



## Ozone absorption in a mechanically stirred reactor

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**Abstract:** Ozone absorption in water was investigated in a mechanically stirred reactor, using both the semi-batch and continuous mode of operation. A model for the precise determination of the volumetric mass transfer coefficient in open tanks without the necessity of the measurement the ozone concentration in the outlet gas was developed. It was found that slow ozone reactions in the liquid phase, including the decomposition of ozone, can be regarded as one pseudo-first order reaction. Under the examined operating conditions, the liquid phase was completely mixed, while mixing in a gas phase can be described as plug flow. The volumetric mass transfer coefficient was found to vary with the square of the impeller speed.

**Keywords:** ozone, absorption, stirred reactor, volumetric mass transfer coefficient.

### INTRODUCTION

When ozone from a gas mixture is absorbed in water of different quality, the appearance of free ozone in the water means that there are no fast reactions of ozone with substances originally present in the water. Very simple Equations describe the ozone transfer from a gas mixture to water in stirred tanks in which liquid phase is completely mixed. For the continuous mode of operation, the Equation is:

$$G_{\text{IN}} c_{G_{\text{IN}}} - G_{\text{OUT}} c_{G_{\text{OUT}}} = K_L a V (c_L^* - c_L) \quad (1)$$

and for the semi-batch mode:

$$\frac{dc_L}{d\tau} = K_L a (c_L^* - c_L) - r_L \quad (2)$$

where  $r_L$  is the overall rate of the slow ozone reactions in the liquid phase. In the case of distilled water  $r_L$  represents the ozone self-decomposition rate. The value of  $r_L$  may be easily determined by using Eq. (3), which also holds for the continuous mode of operation:

$$G_{\text{IN}} c_{G_{\text{IN}}} - G_{\text{OUT}} c_{G_{\text{OUT}}} = L c_L + r_L V \quad (3)$$

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In Eqs. (1) and (3),  $G$  and  $L$  represent the gas and liquid volumetric flow rates, respectively, and  $c_G$  and  $c_L$  the ozone concentration in the gas and liquid phase, respectively. However, the experimental determination of the volumetric mass transfer coefficient from Eqs. (1) or (2) requires the ozone concentration in the liquid phase, which is in equilibrium with ozone partial pressure in the gas phase, to be known. This concentration,  $c_L^*$ , is the product of the solubility ratio  $s$ , and average ozone concentration in the gas bubbles present in the gas–liquid dispersion in the reactor,  $\bar{c}_G$ , according to the Henry law:

$$c_L^* = s \bar{c}_G \quad (4)$$

A variety of data for the equilibrium concentration of ozone in water as a function of temperature is reported in the literature.<sup>1–11</sup> The influence of pH and ionic strength of the liquid phase on the equilibrium ozone concentration was also considered.<sup>11,12</sup>

Literature values of the solubility of ozone in water, converted to a solubility ratio at 20 °C and pH 7, are summarized in Table I.

TABLE I. Literature values of the solubility ratio

Reference	$s$
1	0.340
2	0.334
3	0.355
4	0.290
5	0.309
6	0.245
7	0.243
8	0.241
9	0.251
10	0.240
11.1	0.257
11.2	0.270
11.3	0.240
11.4	0.200
11.5	0.210
11.6	0.220

The values of solubility ratios from Table I can be summarized into two groups. In the first group, values of around 0.3 and above are predicted,<sup>1–5</sup> while in the second group, the values are in the range from 0.2 to 0.27.<sup>6–11</sup>

The value of the solubility ratio suggested by Bin,<sup>10</sup> which approximately represents the mean value of the distribution ratios predicted in the literature,<sup>6–11</sup> and has been adopted by IOA, was used in this work.

On the other hand, the average ozone concentration in gas bubbles present in a gas–liquid dispersion in reactor,  $\bar{c}_G$ , depends on the mixing status in the gas phase. It is evident that the value of the equilibrium ozone concentration calculated on the basis of the ozone concentration in the effluent gas will be lower than that calculated from the ozone concentration in the influent gas. Consequently, these different approaches may result in different obtained values of the volumetric mass transfer coefficients and, furthermore, in different behaviors of the volumetric mass transfer coefficient when some of the operating conditions are changed (impeller speed, power input or superficial gas velocity). In this way, different authors suggested different correlations for predicting the volumetric mass transfer coefficient as a function of power consumption or impeller speed in stirred tank reactors.

Ouederni *et al.*<sup>6</sup> suggested the value of volumetric mass transfer coefficient to vary with impeller speed to the power 0.67, while Anselmi *et al.*<sup>13</sup> suggested the exponent 2. Mallevalle *et al.*<sup>14</sup> and Bouaifi *et al.*<sup>15</sup> suggested that the volumetric mass transfer coefficient vary with the specific power input to the power of 0.5, while Qiu *et al.*<sup>16</sup> suggested exponent 0.4 and Yocum<sup>17</sup> 0.46.

Our assumption was that there is not one reason for the behavior of the ozone and oxygen volumetric mass transfer coefficients to differ when the impeller speed is changed.

Pejanović<sup>18</sup> found that the oxygen volumetric mass transfer coefficient varied with the square of the impeller speed in the same stirred tank reactor as used in this study.

This fact was the basis for the determination of the mixing level in the gas phase in this reactor.

The main objective of this work was to establish a model for precise determination of the ozone volumetric mass transfer coefficient in opened mechanically stirred tanks, without the necessity of measuring the ozone concentration in the effluent gas.

#### EXPERIMENTAL

The experimental set up is schematically shown in Fig. 1. A closed reactor was used for the continuous mode of operation, while semi-batch experiments were performed in an open tank.

The impeller speeds and gas flow rates were chosen in the ranges which provide that mechanical sucking be avoided.

An ozone generator Ozone Lab 100/DS, Yanco Industries Ltd. Burton, Canada, was used. Ozone was absorbed in water in a standard mechanically stirred reactor, equipped with Rushton type 6-bladed impeller. The diameter of the tank was 200 mm and the height 400 mm, while the liquid height in the reactor was around 200 mm, and was measured in each experimental run. In this way, the volume of liquid in the reactor was around 6 dm<sup>3</sup>, but varied from one experiment to another. The impeller speed ranged from 300 to 600 min<sup>-1</sup>, while the gas flow rate was 0.567 dm<sup>3</sup> min<sup>-1</sup> for continuous and 0.25 dm<sup>3</sup> min<sup>-1</sup> for the semi-batch mode of operation. The ozone concentrations in both the liquid and gas phase were measured by standard iodometric titration.

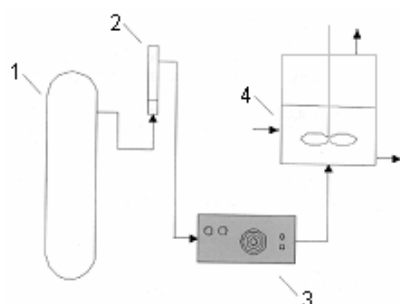


Fig. 1. Experimental set up: oxygen bomb (1), gas flowmeter (2), ozone generator (3) and stirred tank (4).

## RESULTS AND DISCUSSION

### *Continuous mode*

The experiments were performed in the same reactor and with the same “clean” water quality as used in the study of Stankovic.<sup>19</sup> We are of the opinion that Stankovic arbitrarily assumed that the ozone decomposition reaction is zero order with respect to ozone and that there were no fast and slow chemical reactions of ozone with substances present in the “clean” water. This approach resulted in too low values of the volumetric mass transfer coefficients obtained.

The experimentally measured values of  $c_{G_{IN}}$ ,  $c_{G_{OUT}}$  and  $c_L$ , and the two values of  $K_L a$ ,  $(K_L a)_{OUT}$ , calculated on the basis of the average ozone concentration in the gas bubbles being equal to the ozone concentration in the outlet gas flow, and  $(K_L a)_m$ , calculated assuming that  $\bar{c}_G = (c_{G_{IN}} + 5c_{G_{OUT}})/6$ , are summarized in Table II. Only this combination of  $c_{G_{IN}}$  and  $c_{G_{OUT}}$  assures that  $(K_L a)_m$  depends on the square of impeller speed.

TABLE II. Ozone volumetric mass transfer coefficient as a function of impeller speed (gas flow rate:  $0.567 \text{ dm}^3 \text{ min}^{-1}$ , liquid flow rate:  $1.5 \text{ dm}^3 \text{ min}^{-1}$ , temperature:  $18 \text{ }^\circ\text{C}$ , solubility ratio: 0.256). The dependence of  $(K_L a)_m$  on impeller speed is shown in Fig. 2.

$n$ $\text{min}^{-1}$	$c_{G_{IN}}$ $\text{mg dm}^{-3}$	$c_{G_{OUT}}$ $\text{mg dm}^{-3}$	$c_L$ $\text{mg dm}^{-3}$	$V$ $\text{dm}^3$	$(K_L a)_{OUT}$ $\text{min}^{-1}$	$(K_L a)_m$ $\text{min}^{-1}$
300	5.480	4.034	0.168	6.23	0.152	0.142
	6.554	4.846	0.226	6.18	0.154	0.144
	7.627	5.648	0.295	6.32	0.154	0.144
400	5.480	3.593	0.271	5.87	0.281	0.250
	6.554	4.314	0.360	5.93	0.288	0.255
	7.627	5.085	0.440	5.81	0.288	0.256
500	4.944	2.888	0.314	5.86	0.468	0.388
	5.480	3.232	0.362	5.76	0.475	0.394
	6.017	3.606	0.411	5.54	0.482	0.401
600	4.944	2.625	0.380	5.92	0.761	0.568
	5.480	2.948	0.436	5.92	0.761	0.568
	6.017	3.277	0.492	5.92	0.756	0.566

The ozone volumetric mass transfer coefficient is neither affected by the ozone concentration in the inlet and outlet gas flow, nor the free ozone concentration in the water. This means that the ozone self-decomposition and slow chemical reactions in the liquid phase do not influence the value of the physical ozone volumetric mass transfer coefficient.

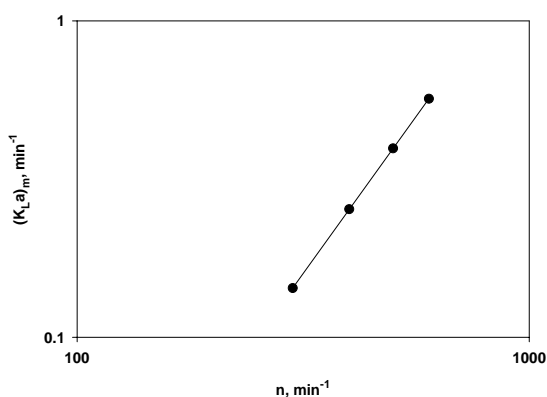


Fig. 2. Dependence of the volumetric mass transfer coefficient on impeller speed.

However, increasing the impeller speed causes a rapid increase of the volumetric mass transfer coefficient. Pejanović<sup>18</sup> determined the oxygen volumetric mass transfer coefficient in the same reactor as used in this work, at 14 °C, and with a gas flow rate of 40 dm<sup>3</sup> h<sup>-1</sup>. These values, converted to the conditions from Table II, are summarized in Table III.

TABLE III. Oxygen volumetric mass transfer coefficient as a function of impeller speed

$n / \text{min}^{-1}$	300	400	500	600
$(K_L a)_{\text{O}_2} / \text{min}^{-1}$	0.175	0.312	0.487	0.706

Pejanović<sup>18</sup> showed that the oxygen volumetric mass transfer coefficient depends on the square of the impeller speed, which also holds for the ozone volumetric mass transfer coefficient  $(K_L a)_m$  from Table II. The ratio of these two coefficients is approximately 0.814. This ratio may also be estimated from the expression given in the literature:<sup>12</sup>

$$\frac{(K_L a)_{\text{O}_3}}{(K_L a)_{\text{O}_2}} = \left( \frac{D_{\text{O}_3}}{D_{\text{O}_2}} \right)^n \quad (5)$$

where  $D_{\text{O}_3}$  and  $D_{\text{O}_2}$  are the molecular diffusivities of ozone and oxygen in water, respectively, and the exponent  $n$  depends on the model of molecular diffusion, being 1 for the two-film model and 0.5 for the surface renewal and penetration model. However, different values of the ozone end oxygen molecular diffusivities are given in the literature. Gottschalk<sup>12</sup> suggests that the ratio between the ozone and oxygen molecular diffusivities in water is 0.622, while Bin<sup>20</sup>

recommends the value of 0.83. Nevertheless, the value obtained in this work seems to be reasonable.

Therefore, a plug flow for mixing in the gas phase is proposed, which was also reported by Wu *et al.*<sup>9</sup> The ozone volumetric mass transfer coefficient may now be determined in an open continuous flow stirred reactor, without measuring of ozone concentration in the outlet gas, from Eq. (1) and with  $c_L^* = s(c_{G_{IN}} + 5 c_{G_{OUT}})/6$ .

#### *Semi-batch mode*

Determination of the ozone volumetric mass transfer coefficient from Eq. (2) requires the overall rate of ozone decomposition and slow chemical reactions in the liquid phase to be known. This rate was determined using Eq. (3) and is expressed by the following equation:

$$r_L = -\frac{dc_L}{d\tau} = k_0 + k_1 c_L \quad (6)$$

where  $k_0$  and  $k_1$  are the pseudo rate constants, being  $0.05 \text{ mg dm}^3 \text{ min}^{-1}$  and  $0.1 \text{ dm}^3 \text{ min}^{-1}$ , respectively, for Belgrade drinking water at  $20^\circ \text{C}$ .

In a recent paper, Bin<sup>21</sup> recommended the method of treatment of experimental data assuming that the equilibrium ozone concentration in water is approximately constant during absorption. Since this is not quite true, a different approach is proposed.

It was found that the change in free ozone concentration in drinking water with time, during an absorption run, may be fitted well by the following expression:

$$c_L = a(1 - e^{-b\tau}) \quad (7)$$

Equation (7) indicates that the free ozone concentration in water is an increasing function of the absorption time. Consequently, the driving force for absorption from Eq. (2) decreases with time, causing an increase in the ozone concentration in the outlet gas flow and the ozone equilibrium concentration with absorption time. The form of Eq. (7) suggests that the change of the ozone equilibrium concentration in water with time may be well represented by a linear increase of this concentration with increasing free ozone concentration in water:

$$c_L^* = c_{L_0}^* + A c_L \quad (8)$$

In this way, Eq. (2) becomes:

$$\frac{dc_L}{d\tau} = K_L a (c_{L_0}^* + A c_L - c_L) - k_0 - k_1 c_L \quad (9)$$

and the solution of this equation is:

$$c_L = \frac{K_L a c_{L_0}^* - k_0}{K_L a (1 - A) + k_1} \left[ 1 - e^{-(K_L a (1 - A) + k_1)\tau} \right] \quad (10)$$

By comparing Eqs. (7) and (10), one may find that:

$$a = \frac{K_L a c_{L_0}^* - k_0}{K_L a (1 - A) + k_1} \quad (11)$$

and:

$$b = K_L a (1 - A) + k_1 \quad (12)$$

The time derivative of Eq. (7) is:

$$\frac{dc_L}{d\tau} = ab e^{-b\tau} \quad (13)$$

This means that this time derivative of the free ozone concentration in water may be found at any given time, if the values of the constants  $a$  and  $b$  are determined from the best fit of the change of free ozone concentration in water with time. The exact values of  $c_{L_0}^*$  and constant  $A$  are not necessary to be known.

Calculation of  $K_L a$  from Eq. (2) requires that the ozone concentration in the outlet gas flow is also known. It is assumed that this concentration may be calculated from the integral balance, as a mean value over a predefined period of time. Since  $G_{OUT}$  differs from  $G_{IN}$  by less than 1 %, the integral balance Equation for any 2 minutes duration of absorption is:

$$c_{G_{OUT},n} = \frac{G c_{G_{IN}}^2 - V(c_{L,n+1} - c_{L,n-1}) - \left( k_0 + k_1 \frac{c_{L,n+1} + c_{L,n-1}}{2} \right) V}{G^2} \quad (14)$$

where  $n$  is the minutes of absorption time and  $V$  is the liquid volume in the reactor. Eq. (14) is valid in time intervals in which the ozone concentration in the liquid phase is close to a linear function of the absorption time, *i.e.*, at the beginning of absorption.

Considering ozone absorption in Belgrade drinking water at 20 °C, the inlet gas flow rate being 0.25 dm<sup>3</sup> min<sup>-1</sup> and the ozone concentration in the inlet gas 33 mg dm<sup>-3</sup>, the data of the change of the free ozone concentration in water with time given in Table IV are obtained.

TABLE IV. The dependence of free ozone concentration in water ( $G_{IN} = 0.25 \text{ dm}^3 \text{ min}^{-1}$ ,  $n = 400 \text{ min}^{-1}$ )

$\tau / \text{min}$	0	2	4	10	15
$c_L / \text{mg dm}^{-3}$	0	1.30	2.03	3.30	3.62

Fitting of experimental data from Table IV in Origin 5.0 software gives the values of parameters  $a$  and  $b$  in Eq. (7), as follows:  $a = 3.827 \text{ mg dm}^{-3}$  and  $b = 0.1962 \text{ min}^{-1}$ . In that way:

$$\left( \frac{dc_L}{d\tau} \right)_1 = 0.6171 \frac{\text{mg}}{\text{dm}^3 \text{ min}},$$

$c_{L_1} = 0.682 \text{ mg dm}^{-3}$  and  $c_{L_2} = 1.242 \text{ mg dm}^{-3}$ , while from Eq. (14), with  $V = 6 \text{ dm}^3$  and  $n = 1 \text{ min}^{-1}$ :

$$c_{G_{\text{OUT},1}} = 15.4056 \frac{\text{mg}}{\text{dm}^3}$$

The ozone volumetric mass transfer coefficient may now be calculated from the following Equation:

$$K_L a = \frac{\left( \frac{dc_L}{d\tau} \right)_1 + k_0 + k_1 c_{L_1}}{s(5c_{G_{\text{OUT},1}} + c_{G_{\text{IN}}})/6 - c_{L_1}} = 0.1977 \text{ min}^{-1}$$

The obtained values of the ozone volumetric mass transfer coefficient agree well with the correlation recommended by Linek *et al.*<sup>22</sup> and with the values obtained by Wu and Masten,<sup>9</sup> but differ from the values given by Bin and Rouston.<sup>23</sup> Since the value obtained in the continuous mode, for a gas flow rate of  $0.567 \text{ dm}^3 \text{ min}^{-1}$  at the same impeller speed, corrected to the temperature of  $20 \text{ }^\circ\text{C}$  is  $0.266 \text{ min}^{-1}$ , the correlation given by Pejanović<sup>18</sup> for oxygen transfer in water in stirred vessels seems to hold for ozone transfer as well:

$$K_L a = \text{const}(n^3 d^2)^{2/3} u_G^{1/3} \quad (15)$$

where  $d$  is the diameter of turbine impeller and  $u_G$  is the superficial gas velocity.

#### CONCLUSIONS

Investigations of ozone transfer to water in a semi-batch and continuous flow stirred reactor were performed in order to determine the ozone volumetric mass transfer coefficient. The flooding regime and mechanical sucking in the reactor were avoided by the correct choice of impeller speed and gas flow rate. The investigations showed that the value of the ozone volumetric mass transfer coefficient is not affected by the liquid flow rate, since the corresponding values were obtained in both types of operation. However, the ozone volumetric mass transfer coefficient was found to vary with the square of the impeller speed and with the third root of the gas flow rate. The same behavior was previously reported for oxygen transfer to water.

#### ИЗВОД

##### АБСОРПЦИЈА ОЗОНА У РЕАКТОРУ СА МЕХАНИЧКИМ МЕШАЊЕМ

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Испитивана је абсорпција озона у води у шаржном и проточном реактору са механичким мешањем. Развијен је модел за прецизно одређивање коефицијента преноса масе озона у отвореним судовима, без потребе за мерењем концентрације озона у излазном гасу. Пока-



зано је да се споре хемијске реакције озона са полутантима присутним у води, укључујући и спонтану декомпозицију озона, могу третирати као једна укупна хемијска реакција псеудо-првог реда. При оперативним условима коришћеним у овом раду, мешање у течной фази је идеално, док се за мешање у гасној фази може применити модел клипног струјања. Констатовано је да запремински коефицијент преноса масе озона расте пропорционално квадрату броја обртаја мешалице.

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