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Degradation of diclofenac by UV-activated persulfate process: Kinetic studies, degradation pathways and toxicity assessments

Xian Lu[a], Yisheng Shao[a,b,*], Naiyun Gao[a], Juxiang Chen[c], Yansen Zhang[a], Huiming Xiang[a], Youluo Guo[a]

[a] State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai, China
[b] China Academy of Urban Planning & Design, Beijing, China
[c] College of Architecture and Civil Engineering, Xinjiang University, Urumqi, China

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ABSTRACT

Diclofenac (DCF) is the frequently detected non-steroidal pharmaceuticals in the aquatic environment. In this study, the degradation of DCF was evaluated by UV-254 nm activated persulfate (UV/PS). The degradation of DCF followed the pseudo first-order kinetics pattern. The degradation rate constant (k_{obs}) was accelerated by UV/PS compared to UV alone and PS alone. Increasing the initial PS dosage or solution pH significantly enhanced the degradation efficiency. Presence of various natural water constituents had different effects on DCF degradation, with an enhancement or inhibition in the presence of inorganic anions (HCO_3^- or Cl^-) and a significant inhibition in the presence of NOM. In addition, preliminary degradation mechanisms and major products were elucidated using LC-MS/MS. Hydroxylation, decarbonylation, ring-opening and cyclation reaction involving the attack of $SO_4^{\bullet -}$ or other substances, were the main degradation mechanism. TOC analyzer and Microtox bioassay were employed to evaluate the mineralization and cytotoxicity of solutions treated by UV/PS at different times, respectively. Limited elimination of TOC (32%) was observed during the mineralization of DCF. More toxic degradation products and their related intermediate species were formed, and the UV/PS process was suitable for removing the toxicity. Of note, longer degradation time may be considered for the final toxicity removal.

1. Introduction

In recent years, the widespread occurrence of pharmaceutical and personal care products (PPCPs) have been referred as one of the most urgent environmental concerns, because of their potentially adverse impacts on the aqueous ecosystem and human health (Kosma et al., 2014; Kumar and Xagoraraki, 2010). As representative PPCPs, the diclofenac (DCF, chemical structure is shown in Fig. S1), an important non-steroidal anti-inflammatory drug (NSAID), is widely used to treat painful inflammatory rheumatoid and non-rheumatoid diseases, largely used clinically as the sodium salt. Besides the conventional sewage treatment plants (STPs) are ineffective in achieving complete degradation of this compound. Due to its extensive use and lower removal (about 30%) by STPs, DCF has been found at different levels in influent and effluent of waste water treatment plants (WWTPs), surface water and groundwater (Huguet et al., 2013). An average concentration of 4.7 μg L^{-1} for diclofenac has been detected in STP effluent while an average concentration of 1.2 μg L^{-1} has been observed in surface water, and even in groundwater and tap water at concentrations of up to 380 ng L^{-1} and below 10 ng L^{-1}, respectively (Aguinaco et al., 2012; Heberer, 2002). Additionally, the formation of harmful disinfection byproducts (DBPs) could be a serious threat to human health during drinking water treatment resulting from the reaction of disinfectants with DCF. Therefore, research on DCF removal in aquatic environment is a critically important issue.

Recently, a promising advanced oxidation technology (AOTs) based on the generation of the sulfate radical ($SO_4^{\bullet -}$) has brought increasing interest to scientific community throughout the world. Compared to $OH^{\bullet}$, sulfate radicals have a high redox potential of 2.5–3.1 V (Neta et al., 1988). Furthermore, sulfate radicals are more selective than $OH^{\bullet}$ for the oxidation of many organic contaminants (Neta et al., 1988; Xie et al., 2015). Usually, $SO_4^{\bullet -}$ can be generated from the activation of peroxydisulfate ($S_2O_8^{2-}$) by using UV (see Eq. (1)), heat (see Eq. (2)) or transition metals (e.g., Fe^{2+}, see Eq. (3)) (Ge et al., 2016; Lau et al., 2007; Waldemer et al., 2007). However, UV activation, which has united quantum efficiency, is more attractive than thermal or chemical

* Corresponding author at: State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai, China.
E-mail address: lucaspp@163.com (Y. Shao).

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activations to produce $SO_4^{\bullet-}$ when considering the cost of heating and the accumulation of metals (e.g., Fe^{3+}) in oxidation system (An et al., 2015; Ghaly et al., 2007).

$$\text{UV activation: } S_2O_8^{2-} + h\upsilon \rightarrow 2\,SO_4^{\bullet-} \quad \begin{matrix}\phi = 1.4 \text{ (de-oxygenated)} \\ \phi = 1.8 \text{ (oxygen saturated)}\end{matrix} \tag{1}$$

$$\text{Thermal activation: } S_2O_8^{2-} + \text{heat} \rightarrow 2\,SO_4^{\bullet-} \tag{2}$$

$$\text{Chemical activation: } S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{\bullet-} + Fe^{3+} + SO_4^{2-} \tag{3}$$

A few examples of DCF degradation process based on persulfate (PS) or peroxymonosulfate (PMS) have been reported. Mahdi Ahmed and co-researches suggested that the Co (II) activated PMS could remove DCF from water effectively (Mahdi Ahmed et al., 2012). Deng et al. demonstrated the $CoFe_2O_4$ magnetic nanoparticles activated PMS could effectively oxidize DCF (Deng et al., 2013). However, to date fewer data have been published to evaluate the degradation mechanism of DCF by UV activated persulfate (UV/PS). It is also important to determine whether the DCF polluted water contains toxic or mutagenic substances after UV/PS treatment, which will allay public health concerns when this oxidation process is employed for water treatment.

The objective of present study was to investigate the degradation of DCF by UV/PS AOT. In a first part, the reaction kinetics and influence of various parameters, such as different PS dosage, solution pH and common natural water constituents (e.g., inorganic anions and natural organic matter (NOM)), were evaluated. In a second part, a mechanistic study of DCF degradation by UV/PS had been done. The oxidation by-products were tentatively identified by LC coupled with UV diode array detector and mass spectrometer, and the degradation pathways of DCF were also proposed. In a third part, the changes in toxicity during the oxidation process were assessed using a Microtox bioassay testing system.

2. Materials and methods

2.1. Reagents and chemicals

All chemicals were at least of analytical grade except as noted. All the solutions were prepared using deionized water (18.2 Ω-cm Milli-Q water, Millipore). Acetonitrile (HPLC grade, ≥99.9%) and ethanol (EtOH, ≥99.7%) were purchased from Sigma-Aldrich. DCF sodium salt (≥98.0%), PS ($Na_2S_2O_8$, ≥99.5%), formic acid (≥99.0%), sodium phosphate (Na_2HPO_4, ≥99.0%), monobasic sodium phosphate (NaH_2PO_4, ≥99.0%), sodium bicarbonate ($NaHCO_3$, ≥99.5%) and sodium chloride (NaCl, ≥99.9%) were obtained from Sinopharm Chemical Reagent Co., China. Humic acid (HA, FA ≥90.0%) was purchased from Aladdin Chemical Co., Ltd, and sodium sulfite (Na_2SO_3, ≥99.0%) from Fluka. The stock solution for DCF (3 mM) and PS (100 mM) were respectively prepared by dissolving the pure compound in deionized water.

2.2. UV collimated beam apparatus

The UV photochemical experiments were conducted using a bench scale collimated beam instrument equipped with a 75 W low-pressure Hg UV lamp (Philips, Netherlands) at 254 nm. The solution was placed under the open end of the collimated tube of the UV beam apparatus center in the center of the beam. In order to make the solution inside have homogeneous UV exposure a small rotor was also placed at the bottom of the circular dish container. Moreover, the irradiance at the surface of solution was measured by a UV intensity radiometer (photoelectric Instrument Factory of Beijing Normal University, Beijing, China). A calibration of the UV irradiance was conducted according to the description of Bolton and Linden (Bolton and Linden, 2003). In this experiment, UV irradiance used was 0.1 mW cm^{-2} after calibration.

2.3. Experimental procedures

All experiments were performed at room temperature (23 ± 1 ℃) in a circular dish reactor with a rotor stirring in it. The solution pH was kept constant by 10 mM phosphate buffer (the inhibiting effect of phosphate species on radical oxidation is negligible) and adjusted to the designated pH by sulfuric acid or sodium hydroxide. To investigate the effect of PS dose (0–2.0 mM), HCO_3^- and Cl^- inorganic anions (0–200 mM), initial solution pH (3–11) and NOM (0–40 mg-HA L^{-1}) on DCF degradation by UV/PS, experiments were initiated by adding the PS stock solution the circular dish containing the 100 mL solution spiked with 0.03 mM DCF and 10 mM phosphate buffer. Then, the circular dish container was exposed to UV irradiation immediately.

Samples (1 mL) were withdrawn at predetermined time intervals, quenched with excess ethanol and stored at 4 ℃ in the dark before HPLC analysis. Control tests of DCF degradation by UV direct photolysis (absence of PS) and PS oxidation (absence of UV light) were conducted in a similar manner, respectively.

To identify the degradation intermediates/products during DCF degradation by the UV/PS, the initial concentration of DCF (0.03 mM), UV intensity (0.1 mW cm^{-2}) and PS (1.0 mM) were used. After a certain reaction time (10, 30, 60, 120 or 180 min), the reaction solution was quenched with 100 mM Na_2SO_3 and a 1 mL samples was collected and immediately analyzed by LC-MS/MS.

2.4. HPLC and mass spectral analysis

The concentration of DCF was analyzed with HPLC (Shimadzu, Japan) equipped with a Shim-pack C_{18} column (250 mm × 4.6 mm, Shimadzu, Japan) by a UV detector at wavelength of 230 nm. The mobile phase consisted of 60/40% (V/V) acetonitrile and 0.1% formic acid at a flow rate of 1.0 mL min^{-1}. The injection volume was 20 μL. The LC-MS/MS analysis was carried out on a Waters e2695 HPLC system coupled with a TSQ Quantum quadrupole mass spectrometer (Thermo Scientific MAX). The mass spectrometer was equipped with an electrospray ionization (ESI) source. Separation was performed by a VP-ODS C_{18} column (4.6 × 250 mm, 5 μm) at the flow rate of 0.2 mL min^{-1}. Mixtures of A (0.1% formic acid in water) and B (acetonitrile) were used as the mobile phase. Gradient elution steps were as follow: 0–5 min 50% A and 50% B, 5–10 min a linear gradient to 25% A and 75% B, 10–20 min 25% A and 75% B, 20–25 min a linear gradient to 50% A and 50% B, 25–30 min 50% A and 50% B. The mass spectra data were obtained in the negative ion mode by scanning from *m/z* 100–400.

2.5. Toxicity measurements

The samples were collected after different times of UV/PS treatment and immediately quenched with Na_2SO_3. Then the toxicity of initial DCF solution and its decomposition products was assessed by using the bioluminescence of the freshwater bacterium Vibrio qinghaiensis. The assays were performed based on the Microtox protocol and the luminescence was determined with a Luminometer DXY-2. Briefly, freeze-dried bacteria pellets were reconstituted and pre-incubated before the analyses. The toxicity data were recorded on 15 min exposure of reconstituted bacteria solution to every sample at 23 ± 1 ℃. The inhibition percentage (I%) of the luminescence, compared with a blank control, was calculated as follows.

$$I\% = \frac{I_0 - I_x}{I_0} \times 100\% \tag{4}$$