



Oxidation of clofibric acid in aqueous solution using a non-thermal plasma discharge or gamma radiation



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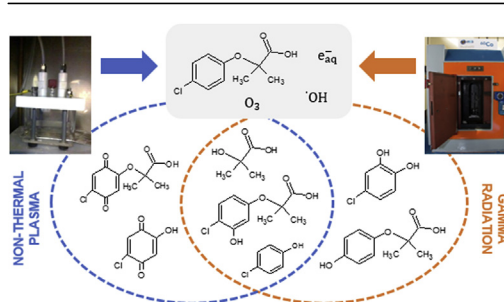
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HIGHLIGHTS

- The degradation of clofibric acid (CFA) in aqueous solution was studied.
- Gamma radiation and a non-thermal plasma were used to promote advanced oxidation processes.
- A new law is proposed to explain the degradation kinetics.
- The degradation products of CFA were assessed.
- The energy was significantly higher for the gamma radiation set-up than for plasma.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, we study degradation of clofibric acid (CFA) in aqueous solution using either ionizing radiation from a ^{60}Co source or a non-thermal plasma produced by discharges in the air above the solution. The results obtained with the two technologies are compared in terms of effectiveness of CFA degradation and its by-products. In both cases the CFA degradation follows a quasi-exponential decay in time well modelled by a kinetic scheme which considers the competition between CFA and all reaction intermediates for the reactive species generated in solution as well as the amount of the end product formed. A new degradation law is deduced to explain the results. Although the end-product CO_2 was detected and the CFA conversion found to be very high under the studied conditions, HPLC analysis reveals several degradation intermediates still bearing the aromatic ring with the chlorine substituent. The extent of mineralization is rather limited. The energy yield is found to be higher in the gamma radiation experiments.

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1. Introduction

Pharmaceutical products are important emerging pollutants due to their large variety and increasing consumption in recent years. Due to the inadequate efficiency of conventional treatment

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processes, some are released into the aquatic environment as primary pollutants, metabolites and transformation products formed during wastewater treatments (Patrolecco et al., 2015; Santos et al., 2009; Salgado et al., 2010) leading to contamination of surface waters, seawaters, groundwater and in some cases also drinking waters (Salgado et al., 2012; Pereira et al., 2015; de Jesus Gaffney et al., 2015; Lolić et al., 2015). They can have toxic effects (Santos et al., 2010) on humans after consumption of contaminated water or of food irrigated with polluted water, and affect aquatic organisms and other animal species.

Clofibric acid (CFA) is the metabolite of the lipid regulators clofibrate, etofibrate and etofyllinclofibrate, used to decrease the level of cholesterol and triglycerides. It was detected in wastewater treatment plants (Salgado et al., 2010; Dordio et al., 2009) in concentrations of up to 41.4 µg/L (Salgado et al., 2011), representing one of the most abundant pharmaceutical compounds in the environment. CFA, which is expected to be fully ionized in natural waters (estimated pKa is 3.18), is non-biodegradable, highly mobile and has high persistence in the environment, with a half-life of 21 years (Winkler et al., 2001).

Advanced oxidation processes (AOPs) use the hydroxyl radical ($\cdot\text{OH}$) for oxidation and are employed in novel technologies for water treatment and especially for the elimination of pharmaceutical products. Different AOPs have been used for this purpose, such as ozonation (Huber et al., 2003), Fenton and photo-Fenton processes (Komtchou et al., 2015), photocatalysis (Elmolla and Chaudhuri, 2010) and ionizing radiations such as gamma radiation and electron-beam and, more recently, non-thermal plasmas (NTPs) produced by electrical discharges inside or in contact with the water to be treated (Magureanu et al., 2015). For example, Mezyk et al. (2008) developed a kinetic model to rationalize the effects of gamma radiation on three types of contaminants, particularly pharmaceuticals, and proposed the degradation mechanisms. Illés et al. (2012) observed an effective degradation of ketoprofen by gamma radiation with no toxicity with 5 kGy dose. The decomposition of diclofenac was studied by gamma radiation (Liu et al., 2011) using different initial conditions and by pulsed corona discharge (Dobrin et al., 2013) and its degradation pathway was proposed. Magureanu et al. (2011) studied the decomposition of three antibiotics (amoxicillin, oxacillin and ampicillin) using a dielectric barrier discharge (DBD) reaching their complete degradation after 10 min for amoxicillin and 30 min for oxacillin and ampicillin, respectively. In recent years, CFA degradation has been studied using different AOPs. Ultraviolet (UV), vacuum ultraviolet, UV/TiO₂ (Li et al., 2012), ozonation (Rosal et al., 2009), different Fenton conditions (Sirés et al., 2007), ionizing radiation such as electron beam (Razavi et al., 2009) or gamma rays (Csay et al., 2014) and plasma from corona discharge (Krause et al., 2011) were reported to be efficient in the elimination of CFA. Mechanisms for CFA decomposition have been proposed. However, the intermediates formed by plasma treatment were not clarified.

In this work, we report and discuss the results of studies of the oxidation of clofibric acid using two technologies: gamma radiation using a ⁶⁰Co source and a non-thermal plasma (NTP) in contact with the liquid. We discuss the decomposition rates, the decomposition products and the energy yield for the two technologies.

2. Material and methods

2.1. Chemicals

Clofibric acid (Fig. 1), 4-chlorophenol and 2-hydroxyisobutyric acid, formic acid and acetonitrile were purchased from Fluka. Ultrapure grade water (milli-Q water) was obtained by filtration of

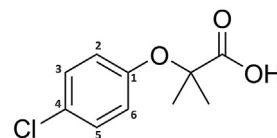


Fig. 1. Structure of the investigated compound, clofibric acid.

deionized water with a Millipore system. Synthetic air (80% nitrogen and 20% oxygen), used in the plasma experiments, was obtained from Air Liquide, with specified impurities of H₂O (<3 ppm) and of C_nH_m (<0.5 ppm).

2.2. Preparation of clofibric acid solutions

Solutions of desired concentration of (0.1, 0.5 and 1) × 10⁻³ M were prepared by dissolving CFA in Milli-Q water, without pH adjustment.

2.3. Experiments of advanced oxidation of clofibric acid

2.3.1. Gamma radiation treatment

Irradiation experiments of clofibric acid solutions were carried out in an equipment previously described by Madureira et al. (2017). The irradiation chamber was a cavity of stainless steel (50 cm depth, 20 cm width and 65 cm height) with four ⁶⁰Co sources placed in four channels on the side walls of the chamber. The irradiations were performed at room temperature with a dose rate of 1.8 kGy/h and different absorbed doses (from 0.1 kGy to 10 kGy). The samples were irradiated in vials with 3 mL of solution in an automatic rotation system to guarantee dose uniformity. The absorbed dose was measured by routine dosimeters (Whittaker and Watts, 2001) while the local dose rate had been previously determined by the Fricke method (ASTM, 1992). The treated solutions were analysed as described in the next paragraphs.

2.3.2. Non-thermal plasma (NTP) treatment

The experimental apparatus was previously described in detail by Marotta et al. (2011b). Briefly, it includes the plasma reactor, the power supply, the gas line used to maintain a constant flow (30 mL/min) of humidified air above the treated solution and the instrumentation for electrical and chemical diagnostics. The reactor has a glass base (95 mm × 75 mm × 60 mm) closed by a teflon cap holding the active electrode (two parallel stainless steel wires with

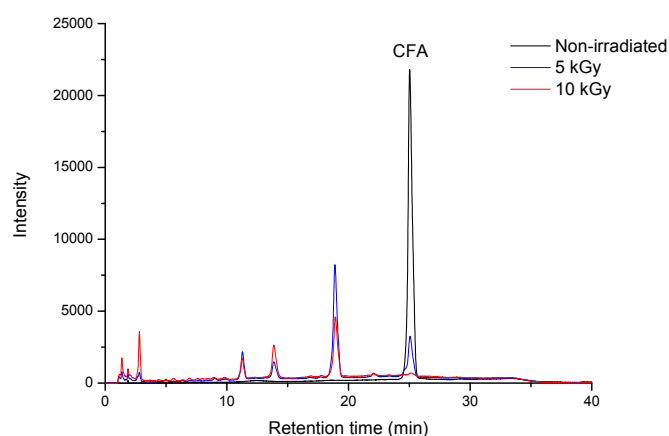


Fig. 2. Chromatograms of solutions, with an initial clofibric acid concentration of 1 × 10⁻³ M, irradiated on a ⁶⁰Co gamma source, as a function of the absorbed dose. The dose rate in the samples was 1.8 kGy/h.

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