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Ceria dispersed on carbon materials for the catalytic ozonation of sulfamethoxazole

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ABSTRACT

Two catalysts containing ceria dispersed on the surface of multi-walled carbon nanotubes and activated carbon were prepared and characterized by several techniques. They were investigated as ozonation catalysts for the mineralization of the antibiotic sulfamethoxazole (SMX). Both materials enhanced the mineralization of SMX relatively to single ozonation. A strong synergetic effect between carbon materials and ceria was observed, leading to higher mineralization degrees. In the catalytic ozonation with these materials both surface and bulk reactions occur. The efficiency of catalysts was mainly affected by the amount of Ce^{3+} species on the surface. The presence of carbon materials containing ceria led to a faster degradation of pyruvic and maleic acids. The original sulfur of SMX was almost completely converted to sulfate and part of nitrogen was converted to NH_4^+ and NO_3^-. Microtox tests revealed that simultaneous use of ozone and the prepared catalysts originated lower acute toxicity.

Introduction

Catalytic ozonation has emerged as a powerful technology for the treatment of pharmaceuticals in water, even for refractory compounds. Activated carbon (AC) by itself, as well as multi-walled carbon nanotubes (MWCNT), have been proven to be efficient ozonation catalysts [1–5]. However, in previous studies, activated carbon/cerium oxide composites in the ozonation of organic compounds showed better results in the mineralization of the mentioned compounds in comparison with single activated carbon or cerium oxide [6,7].

The development of novel synthesis techniques for highly dispersed ceria nanoparticles on carbon materials has been promoted by the increasing application. Namely, CeO_2/AC samples prepared by the impregnation method with cerium nitrate salt [8,9], CeO_2/CNT core–shell nanowires prepared under boiling reflux of ethylene glycol [10], CeO_2/CuO/CNT nanocomposites synthesized using CNTs as templates by a pyridinethermal method [11] and necklace-like CeO_2/CNT composites prepared by a simple solvothermal method [12]. Several materials containing ceria highly dispersed on the activated carbon 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 the ceria-activated carbon composite prepared by the precipitation method [13]. Thus, the present work aimed at the preparation of even more active catalysts by using dispersed cerium oxide on two carbon materials (AC and MWCNTs) and in the assessment of these materials as catalysts for ozonation of sulfamethoxazole (SMX) and to investigate a possible synergetic effect between carbon materials and cerium oxide. This antibiotic was selected because it is one of the most widely prescribed antibiotics. Moreover, a large number of animals are also treated by a combination of drugs containing SMX, not only to prevent and treat infections, but also to promote growth in food-producing animals [14–16]. After use, the substance is metabolized in the liver, and its unmetabolized form (about 15% of the administrated dose [17,18]) and active metabolites [15,16] are excreted with urine or faeces; then enters wastewater and is ultimately discharged into conventional wastewater treatment plants [19].

SMX is refractory to the conventional treatments employed in the sewage treatment plants, since low average removal efficiencies have been obtained [20]. Due to the antibacterial nature of this compound, it shows resistance to conventional biologic water treatment methods [21,22]. Adding these factors to its high use, SMX has been frequently detected in the environment in recent years [23], namely in wastewater and sewage treatment plant effluents [21,22,24] in concentrations of up to 1.9 $\mu g\,L^{-1}$ [25]. In many effluents of municipal sewage treatment plants in Spain, France, Greece, Italy, Sweden and Germany, the detected concentrations of SMX vary from 0.01 to 2 $\mu g\,L^{-1}$ [21,22,26]. This antibiotic has also been identified in natural water and in surface

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water at concentrations varying from 0.03 to 0.48 $\mu g L^{-1}$ [21], and even in drinking water in the low ng L^{-1} range [25]. Residues of SMX and other sulfonamide antibiotics have been reported in different aquaculture environments [27,28].

The abatement of SMX from water has been investigated using different advanced oxidation processes (AOPs), which produce hydroxyl radicals ($OH^{\bullet}$) and effectively either remove SMX or transform it into less toxic and/or more biodegradable intermediates. The treatment technologies that have been commonly used are the chemical oxidation with ferrate [29,30], ozonation [31–42], catalytic ozonation [35,43–46], photocatalytic ozonation [47], O_3/H_2O_2 [33,48], photo-Fenton [49,50], solar photo-Fenton [51–54], TiO_2 photocatalysis [35,47,55–57], UV photolysis [58–60] and UV/H_2O_2 [18,61].

The SMX removal by ozonation in the presence of AC and MWCNTs [43,62] has been reported in the literature, but some of SMX degradation by-products are persistent to ozonation, leading to a slow TOC removal in the system. The use of carbon materials containing ceria as catalysts may enhance the removal of these by-products. In the present work, the concentration of the oxidation compounds identified was monitored and the acute toxicity of the treated solutions evaluated by Microtox assays.

Experimental

Preparation and characterization of the materials

In order to prepare carbon materials containing dispersed cerium oxide on the surface, a commercial AC, Norit GAC 1240 PLUS, and commercial MWCNTs, Nanocyl 3100, were used as initial supports. According to the supplier, these MWCNTs have an average diameter of 9.5 nm, an average length of 1.5 μm and a carbon purity higher than 95%. AC was used with 100–300 μm particle size. These samples were impregnated by the incipient wetness method using an adequate amount of an aqueous solution of 66.6 g L^{-1} $(NO_3)_3{\cdot}6H_2O$ in order to obtain 20 wt.% of ceria in the prepared catalysts (CeO_2/MWCNT and CeO_2/AC samples (CeO_2/MWCNT and CeO_2/AC samples). They were then dried at 110 °C overnight. The catalysts of dispersed ceria oxides on carbon materials were achieved by decomposition the dried ceria/carbon materials under nitrogen flow (100 $cm^3 min^{-1}$) at 400 °C for 4 h, with a heating rate of 5 °C min^{-1}. For comparative purposes, a cerium oxide sample was prepared by precipitation with NaOH using an aqueous solution of $Ce(NO_3)_3{\cdot}6H_2O$ (CeO_2 sample), according to the procedure described by Orge et al. [7].

The resulting materials were characterized by several techniques. The textural properties of the prepared materials were determined by N_2 adsorption–desorption isotherms, determined at −196 °C on a Quantachrome NOVA 4200e apparatus. BET surface areas (S_{BET}), mesoporous surface areas ($S_{\neq \mu pores}$) and micropore volumes ($V_{\mu pores}$) of the samples were calculated. Before measurements, the samples were dried at 110 °C for 12 h and out-gassed at 120 °C under vacuum. The micropore volume and the mesopores surface area were calculated by the *t*-method. The relative amount of metal oxide in the composite was determined by thermogravimetric analysis under air in a STA 409 PC/4/H Luxx Netzsch thermal analyser. XPS was performed with a VG Scientific ESCALAB 200A spectrometer. XPS data corresponding to Ce 3d spectra were fitted using the software *XPS peak*. To minimize the number of degrees of freedom of the curve fitting procedure, constraints on the binding energy (BE), full width at half maximum (FWHM) and peak areas were applied to each doublet pair. XRD spectra were recorded on a Philips X'Pert MPD diffractometer (CuKα = 0.15406 nm).

Catalytic tests

The experiments of SMX ozonation were carried out in a laboratory scale reactor (ca. 1 L) described in a previous work [2]. In each ozonation experiment the reactor was filled with 700 mL of SMX solution with a concentration of 50 mg L^{-1}, at the natural pH (around 4.8). Then, 100 mg of catalyst was introduced in the reactor. The experiments were performed at constant 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. The solution was prepared from ultrapure water obtained in a Milli-Q Millipore system. For comparative purposes, both adsorption on catalysts and ozonation experiments in the presence of *tert*-butanol were performed in the same system, under identical experimental conditions. In the experiments carried out in the presence of *tert*-butanol, a concentration of 2 mM of this radical scavenger was used (concentration ten times higher than the initial SMX concentration) [63]. All experiments were performed at room pressure and temperature. Samples were collected at selected times using a syringe and were centrifuged before analysis. Most of the experiments were carried out in triplicate and the average relative deviations were lower than ±2%.

Analytical methods

Concentrations of SMX and reaction products were followed using a Hitachi Elite LaChrom HPLC equipped with a diode array detector. For SMX, 3-amino-5-methylisoxazole (AMI) and *p*-benzoquinone (BZQ) the stationary phase used was a LiChroCART Purospher STAR RP-18 (250 mm × 4.6 mm, 5 μm) working at room temperature. Oxamic, pyruvic and maleic acids resulting from the SMX degradation were analyzed using a BIO-RAD Aminex HPX 87H column (300 mm × 7.8 mm) working at room temperature. Oxalic acid was quantified using as stationary phase an Alltech OA-1000 column (300 mm × 6.5 mm) working at room temperature. Calibration curves and HPLC conditions are detailed elsewhere [62].

The concentration of the inorganic ions released during ozonation experiments was obtained by ion chromatography. The anions (nitrite, nitrate and sulfate) were identified and quantified in a Dionex ICS-2100 Ion Chromatography System using a Dionex IonPac AS11-HC column (250 mm × 4 mm). For the determination of ammonium, an IonPac CS12A column (250 mm × 4 mm) was used in a Dionex DX-120 Ion Chromatography System.

The degree of mineralization of SMX solutions was obtained by total organic carbon (TOC) measurements in a Shimadzu TOC-5000A analyzer.

Microtox acute toxicity tests were performed by the Microtox basic test (Azure Environmental, USA), using the marine bacteria *Vibrio fischeri* to determine the influence of toxic substances on pure bacteria, according to the procedure described in the standard ISO/DIS 11348-3 [64] and as described elsewhere [62]. Thus, the pH of samples was adjusted to 7.0 ± 0.2 by adding either hydrochloric acid or sodium hydroxide solutions.

Results and discussion

Catalysts characterization

The characterization results are compiled in Table 1. CeO_2/AC presents a higher BET surface area and microporisity than CeO_2/MWCNT. Comparing with the values of BET surface area reported in the literature for these carbon materials [2] (S_{BET} = 809 and 331 $m^2 g^{-1}$, respectively), it is verified that the deposition of CeO_2