Phenol Oxidation in a Slot Type Flow Electrolyzer as Hydrogen Peroxide Generator

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Abstract

Conditions of phenol oxidation with hydrogen peroxide have been studied using a slot type flow electrolyzer with a gas-diffusion electrode to generate hydrogen peroxide from oxygen. The dependences of the rate and efficiency of phenol oxidation on current density have been investigated (pH 12–13). The efficiency factor of a flow type electrochemical cell has been determined.

INTRODUCTION

Previously [1], we have demonstrated that destructive oxidation of phenol occurs in a membrane-free electrochemical cell (ECC) and generates hydrogen peroxide from oxygen inside a gas-diffusion carbon black cathode at pH 12–13. It was established that phenol oxidation is limited by mass transfer, namely, by the delivery of HO_2^- generated in the anodic space area. The kinetic study was performed in a stationary mode of oxidation of the initial phenol solution in the electrochemical cell.

The present work reports on destructive oxidation of phenol in a flow type membraneless electrochemical cell with a reduced distance between the cathode and anode for effective transport of the HO_2^- oxidizer from cathode to anode.

EXPERIMENTAL

Phenol oxidation was investigated in a flow type electrochemical cell with a distance of 2–4 mm between the gas-diffusion cathode and the platinum (plate) anode. To prevent formation of stall zones during release of oxygen at the anode, the cell was equipped with a system of fast delivery of electrolyte through the electrode space (residence time 5 s in that space). For more precise determination of oxidation rates at small degrees of conversion, the system additionally included a closed circuit of electrolyte circulation. The total flow rate of electrolyte was maintained constant. This enabled us to determine variation of the phenol conversion rate at relatively long operation times of the electrochemical cell. The phenol concentration in solution was determined by the procedure of [2]. The concentrations of phenol and its conversion products were also measured by UV spectroscopy.

RESULTS AND DISCUSSION

Figure 1 presents the dynamics of the difference in phenol concentrations at the inlet and outlet of the cell *versus* the operation time for different current densities. It is evident that the rate of phenol oxidation increases during the initial period of operation and then flattens out to a quasistationary mode. This change in the oxidation rate of phenol is probably related to the increase in the rate of hydrogen peroxide formation at the cathode due to surface activation of the gas-diffusion electrode.

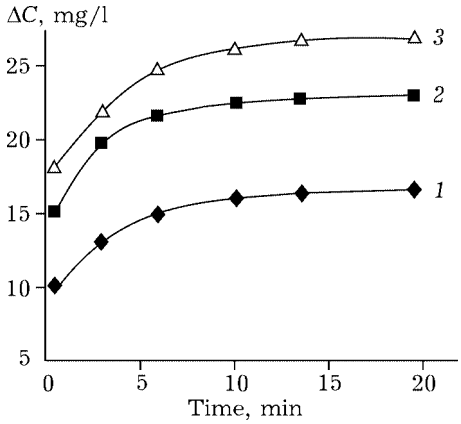

Fig. 1. Difference in phenol concentrations ΔC at the inlet and outlet of ECC *versus* the operation time at different current densities, mA/cm^2: 50 *(1)*, 100 *(2)*, 180 *(3)*.

(All the results given below refer to the steady-state conditions of ECC operation.)

Figure 2 depicts the difference of phenol concentrations $\Delta C = C_0 - C$ between the concentration C_0 at the inlet and the concentration C at the outlet as a function of C_0 at different values of current density. Apparently, the dependence is linear in the region of small values of C_0 and flattens in the region of large values. When the density of current that passes through ECC changes, ΔC is proportional to $\sqrt{i}$ in the range of smaller concentrations, which agrees with the results presented elsewhere [1].

The relationships presented in Fig. 2 fit the radical mechanism of phenol oxidation. In this case, the active radical species generated during passage of current through the cell are spent on mutual recombination and on oxidation of phenol or its conversion products.

In the region of low contents of phenol, mutual recombination of radicals is the prevalent mechanism (dependence of $\sqrt{i}$ on current), while in the region of high contents of organic substrate, the radicals are mostly consumed on oxidation in solution. In this case, one can expect different orders of phenol oxidation depending on reagent concentration.

To determine the order of the phenol oxidation reaction, we use the formal kinetic equation of a chemical reaction

$$\frac{dC}{d\tau} = kC^n \tag{1}$$

where n is the reaction order, which is invariable in the course of the reaction; k is the effective rate constant of oxidation, which depends on current intensity, anode activity, and other cell parameters; and C is the concentration of phenol in the active zone of the cell.

Solution of eq. (1) can be generally presented as

$$\frac{1}{a}[C_0^a - C^a] = k\tau = k\frac{V}{v} \tag{2}$$

where $a = 1 - n$; C_0, C are phenol concentrations at the inlet and outlet of the electrochemical cell, respectively; and τ is the mean residence time of the electrolyte solution in the electrochemical cell, which is equal to V/v (V is the effective volume of the cell, and v is the rate of electrolyte feeding into the cell).

To determine the reaction order for all initial concentrations of phenol C_0, we use the tangent line drawn to an arbitrary point on the curves obtained from experimental data (see Fig. 2). Then in the neighbourhood of any point corresponding to the concentration C_0 on the curves in Fig. 2, $\Delta C(x) = \Delta C + bx$, where b is the slope of the curve at point C_0, x is minor deviation of the initial concentration from C_0. In this case, eq. (2) for this local region may be written as follows:

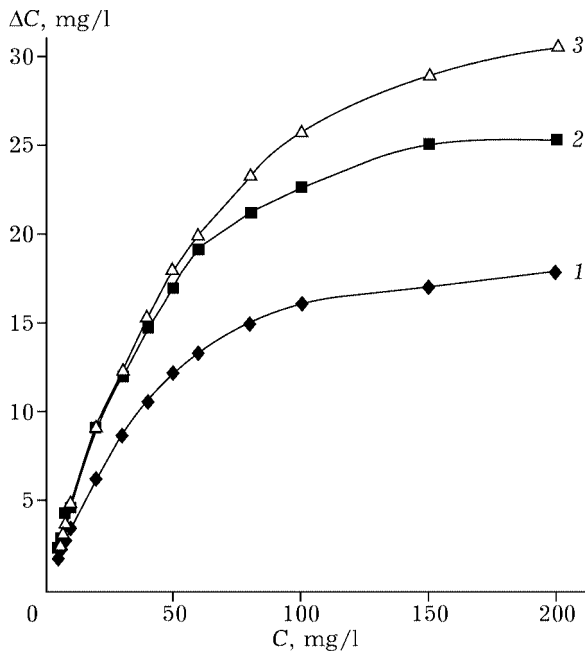

Fig. 2. Difference ΔC of phenol concentrations at the inlet and outlet of ECC *versus* the concentration C_0 at the ECC inlet at different current densities, mA/cm^2: 50 *(1)*, 100 *(2)*, 180 *(3)*.

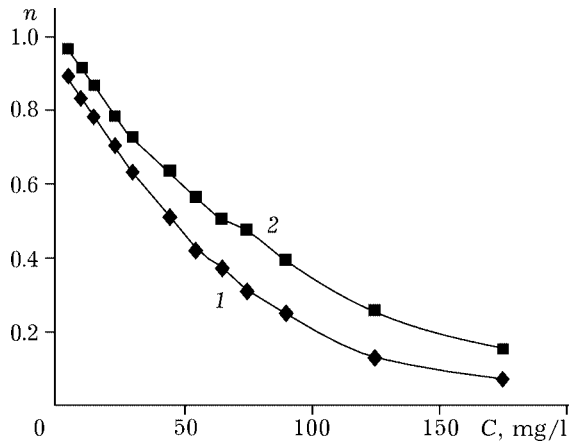

Fig. 3. Dependence of the reaction order n of phenol oxidation on the initial concentration of phenol at different current densities, mA/cm^2: 50 *(1)*, 180 *(2)*.

$$k\tau = \frac{1}{a}[C_0^a - C^a]$$
$$= \frac{1}{a}[(C_0 + x)^a - (C + (1 - b)x)^a] \quad (3)$$

This equation is true if the parameter a is assumed to vary little at small values of x from C_0 to C. Solving eq. (3) for $x \to 0$ gives

$$n = -\frac{\ln\ (1-b)}{\ln(C_0 / C)} \quad (4)$$

The reaction order corresponding to an arbitrary point C_0 may be found from this relation in terms of b – the slope of the curve at that point in Fig. 2.

Figure 3 shows the reaction order of phenol oxidation in ECC as a function of the initial concentration of phenol C_0 at different current densities. It is evident that the reaction order is close to unity in the region of minor concentrations and tends to zero with the increasing initial concentration of phenol. These results are in perfect agreement with the above two mechanisms of active species consumption. The first order is due to the constant concentration of active species in the region of low contents of phenol and its oxidation products. At high concentrations, the zero order is ensured by the involvement of practically all active species in oxidation of organic products.

To estimate the performance of ECC, we determined the efficiency factor (EF) for destructive oxidation of phenol:

$$\eta = 28N_{\mathrm{Ph}}/N_e \quad (5)$$

where N_{Ph} is the number of oxidized phenol molecules, N_e is the number of electrons passed through the ECC, and 28 is the number of electrons required for the formal destructive oxidation of one phenol molecule. Replacement of N_{Ph} and N_e in Eq. (5) gives the following relation:

$$\eta = 28\Delta C_e N_{\mathrm{A}} v/(10^6 MI) \quad (6)$$

where ΔC is variation of concentration, mg/l; M is molar mass, g; I is current intensity, A; e is electron charge; N_{A} is the Avogadro number; v is the electrolyte flow rate through the cell, l/h.

This relation enables one to find EF during phenol oxidation in a cell using the values of ΔC from Fig. 2 and current intensity. The values of h obtained in this way are presented in Fig. 4. Apparently, the EF grows linearly in the region of low phenol contents and reaches the limit in the region of high concentrations. The EF generally grows with decreasing intensity of the current passing through the cell, and reaches 80 % for current density i = 50 mA/cm^2. Hence the performance of a slot type flow cell significantly exceeds the characteristics of phenol oxidation in differently designed cells [1].

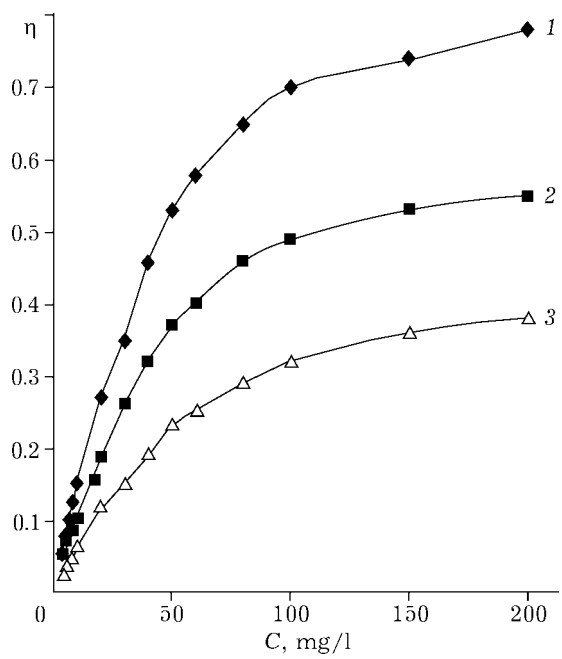

Fig. 4. Dependence of the efficiency factor η of ECC on phenol concentration at different current densities, mA/cm^2: 50 *(1)*, 100 *(2)*, 180 *(3)*.

CONCLUSIONS

1. It has been demonstrated that during the operation of a slot type ECC the oxidation rate of phenol increases, changing to a quasistationary mode with time.

2. The variation ΔC of phenol concentration during oxidation in a slot type cell depends on the initial concentration of phenol and reaches the limiting value in the range of high contents of organic substrate in solution.

3. The effective order of phenol oxidation depends on the concentration of phenol in solution and is governed by the radical mechanism of oxidation.

4. The efficiency factor of an electrochemical cell has been determined for phenol oxidation. The most effective work of the cell corresponds to the range of higher phenol concentrations and lower current densities.

REFERENCES

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