Kinetics and pathways of ibuprofen degradation by the UV/chlorine advanced oxidation process

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ABSTRACT

The UV/chlorine advanced oxidation process (AOP), which forms reactive species such as hydroxyl radicals (HO•) and reactive chlorine species (RCS) such as chlorine atoms (Cl•) and Cl_2^-, is being considered as an alternative to the UV/H_2O_2 AOP for the degradation of emerging contaminants. This study investigated the kinetics and pathways of the degradation of a recalcitrant pharmaceutical and personal care product (PPCP)—ibuprofen (IBP)—by the UV/chlorine AOP. The degradation of IBP followed the pseudo first-order kinetics. The first-order rate constant was 3.3 times higher in the UV/chlorine AOP than in the UV/H_2O_2 AOP for a given chemical molar dosage at pH 6. The first-order rate constant decreased from 3.1×10^{-3} s^{-1} to 5.5×10^{-4} s^{-1} with increasing pH from 6 to 9. Both HO• and RCS contributed to the degradation, and the contribution of RCS increased from 22% to 30% with increasing pH from 6 to 9. The degradation was initiated by HO•-induced hydroxylation and Cl•-induced chlorine substitution, and sustained through decarboxylation, demethylation, chlorination and ring cleavage to form more stable products. Significant amounts of chlorinated intermediates/byproducts were formed from the UV/chlorine AOP, and four chlorinated products were newly identified. The yield of total organic chlorine (TOCl) was 31.6 μM after 90% degradation of 50 μM IBP under the experimental conditions. The known disinfection by-products (DBPs) comprised 17.4% of the TOCl. The effects of water matrix in filtered drinking water on the degradation were not significant, demonstrating the practicality of the UV/chlorine AOP for the control of some refractory PPCPs. However, the toxicity of the chlorinated products should be further assessed.

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1. Introduction

Pharmaceutical and personal care products (PPCPs) have been discovered in wastewater effluent, seawater, surface water and drinking water around the world (Vieno et al., 2007). Many PPCPs are toxic to aquatic organisms and their presence potentially poses a long-term threat to human health (Christen et al., 2010).

Many PPCPs are resistant to conventional water and wastewater treatment such as coagulation, sedimentation, filtration and biological processes (Vieno et al., 2007). Activated carbon adsorbs some PPCPs mainly through hydrophobic interaction, but it has difficulty removing compounds with low hydrophobicity (e.g., naproxen, sotalol, and atenolol) (Vieno et al., 2007; Huerta-Fontela et al., 2011). Ozone, chlorine and chlorine dioxide are selective oxidants that can effectively degrade PPCPs with electron-donating functional groups such as phenolic- and amine-containing compounds (Lee and von Gunten, 2010). However, they work poorly against recalcitrant PPCPs such as ciprofloxacin, phenytoin and atenolol (Vieno et al., 2007; Huerta-Fontela et al., 2011). UV photolysis is also selective but abatement of many PPCPs using this method requires much higher UV fluences (~1500 mJ/cm²) than

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does disinfection (Rosenfeldt and Linden, 2004).

Advanced oxidation processes (AOPs) are effective for the degradation of recalcitrant PPCPs. The UV/peroxide (H_2O_2) AOP producing hydroxyl radicals ($HO^\bullet$) has been reported to unselectively oxidize many PPCPs such as diatrizoic acid, metronidazole, phenazone, phenytoin (Wols et al., 2013; Yuan et al., 2009). However, the radical production is not efficient due to the low UV absorbance of H_2O_2 (for example, εH_2O_2, 254 nm = 19.6 M^{-1} cm^{-1}), which requires excessive H_2O_2 dosing (Barakat et al., 2005). In drinking water practices, only 5–10% of the added H_2O_2 is consumed during treatment (Rosenfeldt et al., 2013). The unreacted H_2O_2 requires quenching, which adds to the treatment cost.

The UV/chlorine AOP producing $HO^\bullet$ and reactive chlorine species (RCS) such as chlorine atoms ($Cl^\bullet$) (Eq. (1)) and $Cl_2^{\bullet-}$, is recently being considered as an alternative to the UV/H_2O_2 AOP (Fang et al., 2014). The remaining chlorine can be used for residual protection in drinking water distribution systems. The UV/chlorine AOP is found to be more efficient in producing reactive species at acidic and neutral pH (Watts et al., 2007; Fang et al., 2014).

$$HOCl/OCl^- + h\nu \rightarrow HO^\bullet/O^{\bullet-} + Cl^\bullet \qquad (1)$$

The diverse reactive species, such as $HO^\bullet$, $Cl^\bullet$ and $Cl_2^{\bullet-}$, that coexist in the UV/chlorine system may complement each other in degrading a variety of contaminants. $HO^\bullet$ is a nonselective oxidant, and it reacts with organic moieties with rate constants close to diffusion-controlled rates (Lee and von Gunten, 2010). $Cl^\bullet$ and $Cl_2^{\bullet-}$ are strong oxidants with oxidation potentials of 2.47 V and 2.0 V, respectively (Hirakawa and Nosaka, 2002; Beitz et al., 1998). $Cl^\bullet$ is a selective oxidant that reacts with electron-rich moieties through one-electron oxidation, H-abstraction, and addition to unsaturated C–C bonds (Grebel et al., 2010). Moreover, $Cl^\bullet$ can react more strongly with benzoic acid and phenol than can $HO^\bullet$ (Fang et al., 2014). The UV/chlorine AOP is more efficient than the UV/H_2O_2 AOP in the degradation of some emerging contaminants such as benzotriazole, tolytriazole and iopamidole (Sichel et al., 2011) and micropollutants such as trichloroethylene (Wang et al., 2012). However, the effectiveness of the UV/chlorine process in degrading recalcitrant PPCPs is less known. The actions of radicals ($HO^\bullet$, $Cl^\bullet$ and $Cl_2^{\bullet-}$), especially RCS ($Cl^\bullet$ and $Cl_2^{\bullet-}$), on the transformation mechanisms of recalcitrant PPCPs in the UV/chlorine AOP are currently unclear. Moreover, whether or not the attacks by the reactive chlorine species (RCS) in the UV/chlorine process would cause undesirable chlorinated byproducts to form is unknown and demands investigation.

Ibuprofen (IBP), a nonsteroidal anti-inflammatory drug, was chosen as the target recalcitrant PPCP for its resistance to conventional water treatment processes, its frequent occurrence in surface water, and its potential long-term adverse effects (Vieno et al., 2007; Ruggeri et al., 2013). The aims of this study were to (1) evaluate the degradation kinetics of IBP by the UV/chlorine AOP under varied conditions; (2) investigate the relative contributions of the reactive species to the degradation; and (3) evaluate the formation of chlorinated byproducts and reveal the degradation pathways of IBP by the UV/chlorine AOP.

2. Materials and methods

2.1. Chemicals

All solutions were prepared from reagent-grade chemicals and deionized water (18.2 Ω-cm) produced from a Milli-Q water purification system (Millipore, Reference). IBP, sodium hypochlorite solution (NaClO), hydroxyl peroxide (H_2O_2), sodium sulfate (Na_2SO_4), sodium chloride (NaCl) and nitrobenzene (NB) were purchased from Sigma–Aldrich. Sodium sulfite (Na_2SO_3) was purchased from Fluka, and sodium hydroxyl (NaOH), sulfuric acid (H_2SO_4) and bicarbonate ($NaHCO_3$) from VWR BDH Prolabo. Phosphoric acid, methanol, acetonitrile and methyl tert-butylether (MtBE) of HPLC grade were purchased from Fisher Scientific.

The IBP stock solution (7 mM) was prepared by adding the pure compound to deionized water containing 7 mM NaOH and stirring overnight. A free chlorine stock solution (about 2000 mg/L as Cl_2) was diluted from the 4% sodium hypochlorite (NaClO) solution and periodically standardized by DPD/FAS titration (USEPA, 1998). A sodium sulfite solution (20 mM) was prepared weekly. A real drinking water sample was collected after sand filtration from a water treatment plant in Guangzhou, China and stored at 4 °C. The water quality parameters of the sample are shown in Supplementary Information Table S1.

2.2. UV irradiation

Figure S1 shows the schematic diagram of the UV reactor used in this study. A low pressure (LP) UV lamp (Heraeus, GPH 212T5L/4, 10W, 254 nm) in a quartz sleeve was placed in the centerline of a 700 mL cylindrical glass reactor with rapid mixing provided at the bottom of the reactor. A water circulating system kept the inner tank temperature at 25 ± 0.1 °C. The photo flux (I_0) was determined to be 0.44 μE s^{-1} for kinetic tests and 0.62 μE s^{-1} for other tests using iodide-iodate chemical actinometry (Bolton and Linden, 2003). The effective path length (L) was determined to be 3.5 cm by measuring the photolysis rate of H_2O_2 (Garoma and Gurol, 2005). The average UV fluence rate (E_p^0) was determined to be 1.05 mW cm^{-2} for kinetic tests and 1.47 mW cm^{-2} for other tests.

2.3. Experimental procedure

All experiments were carried out in the 700 mL photoreactor described above. The UV lamp and the water circulating system were warmed up at least 30 min before experiments. Experiments were initiated by adding the NaClO stock solution to the UV reactor containing the solution spiked with 10 μM IBP and 2 mM phosphate buffer to give an initial chlorine concentration of 10–100 μM and pH of 6, 7 or 9. Samples (1 mL) were collected at different time intervals, quenched with 20 mM Na_2SO_3 (at a molar ratio of sulfite/chlorine of 1.5) and stored at 4 °C in the dark before HPLC analysis. Another test was conducted in the same manner with the initial H_2O_2 concentration of 100 μM at pH 6. Control tests of IBP degradation by UV direct photolysis and dark chlorination were also conducted in a similar manner but in the absence of chlorine and UV light, respectively.

To identify the degradation intermediates/products and quantify the concentrations of total organic chlorine (TOCl) and disinfection by-products (DBPs) during IBP degradation by the UV/chlorine AOP, higher initial concentrations of IBP (50 μM) and chlorine (200 μM) were used. After a certain reaction time (1, 2, 5, 15 or 30 min) in each run, the reaction was quenched with 100 mM Na_2SO_3 and a 400 mL sample was collected and subjected to the pretreatment procedure (Text S1) developed by Zhai and Zhang (2009) for UPLC/ESI-tqMS and UPLC/ESI-QTOF-MS analyses. Additional tests at pH 0 were conducted following the same procedure but with the pH of the reaction mixture adjusted to zero using 95% H_2SO_4 prior to adding the NaClO stock solution to the reactor.

2.4. Analytical methods

Concentrations of IBP and NB were measured using a high performance liquid chromatography (HPLC) system (Agilent Technologies 1260 Series) equipped with a Waters symmetry C18