

# The Prospects of the in situ and ex situ Use of Aqueous Solutions of Hydrogen Peroxide Electrogenerated from Oxygen<sup>1</sup>

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**Abstracts**—The results and prospects of the in situ (in the cell volume) and ex situ (outside the cell) use of aqueous solutions of hydrogen peroxide electrogenerated from oxygen in gas-diffusion electrodes (GDE) of carbon black are discussed. It is shown that using GDE based on technological A-437E carbon (acetylene black) and mesostructured carbon CMK-3 allows the H<sub>2</sub>O<sub>2</sub> solution with the concentration higher than 3 M to be obtained. It is found that electrosynthesized hydrogen peroxide may be used in situ with the high efficiency both in the indirect electrosynthesis of important organic and inorganic target products and in the destruction of organic and inorganic pollutants present in waste waters of different origin. Under the ex situ conditions, it is possible to synthesize the more concentrated solutions of H<sub>2</sub>O<sub>2</sub>, organic peroxyacids, and inorganic peroxosolvates and also to carry out mineralization of exometabolites in autonomous life-support systems. These results may be helpful in selecting the most appropriate versions of using hydrogen peroxide solutions electrogenerated from oxygen for solving particular problems.

**Keywords:** hydrogen peroxide, active forms of oxygen, gas-diffusion electrode, indirect electrosynthesis, current efficiency, mineralization, organic substrates, pollutants, in situ, ex situ

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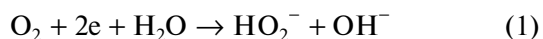
## INTRODUCTION

The concept of the development of modern chemical technologies corresponding to the principles of Green Chemistry and steady development focuses attention on the wide use of aqueous solutions of hydrogen peroxide as the environmentally clean oxidizer [1]. Their application region is extraordinarily wide: the aqueous H<sub>2</sub>O<sub>2</sub> solutions prepared by commercial technologies are used in the pulp and paper industry, in the production of detergents and disinfectants, in hydrometallurgy plants, for cleaning waste waters, in liquid-phase oxidation of exometabolites in closed life-support systems, and in many other life activity fields which require the use of clean oxidizers [2].

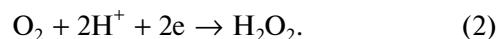
In the recent 20 years, attention was focused on indirect electrolytic oxidation of organic and inorganic substrates by active oxygen forms (AOF) (O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, HO·, HO<sub>2</sub><sup>-</sup>, HO<sub>2</sub><sup>·</sup>, ROOH, etc.), which can be generated at the anodic oxidation of water and hydro-

gen peroxide on Pt electrodes, boron-doped diamond electrodes (BDDE), and electrodes based on dioxides of lead, tin, manganese, etc., and also by the cathodic reduction of oxygen to hydrogen peroxide on carbon-graphite materials [3–8]. It is assumed that based on these solutions, one can carry out highly efficient advanced oxidation processes (OAPs) [8]. However, the wide use of hydrogen peroxide is limited by its relatively high cost when it is produced by traditional technologies [9, 10]. In connection with this, for many years, attempts were undertaken to find the cheaper and easier methods of production of its aqueous solutions with the required concentration.

It is well known [2, 9–12], that hydrogen peroxide can be synthesized relatively easily by electroreduction of oxygen on carbon-graphite electrodes in alkaline solutions (the Berl process [11])

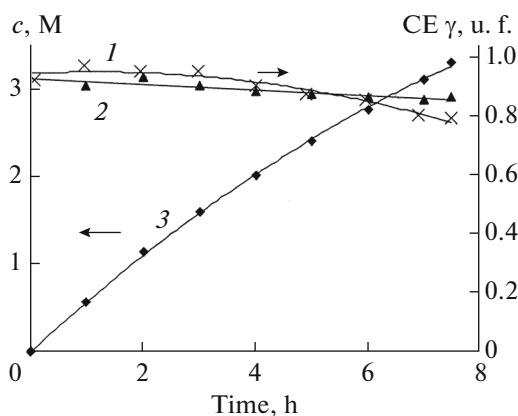


and by the following reaction in acidic solutions:



It deserves mention that this method is wasteless and allows producing H<sub>2</sub>O<sub>2</sub> in the site of its consump-

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**Fig. 1.** Results of preparative electrosynthesis of  $\text{H}_2\text{O}_2$  from  $\text{O}_2$  in a GDE based on CMK-3 with 70 wt % F-4D in an acidic solution at the overall current density of  $1500 \text{ A/m}^2$ : (1)  $\gamma$ , (2) current efficiency of  $\text{H}_2\text{O}_2$ , (3)  $\text{H}_2\text{O}_2$  concentration.

tion in the form of dilute aqueous solutions and using them latter as a commercial product without extracting  $\text{H}_2\text{O}_2$ , which considerably reduces the cost [2, 10, 12]. Such aqueous solutions of hydrogen peroxide can be easily concentrated because the water vapor pressure is higher than that of  $\text{H}_2\text{O}_2$  by one order of magnitude (17 against 1.36 mm Hg,  $20^\circ\text{C}$ ) [13], which allows solutions with the required  $\text{H}_2\text{O}_2$  concentration to be prepared with the high benefit-cost ratio to be used ex situ, i.e., outside the electrolyzer volume.

It is well known that in homogeneous reactions, hydrogen peroxide can interact with substrates and oxygen-containing intermediates  $\text{OH}_2^-$ ,  $\text{HO}_2^-$ ,  $\text{HO}^\cdot$ ; the intrinsic activity of the latter differs by 5–6 orders of magnitude [14]. It is generally accepted that the most active of the mentioned radicals is  $\text{HO}^\cdot$  ( $E^0 \text{HO}^\cdot/\text{H}_2\text{O} = 2.8 \text{ V}$ ) and the least active is  $\text{HO}_2^-$  ( $E^0 \text{HO}_2^-/\text{H}_2\text{O} = 1.65 \text{ V}$ ) [6]. Hence, the use of  $\text{H}_2\text{O}_2$  allows carrying out the oxidation processes of different depth under in situ conditions with the use of the conjugated reactions of the heterogeneous oxygen oxidation to hydrogen peroxide and the homogeneous oxidation of organic and inorganic substrates in the electrolyte volume [15–17]. This was repeatedly discussed in the Russian and foreign literature, for example, in [2–6, 15, 17–32].

This study is aimed at the analysis of experimental results obtained by the research group of the Institute of Chemistry and Technology, Siberian Branch, Russian Academy of Sciences in the course of a long-term complex investigation of the electrosynthesis of aqueous solutions of  $\text{H}_2\text{O}_2$  from  $\text{O}_2$  in carbon-black gas-diffusion electrodes (GDE) and also to the discussion of prospects of practical application of this approach under in situ and ex situ conditions.

## ELECTROSYNTHESIS OF $\text{H}_2\text{O}_2$ FROM $\text{O}_2$

The earlier results on the electrosynthesis of hydrogen peroxide from oxygen in GDE based on carbon-graphite materials produced in Russia (acetylene black A437-E, furnace blacks P268E, P324-E, P701, P602, P805-E, P399-ET) in solutions of different pH are summarized in [12, 17]. The tests of GDE fabricated based on A437-E with the apparent surface area of  $64 \text{ cm}^2$  in an electrolyzer of the filter-press type, in electrolyte containing  $\text{K}_2\text{SO}_4$  (0.5 M) +  $\text{H}_2\text{SO}_4$  (0.2 M) + TBAB (0.005 M) produced the solution of  $\text{H}_2\text{O}_2$  with the concentration 3.0 M in 9 h electrolysis with the current efficiency (CE) approaching 80.0%. The similar results were obtained for the GDE of the analogous composition with the apparent surface of  $900 \text{ cm}^2$ . These results suggest that the considerable increase (by a factor of 14) in the apparent surface of these GDE had virtually no effect on the electrosynthesis efficiency. Moreover, it was shown that acetylene black (A437-E) is the most efficient electrocatalyst among the considered carbon blacks of this type.

In the recent years, we carried on our studies on selecting and testing new types of technological carbon produced by the company Omsktekhuglerod (Russia) as the promising electrocatalysts for electrosynthesis of  $\text{H}_2\text{O}_2$  from  $\text{O}_2$  in GDE [33, 34]. It was found that in GDE based on carbon materials N220, C140, and CH85, the oxygen reduction in alkaline and acidic electrolytes involves the stage of formation of hydroxide ions and hydrogen peroxide with the relatively high selectivity ( $\gamma = 0.8$ ). Thus, in GDE based on technological carbon N220, the hydrogen peroxide solutions with the 0.56 M concentration were obtained in 1 h with the 87% current efficiency. These results demonstrated the good prospects of new types of carbon-graphites as the electrocatalysts in electrosynthesis of  $\text{H}_2\text{O}_2$  from  $\text{O}_2$ . Especially good results were obtained for mesostructured carbon CMK-3. Mesostructured mesoporous carbon materials are the new promising materials for various applications in electrochemistry. The main advantage of mesostructured carbon materials prepared by the template synthesis, as compared with other carbons, is the high surface area, the ordered mesoporous structure, the high conductivity, and relatively low cost [35]. The authors of [36, 37] showed the data on mesostructured carbon CMK-3 (Carbon Mesostructured by KAIST) as the electrocatalysts for electrosynthesis of  $\text{H}_2\text{O}_2$  from  $\text{O}_2$  in a gas-diffusion electrode in alkaline and acidic solutions. Figure 1 shows the results of preparative electrosynthesis of  $\text{H}_2\text{O}_2$ . It is evident that the kinetics of  $\text{H}_2\text{O}_2$  accumulation obeys the parabolic law and the current efficiency and selectivity of this process exceed 80% and 0.8, respectively. The 7.5 h electrolysis at the current density of  $1500 \text{ A/m}^2$  produced hydrogen peroxide with 3 M concentration in the solution containing 0.5 M  $\text{K}_2\text{SO}_4$  : 0.1 M  $\text{H}_2\text{SO}_4$  (3 : 1). The shown

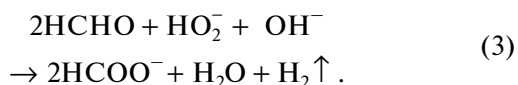
characteristics of the efficiency of synthesizing aqueous  $\text{H}_2\text{O}_2$  solutions considerably exceed the results present in the world literature [38], which points to the good prospects of using this material in gas-diffusion electrodes for many applications important for practice.

### In situ PROCESSES

#### INDIRECT ELECTROSYNTHESIS

##### *Oxidation of Formaldehyde to Formic Acid*

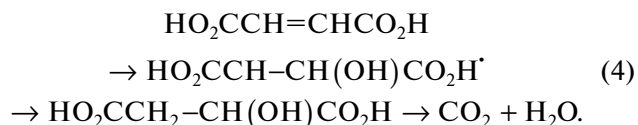
In [39] we studied the oxidation of formaldehyde by  $\text{HO}_2^-$  generated in situ from  $\text{O}_2$  in a carbon-black GDE in 1 M NaOH in cells with cathodic and anodic compartments separated by a cation-exchange MF-4SK-100 membrane at 20°C. It was shown that the formaldehyde oxidation proceeds only to formic acid in quantitative yields according to the equation



The presence of formic acid in the formaldehyde solution volume had virtually no effect on the electrode polarization and generation of  $\text{HO}_2^-$  ions, and the increase in the current from 250 to 2000 A/m<sup>2</sup> did not affect the CE of  $\text{HO}_2^-$ .

##### *Oxidation of Maleic Acid to Malic Acid*

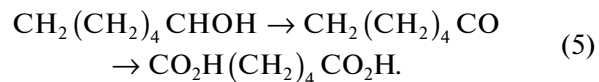
In [40] we studied the kinetics and selectivity of maleic acid oxidation in a cell with a carbon-black gas-diffusion cathode, a platinum anode, and a cation-exchange membrane in 1 M  $\text{Na}_2\text{SO}_4$  at the current density of 500 and 1000 A/m<sup>2</sup>, with the initial substrate concentration of 0.215 M at 12–30°C. The analysis of samples by IR spectroscopy showed that the products represented a mixture of the malic-acid salt as the main product, the unreacted maleic-acid salt, and a small amount of epoxide. It was found that the increase in current density and temperature had virtually no effect on the oxidation rate of the substrate so that its conversion after 12 h electrolysis was by 56–58%. It was shown that electrolysis in a membrane-free cell led to mineralization, where the final products of maleic acid oxidation were only  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , and the following mechanism was proposed:



##### *Indirect Electrosynthesis of Adipinic Acid from Cyclohexanol*

Adipinic acid is used widely, and attempts are still undertaken to develop more environmentally friendly

methods of its synthesis [41]. In [42, 43], the authors studied the possibility of synthesizing adipinic acid by the redox-mediator oxidation of cyclohexanol and cyclohexanone on an oxide-hydroxide nickel electrode (OHNE), i.e., Ni(O)OH anode, and also proposed the mechanism of oxidation of cyclohexanol on the Ni(O)OH electrode in aqueous NaOH solutions. It was shown that the oxidation proceeds via the limiting stage of cyclohexanone formation with its subsequent oxidation to adipinic acid



In [44], we studied the effect of several factors (current density, substrate concentration, the charge passed) on the efficiency of this process when it was carried out on a porous Ni(O)OH electrode in the presence of AOF. It was shown that the current efficiency of adipinic acid reached its maximum at the current density of 220 A/m<sup>2</sup> with the 50.0% current yield and 50.0% substance yield by the reaction scheme involving hydrogen peroxide. The selectivity of adipinic acid formation also increased with the increase in the current density and reached 91.0% at 250 A/m<sup>2</sup> in the presence of  $\text{H}_2\text{O}_2$  in electrolyte solution; however, the current efficiency with respect to the target product decreased to 42%. The side products were glutaric and succinic acids.

Analysis of the results of electron paramagnetic resonance (EPR) has shown that the selectivity of adipinic acid formation can reach 89% at the electrolysis with the optimal current density (220 A/m<sup>2</sup>) and in the presence of AOF sources, i.e., the appearance of additional amounts of AOF increases the selectivity of adipinic acid formation. In this case, two oxidation paths are realized simultaneously - heterogeneous electrocatalytic and homogeneous chemical. The increase in the amount of passed electricity above its theoretical value ( $Q/Q_{\text{theor}}$ ) to 3 leads to a decrease in the selectivity of synthesis of adipinic acid due to the formation of side products (glutaric and succinic acids). Based on these results, it can be concluded that for the redox-mediator mechanism of cyclohexanol oxidation on the OHNE anode containing higher oxides of nickel, which is accompanied by the in situ generation of AOF from  $\text{H}_2\text{O}_2$  and  $\text{O}_2$ , the optimization allows reaching the record-breaking selectivity of 89% and obtaining the target product in a single stage.

##### *Indirect Electrocatalytic Oxidation of Aliphatic Alcohols to Carboxylic Acids*

Aliphatic carboxylic acids, their salts, and esters are widely used in pharmaceutical, vitamin, cosmetic, and food industries [45]. It is well known that the chemical methods of production of carboxylic acids through oxidation of aliphatic alcohols have several drawbacks associated with the use of relatively expensive and toxic

chemical oxidants such as potassium permanganate, chromium compounds, etc. [45, 46]. For this reason, the quest is carried out for alternative methods of synthesis including those electrochemical. As was shown earlier, for the oxidation of alcohols, the OHNE containing specially formed higher oxides of nickel is the most suitable anodic material which can efficiently convert saturated aliphatic alcohols to carboxylic acids in alkaline medium [4, 43, 46].

In [47–50], we studied the indirect oxidation of butyl, hexyl, nonyl, and decyl alcohols to butyric, caproic, pelargonic, and capric acids by active forms of chemically bound oxygen generated in situ from  $O_2$ ,  $H_2O$ , and  $H_2O_2$  on the following anodes: OHNE, lead-dioxide electrode, and BDDE. The following three schemes of electrolysis were realized: (1) oxidation on the anode where the process can proceed under both homogeneous and heterogeneous conditions; (2) oxidation on an anode in the presence of  $H_2O_2$ ; (3) paired electrolysis, i.e., oxidation on the anode with the parallel generation of  $HO_2^-$  on a graphite cathode blown round with oxygen.

It is shown that in the paired electrosyntheses, the oxidation of alcohols proceeds with the high current efficiency and produces the corresponding carboxylic acid according to the pseudo-first order mechanism and also that the optimal current density is 50–100  $A/m^2$ . According to the data of UV spectroscopy and the results on the chemical oxygen demand (COD), in the interval of 150–500  $A/m^2$ , the oxidation proceeds with subsequent mineralization to  $CO_2$  and  $H_2O$ .

Preparative experiments on accumulation and extraction of target products (acids) with the use of the scheme of paired electrolysis showed the following results. The synthesis on OHNE in 1.2 M NaOH produced butyric, caproic, and capric acids with the CE of 168, 148, and 64%, respectively. On BDDE in 0.1 M  $H_2SO_4$ , pelargonic acid was synthesized with 98% CE. In [50], the results of approximate calculations of the charge consumed per t of target product are shown.

Thus, it was found that the highest efficiency in oxidation of alcohols to the target carboxylic acids is achieved under the conditions of paired electrolysis where active oxygen is formed in parallel with the main process, which provides an additional channel for the homogeneous oxidation of substrates.

#### *Indirect Oxidation of Acetic Acid to Peracetic Acid*

Attention paid to peracetic acid is associated with the wide spectrum of its applications as a strong oxidant [51]. Peracetic acid is an ideal disinfectant in medicine and food industry [52]. However, its wide use is prevented by its high cost which is partly associ-

ated with its limited production. Peracetic acid is produced in the reaction of concentrated hydrogen peroxide with glacial acetic acid in the presence of an acidic catalyst



The attention paid to the in situ synthesis of peracetic acid is associated with the fact that it is safer to use dilute solutions of hydrogen peroxide and acetic acid.

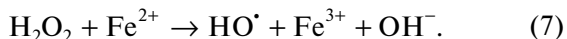
The authors of [53, 54] were the first to demonstrate the possibility of synthesizing peracetic acid with the use of  $H_2O_2$  generated in situ on a gas-diffusion cathode at the reduction of  $O_2$  and a catalyst based on Nafion and Pt. However, the obtained concentrations of peracetic acid were low: 0.0021–0.0062 M for the  $H_2O_2$  concentration of 0.147 M. We studied [55] how the electrolyte composition, the current density, and the nature of catalysts affect the efficiency of indirect electrosynthesis at the higher concentrations of peracetic acid in the presence of hydrogen peroxide generated in situ in a GDE based on technological carbon 437-E and a platinum anode. It was found that the addition of sulfuric acid to the solution as the acidic catalyst increased the concentration of peracetic acid to 0.0092 M. The increase of the acetic acid concentration to 3.5 M had a negative effect on the GDE operation—its electrochemical activity substantially decreased. The addition of ammonium molybdate as the  $H_2O_2$ -activating catalyst had a positive effect on the total efficiency. As the charge passed increased with the increase in the current density to 1500  $A/m^2$ , the produced concentrations of peracetic acid also increased to 0.021 M and the  $H_2O_2$  concentration increased to 1.46 M. It was shown that the ex situ aging of solutions after the electrolysis (10 and 25°C) increased the yield of  $CH_3CO_3H$  to its equilibrium concentration equal to 0.056 M. This suggests that the kinetics of the chemical stage is slow. Moreover, when the concentrations of  $CH_3CO_3H$  and  $H_2O_2$  obtained in electrolysis were higher, the concentration of peracetic acid formed in the “maturing” stage was also higher. The use of two types of catalysts, namely, sulfuric acid and ammonium molybdate increased the rate of peracetic acid formation and their simultaneous use allowed solutions with the concentration of 0.021 M to be obtained, i.e., one order of magnitude higher as compared with [51, 53, 54]. We obtained the close results [56] at the hydrogen peroxide electrogeneration from oxygen in aqueous solutions of  $K_2SO_4 + H_2SO_4$  in the presence of formic, acetic, and butyric acids. These higher results were associated with the higher productivity of the gas-diffusion cathode as regards  $H_2O_2$  generation at the current density of 1500 against 27  $A/m^2$  used in [51, 53, 54].

## DECOMPOSITION OF ORGANIC AND INORGANIC POLLUTANTS

It is known [2] that the consumption of electric energy in disinfection of organic toxicants in waste waters is proportional both to their concentration and to the number of electrons required for their destruction to CO<sub>2</sub>. As a rule, the so deep oxidation of organic molecules requires from 20 to 150 electrons. According to patent [57], the electric energy necessary for electrosynthesizing H<sub>2</sub>O<sub>2</sub> from O<sub>2</sub> is 4.5 kW h per 1 kg of 100% H<sub>2</sub>O<sub>2</sub>. Thus, the synthesis of one H<sub>2</sub>O<sub>2</sub> molecule from O<sub>2</sub> required two electrons, the mineralization of organic pollutants requires from 10 to 75 peroxide molecules. Hence, the use of the method of indirect oxidation at the low concentrations (before sending them to biological cleaning) of organic substrates—"tails" contained in waste water by electrochemically generated H<sub>2</sub>O<sub>2</sub> is economically expedient. As an example of indirect destructive decomposition of organic and inorganic substrates, we studied the processes of oxidation of pollutants encountered most widely in technological and waste waters of various origin.

### *Mineralization of Formaldehyde and Formic Acid*

B [58, 59], the oxidation of formaldehyde was studied in the presence of Fe(II) salts in acidic solutions (electro-Fenton process) where hydroxide radicals can be formed by the reaction



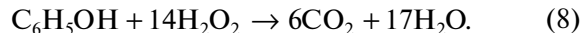
It was shown that the oxidation products are HCOOH, CO<sub>2</sub>, and H<sub>2</sub>O. The optimal conditions are realized at pH 3–4 and 60°C. The increase in the current density from 250 to 2000 A/m<sup>2</sup> did not affect the degree of conversion of formaldehyde, the latter was close to 100% but increased the conversion rate and decreased the time of electrolysis 8-fold. The kinetics of this process was limited by the H<sub>2</sub>O<sub>2</sub> generation rate. The final oxidation products were CO<sub>2</sub> and H<sub>2</sub>O.

In [59] the destructive oxidation of formic acid by intermediates <sup>•</sup>OH and HO<sub>2</sub><sup>•</sup> generated *in situ* from H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> in a diaphragmless cell with a platinum anode and a GDE cathode in electrolytes of different pH is described. It was found that as the current density increased to 1000 A/m<sup>2</sup>, the conversion of HCOOH increased and then remained unchanged; in acidic electrolytes the conversion degree was higher than in alkaline solutions being equal to ~99.0% at pH 3.2. The oxidation products were, as expected, CO<sub>2</sub> and H<sub>2</sub>O.

### *Destructive Oxidation of Phenol*

It is well known that phenol is one of the most abundant and difficult-to-oxidize environmental tox-

icants. Its content can vary widely (0.106–2.12 mM) and it can be oxidized by hydrogen peroxide to CO<sub>2</sub> and H<sub>2</sub>O by the reaction



We studied [60–62] the indirect destructive oxidation of phenol in electrochemical cells with and without cation-exchange membrane, with a carbon-black gas-diffusion cathode, platinum and lead-dioxide anodes, in alkaline, neutral, and acidic media, at current densities of 250–1500 A/m<sup>2</sup> and 20°C. It was found [60] that in the alkaline medium in a three-chamber cell with cation-exchange membrane MF-4SK-100, the oxidation products were organic acids and ketones. The intermediate products with the conjugated double bonds were accumulated when the content of oxidant was insufficient. At these current densities, the efficiency of this process substantially depended on the concentration of sodium hydroxide. The higher efficiency of oxidation (78%) was achieved in 0.1 M NaOH in 3 h electrolysis at the current density of 500 A/m<sup>2</sup>.

In [61], we studied the dependences of the rate and efficiency of destructive oxidation of phenol by hydrogen peroxide generated electrochemically from oxygen in a gas-diffusion electrode in alkaline medium in an electrolyzer without cation-exchange membrane in 0.05, 0.1, and 0.5 M NaOH solutions at the current density of 250, 500, 1000, 1500 A/m<sup>2</sup>. Smooth platinum was used as the anode. In the electrolyzer containing no cation-exchange membrane, HO<sub>2</sub><sup>•</sup> was transferred to the anode to be oxidized there to perhydroxyl radical HO<sub>2</sub><sup>•</sup>. Moreover, the oxidation of OH<sup>-</sup> on the anode produced <sup>•</sup>OH radicals. This is why in an electrolyzer without cation-exchange membrane the presence of a platinum anode allowed one to expect the deeper oxidation of phenol up to its mineralization. The found values of characteristic times of destruction at different current densities showed that the optimal conditions were realized in 0.1 M solution at the current densities of 1000 and 1500 A/m<sup>2</sup>. The efficiency of phenol oxidation decreased with the increase in its initial concentration—at the initial concentration of 0.265, 0.53, 1.06, and 2.12 mM, the efficiency was 86, 85, 70, and 60%, respectively. IR and UV spectroscopic studies have shown that the phenol oxidation proceeds by two pathways: the direct oxidation on the anode to form resinous compounds and its homogeneous oxidation by active intermediates (<sup>•</sup>OH, HO<sub>2</sub><sup>•</sup>) in the near-anode layer. After 2–3 h electrolysis, the electron spectra contained no absorption bands of phenol and intermediates (carboxyl acids with the bands at 3350 and 1725 cm<sup>-1</sup>, β-diketones in the enol form with the bands at 1592 and 2900, quinones and α-diketones), which pointed to the virtually complete mineralization of phenol at the current den-

sity of 1000 and 1500 A/m<sup>2</sup> and for its initial concentration of 0.265–0.53 mM.

In [62], we studied the indirect oxidation of phenol in acidic (pH 2–3) and neutral (pH 6–7) media in a diaphragmless electrolyzer with a gas-diffusion cathode, platinum and lead-dioxide anodes at the current density of 500 and 1000 A/m<sup>2</sup>. The UV spectroscopic data for solutions during their electrolysis at the same charge passed pointed to the different depth of phenol oxidation in acidic and neutral electrolytes. Thus, in acidic electrolytes, the phenol oxidation proceeded to quinone and hydroquinone (as the intermediate products) which was followed by opening of the aromatic ring to form iron complexes with carboxyl ligands and their further decomposition to CO<sub>2</sub> and H<sub>2</sub>O. In neutral solution, the absorption bands typical of diketones and carboxyl acids were observed. It deserves mention that the similar results were obtained in several studies by foreign authors under similar conditions [30, 63–66] but with a GDE less efficient in electrogeneration of hydrogen peroxide.

Thus, we can state that the process of phenol oxidation with 96–98% mineralization to CO<sub>2</sub> and H<sub>2</sub>O can proceed in alkaline electrolyte (0.1 M NaOH) without cation-exchange membrane with involvement of ·OH, HO<sub>2</sub>· radicals and also in acidic electrolytes where HO· is the oxidant, whereas in the neutral medium the oxidation proceeds with involvement of less active radical ions HO<sub>2</sub>·, which allows conversing the poorly oxidizable phenol to simple mono- and dicarboxylic acids which can be utilized by microorganisms in the course of their further biochemical cleaning.

#### *Destructive Oxidation of N-Methyl-p-Aminophenol (Metol)*

Aromatic amines are widely used in industry, e.g., as the precursors and intermediate products in the production of dyes, drugs and are also typical contaminants of the hydrosphere [67].

In [68–70], we studied the indirect electrochemical oxidation of N-methyl-p-aminophenol by active oxygen forms generated in situ from O<sub>2</sub>, H<sub>2</sub>O, and H<sub>2</sub>O<sub>2</sub>. The oxidation of N-methyl-p-aminophenol was carried out in a diaphragmless electrolyzer with a gas-diffusion electrodes of carbon-black and graphite and anodes of Pt and PbO<sub>2</sub> in alkaline and acidic electrolytes. It was shown that the efficiency of oxidation increased with the increase in the current density; moreover, the process was more efficient in alkaline electrolyte as compared with acid electrolyte. In alkaline electrolyte at 700 A/m<sup>2</sup>, the efficiency of mineralization was 98–99%, whereas in acidic electrolyte at 200 A/m<sup>2</sup>, the efficiency was 30%. The indirect oxidation of metol by hydrogen peroxide generally proceeded with mineralization to CO<sub>2</sub> and H<sub>2</sub>O by 98% in

0.1 M NaOH, whereas in 0.2 M NaOH the efficiency of mineralization decreased to 65%.

The results of UV spectroscopic studies showed that the oxidation of metol at different pH proceeded by different pathways of successive oxidation: at pH 2–3, the intermediates were largely of the carboxylate type, whereas at pH 9–10 the metol hydroxylation products were formed and successively transformed to aliphatic acids and the latter were oxidized to CO<sub>2</sub> and water. This scheme of metol oxidation was described in the literature [71, 72]. Summarizing, it should be noted that in the alkaline medium, the metol oxidation with mineralization to CO<sub>2</sub> and H<sub>2</sub>O in diaphragmless cells can proceed with 97–99% efficiency on all anodic materials studied.

#### *Destructive Oxidation of β-Naphthol*

Waste waters of pulp and paper industry contain considerable amounts of naphthol and its content is strictly controlled. The maximum permissible concentration (MPC) of naphthol is 1.39 mM [73]. It is known that the process of destructive oxidation of naphthol is described by the following rough equation [74]:



It follows from the above equation that in the ideal case, the complete mineralization of a β-naphthol molecule requires 46 electrons, i.e., this process is comparatively energy consuming. In connection with this, the more economic version of naphthol neutralization is the interruption of this process at the stage of formation of biologically utilizable aliphatic carboxyl compounds.

In [75, 76], we studied the indirect electrocatalytic oxidation of β-naphthol by active forms of oxygen generated in situ from O<sub>2</sub>, H<sub>2</sub>O, and H<sub>2</sub>O<sub>2</sub> in an diaphragmless electrolyzer with carbon-black gas-diffusion and graphite cathodes and anodes of Pt and Pb/PbO<sub>2</sub> in alkaline and acidic electrolytes of 0.1 M NaOH and 0.5 M H<sub>2</sub>SO<sub>4</sub>. In the cell containing gas-diffusion cathode and Pt anode, we observed the cymbate growth of the β-naphthol oxidation rate with the increase in the current density (i.e., with the increase in the oxidant generation rate). To assess the efficiency of electrochemical-cell operation in the process of β-naphthol destructive oxidation, we determined the efficiency coefficient of the cell (η) as in [77], which allowed comparing the efficiency of different cells and choosing the optimal conditions for electrolysis. For example, for a cell with a gas-diffusion electrode and the naphthol concentration of 1.387 mM, the oxidation is expedient to carry out at the current density of 500 A/m<sup>2</sup>. In this case, η = 16%, while for *i* = 1500 A/m<sup>2</sup>, η = 7.5%. For substrate concentration of 6.94 mM and *i* = 900–1000 A/m<sup>2</sup>, η = 29%. Similar results were obtained in [78]. This suggests that the cell with gas-diffusion cathode best operates in the region

of low current densities. For a cell with graphite cathode and alkaline electrolyte blown through with oxygen, at the current of 0.50 A and the initial naphthol concentrations of 2.081 and 3.47 mM, it is better to use a platinum anode ( $\eta = 18\%$ ), rather than a lead anode ( $\eta = 6.5\%$ ). For acidic electrolytes, one can use both the lead anode and the platinum anode ( $\eta = 15.6\%$ ) at the similar conditions of electrolysis. The value of  $\eta$  is higher when the substrate concentration increases, which is probably determined by the rate of diffusion of dissolved substances to the reaction zone. The results of COD determination have shown that the efficiency of  $\beta$ -naphthol mineralization decreases with the increase in its initial concentration in solution. Thus, at the initial concentration of  $\beta$ -naphthol of 1.389 mM, the efficiency was 95%, and at 6.94 mM, it was 75% for the current density of 900 A/m<sup>2</sup>.

Based on the results of UV spectroscopy, the following scheme of the sequential oxidation of naphthol was proposed:  $\beta$ -naphthol  $\rightarrow$  hydroxylated derivatives of naphthol  $\rightarrow$  quinones  $\rightarrow$  ketones  $\rightarrow$  organic acids  $\rightarrow$  mineralization products (CO<sub>2</sub> and H<sub>2</sub>O). These results suggest that the efficiency of  $\beta$ -naphthol oxidation in a cell with GDE depends on the current density and the substrate concentration. In a cell with a graphite cathode and oxygen bubbling through solutions, Pt is the best anodic material in acid electrolytes and Pb/PbO<sub>2</sub> is the best choice in alkaline electrolytes. The efficiency of oxidation depends on the substrate concentration.

#### *Destructive Oxidation of Benzene*

In [69], we studied the indirect destructive oxidation of benzene by intermediates generated in situ from O<sub>2</sub>, H<sub>2</sub>O, and H<sub>2</sub>O<sub>2</sub> in the two- and three-chamber electrochemical cells containing a carbon-black gas-diffusion cathode capable of generating H<sub>2</sub>O<sub>2</sub> from O<sub>2</sub> and anodes of Pt and lead dioxide in aqueous solutions of different pH. The scheme with H<sub>2</sub>O<sub>2</sub> generated in situ from O<sub>2</sub> and the scheme with the addition of hydrogen peroxide into electrolyte were realized. It was found that benzene hydroxylation to phenol with the use of a gas-diffusion cathode in a two-chamber cell was inefficient due to passivation of the carbon black cathode by adsorbed benzene. The benzene oxidation in the three-chamber cell with a filtering diaphragm that prevented immediate contact of benzene with the GDE proceeded to its mineralization to CO<sub>2</sub> and H<sub>2</sub>O, the degree of oxidation varied from 94.8% (Pb/PbO<sub>2</sub>, pH 2) to 63.5% (Pt anode, pH 2.8,  $c_{\text{Fe}^{2+}} = 7.1 \times 10^{-6}$  M (electro-Fenton version)). The main intermediates were phenol, hydroquinone, resorcinol, *p*-benzoquinone. The authors of [79] observed the similar intermediates of benzene oxidation on a rotating BDD disk anode. The lower efficiency of oxidation for the scheme with electro-Fenton in a cell containing a platinum anode was probably

associated with the use of difficult-to-oxidize oxalate complexes with Fe<sup>3+</sup> the presence of which was confirmed by UV spectroscopic data. The final products of benzene oxidation were CO<sub>2</sub> and H<sub>2</sub>O in all these schemes of destruction. The comparison of our results with literature data [79] made it possible to conclude that depending on the anode materials, the efficient indirect oxidation of benzene can proceed to phenol and further via opening of the benzene ring up to complete mineralization both in the presence of H<sub>2</sub>O<sub>2</sub> and with anodes of metal oxides capable of in situ generation of HO· radicals at the H<sub>2</sub>O oxidation by the rough reaction



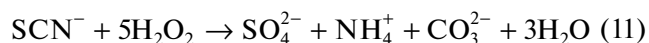
#### *Destructive Oxidation of Aniline*

Aniline is a highly toxic and carcinogenic substance. Its content in water is strictly regulated. In [80], we studied the indirect oxidation of aniline on Pb/PbO<sub>2</sub> and BDDE in sulfuric acid electrolyte in the presence of AOF generated by various schemes in a diaphragmless electrolyzer at current density of 250, 500, and 1000 A/m<sup>2</sup> at 20°C. The initial content of aniline in solutions was 0.537, 1.074, 2.147 mM. It was found that the process of indirect aniline oxidation on the Pb/PbO<sub>2</sub> electrode at pH 2–3 was the most efficient when we used the scheme “anodic oxidation + Fenton reagent.” As the current density increased, the efficiency of this process became almost independent of the method of AOF generation. On BDDE in 0.1 M H<sub>2</sub>SO<sub>4</sub>, the efficiency of aniline oxidation was 90.0% for the oxidation scheme “anodic oxidation + H<sub>2</sub>O<sub>2</sub>.” The UV spectroscopic studies showed that the indirect oxidation of aniline proceeded via the intermediate *p*-benzoquinone; moreover, in the presence of hydrogen peroxide the oxidation rate of all intermediates approximately doubled. Based on the results obtained, we can conclude that the process of indirect aniline oxidation can be considered as a method alternative (to the extraction and adsorption methods) for its degradation in waste waters of industrial plants on electrodes of Pb/PbO<sub>2</sub> and BDD.

#### *Destructive Oxidation of Thiocyanates*

The main source of aqueous solutions of thiocyanates (rhodanides) are the hydrometallurgical processes of gold and silver extraction from sulfide-containing ores and concentrates. Before being discharged or reused, the waste and circulating waters containing thiocyanates should be subjected to deep cleaning from these highly toxic components, which is carried out with the use of chlorine-containing chemicals and the latter results in rapid corrosion of the equipment and complicate the environmental situation.

The destructive oxidation of thiocyanates by hydrogen peroxide proceeds by the rough reaction



and allows achieving a considerable environmental effect because decreases the mineralization of waste waters and lowers down the costs for disinfection by regeneration of cyanide-based chemicals.

In [81, 82], we studied the kinetics and the efficiency of thiocyanate oxidation in alkaline medium with the use of a Pt anode and a gas-diffusion cathode that generated hydrogen peroxide from oxygen, in an electrochemical cell with and without cation-exchange membrane. It was found that when the thiocyanate oxidation was carried out in alkaline medium in a cell with a membrane and the current increased from 0.25 to 0.50 A, the oxidation rate increased approximately 3-fold. The efficiency of destruction of thiocyanates with the initial concentration  $c_0 = 18.36$  mM was 65.0 and 80.0% for the current of 0.25 and 0.50 A, respectively, at the equal charge passed (1 A h). The oxidation products of thiocyanates were mainly  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and also a small amount of  $\text{CNO}^-$ . When the process was carried out in a membraneless cell, in addition to the  $\text{SCN}^-$  oxidation by hydrogen peroxide, its direct oxidation on the Pt anode was possible. Moreover, on the anode, the oxidation of the produced  $\text{HO}_2^-$  was possible as well and the oxidation of water or hydroxyl ions to  $\text{HO}_2^\cdot$  and  $\text{HO}^\cdot$ . The appearance in the system of an additional oxidizing agent in the form of  $\text{HO}_2^\cdot$  increased both the rate of thiocyanate oxidation and its efficiency. For instance, the efficiency of 30 min electrolysis at a current of 0.50 A was 96% when hydrogen peroxide was formed in the gas-diffusion electrode, whereas at the anodic oxidation only, the efficiency was 62%. It was found that in the acidic medium, the oxidation of thiocyanates was more efficient in a membraneless cell as compared with the classical Fenton process in a cell with membrane. The thiocyanate conversion in 30 min electrolysis was 71 and 52%, respectively.

When the process is carried out in a membraneless cell, it should be taken into account that the direct oxidation of  $\text{SCN}^-$  in acidic medium proceeds to  $\text{CN}^-$  ions which can either be oxidized further or hydrolyzed to form toxic hydrogen cyanide.

It should be noted that at the high initial concentration of thiocyanates, the process can be carried out in a membraneless cell with the aim of regeneration of cyanides to be reused in the leaching process [81]. However, at low concentrations, this method is economically unattractive and, without control over evolving HCN-environmentally unsafe. In the latter case, our method of thiocyanate oxidation in alkaline medium is the most advisable.

## Ex situ PROCESSES

### INDIRECT ELECTROSYNTHESIS OF PEROXOSOLVATES—THE PRODUCTS OF MOLECULAR ADDITION

It is well known that  $\text{H}_2\text{O}_2$  can form molecular compounds with a large number of substances, which are highly stable, can be extracted in the solid state (peroxosolvates, peroxohydrates), and stored for a long time [83]. In [84], we studied the electrosynthesis of  $\text{H}_2\text{O}_2$  from oxygen in a gas-diffusion electrode based of technological carbon A437-E in solutions of salts capable of forming molecular compounds with hydrogen peroxide and also the preparation of concentrated solutions of these compounds and their extraction in the solid state. As the electrolytes we took KF, sodium and potassium salts of phosphoric acid with different composition.

After the electrolysis, some of  $\text{H}_2\text{O}_2$  solutions were concentrated. For this purpose, the solutions were kept in air in open polyethylene vessels at room temperature for 10–15 days under the conditions preventing the access of solar light and artificial illumination. As mentioned above, under these conditions, the  $\text{H}_2\text{O}_2$  concentration increases [13]. The concentration of solutions containing KF and KCl was carried out before the extraction of solid compounds and their drying. Concentration of phosphate solutions produced a thick gel-like mass. It was found that when the substances capable of forming molecular compounds with  $\text{H}_2\text{O}_2$  were present at the electrolysis, the latter produced the higher concentrations of hydrogen peroxide with the high current efficiency. The best results were obtained in solutions (pH 7–8) of KF which can form stable compounds with  $\text{H}_2\text{O}_2$ ; the 7.5 h electrolysis at the current density of 1500 A/m<sup>2</sup> produced hydrogen peroxide solution with the concentration of 3.6 M with 92% current efficiency. The close results were obtained in solutions of  $\text{Na}_2\text{HPO}_4$ . The lowest current efficiency and  $\text{H}_2\text{O}_2$  concentration were obtained in solutions of potassium phosphates. The resulting  $\text{H}_2\text{O}_2$  solutions were subjected to concentration; for instance, KF solutions were concentrated to 20 M and higher in 20 days and then stored in closed vessels in order to prevent evaporation of water and  $\text{H}_2\text{O}_2$ . The lowest loss of  $\text{H}_2\text{O}_2$  was observed when concentrating KF solutions. For instance, the concentration of solutions containing KF with the addition of  $\text{H}_3\text{PO}_4$  up to pH 5–6 produced the solution with hydrogen peroxide concentration of 26.9 M; and the solid target product contained ~50.0 wt %  $\text{H}_2\text{O}_2$  in the molar ratio 1 KF per 1.7  $\text{H}_2\text{O}_2$ . It was shown that during the mentioned period, the  $\text{H}_2\text{O}_2$  concentration remained virtually unchanged, which pointed to the high stability of synthesized solutions and solid peroxosolvates. Based on these results, it was concluded that aqueous solutions of salts capable of forming compounds with  $\text{H}_2\text{O}_2$  electrogenerated under in situ



conditions may also find their application in the processes of *ex situ* concentration of  $\text{H}_2\text{O}_2$  solutions up to 26.9 M and also for producing the target product in the solid state, e.g.,  $\text{KF} \cdot 1.7 \text{H}_2\text{O}_2$  with the  $\text{H}_2\text{O}_2$  content of ~50.0 wt % (see Table 2 in [84]).

### ELECTROGENERATION OF $\text{H}_2\text{O}_2$ IN AQUEOUS SOLUTIONS OF MINERALIZED LIQUID AND SOLID DOMESTIC WASTES

One of important problems in the development of autonomous life support systems (ALSS) is the processing of domestic wastes on the basis of biological mass-exchange processes. This problem is solved most efficiently by the liquid-phase oxidation of exometabolites in the presence of 30%  $\text{H}_2\text{O}_2$  under alternating current [85]. At the same time, a substantial drawback of this method is the necessity of storing considerable volumes of hydrogen peroxide in a closed system which is unsafe and also substantially limits the lifetime of the system as a whole. In connection with this, to increase the safety and lifetime of ALSS, it is necessary to produce  $\text{H}_2\text{O}_2$  solutions *in situ* from substances present in closed space and concentrating them under *ex situ* conditions. The electrolysis of  $\text{H}_2\text{O}_2$  from  $\text{O}_2$  and  $\text{H}_2\text{O}$  in GDE satisfies these conditions.

In [86], we studied the process of  $\text{H}_2\text{O}_2$  electro-synthesis in aqueous solutions (pH 1–9) of mineralized liquid and solid solutions of domestic wastes. As the catholyte, we used the solutions of mineralized exometabolites (MEM) prepared in the Institute of Biophysics, Siberian Branch of the Russian Academy of Sciences (Krasnoyarsk, Russia). The anolyte represented 1 M  $\text{H}_2\text{SO}_4$  solution. It was shown that the generation of hydrogen peroxide proceeds at the potentials more positive than the potential of hydrogen evolution under these conditions, which increases the safety and efficiency of its production. It is evident that the rate of  $\text{H}_2\text{O}_2$  accumulation in electrolyte is determined by the difference of the rate of its synthesis in GDE and the rate of its chemical decomposition in electrolyte [12]. In MEM solutions, its higher concentrations and current efficiencies can be reached as compared with the 0.5 M KOH solutions; moreover, the changes in pH have no effect on the efficiency of the target product. The high selectivity of this process in all syntheses demonstrated that no processes of  $\text{H}_2\text{O}_2$  dissolution and or its further reduction to water take place in the electrode volume. This suggests that the presence in MEM of the large number of various compounds does not affect the characteristics of  $\text{H}_2\text{O}_2$  synthesis and even favors its concentration. This phenomenon was observed at electro-synthesis of  $\text{H}_2\text{O}_2$  in alkaline aqueous suspension of brown coal containing a large number of various organic and inorganic compounds [87, 88]. For the current density of 2000 A/m<sup>2</sup>, the value of  $\gamma$  was 0.97–0.95 in this solution.

The electro-synthesis of  $\text{H}_2\text{O}_2$  in GDE with the working surface of 64 cm<sup>2</sup> at the current density of 1000 A/m<sup>2</sup> produced the target product in the concentration reaching 1.6 M at 50% CE. In this case, the lower CE values were associated with the increase in the electrolysis temperature to 40°C and decomposition of peroxide. To test the stability of synthesized  $\text{H}_2\text{O}_2$  solutions, the latter were kept *ex situ* in air in closed polyethylene vessels for 10 days. These experiments showed that the solutions were stable and the target product remained virtually unaffected. When the solutions were stored in open vessels for 5 days, the  $\text{H}_2\text{O}_2$  concentration increased from 2.4 to 11.3 M; the next 5 days of storage increased its concentration to 19 M. The losses of  $\text{H}_2\text{O}_2$  in the process were less than 20%. These experiments showed that hydrogen peroxide can be concentrated in MEM solutions and that the electrolytic method is promising for its synthesis based on biological mass-exchange processes, which is of principal importance for mineralization of exometabolites in ALSS.

These results demonstrate the principal possibility of a considerable extension of the *ex situ* application field of hydrogen peroxide solutions electro-generated in GDE from oxygen, for instance, for their concentration, indirect electro-synthesis of organic peroxyacids, liquid and solid inorganic products with the high content of active oxygen, and mineralization of exometabolites in ALSS.

### CONCLUSIONS

Based on the totality of results known from the literature and obtained in our experimental studies, we can state that hydrogen peroxide solutions electro-generated from oxygen and water can be used *in situ* with the high efficiency in the traditional fields of bleaching of cellulose semi-finished products, indirect electro-synthesis and target organic and inorganic products, and also in destruction and mineralization of organic and inorganic pollutants in technological waste waters of different origin. Under *ex situ* conditions, such solutions can be concentrated to considerable concentrations (26.9 M and higher) and used in the production of organic peroxyacids, inorganic peroxosolvates, and in mineralization of exometabolites in ALSS. It deserves mention that at present, of these two directions of the use of  $\text{H}_2\text{O}_2$  solutions electro-generated from  $\text{O}_2$ , the *in situ* direction is better developed as compared with the *ex situ* direction but we believe that the latter direction is also highly promising.

Furthermore, the highly efficient generation of hydrogen peroxide solutions from oxygen in the concentration above 3 M in carbon-black gas-diffusion electrodes based on acetylene black A437-E or meso-structured carbon CMK-3 in cells-electrolyzers of different design and its use in preparation of active oxygen forms with different oxidation activity allows the

oxidation processes of different depth to be carried out, while the use of different modes of electrolysis (paired electrolysis) makes it possible to carry out this process with the high efficiency. It deserves mention that the production of such solutions can be organized in the sites where they are used, for instance, in inaccessible sufficiently electrified territories from technological oxygen and also from air oxygen with electrolysis characteristics lower by ~25–30%. These results can be used in selecting the most reasonable version of the use of hydrogen peroxide solutions electrogenerated from oxygen in solving concrete problems.

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#### CONFLICT OF INTERESTS

The authors declare the absence of any conflict of interests.

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