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Investigation of the biologically-resistant organic pollution destruction process in wastewater by ozone

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Abstract. During the development of technology of ozone usage for wastewater treatment from organic pollution, it is important to be able to determine the required dose of ozone and the duration of oxidation. Ozonation is used in combination with other methods of water treatment, so it is important to determine the stage at which ozonation is used. Ozone can be used for purification of urban wastewater for the destruction of surfactants and textile dyes. These substances are often biologically resistant and cannot be removed by biological treatment methods. Decomposition of organic matter of dyes and surfactants occurs not as quickly as decrease in color. In such cases, the purification process is usually controlled by indicators such as total organic carbon content, oxidation, COD, etc. It can be difficult to determine the dose of ozone, which is necessary for the destruction of pollution. We examined the material balance of the process of destruction of some contaminants and conducted experimental studies to verify it. The technique is proposed for calculating the required dose of ozone for the destruction of dyes and surfactants in wastewater with a small number of measurements. The method makes it possible to calculate the specific dose of ozone and necessary ozonation period for destruction of pollution in wastewater.

1. Introduction

The development of new effective methods of water purification and adjustment of equipment operation requires indicators describing the decomposition process of complex organic pollution by ozone.

Biologically resistant substances, such as textile dyes and surfactants, enter the wastewater from textile industry [1]. They are poorly removed from urban wastewater at biological treatment facilities and go into water reservoirs. Removing contaminants of this type is a difficult task during creating and modernizing treatment facilities [2]. Generally, decomposition methods [3–6] and separation methods [7-9] are used. Ozonation is used as one of the destruction methods [10-12].

It is known that the destruction of organic substances in water under the action of ozone occurs with the generation of intermediate products by a complex multi-stage processes [13, 14]. Most of the contaminants remain in the water in the form of products of the first stages of destruction [15, 16]. Features and properties according to which the initial contaminants are identified may be lost at the initial stages of destruction. To assess the effectiveness of ozone usage, an indicator that is not associated with the initial identification signs of a pollutant is needed. In one of our researches, it was

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shown that for such difficultly oxidized organic substances as dyes, the use of the intensity of the color of water as an identification feature is not correct. The decrease in color does not correspond to the degree of destruction of the organic matter of the dye in water [17].

The aim of this work was to continue research and find an analytical description for the indicator "chemical demand of ozone". We have finalized the laboratory setup and conducted experimental studies. Indicators and a methodology for their measurement were proposed in order to describe the destruction process.

2. Materials and methods

The studies were carried out both on individual organic substances and on their mixtures with the same total concentration. Aqueous solutions of organic dyes, such as: dis-azo dyes primary — “red straight” and “green straight”, mono-azo dye — “violet straight”, vinyl sulfonic dye — “red-violet active”, dichlorotrisin dye - “orange active” were used us for laboratory studies. In order to study the degradation surfactants substances, aqueous solutions of alkylbenzenesulfonate (ABSK), tetrapropylbenzenesulfonate (TPBS), undecylbenzenesulfonate (UBS), sulfanol (SF), sodium laurylsulfate (SLS) and auxiliary substance OP-10 were taken. These organic compounds decompose slowly under the influence of ozone. The concentration of dyes is reduced by 50% in 1 ... 9 minutes, concentration of surfactants is reduced by 50% - in 4 ... 20 minutes. This is convenient for measuring and analyzing the kinetic characteristics of the process.

The scheme of the experimental equipment is shown in Figure 1.

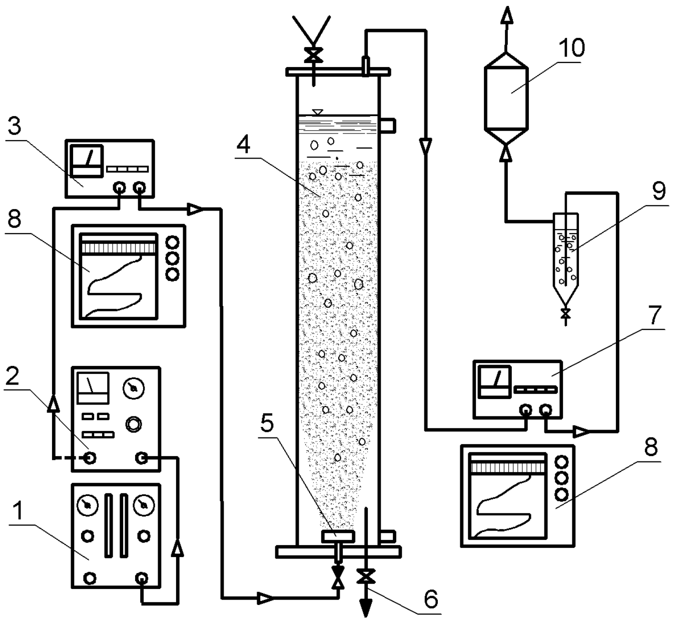

Figure 1. Schematic of experimental equipment: 1 - unit for cleaning and drying air; 2 - ozone generator; 3 - ozone concentration analyzer of gas in the inlet of the contactor; 4 – ozone contactor; 5 - small-bubble ozone dispersant; 6 - sampler; 7 - ozone concentration analyzer of the gas at the outlet; 8 – on-line ozone monitors; 9 – KI wash bottle; 10 - catalytic destructor of ozone.

A bubble column 1.0 meter high was used as a contactor of the experimental equipment. The ozone contactor was flowing in the gas phase and non-flowing in the liquid phase. The concentration of ozone in the ozone-air mixture supplied to the reactor was constant – about 10 mg / l. The ozone-air mixture was supplied to a bubble column with a flow rate of 0.5 l / min. We used an absorber with a KI solution to measure the mass of ozone going out from reactor.

We used standard methodologies for measuring the concentration of the researching substances in water samples and ozone content in gas [20, 21]. Our experimental equipment made it possible to obtain kinetic dependences of the change in concentration of the studied organic substances in water and the dependence of the change in concentration of ozone in the gas leaving the reactor.

3. Discussion

The experiments confirmed that the change in the concentrations of the tested organic substances in the ozonation process proceeds according to the first-order kinetic equation of the chemical reaction:

$$Cx_t = Cx_0 \cdot e^{-k_1 t} \tag{1}$$

where Cx_t is the current concentration of the organic substance being oxidized; Cx_0 - the initial concentration of the oxidized organic substance; k_1 - the reaction rate consumption constant of the studied substances; t - the ozonation period. The experiments were carried out using an excess amount of an oxidizing agent; therefore, the ozone concentration is not included in this equation.

Table 1. Values of the concentration reduction process parameters for the tested organic substances during ozonation according to the first-order kinetic equation.

Substance	Initial substance concentration, (mg /l)	Reaction rates constant, $k_1 .10^3$ (s^{-1})	The period of reducing concentration the substance by 50% (s)	The period of reducing concentration the substance by 95% (s)	Ozone consumption in the decay of the substance by 95% (mg/l)
Dyes:					
Green straight	40.0	1.75	470	1430	82.2
Red straight	35.0	1.69	390	1340	89.5
Violet straight	40.0	3.75	185	750	58.1
Orange active	40.0	12.70	48	250	20.5
Red-violet active	42.0	10.20	67	450	38.7
Wastewater cont. dyes	40.0	9.89	68	512	41.8
Surfactants:					
UBS	24.0	1.25	1325	3350	586
ABSK	37.0	1.20	670	3800	327
TPBS	34.0	1.33	267	3100	254
SF	35.0	2.25	180	2700	124
SLS	25.0	1.67	286	3100	380
OP-10	25.0	1.17	718	4100	455
Wastewater cont. surf.	28.0	1.48	850	3700	496

The analysis of experimental data proved that the dependence of the ozone change concentration at the outlet of the reactor can be written by an equation:

$$C_{ex} = (C_{en} - C_R - C_s)(1 - e^{-k_2 t}) + C_s \quad , \tag{2}$$

where C_{ex} is the concentration of ozone in gas after reactor; C_{en} - the concentration of ozone in front of the reactor; C_R - decrease in ozone concentration due to self-decomposition; C_s – the concentration of ozone slipping through the reactor due to its low height; k_2 - ozone consumption reaction rate constant; t - period of the ozonation process.

A graphical representation of the variables used in equation (2) is shown in Figure 2.

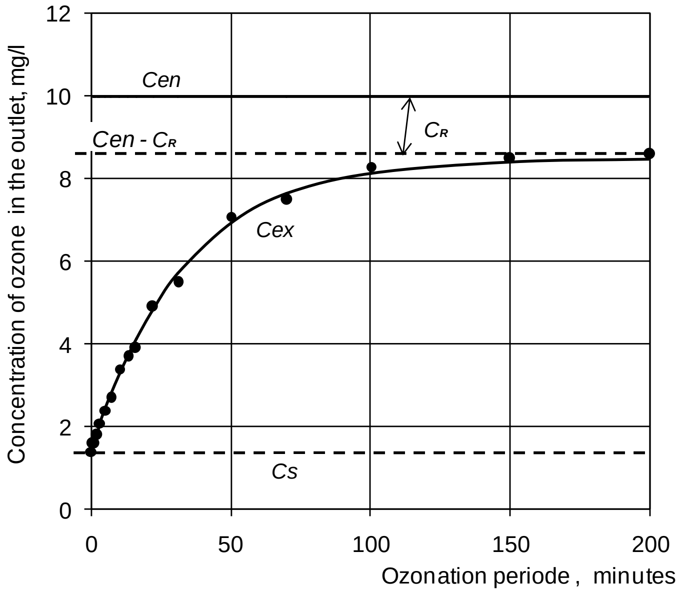

Figure 2. Dependence of ozone concentration in an ozone contactor outlet gas leaving on the ozonation period.

In works of researchers of ozonation processes [13, 18, 19] an indicator that is equal to the ratio of the mass of ozone supplied to the mass of oxidizable substance is often used.

The concentration of oxidizable substances and their mass are determined by individual characteristics, but this does not correspond to the amount of organic matter as a whole and does not reflect the staged nature of the ongoing processes. We obtained experimental data about changes in ozone concentration in the ozone-air mixture stream at the outlet of the contactor. The calculated values of the constants of the equations are shown in Table 2.

Table 2. Parameter values for describing changes in ozone concentration at the gas outlet of contact reactor

Substance	Ozone concentration in front of the reactor, C_{en} (mg/l)	Ozone concentration decrease due to self-decomposition, C_R (mg/l)	Concentration of ozone which slipping through the reactor, C_s (mg/l)	Ozone consumption reaction rate constant, $k_2.10^3$ (s^{-1})
Dyes:				
Green straight	10.0	1.6	0.8	0.21
Red straight	10.4	1.5	1.5	0.40
Violet straight	10.1	1.6	1.1	0.27
Orange active	9.8	1.5	1.45	0.50
Red-violet active	10.1	1.7	0.6	1.00
Wastewater cont. dyes	10.1	1.6	1.4	0.51
Surfactants:				
UBS	9.8	1.7	2.1	0.12
ABSK	9.8	1.8	2.3	0.10
TPBS	10.1	1.9	1.8	0.14
SF	10.0	1.7	1.8	0.15
SLS	9.9	1.5	2.0	0.13
OP-10	10.0	1.8	2.5	0.09
Wastewater cont. surf.	9.9	2.0	2.2	0.11

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Only the first stage of destruction is taken into account, in which substances lose the individual characteristics. Determining the concentration of dyes by the intensity of the color of water. Moreover, the destruction process does not end, but proceeds until the formation of products that do not react with ozone and reactions with active radicals [21, 22].

The conducted made it possible to use a new indicator to characterize the ozonation process - the chemical demand of ozone (CDO_3) *Oz*, mgO_3/l. This indicator reflects the value of the mass of ozone, which can react with organic and inorganic pollutants, referred to 1 liter of ozonated water.

The value of the CDO_3 corresponds to the limit mass of ozone, which can react with organic and inorganic pollutions, in one liter of ozonated water [17].

During the process of wastewater ozonation with ozone, this indicator will depend on the period of ozonation.

$$Oz = (M_r^{\max} - M_r)/V, \tag{3}$$

where $M_r^{\max}$ is the necessary ozone mass for the oxidation of contaminants to persistent products; M_r - the mass of ozone reacted with pollution over a certain period of time; V - the volume of treated water. Analysis of the experimental data performed by us let us to obtain the equations that describe the proposed quantities.

The ozone mass (M_r) reacted with pollutions for a set time period (t) is:

$$M_r = \frac{1}{k_2} q_z (C_{en} - C_R - C_s)(1 - e^{-k_2 t}). \tag{4}$$

The limit ozone mass ($Mz_r^{\max}$), necessary for the oxidation of pollutants to resistant products, is equal to:

$$M_r^{\max} = \frac{1}{k_2} q_z (C_{en} - C_R - C_s), \tag{5}$$

where C_{en} is the ozone concentration in the supplied ozone-air mixture; C_R - decrease in ozone concentration during self-decomposition; C_s - the concentration of ozone slipping through the reactor due to its low height; k_2 - the ozone consumption reaction rate constant; t - period of the process; q_z - volumetric flow rate of the ozone-air mixture.

The use of the CDO_3 indicator in technological calculations of facilities was tested using the ozonation method for the treatment of industrial wastewater from a textile industry containing dyes, organic detergents and oil products, as well as for the post-treatment of urban wastewater in order to reduce the mass of biologically resistant organic substances.

4. Conclusion

According to the results of researches, a methodology for experimental measurement of the indicator "chemical demand of ozone" during the oxidation of organic and inorganic substances to a certain degree of decay has been developed.

The indicator "chemical demand of ozone" can be used for description of the ozonation process of various types of wastewater pollution, regardless of their origin, including biologically resistant organic pollution.

When performing an indicator measurement, there is no need to determine the composition of wastewater. The indicator can be determined by the change in the ozone concentration in the spent ozone-air mixture over a certain period of time.

During the performing technological calculations of water treatment facilities, the use of the CDO_3 indicator allows us to calculate the required period of water treatment and the amount of ozone in order to destroy pollution to the required level.

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