



ELECTROCHEMICAL OXIDATION PRETREATMENT OF REFRACTORY ORGANIC POLLUTANTS

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ABSTRACT

Refractory pollutants, including lignin, tannic acid, chlortetracycline, and EDTA, were destroyed by an electrochemical oxidation method to evaluate the applicability of this method for industrial wastewater pretreatment. Operation parameters, such as supporting electrolyte, current density, and electrolyte concentration, have been investigated for their influences on COD removal efficiencies during electrolysis. In addition, gel permeation chromatography (GPC), Microtox test, and total organic halogen (TOX) analyses were performed to monitor the changes of organic characteristics of these refractory pollutants. Experimental results show that, among sulfate, nitrate, and chloride, chloride was the best supporting electrolyte, and during electrolysis, both COD and color removal efficiencies were improved by increasing current density and chloride concentration. From GPC analysis results, the electrochemical oxidation process readily destroys high-molecular-weight (HMW) organics. Microtox test results also show that the process can reduce the toxicity of these refractory organic compounds. In addition, TOX concentrations were found to increase at the beginning but then decline during the electrolysis. The above results suggest that the electrochemical oxidation process, which has good efficacy for detoxification and destruction of refractory pollutants, is a promising method for wastewater pretreatment. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Refractory pollutants; electrochemical oxidation; chloride; Microtox; TOX.

INTRODUCTION

There are many industries, such as pulp and paper mills, pharmaceutical, and electroplating industries, which discharge wastewaters with certain pollutants which would cause a serious impact to the environment. To minimize the threat to the environment, treatment of the industrial wastewaters has always been conducted. Biological processes are the treatment systems used most and they can usually remove a large fraction of BOD and readily biodegradable organics. However, there are many refractory pollutants present in industrial wastewaters, and they always cause problems in the treatment system. High-molecular-weight (HMW) organics, such as lignin and tannic acid, are the typical refractory pollutants present in the kraft mill. These HMW organics always cause high strength of COD and color in wastewater. Also, the HMW organics are poorly biodegradable, and consequently, they often remain in the effluent from biological treatment processes (Bryant and Amy, 1989; Manka and Rebhun, 1982). In addition to HMW organics, toxic organics

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such as antibiotics (chlortetracycline) and chelating agent (EDTA) from pharmaceutical and electroplating industries are also resistant to biological degradation. These refractory pollutants cannot be readily removed and always remain in the effluent of biological treatment processes, and depress treatment efficiency. Therefore, to enhance the efficacy of biological processes for industrial wastewater treatment, an effective pretreatment process is always in demand to destroy the refractory pollutants.

In recent years, the electrochemical oxidation process had been shown to be promising for wastewater treatment due to the effectiveness and easiness in operation. The process can be applied for decomposing cyanide (Wen, 1990), EDTA (Kusakabe *et al.*, 1986), aniline (Kirk *et al.*, 1985), and color removal (Oehr, 1978). Previous studies also showed that the electrochemical oxidation process is practical for the removal of refractory pollutants in landfill leachate (Chiang *et al.*, 1995a). These investigations concluded that electrochemical oxidation is an appropriate process for the destruction of refractory pollutants.

In this paper, an electrochemical oxidation process was adopted to destroy refractory organic pollutants, including lignin, tannic acid, chlortetracycline, and EDTA. The effects of operating factors, such as supporting electrolyte, current density, and concentration of supporting electrolyte, have been studied. Moreover, Microtox test and total organic halogen (TOX) analysis have been performed to evaluate the feasibility of the process for the pretreatment of industrial wastewater.

MATERIALS AND METHODS

Wastewaters

The wastewaters investigated in this study were prepared at laboratory using pure chemicals, including lignin (TCI, Japan), tannic acid (Merck, Germany), chlortetracycline (Sigma, USA), and EDTA-2 Na (Merck, Germany). The characteristics of the synthetic wastewaters are summarized in Table 1. Pollutant strength for each synthetic wastewaters is set at 2500 ± 200 mg/l COD. As shown in Table 1, all the BOD/COD ratios of the synthetic wastewaters are below 0.2, indicating that the organics are poorly biodegradable, and cannot be readily removed by biological treatment processes. Also, the synthetic wastewaters, except EDTA, contain high color as indicated by the ADMI value.

Table 1. Characteristics of the synthetic wastewaters

Parameters	Synthetic wastewater			
	Lignin	Tannic acid	Chlortetracycline	EDTA
COD (mg/L)	2500 ± 200	2500 ± 200	2500 ± 200	2500 ± 200
TOC/COD	0.46	0.54	0.54	0.65
BOD/COD	0.07	0.14	0.12	0.07
pH	4.34	3.71	2.99	8.64
Color (ADMI value)	2898.6	105.14	687.89	0

Apparatus

The experiments were carried out in a 600 ml batch electrolytic cell. A laboratory D.C. power supply (Goodwill GPD-3030D, Taiwan) with current-voltage monitor is employed to provide the electric power during electrolysis. The cell was equipped with a magnetic stirrer in order to keep the electrolyte well mixed. In electrolysis, lead dioxide coated titanium (PbO_2/Ti) and a steel plate were used as the anode and the cathode. Both electrodes have the approximate geometric surface area of 40 cm^2 and they were placed vertically and parallel to each other in the electrolytic cell. In this study, investigation of organic molecular weight distribution was achieved by gel permeation chromatography (GPC). A peristaltic pump (Gilson minipuls 2, USA) is employed to inject sample and mobile phase (pure water, 107 ml/hr). A column (Pharmacia C16/100, Sweden) packed Sephadex G-25M gel (Pharmacia, Sweden) is used for molecular size

separation. The exclusion from the column was collected by a fractional collector (Pharmacia FRAC-100, Sweden) at every 5 ml. Then the organic strength of the exclusion is determined by detecting the absorption at UV 254 nm (Shimadzu UV1201, Japan). In this study, chlorinated organics and toxicity of the samples are determined by a TOX analyzer (Mitsubishi TSX-10, Japan) and Microtox test (Microtox M500, USA). In Microtox test, *Photobacterium phosphoreum* bacterium was used. The toxicity is expressed as EC50, which is defined as the concentration which causes the depletion of 50% of the phosphorescent intensity of the bacterium. The EC50 concentration is expressed as the dilution percentage of the sample. Therefore, the sample is more toxic as the lower the EC50 becomes, and sample is defined to be nontoxic when the EC50 is over 100%.

Procedures

Firstly, the electrochemical oxidation of wastewaters was conducted with three supporting electrolytes, including sodium sulfate, sodium nitrate, and sodium chloride. Then the operation parameters (current density and supporting electrolyte concentration) were varied over a range to find out their influences. All the electrolysis experiments were operated under the galvanostatic state (constant current operation). Sampling procedure in the electrolysis experiments was based upon the constant charge loading. The wastewater characteristics of the collected samples were determined and all the analytical procedures in this investigation were followed by the methods stated in the "Standard methods" (APHA *et al.*, 1985).

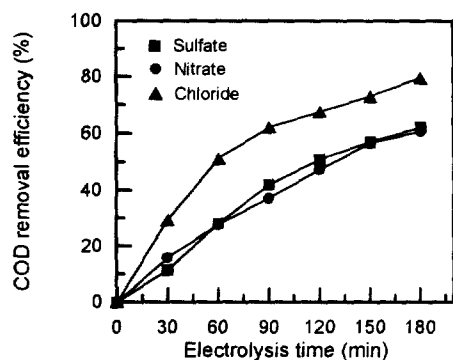


Figure 1. Electrolysis results of lignin for three supporting electrolytes.

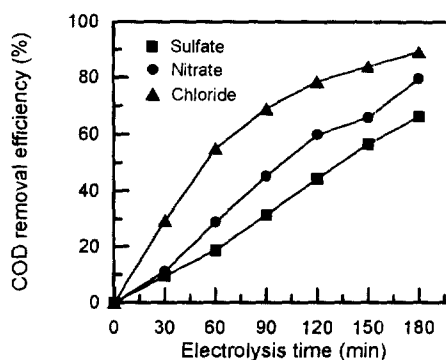


Figure 2. Electrolysis results of tannic acid for three supporting electrolytes.

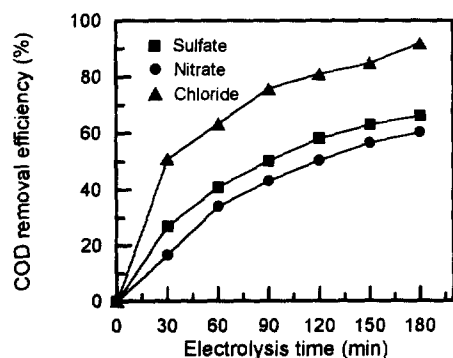


Figure 3. Electrolysis results of chlortetracycline for three supporting electrolytes.

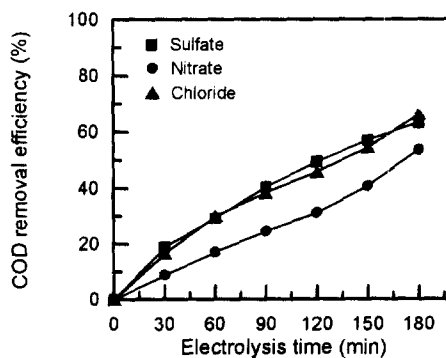


Figure 4. Electrolysis results of EDTA for three supporting electrolytes.

RESULTS AND DISCUSSION

COD removal

Effect of supporting electrolyte. In this study, sodium sulfate, nitrate, and chloride were used as supporting electrolytes to investigate their effects on the removal of COD of refractory pollutants in electrolysis. Figures 1, 2, 3 and 4 show the electrolysis results for lignin, tannic acid, chlortetracycline, and EDTA obtained by electrolysis with three supporting electrolytes of 5000 mg/l at a current density of 7.5 amp/dm², and the results are summarized in Table 2. As shown in Fig. 1, the COD removal efficiencies of lignin are increased as electrolysis time increased, and the COD removal efficiency obtained with chloride is higher than those obtained with sulfate and nitrate. Similar results also can be observed in Figs 2 and 3. The above results suggest that, among the three supporting electrolytes, chloride is the best. Chiang *et al.* (1995b) found that, in the electrolysis of landfill leachate with chloride, an indirect oxidation effect of chlorine/hypochlorite is the main pathway for pollutants removal. Therefore, the superior effect of chloride in this study can also be due to the indirect oxidation effect of chlorine/hypochlorite. In addition to COD, the ADMI values of the refractory pollutants apparently decrease after electrolysis with chloride as indicated in Table 1, inferring that color strengths are also readily removed by the indirect oxidation effect of chlorine/hypochlorite. On the other hand, electrolysis with nitrate or sulfate is ineffective in removing color, and the color strength even increases after electrolysis. Although chloride exhibits excellent results in the electrochemical oxidation process, however, Fig. 4 illustrates that, for EDTA, the COD removal efficiency obtained with chloride is very closed to that obtained with sulfate. This is because EDTA has four carboxylic acid groups (-COOH), which are very resistant to chemical oxidation. As a consequence, COD of EDTA tends to be removed by direct anodic oxidation effect during electrolysis. Nevertheless, chloride is still the most appropriate supporting electrolyte in the electrochemical oxidation process.

Table 2. Experimental results for COD and color removals of refractory organics by electrochemical oxidation process with different supporting electrolyte

Pollutants	Supporting electrolyte	COD removal efficiency (%)	Color strength (ADMI value)	
			before electrolysis	after electrolysis
Lignin	Nitrate	60.9		2519
	Sulfate	62.3	2899	1941
	Chloride	79.1		146
Tannic acid	Nitrate	79.8		1382
	Sulfate	66.5	105	322
	Chloride	89.4		9
Chlortetracycline	Nitrate	60.4		1855
	Sulfate	66.3	688	507
	Chloride	92.0		10
EDTA ^a	Nitrate	53.7		--
	Sulfate	63.4	--	--
	Chloride	66.4		--

a: EDTA is colorless.

Effect of current density. In the electrochemical oxidation process, COD removal rate would be proportional to the pollutant concentration, and be also proportional to the chlorine/hypochlorite concentration when chloride is used as supporting electrolyte, since the pollutant removal is due to the indirect oxidation effect of chlorine/hypochlorite. Therefore, the kinetic for COD removal in the indirect electrochemical oxidation process can be shown as below:

$$-\frac{d[\text{COD}]}{dt} = k[\text{COD}][\text{Cl}_2] \quad (1)$$

During electrolysis, the chlorine/hypochlorite is produced by the anodic oxidation of chloride, and it would convert to chloride as the pollutants have been oxidized. Then the chloride would be anodically oxidized to form chlorine/hypochlorite, which oxidizes pollutants again. Accordingly, the concentration of chlorine/hypochlorite during electrolysis can be assumed to be a constant. Therefore, the term of $[Cl_2]$ and kinetic constant (k) in equation (1) can be merged to simplify equation (1) to a pseudo-first-order reaction kinetic, and a new kinetic constant (k_{obs}) is formed as expressed by equation (2), and then k_{obs} can be obtained by plotting a chart of $\ln([COD]_0/[COD]_t)$ vs time.

$$-\frac{d[COD]}{dt} = k_{obs}[COD] \quad (2)$$

The effect of current density on k_{obs} is tabulated in Table 3. It can be seen from Table 3 that all the k_{obs} values are increased as current density increased. The results imply that the increase of current density enhances the removal of refractory pollutants. Chiang *et al.* (1995b) had found that the chlorine/hypochlorite production rate is improved by increasing current density during the electrolysis of saline water. Therefore, the enhancing effect of current density is attributed to the improvement of chlorine/hypochlorite production rate that enhances the indirect oxidation effect during electrolysis.

Table 3. Effect of current density on k_{obs} for electrochemical oxidation of refractory organics

Current density (amp/dm ²)	k_{obs} for electrochemical oxidation of refractory organics (min ⁻¹)			
	Lignin	Tannic acid	Chlortetracycline	EDTA
2.5	0.0011	0.0015	0.0014	0.0008
5.0	0.0021	0.0036	0.0036	0.0015
7.5	0.0040	0.0043	0.0061	0.0024

Effect of chloride concentration. Table 4 tabulates the experimental results for the electrochemical oxidation of four refractory organics with three different chloride concentrations. It can be seen from Table 4 that the COD removal efficiencies are increased with increasing chloride concentration. It is due to the increase of chloride concentration which benefits chlorine/hypochlorite production during electrolysis, and as a result, the indirect oxidation effect is enhanced.

Table 4. Effect of chloride concentration on the electrochemical oxidation of refractory organics

Chloride concentration (mg/L)	COD removal efficiency (%)			
	Lignin	Tannic acid	Chlortetracycline	EDTA
2500	68.6	82.7	81.5	68.0
5000	79.7	90.5	92.0	66.4
7500	86.5	96.6	97.2	73.9

Destruction of HMW organics

Lignin and tannic acid are composite and HMW organics. To investigate their molecular weight (MW) changes during electrolysis, in this study, gel permeation chromatography (GPC) was employed to analyze the MW distribution of the two refractory organic compounds. Figures 5 and 6 are the GPC profiles for lignin and tannic acid, respectively. From Figs 5 and 6, two peaks can be found in the GPC profiles. One appears at an elution volume of 70 ml which indicates the organic group-I whose MW is more than 5000, and the other appears at elution volume of 170 ml which indicates the organic group-II whose MW is less than 1000. For lignin, the organic group-I (MW > 5000) is predominant as shown in Fig. 5. However, the peak intensity of organic group-I decreases after electrolysis, and it decreases as electrolysis time increased.

Also, the peak intensity of organic group-II (MW < 1000) decreases after electrolysis. The results infer that HMW lignin is readily destroyed by the electrochemical oxidation process. In electrochemical oxidation of tannic acid, it can be found in Fig. 6 that the organic group-I is increased during electrolysis. It suggests that there are HMW organics formed during the electrolysis of tannic acid. The HMW organics are considered to be phenolic oligomers, which were produced by the electrochemical polymerization of phenolic compounds (Gattrell and Kirk, 1990; Chiang *et al.*, 1995c). Nevertheless, the peak intensity of organic group-I is also decreased after electrolysis for 3 hrs. It implies that the HMW organics of tannic acid can also be destroyed by the electrochemical oxidation process. From the above results, the electrochemical oxidation process is concluded to be effective for the destruction of HMW organic pollutants.

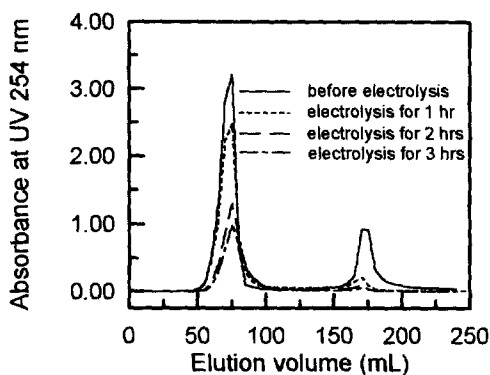


Figure 5. GPC profiles for lignin.

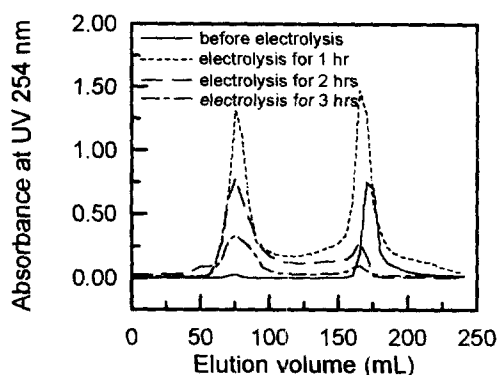


Figure 6. GPC profiles for tannic acid.

Variation of TOX during electrolysis

In the previous discussion, it is pointed out that the refractory pollutants are destroyed mainly by the indirect oxidation effect of chlorine/hypochlorite produced during the electrochemical oxidation process. However, the chlorination reactions have the potential to produce chlorinated organic compounds. Consequently, the electrochemical oxidation process has the possibly adverse effect of chlorinated organic compounds production. In this study, the variation of TOX during electrolysis has been investigated by a TOX analyzer. The TOX concentrations during electrolysis for four refractory pollutants are illustrated in Fig. 7. From Fig. 7, it is found that TOX concentrations increased during the electrolysis of lignin, tannic acid, and chlortetracycline. The results illuminate that chlorinated organics were indeed produced in the indirect electrochemical oxidation process. On the other hand, during the electrolysis of EDTA, TOX concentration did not increase, indicating there is no chlorinated organics produced. This confirms that EDTA destruction pathway is the direct anodic oxidation as previously discussed.

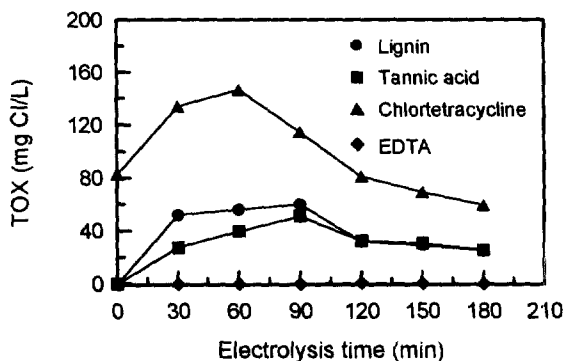


Figure 7. TOX analysis results for refractory pollutants during electrolysis.

Although TOX concentrations increased at the beginning of electrolysis, however, TOX concentrations decreased after electrolysis as shown in Fig. 7, indicating the chlorinated organics were also removed. The decline in TOX concentration reveals that the electrochemical oxidation process has good efficacy for the destruction of chlorinated organics, even though the removal of pollutants in the process is mainly attributed to the chlorine/hypochlorite oxidation.

Detoxification effect of electrochemical oxidation process

The toxic effects of the refractory pollutants before and after electrolysis were determined by Microtox test in this study. The test results are summarized in Table 5, which shows that, before electrolysis, tannic acid, chlortetracycline, and EDTA exhibit significant toxic effect, while lignin is nontoxic. The sequence for toxicity is chlortetracycline > EDTA > tannic acid for 5 min test. In this study, the electrochemical oxidation process demonstrates a good efficacy in detoxification of refractory pollutants. As can be seen in Table 5, after electrolysis, all the EC50 concentrations of the refractory organics were increased to higher than 100%, indicating the organics remaining after electrolysis are nontoxic. The Microtox test results denote that the electrochemical oxidation process can effectively eliminate the toxicity of refractory pollutants and makes the pollutants more amenable to biodegradation.

Table 5. Microtox test results for refractory pollutants before and after electrolysis

Refractory pollutant	EC50 concentration (%) ^a			
	Before electrolysis		After electrolysis	
	5 min ^b	15 min	5 min	15 min
Lignin	>100	>100	>100	>100
Tannic acid	10.27	6.63	>100	>100
Chlortetracycline	2.19	0.50	>100	>100
EDTA	8.66	10.45	>100	>100

a: the dilution percentage of the tested sample.

b: test time.

CONCLUSIONS

In this study, the electrochemical oxidation process presents a good efficacy for the destruction of refractory organic pollutants. The COD and color of lignin, tannic acid, chlortetracycline, and EDTA can be readily removed by the electrochemical oxidation process. It was also found that chloride was the best supporting electrolyte because it can promote the progress of indirect oxidation effect of chlorine/hypochlorite. Also, the increases of current density and chloride concentration improve the COD removal efficiency. In addition, GPC results show that the electrochemical oxidation process is effective in the destruction of HMW organics. Although the destruction of refractory organic pollutants is mainly attributed to the indirect oxidation effect of chlorine/hypochlorite, and TOX concentration increased at the beginning of electrolysis, the chlorinated organics produced during electrolysis can also be removed by the process. The Microtox test results also denote that the process can eliminate the toxicity of refractory pollutants and makes the pollutants more amenable to biodegradation. All the results described in this study reveal that the electrochemical oxidation process has excellent ability for the destruction and detoxification of refractory organic pollutants. Consequently, it is concluded that electrochemical oxidation is a promising process for the pretreatment of refractory pollutants.

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REFERENCES

- APHA-AWWA-WPCF (1985). *Standard methods for the Examination of Water and Wastewater*, 16th ed.
- Bryant, C. W. and Amy, G. L. (1989). Seasonal and in-mill aspects of organic halide removal by an aerated stabilization basin treating a kraft mill wastewater. *Wat. Sci. Tech.*, **21**(4-5), 231-239.
- Chiang, L. C., Chang, J. E. and Wen, T. C. (1995a). Electrochemical treatability of refractory pollutants in landfill leachate. *Hazard. Wastes Hazard. Mater.*, **12**, 71-82.
- Chiang, L. C., Chang, J. E. and Wen, T. C. (1995b). Indirect oxidation effect in electrochemical oxidation treatment of landfill leachate. *Wat. Res.*, **29**, 671-678.
- Chiang, L. C., Chang, J. E. and Wen, T. C. (1995c). Electrochemical oxidation process for the treatment of coke plant wastewater. *J. Environ. Sci. Health*, **A30**, 753-771.
- Gattrell, M. and Kirk, D. W. (1990). The electrochemical oxidation of aqueous phenol at a glassy carbon electrode. *The Can. J. Chem. Enging.*, **68**, 997-1003.
- Kirk, D. W., Sharifian, H. and Foulkes, F. R. (1985). Anodic oxidation of aniline for waste water treatment. *J. Appl. Electrochem.*, **15**, 285-292.
- Kusakabe, K., Nishida, H., Morooka, S. and Kato, Y. (1986). Simultaneous electrochemical removal of copper and chemical oxygen demand using a packed-bed electrode cell. *J. Appl. Electrochem.*, **16**, 121-126.
- Manka, J. and Rebhun, M. (1982). Organic groups and molecular weight distribution in tertiary effluents and renovated waters. *Wat. Res.*, **16**, 399-403.
- Oehr, K. (1978). Electrochemical decolorization of kraft mill effluents. *J. WPCF*, **50**, 286-289.
- Wen, T. C. (1990). Electrodeposited PbO₂ anode for the decomposition of low concentrations of cyanide. *Plat. Surf. Fin.*, **77**, 54-57.