

Study of Phenol Destruction by Means of Oxidation

T. N. VOLGINA, O. S. KUKURINA and V. T. NOVIKOV

*Tomsk Polytechnical University,
Pr. Lenina 30, Tomsk 634050 (Russia)*

E-mail: olskuk@mail.ru

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Abstract

The process of deep phenol oxidation in electrochemically activated medium has been studied in an effort to develop the process for neutralizing the wastes of highly toxic matter. The known scheme of phenol destruction to carbon dioxide and water through the stage of *p*-benzoquinone and carboxylic acid formation has been confirmed. The comparative analysis of specific reaction rates of phenol oxidation has been conducted using the various oxidizers including oxygen, hydrogen peroxide in the presence of Fe^{2+} , and ozone and also by means of electrochemical oxidation.

INTRODUCTION

At present, there is no erosion of interest in the processes of deep oxidation of toxic matter including phenol [1–3]. Chlorine-containing compounds, manganese compounds, ozone, hydrogen peroxide, Fenton's reagent [2] are now in use as oxidizers. Hydrogen peroxide and ozone are recognized to be the most effective oxidizers [3].

The purpose of this work is studying the deep oxidation of phenol by the procedure previously offered in [6] for pesticide neutralization on the basis of glycolic acid phenyl ether derivatives.

The essence of the method suggested consists in generating the complex of oxidizers when passing electric current through sulphuric acid solutions with simultaneous interaction of the produced compounds of peroxide nature [4] with organic matter within the same reaction volume.

EXPERIMENTAL

The deep oxidation of phenol was conducted in a laboratory setup, the basic unit of which represented an electrolytic cell [6]. The conditions

for carrying out the process: 0.1–10 g/l initial content of phenol, 40 vol. % concentration of sulphuric acid, current density of 0.06–0.83 A/cm²; the requisite temperature was maintained by means of a thermostat, under atmospheric pressure. In oxidation by means of hydrogen peroxide, its initial concentration comprised 6 mol/l; in oxidation by air oxygen, its flow rate was equal to 4.2 l/h.

Spectrophotometric measurements were conducted in SF-18, SF-26, KFK-3 devices, in the quartz sample pan, the bed thickness being 1 cm. Phenol concentration in the course of oxidation was determined from the calibration curve for $\lambda = 270$ nm. The concentrations of some intermediate and target products of phenol oxidation (carboxylic acids, carbon dioxide) were determined by the known titrimetric methods [8]. The total content of organic compounds was determined by method of chemical consumption of oxygen (CCO) with pH meter ionomer "ECOTEST-120" applied as the automated analyzer.

RESULTS AND DISCUSSION

While passing electric current through sulphuric acid solutions, the particles with high

oxidation potential are produced, namely, O^{\bullet} , O_3 , H_2O_2 , $H_2S_2O_8$, H_2SO_5 . Consequently, phenol destruction can proceed both in the reaction volume (due to chemical interaction with the above-mentioned particles) and, partially, through electrochemical processes.

The common stage for the processes of phenol deep oxidation is the stage of *o*-, *p*-diphenols (pyrocatechol and hydroquinone) formation and subsequently, formation of *o*-, *p*-quinones. Then the destruction of benzene ring occurs to form di- and monobasic carboxylic acids. Depending on the oxidizer, the composition of phenol destruction products varies. Accordingly, only the traces of oxalic acid [9] have been detected in oxidation by ozone; muconic acid has been detected in oxidation by hydrogen peroxide [10], and muconic, maleinic, and oxalic acid, upon the reaction with Fenton's reagent [11]. Main products of phenol electrooxidation on the Ta/PbO₂ anode were hydroquinone, catechol, 1,4-benzoquinone, maleinic and fumaric acids, and CO₂ [13].

Formation of the first stable intermediate product, *p*-benzoquinone, in phenol oxidation by the activated sulphuric acid is confirmed by a new absorption maximum arising in the region 245 nm (Fig. 1) [7].

The content of *p*-benzoquinone grows during the first minutes of the process and then, upon reaching a maximum, decreases due to further oxidation with the formation of organic acids (Table 1). As the current density increases, *p*-benzoquinone is produced earlier and in smaller concentrations (Fig. 2).

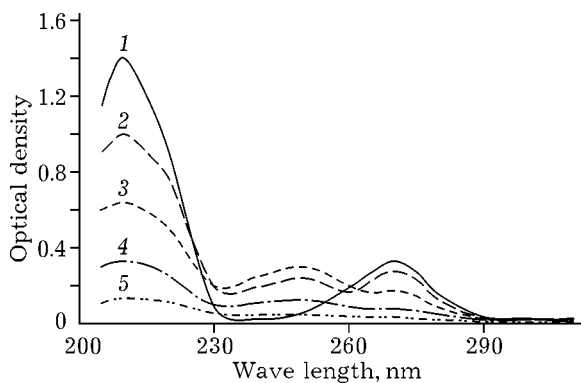


Fig. 1. Absorption spectra of phenol solution. Oxidation time, min: 0 (1), 20 (2), 40 (3), 60 (4), 80 (5).

TABLE 1

Change in the concentration of carboxylic acids in the solution during phenol oxidation, 10^{-3} mol/l

Time, min	C(C ₄ H ₄ O ₄)	C(C ₂ H ₂ O ₄)
0	25.0	120.0
15	7.6	8.9
30	5.3	4.4
60	1.8	2.0

Studying the oxidation process of carboxylic acids as intermediate products in the process of phenol destruction in the reaction mixture is associated with some difficulties, such as low concentration of the produced acids, large losses during the extraction from solutions with low pH value, and also high rate of their oxidation. Therefore, oxidation processes for the model dicarboxylic acids (maleinic and oxalic) with high initial solution strength have been selected as the subject of the research (see Table 1).

As it may be seen from evidence of Table 1, duration of the process being equal to 60 min, the degree of destruction of maleinic and oxalic acid comprises 92.8 and 98.3 %, respectively. Consequently, a suggestion can be made that destruction of carboxylic acids does not limit the process of phenol oxidation.

The CCO method is suggested to judge an effect of some technological parameters on the rate of phenol oxidation process. Since this method reflects the total organic content, both that of initial phenol and oxidation products, it may be considered to be the universal method of control over the neutralization process for

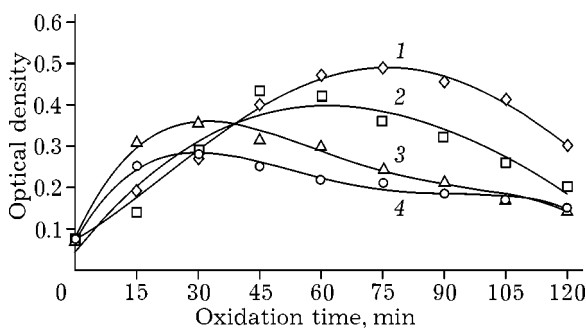


Fig. 2. Absorption spectra of phenol samples with oxidation performed. Current density, A/cm²: 0.06 (1), 0.12 (2), 0.18 (3), 0.3 (4).

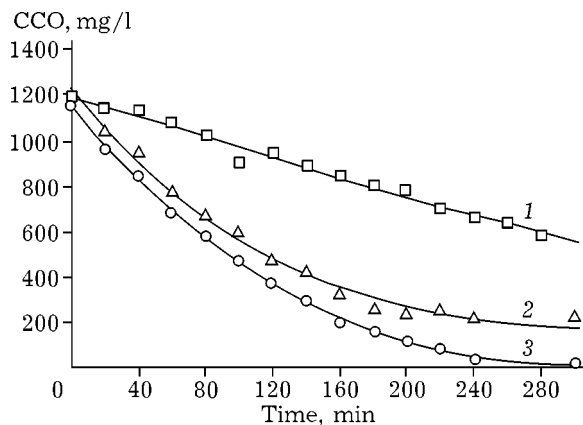


Fig. 3. An effect of current density and the process temperature on phenol oxidation. Current density, A/cm²: 0.17 (1), 0.5 (2), 0.83 (3); temperature, K: 313 (1), 343 (2, 3).

both individual substances (Fig. 3) and the mixtures of organic compounds.

In addition, the waste electrolyte can be recycled. Accordingly, phenol is oxidized with a reasonable rate during 10 cycles of electrolyte re-use.

Also of interest is to compare phenol oxidation rates by various oxidizers (oxygen and hydrogen peroxide) and in the medium of electrochemically activated sulphuric acid under identical conditions (temperature, phenol concentration). The results of experimental measurements (with the initial phenol content of 10 g/l) are presented in Fig. 4.

The associated specific reaction rates of phenol oxidation (Table 2) have been calculated analytically from semi-logarithmic anamorphisms.

Comparison of the values of specific oxidation rates taken from the literature with those calculated allows an inference that during

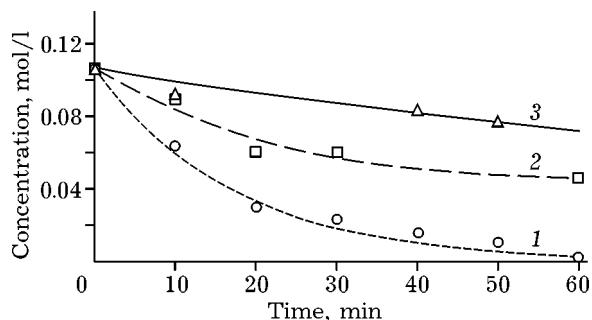


Fig. 4. Kinetic curves of phenol consumption: 1 - activated H₂SO₄, 2 - oxygen, 3 - H₂O.

TABLE 2

The calculated kinetic constants k of phenol destruction by various oxidizers

Oxidizer	k , 10 ⁻³ dm ³ /(mol s)	Ref.
Activated sulphuric acid	0.94	This work
Hydrogen peroxide	0.278	« «
Air oxygen	0.11	« «
Ozonization	0.9	[12]
Electrochemical oxidation	0.0045	[13]

phenol oxidation in electrochemically activated sulphuric acid, the liquid-phase chemical destruction in the reaction volume prevails over electrochemical oxidation of phenol.

CONCLUSION

The potentiality for an offered oxidizing method to be applied for oxidation of such widespread ecotoxicant as phenol was shown. Two processes, namely, electrochemical synthesis of an oxidizer and chemical destruction of organic molecule, are combined in the same reaction volume.

When exposed to the complex of electrochemically synthesized oxidizers, phenol is oxidized in the same way as with the known scheme thus forming the succession of the following oxidation products: *p*-benzoquinone, dicarboxylic acids, carbon dioxide, and water.

The universal method for determination of chemical consumption of oxygen can be employed as the analytical control over the process of deep oxidation of organic matter that is applicable during the destruction of both the individual substances and the mixtures of unknown composition.

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