



## TREATMENT OF HIGH STRENGTH HEXAMINE-CONTAINING WASTEWATER BY ELECTRO-FENTON METHOD

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**Abstract**—A novel Electro-Fenton (EF–Fere) method, applied H<sub>2</sub>O<sub>2</sub> and electrogenerated ferrous ion, was investigated for treating the hexamine-containing wastewater. The performance of Fe<sup>2+</sup> generation in the electrolytic system was first evaluated, including the factors of the cathode material, initial pH, initial ferric concentration (Fe<sub>i</sub>), and current density. When initial pH exceeded 2.5, the current efficiency dramatically decreased, which was due to the formation of Fe(OH)<sub>3</sub>. Between 3000 and 10,000 mg/l of Fe<sub>i</sub>, the initial current efficiency of Fe<sup>2+</sup> generation was almost constant (85–87%), which dropped sharply to 39% at 1000 mg/l. In EF–Fere experiments, the COD removal efficiency attained above 94% after 5 h of reaction. The relationship between the temperature, dissolved oxygen, and COD was discussed. The changes in hexamine and its oxidation intermediates (methanol, formaldehyde, formate, ammonium and nitrate) during the reaction were also investigated. Three additional experiments using H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>, H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup>, and direct electrolysis were also conducted to treat the hexamine-containing wastewater for comparison. The results showed that the EF–Fere method was the most efficient. © 1998 Elsevier Science Ltd. All rights reserved

**Key words**—hydrogen peroxide, electrolysis, oxidation, hexamine, wastewater

### INTRODUCTION

A hexamine-containing waste stream has been identified as the most refractory in a petrochemical factory (factory A) (Huang *et al.*, 1997). The COD concentration of this stream ranges from 15,000 to 40,000 mg/l. Hexamine, (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>, is a nonaromatic heterocyclic compound with a symmetrical three-dimensional molecular structure, as shown in Fig. 1. In acidic condition, it can be hydrolyzed to formaldehyde and ammonia (Pitter and Chudoba, 1990). Smith and Colquhoun (1987) have confirmed that hexamine is resistant to biodegradation, even when sludge has been acclimated for a long period.

Advanced oxidation processes (AOPs) are considered highly promising for treating refractory compounds. Common oxidants involved in AOPs are Fenton's reagent (Walling, 1975), ozone, ozone/H<sub>2</sub>O<sub>2</sub>, and UV/H<sub>2</sub>O<sub>2</sub>, of which the primary intermediate is the hydroxyl radical (OH·) (Huang *et al.*, 1993). Fenton's reagent, a mixture of hydrogen peroxide and a ferrous salt, is an effective and simple oxidant of organic contaminants. It has been proven effective in treating various organic contami-

nants such as dyes, ethers, nitrophenols, chlorinated phenols, aromatic amines, polycyclic aromatics, and photographic wastewater (Korenaga *et al.*, 1989; Ewa, 1991; Sedlak and Andren, 1991; Haag and Yao, 1992; Kuo, 1992; Casero *et al.*, 1997). However, the oxidation of nonaromatic heterocyclic compounds in this way was scarcely investigated (Korenaga *et al.*, 1989). In addition, the application of Fenton's reagent in the destruction of organics has been limited by the slurry system, because ferric hydroxide sludge requires additional separation process and disposal.

Several authors have recently reported the application of the electrochemical method in Fenton's reaction (electro-Fenton method). These studies can be generally divided into three groups. The first group (EF–H<sub>2</sub>O<sub>2</sub> method) uses Fe<sup>2+</sup> and electrogenerated H<sub>2</sub>O<sub>2</sub>, 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; Tzedakis *et al.*, 1989; Hsiao and Nobe, 1993; Brillas *et al.*, 1996). Its disadvantage is the low current efficiency in acidic condition (Do and Chen, 1993). The second group (EF–Feox method) utilizes H<sub>2</sub>O<sub>2</sub> and electrogenerated Fe<sup>2+</sup> which is produced via the oxidation of iron, the sacrificial anode (Pratap and Lemley,

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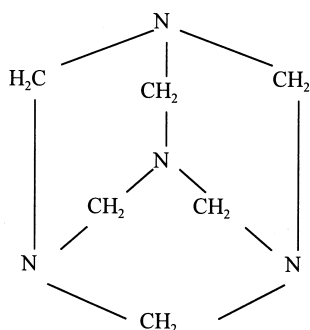


Fig. 1. The molecular structure of hexamine.

1994; Huang *et al.*, 1997). The last group called Fenton sludge recycling (FSR) system (Gnann *et al.*, 1993), involves a Fenton reactor and an electrolytic cell for reducing the ferric hydroxide sludge to ferrous ion.

In our previous study (Huang *et al.*, 1997), we evaluated the performance of five chemical oxidation processes (ozone, ozone/H<sub>2</sub>O<sub>2</sub>, sodium hypochlorite, Fenton's reagent, and EF-Feox) in treating the bioeffluent (COD = 200–400 mg/l) of factory A. The major component of this effluent has been identified as hexamine, which contributed 65% of COD. Among these processes, the EF-Feox process was proven to be the most efficient.

This paper presents a novel electro-Fenton method (EF-Fere method), which combines the Fenton process and the electrolytic cell of FSR-system into one reactor, for treating the high strength hexamine-containing wastewater. It applies H<sub>2</sub>O<sub>2</sub> and electrogenerated Fe<sup>2+</sup> produced via the reduction of ferric sulfate or ferric hydroxide sludge (Huang *et al.*, 1998). Little sludge generates in this system because Fe(OH)<sub>3</sub> sludge can be reused after coagulation and pH adjustment. It has been proven that this system is very effective in treating petrochemical wastewater after 5 times of reuse in our laboratory (Huang *et al.*, 1998).

## EXPERIMENTAL

### Materials

Hydrogen peroxide solution was obtained from the Union Chemical. Ferric sulfate was purchased from Hayashi Pure Chemical. HPLC-grade phosphoric acid was obtained from Merck. HPLC-grade acetonitrile was purchased from Alps Chemical. The characterization of this high strength hexamine-containing stream which was used in this study is listed in Table 1.

### Analytical methods

Hexamine was analyzed using high performance liquid chromatography (HPLC) with a Spherex NH<sub>2</sub> column (25 cm L × 4.6 mm ID, Phenomenex); the mobile phase consisted of 65% acetonitrile and 35% deionized water. Formaldehyde, methanol, and formate ion were analyzed using HPLC with an ion exchange/ion exclusion column (ORH801, 30 cm L × 6.5 mm ID, Interaction Chemical); the mobile phase was 0.1% phosphoric acid. Both of the above analyses applied the refractometer as the detector. The initial ferric concentration was determined with an atomic absorbance spectrophotometer (Varian Spectra AA-30). Chemical oxygen demand (COD) was analyzed according to the Standard Method (16th Ed., 1985). The ferrous concentration was determined through titration with KMnO<sub>4</sub>. Nitrate and nitrite were determined with an ion chromatography (Dionex DX100) and NH<sub>4</sub><sup>+</sup> was analyzed with a portable digital nitrogen meter (CKC, HC-707N).

### Experimental procedures

**Fe<sup>2+</sup> generation.** Batch electrolyses were performed in a rectangular reactor (10 cm L × 10 cm W × 100 cm H) operated at constant current mode. The schematic apparatus is shown in Fig. 2. The anode was a titanium rod coated with RuO<sub>2</sub>/IrO<sub>2</sub> (DSA). As shown in Fig. 2, the cathode is a cylinder located outside the anode. The ratio of the working area on the anode and cathode was maintained at 1:10 in most of the experiments, except in the screening test of the cathode material. Five liters of the solution was used in each trial. The mixing in the electrolytic cell was provided by recycling at 9 l/min. After ferric sulfate was added, the power supply was initiated. Ferric sulfate was applied to simulate the ferric hydroxide sludge produced in the Fenton's reaction. The ferric ion could be reduced and regenerated to ferrous ion.

**EF-Fere method.** The experimental apparatus is the same as the one shown in Fig. 2, except that H<sub>2</sub>O<sub>2</sub> was used in the electrolytic system. High strength hexamine-containing wastewater was mixed with concentrated ferric sulfate to the desired concentration (Fe<sub>i</sub>) before the power supply was started. Then 380 g/l of H<sub>2</sub>O<sub>2</sub> was continuously added at a rate depending on the desired dosage. To elevate the mineralization of the wastewater, H<sub>2</sub>O<sub>2</sub> was so added that at the end of the reaction (6 h), it reached 120% of the theoretical dosage. The H<sub>2</sub>O<sub>2</sub> theoretical dosage was calculated based on the disproportion of H<sub>2</sub>O<sub>2</sub> by catalyst to give 0.5 mole O<sub>2</sub> per mole of H<sub>2</sub>O<sub>2</sub> (Pardieck *et al.*, 1992). The supernatant was analyzed for COD, hexamine, formaldehyde, formate ion, methanol, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>.

## RESULTS AND DISCUSSION

### Performance of Fe<sup>2+</sup> generation

The proposed reactions in the electrolytic system are:

On the anode side:

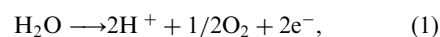


Table 1. Characterization of the hexamine-containing wastewater used in the study

pH	COD (mg/l)	SS (mg/l)	Conductivity (mho/cm)	Hexamine (mg/l)	Formaldehyde (mg/l)	Methanol (mg/l)	NH <sub>4</sub> <sup>+</sup> -N (mg/l)	NO <sub>3</sub> <sup>-</sup> -N (mg/l)
8.5	17100	52	9.7	3680	2298	4851	1235	15
8.97	29640	85	10.1	7380	—	—	—	—

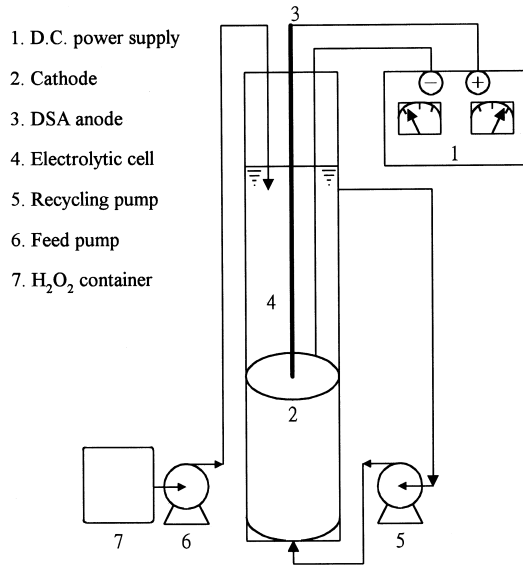
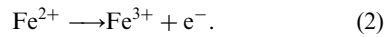
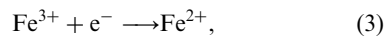


Fig. 2. The experimental apparatus in this study. Hydrogen peroxide is added only in the EF-Fere process.

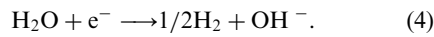
and



On the cathode side:



and



The performance was evaluated by the instantaneous current efficiency ( $\eta$ ) of ferrous ion gener-

ation, which is defined as

$$\eta = (FV/A) \frac{dC_{\text{Fe}}}{dt} \times 100\%, \quad (5)$$

where  $F$  is the Faraday's constant,  $C_{\text{Fe}}$  represents the molar concentration of generated ferrous ion,  $V$  is the volume of the solution,  $A$  is the operating current, and  $t$  is the reaction time. Since the current was kept constant, the amount of  $\text{Fe}^{2+}$  generated was proportional to the time of electrolysis.

Four different cathode materials including lead, sustained steel, titanium, and graphite were tested, because the preferable reaction (equation 3) occurred on the cathode. The ratio of the working area on the anode and the cathode was chosen as 3:8. The larger working area on the cathode was designed to promote the reduction of  $\text{Fe}^{3+}$  (equation 3) and to minimize the oxidation of  $\text{Fe}^{2+}$  on the anode (equation 2). No significant change in pH was observed. Figure 3 shows that  $C_{\text{Fe}}$  increased rapidly initially, but approached a plateau toward the end of the reaction, which indicated that  $\eta$  decreased with the time. The sustained steel cathode possessed the highest initial current efficiency (i.e., 83.6% of  $\eta_i$ ), which would achieve greater  $\text{Fe}^{2+}$  production and subsequently higher degradation rate of organic compounds in the EF-Fere process. Because of the higher  $\eta_i$  and the longer life in acidic condition, we selected sustained steel as the cathode material for the rest of the experiments.

The effect of initial pH ( $\text{pH}_i$ ) on  $\eta_i$  is presented in Fig. 4 ( $\text{pH}$  varied slightly during the reaction).

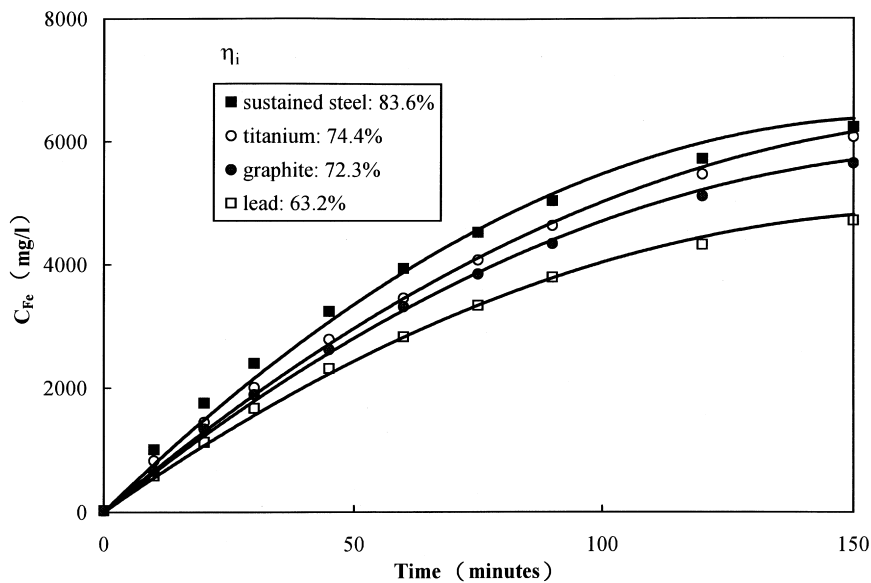


Fig. 3. Effect of cathode material on the change of generated ferrous concentration ( $C_{\text{Fe}}$ ). The solid line is the fit of second-order polynomial model.  $\eta_i$  represents the initial instantaneous current efficiency. Initial ferric concentration ( $\text{Fe}_i$ ) = 5000 mg/l,  $\text{CD}_c = 42 \text{ A/m}^2$ ,  $\text{CD}_a = 112 \text{ A/m}^2$ ,  $\text{pH}_i = 2.1$ .  $\text{CD}_c$  and  $\text{CD}_a$  denote the current densities of cathode and anode, respectively.

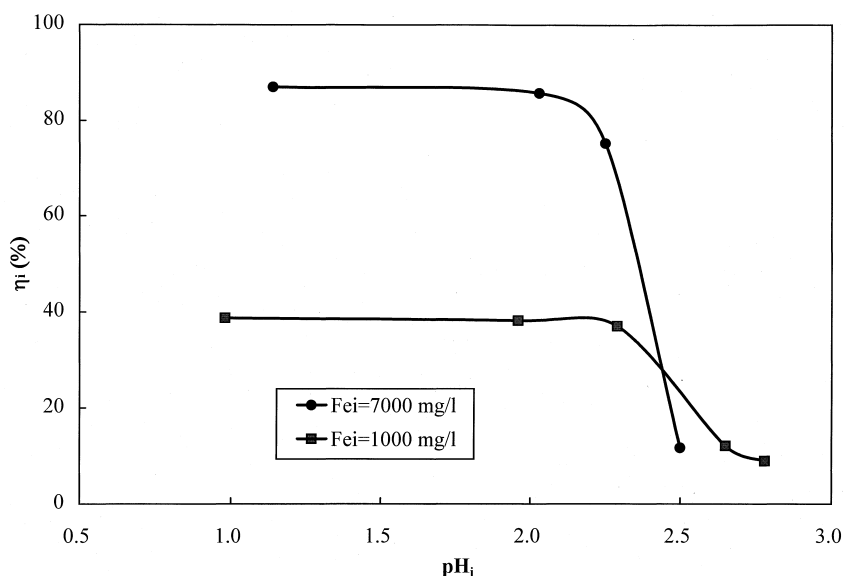


Fig. 4. Effect of initial pH ( $pH_i$ ) on the initial instantaneous current efficiency.  $CD_c=98 \text{ A/m}^2$ ,  $CD_a=980 \text{ A/m}^2$ .

Two ferric concentrations were used, 7000 and 1000 mg/l. In both trials, no significant difference in the current efficiency was noted till pH 2.0 and a sudden drop occurred after that. Note that no sludge was generated at  $pH < 2.0$ . From pH 2.0 to 2.5, a 75% decrease in  $\eta_i$  was observed in the trial of 7000 mg/l ferric concentration and approximately 30% decrease was detected in the 1000 mg/l trial. This phenomenon is due to the formation of  $Fe(OH)_3$  that hardly reduced to  $Fe^{2+}$  (Stumm and Morgan, 1996). The result suggests that this method can provide a wider pH operation range (i.e.,  $pH < 2.5$ ) when comparing with the FSR-system (i.e.,  $pH < 1$ ) (Gnann *et al.*, 1993).

Several initial ferric concentrations ( $Fe_i$ ) were performed to test their effect on  $\eta_i$ , and the result is depicted in Fig. 5. At low  $Fe_i$  (between 1000 mg/l and 3000 mg/l),  $\eta_i$  increased with increasing  $Fe_i$ ; but no change was observed between 3,000 and 10,000 mg/l. The low  $\eta_i$  at low  $Fe_i$ , 39% at 1000 mg/l  $Fe_i$ , is attributed to the limiting mass transfer of  $Fe^{3+}$  ion to the cathode surface when the ferric ion concentration is low (Coin *et al.*, 1996). The electrolytic system would lead to a significantly low current efficiency when  $Fe_i$  was below the critical concentration.

The current density was adjusted to test its effect on  $\eta_i$  using 1000 mg/l of  $Fe_i$  and the result is shown

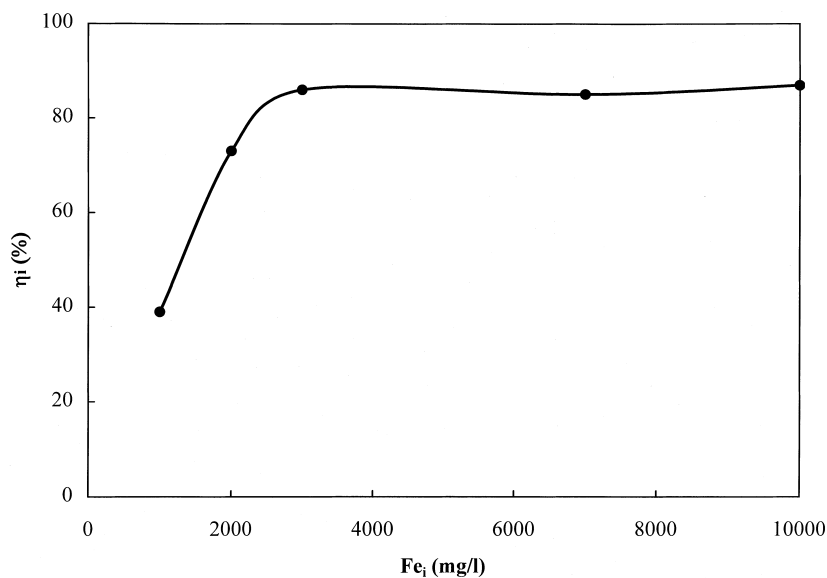


Fig. 5. Effect of initial ferric concentration on the initial instantaneous current efficiency.  $CD_c=98 \text{ A/m}^2$ ,  $CD_a=980 \text{ A/m}^2$ ,  $pH_i=2.0$ .

in Fig. 6. The cell voltage varied from 3 to 7 V depending on the current density chosen. No significant change in  $\eta_i$  was detected (ca. 38–40%) between 50 and 100 A/m<sup>2</sup>. When 150 A/m<sup>2</sup> was used, only 25% of  $\eta_i$  was achieved. Operation under high current density results in low current efficiency and requires smaller cathode area.

#### *Treatment of hexamine-containing wastewater by EF-Fere method*

In this section of study, hexamine-containing wastewater was treated with the EF-Fere method, and the changes in COD and H<sub>2</sub>O<sub>2</sub> dosage are shown (Fig. 7(a)). The cell voltage increased from 9.3 V to 10.4 V during the reaction. In Fig. 7(a), trials I and II have the same operating conditions ( $Fe_i = 5000$  mg/l,  $CD_c = 188$  A/m<sup>2</sup>) but with different initial COD concentration. The trends of COD change in these two trials are very similar. Trial III used the same initial COD as in trial I but lower  $Fe_i$  and higher current efficiency ( $Fe_i = 1000$  mg/l,  $CD_c = 100$  A/m<sup>2</sup>). The slightly lower COD removal of trial III (98.5%, final COD = 271 mg/l) than that of trial I (99.7%, final COD = 100 mg/l) may be due to the limiting mass transfer of  $Fe^{3+}$  to the cathode, as discussed before.

In Fig. 7(b), the changes in pH, temperature, and DO during the treatment process are depicted. The temperature increased from 19.7°C to a maximum of 67.8°C after 3 h of reaction. In contrast, the temperature of the  $Fe^{2+}$  generation system only increased 20°C after 3 h of reaction (not shown in the figure), that was proven due to the heat generated from the recycled pump. The large increase in the temperature of the EF-Fere system suggests

that an exothermic reaction occurred in treating this wastewater. Similar result has been observed in the study of treating high strength wastewater with Fenton's reaction by Korenaga *et al.* (1989).

Dissolved oxygen decreased from 6.0 mg/l to a minimum (i.e., 0.6 mg/l) after 2 h of reaction, and then gradually increased to 2.4 mg/l at 4 h, finally suddenly increased to 16.9 mg/l at 5.5 h (Fig. 7(b)). The reduction in DO could result from the increase in temperature. However, the DO and temperature both increased in the interval of 2–3 h, which suggested that oxygen was indeed consumed in the initial stage by the degradation of hexamine. Decomposition of residual H<sub>2</sub>O<sub>2</sub> by  $Fe^{2+}$  produces oxygen and replenishes DO (Pardieck *et al.*, 1992; Lu *et al.*, 1996), which was depicted in the ascending of DO in the final stage. This finding was echoed by the nearly complete mineralization (in Fig. 7(a), the COD removal efficiency was above 94% at 5 h). Therefore, DO can be used as an index for terminating the EF-Fere system.

*Oxidation intermediates of hexamine.* Hexamine is easily degraded to formaldehyde and ammonium in acidic condition. Do and Chen (1993) has proven that formic acid is the oxidation product of formaldehyde in Fenton's reaction. Figure 8 depicts the variation of methanol, hexamine, formaldehyde, and formate during the treatment. It is shown that only 2.6% of hexamine remained (i.e., from 18.1 mM down to 0.47 mM) after 3 h of reaction. Formaldehyde reached maximum and disappeared earlier than formate. Methanol decreased monotonously during the reaction. The control jar test, conducted in acidic condition without electrolysis, confirmed that hexamine was only slightly

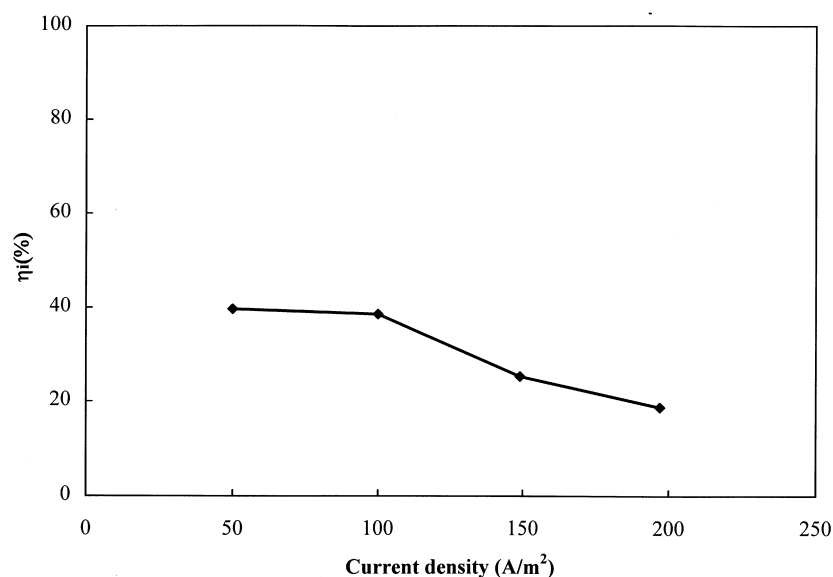


Fig. 6. Effect of current density on the initial instantaneous current efficiency.  $Fe_i = 3000$  mg/l,  $CD_c:CD_a = 1:10$ ,  $pH_i = 1.03$ .

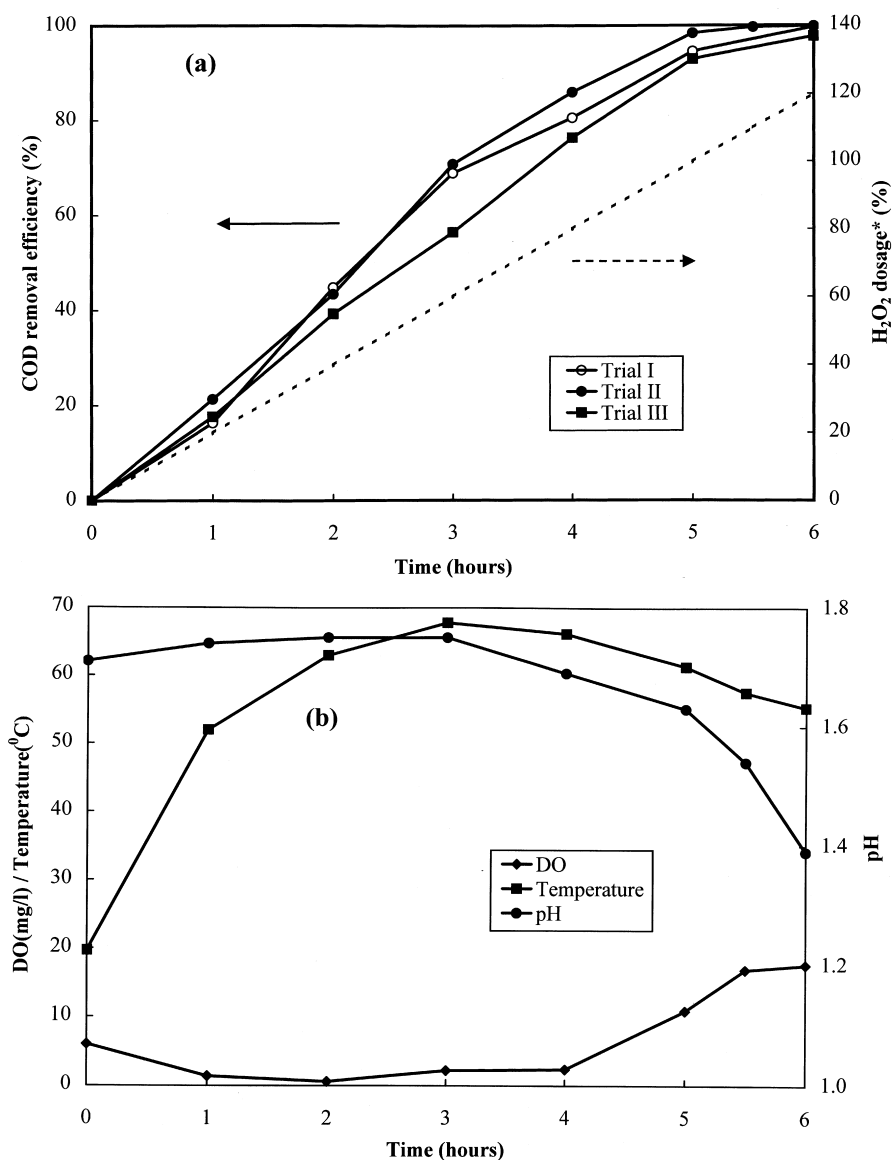
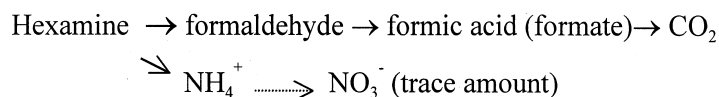


Fig. 7. Changes in (a) COD and H<sub>2</sub>O<sub>2</sub> dosage, (b) pH, temperature, and DO (trial I) during the treatment with the EF-Fere method. H<sub>2</sub>O<sub>2</sub> dosage\* (%) denotes the percentage to the theoretic dosage which can mineralize the wastewater completely. Trial I (COD<sub>i</sub> = 17100 mg/l) and II (COD<sub>i</sub> = 29640 mg/l): Fe<sub>i</sub> = 5000 mg/l, CD<sub>c</sub> = 188 A/m<sup>2</sup>, pH<sub>i</sub> = 1.71. Trial III (COD<sub>i</sub> = 17100 mg/l): Fe<sub>i</sub> = 1000 mg/l, CD<sub>c</sub> = 100 A/m<sup>2</sup>, pH<sub>i</sub> = 1.99.

degraded at pH 1.5 (5% of removal efficiency at 3 h) and no formate was detected. Therefore, we can conclude that those oxidation intermediates were produced mainly from the reactions in the EF-Fere method.

The changes in nitrogen-containing compounds including hexamine, NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> (no NO<sub>2</sub><sup>-</sup> was detected) during the treatment are also studied

(Fig. 9). This finding indicates that NH<sub>4</sub><sup>+</sup> is the major nitrogen-containing intermediate in hexamine degradation. Nitrate only occupies trace amount because NH<sub>4</sub><sup>+</sup> is a refractory compound in the oxidation by hydroxyl radicals, which conforms to the result obtained by Hoigne and Bader (1978). According to the above results, we can propose the mechanism of hexamine degradation as follows:



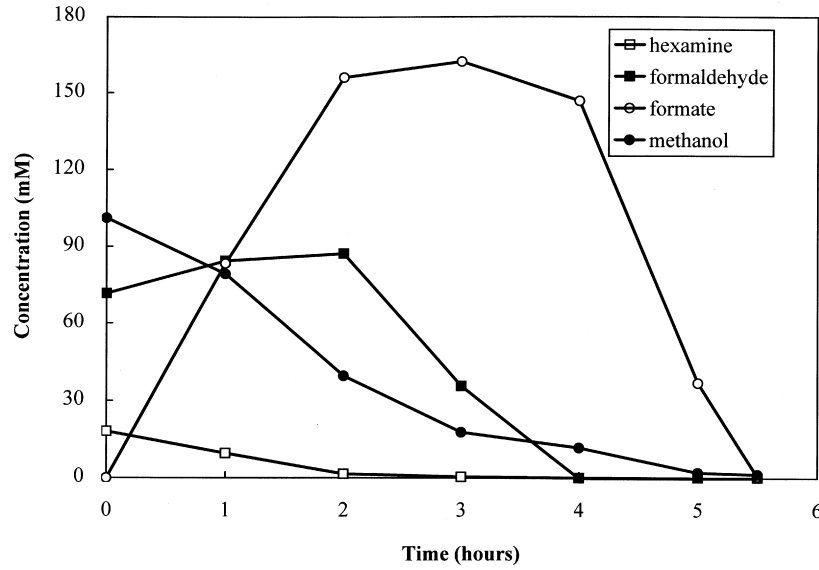
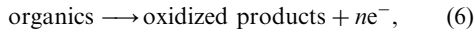


Fig. 8. Changes in hexamine, formaldehyde, methanol, and formic acid during the treatment with the EF-Fere method. The operating condition is the same as that of trial I in Fig. 7.

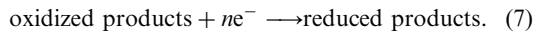
*Comparison experiments with  $H_2O_2/Fe^{2+}$ ,  $H_2O_2/Fe^{3+}$ , and direct electrolysis*

In addition to equations 1–4, the following electrochemical reactions may occur in treating the organic contaminants with the EF-Fere system.

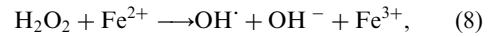
On the electrodes:



and



In the solution phase,  $OH^\cdot$  is produced as below:



which  $OH^\cdot$  can degrade the organic contaminants.

To further understand the reaction mechanism, three comparison experiments ( $H_2O_2/Fe^{2+}$ ,  $H_2O_2/Fe^{3+}$ , and direct electrolysis) were performed in acidic condition to treat the hexamine-containing wastewater. In Fig. 10, the changes in COD of the above comparison experiments are shown. The  $H_2O_2/Fe^{3+}$  trial (trial A) failed to oxidize this

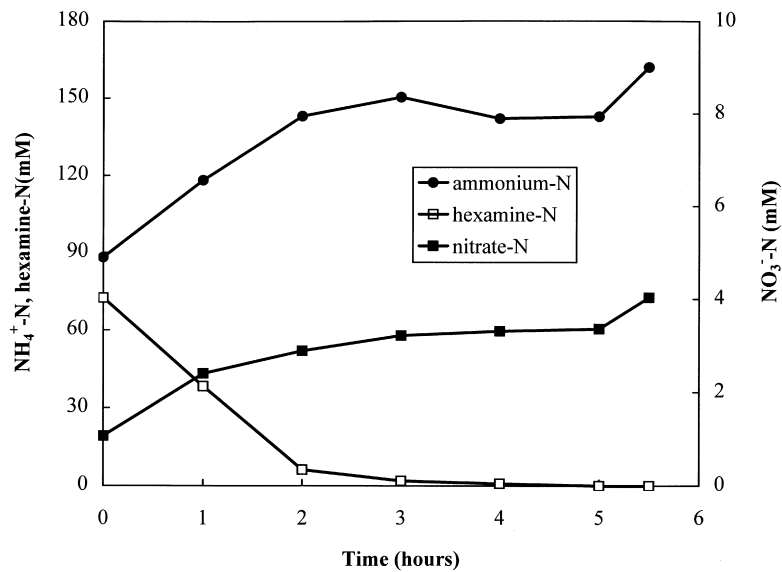


Fig. 9. Changes in hexamine-N,  $NH_4^+$ -N and  $NO_3^-$ -N during the treatment with the EF-Fere method. The operating condition is the same as that of trial I in Fig. 7.

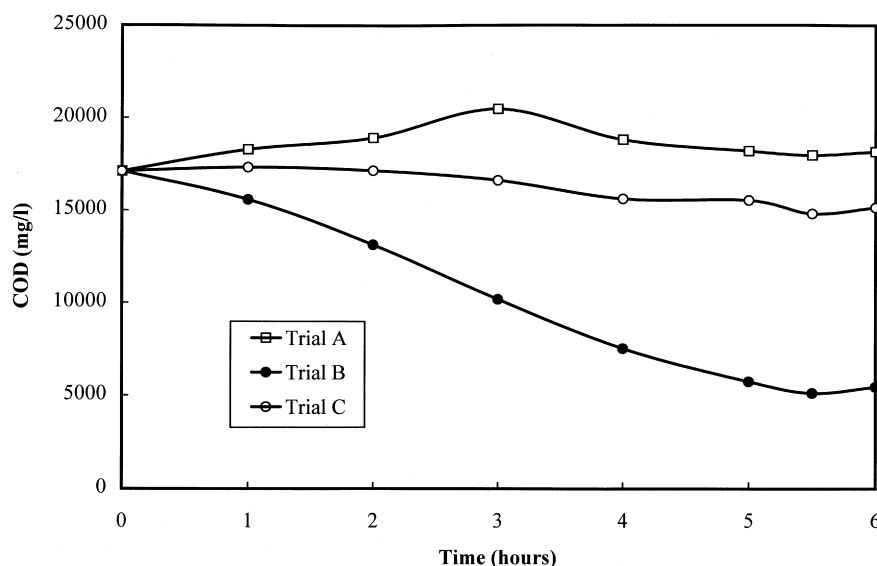


Fig. 10. Changes in COD during the treatment with three comparison experiments. Trial A ( $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ ):  $\text{Fe}^{3+} = 5000 \text{ mg/l}$ , with  $\text{H}_2\text{O}_2$ , no electrolysis,  $\text{pH}_i = 2.65$ . Trial B ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ):  $\text{Fe}^{2+} = 5000 \text{ mg/l}$ , with  $\text{H}_2\text{O}_2$ , no electrolysis,  $\text{pH}_i = 2.46$ . Trial C (direct electrolysis):  $\text{Fe}^{3+} = 5000 \text{ mg/l}$ , no  $\text{H}_2\text{O}_2$ , with electrolysis,  $\text{CD}_c = 188 \text{ A/m}^2$ ,  $\text{pH}_i = 1.57$ .

wastewater; the higher COD than the initial concentration was contributed by the residual  $\text{H}_2\text{O}_2$ . In the direct electrolysis trial (trial C), the low COD removal efficiency (ca. 12%) indicates that the reactions in equations 7 and 8 can be ignored. The COD removal efficiency of the  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  trial (trial B) was the highest (66% at 5 h) but still much lower than that of the EF-Fere method (above 94% at 5 h, as shown in Fig. 7(a)), which was attributed to the presence of formate (instead of formic acid) in the latter. The reaction rate constants of formic acid ( $\text{HCOOH}$ ) and formate ( $\text{HCOO}^-$ ) with  $\text{OH}^\cdot$  are  $1.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  and  $3.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , respectively (Buxton *et al.*, 1988), thus the mineralization rate with the EF-Fere method is higher than that with conventional Fenton's reagent. These results illustrate that the EF-Fere method is the most effective in treating the hexamine-containing wastewater.

#### CONCLUSIONS

This paper has presented a new electro-Fenton method for treating the high strength hexamine-containing wastewater. This EF-Fere method was proven to be the most effective compared with  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ,  $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ , and direct electrolysis. In the electrolytic system of  $\text{Fe}^{2+}$  generation, operations with low current density and high initial ferric ion concentration led to high current efficiency. In addition, the current efficiency decreased significantly when initial pH exceeded 2.5. In treating this wastewater with the EF-Fere method, the variation in DO was related to the change in COD. Hence, DO could be adopted as

an index for monitoring this system. The changes in methanol, hexamine, formaldehyde, and formate during the reaction provide us the information to propose a degradation mechanism of hexamine in this system.

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