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Degradation Mechanism of Phenol in C/PTFE O_2-Fed Cathode by Determining the Product of Oxygen Electroreduction

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Abstract: A terylene membrane which kept pH>12 in cathode compartment was used to construct a divided cell with a carbon/polytetrafluoroethylene (C/PTFE) O_2-fed cathode. The concentrations of hydrogen peroxide (H_2O_2) and hydroxyl radical (HO·) in the catholyte were 8.3 mg/L and 2.15 μmol/L, respectively, which were determined by permanganate titration, electron spin resonance (ESR) spectrum and the fluorescence spectra. The efficiency of the removal of phenol achieved 100% as a result of these two kinds of stronger oxidizer.

Keywords: Electrochemical oxidation, C/PTFE O_2-fed cathode, hydrogen peroxide, hydroxyl radical.

The electrode materials used to O_2 electro-reduction can be divided into two groups. The first one involves electrodes, on which the O_2 electro-reduction proceeds predominantly through the intermediate formation of hydrogen peroxide, while the second one involves electrodes, where both the 4-electron and 2-electron reactions take place[1]. Carbon materials such as C/PTFE and graphite felt are classified in the first group and thus can be used as electrodes for the electrochemical production of H_2O_2. Processes of indirect electrooxidation of organic compounds by H_2O_2, generated during cathodic reduction of oxygen on the C/PTFE O_2-fed cathode, have much promise for treating wastewaters of organic toxicants, owing to their ecologically safe and simple[2]. Generally, electro-Fenton process can be realized in electrolysis cells without a diaphragm, where H_2O_2 is produced in an acid medium and Fe^{2+} is added or offered by Fe anode. The disadvantage of electro-Fenton process is that the problem of iron sludge must be solved. In this paper, a diaphragm is selected to keep pH>12 in cathodic solution of a diaphragm cell with a C/PTFE O_2-fed cathode. The efficiency of the removal of phenol is larger than that of similar report before[3]. The degradation of phenol is confirmed that it is due to the oxidizing reaction of HO_2^- produced by oxygen electroreduction and HO· produced by H_2O_2 autodegradation.

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Experimental

Electrolysis were conducted in a terylene diaphragm cell of 100 mL capacity. The cell consisted of two chambers: a cathodic chamber and an anodic chamber. The anode was Ti/IrO_2/RuO_2 net of 16 cm^2. The cathode was a C/PTFE electrode of 16 cm^2 fed with air.

This cathode was prepared using the following procedure. 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 O_2 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. A laboratory D.C. power supply with current-voltage monitor was employed to provide the electric power. Before an experiment was started, spargeing air was run for 5 min in order to keep dissolved oxygen saturation. And air was sparged into the cell till the electrolysis process was over.

The H_2O_2 concentration accumulated during electrolysis was determined by titration with permanganate using a standard procedure[4]. The chemical oxygen demand (COD) was measured by the standard method.

The radicals were determined by ESR measurements, which were performed in the X-band on a JES-FE3AX ESR spectrometer (JEOL, Tokyo, Japan) at room 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 μL previously filtered with PTFE filters of 0.45 μm 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 × 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).

Results and Discussion

Figure 1 shows the variation of pH value with electrolysis time in cathodic compartment. The terylene diaphragm used in this experiment can keep the pH>12 after 20 min electrolysis whether the original solution was acidic, neutral or alkaline solution.

Figure 1 Variation of pH value with electrolysis time

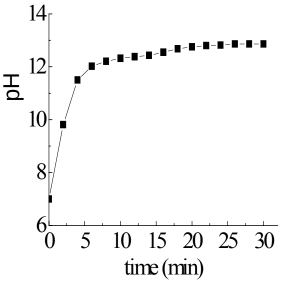
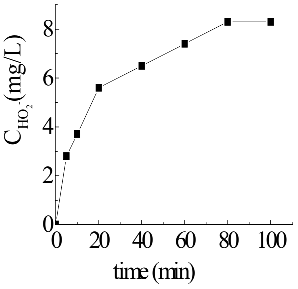


Figure 2 Variation of accumulated HO_2^- concentration with electrolysis time



In basic solutions, oxygen dissolved in the aqueous phase was reduced to basic hydrogen peroxide HO_2^-. **Figure 2** shows the change of HO_2^- concentration with electrolysis time. The amount of HO_2^- is increased within 80 min electrolysis, and then the accumulation HO_2^- tends to steady concentrations of 8.3 mg/L.

In basic electrolyte, H_2O_2 may be converted to HO_2^-、 HO· and $O_2^{-}\cdot$[5] as follows:

$$H_2O_2 + OH^- \rightarrow H_2O + HO_2^- \quad (1)$$

$$H_2O_2 + HO_2^- \rightarrow HO\cdot + O_2^-\cdot + H_2O \quad (2)$$

The oxidizing power of HO_2^-, HO· 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 divided cell. ESR and the fluorescence spectrophotometry combined with HPLC are used to quantitatively determine the free radical.

Figure 3 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· adduct as demonstrated previously[6], confirming that the quartet signal is DMPO-OH· adduct.

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

Figure 3 ESR spectra of HO· radicals trapped by DMPO in electrochemical systems

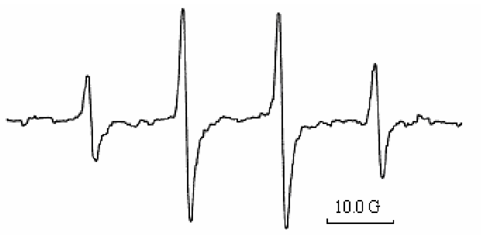
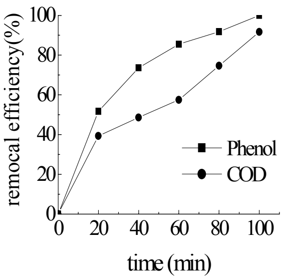


Figure 4 Variations of the phenol and COD *vs.* electrolysis time



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

It can be seen that H_2O_2 and HO· existed in the catholyte during O_2-electroreduction on the C/PTFE cathode. They can be used as oxidizing substances to remove organic pollutant. The efficiencies of the removal of phenol and COD with electrolysis time are given in **Figure 4**. In this electrochemical oxidation system, the degradation fractions of the phenol (100 mg/L) and COD (247 mg/L) in the cathodic compartment were 100% and 91.7% at 100 min, respectively. The degradation of phenol in the divided cell was high. The phenol is supposed to be oxidized by HO_2^- and HO·, produced by oxygen reduction at the C/PTFE O_2-fed cathode.

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