

Mechanism study of electrochemical oxidation in the terylene diaphragm cell

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Abstract: By using a self-made carbon/polytetrafluoroethylene (C/PTFE) O₂-fed as cathode and Ti/IrO₂/RuO₂ as anode, the effects of electrochemical oxidation of phenol and the coal-gas wastewater containing phenol were studied. The terylene diaphragm which kept pH>12 in cathodic compartment and pH<1 in the anodic compartment was selected in the experiment in comparison with the other types of diaphragm. Furthermore, hydroxyl radical (HO·) was determined in the cathodic compartment of the diaphragm cell by electron spin resonance spectrum (ESR) and the fluorescence spectra. Compared with pH, the accumulated H₂O₂ and the COD removal of the no-diaphragm cell, the mechanism of electrochemical oxidation in the terylene diaphragm cell was supposed. The degradation of phenol was supposed to be cooperative oxidation by direct or indirect electrochemical oxidation at the anode and H₂O₂, HO· produced by oxygen reduction at the cathode. The mineralization of phenol in the diaphragm cell was better than that in the no-diaphragm cell. When the coal-gas wastewater was treated by the electrolysis system with terylene diaphragm, the average removal efficiency of the volatile phenol and COD were 100% and 79.6%, respectively.

Keywords: electrochemical oxidation; C/PTFE O₂-fed cathode; terylene diaphragm; hydroxyl radical

Introduction

The demand for new technologies to remove or to detoxify organics, especially those that are toxic to biological treatment processes from aqueous effluents, is widely recognized. The electrochemical method for treatment of such kinds of wastewater has attracted a great deal of attention recently, mainly because of its ease of control, amenability to automation, high efficiency and environmental compatibility (Comminellis and Nerini, 1995). At present, dimensionally stable anodes (DSA), which are typically prepared by thermal deposition of a thin layer of metal oxide (e.g., SnO₂, PbO₂, or IrO₂) on a base metal, have been used for the oxidation of various organic pollutants, mainly phenol, chlorophenol, benzoquinone and dye wastewater (Iniesta and Michaud, 2001; Tahar and Savall, 1999, 1998; Leffrang *et al.*, 1995; Comminellis and Pulgarin, 1993). Usually, electrochemical treatment can actualize the mineralization of organic pollutants by the stronger oxidant of hydroxyl radicals, which are generated by the electrochemical reaction on the electrode surface (Vitt Johnson, 1992).

For anodic oxidation of organic pollutant, it is difficult to achieve total mineralization because of low HO· concentration on the anode. So the study of more efficient electrochemical methods for water treatment based on the indirect electro-oxidation of contaminants, for example electrogeneration of strong

oxidants, is now in progress. The production of O₂ electro-reduction may be H₂O₂ with condition control. The electrode materials used to O₂ electro-reduction can be divided into two groups. The first one involves electrodes, on which the O₂ electro-reduction proceeds predominantly through the intermediate formation of H₂O₂, while the second one involves electrodes, where both the 4-electron and 2-electron reactions take place. Carbon materials such as C/PTFE, graphite felt and reticulated vitreous carbon are classified in the first group and thus can be used as electrodes for the electrochemical production of H₂O₂ (Alcaide *et al.*, 2002; Harrington and Pletcher, 1999; Brillas and Bastida, 1995; Oturan, 2000a; 2000b; Oturan and Pinson, 1995; Do and Chen, 1994; Leon and Pletcher, 1995; Lee *et al.*, 2003; Iniesta and Exposito, 2002). Processes of indirect electrooxidation of organic compounds by H₂O₂, generated during cathodic reduction of oxygen on the C/PTFE O₂-fed cathode, have much promise for treating wastewaters of organic toxicants, owing to their ecologically safe and simple.

With the rationally designed the electrochemical reactor, it can realize the cooperative oxidation of organic pollutant by active anodes and oxidant species electrogenerated on the cathode, which is expected to increase notably the degradation rate of organics with respect to conventional cells with metallic cathodes on which only the reduction of water occurs. The

diaphragms are often used to separate the two compartments and are effective in increasing degradation efficiency for wastewater treatment, such as the glass frit (Harrington and Pletcher, 1999; Oturan, 2000a; 2000b; Oturan and Pinson 1995; Do and Chen, 1994) and the cationic exchange membrane (Albert and Pletcher, 1999; Leon and Pletcher, 1995; Lee *et al.*, 2003; Iniesta and Michaud, 2002). Some authors used a sintered glass frit in the electrolysis cell, but the degradation fractions of the formaldehyde were 99.6% and 98.3% in the diaphragm and no-diaphragm cell, respectively, and the effect of the sintered glass frit on the oxidative degradation of formaldehyde was insignificant (Do and Chen, 1994). The cationic exchange membrane prohibits the penetration of anions and H_2O_2 molecules, but allows cations to penetrate freely through it. The phenol was treated by the electrolysis system with Nafion cationic exchange membrane (Albert and Pletcher, 1999). However the Nafion cationic exchange membrane used now is very expensive. In addition, it is unsuitable for the industrialization of wastewater treatment in the future. Therefore, the cheapness and practicality diaphragm will be considered.

In this paper, we presented a detailed study on the degradation of organic pollutants in the diaphragm cell with the organic synthetic diaphragm, Ti/IrO₂/RuO₂ anode and C/PTFE O₂-fed cathode. H₂O₂ is produced by electro-reduction of dissolved oxygen. The terylene diaphragm was selected in the experiment in comparison with the other types of diaphragm, which kept pH>12 in cathodic compartment and pH<1 in the anodic compartment. In the cathodic compartment, the decomposition of H₂O₂ in the warm alkaline solution can produce the highly reactive hydroxyl radicals during electrolysis. The degradation of organic pollutants was supposed to be cooperatively oxidized by direct or indirect electro-chemical oxidation at the anode and H₂O₂, free radicals produced by oxygen reduction at the cathode. The degradation mechanism of organic pollutants in diaphragm cell has also been investigated comparatively with the no-diaphragm cell. And the degradation of coal-gas wastewater containing phenol was studied.

1 Experimental

1.1 Preparation of cathode

A mixture of 1.2 g of carbon power and 3 g of 10% PTFE was suspended in 0.28 ml of ethanol as dispersant. This suspension was mixed in 60–70°C water bath, and the resulting wet paste was uniformly

painted onto a face of a carbon cloth that was cold-pressed between two laminated steel plates. And further, the O₂ diffusion electrode was composed of two C/PTFE layers stacked onto a stainless steel screen of 200 mesh as current collector. The resulting electrode was then cut to obtain operational C/PTFE cathodes of 4 cm × 4 cm and about 0.4 mm thick.

1.2 Procedures

Electrolysis were conducted in an open, no-diaphragm cell and diaphragm cell of 100 ml. The anode was Ti/IrO₂/RuO₂ net of 16 cm². The cathode was a C/PTFE electrode of 16 cm² fed with air. A schematic diagram of the experimental setup is shown in Fig.1.

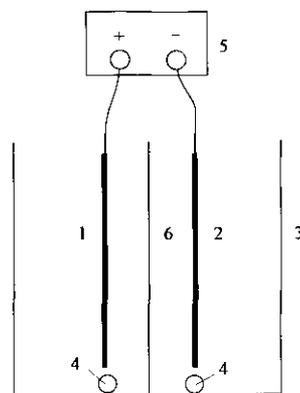


Fig.1 Schematic diagram of apparatus in the diaphragm cell
1. Ti/IrO₂/RuO₂ anode; 2. C/PTFE O₂-fed cathode; 3. electrochemical cell; 4. sparged-air setup; 5. DC power source; 6. diaphragm

A laboratory DC power supply with current-voltage monitor was employed to provide the electric power. The distance between electrodes was 2 cm. The sample wastewater containing phenol removal efficiency was measured in batch sampling. The simulated wastewater was prepared by dissolving an appropriate amount of phenol in distilled water. The initial phenol concentration of 100 mg/L was adopted for most of the experimental runs. The equivalent COD concentration of the initial sample wastewater containing 100 mg/L phenol was measured to be about 247 mg/L. The coal-gas wastewater containing phenol was collected from the gasification plant at a gas-fired industry located in Harbin (China). The coal-gas wastewater, which was diluted with distilled water, had 100 mg/L of volatile phenol and 1600 mg/L of COD. Without being especially specified, the reaction time was 100 min; the current density was 39 mA/cm²; the concentration of supporting electrolyte (Na₂SO₄) was 0.02 mol/L; the initial pH was 7.0. Before an experiment was started, air was sparged for 5 min in order to keep dissolved oxygen saturation. The rate of

sparged-air was 25 ml/s, and air was sparged into the cell till the electrolysis process was over.

1.3 Analytical methods

The resistance for diaphragm in the electrochemical system was determined by impedance/gain-phase analyzer(SI 1260) and electrochemical interface(SI 1287).

The H_2O_2 concentration accumulated during electrolysis was determined by titration with permanganate using a standard procedure (Albert and Pletcher, 1999). The chemical oxygen demand(COD) was measured by the standard method.

The radicals were determined by ESR (electron spin resonance spectrum) measurements, which were performed in the X-band on a JES-FE3AX ESR spectrometer (JEOL, Tokyo, Japan) at ambient temperature. ESR spectrometer was set as follows: microwave frequency, 9.44 GHz; microwave power, 20 mV; modulation frequency, 100 kHz; modulation amplitude, 0.5 G; center field, 3367 G; scan width, 100 G; receiver gain, 2×10^3 ; time constant, 0.3 s; sweep time, 4 min. The ESR spin trapping agent was 5, 5-dimethyl-1-pyrroline-N-oxide (DMPO, 11.1 nmol/L).

The fluorescence spectra and fluorescence intensity were measured with a Shimadzu RF-5000

spectrofluorimeter. The excitation wavelength was set at 305 nm and the emission wavelength at 410 nm. The excitation and emission wavelength bandpasses were both set at 5 nm. The hydroxylated products of the benzoic acid in electrolyzed solutions were analyzed on high-performance liquid chromatography (HPLC, Shimadzu, Japan) by comparing the retention time of the standard compounds. Samples of 10 μ l previously filtered with PTFE filters of 0.45 μ m were injected to the HPLC to determine the hydroxylated products, running with mobile phase of 92% NaH_2PO_4 (50 mmol/L) + 5% methanol + 3% acetic acid. The separation was performed at room temperature using an ODS C18 column (150 mm \times 4 mm) at the flow rate of 1.4 ml/min. An UV detector was used with the wavelength set at 245 nm. The analysis of phenol in electrolyzed solutions was carried out on HPLC (Shimadzu, Japan).

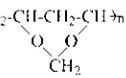
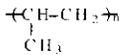
2 Results and discussion

2.1 The choice of diaphragm

The comparative results of the four diaphragms, including the phenol removal efficiency, current density, voltage, resistance and chemical structures, are given in Table 1.

It indicated that the phenol removal efficiencies

Table 1 Comparison of different chemical structure diaphragms (current density, 39 mA/cm²)

Diaphragm	Phenol removal, %			Voltage, V	Resistance, $\Omega \cdot cm$	Chemical structure of diaphragm material
	Anodic	Cathodic	Average			
Terylene	100	100	100	17—19	3.15	$-(CH_2CH_2OOC-C_6H_4-COO)_n$
Cotton	100	98.3	99.2	24—26	4.50	$(C_6H_{10}O_5)_n$
Poly I	100	98.1	99.1	29—32	5.30	$-(CH_2-CH-CH_2-CH)_n$ 
Polypropylene	100	98.4	99.2	64	6.54	$-(CH-CH_2)_n$ 

of anodic compartment, cathodic compartment and average were slightly difference among the four diaphragms for 100 min electrolysis. But the voltage and resistance were obviously difference among them at the same current density. With increasing the voltage and resistance, the energy consumption increased. The voltage and resistance of the terylene diaphragm were the least than other three diaphragms. Compared with chemical structures of the four diaphragms, poly I diaphragm and polypropylene diaphragm have hydrophobic groups, which make against ions to move freely through the diaphragm. Whereas, terylene diaphragm and cotton diaphragm

have hydrophilic groups. Furthermore, the hydrophilicity of terylene diaphragm is stronger than that of cotton diaphragm, which conduce to the H^+ and OH^- move freely through the terylene diaphragm. It was prone to become the acidic solution in anodic compartment and the alkaline solution in cathodic compartment, and formed the optimum environment to degrade organic compounds. According to Table 1, the terylene diaphragm was selected in the following studies.

2.2 Penetrability evaluation of cotton diaphragm

In order to evaluate whether electrolyte solutions in each compartment are mixed or not, the following

controls should be studied with respect to the phenol degradation and COD of the simulated wastewater during the electrolysis: (1) anode: electrolyte without phenol, cathode: electrolyte with phenol; (2) anode: electrolyte with phenol, cathode: electrolyte without phenol. Results are shown in Fig.2 and Fig.3. They show that electrolyte solutions in both anodic compartment and cathodic compartment are mixed after 20 min electrolysis. The removal efficiencies of phenol and COD are slightly difference in the anodic compartment and cathodic compartment. Thus terylene diaphragm is not selective to organic molecules and ions. And the concentration of H_2O_2 did not measured in the anodic compartment during the electrolysis. The one function of the terylene diaphragm can separate the production of two compartments, and prevent H_2O_2 generated on the cathode diffuse to the anode where H_2O_2 is oxidation to O_2 and H_2O . The other function could keep the $pH > 12$ in cathodic compartment and $pH < 1$ in anodic compartment after 20 min electrolysis due to the H^+ and OH^- move freely through the terylene diaphragm. So the terylene diaphragm aids to the electrochemical oxidation of organic pollutants in two compartments.

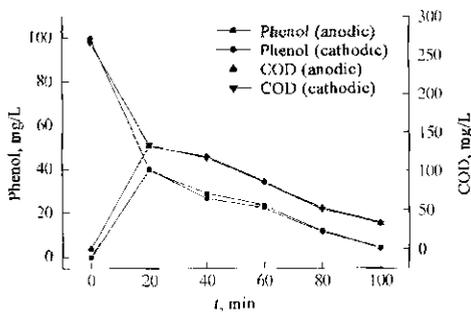


Fig.2 Variations of the phenol and COD vs. electrolysis time in the terylene diaphragm cell when the anodic electrolyte without phenol and cathodic electrolyte with phenol

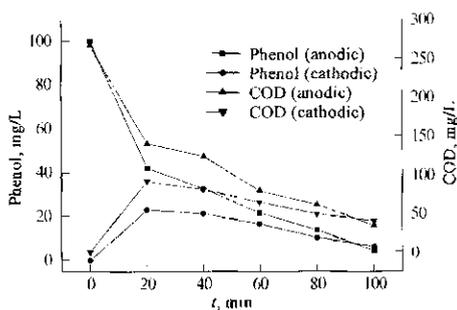


Fig.3 Variations of the phenol and COD vs. electrolysis time in the terylene diaphragm cell when the anodic electrolyte with phenol and cathodic electrolyte without phenol

2.3 Comparative study on diaphragm cell and no-diaphragm cell

Fig.4 shows the variation of pH value with electrolysis time in the no-diaphragm cell and in the cathodic and anodic compartment of the diaphragm cell. In the no-diaphragm cell, pH was near to 3 within 10 min with initial pH values of 1–13. In the diaphragm cell the terylene diaphragm used in this experiment can keep the $pH > 12$ in cathodic compartment and $pH < 1$ in anodic compartment after 20 min electrolysis whether the original solution was acidic, neutral or alkaline solution.

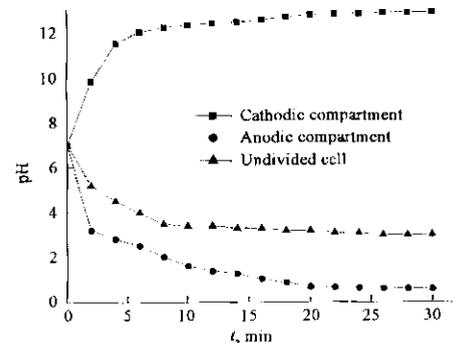
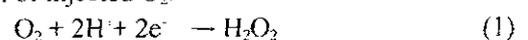


Fig. 4 Variation of pH value with electrolysis time

In general, lower pH aids to the electrochemical oxidation of organic pollutants (Vitt and Johnson, 1992). In the no-diaphragm cell and the anodic compartment of the diaphragm cell, the mechanism of the electrochemical oxidation of organics at the metallic oxide $Ti/IrO_2/RuO_2$ anode is very complex and not yet fully understood. Compared with the previous reports (Ricardo *et al.*, 2003), the conclusion can be drawn about the mechanism of the electrochemical degradation of phenol in this system. It seems to be that two oxidation pathway are involved in direct anodic electrochemical oxidation process by $MO_n(OH\cdot)$ or MO_{n-1} produced on the anode surface. In the presence of oxidizable organic compounds (R), $MO_n(OH\cdot)$ radicals should predominantly cause their complete degradation to carbon dioxide and water (electrochemical cold combustion pathway). And MO_{n-1} is supposed to react with R to generate medium oxidation products via heterogeneous catalytic oxidation at the active sites of the electrodes (chemical oxidation pathway).

The C/PTFE O_2 -fed cathode was used in two types of cells. In the no-diaphragm cell, the whole process was carried out under the acidic condition. The cathode electrogenerates H_2O_2 via a two-electron reduction of injected O_2 :



H_2O_2 is strong oxidant and can oxidize the organic compounds. But in the acidic condition, the reaction rate of Eq.(1) is slower. According to redox potential, the oxidation power of H_2O_2 in the acidic condition is lower than that in the basic condition. In addition, H_2O_2 produced on the cathode can diffuse to the anode where hydrogen peroxide is oxidation to O_2 and H_2O without the diaphragm. So after 80 min, the accumulation H_2O_2 reached to the steady concentrations of 5.6 mg/L in the no-diaphragm cell, which was lower than the concentrations of 8.3 mg/L in the diaphragm cell (Fig.5). The degradation efficiency of phenol was decreased in the no-diaphragm cell.

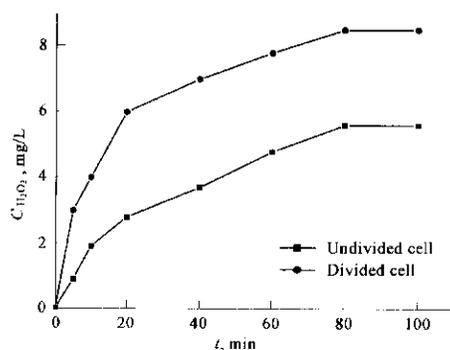
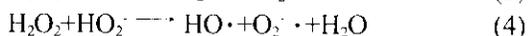
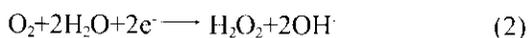


Fig.5 Variation of accumulated H_2O_2 concentration with electrolysis time

In basic electrolyte of the cathodic compartment in the diaphragm cell, C/PTFE O_2 -fed electrode catalyzes the two-electron reduction of O_2 to H_2O_2 and peroxide anion(HO_2^-), and then H_2O_2 and HO_2^- may be converted to $HO\cdot$ and $O_2^{\cdot-}$ as follows (Fang *et al.*, 1999):



The oxidizing power of HO_2^- , $HO\cdot$ and $O_2^{\cdot-}$ are stronger than H_2O_2 , which can oxidize phenol to smaller molecule intermediates or to CO_2 and H_2O .

In the simulated phenol wastewater, the COD (247 mg/L) removal increased with an increase in electrolysis time in both the no-diaphragm cell and diaphragm cell(Fig.6).

However, the varying velocity of the COD removal decreased with an increasing of electrolysis time in two kinds of type cells after 80 min electrolysis. This trend is attributed to the fact that in the initial period of the present experiment, the higher phenol concentration leads to the rate of electrode reactions for the organics removal process increased. And then the molecule structure of the most phenol are destroyed and the phenol concentration are decreased, which leads to the rate of electrode

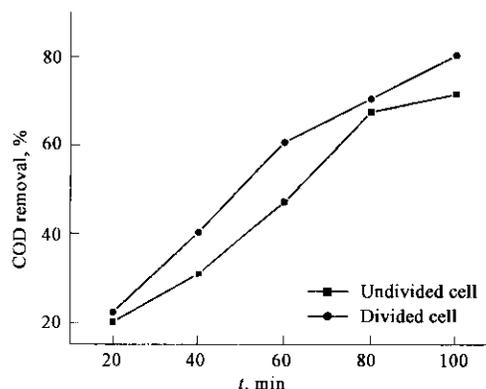


Fig.6 Variation of the COD removal efficiency vs. electrolysis time

reactions decreased after 80 min electrolysis. The COD removal achieved 71.7% and 80.4% in the no-diaphragm cell and the diaphragm cell at 100 min, respectively. It proves that the power of destroying phenol structure in the diaphragm cell is stronger than that in the no-diaphragm cell.

The degradation reaction of phenol in the no-diaphragm cell is supposed to be cooperative oxidized by direct or indirect electrochemical oxidation at the anode and H_2O_2 produced by oxygen reduction at the cathode. However, the degradation reaction of phenol in diaphragm cell is supposed to be cooperative oxidized by direct or indirect electrochemical oxidation at the anode and HO_2^- , $HO\cdot$ produced by oxygen reduction at the cathode. So the mineralization of phenol in the diaphragm cell was better than that in the no-diaphragm cell.

ESR and the fluorescence spectrophotometry combined with HPLC are used to quantitatively determine the free radical in cathodic compartment of the diaphragm cell. Fig.7 shows the typical ESR spectrum obtained by 15 min electrolysis in DMPO solution. The spectrum was composed of quartet lines with the peak height ratio of 1 : 2 : 2 : 1. The ESR parameters (hyperfine constants $a_N = a_H = 14.0$ G and g-value = 2.0065) coincided with those of DMPO-OH \cdot adduct as demonstrated previously (Cheng *et al.*, 2003), confirming that the quartet signal is DMPO-OH \cdot adduct.

But the ESR spectra of the reactive product of

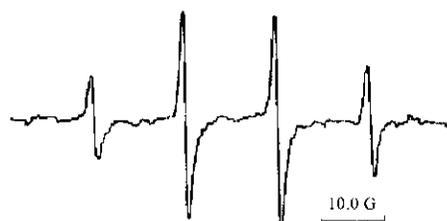


Fig.7 ESR spectrum of hydroxyl radical trapped by DMPO in electrochemical systems

free radical $O_2^{\cdot -}$ and DMPO (DMPO-OOH \cdot adduct) did not be determined. This can be attributed to that the concentration of DMPO-OOH \cdot adduct was very low, or DMPO-OOH \cdot adduct is unstable and it is prone to change to DMPO-OH \cdot adduct.

A fluorescence spectrophotometry method was used to detect HO \cdot produced by C/PTFE O_2 -fed cathode in basic electrolyte. Benzoic acid with weak fluorescence may react on HO \cdot , and the reactive product 3-hydroxybenzoic acid which gave intense fluorescence. The 3-hydroxybenzoic acid was separated from the catholyte by HPLC. Two major hydroxylated products were quantified, corresponding to 3- and 4-hydroxybenzoic acid. Therefore the quantity of HO \cdot in the model reactive system can be primarily calculated. It was 2.15 $\mu\text{mol/L}$ for electrolyzing 60 min.

2.4 Degradation of coal-gas wastewater containing phenol

Electrochemical oxidation of coal-gas wastewater was studied using Ti/IrO $_2$ /RuO $_2$ anode and a carbon/polytetrafluoroethylene(C/PTFE) O_2 -fed cathode in the diaphragm cell with a terylene diaphragm. H $_2$ O $_2$ and HO \cdot exist in the catholyte during O_2 -electroreduction on the C/PTFE cathode. They can be used as oxidizing substances to remove organic pollutant. The variations of the volatile phenol and COD removal efficiency with electrolysis time in the coal-gas wastewater are given in Fig.8. In this electrochemical oxidation system, the degradation fractions of the volatile phenol and COD in the diaphragm cell were 100% and 72% at 100 min, respectively. The coal-gas wastewater is supposed to be cooperative oxidized by direct or indirect electrochemical oxidation at the anode and H $_2$ O $_2$, HO \cdot and $O_2^{\cdot -}$, produced by oxygen reduction at the cathode in the diaphragm cell. Therefore, the cooperative electrochemical oxidation of coal-gas wastewater in the anodic-cathodic compartment achieved better

degradation effects.

3 Conclusions

The mechanism of electrochemical oxidation were studied in the diaphragm cell (a terylene diaphragm) and the no-diaphragm cell with Ti/IrO $_2$ /RuO $_2$ anode and C/PTFE O_2 -fed cathode which generated H $_2$ O $_2$ by a two-electron reduction of oxygen gas fed to the cathode. H $_2$ O $_2$ is electrogenerated and simultaneously destroyed in the system at the same rate without the diaphragm, and HO $_2$ which electrogenerated in the diaphragm cell may be changed to HO \cdot , $O_2^{\cdot -}$. After 80 min, the accumulation H $_2$ O $_2$ reached steady concentrations of 5.6 mg/L and 8.3 mg/L in the no-diaphragm cell and the diaphragm cell, respectively. The COD removal in diaphragm and no-diaphragm cells could reach 80.4% and 71.4%, respectively. The degradation reaction of phenol in the no-diaphragm cell is supposed to be cooperative oxidized by direct or indirect electrochemical oxidation at the anode and H $_2$ O $_2$ produced by oxygen reduction at the cathode. However, in the alkaline solution of the diaphragm cell, the degradation reaction of phenol is supposed to be cooperative oxidized by direct or indirect electrochemical oxidation at the anode and HO $_2$, HO \cdot produced by oxygen reduction at the cathode. The mineralization of phenol in the diaphragm cell was better than that in the no-diaphragm cell. Furthermore, hydroxyl radical (HO \cdot) was determined in the cathodic compartment of the diaphragm cell by electron spin resonance spectrum(ESR) and the fluorescence spectra. The average removal efficiency of the volatile phenol and COD in the coal-gas wastewater were 100% and 79.6%, respectively.

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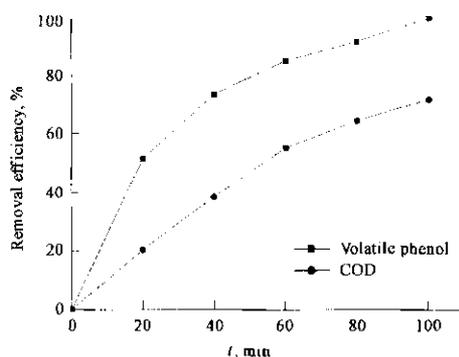


Fig.8 Variations of the volatile phenol and COD in the coal-gas wastewater vs. electrolysis time

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(Received for review April 11, 2005. Accepted May 16, 2005)