

# The Estimation Method of the Ozone Treatment Effectiveness of Wastewater Containing Dyes

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**Abstract.** One of the applications of ozone for wastewater treatment is the destruction of difficult-oxidizing organic contaminants, including dyes. An important stage of development of water purification technology is the determination of the required degree of pollution destruction, effective doses of ozone and the period of water treatment. For example, in some cases when the dyes are degraded in textile sewage, the color reduction occurs with a slight decomposition of the organic substance of the dyes. The purification process is controlled by several indirect indicators, such as oxidizability, total organic carbon content, etc. We have conducted experimental researches and have studied the material balance of the ozonation process for wastewater containing dyes. Generalized method for determination of the consumption of ozone in the oxidation of contaminants in sewage waters and the technological indicator "chemical demand of ozone" are proposed. The method is quite universal and allows, while carrying out trial ozonation of water, to obtain dependence of ozone consumption for the processes of pollution destruction and determine the required specific dose of ozone.

## 1 Introduction

Usage of ozone as a strong oxidant is increasingly used in the technology of purification of industrial wastewater that contain artificial dyes. To develop water purification technology and design equipment, and to assess of the effectiveness of technological methods and equipment, it is necessary to have technological indicators describing the process of destruction of contaminants and ozone consumption.

The main volumes of sewage containing dyes are formed in the enterprise of textile industry. Many industrial dyes are substances with large molecules consisting of cyclic groups connected by a double nitrogen bond (azogroup) or a carbon bond. Such organic substances possess low biodegradability [1]. Reducing the color of waste water, and removing of other biologically non-degradable organic contaminants is a complex technological challenge [2].

Various separation methods [3, 4], destructive methods [5, 6], including ozonation [7, 8] can be used to purify water from biologically persistent organic contaminants. At the first

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stages of interaction with ozone, direct reactions with discontinuity of multiple bonds occur. Then complex radical-chain reactions proceed, up to the formation of inorganic compounds. It has long been established that the process of oxidation of water impurities by ozone proceeds through a complex multistage mechanism with the formation of intermediate products [9]. The properties by which the initial contaminations are identified by standard analytical methods can be already lost in the first stages of oxidation. In this case, the bulk of the oxidized substances remain in the water as products of the first stages of destruction [10]. Because of this, the problem of choosing indicators for determination of the required dose of ozone in wastewater treatment arises. In order to solve it, we carried out experimental studies and identified representative indicators for assessment of the effectiveness of the ozonation process.

## 2 Materials and Methods

For observation after the course of the decomposition of organic compounds and estimation of the depth of their destruction, it is suggested to compare the mass consumption of the incoming and outgoing ozone from the reactor with the content of the test substances in water, which are determined by standard methods.

In the sources of information [9, 11, 12], in description of the ozonation process, the specific dose of ozone  $D_s$ , expressed in terms of ozone mass per unit mass of the oxidizable substance

$$D_s = M_{z_{en}} / M_{x_{en}}, \quad (1)$$

where  $M_{z_{en}}$  – mass of supplied ozone, mg;  $M_{x_{en}}$  – mass of oxidizable substance, mg.

When determining this value, do not take into account how the supplied ozone is consumed and how much oxidized substances are completely degraded.

To adequate characteristics of the process, we propose to use the specific value of consumption of ozone  $R_s$ , mg/mg. It is assumed to be equal to the ratio of ozone masses reacted for the period from the start of the reaction to the current time and the oxidized substance over the same period of time

$$R_s = M_{z_r} / M_{x_r}, \quad (2)$$

where  $M_{z_r}$  - mass of reacted ozone, mg;  $M_{x_r}$  – mass of oxidized substance, mg.

At a significant period of ozonation, the specific consumption of ozone  $R_s$  acquires the meaning of the maximum or maximum value of  $R_s^{lim}$ . Which is equal to the specific consumption of ozone consumed by interaction with organic matter until the formation of substances that do not enter into chemical reactions with ozone.

$$R_s^{lim} = M_{z_r}^{lim} / M_{x_0}, \quad (3)$$

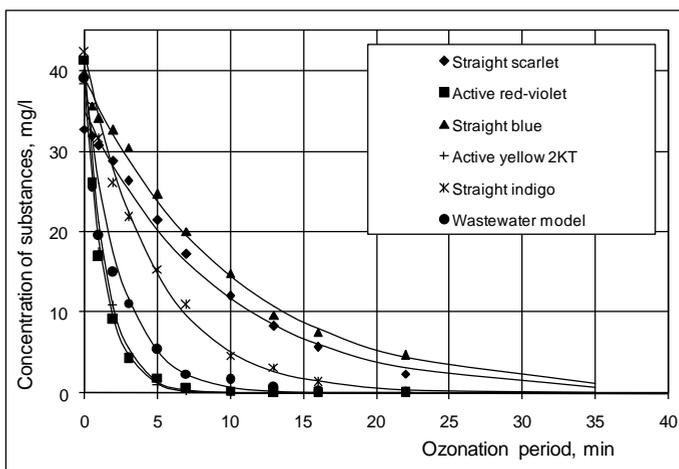
where  $M_{z_r}^{lim}$  - maximum or ultimate consumption of ozone on the oxidation process, mg;  $M_{x_0}$  – initial mass of the substance to be oxidized, mg.

For determination of the value of specific consumption of ozone, it was necessary to study the material balance of the process of destruction of organic contaminants during ozonation under experimental conditions.

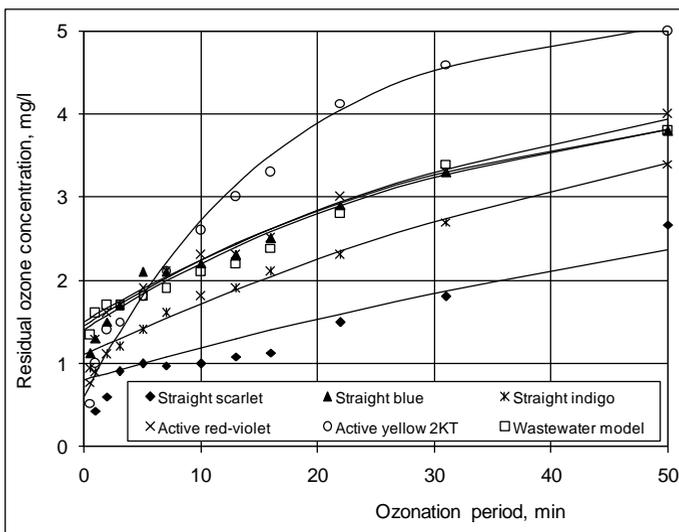
The studies were performed on synthetic dyes used in the textile industry and are biologically stable organic compounds. Also in the studies, a wastewater model of the dyeing from finishing production of a textile enterprise with a known composition of pollutants was used. The effectiveness of removal of synthetic dyes in biological

wastewater treatment is small [1, 2]. These organic compounds slowly decompose under the action of ozone (a half-life of 1 ... 8 minute), which is convenient for obtaining and analyzing the kinetic characteristics of the process. To ensure comparison of the results, laboratory researches were conducted under the same conditions. The initial concentration of dyes is about 40 mg/l, pH = 6.8 ... 7.1. The temperature of treated water is 20 ... 21 °C. As a contact reactor in the experimental setup, a pressure less bubble column with a height of 1 meter was used. The ozone-air mixture was fed through a porous diffuser with a pore size of 70 ... 100 μm, a flow rate of 0.25 l/min and an ozone concentration of 6 ... 6.2 mg/l. The concentration of the ozone-air mixture introduced into the reactor and the outlet from it was measured using instruments. A well-known method for measuring ozone concentration was also used [13].

Some data obtained during the research are presented graphically in Fig. 1 and 2.



**Fig.1.** Change in the concentration of dyes during ozonation.

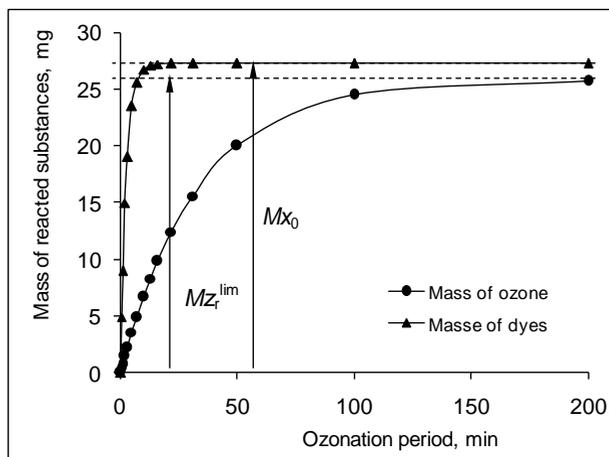


**Fig.2.** Change of ozone concentration in the ozone-air mixture at the reactor output, for the studied dyes.

### 3 Results and discussion

The material balance of the ongoing process of destruction during the experiment was calculated from the change in the masses of the substances that reacted.

Dependences of the change of mass of the test substance and of the reacted ozone are shown in Fig.3.

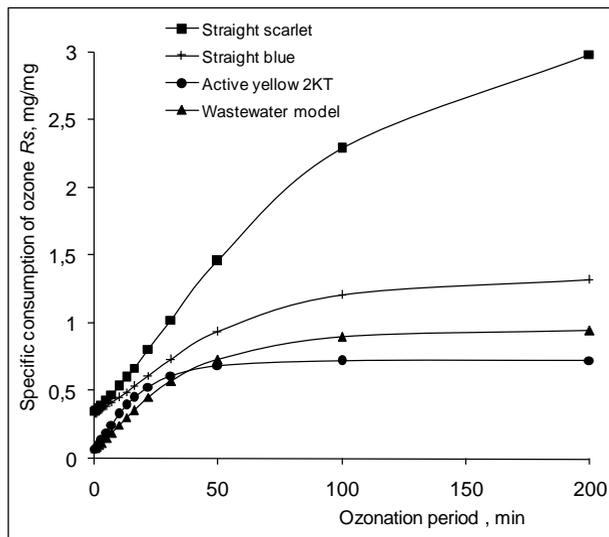


**Fig.3.** Change in the mass of substances that reacted, for example, the ozonation of model wastewater.

Approximation of the change in the mass of the reacted dye, determined by standard analytical methods, to a constant value corresponds to the completion of the process of its destruction as a starting material. This means that all the initial oxidizable substance has reacted and completely lost the identification feature. In the case under consideration, this occurs 13 minutes after the start of the experiment. With a long duration of ozonation, the value of mass of the oxidized substance tends to the mass of the starting material  $Mx_0$ .

The mass of ozone, which enters the  $Mz_r$  reaction, reaches a constant value over a longer period. In this example, it is 200 minutes. Approximation of the dependence of  $Mz_r$  to a constant value indicates the completion of chemical reactions with ozone consumption. This means that in the treated water there were only those compounds (products of destruction of the starting material), which under the given conditions do not interact with ozone.

Figure 4 presents the dependences of specific consumption of ozone for destruction of investigated substances, calculated by equation (2). It can be seen from them that for a long period of ozonation, the value of  $Rs$  tends to an asymptote numerically equal to the limiting consumption of ozone, that is, to the value of its mass per unit mass of the decomposed substance upon complete completion of the process.



**Fig.4.** Effect of the ozonation period on the specific consumption of ozone for some types of dyes.

During the experimental studies and analysis of the results obtained, it was established that the different nature of the change in the mass of the oxidizable substance (Fig. 1), determined by standard analytical methods, and the mass of the reacted ozone indicates that the chemical reaction, in which the substance loses its character, the first stages of interaction with ozone. This reaction proceeds with a lower consumption of the oxidant than the decomposition reactions of the intermediate oxidation products, which are not identified as the starting material. The process of decomposition of organic substances during ozonation can proceed deeper than the observed effect of lowering the concentration of the initial organic matter [14, 15].

The process of decomposition of substances can be estimated indirectly by speed variation of ozone consumption or by change of mass of the reacted ozone. It should be taken into account that the total mass of organic matter is oxidized to final products only by 20 ... 30%, it is mainly degraded with the formation of intermediate decomposition products.

To assess the ability of contaminants in waste water to oxidize by ozone, we proposed a water quality indicator: "chemical demand of ozone" ( $CDO_3$ )  $O_z$ ,  $mgO_3/l$ . This indicator is expressed numerically in mg of ozone per 1 liter of treated water. This value is equal to the amount of ozone that can react with the impurities contained in 1 liter of water, when decomposed to products that do not react with ozone.

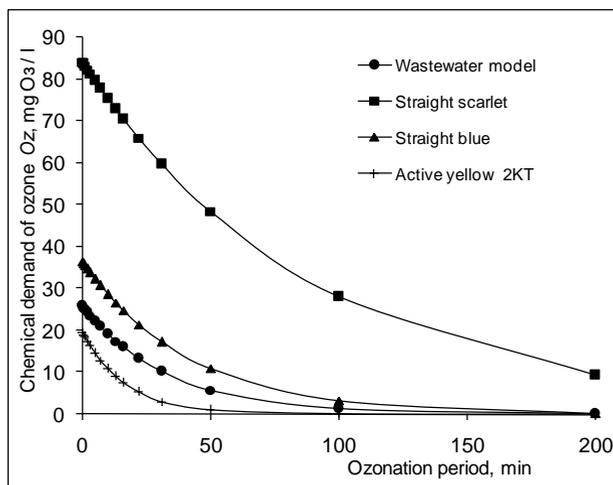
In the process of ozonation, the  $CDO_3$  index decreases in proportion to the amount of ozone reacted with the oxidizable substance. The indicator becomes equal to the difference of the limiting (necessary) mass of ozone for the oxidation of substances originally contained in the solution and the mass of ozone that has reacted to the definite moment of time and is related to the volume of the solution  $W$ , l:

$$O_z = (M_{z,r}^{lim} - M_{z,r}) / W . \quad (4)$$

For the initial sample of water, which has not been ozonated yet,

$$O_z = M_{z,r}^{lim} / W . \quad (5)$$

Figure 5 depicts the dependencies of the  $CDO_3$  index on the ozonation period for some substances.



**Fig. 5.** Change of the indicator of  $CDO_3$  in the process of ozonation of some types of dyes.

## 4 Conclusion

The method and indicator "chemical demand of ozone" ( $CDO_3$ ) offered by us for use in pre-project studies and technological calculations has the following advantages:

- has the universal application for organic and mineral pollution and does not require the availability of detailed data about the composition of waste water, because it can be determined from the dependence of the change in ozone concentration in the spent ozone-air mixture;
- representative of the assessment of the feasibility of using ozone for the purification of specific wastewater species.

Using this indicator, it becomes possible to calculate the required amount of ozone for the decomposition of the substance to a specified degree of destruction.

The use of the indicator "chemical demand for ozone" has also been tested and can be recommended when using the ozonation method for post-treatment of municipal wastewater with a view to decontaminating them and reducing the number of chemically oxidizable organic compounds.

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