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Ozonation of erythromycin over carbon materials and ceria dispersed on carbon materials

Alexandra G. Gonçalves, José J.M. Órfão, Manuel Fernando R. Pereira *

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

HIGHLIGHTS

- MWCNTs and activated carbon containing ceria dispersed on the surface were prepared.
- These materials were tested as catalysts in the ozonation of erythromycin.
- Materials containing ceria showed an interesting catalytic effect.
- A synergetic effect between carbon materials and ceria was observed.
- The lowest toxicity was obtained with the simultaneous use of O_3 and those materials.

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ABSTRACT

Two carbon materials, multi-walled carbon nanotubes (MWCNT) and activated carbon (AC), were investigated as ozonation catalysts for the erythromycin (ERY) mineralization. In addition, in order to evaluate a possible synergetic effect between carbon materials and ceria in the ozonation of this antibiotic, two catalysts containing ceria dispersed on the surface of MWCNT and AC were prepared, characterized and tested. The results were compared with those obtained in the absence of catalyst and in the presence of ceria. The mineralization of ERY solutions was enhanced by addition of the studied catalysts. A synergetic effect between carbon materials and ceria was observed, leading to higher mineralization degrees of ERY, mainly in the presence of MWCNT containing ceria. In the catalytic ozonation with these materials both surface and bulk reactions are supposed to occur. Oxamic, oxalic and pyruvic acids were identified as final by-products during the ozonation process. Part of the original nitrogen of ERY was converted to NO_3^- along with small amounts of NH_4^+ and NO_2^-. Microtox tests revealed that intermediates with higher acute toxicity than ERY are produced in the early stages of single and catalytic ozonation. For longer ozonation times the acute toxicity is similar whether the carbon materials are present or not, whereas it significantly decreases using carbon materials containing ceria. Successive experimental runs of ERY ozonation show that the catalysts surface suffers some limited deactivation.

1. Introduction

Water contamination by pharmaceuticals represents a rising environmental concern. Erythromicyn (ERY) (6-(4-dimethylamino-3-hydroxy-6-methyl-tetrahydropyran-2-yl)oxy-14-ethyl-7,12,13-trihydroxy-4-(5-hydroxy-4-methoxy-4,6-dimethyl-tetrahydropyran-2-yl)oxy-3,5,7,9,11,13-hexamethyl-1-oxacyclotetradecane-2,10-dione) is a glycosidic 14-membered ring macrolide (see Fig. 1), which is widely used as an antibacterial antibiotic [1]. ERY is constituted by several components, being erythromycin A the main one. This antibiotic has been found in concentrations ranging from ng/L to μg/L in effluents of sewage treatment plants, surface water and groundwater [2,3].

There have been few studies on the oxidative treatments of wastewater containing ERY and other pharmaceuticals reporting the use of ozonation alone [4–7], ozone in combination with H_2O_2 [5] or UV [7], UV in combination with H_2O_2 [7] and a combination of anodic oxidation by boron-doped diamond electrodes and ozonation [8]. The individual mineralization of ERY in water has already been investigated by photocatalysis using TiO_2 under

* Corresponding author. Tel.: +351 225 081 468; fax: +351 225 081 449.
E-mail addresses: agg@fe.up.pt (A.G. Gonçalves), jjmo@fe.up.pt (J.J.M. Órfão), fpereira@fe.up.pt (M.F.R. Pereira).

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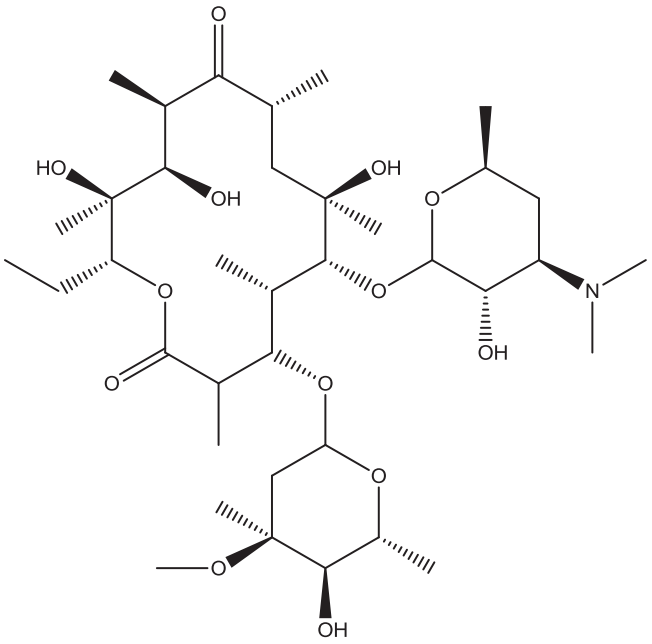

Fig. 1. Molecular structure of erythromycin.

UV-A irradiation [1]. However, to the best of our knowledge, no studies about the individual mineralization of ERY by single or catalytic ozonation have yet been reported in the literature.

Catalytic ozonation has emerged as a powerful technology for the treatment of pollutants in water, even for refractory compounds. Several studies have shown that activated carbon (AC) and multi-walled carbon nanotubes (MWCNT) are efficient ozonation catalysts [9–15]. However, there are few studies using carbon materials as ozonation catalysts of pharmaceutical pollutants. The simultaneous use of ozone and activated carbon to remove this type of compounds, such as diclofenac [16], sulfonamide antibiotics (including the sulfamethoxazole [17,18]), nitroimidazole antibiotics [19,20] and hormones [21] has been successfully investigated, but the application of MWCNT was only studied in removal of sulfamethoxazole [22] and bezafibrate [23].

Moreover, cerium oxide/activated carbon materials showed better results in the mineralization of several organic compounds by ozonation, in comparison to those obtained using activated carbon or cerium oxide. The development of novel synthesis techniques in order to obtain highly dispersed ceria nanoparticles on carbon materials has been promoted by the increasing number of application [27–31]. Several materials containing ceria highly dispersed on activated carbon, prepared by the impregnation method [27,28], were assessed in the catalytic ozonation of oxalic acid, and it was concluded that they are more effective in the mineralization of this compound than a ceria-activated carbon composite prepared by the precipitation method [26]. The ozonation of pharmaceutical compounds catalyzed by cerium oxide/carbon materials has only been reported in [32], where MWCNT and AC containing ceria were tested in the ozonation of the antibiotic sulfamethoxazole showing very promising results.

Thus, the present work aimed at the comparison between the performance of MWCNT and activated carbon as catalysts for the ozonation of ERY. Another goal of this work consisted in the assessment of a possible synergic effect between carbon materials and cerium oxide. The degree of mineralization of ERY solutions was obtained by total organic carbon (TOC) measurements, and the concentrations of the organic acids resultant from the antibiotic oxidation were followed by high performance liquid chromatography (HPLC). In addition, the acute toxicity of the treated solutions was evaluated by Microtox assays.

2. Experimental

2.1. Preparation and characterization of the materials

A commercial activated carbon, Norit GAC 1240 PLUS (sample AC), and commercial multi-walled carbon nanotubes, Nanocyl 3100 (sample MWCNT), were used in the catalytic ozonation of erythromycin. They were also used as supports to prepare carbon materials containing dispersed cerium oxide on the surface. According to the supplier, these MWCNT have an average diameter of 9.5 nm, an average length of 1.5 μm and a carbon purity higher than 95%. Activated carbon was used with 100–300 μm particle size. These samples were impregnated with 20 wt.% of CeO_2 using adequate solutions of $Ce(NO_3)_3{\cdot}6H_2O$ in water (CeO_2/MWCNT and CeO_2/AC samples). The preparation procedure was detailed in a previous work [32]. For comparative purposes, a cerium oxide sample was prepared by precipitation with NaOH using an aqueous solution of $Ce(NO_3)_3{\cdot}6H_2O$ (sample CeO_2) according to the procedure described by Orge et al. [25].

The prepared materials were characterized by N_2 adsorption–desorption at −196 °C, thermogravimetric analysis and, for samples containing ceria, they were also characterized by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD), as described elsewhere [32].

TEM micrographs were obtained using a LEO 906E microscope operating with an accelerating voltage of 120 kV.

2.2. Kinetic experiments

The ozonation experiments were carried out in a laboratory scale reactor (ca. 1 L) equipped with agitation and a circulation jacket. 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 leaving the reactor was removed in a series of gas washing bottles filled with potassium iodide (KI) solution. In each ozonation experiment the reactor was filled with 700 mL of an erythromycin solution with a concentration of 50 ppm. ERY was purchased from Sigma Aldrich and used as received. All solutions were prepared with ultrapure water with a resistivity of 18.2 mΩ cm at room temperature. In catalytic ozonation experiments, 100 mg of catalyst was introduced in the reactor. The experiments were performed at constant gas flow rate (150 $cm^3\ min^{-1}$) and constant inlet ozone concentration (50 $g\ m^{-3}$). The stirring rate was maintained constant at 200 rpm, in order to keep the reactor content perfectly mixed. For comparative purposes, both adsorption on carbon materials and single ozonation experiments were performed in the same system, under identical experimental conditions. All experiments were performed at room pressure and temperature. Samples for analysis were collected at selected times using a syringe and centrifuged. Some experiments were carried out in duplicate and the average relative deviations were lower than ±2%.

2.3. Analytical methods

The degree of mineralization of ERY solutions was obtained by Total Organic Carbon (TOC) analysis in a Shimadzu TOC-5000A analyser.

Concentrations of some organic acids resulting from the ERY degradation were followed by HPLC using a Hitachi Elite LaChrom HPLC equipped with a UV detector. An Alltech