



# Photocatalytic ozonation of model aqueous solutions of oxalic and oxamic acids



C.A. Orge\*, M.F.R. Pereira, J.L. Faria

LCM – Laboratório de Catálise e Materiais – Laboratório Associado LSRE–LCM, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias s/n, 4200–465 Porto, Portugal

## ARTICLE INFO

### Article history:

Received 19 December 2014  
Received in revised form 22 February 2015  
Accepted 27 February 2015  
Available online 28 February 2015

### Keywords:

Photocatalytic ozonation  
Titanium dioxide  
Carbon nanotubes  
Oxalic acid  
Oxamic acid

## ABSTRACT

Degradation of aqueous solutions of oxalic acid (OXA) and oxamic acid (OMA), the final oxidation products of several organic compounds, has been investigated by photocatalytic ozonation. The combined method was carried out comparing P25 to synthesized sol–gel TiO<sub>2</sub>, and composites of TiO<sub>2</sub> and multi-walled carbon nanotubes (MWCNTs) obtained either by the sol–gel method or by the hydration–dehydration technique. Photo-ozonation in the presence of P25 resulted in total conversion of OXA after 15 min. Concerning OMA, P25 and composites containing 80 and 90% wt of P25 led to complete degradation more rapidly. The reaction rate constants,  $k_{app}$ , were  $15 \times 10^{-2} \text{ min}^{-1}$  for P25,  $8.8 \times 10^{-2} \text{ min}^{-1}$  and  $8.2 \times 10^{-2} \text{ min}^{-1}$  for the composite with 80 and 90% wt of P25, respectively. OMA removal by photocatalytic ozonation is here reported for the first time and a remarkable conversion is obtained with complete degradation achieved in a short period of time in the presence of TiO<sub>2</sub>, P25 and composites with 80 and 90%wt of P25 and MWCNTs and with 80%wt of P25 and oxidized MWCNTs. By performing single photocatalysis or single ozonation for selected materials, a synergetic effect of the combined method was identified.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Advanced oxidation processes (AOPs) are efficient in accelerate the non-selective oxidation of organics and thus the mineralization of a wide range of recalcitrant compounds resistant to conventional treatments [1–3]. AOPs are based on the generation of highly reactive free radicals by using chemical and/or other forms of energy, and under appropriate conditions the species to be removed are totally converted to CO<sub>2</sub>, H<sub>2</sub>O and inoffensive mineral salts. Photocatalysis ranks among the AOPs that proved advantageous in remediation of contaminate waste water, although large-scale application remains somewhat expensive owing to the cost of artificial photons and slow oxidation kinetics. The fundamental mechanism of photocatalysis consists in the irradiation of a semiconductor material by light with sufficient energy to excite the electrons from the valence to the conduction band generating electron–hole pairs, which migrate to the surface where they can react with adsorbed OH<sup>−</sup> to produce HO•; or directly oxidize other adsorbed species [4]. In this process, oxygen is widely used as compensatory oxidant to complete the electron balance. The disadvantage is that mineralization normally requires long reaction time

due to the slow electron transfer [5]. In order to improve the performance of photocatalytic processes, different strategies have been followed, such as adding oxidant species as hydrogen peroxide, Fe<sup>2+</sup> ions or ozone (O<sub>3</sub>).

The use of O<sub>3</sub> for the destruction of organic compounds is a recognized water treatment technique. O<sub>3</sub> is a strong oxidative agent ( $E^\circ = 2.07 \text{ eV}$ ) and reacts directly via molecular O<sub>3</sub>, and indirectly by the hydroxyl radicals (HO•), which are a powerful and non-selective oxidant ( $E^\circ = 2.8 \text{ eV}$ ) [6].

Photocatalytic ozonation is an emergent technology that combines two AOPs with the main advantage of this integrate process being the highest HO• yield due to the more powerful oxidant character of ozone compared to oxygen [7]. Thus, an additional and important way of HO• formation is the O<sub>3</sub> capture of electrons in the conducting band of the catalyst to yield the ozonide ion radical (O<sub>3</sub><sup>•−</sup>) that eventually gives rise to HO• [8]. This advantage, on the other hand, minimizes the undesirable recombination reaction of electrons and positive holes in the valence band, which results in the inhibition of the process rate.

Most of the publications on photocatalytic ozonation applied suspensions of fine TiO<sub>2</sub> particles, often in the form of P25 (Evonik; Degussa), the most used photocatalyst, characterized by its non-toxicity, photo-stability, as well as by its low cost and very high efficiency under ultraviolet irradiation. Electron–hole recombination limits the efficiency of TiO<sub>2</sub> photocatalysis. As a strategy to prevent this, TiO<sub>2</sub>/carbon materials in simple mixtures or as

\* Corresponding author. Tel.: +351 225081400; fax: +351 225081440.

E-mail addresses: [carlaorge@fe.up.pt](mailto:carlaorge@fe.up.pt) (C.A. Orge), [fpereira@fe.up.pt](mailto:fpereira@fe.up.pt) (M.F.R. Pereira), [jlfaria@fe.up.pt](mailto:jlfaria@fe.up.pt) (J.L. Faria).

nanocomposites have been investigated. Mixed-phase TiO<sub>2</sub>-based composites tend to show higher photoreactivity in comparison to pure-phase materials, as exhibited by P25, due to the formation of solid–solid interfaces that facilitate charge transfer and spatial separation, reducing electron–hole recombination, and interfacial defect sites that act as “hot spots” [9].

The aim of the present work relies on the investigation of oxalic acid (OXA) and oxamic acid (OMA) degradation by photocatalytic ozonation. For this study, composites with titanium dioxide (TiO<sub>2</sub>) and multi-walled carbon nanotubes (MWCNTs) were prepared by different procedures and with diverse compositions. Experiments only with catalytic ozonation or photocatalysis using the prepared materials were also carried out in order to better understand the results.

Many effluents, especially in metallurgical and textile industrial waste waters contain OXA. Furthermore, OXA is a detectable intermediate in the mineralisation of many pesticides and other organic compounds [10].

On the other hand, OMA is normally generated from the oxidation of organic compounds containing nitrogen functional groups, as aniline, sulfanilic acid and azo dyes [11,12]. OMA is highly refractory to chemical oxidation and conventional processes as ozonation and photolysis did not allow its mineralization. Very few information on this compound was found in the literature and the development of an efficient process capable of removing this compound is an important step to mineralize a vast range of organic pollutants. To the best of our knowledge, no papers in the literature described OMA removal by photocatalytic ozonation. OMA removal by catalytic ozonation in the presence of activated carbon, carbon nanotubes and ceria-activated carbon composites was previously studied [13–16]. The best results allowed 70% and 75% removal after 10 h of reaction in the presence of MWCNTs with basic properties and ceria-activated carbon composite with 10% of cerium oxide, respectively. However, total removal was never achieved even for long reaction times. OMA degradation was also studied by an electrochemical AOP. Total degradation was achieved at 270 min of reaction by anodic oxidation with a boron-doped diamond electrode and Fe<sup>2+</sup> solution under UVA illumination [17]. In another work, OMA was transformed to carbonates and nitrogen with 88.2% conversion, in NaOH medium, with Pd/CNT modified electrode [18].

## 2. Experimental

### 2.1. Reagents and materials

Titanium (IV) isopropoxide (Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>, 97%), nitric acid (HNO<sub>3</sub>, ≥65%), oxalic acid (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>, ≥99%) and oxamic acid (C<sub>2</sub>H<sub>3</sub>O<sub>3</sub>N, ≥98%) were purchased from Sigma–Aldrich. Ethanol (C<sub>2</sub>H<sub>5</sub>OH, 99.5%) was obtained from Panreac. Sulfuric acid was supplied by Fisher Scientific. Commercial TiO<sub>2</sub>, sample P25, was supplied by Evonik Degussa Corporation. The commercial multi-walled carbon nanotubes, MWCNTs, were supplied by Nanocyl (ref. 3100). Ultrapure water was produced on a Direct-Q milipore system.

### 2.2. Catalyst preparation and characterization

Different sets of catalysts were prepared. The composites with TiO<sub>2</sub> and MWCNTs were synthesized by the sol–gel method to match 20, 50 and 80 wt.% of TiO<sub>2</sub> (after designated 20%TiO<sub>2</sub>/MWCNTs, 50%TiO<sub>2</sub>/MWCNTs and 80%TiO<sub>2</sub>/MWCNTs, respectively). Neat sol–gel TiO<sub>2</sub> was also prepared (hereafter referred as TiO<sub>2</sub>).

The composites of P25 and MWCNTs were prepared using the hydration–dehydration technique in the same ratios used for

sol–gel (samples 20%P25/MWCNTs, 50% P25/MWCNTs and 80% P25/MWCNTs) and two additional composites with 90 and 95% of P25 (samples 90% P25/MWCNTs and 95% P25/MWCNTs, respectively).

The TiO<sub>2</sub> sample was prepared by the slowly addition of Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> to ethanol. After 30 min under continuous stirring, nitric acid was added. The solution was loosely covered and kept stirring until the homogenous gel formed. After grinding the xerogel, a fine powder was formed and afterwards it was calcined at 400 °C in a nitrogen flow for 2 h [19].

TiO<sub>2</sub>/MWCNTs composites were prepared by a similar procedure to that described to TiO<sub>2</sub> sample, where a given amount of MWCNTs was dispersed in the metal solution 2 h after adding nitric acid.

In the preparation of P25/MWCNTs composites, a selected amount of MWCNTs was dispersed in water under ultrasonication. P25 was added to the suspension 30 min later and the mixture was heated up to 80 °C and magnetically stirred until the water was completely evaporated. The resulting composite was dried at 110 °C overnight.

The textural characterization of the materials was based on the corresponding N<sub>2</sub> equilibrium adsorption/desorption isotherms, determined at –196 °C with a Quantachrome Instruments NOVA 4200e apparatus. The relative amount of TiO<sub>2</sub> in the catalyst was determined by thermogravimetric analysis (TG) under air in a STA 409 PC/4/H Luxx Netzsch thermal analyser.

### 2.3. Catalytic experiments

Experiments of photocatalytic ozonation (O<sub>3</sub> + UV/catalyst), catalytic ozonation (O<sub>3</sub>/catalyst) and photocatalysis (UV/catalyst) were performed on OXA and OMA. Photo-ozonation (O<sub>3</sub> + UV), single ozonation (O<sub>3</sub>) and photolysis (UV) were also carried on as control. A glass immersion photochemical reactor (diameter: 60 mm; height: 250 mm) loaded with 250 cm<sup>3</sup> of solution. The reactor was equipped with a Heraeus TQ 150 medium-pressure mercury vapor lamp located axially and a DURAN 50<sup>®</sup> glass cooling jacket was placed around the lamp (main resulting emission lines at λ<sub>exc</sub> = 365, 405, 436, 546 and 578 nm). The initial concentration of OXA and OMA was of 1 mM. The agitation was maintained constant at 400 rpm in order to keep the reactor content perfectly mixed. The gas was bubbled in the reactor by a diffuser with 1 cm of diameter. The experiments were performed at constant gas flow rate (150 cm<sup>3</sup> min<sup>–1</sup>) and constant inlet ozone concentration (50 g m<sup>–3</sup>). In O<sub>3</sub> containing experiments, ozone was produced from pure oxygen in a BMT 802X ozone generator. The concentration of ozone in the gas phase was monitored with a BMT 964 ozone analyser. Ozone in the gas phase leaving the reactor was removed in a series of gas washing bottles filled with potassium iodide solution. In direct photolysis and photocatalytic reactions, the ozone-containing stream was replaced by an oxygen stream.

The concentration of selected acids was determined by HPLC with Hitachi Elite Lachrom system equipped with an ultraviolet detector. The stationary phase was an Altech AO-100 column working at room temperature under isocratic elution with H<sub>2</sub>SO<sub>4</sub> 5 mM at a flow rate of 0.5 cm<sup>3</sup> min<sup>–1</sup>. The injection volume was 15 μL and the detector wavelength was 200 nm.

## 3. Results and discussion

### 3.1. Characterization of the catalysts

The TiO<sub>2</sub> average content (determined by thermal analyses) and the BET surface area (from the N<sub>2</sub> adsorption–desorption isotherms) of the prepared composites is collected in Table 1.

Download English Version:

<https://daneshyari.com/en/article/6500072>

Download Persian Version:

<https://daneshyari.com/article/6500072>

[Daneshyari.com](https://daneshyari.com)