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Electrochemical Mineralization of β-Naphthol *in situ* by Active Oxygen Species

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Abstract

An electrochemical method for the oxidation of β-naphthol by active oxygen species generated from O_2, H_2O_2 and H_2O in aqueous media with different pH values was studied in situ using the anodes made of Pt, Pb/PbO_2 with graphite and gas diffusion cathodes based on technical-grade carbon. The effect of reagents concentration, current density and the way of carrying out the process on the efficiency of β-naphthol oxidation was investigated.

Key words: β-naphthol, electrochemical oxidation, active oxygen species, mineralization

INTRODUCTION

The electrochemical technique of water disinfection with the destruction of organic substances present therein with the formation of environmentally safe compounds is considered nowadays to be an alternative method intended for processing diluted wastewater (COD < 5 g/L) [1]. The technology of destructive oxidations involves active oxygen species such as $HO^•$, O_3, as oxidizers obtained by means of electrolysis from H_2O, O_2 and H_2O_2. The authors of [1–5] considered different variants with employing various anode and cathode materials, electrode types and designs as well as different electrolysers.

It is commonly known that reactive oxygen species ($HO^•$, $HO_2^•$, HO_2^-) can be rather readily generated *in situ* in aqueous solutions on the basis of the coupled processes of cathodic O_2 reduction to produce H_2O_2 on the surface of graphitized carbon materials and anodic oxidation of H_2O to yield HO on platinum electrodes and electrodes made of lead, tin, manganese, *etc*. dioxides, diamond electrodes doped with boron (BDDE) [1–5]. It is known that the strongest oxidizer is the $HO^•$ radical ($E^0_{HO^•/H_2O} = 2.80$ V against NHE) capable of non-selective oxidiative destruction with mineralizing organic compounds to produce CO_2 and H_2O.

According to the mechanism of electrochemical mineralization in aqueous media, water is discharged (at the voltage higher than 1.23 V against NHE) on the active centres of an anode with the formation of adsorbed $HO^•$ radicals [1]:

$$H_2O + M \rightarrow M(HO^•)_{ads} + H^+ + e^- \qquad (1)$$

The electrogenerated $HO^•$ radicals are involved in the process of mineralization of organic substances R present in the aqueous solution:

$$R + xM(HO^•)_{ads} \rightarrow xM + \text{products of mineralization} + yH^+ + ye^- \qquad (2)$$

Here x and y are stoichiometric coefficients. The present reaction is in a competition with the side reaction of radicals' discharge on the anode to give O_2:

$$M(HO^•)_{ads} \rightarrow M + 1/2O_2 + H^+ + e^- \qquad (3)$$

The oxidative efficiency of the anodic material is determined by its ability to adsorb $HO^•$ radicals, and the weaker this interaction resulting in a low electrochemical activity in the reaction of O_2 evolution, the higher is the reactivity inherent in the oxidation of organic compounds. An ideal material in this connection could be presented by a novel anodic material such as thin-film boron-doped diamond electrode (BDDE) used while only in laboratory-scale investigations [1].

However, oxidative ability of an anode and the current efficiency could be increased due to involving a cathodic reaction of reduction O_2 into H_2O_2 on carbon materials:

$$O_2 + 2H_2O + 2e^- = H_2O_2 + 2OH^- \quad pH \geq 7 \qquad (4)$$

$$O_2 + 2H^+ + 2e^- = H_2O_2 \quad pH < 7 \qquad (5)$$

The reduction of O_2 occurs *via* the formation of reactive species such as $O_2^{-\bullet}$, $HO_2^\bullet$ those exhibit a lower oxidizing ability as compared to $HO^\bullet$ radical.

It is known, that gas diffusion electrodes-cathodes (GDE) consisting of technical grade carbon and water-repelling agent (fluoroplast-4D, Teflon) to a considerable extent intensify the process of obtaining H_2O_2 due to the fact that there is a three-phase contact surface formed [6].

Hydrogen peroxide H_2O_2 produced on the cathode according to reactions (4), (5) could be oxidized on the anode:

$$H_2O_2 \rightarrow HO_2^\bullet + H^+ + e^- \qquad (6)$$

$$HO_2^\bullet \rightarrow O_2 + H^+ + e^- \qquad (7)$$

It is known, that β-naphthol belongs to toxic, difficultly oxidized compounds, whose maximum permissible concentration (MPC) amounts to 4.0 mg/L [7.] Its electrochemical oxidation with the mineralization to yield CO_2 and H_2O proceeds according to the following scheme:

$$C_{10}H_8O + 19H_2O \rightarrow 10CO_2 + 46H_2O + 46e^- \qquad (8)$$

The purpose of the present work consisted in studying the process of destructive β-naphthol oxidation by highly reactive oxygen species, *in situ* electrochemically generated from O_2, H_2O and H_2O_2 with the use of GDE and spectral graphite as cathodes, with anodes made of Pt and Pb/PbO_2.

EXPERIMENTAL

The experiments were carried out employing electrochemical cells without cathodic and anodic space separation with the use of GDE and graphite for the generation of H_2O_2 from O_2, as well as employing a standard electrochemical cell with a filtering diaphragm in the case of adding H_2O_2 into the anodic chamber.

The gas diffusion cathode represented a flat disk with the total porosity level of 65–70 %, 0.8–0.9 mm thick made of a mixture of soot A 437-E (60 mass %) and FP-4D (40 mass %). The design of a similar cell is described in [6]. The anode represents a platinum plate (4 × 25 mm). The electrode potential was measured at the frontal side of GDE against a silver chloride reference electrode. Current density was calculated per a unit visible frontal surface amounting to 5 cm^2, the volume of an electrolytic cell amounted to 50 mL. In the experiments with GDE, the oxidation of в-naphthol was carried out at the current density equal to 50, 70, 90 and 150 mA/cm^2, without any additional stirring of the electrolyte. The initial content of β-naphthol amounted to 200–500 and 1000 mg/L. 0.1 M NaOH solution was used as the electrolyte.

For electrolysis with a graphite cathode we used a standard electrochemical cell with a magnetic stirrer for agitating a solution. The cathode surface area amounted to 3 cm^2; anodes were made of Pt, Pb/PbO_2. The lead anode was prepared using the technique described in [8]. The oxidation of β-naphthol model solutions was carried out at the current strength value equal to 250–500 мA. The initial content of β-naphthol amounted to 300, 500 and 1000 mg/L. 0.1 M NaOH and 0.5 M H_2SO_4 solutions were used as electrolytes. The cell volume was equal to 50 mL.

Changing in the content of β-naphthol and others organic intermediates in the course electrolysis was determined basing on changing the parameter of chemical oxygen demand (COD) [9] as well as with the help of a photometric analytical method [10]. The composition of oxidation products was analyzed using UV spectrophotometry.

RESULTS AND DISCUSSION

It has been demonstrated in a number of works concerning the destructive oxidation [11, 12], that the electrochemical oxidation of organic substrata could exhibit two types the reaction order such as a zero-order reaction and a first-order reaction. In this connection, the normal kinetics of β-naphthol oxidation is considered due to the two possible mechanisms of this reaction. One mechanism can be described by a first-order reaction; the second mechanism can be described by a zero order reaction and by the general equation of the following form:

$$dC/dt = -k_1C - k_0 \qquad (9)$$

It has been established that the contribution of the k_0 value in the total rate of oxidation is significant only within the range of small C/C_0 ratio values, therefore the kinetic curves for the concentration of β-naphthol have been considered according to the equation

$$\ln (C/C_0) = k_1 t \tag{10}$$

Here C_0, C are the initial and current content of β-naphthol, respectively; k_1 is the reaction rate constant for oxidation.

In order to estimate the operation efficiency of the electrochemical cell in the process of β-naphthol destructive oxidation we determined the performance index of the cell [13] in the reaction of destructive oxidation into CO_2 and H_2O, *i. e.* the current efficiency in the electrolyser (η):

$$\eta = n_e N_{\text{naph}}/N_e \tag{11}$$

Here n_e is the number of electrons (for formal destructive oxidations of one β-naphthol molecule $n_e = 46$); N_{naph} is the number of oxidized β-naphthol molecules; N_e is the number of electrons passed through an electrochemical cell;

$$N_{\text{naph}} = cVN_A,\ \ N_e = It/e \tag{12}$$

Then

$$\mathrm{d}N/\mathrm{d}t = (\mathrm{d}C/\mathrm{d}t)VN_A \tag{13}$$

$$\mathrm{d}N_e/\mathrm{d}t = I/e \tag{14}$$

Thus, the equation (11) can be written in the following manner:

$$\eta = kcVN_A n_e/(I/e) = kcVFn_e/(3600MI) \tag{15}$$

Here c is the content of β-naphthol, mg/L; V is the cell volume; k is the reaction rate constant, h^{-1}; M the molar mass; 3600 is time, s; I is the current strength, A; e is the electron charge; N_A is the Avogadro constant; F is the Faraday constant. Another variant of the equation (11) is:

$$\eta = kCVF46/3600I \tag{16}$$

where C is the initial concentration, mol/L.

This relationship allows one to estimate the current efficiency of the electrochemical cell (η) in the course of β-naphthol oxidation using the values of k_2 and current strength (I) in order to choose optimum electrolysis conditions.

The values of k_1 and η found out with the use of different β-naphthol oxidation schemes are presented in Tables 1, 3, 4.

The data presented in Table 1 demonstrate that the rate of β-naphthol oxidation increases with an increase in current density, *i. e.* with increase in the generation rate of an oxidizer. The decrease of k_1 values at the same current density with the increase in substrate concentration could be caused, first of all, by the presence of diffusion limitations with respect to substrate supply. With the growth of β-naphthol concentration, the performance index of the cell (predictably) increases. At the content of β-naphthol ranging within 200–500 mg/L, the oxidation is appropriately required for the current density equal to 50 mA/cm^2 ($\eta = 15.3$ %). At the content of the substrate amounting to 1000 mg/L, the cell operates much more efficiently at $i = 90$ mA/cm^2 ($\eta = 28.5$ %). It should be noted that in going to the design of slit electrolyser with flowing-through electrolyte the η value of the cell should increase due to decreasing the diffusion limitations with respect to substrate supply, as it was observed in [13] in the case of phenol oxidation.

The estimation of the β-naphthol mineralization efficiency into CO_2 and H_2O depending on the quantity of electricity passed (Q) was carried out basing on the data concerning the COD changing. Data presented in Table 2 indicate that the process with an efficient oxidation into CO_2 and H_2O.

TABLE 1

Data concerning the oxidation reaction rate constant (k_1) and the current efficiency (η) in the electrolysis processes with GDE in 0.1 M NaOH solution, Pt anode

C_{naph}, mg/L	k_1, h^{-1}				η, %			
	i, mA/cm^2				i, mA/cm^2			
	50	70	90	150	50	70	90	150
200	0.45	0.5	0.6	0.6	15.3	12.15	11.3	6.8
500	0.2	0.25	0.3	0.5	17.1	15.27	14.3	11.1
1000	0.15	0.20	0.3	0.4	25.8	24.4	28.5	22.8

TABLE 2

Efficiency of β-naphthol mineralization (η) with the use of the GDE cathode and Pt anode in 0.1 M NaOH solution depending on the quantity of electricity passed (Q)

Q,	η, %	
A · h	i = 50 mA/cm^2	i =150 mA/cm^2
0.75	48.8/40.2	51.3/40.6
1.25	60.6/50.0	62.0/54.7
3.75		90.4/78.3

Note. The first value is determined at the content of β-naphthol equal to 500 mg/L; the second value being obtained at 1000 mg/L.

Table 3 demonstrates the results concerning the oxidation of β-naphthol with a graphite cathode for obtaining H_2O_2 from O_2 and anodes made of Pt and Pb/PbO_2.

The comparative analysis of the data from Tables 1 and 3 for electrolysis in NaOH solution with Pt anode demonstrates that the decrease of diffusion limitations with respect to mass transfer due to stirring the solution (the cell with graphite cathode) is levelled by a low efficiency of this cathode in the reaction of H_2O_2 generation. The diaphragmless electrolyser provides $C_{H_2O_2} = 6 \cdot 10^{-3}$ mol/L in the alkaline medium (pH 10.5); $C_{H_2O_2} = 2 \cdot 10^{-3}$ mol/L in the acidic medium (pH 2–3); $7.1 \cdot 10^{-2}$ mol/L in the cell with GDE at pH 10.5, when the current strength amounting to 500 mA after 0.5 h of operation. As a result, the з value decreases down to 12.8 % (I = 250 mA) as compared to the electrolysis with GDE (η = 17.1 %). The parallel determination of H_2O_2 concentration in the course of electrolysis has demonstrated that in the experiments with the graphite cathode all the H_2O_2 produced is consumed during the electrolysis, whereas in the case when GDE is employed, a residual content of H_2O_2 is registered. For Q = 1.25 A · h at the content of β-naphthol equal to 1000 mg/L, the concentration of H_2O_2 amounts to $8.5 \cdot 10^{-2}$ mol/L.

The comparison of data concerning the kinetics of β-naphthol oxidation in both cells indicates the possibility of controlling the process of oxidation. So, at the initial content of β-naphthol amounting to 500 mg/L and the quantity of electricity passed Q = 0.175 A · h (in the cell with GDE, with no forced stirring of the solution) the residual content of β-naphthol amounted to 347.1 mg/L, whereas in the electrolyser with the graphite cathode (O_2 bubbling) this value was equal to 265.8 mg/L. At Q = 0.7 A · h the residual content of β-naphthol in the cell with GDE and in the cell with the graphite cathode amounted to 125.0 and 62.1 mg/L, respectively. At Q = 1.75 A · h the content of β-naphthol in the cell with GDE reached 37.2 mg/L, whereas β-naphthol was not found out in the cell with the graphite cathode. According to UV spectrometric data, only aliphatic carboxylic compounds are determined in the products after the electrolysis with the graphite cathode (rather weak absorption within the range of 240–200 nm). In the solution with GDE there are β-naphthol and intermediates

TABLE 3

Electrolysis processes with the graphite cathode for the generation of H_2O_2 from O_2

C_{naph}, mg/L	I, mA	Electrolyte	Anode	k_1, h^{-1}	η, %
500	250	0.1 M NaOH solution	Pt	0.15	12.8
	500			0.35	14.9
300	250	0.1 M NaOH solution	Pt	0.20	10.3
	500			0.40	10.3
500	250	0.1 M NaOH solution	Pb/PbO_2	0.08	6.8
	500			0.15	6.4
300	250	0.1 M NaOH solution	Pb/PbO_2	0.20	10.3
	500			0.30	7.7
300	250	0.5 M H_2SO_4 solution	Pt	0.30	15.4
	500			0.45	11.6
300	250	0.5 M H_2SO_4 solution	Pb/PbO_2	0.15	7.7
	500			0.25	6.4

TABLE 4

Electrolysis processes with adding H_2O_2 solution to the anodic chamber

C_{naph}, mg/L	Anode	Electrolyte	I, mA	k_1, h^{-1}			η, %		
				$C_{H_2O_2}$, mol/L			$C_{H_2O_2}$, mol/L		
				0.1	0.2	0.1*	0.1	0.2	0.1*
300	Pb/PbO_2	0.5 M H_2SO_4 solution	250	0.11	0.24	–	7.6	12.3	–
			500	0.15	0.25	0.65	3.8	6.4	16.6
500	Pt	0.1 M NaOH solution	250	0.22	0.39	–	18.8	33.3	–
			500	0.41	0.48	–	9.4	20.5	–
	Pb/PbO_2	0.1 M NaOH solution	250	0.10	0.21	–	8.6	17.9	–
			500	0.14	0.18	0.22	6.0	7.7	9.5
1000	Pt	0.1 M NaOH solution	500	0.36	0.41		30.7	35.0	–

* H_2O_2 adding was dosed by 0.1 mL every 0.5 h.

of its oxidation, in particular compounds with quinoid structure (λ = 320–360 nm). This fact could be connected with the presence of stagnant zones in a cell with GDE because of its constructional imperfection. It is known that the hydroxylation of the benzene ring and its subsequent opening occur faster, than the mineralization of biodegradable aliphatic acids [14, 15] by $HO^{\bullet}$ radicals. Thus, the electrolysis could be stopped at the stage of the formation of biodegradable aliphatic acids, which would require for a smaller number of electrons.

The increase in the oxidizing ability of the anode could also be achieved due to adding H_2O_2 into the anodic chamber of the electrolyser which H_2O_2 being oxidized on the anode produces additionally highly reactive radicals in the bulk of electrolyte according to reactions (6), (7). The results electrolysis are presented in Tables 4, 5.

TABLE 5

Results of β-naphthol mineralization with adding H_2O_2 into the anodic chamber

C_{naph}, mg/L	Anode	Electrolyte	I, mA	Q, A · h	η, %		
					$C_{H_2O_2}$, mol/L		
					0.1	0.2	0.1*
300	Pb/PbO_2	0.5 M H_2SO_4 solution	250	0.75	21.0	50.3	–
				1.25	34.1	68.3	–
			500	0.75	24.1	50.0	31.0
				1.25	62.0	75.8	67.2
				2.00	99.9	99.9	99.9
500	Pb/PbO_2	0.1 M NaOH solution	250	0.75	19.1	20.2	–
				1.25	40.4	46.8	–
			500	0.75	6.8	10.6	25.5
				1.25	27.6	36.2	47.9
				2.50	57.7	59.6	68.1
500	Pt	0.1 M NaOH solution	500	0.75	63.8	67.9	–
				1.25	68.0	74.5	–
				2.50	77.7	81.9	–
1000	Pt	0.1 M NaOH solution	500	0.75	53.8	56.0	–
				1.25	56.5	67.1	–
				2.50	58.3	82.9	–

*H_2O_2 adding was dosed by 0.1 mL every 0.5 h.

From data presented in Table 4, one can see that the electrolysis processes in the alkaline electrolyte proceed much more efficiently with the use of platinum anode. In this case, it is better to add H_2O_2 to the solution dosing by small portions.

The influence of added H_2O_2 upon the efficiency of β-naphthol (300–500 mg/L) mineralization is more significant (see Table 5) in the acidic medium (0.5 M H_2SO_4 solution). In this case, the electrolysis with periodic H_2O_2 adding into the bulk of electrolyte the η value (see Table 4) and the efficiency of mineralization increase.

After passing $Q = 1.25$ A · h there were no β-naphthol and its aromatic derivatives revealed in the composition of electrolysis products a (0.1 M NaOH solution, Pb/PbO_2 anode, dozed H_2O_2 addition), the efficiency of mineralization amounted to 47.9 %.

Basing on the data we obtained and data available from the literature concerning the oxidation on BDDE [16, 17] we have proposed the following reaction scheme for the oxidation of β-naphthol: β-naphthol > hydroxylated naphthol derivatives > quiniones > ketones > aliphatic organic acids > the products of mineralization (CO_2 and H_2O).

The rate of benzene ring opening and quinoid structure destruction up to carboxylic compounds is determined by the current density of electrolysis and by the mode of stirring the solution.

CONCLUSION

It has been demonstrated by the example of β-naphthol oxidation that the method under consideration represents an environmentally safe way to utilize toxic organic substances and allows one either to perform the mineralization into CO_2 and H_2O or to stop the electrolysis at a stage of forming biodegradable aliphatic carboxylic compounds.

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