

## Research Article

# Coprecipitation Preparation of Cu/Zn/Al-Hydrotalcite-Like Compound for Copper Removal from Electroplating Wastewater

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Cu/Zn/Al-hydrotalcite-like compound (Cu/Zn/Al-HTlc) was prepared by the coprecipitation method with Zn<sup>II</sup>, Al<sup>III</sup> cations solution, and electroplating wastewater containing Cu<sup>II</sup> cation. The preparation conditions of Cu/Zn/Al-HTlc were optimized. The metal ion pollutants removal effect and iodide maximum adsorption capacity of Cu/Zn/Al-HTlc were also studied. The physicochemical properties of the Cu/Zn/Al-HTlc were analyzed by X-ray diffraction, FTIR, SEM, N<sub>2</sub> adsorption-desorption isotherms, and TG-DTG. The results showed that Cu/Zn/Al-HTlc should be prepared with the Zn<sup>II</sup>-Al<sup>III</sup> molar ratio of 1.5 : 1, pH = 11, and aged at room temperature for 0.5 d. Structural analysis showed that the Cu/Zn/Al-HTlc was a layered compound. Cu<sup>II</sup> and other metal ion pollutants can also be successfully removed from electroplating wastewater in the preparation process of Cu/Zn/Al-HTlc and reached Chinese National Emission Standard (GB 21900-2008). The optimal adsorption condition of calcinated Cu/Zn/Al-HTlc for iodide was as follows: the solid-liquid ratio was 1 : 250, the pH value was 8, and the adsorption process was carried out at 25°C for 30 min. The saturated adsorption capacity reached 1000 mg·g<sup>-1</sup> at the optimal adsorption condition. The main reason for this high-saturated adsorption capacity of Cu/Zn/Al-HTlc was that iodide penetrated into the layered structure of Cu/Zn/Al-HTlc by physical adsorption and Cu<sup>II</sup> undergoes a specific redox reaction, producing CuI. Hence, coprecipitation synthetic technology and prepared Cu/Zn/Al-HTlc could be potentially used for electroplating wastewater treatment.

## 1. Introduction

Heavy metal ions and organic substances are discharged by industrial activities, which could be consumed and accumulated in tissues of living organisms through the food chain [1–5]. Heavy metal ions entered waterbody through industrial wastes [6], among which electroplating wastewater needs the most attention [7]. Some heavy metal ions, such as copper, were necessary elements for human body, but excessive intake of Cu<sup>II</sup> may bring about chronic copper poisoning [8, 9]. The Chinese National Electroplating Wastewater Discharge Standard (GB21900-2008) made clear regulations that Cu<sup>II</sup> concentration must be less than 0.5 mg·L<sup>-1</sup> [10]. Therefore, the electroplating wastewater which can lead to health lesion must be properly treated and must be less than 0.5 mg·L<sup>-1</sup> prior to discharge. There are a lot of methods for heavy metal ions removal from electroplating wastewater [11], such as

precipitation [12], ion exchange [13], membrane separation [14], trapping, and electrochemical reduction [15]. However, these methods need high cost and may produce the secondary pollution. Therefore, efficient, low cost, and easy-to-operate electroplating wastewater treatment methods need to be urgently developed.

Iodine is one of the nuclides causing most concern among radioactive anions. <sup>129</sup>I was especially considered as one of the key radionuclides that dominates the long-term radiation in underground radioactive. The radioactive iodine can be introduced into the environment via accidents in nuclear facilities and was then absorbed by humans. Adsorption has been the most competitive method for removal of iodide in aqueous solution because of its simplicity, high efficiency, and availability [16, 17]. In recent years, various adsorbents capable of isolating iodide pollutants from aqueous solution, such as zeolite-based materials,

minerals, and layered double hydroxide, have been investigated [18–21].

The hydrotalcite (HT) and hydrotalcite-like compounds (HTLcs) are double hydroxide-layered structure compounds [22]. Due to the layered structure, they have good adsorption property. As adsorbents, they have been used to remove some metal ions and inorganic and organic anionic pollutants in recent years [23–27]. In addition, calcinated HTLcs have larger surface areas and alkaline centers. They also can reconstruct the layered structure by incorporating with available ions in the solution [28]. So a rational preparation technology should be developed, the technology is essential to reduce heavy metal ions concentration of electroplating wastewater, and the product HTLcs could be applied to iodide pollutants adsorption.

In this study, the preparation of Cu/Zn/Al-HTlc, optimum conditions, heavy metal ions removal capability, and iodide adsorption capacity were first reported.

## 2. Experimental

**2.1. Materials.** All chemicals were pure commercial products obtained from Aladdin. Deionized water was used in the experiment. Electroplating wastewater was obtained from electroplating enterprises.

**2.2. Preparation of HTlc.** The HTlc was prepared by the coprecipitation method. Firstly, different metal ion systems ( $\text{Zn}^{\text{II}}$ ,  $\text{Ca}^{\text{II}}$ ,  $\text{Fe}^{\text{III}}$ ,  $\text{Zn}^{\text{II}}\text{-Al}^{\text{III}}$ , and  $\text{Cd}^{\text{III}}\text{-Al}^{\text{III}}$ ) were selected together with electroplating wastewater (15.0 mL), and deionized water (30.0 mL) was placed in a beaker. Then, mixed solution was added dropwise into an aqueous solution of  $\text{NaCO}_3$  ( $0.25 \text{ mol}\cdot\text{L}^{-1}$ , 90.0 mL) under vigorous stirring, and the pH value was adjusted to 10 by adding  $\text{NaOH}$  ( $0.1 \text{ mol}\cdot\text{L}^{-1}$ ). The mixture solution was stirred for 30 min and left to age for 24 h at  $60^\circ\text{C}$ . The mixture was filtered, and the precipitate was washed with deionized water. Finally, the residue was dried and calcinated at  $400^\circ\text{C}$  for 3 h in a muffle furnace.

**2.3. Iodide Adsorption.** Calcinated HTlc (0.1 g) was placed in a 50 mL volumetric flask, and then different concentrations of KI solution (25.0 mL) were added. The mixture was shaken for 60 min and centrifuged. Subsequently, the supernatant (1.0 mL), deionized water (10.0 mL), and bromine water (2 drops) were added in a 50 mL volumetric flask. The mixed solution was shaken for 5 min. Formic acid (1.0 mL) was added in the mixture and shaken until the solution was colorless. Phosphate (2.0 mL) was then added and shaken up again. Finally, the aqueous solution of KI ( $1.0 \text{ mL}$ ,  $200 \text{ mg}\cdot\text{L}^{-1}$ ) was added and diluted to deionized water (50.0 mL). The reaction was proceeded for 30 min and then was measured by a UV-Vis spectrophotometer at 350 nm.

**2.4. Characterization of HTlc.** X-ray diffraction (XRD) patterns of the products were recorded by the X'pert PRO X-ray diffractometer at a scanning range of  $3\text{--}80^\circ \text{ min}^{-1}$ ,

operated at 40 kV and 40 mA. The Brunauer–Emmett–Teller (BET) surface area was measured by the  $\text{N}_2$  adsorption-desorption method using NOVA 3000 specific surface area analyzers. Scanning electron microscopy (SEM) was performed using a ZEISS Ultra55 emission-scanning electron microscope scanned at an acceleration voltage of 15 kV. Infrared spectrum was obtained using a TENSOR27 Fourier transform infrared spectrometer in the range of  $400\text{--}4000 \text{ cm}^{-1}$  employing the KBr dilution technique (1.5%, w/w). Thermogravimetric analysis was carried out at a heating rate of  $15^\circ\text{C min}^{-1}$  up to  $600^\circ\text{C}$  using a SDTQ600 thermal analyzer. The metal ions concentration was determined directly by inductively coupled plasma optical emission spectrometry (ICP-OES 710ES, Varian).

## 3. Results and Discussion

**3.1. Preparation of HTlc.** In this study,  $\text{Zn}^{\text{II}}$ ,  $\text{Ca}^{\text{II}}$ ,  $\text{Fe}^{\text{III}}$ ,  $\text{Zn}^{\text{II}}\text{-Al}^{\text{III}}$ , and  $\text{Cd}^{\text{III}}\text{-Al}^{\text{III}}$  were added in electroplating wastewater for HTlc preparation with the coprecipitation method, respectively. All coprecipitation products were characterized by X-ray diffraction (XRD), as shown in Figure 1. HTLcs have an X-ray diffraction peak at low angle  $2\theta$  [29]. However, coprecipitation products of electroplating wastewater or electroplating wastewater with  $\text{Zn}^{\text{II}}$ ,  $\text{Ca}^{\text{II}}$ ,  $\text{Fe}^{\text{III}}$ , and  $\text{Cd}^{\text{III}}\text{-Al}^{\text{III}}$  did not show the characteristic peak of HTLcs in corresponding XRD. In contrast, the coprecipitation product of electroplating wastewater and  $\text{Zn}^{\text{II}}\text{-Al}^{\text{III}}$  showed a sharp diffraction peak at low angle  $2\theta$ , and its interplanar distance was 0.7514 nm, which was attributed to the typical HTlc-stratified structure [27, 29]. The sharp and intense diffraction peak and corresponding interplanar distance were similar with standard Zn/Al-HT. At the same time, HTLcs was an important layered matrix represented by the general formula  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}[\text{A}^{n-}]_{x/n}\cdot m\text{H}_2\text{O}$ , where  $\text{M}^{2+}$  was a divalent cation such as  $\text{Mg}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$ , or  $\text{Co}^{\text{II}}$ ;  $\text{M}^{3+}$  is a trivalent cation such as  $\text{Al}^{\text{III}}$ ,  $\text{Cr}^{\text{III}}$ ,  $\text{Fe}^{\text{III}}$ , or  $\text{Ga}^{\text{III}}$ ; and  $\text{A}^{n-}$  is an anion of charge  $n$ , and they maintain charge neutrality by positively charged layers and exchangeable interlayer anions [30–32]. Consequently, the results of the XRD indicated that  $\text{Cu}^{\text{II}}$  exchanged parts of  $\text{Zn}^{\text{II}}$  together with  $\text{Zn}^{\text{II}}$  and  $\text{Al}^{\text{III}}$  constitute the layered Cu/Zn/Al-HTlc. It also shows that exogenous  $\text{Zn}^{\text{II}}\text{-Al}^{\text{III}}$  provides the good route to  $\text{Cu}^{\text{II}}$  of electroplating wastewater removal via the formation of Cu/Zn/Al-HTlc with layered structures.

**3.1.1. Effect of the  $\text{Zn}^{\text{II}}/\text{Al}^{\text{III}}$  Molar Ratio.** The XRD pattern of the three products, which were prepared by coprecipitation of electroplating wastewater and  $\text{Zn}^{\text{II}}\text{-Al}^{\text{III}}$  solution (molar ratio = 5 : 1, 2 : 1, 1.5 : 1), is shown in Figure 2(a). The XRD pattern result indicated that the diffraction angle of the three prepared products have sharp and symmetric peaks at low  $2\theta$  angles and broad and asymmetric peaks at higher  $2\theta$  angles which are characteristic of the layered structure, and they were similar to Zn/Al-HT [29]. It also can be seen that three products have intense diffraction peak, which indicated they have good degree of crystallization. All diffraction peak intensity and interplanar distance have no significant

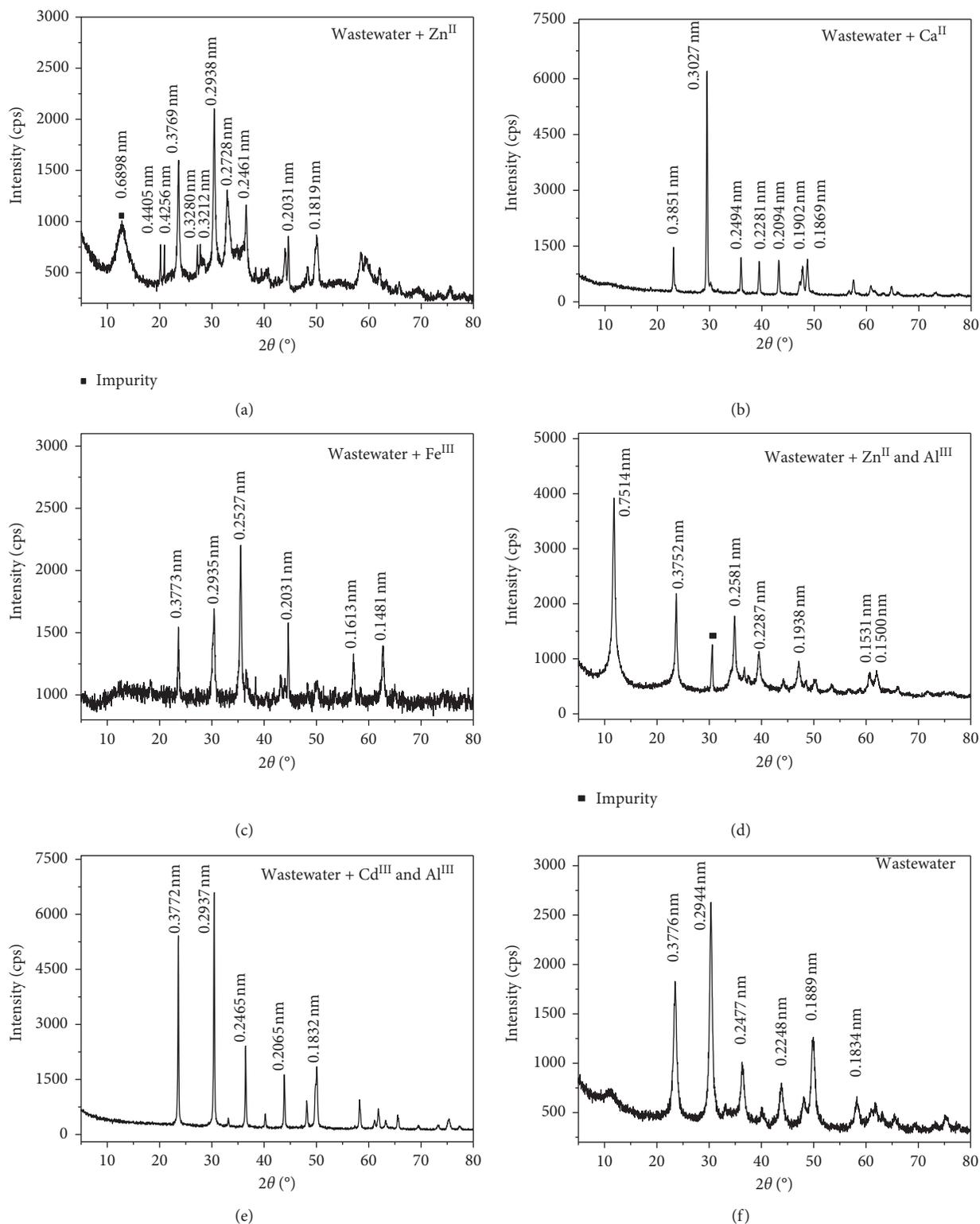


FIGURE 1: XRD pattern of precipitation of (a) Zn<sup>II</sup> and wastewater, (b) Ca<sup>II</sup> and wastewater, (c) Fe<sup>III</sup> and wastewater, (d) Zn<sup>II</sup>-Al<sup>III</sup> and wastewater, (e) Cd<sup>III</sup>-Al<sup>III</sup> and wastewater, and (f) wastewater.

difference in the XRD pattern of three products (Figure 2(a)). At low molar ratio, good degree of crystallization can also be obtained. Therefore, the Zn<sup>II</sup>-Al<sup>III</sup> molar ratio of 1.5:1 was used for Cu/Zn/Al-HTlc preparation.

**3.1.2. Effect of the pH Value.** The coprecipitation preparation of HTlcs needs to be achieved at a constant pH [33]. Consequently, different pH values (pH = 7, 8, 9, 10, 11, and 12) were chosen to evaluate the effect of the pH value to

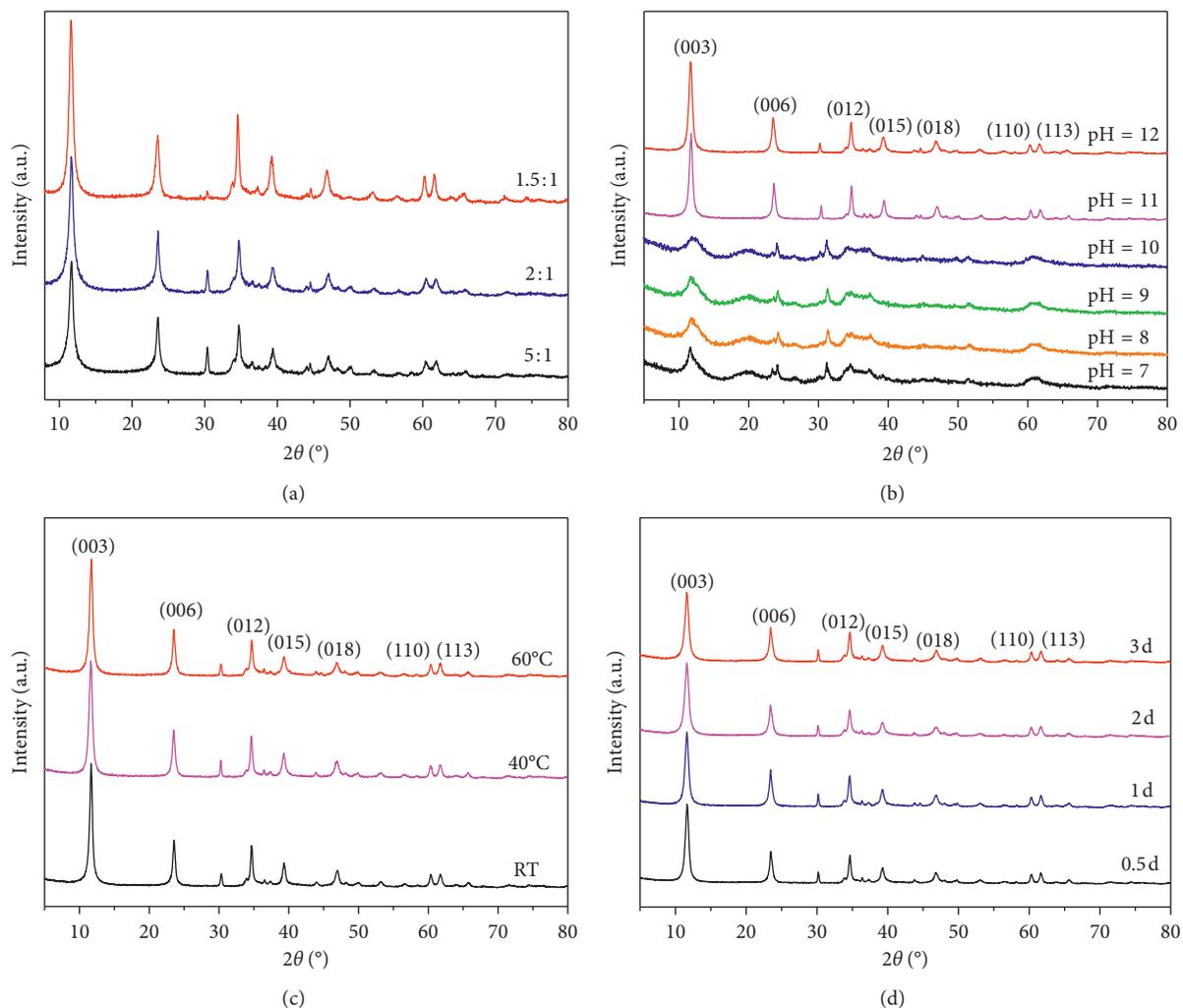


FIGURE 2: XRD pattern of Cu/Zn/Al-HTlc of different (a)  $Zn^{II}/Al^{III}$  molar ratios, (b) pH values, (c) aging temperatures, and (d) aging time periods.

Cu/Zn/Al-HTlc and then determined the optimal pH value. Figure 2(b) showed the effect of the pH value on Cu/Zn/Al-HTlc preparation. With the initial pH ranging from 7 to 10 in the preparation process, the yield of Cu/Zn/Al-HTlc increased and reached constant until pH 10. And it can be observed that their products have a weak diffraction peak, which indicated that they have low crystallinity at pH between 7 and 10. But two products have a sharp diffraction peak at the pH value of 11 and 12, and the crystallinity of product was better at the pH value of 11, which attributed to its higher diffraction peak. Therefore, the pH value of 11 was an ideal parameter for preparation Cu/Zn/Al-HTlc.

**3.1.3. Effect of Aging Temperature.** The three temperatures (room temperature, 40°C, and 60°C) were used to investigate the effect of the aging temperature for Cu/Zn/Al-HTlc preparation. The XRD pattern of products at the corresponding temperature was shown in Figure 2(c). It can be seen that three products have a high diffraction peak, and their intensity have no obvious difference in the XRD pattern, which indicated products have good crystallinity at three aging temperatures. At the same time, it was also found

that their yield was almost the same. Considering the convenience of the operation, the optimum preparation temperature was set at room temperature.

**3.1.4. Effect of Aging Time.** The aging time periods (0.5 d, 1 d, 2 d, and 3 d) were researched for Cu/Zn/Al-HTlc preparation. Figure 2(d) showed the XRD pattern of the corresponding product of four aging time periods. The diffraction peak intensity of all products was high and has no obvious difference, which demonstrated the aging time has not a certain effect on the crystallinity of Cu/Zn/Al-HTlc. In order to rapidly obtain Cu/Zn/Al-HTlc, 0.5 d was selected as the optimum aging time.

Therefore, the results of metal ions molar ratio, pH value, aging temperature, and aging time indicated that Cu/Zn/Al-HTlc can be prepared with the  $Zn^{II}/Al^{III}$  molar ratio of 1.5:1, pH = 11, and aging at room temperature for 0.5 d.

**3.2. Characterization of Cu/Zn/Al-HTlc.** The structure and thermal stability of Cu/Zn/Al-HTlc were confirmed by XRD, FTIR, SEM, EDS, and TG. The XRD diffraction parameters of

Cu/Zn/Al-HTlc and Zn/Al-HT were shown in Table 1. It can be observed that XRD diffraction parameters of Cu/Zn/Al-HTlc and Zn/Al-HT were similar, which could be attributed to similar ion radius of  $\text{Cu}^{\text{II}}$  and  $\text{Zn}^{\text{II}}$ . At the same time,  $\text{Cu}^{\text{II}}$  together with  $\text{Zn}^{\text{II}}$  constructed layers structure of the Cu/Zn/Al-HTlc, which leads to smaller change of interplanar distance, layer distance, and crystal cell size. It can be seen that  $d_{003}$ ,  $d_{006}$ , and  $d_{012}$  have good multiple relationship for the Cu/Zn/Al-HTlc, which indicated it has an excellent layer structure [29].

The FTIR spectrum of Cu/Zn/Al-HTlc was shown in Figure 3. As shown in the FTIR spectrum, the broad band is observed at  $3353\text{ cm}^{-1}$ , which was ascribed to the O-H stretching vibration of interlayer water molecules. There was also a vibration band at  $1632\text{ cm}^{-1}$ , assigned to the O-H bending vibration. The strong vibration band at  $1353\text{ cm}^{-1}$  was ascribed to interlayer  $\text{CO}_3^{2-}$  anions. The sharp bands at around  $772$ ,  $552$ , and  $428\text{ cm}^{-1}$  were caused by various lattice vibrations associated with metal hydroxide sheets [34].

The porous structures of calcinated Cu/Zn/Al-HTlc was analyzed by  $\text{N}_2$  adsorption-desorption curves in Figure 4(a). According to the IUPAC classification, the isotherm of calcinated Cu/Zn/Al-HTlc is classified as the type IV adsorption isotherm, indicating that it is a mesoporous material [35, 36]. The Brunauer-Emmett-Teller (BET) surface area of Cu/Zn/Al-HTlc reached  $60.16\text{ m}^2\cdot\text{g}^{-1}$ , which was closed to calcinate Mg/Al-HT [25]. The big surface area was crucial for the adsorption capacity because of more active sites. To further analyze the microstructural features of the material, the SEM image of Cu/Zn/Al-HTlc was studied. As shown in Figure 4(b), the expected platelet-like morphology of Cu/Zn/Al-HTlc was observed, which possess a relatively small average platelet size. The layered structure of Cu/Zn/Al-HTlc was in line with the typical hydroxalite morphology with irregular edges.

Furthermore, the energy dispersive X-ray spectra (EDS) of Cu/Zn/Al-HTlc demonstrated that the prepared Cu/Zn/Al-HTlc contained Mg, Al, Cu, Zn, Cd, and Cr elements, which indicated the layered structure of prepared Cu/Zn/Al-HTlc was also composed of Mg, Cd, and Cr elements of the electroplating wastewater.

Here, TG-DTG analyses were performed to evaluate thermal stability of Cu/Zn/Al-HTlc. The TG-DTG curve is shown in Figure 5. The results indicated that the Cu/Zn/Al-HTlc decomposed mainly in three stages. The first stage with 8.18% weight loss at about  $92.2^\circ\text{C}$  corresponded to the loss of physical adsorption water. The second stage with 7.43% weight loss centering at  $170.6^\circ\text{C}$  was due to the loss of interlayer water molecules without collapse of the hydroxalite structure. And the last stage with 10.24% weight loss after  $227.1^\circ\text{C}$  was due to the removal of the interlayer anions and hydroxyl groups [25, 37].

**3.3.  $\text{Cu}^{\text{II}}$  Removal from Electroplating Wastewater.** The  $\text{Cu}^{\text{II}}$  was removed from electroplating wastewater by preparation of Cu/Zn/Al-HTlc. And electroplating wastewater containing  $\text{Cu}^{\text{II}}$  together with exogenous  $\text{Zn}^{\text{II}}$  and  $\text{Al}^{\text{III}}$  formed the layered Cu/Zn/Al-HTlc by the coprecipitation method. At the same time, it was found that the best condition of  $\text{Cu}^{\text{II}}$

TABLE 1: The XRD diffraction parameters of Cu/Zn/Al-HTlc and Zn/Al-HT.

Parameters	Cu/Zn/Al-HTlc	Zn/Al-HT (standard card)
$d_{003}$ (nm)	0.7554	0.7550
$d_{006}$ (nm)	0.3789	0.3770
$d_{012}$ (nm)	0.2587	0.2587
$d_{110}$ (nm)	0.1534	0.1536
$a$ (nm)	0.3063	0.3072
$c$ (nm)	2.274	2.265
$\alpha$ ( $^\circ$ )	90	90
$\beta$ ( $^\circ$ )	90	90
$\gamma$ ( $^\circ$ )	120	120
Average particle size (nm)	21.7	—

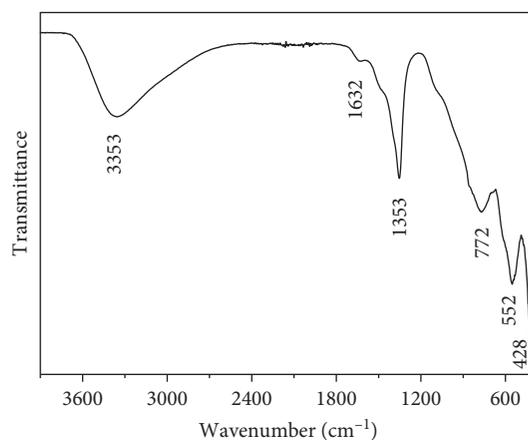


FIGURE 3: FTIR spectra of Cu/Zn/Al-HTlc.

removal was the same with the optimal preparation condition. To evaluate the  $\text{Cu}^{\text{II}}$  removal effect from the electroplating wastewater, the metal ion content of the Cu/Zn/Al-HTlc, electroplating wastewater, and residual liquid were determined by ICP-OES. The results of these measurements are presented in Tables 2 and 3. Table 2 showed that Cu/Zn/Al-HTlc contains  $\text{Zn}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Mg}^{\text{II}}$ ,  $\text{Al}^{\text{III}}$ ,  $\text{Cd}^{\text{II}}$ ,  $\text{Fe}^{\text{III}}$ , and  $\text{Cr}^{\text{III}}$  metal ion. Its mass ratio was identified as 1.442 : 0.129 : 0.103 : 0.007 : 1 : 0.082 : 0.002 : 0.038 by calculating metal ion content. Therefore, the chemical molecular formula of the Cu/Zn/Al-HTlc can be represented as  $\text{Zn}_{0.515}\text{Cu}_{0.046}\text{Ni}_{0.037}\text{Mg}_{0.002}\text{Cd}_{0.029}\text{Fe}_{0.001}\text{Al}_{0.357}\text{Cr}_{0.013}(\text{OH})_2(\text{CO}_3)_{0.185}\cdot 0.5\text{H}_2\text{O}$ .

Table 3 showed the concentrations of remaining  $\text{Zn}^{\text{II}}$  and  $\text{Al}^{\text{III}}$  of residual liquid were high. This result can be attributed to exogenous  $\text{Zn}^{\text{II}}$  and  $\text{Al}^{\text{III}}$  in the preparation process of Cu/Zn/Al-HTlc. But compared with electroplating wastewater, the concentrations of  $\text{Zn}^{\text{II}}$  and  $\text{Al}^{\text{III}}$  were greatly reduced, which indicated exogenous  $\text{Zn}^{\text{II}}$  and  $\text{Al}^{\text{III}}$  have not brought about secondary pollution. And the residual  $\text{Mg}^{\text{II}}$ ,  $\text{Al}^{\text{III}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$ ,  $\text{Fe}^{\text{III}}$ , and  $\text{Ni}^{\text{II}}$  concentrations have reached the national emission standards. The calculating result of chromium was little lower than electroplating wastewater, which due to  $\text{Cr}^{\text{VI}}$  exists in electroplating wastewater and have not participated in the preparation process of Cu/Zn/Al-HTlc. The analysis result indicated  $\text{Cu}^{\text{II}}$  and other metal ion pollutant can be successfully removed by Cu/Zn/Al-HTlc preparation, and all

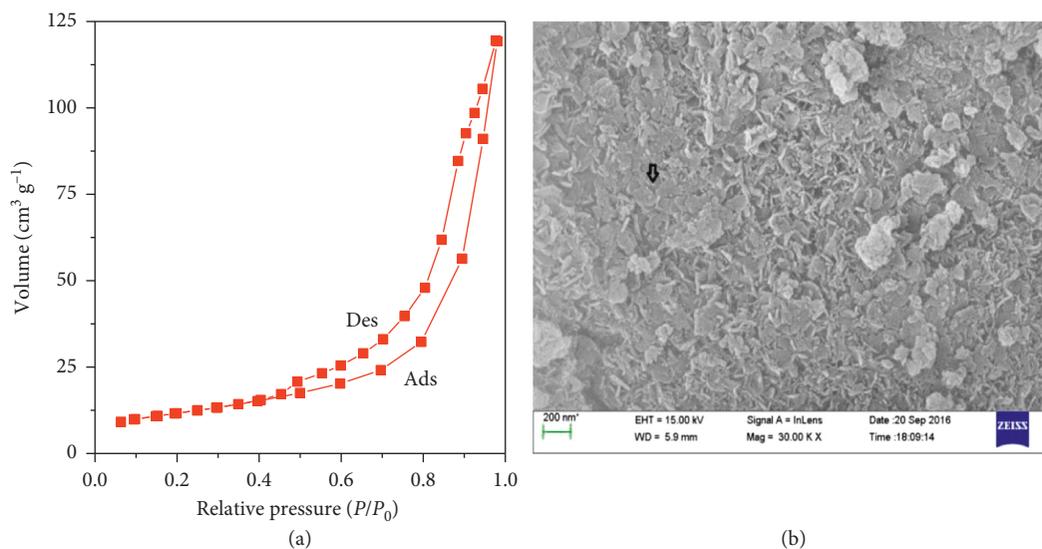


FIGURE 4: (a)  $N_2$  adsorption-desorption curves of calcinated Cu/Zn/Al-HTlc and (b) SEM images of typical platelet-like Cu/Zn/Al-HTlc.

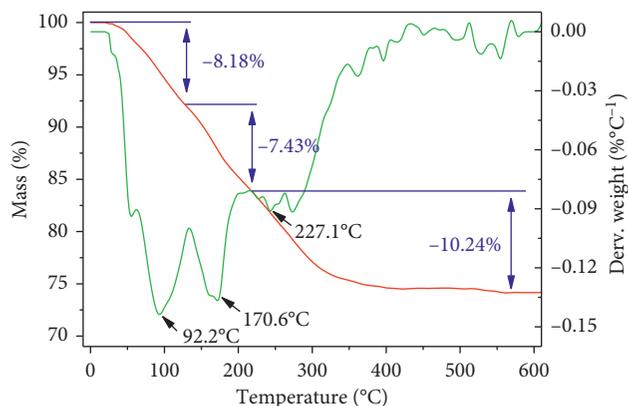


FIGURE 5: The TG-DTG curve of the Cu/Zn/Al-HTlc.

TABLE 2: The metal ions content of Cu/Zn/Al-HTlc.

Ions concentration ( $\text{mg}\cdot\text{kg}^{-1}$ )	Zn <sup>II</sup>	Cu <sup>II</sup>	Ni <sup>II</sup>	Mg <sup>II</sup>	Al <sup>III</sup>	Cd <sup>II</sup>	Fe <sup>III</sup>	Cr
Cu/Zn/Al-HTlc	400000	35200	25975	673.5	115222	39025	490.75	8482.5

TABLE 3: The metal ions concentration of the electroplating wastewater and remaining metal ions concentration of residual liquid.

Ions concentration ( $\text{mg}\cdot\text{L}^{-1}$ )	Zn <sup>II</sup>	Cu <sup>II</sup>	Ni <sup>II</sup>	Mg <sup>II</sup>	Al <sup>III</sup>	Cd <sup>II</sup>	Fe <sup>III</sup>	Cr
Electroplating wastewater	1487.7	2689.4	1946.8	38.9	185.7	3081.4	28.5	1177.3
Residual liquid	0.31	0.46	0.10	1.81	1.23	0.00	0.00	48.07

metal ions except Cr reached the Chinese National Electroplating Wastewater Discharge Standard (GB21900-2008).

**3.4. Iodide Adsorption of Cu/Zn/Al-HTlc.** Generally, Cu/Zn/Al-HTlc has good adsorption property. Firstly, the paper researched the adsorption condition (adsorption time, pH, solid-liquid ratio, and adsorption temperature) for iodide. Then, the maximum adsorption capacity was determined by the Langmuir model.

**3.4.1. Effect of the Adsorption Condition.** The adsorption time effect was evaluated from 0 to 120 min. The effect of solution pH on iodide adsorption was monitored at pH 4, 5, 6, 7, 8, 9, and 10, respectively. The effect of the solid-liquid ratio on iodide adsorption was evaluated by using different ratios (1:100, 1:150, 1:200, 1:250, and 1:300). The adsorption temperature effect was studied at 25°C, 35°C, 45°C, 55°C, and 65°C, respectively. The results were shown in Figure 6. As shown in Figure 6(a), when Cu/Zn/Al-HTlc was mixed with

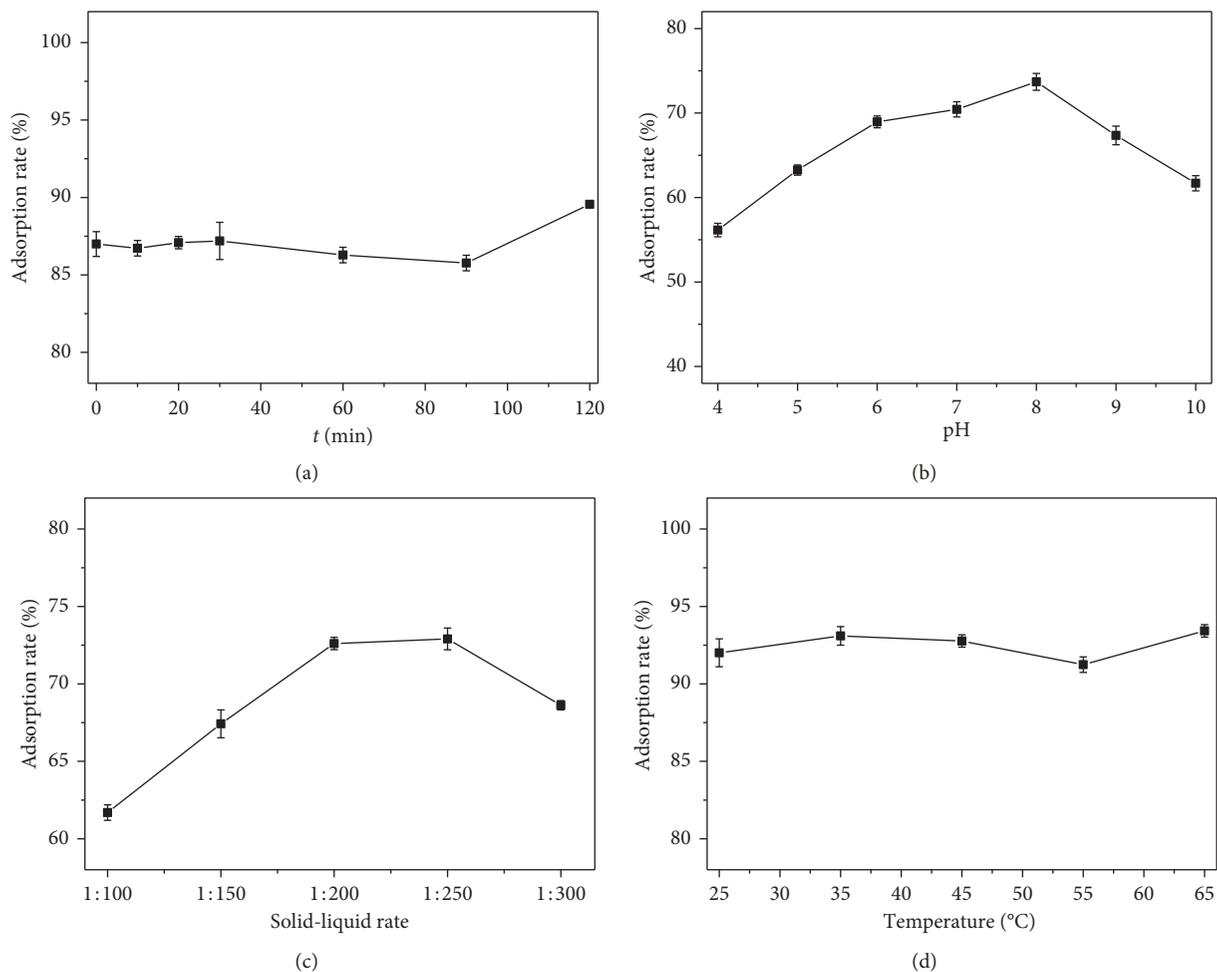


FIGURE 6: Effect of (a) adsorption time, (b) pH value, (c) solid-liquid ratio, and (d) adsorption temperature on the iodide adsorption.

iodide solution, adsorption rate achieved more than 85%. But because the surface adsorption activity of the Cu/Zn/Al-HTlc decreased, the adsorption efficiency had no obvious changes after 30 min. So the adsorption time of 30 min was chosen in this study. As shown in Figure 6(b), with the increasing pH value, the adsorption rate increased in the acidic condition, which was attributed to the reaction of the metal ion of the Cu/Zn/Al-HTlc with iodide. The adsorption rate reached a maximum value of 73.7% at pH = 8. As shown in Figure 6(c), with the increasing solid-liquid ratio, the adsorption rate increased. When the solid-liquid ratio was 1:250, the adsorption rate reached 72.9%. The adsorption rate was decreased when solid-liquid ratio was more than 1:250. So the optimal solid-liquid ratio was chosen to be 1:250. As shown in Figure 6(d), the adsorption rate curve indicated that the adsorption temperature has no obvious influence on adsorption rate. The iodide adsorption can proceed at room temperature. Consequently, the iodide adsorption experiment can be completed on the condition of 25 $^{\circ}\text{C}$ , pH = 8, solid-liquid ratio of 1:250, and adsorption time of 30 min.

**3.4.2. Adsorption Capacity.** The adsorption capacity of Cu/Zn/Al-HTlc for different concentration iodide solutions was measured. The results were shown in Figure 7. As shown in

Figure 7, the iodide concentration was 200 to 1400  $\text{mg}\cdot\text{L}^{-1}$ , and the iodide adsorption capacity of Cu/Zn/Al-HTlc was increased with the increasing iodide concentration. When iodide concentration reached 1400  $\text{mg}\cdot\text{L}^{-1}$ , adsorption capacity did not reach equilibrium, which indicated Cu/Zn/Al-HTlc has an excellent adsorption capacity.

In order to measure specific adsorption capacity, saturated adsorption capacity of Cu/Zn/Al-HTlc to iodide should be determined. Freundlich and Langmuir equations are common models to analyze the adsorption isotherm [22]. In this study, the two models were used to fit the experimental data. The Freundlich equation can be expressed in a linear form as shown in equation (1), where  $q_e$  ( $\text{mg}\cdot\text{g}^{-1}$ ) is the equilibrium adsorption capacity,  $C_e$  ( $\text{mg}\cdot\text{L}^{-1}$ ) is the equilibrium concentration, and  $k_f$  ( $\text{L}\cdot\text{mg}^{-1}$ ) and  $1/n$  are the Freundlich constant and heterogeneity factor:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e, \quad (1)$$

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{q_e}{q_m}. \quad (2)$$

The Langmuir isotherm model can be expressed in a linear form as shown in equation (2), where  $b$  ( $\text{mg}\cdot\text{L}^{-1}$ ) is the Langmuir adsorption constant and  $q_m$  ( $\text{mg}\cdot\text{g}^{-1}$ ) is the

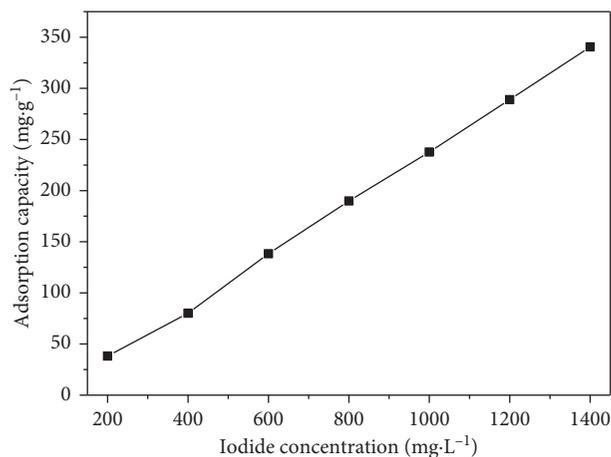


FIGURE 7: The curve of iodide adsorption capacity of Cu/Zn/Al-HTlc.

maximum adsorption capacity. By using equations (1) and (2), the iodide-saturated adsorption experiment results were fitted. The fitted results indicated the correlation coefficient of the Langmuir model and Freundlich model was 0.9990 and 0.9959, respectively. The results indicated that the Cu/Zn/Al-HTlc adsorption with iodide was effective monolayer sorption. The maximum adsorption capacity of iodide calculated by the Langmuir model for Cu/Zn/Al-HTlc was 1000 mg·g<sup>-1</sup>. It was higher than the reported iodide adsorbent [20, 21], which was attributed to iodide penetrated into the layered structure of Cu/Zn/Al-HTlc, and Cu<sup>II</sup> undergoes a specific redox reaction, producing CuI and indirectly enhancing the adsorption capacity for iodide. So Cu/Zn/Al-HTlc has better iodide adsorption property [38]. Hence, Cu/Zn/Al-HTlc could effectively treat iodide pollution in wastewater.

#### 4. Conclusions

Cu/Zn/Al-HTlc was successfully prepared by the coprecipitation method, and Zn<sup>II</sup>, Al<sup>III</sup>, and Cu<sup>II</sup> of electroplating wastewater contributed to the formation of the layered structure. Cu<sup>II</sup> pollutant was successfully removed from electroplating wastewater in the coprecipitation preparation process and reached Chinese National Emission Standard (GB 21900-2008). And the prepared Cu/Zn/Al-HTlc has good adsorption capacity for iodide. The maximum iodide adsorption capacity reached 1000 mg·g<sup>-1</sup> at the optimized condition by the Langmuir model. Consequently, it was a good technology for removal of the metal ion pollutant of the electroplating wastewater by using electroplating wastewater to prepared Cu/Zn/Al-HTlc. And the Cu/Zn/Al-HTlc also could be potentially used as an effective adsorbent of anion pollutants for electroplating wastewater.

#### Data Availability

The data used to support the findings of this study are included within the article.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

#### Authors' Contributions

D. B. and X. W. directed the project. D. B. and Q. Y. proposed and designed the project. D. B., D. H., N. W., B. X., and X. Z. carried out the experiment and analyzed the data through discussion with D. B. and X. W. All the authors discussed the results and contributed to the final version of the manuscript.

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