

Destructive Oxidation of Phenol by Hydrogen Peroxide in Alkaline Medium in a Membrane-Free Electrolyzer

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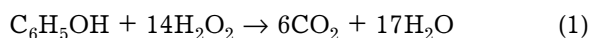
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Abstract

The conditions of indirect destructive oxidation of phenol by hydrogen peroxide generated electrochemically from oxygen in gas diffusion electrode in alkaline medium in an electrolyzer without cation-exchange membrane are considered. The dependence of phenol oxidation rate and efficiency on current density, concentration and composition of electrolyte is investigated. The major routes of the activation of phenol oxidation and conditions for utilization of organic components from aqueous solutions are determined.

INTRODUCTION

Modern technology of waste water purification from phenol and its derivatives pays much attention to the use of ecologically pure oxidizers, such as H_2O_2 , O_3 [1, 2]. The authors of [3] subjected industrial waste water to ozone-peroxide electrochemical treatment in an electrolyzer with diaphragm; oxidation rate during the ozone-peroxide treatment was four times higher than that during simple ozonation. It is demonstrated in [4] that electrochemically generated hydrogen peroxide in a cell with porous glass carbon cathode is able to destructively oxidize phenol into CO_2 and H_2O according to the equation



The authors of [5] report comparative results on the oxidation of aniline and 4-chloroaniline without hydrogen peroxide, with hydrogen peroxide added, and with hydrogen peroxide obtained by the cathode reduction of oxygen in carbon polytetrafluoroethylene electrodes. It is demonstrated that the anode

oxidation with hydrogen peroxide involves destructive oxidation of the mentioned compounds.

In [6], we describe results of indirect oxidation of phenol by hydrogen peroxide generated electrochemically from oxygen in gas diffusion electrode in alkaline medium in an electrolyzer with cation-exchange membrane. It is stated that oxidation products are organic acids and ketones; intermediate products with conjugated double bonds are accumulated in the case of the lack of oxidizer; the efficiency of the process is substantially affected by the concentration of alkali and by the current density.

It is known [7] that oxygen is reduced in an alkaline medium to form peroxide ion; in case if cation-exchange membrane is used, it is the major oxidizing agent within the catholite volume. In an electrolyzer without cation-exchange membrane, according to the electrolysis conditions HO_2^- will be transferred to the anode and oxidized to perhydroxyl radical HO_2^\cdot . Besides, HO^- will be oxidized at the anode and will form hydroxyl radicals HO^\cdot [5]. The peroxide intermediate particles are known to exhi-

bit different reactivity [8]. Because of this, an electrolyzer without cation exchange membrane equipped with platinum anode may be expected to provide a deeper oxidation of phenol till its mineralization.

The present investigation continues the studies described in [6]; the aim of the investigation is to study the dependence of the rate and efficiency of destructive oxidation of phenol by hydrogen peroxide generated electrochemically from oxygen in gas diffusion electrode in an alkaline medium in electrolyzer without cation-exchange membrane.

EXPERIMENTAL

Experimental conditions, the procedure according to which gas diffusion electrodes were manufactured, and the analysis of initial substances and products are described in [6]. Smooth platinum was used as the anode. Model phenol solutions with concentrations 25, 50, 100 and 200 mg/l were oxidized in NaOH solutions (0.05, 0.1, 0.5 mol/l) at current densities of 25, 50, 100 and 150 mA/cm².

RESULTS AND DISCUSSION

Figure 1 shows kinetic curves of the accumulation of hydrogen peroxide in the mem-

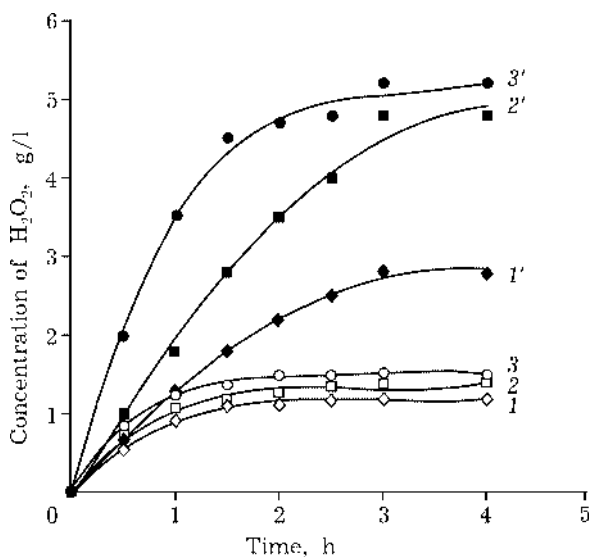


Fig. 1. Kinetic curves of the accumulation of hydrogen peroxide in NaOH solutions. i , mA/cm²: 25 (1, 1'), 50 (2, 2'), 100 (3, 3'); NaOH concentration, mol/l: 0.1 (1-3), 0.5 (1'-3').

brane-free cell in 0.5 M and 0.1 M NaOH. One can see that the equilibrium concentration of hydrogen peroxide is much less in the cell without membrane; it is 1-1.5 g/l. A sharp decrease of H₂O₂ concentration points to the decomposition of the formed HO₂⁻ in the region near the anode. The decomposition of hydrogen peroxide in the region near the anode can be described by the following equations:

$$\dot{C}_{\text{HO}_2^-} = ik_C - ik_A C_{\text{HO}_2^-} - k_d C_{\text{HO}_2^-} C_A \quad (2)$$

$$\dot{C}_a = i(k_A C_{\text{HO}_2^-} + k'_A C_{\text{HO}^-}) - k_{r,a}^2 - k^* C_A C^* \quad (3)$$

Here k_C is the coefficient determining the rate of hydrogen peroxide formation at the cathode, i is current density, mA/cm²; k_A and k'_A are rate constants of electron transfer from HO₂⁻ and HO⁻, respectively, to the anode; k_d is rate constant of H₂O₂ decomposition due to the interaction with active particles (HO₂⁻, HO⁻); C_a is the concentration of active particles determined according to the equation (3); $k_{r,a}$ is the constant of mutual recombination of active particles; k^* is rate constant of the interaction of active particles with various products; C^* is the concentration of products (phenol and others) reacting with active particles.

Radical recombination rate is known to be high; because of this, their concentration will be equilibrium; it is approximately defined on the basis of equation (3) by the following relation:

$$C_A = \frac{\sqrt{i}(k_A C_{\text{HO}_2^-} + k'_A C_{\text{HO}^-})}{\sqrt{k_{r,a}}} \quad (4)$$

The rate of oxidation of the organic components in solution is proportional to the concentration of radicals; because of this, the rate constant of phenol transformation depends on \sqrt{i} , which is in agreement with the data shown in Fig. 2. Besides, one should expect under these conditions that the transformation of the organic component will occur by the reaction with the order close to unity with respect to this component, which agrees with the results shown in Fig. 3. It should be noted that the equilibrium concentration of hydrogen peroxide in the cell decreases by an order of magnitude in the presence of phenol and its oxidation products, which is a direct indica-

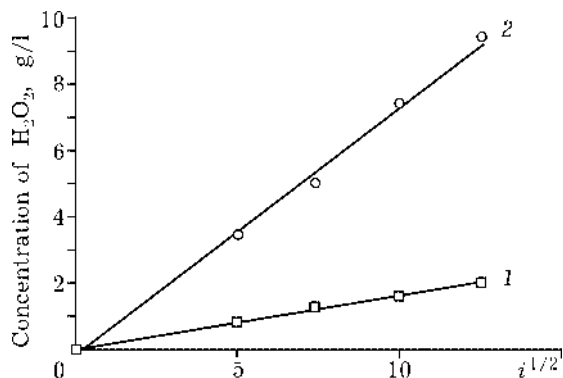


Fig. 2. Dependence of the equilibrium concentration of hydrogen peroxide on current density. NaOH concentration, mol/l: 0.5 (1), 0.1 (2).

tion of the participation of peroxide ions in the oxidation of organic components.

Figure 3 shows the curves of phenol oxidation in 0.05 M NaOH at the initial phenol concentration of 50 mg/l. The analysis of curves indicates the pseudo-first order of reaction; the mentioned dependence is described by the equation:

$$\ln \frac{C_0}{C} = kt \quad (5)$$

where C_0 is the initial phenol concentration, mg/l; C is phenol concentration after a time interval t , mg/l; k is the rate constant of oxidation.

The determined values for the constant at different current density and different NaOH concentration are shown in Table 1. One can see that more optimal conditions are realized

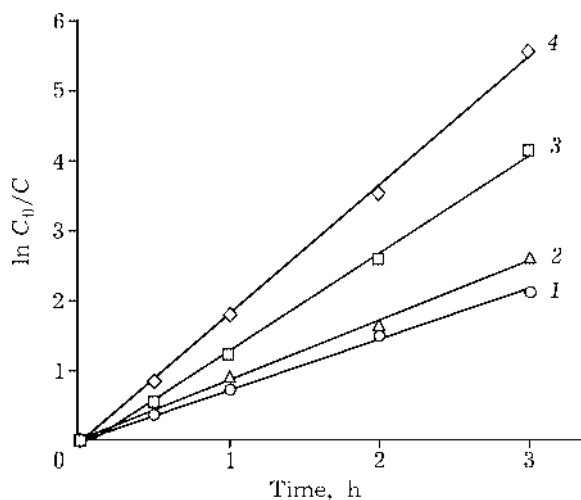


Fig. 3. Kinetic curves of phenol oxidation in 0.05 M NaOH. Initial phenol concentration: 50 mg/l. i , mA/cm²: 25 (1), 50 (2), 100 (3), 150 (4).

TABLE 1

Rate constant of phenol oxidation at different current densities and NaOH concentrations, h⁻¹

i , mA/cm ²	NaOH concentration, mol/l		
	0.5	0.1	0.05
150	1.7	2.0	1.8
100	1.4	1.8	1.4
50	0.9	1.0	0.8
25	0.5	0.5	0.7

in 0.1 M NaOH at current density of 100 and 150 mA/cm².

We investigated the kinetic dependencies of the oxidation of phenol with different initial concentrations (25 to 200 mg/l) on current density in 0.1 M NaOH. The determined reaction rate constants are shown in Table 2. One can see that the oxidation efficiency decreases with increasing initial phenol concentration, which is especially evident within the first hour of electrolysis. The efficiency of phenol oxidation at its initial concentration of 25, 50, 100 and 200 mg/l was 86, 85, 70 and 60 %, respectively.

The data shown in Table 1 were plotted in $\sqrt{i} - k$ coordinates as shown in Fig. 4. One can see that it is better to use 0.1 M NaOH solution for phenol oxidation. Current density has a substantial impact on oxidation efficiency, especially within the first hour of electrolysis. At the current density of 100 mA/cm², the oxidation efficiency within the first hour of electrolysis was 85 %, while at 25 mA/cm² it was 38 % in 0.1 M NaOH at the initial phenol concentration of 50 mg/l.

In order to increase electrical conductance of 0.1 M and 0.05 M NaOH solutions, we used the 1 M Na₂SO₄ and 1 M Na₂CO₃ (4 : 1) solu-

TABLE 2

Rate constant of phenol oxidation at its different initial concentrations, h⁻¹

i , mA/cm ²	C_0 , mg/l			
	25	50	100	200
150	1.8	1.8	1.5	0.9
100	1.8	1.8	1.5	0.9
50	1.5	1.0	1.0	0.5
25	—	0.5	0.5	—

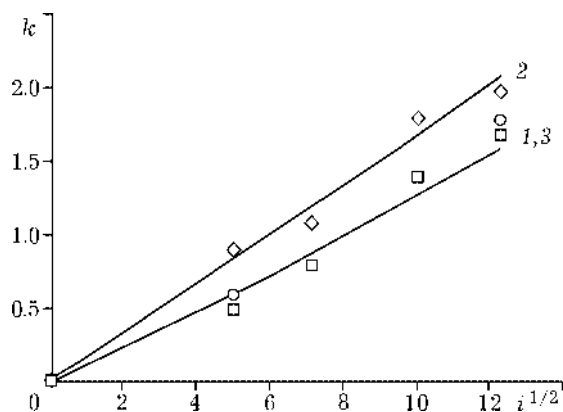


Fig. 4. Changes of the oxidation rate constant depending on current density. NaOH concentration, mol/l: 0.5 (1), 0.1 (2), 0.05 (3).

tions. It should be noted that the oxidation efficiency for the first hour of electrolysis is higher for Na_2CO_3 , being 82 %; while with Na_2SO_4 it is 69 % at the current density of 100 mA/cm^2 . The presence of carbonates in solution increases the electrode polarization by 0.6–0.8 V at current density of 100 mA/cm^2 . This happens because carbonates get deposited in the pore volume of the electrode [9].

Along with transitions from phenolate anion, the electronic spectra of phenol oxidation products contain additional weak lines with $\lambda_1 = 365$ nm, $\lambda_2 = 325$ nm, and transitions at the wavelengths $\lambda_3 = 276$ nm, $\lambda_4 = 254$ nm, $\lambda_5 = 238$ nm. Besides the mentioned transitions, there is a background line connected with the presence of scattering factor. This can be explained by the formation of polymeric compounds (tar); this factor is actual for the initial phenol concentration of 200 mg/l. The highest intensity of absorption bands corresponding to intermediate products of oxidation is observed at the initial period of phenol oxidation, its initial concentration being 100–200 mg/l, which can be connected with direct oxidation of phenol at the anode because of the lack of oxidizer in the layer near anode at this moment.

Thus, phenol oxidation process follows two routes: direct oxidation of phenol at the anode with the formation of tar compounds, and its oxidation by active intermediates (HO_2 , HO) in the layer near the anode. Addition of the oxidizer (H_2O_2) into the electrochemical cell before the experiment leads to the absence of absorption bands related to intermediate pro-

ducts and tar compounds in the electronic spectra, which points to the suppression of tar formation reaction and to more efficient oxidation of intermediate products.

Investigation of the intermediate products of phenol oxidation by means of IR and UV spectroscopy revealed the presence of carboxylic acids with absorption bands at 3350 and 1725 cm^{-1} , β -diketones in the enolic form with bands at 1592 and 2900 cm^{-1} . For these compounds, transitions at $\lambda = 254$ nm are observed, along with a weak transition at $\lambda = 325$ nm. Besides the bands related to the mentioned compounds, absorption bands related to quinones and α -diketones are sometimes present. After electrolysis for 2–3 h, electronic spectra do not contain absorption bands of intermediate products, which is the evidence of complete mineralization of phenol at current density of 100–150 mA/cm^2 and initial phenol concentration of 25–50 mg/l.

CONCLUSIONS

1. It is demonstrated that the process of indirect electrochemical oxidation of phenol occurs efficiently in a cell without cation-exchange membrane.
2. It is stated that the efficiency of oxidation in non-separated cell depends on alkali concentration and current density.
3. Destructive oxidation of phenol is most efficient in a 0.1 M NaOH solution at the current density of 100–150 mA/cm^2 .

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