

Characterization of ozonation processes by oxygen demand of compounds

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Abstract. Systematization of kinetic data of ozonation processes of wastewater is discussed. Literary and experimental data on the ozonation kinetics of aqueous solutions and wastewater were analysed. Chemical oxygen demand (COD) was used as the generalized kinetic parameter for ozonation processes of water solution and wastewater. To compare the theoretical considerations with experimental results, the rate constants of the ozonation of nitrobenzene and glyoxylic and oxalic acids as well as of real wastewater from aniline dye production were measured. The main conclusion of this study is that the use of COD as a generalized kinetic parameter for ozonation processes of water solution and wastewater is justified. The rate coefficient ζ_{O_3} in the equation of ozonation kinetics for water solution with several compounds or wastewater is not constant and it depends on the formation of compounds richer in oxygen and more resistant to ozone, i.e. on the COD of the solution. With decreasing COD also the rate coefficient ζ_{O_3} decreases. The reaction order with respect to the COD of the solution was shown to be equal to the reaction order with respect to the pure compound.

Key words: theoretical oxygen demand, ozonation rate constant, wastewater, rate coefficient, chemical oxygen demand.

INTRODUCTION

The design of the wastewater ozonation process and equipment in a pilot or full scale presumes availability of microkinetic data on the ozonation reactions (reaction mechanism, rate constant, reaction orders, stoichiometric coefficient). So far the exact mechanism, the mutual effect of oxidation intermediates, as well as the composition of ozonation products, even that of pure individual compounds, have remained problems of quite complicated nature.

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In order to avoid the effect of simultaneous interaction of oxidation intermediates on the results of investigation of the primary reaction of ozone with an organic compound, its kinetics is studied as a rule during the first seconds or minutes, i.e. at the initial rate. However, it is practically impossible to keep intermediates from affecting the course of the primary reaction, and this is why a rate coefficient is needed that takes into consideration the formation of by-products and the retarding of the oxidation process caused by it. Such a rate coefficient is especially useful for describing the ozonation process of wastewaters as multicomponent solutions.

In our earlier publication [1] we applied chemical oxygen demand (COD) for the description of the ozonation reactions of the wastewater with unknown compounds in a form of the following equation:

$$d[\text{O}_3]/dt = \zeta_{\text{O}_3} \text{COD}_{\text{mix}}^n [\text{O}_3]^m, \quad (1)$$

where ζ_{O_3} is the rate coefficient of the reaction by ozone in L/mol O₂ s, provided that $n = m = 1$.

The rate coefficient may also be expressed by the COD of the solution, ζ_{COD} , which differs from the rate coefficient for ozone because of the apparent stoichiometric ratio $z = \zeta_{\text{O}_3} / \zeta_{\text{COD}}$. This ratio is usually in the range 2–6 mgO₃/mgCOD.

Equation 1 has been disputed by some specialists of classical chemical kinetics. Their main objection has been that there is no chemical reaction between ozone and COD, the oxidation reactions occur between ozone and organic compounds in the water solution.

On the one hand this is of course true. On the other hand, however, engineers really need some kinetic expression for the modelling and design of wastewater ozonation processes. Unlike total organic carbon (TOC), COD depends unequivocally on the extent of wastewater ozonation, as ozonation, due to the formation of richer-in-oxygen compounds, inevitably leads to the reduction of the COD values. Later, Beltran et al. [2–4] applied COD for the description of ozonation kinetics of distillery and tomato wastewaters.

This paper focuses mainly on the meaning and determination of the rate coefficient ζ_{O_3} in Eq. 1 (it cannot be constant during the ozonation reaction as it is in the classical kinetic equation). Strictly speaking, even the rate constant in the ozonation reaction equation of one pure compound (benzene, phenol, aniline, etc.) can be considered constant only during the first seconds or minutes of the process.

As soon as the first oxidation intermediates are formed, the rate constant cannot be the same any more. Therefore, below we will actually discuss the following rate constants (coefficients): *rate constant* for a pure organic compound during the first minutes (seconds) of ozonation, *rate coefficient* for an ozonated solution of this compound, and *rate coefficient* for the ozonation of the real wastewater with many (often unknown) compounds.

THEORETICAL CONSIDERATIONS

First we shall try to bring reasons why the COD of wastewater may be used for mathematical description of the kinetics of its ozonation process.

In this study as a basis on the side of the chemical compound i the theoretical value of the oxygen demand ThOD_i (gO_2/mol) was taken. This parameter is constant for a given compound i and does not depend on isomerization. The theoretical oxygen demand (ThOD_i), which represents the amount of oxygen (in mg) needed for the complete oxidation of 1 mg of a given substance to CO_2 and H_2O , can be calculated for every single organic compound.

Thus, the amount of oxygen in milligrams per litre of solution can be brought into line with every concentration unit of the organic compound i in the solution C_i (mg/L), according to the equation:

$$[C_i] \text{ThOD}_i = \text{COD}_i. \quad (2)$$

In most cases the reaction rate of the organic compound i with dissolved ozone is described by the second order equation:

$$W = d[C_i]/dt = k_2 [C_i] [O_3] \quad (3)$$

or

$$W_1 = d[O_3]/dt = z k_2 [C_i] [O_3], \quad (4)$$

where k_2 is second order reaction rate constant, $\text{L}/\text{mol s}$; z is stoichiometric coefficient, $\text{mol O}_3/\text{mol } C_i$; and $[C_i]$ and $[O_3]$ are concentrations, mol/L .

Considering Eq. 2, the concentration of the compound i , C_i , can be expressed by the ratio:

$$[C_i] = \text{COD}_i / \text{ThOD}_i.$$

Then, for example, Eq. 4 will be:

$$W_1 = d[O_3]/dt = z k_2 \text{COD}_i / \text{ThOD}_i [O_3]. \quad (5)$$

Considering that ThOD_i is constant for a given component, it can be expressed as the constant of the equation:

$$W_1 = d[O_3]/dt = (z k_2 / \text{ThOD}_i) \text{COD}_i [O_3] = k'_2 \text{COD}_i [O_3], \quad (6)$$

where COD is in molO_2/L and k'_2 is in $\text{L}/\text{mol s}$.

Equation 6 expresses the rate of the ozonation reaction of the compound i through the COD of its solution in a manner similar to the classical equation of chemical kinetics.

For a mixture of n components (wastewater), the kinetic Eq. 3 may be expressed as follows:

$$W = d[\text{O}_3]/dt = \sum_{i=1}^n k_2 [C_i] [\text{O}_3]. \quad (7)$$

After multiplying and dividing the items on the right of Eq. 7 by the values of molar theoretical oxygen demand (ThOD_i^M , molO₂/mol) and using the designation k_2' , the equation will become:

$$d[\text{O}_3]/dt = \sum_{i=1}^n k_2' [C_i] \text{ThOD}_i^M [\text{O}_3]. \quad (8)$$

According to the Eq. 2, the multiplication $[C_i] \text{ThOD}_i^M$ represents the value of the COD of component i , and the sum total of the COD values of all components gives the COD of the mixture (wastewater):

$$\sum_{i=1}^n \text{COD}_i = \text{COD}_{\text{mix}}. \quad (9)$$

As Eqs. 2 and 9 indicate, Eq. 8 can be reduced to the following expression (see Eq. 1):

$$d[\text{O}_3]/dt = \zeta_{\text{O}_3} \text{COD}_{\text{mix}}^n [\text{O}_3]^m. \quad (10)$$

This is what was actually necessary to prove. The rate coefficient ζ_{O_3} depends on the quantitative and qualitative composition of wastewater, and will change (decrease) with changing (decreasing) COD_{mix} .

EXPERIMENTAL

Ozonation of model solutions of nitrobenzene, glyoxylic and oxalic acids, and their mixtures was carried out [1]. The rate constants of individual components differed radically. Some control experiments were conducted with a real biologically treated wastewater (BTW) of aniline dye production ($\text{COD}_0 = 144 \text{ mgO}_2/\text{L}$, $\text{BOD}_5 = 20 \text{ mgO}_2/\text{L}$, $\text{pH} = 7.1$, total nitrogen $\text{N} = 80 \text{ mg/L}$, initial colour = 500 deg.). The pH was adjusted with KOH or H₂SO₄ solutions. Ozonation was carried out in a 1.5-L semibatch bubble reactor. The ozone concentration in the gas stream was measured spectrophotometrically and kept constant in the range 4 to 40 mg/L. The dissolved ozone concentration was measured by the indigo method.

The rate constants for ozone were determined using the bubble method [5] and in the static conditions, using a spectrophotometer SPECORD UV/VIS/M-40, in a quartz cell with an optical length of 50 mm at the temperature of 20°C. Nitrobenzene in the solutions was determined spectrophotometrically ($\nu = 38440 \text{ cm}^{-1}$), while for oxalic acid titration with KMnO₄ and for glyoxylic acid the iodometric method was used. COD was determined according to the standard method [6].

RESULTS AND DISCUSSION

In order to check the reaction order with respect to COD of wastewater and ozone in Eq. 10, experiments of ozone decomposition in model solutions of nitrobenzene, glyoxylic acid, oxalic acid, and real wastewater from aniline dye production were carried out. We tried to find answers to the following questions:

– What is the difference between the values of the rate constant for a pure compound concentration and the rate coefficient for COD of the compound's solution?

– Is the reaction order in the case of a pure substance and COD of the substance solution the same or not?

Table 1 gives answers to these questions.

The rate constants k_2 in Table 1 correspond to the ozonation reaction's rate Eq. 3 and the rate coefficients ζ_{COD} in this table to the rate equation:

$$d[\text{COD}]/dt = \zeta_{\text{COD}} \text{COD} [\text{O}_3]. \quad (11)$$

Differently from nitrobenzene and oxalic acid ozonation of glyoxylic acid followed to our surprise zero order in the range of the tested initial concentration $(2-16) \times 10^{-3}$ mol/L in acid (pH = 3), neutral (pH = 7–8), as well as basic media (pH = 11–12). Unfortunately, no reasonable explanation for this phenomenon exists.

Table 1 shows that the values of the rate coefficient ζ_{COD} for the COD of the pure compound solution are somewhat lower than the values of the rate constant k_2 for the compound itself. This is due to the formation of more slowly reacting oxidation intermediates which are taken into account in the COD of the solution.

It was also established that in the case of ozonation of a mixture of compounds (such as wastewater), containing a faster reacting compound (for example, glyoxylic acid or nitrobenzene) and a slower reacting compound (for example, oxalic acid), the compound reacting faster plays the decisive role.

The reaction order with respect to the COD of the mixture is equal to the reaction order with respect to the COD of the component reacting faster. The value of the rate coefficient for the COD of the mixture ζ_{COD} is equal or close to the value of the rate coefficient for the COD of the compound reacting faster (Table 2).

Table 1. Values of rate constants and coefficients of model solutions of some compounds

Compound	C_0 , 10^3 mol/L	COD_0 , molO ₂ /L	pH	Order by compound	Rate constant k_2 , L/mol s, for compound	Rate coefficient ζ_{COD} , L/mol s, for COD
Nitrobenzene	4.86	35.45	9.0–9.5	1	3.3	2.8
Glyoxylic acid	13.94	14.22	7.0–8.0	0	0.019*	0.009*
Oxalic acid	13.75	6.90	6.5–8.0	1	0.2	0.1

* for zero order k_2 and ζ_{COD} are in 1/s.

Table 2. Values of rate coefficients for compounds and their mixtures at the initial stage of ozonation

Model solution	pH	$\zeta_{\text{C}_6\text{H}_5\text{NO}_2}$, L/mol s	ζ_{CHOCOOH} , L/mol s	ζ_{CODmix} , L/mol s
[CHOCOOH] = 13.9 mM; [(COOH) ₂] = 2.76 mM	6.5–7.5		0.009	0.009
[C ₆ H ₅ NO ₂] = 4.9 mM; [(COOH) ₂] = 4.3 mM	9.0–9.5	2.8		2.6
[C ₆ H ₅ NO ₂] = 4.9 mM; [(COOH) ₂] = 18 mM	9.0–9.5	2.8		2.0

For comparison the values of the rate coefficient were determined for a real BTW of aniline dye production. It was experimentally established (7 runs) that the rate coefficient for the COD of wastewater, ζ_{COD} , can be expressed as follows (see Fig. 1):

$$\zeta_{\text{COD}} = A \text{COD}^n = 0.06 \text{COD}^{1.25}, \text{ L/molO}_2 \text{ s.} \quad (12)$$

The values of A and n were obtained after linearization of Eq. 12 in the coordinates $\log \zeta_{\text{COD}} = \log A + n \log \text{COD}$ with the correlation coefficient 0.96.

In their paper published in 1992 Beltran et al. [2] determined the rate coefficients for distillery wastewater (7.61×10^3) and for tomato wastewater (3.90×10^4) at neutral pH, and compared these values to the rate constant value for phenol ozonation at pH = 7 (1.0×10^6 [7]). However, they did not discuss the possible change in the rate coefficient values during the process when the COD is decreasing.

In their next paper [3] Beltran et al. already presented a curve of the reduction of the rate coefficient of distillery wastewater ozonation reaction in time. The curve showed that during a 2-hour oxidation process the rate coefficient decreased from 8×10^3 to 0.5×10^3 L/mol s, i.e. 16 times.

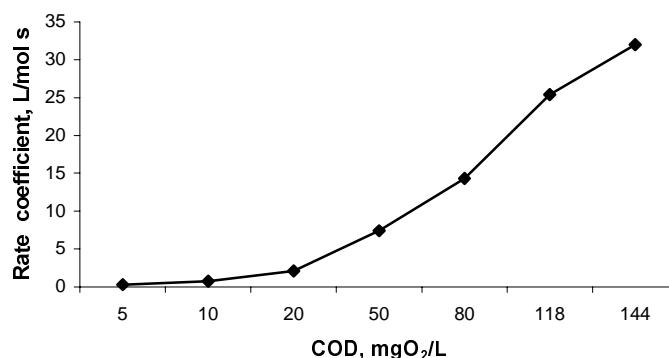


Fig. 1. Rate coefficient ζ_{COD} of the ozonation reaction of biologically treated wastewater versus COD.

The values of the rate coefficient ζ_{COD} for our BTW of aniline dye production are much lower, because after biological oxidation the solution contains mainly final oxidation products, aldehydes, ketones, and carbocyclic acids. Table 3 presents some rate constant values for the ozonation reaction of such compounds. In our experiments the values of ζ_{COD} were in the range 32 to 0.3 L/mol s depending on the COD, as it was expected for BTW.

As BTW contains oxygen-rich compounds (aldehydes, ketones, carboxylic acids) the rate of its COD reduction is always slower than the rate of ozone consumption. Figure 2 presents the curve of ozone decomposition in BTW with $\text{COD}_0 = 64 \text{ mgO}_2/\text{L}$ at the initial concentration of dissolved ozone $[\text{O}_3]_0 = 2.9 \text{ mg/L}$.

Table 3. Rate constant values for the ozonation of aldehydes and acids

Compound	pH	k_2 , L/mol s	Reference
Formaldehyde	5	36	[8]
	<7	0.1	[9]
Acetaldehyde	2	1.5	[9]
Glyoxal	5	42	[8]
Formic acid	<7	5	[9]
Acetic acid	<5	$3 \cdot 10^{-5}$	[9]
Glyoxylic acid	<7	20	[5]
Oxalic acid	5-6	<0.04	[9]

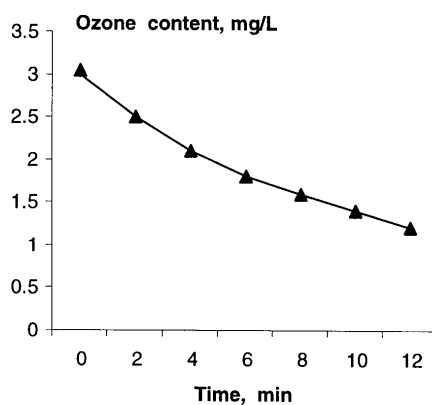


Fig. 2. Ozone decomposition in biologically treated wastewater with $\text{COD}_0 = 64 \text{ mgO}_2/\text{L}$ at the initial ozone concentration $[\text{O}_3]_0 = 2.9 \text{ mg/L}$.

CONCLUSIONS

The use of COD as a substitute of the effective concentration in the equation of ozonation of mixtures of organic compounds and wastewaters

$d[\text{O}_3]/dt = \zeta_{\text{O}_3} \text{COD}_{\text{mix}}'' [\text{O}_3]^m$ is justified because it takes into consideration the decrease in the ozonation rate due to the formation of less readily oxidizable intermediate products. The values of the rate coefficient ζ_{COD} for the COD of a pure compound solution are somewhat lower than the values of the rate constant k_2 for the compound itself. This is due to the formation of less rapidly reacting oxidation intermediates, which are taken into account in the COD of the solution. In the case of the ozonation of a mixture of compounds (such as wastewater) containing a faster reacting compound (for example, glyoxylic acid or nitrobenzene) and a slower reacting compound (for example, oxalic acid), the faster reacting compound plays the decisive role. The reaction order with respect to the COD of the mixture is equal to the reaction order with respect to the COD of the faster reacting component. The value of the rate coefficient for the COD of the mixture ζ_{COD} is equal or close to the value of the rate coefficient for the COD of the faster reacting compound. The values of ζ_{COD} for the biologically treated wastewater from aniline dye production were in the range 32 to 0.3 L/mol s depending on the COD. Such values were expected for a mixture containing aldehydes, ketones, and carbocyclic acids.

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Osoonimisprotsesside iseloomustus ühendite hapnikutarbe järgi

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On käsitletud reovee osoonimisprotsesside kineetikat. Eeldati, et keemilise ühendi osooniga reageerimise kiirus peab olenema muude näitajate kõrval ka selle aine teoreetilisest hapnikutarbest. Samast loogikast lähtudes on põhjendatud reovee keemilise hapnikutarbe (KHT) kasutamist osoonimisprotsessi kineetilise näitajana. Ainete segu ja reaalse heitvee puhul on osoonimisreaktsiooni järk ja kiiruskoefitsient määratud osooniga kõige kiiremini reageeriva komponendi KHT poolt. Aniliinvärvitööstuse bioloogiliselt puhastatud reovee osoonimisreaktsiooni kiiruskoefitsient oli piirides $32-0,3$ l/mol s, olenevalt reovee KHT-st. Leitud kiiruskoefitsiendi väärtused vastavad hästi hapnikurikaste ühendite (aldehüüdid, ketoonid, karboonhapped) ja osooni reageerimise kiiruskonstantide kirjanduses toodud väärtustele, kuna nimetatud ühendid ongi reovete biopuhastusprotsessi tüüpilised lõppproduktid.