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APPLIED ELECTROCHEMISTRY AND METAL CORROSION PROTECTION

Indirect Electrochemical Oxidation of Aniline in Acid Electrolyte with Active Oxygen Species

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Abstract—Kinetics and selectivity of the aniline oxidation on a boron-doped diamond electrode and lead dioxide anode (Pb/PbO_2) in an acid electrolyte were studied under various generation conditions of active oxygen species. The resulting kinetic dependences can be described by a pseudo-first-order equation. The apparent rate constants of the process were determined for two electrolysis modes: direct anodic oxidation and oxidation with addition of hydrogen peroxide. UV spectroscopy was used to determine that the aniline destruction process occurs via formation of a number of intermediate products (benzoquinone, carboxylic acids). It was shown that the aniline destruction process can occur with a rather high efficiency (~80–90%) on the electrode types under study.

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During the recent decades, the interest has not slackened in studies aimed to employ electrochemical methods for synthesis of new organic and inorganic compounds [1, 2] and treat industrial wastewater both to recover valuable components and perform its decontamination to remove toxic components [3, 4].

The increased interest in these technologies is due to the fact that numerous electrochemical processes conform to main concepts of green chemistry. As regards their industrial implementation, the electrochemical reactions have a number of advantages: mild conditions, comparatively high rates, easy control by the current density and potential, high selectivity, and easy automation of the process.

The electrochemical treatment of wastewater to destruct toxic and difficulty biodegradable organic ecopollutants is an alternative to chemical processes using various comparatively toxic oxidizing systems [6].

It is known that the oxidation of organic compounds occurs with high efficiency in aqueous electrolyte solutions with the use of active oxygen species (AOSs): $^{\bullet}OH$, $HO_2^{\bullet}$, HO_2^-, O_3, which can be comparatively simply generated in situ from O_2 and H_2O by conjugated reactions with a carbon-graphite cathode and anodes with high oxygen evolution overvoltage, such as Pt, Pb/PbO_2, SnO_2, MnO_2 and boron-doped diamond electrode (BDDE) [7–10]. It is known that the strongest oxidizing agent among the AOSs is the $^{\bullet}OH$ radical ($E^0_{HO^{\bullet}/H_2O} = 2.80$ V relative to s.h.e.) capable of a nonselective oxidative destruction of organic compounds to CO_2 and H_2O [11].

According to the existing concepts, water is discharged (at potentials higher than 1.23 V relative to s.h.e.) at active centers of the anode to give adsorbed $HO^{\bullet}$ radicals [7]:

$$H_2O \rightarrow {}^{\bullet}OH + H^+ + e. \tag{1}$$

It is known that the characteristics of this process are largely determined by the electrode material. Depending on the ability to adsorb $^{\bullet}OH$ radicals, the electrode materials are commonly divided into two types: active electrodes, such as Pt, and inactive electrodes, such as PbO_2, SnO_2, and BDDE [12].

On active electrodes, the active centers (M) can be transformed by the reaction with chemisorbed hydroxy radicals into surface oxides (MO_x), which can react with other compounds thereby being reduced to the initial state:

$$M + x^{\bullet}OH \rightarrow MO_x + H^+ + e, \quad (2)$$

$$R + MO_x \rightarrow RO_x + M. \quad (3)$$

On inactive electrodes, the active centers do not interact chemically with hydroxy radicals (physical adsorption), and, therefore, the chemical state of the electrode remains unchanged when the substrate R is oxidized:

$$MO_x + H_2O \rightarrow MO_x(^{\bullet}OH)_{ads} + H^+ + e, \quad (4)$$

$$R + MO_x(^{\bullet}OH)_{ads} \rightarrow MO_x + \text{oxidation products} + yH^+ + ye. \quad (5)$$

In addition to hydroxy radicals, other oxygen-containing species can also be formed on the electrode surface, such as ozone, atomic oxygen, and peroxo compounds ($HOO^{\bullet}$ and H_2O_2). Wabner and Grambow [13] found that the products of water oxidation on PbO_2 are O_2, O_3, $^{\bullet}OH$ radicals and atomic oxygen, whereas only trace amounts of hydroxy radicals and ozone are observed on platinum, and peroxide compounds and atomic oxygen are the main intermediates.

Depending on the composition of a supporting electrolyte, stable oxidizing agents are formed, which can diffuse into the bulk of the electrolyte, with the overall oxidation rate thereby raised. For example, it has been shown [2, 14] that the electrolysis of sulfate solutions on BDDE is accompanied by the formation of the peroxydisulfide anion whose concentration depends on the current density and on the concentration of sulfuric acid:

$$2HSO_4^- \rightarrow S_2O_8^{2-} + 2H^+ + 2e. \quad (6)$$

When hydrogen peroxide and Fe^{2+} ions are added to the electrochemical cell, there appears an additional source of $^{\bullet}OH$ radicals in accordance with the known Fenton reaction

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {^{\bullet}OH} + OH^- \quad (7)$$

and the destruction rate of organic substrate in the solution bulk increases.

It is known that aniline is a highly toxic and carcinogenic substance. Its content in water is strictly regulated (MPC for drinking-and-household and cultural-and-general water basins).

Studies concerned with the electrochemical oxidation of aniline and other aromatic compounds have been rather widely reported abroad. The interest in studies of this kind is due to the complex mechanism of the process, formation of a number of intermediates possessing a higher resistance to further destruction as compared with the starting substance, and influence exerted by a substantial number of parameters on the kinetics and mechanism of electrolysis.

The goal of the present study was to examine the kinetics and selectivity of the electrochemical oxidation of aniline on Pb/PbO_2 and BDDE in a sulfuric acid electrolyte, with AOSs involved in various schemes of their generation.

EXPERIMENTAL

Model solutions of aniline were oxidized in a diaphragmless electrolyzer at current densities of 25, 50, and 100 mA cm^{-2} and temperature of 20°C. As anodes served lead dioxide (Pb/PbO_2) with a working surface of 8 cm^2, fabricated by the procedure described in [15], and boron-doped diamond electrode with area of 4.16 cm^2 [16].

The initial content of aniline in solutions was 50, 100, and 200 mg L^{-1}. The change in the aniline concentration in solution was determined by the photometric method. The composition of the reaction products was analyzed by UV spectroscopy on a Varian Cary 100 Scan spectrophotometer. The electrode potential at the anodes was measured relative to the silver chloride reference electrode (s.c.e.), with a graphite rod as the cathode. Aniline was oxidized in a 0.7 H_2SO_4 solution on Pb/PbO_2 and in 0.1 M H_2SO_4 on the BDDE. Three AOS generation schemes were used in oxidation on Pb/PbO_2: anodic oxidation (A), anodic oxidation with portionwise addition of H_2O_2 (CH_2O_2 = 0.025 M) once in an hour (A + H_2O_2), and anodic oxidation + Fe^{2+} + H_2O_2 (A + Fenton reagent). Two AOS generation schemes were used in oxidation on the BDDE: anodic oxidation and anodic oxidation with addition of H_2O_2.

It is known that the oxidation of organic substrates is strongly affected by the state of the surface of the anodes being used. Both the physical adsorption of $^{\bullet}OH$ and the chemisorption may occur on Pb/PbO_2 electrodes,

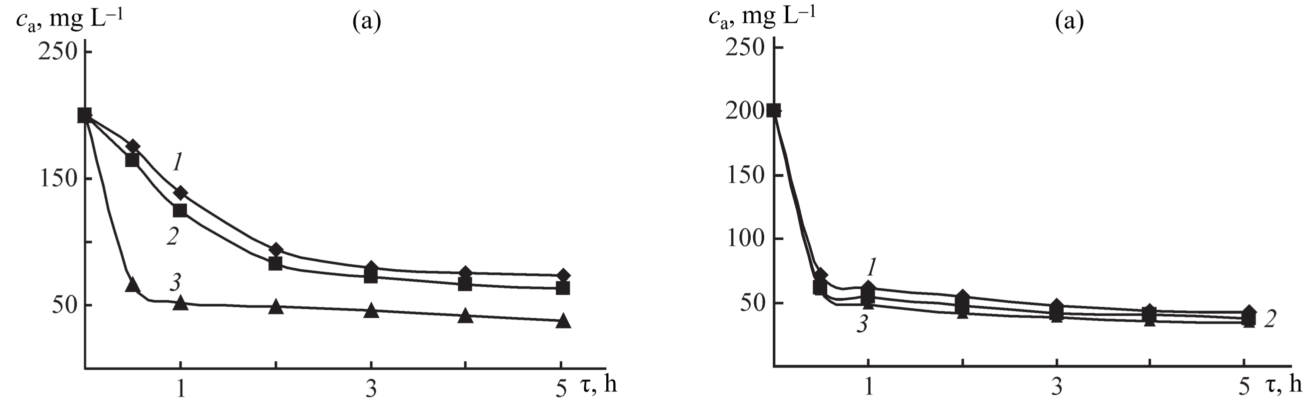

Fig. 1. Kinetic curves for aniline oxidation on a Pb/PbO_2 electrode at current density of (a) 25 and (b) 100 mA cm^{-2}. Initial aniline concentration 200 mg L^{-1}. (c_a) Aniline concentration and (τ) time; the same for Fig. 2. (*1*) Anodic oxidation, (*2*) oxidation with addition of hydrogen peroxide, and (*3*) anodic oxidation + Fe^{2+} + H_2O_2.

depending on a modification of the electrode, solution pH, and electrode potential [17]. The oxidation potential of organic substances is 1.3–2.0 V relative to s.h.e. for Pb/PbO_2 and 2.2–2.7 V relative to s.h.e. for the BDDE [7].

The kinetic curves describing the oxidation of aniline on a Pb/PbO_2 anode at current densities of 25 and 100 mA cm^{-2} and initial concentration of 200 mg L^{-1} are shown in Figs. 1a and 1b for different AOS generation schemes. It can be seen that the aniline oxidation rate grows as the current density and the concentration of oxidizing species in the solution bulk become higher. For the purely anodic oxidation (curves *1*), this increase may be due to the rise in the rate of the direct oxidation of aniline at the anode. An increase in the AOS concentration in the bulk of the electrolyte exerts a strong influence at low current densities, with a higher oxidation rate observed when the process is performed by the A + Fenton reagent scheme. It should be noted that the oxidation rate of aniline substantially decreases already after the first hour of electrolysis, which is due, in our opinion, to the appearance in solution of intermediate products formed in the destruction of aniline and to the involvement of these in reactions with $^{\bullet}OH$ radicals.

Table 1 presents the results obtained in determining the aniline oxidation efficiency on Pb/PbO_2 in relation to the current density, electrolysis duration, and process scheme.

It can be seen in Table 1 that the efficiency of aniline destruction is higher in processes with additional AOS generation in the cell volume, especially during the first half-hour of electrolysis at low current density. For example, at aniline concentration of 200 mg L^{-1} and current density of 25 mA cm^{-2}, the efficiencies were 12, 18, and 67% for the processes A, A + H_2O_2, and A + Fenton reagent, respectively. The additional generation of AOSs in the electrolyte by the Fenton reaction enabled 81% oxidation of aniline in 5 h at a current density of 25 mA cm^{-2}, whereas in the case of a direct oxidation at the anode, the same efficiency was reached on raising the current density to 100 mA cm^{-2}. It should be noted that, as the current density is raised, the aniline oxidation efficiency depends to a lesser extent on the AOS generation scheme, i.e., on the AOS concentration. A similar effect was also observed on raising the quantity of passed electricity. Probably, this is due to the increase in the amount of intermediate products formed in the destruction of aniline, whose oxidation consumed a part of AOSs, and to the occurrence of side reactions in which $^{\bullet}OH$ radicals recombine. An increase in the aniline concentration from 100 to 200 mg L^{-1} led to a higher efficiency of the direct anodic oxidation and had nearly no effect on the process efficiency for other AOS generation schemes. Figures 2a and 2b show kinetic curves describing the oxidation of aniline on the BDDE at current densities of 25 and 100 mA cm^{-2} and initial aniline concentration of 100 mg L^{-1} for two AOS generation schemes: anodic (A) and anodic with addition of hydrogen peroxide (A + H_2O_2).

It can be seen in Fig. 2 that the aniline destruction rate grows as the AOS concentration increases due to the additional AOS formation in the solution bulk (A + H_2O_2). Raising the current density in the case of a purely anodic oxidation also led to an increase in the process rate, but this occurred to a lesser extent as compared with the addition of hydrogen peroxide.

Table 2 presents data on the aniline oxidation efficiency on the BDDE in relation to the current density, electrolysis duration, and scheme of the oxidation process.

Table 1. Oxidation of aniline on a Pb/PbO$_2$ anode in 0.7 M H$_2$SO$_4$

AOS generation scheme	Current density *i*, mA cm^{-2}	Potential φ, V	Time τ, h	Oxidation efficiency, %
		c_a = 100 mg L^{-1}		
A	50	2.2	0.5	38
		2.2	5	63
	100	2.5	0.5	42
		2.5	5	71
A + H$_2$O$_2$	50	1.8	0.5	54
		2.1	5	74
	100	1.9	0.5	55
		2.5	5	77
		c_a = 200 mg L^{-1}		
A	25	1.8	0.5	12
		1.8	5	63.5
	50	1.8	0.5	42.5
		1.8	5	73.5
	100	1.7	0.5	64
		1.85	5	78.5
A + H$_2$O$_2$	25	1.8	0.5	18
		1.85	5	68.4
	50	1.8	0.5	20.5
		1.8	5	70.5
	100	1.8	0.5	69
		1.9	5	81.5
A + Fenton reagent	25	1.7	0.5	67
		1.8	5	81
	100	2.1	0.5	70
		2.1	5	83

It can be seen in Table 2 that, at c_a = 100 mg L^{-1}, the aniline oxidation efficiency in 30 min of electrolysis upon addition of H$_2$O$_2$ reached 68.5 and 72% for current densities of 50 and 100 mA cm^{-2}, whereas with the anodic scheme of AOS generation, these values were 10 and 29%, respectively. Addition of hydrogen peroxide to the electrolyte can, on the one hand, raise the AOS concentration for oxidation of organic substances, and on the other, favor cleaning of the surface to remove tarring products by being decomposed at the anode.

As the initial concentration was lowered and the current density was raised, the aniline oxidation efficiency decreased, with addition of H$_2$O$_2$ to the electrolyte volume having no effect on this parameter.

At the same time, the oxidative destruction efficiency in the anodic scheme of AOS generation was higher for a lower aniline concentration, whereas the opposite dependence was observed for Pb/PbO$_2$ (Table 1). This is probably due to the somewhat different mechanism by which organic substances are oxidized at these anodes.

At a lower content of aniline, its oxidation presumably occurs mostly at the electrode surface due to the interaction with adsorbed radicals. In this case, the [$^{\bullet}$OH] : [aniline/intermediates] ratio remains rather high

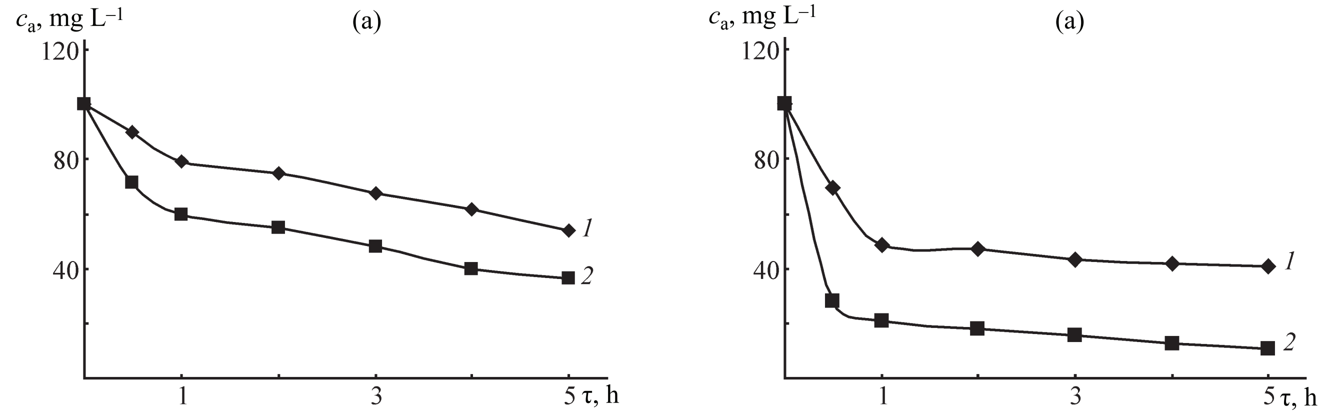

Fig. 2. Kinetic curves for aniline oxidation on a BDDE at current density of (a) 25 and (b) 100 mA cm^{-2}. Initial aniline concentration 100 mg L^{-1}. (*1*) Anodic oxidation and (*2*) oxidation with addition of hydrogen peroxide.

and introduction of an additional amount of AOSs has no significant effect.

The kinetic dependences were used to determine the apparent rate constants of aniline oxidation at current densities of 25, 50, and 100 mA cm^{-2} and various schemes for generation of active oxygen species (Table 3). An analysis of the kinetic curves demonstrated rather good linear dependences with a correlation coefficient of about

Table 2. Oxidation of aniline on a BDDE anode in 0.1 M H_2SO_4

AOS generation scheme	Current density *i*, mA cm^{-2}	Potential φ, V	Time τ, h	Oxidation efficiency, %
		c_a = 100 mg L^{-1}		
A	25	2.1	0.5	10
		2.1	5	46
	50	2.4	0.5	10
		2.5	5	55
	100	2.4	0.5	30
		2.4	5	59
A + H_2O_2	25	2.1	0.5	29
		2.4	5	63.5
	50	2.5	0.5	68.5
		2.5	5	85
	100	2.4	0.5	72
		2.4	5	89.5
		c_a = 200 mg L^{-1}		
A	25	2.3	0.5	36
		2.1	5	61
	100	2.8	0.5	49
		2.9	5	62
A + H_2O_2	25	2.3	0.5	46
		2.5	5	54
	100	2.8	0.5	52
		2.8	5	63

Table 3. Rate constants kI of aniline oxidation on Pb/PbO_2 and BDDE anodes with different AOS generation schemes

Current density i, mA cm^{-2}	k_1, h^{-1}			
	A		A + H_2O_2	
	Pb/PbO_2	BDDE	Pb/PbO_2	BDDE
25	0.28	0.17	0.41	0.54
50	0.37	0.23	0.43	1.37
100	1.0	0.53	1.12	1.61

0.97 for the pseudo-first-order reaction described by the equation

$$\ln c_0/c = k\tau, \quad (8)$$

where c_0 is the initial aniline concentration (mg L^{-1}); c, aniline concentration after a time τ (mg L^{-1}); and k, apparent rate constant of oxidation (h^{-1}).

The difference between the values of k, obtained for dissimilar electrolysis schemes at the same current density indicates that the pathways of the aniline oxidation process are possibly different because of the difference in the composition and amount of AOSs being generated. It can be seen that the aniline oxidation process is the most efficient in the schemes in which the anodic generation of $^{\bullet}OH$ radicals (1) is supplemented with perhydroxy $HO_2^{\bullet}$ radicals formed by the reactions

$$H_2O_2 \rightarrow HO_2^{\bullet} + H^+ + e, \quad (9)$$

$$H_2O_2 + HO_2^{\bullet} \rightarrow {}^{\bullet}OH + H_2O + O_2. \quad (10)$$

UV spectroscopic data demonstrate that a number of intermediate products are formed in aniline destruction in the case of anodic oxidation of aniline on the BDDE. A number of new absorption bands appear in electronic absorption spectra (λ_1 = 250 nm and λ_2 = 280 nm). The appearance of the new absorption band with λ_1 = 250 nm can be attributed to the formation of phenylhydroxylamine in the cationic form as the intermediate product. Further oxidation of this product yields phenol and its derivatives (λ_2 = 280 nm), including those contained in the polymeric product, in agreement with the presence of a broad absorption band in the spectra in this range. Comparison of the relative contents of various intermediate products formed in oxidation in the presence of hydrogen peroxide and without it indicates that the oxidative destruction rate of all intermediate products becomes approximately twice higher. This means that the oxidative destruction process of the organic components occurs by the radical mechanism.

The electronic absorption spectra of the electrolyte upon oxidation of aniline on Pb/PbO_2 show, in contrast to the case of BDDE, a rather strong absorption at λ = 240–250 nm and a noticeable increase in the intensity of absorption bands at λ = 290 and 310 nm. With consideration for the strong absorption at λ = 240–250 nm, the absorption band at λ = 290 nm can be attributed to p-benzoquinone (nitrobenzene has similar spectral characteristics). The absorption at λ = 310–315 nm can be attributed to the presence of nitrobenzene in trace amounts or to the formation of separate units when a polymeric product (tarry substances) is formed. The fact that this band is not observed in the presence of hydrogen peroxide indicates that this compound is actively involved in the oxidation of these intermediate products. These results agree with those obtained in the oxidation of aniline on the BDDE. However, the difference in the composition of the intermediate products formed in the oxidation of aniline on different anode shows that the mechanisms of the electrochemical oxidation on their surface are not the same. Mostly one-electron oxidation processes occur on the BDDE to give $^{\bullet}OH$ radicals, whereas on Pb/PbO_2, many-electron processes additionally occur to produce intermediate products in a deeper oxidation state.

CONCLUSIONS

(1) It was shown that the process of the indirect electrochemical oxidation of aniline on the Pb/PbO_2 electrode at pH 2–3 occurs with the highest efficiency (81–83%) when active oxygen species are generated by the scheme with anodic oxidation and the Fenton reagent. At higher current densities, the process efficiency is little dependent on the scheme by which active oxygen species are generated.

(2) It was found that the efficiency of the aniline oxidation process on a boron-doped diamond electrode in 0.1 M H_2SO_4 is 89.5% upon addition of hydrogen peroxide to the electrolyte: (anodic oxidation + H_2O_2) scheme.

(3) UV spectroscopy demonstrated that p-benzoquinone is the intermediate product in the indirect electrochemical oxidation of aniline. Addition of hydrogen peroxide leads to a decrease in the concentration of intermediate products, which means that hydrogen peroxide is involved in the oxidative destruction of aniline.

(4) It was found that the rate of the oxidative destruction of all intermediate products becomes approximately twice higher on the boron-doped diamond electrode in the presence of hydrogen peroxide.

(5) It was shown that the process of the electrochemical oxidation of aniline can be regarded as an alternative way to degrade aniline in industrial wastewater, and studies aimed to improve its efficiency form a promising area of research in the field of applied electrochemistry.

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