

STUDY OF DESTRUCTION PROCESSES OF SYNTHETIC SURFACE-ACTIVE SUBSTANCES (SURFACTANTS) IN BARRIER DISCHARGE

V.I. Grinevich*, A.A. Gushchin, T.V. Izvekova, V.Y. Shulyk

Ivanovo State University of Chemistry and Technology

Phone/fax: +7 (4932) 416693

Email: grin@isuct.ru

Abstract: Kinetic data on degradation of aqueous solutions of surfactants in the plasma of barrier discharge are presented. The possible mechanism of proceeding processes is offered and considered. It is shown that the treatment in a barrier discharge results in decomposition efficiency of 95%. It is established that the main product of degradation are carboxylic acids.

Keywords: water, barrier plasma discharge, pollutants, surfactants

1. Introduction

A pollution of natural waters is one of the global environmental problems. Also, the problem becomes aggravated that the world enters an era of deficiency of pure water. This is the problem for 40% of world population. And it will be the problem for the 60% of population on keeping this rate. Situation aggravates by a constant increase in technogenic loading at natural sources of water. Therefore, the problem of providing of the population with qualitative drinking water has been recognized as one of priority at last session of National Security Council.

Considerable part of the anthropogenic loading on superficial water objects falls on the sewage containing synthetic surface-active substances which are a part of all domestic and the majority of industrial wastewater. Thereby 95-98 % of total applied in our country detergents is the synthetic washing-up liquids manufactured by the industry, both anionic and nonionic detergent agents on their basis which, as a rule, are characterized by low biological degradability and owing to the chemical nature have essential negative influence on water objects. A stability of surfactants to the biochemical oxidation is the cause of their accumulation in water objects especially in the bottom sediments, which in turn leads to a decrease in self-purification capacity of natural waters and creates the risk of secondary contamination of water bodies and watercourses. Therefore the aim of this study was to investigate the processes of destruction of aqueous solutions of surfactants in a dielectric barrier discharge.

2. Experimental part

The object of investigation was a sulfonol aqueous solution (sodium salt alkylbenzolsulfoacid) ($C_{12}N_{25}S_6N_4SO_3Na$). Experiment was carry out on the set-up as the basic element of which was a plasma-chemical reactor (Fig. 1). The outer tube of the reactor was made from molybdenum glass. For feeding plasma forming gas and the removing gaseous products in a glass reactor tube (insulator) were welded two sockets. A charge device was tightly closed by covers made from PTFE, the center of which was fixed with non-isolated electrode made from aluminum alloy. It was contained a hole with the depth of 50 mm, for passing treated solution (the object of research) coming from the tank directly on a layer of porous hydrophilic material (fiberglass) by 1 mm of thickness covering the central electrode.

The extraction of purified solution was carried out through the hole located at the bottom of the electrode. Flow rate of solution ranged from 0.02 to 2 mL/s. In case of increase in consumption of water containing a pollutant, there was malfunction of a film mode of fluid flow partial filling by solution of reactor volume and consequently the burnout barrier discharge.

The barrier discharge was excited by high-voltage transformer, the value of the variable (current at 50 Hz) voltage between the electrodes (U) was varied within the limits of 5 ÷ 20 kV. The control of voltages was carried out with a voltmeter. The length of the discharge zone was 120 mm. As the carrier gas the technical oxygen was used the flow rate of which was varied from 1.1 to 5.3 cm³/s. A residence time (τ_l) of the treated solution with the discharge zone was determined as follows

$$\tau_l = \frac{\pi \cdot D \cdot h \cdot l}{Q}$$

where l - length of the discharge zone, m;

Q - flow rate, m³/s;

D - diameter of the inner electrode, m;

h - thickness of the liquid layer, m.

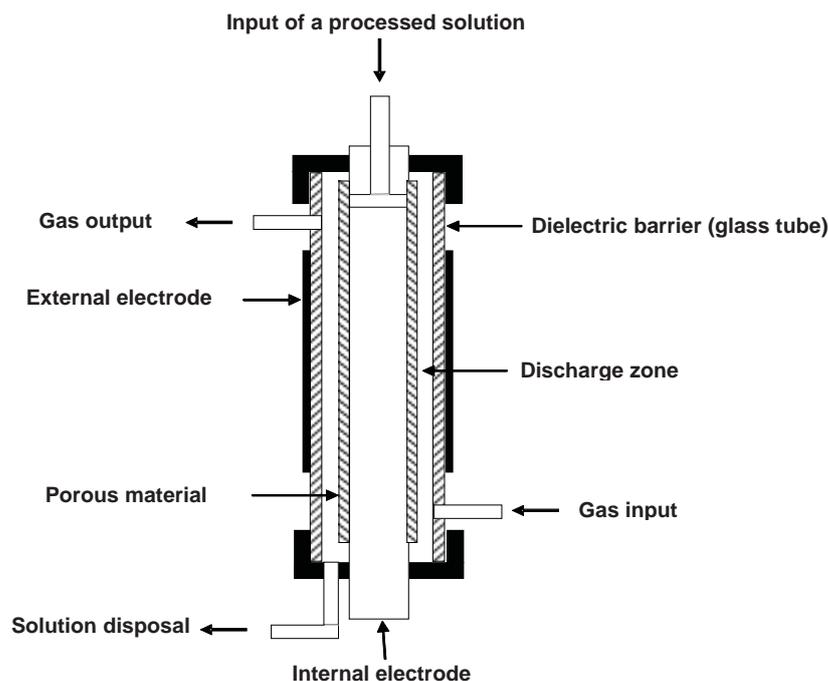


Fig. 1. An element of the reactor with a coaxial arrangement of electrodes.

The determination of the sulfonol concentration and formaldehyde in aqueous solution was based on the fluorescence method using fluorometer "Fluorat-02-3M" [1].

Monobasic carboxylic acids were determined spectrophotometrically (spectrophotometer KFK-2MP, Russia). The method is based on the color reaction of the compounds with m-vanadate of ammonium [2].

The determination of carbon dioxide (converted to bicarbonate ion) in water was carried out potentiometrically [3]. The value of the pH of the solution before and after treatment was determined by ionometer IPL-311.

The method for determination of free CO₂ in the gas phase is based on the conversion of barium carbonate into a soluble chloride, after the absorption of carbon dioxide with cold ammonia solution of barium chloride (5 g BaCl₂·2 H₂O and 27.5 ml of 25% NH₄OH in 100 ml of solution) [4].

Measurements of ozone in gaseous and liquid phases was accomplished by the method of absorption spectroscopy - on the absorption of light at $\lambda=253,7$ nm attributable to the maximum of the photoabsorption cross section O₃ ($\sigma=7,8 \cdot 10^{-18}$ cm² [5]). Ozone concentration was calculated from the expression:

$$N_{O_3} = \frac{\ln(I_0 / I)}{\sigma \cdot l}, \text{ cm}^{-3},$$

where I_0 - initial intensity of the line Hg resonance without ozone, rel. units.;

I - then the same, but at ozone presence rel. units.;

σ - Photoabsorption cross section, cm²;

l - length of a cell from 5.9 cm - in the case of measuring the concentration of O₃ in the gas phase or 0.999 cm - in the case of measuring the concentration of O₃ dissolved in an aqueous solution

$$C_{O_3} = \frac{M_{O_3} \cdot N_{O_3} \cdot 10^9}{N_A}, \text{ mg/m}^3,$$

where M_{O_3} - molecular weight of ozone (48 g/mol), and N_A - Avagadro number ($6,02 \cdot 10^{23}$ mol⁻¹).

The efficiency of decomposition surfactants were determined by the formula:

$$\alpha = \frac{C_i - C_f}{C_i}, \%,$$

where C_i, C_f - the concentration of phenol before and after treatment, respectively, mg·l⁻¹.

Figure 2 shows the decomposition kinetics of surfactants dissolved in the water under the impact of a barrier discharge. From the presented data it follows that degradation of surfactants is described by the reaction of pseudo-first order. The experimental data show that the decrease in flow of model solution, and, consequently, an increase in residence time of the treated liquid with the discharge zone influences on the degree of degradation of surfactants. So

the increase in residence time of a liquid with a discharge zone in the 3-fold (from 1.7 to 5.4 seconds) resulted in the decrease in concentration of the pollutant in solution in an average of 5 times.

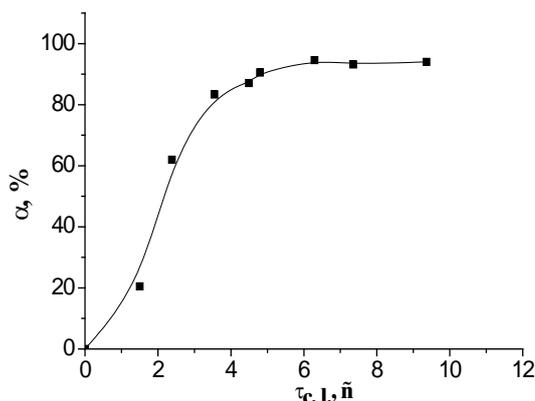


Fig 2. The degree of decomposition of the surfactants in the solution vs the residence time of the liquid with the zone of discharge.

Figure 3 shows the kinetic dependences of the concentration of the pollutant – surfactant and primary oxidizing agent - ozone in a model solution at processing. It is known [6], that with increasing the power, whose magnitude is directly proportional to the applied, the output of active particles involved in chemical processes is increased, therefore, the efficiency and expansion of surfactants in aqueous solutions, was to be increased as observed during the experiments.

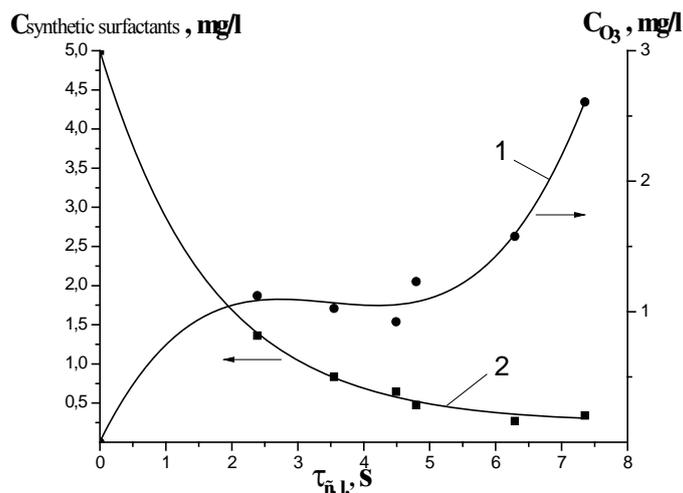


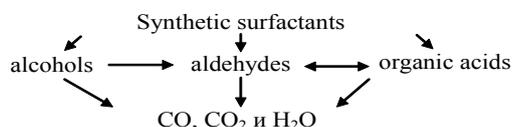
Fig 3. The change in concentration of ozone (1) and the synthetic surfactants (2) in a solution vs the residence time of the solution with the zone of discharge.

The dependence (Fig. 3) suggests that at short residence times there is a high consumption of dissolved ozone on the oxidation of synthetic surfactants (the initial part of the curve from 0 to 2.5 s). Later, with increasing time of residence rate of degradation falls, and runs a stationary process of oxidation (the smooth decrease in concentration of synthetic surfactants and the steady-state concentration of ozone at exposure time range of 2.5 - 5.6 s). At achievement of the maximum degrees of decomposition of synthetic surfactants, a concentration of ozone in water is increased (5.6 - 7.6 s). Hence, it is possible to assume that at times of contact more than about 6.2 ozone starts to participate in oxidation processes, both with a pollutant itself, and products of its decomposition (such as carboxylic acids and aldehydes), therefore the oxidation process does not proceed completely to CO_2 and H_2O . It agrees with experimental data on determination of the final and intermediate products of oxidation.

According to the stoichiometric equation for the complete oxidation of one molecule of sulfonol it needs 16 molecules of O_3 . Therefore, the complete oxidation of 14 mmol of sulfonol requires 224 mmol of O_3 . Maximum ozone concentration in the liquid phase, which is observed during the experiments was 52 mmol/L. Consequently the existing O_3 in these experiments is not sufficient for complete oxidation of synthetic surfactants (4.3 times the stoichiometric ratio). From experimental data follows that the maximum flow rate of ozone is observed in the initial period of treatment

and approximately 70% of the incoming ozone in the reactor. Thus, practically all ozone is consumed in the oxidation of synthetic surfactants and its degradation products. Straight in the range of residence time of 2.5 s to 5.6 s a maximum rate of oxidation of synthetic surfactants is observed (which is confirmed by the kinetic curves of oxidation of synthetic surfactants (Fig. 3).)

A model scheme of the process of oxidation of synthetic surfactants in the barrier discharge reactor can be represented in the following:



No alcohols in the processing of these compounds within the sensitivity of the measurement methods have been found. In fig. 4 the kinetics of formation of monobasic carboxylic acids (acetic acid), carbon dioxide and formaldehyde is presented in terms of carbon. The experimental data indicate that the kinetics of accumulation of carboxylic acids, as well as the kinetics of accumulation of carbon dioxide and formaldehyde was described by a curve with saturation. This suggests that carboxylic acid and formaldehyde, along with carbon dioxide, are the final products of oxidation of surfactants.

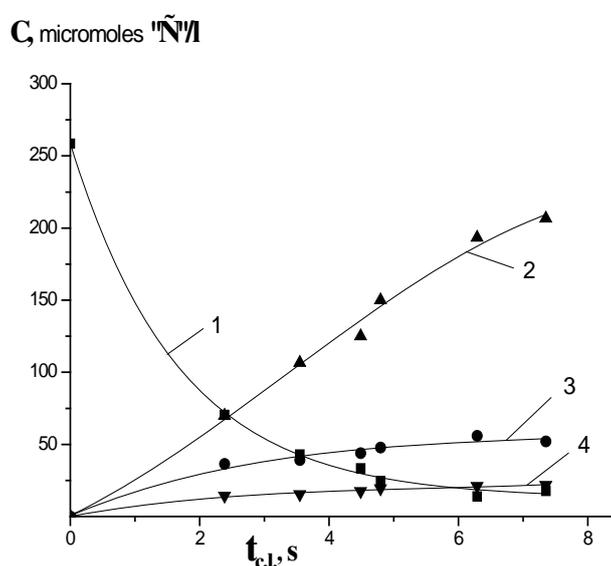


Fig. 4. Dependence of synthetic surfactants concentrations (1), carboxylic acids (2), the dioxide of carbon (3) and formaldehyde (4) in terms on carbon from the time of residence.

Complete chemical oxidation of organic compounds should proceed with the formation of carbon dioxide and water. Formation of CO_2 in the system depends on the pH. Under the conditions of the experiment (pH value of the solution after treatment in barrier discharge was 4.5) the carbonate system in solution was presented in the form of gaseous CO_2 [7].

Experiments have shown that the increase in processing time of model solution the value of the CO_2 concentration is increased, indicating the increase in the completeness of the destruction of organic compounds presented in the treated water. With increasing the processing time in 5 times the concentration of CO_2 has increased 1.7 times. While reducing the concentration of surfactants in 2 times. Maximum yield of carbon dioxide in the gas phase was 2.7 mg/L.

The maximum concentration of carboxylic acid was 6.2 mg/l (207 mol 'C' /L), the maximum CO_2 concentration was 2.3 mg /L (52.1 mol 'C' /L), and a maximal concentration of formaldehyde under study was 0.651 mg/L (21.7 mol 'C'/L). We can conclude that the main product of decomposition of sulfonol in the barrier discharge reactor under study, are monobasic carboxylic acids. The reliability of our data is based on the fact that the average convergence of the material balance on carbon in this case is 85%.

As it can be seen from the experimental data, we did not reach 100% destruction of organic compounds (maximum degree of decomposition was about 95%). This result can be explained by the fact that the solution contains an insufficient quantity of active particles, which are responsible for the oxidation of organic compounds. Results of experiments showed that the barrier discharge is effective for destruction of organic pollutants (for example, surfactants) in model solutions. However, at the transition from model experiments to the conditions of real systems it can be expected the

change in the efficiency of oxidative processes because of the increase in the number of reversible reactions due to a more complex component composition.

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