

Methodology Of Ozone Introduction Into Water And Wastewater Treatment

R. Munter, S. Preis, S. Kamenev and E. Siirde

Tallin Technical University
EE 0108 Tallin, ESTONIA

Received for Review : 28 April 1991
Accepted for Publication : 7 October 1992

Abstract

Theoretical basis and methodology for calculation and modeling of ozonation processes and contact equipment have been elaborated. Methodology of determination of reaction rate constant, stoichiometric coefficient, optimum values of pH, intermediate and final products, regimes of chemisorption, etc., for certain typical fast and slow reacting organic compounds (aniline, toluidine, humic acids, nitrobenzene, glyoxalic, oxalic and acetic acid) and wastewaters have been proposed. For calculation of the wastewater ozonation process, the value of chemical oxygen demand (COD) was suggested to be as a kinetic parameter from the solution side. On the basis of kinetic information, recommendations for the choice of the construction of contact equipment for the different chemisorption regimes of ozonation have been presented. Some new contact apparatuses have been proposed.

Introduction

Due to its high chemical activity, ozone is widely used in drinking water and municipal wastewater treatment. For a successful introduction of ozone into water and wastewater treatment, new high-capacity ozone generators and effective ozonation processes are required. In recent years, numerous studies have been concerned with either the kinetics of ozonation reactions or the calculation and modeling of contact systems. A better relationship between these two factors should be found. The designer of a water purification plant has to consider all the purposes of ozonation along with the treatment line to determine the best solutions, both as concerns the different points of application and the different types of contactors to be used. Some laboratory and pilot-plant tests can help make this choice.

Transformation from laboratory-scale studies of ozonation to an industrial-scale process consists of at least six stages (Figure 1). The selection and calculation of the contact equipment for water or wastewater ozone systems will be possible only if

sufficient information on the microkinetics of the process is available, and this assumes a thorough study in this field .

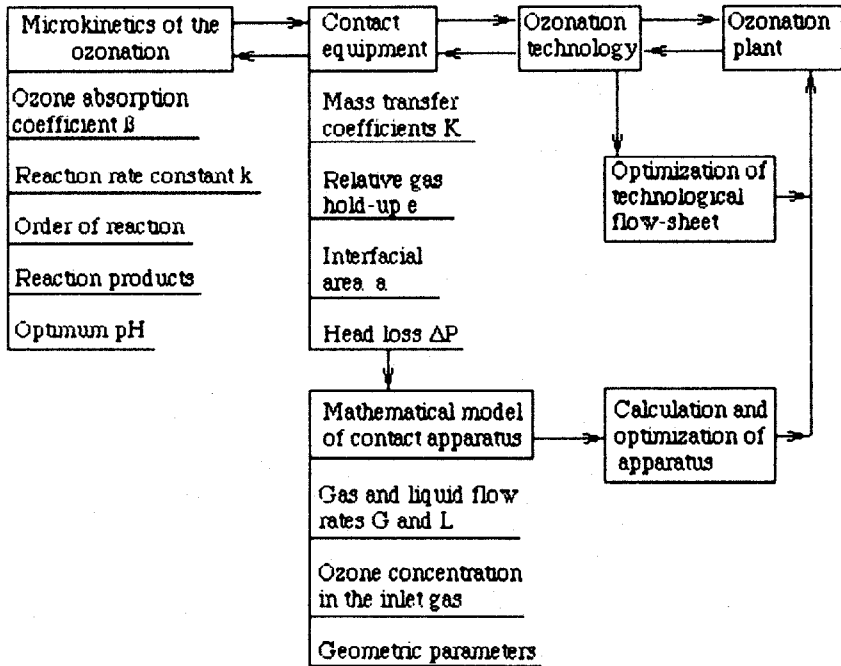


Figure 1. Scheme of water ozonation process investigation and introduction.

Theoretical And Experimental Investigation Of Fast Ozonation Processes

KINETICS OF OZONATION

For determination of reaction rate constants of fast reactions, the method using the wetted-wall column was used. The reaction rate constant, k_2 , may be calculated from the expression for the chemisorption parameter R :

$$R = K_L^{-1} (D_{O_3} \cdot k_2 \cdot C_B)^{1/2} \quad [1]$$

where C_B = the mean value of organic compound concentration,
 K_L = mass transfer coefficient of ozone for physical absorption;
 D_{O_3} = coefficient of ozone diffusion.

In turn, the value of R may be found from the expression:

$$a' = R[1 - (Ha - 1)/M]^{1/2} \quad [2]$$

where a' = a parameter, defined by the Hatta number, Ha:

$$Ha = K_L' / K_L; \quad Ha = [1 + (a')^2]^{1/2} \quad [3]$$

where K_L' = mass transfer coefficient of ozone for absorption accompanied with chemical reaction (chemisorption).

M = another chemisorption parameter, defined by the expression:

$$M = C_B(m.\beta.C_G)^{-1}(D_B/D_{O_3})^{1/2} \quad [4]$$

where m = stoichiometric coefficient;

C_G = mean value of ozone concentration in the gas;

β = solubility coefficient of ozone ($\beta = 0.32 \pm 0.02$ at 20°C);

D_B = coefficient of diffusion of organic compound.

Unlike the "stopped flow" method, the method described above does not need complicated measuring equipment.

As examples of fast reaction, the cases of ozonolysis of humic acids in lake water and also aniline and *p*-toluidine solutions were investigated. The curves of color reduction of lake water can be divided into two stages: fast oxidation of humic acids and slow oxidation of more resistant fulvic acids. Expressing the rate of chemical reaction of color reduction by color degrees, the following kinetic results were obtained in the wetted-wall column for humic acids oxidation: $k_2 = 0.94 \pm 0.6$ (deg.s)⁻¹, stoichiometric factor $m = 1.63.10^5$ m³.deg/kmole O₃. For determination of the reaction rate constant, k_2 , for decolorization of lake water, it was assumed that humic acids in the water consist mainly of pure polyphenol with a varying number of groups, $n = 5$ and $n = 200$. The unknown concentration of humic acids in lake water was substituted by color degrees at wave length 360 nm. Kinetic decoloration experiments were carried out in the wetted wall column with inner diameter $D = 0.015$ m and height $H = 0.34$ m at pH = 8 and $T = 283^\circ\text{K}$. Stoichiometric factor m was measured in the semi-continuous bubble column ($V = 1.5 \cdot 10^{-3}$ m³, pH = 8, $T = 283^\circ\text{K}$). Experimental results are presented in Tables I and II. The obtained values of the factors M, R, α , and a' show also that lake water decolorization process proceeds in the regime of a fast reaction, or between that of a fast and an instantaneous reaction.

The ozonation process of aromatic amines also can be divided into two stages (Figure 2). The first may be characterized by intensive foaming, formation and flotation of precipitate independent of pH and sharp increase of color. During this stage, the extent of ozone absorption is 100%. Ozone consumption for aniline degradation does not depend on pH and has the mean value 1.7 kmole O₃/kmole, but for the solution of *p*-toluidine increases from 1.2 kmole O₃/kmole at pH = 2 up to 5.6 kmole O₃/kmole at pH = 13. Ozone consumption for COD reduction depends only slightly on pH during the first stage, and has the following mean values: for aniline 0.7 g O₃/g O₂ and for *p*-toluidine 1.1 g O₃/g O₂. At the end of the first stage, the flotation of the precipitate stops and foam disappears.

TABLE I. DETERMINATION OF THE REACTION RATE CONSTANT k_2 IN THE WETTED-WALL COLUMN (pH = 8, T = 283°K)

$K_L \cdot 10^4$, m/s	$K_L \cdot 10^5$ m/s	Ha	a'	M		R		k_2 (deg.s) ⁻¹	
				n=5	n=200	n=5	n=200	n=5	n=200
1.38	4.18	3.30	3.15	11.34	3.75	3.53	5.07	0.37	0.77
1.82	6.08	2.99	2.82	11.81	3.90	3.09	4.03	0.60	1.01
2.03	6.49	3.13	2.96	11.48	3.80	3.28	4.47	0.77	1.43
2.31	7.99	2.89	2.71	11.88	3.93	2.96	3.76	0.93	1.51
Average $k_2 = 0.94 \pm 0.6$ (deg.s) ⁻¹									

TABLE II. DETERMINATION OF THE STOICHIOMETRIC FACTOR M IN THE SEMICONTINUOUS BUBBLE COLUMN (V = 1.5.10⁻³ m³, pH = 8, T = 283°K)

Time, s	C_G^{in} , g/m ³	C_G^{out} , g/m ³	Color, deg.	G, m ³ /h	O ₃ Dose consumed, g/m ³	Stoichiometric Factor, m
0	4.65	0	50.0	0.012	0	---
20	4.65	0.21	49.5	0.012	0.21	1.95
40	4.65	0.41	48.6	0.012	0.41	3.21
60	4.65	0.62	48.0	0.012	0.60	3.16
90	4.65	0.78	46.5	0.012	0.89	3.83
120	4.65	0.93	45.0	0.012	1.17	4.20
150	4.65	1.36	44.0	0.012	1.43	4.12
Average m = 3.4 m ³ .deg/g O ₃ or 1.63.10 ⁶ m ³ .deg/kmole O ₃						

From the beginning of the second stage, ozone appears in the outlet gas. Ozone consumption for COD reduction increases due to the oxidation of less readily oxidizable intermediates and reaches 1.8 g O₃/g O₂ for aniline and 3.0 g O₃/g O₂ for *p*-toluidine. As an illustration, the COD reduction versus consumed ozone dosage for aniline solution is shown in Figure 3. The final products of aniline destruction were oxalic and ortho-phthalic acids. The end products of *p*-toluidine destruction were oxalic and succinic acid. Up to the end of the second stage, the solution becomes colorless. The reaction rate constant at 20°C for aniline oxidation is (6±3).10⁶ m³/kmole and for *p*-toluidine (5±2).10⁷ m³/kmole. The reaction is first order with respect to amine and ozone. The ozone process at the first stage (up to 90% degradation of amines) proceeds in the regime of a fast or instantaneous reaction.

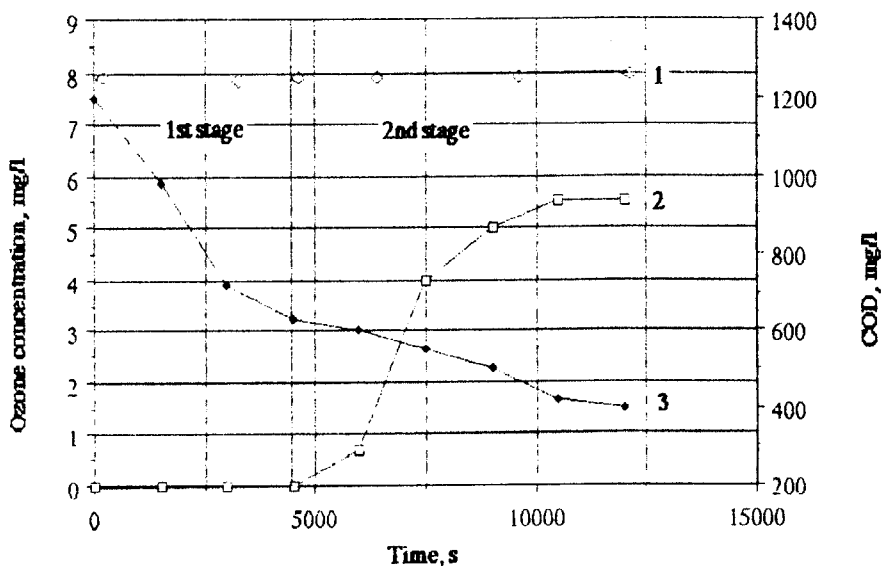


Figure 2. Ozone concentration in outlet gas and COD versus ozonation time for aniline for aniline solution (pH = 4). 1 = ozone inlet; 2 = ozone outlet; 3 = COD.

CONTACT EQUIPMENT

Although the phenomenon of ozone transfer in water has become better known, it must be admitted that in most cases, the choice of a particular contact system is based much more on habit than on the result of an analysis of the chemisorption process. Fast and instantaneous reactions are rate-limited by mass transfer of ozone from the gas phase to the liquid boundary layer. The ozonation reactions occur then at the interface or in the thin liquid boundary layer and the concentration of dissolved ozone is either zero or close to zero. Venturi scrubbers, jet reactors, packed and plate columns, as well as agitated vessels have been used for ozone transfer in water in this case (1). Basic research of the downward vertical flow of ozone-water mixtures has shown that both a considerably higher relative gas holdup and interfacial area, as well as liquid phase mass transfer coefficient can be achieved in a downflow bubble column (2,3). Experimental investigations showed that the most effective construction was the downflow bubble reactor, sectionalized by sieve plates of relatively large free area $S = 60\text{-}70\%$. The main advantage of this type of reactor is rather high values of the specific interfacial areas at low and moderate values of energy dissipation (4).

For mathematical modeling of the process in the downflow cocurrent reactor, the stagewise backmixing model was used (4). It took into consideration the continuous change of the absorption regime along the column because of the reagent concentration decrease in the liquid phase and the formation of less readily oxidizable intermediates (by the value of the reaction rate constant). The validity of the model

was verified by experiments with raw lake water in two columns with $D = 0.06$ m, $H = 0.4$ m, 4 plates and $D = 0.06$ m, $H = 0.6$ m, 6 plates, respectively. A good correlation between calculated and experimental values of ozone concentration in the outlet gas and of the color degrees of the outlet water was obtained.

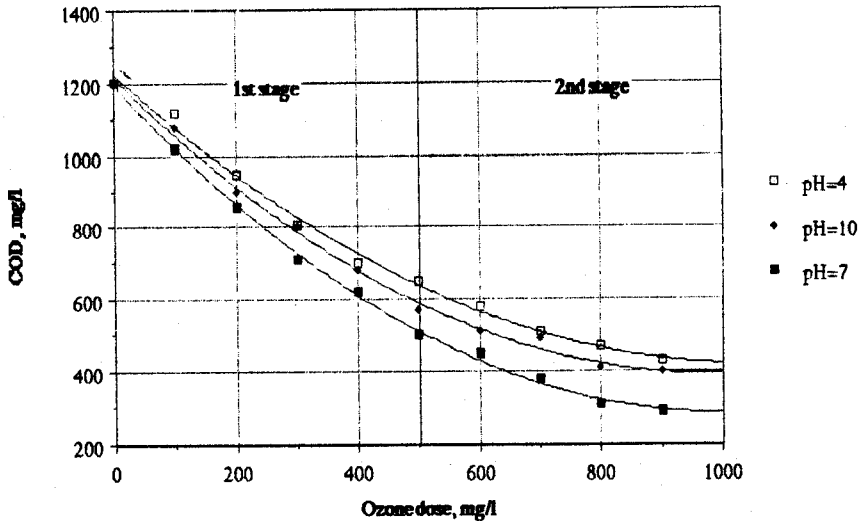


Figure 3. COD reduction versus consumed dose of ozone for aniline solution.

For the design and calculation of full-scale contact equipment, the above-mentioned mathematical model was used. The dimensions of the contact column and ozone concentration in the inlet gas were optimized.

For ozonation of Lake Ülemiste water, the downflow staged bubble column ($D = 0.31$ m, $H = 0.6$ m, 3 plates, $S = 60\%$, diameter of holes $d_0 = 3$ mm) was designed. Water throughput up to 530 m³/h was achieved in the tests at the Water Purification Plant. Ozone concentration in the inlet gas was optimized using the following expression for annual expenses (S):

$$S = 365 \cdot 24 \cdot L \cdot d_{O_3} \cdot \delta \cdot 10^{-3} \cdot \pi_{O_3}^{-1} \cdot [(C_G^{\text{in}} + 35)/3 + 65/C_G^{\text{in}}] + (S_{\text{sp}} \cdot 24 \cdot d_{O_3} \cdot L \cdot \pi_{O_3}^{-1} \cdot 10^{-3}) \cdot [p + 0.01 \cdot (g + h)] \quad [5]$$

where:

- π_{O_3} = degree of ozone absorption;
- C_G^{in} = concentration of ozone in the inlet gas;
- S_{sp} = specific capital investments for construction of ozonation equipment;
- d_{O_3} = dose of absorbed ozone;
- δ = cost of 1 kWh;

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- p = coefficient of effectiveness of investments;
 g = rate of depreciation
 h = coefficient of current repairs;
 L = volumetric flow rate of water, m³/h.

The annual expenses S consists of two parts - capital investments and operational expenses:

$$S = p.K + E \quad [6]$$

where K = capital investments.

Operating expenses E can be calculated as the sum of the following components:

$$E = E_1 + E_2 + E_3, \quad [7]$$

where E_1 = cost of electrical energy;
 E_2 = cost of amortization;
 E_3 = cost of running repairs.

E_1 can be found on the basis of the energy consumption and its cost:

$$E_1 = 365 E_d \cdot \delta, \quad [8]$$

where E_d = daily electric energy consumption, kWh.

$$E_d = E_{\text{spec}} \cdot Q_{O_3} \quad [9]$$

where E_{spec} = specific energy consumption for ozone production, kWh/kg O₃;
 Q_{O_3} = daily ozone consumption, kg.

Specific energy consumption for ozone production depends on the type of ozone generator used. For ozone generators made in Russia (type OP-121, OP-315, OP-510) the following correlation has been found (5):

$$E_{\text{spec}} = (C_G^{\text{in}} + 35)/3 + 65/C_G^{\text{in}} \quad [10]$$

Daily ozone consumption:

$$Q_{O_3} = 24 \cdot d_{O_3} \cdot L / (\pi_{O_3} \cdot 1000) \quad [11]$$

Capital investments can be estimated roughly as the cost of ozone generators considering the cost of contact column and installation expenses as negligible:

$$K \approx S_{\text{gen}} \quad [12]$$

The degree of ozone absorption was calculated from the equation:

$$\pi_{O_3} = 0.068 \cdot L^{0.28} \cdot (L/G)^{0.83} \cdot C_G^{-0.35} \cdot H^{0.56} \quad [13]$$

where G = volumetric flow rate of gas, m^3/h ;

H = height of the downflow bubble column, m.

Equation [13] was verified in the following range of parameters:

$$L = 15\text{-}600 \text{ m}^3/\text{h}; L/G = 1\text{-}10; C_G = 5\text{-}35 \text{ g/m}^3; H = 0.4\text{-}2.0 \text{ m}.$$

The needed dose of absorbed ozone and coefficient of turbidity of water A were calculated on the basis of the following expressions:

$$d_{O_3} = \pi_s \cdot B_0 \cdot A^{-1} \cdot 10^{-2} \quad [14]$$

$$A = 4.1 \cdot \exp[-0.037 \cdot T] \quad [15]$$

where: π_s = degree of decoloration;
 B_0 = initial color of water;
 T = turbidity, g/m^3 .

The minimum value of the annual expenses S was found at $C_G = 5 \text{ g/m}^3$.

Theoretical And Experimental Investigation Of Moderate And Slow Ozonation Processes

KINETICS OF OZONATION

Moderate and slow ozonation processes are influenced by the decomposition of ozone, catalyzed by OH^- ions. OH^\cdot free radicals are formed, but they are not able to destroy the aromatic ring. At the same time they react very intensively with the intermediates and products of aromatic ring destruction. The following relationship between the pseudo-first order reaction rate constant k_1 of ozone decomposition and pH were found:

$$\ln k_1 = -13.34 + 0.974 \cdot \text{pH} \quad \text{at } \text{pH} \leq 10.5 \quad [16]$$

$$\ln k_1 = -28.71 + 2.43 \cdot \text{pH} \quad \text{at } \text{pH} \geq 10.5 \quad [17]$$

Depending on electrolyte concentration, the decomposition of ozone accelerated 3-4 times. Between the rate constant of decomposition and electric conductivity of the solution, the linear relationship was determined as it results from the experimental data in Table III. Ozone decomposition in this case was approximated to the 1.5th order reaction.

As an example of moderate and slow reactions, ozonolysis of nitrobenzene, glyoxylic, oxalic and acetic acids was studied. Some results are presented in Table IV.

It is practically impossible to keep intermediate products from affecting the course of the primary reaction. Therefore, a parameter is needed to characterize ozonation kinetics throughout the entire process and to make the calculation of the equipment

possible. COD, unlike TOC, depends unequivocally on the extent of wastewater ozonation, as ozonation, due to the formation of compounds high in oxygen content, leads invariably to reduction of the COD values. As it was shown (6), the rate of the ozonation process may be expressed by COD and dissolved ozone concentration. Experiments carried out with model solutions and real wastewater from aniline dye production showed that the rate coefficient of COD of the solution was slightly lower than the rate constants of the pure component because of the effect of the intermediates. At the same time, the reaction order with respect to COD coincided with the reaction order of the pure component. The rate coefficient of the reaction of COD of the wastewater was constant during the separate stages of the process. A spasmodic change of the rate coefficient took place, caused by the consumption of the faster reacting components. For example, at the first stage of ozonation of the biologically treated aniline dye production wastewater, the rate coefficient was 4.5 ± 1.0 L/mole O_2 .s; at the second stage it was 1.1 ± 0.1 L/mole O_2 .s.

TABLE III. RATE CONSTANT OF OZONE DECOMPOSITION vs ELECTROLYTE CONCENTRATION (Na_2SO_4)

[Na_2SO_4] solution, N	pH	Specific Conductivity $\Omega^{-1}.m^{-1}$	Rate Const. $k_{3/2}$, $M^{-0.5}.min^{-1}$
0.001	7.47	$1.22.10^{-4}$	0.660
0.01	7.43	$9.54.10^{-4}$	0.823
0.1	7.50	$3.72.10^{-3}$	0.949

The process of ozonation of slowly oxidizable organic substances (nitro compounds, carboxylic acids, etc.) in wastewaters meets difficulties and requires large amounts of ozone. The use of heterogeneous catalysts makes it possible to shorten the process and decrease the ozone consumption, but pollution of the water being treated due to metal cations renders impossible the practical use of catalytic ozonation. Another method for acceleration of the ozonation process is conversion of molecular ozone into OH° radicals, having greater degradative action with respect to organic compounds. OH° radicals can be formed during the irradiation of ozone dissolved in water by UV-light with wavelengths from 200 to 300 nm, because of which the use of ozone with simultaneous UV irradiation may be advantageous in acid and neutral media.

Solutions of nitrobenzene and oxalic and acetic acids were chosen for investigation (3). Experiments were also carried out with biologically treated wastewater from the aniline dye industry (ADIBTW) and wastewater from the manufacture of leather products (WMLP). The results of investigations suggested that the formation of OH° radicals which was due to the effect of UV radiation on the ozone dissolved in water occurred via a stage of the formation of hydrogen peroxide in acid and neutral media, with its subsequent photolytic decomposition. Experiments on the ozonation of nitrobenzene solutions showed that the presence of UV irradiation did not affect the course of the process, regardless of the type of UV-radiation source. This was due to the high optical activity of nitrobenzene in the entire range of UV-radiation. In the absence of UV irradiation, the acetate ion underwent ozonolysis only in highly

alkaline medium (pH 11-12). When UV irradiation was used it also decomposed in neutral and acid media. The oxidation of oxalic acid also occurred better than without irradiation, with the maximum effect being attained in an acid medium. Experiments with ADI BTW showed that the process proceeds approximately three times faster in the presence of UV irradiation than without it. Of significant interest is the fact that the simultaneous use of ozone and UV irradiation made it possible to bring the COD of the water to lower values than could be attained by using ozone alone (5 and 30 mg O₂/L, respectively). The UV irradiation did not give a significant effect when the solution being ozonized (WMLP) contained substances optically active in the range of the optical activity of ozone (250-270 nm).

TABLE IV. RESULTS OF OZONATION OF INDIVIDUAL SUBSTANCES IN AQUEOUS SOLUTIONS AT DIFFERENT pH VALUES

pH	Reaction order with respect to compound	Reaction order with respect to ozone	Rate Constant k_2 , M ⁻¹ .s ⁻¹	
			by substance	by ozone
Nitrobenzene				
2-3	1	1	2.5 ± 0.5	9.0 ± 0.5
6-8	1	1	5.5 ± 0.5	18.5 ± 0.5
9-9.5	1	---	3.3 ± 0.4	---
11-12	1	---	3.0 ± 1.0	48 ± 1
Glyoxylic Acid				
7-8	0	1	0.019 ± 0.002*	---
11.5-12.0	0	1	0.018 ± 0.003*	---
Oxalic Acid				
2-2.5	1	1	0.013 ± 0.008	---
6.5-8.0	1	1	0.20 ± 0.02	0.1 - 0.4
9.5-10.5	1	---	0.36 ± 0.05	---
13.5	1	---	0.21 ± 0.03	---

* Dimension of k_2 -s⁻¹

CONTACT EQUIPMENT

For moderate and slow reactions of ozonolysis, the ozone concentration differs from zero, and the enhancement factor Ha is close to one. Several devices for promoting the gas-liquid contacting have been employed for moderate and slow reactions: countercurrent bubble columns, plate columns etc. In this work, two different constructions have been investigated - a semibatch bubble column and a continuous flow countercurrent plate column. Equations for the calculation of head loss, the

mass transfer coefficients and power dissipation have been proposed. For mathematical modeling ideal mixing and ideal plug-flow models were used. The composed programs took into consideration possible evaporation (volatilization) of organic compounds with a gas stream. As a kinetic parameter of ozonation from the liquid side the concentration of organic compound as well as COD of the solution were used.

The process of ozonation in the continuous-flow countercurrent plate column was described by the following system of equations:

$$\begin{aligned}
 L \cdot dC/dz &= F \cdot [K_L a \cdot (C_L^* - C_L) - m \cdot k_2 \cdot C_{SL} \cdot C_L] \\
 L \cdot dC_{SL}/dz &= F \cdot [k_2 \cdot C_{SL} \cdot C_L + (K_L a)_S \cdot (C_{SL} - C_{SL}^*)] \\
 G \cdot dC_G/dZ &= F \cdot K_L a \cdot (C_L^* - C_L) \\
 G \cdot dC_{SG}/dz &= -F \cdot [(K_L a)_S \cdot (C_{SL} - C_{SL}^*)]
 \end{aligned}
 \tag{18}$$

with equilibrium conditions:

$$C_{SL}^* = C_{SG}/\beta_S; \quad C_L^* = \beta \cdot C_G;$$

At the following boundary conditions:

$$\text{when } z = 0, \quad C_L = C_L^0 = 0; \quad C_{SL} = C_{SL}^0;$$

$$\text{when } z = z_0, \quad C_G = C_G^0; \quad C_{SG} = 0,$$

where: L, G = flow rate of the liquid and gas phase;
 C_L, C_G = ozone concentration in the liquid and gas phase;
 C_{SL}, C_{SG} = concentration of the volatile organic compound in the liquid and gas phase;
 F = effective cross-sectional area of the column;
 $(K_L a)_S$ = mass transfer coefficient of evaporation of the organic compound;
 β_S = equilibrium coefficient of evaporation.

The effective cross-sectional area of the column F was calculated as:

$$F = F_{c.s.} \cdot (1-e) \tag{19}$$

where: $F_{c.s.}$ = cross-sectional area of the column; and
 e = porosity.

The validity of the model was verified by experiments with the solutions of oxalic acid and nitrobenzene. Experiments were carried out in the laboratory scale column with the following parameters: diameter of the column $D = 0.1$ m; height $H = 2.0$ m; number of plates 11; free cross-sectional area $S = 1\%$; diameter of holes $d_0 = 1.5$ mm. The gas flow rate was varied from $4.2 \cdot 10^{-3}$ to $8.4 \cdot 10^{-3}$ m/s and the liquid flow rate from $1.8 \cdot 10^{-4}$ to $1.4 \cdot 10^{-3}$ m/s. Within the given limits, the following correlations were derived:

$$e = 285.w_G^{1.75} \quad [20]$$

$$a = 1.2 \cdot 10^4 \cdot w_G + 18 \quad [21]$$

where: w_G = linear flow rate of the gas phase, and
 a = specific interfacial area, m^{-1} .

To calculate the volumetric mass transfer coefficient $K_L a$, the following correlation was taken (8):

$$K_L a = 0.467 \cdot w_G^{0.82} \quad [22]$$

and verified experimentally for the 'ozone-water' system in several points. Deviations did not exceed 25%.

The numerical solution of the system of equations [18] was realized by the Runge - Kutta method of the fourth order. In general, the number of iterations from 8 to 10 was sufficient to meet the desired error of tolerance. A good correlation between calculated and experimental values of ozone concentration in the outlet gas and organic compound concentration in the outlet water was obtained. Figure 4 presents the practical and calculated values of oxalic acid concentration in the outlet water as an example of model verification. The experimental conditions are presented in Table V. Investigation of countercurrent bubble columns showed that these constructions, although guaranteeing the possibility of regulation of water residence time in the wide range, did not guarantee high values of oxidation degree and ozone utilization. For instance, the effectiveness of ozone absorption in the present laboratory scale experiments did not exceed 9-16% for oxalic acid solutions.

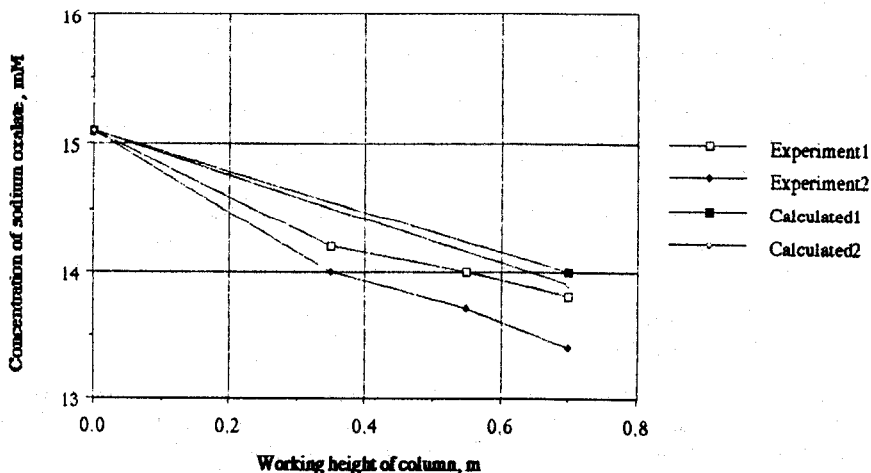


Figure 4. Results of verification of the countercurrent reactor model.

TABLE V. EXPERIMENTAL CONDITIONS FOR EXPERIMENTS WITH OXALIC ACID FOR VERIFICATION OF THE COUNTERCURRENT COLUMN MODEL

Experiment No.	Ozone Concentration in the Inlet Gas, mole.L ⁻¹	Gas Flow Rate, L.s ⁻¹	Liquid Flow Rate, L.s ⁻¹
1	7.5 x 10 ⁻⁴	3.3 x 10 ⁻²	3.1 x 10 ⁻³
2	6.5 x 10 ⁻⁴	6.7 x 10 ⁻²	3.1 x 10 ⁻³

In this work a new construction of a cocurrent contact column for moderate and slow ozonation reactions was elaborated. It was called "tube in tube" (Figure 5), consisting of a short part sectionalized with perforated plates and of longer tubes with downward and upward flow. For mathematical modeling, the stagewise model was used. Previously, the number of stages of ideal mixing was determined experimentally. The process of ozonation in the cocurrent contact apparatus was described by the following system of equations:

for the liquid phase:

$$\begin{aligned}
 & L.C_{SL0} + L.\Omega_L.C_{SL2} - L.(1 + \Omega_L).C_{SL1} - f_1 = 0 \\
 & \hline
 & L.(1 + \Omega_L).C_{SL(i-1)} + L.\Omega_L.C_{SL(i+1)} - L.(1 + 2\Omega_L).C_{SLi} - f_i = 0 \\
 & \hline
 & L.(1 + \Omega_L).C_{SL(n-1)} - L.(1 + \Omega_L).C_{SLn} - f_n = 0
 \end{aligned} \tag{23}$$

for the gas phase:

$$\begin{aligned}
 & G.C_{G0} + G.\Omega_G.C_{G2} - G.(1 + \Omega_G).C_{G1} - r_1 = 0 \\
 & \hline
 & G.(1 + \Omega_G).C_{G(i-1)} + G.\Omega_G.C_{G(i+1)} - G.(1 + 2\Omega_G).C_{Gi} - r_i = 0 \\
 & \hline
 & G.(1 + \Omega_G).C_{G(n-1)} - G.(1 + \Omega_G).C_{Gn} - r_n = 0
 \end{aligned} \tag{24}$$

with an equilibrium condition:

$$C_{Li} = \beta.C_{Gi} \tag{25}$$

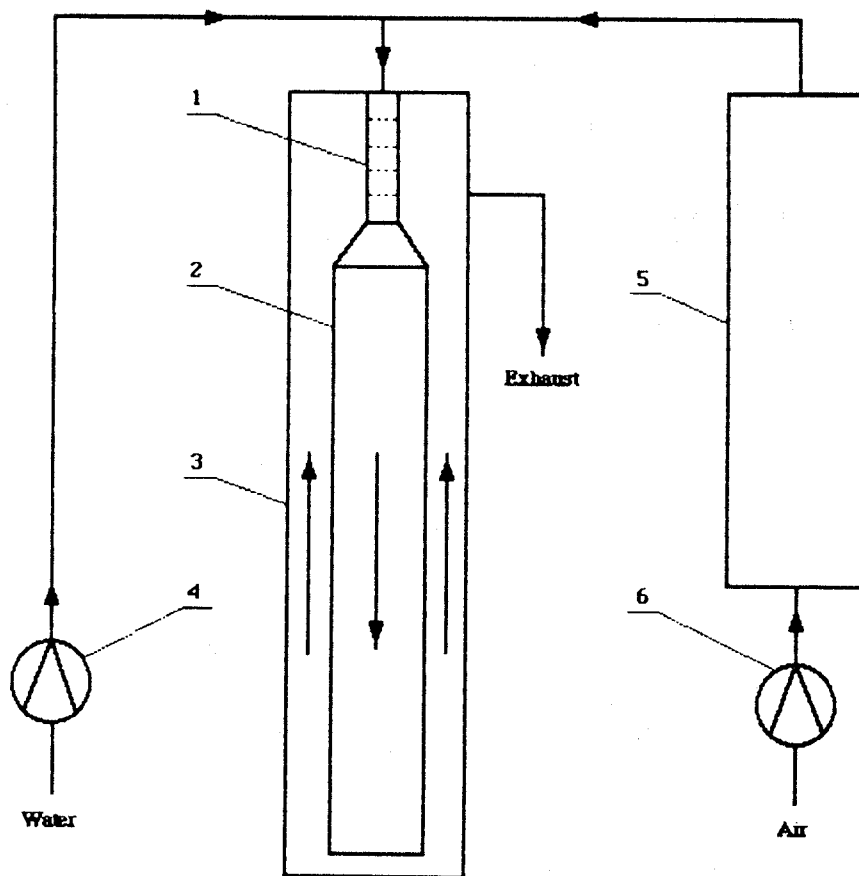
where Ω_G, Ω_L = the coefficient of back-mixing for the gas and liquid phases, respectively.

The form of the functions f_i and r_i depends on the chemisorption regime, and for the slow reaction kinetic regime is the following:

$$f_i = d \cdot H_a \cdot k_2 \cdot C_{SLi} \cdot C_{Li} \cdot V_{Li} \quad [26]$$

$$r_i = H_a \cdot k_2 \cdot C_{SLi} \cdot C_{Li} \cdot V_{Li} \quad [27]$$

where: d = stoichiometric coefficient;
 k_2 = second order reaction rate constant
 V_{Li} = volume of liquid phase in the i -stage.



1 = sectionalized part; 2 = inner tube; 3 = outer tube; 4 = pump; 5 = ozone generator; 6 = air compressor

Figure 5. Flow sheet of the cocurrent contact chamber (tube in tube).

Measurements of the porosity and the specific interfacial area led to the following equations:

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$$e = 67.82 \cdot w_L^{-1.8} \cdot w_G \quad [28]$$

$$a = 3200 \cdot w_G^{0.24} \cdot w_L - 230 \quad [29]$$

To calculate the volumetric mass transfer coefficient in the inner tube, the following correlation was taken (9) and verified experimentally in several points:

$$K_L a = 7.1 \cdot 10^{-3} \cdot e, s^{-1} \quad [30]$$

Deviations did not exceed 10%.

The validity of the model was verified by experiments with solutions of nitrobenzene and oxalic acid. The experimental conditions are presented in Table VI. Experiments were carried out in the laboratory-scale apparatus with the following parameters:

sectionalized part: $D = 0.04$ m; $H = 0.3$ m; $n = 2-5$; $d_0 = 1.0$ mm; $S = 62\%$;
 inner tube $D = 0.08$ m; $H = 1.4$ m;
 outer tube $D = 0.14$ m; $H = 2.0$ m.

TABLE VI. EXPERIMENTAL CONDITIONS FOR MODEL VERIFICATION OF THE COCURRENT DOWNFLOW REACTOR

Experiment No.	Compound	Liquid Flow Rate, L.s ⁻¹	Gas Flow Rate, L.s ⁻¹	Ozone Concentration in Gas, C ₀ ^m , mM
1	nitrobenzene	1.36	0.12	0.38
2	nitrobenzene	1.89	0.34	0.13
3	Na oxalate	1.50	0.12	0.39

In the column "tube in tube", high efficiency of ozone absorption was achieved. For example, during experiments with nitrobenzene, ozone concentration in the outlet gas was equal to zero, and during experiments with oxalic acid it was 20-30% of the inlet concentration. Differences between parameters calculated on the basis of the model process and their experimental values did not exceed 30 - 45% (Figure 6).

Conclusions

The theoretical basis and united methodology for calculation and modeling of ozonation processes and contact equipment have been elaborated. For the kinetic description of natural and wastewater ozonation processes, general parameters like color degree, COD, etc., are needed. The use of COD as a kinetic parameter of ozonation of wastewaters is possible and feasible because it takes into consideration the decrease in ozonation rate due to the formation of less readily oxidizable intermediate products. The use of simultaneous ozonation and UV irradiation makes possible to bring the COD of some wastewaters to very low final values (5-10 mg O₂/L).

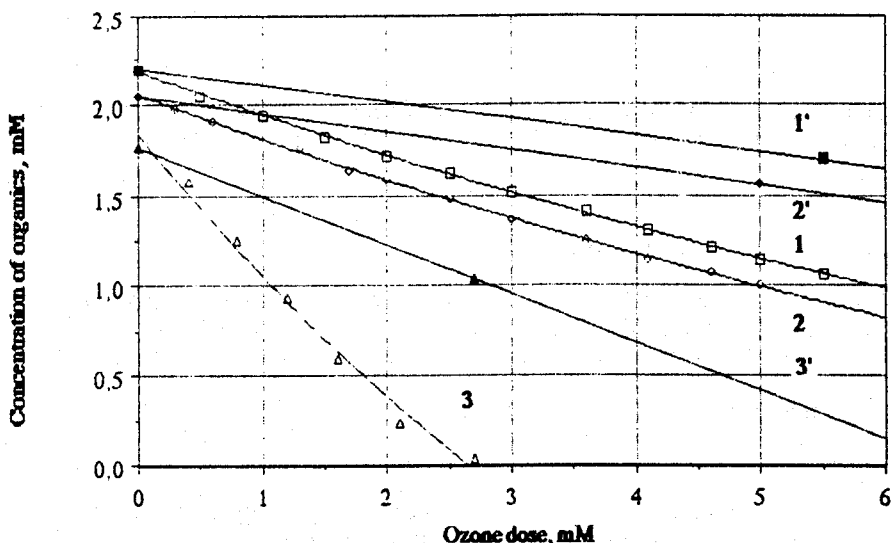


Figure 6. Results of verification of cocurrent downflow reactor model.
 1 & 2 = nitrobenzene, experimental; 1' & 2' = nitrobenzene, calculated;
 3 = sodium oxalate, experimental; 3' = sodium oxalate, calculated.

Cocurrent downflow of ozone and water has remarkable advantages - high values of porosity (gas content) and interfacial area, moderate head losses, etc. Sectionalization of the downflow by sieve plates of relatively large free areas causes very intensive turbulence and a large interfacial area. The mathematical models composed can be used for optimization of the contact equipment.

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Key Words

Ozone; Contacting; Water Treatment; Wastewater Treatment; Kinetics Modeling; Aniline; Toluidine; Humic Acids; Nitrobenzene; Glyoxylic Acid; Oxalic Acid; Acetic Acid; Chemical Oxygen Demand; Cocurrent Flow Ozone Contactor; "Tube In Tube" Ozone Contactor;

Résumé

Il a été élaboré dans cette étude la base théorique et la méthode de calcul et de modélisation des procédés d'ozonation et des équipements de contact. Il a été également proposé une méthode de détermination des constantes de vitesse des réactions, des coefficients stœchiométriques des valeurs optimales de pH, les produits intermédiaires et finaux, les régimes de chimisorption, etc. pour certains composés organiques typiques à réaction rapide ou lente (aniline, toluidine, acides humiques, nitrobenzène, acides glyoxalique, oxalique, et acétique) et pour les eaux usées. Pour le calcul du procédé d'ozonation des eaux usées, la demande chimique en oxygène (DCO) a été suggérée comme paramètre cinétique des solutions à ozoner. A partir des informations cinétiques, des recommandations concernant les équipements de contact - pour différents régimes de sorption chimique d'ozonation ont été présentées. Plusieurs nouveaux systèmes de contact ont été proposés.

Zusammenfassung

Die theoretische Grundlage und Methodik für Modellierung und Berechnung von Ozonierungsprozessen und Kontaktausrüstungen wurden erarbeitet. Methoden der Bestimmung von Geschwindigkeitskonstanten stöchiometrischer Koeffizienten, optimaler pH-Bedingungen, intermediärer und Finalprodukte, Chemisorptionsregime, etc., für bestimmte typische schnell und langsam reagierende organische Verbindungen (Anilin, Toluidin, Huminsäuren, Nitrobenzol, Glyoxal-, Oxal- und Essigsäure) sowie Abwasser werden vorgeschlagen. Zur Berechnung der Abwasser-ozonierung wird vorgeschlagen den Wert des chemischen Sauerstoffbedarfs (COD) als kinetischen Parameter der Lösungsseite zu verwenden. Auf der Grundlage der kinetischen Informationen werden verschiedene Vorschläge für die Auswahl und Konstruktion der Kontaktausrüstung bei verschiedenen Chemisorptionsregimen der Ozonierung gemacht. Es werden einige neuartige Kontaktapparaturen vorgestellt.

