

Treatment of non-biodegradable wastewater by electro-Fenton method

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Abstract A novel electro-Fenton method, called the Fered-Fenton method, applying H_2O_2 and electrogenerated ferrous ions for treating organic-containing wastewater was investigated. By combining electrochemical reduction and chemical oxidation, the process can regenerate ferrous ions and remove organic compounds simultaneously in a batch reactor. Because the generation rate of ferrous ions is one of the key parameters in evaluating the oxidation efficiency of the reaction system, the initial current efficiencies (η_i) for iron (III) reduction are examined first. It shows that increasing initial ferric ion concentration can achieve high initial current efficiency. In addition, η_i decreased (ca. 20–100%) with increasing current density of cathode (ca. 40–199 A/m²). For illustration, the wastewater from chemical (i.e. electroless) nickel plating was treated in this investigation owing to its non-biodegradability and high organic concentration. The average pH, COD and Ni concentrations of this wastewater were about 5.0, 30,000 and 2,000 mg/L, respectively. Experimental results indicate that traditional Fenton method only removed 60% of COD when using 5,000 mg/L of ferrous ions. However, the COD removal efficiency was promoted after the electricity was introduced into the system (i.e. Fered-Fenton method). Moreover, Ni concentration was reduced from 2,080 to 0.3 mg/L, indicating that the removal efficiency was higher than 99.9%.

Keywords Chemical plating; electro-Fenton; electrolysis; hydrogen peroxide; wastewater

Introduction

Fenton's reagent, a combination of H_2O_2 and a ferrous salt, is an effective and simple oxidant for various types of organic contaminants. In this system, the hydroxyl radical ($\bullet OH$) is generated by reducing H_2O_2 with a ferrous ion. It has been proved effective in treating various organic contaminants such as chlorobenzenes, nitrophenols, and aromatic amines (Casero *et al.*, 1997; Ewa, 1991; Sedlak and Andren, 1991). However, application of Fenton's reagent in the destruction of organic compounds has been limited by the slurry system because it produces a substantial amount of $Fe(OH)_3$ sludge which requires further separation and disposal.

The electro-Fenton method has received considerable attention (Sudoh *et al.*, 1986; Huang *et al.*, 1997; Brillas *et al.*, 1996), and can be divided into three types. The first type, i.e. EF- H_2O_2 method, uses Fe^{2+} and electrogenerated H_2O_2 , that can be produced from the two-electron reduction of sparged oxygen on graphite, reticulated vitreous carbon, or carbon-PTFE cathodes (Sudoh *et al.*, 1986; Hsiao and Nobe, 1993; Brillas *et al.*, 1996). Its main drawback is the low current efficiency in the acidic solution (Do and Chen, 1993). The second type, i.e. EF-Feox method, utilizes H_2O_2 and electrogenerated Fe^{2+} which is produced via the oxidation of iron, the sacrificial anode (Pratap and Lemley, 1994; Huang *et al.*, 1999). However, this method has the same limitations as the aforementioned Fenton's reagent. The final type is a novel electro-Fenton method (Fered-Fenton process) which applies H_2O_2 and electrogenerated Fe^{2+} produced via the reduction of ferric sulfate or ferric hydroxide sludge (Chou *et al.*, 1999). Only a slight amount of sludge will be generated in

this system because $\text{Fe}(\text{OH})_3$ sludge can be reused after coagulation and pH adjustment. Our previous investigation has confirmed that this system can still effectively treat petrochemical wastewater after 5 cycles of reuse (Huang *et al.*, 1997). However, it is still an open question as to whether or not the Fered-Fenton process can be used in the wastewater containing large amount of heavy metals. In this study, the Fered-Fenton process will be compared with other methods, including coagulation, reduction, direct electrolytic oxidation, and Fenton's method.

Materials and methods

Materials

Hydrogen peroxide (35%) solution was obtained from Union Chemical Works (Taiwan). Ferric sulfate (194 g-Fe/l) and ferrous chloride (208 g-Fe/l) were purchased from Hayashi Pure Chemical (Taiwan).

The wastewater of the chemical nickel plating process was generated from a local plant. The average pH, COD and Ni concentrations of this wastewater were about 5.0, 30,000 and 2,000 mg/L, respectively.

$\text{IrO}_2/\text{RuO}_2$ composite electrode was prepared by thermal decomposition of the following precursors: $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ (Johnson Matthey, 51.6% Ir) and $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (Johnson Matthey, 42.25% Ru).

Analytical methods

The initial ferric and nickel concentrations were determined with an atomic absorbance spectrophotometer (Varian Spectra AA-30). Chemical oxygen demand (COD) was analyzed according to *Standard Methods* (16th edn, 1985). The ferrous concentration was determined through titration with KMnO_4 .

Procedure

Fe²⁺ generation. Batch electrolyses were performed in a rectangular reactor (10.5 cm-L × 10.5 cm-W × 120 cm-H) operated at constant current mode. The apparatus is schematically shown in Figure 1. The anode was a titanium rod coated with $\text{IrO}_2/\text{RuO}_2$ (DSA), which was supported on a distributor. The cathode is a cylinder located outside the anode and the distributor. The ratio of the working area on the anode and cathode was maintained at 1:8. Mixing in the electrolytic cell was performed by recycling at 9 l/min. After ferric sulfate was added, the power supply was initiated. Ferric sulfate was applied to simulate the ferric

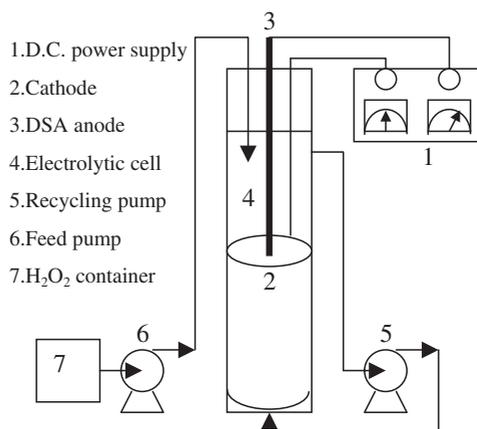


Figure 1 The experimental apparatus

hydroxide sludge produced in Fenton's reaction. The ferric ion could be reduced and regenerated to ferrous ion.

Fered-Fenton process. The experimental apparatus is the same as in Figure 1, except that H_2O_2 was used in the electrolytic system. The wastewater was mixed with concentrated ferric sulfate to the desired concentration before the power supply was started. Then 380 g/l of H_2O_2 was continuously added at a rate depending on the desired dosage. The H_2O_2 theoretical dosage was calculated on the basis of the disproportion of H_2O_2 by catalyst to give 0.5 mole O_2 per mole of H_2O_2 (Pardieck *et al.*, 1992). Fenton's test was also conducted in the same apparatus.

Results and discussion

Performance of Fe^{3+} reduction for the Fered-Fenton process

The proposed reactions in the electrolytic system for the Fered-Fenton process are as follows:

On the anode side:



On the cathode side:



The performance was evaluated by the instantaneous current efficiency (η) for iron (III) reduction, which is defined as

$$\eta = (\text{FV} / \text{A}) \frac{\text{dFe}^{2+}}{\text{dt}} \times 100\% \quad (5)$$

where F denotes the Faraday constant; Fe^{2+} represents the molar concentration of generated ferrous ion; V is the volume of the solution; A denotes the operating current; and t represents the reaction time. Since the current was kept constant, the amount of iron (II) generated was proportional to the time of electrolysis.

Our previous study (Chou *et al.*, 1999) suggested that Fered-Fenton process can provide a wider range of pH operation ($\text{pH} \leq 2.0$) and low iron (III) concentration ($\text{Fe}^{3+} \geq 3,000$ mg/l) than the system of Fenton sludge recycling ($\text{pH} \leq 1$, $\text{Fe}^{3+} \geq 10,000$ mg/l) (Gnann *et al.*, 1993). That investigation also revealed that the stainless steel cathode possesses the highest current efficiency among four different cathode materials including lead, stainless steel, titanium, and graphite. Therefore, in this study, we selected stainless steel as the cathode material and at the operating condition of $\text{pH} \leq 2.0$ for the remaining experiments.

Although the Fered-Fenton process has the above advantages, in terms of the low operating cost, the iron (III) concentration should be reduced as low as possible. Figure 2 illustrates the generated ferrous ion concentration as a function of the reaction time, where CDc and CDa represent the current densities of cathode and anode, respectively.

According to Eq. (5), the initial current efficiencies (η_i) in Figure 2 were then calculated. The effects of the current densities of cathode on η are depicted in Figure 3. It depicts that significant change in η was detected (ca. 20–80%) between 40 and 199 A/m² current density, and

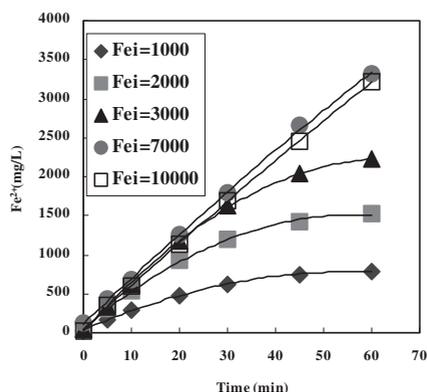


Figure 2 Effects of initial ferric concentration on the change of generated ferrous concentration (Fe^{2+}). $\text{CD}_c = 42 \text{ A/m}^2$, $\text{CD}_a = 336 \text{ A/m}^2$, $\text{pH}_i = 2$

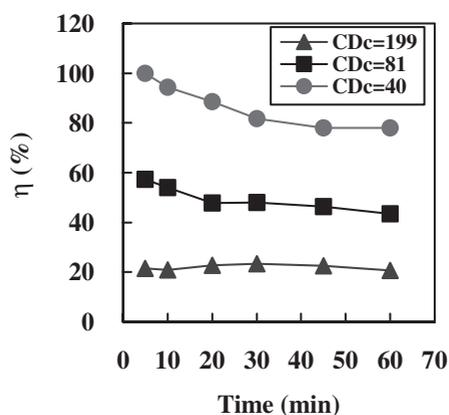


Figure 3 Effects of the current density of cathode on the change of current efficiency. $\text{Fe}^{3+} = 3,000 \text{ mg/L}$, $\text{pH}_i = 2$

the efficiency decreased with increasing the current density. In addition, η_i decreased (ca. 20–100%) with increasing the current density of cathode (ca. 40–199 A/m^2).

Screening tests for treating the wastewater from the chemical nickel plating process

The respective average COD and Ni concentrations of wastewater were 30,000 mg/l and 3,000 mg/l, respectively, implying that this wastewater is non-biodegradable and has high organic concentration. The major component of the wastewater was nickel–citric acid complex, which is difficult for alkali or coagulants to destroy. Conventional methods of isolating Ni with chelating agent were employed to treat this wastewater in a series of screening tests. Coagulation processes by calcium and ferric salts both failed to decompose the complex. Although reduction processes by sodium borohydride and sodium sulfide could reduce complex Ni to metal Ni, the COD removal was still less than 40%. Moreover, they were not feasible due to the high cost with the former process and the poor settleability with the latter one. Although direct electrolytic oxidation failed, more than 90% of complex Ni was removed with NH_4OH addition after 18 hours of electrolysis, while ammonia gas and the high COD effluent still need further treatment.

Figure 4 shows the changes in COD, CODr, temperature, and DO at pH 3.5 for the Fenton method where CODr denotes the COD removal efficiency. The wastewater was treated with 5,000 mg- Fe^{2+}/l , and H_2O_2 was continuously added into the reactor during a

six-hour reaction time. Experimental results indicate that 62 % of COD was removed after four hours of treatment. The higher COD at the final stage than that at 4h was due to the unreacted H₂O₂. The DO curve demonstrates a similar trend to that of COD. Coincidentally, the temperature showed a maximum value (51.1°C) at 3 h, then decreased owing to the slow or no chemical reaction at the final stage.

Treatment of chemical nickel plating wastewater by Fered-Fenton process

In the experiments using the Fered-Fenton process, the changes in COD, CODr, temperature, and DO during the reaction are shown in Figure 5. The cell voltage decreased from 5.8 V to 4.2 V during the reaction. The iron concentration (5,000 mg-Fe³⁺/l) was the same as that in the Fenton process. The COD concentration decreased dramatically from 27,900 mg/l to 3,070 mg/l after five hours of the reaction. Its final COD removal efficiency (93%) was found to be superior to that in the Fenton process (62%). Moreover, Ni concentration was reduced from 2,080 to 0.3 mg/L; the removal efficiency was greater than 99.9%. The temperature increased from 18.6°C to a maximum of 63.2°C after four hours of reaction. The significant increase in the temperature of the Fered-Fenton system suggests that an

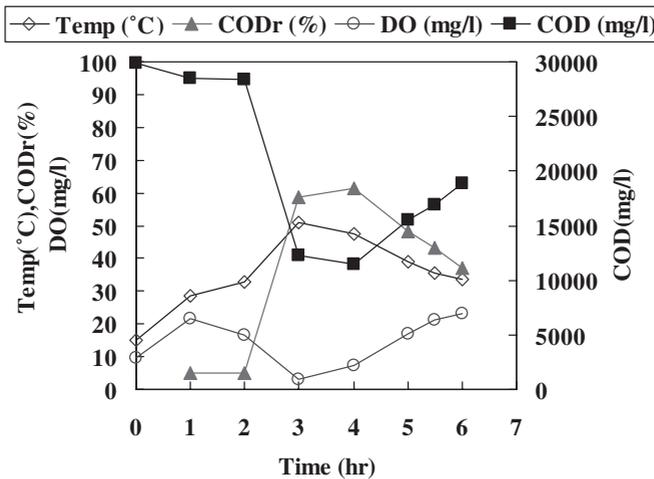


Figure 4 Changes in COD, CODr, temperature, and DO during the treatment with Fenton's method. Fe²⁺ = 5,000 mg/l, pH = 3.5

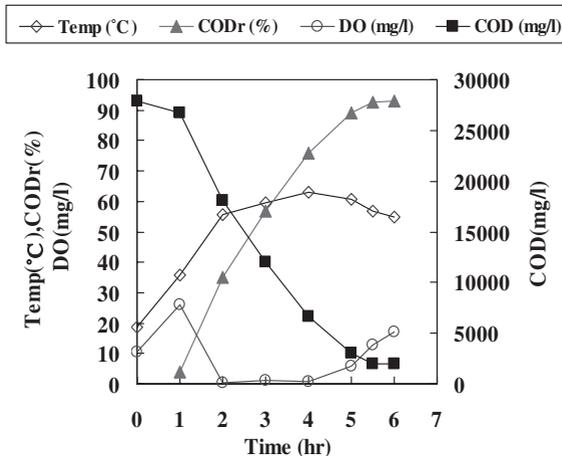


Figure 5 Changes in COD, CODr, temperature, and DO with Fered-Fenton process. Fe = 5,000 mg/l, CD_c = 160 A/m², CD_a = 1,250 A/m², pH_i = 1.6

exothermic reaction occurred in treating this wastewater. Korenaga *et al.* (1989) also observed a similar phenomenon when treating high strength wastewater with the Fenton reaction.

Conclusions

A novel electro-Fenton method, the Fered-Fenton method, applying H_2O_2 and electrogenerated ferrous ions in treating the organic-containing wastewater was investigated. By combining electrochemical reduction and chemical oxidation, the process can regenerate ferrous ions and remove organic compounds simultaneously in a batch reactor. Conventional methods using calcium and ferric salt as coagulants fail to treat the wastewater from the chemical nickel plating process in this work. Although reduction processes by sodium borohydride and sodium sulfide could reduce complex Ni to metal Ni, the COD removal was less than 40%. However, the Fenton method can attain 62% of COD removal efficiency. Furthermore, the Fered-Fenton process attained 93% of COD removal efficiency in treating this wastewater. Ni concentration was reduced from 2,080 to 0.3 mg/L in the same reaction time; the removal efficiency was greater than 99.9%. Consequently, combination of electrolytic and Fenton processes has potential in the field of treating wastewater containing organic and metallic pollutants.

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