

Article

Electrochemical Processes for the Treatment of Hazardous Wastes Exemplified by Electroplating Sludge Leaching Solutions

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Abstract: The solidified landfill disposal of hazardous solid waste such as electroplating sludge in arid/semi-arid areas has potential risks and hazards. In this study, the electrochemical method was used to destroy the structures of metal complexes in electroplating sludge and release metal ions so that the organics were removed by direct mineralization in the anode while the metal was recovered in the cathode. A SnO₂/Ti electrode was used as the anode during the electrolysis process. The effect of different current densities (10, 20, 30, 40, 50, 60 A/m²), different pH values (2, 3, 4, 5, 6), and the presence of chloride (0.1 or 0.2 M NaCl) and sulfate (0.1 or 0.2 M Na₂SO₄) on treatment were investigated. Under the optimal treatment conditions (current density = 50 A/m², pH = 3), the removal rates of COD_{Cr}, TOC, and Ni²⁺ reached 88.01%, 85.38%, and 97.57%, respectively, with a metal recovery of 97.01%. Further studies showed that active chlorine and active persulfate generated in the presence of chloride and sulfate had less effect on the removal of organics, while hydroxyl radicals played a major role. The dilution of the leachate would be detrimental to electrochemical treatment. The by-products of organic chlorination were produced in low amounts, mainly CHCl₃. This method can be used to treat electroplating sludge in various areas to recover valuable metals while removing organic pollutants, complying with the concept of sustainable development. This method provides a new solution for the treatment of metal-containing hazardous solid waste such as electroplating sludge from the perspective of practical application.

Keywords: arid/semi-arid areas; hazardous solid wastes; electroplating sludge; electrochemistry; environmentally friendly disposal



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1. Introduction

Electroplating sludge is listed in the National Hazardous Waste List (2021) in the HW17 and HW21 waste categories due to the presence of heavy metals such as Ni, Pb, Cu, and other toxic substances that are classified as hazardous solid wastes. Heavy metals in electroplating sludge are often not in the form of single metal ions but in the form of metal complexes, metal chelates, and other organic heavy metals, which are biomethylated under natural conditions, are lipid soluble, and have strong biological toxicity. Disposal must be carried out, and common methods include solidification landfills, thermochemical treatment, and materialization techniques [1–5]. Solidified landfill is an important final disposal method for solid wastes (including hazardous wastes). If the site selection or engineering measures are not appropriate in the process of landfill disposal, the impermeable layer will be damaged and leaked with the resultant extension of operation

time, leading to the contamination of soil and groundwater in the area due to the infiltration of contaminants [6–9]. The infiltrating pollutants include a variety of contaminants such as heavy metals, aromatic hydrocarbons, and phenols, which seriously damage the fertility of soil and endanger human health through the food chain. Treating hazardous solid wastes such as electroplating sludge by solidified landfill is potentially harmful, and a method that can address such metal-containing hazardous solid wastes from the source is urgently needed.

It is generally believed that solid wastes are more suitable for landfill disposal in arid/semi-arid areas than in wet areas because arid/semi-arid areas have desert-like topography, and it is very easy to find suitable sites for landfill [10–13]. Nevertheless, since the soil moisture in arid/semi-arid areas is less than that in wet areas, the dilution capacity of soil is weak, the infiltration pollutants are more concentrated in the soil, the pollution level increases due to a high concentration of pollutants in the local area, and the pollution multiplier is much higher than that in wet areas. This kind of concentrated pollution due to the lack of natural dilution conditions causes the pollutant concentration to increase with the prolonged operation time. This can lead to persistent pollution, and when encountered with heavy rainfall or floods, the concentrated release of pollutants can easily occur, causing a wide range of soil, groundwater, and surface water pollution, resulting in much greater damage to the environment than in wet areas. In dry climates, rising groundwater levels may produce more leachate, especially persistent contaminants including pesticides and heavy metals that are more hazardous [14–18]. Hence, landfills alone are not sufficient in arid/semi-arid areas, especially for the environmentally sound disposal of hazardous solid wastes. Arid/semi-arid areas generally have a low resource carrying capacity, and once contamination occurs, it will cause serious, even irreversible, ecological damage. Additionally, due to the unique climatic characteristics of these areas, surface water resources are less available, and the demand for groundwater is more intense than in the wetter areas, which requires a higher degree of groundwater protection [19]. Therefore, hazardous wastes should be disposed of with more attention given to the selection of process management and disposal technologies in arid/semi-arid areas. Currently, the quantity of hazardous wastes produced is increasing year by year, but there are few studies on how to treat hazardous wastes rationally, effectively, and harmlessly under arid/semi-arid conditions. The existing studies have mainly focused on how to treat contaminated soil and groundwater, and few studies have explored how to reduce or solve the issue of hazardous wastes at the source [4,5].

Gansu Province in northwestern China was studied in this research because the central and northern part of the province are typical semi-arid/arid regions, and rainfall occurs mostly in the summer, which can easily cause heavy rain and floods in mountainous and central arid areas. The region is rich in mineral resources, with 35 types of metal minerals identified. There are large enterprises such as Jinchuan Group and Jiugang Group, among which Jinchuan ranks second in the world in Co production and fourth in Ni production, making it an important non-ferrous metallurgical production base in China [20]. The climatic characteristics and industrial features of this area indicate an urgent need for a non-hazardous technology for the treatment of metallic solid waste. Heavy metals in wastewater are usually treated by electrochemical cathode reduction. Additionally, electrochemical processes can be used to partially degrade or completely mineralize organics using anode oxidation. However, these two types of studies are often carried out separately. At present, it is rare to see studies on the mineralization of organics and the reduction of heavy metals in one system [21,22]. In this study, in light of the regional industry, climatic characteristics, and the advantages of electrochemical techniques, solid wastes such as electroplating sludge were selected as the research object, given their toxicity, difficult treatment, and high recovery value. Electrochemical technology was used to directly oxidize organics from which metals could be recovered, and a technically feasible, economically reasonable disposal scheme was designed to solve the problem of the harmless disposal of metal-containing solid wastes and recycling heavy metals. The results can provide theoretical

and technical support for the practical application of such pollutant treatment projects and a solution for the harmless disposal of electroplating sludge.

2. Experiment and Theories

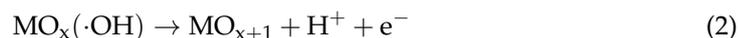
2.1. Electrochemical Oxidation and Reduction

During the electrochemical reaction, the anode undergoes an oxidation reaction, and under the catalytic effect of a special electrode, various active substances are released including active oxygen, active chlorine, and active peroxydisulfate, depending on the electrode material or the nature of the solution. They have strong oxidizing properties and are capable of treating difficult-to-degrade organics. In the case of $\cdot\text{OH}$, for example, the first step of the reaction is to release water molecules and form adsorbed hydroxyl radicals:



The following reactions were divided into two categories according to the nature of electrode materials: one was the active anode (e.g., IrO_2 , RuO_2) [23–25], and the other was the non-active anode (e.g., SnO_2 , PbO_2) [26–28].

(a) On the active anode, the chemically adsorbed hydroxyl radicals might interact with the anode to form higher valence oxides, which then undergo conversion or selective oxidation of the organics:



(b) On the non-active anode, higher valence oxides cannot be generated, and the active oxygen radicals of physical adsorption can carry out non-selective oxidation of organics, which might lead to complete combustion of organics into CO_2 [29,30];



For both anodes, the side reaction of oxygen evolution occurs in the oxidation reaction, affecting the oxidation effect [30]. In the cathode, the reduction reaction occurs, and low-valent metals with low oxidation potential (e.g., Ni, Co, Zn, Cu) are precipitated directly, leading to the following reaction:



2.2. Non-Active Anode

The active anode can induce the electrochemical conversion of organics to more biodegradable molecules such as short-chain carboxylic acids, which cannot achieve complete mineralization or organic combustion to CO_2 , while the non-active anode reaction generates $\cdot\text{OH}$ radicals, which are physically adsorbed on the anode surface, which has high instability, strong reactivity, and high oxidation power, facilitating the complete electrochemical oxidation of organic pollutants to CO_2 . The non-active anode inhibits the production of active chlorine and effectively reduces the production of undesirable organic chlorinated by-products (e.g., halo-acetic acid, halo-methane) and harmful ionic substances (e.g., chlorate, perchlorate) from the oxidation of active chlorine organics (e.g., methane) and harmful ionic substances (e.g., chlorate, perchlorate) [29–31].

The presence of organics in electroplating sludge is caused by the addition of additives, brighteners, and coating agents in the electroplating process. These polymers and their monomers contain primary amines, quaternary amines, and amide groups, which have been shown to be precursors for the formation of organochlorinated by-products. At the same time, electroplating sludge has chloride ions, and active chlorine formed during the oxidation of the electrochemical anode might generate organochloride by-products

with these precursors. It is therefore necessary to monitor the content of trihalomethanes (THMs) after electrochemical treatment [32–34].

The SnO₂/Ti electrode is a typical non-active anode, and ·OH precipitated on its surface has a strong oxidizing ability, which is non-selective for the oxidation of organics and leads to complete combustion to CO₂. Less chlorine is generated in chlorinated media, and the potential for harmful chlorinated organic by-products is smaller, making it the ideal anode for industrial wastewater treatment [27,28,30].

2.3. Experimental Hypothesis

Electrochemical treatment begins by dissolving the electroplating sludge into a solution, using nitric acid to avoid the use of hydrochloric acid to form a chlorine-containing system, and then the electrochemical process is used to separate the organics and heavy metals in the electroplating sludge by oxidation and reduction, respectively. The organics and heavy metals in the electroplating sludge are separated and disposed of harmlessly by electrochemistry. After the electroplating sludge is dissolved, the metal complexes are destroyed by the action of ·OH generated by the anode to release heavy metal ions. The released heavy metal ions are reduced to metal in the cathode. In addition to Ni, Co, Pb, Zn, and Cu, which are attached to the cathode, some ions (Cr₂O₇²⁻, Cd²⁺) are precipitated in the form of powder at the bottom of the cathode by controlling the current and pH value, and the metals are obtained by filtration. As a result of continuous energization, the toxic substances in electroplating sludge can be completely disposed of, and various types of electroplating sludge can be disposed of by changing the electrode materials and operating parameters, thus changing the existing electroplating sludge solidification and landfill treatment method, transforming the electroplating sludge morphology, eliminating potential hazards, and recovering useful metals. This method overcomes the difficulties of the cumbersome treatment process and low separation efficiency demonstrated by some studies in which the morphology of the electroplating sludge was destroyed first, then the separation of organics and heavy metals was carried out before the separate treatment of heavy metals and organics.

3. Materials and Methods

3.1. Dissolution of Solid Waste Samples

The electroplating sludge of an electroplating enterprise in Gansu Province was used as the raw material. The pH value of the untreated electroplating sludge was 7.09, water content was 82.65%, and ash content was 75.44%. According to the Classification of Electroplating Sludge Treatment and Disposal (GB/T38066-2019), the sludge can be classified as nickel sludge in electroplating sludge. A small amount was slurried and pretreated with 1 M nitric acid for 0.5 h. After nitric acid leaching, the metal components were dissolved into the solution, and some impurities were removed [35]. In this study, the electroplating sludge leaching solution was studied, and Ni was present in the form of ethylene diamine tetraacetic acid (EDTA) complexes and ions. Table 1 shows the main characteristics of the leaching solution.

Table 1. Leaching solution wastewater characteristics.

	Unit	Value
Chemical oxygen demand (COD)	mg/L	28,000
EDTA	mg/L	35,000
Total organic carbon (TOC)	mg/L	9500
Ni ²⁺	mg/L	47,300
Al ³⁺	mg/L	4120
Ca ²⁺	mg/L	2380
Cu ²⁺	mg/L	48
PO ₄ ³⁻	mg/L	17,300
SO ₄ ²⁻	mg/L	761
Cl ⁻	mg/L	318
pH		3.04

3.2. Experimental Setup

Experiments were performed in a single-chamber electrochemical reactor with a size of $6 \times 6 \times 6 \text{ cm}^3$. The anode was a SnO_2/Ti electrode, the cathode was an Ni electrode, and the size of the electrode was $4 \times 4 \times 0.1 \text{ cm}^3$. Electrode spacing was 3 cm.

In the experiments, the current density was 10, 20, 30, 40, 50, 60 A/m^2 ; the initial pH value was 2, 3, 4, 5, 6; and the NaCl or Na_2SO_4 concentration was 0.1 or 0.2 M, respectively. The volume ratios of leachate to deionized water (DI water) were 100:0, 75:25, 50:50, and 25:75. The initial pH value was adjusted using nitric acid or sodium hydroxide. Samples were taken from the electrolytic cell at 0 (initial), 5, 10, 20, 30, 45, 60, 90, 120, and 150 min.

3.3. Analysis

COD_{Cr} was measured using a COD_{Cr} tester (version 5B-3A, Lianke, Beijing, China), TOC was measured with a TOC/TN analyzer (MULTI N/C2100, Analytik Jena, Jena, Germany), and a pH meter (BPH-7200, Bell, Dalian, China) was used for pH measurement. Ni^{2+} was measured using a flame atomic absorption spectrophotometer with a wavelength of 324.7 nm (AA-7000, Shimadzu, Kyoto, Japan). Organic chlorinated by-products including CHCl_3 , CHCl_2Br , CHClBr_2 , and CHBr_3 were measured by using gas chromatography (GC-MS 7000C, Agilent, Palo Alto, CA, USA) with a capillary column of $30 \text{ m} \times 320 \mu\text{m} \times 0.25 \mu\text{m}$ (HP-5, Agilent, Palo Alto, CA, USA).

The effect of COD_{Cr} , TOC, and heavy metal was characterized by residual rate (i.e., C_t/C_0 , where C_0 and C_t are the initial concentrations and concentrations at t-time, respectively, of COD_{Cr} , TOC, and Ni^{2+}).

The instantaneous current efficiency (ICE) obtained from COD_{Cr} measurements, was calculated as follows [30]:

$$\text{ICE} = FV \frac{\text{COD}_0 - \text{COD}_t}{8I\Delta t} \times 100\% \quad (6)$$

where F is the Faraday constant (96,487 C/mol); V is the volume (L); COD_0 and COD_t represent the COD concentration (mg/L) at the beginning of the experiment and after t time of electrolysis (mg/L); 8 is the equivalent weight of oxygen (g/eq); I is the current (A); and Δt is the electrolysis time (s).

4. Results and Discussion

4.1. Effects of Current Density

Figure 1 shows the removal effect of COD_{Cr} , TOC, and Ni^{2+} at different current densities; with the increase in current density, the residual rate of organics and heavy metal in wastewater decreased significantly. As shown in Figure 1a, as the current density increased from 10 to 50 A/m^2 , the removal efficiency of COD_{Cr} increased from 50% to 85% after 120 min of electrolysis. The oxidation effect was not only related to the oxidizing ability of the oxidant itself, but also to the concentration of the oxidant. Increasing the current density could accelerate the electrochemical reaction of the anode, promote the production rate of $\cdot\text{OH}$ radicals, and increase the concentration of the oxidant. Increasing the current density not only accelerated the production of the oxidant, but also promoted the electron transfer between organic pollutants and the electrode, which improved the oxidation effect. According to reports, EDTA was first degraded to R_3N by the action of strong oxidizing agents and then underwent the mineralization process of $\text{R}_3\text{N} \rightarrow \text{R}_2\text{NH} \rightarrow \text{H}_2\text{NR} \rightarrow \text{NH}_4^+ + \text{HOOC-COOH} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{NH}_3$, and the main oxidation intermediates were amino acids [36,37]. $\cdot\text{OH}$ had a strong electron affinity and could easily attack high electron cloud density sites. Hydroxyl radicals extracted hydrogen from the alkyl groups. The structure was destroyed, converted to intermediates, and then mineralized [38,39]. Compared with 50 A/m^2 , the COD_{Cr} removal effect at 60 A/m^2 was not significantly increased. This might be attributed to the fact that at higher current density, the anode underwent more side reactions of oxygen evolution with weak oxidation capacity, which competed with the main reaction, while the electrode surface generated various bubbles, reducing the electrode

area involved in the reaction [40,41]. The significant occurrence of oxygen evolution side reactions led to a decrease in current efficiency. As shown in Figure 1b, the ICE did not increase with the increase in current density when the current density increased from 50 to 60 A/m².

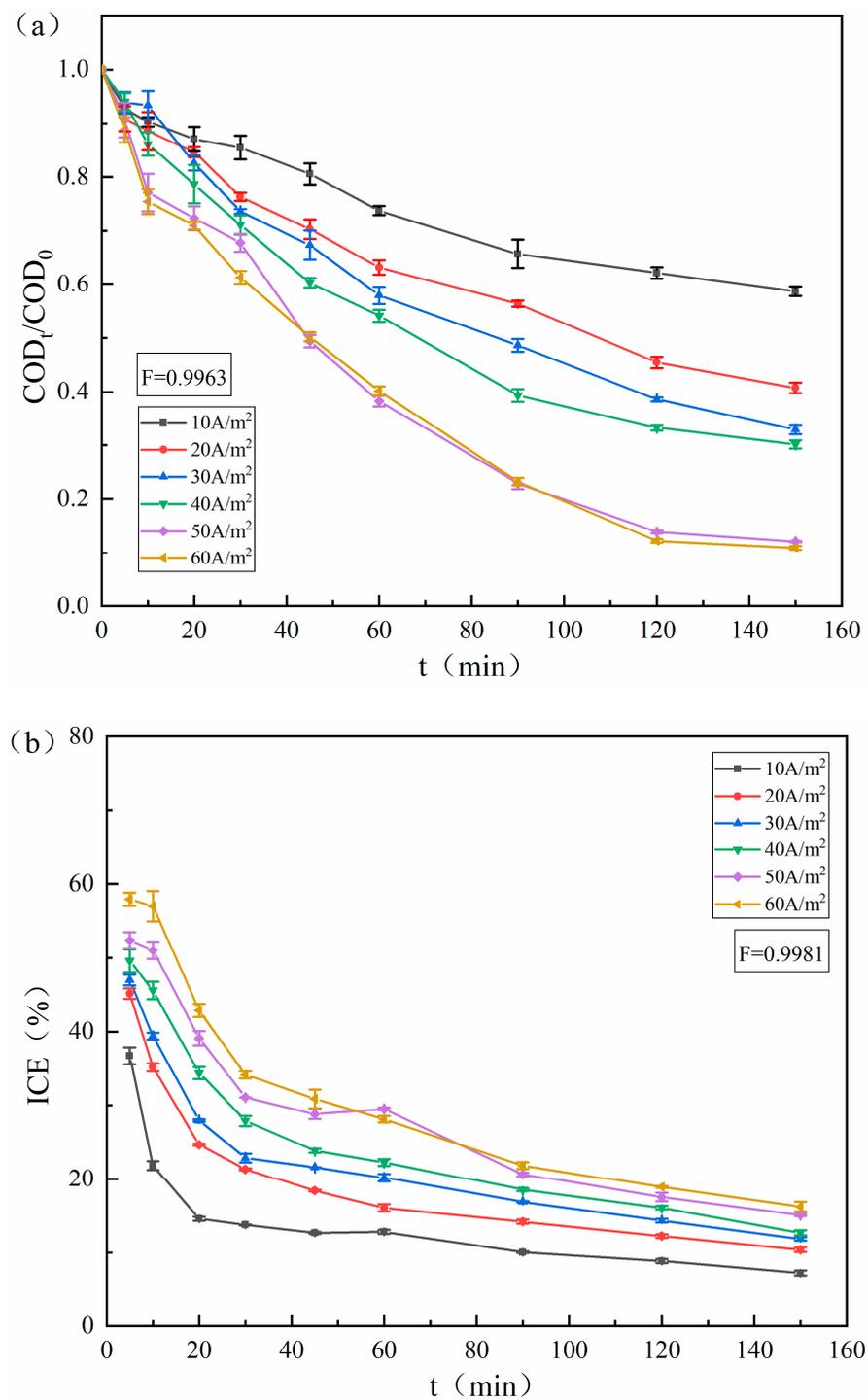


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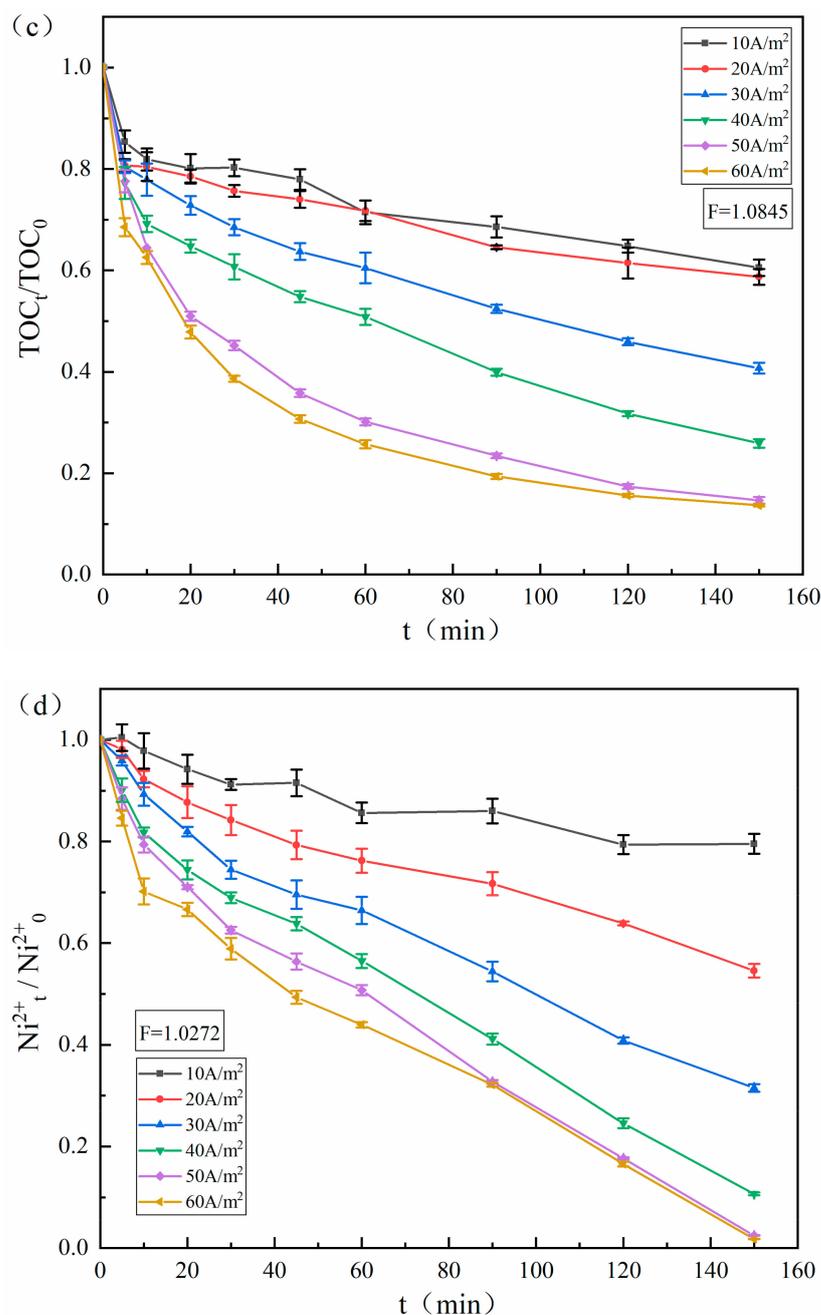


Figure 1. Evolution of COD_{Cr} (a), ICE (b), TOC (c), and Ni²⁺ (d) as a function of time at different current densities. Electrolysis conditions: electroplating sludge leaching solution (180 mL), temperature 25 °C and pH 3.

The removal of TOC showed a similar pattern to COD_{Cr}. The removal rate of TOC increased with the increase in current density; when the current density was 50 A/m², the increase was no longer obvious, reaching more than 85%, as shown in Figure 1c. The high removal rate of TOC indicated that the generated ·OH was highly oxidizable and could be oxidized without any selection, which in turn led to a better mineralization of organics. However, the removal rates of COD_{Cr} and TOC could reach 95.17% and 91.89% when Luu applied electrochemical oxidation to treat waste leachate. Compared with Luu's study, the removal rate of organic matter in this method still needs to be improved, and the next step is to conduct further study on anode modification, etc. [42].

Under the action of ·OH, the structure of EDTA-Ni was disrupted to release Ni²⁺, which created conditions for Ni²⁺ deposition in the cathode. With the increase in current

density and energization time, the Ni^{2+} removal rate increased continuously. As shown in Figure 1d, when the current density was 60 A/m^2 , the removal rate of Ni^{2+} was larger than that of 50 A/m^2 for 60 min, but the final removal rate was basically the same, mainly because the total amount of Ni^{2+} in wastewater was fixed. According to Faraday's first law, $m = Mit/zF$, when the current density is larger, the Ni in the cathode deposition inevitably increases, hence, the Ni^{2+} removal rate can be increased by increasing the current density in the early stage. As the concentration of Ni^{2+} in water decreases with electrolysis, the Ni can be deposited in the cathode, so the final removal rate is basically the same. When the concentration of Ni^{2+} in the electrolyte is small, the large current density leads to an increase in cathode hydrogen evolution side reactions, which competes with metal deposition [43].

4.2. Effects of pH Value

The pH value of the solutions affects the electrochemical process in two ways. First, it affects the oxygen evolution potential of the anode, and second, it affects the deposition and recovery efficiency of the cathode metal. At low pH value, the oxygen evolution reaction does not easily occur, but the increase in the cathode hydrogen evolution reaction affects the metal recovery rate at the cathode. High pH value affects the current efficiency and may exceed the metal solubility product, which may lead to precipitation and reduce the recovery rate. To better investigate the removal effect, the effect of different pH values (2, 3, 4, 5, 6) on the treatment effect was investigated at a current density of 50 A/m^2 .

Figure 2a,b shows the effect of pH on COD_{Cr} and TOC, and it is easy to conclude that a lower pH value is beneficial to improving the oxidation effect of the electrochemical anode. During the degradation of the anode, $\cdot\text{OH}$ oxidation of organics and oxygen evolution were two competing reactions. Under normal conditions, the higher the oxygen evolution potential of the anode under acidic conditions, the harder it is for the oxygen evolution reaction caused by the electrolysis of solvent water to occur, and the more $\cdot\text{OH}$ is generated. The increase in the oxygen evolution reaction at a higher pH value led to a decrease in current efficiency, which was reflected by the decrease in the removal rate for COD_{Cr} and TOC after the increase in pH. At the same time, the adsorption and reaction activity of organics on the electrode surface were also affected by pH value; specifically, pH value affected redox potential and electrode surface charge. The rapid decrease in TOC at $\text{pH} = 2$ indicates that the acidic solution accelerated the removal of organic pollutants and mainly afforded easily degradable products [44–46].

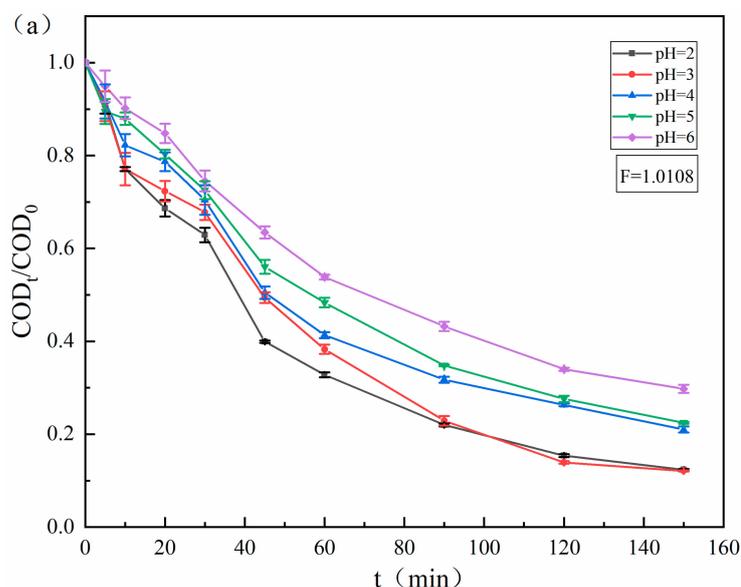


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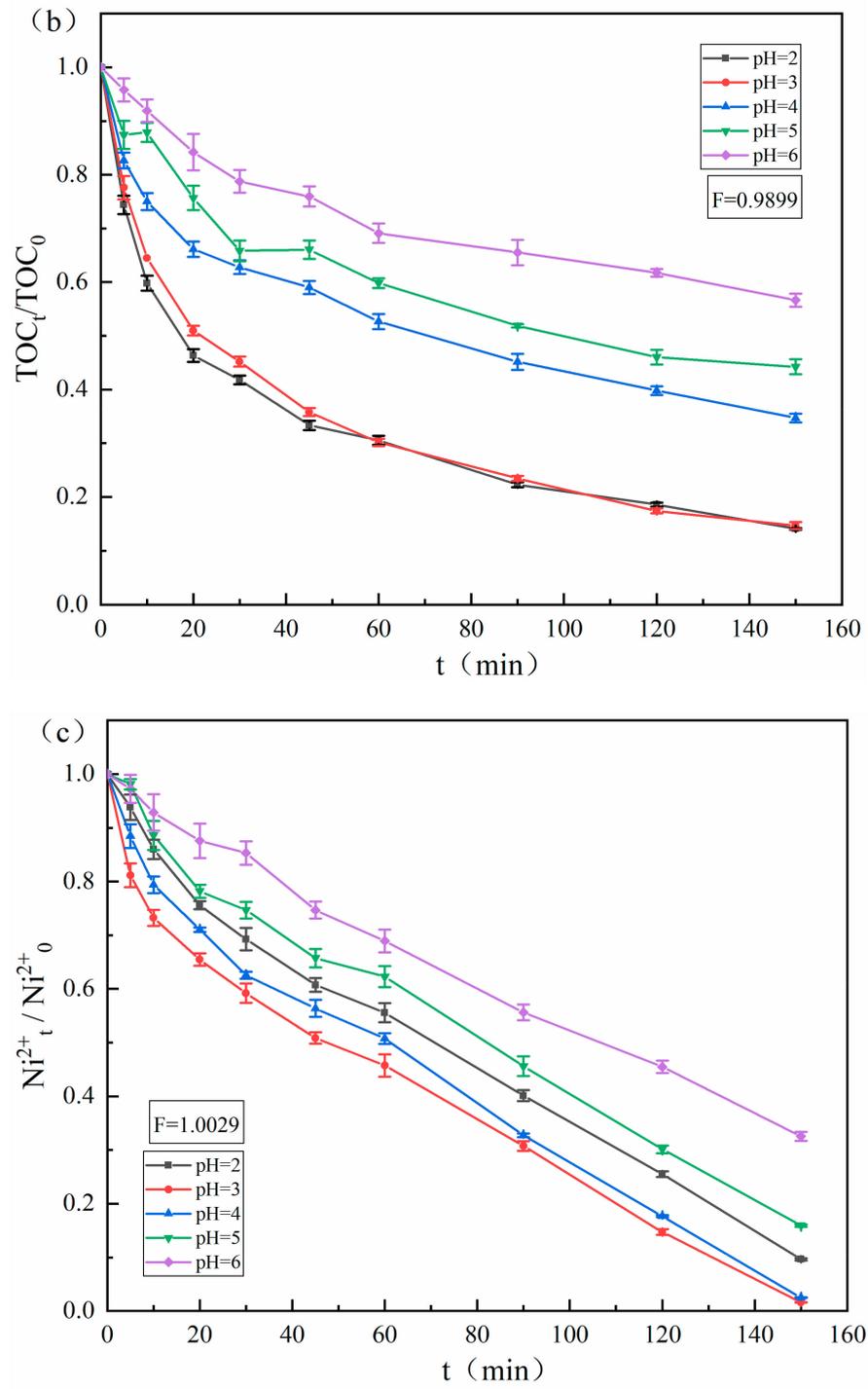


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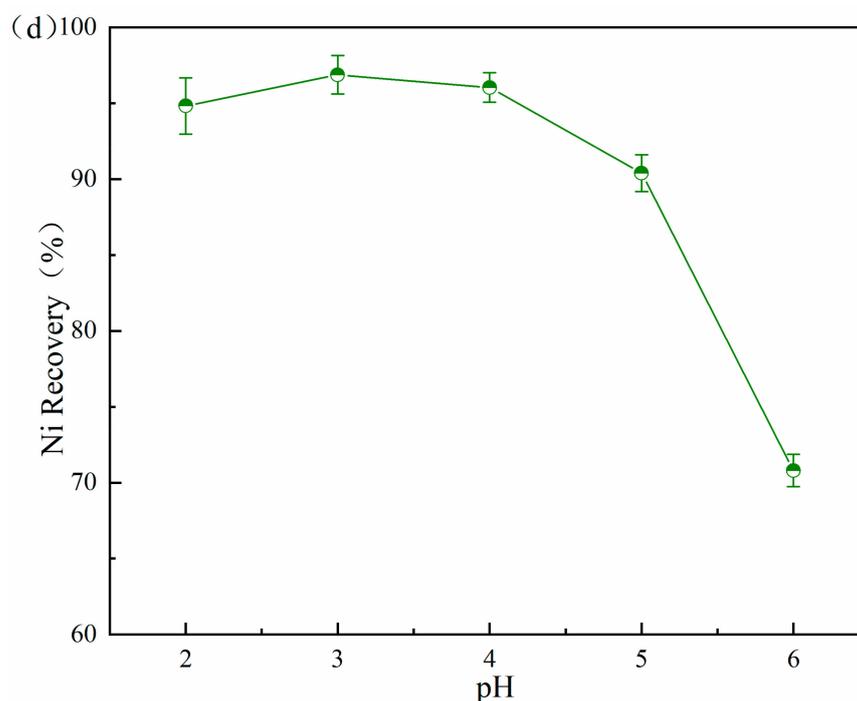


Figure 2. Evolution of COD_{Cr} (a), TOC (b), and Ni²⁺ (c) as a function of time at different initial pH. (d) The relationship between the Ni²⁺ recovery rate and pH. Electrolysis conditions: electroplating sludge leaching solution (180 mL), temperature 25 °C, and current density 50 A/m².

The effect of pH value on cathode deposition was completely different, as higher or lower pH was not conducive to metal deposition or recovery (Figure 2c). At lower pH conditions, the proportion of cathode hydrogen evolution side reactions increased significantly, and various bubbles were clearly observed on the electrode surface and escaped from the electrode surface that competed with the metal deposition reaction in the cathode and affected the metal removal and recovery. At higher pH values, the cathode zone was alkalinized, and the metal recovery was reduced. As shown in Figure 2d, higher pH reduced the recovery by more than 20% [43]. Under the optimal conditions, the metal recovery of this method was 96.88%. However, Yu et al. used chlorine with thermal regulation and directional phase conversion for the recovery of metals from electroplating sludge; the recovery rate was 97%, which was comparable to the metal recovery of the present method [47].

4.3. Effects of Chloride and Sulfate

Due to the different production processes, electroplating sludge contains some chloride or sulfide in the production process, which will produce active chlorine or active sulfide in the electrochemical oxidation process. As the concentrations of sulfate and chloride in the leaching solution used in this study were below 0.01 M, the effect of the presence of chloride and sulfate on the electrochemical treatment was investigated by adding 0.1 M, 0.2 M NaCl and Na₂SO₄ to the solution. The current density was 50 A/m², with pH = 3. The results are shown in Figure 3.

Figure 3a,b shows that the effects of chloride and sulfate on the removal of organics were reversed, and sulfate could increase the removal rate of organics, while chloride could weaken the removal of organics. This was mainly due to the difference in the oxidation capacity of the electrochemical anode to produce active chlorine and sulfate radicals ($\cdot\text{SO}_4^{2-}$) [48]. The standard electrode potential of $\cdot\text{SO}_4^{2-}$ ($E_0 = 2.7\sim 2.8$ eV) was close to that of $\cdot\text{OH}$ and had almost the same oxidation capacity. It was shown that the presence of $\cdot\text{SO}_4^{2-}$ was longer than that of $\cdot\text{OH}$, which prolonged the reaction time with organics, and $\cdot\text{SO}_4^{2-}$ had a higher sustained oxidation capacity and therefore a higher

degree of mineralization than that of $\cdot\text{OH}$. At the same time, the sulfate radical had a wider oxidation range than $\cdot\text{OH}$ and oxidized organics that could not be oxidized by hydroxyl radicals. Hence, after adding sulfate, the anode produced both $\cdot\text{OH}$ and $\cdot\text{SO}_4^{2-}$, forming a cross synergistic oxidation, and the oxidation capacity of radicals was enhanced. The increase in the removal rate for COD_{Cr} was higher than the increase in the removal rate for COD_{Cr} , which indicated that the mineralization ability of $\cdot\text{SO}_4^{2-}$ was stronger [49,50]. The active chlorine ($E_{\text{HClO}} = 1.49$) was significantly less oxidizing than $\cdot\text{OH}$, and the active chlorine produced in the anode competed with $\cdot\text{OH}$ and affected the removal effect [51,52]. Notably, the presence of chloride and sulfate did not particularly affect the removal of organics, and the main removal effect relied on $\cdot\text{OH}$.

The addition of chloride and sulfate did not significantly promote the removal of Ni^{2+} . Although the addition of NaCl or Na_2SO_4 is usually used to increase electrical conductivity, the addition of sodium salts reduced the solution resistance but hardly affected the charge transfer coefficient and did not change the reaction mechanism of Ni deposition. As shown in Figure 3c, after adding sodium salt, the removal rate of Ni^{2+} only slightly increased.

4.4. Effect of Leachate Dilution

Figure 4 shows the effect of the leachate after dilution on treatment effect. The removal rates of COD_{Cr} , TOC , and Ni^{2+} showed a decreasing trend with the increase in dilution, and the removal rate of Ni^{2+} decreased most significantly. When the volume ratio of leachate to deionized water was reduced from 100:0 to 25:75, the removal rates of COD_{Cr} , TOC , and Ni^{2+} decreased by 7.98%, 6.77%, and 83.81%, respectively. This was because the conductivity of the diluted solution decreased and the electrochemical process slowed down, which led to a decrease in the quantity of reactive oxygen species produced by the anode and a weakening of oxidation capacity. The concentration of organic matter decreased after dilution, and the chance of collision between organic molecules with electrodes or electrochemically generated reactive oxygen species near the electrode surface decreased, resulting in a decrease in removal rates for COD_{Cr} and TOC . When the concentration of metal ions in solution was small, the charge transfer in the solution during electrolysis slowed down, resulting in a slower cathodic electrodeposition reaction process that directly affected the degradation efficiency of Ni^{2+} , which was consistent with the law of mass action of the reaction.

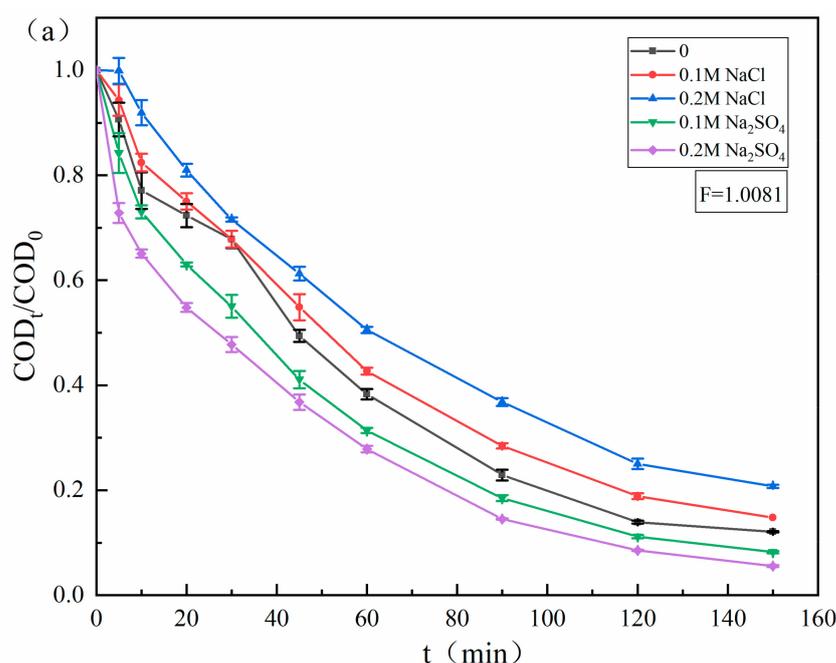


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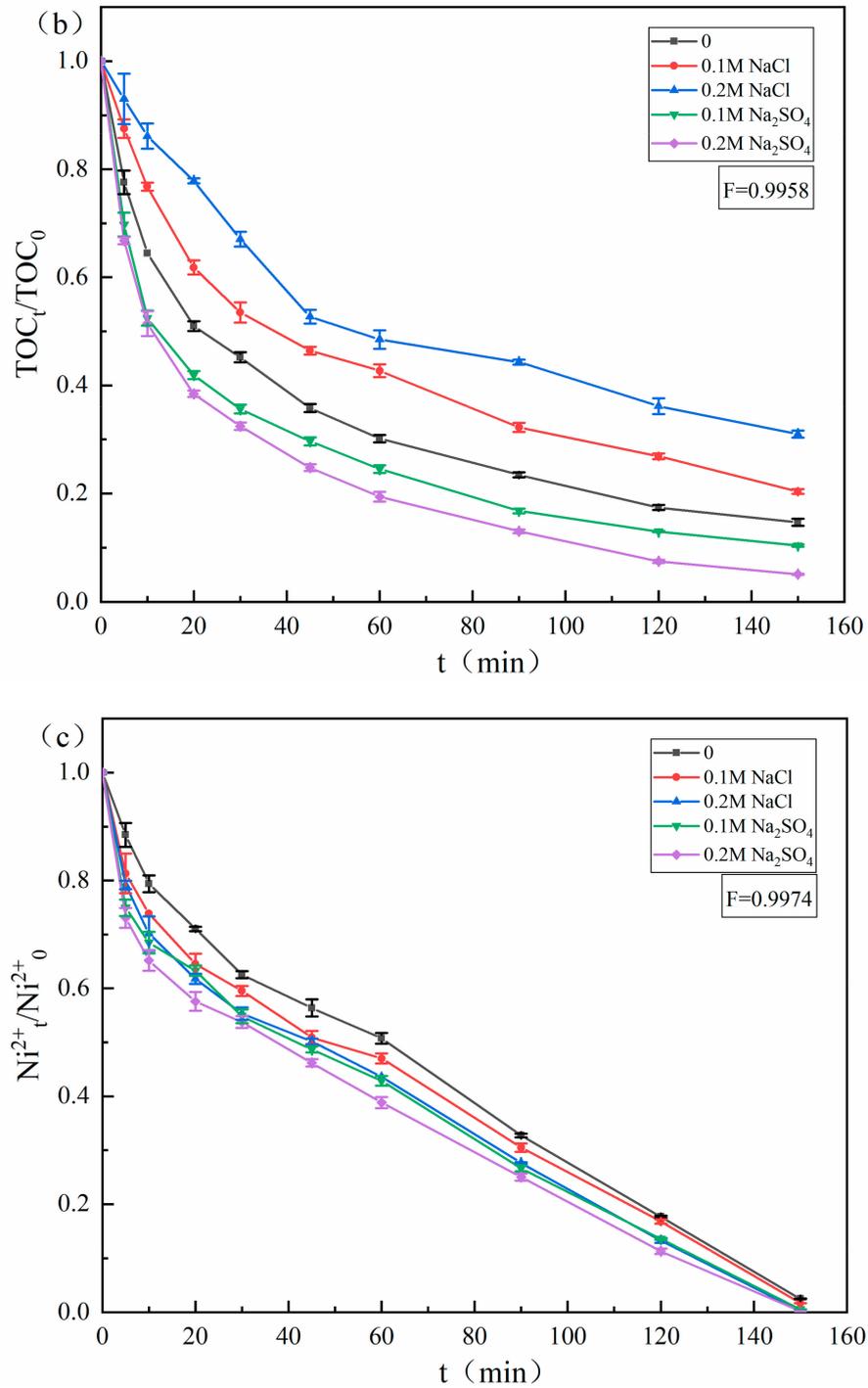


Figure 3. Evolution of COD_{Cr} (a), TOC (b), and Ni²⁺ (c) as a function of time in different supporting media. Electrolysis conditions: electroplating sludge leaching solution (180 mL), current density 50 A/m², temperature 25 °C, and pH 3.

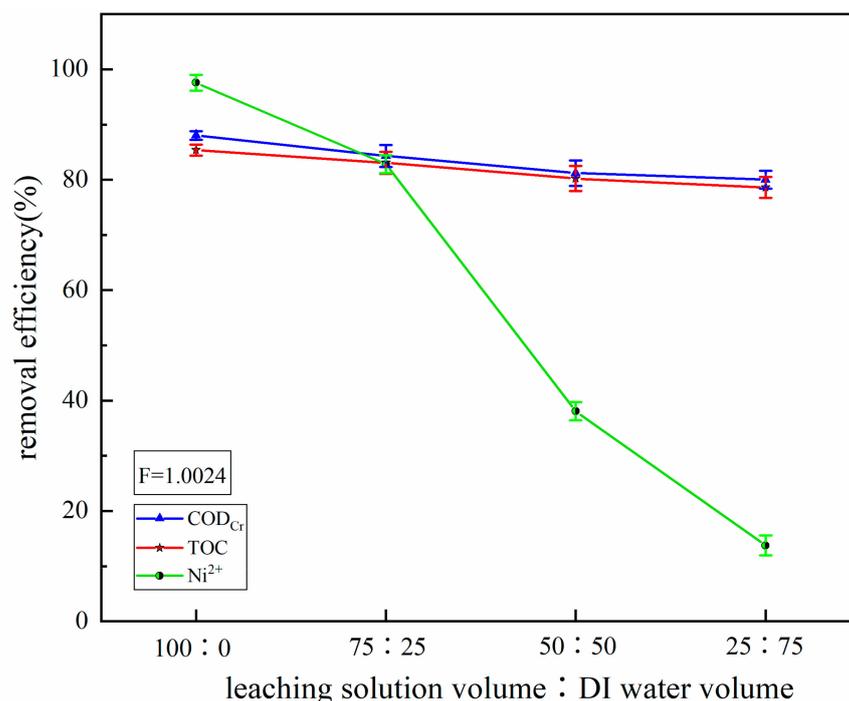


Figure 4. Relationship between the removal efficiency of COD_{Cr}, TOC, and Ni²⁺ and dilution ratio. Electrolysis conditions: solution 180 mL, current density 50 A/m², temperature 25 °C, and pH 3.

4.5. Inhibition of the Production of Organochloride By-Products

Harmful organic chlorinated by-products, most commonly trihalomethanes (THMs), are produced after electrochemical treatment in some chlorine-containing systems. In this study, the primary amine group may have appeared in the degradation process of EDTA, which is a precursor of organochlorinated by-products. In order to investigate the inhibitory ability of the selected SnO₂/Ti electrode for organic chlorinated by-products, 0.1 M NaCl was added to the electrolysis, and then the content of trihalomethanes (THMs) was measured after 150 min of electrolysis. The results are shown in Table 2. The experimental results showed that all the THMs were CHCl₃, which would produce some harmful by-products in chlorine-containing systems; however, according to the literature, the quantity of by-products produced was lower than that of the other anode, and the non-active electrode had a better effect of inhibiting the production of by-products [53,54].

Table 2. The number of THMs formed during the electrochemical oxidation under the optimal conditions (50 A/m², pH = 3, 25 °C, and supporting electrolyte of 0.1 M NaCl) after 150 min.

Parameter	Unit	Value
CHCl ₃	µg/L	128
CHCl ₂ Br	µg/L	0
CHClBr ₂	µg/L	0
CHBr ₃	µg/L	0

5. Conclusions

From the above results, it can be seen that the electrochemical redox designed in this study was an effective method for the treatment of electroplating sludge. Optimizing the design of electrochemical system parameters could further improve the prospects of its industrial application. Electrochemistry was used to achieve an effective, environmentally friendly disposal of electroplating sludge. Under optimal treatment conditions (current density = 50 A/m², pH = 3), the removal rates for COD_{Cr}, TOC, and Ni²⁺ reached 88.01%, 85.38%, and 97.57%, and the metal recovery was 97.01% within 150 min. Increasing

the current density and decreasing the pH value promoted the treatment of COD_{Cr} and TOC. The removal rate of heavy metal was directly proportional to the current density. Too high or too low pH values were not conducive to metal recovery. However, the optimal pH value for the treatment of metals could meet the requirements for the treatment of organics. The removal of organics mainly relied on hydroxyl radicals generated by the anode oxidation process, while active chlorine and active persulfate generated by chloride and sulfate had less effect on the removal of organics. Dilution of the leachate would be detrimental to electrochemical treatment. The detection of organochloride by-products after electrolysis showed that the SnO₂/Ti electrode well inhibited the generation of organochloride by-products, which were mainly CHCl₃. After electrochemical treatment, the metal complex in electroplating sludge was destroyed, and the concentration of organics decreased significantly. The metal content was significantly reduced, which eliminated the toxicity and hazards of the electroplating sludge and provided the conditions for the next step of the biological method. More importantly, heavy metal wastes need to be properly disposed of in various areas including arid/semi-arid areas. In the disposal process, significantly polluted areas should be designated to prevent potential risks and hazards, with emphasis on reducing or eliminating the toxicity of heavy metal wastes while giving priority to the recovery of valuable metals to help achieve sustainable development.

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