ISSN 1009 - 3095 *Journal of Zhejiang University SCIENCE* V.3, No.2, P.194 - 198, Apr. - June, 2002
http://www.periodicals.com.cn; http://www.zju.edu.cn/English
http://www.zjupress.com; http://lib.zju.edu.cn/eindex.htm; jzu_s@mail.hz.zj.cn

Electrocatalysis method for wastewater treatment using a novel *beta*-lead dioxide anode*

WU Zu-cheng(吴祖成)†, ZHOU Ming-hua(周明华),
HUANG Zhi-wei(黄志玮), WANG Da-hui(汪大翚)
(*Institute of Environmental Science & Engineering, Zhejiang University, Hangzhou 310027, China*)
† E-mail: wuzc@che.zju.edu.cn

Received Mar. 26, 2001; revision accepted July 12, 2001

Abstract: A novel β-PbO_2 anode modified with fluorine resin was developed for typical pollutant electrocatalytic degradation and wastewater treatment. Various operating parameters such as applied voltage (3.5 - 10.5 V), pH (2 - 6), salinity of the electrolyte (0.5 - 2 g/L K_2SO_4) and initial phenol concentration (100 - 400 mg/L) were investigated to explore the electrocatalytic ability of the anode by taking phenol as sample. A preliminary study on dyeing wastewater treatment by this method indicated that the biodegradability could be increased to suit subsequent biological treatment. The stability of the anode has been proved to be high against acidity. The anode showed promising application for treatment of wastewater, especially of high salinity and high acidity wastewater.

Key words: Electrocatalysis, Anodic oxidation, Phenol, Dyeing wastewater treatment
Document code: A **CLC number:** TQ150.9, O646.5, X783

INTRODUCTION

The treatment of biorefractory wastewater such as dyeing and phenols wastewater is of considerable importance in environmental protection. Many of these industrial wastewaters are well known to be characterized by high salinity, high acidity, high COD (chemical oxygen demand) and low biodegradability; which means that the effluent cannot be treated by conventional biological process (Liakou et al., 1997). Therefore, it would be of practical interest to look for more effective processes to treat such wastewater.

Electrochemical method for treating such kinds of wastewater has recently attracted a great deal of attention (Hsiao et al., 1993; Comninellis et al., 1994; Awad et al., 1999), mainly because of its easy applicability to automation, high efficiency, and environmental compatibility (Rajeshwar et al., 1994). The treatment efficiency of the process is strongly dependent on the anode. Some researchers (Sharifian et al., 1986; Gattrell et al., 1990; Tahar et al., 1998) studied the degradation of phenol on various kinds of electrodes such as PbO_2 and glassy carbon electrodes. However, the problem of electrode fouling that decreased the efficiency of the process (Soriaga et al., 1983), was encountered. One solution was to treat the contaminants in high acidic medium (Comninellis et al., 1991; Gattrell et al., 1996), so electrode with good catalytic characteristics and good resistance to high acidity would be ideal for this purpose.

The common β-PbO_2 electrode is widely used in the electrochemical industry because of its good conductivity, perfect chemical stability and favorable reaction activity; but has disadvantages of corrosion, brittleness and flake-off. To overcome these problems, a novel modified β-PbO_2 electrode co-deposited with fluorine resin, which was cheaper and had electrode activity similar to that of platinum, and long lifetime even in highly acidic media, was adopted in our experiment. This study was aimed to explore the electro-

* Project supported by Foundation of Education Ministry of China (No. 98679) and Zhejiang Provincial Natural Science Foundation (No. 200043).

catalytic characteristics of the novel anode and the feasibility of the anodic oxidation method for treatment of dyeing process wastewater by using phenol as the sample. Operating parameters such as pH, applied voltage and initial phenol concentration were investigated to find the optimum conditions for oxidation.

METHODS

Apparatus

Figs. 1 and 2 are the schematics of the experimental setup. The anode of β-PbO_2 and the cathode of Ni-Cr-Ti alloy grid (20 mesh) were concentrically assembled into the undivided electrolytic reactor with final volume of about 0.33 dm^3. The anode used here was a modified β-PbO_2 electrode (ø 45 × 200 mm), which was co-deposited with fluorine resin on a cylindrical ceramic tube. The details of the anode preparation are given in Wu et al. (2001). The solution of wastewater was pumped through the reactor and then returned to the reservoir for recycling. The reservoir was placed in a water bath to regulate the reaction temperature desired. Constant current was maintained at the desired level with only minor adjustments of the applied voltage. During each run, samples were taken from the sampling port in the reservoir for analysis at appropriate intervals.

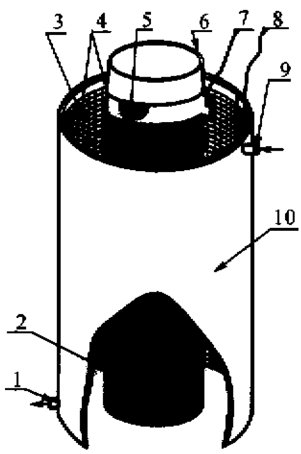

Fig. 1 The electrocatalysis reactor
1. outlet; 2. modified β-PbO_2 anode; 3. stainless steel net cathode; 4. fastener; 5. graphite foil; 6. ceramic; 7. positive connection; 8. negative connection; 9. inlet; 10. polyethylene cylinder

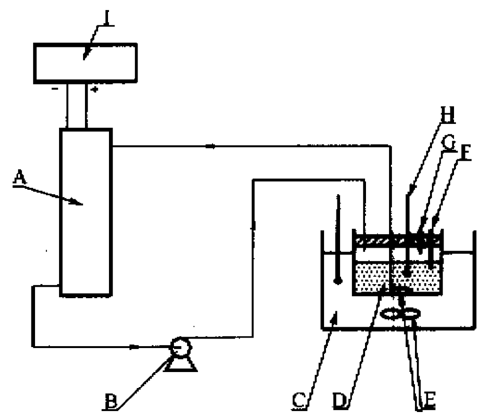

Fig. 2 Flowchart schematic
A. electrocatalysis reactor; B. circulation pump; C. water batch; D. reservoir; E. magnetic stirrer; F. sampling port; G. gas outlet; H. thermometer; I. power supply

Analysis

The COD (chemical oxygen demand) and BOD_5 (biochemical oxygen demand) were determined according to the Standard Methods for Examination of Water and Wastewater (APHA, 1995).

RESULT AND DISCUSSION

Electrocatalytic ability of the anode

Operating parameters such as salinity of the electrolyte, pH, initial concentration of phenol and applied voltage on phenol degradation were considered in this study on the electrolytic ability of the β-PbO_2 using phenol in water as model wastewater.

Effect of K_2SO_4 concentration

Among many kinds of salts in wastewater, sulfate is the most common one. Therefore K_2SO_4 was selected as supporting electrolyte in our experiment. The influence of K_2SO_4 concentration on COD removal is shown in Fig. 3. Under these conditions, COD could be removed to lower than 50 mg/L in no more than 60 min. Among all the K_2SO_4 concentrations investigated, the higher the concentration， the faster was COD removed. These may due to the increase of the solution conductivity as the supporting electrolyte was added. Moreover， lower current was observed at higher concentration of the supporting electrolyte， for the same voltage applied. Therefore the power consumption for treatment of the wastewater containing phenol could be decreased in case of high salinity. Furthermore， such a process could be an alternative for the common biological treatment of high salinity wastewater (salt concentration > 5000 mg/L) at prohibitory high cost.

Effect of initial pH

The pH of the wastewater often plays an important role in wastewater treatment. Fig.4 shows the effects of initial pH of the solution on COD removal. Faster COD removal rate was achieved at the relatively higher acidity quite common for phenolic wastewater. So the treatment will be more cost-effective at pH 2 rather than pH 6. Therefore， the method developed has met the requirements for treatment of high acidity wastewater and shows promising application even without pH adjustment.

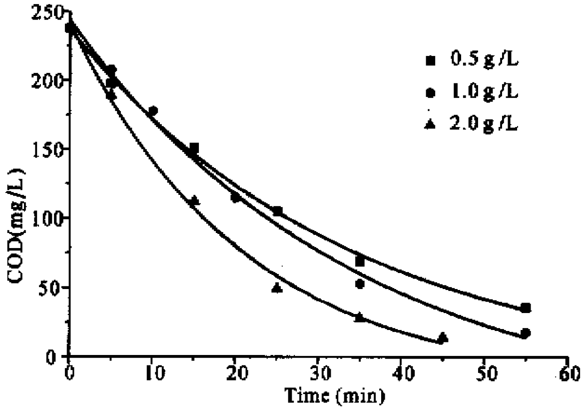

Fig.3 Effects of K_2SO_4 concentration on COD removal

Operating conditions: initial phenol concentration 100 mg/L， applied voltage 10.5 V， circulation rate 1800 ml/min， pH 6; temperature 25 ℃

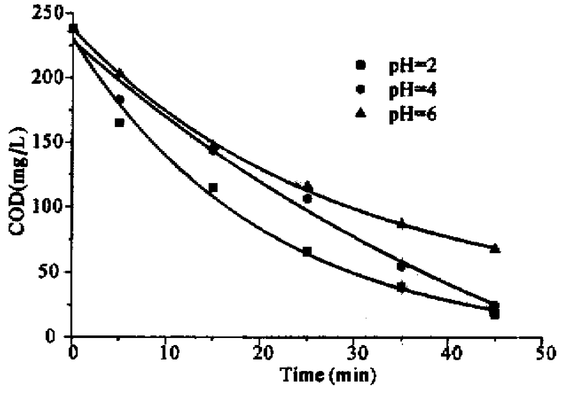

Fig.4 Effects of pH on COD removal

Operating conditions: initial phenol concentration 100 mg/L， applied voltage 7.0 V; circulation rate 1800 mL/min， temperature 25℃; K_2SO_4 2 g/L

Effect of the initial concentration of phenol

Different initial phenol concentrations (100 mg/L， 200 mg/L， and 400 mg/L) were employed to examine how the initial phenol concentration affected the COD removal. As shown in Fig.5， low initial phenol concentration resulted in higher COD removal rate. After 60 min treatment， COD removal for the phenol at 100 mg/L initial concentration dropped from about 238 mg/L down to around 40 mg/L， i.e.， about 83% of COD were removed， while for 400 mg/L， it was only 56%. Such a decrease in the COD removal rate was apparently attributable to an increase in the oxidation load at high initial phenol concentration. However， the total COD removal was favored at higher initial phenol concentration， in view of which， the oxidation process would be much more effective for the treatment of higher concentration pollutants.

Effect of applied voltage

Fig.6 shows that the applied voltage significantly affects COD removal. Faster phenol degradation was observed at higher current density. It can be explained that， at higher voltage， more electrons are transferred to the anode， thus promoting the degradation of phenol.

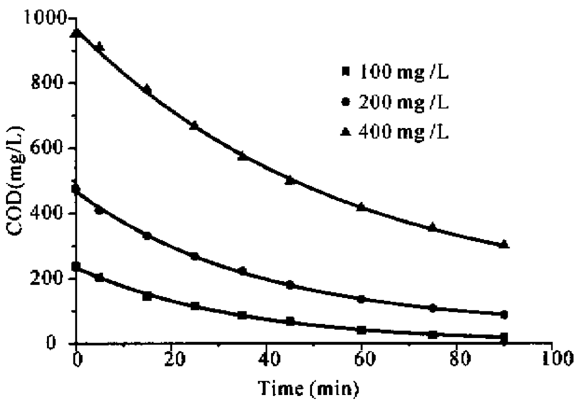

Fig.5 Effects of initial phenol concentration on COD removal

Operating conditions: voltage 7.0 V, circulation rate 1800 ml/min, temperature 25℃, pH = 6, K_2SO_4 2 g/L

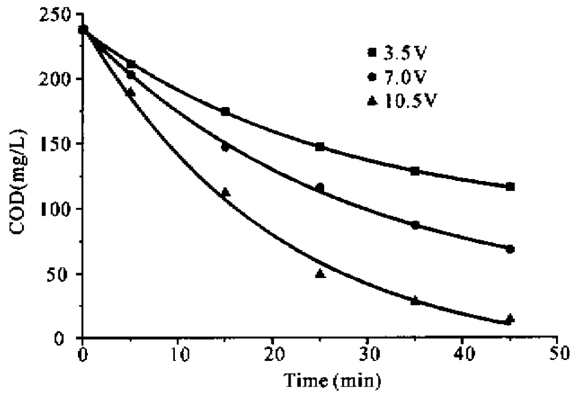

Fig.6 Effects of applied voltage on COD removal

Operating conditions: initial phenol concentration 100 mg/L, circulation rate 1800 ml/min, temperature 25℃, pH = 6, K_2SO_4 2g/L

Stability of the anode

The anode developed showed good electrocatalytic activity, especially at high acidity and high salinity. The apparatus assembled in our laboratory has been used for more than 600 hours and no evident declination in the catalytic character was observed. To evaluate the lifetime of the electrode in high acidic media, the mass loss of the electrodes were measured at current density 1.20 A/cm^2 in the medium of 9 mol/L H_2SO_4 at 90℃. Data on the two kinds of electrode are listed in Table 1, showing that the modified electrode has better resistance against acidity than the unmodified one and that the rate of mass loss was 0.58% per day at the conditions mentioned above. Therefore this kind of electrode showed promising application in acidic medium.

Table 1 Comparison of mass loss in two kinds of electrodes

Day	0	1	2	3	4	5	6	7	8	9	10
1	47.883	47.882	47.876	47.870	47.864	47.850	47.830	47.793	47.755	47.724	47.603
2	50.769	49.135	47.348	43.857	38.634	32.147	–	–	–	–	–

1. the modified β-PbO_2 electrode; 2. unmodified β-PbO_2 electrode.

Applicability

The anode had showed good electrocatalytic characteristics for typical pollutant degradation and also perfect stability against high acidity; so we employed such an anodic oxidation method for actual dyeing wastewater treatment to examine the applicability of the anode. Dyeing wastewater is one of the major biorefractory industrial wastes. It is far from being satisfactorily treated with conventional methods such as biological oxidation, adsorption or coagulation because of its high acidity and salinity. The anodic oxidation method developed here gives good performance under such conditions without additional pretreatment process. Dyeing wastewater is obtained from a Chinese corporation. The characteristics of the wastewater are listed in Table 2.

Table 2 Dyeing wastewater parameters

Parameters	Values
pH	2.3
COD (mg/L)	8500
BOD_5 (mg/L)	1870
BOD_5/COD	0.22
Salinity (g/L)	10.2

As shown in Fig. 7, COD dropped from 8500 mg/L to about 2600 mg/L within 2 hours treatment applying voltage at 4.2 V. The COD removal rate decreased with time, and no further treatment was necessary, thus limiting operation costs. It was found that BOD_5 was around 980 mg/L after 2-hours treatment, i.e., the biodegradability BOD_5/COD had reached to about 0.38, indicating that the effluent had been improved to be suitable for subsequent biological treatment.

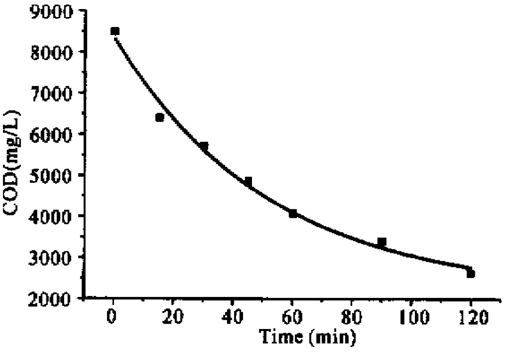

Fig.7 Dyeing wastewater treatment by anodic oxidation

Operating conditions: voltage 4.2 V, circulated rate 1800 ml/min, temperature 25℃, pH = 2.34

The anode modified with fluorine resin showed good electrocatalytic ability for the degradation of wastewater of high salinity and high acidity. Both phenol and dyeing wastewater treatment indicated that the method would be more cost-effective if anodic oxidation is used for pretreatment, followed by biological treatment.

CONCLUSIONS

The β-PbO_2 anode modified with fluorine resin has high stability and strong electrocatalytic ability, indicating promising application for wastewater treatment. For phenol at 100 mg/L, COD can be completely removed within 60 minutes under voltage 7.0 V with the addition of 2.0 g/L K_2SO_4 at pH 2. Moreover, the electrocatalytic method will be cost-effective to serve as the wastewater pretreatment to improve its biodegradability.

References

APHA; AWWA; WEF, 1995. Standard Method for the Examination of Water and Wastewater, 19th ed. APHA. Washington, DC.

Awad, Y.M., Abuzaid, N., 1999. Electrochemical oxidation of phenol using graphite anodes. *Sep. Sci. Technol*. **34**: 699 – 708.

Comninellis, Ch., Pulgarin C., 1991. Anodic oxidation of phenol for wastewater treatment. *J. Appl. Electrochem*. **21**: 703 – 708.

Comninellis, Ch., Nerini, A., 1995. Anodic oxidation of phenol in the presence of NaCl for wastewater treatment. *J. Appl. Electrochem*. **25**: 23 – 28.

Gattrell, M., Kirk, D. W., 1990. The electrochemical oxidation of aqueous phenol at a glassy carbon electrode. *The Canadian Journal of Chemical Engineering*. **68**: 997 – 1003.

Hsiao, Y. L., 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.

Liakou, S., Pavlou, S., Lyberatos, G., 1997. Ozonation of azo dyes. *Wat. Sci. Technol*. **35**(4): 279 – 296.

Sharifian, H., Kirk D. W., 1986. Electrochemical oxidation of phenol. *J. Eelectrochem. Soc*. **133**: 921 – 924.

Soriaga, M. P., Stickney, J. L., Hubbard, A. H., 1983. Electrochemical oxidation of aromatic compounds adsorbed on platinum electrodes: The influence of molecular orientation. *J. Electroanal. Chem*. **144**: 207 – 215.

Tahar, N. B., Savall, A., 1998. Mechanistic aspects of phenol electorchemical degradation by oxidation by oxidation on a Ta/PbO_2 anode. *J. Electrochem. Soc*. **145**: 3427 – 3434.

Wu, Z.C., Zhou, M.H., 2001. Partial degradation of phenol by advanced electrochemical oxidation process. *Environ. Sci. Technol*., **35**: 2698 – 2703.