Journal of Environmental Management 137 (2014) 197–203

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Degradation of drugs in water with advanced oxidation processes and ozone

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ARTICLE INFO

Article history:
Received 5 September 2013
Received in revised form
30 January 2014
Accepted 10 February 2014
Available online 28 March 2014

Keywords:
Drugs
Ozone
Toxicity
Mineralization
AOP

ABSTRACT

The aim of this paper is to assess the degradation of a mixture of ibuprofen and clofibric acid and to study the mineralization and toxicity following ozone treatment. To this end, a comparison is presented of the experimental results obtained from ozone treatment using atmospheric air as the feed gas (Experiment I, $[O_3] = 15$ gN/m^3), with and without addition of H_2O_2, and those obtained under the same conditions but using concentrated oxygen as the feed gas, obtained by pressure swing adsorption technology (Experiment II, $[O_3] = 200$ gN/m^3). All tests were conducted using a pilot scale reactor.

Under (Experiment II) conditions, degradation exceeded 99% and up to 60% mineralization was achieved for initial compound concentrations, and hydraulic retention time was reduced by 75% compared to (Experiment I).

The results of toxicity tests show through increasing the production of ozone gas in (Experiment II), toxicity was eliminated at initial study concentrations of $\leq$1 mg/l for all treatment times studied.

1. Introduction

Concern has grown in recent years among those responsible for the water supply due to increasing research evidence of the presence of pharmaceutical products in natural aquatic systems (Ternes et al., 1998, Ternes, 1998, 2001; Daughton and Ternes, 1999; Heberer, 2002; Kolpin et al., 2002; Kümmerer, 2010). Among the substances detected in surface waters, large quantities of medicinal drugs have been reported (Ternes, 1998; Cleuvers, 2004), which are administered to living organisms via different routes (oral, inhalation, skin, injections, etc.). Following administration of the drug, the molecules are adsorbed, distributed and metabolised by the recipient organisms and eventually excreted.

Excretion, uncontrolled drug disposal, discarding excess medicines in households and veterinary applications (Daughton and Ternes, 1999) constitute the main pathways by which pharmaceuticals and other recalcitrant compounds reach wastewater treatment plants. Studies carried out on the capacity of these facilities to remove such compounds have reported that present technologies do not eliminate sufficient quantities (Ternes, 1998; Mohle et al., 1999). As a consequence, these compounds enter the surface water, which is then used for obtaining drinking water. Since drinking water treatment plants are also unable to remove these products, very low concentrations are beginning to be detected in drinking water (Heberer and Stan, 1996), which could lead to public health risks in the future.

Ibuprofen (IBP) and clofibric acid (CLF) (Hignite and Azarnoff, 1977; Heberer and Stan, 1996; Tixier et al., 2003; Cleuvers, 2004) are among the compounds most commonly detected in natural waters. Ibuprofen, or 2-(4-isobutyl phenyl) propionic acid (IBP), is the leading nonsteroidal anti-inflammatory drug (NSAID) derived from propionic acid and is sold in most countries. It is widely used throughout the world (Zwiener and Frimmel, 2000), and numerous studies have reported surface water concentrations ranging from 0.05 to 0.28 mg/l (Daughton and Ternes, 1999). A metabolite of clofibrate, clofibric acid (CLF) is mainly used to reduce the levels of triglyceride-rich lipoproteins and to raise HDL-cholesterol levels slightly. There is a high social demand for this compound and it is frequently present in the environment (Zwiener and Frimmel, 2000), having been detected at concentrations of 0.049–0.066 mg/l in surface water (Ternes, 1998; Tixier et al., 2003) and at maximum concentrations of 270 ng/l in drinking water.

Some organic pollutants can be degraded by advanced oxidation processes (AOP). These methods are now considered an alternative

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http://dx.doi.org/10.1016/j.jenvman.2014.02.011
0301-4797/

to conventional treatments for the removal of organic contaminants. The use of ozone to remove pollutants present in water began to be developed in the late 1970s, and over time it has proved to be an efficient technique for the removal of emerging contaminants, including pharmaceuticals (Zwiener and Frimmel, 2000; Ternes et al., 2002, 2003; Huber et al., 2005; Westerhoff et al., 2005; Hua et al., 2006), so ozone is an efficient oxidant of pharmaceutical compounds (Rivas et al., 2003).

The aim of this study was to assess the degradation of a mixture of ibuprofen and clofibric acid using a conventional ozone generator and to compare these results with those obtained using an oxygen concentrator and one of the most widely used oxidation processes, the combination of ozone with hydrogen peroxide (O_3/H_2O_2).

A further objective was to assess the degradation and mineralization of the IBP and CLF mixture and the toxicity of the intermediate compounds generated during the treatment processes. The ultimate goal is to apply this knowledge in order to improve waters treatment processes.

2. Materials and methods

2.1. Reagents

Ibuprofen and clofibric acid, in solid state, were provided by Sigma Life Science (Madrid, Spain) with a purity in excess of 97%. Fig. 1 shows the chemical structure of both compounds. Super-pure hydrogen peroxide (H_2O_2) and the other analytical or HPLC grade reagents and solvents used were supplied by Merck (Madrid, Spain).

2.2. Oxidation treatment

Tests were performed using a pilot scale plant (Fig. 2) constructed with inert materials resistant to the action of ozone.

The ozone generator used had two different air treatment units, one supplied by dry atmospheric air (Experiment I) and the other supplied by concentrated oxygen obtained using pressure swing adsorption technology (PSA) (Experiment II). The supply of oxygen yields higher ozone concentrations. Ozone was generated by high frequency corona discharge. The characteristics of the equipment and supply units are shown in Table 1.

An Ebara Fesx M6 centrifugal pump (Fig. 2, VII) ($Q = 5–45$ l/min, $H = 31.5–13.5$ m and V- 230–240) was used to pump water from an external 25 L capacity tank into the reactor (Fig. 2, XIV), where it was mixed with the drugs and then circulated continuously through a closed circuit in the plant. The ozone was mixed with the water-drug solution using a venturi device (Fig. 2, X) and then passed through a micro-bubble generator (Fig. 2, XI), a mixing chamber (Fig. 2, XII) to ensure contact between the compounds, and the ozone reactor (Fig. 2, XIII) which consisted of a 2 m high contact column and a usable volume of 50 L, which was where the oxidation process occurred. The plant also had a visual mechanical rotameter (Fig. 2, VIII) supplied by Korus (Cadiz, Spain) to measure the flow of water entering the mixing chamber and a Mini-Hicon Ozone Analyzer (Fig. 2, VI) to continuously monitor ozone generator output, supplied by Hicon (Alaska, USA).

Construction of the entire facility was carried out by Zonosistem, Ingeniería del Ozono S.L. (Cadiz, Spain).

2.3. Tests

Two types of experiment were conducted. In Experiment I tests, the mixture of both drugs was subjected to ozone oxidation using atmospheric air as the ozone generator feed gas. These tests were conducted without and with addition of H_2O_2 and were denominated I_A and I_B, respectively. In Experiment II tests, the mixture was subjected to oxidation treatment using concentrated oxygen as the ozone generator feed gas. The experiments were performed using 20 L of MilliQ type water (Zwiener and Frimmel, 2000; Quero-Pastor et al. 2014). A working pH of 9 was obtained using a solution of sulphuric acid and sodium hydroxide, and sodium chloride was used to adjust conductivity. Stock solutions of both compounds were prepared and added to the aqueous solution in the ratio required to achieve concentrations of 0.1, 1.0 and 10 mg/l for the tests. The stock solutions consisted of 100 g/l of IBP in methanol and 40 mg/l of clofibric acid in water. Table 1 shows the characteristics of the experiments carried out in this study.

In all experiments, the IBP was poured into the aqueous solution from the top of the reactor (Fig. 2, XIII) while the CLF was pumped in from the bottom (Fig. 2, X).

The IBP was added first, and after stirring for 20 min at 2800 rpm, the CLF was added and the solution was stirred for a further 5 min. The mixing protocol for obtaining a homogenous solution had been established previously in earlier tests on the individual compounds. Once the mixtures were homogenized, ozone treatment commenced and a constant dose, depending on the experiment, was injected in order to maintain a sufficient minimum concentration in the medium (Table 1). In tests using hydrogen peroxide, this was added from the top of the reactor (Fig. 2, XIII) at the beginning of the experiment. All tests ran continuously in a closed circuit at 25 ± 2 °C.

2.4. Test variables

Conductivity, pH and hydraulic retention time (HRT) values are given in Table 2 and were established following the same criteria for both compounds (Quero-Pastor et al., 2014). Lastly, the pH value was selected in accordance with the literature (Hoigne, 1998;

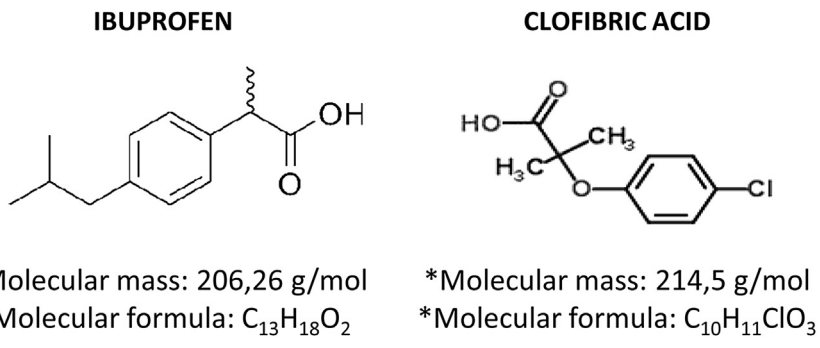

Fig. 1. Chemical structure of the compounds.