Efficient treatment of an electroplating wastewater containing heavy metal ions, cyanide, and organics by H₂O₂ oxidation followed by the anodic Fenton process

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ABSTRACT

A real electroplating wastewater, containing heavy metals, cyanide, and organic contaminants, was treated by electrocoagulation (EC), H₂O₂ oxidation, H₂O₂ pre-oxidation followed by EC, and the anodic Fenton process and the efficacy of the processes was compared. Concentration of cyanide, Cu, Ni, Zn, and Cr was largely decreased by EC within 5 min. When the reaction time was extended, removal of residual cyanide, Cu, and Ni was limited. In H₂O₂ oxidation, the concentration of cyanide decreased from initial 75 to 12 mg L⁻¹ in 30 min. The effluents from the H₂O₂ oxidation were further treated by EC or anodic Fenton. In EC, the concentration of total cyanide, Ni, and Cu decreased to below 0.3, 0.5, and 1.5 mg L⁻¹, respectively. Removal efficiency of chemical oxygen demand by EC was less than 20.0%. By contrast, there was 73.5% reduction by the anodic Fenton process with 5 mM H₂O₂ at 30 min; this can be attributed to the oxidation induced by hydroxyl radicals generated by the reaction of H₂O₂ with the electrogenerated Fe²⁺. Meanwhile, residual cyanide, Cu, and Ni can also be efficiently removed. Transformation of organic components in various processes was analyzed using UV-visible and fluorescence excitation-emission spectra.

Key words | anodic Fenton process, cyanide, electrocoagulation, electroplating wastewater, heavy metals

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INTRODUCTION

Electroplating wastewater contains various toxic substances such as cyanide, degreasing solvents, and heavy metals. Heavy metals are bound to strong organic and inorganic complexing agents and cannot be efficiently removed by the individual precipitation, coagulation, and filtration processes (Chareerntanyarak 1999; Wong *et al.* 2002).

Electrocoagulation (EC) has been shown to be effective in removing oil and grease, chemical oxygen demand (COD), heavy metals, fluoride, and bacteria from drinking water and wastewater (Chen 2004; Remoundaki *et al.* 2007; Durante *et al.* 2010; Tanneru & Chellam 2012). EC involves the generation of coagulants in situ by dissolving electrically either aluminum or iron ions from aluminum or iron electrodes, respectively. If iron electrodes are used, the Fe³⁺ ions generated will undergo further spontaneous reactions to produce corresponding hydroxides and/or

polyhydroxides (Mollah *et al.* 2004). This has been shown to be a promising technology for the removal of heavy metals from a vast range of effluents (Pociecha & Lestan 2010). EC coupled to pre- or post-oxidation has been examined with the aim of efficiently removing complexed heavy metals and organic contaminants (Kabdasli *et al.* 2010; Durante *et al.* 2011).

Recently, the anodic Fenton (AF) process for treatment of refractory organics has attracted considerable research interest (Saltmires & Lemley 2000; Brillas *et al.* 2009). In the AF process, Fe²⁺ ions are delivered into the cell by electrolysis from a sacrificial iron anode, as shown in the following:

H₂O₂ solution is pumped into the cell to initiate the Fenton reaction:

In the AF process, the amount of the Fe²⁺ ions can be easily controlled by adjustment of current density, and Fe³⁺ can be reduced to Fe²⁺ to some extent by the electrochemical process at the cathode. As far as we know, application of the AF process in treating a real electroplating wastewater has not been reported previously.

In the present study, treatment of a real electroplating wastewater containing heavy metals, cyanide, and organics by three processes was compared: EC; H₂O₂ pre-oxidation followed by EC (H₂O₂-EC); and anodic Fenton (H₂O₂-AF). A preferred process is proposed with efficient removal of heavy metals, cyanide, and COD from the electroplating wastewater, and the removal mechanism is discussed.

MATERIAL AND METHODS

The electroplating effluent was collected from an electroplating factory located in Quanzhou City (Fujian Province, China). The pH of the effluent was 1.5; concentrations of cyanide and COD were 75 and 245 mg L⁻¹. The concentrations of Cu, Ni, Cr, and Zn were 185, 64, 13, and 148 mg L⁻¹, respectively. All chemicals used in the present work were of at least reagent grade purity.

Electrochemical experiments

A schematic diagram of the experiment setup is shown in Figure SM-1 (available online at <http://www.iwaponline.com/wst/068/296.pdf>). Stainless steel plates with an active area of 25 cm² were used as anode and cathode, respectively. Three iron plates were used as an induced electrode between the anode and cathode. The gap between the electrodes was 15 mm. For each experiment, the electroplating wastewater (400 mL) was stirred by a magnetic stirring bar in the cell. The solution pH was adjusted by adding 1.0 M HNO₃ or NaOH. Samples were collected from the cell at various intervals for chemical analysis. In the case of H₂O₂ oxidation, a given amount of H₂O₂ was added. At a given reaction time, the reaction cell was quickly dosed with KI to quench the residual H₂O₂ and stop the oxidation reactions.

Analytical methods

All experiments were performed in duplicate, and the analysis of each parameter was done in triplicate for each run. pH was measured using a pH meter (310P-02, Thermo Fisher, USA). Total cyanide concentration was determined through a standard colorimetric method using a pyridine–barbituric acid reagent to form a highly colored complex with maximum absorbance at 575 nm (Clesceri *et al.* 1998). UV–visible (UV-Vis) analysis was performed using an UV-Vis spectrophotometer (U-3010, Hitachi). COD was measured by a titrimetric method (Hach Corporation, USA). In order to remove interference from residual H₂O₂ on COD analysis, the pH of the samples was adjusted to 9.0 and they were left overnight. There was no residual H₂O₂ according to the method of Bader *et al.* (1988). Concentration of the heavy metal ions was measured using a 700 Series inductively coupled plasma optical emission spectrometer (Agilent Technology). Fluorescence excitation–emission spectroscopy was determined using a fluorescence spectrophotometer (Hitachi F-2000), equipped with a 150 W xenon lamp. Excitation–emission matrices (EEMs) were plotted to identify the organic components based on the peaks characterized by Chen *et al.* (2003). Total organic carbon (TOC) was analyzed by a TOC analyzer (TOC-VCPh, Shimadzu, Japan).

RESULTS AND DISCUSSION

Electrocoagulation treatment

Firstly, treatment of the effluent by the EC process with various current densities was examined at pH 4.0 and samples were taken at various time points up to 30 min. After pH had been adjusted to 8.5, the samples were filtered using a 0.45 µm membrane and used for analysis. It can be seen from Figure 1(a) that the removal efficiency of total cyanide for 3 and 5 mA cm⁻² was 46.0 and 46.8%, respectively, at 5 min. A greater removal of total cyanide was observed at the current density of 10 mA cm⁻². As shown in Figure 1(b) and (c), a large amount of Ni and Cu was efficiently removed via the EC process at 5 min for all selected current densities. The concentration of Ni and Cu decreased to less than 10 and 40 mg L⁻¹, respectively. As shown in the inset of Figure 1(b), the concentration of Ni decreased continuously over time. At 30 min, the concentration of Ni was determined to be

Figure 1 | Variation in concentration of pollutants in electroplating wastewater treated by electrocoagulation process with reaction time under various current densities at pH 4.0: (a) cyanide (CN); (b) Ni; (c) Cu.

0.29 mg L⁻¹ with the current density of 10 mA cm⁻². By contrast, concentration of residual Cu was still as high as 11.98 mg L⁻¹ (see Figure 1(c)). The concentrations of Cr and Zn decreased to 0.12 and 0.18 mg L⁻¹ at 5 min, which may be due to the hydroxide precipitation.

The pH value of the raw water was adjusted to 8.5 and the water samples were stirred for 20 min to examine the

Figure 2 | Variation in concentration of cyanide (CN) with reaction time under various conditions using raw water at pH 1.5: (a) various pH (H₂O₂ dosage, 3 mg L⁻¹); (b) various ratio of H₂O₂ to cyanide.

treatment efficiency of precipitation of simple hydroxides. After being filtered by 0.45 μm membrane, the filtrate obtained was analyzed. The concentration of Cu, Ni, Cr, and Zn was determined to be 20.1, 34.6, 6.7, and 4.8 mg/L, respectively. The above results indicated that the EC process was superior to the simple precipitation.

In the EC process, heavy metal ions are removed by a combined process of precipitation with iron ions, coagulation, and adsorption by iron flocs (Akbal & Camci 2011). In our case, residual Cu and Ni may be present as species of Cu/Ni-cyanide and Cu/Ni-organics complexes, which cannot be efficiently removed by the EC process. However, the surface complexation of cyanide ions with iron precipitates and cyanide enmeshment in the porous hydroxide precipitates might be responsible for removal of cyanide (Moussavi *et al.* 2011). Residual cyanide may be present as species of metal-cyanide, which cannot be easily removed by the EC process. COD was reduced from 245 to 208.3 mg/L (15.0% reduction) after 30 min. The TOC

values decreased from 141.4 to 116.4 mg/L (17.7% reduction) under the same conditions. Thus, it was concluded that the COD abatement was mainly due to cyanide removal.

H₂O₂ oxidation

It has been reported that free cyanide and complexed metal cyanides (i.e., nickel, copper, cadmium) can be oxidized by H₂O₂, leading to the generation of cyanate, nitrite, carbonate, and, eventually, nitrate when added in excess (Mudliar *et al.* 2009). Therefore, removal of the cyanide with the addition of H₂O₂ (3 mg L⁻¹) was tested at various pH values. It can be seen from Figure 2(a) that about 60% of the cyanide was removed within 10 min at all pH values. The difference between various pH conditions was slight. When the reaction time was extended, the increase in the removal of total

cyanide was limited at pH 5 and 6. By contrast, it increased to 76.6 and 80.1% at pH 3 and 4, respectively.

Next, removal of the cyanide with various ratios of total cyanide to H₂O₂ at pH 4 was investigated. As shown in Figure 2(b), the rapid removal of total cyanide occurs under all selected ratios of total cyanide to H₂O₂ at the initial 20 min. With prolonged reaction time, the removal efficiency of the cyanide increased with the increase of the ratio of total cyanide to H₂O₂. The difference in the cyanide removal with the ratio of 1.5:1 and 3:1 was slight. Therefore, the ratio of 1.5:1 was selected to use in the next experiment.

It is known that soluble copper may increase cyanide destruction rates significantly, like a Fenton process (Kitis *et al.* 2005). In our wastewater, the concentration of Cu is mostly higher than that of total cyanide. Therefore, the destruction of the cyanide by H₂O₂ oxidation may be catalyzed by the Cu–cyanide complexes.

Figure 3 | Effect of current density on removal of pollutants from effluent treated by H₂O₂ oxidation at pH 4.0: (a) cyanide; (b) Cu; (c) Ni; (d) COD.

Treatment of the effluent from the H₂O₂ oxidation followed by electrocoagulation and the anodic Fenton process

The above results indicated that removal of cyanide, heavy metals, and COD by EC or H₂O₂ oxidation separately was limited. Therefore, treatment of the wastewater by the combined processes of H₂O₂-EC and H₂O₂-AF was tested. Firstly, removal of residual cyanide, Cu, Ni, and COD using the H₂O₂-EC process with various current densities at pH 4 was tested. As shown in Figure 3(a), residual cyanide from the H₂O₂ oxidation can be removed by the EC process, and this increases with the current density. At 5 mA cm⁻², the concentration of total cyanide was reduced from 12 mg L⁻¹ to below 0.3 mg L⁻¹ within 30 min. As shown in Figure 3(b) and (c), efficient removal of Cu and Ni occurred at 5 min, and this effect increased with the current density (see inset of Figure 3(b) and (c)). At 30 min, the concentration of Ni and Cu was below 0.5 and 1.5 mg L⁻¹ at 20 mA cm⁻², respectively. For COD, 18.4% removal was observed at 20 mA cm⁻² (Figure 3(d)).

In the H₂O₂-AF process, the effluent from H₂O₂ oxidation was further treated by the AF process. At the current density of 5 mA cm⁻², doses of 5, 15, or 30 mM H₂O₂ were added to the electrochemical system at an initial pH of 4. As shown in Figure 4(a), residual cyanide in the effluent was removed via the addition of H₂O₂. At the same time, the concentration of Cu decreased to below 1 mg L⁻¹ (Figure SM-2(a), available online at <http://www.iwaponline.com/wst/068/296.pdf>). It is proposed that the liberated Cu ions can be efficiently removed by co-precipitation with iron ions via hydroxide or polyhydroxide formation. In addition, adsorption and surface hydroxyl complex formation may be responsible for removal of the metal ions. By contrast, with the addition of H₂O₂, the concentration of Ni was higher than that in the separate EC process at the same pH values of 8.5 (shown in Figure SM-2(b), available online at <http://www.iwaponline.com/wst/068/296.pdf>).

Removal of COD increased greatly with the addition of H₂O₂ into the electrochemical system with initial pH 4 and a constant current density of 5 mA cm⁻² (Figure 4(b)). At 30 min, COD decreased from 245 to 65 mg L⁻¹ with 3.0 mg L⁻¹ H₂O₂. COD removal increased slightly with the H₂O₂ dosage. Hydroxyl radicals (OH) generated in the AF reaction may be responsible for the COD reduction.

Transformation characteristics of the organic components

The UV-Vis spectra of the untreated wastewater and the samples treated by EC, H₂O₂ oxidation, H₂O₂-EC, and

Figure 4 | Effect of H₂O₂ dosage on removal of cyanide (CN) (a) and COD (b) from effluent treated by H₂O₂ oxidation at a current density of 5 mA cm⁻².

H₂O₂-AF are given in Figure SM-3 (available online at <http://www.iwaponline.com/wst/068/296.pdf>). There are peaks at 215 and 258 nm for the untreated samples. The intensities remain nearly the same after H₂O₂ oxidation. After treatment by H₂O₂-EC, the intensities of the peaks obviously decreased and the peaks at 215 and 258 nm nearly disappeared. After being treated by the H₂O₂-AF, the peak at 258 nm nearly disappeared and a blue shift occurred for the peak at 215 nm, indicating that the organic contaminants were efficiently destroyed.

Variations in EEMs of the untreated sample and the samples treated by EC, H₂O₂ oxidation, H₂O₂-EC, and H₂O₂-AF are presented in Figure 5. Excitation and emission boundaries were defined into five regions (Wen et al. 2003). As shown in Figure 5(a), two peaks (excitation (Ex)/emission (Em) (nm)) at 349/229 in region II and 334/281 in region IV were observed for the untreated wastewater. These peaks suggest that the untreated wastewater primarily contained aromatic protein-like and humin-like substances.

Figure 5 | EEMs of the electroplating wastewater treated by various processes for 30 min: (a) untreated electroplating water; (b) electrocoagulation; (c) H_2O_2 oxidation; (d) H_2O_2 oxidation followed by electrocoagulation; (e) H_2O_2 oxidation followed by anodic Fenton.

Almost no variation was observed for the sample treated by the EC (Figure 5(b)). The fluorescence intensity of the peaks in region II and region IV decreased and a new peak appeared at 423/276 in region V at 30 min in the H_2O_2 oxidation process (Figure 5(c)). In comparison with the sample

treated by H_2O_2 -EC, the fluorescence intensity of these peaks decreased sharply in H_2O_2 -AF; all the peaks disappeared at 30 min (Figure 5(d) and (e)). These results indicate the components with aromatic and conjugated structure in the wastewater have been efficiently destroyed.

CONCLUSIONS

The results indicate that Cr and Zn can be efficiently removed in the EC process. Complexes of Cu/Ni-cyanide or Cu/Ni-organics cannot be removed by the EC process alone. H₂O₂ oxidation can efficiently destroy cyanide instead of organic contaminants. In the case of H₂O₂-EC, the concentration of the residual cyanide, Ni, and Cu was efficiently reduced. COD removal is still limited, but it decreased to 65 mg L⁻¹ within 30 min in H₂O₂-AF process. The organic components with aromatic and conjugated structures in the wastewater were efficiently destroyed. Our results indicated that H₂O₂ oxidation followed by the anodic Fenton process would be a suitable method for treating electroplating wastewater containing Cu, Ni, cyanide, and organic contaminants.

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