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ORIGINAL PAPER

# Mechanistic aspects of oxalic acid oxidation by photocatalysis and ozonation

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**Abstract** Oxalic acid has been oxidised in acidic aqueous solutions (pH 3) using photocatalysis and ozonation alone or coupled. The simultaneous presence of ozone, titanium dioxide and near UV irradiation increases the oxidation rate of oxalic acid to values greater than those deriving from the single contributions of photocatalysis and ozonation. In particular in the present paper ozonation alone, heterogeneous photocatalysis and also combined ozonation with heterogeneous photocatalysis have been used for the oxidation of oxalic acid at acidic pH in the presence of $TiO_2$ Degussa P25. A likely mechanism, able to explain both the homogeneous and heterogeneous processes, is discussed.

**Keywords** Oxalic acid degradation · Ozonation · Photocatalysis · Titanium dioxide

## 1 Introduction

Heterogeneous photocatalysis, based on polycrystalline semiconductor oxides irradiated with UV light, is an advanced oxidation process recently developed [1, 2]. Oxidation processes such as ozonation and methods aimed at an enhancement of its efficiency have recently received much attention [3]. The use of ozone in combination with heterogeneous photocatalysis has also been studied and a significant improvement in the oxidation process performance has been reported [4, 5].

Oxalic acid has been detected during the mineralization of a large variety of organic compounds. It is a water pollutant resulting from some industrial treatment processes (textile industry, metallurgy, etc.): $Na_2C_2O_4$, for instance, is present during alumina processing (Bayer process) and its removal for the reuse of the caustic solution is very important for the plant economy [6].

The photocatalytic method is effective for the degradation of oxalic acid in suspension of $TiO_2$ irradiated with near-UV light [7, 8]. Ozonation has also been used to oxidise oxalic acid both in the absence and presence of $TiO_2$ [9]. The simultaneous presence of photocatalysis and ozonation produces a significant increase in the oxalate ion degradation rate at basic pH [10]. A kinetic model considering both homogeneous and heterogeneous processes for oxalate ion oxidation in alkaline solution was developed and the kinetic and thermodynamic parameters were reported [10]. Notwithstanding the existence of studies on oxalic acid degradation at acidic pH in the presence of $TiO_2$ or $O_3$, up to date no detailed investigation has been carried out on the simultaneous presence of $O_3$, $TiO_2$ and UV light.

In the present paper heterogeneous photocatalysis has been combined with ozonation for the oxidation of oxalic acid used as a probe molecule in acidic media in the presence of $TiO_2$ Degussa P25.

## 2 Experimental

A Pyrex batch photoreactor ($V = 2.5$ dm$^3$) of cylindrical shape was used. A medium pressure Hg lamp (Helios Italquarz, Italy) of 700 W was immersed in an axial

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position inside the photoreactor. The emitted photon flow of the lamp (measured by a Digital UVX radiometer) was 17 mW cm$^{-2}$. The initial oxalic acid concentrations were in the 0.2–2.0 mM range. The pH of the solutions ranged between 2.7 and 3; in this pH range oxalic acid is partially ($\sim$85%) dissociated in $HC_2O_4^-$ anion. Air or air-ozone mixtures were bubbled in the reacting suspension at a flow rate of 0.030 L min$^{-1}$. Ozone was produced by feeding synthetic air to an ozonator (Microlab) able to vary the ozone production rate in the 1 to 20 mmol h$^{-1}$ range. In order to determine the concentration of ozone in the gas phase introduced to the reacting system, the absorbance of gaseous ozone was measured at 254 nm 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 oxidised by the ozone to iodate. The values of ozone concentration measured in the air entering the reactor were in the 0.06–0.16 mM range. The concentration values of ozone and oxygen dissolved in the liquid phase, calculated using Henry's law [11], were in the range 0.013–0.047 mM and 0.025–0.026 mM, respectively.

The amount of catalyst ($TiO_2$ Degussa P25) was 0.24 g L$^{-1}$. This mass was able to absorb all the photons emitted by the lamp during the photoreactivity runs that lasted 5 h. Before turning on the lamp, the system was maintained in the dark for 30 min by bubbling air or air-ozone mixtures in order to reach steady state conditions. Samples of 5 mL were withdrawn at fixed intervals of time and quantitative analyses of anionic species were carried out by ionic chromatography after catalyst separation by means of a cellulose acetate filter (Millipore) with pore diameter of 0.45 μm. The ionic chromatograph (Dionex DX 120) was equipped with an Ion Pac AS14 column (4 mm × 250 mm, Dionex). A buffer solution of $NaHCO_3$ (1 mM) and $Na_2CO_3$ (8 mM) was used as mobile phase at a flow rate of 1.0 cm$^3$ min$^{-1}$.

## 3 Results

Preliminary runs, carried out without catalyst and by bubbling air in the solution both in the presence or in the absence of UV light or in the presence of $TiO_2$ in the dark, showed that no degradation of oxalic acid occurred. In contrast, as shown in Fig. 1, degradation of the substrate was observed by irradiating the system in the presence of the catalyst and by bubbling air.

Runs carried out in the dark by bubbling $O_3$ showed a very small degradation of oxalic acid that slightly increased when $TiO_2$ was also present, indicating some catalytic activity of titanium dioxide. In contrast, when the ozonated solution was also irradiated, a noticeable increase in reactivity was observed. This reactivity increased with increasing $O_3$ concentration in the solution. Figure 2 reports some results concerning the oxidation of oxalic acid with ozone carried out in the homogeneous phase both in the absence and presence of UV light.

The highest reactivity was, however, observed when $O_3$, air, $TiO_2$ and UV light were simultaneously present. Figure 3 reports the concentration values of oxalic acid versus time for runs carried out in these conditions at the two different ozone concentrations in the liquid phase studied in this paper.

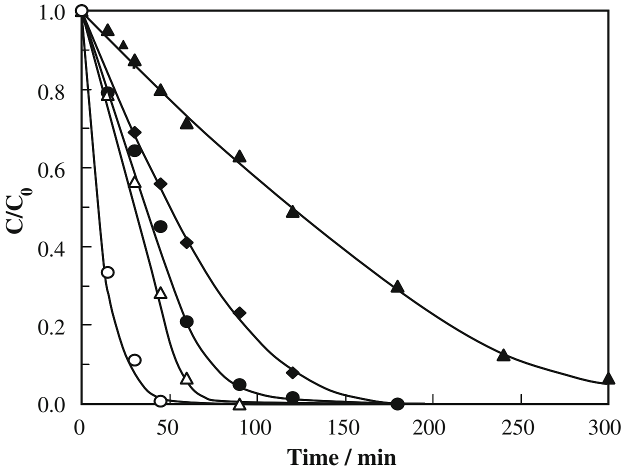

**Fig. 1** Normalized oxalic acid concentration versus irradiation time for runs carried out in the presence of air and $TiO_2$. Initial concentrations of $H_2C_2O_4$: (▲) 2.0 mM; (♦) 1.0 mM; (●) 0.63 mM; (Δ) 0.46 mM; (O) 0.16 mM

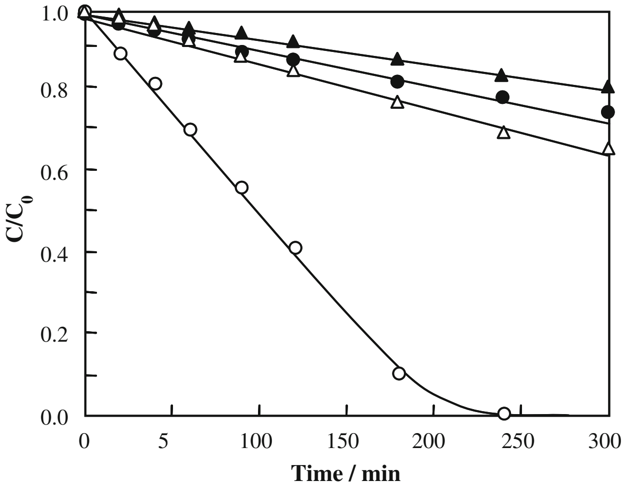

**Fig. 2** Normalized oxalic acid concentration versus time for runs carried out in homogeneous conditions in the presence of $O_3$/air mixtures at the different $O_3$ concentrations of (▲) 0.013 mM; (●) 0.047 mM; (Δ) 0.013 mM in the presence of UV; (O) 0.047 mM in the presence of UV. Initial $H_2C_2O_4$ concentration 2 mM

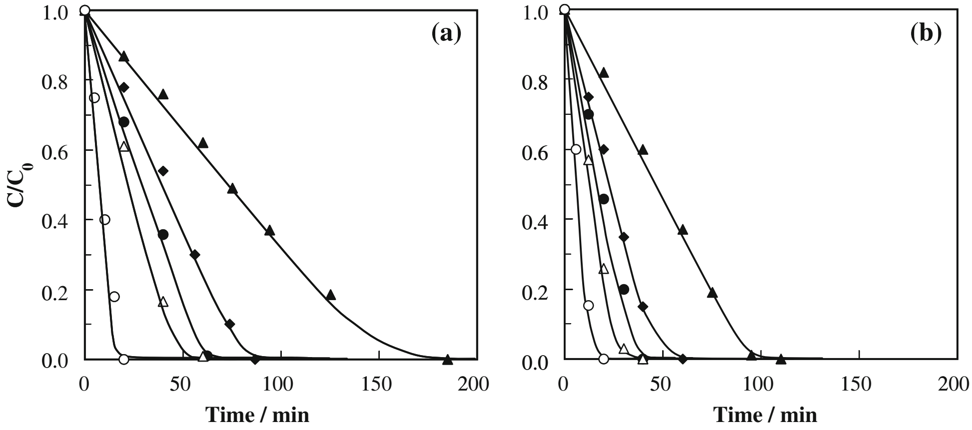

**Fig. 3** Oxalic acid concentration versus irradiation time for runs carried out in the simultaneous presence of $O_3$, air, $TiO_2$ and UV at different ozone concentrations: (**a**) 0.013 mM and (**b**) 0.047 mM. Initial $H_2C_2O_4$ concentrations: (▲) 2.0 mM; (◆) 1.0 mM; (●) 0.63 mM; (Δ) 0.46 mM; (O) 0.16 mM

## 4 Discussion

### 4.1 Homogeneous system

The reactivity runs carried out in the homogeneous system revealed that oxalic acid is degraded in the presence of $O_3$ and that UV irradiation increases the decomposition rate. Ozone is one of the most powerful oxidants, due to its high redox potential ($E_0 = 2.07$ V). Two possible oxidation pathways can be considered [9, 12]: the direct reaction between substrate (if it possesses specific functional groups such as double bonds or nucleophilic positions) and ozone and/or the reaction between substrate and the hydroxyl radicals produced in ozone decomposition. In the case of oxalic acid which does not posses any of these specific groups, direct reaction between $O_3$ and the substrate can be neglected and consequently only indirect ozone attack should be considered. The formation of hydroxyl radicals due to ozone decomposition proceeds according to the following reactions [13]:

$$O_3 + H_2O \rightarrow 2HO^\bullet + O_2 \tag{1}$$

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

$$O_3 + HO_2^\bullet \rightarrow 2O_2 + HO^\bullet \tag{3}$$

$$2HO_2^\bullet \rightarrow O_2 + H_2O_2 \tag{4}$$

In our experimental conditions the degradation of oxalic acid by ozonation proceeds slowly in acidic medium (See Fig. 2). Coupling ozone and UV light causes an increase in HO radical production, due to the decomposition of $H_2O_2$ by the following reaction:

$$H_2O_2 \xrightarrow{hv} 2HO^\bullet \tag{5}$$

and consequently the degradation of the substrate increases. Moreover, UV light can promote the photolysis of $O_3$ producing atomic oxygen which reacts with $H_2O$ and gives rise to further formation of $H_2O_2$ [14]:

$$O_3 \xrightarrow{hv} O + O_2 \tag{6}$$

$$O + H_2O \rightarrow H_2O_2 \tag{7}$$

The strong oxidant OH radical species mineralize the hydrogen oxalate anion:

$$HC_2O_4^- + 2HO^\bullet + H^+ \rightarrow 2CO_2 + 2H_2O \tag{8}$$

### 4.2 Heterogeneous system

The experimental results have shown that the oxalic acid degradation in the dark and in the presence of $O_3$ slightly increases when $TiO_2$ is added to the reacting medium. These results are in agreement with those reported by Beltrán et al. [9] who studied oxalic acid degradation in systems containing $O_3/TiO_2$ without irradiation. The efficiency of this process depends on the kind of catalyst and its surface properties and on the pH of the solution. In particular the pH of the reacting medium can affect the amount of oxalic acid adsorbed onto the catalyst surface. The higher photoreactivity observed at acidic pH with respect to that reported at pH 10 [10] can be explained by taking into account the significant adsorption [15] of hydrogen oxalate (which is the main species present at pH 3) onto the $TiO_2$ surface. In fact, the initial reaction rates of the photocatalytic process for an initial concentration of substrate 2 mM at pH 3 and 10 were $14.1 \times 10^{-8}$ and $5.75 \times 10^{-8}$ M $s^{-1}$ [10], respectively.

As far as the photocatalytic process (in the simultaneous presence of $TiO_2$, UV light and air) is concerned, electron-hole pairs are generated after absorption of the radiation by the semiconductor and they can be trapped by adsorbed water and $O_2$ forming radical species such as $HO^\bullet$:

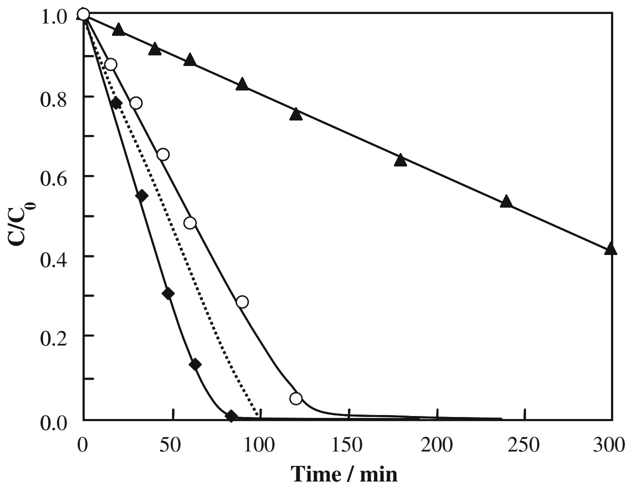

**Fig. 4** Disappearance of normalized oxalic acid concentration vs. irradiation time: (▲) $O_3$/UV; (O) air/$TiO_2$/UV; (♦) $O_3$/$TiO_2$/UV. The dotted line corresponds to the sum of the contributions $O_3$/UV and air/$TiO_2$/UV. Concentration of dissolved $O_3$ 0.013 mM. Initial $H_2C_2O_4$ concentration 1 mM

$$TiO_2 \xrightarrow{h\nu} TiO_2(h^+ + e^-) \tag{9}$$

$$H_2O + h^+ \rightarrow HO^\bullet + H^+ \tag{10}$$

$$O_2 + e^- \rightarrow O_2^{\bullet-} \tag{11}$$

$$O_2^{\bullet-} + H^+ \rightarrow HO_2^\bullet \tag{12}$$

$$2HO_2^\bullet \rightarrow O_2 + H_2O_2 \tag{13}$$

$$H_2O_2 + O_2^{\bullet-} + H^+ \rightarrow HO^\bullet + H_2O + O_2 \tag{14}$$

that oxidize the hydrogen oxalate anion as in reaction (8).

It is worth noting that a direct attack on the substrate by the holes generated on the surface of the solid cannot be excluded, especially when strong adsorption of the substrate occurs. In the simultaneous presence of $TiO_2$, UV irradiation and $O_3$, the adsorbed ozone acts as a very strong electrophilic agent, forming ozonide radicals [16] which lead to hydroxyl radicals:

$$O_3 + e^- \rightarrow O_3^{\bullet-} \tag{15}$$

$$O_3^{\bullet-} + H^+ \rightarrow O_2 + HO^\bullet \tag{16}$$

Moreover, homogeneous reactions (1–7) also occur in the heterogeneous system. The above reported mechanism gives rise to the formation of one hydroxyl radical for each trapped electron (reactions 15 and 16), whereas three electrons are needed for the generation of a hydroxyl radical when oxygen acts as electron trap (reactions 11–14). 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 finding justifies the effectiveness of photocatalysis coupled with ozonation on the oxidation rate of oxalic acid. Figure 4 shows the disappearance of oxalic acid with irradiation time for runs carried out in different experimental conditions. The oxalic acid degradation was faster when ozone, air, UV irradiation and photocatalyst were contemporaneously present. The synergistic effect observed when photocatalysis and ozonation were simultaneously used is evident; indeed in this case the decrease in oxalic acid concentration was larger than that expected from a simple sum of the single contributions due to photocatalysis and ozonation in the presence of UV light.

## 5 Conclusions

Oxalic acid was mineralised in aqueous acidic solutions by photocatalysis and/or ozonation. $TiO_2$ was used as the photocatalyst in the presence of air or air/ozone mixtures. A significant increase in oxidation rate was observed in the simultaneous presence of $O_3$, air, $TiO_2$ and UV light compared to the other experimental conditions studied. The beneficial effect of the presence of $O_3$ was explained by a higher production of hydroxyl radicals. The larger adsorption of oxalic acid in the acidic medium justifies the increased photoactivity compared to that observed in the alkaline medium.

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