Comparison of a novel electro-Fenton method with Fenton's reagent in treating a highly contaminated wastewater

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Abstract This study applied a novel electrochemical process called the Fered-Fenton method to treat a highly concentrated wastewater. By combining electrochemical reduction and chemical oxidation, the process can remove organic compounds and heavy metals in a batch reactor. A PVC-stabilizer processing wastewater was treated in this investigation owing to its high heavy metal concentration (Pb = 7,500 mg/l) and high organic concentration (COD = 11,000 mg/l). The major organic component was acetate. Direct anodic oxidation showed no effect on COD removal. Fenton's method only removed 36% of COD using 4,000 mg-Fe^{2+}/l and 28,000 mg-H_2O_2/l dosage. In the Fered-Fenton process, about 89% of COD was removed with 2,000 mg-Fe^{3+}/l and 28,000 mg-H_2O_2/l. Furthermore, the COD removal attained an efficiency of about 98% for 56,000 mg-H_2O_2/l used. Results presented herein demonstrate that the Fered-Fenton method is superior to direct anodic oxidation and Fenton's method in this case. Furthermore, the changes of the intermediate compounds including acetate, oxadate, and formate during the reaction were analyzed, which provided us with the information to propose degradation reactions of the wastewater in this system.
Keywords Electro-Fenton; hydrogen peroxide; electrochemical oxidation; wastewater.

Introduction

Fenton's reagent (Fenton, 1894), a mixture of H_2O_2 and a ferrous salt, has been proved an effective and simple oxidant for various types of organic contaminants (Buxton *et al.*, 1988). In this system, hydroxyl radical (•OH) is generated by reducing of H_2O_2 with ferrous ion (reaction 1)).

$$H_2O_2 + Fe^{2+} \rightarrow •OH + OH^- + Fe^{3+} \qquad (1)$$

Fenton's reagent has been proved effective at treating various aromatic compounds such as chlorobenzenes, nitrophenols, and aromatic amines (Casero *et al.*, 1997; Ewa, 1991; Sedlak and Andren, 1991). 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. Another drawback of Fenton's reagent is that the overall oxidation process is considerably slowed down after conversion of Fe^2 to Fe^{3+} (reaction (1)), as the reduction of Fe^{2+} to Fe^{3+} by hydrogen peroxide (reaction 2)) is much slower than reaction (1) (Barb *et al.*, 1951).

$$H_2O_2 + Fe^{3+} \rightarrow •O_2H^+ + H^+ + Fe^{2+} \qquad (2)$$

Recently, the electro-Fenton method has received considerable attention (Sudoh *et al.*, 1986; Huang *et al.*, 1997; Brillas, 1996), and can be divided into three types. The first type uses Fe^{2+} and electrogenerated H_2O_2 (Sudoh *et al.*, 1986; Hsiao and Nobe, 1993; Brillas, 1996). The second type 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). The final type (Fered-Fenton process) applies H_2O_2 and electrogenerated Fe^{2+} produced via the

reduction of ferric sulfate or ferric hydroxide sludge (Chou *et al.*, 1999). Our previous investigation has verified that this system can effectively treat petrochemical wastewater after 5 times of reuse (Huang *et al.*, 1997). This study evaluated the treatment of a PVC-stabilizer processing wastewater using the Fered-Fenton process, direct anodic oxidation, and Fenton's reagent.

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 was the raw wastewater generated from a PVC-stabilizer plant. The COD and Pb concentrations of this wastewater were 11,000 mg/l and 7,500 mg/l, respectively.

IrO_2/RuO_2 composite electrode was prepared by thermal decomposition of the following precursors: $IrCl_3$ xH_2O (Johnson Matthey, 51.6% Ir) and $RuCl_3$ xH_2O (Johnson Matthey, 42.25% Ru).

Analytical methods

The ferric and lead concentrations were 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 $KMnO_4$. Volatile acids were analyzed using high performance liquid chromatography (HPLC) with an ion exchange/ion exclusion column (ORH8u01, 30 cm-L $\times$ 6.5 mm-ID, Interaction Chemical Company); the mobile phase was 0.1% phosphoric acid. The analyses applied the refractometer as the detector.

Apparatus

Batch electrolyses were performed in a rectangular reactor (11 cm-L $\times$ 11 cm-W $\times$ 120 cm-H) operated at constant current mode. The schematic apparatus is shown in Figure 1. The anode was a titanium rod coated with IrO_2/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.

Method

Fered-Fenton process. Five to ten litres of the wastewater was employed for the system. After ferric sulphate was added and pH was adjusted to about 2.0, the power supply was initiated. The pH in the reactor was not controlled during the reaction. Ferric sulfate was applied to simulate the feric hydroxide sludge produced in the Fenton's reaction. The ferric ion could be reduced and regenerated to ferrous ion. 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 process. The same apparatus and procedures used in the Fered-Fenton process were applied here, except that power supply was not operated during the reaction. Furthermore, ferrous chloride was used instead of ferric sulfate.
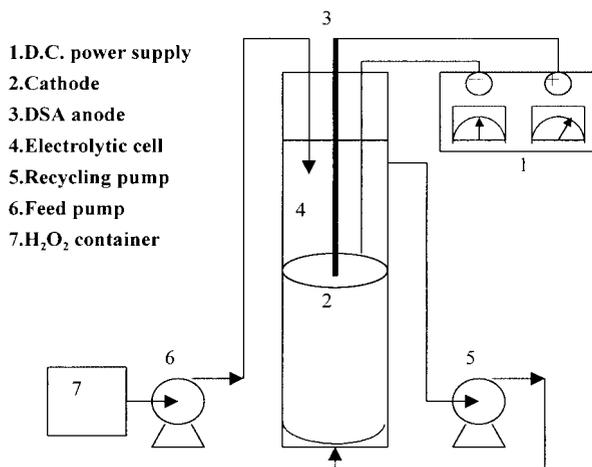
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Figure 1 The experimental apparatus in this study

1. D.C. power supply
2. Cathode
3. DSA anode
4. Electrolytic cell
5. Recycling pump
6. Feed pump
7. H_2O_2 container

Direct anodic oxidation. The experiment was conducted in the same apparatus and procedures as the Fered-Fenton process, except that neither iron solution nor H_2O_2 was added to the system.
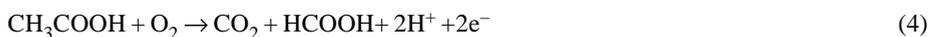
Results and discussion

Pretreatment for the PVC-stabilizer processing wastewater
The respective pH, Pb and COD concentrations of this chemical factory wastewater were 7.2, 7,500 mg/l and 11,000 mg/l, implying that this wastewater contains high strength of metal and organic compounds. Therefore, Pb must be separated from the organic compounds first. Conventional methods of isolating Pb were coagulation processes by adding calcium hydroxide and/or sodium hydroxide to form $PbCO_3$ and/or $Pb(OH)_2$. Although these processes could remove Pb, it produced a substantial amount of sludge which requires further separation and treatment before disposal. This work applied H_2SO_4 instead of the basic reagents mentioned above to produce $PbSO_4$ precipitation. The Pb concentration in the wastewater was reduced from 7,500 mg/l to 26 mg/l with 99.7% removal efficiency at pH 2. Moreover, $PbSO_4$ precipitation could be reused in the factory because it is a raw material of another process.

Performance of COD removal by direct anodic oxidation
After the pretreatment, the wastewater was initially treated by direct anodic oxidation. The major organic component was acetate. The proposed reactions in the electrolytic system for the direct anodic oxidation are as follows:

On the anode side:

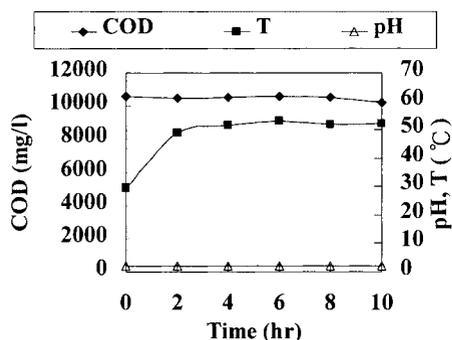$$H_2O \rightarrow 2\,H^+ + 1/2\,O_2 + 2e^-, \text{ and} \tag{3}$$

$$CH_3COOH + O_2 \rightarrow CO_2 + HCOOH + 2H^+ + 2e^- \tag{4}$$

On the cathode side:

$$H_2O + e^- \rightarrow 1/2\,H_2 + OH^- \tag{5}$$

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Figure 2 Changes in COD, pH, and temperature by direct anodic oxidation. CDc = 150 A/m^2, CDa = 1,200 A/M^2. CDc and CDa denote the current densities on the cathode and the anode, respectively

Figure 2 shows the changes in COD, pH, and temperature (in terms of T) by direct anodic oxidation. Experimental results display no effect on the COD removal after ten hours of the treatment. The pH value was unchangeable during the reaction. The increase in temperature was mainly due to the electrolysis.

Performance of COD removal by Fenton's reagent

Next, the wastewater was treated by Fenton's reagent with 1,000 mg-Fe/l and 4,000 mg-Fe/l, respectively. The changes in COD and H_2O_2 during the treatment are depicted in Figure 3a, which displays a little effect on the COD removal. The increase of COD in the initial range was due to the unreacted H_2O_2, especially under the low iron concentration of 1,000 mg/l.

The changes in CODm and temperature during the reaction are shown in Figure 3b, where CODm is the modified COD. From the analyses of COD and H_2O_2 during the reaction, the CODm can be calculated using the relation:

$$CODm = COD - H_2O_2/2.125 \tag{6}$$

The temperature increased from 30°C to a maximum of 43°C after six hours of reaction for both cases (1,000 mg-Fe/l and 4,000 mg-Fe/l). The CODm concentration linearly decreased from 10,500 mg/l to about 7,000 mg/l for both cases. Figure 3b shows that little difference appears on the changes of COD and temperature with 1,000 mg-Fe/l and 4,000
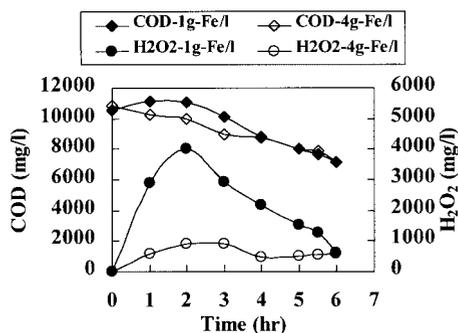

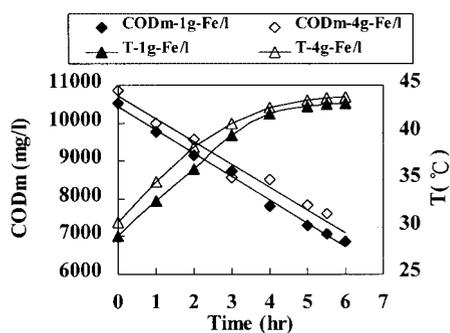**Figure 3a** Changes in COD, and H_2O_2 with Fenton's reagent. $pH_i = 2$

Figure 3b Changes in temperature, and CODm with Fenton's reagent. $pH_i = 2$

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mg-Fe/l. However, the final COD removal efficiency (33%) by Fenton's reagent was found to be superior to that by direct anodic oxidation (3.3%).

Performance of COD removal by the Fered-Fenton process

In addition to the equations mentioned above, the additional reaction on the cathode side for the Fered-Fenton process is as follows:

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{7}$$

First, this study applied a constant current of 22.5A for the Fered-Fenton method. Changes in CODm and temperature for Fenton's method and Fered-Fenton method during the reaction are shown in Figure 4. Both methods were conducted at the same operating conditions except that the Fenton method used 4 g-Fe/l, however the Fered-Fenton method used 2 g-Fe/l. The cell voltage of the Fered-Fenton method decreased from 7.7 V to 6.2 V during the reaction and the pH smoothly decreased from 1.98 to 1.76. Its final COD removal efficiency (89%) was found to be superior to that of Fenton method (33%). The temperature also showed a dramatic increase to a maximum of 65°C which was higher than that (43°C) of the Fenton method. The significant increase in the temperature of the Fered-Fenton system suggests that an exothermic reaction occurred in treating this wastewater. Korenaga *et al.* (1989) observed a similar finding when treating high strength wastewater with Fenton's reagent.

Next, the current density of the cathode was changed between 65 A/m^2 and 200 A/m^2. From the measure of COD during the reaction, the utilization efficiency of H$_2$O$_2$, E$_H$, can be calculated using equation (8).

$$E_H (\%) = \frac{actual\ COD\ removal}{theoretically\ removable\ COD\ by\ inlet\ H_2O_2} \times 100\%$$

$$= \frac{COD_i - COD}{H_2O_2 \times 0.47} \times 100\% \tag{8}$$

where COD$_i$ and COD denote the initial COD and the COD at time t, respectively. H$_2$O$_2$ represents the dosage concentration of H$_2$O$_2$ at time t. Table 1 lists the COD removal efficiency (CODr) and E$_H$ under different operating conditions with the Fered-Fenton method. Results of run 1 and 2 show that there were no differences in CODr and E$_H$ when CDc was
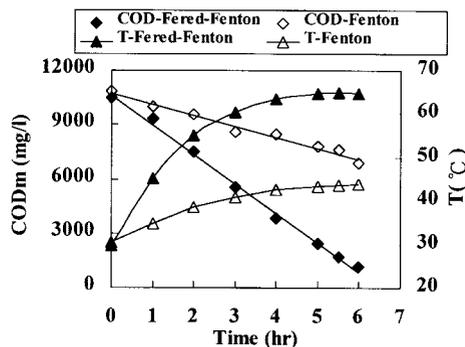

Figure 4 Changes in CODm and temperature for Fenton's method and the Fered-Fenton method. Fered-Fenton method: Fe = 2,000 mg/l, CDc = 100 A/m^2, CDa = 800 A/m^2, pH$_i$ = 2. Fenton method: Fe = 4,000 mg/l, pH$_i$ = 2

below 100 A/m^2 at Iron(II)$_{th}$/H$_2$O$_2$ = 1, where Iron(II)$_{th}$ is the theoretical amount of ferrous ion produced on the cathode. However, results of runs 3 and 4 demonstrated that CODr and E$_H$ decreased with increasing CDc at Iron(II)$_{th}$/H$_2$O$_2$ = 0.5. In addition, results of runs 2 and 3 demonstrated that CODr and E$_H$ decreased with decreasing Iron(II)$_{th}$/H$_2$O$_2$ value at the same CDc. The last four runs show that CODr increased but E$_H$ decreased with increasing H$_2$O$_2$ dosage.

Table 1 The CODr and E$_H$ under different operating conditions with Fered-Fenton method

	Operating conditions			Results	
Run	CDc (A/m^2)	H$_2$O$_2$ (mg/l)	Iron(II)$_{th}$/H$_2$O$_2$ (wt/wt)	CODr (%)	E$_H$ (%)
1	65	28,000	1	89.0	73.3
2	100	28,000	1	89.1	73.4
3	100	28,000	0.5	72.9	60.0
4	200	28,000	0.5	62.9	51.8
5	200	37,400	0.5	79.1	48.9
6	200	46,800	0.5	90.6	44.8
7	200	51,000	0.5	97.8	40.3

COD$_i$ = 11,000 mg/l, Fe = 2,000 mg/l, pH$_i$ = 2.

Finally, the major component of the wastewater and the changes of intermediate compounds including acetate, oxalate, and formate during the treatment were also studied. Figure 5 shows the changes in COD, COD-sum, COD-acetate, COD-formate, and COD-oxalate for the Fered-Fenton method, where COD-sum is the summation of acetate, formate and oxalate in COD. The quality analysis of raw wastewater indicates that acetate was the major component (95.5%) in the wastewater, and no other volatile acids such as formate and oxalate were detected. The change of COD-sum is consistent with that of analyzed COD. It indicates that the major components during the treatment by Fered-Fenton method are acetate, formate and oxalate.

Do and Chen (1993) have proven that formate is the oxidation product of formaldehyde by Fenton's reagent. Our studies also found that formate is the major product in the wastewater in Fenton's reaction. During the treatment of this wastewater by the Fered-Fenton method, formate was also the major product, but it could be further reduced to oxalate.
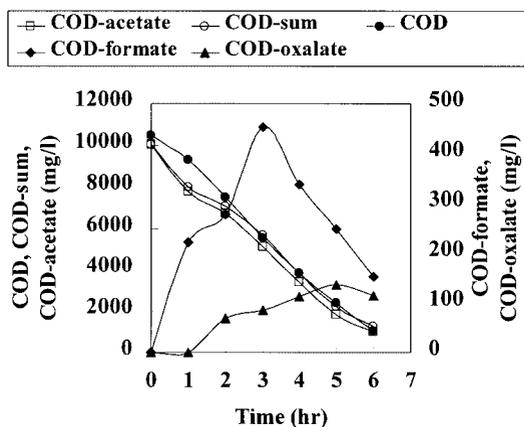

Figure 5 Changes in COD, COD-sum, COD-acetate, COD-formate, and COD-oxalate for Fered-Fenton method. Fe = 2,000 mg/l, CDc = 100 A/m^2, CDa = 800 A/m^2, pH$_i$ = 2
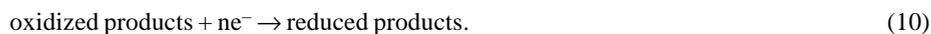
Figure 5 shows that formate reached a maximum of 1,133 mg/l (COD = 453 mg/l) at half of the total reaction time and then linearly decreased to 380 mg/l (COD = 152 mg/l). Oxalate didn't appear until two hours of the reaction. After that, it slowly increased to a maximum at five hours of the reaction and then decreased. Table 2 lists the rate constants for reactions of hydroxyl radicals in acetate, formate, and oxalate (Buxton *et al.*, 1988). These acids in dissociated form show higher rate constants than those in nondissociated form. In the Fered-Fenton process, these three volatile acids may exist in dissociated form due to the electrolysis; this could explain why the Fered-Fenton method is better than conventional Fenton's reagent.

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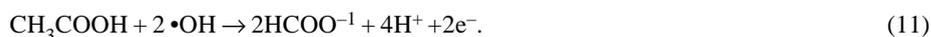**Table 2** Rate constants for reactions of hydroxyl radicals in acetate, formate, and oxalate (Buxton *et al.*, 1988)

	k ($M^{-1}S^{-1}$) dissociated form (B^- or B^{2-})	K ($M^{-1}S^{-1}$) non dissociated form (HB)
Acetate	8.5×10^7	1.6×10^7
Formate	3.2×10^9	1.3×10^8
Oxalate	7.7×10^6	1.4×10^6

In addition to equations (3)-(5) and (7), the following electrochemical reactions may occur in treating the organic contaminants with the Fered-Fenton process.

On the electrodes:

$$\text{organics} \rightarrow \text{oxidized products} + n e^-, \text{ and} \tag{9}$$

$$\text{oxidized products} + n e^- \rightarrow \text{reduced products.} \tag{10}$$

In the solution phase, •OH can degrade the organic contaminants. According to the above results, we can propose the main reactions of acetate degradation by the Fered-Fenton method as follows:

$$CH_3COOH + 2 \bullet OH \rightarrow 2HCOO^{-1} + 4H^+ + 2e^-. \tag{11}$$

$$HCOO^- + \bullet OH \rightarrow \bullet COO^- + H_2O. \tag{12}$$

$$\bullet COO^- + \bullet COO^- \rightarrow {}^-O_2CCOO^-. \tag{13}$$

$${}^-O_2CCOO^- + 2\bullet OH \rightarrow 2CO_2 + 2OH^-, \text{ and} \tag{14}$$

$$\bullet COO^- + \bullet OH \rightarrow CO_2 + OH^-. \tag{15}$$

Conclusions

Based on the results presented herein, we can conclude the following. Direct anodic oxidation fails to treat the chemical wastewater in this study with less than 3.3% of COD removal. Fenton's method attains 33% of COD removal efficiency. The novel Fered-Fenton process is the most effective in treating this wastewater with 89% of COD removal efficiency. According to experimental results, the changes in acetate, oxalate, and formate during the reaction provide us with the information to propose some degradation reactions of this wastewater using the Fered-Fenton method.

References

Barb, W.G., Baxendale, J.H., George, P. and Hargrave, K.R. (1951). Reaction of ferrous and ferric ions with hydrogen peroxide. *Trans. Faraday Soc.* **47**, 462–500 and 591–616.

Brillas, E., Mur, E. and Casado, J. (1996). Iron (II) catalysis of the mineralization of aniline using a carbon-PTFE O_2-fed cathode. *J. Electrochem. Soc.* **143**, 973–982.

Buxton, G.V., Greenstock, C.L., Helman, W.P. and Ross, A.B. (1988). Critical review of rate constants for reaction of hydrated electrons, hydrogen atoms and hydroxyl radicals (•OH/•O⁻) in aqueous solution. *J. Phys. Chem. Ref. Data* **17**(2), 513–886.

Casero, I., Sicilia, D., Rubio, S. and Perez-Bendito, D. (1997). Chemical degradation of aromatic amines by Fenton's reagent. *Water Res.* **31**, 1985–1995.

Chou, S.S., Huang, Y.H., Lee, S.N., Huang, G.H. and Huang, C.P. (1999). Treatment of high strength hexa-mine-containing wastewater by electro-Fenton method. *Water Res.* **33**(3), 751–759.

Coin, R.J., Niksa, M.J. and Elyanow, D.I. (1996). Wastewater treatment enhanced by electrochemistry. *Environmental Progress* **15**, 122–127.

Do, J.S. and Chen, C.P. (1993). *In situ* oxidative degradation of formaldehyde with electrogenerated hydro-gen peroxide. *J. Electrochem. Soc.* **140**, 1632–1637.

Ewa, L.K. (1991). Degradation of aqueous nitrophenols and nitrobenzene by means of the Fenton reaction. *Chemosphere* **22**, 529–536.

Fenton, H.J.H. (1894). Oxidation of tartaric acid in the presence of iron. *J. Chem. Soc.* **65**, 899–910.

Gnann, M., Gregor, C.H. and Schelle, S. (1993). Chemical oxidative process for purifying highly contami-nated wastewater. WO patent 93/08129, Peroxid-Chemie GmbH, DE.

Hsiao, Y.L. and Nobe, K. (1993). Hydroxylation of chlorobenzene and phenol in a packed bed flow reactor with electrogenerated Fenton's reagent. *J. Appl. Electrochem.* **23**, 943–946.

Huang, Y.H., Chou, S.S., Peng, M.G., Huang, G.H. and Cheng, S.S. (1999). Case study on the bioeffluent of petrochemical wastewater by electro-Fenton method. *Water Sci. Technol.* **39**(10–11) 145–149.

Huang, Y.H., Huang, G.H., Lee, S.N. and Lin, S.M. (1997). Method of wastewater treatment by electrolysis and oxidation. ROC patent: 088151.

Pardieck, D.L., Bouwer, E.J. and Sloane, A.T. (1992). Hydrogen peroxide use to increase oxidant capacity for in situ bioremediation of contaminated soils and aquifers: a review. *J. Contam. Hydrol.* **9**, 221–242.

Pratap, K. and Lemley, A.T. (1994). Electrochemical peroxide treatment of aqueous herbicide solutions. *J. Agric. Food Chem.* **42**, 209–215.

Sedlak, D.L. and Andren, A.W. (1991). Oxidation of chlorobenzene with Fenton's reagent. *Environ. Sci. Technol.* **25**, 777–782.

Sudoh, M., Kodera, T., Sakai, K., Zhang, J.Q. and Koide, K. (1986). Oxidative degradation of aqueous phe-nol effluent with electrogenerated Fenton's reagent. *J. Chem. Eng. Jpn.* **19**, 513–518.