



Removal of EDTA-chelated copper from aqueous solution by interior microelectrolysis

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ABSTRACT

The efficient removal of EDTA-chelated copper from aqueous solution was achieved using waste iron scraps in interior microelectrolysis. The experimental results show that the appropriate ranges for the cast iron scrap (CIS) dosage and the Fe/C mass ratio are 20–40 g/L and 2:1–4:1, respectively. This method proved effective over a wide range of pH, from 2.0 to 10.0, and copper removal efficiency decreased unevenly as pH increased. Copper removal accelerated as dissolved oxygen (DO) was increased from 0.15 mg/L to 5.25 mg/L, but it decelerated as DO was further increased from 5.25 mg/L to 9.0 mg/L. Additionally, the Taguchi method was used for a L_9 (3^4) orthogonal array design to determine the optimum microelectrolytic conditions for copper removal, and it was found that 98.2% of copper and 32.3% of EDTA (in terms of TOC) were removed under the following optimum microelectrolytic conditions: a pH of 3.0, a CIS dosage of 40 g/L, 40 min of reaction time and a Fe/C mass ratio of 2/1. The results of the Fourier transform infrared (FT-IR) and UV–Visible spectra confirmed the existence of Fe^{2+} -based replacement-precipitation and electrocoagulation during interior microelectrolysis, and these processes contributed to the removal of EDTA-chelated copper from aqueous solution. Economic analysis indicated that interior microelectrolysis was cost-effective and had great potential for practical application in the pretreatment of EDTA-chelated copper in wastewater.

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1. Introduction

Ethylenediaminetetraacetic acid (EDTA) is a synthetic chelating ligand widely used in the electroless copper deposition process, and it can bind with cupric ions to form strong complexes at a molar ratio of 1:1 [1]. The presence of the copper–EDTA complex can cause great difficulties in the treatment of effluent. Although regarded as the most economical methods for the disposal of metal-rich effluents, conventional chemical precipitation methods for the removal of cupric ions are rendered ineffective by EDTA [2]. Moreover, the toxicity of copper–EDTA chelate in effluents can prevent the removal of COD by subsequent biological treatment processes [3–5]. Further, no existing chemical or biochemical methods can easily decompose this compound.

Traditional methods such as membrane filtration [6], ion exchange [7,8], adsorption [9,10] and reduction and oxidation processes [11,12] have been successfully applied to treat metal–EDTA

compounds in wastewater. However, these methods are limited by high costs, long treatment times and the toxicity of the chemicals, inhibiting their widespread application and limiting their availability in developing countries. Hence, there is an urgent need to explore new methods that have low capital investments and environmental risks. Recently, much attention has been directed at the electro-coagulation (EC) process and the replacement-precipitation (RP) method for chelated copper treatment. Yeh and Kabdasli effectively treated effluent containing Cu–EDTA compounds with the electro-coagulation process [13,14], but this process required a large amount of electricity, making it less attractive in areas with limited electricity supplies. Some researchers have attempted to use FeSO_4 in the place of the cupric ion in chelated solutions before raising the pH to form $\text{Cu}(\text{OH})_2$ precipitate [15,16]. However, large quantities of FeSO_4 were consumed, and EDTA remained in the solution after treatment. Moreover, the high buffer capacity of EDTA necessitated excess amounts of chemicals to neutralize alkalinity.

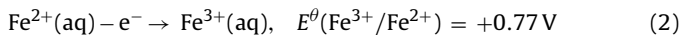
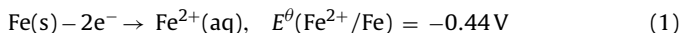
Interior microelectrolysis seems to operate on a principle similar to the combined effects of the EC process and the RP method. For example, when a mixture of iron scraps and activated carbon comes in contact with wastewater, numerous microscopic galvanic cells are formed between iron and carbon particles. The electrode

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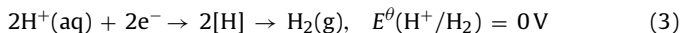
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reactions can be represented as follows [17,18]:

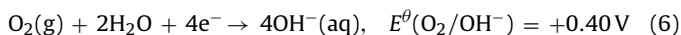
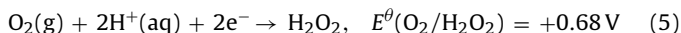
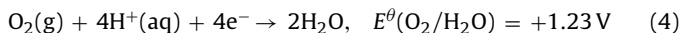
Iron anode (oxidation):



Carbon cathode (reduction):



In the presence of oxygen:



With the dissolution of iron scraps (Eq. (1)), ferrous ions (Fe^{2+}) are released rapidly into solution. Although active Fe^{2+} generated during the anodic reaction drives electro-coagulation, Fe^{2+} can act as a precursor in the replacement of Cu^{2+} in the Cu-EDTA by Fe^{3+} . The free Cu^{2+} is then precipitated by OH^- produced at the cathode. Additionally, based on Eq. (5), H_2O_2 is generated and subsequently combined with Fe^{2+} to form Fenton's reagents, which, theoretically, can decompose EDTA and release copper that was previously bound to EDTA into solution in a free state. Thus, interior microelectrolysis can be used for EDTA-chelated copper treatment.

Interior microelectrolysis is substantially different from the EC process and the RP method because it does not require an external power supply or the addition of FeSO_4 and alkaline chemicals. The merits of the interior microelectrolysis process, including (1) the availability of plentiful, low-cost iron scraps, (2) low operating costs, (3) a high process efficiency, (4) the enhancement of the biodegradability of wastewater, and (5) the simple reactor construction, have been documented in previous studies and applications [17–21].

Based on the analysis and merits mentioned above, interior microelectrolysis is likely to be a low-cost, effective and novel technology for the treatment of EDTA-chelated copper effluent. Thus, in this research, the removal of EDTA-chelated copper by interior microelectrolysis was studied, which to our knowledge, has not yet been reported.

Batch experiments were conducted to investigate the performance of interior microelectrolysis and the removal mechanisms of copper and EDTA were studied. The optimum conditions for copper removal from EDTA-chelated solution were determined by the Taguchi method using an $L_9(3^4)$ orthogonal array. In addition, an economic analysis of interior microelectrolysis was conducted. Overall, this research provides a theoretical basis and the technical parameters for the treatment of rinse water originating in the electroless copper plating process.

2. Experimental

2.1. Materials and solutions

All chemicals were of analytical grade and used without further purification. Distilled water was used for the preparation and dilution of solutions. To adjust pH, solutions of 1 M HCl and 1 M NaOH were used.

Waste CIS pieces obtained from a metal machining shop in Nanhai, Guangdong province, China were 1–3 mm in length and 0.5–1.0 mm in width. Scraps were degreased in a heated 10% sodium hydroxide bath for 30 min before rust was removed in a diluted (2%) hydrochloric acid solution. Finally, the pieces were cleaned with distilled water and dried in a vacuum drying oven at 80 °C for 12 h. The scraps were placed in a drying chamber for later use. The granular activated carbon (GAC) had a mean particle

diameter of 2–3 mm. The bulk densities of the CIS and GAC were 1.65 g/cm³ and 0.55 g/cm³, respectively.

The EDTA-chelated copper stock solution, with an initial Cu^{2+} concentration of 1000 mg/L, was prepared by dissolving 3.932 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 5.862 g of EDTA-2Na $2\text{H}_2\text{O}$ in 1 L of distilled water ($\text{Cu}^{2+}/\text{EDTA}$ molar ratio of 1:1). The stock solution was diluted with distilled water prior to experiments.

2.2. Experimental methods

2.2.1. Batch experiments

To investigate the effect of CIS dosage on the removal of EDTA-chelated copper from aqueous solution, the CIS dosage, Fe/C mass ratio and the pH were varied using interior microelectrolysis. Batch experiments were conducted in 250-mL ground-glass stoppered flasks under the following conditions: the solution contained 100 mg/L of copper and 457 mg/L of EDTA; the solution volume was 100 mL; the original solution pH was 3.1 ± 0.2 ; and the temperature was 25 ± 0.5 °C. CIS pieces were thoroughly mixed with GAC particles in the desired proportion before being added to the flasks. The flasks were immediately placed into a thermostatic oscillator at a rate of 160 rpm. All batch experiments were conducted in duplicate and the averaged data reported.

To study the effect of DO, 200 mL of untreated solution was poured into each flask marked A, B, C, D and E for a total of five groups of flasks. Then, solutions A (referring to the solution in flask A), B and C were purged with N_2 for 25, 15 and 5 min, respectively. Solution D was used without any pretreatment, and solution E was purged with air for 30 min. Finally, the flasks were closed and the experiments were conducted under the conditions described above. DO was measured by a dissolved oxygen analyzer, and the DO concentrations in flasks A, B, C, D and E were 0.15 ± 0.05 mg/L, 2.06 ± 0.08 mg/L, 5.25 ± 0.10 mg/L, 7.25 ± 0.15 mg/L and 9.00 ± 0.10 mg/L, respectively (each value of DO was the mean of three repetitions \pm the standard deviation).

2.2.2. Orthogonal array experiment

The technique for designing experiments with multiple factors is known as the factorial design of experiments. This method incorporates potential combinations of factors and identifies the best combination [22]. To simplify and standardize experimental design and to minimize the number of factor combinations required to test the factor effects, the Taguchi method uses a special design of orthogonal arrays to study the entire factor space with only a small number of experiments [23].

Based on the Taguchi method, an orthogonal array experiment $L_9(3^4)$ was designed to determine the optimum microelectrolytic conditions for the removal of copper from an EDTA-chelated aqueous solution. Four significant factors were selected, and the following conditions were established: (A) iron scrap dosage: 20, 30 and 40 g/L; (B) initial pH: 2.0, 3.0 and 4.0; (C) reaction time: 20, 40 and 60 min; and (D) Fe/C mass ratio: 2/1, 3/1 and 4/1. These levels were selected based on the experimental data of batch experiments.

To evaluate the effect of each factor on the performance of the interior microelectrolysis, the Statistical Package for the Social Sciences (SPSS) 16 statistical software was used. The experiment was conducted three times to ensure the accuracy of the experimental data.

2.2.3. Analysis of solutions

All samples were filtered through 0.45- μm nitrocellulose membrane filters before analysis. The copper concentration and the total organic carbon (TOC) concentration were measured with an atomic adsorption spectrophotometer (AA6000, Techcomp) and

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