Application of catalytic destruction methods in wastewater treatment

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Abstract. The objective of the present work is to study the process of removing wastewater pollutants of peroxide nature chemical compounds by catalytic destruction method. To achieve this the following tasks were solved: a) to study qualitative and quantitative composition of wastewater, as well as composition stability over time; b) to study the possibility of applying methods of peroxide catalytic destruction in the wastewater medium; c) to determine optimal conditions for peroxide catalytic destruction; d) to determine the possibility of such wastewater purification at biological treatment plants. As a result of the research, it was established that wastewater has a variable quantitative composition of pollutants both at the moment of their formation and over time, which significantly complicates selection of reagents for peroxide catalytic destruction. Optimal conditions for catalytic decomposition of peroxides in the wastewater medium were determined. Thermal decomposition of peroxide compounds in the presence of iron-ion catalyst - Fe(II) was studied. The proposed methods of peroxide destruction allow achieving a high degree treatment of wastewater from these components, and to use biological methods of decontamination in further post-treatment of effluents.

Keywords: destruction, wastewater, peroxides, catalyst, metals of variable valence, research.

1 Introduction

Currently, violation of ecological balances in the biosphere causes bringing up a number of complex and important issues related to environmental protection, which makes it necessary to raise requirements for water, soil and atmosphere protection [1-6]. Requirements for both the purity of wastewater discharged into reservoirs, and their size are growing.

The growing rate of industrial emissions from operating enterprises explains a high level of atmosphere, hydrosphere and lithosphere pollution. To maintain the standard level of possible environmental pollution, it is necessary to apply widely complex methods of processing and disposal of pollutants based on new approaches to proven methods of cleaning. Difficulties in solving wastewater treatment issues are undoubtedly related to the complexity and variability of the composition, as well as impressive economic costs of equipment and reagents [7-11]. The diversity of systems by chemical composition and formation conditions dictates the conduct of individual studies for each specific case. The multi-component composition of wastewater does not allow using standard water treatment technologies and requires a complex approach to treatment methods [12-17]. Wastewater discharged by enterprises into reservoirs or for flaring creates many environmental problems. Solution of the environmental protection problem by such methods becomes inadvisable, even – unacceptable, if to say outright. Stricter environmental regulations force the company to pay due attention to solving the problem of high-quality treatment of generated wastewater when it is discharged into natural reservoirs [18-20].
2 Materials and methods
Experimental studies were carried out on real wastewater from production of styrene and propylene oxide. The amount of peroxides in wastewater was determined by iodometric titration method. To determine the qualitative composition of peroxides in wastewater, we developed and applied a polarographic method. The pH value of effluents was determined by a pH meter.

The research was carried out on different samples of wastewater from the same production site of styrene and propylene oxide, which have different values of peroxide concentration and pH.

3 Results
Wastewater of a multi-component mixture is formed at the production of styrene and propylene oxide. Complexity of such wastewater treatment is connected with a high content of organic components and peroxide compounds, which prevent wastewater treatment at biological treatment plants [21]. In this regard, the composition of wastewater was studied (table 1). The data in table 1 show that the composition of both organic and peroxide components of wastewater samples is not constant. The studies showed unstable quantitative characteristics of the above components in wastewater samples taken from the same node of the technological production scheme at different times. Instability of the wastewater composition provides difficulties in treatment of such effluents by standard methods and requires an individual approach.

| № wastewater samples | Quantity of organic substances by COD, gO₂/l | Peroxide concentration, mol/l |
|----------------------|--------------------------------------------|-----------------------------|
| 1                    | 18,21                                      | 0,07                        |
| 2                    | 69,36                                      | 0,09                        |
| 3                    | 23,47                                      | 0,05                        |
| 4                    | 28,36                                      | 0,48                        |
| 5                    | 36,49                                      | 0,06                        |

To identify and determine the quantitative ratio of peroxide compounds in wastewater, we developed a polarographic method which analyses joint determination of organic and inorganic peroxides. Polarographic analysis made it possible to determine that the effluents contain hydrogen peroxide (H₂O₂) and ethylbenzene hydroperoxide (EBHP) in different molar ratios (table 2).

| № wastewater samples | Quantity of H₂O₂, mol | Quantity of H₂O₂, mol |
|----------------------|-----------------------|-----------------------|
| 1                    | 1                      | 3                     |
| 2                    | 1                      | 10                    |
| 3                    | 1                      | 4                     |
| 4                    | 1                      | 10                    |
| 5                    | 1                      | 2                     |
| 6                    | 1                      | 5                     |
| 7                    | 1                      | 10                    |
| 8                    | 1                      | 7                     |
| 9                    | 1                      | 9                     |
| 10                   | 1                      | 3                     |

Peroxides are highly active chemicals that have a detrimental effect on the active sludge in the biological wastewater treatment system. To avoid destructive effects on colonies of bacteria and protozoa in the active sludge, peroxide-containing effluents must be neutralized in local treatment conditions. Methods that are often used for wastewater treatment from peroxide compounds are
described in the References [1, 22]. The authors [23] point out that catalysts are used in peroxide decomposition reactions. Most often metals with variable valence are used as an agent in catalytic complexes. And these are iron ions to be most active in the processes that they catalyze. Samples of existing effluents of styrene and propylene oxide production with a high content of organic impurities and components of organic and inorganic peroxides with the content in the range of 0.04-0.52 mol/l were used in the experiment. Iron sulphate (FeSO$_4$) was used as a catalytic agent. At the beginning of the tests, at the first stage of the experimental study, we studied influence of the hydrogen pH value of the treated water medium on catalytic oxidation methods of peroxide components of effluents under normal temperatures and barometric pressure using iron in the catalytic complex. The analysis and processing of the obtained experimental data of the work first stage (figure 1) showed that peroxide compounds decompose most intensively in the medium where the hydrogen index of wastewater is pH =3 and pH =6.

![Figure 1. Peroxide decomposition schedule in wastewater medium.](image)

Analyzing the results of the experiment, it was found that the rate of decomposition of peroxide compounds in the medium with an increased pH level (pH=11) was very low. Inefficiency of decomposition of such compounds in an alkaline medium is justified by transition of an iron ion to the trivalent state, in particular to iron hydroxide Fe(OH)$_3$. Confirmation of this is the precipitation of reddish-brown color, which is a qualitative reaction to Fe$^{3+}$ ion.

Thus, having determined that the result of rapid decomposition of peroxide compounds by catalytic oxidation of such wastewater components is the highest in acidic and neutral mediums, subsequent studies were conducted on wastewater samples with pH=7 and pH=3. Based on these samples, we studied the influence of iron ions (Fe$^{2+}$) content in the catalytic complex on the degree of peroxide destruction.

The second stage of the experiment was performed with a sample of wastewater with pH=6, that is, in a neutral medium. In the course of the experiment, changes in the catalytic component content in the process of oxidation of effluent peroxide components were studied and analyzed. The main results of the experiments are shown in figure 2, from which we can see that the highest values of intensity level of peroxide decomposition under conditions of catalytic oxidation are found at the molar ratio of peroxide components and catalyst 1:1.

At the third stage of the research we studied the influence of iron ions (II) content on the level of catalytic oxidation of wastewater peroxide components under low pH value conditions (figure 3).
The experiment showed that in wastewater with a low hydrogen pH value (acidic medium), even with an insignificant content of the catalyst component (Fe²⁺), the level of peroxide decomposition can be within 98%, provided that their oxidation by the catalyst is not less than 30 minutes, which indicates that the catalytic activity of iron is significantly higher in an acidic medium.

The fourth stage of the experiment was to study the effect of temperature increase on the intensity of peroxide components oxidation of wastewater. This experiment was performed with a sample of effluents having an acidic reaction of the medium (pH=3). The results are shown in the table 3.

| Concentration of iron ions, mol/l | Temperature, °C | Time, min | Destruction degree, % |
|----------------------------------|-----------------|-----------|----------------------|
| 0,010                            | 25              | 5         | 8                    |
|                                  |                 | 10        | 10                   |
|                                  |                 | 30        | 11                   |
|                                  |                 | 60        | 20                   |
Various combinations of temperature and concentration of the catalyst were studied and tested in the experiments. The results showed that the catalyst is most active at high temperatures, as well as at high concentrations of iron ions and at a combination of high temperatures and high concentrations of the catalytic agent.

The experiments confirmed that the ratio of the catalyst concentration to peroxides should be 1:1 for effective wastewater treatment. In addition, the experiment indicated that temperature effects contribute to peroxide destruction. For example, at $70^\circ C$, a 10-minute temperature effect is sufficient for 100% decomposition degree.

4 Conclusions
1. The possibility of catalytic destruction of peroxides in the medium of wastewater and metals of variable valence was revealed.
2. The optimal pH value of the medium for catalytic destruction of peroxides in wastewater was experimentally determined, which is within the range of 3-7 pH.
3. Experiments established the effect of the ratio of catalyst concentration and peroxide compounds on destruction rate of the latter. The optimal concentration rate is 1:1.
4. Increasing the temperature of wastewater up to $70^\circ C$ leads to 100% peroxide decomposition within 10 minutes of temperature effect in the catalyst and wastewater medium.
5. Wastewater treated from peroxides by catalytic destruction can be sent for further treatment at biological decontamination plants.
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