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Removal of diclofenac from surface water by electron beam irradiation combined with a biological aerated filter

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HIGHLIGHTS

- DCF cannot be removed from surface water by biological aerated filter.
- Electron beam (EB) can effectively decompose DCF in surface water.
- Both EB and biological treatment can reduce the toxicity of treated water.
- The combined EB and BAF can eliminate DCF from surface water.

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ABSTRACT

The degradation of DCF was investigated in aqueous solution by using electron beam (EB) technology. When the initial concentration was between 10 and 40 mg/L, almost 100% of the DCF was degraded at a dose of 0.5 kGy. However, only about 6.5% of DCF was mineralized even at 2 kGy according to total organic carbon (TOC) measurements. A combined process of EB and biological aerated filter (BAF) was therefore developed to enhance the treatment of DCF contaminated surface water. The effluent quality of combined process was substantially improved by EB pretreatment due to the degradation of DCF and related intermediates. Both irradiation and biological treatment reduced the toxicity of the treated water. The experimental results showed that EB is effective for removing DCF from artificial aqueous solution and real surface water.

1. Introduction

The huge consumption of pharmaceuticals and personal care products (PPCPs) provides a continuous release of both unmetabolized and as active metabolites to the receiving rivers, lakes, groundwater and even drinking water supplies (Benotti et al., 2009; Kim et al., 2007; Makris and Snyder, 2010). Public and scientific concern is increasing gradually due to their potential impact on aqueous ecosystems and human health (Carballa et al., 2004; Kumar and Xagoraraki, 2010). As a consequence, various techniques have been developed to eliminate PPCPs from wastewater and waters. It is well known that physical treatments, such as filtration (including recently developed nanofiltration and reverse osmosis) and adsorption, can only transfer PPCPs from one phase to another phase, unable to decompose them (Behera et al., 2011; Matamoros et al., 2009). Biological process in WWTPs, such as activated sludge, is not originally designed to remove such kinds of emerging contaminants; therefore, their treatment performance is usually limited for these compounds (Vieno et al., 2007).

Advanced oxidation processes (AOPs), mostly dependent on the generation of hydroxyl radicals (•OH), including ozonation, Fenton reaction (Li et al., 2012), photolysis (Salgado et al., 2013), sonolysis (Guyer and Ince, 2011), have been studied as possible alternatives to destroy PPCPs in water (Yang et al., 2011). The ionizing radiation process also belongs to the AOPs family. A number of researches have been conducted at bench-scale and pilot-scale on irradiation induced decomposition of PPCPs in aqueous solution (Kimura et al., 2012; Kurucz et al., 2002; Liu et al., 2011).

This study focused on diclofenac (2-(2,6-dichlorophenylamino) phenyl acetic acid, DCF), one of the most widely used non-steroidal anti-inflammatory drugs. As previous reports shown, irradiation process succeeded to decompose DCF in aqueous solution but it was rather ineffective in mineralization (Homlok et al., 2011, Yu, et al., 2008). In this regard, a following biological aerated filter (BAF) was developed to remove the DCF and

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its intermediates from wastewater samples. Biological aerated filter (BAF), a type of immobilization reactor, has been demonstrated to be a cost-effective way for the treatment of micro-polluted surface water (Han et al., 2012; Lu et al., 2012; Zhang et al., 2012). The main objectives of this study were to investigate the electron beam (EB) irradiation induced degradation of DCF as well as the change of TOC, COD_{Mn}, Cl^-, NH_4^+-N in aqueous solution. The performance of BAF alone in parallel with a combined process of EB+BAF for the treatment of DCF contaminated surface water was compared.

2. Materials and methods

2.1. Materials

DCF was obtained from Adamas Reagent Co. Ltd with purity > 98%. All other chemicals were of analytical or the highest grade available. *Vibrio fischeri* for toxicity assays was obtained from Institute of Soil Science, Chinese Academy of Sciences. In order to investigate the decomposition of DCF as well as the change of TOC, COD_{Mn}, Cl^-, NH_4^+-N in aqueous solution, 10–40 mg/L DCF was prepared with double-distilled water. As for the combined process of EB+BAF, DCF was dissolved into real surface water to achieve 5–10 mg/L DCF contained water samples as shown in Table 1.

2.2. Equipment

Electron beam irradiation was carried out with a Rhodotron TT200 accelerator (energy 10 MeV, beam current 10 mA, beam power 100 kW). The accelerator was equipped with a track transport system to send the water samples to the irradiation room. The absorbed dose was calibrated by a GEX B3 dosimeter.

Biological treatments were performed using two same size BAF reactors, diameter of 100 mm, length of 700 mm , and effective volume of 5.5 L. The first column (1#) was tested for the biological treatment alone, while the second column (2#) was tested for the combined process of EB+BAF. The surface water containing DCF was pumped into the reactors via a peristaltic pump. Air stream was continuously introduced at the bottom of the BAF. The ratio of air to water was fixed at 3:1. For the flow rate of 0.58 L/h, the hydraulic retention time (HRT) of BAF was approximately 9 h.

2.3. Analysis methods

The DCF concentration was measured by high performance liquid chromatography (HPLC, Agilent 1200 Series, Agilent, USA) equipped with an XDB-C18 column and a diode array detector (DAD). The injection volume was 10 μL and the column temperature was 30 °C. Mobile phase of this analysis was a mixture of methanol and distilled water at a ratio of 90:10 (v/v). The DCF was measured at a flow rate of 1.0 mL/min at a wave length of 275 nm for 4.5 min.

The ammonia (NH_4^+-N) was analyzed by a phenate method (Lee and Lee, 2005). UV_{254} was obtained using a Mapada UV-1600 spectrophotometer (Mapada, China). Chloride ions released from the degradation of DCF were analyzed by ion chromatography. Total organic carbon (TOC) was measured by Shimadzu TOC-VCPH.

Table 1
Characteristic of DCF contaminated surface water.

pH	NH_4^+-N (mg/L)	COD_{Mn} (mg/L)	TOC (mg/L)	UV_{254}	DCF (mg/L)
6–8	0.56–0.98	9–22	12–15	0.21–0.35	5–10

Chemical oxygen demand (COD_{Mn}) was determined according to the standard method (GB 11892-89, 1990).

The toxicity of the samples was determined by the bioluminescence of the marine bacterium *V. fischeri* with a luminometer Glomax Multi Detection System. A 200 μL water sample with different dilution ratios and 50 μL bacterial suspensions was thoroughly mixed in a microplate and the luminescence was recorded after 5 min of incubation at 25 °C. The luminescence inhibition ratio LIR (%) was obtained according to the following equation:

$$\mathrm{LIR}(\%) = \left(1 - \frac{\mathrm{RLI_{sam}}}{\mathrm{RLI_{ref}}}\right) \times 100\%$$

where RLI_{sam} *and* RLI_{ref} are the relative light intensities of the luminescence of bacteria on reacting with the wastewater sample and reference compound, respectively.

3. Results and discussion

3.1. Degradation of DCF by electron beam irradiation

Electron beam irradiation-induced degradation of DCF in aqueous solution is shown in Fig. 1. The results indicated that DCF was degraded quickly in a range of 10–40 mg/L. The removal efficiency was almost 100% for all the samples at 0.5 kGy. For the gamma irradiation (Kimura et al., 2012), 5 μmol/L DCF in real wastewater samples was eliminated with 1 kGy. In another report, at 0.1 mM DCF concentration, an ~1 kGy absorbed dose is needed for the degradation of DCF molecules (Homlok et al., 2011). If compared the present results and the above reports, it seems almost equal efficiency between the EB and gamma irradiation.

In order to investigate the degradation of DCF as well as the decrease of TOC and COD_{Mn}, the initial concentration of 40 mg/L

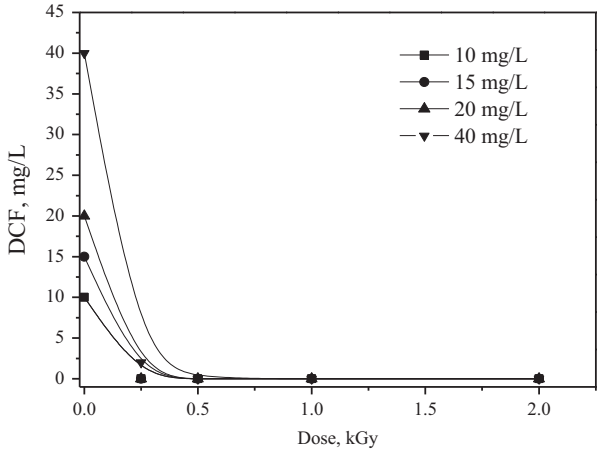

Fig. 1. Effect of absorbed dose on DCF degradation.

Table 2
Decrease of DCF, TOC, COD_{Mn} and the release of Cl^-, NH_4^+-N during EB irradiation.

Dose (kGy)	DCF (mg/L)	TOC (mg/L)	COD_{Mn} (mg/L)	Cl^- (mg/L)	NH_4^+-N (mg/L)
0	38.1	25	45	bdl	bdl
0.25	1.8	24.6	41	0.35	0.1
0.5	bdl	24.2	39	1.38	0.20
1	bdl	23.7	38	2.34	0.21
2	bdl	23.4	37	3.86	0.27

bdl: below detection limits.