



Electron beam irradiation induced degradation of antidepressant drug fluoxetine in water matrices



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H I G H L I G H T S

- The radiolytic degradation of emerging pharmaceutical pollutants fluoxetine was investigated via electron beam irradiation.
- The influences of various environmental factors on the degradation processes were conducted.
- Natural surface water matrix displayed reserve effects on the degradation process.
- The degradation mechanisms of fluoxetine in water matrix were proposed.

A R T I C L E I N F O

Article history:

Received 5 July 2017

Received in revised form

1 September 2017

Accepted 27 September 2017

Available online 3 October 2017

Handling Editor: Jun Huang

Keywords:

Emerging pollutants

Advanced oxidation processes (AOPs)

Influence factors

Kinetics and mechanisms

By-product identification

A B S T R A C T

With the development of psychiatric disorder in the current society, abuse of antidepressant drug fluoxetine (FLX) has made such compound an emerging contaminant in natural waters, and causes endocrine systems disturbance on some aquatic species. Herein, an efficient advanced oxidation process (AOP), electron beam irradiation was carried out to investigate the decomposition characteristics of such novel environmental pollutant, including the effects of initial concentration, pH, radical scavengers and anions. The results showed that FLX degradation followed pseudo-first-order kinetics. The degradation rate and dose constant decreased with increasing initial FLX concentration; and G-values elevated with the increase of initial concentration but reduced with increase of absorbed dose. Acidic condition was more conducive to FLX destruction than neutral and alkaline. The radical scavenger experiments indicated $\cdot\text{OH}$ was the main reactive species for the decomposition of FLX, while the reductive species e_{aq}^- and $\cdot\text{H}$ played an adjuvant role. The presence of anions slightly decreased or even no impact on FLX degradation rate. Various water matrices influenced degradation processes of FLX. Experimental results suggested radiolytic degradation showed the best performance in pure water rather than natural water no matter with filtration or not. Moreover, with the occurrence of defluorination and dealkylation during degradation process, some organic and inorganic intermediates were detected, and the possible degradation mechanisms and pathways of FLX were proposed.

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1. Introduction

Pharmaceutical compounds have been frequently detected as emerging contaminants in surface water (Boyd et al., 2004; Henzler

et al., 2014; Iglesias et al., 2014; Petrović et al., 2014; Shanmugam et al., 2014; Wu et al., 2015), drinking water (Zuhlke et al., 2004; Schaider et al., 2014), wastewater especially in the case of hospital effluents (Nam et al., 2014; Silva et al., 2014), effluents from wastewater treatment plants (WWTPs) (Kostich et al., 2014; Silva et al., 2014), as well as sediments (Schultz et al., 2010; Chen and Zhou, 2014), which have been a major concern to the public and scientific community as their highly resistant to biodegradation and potential adverse impacts to the flora and fauna in aquatic systems (Simazaki et al., 2015; der Beek et al., 2016). Furthermore,

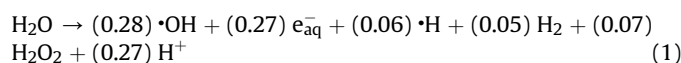
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human exposure to pharmaceuticals is also unnegligible, which may occur via various routes, such as drinking water, food chain, wastewater reuse for household purposes and even inhalation. Since the WWTPs exhibited limited capability to remove these novel contaminants, the environmental pollution caused by the emerging pharmaceutical pollutants aroused widespread social concerns.

In recent years, fluoxetine (FLX) is widely used as antidepressant to address anxiety and depression; however, plenty of researchers have shown that such compounds performed both acute and chronic toxicity to aquatic ecosystems (Melvin, 2017; Varano et al., 2017; Zhao et al., 2017). Unfortunately, quantities of FLX cannot be easily eliminated using traditional means at WWTPs (Loos et al., 2013; Kostich et al., 2014), thus making it easily release into the environment via effluent discharge into surface waters and some other agricultural ways (Carballa et al., 2004; Lishman et al., 2006). Under the circumstances, advanced oxidation processes (AOPs) have been developed to treat with pharmaceutical contaminants including FLX, such as ozone/H₂O₂ (Aghaeinejad-Meybodi et al., 2015), sonochemical (Serna-Galvis et al., 2015), photochemical processes (Keen and Linden, 2013) and so on. However, the degradation efficiency of FLX by these traditional AOPs still remains low. This situation has encouraged the search for more efficient approaches with capacity of promoting mineralization of these contaminants. The electron beam (EB) irradiation technology, one of the AOPs, has been proved to be an efficient, safe, simple and completely mineralized method and shown great advantage during the last three decades for efficient treatment of persistent organic pollutants (POPs), especially for the thorough decomposition of biorefractory compounds (Xu et al., 2011). Generally, three main reactive species could be generated in aqueous media by the irradiation process, including e_{aq}⁻, •OH, and •H, and some other less reactive species (Eq. (1)) (Buxton et al., 1988), the values in square brackets are radiation yield (G-value) of each species in μmol J⁻¹ absorbed energy. The main reactive species can react with each other as well as other solutes present in the reaction systems so as to influence the entire degradation process (Buxton et al., 1988).



Most researches have demonstrated that the oxidative •OH radicals are the most important species during the process; moreover, in most cases pollutants can be degraded to less toxic substances and in some cases into more biodegradable compounds by EB irradiation, and finally, the organic pollutants can be converted to simply carbon dioxide and water (Basfar et al., 2007; Zheng et al., 2014; Xu et al., 2015).

In the present work, EB irradiation technology was employed to evaluate the complete mineralization applicability of the AOP to FLX, which can enlarge the knowledge of efficient treatment methods to such contaminant. The influence factors during the irradiation process such as irradiation dose, initial contaminant concentration, pH, radical scavengers, inorganic ions, and H₂O₂ additive amounts were comprehensively evaluated. Additionally, since the natural surface water is a complex system that contains a variety of constituents, such as ions, dissolved organic matter (DOM) and suspended solids (SS), to test the performance of the EB process in conditions closer to those in an applicable system, degradation of FLX in natural water with and without any filtration was also investigated. Moreover, the main intermediates, inorganic ions and organic acids formed during EB irradiation process were identified, and the potential decomposition pathways of FLX were also proposed based on its degradation mechanisms.

2. Experimental section

2.1. Materials and reagents

FLX was purchased from CNW Technologies GmbH (Duesseldorf, Germany) with >98% purity without any further purification before use. All chemical reagents were analytical grade unless otherwise stated. Sodium sulfite, sodium sulfate, sodium nitrite, sodium nitrate, sodium carbonate, sodium bicarbonate, sodium chloride, ammonium chloride, hydrogen peroxide (H₂O₂, 30%, w/w) and isopropanol were obtained from ANPEL Laboratory Technologies (Shanghai) Inc. The pH of the solution was adjusted using sodium hydroxide or sulfuric acid when needed. All the solutions were prepared by Ultra-pure water throughout the study using a Milli-Q-Plus ultra-pure water system (resistance >18.2 MΩ cm) from Millipore (Sartorius 611, Germany). High purity N₂ and O₂ (>99.999% purity) were used.

2.2. Irradiation performance

All irradiation experiments were conducted using electron accelerator (GJ-2-II, Xianfeng electrical plant) with beam energy of 1.8 MeV and variable current (0–10 mA), which belonged to Institute of Applied Radiation, Shanghai University, China. Aqueous fluoxetine solutions were irradiated at different doses and all experiments were performed at room temperature (20 ± 2 °C).

2.3. Analytical methods

The concentrations of FLX before and after irradiation were quantified by HPLC (Agilent 1200) using a C₁₈ reversed phase column (250 mm × 4.6 mm × 5 μm). Based on previous researches with some modifications (Aymard et al., 1997), the mobile phase was 0.067 M KH₂PO₄ buffer (adjust to pH 3.0 with H₃PO₄ and filtered with 0.22 μm membrane) and acetonitrile mixture (62:38, v/v) at flow rate of 1.1 mL min⁻¹. UV detector wavelength was set at 226 nm and injection volume was 10 μL.

The organic acids and inorganic ions formed during FLX degradation by electron beam irradiation were determined by ion chromatography (Dionex ICS1100) using hydrophilic anion exchange column. The eluent was mixed with 4.5 mM Na₂CO₃ and 1.4 mM NaHCO₃ at a flow rate of 1.2 mL min⁻¹. The injection volume was 25 μL.

Intermediate identification was carried out with HPLC (Agilent 1260) coupled with Triple Quad MS (Agilent 6460) using ESI-ionization operating in full-scan mode. Separation was carried out using a C₁₈ column (100 mm × 3.0 mm × 2.7 μm) at a flow rate of 0.4 mL min⁻¹; and a mixture of acetonitrile and water (35:65, v/v) as used as the mobile phase.

3. Results and discussion

3.1. Radiolytic degradation kinetics

The radiolytic degradation of FLX was carried out in four various concentrations (50, 75, 100 and 125 mg L⁻¹) with irradiation dose ranging from 0 to 5 kGy. Apparently, FLX could be effectively degraded with a relatively low dose as shown in Fig. 1. Specifically, the removal of 50 mg L⁻¹ of FLX was nearly 90% at the irradiation dose of 0.5 kGy, and even reached 98% at 1 kGy; furthermore, FLX can be nearly completely degraded at 2 kGy when the initial concentration was doubled to 100 mg L⁻¹, implying EB was an effective method for FLX decomposition comparing with the traditional biochemical or other AOP approaches. However, the change rate of FLX degradation rate decreased with increasing absorbed dose at any

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