Effect of Cu$^{2+}$ on the Activation to Muscovite Using Electrochemical Pretreatment

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Abstract: In this study, electrochemistry pretreatment flotation of muscovite was carried out and the flotation behavior and mechanism of muscovite in the system of sodium oleate and Cu$^{2+}$ ion was characterized by solution pH value detection, solution conductivity detection, zeta potential, infrared spectrum and the electronic energy spectrum. The results indicated that under the conditions of muscovite mass of 10.00 g, pulp mass concentration of 13.33%, flotation speed of 1750 r/min, sodium oleate concentration of 9.20 $\times$ 10$^{-4}$ mol/L and Cu$^{2+}$ concentration of 6 $\times$ 10$^{-5}$ mol/L, electrochemical pretreatment of Cu$^{2+}$ could strengthen the activation of muscovite. Electrochemical pretreatment of Cu$^{2+}$ solution can inhibit the hydrolysis of copper ions, increase the content of Cu$^{2+}$ in the solution, strengthen the adsorption of Cu$^{2+}$ on the muscovite surface, and enhance the electrostatic adsorption of sodium oleate on the muscovite surface, thereby strengthening the physical and chemical adsorption of sodium oleate on the muscovite surface.

Keywords: electrochemical pretreatment; copper sulfate; muscovite; action mechanism

1. Introduction

Electrochemical flotation process is a hotpot in the field of mineral processing in recent years. It mainly focuses on the electrochemical pretreatment of flotation medium, pulp or pharmacy, which plays a boosting role in improving the index of flotation concentrate [1–4].

Ahmadi [5] pointed out that compared with the conventional bioleaching, the electrochemical bioleaching of chalcopyrite flotation concentrate leads to about 35% more copper recovery. It seems that the main reason for increasing copper recovery by electrochemical bioleaching is the control of redox potential between 400 and 425 mV. In this range of potential, the precipitation of ironoxy-hydroxides on the chalcopyrite surface, which act as a diffusion barrier and prevent chalcopyrite dissolution, is significantly reduced. This leads to a higher electrochemical reduction of chalcopyrite and improves dissolution. Chander and Fuerstenau [6] found that chalcocite could be separated from molybdenite through appropriate choice of the potential of flotation. Meng et al. [7] found that chalcopyrite began to oxidize quickly at a much lower potential than enargite. Enargite was floated well at a potential higher than +0.2 V vs. SCE (Saturated calomel electrode) while chalcopyrite was completely depressed at a potential higher than +0.2 V vs. SCE. Selective flotation revealed that enargite can be successfully removed from chalcopyrite through controlling the pulp potential higher than +0.2 V and lower than +0.55 V vs. SCE. In order to exploit the Northparkes copper and gold mine in New South Wales, Australia, containing arsenopyrite, it is necessary to remove the arsenopyrite existing in the raw
ore. Smith et al. [8] separated arsenopyrite from chalcopyrite and bornite by electrochemical control flotation process. At the potential of −150 mV and the pH value of 12, about 52% of the low arsenic and high copper concentrate was obtained, which provided a good way for the removal of arsenic from copper minerals. Nguyen et al [9] carried out a study on the adsorption of electrochemically regulated flotation collectors for arsenopyrite. The results indicated that when the oxidation potential was +516 mV, the mineral recovery reached the highest. This experiment proves that arsenic can be effectively separated by potential regulation. Zhou et al. [10] conducted a flotation test study on a complex lead–zinc ore in Jing Dong Tailings Company of Fujian province. The result showed that in the electrochemical potential controlling flotation processing, using DDTC as collector, the separation potential range of galena and sphalerite with pyrrhotite can be achieved. Flotation circuit of lead–zinc–silver tailing ore was achieved. Li et al. [11] showed that in the presence of Cu\(^{2+}\) ion, and a wide pH range of 2.0 to 12.0, the floatability of pyrrhotite and marmatite was strong, so marmatite could not be separated from pyrrhotite. The technique of electrochemical flotation was used to separate marmatite from pyrrhotite in the presence of Cu\(^{2+}\). Pyrrhotite can be depressed and marmatite be floated through controlling the potential of flotation. Marmatite can be separated from pyrrhotite in the pulp potential range of −0.25 V to 0 V vs. SHE (Normal Hydrogen Electrode) at pH 11.2 solution.

Different studies have found that electrochemical treatment can change the properties of the flotation agent, therefore changing the state of the drug itself, the chemical composition, the pH value and the redox potential value, as well as the proportion of ions, molecules and colloidal particles formed in the flotation agent solution, and thereby affecting the flotation effect of the target mineral [12–14]. Conventional flotation methods of mica include the acid cation method, basic anion and cation method and the combined flotation method [15].

However, there are few studies on the application of electrochemical flotation technology for the flotation of muscovite. Some studies have shown that adding a certain amount of Cu\(^{2+}\) can activate the target mineral in the flotation process of muscovite [16]. Based on this finding, the paper takes the flotation behavior of muscovite in the sodium oleate system as the entry point, and reveals the activation mechanism of Cu\(^{2+}\) with electrochemical pretreatment for enhancing the activation of muscovite, which is expected to provide a reference for the actual mineral flotation of muscovite [17].

2. Materials and Methods

2.1. Materials and Reagents

Coarse concentrate of hand separation in a muscovite mine from Henan province was used in this experiment. First, the original ore sample was processed by the processes of crushing, shaking table purification, screening and acid pickling, and then the acid pickling muscovite sample was washed to neutral by distilled water. Finally, the ore sample was filtered and dried at low temperature for flotation tests. In order to understand the chemical composition and crystallization of the mica ore, the test conducted multi-element analysis and XRD characterization of the samples, and the results are shown in Figure 1 and Table 1.

Figure 1 shows that the muscovite owned high purity and good crystallinity. According to Table 1, the muscovite samples mainly contained elements of K, Si, Al, etc., and the combined Na\(_2\)O and K\(_2\)O content was 11.34%; combined with the theoretical content of potassium and sodium, muscovite purity can reach more than 95%.

The sodium hydroxide (NaOH), copper sulfate (CuSO\(_4\)·5H\(_2\)O) and sodium oleate (C\(_{18}\)H\(_{33}\)NaO\(_2\)) used in this study were all analytically pure. They were purchased from Tianjin BASF reagent plant, Tianjin Guangfu Research Institute and Tianjin Zhiyuan chemical reagent plant, respectively. Distilled water was used in all tests.
Figure 1. XRD pattern of muscovite.

Table 1. Results of chemical composition analysis of samples.

<table>
<thead>
<tr>
<th>Chemical Constituents</th>
<th>SiO&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Na&lt;sub&gt;2&lt;/sub&gt;O</th>
<th>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>K&lt;sub&gt;2&lt;/sub&gt;O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition content/(wt)%</td>
<td>48.16</td>
<td>0.72</td>
<td>32.50</td>
<td>10.62</td>
</tr>
</tbody>
</table>

2.2. Methods

2.2.1. Electrolysis Experiment

The electrochemical pretreatment of flotation reagent solution was studied by using DC regulated power supply (ka3005p, Shenzhen preeminent Instrument Co., Ltd., Shenzhen, China), which is shown in Figure 2. During the pretreatment, a certain concentration of CuSO<sub>4</sub> solution was prepared first, and a certain amount of CuSO<sub>4</sub> solution was added into the electrolytic cell. Then, the current and electrolysis time were adjusted, the type of electrode plate was selected and the distance between the plates was fixed, and then the electrode plate and DC voltage were stabilized. The power supply was connected with electrode wire, the switch pressed, and electrolysis started. Its process can be expressed by the following reaction formula:

\[
CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-} \quad (1)
\]

\[
Cu^{2+} + H_2O \rightleftharpoons Cu(OH)^+ + H^+ \quad (2)
\]

\[
Cu(OH)^+ + H_2O \rightleftharpoons Cu(OH)_2 + H^+ \quad (3)
\]

\[
Cu(OH)_2 + H_2O \rightleftharpoons Cu(OH)_2^- + H^+ \quad (4)
\]

\[
Cu(OH)_2^- + H_2O \rightleftharpoons Cu(OH)_4^{2-} + H^+ \quad (5)
\]

When the two plates are made of graphite, the following reactions will take place near the cathode plate and anode plate:

- cathodic reaction: \( Cu^{2+} + 2e^- = Cu \downarrow \) (6)
- anodic reaction: \( 2OH^- = O_2 \uparrow + 2H^+ \) (7)

The electrochemical pretreatment conditions of Cu<sup>2+</sup> are shown in Table 2.
Table 2. Electrochemical pretreatment conditions.

<table>
<thead>
<tr>
<th>Test Number</th>
<th>Electric Current Magnitude/A</th>
<th>Electrolysis Time/min</th>
<th>PLATE DISTANCE/cm</th>
<th>Electrode Material Types (Anode–Cathodic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>variable</td>
<td>5</td>
<td>4.5</td>
<td>graphite–graphite</td>
</tr>
<tr>
<td>b</td>
<td>0.1</td>
<td>variable</td>
<td>4.5</td>
<td>copper–graphite</td>
</tr>
<tr>
<td>c</td>
<td>0.1</td>
<td>5</td>
<td>variable</td>
<td>lead board–graphite</td>
</tr>
<tr>
<td>d</td>
<td>0.1</td>
<td>5</td>
<td>4.5</td>
<td>variable</td>
</tr>
</tbody>
</table>

Finally, the electrolyzed copper sulfate solution was taken out from the electrolytic cell and placed in a beaker for the subsequent flotation test and related solution property detection.

![Image](image-url)

**Figure 2.** The electrolysis equipment and experimental process. (a), Electrochemical pretreatment of reagents; (b), DC regulated power supply.

2.2.2. Micro-Flotation Tests

In the flotation tests, the hanging cell flotation machine FGC(5-35) (Wuhan lock grinding equipment manufacturing Co., Ltd, Wuhan, China) was used, with the rotating speed of 1750 r/min. In each test, the muscovite 10.00 g was placed into the flotation cell, adding appropriate distilled water to adjust the pulp concentration to 13.33%. After stirring 1 min, sodium hydroxide was added to the pulp to achieve the best pH value in 2 min, then the proper amount of the collector and adjustment agent were added after electrochemical pretreatment and mixing the slurry. Finally, the foam products were filtered and dried, and the recovery rate after weighing was calculated. The flotation test flow is shown in Figure 3.

![Image](image-url)

**Figure 3.** Flowchart of flotation test.
2.2.3. Zeta Potential Characterization

The zeta potential on the muscovite surface was determined with a ZetaSizer 3000 Malvern Instrument (Malvern Instruments, Malvern, UK). The overcrushing samples were ground to less than 5 µm by agate grinding. The suspension was prepared by adding 20 ± 1 mg of muscovite sample to 20 mL of distilled water and adding pH adjusting agent in turn, after electrochemical pretreatment of adjusting agent. The suspension was conditioned for 15 min. Suspension with or without 200 or 400 mg/L of muscovite was placed on a rotating shaker for 30 min. The zeta potential was measured in accordance with the procedures described in the instrument manual. The reported results were the average of at least three full repeats of the experiment.

2.2.4. FTIR Spectroscopy Characterization

FTIR spectra of muscovite were recorded to examine the functional groups of muscovite before and after adsorbing electrochemical regulator. The experimental samples of 2.00 g were added into the 100 mL centrifuge tube with 40 mL of liquid, where the concentration of electrochemical regulator was 8000 mg/L (400 mg/L × 20 times). Then, the samples were shaken at a centrifugal speed of 100 rpm for 30 min. FTIR spectra were recorded over the region of 600–4000 cm⁻¹. The samples were examined in KBr pellets (3 mg/300 mg KBr). All samples were analyzed with a Lumex FTIR-08 spectrophotometer [18].

2.2.5. XPS Measurements

The chemical compositions of the muscovite surfaces were determined by XPS on a Thermo Scientific ESCALAB 250Xi, using an Al Kα X-ray source operated at 200 W with 20 eV pass energy. The sample preparation method was the same as that of the FTIR spectra experiment, with the vacuum pressure ranging from 10⁻⁹ to 10⁻⁸ Torr and a take-off angle of 90°, which was used for collecting and analyzing data using Thermo Scientific Avantage 4.52 software.

3. Results and Discussion

3.1. Influence of Cu²⁺ on Flotation Behavior of Muscovite without Electrochemical Pretreatment

In order to compare the effect of copper ion on the floatability of muscovite before and after electrochemical pretreatment, the effects of different concentrations of Cu²⁺ on the floatability of muscovite before electrochemical pretreatment were tested. The test conditions were as follows: the muscovite sample was 10.00 g, pulp concentration 13.33%, Cu²⁺ concentration 6 × 10⁻⁵ mol/L, and sodium oleate (without pretreatment) concentration 9.20 × 10⁻⁴ mol/L. Electrochemical pretreatment conditions, test flow and the results are shown in Table 2, in Figure 3, and in Figure 4, respectively.

Figure 4 shows that the recovery rate of muscovite gradually increased with the increase of Cu²⁺ concentration when the pH value of the pulp was 12. When the concentration of Cu²⁺ was 8 × 10⁻⁵ mol/L, the recovery rate of muscovite was 80.90%, which indicated that Cu²⁺ can greatly improve the floatability of muscovite.
Distinct Conditions first and then decreased with the increase of electrolysis current. When the electrolysis current was 0.1A, the recovery of muscovite reached the maximum (about 80.40%). It indicates that electrochemical pretreatment of Cu\textsuperscript{2+} can enhance sharply the activation of muscovite during a electrolysis current, time, plate distance and electrode material type are shown in Figure 5.  

3.2. Effects of Electrochemical Pretreatment for Cu\textsuperscript{2+} on Flotation Behavior of Muscovite under Distinct Conditions

When the pH value was 12, the effects of Cu\textsuperscript{2+} on the floatability of muscovite as a function of electrolysis current, time, plate distance and electrode material type are shown in Figure 5.

![Figure 4. Effects of different concentrations of Cu\textsuperscript{2+} on the recovery of muscovite (pH = 12, c (Sodium oleate) = 9.20 × 10\textsuperscript{-4} mol/L).](image)

![Figure 5. Effects of Cu\textsuperscript{2+} on floatability of muscovite under different electrochemical treatment conditions (pH = 12, c (Sodium oleate) = 9.20 × 10\textsuperscript{-4} mol/L, c (Cu\textsuperscript{2+}) = 6 × 10\textsuperscript{-5} mol/L).](image)
As shown in Figure 5a, the recovery of muscovite was basically unchanged with the increasing of electrolysis current from 0 A to 0.05 A. From 0.05 A to 0.2 A, the recovery of muscovite increased first and then decreased with the increase of electrolysis current. When the electrolysis current was 0.1 A, the recovery of muscovite reached the maximum (about 80.40%). It indicates that electrochemical pretreatment of Cu$^{2+}$ can enhance sharply the activation of muscovite during a suitable current range. Figure 5b shows that the recovery of muscovite decreased with the increase of electrolysis time. When the pretreatment time increased from 5 min to 20 min, the recovery of muscovite decreased from 80.40% to 54.70%. Therefore, prolonging the electrolysis time is not conducive to strengthening the activation of muscovite by Cu$^{2+}$. Figure 5c shows that the recovery of muscovite decreased first and then increased with the increase of the distance between the plates. When the electrode plate spacing was 5.5 cm, the recovery of muscovite was reduced to 58.60%. This indicates that plate spacing can influence activation properties of Cu$^{2+}$, but changing the plate spacing is not a good choice. In addition, it can be seen from Figure 5d that the electrode plate material type had little effect on the activation of Cu$^{2+}$.

3.3. Effect Mechanism of Electrochemical Pretreatment of Cu$^{2+}$ on Flotation Behavior of Muscovite

The pH value of copper sulfate solution was detected by acidity meter to understand the effect of the distinct pretreatment conditions. The results are shown in Figure 7. Before that, the paper calculated the distribution coefficient of Cu$^{2+}$ components under different pH values, and the results are shown in Figure 6.

![Figure 6. Distribution chart of Cu$^{2+}$ composition and solution pH value.](image)

Figure 6 shows that Cu$^{2+}$ existed in many forms in the solution. When the pH value was less than 4, Cu$^{2+}$ was the main component in the solution. When the pH value was more than 4 and less than 10, the content of Cu$^{2+}$ decreased with the increase of the pH value, while the content of Cu(OH)$_2$ and Cu(OH)$^+$ increased. In addition, when the pH value was more than 9, Cu(OH)$_3^−$ and Cu(OH)$_4^{2−}$ began to form in the solution, in which the content of Cu(OH)$_3^−$ increased first and then decreased with the increase of the pH value, and the content of Cu(OH)$_4^{2−}$ increased with the increase of the pH value [19].

It can be seen from Figure 7a that the pH of the solution was about 3.3 when the copper sulfate solution was not electrochemically pretreated. After electrochemical pretreatment with distinct electrolysis current, the pH of the copper sulfate solution decreased. According to the relationship between the Cu$^{2+}$ component distribution coefficient and the pH value of solution, the Cu$^{2+}$ content in the solution increased with the increase of electrolytic current. According to Figure 6, the Cu$^{2+}$ content in the solution increased with the increase of electrolytic current. As shown in Figure 7b, when the electrolysis time increased from 5 min to 20 min, the pH value of the copper sulfate solution
gradually decreased. Since $H^+$ was generated in the vicinity of the anode plate during electrochemical pretreatment of the copper sulfate solution, the concentration of $H^+$ in the solution increased, so that the pH of the solution decreased, but the $Cu^{2+}$ content increased. According to Figure 6, the $Cu^{2+}$ content in the solution increased with the increase of electrolysis time. Figure 7c exhibits that the pH value of the copper sulfate solution changed little as the distance increased between the plates. According to Figure 6, the $Cu^{2+}$ content in the solution did not change much under this condition. It can be seen from Figure 7d that when the copper sulfate solution was electrochemically pretreated, the anode plate material influenced the pH value of the solution. Taking copper or lead plate as anode plate materials, the pH value of the copper sulfate solution was higher than that of graphite and stainless steel as the anode, which can be ascribed to oxidation dissolution of copper and oxidation behavior of lead. According to Figure 6, when the anode plate was made of copper and lead, the content of $Cu^{2+}$ in the $CuSO_4$ solution was higher than that of graphite and stainless steel.

![Figure 7](image_url)

**Figure 7.** Influence of electrochemical pretreatment on pH value of copper sulfate solution. ($c(Cu^{2+}) = 6 \times 10^{-5}$ mol/L). (a), electrolysis current; (b), electrolysis time; (c), plate distance; (d), electrode material types.

3.4. Zeta Potential Effect of $Cu^{2+}$ on Muscovite Surface under Different Electrochemical Pretreatment Conditions

For understanding the influence of $Cu^{2+}$ on zeta potential on the muscovite surface under distinct electrochemical pretreatment conditions, zeta potential of the muscovite surface was detected after electrochemical pretreatment, and the concentration of $Cu^{2+}$ was $6 \times 10^{-5}$ mol/L with a pH value of 12. The tested results are shown in Figure 8.
Figure 7. Influence of electrochemical pretreatment on pH value of copper sulfate solution. (c(Cu<sup>2+</sup>) = 6 × 10<sup>−5</sup> mol/L). (a), electrolysis current; (b), electrolysis time; (c), plate distance; (d), electrode material types.

3.4. Zeta Potential Effect of Cu<sup>2+</sup> on Muscovite Surface under Different Electrochemical Pretreatment Conditions

For understanding the influence of Cu<sup>2+</sup> on zeta potential on the muscovite surface under distinct electrochemical pretreatment conditions, zeta potential of the muscovite surface was detected after electrochemical pretreatment, and the concentration of Cu<sup>2+</sup> was 6 × 10<sup>−5</sup> mol/L with a pH value of 12. The tested results are shown in Figure 8.

Figure 8. Effect of electrochemical pretreatment on zeta potential of the muscovite surface with Cu<sup>2+</sup> (pH = 12, c(Cu<sup>2+</sup>) = 6 × 10<sup>−5</sup> mol/L). (a), electrolysis current; (b), electrolysis time.

According to Figure 8a, zeta potentials on the muscovite surface first increased positively and then slightly negatively with the increase of electrolysis current of Cu<sup>2+</sup>. At the electrolysis current of 0.1 A, the maximum zeta potential of −23.36 mV was obtained. According to Figure 8b, zeta potential on the muscovite surface increased negatively with the increase of electrolysis time for Cu<sup>2+</sup>. When the electrolysis of Cu<sup>2+</sup> solution was 20 min, zeta potential on the muscovite surface was −36.52 mV.

According to the analysis of the hydrolysis reaction, electrode reaction and solution pH value of copper ions, the small electrochemical pretreatment current and the short pretreatment time will result in a low precipitation rate of copper near the cathode plate, and the amount of precipitation was very small. The small consumption of Cu<sup>2+</sup> in the solution resulted in the content of Cu<sup>2+</sup> in the solution as very small, while oxygen was released and hydrogen ions were generated near the anode plate. The increase of hydrogen ions in the solution led to the left movement of the hydrolysis reaction of copper ions, which led to the increase of the overall content of Cu<sup>2+</sup> in the solution. The decrease of the content of Cu(OH)<sub>3</sub><sup>−</sup> and Cu(OH)<sub>2</sub> led to the increase of the adsorbed Cu<sup>2+</sup> on the muscovite surface, so that the zeta potential on the muscovite surface increased negatively. At a high electrochemical pretreatment current or a longer pretreatment time, the excessive deposition rate of elemental copper near the cathode plate will consume large amounts of Cu<sup>2+</sup>, making Cu<sup>2+</sup> in the solution decrease as a whole, thereby decreasing its adsorption on the muscovite surface.

3.5. Infrared Spectrum Analysis of Muscovite Samples

Infrared spectroscopy was employed to study the adsorption state of sodium oleate and Cu<sup>2+</sup> on the muscovite surface. The conditions of this action are shown in Table 3, and the results are shown in Figure 9.

<table>
<thead>
<tr>
<th>Sample Numbers</th>
<th>Sodium Oleate/ mol/L</th>
<th>Cu&lt;sup&gt;2+&lt;/sup&gt;/ mol/L</th>
<th>Electrolysis Current/A</th>
<th>Electrolysis Time/min</th>
<th>Plate Distance/cm</th>
<th>Electrode Material Types (Anode–Cathodic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>9.20 × 10&lt;sup&gt;−4&lt;/sup&gt;</td>
<td>6 × 10&lt;sup&gt;−5&lt;/sup&gt;</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>B</td>
<td>9.20 × 10&lt;sup&gt;−4&lt;/sup&gt;</td>
<td>6 × 10&lt;sup&gt;−5&lt;/sup&gt;</td>
<td>0.1</td>
<td>5</td>
<td>4.5</td>
<td>graphite plate–graphite plate</td>
</tr>
<tr>
<td>C</td>
<td>9.20 × 10&lt;sup&gt;−4&lt;/sup&gt;</td>
<td>6 × 10&lt;sup&gt;−5&lt;/sup&gt;</td>
<td>0.2</td>
<td>5</td>
<td>4.5</td>
<td>graphite plate–graphite plate</td>
</tr>
<tr>
<td>D</td>
<td>9.20 × 10&lt;sup&gt;−4&lt;/sup&gt;</td>
<td>6 × 10&lt;sup&gt;−5&lt;/sup&gt;</td>
<td>0.1</td>
<td>15</td>
<td>4.5</td>
<td>graphite plate–graphite plate</td>
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</tbody>
</table>
Infrared spectra of different muscovite samples (pH = 12, $c(\text{Sodium oleate}) = 9.20 \times 10^{-4}$ mol/L, $c(\text{Cu}^{2+}) = 6 \times 10^{-5}$ mol/L).

Sample A underwent the joint action of untreated copper ions and sodium oleate. As can be seen from Figure 9, the absorption peak of wave number 3629 cm$^{-1}$ corresponds to the vibration absorption peak of hydroxyl, and the other two peaks at 2935 cm$^{-1}$ and 2860 cm$^{-1}$ can be attributed to the vibration absorption peak of the C–H bond in the methyl group and methylene in sodium oleate, respectively [20,21]. Sample B, sample C and sample D had the joint action of treated copper ions and sodium oleate. Compared with sample A, the intensity of vibration absorption peak of the C–H bond corresponding to methylene and methyl groups of sodium oleate in sample B and C is significantly enhanced, indicating that the increased adsorption of sodium oleate on the sample surface. According to electrode reaction analysis, solution conductivity analysis, solution pH analysis and potential analysis, the reason is that electrochemical pretreatment conditions of the copper sulfate solution can inhibit the hydrolysis of copper ions, increase the Cu$^{2+}$ content in the copper sulphate solution, strengthen the Cu$^{2+}$ adsorption on the muscovite surface, and enhance electrostatic adsorption of sodium oleate on the muscovite surface, thereby strengthening the physical and chemical adsorption of sodium oleate on the muscovite surface.

3.6. XPS Analysis of Muscovite Samples

To understand the valence bond morphology of Cu$^{2+}$ on the muscovite surface before and after electrochemical pretreatment, XPS characterization was carried out on the muscovite samples treated with sodium oleate and untreated Cu$^{2+}$ and the electrochemically pretreated muscovite samples treated with Cu$^{2+}$. The conditions of activation are shown in Table 3, and the results are shown in Figure 10.

As can be seen from sample A in Figure 10, copper elements appeared on the surface of the sample after the action of copper ions, indicating that copper ions adsorbed on the surface of muscovite. Compared with sample A, the characteristic peaks of each element on the surface of sample B were changed. Therefore, the electron binding energy and relative content of the main elements on the surface of the sample were analyzed. The results are shown in Table 4.
which indicates that the chemical environment of Cu is changed by electrochemical pretreatment with appropriate conditions. In order to further understand the valence bond morphology of Cu on the muscovite surface after electrochemical pretreatment significantly increased. Compared with sample A, the content of carbon and copper on the surface of sample B increased by 11.26% and 0.34%, respectively. Copper ions and oleate ions adsorbed on the sample after the action of copper ions, indicating that copper ions adsorbed on the surface of sample B were changed. Therefore, the electron binding energy and relative content of the main elements on the surface of sample were analyzed. The results are shown in Table 4.

According to Table 4, compared with sample A, the content of carbon and copper on the surface of sample B increased by 11.26% and 0.34%, respectively. Copper ions and oleate ions adsorbed on the muscovite surface after electrochemical pretreatment significantly increased. Compared with sample A, it was also found that the binding energy of Cu2p3/2 on the surface of sample B was changed, which indicates that the chemical environment of Cu is changed by electrochemical pretreatment with appropriate conditions. In order to further understand the valence bond morphology of Cu on the muscovite surface, the paper divided the peak of the spectrogram of the copper element, and the results are shown in Figure 11 and Table 5.

![Figure 10](image1.png)

**Figure 10.** XPS spectra of muscovite samples (pH = 12, c(Sodium oleate) = 9.20 × 10^-4 mol/L, c(Cu^2+) = 6 × 10^-5 mol/L).

**Table 4.** Electron binding energy and relative content of major elements on the surface of the sample.

<table>
<thead>
<tr>
<th>Sample Numbers</th>
<th>C/(wt)%</th>
<th>Cu/(wt)%</th>
<th>Cu2p3/2/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>19.54</td>
<td>0.57</td>
<td>934.07</td>
</tr>
<tr>
<td>B</td>
<td>30.80</td>
<td>0.91</td>
<td>933.28</td>
</tr>
</tbody>
</table>

According to Table 4, compared with sample A, the content of carbon and copper on the surface of sample B increased by 11.26% and 0.34%, respectively. Copper ions and oleate ions adsorbed on the muscovite surface after electrochemical pretreatment significantly increased. Compared with sample A, it was also found that the binding energy of Cu2p3/2 on the surface of sample B was changed, which indicates that the chemical environment of Cu is changed by electrochemical pretreatment with appropriate conditions. In order to further understand the valence bond morphology of Cu on the muscovite surface, the paper divided the peak of the spectrogram of the copper element, and the results are shown in Figure 11 and Table 5.

![Figure 11](image2.png)

**Figure 11.** Peak-splitting fitting diagram of Cu2p3/2 on the muscovite surface. (a), without electrochemical pretreatment; (b), electrochemical pretreatment.
Table 5. Valence bond and proportion of Cu on mineral surface.

<table>
<thead>
<tr>
<th>Sample Numbers</th>
<th>Total Peak Area</th>
<th>Cu-OOCR Peak Area</th>
<th>Cu-OH Peak Area</th>
<th>Cu-OOCR Relative Content/%</th>
<th>Cu-OH Relative Content/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4166.69</td>
<td>1518.25</td>
<td>2648.44</td>
<td>36.44</td>
<td>63.56</td>
</tr>
<tr>
<td>B</td>
<td>6820.16</td>
<td>3205.89</td>
<td>3614.27</td>
<td>47.01</td>
<td>52.99</td>
</tr>
</tbody>
</table>

According to Figure 11 and Table 5, the Cu–OOCR valence bond appeared at the sample surface after the action of copper ions, indicating that the oleic acid group had chemical adsorption on the muscovite surface. Compared with sample A, the Cu–OOCR ratio on the surface of sample B was increased by 10.57%, which indicates that the content of copper oleate on the surface of muscovite increased after the electrochemical pretreatment of copper ions. The main reason lies in that electrochemical pretreatment of copper ion solution will inhibit the hydrolysis of copper ion and increase the concentration of copper ion in the solution, which will lead to the increase of adsorbed copper ion content on the muscovite surface and further strengthen the physical and chemical adsorption of oleic acid root on the muscovite surface [22].

4. Conclusions

(1) In $9.20 \times 10^{-4}$ mol/L sodium oleate system, electrochemical pretreatment of Cu$^{2+}$ solution can greatly enhance the activation of copper ions on muscovite when the electrolysis current is 0.1 A at the short electrolysis time.

(2) The electrochemical pretreatment of the Cu$^{2+}$ solution can inhibit the hydrolysis of copper ions, increase the content of Cu$^{2+}$ in the solution, strengthen the adsorption of Cu$^{2+}$ on the muscovite surface. The electrostatic adsorption of sodium oleate on the mica surface is enhanced, and then the physical and chemical adsorption of sodium oleate is also strengthened.

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References


