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Oxidation of oxalate ion in aqueous suspensions of TiO_2 by photocatalysis and ozonation

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Abstract

Oxalate anion has been oxidized in aqueous alkaline solution by using ozonation and photocatalysis in the presence of TiO_2. A batch annular reactor has been used for carrying out reactivity runs in the presence of air/ozone, air/ozone/near UV irradiation, air/ozone/TiO_2, air/near UV-irradiated TiO_2 and air/ozone/near UV-irradiated TiO_2. The Langmuir–Hinshelwood kinetic model adequately describes the photocatalytic results obtained at different reaction conditions and allows determining the values of the kinetic and equilibrium adsorption constants. The contemporary presence of photocatalysis and ozonation shows a significant improvement of the process performance as the oxidation rate of oxalate anion is greatly enhanced compared with the photocatalysis or ozonation processes alone. A likely explanation of this result may be that the presence of ozone on UV-irradiated surface of TiO_2 enhances both the photogeneration of hydroxyl radicals and the photoadsorption of oxalate anions, due to its higher electrophilic nature with respect to O_2.

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1. Introduction

Heterogeneous photocatalysis is one of the advanced processes of oxidation more developed in the last two decades [1,2]; this catalytic process uses semiconductor oxides irradiated with UV or near-UV light at ambient temperature and pressure and in the presence of oxygen. The fundamental mechanism of photocatalysis consists in the generation of electron–hole pairs, which determine the occurrence of redox reactions of species adsorbed on the photocatalyst surface. This method has been successfully used for wastewater treatment and it is suitable to perform the complete degradation of organic and inorganic pollutants, the reduction of metal ions, the inactivation of many aerobic bacteria, etc. [3–6].

Titanium dioxide is extensively used as photocatalyst due to its high chemical stability, optical and electronic properties [7], low cost, and absence of toxicity. Nevertheless, TiO_2 uses only a small fraction of the solar spectrum, due to its relatively high band-gap. In order to improve the performance of the photocatalytic process, different strategies have been used. The efficiency of TiO_2 in the photocatalytic process has been improved, for example, modifying its electrical properties by doping with transition metals [8] or noble metal elements [9]. These modifications can induce a displacement of TiO_2 absorbance towards the visible region of the spectrum. Another strategy consists of increasing the life of the photogenerated electron–hole pair; this goal is carried out by favoring the presence of hetero junctions [10], by using photosensitizers [11] or by depositing particles of noble metals on the surface of the oxide semiconductor [12]. The previous modifications affect the quantum yield of the photocatalytic process and/or the absorption rate of the photons. An alternative option to

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increase the performance of the photocatalytic system is to change the reaction ambient by adding very oxidant species as hydrogen peroxide [13] also in the presence of Fe(II) ions [14], peroxodisulfate and periodate ions [15], or ozone.

Oxidation processes based on ozonation and methods aimed at an enhancement of its efficiency have recently received much attention [16,17]. The use of ozone in combination with the heterogeneous photocatalysis [18–20] has been recently studied in liquid phase to treat aniline [21], phenol [22], formic acid [23], and cyanide ions [24]. In all cases a significant improvement of oxidation process performance has been reported as the mineralization rate of organic and inorganic substances is greatly enhanced. Likely explanation of the onset of this effect [18–21] is that ozone is able to generate $HO^{\bullet}$ radicals on the TiO_2 surface through the formation of an $O_3^{\bullet}$ ozonide radical. The production of $HO^{\bullet}$ radicals on the irradiated surface of photocatalyst would be more effective in the presence of ozone than in that of oxygen.

It is well known that the photocatalytic method is effective for the degradation of oxalic acid in suspension of TiO_2 irradiated with near-UV light [25–28]. Bangun and Adesina [28] investigated the kinetics of oxalate photodegradation by using commercial TiO_2 (Aldrich) under irradiation in the 250–310 nm wavelength range and reported that initial solution pH, light intensity, oxygen partial pressure, catalyst loading and oxalate concentration have strong effects on the decomposition rate. Oxalic acid has been detected during the mineralization of a large variety of organic compounds [29,30]. Moreover, it is a water pollutant resulting from some industrial treatment processes (textile industry, metallurgy, etc.); indeed, sodium oxalate is an important toxic pollutant in Bayer liquor during alumina processing and its removal and possible rejuvenation of the caustic solution is vital to plant economics [28]. It is easy to be oxidized as indicated by the redox potential at acidic pH (−0.49 V) of the $H_2C_2O_4(aq)/CO_2(g)$ couple [25]. For this reason anions of simple carboxylic acids, i.e. methanoic, ethanoic and oxalic acids, have been used as hole scavengers in photoelectrochemical cells with anodes formed by single TiO_2 crystals [31]. Ozonation has been also used to oxidize oxalic acid both in the absence [32] and in the presence of TiO_2 as the catalyst [33]. Notwithstanding the existence of the above reported studies on oxalic acid (photo)degradation at acidic pHs in the presence of TiO_2 or O_3, no detailed investigation up to date has been carried out in the presence of O_3, TiO_2 and near-UV light. In the present paper heterogeneous photocatalysis combined with ozonation has been used for the oxidation of oxalate anion at pH 10 in the presence of TiO_2 Degussa P25. The contemporary presence of photocatalysis and ozonation determines a significant increase of the substrate oxidation rate. A kinetic model considering the homogeneous and the heterogeneous processes for oxalate anion degradation under different reaction conditions is reported.

2. Experimental

For the experimental runs a Pyrex batch photoreactor of cylindrical shape has been used. The photoreactor, containing 2.5 dm^3 of aqueous suspension, was provided with ports in the upper part in order to feed gases, to measure pH and temperature and to withdraw aliquots of the reacting suspension. A medium pressure Hg lamp (Helios Italquartz, Italy) of 700 W was immersed in axial position inside the photoreactor. The photon flow emitted by the lamp has its maximum value at 365 nm; it was measured with a radiometer (Digital UVX) placed at different heights of the outer wall of the reactor. The average value was 17 $mW\ cm^{-2}$. Four series of photoreactivity runs were carried out by varying both the initial oxalate anion concentration and the gas bubbled within the suspension. Synthetic air (20% O_2, 80% N_2), pure oxygen or ozone–air mixture of two different compositions were continuously bubbled within the liquid phase during the course of the runs at a constant flow rate of 300 $cm^3\ min^{-1}$. The concentration of dissolved oxygen in the liquid phase was 2.6×10^{-4} M when air was bubbled in the solution and 1.3×10^{-3} M in the case of pure oxygen. Ozone was produced by feeding synthetic air to an ozonator (Microlab) able to vary the ozone production rate in the 1–20 $mmol\ h^{-1}$ range. The values of ozone concentration in the air entering the reactor were 2.2×10^{-4} and 8.3×10^{-4} M. For the runs carried out with ozone, the concentration values of ozone and oxygen in the liquid phase, calculated by using the Henry's constants [34], were 0.26×10^{-4} and 1.0×10^{-4} and 2.5×10^{-4} and 2.2×10^{-4} M, respectively. The initial oxalate concentrations were: 0.22, 0.48, 0.68, 1, and 2 mM. The reagent used was $H_2C_2O_4{\cdot}2H_2O$ (Riedel de Haën). The pH of the solution was 10 and it was adjusted by addition of NaOH (Fluka). The temperature of the suspension was 300 ± 2 K. TiO_2 Degussa P25 (ca. 80% anatase and 20% rutile, BET specific surface area: 50 $m^2\ g^{-1}$) was used without any preliminary treatment. For all of the runs the amount of photocatalyst was 0.24 $g\ l^{-1}$ and this mass was able to absorb all the photons emitted by the lamp. The photoreactivity runs lasted 5 h. Before turning on the lamp, the system was maintained in the dark for 30 min in order to reach steady state conditions. Samples (5 cm^3) of the dispersion were withdrawn at fixed intervals of time. The photocatalyst was immediately separated by means of a cellulose acetate filter (Millipore) with pore diameter of 0.45 μm.

The quantitative determination of anionic species was carried out by using an ionic chromatograph system (Dionex DX 120) equipped with an Ion Pac AS14 4 mm column (250 mm long, Dionex). Aqueous solutions of $NaHCO_3$ (8 mM) and Na_2CO_3 (3.5 mM) were used as eluents at a flow rate of $1.67 \times 10^{-2}\ cm^3\ s^{-1}$. In order to determine the concentration of ozone in the gas phase introduced in the reacting system, the absorbance of gaseous ozone was measured at 254 nm by using a UV–vis spectrophotometer (Shimadzu). A previous calibration was performed by bubbling the air–O_3 mixture in KI aqueous solution and measuring the quantity of iodide anion oxidized by the ozone to iodate.

3. Results

Preliminary runs carried out in the absence of light with the aim to determine the quantity of oxalate adsorbed on the TiO_2 surface, indicated that the adsorption of oxalate anion was negligible under these conditions. For runs carried out in the absence of catalyst, it was observed that the concentration of oxalate remained constant by bubbling air in the solution and/or by irradiating the solution. The presence of ozone in the reaction medium led to a decrease of the concentration of the oxalate anion and the extent of this decrease did not change if the system was also irradiated with UV light. These results demonstrate that a homogeneous oxidation of the oxalate anion takes place when ozone is present in the reaction medium and that UV radiation does not affect this homogeneous process. Fig. 1 reports the values of oxalate ion concentration versus reaction time for runs carried out without photocatalyst in the presence of ozone, air, and near-UV irradiation.

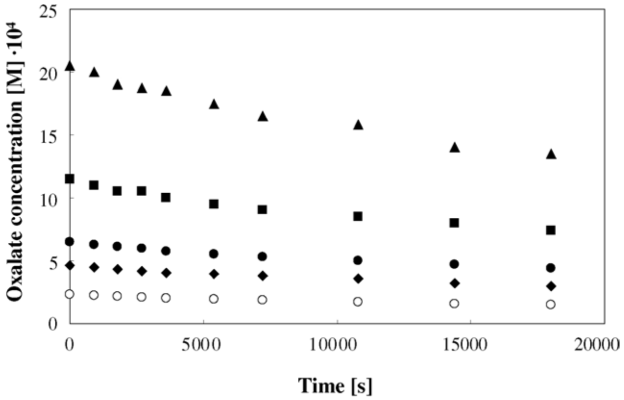

Fig. 1. Experimental values of oxalate ion concentration vs. reaction time for runs carried out in the contemporary presence of O_3, air and near-UV irradiation. Ozone concentration in the gas phase: 8×10^{-4} M. Initial concentrations of oxalate ion: (▲) 20.4×10^{-4} M; (■) 10×10^{-4} M; (●) 6.8×10^{-4} M; (◆) 4.8×10^{-4} M; (○) 2.27×10^{-4} M.

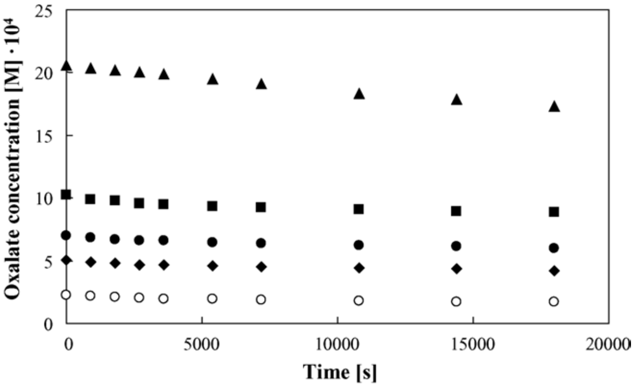

Fig. 2. Experimental values of oxalate ion concentration vs. reaction time for runs carried out in the contemporary presence of TiO_2, air and near-UV irradiation. Initial concentrations of oxalate ion: (▲) 20.4×10^{-4} M; (■) 10×10^{-4} M; (●) 6.8×10^{-4} M; (◆) 4.8×10^{-4} M; (○) 2.27×10^{-4} M.

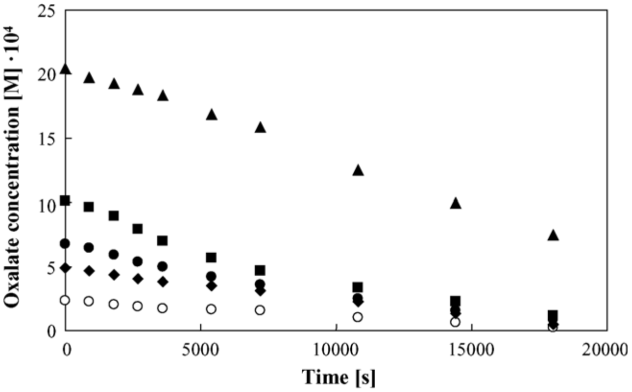

Fig. 3. Experimental values of oxalate ion concentration vs. reaction time for runs carried out in the contemporary presence of TiO_2, ozone, air near-UV irradiation. Ozone concentration in the gas phase: 8×10^{-4} M. Initial concentrations of oxalate ion: (▲) 20.4×10^{-4} M; (■) 10×10^{-4} M; (●) 6.8×10^{-4} M; (◆) 4.8×10^{-4} M; (○) 2.27×10^{-4} M.

For runs carried out in the presence of TiO_2 and ozone, without irradiating the system, the decrease of the concentration of oxalate was determined only by the homogeneous reaction thus indicating that a catalytic reaction between ozone and oxalate ion on TiO_2 surface plays a negligible role.

Fig. 2 shows the values of oxalate ion concentration versus reaction time for photocatalytic runs carried out in the presence of TiO_2, air and near-UV irradiation, while Fig. 3 reports the results of runs carried out in the presence of TiO_2, O_3, air and near-UV irradiation.

For the sake of comparison, Fig. 4 reports the concentration values of oxalate ion versus reaction time for runs carried out in the following operative conditions: (i)

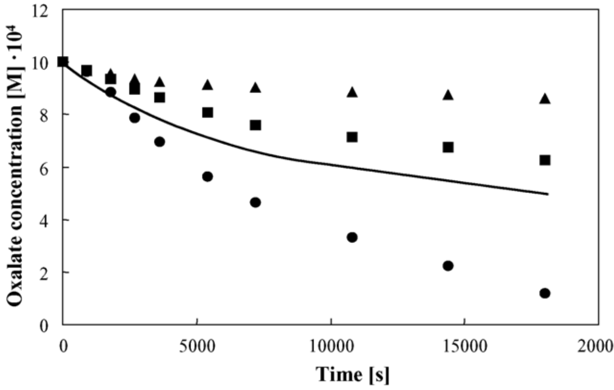

Fig. 4. Comparison between oxalate ion degradation runs both in homogeneous and heterogeneous regimes: (■) O_3/air/near-UV; (▲) TiO_2/air/near-UV; (●) TiO_2/O_3/air/near-UV; (—) sum of the contribution of the substrate degradation of O_3/air/near/UV and TiO_2/air/near-UV.

ozonation without catalyst; (ii) near-UV irradiation in the presence of photocatalyst and air; (iii) near-UV irradiation in the presence of photocatalyst and a mixture of air and ozone. From the observation of data of Fig. 4, it can be noted that the highest decrease of oxalate concentration takes place in the presence of ozone, air, near-UV irradiation and photocatalyst.

For all the runs in which a decrease of oxalate ion concentration was observed, no intermediate products of oxalate ion oxidation were detected in solution, indicating that both the homogeneous and heterogeneous processes are able to completely mineralize the substrate.

4. Discussion

4.1. Mechanistic aspects: homogeneous system

The reactivity runs carried out in homogeneous system indicated that oxalate oxidation occurred in the presence of ozone and that the presence of near-UV irradiation did not influence the homogeneous degradation rate.

It is well known [16] that ozone reacts in water solution with organic or inorganic compounds by following two pathways, the first one is the direct selective reaction with specific functional groups (double bonds, nucleophilic positions) and the second one is the reaction through free radicals generated from ozone decomposition. Hoigne and Bader [32] investigated the ozonation of oxalic acid at pHs ranging from 2 to 8 and concluded that the direct reaction of ozone with oxalate anion can be considered negligible. On this basis it may be assumed that the oxidation of oxalate anion in homogeneous conditions is due to attack by free radicals generated by O_3 decomposition. It is known [35] that at alkaline pHs O_3 molecules react with hydroxyl ions eventually producing the strong oxidant hydroxyl radicals:

$$O_3 + OH^- \rightarrow O_2^{\bullet -} + HO_2^{\bullet} \tag{1}$$

$$O_3 + HO_2^{\bullet} \rightarrow 2O_2 + {}^{\bullet}OH \tag{2}$$

or alternatively:

$$2HO_2^{\bullet} \rightarrow O_2 + H_2O_2 \tag{3}$$

$$H_2O_2 + O_2^{\bullet -} \rightarrow OH^- + {}^{\bullet}OH + O_2 \tag{4}$$

The produced oxidant species can mineralize the oxalate anion:

$$C_2O_4^{2-} + 2{}^{\bullet}OH \rightarrow 2CO_2 + 2OH^- \tag{5}$$

4.2. Mechanistic aspects: heterogeneous system

The oxalate degradation rate in the presence of ozone was not affected by the presence of the catalyst without irradiation. This result is in contrast with that reported by Beltrán et al. [33]; in fact, they studied the O_3/TiO_2 system without irradiation for oxalic acid degradation and found that at acidic pH the oxidation efficiency was greater than that of the homogeneous ozonation. It is well known [16] that the efficiency of the catalytic ozonation depends to a great extent both on the type of catalyst and its surface properties and the pH of the solution. Both Brönsted and Lewis acid–basic sites can work as catalytic centers for the adsorption on the metal oxide surface. An explanation can be found by considering that the extent of adsorption of oxalate anion and ozone onto TiO_2 surface changes at different pHs. Hug and Sulzberger [36] confirmed by FT-IR spectroscopy a significant adsorption of oxalic acid at pH around 3 and a negligible adsorption at pHs higher than 8. By considering that all the experimental runs were carried out at alkaline pH, the negligible role of the catalytic reaction between ozone and oxalate ion on TiO_2 surface may be justified by the practical absence of oxalate ion on the catalyst surface.

As far as the photocatalytic process is concerned, electron–hole pairs are generated after absorption of radiation by the semiconductor and they can be trapped by particular species. Hydroxyl groups act as traps for the holes, forming oxidant hydroxyl radicals; oxygen molecules adsorbed on TiO_2 surface, instead, can trap photogenerated electrons. O_2 is transformed in $O_2^{\bullet -}$ that produces $HO_2^{\bullet}$ and ${}^{\bullet}OH$ radicals:

$$TiO_2 + h\nu \rightarrow TiO_2 + e^- + h^+ \tag{6}$$

$$OH^- + h^+ \rightarrow {}^{\bullet}OH \tag{7}$$

$$O_2 \rightarrow O_{2(ads)} \tag{8}$$

$$O_{2(ads)} + e^- \rightarrow O_2^{\bullet -} \tag{9}$$

$$O_2^{\bullet -} + H_2O \rightarrow HO_2^{\bullet} + OH^- \tag{10}$$

$HO_2^{\bullet}$ evolves producing the hydroxyl radical according to reactions (3) and (4).

When ozone is present in the photocatalytic suspension, in addition to the homogeneous pathway described by reactions (1)–(4), it must be considered the role of O_3 as electron trap. FT-IR studies [31,37] report different modes of ozone interaction with TiO_2 surface such as: (i) physical adsorption; (ii) formation of weak hydrogen bonds with surface hydroxyl groups of the catalyst surface; (iii) molecular or (iv) dissociative adsorption into Lewis acid sites. Strong surface Lewis acid sites lead to distortion of the ozone molecule affording its decomposition with formation of a free oxygen molecule and a surface oxygen atom that remains attached to the site [37]. In the presence of TiO_2 and irradiation, ozone acts as a very strong electrophilic agent forming $O_3^{\bullet -}$ ozonide radicals [24] that lead to hydroxyl radicals:

$$O_{3(ads)} + e^- \rightarrow O_3^{\bullet -} \tag{11}$$

$$O_3^{\bullet -} + H_2O \rightarrow HO^{\bullet} + OH^- + O_2 \tag{12}$$

It is worth noting that the above reported mechanism gives rise to the formation of an hydroxyl radical for each trapped electron (reactions (11) and (12)), whereas three electrons are needed for the generation of a hydroxyl radical when oxygen acts as the electron trap (reactions (3), (4), (9) and (10)). Moreover, EPR studies [24] confirmed that oxygen is less electrophilic than ozone for photogenerated electrons onto TiO_2 surface. Therefore, when the catalyst is irradiated in the presence of ozone, a greater amount of hydroxyl radicals is formed with respect to that produced in the presence of oxygen. This fact can justify the significant positive effect of photocatalysis coupled with ozonation on the oxidation rate of oxalate anion. This effect is evident from the results reported in Fig. 4 where the decrease of oxalate concentration determined by both the homogeneous ozonation process and the heterogeneous photocatalytic one in the presence of oxygen is far less with respect to the decrease determined by the photocatalytic process combined with ozonation.

4.3. Kinetic aspects

zKinetic models of different orders with respect to oxalate concentration (zero, first and second order) have been tentatively applied to the experimental data obtained in homogeneous ozonated solutions (see Fig. 1). The degradation rate of oxalate anion, at the used operative conditions, can be best described by a first-order kinetic equation:

$$r_{\mathrm{homo}} \equiv -\frac{1}{V}\frac{\mathrm{d}N}{\mathrm{d}t} = -\frac{\mathrm{d}C}{\mathrm{d}t} = k_{\mathrm{homo}}C \qquad (13)$$

where r_{homo} is the homogeneous reaction rate, V the reaction volume, N the oxalate moles, t the time, C the molar concentration of oxalate, and k_{homo} is the kinetic constant. The values of k_{homo} have been determined by a least squares best fitting procedure applied to the experimental results. The average value obtained is equal to $(2.24 \pm 0.11) \times 10^{-5}$ s^{-1} $^{-1}$ being the R^2 values higher than 0.98 for all the runs.

In accord with Bangun and Adesina [28] the kinetics of oxalate photocatalytic oxidation, when oxygenated suspensions were irradiated, depends on the coverages by oxygen and oxalate anion. These species adsorb on different types of sites existing on the irradiated catalyst surface: the oxalate anions onto positively charged sites and oxygen onto electron-rich sites. The second-order surface reaction rate, $r_{\mathrm{S-Ox}}$, i.e. the oxalate moles reacted per unit time and active surface area, can be written in terms of Langmuir–Hinshelwood kinetics as

$$r_{\mathrm{S-Ox}} \equiv -\frac{1}{S_{\mathrm{A}}}\frac{\mathrm{d}N}{\mathrm{d}t} = -\frac{V}{S_{\mathrm{A}}}\frac{\mathrm{d}C}{\mathrm{d}t} = k''_{\mathrm{Ox}}\theta_{\mathrm{Ox}}\theta \qquad (14)$$

in which k''_{Ox} is the surface second-order rate constant, and θ_{Ox} and θ are the fractional sites coverages by oxygen and oxalate anion on irradiated TiO_2, respectively. S_{A} is the catalyst surface area able to adsorb oxygen and oxalate anion under irradiation; owing to the fact that S_{A} is very difficult to be determined, this parameter is substituted with the BET surface area (S) which is proportional to S_{A}. The θ_{Ox} and θ terms are related to oxygen and oxalate concentration in solution by the Langmuir model:

$$\theta_{\mathrm{Ox}} = \frac{K_{\mathrm{Ox}}C_{\mathrm{Ox}}}{1 + K_{\mathrm{Ox}}C_{\mathrm{Ox}}} \qquad (15)$$

$$\theta = \frac{KC}{1+KC} \qquad (16)$$

in which K_{Ox} and K are the equilibrium adsorption constants, and C_{Ox} and C the concentrations of oxygen and oxalate anion, respectively. As all the experiments were performed in a batch reactor by continuously bubbling oxygen, it can be assumed that for all the runs the θ_{Ox} term is constant during the occurrence of oxalate photooxidation.

By substituting Eqs. (15) and (16) into Eq. (14) and integrating with the limit condition that $C = C_0$ at $t = 0$, the following relationship between C and t is obtained:

$$t = \frac{1}{k'_{\mathrm{Ox}}\frac{S}{V}K}\ln\frac{C_0}{C} + \frac{1}{k'_{\mathrm{Ox}}\frac{S}{V}}(C_0 - C) \qquad (17)$$

in which k'_{Ox} (equal to $k''_{\mathrm{Ox}}\theta_{\mathrm{Ox}}$) is the surface pseudo-first-order rate constant.

By applying least-squares best fitting procedure to the photoreactivity experimental data, for each run the values of K and k'_{Ox} have been determined; the K value is reported in Table 1. The fitting of the model to the experimental data may be observed in Fig. 5 where the full lines drawn through the data represent the values of oxalate anion concentration obtained from Eq. (17) in which the fitted values of k'_{Ox} and K have been substituted. A good fitting of the model to the experimental data may be observed thus confirming the Langmuir–Hinshelwood nature of the photoreaction

Table 1
Kinetic parameters calculated according to the Langmuir–Hinshelwood kinetic model for the processes carried out by using TiO_2, in the presence of air and near-UV irradiation and in the contemporary presence of air, ozone and near-UV irradiation

	Photocatalysis	Photocatalysis and ozonation $C_{\mathrm{Oz}} = 0.26 \times 10^{-4}$ M	Photocatalysis and ozonation, $zC_{\mathrm{Oz}} = 1.0 \times 10^{-4}$ M
Second-order rate constant (k''_{Ox} or k''_{Oz}) ($\times 10^{-8}$ mol m^{-2} s^{-1})	1.00	1.50	1.50
Equilibrium adsorption constant of oxalate anion (K or K^*) (M^{-1})	400	800	1500
Equilibrium adsorption constant of oxygen, K_{Ox} (M^{-1})	1960	1960	1960
Equilibrium adsorption constant of ozone, K_{Oz} (M^{-1})	–	3000	3000

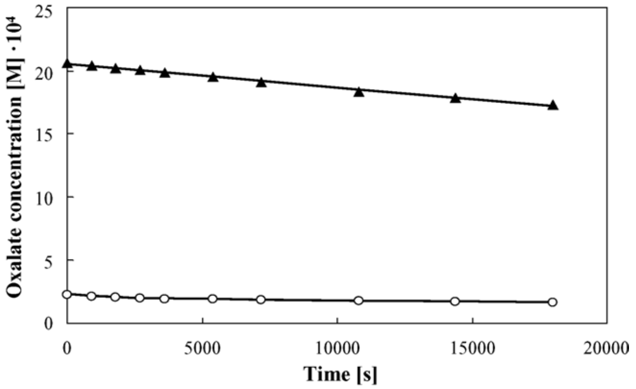

Fig. 5. Comparison between the experimental data and the Langmuir–Hinshelwood model of selected runs. Initial concentrations of oxalate ion: (▲) 20.4×10^{-4} M; (○) 2.27×10^{-4} M.

mechanism. The k'_{Ox} values depend on the oxygen concentration in the solution, and this dependence can be expressed by the following relationship:

$$\frac{1}{k'_{\mathrm{Ox}}} = \frac{1}{k''_{\mathrm{Ox}}K_{\mathrm{Ox}}}\frac{1}{C_{\mathrm{Ox}}} + \frac{1}{k''_{\mathrm{Ox}}} \tag{18}$$

which indicates a linear dependence of $1/k'_{\mathrm{Ox}}$ on $1/C_{\mathrm{Ox}}$. By using the $1/k'_{\mathrm{Ox}}$ values obtained from the series of runs carried out at two different oxygen concentrations, the figures of k''_{Ox} and K_{Ox} have been determined and they are reported in Table 1.

When dissolved ozone and oxygen are present in the irradiated suspensions, it must be taken into account that the oxalate oxidation occurs through three routes: (i) the homogeneous process; (ii) the heterogeneous photocatalytic one in the presence of oxygen; (iii) the heterogeneous photocatalytic one in the presence of ozone. The assumption is here made that ozone and oxygen competitively adsorb on the same sites of $\mathrm{TiO_2}$ surface so that their fractional coverages are expressed by the following relationships:

$$\theta^*_{\mathrm{Ox}} = \frac{K_{\mathrm{Ox}}C_{\mathrm{Ox}}}{1 + K_{\mathrm{Ox}}C_{\mathrm{Ox}} + K_{\mathrm{Oz}}C_{\mathrm{Oz}}} \tag{19}$$

$$\theta^*_{\mathrm{Oz}} = \frac{K_{\mathrm{Oz}}C_{\mathrm{Oz}}}{1 + K_{\mathrm{Oz}}C_{\mathrm{Oz}} + K_{\mathrm{Ox}}C_{\mathrm{Ox}}} \tag{20}$$

in which θ^*_{Ox} and θ^*_{Oz}, are the fractional coverages by oxygen and ozone when both compounds are present in the solution. K_{Oz} and C_{Oz} are the equilibrium adsorption constant of ozone on $\mathrm{TiO_2}$ surface and the concentration of ozone in the aqueous solution, respectively.

On this basis, the overall reaction rate per unit volume (r_{Ov}) for first-order homogeneous reaction and second-order surface reaction of oxalate can be written as

$$r_{\mathrm{Ov}} = -\frac{\mathrm{d}C}{\mathrm{d}t} = k_{\mathrm{homo}}C + \frac{S}{V}[k''_{\mathrm{Ox}}\theta^*_{\mathrm{Ox}}\theta^* + k''_{\mathrm{Oz}}\theta^*_{\mathrm{Oz}}\theta^*] \tag{21}$$

where k''_{Oz} is the second-order kinetic constant of the photocatalytic reaction between adsorbed ozone and oxalate ion and θ^* the fractional site coverage by oxalate ion when also ozone is present in the solution. By considering that ozone and oxygen concentrations were always constant, Eq. (21) may be simplified by substituting the $(k''_{\mathrm{Ox}}\theta^*_{\mathrm{Ox}} + k''_{\mathrm{Oz}}\theta^*_{\mathrm{Oz}})$ term with k'_{Oz} so that it may be written as

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = k_{\mathrm{homo}}C + \frac{S}{V}k'_{\mathrm{Oz}}\frac{K^*C}{1 + K^*C} \tag{22}$$

where K^* is the equilibrium adsorption constant of oxalate ion when ozone is also present in the reacting medium. The integration of Eq. (22) with the limit condition that for $t = 0$ the oxalate concentration is the initial one, C_0, gives

$$t = \frac{1}{D}\ln\frac{C_0}{C} + \left(\frac{1}{D} - \frac{K^*}{E}\right)\ln\frac{D + EC}{D + EC_0} \tag{23}$$

where $D = [(S/V)k'_{\mathrm{Oz}}K^* + k_{\mathrm{homo}}]$ and $E = k_{\mathrm{homo}}K^*$. By applying a least-squares best fitting procedure to the two sets of photoreactivity runs carried out with different ozone concentration, the values of the k'_{Oz} and K^* terms have been obtained; the K^* values are reported in Table 1. It is worth noting that the concentration of dissolved ozone affects not only the figures of k'_{Oz} $(= k''_{\mathrm{Ox}}\theta^*_{\mathrm{Ox}} + k''_{\mathrm{Oz}}\theta^*_{\mathrm{Oz}})$, as expected, but also the values of K^*, the equilibrium adsorption constant of oxalate anion. From the definition of k'_{Oz} and the previously obtained values of k''_{Ox} and K_{Ox}, the values of k''_{Oz} and K_{Oz} have been determined; they are reported in Table 1.

It can be noticed that in the case of photocatalysis in the presence of ozone the values of kinetic constant and oxalate adsorption constant are higher than those of photocatalysis in the presence of oxygen. The values of equilibrium adsorption constant of oxalate anion increase by increasing the ozone concentration in the liquid phase. These findings might be justified by the higher electrophilic nature of ozone on respect to oxygen. It is well known [16] that the reaction rate of ozone with photogenerated electrons is higher than that of oxygen. Therefore, in the presence of adsorbed ozone, the production rate of strong oxidant species, such as hydroxyl radicals, is enhanced giving rise to an enhancement of oxalate oxidation rate. The strong electrophilic nature of ozone determines that, when it is adsorbed on the irradiated photocatalyst surface, photogenerated electrons are displaced towards the ozone adsorption sites so that positive holes may be stabilized by surface centers, which in this way get able to adsorb an anion species as oxalate. The important increase of the adsorption equilibrium constant in the photocatalytic reaction combined with the ozonization is a clear clue that in the field of heterogeneous photocatalysis the photoadsorption phenomenon may be strongly affected by the reaction environment.

5. Conclusions

Oxalate anion has been mineralized in water solution at pH 10 by ozonation and by heterogeneous photocatalysis in combination also with ozonation. $\mathrm{TiO_2}$ was used as photocatalyst in the presence of oxygen or an oxygen/ozone mixture. An important increase on the rate of the oxidation process was observed in the presence of O_3, ultraviolet radiation and TiO_2 with respect to the other experimental conditions studied. The Langmuir–Hinshelwood kinetic model adequately describes all the photoreactivity results of heterogeneous systems and allows obtaining the values of the kinetic constant and of the equilibrium adsorption constant. The kinetic constant of the photocatalytic reaction in the presence of ozone is higher than that obtained in the presence of oxygen only; moreover, the value of the adsorption constant of oxalate anion increases by increasing the ozone concentration. These results allow hypothesizing a higher adsorption capacity of oxalate anion on the surface of the photocatalyst in the presence of ozone and UV irradiation. On the other hand, ozone acts as trap for the electrons photogenerated on the surface of the photocatalyst in a more effective way than oxygen, forming an ozonide radical that is an intermediate for the production of hydroxyl radicals. The higher production of hydroxyl radicals in the presence of ozone and UV irradiation on the TiO_2 surface in comparison to other conditions can justify the important beneficial effect observed when photocatalysis and ozonation are both used for the oxalate anion degradation.

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References

[1] M. Schiavello (Ed.), Heterogeneous Photocatalysis, John Wiley & Sons, New York, 1995.

[2] A. Fujishima, K. Hashimoto, T. Watanabe, TiO_2 Photocatalysis: Fundamentals and Applications, Bkc, Tokyo, 1999.

[3] V. Augugliaro, A. Bianco Prevot, J. Cáceres Vázquez, E. García-López, V. Loddo, S. Malato-Rodrigúez, G. Marcì, L. Palmisano, E. Pramauro, Adv. Environ. Res. 8 (2004) 329.

[4] V. Augugliaro, J. Blanco-Gálvez, J. Cáceres-Vásquez, E. García-López, V. Loddo, M.J. López-Muñoz, S. Malato-Rodríguez, G. Marcì, L. Palmisano, M. Schiavello, J. Soria-Ruiz, Catal. Today 54 (1999) 245.

[5] D. Chen, A.K. Ray, Chem. Eng. Sci. 56 (2001) 1561.

[6] K. Sunada, T. Watanabe, K. Hashimoto, J. Photochem. Photobiol. A: Chem. 156 (2003) 227.

[7] A.L. Linsebigler, G. Lu, J.T. Yates, Chem. Rev. 95 (1995) 735.

[8] A. Di Paola, E. García-López, S. Ikeda, G. Marcì, B. Othani, L. Palmisano, Catal. Today 75 (2002) 87.

[9] S. Sakthivel, H. Kisch, Angew. Chem. Int. Ed. 42 (2003) 4908.

[10] A. Di Paola, L. Palmisano, V. Augugliaro, Catal. Today 58 (2000) 141.

[11] G. Mele, R. Del Sole, G. Vasapollo, E. García-López, L. Palmisano, M. Schiavello, J. Catal. 217 (2003) 334.

[12] S. Sato, J.M. White, Chem. Phys. Lett. 72 (1980) 83.

[13] V. Augugliaro, E. Davì, L. Palmisano, M. Schiavello, A. Sclafani, Appl. Catal. 65 (1990) 101.

[14] J. Pignatello, Environ. Sci. Technol. 26 (1992) 944.

[15] E. Pelizzetti, V. Carlin, C. Minero, M. Grätzel, N. J. Chem. 15 (1991) 351.

[16] S.T. Oyama, Catal. Rev. Sci. Eng. 42 (2000) 279.

[17] J. Araña, J.A. Herrera Melián, J.M. Doña Rodríguez, O. González Díaz, A. Viera, J. Pérez Peña, P.M. Marrero Sosa, V. Espino Jiménez, Catal. Today 76 (2002) 279.

[18] K. Tanaka, K. Abe, T. Hisanaga, J. Photochem. Photobiol. A 101 (1996) 85.

[19] M. Klare, G. Waldner, R. Bauer, H. Jacobs, J.A.C. Broekaert, Chemosphere 38 (19992013).

[20] E. Piera, J.C. Calpe, E. Brillas, X. Domènech, J. Peral, Appl. Catal. B: Environ. 27 (2000) 169.

[21] L. Sanchez, J. Peral, X. Domenech, Appl. Catal. B: Environ. 19 (1998) 59.

[22] J. Villaseñor, P. Reyes, G. Pecchi, Catal. Today 76 (2002) 121.

[23] S. Wang, F. Shiraishi, K. Nakano, Chem. Eng. J. 87 (2002) 261.

[24] M.D. Hernandez-Alonso, J.J. Coronado, A.J. Maira, J. Soria, V. Loddo, V. Augugliaro, Appl. Catal. B: Environ. 39 (2002) 257.

[25] J.-M. Herrmann, M.N. Mozzanega, P. Pichat, J. Photochem. Photobiol. 22 (1983) 333.

[26] I. Franch, J.A. Ayllon, J. Peral, X. Domenech, Catal. Today 76 (2002) 221.

[27] M. Kosanic, J. Photochem. Photobiol. A: Chem. 119 (1998) 119.

[28] J. Bangun, A.A. Adesina, Appl. Catal. A: Gen. 175 (1998) 221.

[29] J.-M. Herrmann, H. Tahiri, C. Guillard, P. Pichat, Catal. Today 54 (1999) 131.

[30] E. Brillas, E. Mur, R. Sauleda, L. Sanchez, J. Peral, X. Domenech, J. Casado, App. Catal. B: Environ. 16 (1998) 31.

[31] Y. Maeda, A. Fujishima, K. Honda, J. Electrochem. Soc. 128 (1981) 1731.

[32] J. Hoigne, H. Bader, Water Res. 17 (1983) 185.

[33] F. Beltrán, F.J. Rivas, R. Montero de Espinosa, Appl. Catal. B: Environ. 39 (2002) 221.

[34] D.R. Lide (Ed.), Handbook of Chemistry and Physics, CRC Press Inc., Boca Raton, 1994.

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

[36] S.J. Hug, B. Sulzberger, Langmuir 10 (1994) 3587.

[37] K.M. Bulanin, J.C. Lavalley, A.A. Tsyganenko, Colloid Surf. A 101 (1995) 153.