Enhancement of gas-liquid mass transfer during the unsteady-state catalytic decomposition of ozone in water

Please, cite as follows:

R. Rosal, A. Rodríguez, M. Zerhouni, Enhancement of gas–liquid mass transfer during the unsteady-state catalytic decomposition of ozone in water, Applied Catalysis A: General, Volume 305, Issue 2, 24 May 2006, Pages 169-175, ISSN 0926-860X, 10.1016/j.apcata.2006.02.059.

http://www.sciencedirect.com/science/article/pii/S0926860X0600158X

Enhancement of gas-liquid mass transfer during the unsteady-state catalytic decomposition of ozone in water

Roberto Rosal[*], Antonio Rodríguez, Mohamed Zerhouni

Department of Chemical Engineering, University of Alcalá, E-28871 Alcalá de Henares, Spain.

[*] Corresponding author: roberto.rosal@uah.es

Abstract

Unsteady mass transfer and kinetic experiments were conducted in a gas-liquid reactor to study the catalytic and non-catalytic decomposition of ozone in water. In the absence of catalyst, first-order decomposition constants and volumetric mass transfer coefficients were determined at temperatures between 20ºC and 30ºC. Catalytic runs were performed on fumed colloidal TiO_2, which primary particles had an average diameter of 20 nm. The evolution of the concentration of ozone in water after introducing a given amount of catalyst was fitted to a kinetic model that assumed two-stage adsorption-decomposition on the catalytic surface. Runs were performed under slightly acidic conditions allowing the adsorption of ozone molecules on Lewis acid sites. A significant enhancement of mass transfer has been linked to the presence of particles. This effect could be attributed to a physical shuttle mechanism involving the adsorption of ozone on surface adhering particles. For bulk concentrations of catalyst up to 0.65 kg m^{-3}, the fraction of interface coverage did not reach saturation. The observed behaviour is consistent with the hydrophilic character of titanium oxide. Reaction constants and activation energies were determined for the two chemical steps describing catalytic ozone decomposition.

Keywords: Adsorption, Catalysis, Ozonation, Enhancement, Titanium Oxide

1. Introduction

Ozone has recently received much attention in water treatment technology due to its high capacity for oxidation and disinfection. Commercial applications focus on iron and manganese oxidation, odour control and disinfection, but a more widespread use is expected [1, 2]. Two physicochemical factors determine the concentration of ozone in aqueous systems. First, the low solubility of ozone in water limits the mass transfer driving force of gaseous ozone into water and consequently, typical concentrations of ozone during water treatment range from < 0.1 to 1mg/L. Second, ozone is unstable in water, being the subject of extensive basic chemical research. It has been shown that ozone decomposes spontaneously during water treatment by a complex mechanism that involves the generation of hydroxyl free radicals [3-5].

Municipal and industrial wastewaters usually contain compounds refractory to the conditions of homogeneous ozonation processes. Moreover, conventional ozonation applied to degradable organic matter led to carboxylic acids and other oxygenated compounds with low rate of mineralization. Another drawback of homogeneous ozonation processes is that alkaline conditions are required for reactions to proceed at a reasonable rate [3-4]. Advanced oxidation processes are intended to oxidize persistent pollutants or their reaction products by enhancing the concentration of hydroxyl radicals or other strong oxidant species [6]. Among other advanced oxidation processes, catalytic ozonation has received particular attention during the last few years in the search for lower costs and simpler operation [7]. Many authors reported promising results using metal oxides, supported metals or carbon catalysts [8]. As for metal oxides, TiO_2, MnO_2 and Al_2O_3 received major attention [9-12]. The surface of metal oxides contains hydroxyl groups that act as Brönsted acid sites and determine the charge of the surface as a function of pH. In addition to this, metal oxides have Lewis acid sites that, in an aqueous solution, allow water molecules to coordinate on their surface [13]. The adsorption of ozone or dissolved organic molecules on the surface of metal oxide requires the displacement of coordinated water and is strongly dependent on the presence of other bases. In the case that a Lewis site is accessible to ozone, the mechanism for its adsorption-decomposition on a catalytic surface would follow a mechanism similar to that used for explaining gas-phase decomposition [10, 14]:

$$O_3 \rightarrow (O_3)_{ads} \qquad (1)$$

$$(O_3)_{ads} \rightarrow (O)_{ads} + O_2 \qquad (2)$$

$$O_3 + (O)_{ads} \rightarrow 2O_2 \qquad (3)$$

In aqueous solution, the hydroxide ion is expected to act as a strong inhibitor of the adsorption ability of the catalyst by blocking Lewis acid sites. Therefore, the catalytic activity at high pH should proceed by a redox mechanism involving surface hydroxyl groups [12]. Ozone would react with them to yield an ozone anion radical or another active species able to oxidize organic compounds either in solution or on the surface [10, 15].

The presence of fine particles in a gas-liquid reactor enhances gas-liquid mass transfer due to an effect that was first described by Kars et al. [16]. The mechanism

Appl. Catal. A: General 305, 169-175, 2006

involves the physical adsorption of the transferred component from the gas phase and its subsequent desorption to the bulk of the liquid. Hydrophobic particles tend to adhere to the interface and accumulate in the mass transfer zone leading to higher enhancement factors but the effect was also described with relatively hydrophobic particles [17]. In the case of catalytic solids, the enhancement can be due to the increased reaction rate near the interface originated by a greater concentration of catalyst [18].

The aim of this paper is to obtain a kinetic expression for the aqueous decomposition of ozone using fine particles of titanium oxide as catalyst. The influence of temperature over the range of practical interest in ozonation has been studied to determine the activation energies of catalytic and non-catalytic reactions. Catalytic reactions were carried out in unsteady state by adding an aqueous suspension of the catalyst to a stirred bubble reactor operating in semicontinuous mode. Special attention was paid to the influence of the amount of catalyst on the mass transfer rate. The assumption underlying the approach followed in this paper is that under slightly acidic conditions, Lewis acid sites on titanium dioxide may adsorb ozone both dissolved in the liquid and directly from the gas phase. The concentration of ozone in water was then considered the result of the simultaneous mass transfer, physical adsorption and simultaneous homogeneous and catalytic decomposition reactions.

2. Experimental

2.1. Materials, experimental setup and procedure

Titanium dioxide Degussa P25 (80/20 anatase-to-rutile ratio) was used as a catalyst to decompose ozone in double distilled water. The powder has an average particle size of approx. 20 nm and a BET surface of 50 m^2/g. Ozone decomposition reactions were carried out in a 20 L glass jacketed reactor whose temperature was controlled by a Huber thermostatic regulator. The temperature of the liquid inside the reactor was also monitored throughout the experiment. Ozone was produced by a corona discharge ozonator (Ambiozon, GMF10) that was fed by oxygen from a compressed cylinder supplied by Air Liquide (99.995%).

The mixture of ozone and oxygen was bubbled into the liquid by means of a porous glass disk with a total gas flow that varied from 40 to 90 NL/h. The content of the vessel was agitated with a two-blade impeller operating at velocities of 100-200 rpm. The ozone decomposition experiments were conducted in a semicontinuous mode using a fixed volume of water. Catalytic decomposition runs were performed by introducing the catalyst once the steady state was reached for the reaction in pure water. Experiments were carried out under slightly acidic conditions (pH = 5, at which this variable has a minor effect on ozone decomposition rate) [19]. The pH of the reaction mixture was controlled by adding small amounts of diluted sodium hydroxide.

2.2. Analytical

The concentration of ozone in the liquid was measured using a Rosemount 499A OZ Ozone amperometric sensor equipped with Pt 100 RTD temperature compensation and checked against the Indigo Colorimetric Method (SM 4500-O_3 B). The signal was transmitted to a recorder by means of a Rosemount 1055 Dual Input Analyzer. The concentration of ozone in gas was determined with a non-dispersive UV Photometer Anseros Ozomat GM6000 Pro calibrated and tested against a chemical method.

3. Results and discussion

3.1. Decomposition of ozone in pure water

Ozone decomposition reaction in water has been studied by a number of authors and their results compiled by Gurol and Singer [20] and by Sotelo et. al [19]. Most modern studies have found first order with respect to ozone. Some researchers, however, have reported higher orders (1.5 or 2.0) even in experiments performed under similar conditions [20, 21]. Hewes and Davison [22] reported a change from second order at low pH values to first order under basic conditions. Kuo et al. [21] obtained a fractional order of 1.5 at least under slightly acid conditions. The reason for such differences in kinetic expressions is because of the complexity of the radical chain mechanism of ozone decomposition in water which involves different initiation and termination mechanisms. The chain is initiated by a reaction between ozone and hydroxide ions or a molecule of water depending on pH and follows a complex network studied by Bühler et al. [23] and Stahelin et al. [24], among others. Nadezhdin [25] suggested that a balance between different chain termination processes may explain the simultaneous observations of orders of 1.0 and 1.5 around neutral pH. Finally, the presence of radical scavengers may account for the observations of second order kinetics.

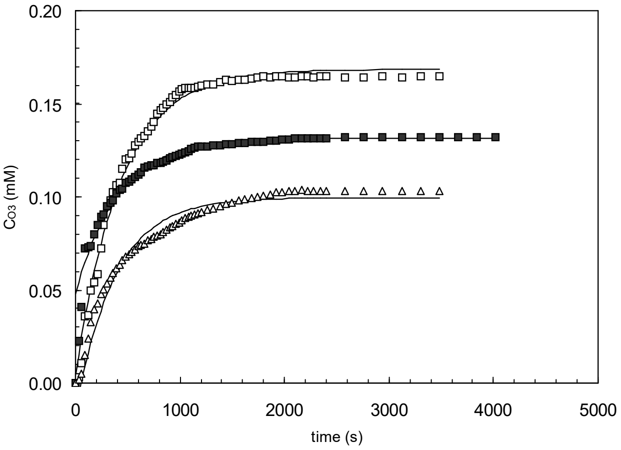

Figure 1. Self-decomposition of ozone at three different flows: 60 (□) 70 (■) and 80(△) NL h^{-1}. The temperature was 20ºC and no catalyst was used.

In this work, a set of runs was performed at $pH = 5$ and at temperatures between 20 and 30ºC. Different concentrations of ozone in gas ranging from 25 to 73 g/Nm^3 were used for flow rates of 40 to 90 NL/h. The gaseous mixture of oxygen and ozone was bubbled in pure water previously saturated with oxygen and the evolution of the concentration of ozone dissolved in the liquid was continuously monitored by means of amperometry with a general sampling period of 30 s. Hatta number was first estimated using first order constants from several sources [26]. The diffusivity of ozone in water was calculated according to the Johnson and Davis equation [27]. The individual liquid side mass transfer coefficient was estimated as $k_L = 5.5 \times 10^{-5}$ m s^{-1} using the correlation proposed by Dankwerts [28]. In all cases $Ha < 0.04$ indicating a slow kinetic regime where reaction only takes place significantly in the bulk. The changes in ozone concentration during bubbling were shown to be negligible. The concentration of ozone in the liquid phase is subsequently described by the following differential equation:

$$\frac{d\,C_{O_3}}{d\,t} = k_L a\left(C^*_{O_3} - C_{O_3}\right) - k_d\, C^n_{O_3} \qquad (4)$$

The dependence of gas-liquid interfacial area with the gas velocity [29] predicts a linear relationship of volumetric mass transfer coefficients, k_La, with gas flow rate. This dependence was incorporated as a constraint in the simultaneous fitting of experiments at different total flows and temperatures. Least square fitting yielded a reaction order of 0.976 ± 0.085, the boundaries corresponding to the 95% confidence interval. Besides the kinetic expression included in eq. 4, we also tested the more complex model proposed by Sotelo et al. [19] that was based on the individual stages of a chain mechanism. They considered initiation, propagation, and termination steps to derive a four-parameter kinetic expression in which first-order with respect to ozone was obtained as limit solution at pH < 3. The fitting to this equation did not represent a significant improvement and therefore, first-order decomposition rate law was used in what follows. Fig. 1 shows the evolution of the concentration of ozone dissolved in water at 20ºC for three different flow rates of gas. Solid lines represent the fitting for first order kinetics. A complete fitting requires the equilibrium concentration of ozone calculated from the concentration of ozone in the gas phase. Henry's constant was taken from the correlation proposed by Richsbieter et al. [30]. Without introducing Henry's constant, the integration of eq. 4 may provide only an independent estimation of $k_La + k_d$. The dependency of mass transfer coefficients on the agitation rate allowed to verify the results obtained by means of Richsbieter equation. According to the correlations of Koetsier et al. [31] and Koetsier and Thoenes [32], the liquid side mass transfer coefficients are almost linear with the agitation rate, so that runs at a different agitation rate should yield values of $k_La + k_d$ linear with stirring rate. The intercept is expected to be close to k_d. Fig. 2 represents the result of runs performed at different agitation rates for equal temperature, ozone concentration and gas flow. For lower agitation rates, the ozone sensor did not yield a stable reading which is probably due to the tendency of primary particles to form aggregates that in water may reach 50-100 nm at lower stirring rates. The linear behaviour observed was consistent with predictions and the intercept yielded a value close to the value of k_d presented by Bin [26] that was based on the fitting of data from several sources. The value obtained in the global fitting of this work was 8.74×10^{-3} s^{-1} at 20ºC. The activation energy was 41.6 ± 2.0 kJ mol^{-1} and, together with the rest of the parameter estimations of this paper, is presented in Table I. With respect to activation energies for self-decomposition of ozone in water, a considerable scatter exists in the literature, but our value agrees well with recent results [19, 33, 34].

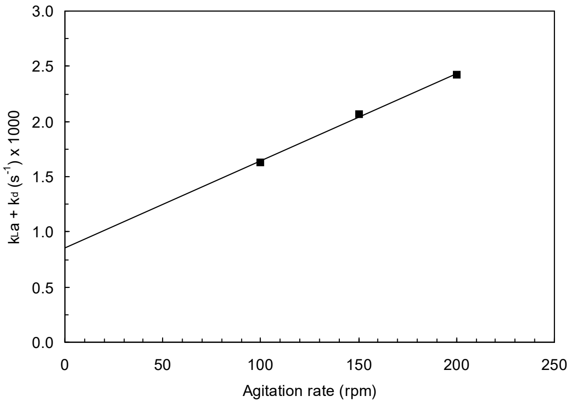

Figure 2. Effect of the agitation rate on the non-catalytic self-decomposition of ozone in water.

3.2. *Ozone decomposition on titanium catalyst*

Transient ozone decomposition was studied by introducing a predefined amount of a catalyst suspension in a semicontinuous reactor operating with pure water in steady state. Runs were performed at 10, 20, 25 and 30ºC with different catalyst loading in the range 0.20-0.65 kg m^{-3}. Small additions of sodium hydroxide allowed to keep the value of $pH = 5$ throughout the reaction. The model of catalytic decomposition assumes that simultaneous non-catalytic reaction follows a first order kinetic expression. The homogeneous rate constant was taken from experiments described in the section above. As was previously mentioned, ozone was supposed to adsorb on the surface of titanium dioxide, so that its decomposition takes place according to the mechanism indicated in eqs. 1-3. In the absence of data on adsorbed intermediates, eqs. 1 and 2 were coupled in a single rate step: $O_3 \rightarrow (O)_{ads} + O_2$. The concentration of ozone was then calculated by solving the following system of differential equations:

$$\frac{dC_{O_3}}{dt} = k_L a\, E\left(C^*_{O_3} - C_{O_3}\right) - k_1\, c_s\, C_{O_3}\,(1-\theta) - k_2\, c_s\, C_{O_3}\,\theta - k_d\, C_{O_3} \qquad (5)$$

$$-c_t \frac{d\theta}{dt} = -k_1\, C_{O_3}\,(1-\theta) + k_2\, C_{O_3}\,\theta \qquad (6)$$

where θ is the fraction of catalyst-free surface sites, k_1 and k_2 are the rate constants for the catalytic reactions (1+2) and (3) and c_s is the bulk concentration of solids. Least square fitting was performed including a fourth-order Runge-Kuttta routine for the integration of eq. 5 and 6. The introduction of reversible reactions did not result in a significantly better fitting and were therefore not considered. Kinetic constants and activation energies resulting from the fitting of experimental results are listed in Table 1 together with their 95% individual confidence intervals. Fig. 3 shows the effect of introducing 0.50 g/L of catalyst into a stirred bubbling reactor operating at three different temperatures and with a total gas flow rate of 70 NL/h. Immediately after the introduction of catalyst, the concentration of ozone drops reflecting the fact that the rate of adsorption is maximum when the fractional coverage of the catalyst is still low. Afterwards, as the fractional coverage increases, the positive transport term of eq. 5 becomes prevailing. The non-linear dependence with temperature reflects the fact that k_LaE is almost constant, but the rate constants k_1, k_2 and k_d follow Arrhenius-type expressions. The fitting of experimental data to eqs. 5 and 6 shows an increase in the rate of ozone transfer to the liquid phase that depended on the bulk concentration of catalyst. The enhancement factor, E, included in eq. 5, represents the actual molar flux of solute, referring to the physical liquid-phase mass transfer rate:

$$E = \frac{J_{O_3}}{k_L\left(C^*_{O_3} - C_{O_3}\right)} \qquad (7)$$

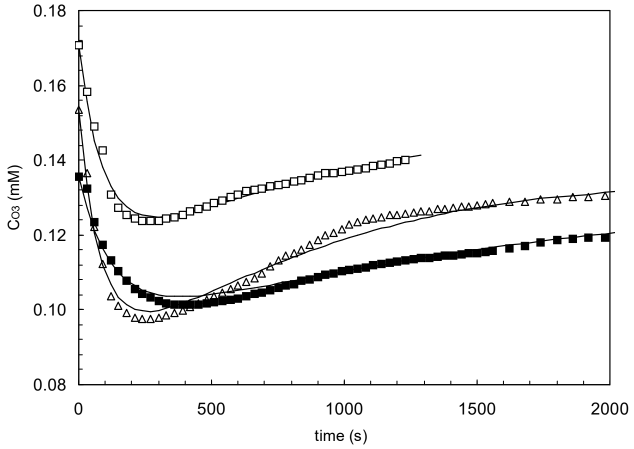

Figure 3. Catalytic decomposition of ozone on TiO_2 at different temperatures: 20ºC (■), 25ºC (□) and 30ºC (△). The bulk concentration of catalyst was 0.50 kg m^{-3}.

Fig. 4 shows the evolution of ozone in the liquid phase for reactions performed with different concentrations of catalyst. Catalytic particles may concentrate at the interface and enhance the mass transfer due to the chemical reaction. The modelling of this classical chemical enhancement considers that particles may be more or less attracted to the gas-liquid interface depending on their surface properties [35]. Wimmers and Fortuin [18] developed a model that described this effect. For enhancement due to first- or pseudo-first order reactions, they defined the following modified Hatta number:

$$Ha' = \frac{\sqrt{k\, c_{s,i}\, D_{O_3}}}{k_L} \qquad (8)$$

Table I. Parameter estimates for the decomposition of ozone

Non catalytic decomposition	*Reaction on titanium catalyst*
$k_La = 1.62 \times 10^{-3} \pm 2.5 \times 10^{-4}\ s^{-1}$	k_1 (20 ºC) = $7.21 \times 10^{-3} \pm 3.1 \times 10^{-4}\ m^3\ kg^{-1}\ s^{-1}$
(at 70 NL h^{-1} and 20ºC)	k_2 (20 ºC) = $2.73 \times 10^{-4} \pm 2.5 \times 10^{-5}\ m^3\ kg^{-1}\ s^{-1}$
k_d (20ºC) = $8.74 \times 10^{-3} \pm 1.3 \times 10^{-4}\ s^{-1}$	$E_1 = 50.2 \pm 2.6$ kJ mol^{-1}
$E_a = 41.6 \pm 2.0$ kJ mol^{-1}	$E_2 = 49.3 \pm 6.8$ kJ mol^{-1}
(The boundaries correspond to 95% confidence intervals)	

where k is the first-order rate constant and $c_{s,i}$ represents the concentration of solids in the mass transfer film that may substantially differ from their bulk mean concentration. Wimmers et al. [36] found film concentration of solids up to two orders of magnitude over bulk particle loadings, but this effect should be considerably less pronounced in the case of hydrophilic particles. It has also been pointed out that the preceding analysis would be strongly affected by an unequal distribution of solids near the interface [37]. For the estimation of pseudo-first order Hatta numbers, it has been considered that the adsorption-reaction of ozone with free catalytic sites is the fastest step of the mechanism. The maximum rate of ozone dissociation takes place immediately after the introduction of the catalyst allowing the use of the rate constant of the first reaction step, k_1, in eq. 8 to obtain an upper limit for pseudo-first order Hatta number. On the other hand, the hydrophilic character of titanium dioxide supports the assumption that the concentration of solids at the interface would be similar to their bulk concentration. The later ideas led to $k\, c_{s,i} \approx k_1\, c_s$ allowing an rough estimation of Hatta number. In all cases, $Ha' < 0.05$ and the corresponding initial enhancement factor calculated from the expression proposed by Wimmers and Fortuin [18] would account for no more than half of the observed enhancement. Greater enhancement factors may be associated to an accumulation of particles near the interface but this is not the expected behaviour of hydrophilic particles. Moreover, from Wimmers and Fortuin's results, it can be stated that the enhancement factor should increase considerably with temperature by means of the activation energy of the catalytic reaction. For a hydrogenation reaction with palladium on activated carbon as catalyst, it was found that this enhancement factor doubles when the temperature increases from 20ºC to 40ºC [18]. As indicated below, greater enhancement was not found when changing the temperature from 20ºC to 30ºC.

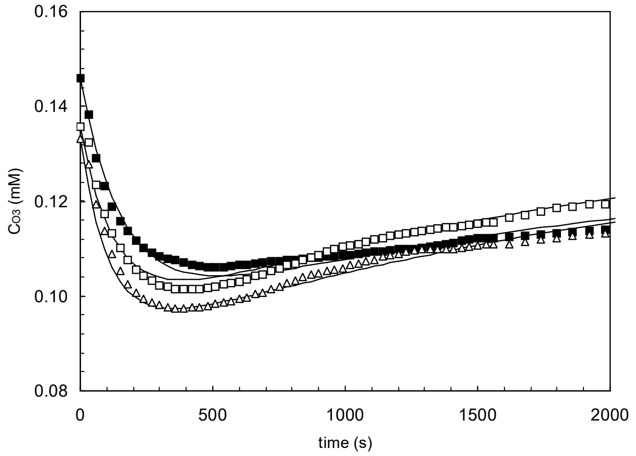

Figure 4. Catalytic decomposition of ozone on TiO_2 with variable catalyst masses: 0.35 (■), 0.50 (□) and 0.65 (△) kg m^{-3}. The temperature was 20ºC for these runs.

Enhancement of gas absorption by fines has also been attributed to the adsorption of the transferred component on the particles located near the gas-liquid interface. The mechanism, called "grazing" or "shuttle" effect, is supposed to involve the adsorption of solute at the interface followed by subsequent desorption in the bulk of the liquid [34]. Several models based on film theory, Dankwerts' surface renewal and Higbie's penetration theory have been proposed to describe this effect [38-40]. All of these models consider that a fraction of the surface is covered by particles whose renewal rate from the bulk of the suspension depends on the agitation rate. Through the part of the surface covered by clear liquid, mass transfer takes place from gas bubbles to the ideally mixed bulk liquid and then from it to the catalyst particle according to conventional mass transfer theory. In the part of the interface covered by particles, adsorption on the catalyst takes place directly from gas phase. Both processes act as strictly parallel resistances, without lateral mixing.

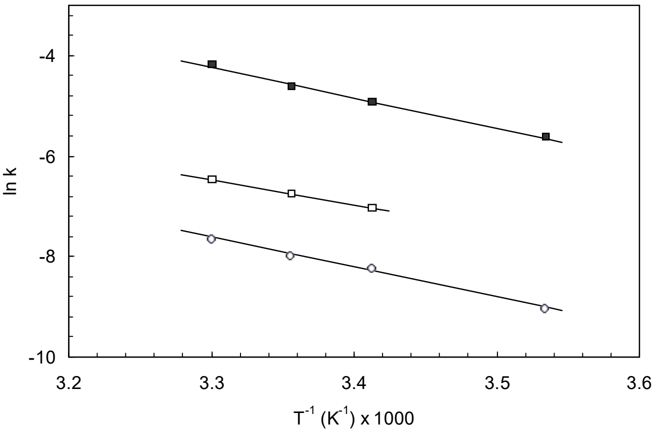

Figure 5. Arrhenius plot for catalytic and non-catalytic decomposition of ozone. Without catalyst (□) and on TiO_2

The molar flux of ozone through the entire surface can then be expressed as:

$$J_{O_3} = (1-\varsigma)\, k_L \left(C^*_{O_3} - C_{O_3}\right) + \varsigma\, J^p_{O_3} \qquad (9)$$

where ζ is the fraction of the interface covered by adhering particles and $J^p_{O_3}$ the rate of absorption through the part of the surface covered by particles. A common assumption of most physical enhancement models is the use of a Langmuir-type adhesion isotherm connecting interfacial and bulk concentration of solids, a model first proposed by Schumpe et al. [41]. This is usually combined with the further assumption that the fraction of the interfacial surface covered by particles reaches a limiting value, ζ_s, that decreases with an increase in the intensity of stirring. These ideas combine in an expression relating the bulk concentration of solids with the fraction of surface covered by adhering particles:

$$\frac{\varsigma}{\varsigma_s} = \frac{K_s\, c_s}{1 + K_s\, c_s} \qquad (10)$$

where K_s is the particle-to-bubble adhesion constant. Both ζ_s and K_s are also supposed to depend on the surface curvature, the surface properties of particles and the presence of dissolved surface active substances among others. All of these effects alter the equilibrium of particles moving towards and away from the interface. Vinke et al. [38] and Demmink et al. [39] proposed models based on eqs. 9 and 10 that yielded expressions for the enhancement factor as a function of ζ, the partition coefficient, m, and a dimensionless mass transfer coefficient K_L defined as follows:

$$K_L = \frac{k_L\, d_p}{D_{O_3}} \qquad (11)$$

The general form of the expression obtained by both authors is:

$$E = 1 + \varsigma\, f(m, K_L) \qquad (12)$$

For the experimental conditions used in this work, $K_L \approx 10^{-3}$, a value that makes difficult to simplify the proposed forms of eq. 12 or to try to theoretically predict the maximum enhancement factor that takes place for complete surface coverage. The combination of eq. 12 and 10 yields the following expression for the enhancement factor:

$$E = 1 + \frac{\varsigma_s\, K_s\, c_s}{1 + K_s\, c_s} f(m, K_L) \qquad (13)$$

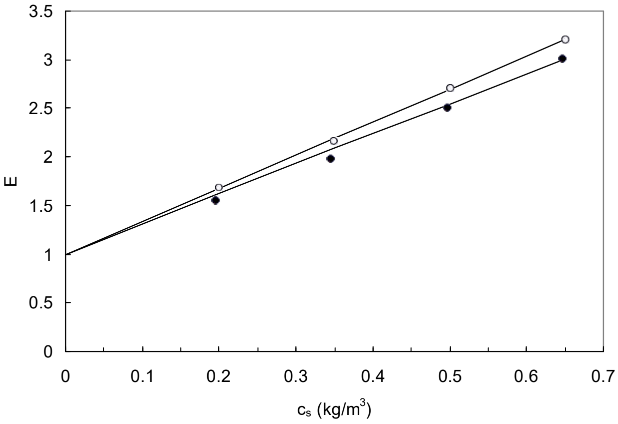

Figure 6. Enhancement factor for the catalytic decomposition with different concentrations of TiO_2 at 20ºC (○) and 30ºC (●). Solid lines correspond to the fitting to a Langmuir-type expression (eq. 13).

Enhancement factors obtained from the fitting of experimental data are represented in Fig. 5 as a function of the bulk concentration of solids. A linear relationship following the form of eq.13 was clearly obtained with the adhesion constant large enough to assume that $1 >> K_s\, c_s$ within the experimental range explored in this work. Experimental data represented in Fig. 5 show a slight decrease in the enhancement factor with temperature. This behaviour is not consistent with a chemical explanation of the enhancement like the one encountered by Wimmers and Fortuin [18]. For physical enhancement, the dependence of the enhancement factor on temperature depends on the dimensionless mass transfer coefficient, the partition coefficient and the actual degree of coverage of the interface by particles. The sign of the dependency depends on the form adopted by $f(m, K_L)$ and, therefore, on the theoretical background of the interface model, though the effect of temperature is expected to be less pronounced than that encountered in a situation of chemical enhancement. The degree of surface coverage is expected to depend on the hydrophobic/hydrophilic character of particles. TiO_2 fumed colloidal titanium dioxide is considered to be relatively hydrophilic. However, it was already shown that it may adhere to the interface during mass transfer from gas to aqueous suspension originating a physical enhancement of mass transfer [17].

4. Conclusions

The research done demonstrated that titanium dioxide fine particles, a material commonly used in photocatalysis, may enhance the absorption rate of ozone under the conditions typically encountered in ozonation processes. The maximum enhancement level reached represents three times the mass transfer rate of ozone in a particle-free liquid. The effect described in this work could be attributed to a "shuttle" mechanism involving the physical adsorption of ozone on the surface of particles. This is supported by the slight reduction of enhancement factors with temperature since a mechanism based on chemical enhancement due to the accumulation of particles near the interface should yield the opposite behaviour. It has been determined that, in accordance with the hydrophilic character of titanium dioxide, the interface is not saturated with particles in the experimental range studied in this work. Therefore, enhancement factors remain linear with bulk catalyst concentration as expected from a Langmuir-type surface adhesion model.

Unsteady absorption-reaction experiments allowed reaction constants and activation energies to be calculated for a two-step mechanism of ozone decomposition on the catalytic surface. The proposed mechanism involves the adsorption-decomposition of ozone on catalytic surface sites followed by the reaction of non-adsorbed ozone on oxidized sites. The results suggest that acidic sites, probably titanium surface atoms, act as Lewis adsorption sites for the ozone molecule even in the presence of water. Hydroxide ions are expected to block coordination sites, but at the slightly acidic reaction conditions used in this work this catalyst blocking did not occur. The model allowed an estimation of the steady state fraction of occupied sites of about $\theta_{t\to\infty} \approx 0.8$ with minor variations depending on temperature and gas phase concentration of ozone. The equilibrium degree of catalyst coverage is due to the fact that the adsorption-decomposition rate is one order of magnitude greater than the reaction rate of oxidized sites. The activation energies for the catalytic reaction steps are very similar, probably reflecting the fact that both involve breaking an ozone molecule.

Acknowledgement

Financial support was provided by the Dirección General de Universidades e Investigación de la Comunidad de Madrid under Contract No. GR/AMB/0811.

Notation

C_{O_3}:	Concentration of ozone, mol m^{-3}
$C^*_{O_3}$:	Equilibrium concentration of ozone, mol m^{-3}
C_{OH^-}:	Concentration of hydroxide ions, mol m^{-3}
c_s:	Bulk concentration of solids in the liquid phase, kg_{solids} m^{-3}_{liquid}

$c_{s,i}$: Concentration of solids at gas-liquid interface, $kg_{solids}\ m^{-3}{}_{liquid}$

c_t: Total concentration of active sites, mol kg^{-1}

D_{O_3}: Diffusivity of ozone in water, $m^2\ s^{-1}$

E: Enhancement factor, dimensionless

Ha: Hatta number, $Ha=\frac{\sqrt{k_d\, D_{O_3}}}{k_L}$, dimensionless

Ha': Hatta number defined by eq. 9, dimensionless

J_{O_3}: Mass transfer rate of ozone, kmol $m^{-2}\ s^{-1}$

$J_{O_3}^p$: Mass transfer rate of ozone through the part of the surface covered by particles, kmol $m^{-2}\ s^{-1}$

K_s: Langmuir-type adhesion constant defined in eq. 10, $m^3\ kg^{-3}$

K_L: Dimensionless mass transfer coefficient defined by eq. 11, dimensionless

k, k_i: Kinetic constants for heterogeneous reactions, $m^3\ kg^{-1}\ s^{-1}$

k_d: Kinetic constant of ozone decomposition, s^{-1}, $mol^{1-n}\ m^{3n-3}\ s^{-1}$

k_La: Volumetric mass transfer coefficient in the liquid phase, s^{-1}

m: Partition coefficient of the solute between solid and liquid phases, (kmol $m^{-3}{}_{solid}$) (kmol $m^{-3}{}_{liquid}$)$^{-1}$

Greek letters

ζ: Interface fractional coverage by adhering particles, dimensionless

ζ_s: Maximum possible interface fractional coverage, dimensionless

θ: Fractional coverage of catalyst surface, dimensionless

References

[1] U. Gunten, Water Res., 37 (2003) 1443.

[2] U. Gunten, Water Res., 37 (2003) 1469.

[3] J. Hoigné, H. Bader, Water Res., 17 (1983) 173.

[4] J. Hoigné, H. Bader, Water Res., 17 (1983) 185.

[5] B. Kasprzyk-Hordern, M. Ziólek, J. Nawrocki, Appl. Catal., B: Environ., 46 (2003) 639.

[6] S. Esplugas, J. Giménez, S. Contreras, E. Pascual, M. Rodríguez, Water Res., 36 (2002) 1034.

[7] B. Legube, N.V. Leitner, Catal. Today, 53 (1999) 61.

[8] F.J. Beltrán, Ozone Reaction Kinetics for Water and Wastewater Systems, CRC Press, London, 2003, pp 231-239.

[9] F.J. Beltrán, F.J. Rivas, R. Montero, R., Appl. Catal. B: Environ., 39 (2003) 221.

[10] F.J. Beltrán, J. Rivas, P. Álvarez, R. Montero, Ozone Sci. Eng., 24 (2002) 227.

[11] R. Andreozzi, R. Marotta, R. Sanchirico, J. Chem. Tech. Biotechnol., 75 (2000) 59.

[12] M. Ernst, F. Lurot, J.C. Schrotter, Appl. Catal. B: Environ., 47 (2004) 15.

[13] B. Kasprzyk-Hordern, M. Ziolek, J. Nawrocki, Appl. Catal. B: Environ., 46 (2003) 639.

[14] R. Gracia, S. Cortés, J. Sarasa, P. Ormad, J.L. Ovellieiro, Ozone Sci. Eng., 19 (2000) 1525.

[15] J. Ma, J.D. Graham, Wat. Res., 33 (1989) 785.

[16] R.L. Kars, R.J. Best, A.A.H. Drinkenburg, Chem. Eng. J., 17 (1979) 201.

[17] M.V. Dagaonkar, H.J. Heeres, A.A.C.M. Beenackers, V.G. Pangarkar, Chem. Eng. J., 92 (2003) 151.

[18] O.J. Wimmers, J.M.H. Fortuin, Chem. Eng. Sci., 43 (1988) 313.

[19] J.L. Sotelo, F.J. Beltrán, F.J., Benítez, J. Beltrán, Ind. Eng. Chem. Res., 26 (1987) 39.

[20] M.D. Gurol, P.C. Singer, Environ. Sci. Technol., 16 (1982) 377.

[21] C.H. Kuo, K.Y. Li, C.P. Wen, J.L. Weeks, J.L., AIChE Symp. Ser., 73 (1976) 230.

[22] C.G. Hewes, R.R. Davison, AIChE J., 17 (1981) 141.

[23] R.E. Bühler, J. Staehelin, J. Hoigné, J, J. Phys. Chem., 88 (1984) 2560.

[24] J. Staehelin, R.E. Bühler, J. Hoigné, J. Phys. Chem., 88 (1984) 5999.

[25] A. Nadezhdin, Ind. Eng. Chem. Res., 27 (1988) 548.

[26] A.K. Bin, Experimental Thermal and Fluid Science, 28 (2004) 395.

[27] P.N. Johnson, R.A Davis, J. Chem. Eng. Data, 41 (1996) 1485.

[28] P.W. Danckwerts, Ind. Eng. Chem., 43 (1951) 1460.

[29] G.F. Froment, K.B. Bischoff, Chemical Reactor Analysis and Design, John Wiley and Sons, New York, 1990, pp, 637.

[30] E. Richsbieter, H. Stein, A. Schumpe, J. Chem. Eng. Data, 45 (2000) 338.

[31] W.T. Koetsier, D. Thoenes, J.F. Frankena, The Chem. Eng .J., 5 (1973) 61.

[32] W.T. Koetsier, D. Thoenes, The Chem. Eng. J., 5 (1973) 71.

[33] J.A. Roth, D.E. Sullivan, Ozone Sci. Eng., 5 (1983) 37.

[34] F. de Smedt, S. de Gendt, I. Cornelissen, M.M. Heyns, C. Vinckier, Solid State Phenom., 76-77 (2001) 211.

[35] A.A.C.M. Beenackers, W.P.M. van Swaaij, Chem. Eng. Sci., 48 (1993) 3109.

[36] O.J. W.immers, H.J.J.S. Notting, J.M.H. Fortuin, Chem. Eng. Sci., 43 (1988) 2155.

[37] S. Karve, V.A. Juvekar, Chem. Eng. Sci., 45 (1990) 587.

[38] H. Vinke, P.J. Hamersma, J.M.H. Fortuin, Chem. Eng. Sci., 48 (1993) 2197.

[39] J.F. Demmink, A. Mehra, A.A.C. Beenackers, Chem. Eng. Sci., 16 (1998) 2885.

[40] K.C. Ruthiya, J. Schaaf, B.F.M. Kuster, J.C. Schouten, Ind. Eng. Chem. Res., 44 (2005) 6123.

[41] A. Schumpe, A.K. Saxena, K.D.P. Nigam, AIChE J., 33 (1987) 1916.