Analysis of Highly Efficient Adsorption of \(\text{Au(S}_2\text{O}_3\text{)}_2^{3-}\) by Calcined Cu/Fe Layered Double Hydroxides

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1. INTRODUCTION

The gold thiosulfate extraction method has a good leaching effect for low-grade and difficult-to-treat gold ore-containing copper, arsenic, antimony, carbon, and so forth.\(^1\) Compared to the cyanidation method, it is a more environmentally friendly and efficient leaching strategy.\(^2\) However, the process of recovering gold ions in thiosulfate leaching solution is still a very challenging problem to overcome. In recent years, the adsorption method has garnered a lot of research interest in the recovery of \(\text{Au(S}_2\text{O}_3\text{)}_2^{3-}\). Activated carbon has developed a porous structure, abundant surface functional groups, and huge specific surface area, so it is widely used as an adsorption material.\(^14\)\(^15\) The activated carbon adsorption method is used in gold extraction via cyanidation, which represents a mature technology, that is of low cost and relatively simple to carry out.\(^16\) However, activated carbon has poor affinity for gold ions in the thiosulfate leaching solution and poor adsorption rate.

In recent years, many scholars have conducted in-depth research on the ability of activated carbon to adsorb \(\text{Au(S}_2\text{O}_3\text{)}_2^{3-}\), which has greatly improved the recovery effect of activated carbon. For example, a Prussian blue-like compound was used to modify activated carbon to improve the adsorption of \(\text{Au(S}_2\text{O}_3\text{)}_2^{3-}\).\(^17\) However, the modification process is relatively complicated, and the gold loading is only improved within a limited range. 2-Mercaptobenzothiazole was grafted onto activated carbon to improve the targeted recovery of \(\text{Au(S}_2\text{O}_3\text{)}_2^{3-}\).\(^18\) It emerged that in a solution with a pH of 9.0 and a \(\text{Na}_2\text{S}_2\text{O}_3\) concentration of 0.1 mol/L, the cumulative amount of gold adsorbed by activated carbon is 18.4 mg/g. In their study, Chen et al.\(^19\) used 1-phenyl-5-mercaptotetrazole to modify coconut shell activated carbon. Their results confirmed that under the conditions of pH 9.0, a temperature of 25 °C, and \(\text{Na}_2\text{S}_2\text{O}_3\) concentration of 0.1 mol/L, the cumulative amount of gold adsorption by activated carbon is 25.8 mg/g. Using 2-mercaptopbenzothiazole and 1-phenyl-5-mercaptotetrazole to modify activated carbon is still time-consuming and expensive.

Wang et al.\(^20\) employed chemical vapor deposition to modify activated carbon to recover \(\text{Au(S}_2\text{O}_3\text{)}_2^{3-}\). In this method, thiourea is loaded on activated carbon by heating, and the adsorption rate is greatly improved. However, the exchangeability of anions between their layers is a challenging problem to overcome. In recent years, the adsorption isotherm fitting experiment indicates that the adsorption by Cu/Fe-CLDH of \(\text{Au(S}_2\text{O}_3\text{)}_2^{3-}\) conforms to the Langmuir model. During the process of Cu/Fe-CLDH adsorbing \(\text{Au(S}_2\text{O}_3\text{)}_2^{3-}\), CLDH restored part of the layered structure, and \(\text{Au(S}_2\text{O}_3\text{)}_2^{3-}\) was inserted between the layers as a counteranion. Furthermore, the reduction of \(\text{Au(S}_2\text{O}_3\text{)}_2^{3-}\) by low-valent iron compounds in the adsorbent promoted the process of Cu/Fe-CLDH adsorbing \(\text{Au(S}_2\text{O}_3\text{)}_2^{3-}\).
research results show that the original layered structure of Mg/Al-LDH can be restored in an anion-containing solution after calcining. The memory effect can be used for Au(S$_2$O$_3$)$_2^{2−}$ adsorption. The Mg/Al-LDH loaded with Au(S$_2$O$_3$)$_2^{2−}$ can be eluted with CO$_3^{−}$ with strong exchange capacity to realize the recycling of adsorption materials.

The type of divalent and trivalent metal ions in the layer of LDHs and the change of interlayer anions will affect the adsorption of Au(S$_2$O$_3$)$_2^{2−}$ in an endothermic reaction process, as discussed below. Also, according to the change in pH of the solution after adsorption, (when the pH is greater than 9), the adsorption process will release hydrogen ions, causing the pH to fall, as shown in Figure 1c. Therefore, a higher pH value can consume hydrogen ions, and this subsequently promotes the adsorption process. When, however, the pH of the solution is 11, the CLDH surface has more negative charges. Due to the electrostatic repulsion forces, this affects the adsorption of gold ions. When the pH of the solution is 8, although the surface of the CLDH is positively charged, it can be seen from Figure 1c that hydroxyl radicals are released during the adsorption process. Therefore, in this scenario, the adsorption effect of gold is lower than that at pH 9. In the experiment involving Cu/Fe-CLDH adsorption of gold, the best pH value is 10.

### 2. RESULTS AND DISCUSSION

#### 2.1. Adsorption Effect of Different Types of CLDH on Au(S$_2$O$_3$)$_2^{2−}$

A total of 0.5 g of the adsorbent was put into a solution with a 20 mg/L initial gold concentration, 0.01 mol/L sodium thiosulfate, pH 10, and 30 °C. After 2 h, the adsorption results of different CLDHs to Au(S$_2$O$_3$)$_2^{2−}$ are shown in Table 1.

| M$^{2+}$       | M$^{3+}$       | A$^{−}$       | adsorption rate (%) |
|---------------|---------------|--------------|---------------------|
| copper sulfate| ferric sulfate| sodium hydroxide and sodium thiosulfate | 98.00 |
| nickel sulfate| ferric sulfate| sodium hydroxide and sodium thiosulfate | 86.39 |
| zinc sulfate  | ferric sulfate| sodium hydroxide and sodium thiosulfate | 1.58  |
| manganese sulfate | ferric sulfate | sodium hydroxide and sodium thiosulfate | 52.98 |
| copper sulfate| aluminum sulfate| sodium hydroxide and sodium thiosulfate | 78.16 |
| nickel sulfate| aluminum sulfate| sodium hydroxide and sodium thiosulfate | 50.55 |
| zinc sulfate  | aluminum sulfate| sodium hydroxide and sodium thiosulfate | 0.46  |
| manganese sulfate | aluminum sulfate | sodium hydroxide and sodium thiosulfate | 7.92  |

It can be seen that different CLDHs have varied adsorption capacities for Au(S$_2$O$_3$)$_2^{2−}$. Copper sulfate and iron sulfate as the salt solution and sodium hydroxide and sodium thiosulfate as the alkaline solution to prepare the precursor (Cu/Fe-LDH) were used, and then, calcining was done at 400 °C for 2 h to obtain Cu/Fe-CLDH. It emerged that Cu/Fe-CLDH has the best adsorption effect on Au(S$_2$O$_3$)$_2^{2−}$.

#### 2.2. Effect of Different Conditions on the Adsorption of Au(S$_2$O$_3$)$_2^{2−}$ by Cu/Fe-CLDH

##### 2.2.1. Effect of pH

With the initial gold concentration at 20 mg/L, the sodium thiosulfate concentration at 0.01 mol/L, and the adsorption temperature at 40 °C, the effect of different pH values on the Au(S$_2$O$_3$)$_2^{2−}$ adsorption by Cu/Fe-CLDH is shown in Figure 1. Any change in pH exerts a great influence on the adsorption of Au(S$_2$O$_3$)$_2^{2−}$ by Cu/Fe-CLDH. When the pH value increases from 8 to 10, the gold loading rises from 8.8 to 10.43 mg/g. When the pH level is 11, the ability of Cu/Fe-CLDH to adsorb Au(S$_2$O$_3$)$_2^{2−}$ declines significantly. As shown in Figure 1b, the pH of the CLDH surface is about 9. When the pH of the solution is greater than 9, the CLDH surface is negatively charged, but the adsorption effect of gold is best when the pH is 10. This is because the gold adsorption process may be controlled by the chemical reaction process, as discussed below. Also, according to the change in pH of the solution after adsorption, (when the pH is greater than 9), the adsorption process will release hydrogen ions, causing the pH to fall, as shown in Figure 1c.

##### 2.2.2. Effect of Gold Concentration

Figure 2 illustrates the effect of different gold concentrations on the adsorption of Au(S$_2$O$_3$)$_2^{2−}$ by Cu/Fe-CLDH. It can be observed that under different conditions, the amount of Au(S$_2$O$_3$)$_2^{2−}$ loaded on Cu/Fe-CLDH gradually rises as time passes. In the first hour, the loading of gold gradually increased and then basically reached saturation. As the concentration of gold in the solution increases, the gold loading on Cu/Fe-CLDH also increases. The reason for this is that more thiosulfate ions in the solution can be complexed when the gold concentration is higher, thereby weakening the competitive adsorption of S$_2$O$_3^{−}$ to Au(S$_2$O$_3$)$_2^{2−}$ on Cu/Fe-CLDH. Also, the increase in the concentration of Au(S$_2$O$_3$)$_2^{2−}$ in the solution can accelerate its diffusion to the adsorbent material.

##### 2.2.3. Effect of Temperature

The influence of different temperatures on adsorption of Au(S$_2$O$_3$)$_2^{2−}$ by Cu/Fe-CLDH is shown in Figure 3. When the adsorption temperature is 30 °C, the adsorption rate of Cu/Fe-CLDH is lower, reaching saturation in 5 h, and furthermore, the adsorption capacity is lower. When the solution temperature increases, the adsorption rate of Au(S$_2$O$_3$)$_2^{2−}$ by Cu/Fe-CLDH improved significantly, and the adsorption process reached equilibrium within 1 h. When the temperature rose from 40 to 60 °C, the adsorption capacity increased slowly, and the adsorption capacity of Cu/Fe-CLDH for Au(S$_2$O$_3$)$_2^{2−}$ reached its maximum at 60 °C. This confirms that Cu/Fe-CLDH is more conducive to the adsorption of Au(S$_2$O$_3$)$_2^{2−}$ in a higher temperature environment. The adsorption process is an endothermic reaction.

#### 2.3. Adsorption Isotherms, Kinetics, and Thermodynamic Simulations

##### 2.3.1. Adsorption Isotherms

The fitting results of the Langmuir and Freundlich models of Au(S$_2$O$_3$)$_2^{2−}$...
isotherms adsorbed by 0.15 g of Cu/Fe-CLDH are shown in Figure 4a,b, respectively. The corresponding fitting parameters are summarized in Table 2. According to the overall trend of the curve in Figure 4, it is evident that both Langmuir and Freundlich models can fit the adsorption process well, but the correlation coefficients of the Langmuir fitting line are 0.998, 0.995, 0.997, and 0.999. They do not differ that much from the Freundlich fitting results (0.999, 0.994, 0.997, and 0.997). The adsorption isotherm shown in Figure 8 reveals that the surface structure of CLDH is more complicated, and it is not in fact an ideal adsorption surface. During the process of adsorption of gold ions, it may deviate from single-layer adsorption due to the existence of complex void structures on the surface. Judging by the influence of change in pH on the gold adsorption effect, we can see that the physical changes occurring in the adsorption process cannot be ignored. However, it can be seen from the analysis results of X-ray photoelectron spectroscopy (XPS) that a chemical reaction did occur during the adsorption process. Although the simulation results of the two adsorption isotherms are not that much different, according to the simulation results.

Figure 1. (a) Influence of pH on the gold adsorption (C_{Au} = 20 mg/L; C_{Na2S2O3} = 0.01 mol/L; m_{CLDH} = 0.15 g; T = 40 °C); (b) determination of pH_{pzc} for Cu/Fe-CLDH; and (c) pH change of the solution after the adsorption.

Figure 2. Infl.ence of gold concentration on the gold adsorption (C_{Na2S2O3} = 0.01 mol/L; pH = 10; T = 40 °C; m_{CLDH} = 0.15 g).

Figure 3. Effect of temperature on the adsorption of gold by Cu/Fe-CLDH (C_{Au} = 20 mg/L; C_{Na2S2O3} = 0.01 mol/L; pH = 10; m_{CLDH} = 0.15 g).
of adsorption kinetics, the adsorption isotherm is more inclined to the Langmuir model. It means that Au(S$_2$O$_3$)$_2$$_3^{−}$ has monolayer adsorption on the Cu/Fe-CLDH surface.

### 2.3.2. Adsorption Kinetics

Figure 5a,b depicts the pseudo-first-order and pseudo-second-order kinetic fitting equations of gold adsorption at 40 °C for 0.15 g of Cu/Fe-LDO, respectively. Table 3 corresponds to the calculation results of the fitting parameters. Through the comparison of $R^2$ values, it can be ascertained that the pseudo-second-order kinetic curve fits the experimental data better compared to the pseudo-first-order kinetic equation. In addition, the theoretical value (48.123 mg/g) of the adsorption capacity determined by the pseudo-second-order kinetic equation is closer to the experimental value (48.6 mg/g). It further demonstrates that the pseudo-second-order kinetic model is more suitable for describing the adsorption process of Au(S$_2$O$_3$)$_2$$_3^{−}$ by Cu/Fe-CLDH.

### 2.3.3. Adsorption Thermodynamics

The adsorption behavior of Cu/Fe-CLDH at different temperatures (303, 313, 323, and 333 K) was further studied, and the corresponding thermodynamic parameters were analyzed and calculated. Results are shown in Table 4. It can be seen that when the temperature increased, the value of $\Delta G$ dropped from 6.425 to 6.219 KJ/mol, strongly suggesting that higher temperature greatly encourages the adsorption process. Moreover, $\Delta H > 0$ means that the adsorption of Au(S$_2$O$_3$)$_2$$_3^{−}$ by Cu/Fe-CLDH is

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**Table 2. Adsorption Isotherm Model Parameters of Cu/Fe-CLDH**

| isotherm          | temperature (°C) | $R^2$  | $q_{max}$ (mg/g) | $k_L$  | $R^2$  | $n$  | $k_F$  |
|-------------------|------------------|--------|------------------|--------|--------|------|--------|
| Langmuir          | 30               | 0.998  | 46.948           | 0.073  | 0.998  | 42.176| 0.092  |
|                   | 40               | 0.995  | 42.176           | 0.092  | 0.999  | 40.584| 0.106  |
|                   | 50               | 0.997  | 40.584           | 0.106  | 0.999  | 50.891| 0.097  |
|                   | 60               | 0.999  | 50.891           | 0.097  | 0.999  | 50.891| 0.097  |
| Freundlich        | 30               | 0.775  | 0.744            | 4.508  | 0.775  | 0.744 | 4.508  |
|                   | 40               | 0.744  | 0.730            | 5.272  | 0.744  | 0.730 | 5.272  |
|                   | 50               | 0.761  | 0.761            | 5.272  | 0.761  | 0.761 | 5.272  |

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**Table 4. Adsorption Thermodynamic Parameters of Au(S$_2$O$_3$)$_2$$_3^{−}$ Adsorption on Cu/Fe-CLDH**

| parameter | $\Delta H$ (KJ/mol) | $\Delta S$ (KJ/mol) | $\Delta G$ (KJ/mol) |
|-----------|----------------------|----------------------|----------------------|
| 303 K     | 72.194               | 140.346              | 6.425                |
| 313 K     | 66.826               | 134.055              | 6.219                |
| 323 K     | 61.691               | 128.458              | 6.010                |
| 333 K     | 56.791               | 123.230              | 5.801                |

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**Figure 4.** Cu/Fe-CLDH adsorption models, (a) Langmuir and (b) Freundlich models ($C_{Na_2S_2O_3}=0.01$ mg/L; pH = 10; $m_{CLDH} = 0.15$ g).

**Figure 5.** Gold adsorption kinetics by Cu/Fe-CLDH, (a) pseudo-first-order kinetics and (b) pseudo-second-order kinetics.
an endothermic reaction. As the adsorption temperature increases, the adsorption capacity tends to increase, and $\Delta S$ is a positive value, indicating that the process of Au(S\textsubscript{2}O\textsubscript{3})\textsubscript{2}\textsuperscript{3−} adsorption by Cu/Fe-CLDH is an entropy-increasing process.

### 2.4. Cu/Fe-CLDH Characterization

#### 2.4.1. XRD Analysis

The X-ray diffraction (XRD) patterns of Cu/Fe-LDHs, Cu/Fe-CLDH, and Cu/Fe-CLDH-Au (Cu/Fe-CLDH with Au(S\textsubscript{2}O\textsubscript{3})\textsubscript{2}\textsuperscript{3−} adsorption) are shown in Figure 6a−c, respectively. It can be seen from (a) that there are characteristic peaks of LDHs around 11 and 23°, corresponding to Cu/Fe-LDHs (0 0 3) and (0 0 6) crystal planes, respectively. The diffraction peaks at 27.6, 29.2, 31.7, 32.8, 47.9, 52.7, and 59.3° correspond to (1 0 0), (1 0 2), (1 0 3), (0 0 6), (1 1 0), (1 0 8), and (1 1 6) crystal planes in CuS, indicating that the synthesized product contains CuS. In (b), the characteristic peaks of LDHs disappeared after calcination at 400 °C lasting for 2 h, strongly suggesting that at this temperature, the interlayer anions were removed and the layered structure was destroyed. Also, the CuS diffraction peak disappeared, and the CuSO\textsubscript{4} diffraction peak with a narrow peak shape and high intensity appeared. In order to verify the CuSO\textsubscript{4} on gold adsorption, a solution of 0.15 g of CuSO\textsubscript{4}, 0.01 mol/L Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}, and 20 mg/L Au(S\textsubscript{2}O\textsubscript{3})\textsubscript{2}\textsuperscript{3−} with pH = 10 was prepared. The change in the gold concentration in the solution was detected, and the result showed that this concentration did not change within 5 h. It further confirms that the CuSO\textsubscript{4} which appears after roasting does not explain the adsorption of gold. In Figure 6c, the characteristic peaks of LDHs reappear at about 11

| Table 3. Kinetic Parameters of Gold Adsorption by Cu/Fe-CLDH |
| --- |
| kinetic model | temperature (°C) | parameter | 10 | 20 | 40 | 80 |
| --- | --- | --- | --- | --- | --- | --- |
| Pseudo-first-order dynamics | 30 | $R^2$ | 0.995 | 0.987 | 0.960 | 0.957 |
| | | $k_1$ | 0.009 | 0.018 | 0.010 | 0.028 |
| | | $q_{e,c}$ (mg/g) | 4.710 | 11.209 | 18.242 | 54.065 |
| | 40 | $R^2$ | 0.909 | 0.584 | 0.698 | 0.775 |
| | | $k_1$ | 0.022 | 0.013 | 0.018 | 0.018 |
| | | $q_{e,c}$ (mg/g) | 4.372 | 3.747 | 8.828 | 13.877 |
| | 50 | $R^2$ | 0.923 | 0.343 | 0.476 | 0.588 |
| | | $k_1$ | 0.018 | 0.009 | 0.017 | 0.017 |
| | | $q_{e,c}$ (mg/g) | 3.794 | 2.426 | 2.808 | 9.901 |
| | 60 | $R^2$ | 0.599 | 0.088 | 0.326 | 0.102 |
| | | $k_1$ | 0.014 | 0.005 | 0.012 | 0.008 |
| | | $q_{e,c}$ (mg/g) | 2.042 | 1.096 | 1.273 | 2.350 |
| Pseudo-second-order dynamics | 30 | $R^2$ | 0.993 | 0.992 | 0.949 | 0.995 |
| | | $k_2$ | 0.001 | 0.001 | 0.001 | 0.001 |
| | | $q_{e,c}$ (mg/g) | 6.283 | 12.367 | 23.343 | 51.653 |
| | 40 | $R^2$ | 0.984 | 0.990 | 0.994 | 0.999 |
| | | $k_2$ | 0.004 | 0.005 | 0.002 | 0.003 |
| | | $q_{e,c}$ (mg/g) | 6.105 | 11.121 | 23.100 | 48.733 |
| | 50 | $R^2$ | 0.990 | 0.990 | 0.562 | 0.998 |
| | | $k_2$ | 0.006 | 0.009 | 0.003 | 0.003 |
| | | $q_{e,c}$ (mg/g) | 5.907 | 11.007 | 23.607 | 49.188 |
| | 60 | $R^2$ | 0.997 | 0.99986 | 0.99998 | 0.99994 |
| | | $k_2$ | 0.016 | 0.120 | 0.141 | 0.004 |
| | | $q_{e,c}$ (mg/g) | 5.670 | 10.949 | 23.180 | 48.123 |

| Table 4. Gold Adsorption Thermodynamic Parameters by Cu/Fe-CLDH |
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| $T$ (K) | $\Delta G$ (KJ/mol) | $\Delta H$ (KJ/mol) | $\Delta S$ [J/(mol·K)] |
| --- | --- | --- | --- |
| 303 | 6.425 | 1.888 | 6.297 |
| 313 | 6.356 | 1.888 | 6.297 |
| 323 | 6.288 | 1.888 | 6.297 |
| 333 | 6.219 | 1.888 | 6.297 |

Figure 6. XRD patterns of (a) Cu/Fe-LDHs, (b) Cu/Fe-CLDH, and (c) Cu/Fe-CLDH-Au.
and $23^\parallel$, and the intensity is lower than that of the characteristic peaks in Figure 6a, meaning that Cu/Fe-CLDH restores a certain layered structure in the process of adsorbing Au($S_2O_3$)$_2$ $^{3-}$. In addition, following adsorption, the CLDH layer spacing (0.86, 0.45) becomes larger than before adsorption (0.75, 0.37), indicating that Au($S_2O_3$)$_2$ $^{3-}$ has entered the interlayer of CLDH. Furthermore, there are diffraction peaks of Fe$_2$O$_3$ crystals, yet there is no iron-containing crystalline substance evident in Figure 6b. Although this part of cryptocrystalline iron cannot be shown in the XRD results, 85% of the gold adsorption effect is caused by this part of iron-containing material, which will be proved in Figure 9.

2.4.2. FTIR Analysis. The Fourier transform infrared (FTIR) spectra of Cu/Fe-LDHs, Cu/Fe-CLDH, and Cu/Fe-CLDH-Au (400–4000 cm$^{-1}$) are shown in Figure 7a–c, respectively. In (a), the peaks at 3442 and 1617 cm$^{-1}$ are attributed to OH-stretching vibration and interlayer water bending vibration in water molecules, respectively. The peak near 1100 cm$^{-1}$ is the asymmetric vibration absorption peak of S=O in thiosulfate. A characteristic peak caused by the Cu–S stretching vibration appeared at 616 cm$^{-1}$, indicating the presence of the CuS material, which was consistent with the XRD results. In Figure 7b, the absorption peak intensity of water molecules and thiosulfate radicals decreases, and the characteristic absorption peaks of SO$_4^{2-}$ appear at 1152 and 1077 cm$^{-1}$, which is consistent with the formation of copper sulfate in the XRD pattern of Cu/Fe-CLDH. Figure 7c is the spectrum of Cu/Fe-CLDH after adsorption of Au($S_2O_3$)$_2$ $^{3-}$. At 1113 cm$^{-1}$, the asymmetric vibrational absorption peak of S=O in thiosulfate reappeared. Compared with the position of the vibration peak in Figure 7a, a red shift occurred, indicating that S=O $^{3-}$ has formed a bond with gold ions. It proves that Au($S_2O_3$)$_2$ $^{3-}$ entered the interlayer of LDHs successfully.

2.4.3. BET Analysis. The size of the parameters such as pore size, pore volume, and specific surface area will have a certain impact on the adsorption capacity of the material. Therefore, Brunauer–Emmett–Teller ( BET) analysis was done on Cu/Fe-LDH, Cu/Fe-CLDH, and Cu/Fe-CLDH-Au materials, and the results are shown in Figure 8a–c, respectively. In Table 5 summarizes the relevant parameters of the BET results. Following calcination, similar changes occurred in the specific surface area (increased from 57.335 to 83.344 m$^2$/g) and the total pore volume (increased from 0.556 to 0.751 m$^3$/g). The pore volume of Cu/Fe-CLDH-Au (0.496 m$^3$/g) is lower than that of Cu/Fe-CLDH, indicating that during the adsorption process, Au($S_2O_3$)$_2$ $^{3-}$ is added to the voids of Mg/Al-CLDH.

2.4.4. XPS Analysis. In order to characterize the surface chemical elements and document the valence state of the adsorbent material in different states, Figure 9 depicts the XPS energy spectra of the elements Fe 2p, S 2p, and Au 4f contained in the material. In the Au 4f spectrum, the two small peaks at 88.8 eV and 85.3 eV are the characteristic peaks of Au(I), while the two higher characteristic peaks at 84.2 and 87.8 eV represent Au 4f$_{7/2}$ and Au 4f$_{5/2}$ of gold element, respectively. According to the peak area, it is understood that the elemental gold content on the adsorbent is 85%, and the monovalent gold content is 15%. This demonstrates that part of the Au($S_2O_3$)$_2$ $^{3-}$ is reduced during the adsorption process, so there must be chemical substances in the adsorption material that will be oxidized. The peaks of Cu 2p before and after adsorption are basically the same (not given here). However, the peaks of Fe 2p located at 724.1 and 710.8 eV (before adsorption) become 725 and 711.68 eV (after adsorption), respectively, which means that the divalent iron in the adsorbent turns into trivalent iron. This transformation is consistent with the XRD results in Figure 6. After the gold is adsorbed, the iron-containing material in the adsorbent becomes Fe$_2$O$_3$. It confirms that the iron-containing material in the adsorbent acts as a gold ion-reducing agent, and the reduction of divalent iron ions contributes to the adsorption outcome of 85%. The S 2p peaks in Cu/Fe-LDHs are located at 168.3, 163.1, and 162.1 eV, corresponding to the S=O $^{2-}$ between the layers. After adsorption, the peaks of S 2p are located at 168.7, 163.4, and 162.3. This change indicates that the anions entering the interlayer are Au($S_2O_3$)$_2$ $^{3-}$.

2.4.5. SEM–EDS Characterization. Figure 10 shows the scanning electron microscopy–energy-dispersive X-ray spectroscopy (SEM–EDS) characterization results of Cu/Fe-LDHs, Cu/Fe-CLDH, and Cu/Fe-CLDH-Au. It can be seen from (a–c) that in addition to the characteristic layered morphology of hydrotalcite, Cu/Fe-LDHs have many closely connected slender columnar tubes, which may correspond to the CuS present in the material. It can be seen from Figure 10e that Cu/Fe-CLDH has two morphologies, as shown in (d) and (f). The crystal morphology in (d) is very good, belonging to a regular cuboid structure, corresponding to the CuSO$_4$ present in the product, while in (f), there is a slightly rough lamella, attributable to the roasting stage. Figure 10g presents the morphology of Cu/Fe-CLDH-Au; the degree of order is greatly reduced, the particles are small and broken, and the level of agglomeration is serious, which may be related to the Cu/Fe-CLDH adsorption process. At the same time, according to the energy spectrum of Cu/Fe-CLDH-Au in (i), it is proven that gold is successfully loaded onto Cu/Fe-CLDH.

2.5. Cu/Fe-CLDH Adsorption Mechanism. It can be seen from the XRD analysis in Figure 6 that as Au($S_2O_3$)$_2$ $^{3-}$ enters the CLDH interlayer, the interlayer spacing becomes larger after adsorption. Because the interlayer anions of LDHs change from S=O $^{2-}$ to Au($S_2O_3$)$_2$ $^{3-}$, consequently, the position of the S=O vibration peak shown in Figure 7 has a red shift. Added to this,
the binding energy of S 2p in Figure 9 changed from 168.3, 163.1, and 162.1 eV to 168.7, 163.4, and 162.3 eV, respectively, which proves again that Au(S2O3)2−3− entered the CLDH interlayer. According to the results of the XPS analysis in Figure 9, due to the reduction of iron-containing substances in the adsorbent, gold ions are turned into elemental gold, which contributes 85% of the adsorption effect. The adsorption mechanism of gold ions by Cu/Fe-CLDH is shown in Figure 11. Due to the combined result of the two effects, Cu/Fe-CLDH’s adsorption of gold is much greater than that of Mg/Al-CLDH.

3. CONCLUSIONS

Based on the controllability of LDHs’ structure, Cu/Fe-LDHs were synthesized utilizing the co-precipitation method, and Cu/Fe-CLDH was obtained by calcination at 400 °C that lasted for 2 h. XRD, FTIR, SEM, XPS, and other methods helped to systematically characterize the microstructure and surface chemistry of Cu/Fe-CLDH in different states. The effects of thiosulfate concentration, initial gold concentration, solution pH, and adsorption temperature on the process of Au(S2O3)2−3− adsorption on Cu/Fe-CLDH were investigated, and the corresponding adsorption mechanism was further analyzed. Subsequently, the following research conclusions can be reported:

1. Cu/Fe-CLDH has a single adsorption capacity of 48.6 mg/g for Au(S2O3)2−3− at a solution of 80 mg/L Au(S2O3)2−3−, 0.01 mol/L S2O32−, 60 °C, and pH 10. Compared with the adsorption capacity of 11.6 mg/g of Mg/Al-CLDH, its adsorption capacity is quadrupled.

2. The increase in both the concentration of gold in the solution and temperature are conducive to the adsorption of Au(S2O3)2−3− by Cu/Fe-CLDH. When the pH value of the solution is greater than 11, the CLDH surface has more negative charges. This weakens the effective adsorption of Au(S2O3)2−3− by Cu/Fe-CLDH.

3. The pseudo-second-order kinetic model is ideal for describing the adsorption process of Au(S2O3)2−3− by Cu/Fe-CLDH. The adsorption isotherm fitting study found that the adsorption process of Au(S2O3)2−3− on Cu/Fe-CLDH conforms to the Langmuir model.
The two effects together promote the adsorption of \( \text{Au(S}_2\text{O}_3\text{)}_2^{3-} \) by Cu/Fe-CLDH. On one hand, \( \text{Au(S}_2\text{O}_3\text{)}_2^{3-} \) is inserted between the layers as a counteranion during the recovery process of the layered structure of Cu/Fe-CLDH; on the other hand, it is the reduction of \( \text{Au(S}_2\text{O}_3\text{)}_2^{3-} \) by the divalent iron ion in the adsorbent.

4. EXPERIMENTAL SECTION

4.1. Reagents. Au (99.99%), HCl, HNO₃, NaOH, H₂SO₄, KCl, Na₂S₂O₃, H₂O₂, CuSO₄·5H₂O, NiSO₄·6H₂O, ZnSO₄·7H₂O, MnSO₄·H₂O, Fe₂(SO₄)₃·xH₂O, Al₂(SO₄)₃·18H₂O, and Na₂CO₃ were all analytically pure. Furthermore, deionized water was used throughout the experiments.

4.2. Experimental Methods. The divalent metal salt and trivalent metal salt reagent was dissolved with a molar ratio of 2:1 in 250 mL solution. Then, NaOH and Na₂S₂O₃ reagents with a molar ratio of 3:1 were taken and dissolved in 250 mL of deionized water to form an alkaline solution. It was necessary to mix and stir the prepared salt solution and alkali solution quickly to produce a colloidal slurry and place it in a constant-temperature water bath. With the use of a mechanical stirrer, the mixture was stirred and crystallized at a constant temperature of 80 °C for 24 h. Following this, the crystallization slurry was filtered, washed with deionized water to achieve neutrality, and Na₂CO₃ were all analytically pure. Furthermore, deionized water was used throughout the experiments.

Figure 9. XPS profiles of Cu/Fe-LDHs, Cu/Fe-CLDH, and Cu/Fe-CLDH-Au.
then dried to obtain LDHs. Lastly, the LDHs were put into a muffle after being ground to powder and subsequently calcined at 400 °C for 2 h to obtain CLDH.

4.3. Gold Adsorption Test. A specific amount of adsorbent LDO was added to 100 mL of 0.01 mol/L Na$_2$S$_2$O$_3$ solution containing different concentrations of Au(S$_2$O$_3$)$_2^{3-}$. An aqueous solution of Au(S$_2$O$_3$)$_2^{3-}$ was prepared as described previously. In the gold ion adsorption experiments, the pH of the solution was adjusted to 10 using NaOH. The concentration of Au(S$_2$O$_3$)$_2^{3-}$ was adjusted according to the experimental requirements. The mixture was then mechanically stirred at 300 rpm and different temperatures. After a period of time, part of the solution was used for gold ion analysis. The gold percentage recovery was calculated using eq 1

$$R = \frac{C_0V_0 - CV_t}{C_0V_0}$$

where $R$ is the percentage of CLDH-adsorbed Au(S$_2$O$_3$)$_2^{3-}$, $C_0$ and $C_t$ are the gold concentration at the beginning and at time $t$, respectively, and $V_0$ and $V_t$ are the initial volume of the solution and volume of the solution at time $t$, respectively.

The loading capacity of the CLDH was calculated with eq 2

$$Q = \frac{C_0V_0 - CV_t}{M}$$

where $Q$ (mg g$^{-1}$) is the gold loading capacity of the CLDH and $M$ (g) is the mass of the adsorbent.

4.4. Adsorption Kinetics. The adsorption kinetics can reflect the influence of various factors such as adsorption temperature and initial gold concentration of the solution on the reaction rate, which makes possible to analyze the adsorption mechanism. Two well-known kinetic models, namely, pseudo-first-order (eq 3) and pseudo-second-order (eq 4), were used for fitting the kinetic data of Au(I) adsorption on CLDH

$$\log(q_e - q_t) = \log q_{e,c} - \frac{k \cdot t}{2.303}$$

Figure 10. SEM images of (a–c) Cu/Fe-LDHs, (d–f) Cu/Fe-CLDH, and (g,h) Cu/Fe-CLDH-Au and SEM–EDS image of (i) Cu/Fe-CLDH-Au.
respectively, and the kinetic constants respectively, while respectively.

4.5. Adsorption Isotherms. At present, the most widely used adsorption isotherm models are the Langmuir and Freundlich variants. They are written below as follows

Langmuir model: \[ \frac{q_e}{c_e} = \frac{1}{k_L q_{max}} + \frac{c_e}{q_{max}} \] (5)

where the gold concentration in solution at equilibrium is represented by \( c_e \), \( q_{max} \) is the maximum load of gold ions in CLDH (mg/g), and \( k_L \) and \( k_F \) are the Langmuir and Freundlich isotherm constants, respectively, while \( n \) is a corresponding constant of the Freundlich model.

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Notes
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