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OZONE ABSORPTION IN RAW WATERS

The ozone absorption in raw water entering the main ozonization step at the Belgrade drinking water supply plant was investigated in a continuous stirred tank reactor (CSTR). A slow chemical reaction rate of dissolved ozone and pollutants present in raw water have been experimentally determined. The modified Hatta number was defined and calculated as a criterion which determines whether and to which extent the reactions of ozone and pollutants influence the rate of the pure physical ozone absorption.

Key words: ozone, absorption, chemical reactions, raw water, continuous stirred tank reactor (CSTR).

The ozone absorption in raw waters of different unknown compositions is accompanied by chemical reactions of dissolved ozone and different substances - pollutants present in water. Simultaneously, the ozone self-decomposition in the water occurs [1]. Depending on the nature and the concentration of these pollutants, chemical reactions could be so fast and the ozone consumption so large that the residual ozone concentration in the bulk liquid is negligibly small. In that case, the rate of the mass transfer and thus the volumetric ozone mass transfer coefficient are enhanced, compared to their values for the pure physical ozone absorption [2]. However, in the case of slow chemical reactions, when the amount of the absorbed ozone becomes higher than the amount reacted, the dissolved ozone appears in the bulk liquid as the residual ozone concentration. In the case of very slow chemical reactions, the ozone transfer from a gas to a liquid is not anymore affected by chemical reactions, and the volumetric ozone mass transfer coefficient is equal to that of the physical ozone absorption.

The volumetric ozone mass transfer coefficient has been recently shown to be a function of impeller speed [3], and a detailed literature review has been presented as well [3]. It was found that the ozone mass transfer and thus the ozone volumetric mass transfer coefficient depended neither upon the ozone concentration in the inlet and outlet gas flow nor on the residual ozone concentration in the liquid phase.

Such information indicated that the ozone self-decomposition and slow chemical reactions with pollutants present in water did not influence the volumetric ozone mass transfer coefficient characterizing the pure physical ozone absorption. However, this conclusion was not explicitly proved.

The present study is related to the ozone absorption in raw water in a continuous stirred tank reactor (CSTR). The main objective was to define and calculate a criterion which could be used for estimating whether the chemical reactions of dissolved ozone and pollutants present in raw water influence the rate of the physical ozone absorption or not. For this purpose, the model of the ozone absorption in raw water, accompanied by chemical reactions in the liquid phase based on the overall ozone mass balance for the reactor was developed.

THEORETICAL MODEL

If the liquid phase is perfectly mixed, the overall ozone mass balance for its absorption from a gas phase in a continuous stirred tank reactor (CSTR) may be represented by the following equation:

$$G_{IN}c_{G,IN} - G_{OUT}c_{G,OUT} = Lc_L + r_L V_L = K_L a(c_L^* - c_L) V_L \quad (1)$$

The overall rate of the ozone chemical reactions in the liquid phase, r_L , may be calculated from the equation (1), provided that the gas and liquid flow rates, G_{IN} , G_{OUT} and L , the ozone concentrations in the inlet and outlet gas flows, $c_{G,IN}$ and $c_{G,OUT}$, as well as the dissolved ozone concentration, c_L , are measured; the liquid volume in the reactor, V_L , should be also known.

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If n pollutants are present in the raw water at the concentrations of c_1, c_2, \dots, c_n , all reacting with the dissolved ozone by a second order reaction rate mechanism (the first order with respect to both ozone and each pollutant), the overall rate of slow chemical reactions in raw water, r_{SC} , will be the sum of the ozone reaction rates with respect to each pollutant:

$$r_{SC} = k_{21}c_Lc_1 + k_{22}c_Lc_2 + \dots + k_{2n}c_Lc_n = c_L \sum_{i=1}^n k_{2i}c_i \quad (2)$$

The sum of the products, $\sum_{i=1}^n k_{2i}c_i$, can be symbolically signed as k_2c_B .

Simultaneously, the ozone self-decomposition in the raw water occurs. The rate of the ozone self-decomposition is defined as [4]:

$$r_D = k_0 + k_1c_L \quad (3)$$

The pseudo first order reaction rate constants, k_0 and k_1 , for the ozone self-decomposition for distilled water at 18 °C were determined to be 0.021 mg dm⁻³ min⁻¹ and 0.0325 min⁻¹, respectively. Thus, if the dissolved ozone concentration is measured, the ozone self-decomposition rate could be calculated by the equation (3).

The overall rate of the ozone reactions in the water is the sum of the slow chemical reaction rate and the ozone self decomposition rate:

$$r_L = r_{SC} + r_D \quad (4)$$

By combining the equations (2) and (4), one obtains

$$r_{SC} = r_L - r_D = k_2c_Bc_L \quad (5)$$

If the dissolved ozone concentration is known, the product k_2c_B can be calculated by the equation (5). The increase in the residual ozone concentration in the water, caused by increasing the ozone concentration in the inlet gas flow or by increasing the impeller speed thus increasing the ozone mass transfer, will cause the decrease in the concentration of each pollutant present in the water, and consequently the decrease in the product k_2c_B .

According to Danckwerts [2], the value of the modified Hatta number for given the operating conditions should be checked in order to estimate with confidence whether the slow chemical reactions of the ozone affect the ozone absorption or not. The modified Hatta number is defined as follows:

$$\sqrt{M} = \frac{\sqrt{D_A k_2 c_B}}{k_L^0} \quad (6)$$

From equation (6) it follows that the value of the modified Hatta number can be calculated if the values of the ozone diffusivity, D_A , and the ozone mass trans-

fer coefficient for physical absorption, k_L^0 , are known, and if the product k_2c_B is experimentally determined. The value of the ozone diffusivity in the water at 18 °C of 1.62·10⁻⁵ m²/s [5], which is somewhat higher than that published by Gottschalk et al. [1], was used to calculate the modified Hatta number. The value of the ozone mass transfer coefficient for physical absorption can be approximated by the corresponding value of the oxygen mass transfer coefficient obtained experimentally in the same reactor as used in this study, being 4·10⁻² cm/s [6]. A similar value could be obtained by using Calderbank and Moo-Young expression for bubbles, diameters of which are larger than 2.5 mm [7]. However, they suggested the value of approximately 1·10⁻² cm/s, for smaller bubbles which behave like rigid spheres, so this value was used as a more severe value for estimating the modified Hatta number.

If $\sqrt{M} \ll 1$, then the enhancement factor for the absorption accompanied by the chemical reaction in liquid phase is equal to one [2]. It means that slow chemical reactions have no influence on the rate of the physical absorption and that the volumetric mass transfer coefficient in the case of the absorption followed by chemical reactions is equal to the value for the physical absorption.

EXPERIMENTAL

The experimental set up, schematically shown in Fig. 1, consisted of an oxygene bomb, an ozone generator (Ozone Lab 100/DS, Yanco Industries Ltd. Burton, Canada) and a closed reactor with a continuous mode of the operation. The stirred tank of a standard dimension was equipped with a Rushton type 6-bladed impeller. The diameter and the height of the tank were 200 and 400 mm, respectively. Ozone was absorbed in a raw water continuously flowing through the reactor. The liquid height in the reactor was held constant (around 200 mm). The liquid volume in the reactor was about 6 dm³ and was measured in each experimental run. The impeller speed varied in a range from 300 to 600 min⁻¹ and was measured by a counter. The gas and liquid flow rates were 0.567 and 1.5 dm³/min, respectively and were measured by rotameters. Under the operating conditions employed, a flooding regime was avoided and the surface aeration was not observed. All experiments were performed at 18 °C and at atmospheric pressure. The ozone concentrations in both liquid and gas phases were measured by the standard iodometric titration. Experimentally measured values of $c_{G,IN}$, $c_{G,OUT}$, c_L and V_L , as well as the values of r_L and r_{SC} calculated from equations (1) and (5), respectively are summarized in Table 1. The values

of the product k_2c_B and the modified Hatta number, calculated by equations (5) and (6), respectively are also shown in Table 1.

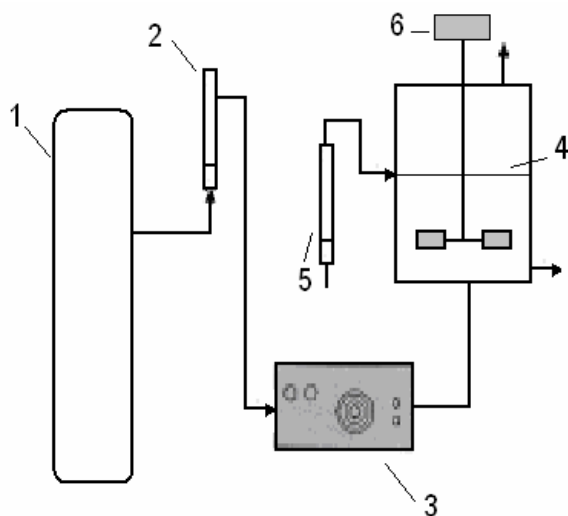


Figure 1. Experimental set up: oxygen bomb (1), gas flowmeter (2), ozone generator (3) stirred tank (4), liquid flowmeter (5) and rotational speed counter (6)

RESULTS AND DISCUSSION

Dependence of the overall rate of the ozone slow chemical reactions in raw water on the residual ozone concentration is shown in Figure 2. An analytical expression for this dependence could be obtained by combining equations (1), (3), (4) and (5), but the straight conclusions are not possible since the equilibrium ozone concentration increases with increasing the residual ozone concentration. It seems that at very low values of c_L , when it is much less than c_B , the

slope of the curve is k_2c_B . As it can be seen, the overall rate of slow chemical reactions is an increasing function of the residual ozone concentration, in the range of the operating conditions.

The dependence of k_2c_B on the ozone residual concentration in water is shown in Figure 3. As it can be seen, the product k_2c_B decreased with increasing the residual ozone concentration in raw water. One may expect that at high values of the ozone residual concentration the value of the product k_2c_B declines to zero. In such a case the rate of slow chemical reactions will decline to zero as well, indicating that the curve shown in Figure 2 would have its maximum value and then decreases with a further increase of c_L until the rate of slow chemical reactions declines to zero.

Figure 3 (or Table 1) show that the maximum value of k_2c_B was obtained at the minimum impeller speed employed and the lowest value of the ozone concentration in the inlet gas flow, producing the minimum value of the residual ozone concentration in the water. Using values of the product k_2c_B , the values of the modified Hatta number were calculated (Table 1). For instance, for the maximum value of k_2c_B , the following value of the modified Hatta number was calculated:

$$\sqrt{M} = \frac{\sqrt{1.62 \cdot 10^{-5} \cdot 6.42 \cdot 10^{-3}}}{10^{-2}} \approx 0.032 \ll 1$$

Since the modified Hatta number calculated is much less than unity for all operating conditions applied, it was proved that the values of the volumetric ozone mass transfer coefficient for the absorption accompanied by slow chemical reactions were equal to those for the pure physical ozone absorption.

Table 1. The rate of slow chemical reactions as a function of residual ozone concentration

n (min^{-1})	$c_{G,IN}$ mg/dm^3	$c_{G,OUT}$ mg/dm^3	c_L mg/dm^3	V_L dm^3	r_L $\text{mg dm}^{-3} \text{min}^{-1}$	r_{SC} $\text{mg dm}^{-3} \text{min}^{-1}$	k_2c_B min^{-1}	\sqrt{M}
300	5.480	4.034	0.168	6.23	0.091	0.065	0.385	0.0322
	6.554	4.846	0.226	6.18	0.102	0.074	0.326	0.0297
	7.627	5.648	0.295	6.32	0.108	0.077	0.261	0.0265
400	5.480	3.593	0.271	5.87	0.113	0.082	0.307	0.0288
	6.554	4.314	0.360	5.93	0.123	0.090	0.251	0.0260
	7.627	5.085	0.440	5.81	0.134	0.099	0.226	0.0247
500	4.944	2.888	0.314	5.86	0.119	0.087	0.278	0.0274
	5.480	3.232	0.362	5.76	0.127	0.094	0.260	0.0265
	6.017	3.606	0.411	5.54	0.136	0.101	0.246	0.0258
600	4.944	2.625	0.380	5.92	0.126	0.092	0.243	0.0256
	5.480	2.948	0.436	5.92	0.132	0.097	0.221	0.0244
	6.017	3.277	0.492	5.92	0.138	0.101	0.205	0.0235

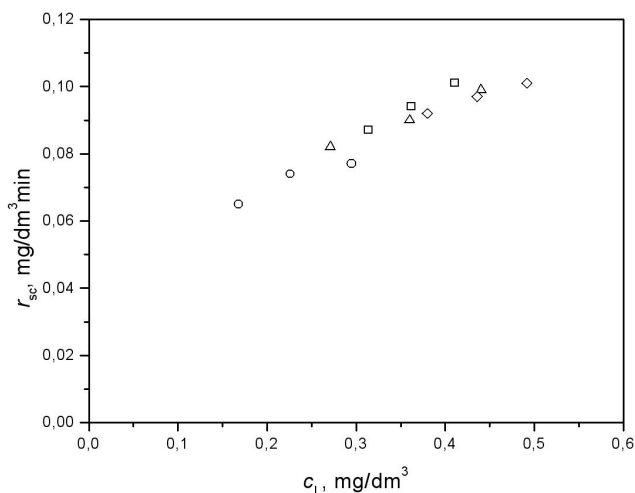


Figure 2. The overall rate of the ozone slow chemical reactions in water as a function of a residual ozone concentration in water (impeller speed, min^{-1} : 300 - O; 400 - Δ ; 500 - \square ; and 600 - \diamond)

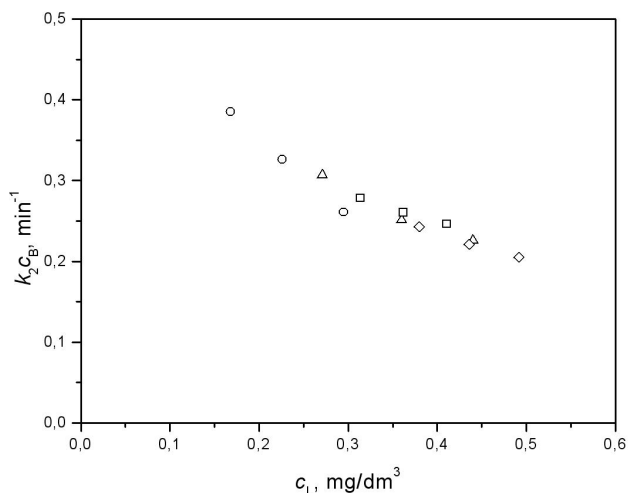


Figure 3. The dependence of $k_2 c_B$ on the residual ozone concentration in water (symbols are the same as in Figure 2)

CONCLUSIONS

The ozone absorption in raw waters of different purities and from different sources can be followed by determining the modified Hatta number for the absorption accompanied by slow chemical reactions in the liquid phase. The value of this criterion will show whether the chemical reactions of dissolved ozone and pollutants present in raw water enhance the rate of physical ozone absorption in the water or not. In that way, it is not necessary to evaluate the composition of any single raw water, in order to determine the ozone demand for purification.

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