

Indirect Electrochemical Oxidation of Phenol by Hydrogen Peroxide *in situ* Generated from Oxygen in a Gas Diffusion Electrode in Acid and Neutral Media

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Abstract

Indirect electrochemical oxidation of phenol is studied in acid (pH 2–3) and neutral (pH 6–7) media with platinum and lead oxide anodes. In the acid electrolyte oxidation is found to occur through mineralization to CO₂ and H₂O, while in neutral electrolyte phenol is oxidized to organic acids.

INTRODUCTION

With increasing man-caused effect on the environment it is necessary to use environmentally harmless reagents. With this regard hydrogen peroxide H₂O₂ seems to be rather attractive, since it is not only harmless to environment, but possesses a rather high oxidative potential combined with high efficiency and selectivity. An indirect oxidation of organic compounds, assisted by *in situ* generated H₂O₂ based reactive inorganic intermediates, allows reaction performance at potentials with absolute values lower than that required for the direct anode oxidation.

The essence of this approach is that anode (HO[•]) generation from H₂O₂ and water, combined with cathode O₂ reduction to ion HO₂⁻, favours a higher concentration of reactive radicals in electrolytic cell with no diaphragm. It is shown [1–3] that under these conditions organic substrates are oxidized to CO₂ and H₂O.

It is well known that phenol is a widely spread hard to oxidize toxic reagents. Its content in various media may range from 10 to 200 mg/l. As reported in the literature [4], when phenol is present in low concentrations it is preferable

to oxidize it with environmentally harmless reagents such as ozone, hydrogen peroxide, or with UV irradiation [5].

Earlier [6] we studied the indirect electrochemical phenol oxidation by H₂O₂ *in situ* generated from O₂ in the gas diffusion electrode in alkali electrolytic cell with platinum anode, but containing no cation exchange membrane. We have shown that destructive oxidation is rather efficient in the 0.1 M NaOH solution at a current density of 100–150 mA/cm².

In the present study we focus on the indirect phenol oxidation by H₂O₂ *in situ* generated from O₂ in the gas diffusion electrode in acid and neutral media in the diaphragm less electrolytic cell with platinum and lead (Pb/PO₂) anodes. Electrodes based on lead dioxide show high chemical resistance to various media, thus allowing process performance in a wide pH range, and may be regarded as a good alternative to platinum anodes.

EXPERIMENTAL

Experimental conditions, method for manufacturing gas diffusion electrodes, analysis of reagents and products are described elsewhere

[7]. We used platinum plate and lead system (Pb/PbO₂) as anodes. The latter was produced by the anode oxidation of a lead plate (2 × 10 × 25 mm in size) in solution containing 1 M H₂SO₄ at a current of 500 mA for 1 h at 20–25 °C. Anode composition was determined with X-ray phase analysis: PbO-α-PbO₂ (3 : 1).

In experiments we used either neutral solution (1 M Na₂SO₄) or acid electrolyte. The latter contained 1 M Na₂SO₄ acidified by H₂SO₄ to pH 2–3 and sulphate of iron (II) ($C_{\text{Fe}^{2+}} = 2.4 \cdot 10^{-3}$ mg/l).

Solutions oxidation was performed at 20 °C in diaphragm less electrolytic cell at current densities 50 and 100 mA/cm². Phenol starting concentration was 100, 200, 400 and 800 mg/l. Phenol content decrease was registered by photo colorimetry. Oxidation products were analyzed with the UV–VIS spectroscopy.

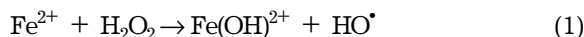
In order to study the lead anode efficiency in phenol oxidation at various pH we used solutions with starting phenol content 100 mg/l, electrolysis current density being 50 mA/cm².

RESULTS AND DISCUSSION

According to Fig. 1 as pH decreases, phenol oxidation on the lead oxide electrode becomes more efficient. Thus, at pH 13 oxidation efficiency is 55 %, while at pH it attains 80 %.

Figure 1, b shows the kinetic curves of anode phenol oxidation at pH 7 without H₂O₂ and with it. Apparently, hydrogen peroxide addition increases phenol oxidation efficiency during the first hour of electrolysis from 55 % (curve 1) to 70–75 % (curves 2, 3). Apparently, anode Pb/PO₂ allows efficient phenol oxidation performance at various pH. H₂O₂ introduction improves phenol oxidation efficiency from 78–80 to 96–98 % in 3 h.

Phenol is known to be destructively oxidized in acid solutions by hydrogen peroxide in the presence of Fe(II) ions (Fenton reagent) [8, 9]. In system H₂O₂ + Fe²⁺ most reactive radicals HO• form:



Certain reactions may go on the anode surface:

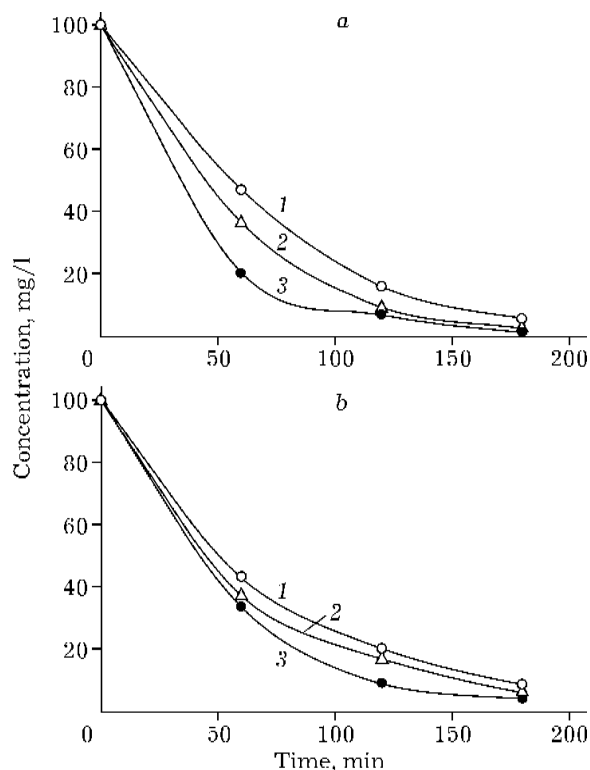
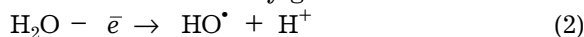


Fig. 1. Kinetic curves of phenol oxidation depending on pH (a) and hydrogen peroxide concentration (b). Current density 50 mA/cm², initial phenol content 100 mg/l: a – pH: 13 (1), 10 (2), 5 (3); b – H₂O₂ concentration, mol/l: 0 (1), 0.14 (2), 0.3 (3), lead-oxide anode.

It is well known that hydroxyl radicals are capable of phenol oxidation to CO₂ and water through several intermediate stages [10].

Figure 2 shows the kinetic curves of phenol oxidation by *in situ* generated H₂O₂ in the gas diffusion cathode in acid and neutral electrolytes in the diaphragm less electrolysis cell with platinum anode.

Apparently, in both acid and neutral electrolytes phenol oxidation efficiency increases with the growing current density. This effect is most vivid during the first hour of electrolytic cell operation. Thus, in the acid electrolyte at initial phenol content 200 mg/l efficiency is 84 % at a current density of 50 mA/cm², and 92 % – at 100 mA/cm². In the neutral electrolyte with the same initial phenol concentration during the first hour of electrolysis efficiency is 48 % at a current density of 50 mA/cm², and 77 % – at 100 mA/cm². Data comparison shows that phenol oxidation at pH 2–3 is far more efficient than in the neutral solution.

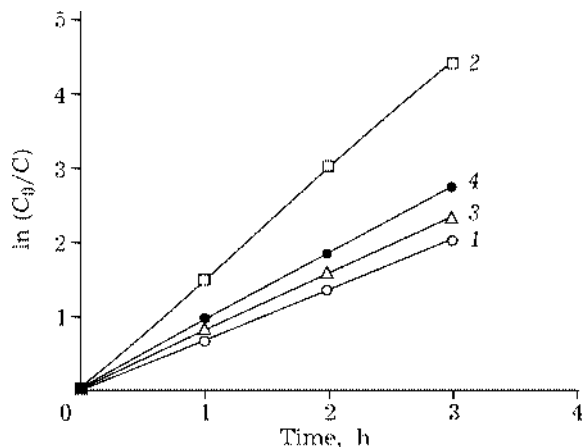


Fig. 2. Phenol oxidation kinetics at pH 2-3, pH 7, current density, mA/cm²: 50 (1, 3), 100 (2, 4). Initial phenol content, mg/l: 200 (1, 2), 400 (3, 4); platinum anode.

Most likely, depending on pH oxygen reduction in water electrolyte yields intermediates differing by their reactivity. Thus, in the acid medium these intermediates are HO₂[•] and HO[•], produced in reactions (1)–(3). In the neutral media HO₂[•] is the oxidizing species, forming on the cathode *via* reaction:



And on the anode via reaction:



Therefore, HO₂[•], HO₂[•] and HO[•] are responsible for the oxidation performance, but they differ by their reactivity by 5–6 orders of magnitude. Among them radical HO[•] is the most active species [11].

Analyzing curves in Fig. 2, we observe the pseudo first order of phenol oxidation reaction, indicated dependence following equation:

$$\ln C_0/C = k\tau$$

where C₀ is initial phenol concentration, mg/l; C is phenol concentration at time τ, mg/l; k is reaction rate constant, h⁻¹.

TABLE 1

Reaction rate constants *k* at various current density and pH, h⁻¹

Current density, mA/cm ²	C ₀ [*] , mg/l	
	200	400
50	1.4/0.66	1.3/0.8
100	1.8/1.47	1.6/0.9

*First value – at pH 2-3, second value – at pH 7.

Table 1 lists the values of reaction rate constants obtained at different current densities.

In order to confirm that phenol is indeed oxidized to CO₂ and water, electrolysis gas was collected in a trap with a solution of CaCl₂. Calcium carbonate precipitate was analyzed for the content of CO₂ and Ca²⁺ using method [12] (see Table 2 for the results obtained).

Obviously, initial phenol concentration and electricity passing through the cell are the main factors, determining the efficiency of phenol conversion to CO₂ and water.

UV spectroscopy data, obtained for the solutions at the same quantity of electricity passed through the cell, show that phenol oxidation routes depend on solution pH. Thus, in acid media phenol oxidation goes through the formation of quinone and hydroquinone as intermediates, and is followed by the aromatic ring opening, yielding intermediate iron complexes with carboxyl ligands then converted to CO₂ and H₂O. Since electronic spectra show no bands of quinones, hydroquinones and carbonic acids, which are phenol oxidation intermediates [6, 7], phenol is indeed oxidized to CO₂ and water. Neutral solutions are characterized by absorption bands typical for diketones and carbonic acids. Quality reactions [13] prove oxalic acid to be present as well.

TABLE 2

Phenol mineralization efficiency

C ₀ , mg/l	Q, C	CO ₂ mass, mg		Mineralization degree, %
		Stoichiometry	Evolved	
200	10 802	14	12.5	89
400	10 802	28	11.5	41
400	21 604	28	25.2	90
800	10 802	56	6.2	11

CONCLUSION

Indirect electrochemical method was applied for phenol oxidation in acid and neutral media. Oxidation process is found to go more efficiently in acid electrolytes ($k = 1.6 \text{ h}^{-1}$) and yields CO_2 and water. In neutral media electrochemical process transforms hard to oxidize phenol to simple mono- and dicarbonic acids, which may be utilized by microorganisms during the subsequent biochemical purification.

Lead oxide electrode is shown to be quite efficient as anode for the indirect electrochemical oxidation of organic substrates in solutions with different pH.

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