Investigation of the ozone treatment effectiveness of urban wastewater containing biologically-resistant organic pollution

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Abstract. When developing the technology of using ozone for the subsequent purification of municipal wastewater from biologically resistant organic pollutants, it is important to determine the required ozone dose and the duration of oxidation. Post-treatment of wastewater after biological treatment is used, for example, for the destruction of biologically resistant textile dyes and surfactants. It is known that, for example, during the process of ozonation, decrease in color occurs earlier than the decomposition of the organic matter of the dyes. Therefore, the water treatment process is controlled by several indirect indicators, such as oxidation, total organic carbon, etc. It is difficult to determine the necessary dose of ozone for the decomposition of pollutants. We carried out the experimental studies and examined the material balance of the process of destruction of pollution by ozone. A method is proposed for measuring and calculating ozone consumption in the destruction of pollution in wastewater. According to the results of test ozonation of waste water, the dependence of ozone consumption on the processes of pollution destruction is built. The method allows to determine the required specific dose of ozone for the destruction of pollution and the duration of ozonation for equipment design.
1 Introduction

The ozone treatment technology is increasingly being used to purify drinking and municipal wastewater. The development of the effectiveness of technological methods and the adjustment of equipment operation require the availability of technological indicators describing the process of organic pollutants destruction.

Organic biologically resistant substances are characteristic contaminants of biologically treated municipal wastewater. These are substances with large molecules and consisting of cyclic groups interconnected by a double nitrogen bond (azo group) or a carbon bond. For example, surfactants and textile dyes come from sewage from the textile industry [1]. Removal of dyes, surfactants and other biologically persistent organic pollutants from wastewater is a difficult task when developing a purification technology [2].

Various methods of separation [3-5] and methods of destruction [6–9], including ozone [10, 11], are used at modern treatment plants to purify wastewater from biologically persistent organic pollutants. It has long been established that the process of decomposition of organic pollutants in water under the action of ozone occurs with the formation of intermediate products through a complex multistage mechanism [12, 13].

In this case, the bulk of the oxidized substances remain in water in the form of products of the first stages of destruction [14]. Because of this, the problem of choosing indicators for determination of the required dose of ozone in wastewater treatment arises. Therefore, there is the problem of selecting indicators for assessing the effectiveness of ozone use. In one of our works, we have shown that the evaluation of the effectiveness of the ozonation process, for such difficult-to-oxidize organic pollutants as dyes, to reduce the color of their solution is incorrect. It does not correspond to the destruction of the main mass of their substance to water. We have proposed the use of the indicator “chemical demand of ozone” (CDO₃) measured by the consumption of ozone in the process of destruction [15]. The objective of this work was to find an analytical description of the indicator “chemical demand of ozone”.

To solve it, we carried out experimental studies in a laboratory setting, proposed indicators for describing the ozonation process, and developed a technique for measuring and calculating them.

2 Materials and Methods
Aqueous dye solutions such as: primary dis-azo dyes — “straight scarlet” and “straight blue”, mono-azo dye — “straight blue”, vinyl sulfonic dye — “active red-violet”, dichlorotrisin dye - “active yellow” were used for laboratory studies. To study the degradation of anionic surfactants substances, aqueous solutions of undecylbenzenesulfonate (UBS), dodecylbenzenesulfonate (DBS) and tetrapropylbenzenesulfonate sodium (TPBS) were taken. The studies were carried out both on individual substances and on their mixtures with the same total concentration. Chosen for research organic compounds are rather slowly decomposed by the action of ozone (the half-life of dyes is 1 ... 8 minutes, the surfactant is 5...20 minutes), that is convenient for obtaining and analyzing the kinetic characteristics of the process.

The scheme of the laboratory experimental setup is shown in Fig.1.

Figure 1. Scheme of the experimental setup: 1 - compressor; 2 - unit for cleaning and drying air; 3 - ozone generator; 4, 7 - ozone concentration analyzers at the inlet and outlet of the reactor; 5 - reactor; 6 - sampler; 8 - ozone concentration recorder at the reactor exit; 9 - absorber with KJ solution; 10 - catalytic destructor of ozone.

A bubbling column was used as the reactor of the laboratory unit. The ozone-air mixture was supplied with a flow rate of 0.3 l / minute. The concentration of ozone in the ozone-air mixture at the entrance to the column was constant - 6 mg / l. To determine the mass of ozone leaving the reactor, an absorber with KJ solution was used.
The concentrations of the studied substances in water samples taken from the reactor and the ozone content in the gas were measured using the appropriate standard methods [18, 19]. When using this equipment, we were able to obtain the kinetic dependences of the change in the concentration of the pollutants in question in the treated water and the kinetic dependences of the concentration of ozone in the gas leaving the reactor. The total mass of ozone not consumed in and leaving the reactor was also measured.

3 Discussion

Analysis of the ozonation process data for solutions containing dyes and surfactants showed that the change in the concentration of substances proceeds according to the first-order kinetic equation.

\[ \dot{N}x_t = Cx_0 \cdot e^{-k_1t} \]  

where \( Cx_t \) is the current concentration of the substance being oxidized; \( Cx_0 \) is the initial concentration of the oxidized substance; \( k_1 \) is the reaction rate constant of pollutant consumption; \( t \) - is the ozonation period. The equation in question does not include ozone concentration. Experiments were performed using an excess amount of oxidizing agent.

According to the data obtained during the experiments, the parameters of the research process were determined using kinetic equations.

Table 1. The destruction parameters of the studied organic substances in the process of ozonation.

| Substance     | Initial concentration, mg/l | Constant reaction rates, \( k_1 \cdot 10^3 \), sec\(^{-1} \) | The period of reducing the concentration by half, sec. | The period of decomposition of the substance on 95%, sec | Ozone consumption in the decay of a substance 95%, mg/l |
|---------------|-----------------------------|--------------------------------------------------------|------------------------------------------------------|------------------------------------------------------|------------------------------------------------------|
| Dyes:         |                             |                                                        |                                                      |                                                      |                                                      |
| Straight blue | 39,1                        | 1,65                                                   | 480                                                  | 1330                                                 | 78,2                                                 |
| Straight scarlet | 35,0                    | 1,82                                                   | 330                                                  | 1230                                                 | 73,5                                                 |
| Straight blue | 39,0                        | 3,50                                                   | 210                                                  | 900                                                  | 62,1                                                 |
| Active        | 38,5                        | 11,67                                                  | 50                                                   | 270                                                  | 21,5                                                 |
The analysis of experimental data on the ozone content in the spent ozone-air mixture showed that the dependence of the change in ozone concentration at the reactor exit can be written by an equation similar in structure to the chemical equation of the first order:

\[
\frac{\Delta C_z}{C_{zen}} = (C_{zen} - \Delta C_z - \Delta C_z) (1 - e^{-k_z t}) + C_{z_s},
\]

where \( C_{zen} \) is the ozone concentration in the gas leaving the reactor; \( C_{zen} \) is the concentration of ozone in the ozone-air mixture which is fed to the reactor; \( \Delta C_z \) - reduction of ozone concentration during self-decomposition without participation in chemical reactions; \( C_{z_s} \) - the initial concentration of ozone in the gas leaving the reactor; \( k_z \) is the ozone consumption reaction rate constant; \( t \) is the period of the ozonation process.

Graphic interpretation of the described values is shown in Fig. 2.

![Figure 2](image)

**Figure 2.** Dependence of ozone concentration in the gas leaving the reactor on the ozonation period.
The presence of the initial $C_{z_0}$ concentration is due to the accumulation of ozone in the treated water to create the necessary value of the redox potential of the system.

Many researchers in their works [12, 16, 17] to describe the process of ozonation use the indicator “specific dose of ozone”, which is numerically equal to the mass of ozone fed to the reactor, referred to per unit mass of the oxidized substance. It was noted that the determination of the concentration of oxidizable organic substances in the process of destruction by their individual characteristics does not reflect the presence of organic matter in general and the staging of the processes taking place, but shows the passage through only the first stages of destruction, in which substances lose their individual characteristics. For example, discoloration of water occurs. However, the oxidation process does not end there, but proceeds further until the formation of the final oxidation products or ozone-resistant compounds [19-21].

Based on our study of the material balance of the ozonation process, indicators have been established that best characterize the destruction of pollution and ozone consumption, such as: specific ozone consumption (see paper [15]) and chemical demand of ozone (CDO₃) $O_{z_0}$ ozO₃ / l.

The value of the indicator CDO₃ corresponds to the maximum mass of ozone, which can react with pollution, in 1 liter of treated water. In this case, the reaction products do not react with ozone [15]. In the process of water ozonation, this indicator will decrease in proportion to the mass of ozone, which reacted with pollution.

$$O_{z_0} = (M_{z_0}^{\text{max}} - M_{z_0}) / W$$

where $M_{z_0}^{\text{max}}$ is the maximum mass of ozone necessary for the oxidation of pollution to resistant products; $M_{z_0}$ - ozone mass reacted with pollution for a certain period of time; $W$ is the volume of treated water. Analysis of experimental data and their mathematical description allowed us to obtain equations that describe these quantities.

The mass of ozone reacted with pollution ($M_{z_0}$) is:

$$M_{z_0} = \frac{1}{k_2} q_z (C_{z_0} - \Delta N_{z_0} - \tilde{N}_{z_0})(1 - e^{-k_2 t})$$

The maximum mass of ozone ($M_{z_0}^{\text{max}}$), necessary for the oxidation of pollution to resistant products, is equal to:

$$M_{z_0}^{\text{max}} = \frac{1}{k_2} q_z (C_{z_0} - \Delta N_{z_0} - \tilde{N}_{z_0})$$
where $C_{ze}$ and $C_{zex}$ is the ozone concentration in the ozone-air mixture fed to the reactor and the gas leaving the reactor, respectively; $\Delta C_z$ - reduction of ozone concentration during self-decomposition without participation in chemical reactions; $C_{z_0}$ - the initial concentration of ozone in the gas leaving the reactor; $k_2$ is the ozone consumption reaction rate constant; $t$ is the duration of the ozonation process; $q_z$ is the volume flow rate of the ozone-air mixture.

A technique has been developed to experimentally determine the “chemical demand of ozone” indicator and the value of “specific ozone consumption” during the oxidation of organic substances to a certain degree of decomposition used to assess the feasibility and effectiveness of using ozonation for the destruction of pollution.

4 Conclusion

The use of the indicator "chemical demand of ozone" for technological calculations has also been tested and can be recommended using for the treatment of industrial wastewater containing dyes, organic detergents and petroleum products in order to reduce the amount of biologically resistant organic compounds.

The indicator "chemical demand of ozone" proposed by us for technological calculation has the following advantages:
- The indicator can be applied to describe the process of ozonation of both organic and mineral pollution;
- Measurement of the indicator does not require determination of the composition of wastewater, since it can be determined from the dependence of the change in the concentration of ozone in the spent ozone-air mixture;
- The indicator allows you to assess the feasibility of using ozone for the treatment of specific types of wastewater;
- When used in technological calculations of the considered indicator of CDO$_3$, it is possible to calculate the required amount of ozone in order to decompose the substance to a given level.

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