Chemosphere 113 (2014) 71–78

Contents lists available at ScienceDirect

Chemosphere

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

Solar photocatalytic ozonation of a mixture of pharmaceutical compounds in water

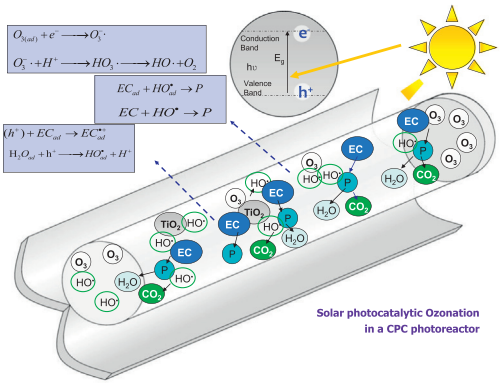
Gracia Márquez, Eva M. Rodríguez, Fernando J. Beltrán, Pedro M. Álvarez *

Departamento de Ingeniería Química y Química Física, Universidad de Extremadura, 06006 Badajoz, Spain

HIGHLIGHTS

- Ozone and solar radiation systems are compared to remove pharmaceuticals from water.
- Ozone systems led to 95% removal of ECs in less than 30 min.
- O_3/TiO_2/Solar radiation showed the lowest ozone consumption and the highest TOC removal rate.
- The organic matrix of water significantly affected pharmaceutical oxidation rates.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 July 2013
Received in revised form 20 March 2014
Accepted 24 March 2014
Available online 14 May 2014

Handling Editor: Hyunook Kim

Keywords:
Ozonation
Solar photocatalytic ozonation
Pharmaceuticals
Water treatment

ABSTRACT

Aqueous solutions of mixtures of four pharmaceutical compounds (atenolol, hydrochlorothiazide, ofloxacin and trimethoprim) both in Milli-Q ultrapure water and in a secondary effluent from a municipal wastewater treatment plant have been treated at pH 7 by different oxidation methods, such as conventional ozonation, photolytic ozonation, TiO_2 catalytic ozonation, TiO_2 photocatalytic oxidation and TiO_2 photocatalytic ozonation. Experiments were carried out using a solar compound parabolic concentrator. The performance results have been compared in terms of removal of emerging contaminants (ECs), generation rate of phenolic intermediates, organic matter mineralization, ecotoxicity removal and enhancement of biodegradability. Also, the consumption of ozone to achieve certain treatment goals (95% removal of ECs and 40% mineralization) is discussed. Results reveal that solar photocatalytic ozonation is a promising oxidation method as it led to the best results in terms of EC mineralization (~85%), toxicity removal (~90%) and efficient use of ozone (~2 mg O_3 mg EC^{-1} to achieve complete EC removal and ~18 mg O_3 mg TOC^{-1} to achieve 40% EC mineralization, respectively).

1. Introduction

There is a growing body of evidence of the occurrence of emerging contaminants (ECs) in effluents from municipal wastewater treatment plants (MWWTPs) and other water bodies, which have raised significant concerns about the impact of these substances on the environment (Stuart et al., 2011). ECs are substances such as drugs, personal care products or pharmaceuticals that are introduced continuously into the water environment. In general, they are hardly biodegradable and suspected of causing adverse effects on human health and safety of ecosystems.

* Corresponding author. Tel.: +34 924289387; fax: +34 924289385.
E-mail addresses: graciamm@unex.es (G. Márquez), evarguez@unex.es (E.M. Rodríguez), fbeltran@unex.es (F.J. Beltrán), pmalvare@unex.es (P.M. Álvarez).

http://dx.doi.org/10.1016/j.chemosphere.2014.03.093
0045-6535/

In recent years, many studies have dealt with the removal of ECs from water by advanced oxidation processes (AOPs). Particularly, TiO_2 photocatalytic oxidation under sunlight has attracted great interest as a method capable to transform many ECs into other less toxic compounds (Malato, 2008). Despite the great potential of the solar TiO_2 photocatalytic oxidation process, some drawbacks have limited its practical use. Among these limitations is the long hydraulic detention time needed to achieve complete EC removal. A novel process, which combines ozone and solar TiO_2 photocatalysis, can overcome this difficulty as it may significantly increase the overall degradation rate of ECs (Rodríguez et al., 2013). Ozone is a powerful oxidizing agent, which can react with organic compounds in water through direct reactions and indirect reactions involving reactive free radicals generated from the decomposition of ozone in water (Staehelin and Hoigné, 1985). Several studies have shown that direct reactions of ozone are very efficient to remove many ECs, transforming them into less complex organic compounds (Huber et al., 2005). If combined with radiation and/or a proper catalyst, the decomposition of ozone into oxidizing free radicals (mainly hydroxyl radical) is promoted. Hydroxyl radicals are able to react with organic compounds, including ozonation by-products, to transform them to CO_2 and H_2O. Therefore, the combination of ozone, TiO_2 and solar radiation constitutes an AOP, called solar photocatalytic ozonation, which deserves further investigation. Although a few studies of the application of TiO_2 photocatalytic ozonation to remove organic compounds from water using different UV-lamps have already been reported, there is a lack of studies where sunlight has been directly used as radiation source despite the fact that this would considerably reduce the treatment cost (Encinas et al., 2013).

Four pharmaceutical compounds, i.e., atenolol (ATL), hydrochlorothiazide (HCT), ofloxacin (OFX) and trimethoprim (TMP), whose occurrence in effluents of MWWTPs is well documented (e.g., Deblonde et al., 2011), have been selected as model ECs for this work. All these compounds show high reactivity with ozone (rate constants at pH 7 are in the 10^3–10^6 M^{-1} s^{-1} range) with a number of intermediates being identified as ozonation by-products (Dodd et al., 2006; Benner et al., 2008; Radjenovic et al., 2009a; Real et al., 2010; Tay et al., 2011; Márquez et al., 2013). In a previous work, the photocatalytic ozonation process using UV lamps emitting primarily at 365 nm has been shown promising to degrade a mixture of these four compounds (Rodríguez et al., 2013). In this new study, sunlight is used as source of radiation and the efficiency of solar photocatalytic ozonation is investigated and compared to those obtained with other AOPs, such as conventional ozonation (O_3), catalytic ozonation (O_3/TiO_2), photolytic ozonation (O_3/Solar radiation) and solar photocatalytic oxidation (TiO_2/Solar radiation).

2. Material and methods

The four pharmaceutical compounds used in this investigation were obtained from Sigma–Aldrich and used as received. The photocatalyst (Aeroxide TiO_2 P25) was used as supplied by the manufacturer (Evonik Industries AG Silica, Darmstadt, Germany). Experiments to study the efficiency of AOPs were carried out using aqueous solutions of the target pharmaceutical compounds in both ultrapure water (UPW) and a secondary effluent from an MWWTP (WWSE). UPW was obtained from a Milli-Q water system and buffered with sodium dihydrogen phosphate (ion strength of 0.05 M) to reach pH 7. WWSE was collected from the MWWTP of Badajoz, Spain. WWSE was characterized according to standard methods (APHA, 2005). Some main characteristics of the WWSE were as follows (average values from 24 samples): pH = 7.4; turbidity = 14.7 NTU; COD = 47 mg L^{-1}; BOD = 11 mg L^{-1}; TOC = 20 mg L^{-1}; Total inorganic carbon (TIC) = 12 mg L^{-1}; Total nitrogen (TN) = 17.2 mg L^{-1}; NH_4^+-N = 14.6 mg L^{-1}; Total phosphorus (TP) = 5.1 mg L^{-1}. Before the experiments, both, UPW and WWSE were spiked with amounts of the four pharmaceutical compounds to reach the desired initial concentrations (from 0.5 to 10 mg L^{-1} each).

Fig. 1 shows details of the experimental set-up used for semi-batch degradation experiments. In a typical experiment, 5 L of the solution to be treated was loaded into the photoreactor tank (gas–liquid separator). After adding the photocatalyst (if needed), the liquid was recirculated through the compound parabolic concentrator (CPC) for 30 min in the dark (i.e., the CPC tubes were covered). The CPC (Ecosystem–Environmental, Barcelona, Spain), with 0.25 m^2 of irradiated surface, was mounted on a fixed platform tilted 45° (local latitude) and, as seen in Fig. 1, it comprised 4 parallel borosilicate glass tubes (75 cm length, 2.92 cm i.d.) in series connected to a gas–liquid separator. Ozone was generated from dry air with an ozone generator (Ozonfilt OzVa, Prominent GmbH, Heidelberg, Germany). Thirty min after adding the catalyst, the CPC tubes were uncovered and the ozone containing gas was fed through two porous plates situated at the entrance of tubes of the CPC. The solution to be treated was kept recirculating at a rate of 300–400 L h^{-1}, which provided good mixing. The gas flow rate was set at 45 L h^{-1} by means of a mass controller and the ozone inlet concentration was kept at about 20 mg L^{-1} by fixing the voltage applied in the ozone generator. Ozone concentrations in the gases entering and leaving the photoreactor were continuously monitored with Ozomat GM-6000-RTI and Ozomat GM-6000-PRO ozone analyzers (Anseros, Tübingen, Germany), respectively. The intensity of solar UVA radiation and the temperature were continuously measured by an ACADUS85 UV radiometer (Ecosystem–Environmental, Barcelona, Spain) and a Pt-100 probe, respectively. The average incident UVA radiation was typically about 35 ± 5 W m^{-2}, while the temperature varied in the 18–30 °C range during each experiment. A pH&redox 26 probe (Crison Instruments, Barcelona, Spain) was used to continuously measure pH during the course of each experiment. Also, pH was controlled at about 7 (set point) by adding appropriate amounts of NaOH or H_3PO_4 aqueous solutions. At different reaction times, samples were withdrawn from the gas–liquid separator and analyzed for the concentration of ECs, total polyphenol concentration (TPC), TOC and ozone concentration. In addition, COD and BOD were analyzed when working with WWSE.

ATL, HCT, OFX and TMP were analyzed by HPLC with an L-2455 Hitachi diode array detector as reported previously (Rodríguez et al., 2013). TPC was determined by the Folin Ciocalteau method (Singleton and Rossi, 1965) and expressed as equivalent concentration of OFX. TOC was analyzed with a TOC-VSCH Shimadzu carbon analyzer. COD was measured by the dichromate method using the LCK 414 Hach Lange cuvette test. BOD was determined following a manometric method using an OxiTop® measuring system (OECD, 1992). Dissolved ozone concentration was measured following the indigo method proposed by Bader and Hoigné (1981). In order to assess ecotoxicity of initial and treated samples to *Daphnia magna*, some experiments were completed with non-buffered solutions, as the phosphate buffer is toxic to *D. magna* (EC_{10} = 1.5–7.4 mM, 24 h and pH 7; Rendal et al., 2012). Ecotoxicity of samples to *D. magna* was determined by an immobilization test performed in accordance with the OECD *Daphnia* sp. Acute Immobilisation Test (OECD, 2004). $K_2Cr_2O_7$ was used as reference chemical to ensure test validity.

3. Results and discussion

3.1. Removal of ECs in UPW by different AOPs

Experiments of adsorption, photolysis and/or oxidation of a mixture of the four pharmaceutical compounds in UPW were