WATER RESEARCH 42 (2008) 585–594

Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Photocatalytic degradation of non-steroidal anti-inflammatory drugs with TiO_2 and simulated solar irradiation

*Fabiola Méndez-Arriaga**, *Santiago Esplugas*, *Jaime Giménez*

Chemical Engineering Department, University of Barcelona, Martí i Franquès 1, 08028 Barcelona, Spain

ARTICLE INFO

Article history:
Received 4 January 2007
Received in revised form
29 June 2007
Accepted 1 August 2007
Available online 6 August 2007

Keywords:
Diclofenac
Ibuprofen
Naproxen
NSAID
Photocatalysis
Solar
TiO_2

ABSTRACT

The aim of this work is to evaluate and compare the degradation achieved for three non-steroidal anti-inflammatory drugs (NSAIDs) by heterogeneous TiO_2 photocatalytic means in aqueous solution at laboratory scale. The selected pharmaceutical compounds were diclofenac (DCF), naproxen (NPX) and ibuprofen (IBP). These compounds were used in their sodium salt chemical form.

Previous experiments (adsorption, photolysis and thermodegradation) were developed to evaluate non-catalytic degradation for each NSAID. Photocatalytic experiments were carried out in a Xe-lamp reactor in order to study the influences of different operational conditions (catalyst load, temperature and dissolved oxygen concentration). These results showed that the optimum amount of TiO_2, to achieve maximum degradation, of IBP was 1 g/L. In contrast, the maximum degradation for DCF or NPX was observed at a TiO_2 loading of 0.1 g/L. Temperature had a significant effect only for NPX degradation, achieving almost 99% phototransformation. No significant differences were observed for DCF and IBP at 20, 30 and 40 °C. Dissolved oxygen concentration was an important parameter to increase the degradation for NPX and IBP. However, it was observed that its rate of mineralization did not increase. Intermediate metabolites were detected in all cases. Hydroxyl metabolites were the most important residual compounds after the photocatalytic treatment of IBP. The inhibition percentage of bioluminescence from *Vibro fischeri*—as a toxicity parameter—increased during the irradiation time due to the residual concentration of the hydroxyl metabolites generated. However, after 120 min, in experiments with 40 mg/L of dissolved oxygen, a decrease of the % inhibition was observed. Only photocatalytic treatment of IBP drives to a satisfactory biodegradability index BOD_5/COD (between 0.16 and 0.42) and, only in this case, a post-biological treatment could be suggested.

1. Introduction

Recent studies have demonstrated the presence of pharmaceutical compounds in rivers, lakes and superficial freshwater (Halling-Sorensen et al., 1998; Ternes, 1998; Daughton and Ternes, 1999; Carballa et al., 2004). Non-steroidal anti-inflammatory drugs (NSAIDs) are a special group of pharmaceuticals that are often found as a persistent toxic waste and are one of the most widely available drugs in the world. In Spain, 55% of the consumed Top 200 drugs are ingested orally, and approximately 5% of them correspond to NSAIDs (Takagi et al., 2006). Some important examples of this family of medicines are ibuprofen, naproxen, diclofenac and ketoprofen, although there are more than 50 different types available commercially.

**Corresponding author.* Tel.: +34 93 402 1293; fax: +34 93 402 1291.
E-mail addresses: fmendeza@ub.edu (F. Méndez-Arriaga), gimenez@angel.qui.ub.es (J. Giménez).

0043-1354/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.watres.2007.08.002

In the environment, NSAIDs have been detected in hospital wastewaters (Kummerer, 2001), in and out STP (sewage treatment plant) effluents (Carballa et al., 2004), in surface water such as rivers and lakes (Boyd et al., 2003), in marine waters (Weigel et al., 2004) as well as in soil matrices (Scheytt et al., 2006).

The detection levels rarely exceed the μg/L levels (Stumpf et al., 1998; Ternes, 1998; Tixier et al., 2003); however, their presence at low or high concentrations could bring about harmful toxicological consequences (Fent et al., 2006; Prakash Reddy et al., 2006).

Frequently, NSAIDs are prescribed for skeletal–muscle pain and inflammatory rheumatic disorders; however, they also present analgesic and antipyretic effects. The main common characteristic in the NSAID group is the carboxylic aryl acid moiety that provides their acidic properties.

Investigations on physical and chemical remediation technologies had recently reported the removal of some NSAIDs. Filtration, adsorption, coagulation–flocculation and flotation (Carballa et al., 2005) are some examples. On the other hand, advanced oxidation processes (AOPs) appear to be an alternative for the degradation of hazardous pollutants (Bauer et al., 1999) and are usually clean technologies with an economic advantage when AOPs are used with a natural light source (Malato et al., 2001). AOPs are a potential alternative for the degradation of NSAIDs by non-selective hydroxyl radical attack on organic molecules and, sometimes, complete mineralization is achieved (Ravina et al., 2002). Actually, AOPs have been employed to remove NSAIDs. Special development did show the ozonation process (Huber, 2003; Ternes, 2003; Zweiner, 2000) and recently the photo-Fenton solar process (Pérez-Estrada et al., 2005a, b).

Studies with TiO_2 heterogeneous catalysts have also been reported. Oxidation of organic compounds by means of TiO_2 was achieved by hydroxyl radical generation through the e^-/h^+ pair generated when the semiconductor is exposed to UV radiation. In a recent study, Calza et al. (2006) present an exhaustive study on the heterogeneous photocatalytic degradation of DCF over TiO_2 aqueous suspension at low DCF concentrations (0.07–9.24 ppm).

In our study, relatively high initial concentrations of NSAID were tested to obtain the most plausible amount of photoproducts and their subsequent characterization in order to measure the final toxicity and biodegradability achieved. The aim of this research is to describe the capability of TiO_2 to remove pollutants in aqueous solutions with high NSAID concentrations, as well as to compare the degradation degree of three separate NSAIDs, at different operation conditions in a tubular laboratory reactor with a solar-simulated light source.

2. Experimental section

2.1. Materials

Synthetic amorphous titanium dioxide (Degussa P-25) was used as received. The NSAIDs DCF (2-[2-[(2,6-dichlorophenyl)amino]phenyl]acetic acid), NPX ((S)-6 methoxy-α-methyl 2 naphthaleneacetic acid)) and IBP (2-[3-(2-methylpropyl)phenyl]propanoic acid), all of them in their sodium salt form, were purchased from Sigma-Aldrich and used without pretreatment (Fig. 1).

2.2. Analytical procedures

NSAID concentrations were monitored after sample filtration (Durapore PVDF Millipore 0.22 μm) in a high-performance liquid chromatograph (HPLC) from Waters using a C18 RP Trace Extrasil OD52-5 Micromet 25 × 0.46 Teknockroma column, and a Waters 996 photodiode array detector using the Empower Pro software 2002 Water Co. Conditions of each HPLC analysis are shown in Table 1.

Total organic carbon (TOC) was measured in a Shimadzu TOC-V CNS instrument. Spectrophotometric measurements to obtain the absorption spectrum were carried out in a Perkin-Elmer UV/VIS Lambda 20 (220–700 nm range) spectrophotometer. BOD_5 determinations were carried out according to the Standard Methods (5120) by a respirometric single measuring system and OxiTop procedure. COD determination was carried out according to Norm. France NFT 90–101. Multi-temperature measurements (Crison 621) and pH (Crison GLP 22) were monitored online. Air and pure oxygen sparged through the system were purchased at Air Liquide, both were used to vary the dissolved oxygen concentration. Dissolved oxygen concentration was measured online by Crison Oxi 330i WTW Oxi Cal-SL sensor. Microtox tests were employed to obtain the inhibition of bioluminescence of *Vibrio fischeri* at 15 min of incubation time. Millipore water quality (18 MΩ) was used during all experiments. For the identification of by-products, the final sample mixture was analyzed by electrospray ionization/mass spectrometry using a PerSeptive, TOF Mariner Jasco AS-2050 plus IS mass spectrometer.

2.3. Photoreactor

A stirred tank (1.5 L) was filled with the NSAID–TiO_2 solution. The aqueous suspension was continuously pumped (Heidolph Pumpdrive 5130 120–300 rpm) to the Solarbox (Co.fo.me.gra 220 V 50 Hz) and recirculated to the batch tank. In the Solarbox, the Duran tubular photoreactor (0.078 L) was irradiated by the Xe-OP lamp (Phillips 1 kW) with a photon flux equal to 6.9 μEinstein/s (290–400 nm). The jacket temperature of the stirred tank was controlled with an ultrathermostat bath (Selecta; Frigiterm-10). All connections and pipes employed were made of Teflon and/or glass material to avoid losses by adsorption. The different types of equipment and instruments employed in our installation are depicted in Fig. 2.

3. Results and discussion

3.1. Previous experiments: photolysis, thermodegradation and adsorption

To avoid confusion between photocatalytic and other degradation phenomena, it was necessary to evaluate the non-photocatalytic influence of photolysis, thermodegradation and adsorption of each NSAID onto the TiO_2 catalyst.