

## THE DEVELOPMENT OF LIQUID-PHASE METHOD FOR PHENOL DEEP OXIDATION

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*The reaction of deep oxidation of toxic organic compounds-phenol and its nitro- and chloroderivatives in oxidizing medium electrochemically generated in situ has been studied. Kinetic parameters of the process and oxidation end products are determined. Standard method of determining a demand of chemical oxygen in a sample is suggested as an analytical testing method of phenol decomposition.*

Environment is contaminated with phenols while producing and using fertilizers, pesticides, paints, pharmaceuticals [1]. Therefore, destruction of phenol and its derivatives with different oxidation agents still attracts attention of researchers. Fenton reagent [2, 3], hydrogen peroxide [4], UV-radiation [5], ozone [6], electrochemical oxidation [7] as well as their various combinations are usually used as oxidation agents [8].

Ozone and hydrogen peroxide are recognized as the most efficient and technological oxidizers. Application restrictions of these oxidizers are connected first of all with their fire and explosion hazard.

Recently the processes of indirect oxidation of organic substances are of interest. The suggested technique allows combining several reactions into one process. And namely, electrosynthesis of peroxide compound complex and phenol oxidation in solution and partially at electrodes escaping the stage of pure oxidizer extraction. Oxidizer is synthesized by electric current transmission through sulfuric acid solution. The oxidizer complex is formed: hydrogen peroxide, ozone, mono persulfuric and persulfuric acids as well as particles of their decay (hydroxide-ion, peroxymonosulphate-ion, peroxydisulphate-ion and oxygen radical) which decompose dissolved organic substance. But efficiency of oxidation increases many times in comparison with purely electrochemical or chemical oxidation.

## Experimental part

Phenol deep oxidation was carried out at the laboratory set the main device of which was electrolyzer (reaction zone volume was 100 ml) with lead electrodes (electrode working surface was 7,23 cm<sup>2</sup>) [9]. The conditions of the process: sulfuric acid concentration was 40 rev. %; voltage was 6 V; current density was 0,83 A/cm<sup>2</sup>; electrolyte temperature was 40 °C; atmospheric pressure.

For investigations phenol «ch.p», ortho-, meta-, para- and dinitrophenols «ch.p», 2,4,6-trichlorophenol «ch.p», sulfuric acid «ch.p», Griss reagent, Nessler reagent were used.

Spectral investigations of samples selected at oxidation process of model compounds were carried out in UV-region ( $\lambda=200\ldots300$  nm) using spectrophotometer SP-26 and visible region ( $\lambda=300\ldots500$  nm) using photocolimeter – KFC-3.

Spectrophotometer analysis of dried solid oxidation products filtered at Chott filter was carried out at the de-

vice «Specord M80» (IR-region,  $\nu=500\ldots4000$  cm<sup>-1</sup>) in tablet KBr (1:300).

Gaseous products were analyzed by titrometric method.

Demand of chemical sample oxygen at phenol oxidation was carried out with the help of pH-metra-ion meter «ECOTEST-120»; direct potentiometric measurements in boiling solution which consists of components of oxidation-reduction systems  $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ ,  $\text{Ce}^{4+}/\text{Ce}^{3+}$ ,  $\text{Mn}^{3+}/\text{Mn}^{2+}$ ,  $\text{Ag}^2/\text{Ag}^+$  are in the basis of this device.

## Results and discussion

Oxidizing phenol in the medium of electrochemically generated oxidizers optical density ( $D$ ) increases in the region 245 nm that indicates the formation of the first stable intermediate product (Fig. 1) p-benzoquinone [10–13] which is later oxidized by classical scheme to  $\text{CO}_2$ .

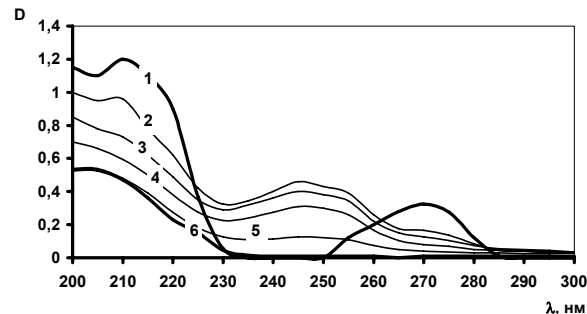


Fig. 1. Absorption spectra of phenol solution with initial concentration  $C_0=0,05$  mole/l after oxidation, min: 1) 0; 2) 30; 3) 45; 4) 60; 5) 90; 6) 135

Known scheme of phenol oxidation reaction is complicated by solid precipitate formation. To study solid precipitate after phenol electrolysis on composition of mineral and organic nature the obtained substrate underwent thermal treatment at 500 °C to constant mass. Precipitate thermal treatment showed that 67,9 % is mineral constituent and the rest 32,1 % is the organic one. IR-spectra of mineral part of precipitates show that they are identical to IR-spectrum  $\text{PbSO}_4$  which is formed owing to electrode destruction. Lead sulfate formation was revealed at oxidation of both phenol itself and its chlor- and nitroderivatives as well as their mixture.

Voltamperometric investigation showed that  $\text{Pb}^{2+}$  ions content in solid products of reaction amounted to 1...1,5 g/kg. Lead sulfate formed at electrolysis may be extracted and utilized by standard methods.

It was interesting to check the possibility of electrolyte reuse. So phenol is oxidized with considerable velocity and during 10 cycles of electrolyte reuse. At the same time amount of solid precipitate increased. The obtained IR-spectra of precipitates coincide with IR-spectra of the film formed by phenol electro-oxidation in paper [10] (Table. 1). On the basis of the obtained spectra the conclusion may be made about the presence of poly-nuclear structure with hydroxyl groups participating in formation of hydrogen bonds in precipitate organic constituent.

**Table. 1.** Magnitudes of absorption frequencies of IR-spectra of polyphenolic products,  $\text{cm}^{-1}$

Magnitudes of frequencies of IR-spectra of the film obtained at phenol electro-oxidation [10]		Magnitudes of frequencies of precipitate IR-spectra in the given paper	
615	w.	600	av.
—	—	700	w.
754	v. st.	760	v.st.
830	wd.	820	av.
830	av.w.	850	av.w.
971	av.	980	w.
1080	w.	1070	w.
1101	av.	1090	av.
1152	av.w.	—	—
1212	v.st.	1190	v.st.
1265	av.	1235	arm
1288	av.	1300	arm
1448	av.w.	1440	av.w.
1488	st.	1490	st.
1504	—	1520	av.
1610	av.	1620	av.w.
1648	av.w.	1648	av.
3374	av.	3350	av.w.

Note: v.st. – very strong; av. – average; w. – weak; wd. – wide; av.w. – average wide; st. – strong

The quantity of formed precipitate of polymeric structure at phenol electrolysis amounted to less than 5 % (from loaded phenol).

Kinetics of phenol oxidation reaction was determined only by substrate disappearance as it was not possible to consider phenol interaction with each oxidizer separately ( $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{S}_2\text{O}_8$ ,  $\text{H}_2\text{SO}_5$ ,  $\text{O}_3$  as well as electrochemical processes). Owing to phenol excess over oxidizer the reaction has pseudofirst order and determined velocity constant of this reaction  $k$  is observable (efficient).

**Table. 2.** Conditions and characteristics of phenol oxidation reaction with various agents

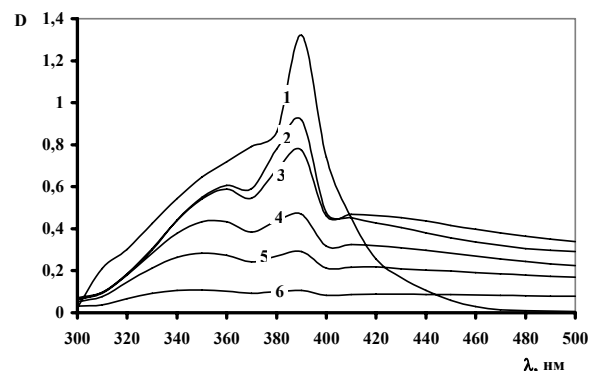
Comparison parameters	Ozonation [11]	Electrochemical oxidation [12]	Photolysis ( $h\nu$ )+ $\text{H}_2\text{O}_2$ [13]	Results of the given paper
$[\text{PhOH}]_0$ , mole/l	0,0004	0,021	$10^{-4}$	0,05
$k \cdot 10^3$ , $\text{C}^{-1}$	0,9	0,67	$h\nu$ 0,011 $\pm$ 0,001 $h\nu$ + $\text{H}_2\text{O}_2$ 0,93 $\pm$ 0,08	0,436 $\pm$ 0,014
Temperature, $^{\circ}\text{C}$	18	60	—	40

Comparative analysis of oxidation reaction kinetic parameters in the medium of electrochemically generated oxidizer with ozonolysis, photolysis and electrochemical

oxidation (in the medium of  $\text{H}_2\text{SO}_4$  with  $\text{pH}=2,0$ ) showed that the same order of pseudomonomolecular velocity constants of the above-listed processes and oxidation technique of the studied one may indicate the identity of the processes occurring both in reactionary volume and at electrodes.

The most toxic phenol nitroderivatives practically indestructible by microbiological methods were oxidized.

P-nitrophenol oxidation was controlled by absorption spectra in UV-and visible region (Fig. 2).



**Fig. 2.** Spectra of p-nitrophenol samples ( $C_0=0,05$  mole/l) after oxidation, min: 1) 0; 2) 30; 3) 60; 4) 90; 5) 120; 6) 180

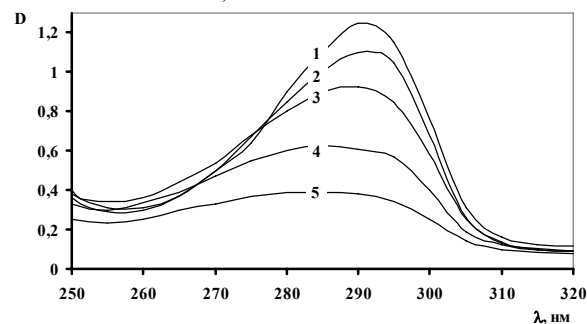
Under the influence of hydroxide-ions in acidic medium [3] which are formed in the given conditions, nitrophenols are oxidized with nitrogroup substitution by hydroxide one with formation of hydroquinones then corresponding quinones and then aromatic ring is destructed forming carboxylic acid (oxalic, maleic, muconic). It is known that under the influence of ozone nitrophenols [6, 8] are destructed forming  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and nitrite-ion. Thus, it could be supposed that nitro compounds are destructed by the researched technique to complete mineralization. And nitro group, which can be easily reduced, forms amides on cathode with its further detachment [14]. So at p-nitrophenol oxidation  $\text{NH}_4^+$  ions were determined in solution. And in gaseous products neither nitrogen oxides (with Griss reagent) nor ammonia (with Nessler reagent) were not revealed.

Proper comparative analysis of kinetic data of p-nitrophenol oxidation with various oxidizers and at the above given conditions is not possible. As the data given in paper [8] for oxidation reactions at supersonic influence are found for p-nitrophenol solutions with initial concentration  $1 \cdot 10^{-4}$  mole/l and equal for oxygen  $1,7 \cdot 10^{-3} \text{ min}^{-1}$ , ozone  $7,8 \cdot 10^{-2} \text{ min}^{-1}$  and for simple ozonation  $4,5 \cdot 10^{-2} \text{ min}^{-1}$ . The calculated oxidation rate constant in the studied conditions amounts to  $1,3 \cdot 10^{-2} \text{ min}^{-1}$ , the obtained one at oxidation of p-nitrophenol suspension with initial substance content 6,9 g/l (0,05 mole/l). It is seen from the given data that destruction rate of toxic compound in suspension by the researched technique is rather high.

It was interesting to study the possibility of decomposition of the most widespread phenol derivatives – chlorphenols, by the example of 2,4,6-trichlorophenol by the suggested technique.

As it is seen from the data of spectrophotometric investigation (Fig. 3) even in such severe conditions solution of 2,4,6-trichlorophenol (with initial 0,01 mole/l) is

hardly oxidized. Rate constant of pseudofirst order reaction amounts to  $1,02 \cdot 10^{-4} \text{ s}^{-1}$ .



**Fig. 3.** Absorption spectra of solution of 2,4,6-trichlorophenol ( $C_0=0,01 \text{ mole/l}$ ) after oxidation, min: 1) 0; 2) 15; 3) 60; 4) 120; 5) 240

However, application of only spectral methods for analyzing mixtures with unknown composition requires bulk preliminary work on describing characteristics of individual compounds, supposed mixture components and reaction products. Therefore it is more sensible to estimate destruction degree of the original mixture of organic compounds on content of total organic carbon in the sample.

Bichromatic method of determining demand of chemical oxygen (DCO) using ion meter ECOTEST-120 as an automatic tester of DCO was suggested as analytic control over organic compound neutralization process. The method was tested for controlling neutralization of phenol and mixture of its most toxic nitro- and chloroderivatives (Table 3).

Oxidizing mixture of phenol, o-nitrophenol and 2,4,6-trichlorophenol (with initial concentration  $10 \text{ g/l}$ ) significant differences from individual compound oxidation were not observed.

**Table 3.** Magnitudes of DCO samples at phenol oxidation

Phenol compound	Initial concentration, g/l	Oxidation time of organic compound, min								
		0	30	60	90	120	180	300	420	480
		DCO values, mgO <sub>2</sub> /dm <sup>3</sup>								
o-NO <sub>2</sub>	6,0	3435	2463	888	209	62	<30	–	–	–
m-NO <sub>2</sub>	1,25	1471	576	129	<30	–	–	–	–	–
p-NO <sub>2</sub>	6,0	3470	2350	1118	673	<30	–	–	–	–
2,4-diNO <sub>2</sub>	9,2	9257	6498	5814	1606	287	<30	–	–	–
	1,65	1010	609	<30	–	–	–	–	–	–
2,4,6-triCl	1,98	3297	1664	1284	–	492	<30	–	–	–
Phenol mixture	10,0	11384	11183	9467	7847	6644	5468	3660	795	<30

The main advantage of the developed method is its applicability for the most part of organic compounds as at electrochemical synthesis the complex of oxidizers capable of destructing organic compound of practically any structure to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  is generated. The suggested method also allows decreasing danger class of pesticide wastes; their amount is decreased in 950...1000 times.

### Conclusion

1. The possibility of deep oxidation of phenol and its nitro- and chloroderivatives with oxidizer complex synthesized by electrochemical method *in situ* is shown. Process kinetic parameters are determined.
2. Precipitate consisting of phenol condensation products and lead sulfate is formed at phenol liquid-phase electrochemical oxidation using lead electrodes.
3. The COD method is suggested to be used as the main analytical control method over the process of neutralization of toxic organic wastes.

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