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A STUDY ON THE KINETICS OF OZONE DECOMPOSITION IN WATERS OF DIFFERENT QUALITY

The kinetics of ozone decomposition in waters of different quality, namely distilled water, tap water previously treated with ozone, tap water not treated with ozone and raw water from an accumulation lake, were studied in a batch stirred reactor at different temperatures (18–28°C). The dissolved ozone concentration was measured by the iodometric titration method. It was determined that an empirical kinetic equation of the form:

$$-\frac{dc(O_3)}{dt} = k_0 + k_1c(O_3)$$

fitted the experimental data better than a first-order reaction rate equation. The apparent reaction rate constants in the case of ozone decomposition in distilled water were shown to be a function of temperature in accordance with the Arrhenius equation.

The ever-increasing need for good quality water and the intensive pollution of rivers and waterways in our country have rendered indispensable the application of new water processing technologies. Prechlorination, coagulation, flocculation, precipitation, filtration and final chlorination used in the process of eliminating phenols, pesticides, detergents, hydrocarbons, organic chlorine compounds, dissolved organic compounds, heavy metals and compounds giving certain taste and odor to drinking water, do not give hygienically proper drinking water. The traditional procedure of drinking water processing includes a pre-ozonation stage (elimination of odor and taste, degradation of metal-organic complexes, destabilization of colloid and colored substances, inactivation of algae and partial disinfection, etc.) and the main ozonation stage (chemical oxidation and complete disinfection), which substantially improves water quality.

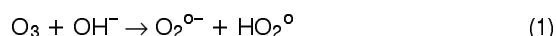
In order to process raw water by the ozonation procedure, it is necessary to introduce a stream of gas containing ozone into the water and to achieve efficient ozone mass transfer from the gas into the liquid. During the contact of ozonated air with water, several processes occur, namely, the absorption of ozone from the gas into the liquid, the desorption of volatile organic matters from water into the gas phase, the chemical reaction of ozone with the organic and inorganic matters contained, the decomposition of ozone and free radical reactions as a result of the decomposition of ozone. The efficiency of ozonation is determined by the following parameters: the raw water quality, the chemical reactivity of the substances (rate constants of direct and indirect reactions), the volatility of the substances, the ozone

mass transfer coefficient in the contactor, the gas-liquid contact area and the residual ozone concentration in the liquid phase.

Ozone reacts in water in two ways: by direct, highly selective reactions of molecular ozone, and by less selective reactions of OH radicals formed as a result of ozone decomposition [1]. Several seconds after introducing ozone into the water, part of the ozone reacts immediately with the dilutes, and the other part decomposes into further reacting radicals. Surface waters, which are most frequently analyzed, include both types of reactions.

Indirect reactions occur in the presence of radicals (OH° , HO_2° , HO_3 , HO_4 , $O_2^{\circ-}$, $O_3^{\circ-}$), produced in chain reactions, by the decomposition of ozone initiated by OH^- ions from water. Ozone decomposition takes place by the mechanism of indirect ozone reactions. The free radicals react non-selectively and promptly. In the water treatment process, the indirect mechanism is dominant, the direct reaction having little or negligible importance.

The mechanism and kinetics of ozone dissociation in water have been investigated by many researchers, starting with the experimental work of Weiss, Stumm and Kilpatrick in 1935 [1]. The decomposition of ozone is presented by a chain reaction initiated by a present hydroxyl ion, whereby free radicals are produced, which become chain carriers in further reactions. The initial stage, in which ozone reacts with hydroxyl ions, is the stage controlling the decomposition reaction rate and is described by the following equation:



Free OH radicals are produced as intermediaries of the decomposition reaction, and 1 mole of ozone produces 1.5 moles of hydroxyl radicals.

The ozone decomposition degree depends on the following process conditions: temperature, pH, ozone concentration, and the concentrations of the decomposition promoter and inhibitor in water. The decomposition rate depends largely on pH and the concentration of the reaction inhibitor or promoter. The decomposition rate increases with increasing

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temperature, but no significant effect of the temperature has been observed in the interval from 15 to 35°C [2].

The understanding of kinetic parameters (reaction order and reaction rate constant) helps to determine the feasibility and to optimize the application of ozone in raw water treatment in a wide range of temperatures to obtain good quality drinking water. Determination of the kinetics of ozone decomposition in water is important in practice when it is necessary to improve mass transfer and/or to achieve the optimal concentration of ozone in the processed water.

Several equations for the ozone decomposition reaction rate can be found in the literature. According to some authors, based on the assumed reaction mechanism, the following equation of the ozone decomposition reaction was developed [1]:

$$-\frac{dc(O_3)}{dt} = k_A \cdot c(O_3) + k_B \cdot c(OH)^{0.5} \cdot c(O_3)^{1.5} \quad (2)$$

where k_A is the reaction rate constant as related to the ozone concentration, and k_B is the decomposition reaction rate constant. Some other authors do not take into account the ozone decomposition mechanism and represent the reaction rate by the empirical kinetic equation [1]:

$$-\frac{dc(O_3)}{dt} = kc(O_3)^n \cdot c(OH)^m \quad (3)$$

where k is the reaction rate constant, n is the order of the reaction with respect to ozone ($1 < n < 2$), and m is the reaction order with respect to OH ions ($0.36 < m < 1$, $m \rightarrow 1$ with decreasing pH).

If the ozone decomposition reaction occurs at constant pH, the differential equation (3) can be simplified:

$$-\frac{dc(O_3)}{dt} = k_1' \cdot c(O_3)^n \quad (4)$$

where $c(O_3)$ is the actual ozone concentration and k_1' is the apparent reaction rate constant. Table 1 gives a survey of the results of a number of investigations regarding the reaction order of ozone decomposition in deionized water at various pH and temperatures. In all the investigations, a reaction order with respect to ozone between 1 and 2 was obtained, but the results gave no information on the influence of temperature or pH on the reaction order. Different experimental conditions, lack of information on specific conditions, as well as the application of different analytical methods, make these results incomparable.

Assuming that the concentration of OH⁻ ions is constant, the ozone decomposition reaction rate was assumed to be a linear function of the dissolved ozone concentration, i.e.:

$$-\frac{dc(O_3)}{dt} = k_0 + k_1c(O_3) \quad (5)$$

the integral form of the equation being:

Table 1. Reaction order of ozone decomposition with respect to ozone in deionized water [1,3]

Temperature, °C	pH	Reaction order with respect to O ₃	Investigators
0	2-8	1,5	Weiss
0-27	1-2.8	1	Aldler & Hill
0.2-19.8	7.6-10.4	1	Stumm
25	0-6.8 8-10	1,5	Klipatrick et al.
5-25	5.4-8.5	1,5	Rankas
10-20	2-4 6 8	2 1,5-2 1	Hewes & Davies
15-35	2,2-11	1,5	Kuo et al.
3.5-60	0,5-10	1	Sullivan
20	2,2-9,5	2	Guroł & Singer
20	8-10	1	Staehelein & Hoigne
10-40	2,5-9	1,5-2	Sotelo et al.
-	6,65	2	Minchews et al.
-	5-9	1	Grasso & Webber
20	7	1-2	Gottschalk

$$c(O_3) = \frac{k_0 + k_1c(O_3)_0}{k_1} \cdot e^{-k_1t} - \frac{k_0}{k_1} \quad (6)$$

where k_0 and k_1 are apparent reaction rate constants, which include the influence of hydroxyl ions and $c(O_3)_0$ is the initial concentration of ozone in water. At low ozone concentrations ($c(O_3) \rightarrow 0$), the reaction rate does not depend on the ozone concentration and the reaction is pseudo-zero order with respect to ozone. However, if $k_0 \ll k_1c(O_3)$, then the ozone decomposition reaction is pseudo-first order with respect to ozone ($k_0 = 0$) and equation (6) becomes:

$$c(O_3) = c(O_3)_0 \cdot e^{-k_1t} \quad (7)$$

The kinetics of ozone decomposition in distilled water, drinking water previously treated with ozone (from the Belgrade water supply network), in drinking water previously not treated with ozone (from the Leskovac water supply) and in raw water from the accumulation lake of Barje (Leskovac surroundings) were investigated at various temperatures in this paper. The scope of this experiment was to determine the reaction order and apparent reaction rate constants of ozone decomposition in waters of different purity, as well as the dependence of the apparent reaction rate constants on temperature.

EXPERIMENTAL

The layout of the experimental ozonation plant is given in Figure 1. The reactor was equipped with a Rushton turbine stirrer with six flat blades and four baffles. The geometric characteristics of both the reactor and stirrer, as well as the operating conditions, are given

in Table 2. All the equipment parts coming into contact with ozone were made of non-corrosive material, resistant to ozone, which did not cause increased ozone decomposition. Waters of various quality were used as the liquid phase: distilled water, drinking water previously treated with ozone (from the Belgrade water supply network), in drinking water previously not treated with ozone (from the Leskovac water supply) and raw water from the accumulation lake of Barje (Leskovac surroundings). The experiments were carried out at different temperatures, ranging from 18 to 28°C. By passing oxygen through an ozone generator (Ozone Lab 100/DS, Yanco Industries Ltd., Burton, Canada), a mixture of oxygen and ozone with known ozone concentration was obtained, which was introduced into a batch reactor by a nozzle below the stirrer. The gas flow rate was measured by a rotameter placed before the ozone generator. The gas pressure was measured by a pressure gauge before entering the rotameter. The gas mixture was passed through the reactor for a predetermined period of time, and then the gas flow was cut off and samples of water were taken from the reactor

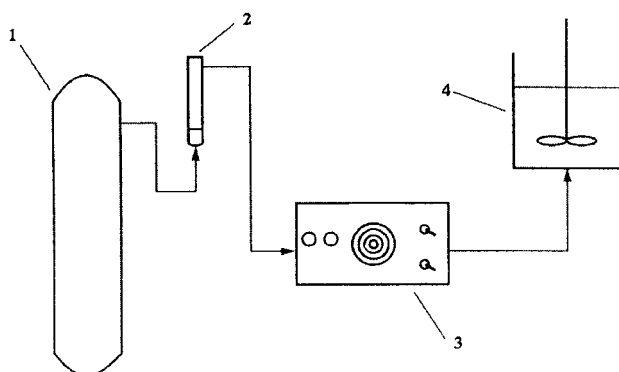


Figure 1. Experimental set up for ozone decomposition in water: oxygen bomb (1), rotameter (2), generator of ozone (3) and stirred tank (4)

Table 2. Geometric characteristics of the stirred reactor and the operating conditions

Characteristic	
Diameter of tank, cm	20
Height of tank, cm	40
Liquid height, cm	20
Liquid volume, dm ³	6,1
Diameter of agitator, cm	6,7
Length of blade, cm	1,61
Width of blade, cm	1,34
Distance from bottom, cm	6,7
Width of baffle, cm	2
Diameter of nozzle, cm	0,2
Height of nozzle, cm	4,7
Agitation speed, rpm	400
Gas flow rate, dm ³ /h	30
Inlet ozone concentration in the gas phase, mg/dm ³	36

bottom at time intervals to determine the dissolved ozone concentration. The ozone concentration in the water was determined by the iodometric titration method based on the volume of sodium thiosulfate solution (0.00206 mol/dm³) used to discolor the sample (1 cm³ of solution corresponds to 5.494 mg O₃/dm³). To each 9 cm³ sample of water, 1 cm³ of potassium iodide (0.1 mol/dm³) and starch solution were added and then titrated with sodium thiosulfate solution.

RESULTS AND DISCUSSION

Due to ozone decomposition, the dissolved ozone concentration decreased with time, as shown in Figure 2. By introducing the oxygen and ozone mixture into the reactor at various temperatures, various conditions for ozone mass transfer into the liquid phase were obtained, so that the initial dissolved ozone concentrations were different for individual tests. The change of dissolved ozone concentration, regardless of water quality and temperature, can be presented by a decreasing first order exponential function as follows:

$$c(\text{O}_3) = c(\text{O}_3)_0 + A \exp\left(-\frac{t-t_0}{B}\right) \quad (8)$$

where $c(\text{O}_3)$ is the concentration of ozone at time t , $c(\text{O}_3)_0$ – the concentration of ozone at time t_0 , A and B – parameters. The parameters of equation (8) were calculated using the program ORIGIN 5.0, presuming that $t_0 = 0$.

Equations (5) and (7) were used to calculate the kinetic parameters. In the first case, $dc(\text{O}_3)/dt$ was calculated for different times, by differentiating equation (8), and the kinetic parameters k_0 and k_1 were then calculated by the method of linear regression, using the program ORIGIN 5.0. In the second case, equation (7) was first linearized, and then the parameter k' was calculated by the linear regression method using the program ORIGIN 5.0. The procedures for calculating kinetic parameters using equations (5) and (7) are shown in Figures 3 and 4, respectively. The values of the kinetic parameters at certain pH and temperature conditions are given in Table 3. Comparing the values of the linear correlation coefficient, it can be seen that equation (5) better fits the experimental data better than equation (7). In other words, the kinetics of ozone decomposition, regardless of water quality and temperature, comply with a law that combines zero (at low ozone concentration) and first (at high ozone concentration) order kinetics with respect to ozone.

As seen in Figure 5, the apparent ozone decomposition reaction rates in distilled water, which include the influence of water pH and the pollutants present in the water, depend on the temperature, in accordance with the Arrhenius equation:

$$k_0 = 4.736 \cdot 10^{13} \exp\left(-\frac{10333}{T}\right) \frac{\text{mg}}{\text{dm}^3 \text{ min}} \quad (9a)$$

$$k_1 = 2.450 \cdot 10^4 \exp\left(-\frac{3899}{T}\right) \frac{1}{\text{min}} \quad (9b)$$

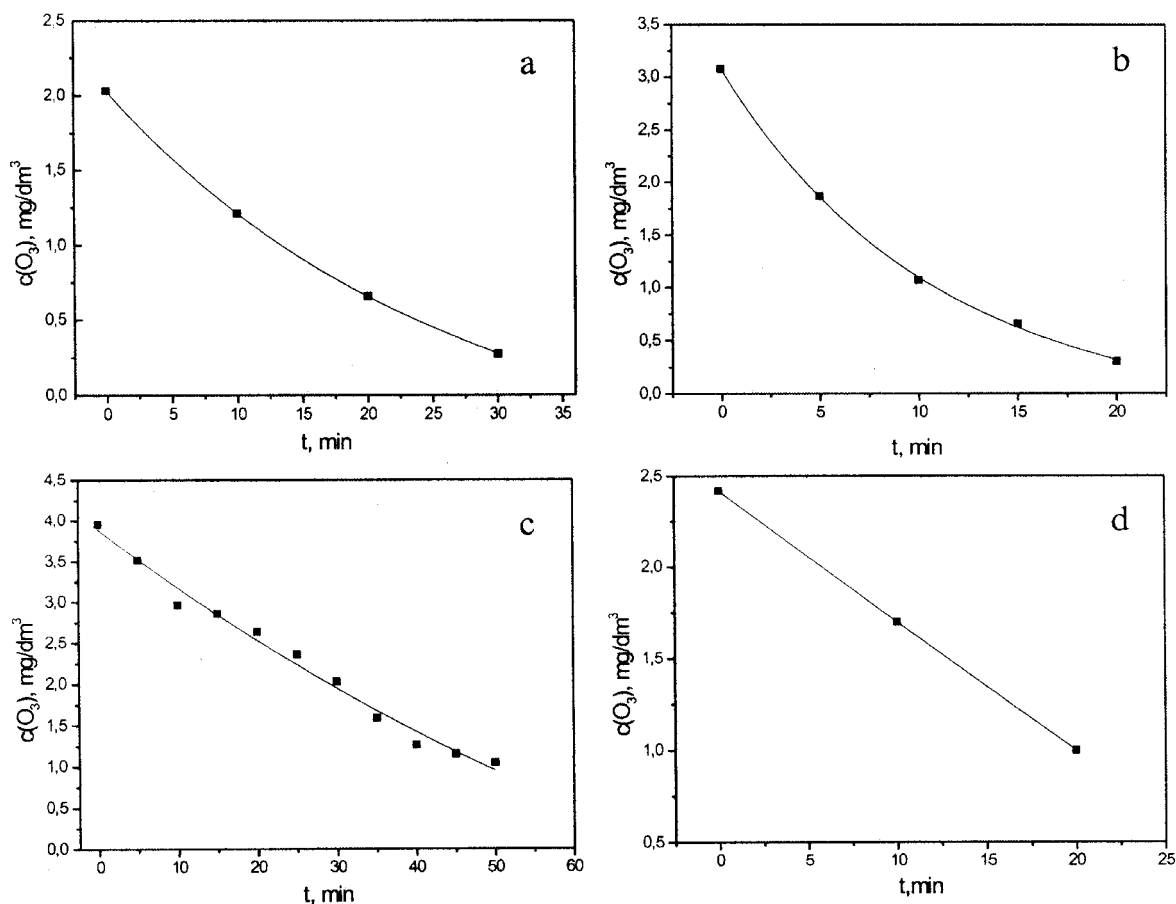


Figure 2. Variation of the dissolved ozone concentration during its decomposition in a) distilled water ($19^\circ C$), b) tap water previously treated with ozone (Belgrade water system; $27^\circ C$), c) tap water previously not treated with ozone (Leskovac water system; $18^\circ C$) and d) raw water from the Barje accumulation lake ($23^\circ C$)

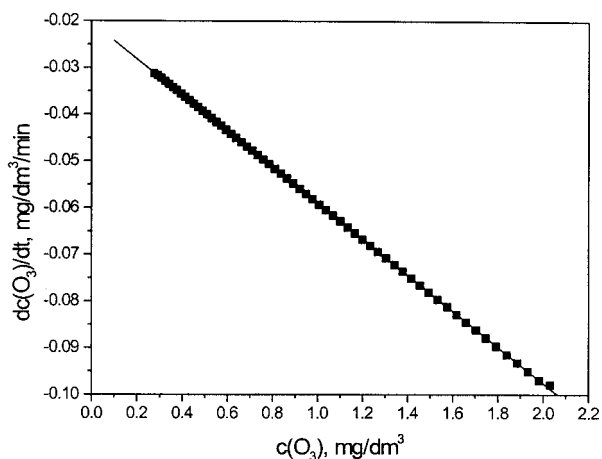


Figure 3. Reaction rate of ozone decomposition in distilled water ($19^\circ C$) as a function of the dissolved ozone concentration

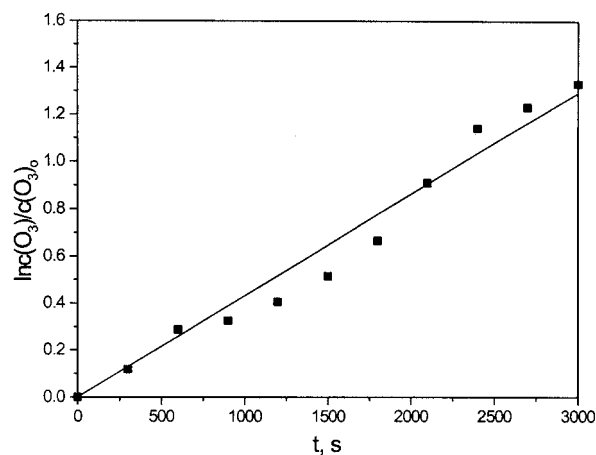


Figure 4. Determination of the apparent reaction rate constant for ozone decomposition in tap water previously not treated with water (Leskovac water system; $18^\circ C$) assuming a first-order reaction

Figure 5 enables comparison of the apparent constants for waters of different quality, assuming that the Arrhenius equation applies to all the waters tested. Thus, the k_1 constant values decrease, and the k_0 constant values increase in the sequence

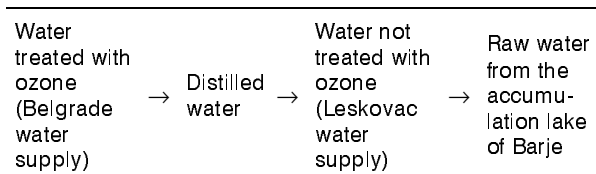


Table 3. Values of the apparent reaction rate constants, k_0 and k_1 , for waters of different quality

Type of water	T °C	pH	k_0 mg/dm ³ /min	k_1 min ⁻¹	r^2 Equation (5)	k_1' min ⁻¹	r^2 Equation (7)
Distilled water	19	7	0.0204	0.0386	1.000	0.5460	0.773
	24		0.0393	0.0465	1.000	0.0920	0.271
	25		0.0373	0.0553	1.000	0.0783	0.741
	28		0.0602	0.0563	1.000	0.0865	0.610
Tap water from Leskovac water supply	18	5.8	0.0356	0.0101	1.000	0.0258	0.987
Tap water from Belgrade water supply	27	7	0.0178	0.0928	1.000	0.1060	0.996
Raw water from the Barje accumulation lake	23	8.9	0.0662	0.00283	1.000	0.0526	0.988

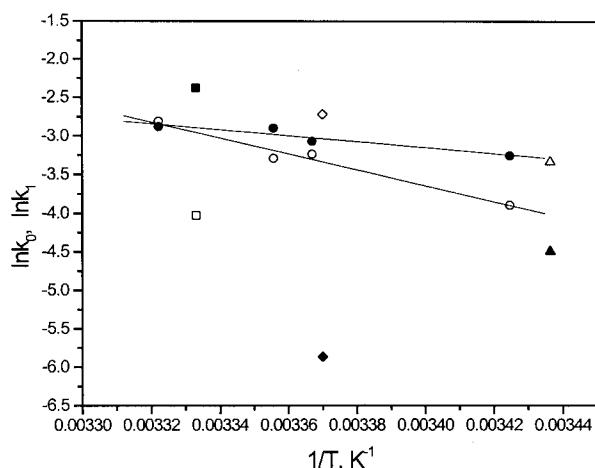


Figure 5. Dependence of the apparent reaction rate constants, k_0 and k_1 , on the reciprocal absolute temperature for waters of different quality (o – distilled water, Δ – tap water previously treated with ozone, \diamond – tap water previously not treated with ozone and \square – raw water from the Barje accumulation lake; k_0 – open symbols and k_1 – black symbols)

CONCLUSION

In this paper an experimental investigation of the kinetics of ozone decomposition in waters of different

quality (distilled water, drinking water treated with ozone, drinking water that had not been treated with ozone and raw water from the accumulation lake of Barje) was carried out in order to determine the ozone decomposition reaction rate. The ozone decomposition kinetics, regardless of the water quality and temperature, complied with a law combining zero (at low ozone concentration) and first (at high ozone concentration) order kinetics with respect to ozone. The apparent reaction rate constants for ozone decomposition in distilled water depend on temperature, in accordance with the Arrhenius equation. The values of the apparent constants depend on the water quality.

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IZVOD

ISPITIVANJE KINETIKE DEKOMPOZICIJE OZONA U VODAMA RAZLIČITOG KVALITETA

(Naučni rad)

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U radu su dati rezultati analize kinetike dekompozicije ozona u vodama različitog kvaliteta (destilovana voda, pijaća voda prethodno tretirana ozonom, pijaća voda koja nije tretirana ozonom i sirova voda iz akumulacionog jezera Barje) u šaržnom reaktoru sa mešanjem, praćenjem promene koncentracije slobodnog ozona u vodi sa vremenom, na temperaturama u intervalu od 18 do 28°C. Određen je zakon brzine reakcije dekompozicije ozona:

$$-\frac{dc(O_3)}{dt} = k_0 + k_1 c(O_3)$$

koji bolje "fituje" eksperimentalne podatke od jednačine za brzinu reakcije prvog reda. Prividne konstante brzine dekompozicije ozona u destilovanoj vodi, k_0 and k_1 , pokoravaju se Arenijusovoj zavisnosti od temperature.

Ključne reči: Ozon • Razlaganje • Kinetika • Otpadne vode • Česmenska voda •

Key words: Ozon • Decomposition • Kinetics • Waste water • Tap water •