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Non-catalytic and catalytic wet air oxidation of pharmaceuticals in ultra-pure and natural waters

F. Javier Benitez^{a,*}, Juan García^b, Juan L. Acero^a, Francisco J. Real^a, Gloria Roldan^a

^a Universidad de Extremadura, Departamento de Ingeniería Química, Avda. de Elvas s/n, 06071 Badajoz, Spain

^b Universidad Complutense de Madrid, Departamento de Ingeniería Química, Avda. Complutense s/n, 28040 Madrid, Spain

A B S T R A C T

A wet air oxidation (WAO) process was applied to four selected pharmaceuticals (metoprolol, naproxen, amoxicillin, and phenacetin) individually dissolved in ultra-pure water, varying the temperature and oxygen pressure. Due to the moderate (amoxicillin) or low (metoprolol, naproxen, and phenacetin) efficiency found in the oxidation of these pollutants, a catalytic wet air oxidation (CWAO) process was then tested using a platinum catalyst supported on multi-walled carbon nanotubes (CNT). In this CWAO process, the pharmaceuticals were dissolved together in ultra-pure water and in four natural water matrices—a reservoir water, a groundwater, and two waters from different municipal wastewater treatment plants. On the basis of the measurements of their removals, a discussion is given of the influence of the main operating variables: the presence or absence of catalyst, type of catalyst (the synthesized Pt/CNT or a commercial Pt/AC), catalyst dosage (0.005–0.050 g), temperature (120–140 °C), and oxygen pressure (20–40 bar). In most experiments, the removals were in the sequence: amoxicillin > naproxen > phenacetin. In addition, total organic carbon (TOC) removal measurements were made of some of the natural waters tested.

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1. Introduction

The extensive use of pharmaceutical chemicals in humans and animals has led to the identification of various amounts of these products in natural water systems worldwide (Halling-Sorensen et al., 1988; Kolpin et al., 2002; Batt et al., 2006). Thus, Kolpin et al. (2002) found 22 antibiotics in their survey of 139 rivers and streams in the US, and Lin et al. (2008), investigated eleven antibiotics in three rivers in Taiwan, finding a consistent presence of erythromycin and sulfamethoxazole. The effluents from municipal wastewater treatment plants (WWTPs) have also been identified as a major source of micropollutants, including hormones and personal care products as well as pharmaceuticals, and these substances have been detected in surface and groundwater drinking water sources, thus constituting a potential risk for human health (Ternes and Joss, 2006).

Traditionally, chemical oxidants, such as chlorine, chlorine dioxide, ozone, and hydroxyl radicals, have been used

to disinfect drinking waters and wastewaters by transforming or eliminating undesired micropollutants in general, and pharmaceutical compounds in particular (Esplugas et al., 2007; Deborde and von Gunten, 2008). Such oxidation treatments now also include ferrate (Sarmah et al., 2006), titanium dioxide as photocatalyst (Abellan et al., 2007), UV photolysis (Pereira et al., 2007), etc. Numerous studies have found ozonation in particular to be very effective for such elimination, with over 90% degradation being attained for a wide variety of compounds (Huber et al., 2005; Nakada et al., 2007).

However, pharmaceutical micropollutants can vary greatly chemically, with the differences in size, structure, polarity, solubility, and other electronic properties influencing their susceptibility to any specific treatment. Given the potential risks of their presence in aquatic systems, it is therefore recommendable to test different techniques for their elimination in addition to the use of classic oxidants. One such technique, wet air oxidation (WAO), has shown itself to be very effective in treating a wide variety of refractory organic pollutants in

* Corresponding author. Tel.: +34 924289384.

E-mail address: javben@unex.es (F.J. Benitez).

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waters (Luck, 1999), but the high pressure and temperature it requires limit its application in practice. Catalytic wet air oxidation (CWAO) has been proposed as a form of reducing these extreme WAO operating conditions, and has been described as a promising technique for the removal of toxic and non-biodegradable organic compounds from waters (Levec and Pintar, 2007). In the three-phase CWAO process at its usual temperatures of 120–250 °C and pressures of 10–50 bar, organic pollutants are oxidized by activated O₂ species in the presence of a solid catalyst, forming biodegradable intermediates (such as low molecular weight carboxylic acids), or are mineralized into CO₂, water, and associated inorganic salts. Several recently developed heterogeneous catalysts, including transition metal oxides and noble metals deposited onto different supports, have shown good catalytic activity in the CWAO of organic pollutants present in drinking waters and wastewaters (Gomes et al., 2002; Levec and Pintar, 2007; Liu et al., 2010).

Among the noble metal catalysts used, supported-platinum catalysts would seem to be particularly interesting because they are highly effective in the oxidation of organic compounds (Garcia et al., 2005; Mikulová et al., 2007). Nonetheless, there is as yet no data available on the specific application of such catalysts in CWAO processes for the oxidation of pharmaceuticals in water matrices. Given this context, an extensive study was designed to investigate the capacity of different oxidation treatments to remove some frequently occurring pharmaceuticals from waters. Four representative compounds were selected as test pollutants: the beta-blocker metoprolol, the non-steroidal anti-inflammatory (NSAID) naproxen, the antibiotic amoxicillin, and the analgesic phenacetin. In earlier studies, these pollutants were oxidized by monochromatic UV radiation and Fenton's reagent (Benitez et al., 2009a), by ozone and hydroxyl radicals (Benitez et al., 2009b), and by chlorine (Acero et al., 2010).

The objective of the present study was to investigate the performance of the WAO and CWAO processes in removing the aforementioned pharmaceuticals in a batch stirred-tank microreactor, by dissolving them in ultra-pure water and in different natural waters. A catalyst consisting of Pt supported on multi-walled carbon nanotubes (Pt/CNT) was custom synthesized and characterized. How the operating conditions (catalyst dosage, temperature, oxygen pressure, and nature of the catalyst whether commercial or custom synthesized) affected the removals was studied, and the reductions of the TOC in some of the natural water matrices were also evaluated.

2. Materials and methods

2.1. Catalysts

The first of the two catalysts tested was a commercial catalyst supplied by Sigma-Aldrich which consisted of Pt 1 wt% supported on activated carbon (Pt/AC). The second was Pt supported on multi-walled carbon nanotubes (MWNT) synthesized for the present work, following the procedure described by Ovejero et al. (2006). Basically, the synthesis protocol started with the raw carbon nanotubes (CNTs; supplied by Sun Nanotech Co. Ltd., Beijing, Republic of China) prepared by chemical vapour deposition of carbon atoms from ethylene, and using iron supported on alumina as catalyst. The surface chemistry of the CNTs was then modified by introducing carboxylic acid groups (–COOH) via an acidic treatment consisting of an aque-

ous solution of HNO₃ refluxed for 6 h at 130 °C. The catalyst was finally prepared by incipient wetness impregnation of the CNT support with a platinum metal precursor. The precursor mass was calculated so as to provide 1 wt% metal in the catalyst. The metal precursor was subsequently reduced to its ground state by drying the wet solid overnight at 110 °C, and then activated under a N₂/H₂ (3:1) flow at 350 °C for 3 h in a furnace.

2.2. Catalyst characterization

Several techniques were applied to characterize the catalyst (the results will be described in Section 3.1): the metal loading was determined by X-ray fluorescence (XRF); transmission electron microscopy (TEM) analyses were made using a JEOL JEM 2010 electron microscope; X-Ray diffraction (XRD) patterns were recorded on a Siemens D-501 diffractometer; the N₂ adsorption–desorption at 77 K (BET) was determined using a Micromeritics ASAP 2010 apparatus; and an EXTAR 6000 Seiko thermal analyzer was used for the thermogravimetric analysis (TGA).

2.3. Pharmaceuticals and water systems

As mentioned above, the pharmaceuticals selected were metoprolol, naproxen, amoxicillin, and phenacetin. They were purchased from Sigma-Aldrich, and were of the highest purity available (99%). In a first group of experiments, they were dissolved (individually and in mixtures) in ultra-pure water produced from a MilliQ (Millipore) water purification system. In a second group of experiments, they were dissolved together in four different natural waters in an attempt to approach oxidation under realistic water treatment conditions. These waters were: a groundwater (PZ), a surface water from the public municipal water supply reservoir “Peña del Aguila” (PA), and two secondary effluents from municipal wastewater treatment plants, one in the medium-sized city of Badajoz (BA) and the other in the small town of La Albuera (LA) (both in the Extremadura Community, south-west Spain).

2.4. Experimental procedures

All the experiments (with and without catalysts) were done in a Hastelloy high-pressure 100 mL reactor, equipped with an electrically heated jacket to control the temperature, and a variable speed magnetic stirrer drive. Inlets are located at the top of the reactor for the gas and cooling water feeds, together with a pressure gauge and a rupture disk. A thermocouple and the liquid sample extraction device were immersed in the reaction mixture.

Similar procedures were followed for all the experiments. A first group of experiments was with the pharmaceuticals dissolved in ultra-pure water (each compound individually, or in mixtures), and a second group with them dissolved together in the selected water systems. For the latter group of experiments, each water was previously filtered through a 0.45 μm cellulose nitrate filter within 24 h after collection and then stored at 4 °C until use.

At the beginning of each experiment, the reactor was loaded with 100 mL of the solution (plus the catalyst in the CWAO experiments), and the system was pressurized with nitrogen to ensure an inert atmosphere and heated to the desired temperature. Commercial oxygen (99.999% purity, supplied by Linde Co., Spain) was then fed to the reactor and

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