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Upcycling of Electroplating Sludge to Prepare Erdite-Bearing Nanorods for the Adsorption of Heavy Metals from Electroplating Wastewater Effluent

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Abstract: Electroplating sludge is a hazardous waste produced in plating and metallurgical processes which is commonly disposed of in safety landfills. In this work, electroplating sludge containing 25.6% Fe and 5.5% Co (named S1) and another containing 36.8% Fe and 7.8% Cr (S2) were recycled for the preparation of erdite-bearing particles via a facile hydrothermal route with only the addition of Na₂S·9H₂O. In the sludges, Fe-containing compounds were weakly crystallized and spontaneously converted to short rod-like erdite particles (SP1) in the presence of Co or long nanorod (SP2) particles with a diameter of 100 nm and length of $0.5-1.5 \ \mu m$ in the presence of Cr. The two products, SP1 and SP2, were applied in electroplating wastewater treatment, in which a small portion of Co in SP1 was released in wastewater, whereas Cr in SP2 was not. Adding 0.3 g/L SP2 resulted in the removal of 99.7% of Zn, 99.4% of Cu, 37.9% of Ni and 53.3% of Co in the electroplating wastewater, with residues at concentrations of 0.007, 0.003, 0.33, 0.09 and 0.002 mg/L, respectively. Thus, the treated electroplating wastewater met the discharge standard for electroplating wastewater in China. These removal efficiencies were higher than those achieved using powdered activated carbon, polyaluminum chloride, polyferric sulfate or pure Na₂S·9H₂O reagent. With the method, waste electroplating sludge was recycled as nanorod erdite-bearing particles which showed superior efficiency in electroplating wastewater treatment.

Keywords: electroplating sludge; hydrothermal process; heavy metal; electroplating wastewater; upcycling

1. Introduction

Electroplating is a basic process in the machine manufacturing industry and uses various heavy metals to protect plating pieces [1–4]. High volumes of electroplating wastewater are generated, which is an extremely hazardous type of wastewater containing multiple heavy metals [5]. Electroplating wastewater can be categorized into acidic or alkaline wastewater in accordance with the electroplating technology used. Acidic wastewater is easily treated through pH adjustment and coagulation, which transfer heavy metals from wastewater to sludges [2,3]. By contrast, alkaline wastewater comprises complex agents, such as citric acid, ethylene diamine tetra-acetic acid (EDTA) and tartaric acid [6,7], which react with heavy metals to form heavy metal–organic complexes. Thus, heavy metals cannot be hydrolyzed even after adjusting wastewater pH to values above 12. Therefore, heavy metals are difficult to precipitate in alkaline wastewater through pH adjustment and are commonly



treated using time-consuming processes, including pH adjustment, cationic exchange, extraction and/or precipitation with special agents [8–12]. Although the amount of heavy metals detected from the effluents of an electroplating workplace is usually low [10,13], heavy metals should be further removed until the discharge standard for electroplating wastewater is met.

The removal of heavy metals from alkaline electroplating wastewater generally involves two methods [14–21]. One is the decomposition of organic complex reagents by the Fenton reaction and/or wet oxidation [15–17]. For instance, Shin et al. [15] investigated the removal of a citrate–Ni complex in alkaline electroplating wastewater and found that, after the wastewater was adjusted to pH 3, 95% citrate removal was achieved by Fenton oxidation with the addition of 20 mM Fe^{2+} and 1080 mM H₂O₂, and subsequently 99.9% of Ni precipitation occurred when the wastewater was adjusted back to pH 10. Yong et al. also reported that more than 90% of Cu was precipitated after the decomposition of complex gluconic acid in a micro-electrolysis system [17]. Similarly, the derivatives of gluconic acid in the molasses-based distillery wastewater were effectively broken down by wet oxidation at a temperature above 150 °C [16]. Another method is the removal of heavy metals by adding special agents and/or functionalized resin [18–21]. For example, Li et al. [18] found that at a sodium diethyldithiocarbamate/Cu molar ratio of 1, approximately 99.6% of complex Cu (with EDTA as the coordination agent) is trapped by sodium diethyldithiocarbamate and precipitates during coagulation after the addition of polyferric sulfate and polyacrylamide. A few aminopolycarboxylic acids, such as iminodiacetic acid, nitrilotriacetic acid, and diethylenetriaminepentaacetic acid, include the necessary functionalized groups (e.g., carboxyl and amino) to chelate heavy metals [19]. Such organics were also grifted on the resin surface to considerably improve its affinity for heavy metals recycling from electroplating wastewater [20,21]. Although these methods can efficiently remove heavy metals from alkaline wastewater, they require expensive agents and complicated devices. Thus, their applications are limited. By contrast, adsorption is a low-cost process and has a simple operating method. Many adsorbents, such as natural minerals, carbon materials and artificial composites, exhibit a variety of surface groups (such as -OH and -COOH) to adsorb free heavy metals. These surface groups show relatively low affinity to heavy metals compared with complex agents and have low removal efficiencies in alkaline electroplating wastewater treatment [22]. Therefore, a novel adsorbent that can remove complex heavy metals should be urgently developed.

The resource reutilization of electroplating sludge for the preparation of novel adsorbents for electroplating wastewater treatment is a green route involving the "waste to treat wastewater" approach. This type of sludge is composed of heavy metals, precipitant reagent and hydrolyzed flocculant [23–25]. Fe/Al oxyhydroxide from hydrolyzed flocculants are usually used to adsorb free heavy metals in the absence of complex agents [24,25]. However, the reutilization of heavy metal-bearing sludges in alkaline electroplating wastewater has not yet been reported.

The aim of this study is to recycle Co/Cr-bearing sludge for the preparation of a novel erdite material that can be used in the advanced treatment of electroplating wastewater effluent. In contrast to conventional adsorbents, the novel erdite material can be spontaneously hydrolyzed in neutral solutions, thereby generating Fe/S-bearing oxyhydroxide with plenty of –SH groups for heavy-metal coordination. The release of Co and Cr in the prepared erdite materials was investigated during wastewater treatment.

2. Materials and Methods

2.1. Electroplating Sludge Pre-Treatment

The Co-bearing sludge, denoted as S1, was precipitated from the wastewater of a rolling-anode plant (Sanhe company, Changchun, China). The wastewater was first treated with a resin filter (CH-90, Kaiping company, Shanghai, China) to recycle Co, and then coagulated with the addition of polyferric sulfate and polyacrylamide. A yellowish precipitate was generated after coagulation treatment and pumped to a plate and frame filter (XAMY6/450-30U, Runnan company, Shanghai, China)

to perform mechanical dewatering. Thus, the yellowish cake of S1 was generated and stored in the northwestern corner of the waste yard before transport and landfilling. The Cr-bearing sludge, named S2, was generated from the wastewater of the electroplating workshop (Sanhe company, Changchun, China). For Cr recovery, a resin filter (RS10, Kaiping company, Shanghai, China) was also employed to treat the wastewater, and then the effluent was further treated with the coagulation and dewatering process with the abovementioned procedures. The generated Cr-bearing sludge cake was placed at the south side of the waste yard.

The two sludges, S1 and S2, were vacuum-dried at 50 °C overnight and ground to pass through a 1 mm mesh. The powder of each sludge was analyzed by X-ray fluorescence (XRF, S4-Explorer, Bruker, Karlsruhe, Germany); only the diffraction intensity of metallic elements was recorded, except for the nonmetal elements C, H and O. For S1, the percentage of total metallic elements was about 36.31%, whilst the residual in S1 was affiliated with the coordinated groups (e.g., oxide/oxyhydroxide, sulfate and chloride) and the added polymeric flocculant. S2 showed a similar composition to S1, and the major elements are summarized in Table 1. S1 contains 25.6% Fe and 5.5% Co, demonstrating that S1 is a Fe/Co-rich sludge, whereas S2 is a Fe/Cr-rich sludge with 36.8% Fe and 7.8% Cr.

Element	Relative Weight Percentage (wt.%)	
	S 1	S2
Fe	25.6	36.8
Cr	0.06	7.8
Co	5.5	0.04
Ca	0.5	1.3
Si	0.9	1.1
Al	2.05	2.78
Na	1.7	1.4

Table 1. Sludge composition.

2.2. Hydrothermal Conversion of Sludge

S1 and S2 were hydrothermally treated in accordance with our previous method [26,27] with the replacement of NaOH by Na₂S. In brief, S1 (1 g), Na₂S·9H₂O (2.4 g) and deionized water (30 mL) were mixed in a 50 mL Teflon vessel. Then, the vessel was sealed and heated at 180 °C for 10 h in a drying oven (DHG-9037A, Jinghong company, Shanghai, China) and water-cooled to below 25 °C. Finally, the blackish particles at the vessel bottom were collected, freeze-dried at -80 °C in a freeze dryer (FDU-2110, EYELA, Tokyo, Japan) overnight and denoted as SP1. SP2 was hydrothermally treated in accordance with the abovementioned steps, and the obtained product was named SP2.

2.3. Heavy Metal Release

In the Sanhe company, heavy-metal-bearing wastewaters were mixed in a storage tank to generated a comprehensive electroplating wastewater, in which Zn, Cu, Ni, Co and Cr values were 711.5, 36.8, 131.2, 2.7 and 0.9 mg/L. The comprehensive electroplating wastewater was alkaline at pH 13.5, and adjusted to pH 7–7.5 by adding hydrochloric acid (9.8 M, Binghai chemical Group, Jinhua, China), in accordance with the optimal pH range of the resin filter (KP752, Kaiping company, Shanghai, China) operation. The wastewater was then treated with resin (KP752, Kaiping company, Shanghai, China) for the recycling of heavy metals and precipitated with polyferric sulfate. After treatment, the pH of the electroplating wastewater effluent was 7.3, and the concentrations of Zn, Cu, Ni, Co and Cr were 3.03, 0.51, 0.56, 0.19 and 0.003 mg/L, respectively. In the effluent, the concentrations of Zn, Cu and Ni exceeded the emission standard of pollutants for electroplating in China (GB21900-2008). Thus, the effluent needed to be further treated before discharge.

In total, 0.8 g/L of SP1 and SP2 adsorbents were added to 100 mL of electroplating wastewater, and the mixture was magnetically stirred at 90 rpm for 2 h; then, SP1 and SP2 were collected and

freeze-dried after the reaction. The dried SP1 and SP2 were respectively put into 50 mL deionized water until the concentration was 0.3 g/L and stirred magnetically for 24 h. Then, the concentration of heavy metals in the supernatant was determined by an inductively coupled plasma optical emission spectrometer (ICP-OES, AVIO-200, PerkinElmer, Waltham, MA, USA).

2.4. Electroplating Wastewater Treatment

The effluent was treated by placing SP1 in 50 mL of effluent until the SP1 concentration was 0.05 g/L. The mixture was magnetically stirred at 90 rpm for 2 h, and SP1 was separated by centrifuging at 6000 rpm for 5 min. Subsequently, the supernatant was collected, and the residual heavy metals in the supernatant were determined. According to the aforementioned steps, heavy metal removal was optimized by varying the SP1 dosage from 0.05 g/L to 0.8 g/L. Then, the dosage of SP2 on the effluent treatment was also investigated according to the abovementioned steps. Powdered activated carbon is a commercial adsorbent and is used in mass production in the project-scale advanced treatment of electroplating wastewater [28,29]; thus, it was targeted as the control in the experiment. After that, several common chemical reagents and the raw sludge were used to treat the electroplating wastewater, including polyaluminum chloride (PAC) [30], polyferric sulfate (PFS) [31] and Na₂S·9H₂O [32]. The experimental conditions are similar to the above, but the dose of the chemical reagent was 0.8 g/L, and the mixture was magnetically stirred at 90 rpm for 2 h.

2.5. Kinetic Experiment

A dose of 0.05 g/L SP2 was added to 50 mL electroplating wastewater, and the mixture was magnetically stirred at 90 rpm. The heavy metal concentration in the supernatant was measured at 0.25 h, 0.5 h, 1 h, 1.5 h and 2 h, respectively.

2.6. Adsorbent Regeneration

Adsorbent regeneration was carried out by treating with 15% NaCl of pH 5 for 48 h or calcining at 450 °C for 2 h. The adsorbent after regeneration treatment was put into 50 mL electroplating wastewater with a dose of 0.8 g/L and a reaction time of 2 h. After the reaction, the residual heavy metal concentration in the supernatant was measured.

2.7. Zeta Potential Measurement

In total, 0.5 g/L of SP2 was added to deionized water at pH 5 and magnetic stirring was performed, and the zeta potential of SP2 was measured by a zeta potential analyzer (Zetasizer Nano ZSP, Malvern, UK) at 30 min, 60 min, 180 min and 300 min, respectively.

2.8. Characterisation

The conversion mechanism was explained by characterizing the sludge and products by scanning electron microscopy (SEM, JSM-6400, Jeol, Tokyo, Japan), X-ray diffraction (XRD, Rint2200, Rigaku Corporation, Tokyo, Japan) and X-ray photoelectron spectroscopy (XPS, ADES-400, VG Scientific, Birmingham, Britain).

3. Results and Discussion

3.1. Conversion of the Two Types of Sludge to Erdite-Bearing Particles

The morphology and compositions of the sludges are shown in Figures 1 and 2. S1 was an irregular block (Figure 1a) and did not show the obvious peaks of Fe/Co-bearing compounds (Figure 2, S1). The Fe/Co-bearing compounds in S1 exhibited weakly crystallized forms. S2 showed fine particles (Figure 1b), and its XRD patterns were similar to those of S1 (Figure 2, S2) and corresponded to weakly crystallized Fe/Cr-bearing compounds. After hydrothermal treatment, SP1 synthesized using S1 as raw sludge was characterized by short rod-like particles (Figure 1c), with obvious peaks of erdite and

sulfur (Figure 2, SP1). In comparison with SP1, SP2 from S2 showed long nanorods with diameters of 100 nm and lengths of 0.5–1.5 μ m (Figure 1d). These products corresponded to the sharp peaks of erdite in the curve of SP2 (Figure 2, SP2). These findings demonstrated that Fe was involved in the formation of amorphous Fe-bearing compounds in S1 and S2. These Fe-bearing compounds were converted to well-crystallized erdite particles, which were short in SP1 and lengthened in SP2.



Figure 1. Scanning electron microscope (SEM) images of (a) S1, (b) S2, (c) SP1 and (d) SP2.



Figure 2. X-ray diffraction (XRD) patterns of S1, S2, SP1 and SP2.

The two types of sludge and the prepared SPs (SP1 and SP2) were further characterized by XPS. The Fe 2p spectra of S1 and S2 showed that the indicative peak at the binding energy of 710.5 eV (Figure 3a, S1 and S2) corresponded to Fe³⁺ in the Fe–O bond and was similar to that in ferrihydrite [33]. After the hydrothermal process, SP1 showed a new peak at the binding energy of 707.8 eV (Figure 3a, SP1). The peak belongs to Fe³⁺ in the Fe–S bond, in accordance with erdite formation. Compared with SP1, SP2 showed an intensified peak of Fe³⁺ in Fe–S bond (Figure 3a, SP2), in agreement with the long rod-sharped erdite. For the S 2p spectra, SP1 and SP2 showed the four major peaks at binding energies of 160.4, 161.3, 163.2 and 167.4 (Figure 3b) corresponding to the S in the Fe–S bond of the (FeS2)nⁿ⁻ structure, and S²⁻, sulfur and S in sulfate, respectively. In the Co 2p spectra, a major peak at 782.1 eV with a satellite peak was observed at the curve of S1 (Figure 3c, S1). The peak was related to the Co–O bond [34]. After hydrothermal treatment, new peaks related to Co in the Co–S bond appeared in SP1 at 778.6 eV (Figure 3c, SP1) [34], indicating the involvement of Co in CoS and/or CoS₂ after the addition of Na₂S. In the Cr 2p spectra, S2 exhibited two major peaks at 577.3 and 579.8 eV (Figure 3d,

S2). The peaks were attributed to the Cr(III) and Cr(VI) [35], respectively. However, the peak of Cr(VI) disappeared during the hydrothermal process, and only the peak of Cr(III) remained in SP2 (Figure 3d, SP2), indicating the reduction of Cr(VI) to Cr(III) by Na₂S·9H₂O.



Figure 3. High resolution (**a**) Fe 2p, (**b**) S 2p, (**c**) Co 2p and (**d**) Cr 2p X-ray photoelectron spectroscopy (XPS) curves of S1, S2, SP1 and SP2.

Fe-bearing compounds were rich in S1 and S2 and converted into erdite in four steps. Firstly, the added Na₂S was hydrolyzed to release OH⁻ and HS⁻ to the solution, increasing the solution pH to above 13.6. Thus, many OH⁻ ions in the solution attacked the surface Fe at the Fe-bearing mineral and generated $Fe(OH)_4^-$ (Equation (1)) in the solution [36]. This result indicated the presence of residual Fe (approximately 15 mg/L) in the solution after the hydrothermal process (Figure 4). Secondly, a replacement reaction between free HS⁻ and the hydroxyl group of Fe(OH)₄⁻ occurred, thereby generating $Fe(OH)_3HS^-$ (Equation (2)), followed by the conjunction reaction between two adjacent $Fe(OH)_3HS^-$ compounds. Thus, $Fe_2S_2(OH)_4^{2-}$ was generated with the dewatering of two water molecules (Equation (3)) [37]. Finally, the conjunction reaction continued in the presence of sufficient $Fe(OH)_4^-$ to form the final product $(FeS_2)_n^{n-1}$. Na⁺ neutralized the free charge of $(FeS_2)_n^{n-1}$, and free water molecules occupied the free channels in the structure of $(FeS_2)_n^{n-1}$, resulting in erdite nanorod formation. Cr(VI) was reduced by free HS⁻ in SP2, thereby generating Cr(III) with the generation of OH⁻. This reaction employed plenty of OH⁻ during the Fe(OH)₄⁻ formation, thereby increasing the length of the erdite nanorods in SP2. Conversely, the reaction between Co and HS⁻ in SP2 also occurred without OH⁻ generation, the contribution of which in erdite formation was negligible. During the hydrothermal process, Si/Al-bearing compounds were dissolved [38], thereby forming $Si(OH)_4$ and $Al(OH)_4^-$ in accordance with the high concentration of Si/Al in the supernatant (Figure 4). The dissolved Si/Al was not involved in erdite formation.

$$Fe(OH)_3 + OH^- \to Fe(OH)_4^- \tag{1}$$

$$\operatorname{Fe}(\operatorname{OH})_{4}^{-} + \operatorname{HS}^{-} \to \operatorname{Fe}(\operatorname{OH})_{3}\operatorname{HS}^{-} + \operatorname{OH}^{-}$$
 (2)

$$2Fe(OH)_3HS^- \rightarrow 2H_2O + (Fe_2S_2(OH)_4)^{2^-}$$
 (3)



Figure 4. Concentrations of heavy metals in the supernatant after the hydrothermal process.

3.2. Adsorption of Cu, Zn, Ni and Co from Electroplating Wastewater Effluent

In order to study the adsorption stability of SP1 and SP2, the release of heavy metals in used SP1/SP2 after electroplating wastewater treatment was investigated. After stirring at 90 rpm for 24 h, Co was apparently released from used SP1, and its concentration was close to 0.7 mg/L, whist only 0.003 mg/L Co was released from used SP2. Other heavy metals—e.g., Zn, Cu, Ni and Cr—were at a level lower than 0.01 mg/L (Figure 5). This demonstrated that the used SP2 showed a stable adsorption performance in the electroplating wastewater treatment.



Figure 5. Heavy metals released from SP1/SP2 after electroplating wastewater treatment.

The electroplating wastewater contained 3.03 mg/L Zn, 0.51 mg/L Cu, 0.56 mg/L Ni and 0.19 mg/L Co. The first three heavy metals needed to be treated further because their concentrations exceeded the discharge standard for electroplating wastewater in China (GB21900-2008), and the concentration of Co met the discharge standard. The prepared adsorbents, SP1 and SP2, were employed to remove the first three heavy metals form electroplating wastewater, with powdered activated carbon as reference. At a dose of 0.05 g/L, the removal efficiency of Zn was 77.8% for SP2, 69.1% for SP1 and 29.1% for powdered activated carbon (Figure 6a). SP2 showed a high Zn removal efficiency in comparison with SP1 due to the formation of a well crystallized erdite nanorod in SP2. The mechanism for heavy metals removal by the erdite nanorod will be detailed in the next section. With the dosage increased from 0.05 to 0.3 g/L, the removal efficiency of Zn was elevated to nearly 100% for both SP1 and SP2, but only to 56.5% for powdered activated carbon (Figure 6a). In addition, a comparison experiment between SP2 and other materials were also performed, and their effects on Zn removal were sorted in the following order: $SP2 > polyaluminum chloride (PAC) > Na_2S \cdot 9H_2O > Polymeric ferric sulfate$ (PFS) > S2 > S1. As mentioned in Section 1, Zn was complexed with organic reagents (e.g., citric acid, EDTA and tartaric acid) in the alkaline electroplating process, and thus was not spontaneously precipitated in the generated alkaline wastewater. For the advanced treatment of electroplating wastewater, powdered activated carbon was widely used because it has plenty of surface functional groups; e.g., –COOH, –C=O and –OH, for Zn coordination. However, it showed a low Zn removal

efficiency (<64.7%), even though its dosage was increased to 0.8 g/L, in comparison with SP1 and SP2 (Figure 6a). This demonstrated that these surface groups on powdered activated carbon had a normal affinity to adsorbing Zn in comparison with the complexed organic reagents in wastewater. Ibrado et al. reported that the adsorption capacity of Zn on coconut-derived carbon was nearly 5 mg/g, but this decreased rapidly to 1.7 mg/g in the presence of cyano due to the formation of cyano complexes of Zn [39]. Therefore, the residual Zn was stable in the Zn-complex ligands and did not react with the surface groups of powdered activated carbon [40]. In electroplating wastewater treatment, PAC and PFS were common coagulants, and spontaneously hydrolysed to generate Al/Fe-bearing flocs. The raw sludge, S1 and S2, was rich in weakly crystallized Fe oxyhydroxides. Such Al/Fe-bearing flocs and Fe oxyhydroxides contained abundant of surface hydroxyl groups, similar to powdered activated carbon, for heavy metals adsorption [41]. In addition, Na₂S·9H₂O was an industrial chemical, and decomposed to HS⁻ in water, followed by reacting with free Zn to form ZnS precipitate [42], which was in accordance with the removal efficiency of 52.7% for Zn. In summary, the surface functional groups on powdered activated carbon, hydrolysed PAC and PFS, S1 and S2, along with free HS⁻ from Na₂S, were not particularly efficient in the removal of Zn from electroplating wastewater.

In the electroplating wastewater, Cu was at a low level in comparison with Zn, and was removed at a rate of nearly 100% with the addition of SP1 and SP2 at the dosage of 0.3 g/L. However, only 25.5% Cu removal was achieved by powdered activated carbon in the presence of chelating organics in wastewater (Figure 6b). Chu et al. employed coal-based carbon for Cu-bearing wastewater treatment and found that by adding EDTA at the M_{EDTA}/M_{Cu} ratio of 10, the Cu removal efficiency dropped dramatically from 83.7% to 16.5% [43]. The abovementioned materials—e.g., PAC, PFS, Na₂S·9H₂O, S2 and S1—were also employed for Cu removal, showing similar values to those achieved for Zn removal. The atomic radius of Cu is 1.28 pm, which is close to that of Zn (1.39 pm), and thus Cu showed similar complex performance and removal efficiency to that of Zn in wastewater.

Although Ni was at a low level in wastewater—similar to Cu—its removal efficiency was apparently lower than that of Cu. As shown in Figure 6c, at the maximum dosage of 0.8 g/L, the removal efficiency of Ni was 49.6% for SP2, 44.3% for SP1 and 27.4% for powdered activated carbon. In the comparison experiment, the removal efficiency of Ni was ranked as follows: SP2 > PFS > PAC > Na₂S·9H₂O > S2 > S1. Compared with Cu and Zn, Ni has a smaller atomic radius (1.24 pm) and easily reacts with chelating organics to form more stable Ni-complexed ligands. For instance, in citric acid, the stability constant of Ni in citric acid is $log K_{NiH_3A}^{Ni}$ 1.75, which is higher than that of Zn (1.25) [44]. In terms of Ni removal efficiency, Na₂S·9H₂O only achieved 7.5%, which was lower than that of PAC and PFS and close to that of S1 and S2. This is because NiS was metastable in aqueous solution and easily converted to an Ni₂S₃ and Ni-S-bearing mixture to redissolve in wastewater [45]. S1 and S2 showed low removal efficiencies for Ni in comparison with PAC and PFS due to the inadequacy of surface hydrogen groups.

The Co concentration was less than 0.5 mg/L, which met the discharge standard. Approximately 60% of Co was removed by adding SP2, which is higher than the value for powdered activated carbon (nearly 20%) (Figure 6d). However, by adding 0.8 g/L SP1, the Co concentration in the treated wastewater was 0.77 mg/L (Figure 6e), which was apparently higher than that in the raw wastewater (0.19 mg/L), suggesting the release of Co from SP1 to wastewater, probably from the dissolution of CoS and/or CoS₂. Thus, SP1 was not an ideal adsorbent for the effluent treatment. The abovementioned materials were also used for Co removal, as shown in Figure 6f, and showed a similar value as Ni due to the similar radius and chelating performance of Co and Ni [44].



Figure 6. Application of SP1 and SP2 in electroplating wastewater treatment. (\mathbf{a} - \mathbf{d}) represent the removal efficiencies of Zn, Cu, Ni and Co, respectively, by SP1 and SP2, whilst (\mathbf{e}) shows the concentration of Co in the supernatant with the addition of SP1; (\mathbf{f}) shows the removal of heavy metals by adding SP2 in comparison with polyaluminum chloride (PAC), polyferric sulfate (PFS), the raw sludge S1 and S2 and Na₂S·9H₂O of chemically pure grade.

In comparison with the abovementioned materials, SP2 exhibited desirable removal efficiencies of Zn, Cu, Ni and Co. By adding 0.3 g/L SP2, the residual concentrations of Zn, Cu, Ni, Co and Cr in the wastewater were 0.007, 0.003, 0.33, 0.09 and 0.002 mg/L, respectively, which met the discharge standard [13]. This demonstrated that SP2 was an efficient reagent in smelting wastewater treatment.

The kinetic experiment of SP2 was investigated as shown in Figure 7, and the adsorption of heavy metal on SP2 was simulated using a pseudo-second-order model (Equation (4)). The kinetic model was expressed as follows:

$$q_t = \frac{kq_e^2 t}{1 + kq_e t} \tag{4}$$

where q_e and q_t are the adsorption capacity (mg/g) of the heavy metal at equilibrium and at any time, t, respectively; and k is the pseudo-second-order adsorption rate constant (g/mg h).



Figure 7. Non-linear plots of the pseudo-second-order model for the adsorption of Zn/Cu on SP2.

The adsorption data of Zn, Cu, Ni and Co on SP2 fitted well with the pseudo-second-order model (Figure 7) with correlation coefficients (\mathbb{R}^2) of 0.995, 0.997, 0.991 and 0.989, respectively. This finding indicates the importance of heavy metals chemisorption on SP2. However, the calculated q_e values were in the following order: Zn > Cu > Ni > Co. The value of Zn was 3.03 mg/L in the electroplating wastewater, which was about six times the value of Cu and Ni, and thus showed the highest q_t . In comparison with Cu, Ni and Co have small ionic radii and are easily complexed with organics (e.g., ethylene diamine tetra-acetic acid) to form a stable complex product [6], resulting in a low q_t in comparison with Cu.

The used SP2 was regenerated with 15% NaCl solution at pH 5 for 48 h or calcinated at 450 °C for 2 h. The results showed that SP2 was regenerated easily using NaCl solution as the desorption agent. However, the removal efficiency of Zn, Cu, Ni and Co was dramatically decreased to 33.2%, 27.5%, 11.3% and 18.6% (Figure 8). After being calcinated at 450 °C, the regenerated SP2 also showed a similar low removal efficiency of heavy metals. This indicated that SP2 cannot feasibly be reused.



Figure 8. Reuse of the precipitate of hydrolyzed SP2 for electroplating wastewater treatment. In the figure, Methods 1 and 2 represent NaCl solution elution and high-temperature calcination, respectively.

The zeta potential measurement of SP2 showed that SP2 had a negative charge on the surface after hydrolysis (Figure 9), which showed a strong adsorption capacity for positively charged heavy metals. In addition, SP2 can compete with chelates for binding heavy metals and then remove heavy metals from wastewater.



Figure 9. Zeta potential of SP2 in deionized water.

3.3. SP1 and SP2 Characterisation after Electroplating Wastewater Treatment

SP1 and SP2 were collected after wastewater effluent treatment and characterized by SEM, XRD and XPS, and the removal mechanism of heavy metals was investigated. The used SP1 and SP2 were irregular aggregates (Figure 10a,b); the peaks of erdite disappeared, and only peaks of element sulfur remained (Figure 11). Thus, erdite was spontaneously hydrolyzed. SP1 and SP2 spectra showed that

the peaks of Fe^{3+} in the Fe–S bond of erdite were absent; instead, a new peak with a binding energy of 710.2 eV appeared (Figure 12), corresponding to the Fe^{2+} generated from the redox reaction of Fe^{3+} –S [46]. The typical peak of structural S in erdite also disappeared, and the peaks of S^{2-} and S were recorded in the curve of SP1 and SP2, in agreement with erdite hydrolysis (Figure 12). In addition, the peaks of Co and Cr did not change obviously in SP1 and SP2, respectively, indicating that Co/Cr oxidation did not occur (Figure 13).



Figure 10. SEM images of (a) SP1 and (b) SP2 after smelting wastewater treatment.



Figure 11. XRD patterns of SP1 and SP2 after electroplating wastewater treatment.



Figure 12. High resolution (**a**) Fe 2p, (**b**) S 2p XPS spectrum of SP1 and SP2 after smelting wastewater treatment.





Figure 13. High resolution (a) Co 2p, (b) Cr 2p XPS spectrum of SP1 and SP2 after smelting wastewater treatment.

In the electroplating wastewater effluent, the residual heavy metals included Zn, Cu, Ni and Co and were chelated with organic matters, such as nitrilotriacetic acid and citric acid [6,7]; as such, they did not precipitate even at an effluent pH of >7.3. When the prepared SPs were introduced to the effluent, erdite was rich in SPs and spontaneously hydrolyzed and generated various Fe/S-bearing complexes and clusters, such as $=Fe(SH)_2$, =Fe(OH)(SH) and $=Fe(SH)^+$ [47]. These products, which are metastable, were further converted to Fe/S-bearing oxyhydroxide (such as =Fe-SH and =Fe-OH) through the homolytic cleavage of Fe–S–Fe bonds [48] after the release of OH⁻ and HS⁻ to the effluent (Figure 14). This phenomenon corresponds to the increase in the treated effluent pH from 7.3 to 8.6. During erdite hydrolysis, a redox reaction between surface Fe³⁺ and the adjacent free SH⁻ occurred [47], and thus surface-associated Fe²⁺, which stabilized the new Fe/S-bearing oxyhydroxide, was generated. Surface functional groups (Fe-SH and Fe-OH) are rich in new Fe/S-bearing oxyhydroxide, and H⁺ ions on their sides were dissociated with vacuum surface sites $(Fe-S^- \text{ and } Fe-O^-)$ under alkaline conditions [26]. The adjacent vacuum sites exhibited high affinity to complex Cu and Zn (Figure 14) and competed with chelates, such as EDTA [49], leading to nearly 100% removal of Cu and Zn from the wastewater. However, Ni and Co have small ionic radii and easily react with complex agents to form stable complex products with high stability constants [6]; these products only break with difficulty in the presence of HS⁻ and hydrolyzed Fe/S-bearing oxyhydroxide, leading to the production of residual Co and Ni in treated effluents. Polyaluminum chloride and polyferric sulfate were hydrolyzed and formed Al/Fe flocs, exhibiting plenty of hydroxyl groups for heavy metal coordination; however, they showed low Zn, Cu, Ni and Co removal efficiencies (Figure 6f) given the absence of an –SH bond on the surface of the hydrolyzed Fe/Al flocs. In addition, the released HS⁻ from the hydrolyzed erdite can react with heavy metals, such as Zn and Cu, to form S-bearing precipitates; however, they play a minor role in heavy metal removal. For instance, with the addition of Na₂S, approximately 50% of Zn and Cu was removed, whereas lower than 10% of Ni and Co was removed (Figure 6f). Thus, the role of HS⁻ in the removal of heavy metals is minimal. The Fe/S-bearing oxyhydroxide of hydrolyzed erdite plays a key role in the removal of residual heavy metals.



Figure 14. Illustration graph of SP2 for heavy metals removal from electroplating wastewater.

4. Conclusions

Two types of electroplating sludge, namely S1 with 25.6% Fe and 5.5% Co and S2 with 36.8% Fe and 7.8% Cr, were recycled as erdite-bearing particles for the advanced treatment of electroplating wastewater effluent. The weakly crystallized Fe-bearing minerals were rich in sludge and hydrothermally converted to well-crystallized erdite particles through the addition of Na₂S. In S1, Co was involved in CoS and/or CoS₂ formation, and the corresponding product SP1 was characterized by short rod-like particles. However, Cr had two valance states in S2, namely Cr(VI) and Cr(III). Cr(VI) was reduced to Cr(III) by Na₂S, and abundant OH⁻ was generated, which steadily promoted the conversion of Fe-bearing minerals to erdite. Consequently, the lengths of the erdite nanorods increased, and the corresponding product SP2 was characterized by long nanorods with a diameter of 100 nm and length of $0.5-1.5 \mu m$.

When SP1 was added to the electroplating wastewater effluent, a fraction of Co was released to the effluent, and Zn and Cu were removed efficiently. Compared with SP1, SP2 showed ideal Zn, Cu, Ni and Co removal efficiencies without releasing Co and Cr. When the SP2 dosage was 0.3 g/L, 100% Zn and Cu removal efficiencies were nearly achieved, and 37.9% Ni and 53.3% Co removal efficiencies were observed—higher than those of powdered activated carbon, polyaluminum chloride, polyferric sulfate and Na₂S. After treatment, the concentrations of Zn, Cu, Ni and Co met the emission standard, and the treated effluent was dischargeable. Through the proposed method, the Cr-bearing electroplating sludge was recycled as erdite nanorod particles, and the product was efficient in the advanced treatment of electroplating wastewater.

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