; MFC-S, superparamagnetic-mercapto-functionalized magnetic Zr-MOF; MWCNT-AA, amidoamine-functionalized multiwalled carbon nanotubes; Fe$_3$O$_4$@PPy, functional magnetic Fe$_3$O$_4$@polypyrrole microspheres; CHS$@$Cu$_3$(BTC)$_2$–DMTZ, 2,5-dimercapto-1,3,4-thiadiazol functionalized copper hydroxy sulfate$@$Cu$_3$(BTC)$_2$; MCP, tannic acid crosslinking cellulose/polyethyleneimine functionalized magnetic composite; MPTMS–VER, 3-mercaptopropyltrimethoxysilane functionalized vermiculites.”

Figure 8. XPS full scanning spectra (a) of H-PAMAMs, CHAP-SH, and CHAP-SH–Hg and the high-resolution scanning spectra of C 1s (b), O 1s (c), N 1s (d), and S 2p (e).
of the simulated aqueous solution with the coexistence of multimetal ions. The outstanding selectivity was mainly due to the introduction of functional groups containing S. XPS and FT-IR showed that CHAP-SH had the synergistic adsorption of N, S, and O groups for Hg(II). In conclusion, CHAP-SH showed considerable promise for the removal of heavy metals in the future. Meanwhile, it can also be a good supplement to the adsorbents for mercury ion removal.

4. MATERIALS AND METHODS

4.1. Materials and Instruments. All chemical solvents and reagents used in this research were analytically pure and were not further purified, and all the solutions were prepared with distilled water during the experiment. Methyl acrylate was obtained from Tianjin Guangfu Chemistry Reagent Co., Ltd. (Tianjin, China). Ethylenediamine (EDA) and anhydrous methanol (CH₃OH) were obtained from Tianjin Fuyu Chemistry Reagent Co., Ltd. (Tianjin, China). Epichlorohydrin (ECH) and mercury dichloride (HgCl₂) were provided by Sinopharm Chemistry Reagent Co., Ltd. (Beijing, China). Zinc nitrate [Zn(NO₃)₂], cupric nitrate [Cu(NO₃)₂], and cadmium nitrate [Cd(NO₃)₂] were obtained from Tianjin Kemio Reagent Co., Ltd. (Tianjin, China). Lead nitrate [Pb(NO₃)₂] was provided by Shanghai Qiangshun Reagent Co., Ltd. (Shanghai, China). Thiourea (CH₄N₂S) was provided by Shanghai Aladdin Co., Ltd. (Shanghai, China). Sodium hydroxide (NaOH) and nitric acid (HNO₃) were obtained from Chengdu Jinshan Chemistry Reagent Co., Ltd. (Chengdu, China).

The instruments and apparatus used in this research were as follows: an atomic absorption spectrophotometer (FAAS, AA-6300C, Shimadzu, Japan), a Fourier transform infrared spectrometer (iS10, Nicolet, USA), an X-ray photoelectron spectrometer (ESCALAB Xia, ThermoFischer, USA), a scanning electron microscope/an X-ray energy spectrometer (SEM/EDS, s-3400N, Hitachi, Japan), a cold-atomic absorption mercury determinator (P732-VJ, Huaguang, China), a thermogravimetric analyzer (Mettler Toledo, USA), and a pH meter (PHSJ-4A, Eutech Instrument, China).

4.2. Preparation of CHAP-SH Composites. H-PAMAMs were synthesized through a modified one-pot hydrothermal method. H-PAMAMs were mixed with ECH, stirred for 2 h at 50 °C with a mass ratio of 13:7, and ripened for 30 min at ambient temperature (30 °C). Then, thiourea was slowly added to the mixture solution with constant stirring for 24 h at 80 °C and dried in an oven at 95 °C for 12 h. To this yellow colloid, NaOH (1 M) was processed for 2 h at 75 °C. Finally, the adsorbent particles were separated using a 3000 rpm centrifuge, washed successively three times with water and 5% HNO₃, and dried in a vacuum freeze drier. The synthesis process of CHAP-SH is presented in Scheme 1.

4.3. Adsorption Experiments. The effect of pH values ranging from 3.0 to 5.5 on the adsorption of Hg(II) was investigated, and the ideal pH values of the stock solution were controlled by 0.1 M HCl or 0.1 M NaOH, with the initial concentration (100 mg/L) of Hg(II) and a temperature of 298 K. The selectivity experiments were carried out in a mixed solution containing equal concentrations (100 mg/L) of Hg(II), Cu(II), Pb(II), Zn(II), and Cd(II). The influence of coexisting ions (Na⁺, Ca²⁺, Mg²⁺, K⁺, Cl⁻, NO₃⁻, and SO₄²⁻) and initial concentration range (60–300 mg/L) of Hg(II) on the adsorption process was investigated. The adsorption kinetic experiments were studied by adding 50 mL of the Hg(II) (300 mg/L) solution to 50 mg of CHAP-SH at 298 K and at the predetermined intervals (5, 10, 15, 20, 25, 30, 60, 90, 120, 180, 300, and 360 min). Also, the adsorption isotherm study was performed by immersing the 50 mg adsorbent into 50 mL of Hg(II) solution with different initial concentrations (100–330 mg/L) and controlling the reaction temperature at 298, 308, and 318 K, respectively. After adsorption equilibrium was reached, the solution of the specified conical flask was taken out and filtered. Finally, the final concentration of the metal ion was determined by a cold-atomic absorption mercury determinator and a flame atomic absorption spectrometer, and all the experiments were implemented in triplicate.

The adsorption capacity Qₑ and Qₜ, and the removal rate R (%) can be calculated by eqs 10–12, respectively, as follows

\[
R = \left(1 - \frac{C_f}{C_0}\right) \times 100\% \tag{10}
\]
\[ Q_e = \frac{(C_0 - C_f) V}{m} \]  
(11)  
\[ Q_t = \frac{(C_0 - C_t)V}{m} \]  
(12)  
where \( C_0, C_f \), and \( C_t \) (mg/L) are concentrations of metal ions in the solution at initial, final equilibrium, and time \( t \), respectively. \( Q_e \) and \( Q_t \) are the adsorption capacities at \( t_e \) and \( t \) (min), respectively, \( R \) (%) is the adsorption percentage, \( V \) (L) is the volume of the solution, and \( m \) (g) is the mass of the adsorbents.

4.4. Adsorption and Desorpcion Studies. The metal-laden CHAP-SH was desorbed with 0.1 M HCl for 30 min and repeated three times. Then, the desorbed adsorbents were washed with deionized water until neutral for the next recycle adsorption. On the basis of the above operation, the regenerated adsorbents were used for five adsorption-desorption cycles to determine the reusability of CHAP-SH.

**ASSOCIATED CONTENT**

Supporting Information  
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c00622.

Effect of coexisting ions on adsorption of Hg(II) ions, and changes of Hg(II) concentration in CHAP-SH after desorption at different temperatures (PDF)

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**Notes**  
The authors declare no competing financial interest.

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