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Investigation of clofibric acid removal by UV/persulfate and UV/chlorine processes: Kinetics and formation of disinfection byproducts during subsequent chlor(am)ination

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ABSTRACT

This study investigated the UV/persulfate (UV/PS) and UV/chlorine processes as alternative method for the removal of clofibric acid (CA). The formation of disinfection byproducts (DBPs) during subsequent chlor(am)ination was also evaluated. The degradation of CA followed the pseudo-first order kinetics. The second-order rate constants of CA with $SO4^{\cdot -}$, $OH^{\cdot}$ and $Cl^{\cdot}$ were respectively determined as $k_{SO4^{\cdot -},CA} = (1.73 \pm 0.01) \times 10^9\ M^{-1}\ s^{-1}$, $k_{OH^{\cdot},CA} = (2.72 \pm 0.08) \times 10^9\ M^{-1}\ s^{-1}$ and $k_{Cl^{\cdot},CA} = (9.76 \pm 0.15) \times 10^{10}\ M^{-1}\ s^{-1}$. The degradation rate constant increased with increasing oxidant dosage in UV/PS and UV/chlorine processes. The degradation rate constant was found to be the highest at pH 9 and decreased dramatically at pH 11 in UV/PS process. For UV/chlorine, the rate constant continuously decreased with increasing pH from 3 to 11. Presence of HCO_3^- and Cl^- had different effects (promotion and/or inhibition) on CA degradation in both processes. An inhibition effect was observed in the presence of NOM for the two UV-based processes. The higher CA removal in real water suggested the two processes were suitable for treating water containing CA, and the UV/chlorine was more cost-effective than UV/PS based on the total cost of electrical energy. Compared with the chlor(am)ination of CA, the UV/PS and UV/chlorine pre-oxidation significantly impacted the DBP formation during subsequent chlor(am)ination, which indicated the application of the two UV-based processes needs to be carefully balanced against the downstream effect on DBP formation.

1. Introduction

Pharmaceuticals, like lipid regulators (LRs), are frequently used in large quantities for therapeutic purposes of treating angiocardiopathy problem (e.g., high blood pressure, coronary heart disease and arrhythmia) [1,2]. The common LRs included clofibrate, etofibrate and etofylline clofibrate. Clofibric acid (CA), as the active metabolite of clofibrate and other widely used LRs, has been detected repeatedly in the aquatic environment [3,4]. Unfortunately, the biodegradation of CA in wastewater treatment plant (WWTP) is limited due to the complex structure of CA and its intermediates [5]. Therefore, significantly irreversible adversity (e.g., the resistance of bacteria and the adverse change of current ecological system) might be induced because of its accumulation in real water environment, and hence further threatening the human health [2,6,7]. As a result, it is urgent need to develop effective treatment methods to remove CA in order to avoid the potential risk to water ecosystem and human health.

Various chemical oxidation and advanced oxidation processes (AOPs), including ozonation [8], UV/H_2O_2 process [2,9], electro-Fenton process [10] and photoelectron-Fenton process [10,11], were effective for the elimination of CA in aqueous medium. Among these AOPs, the UV/H_2O_2 process has been extensively studied and applied in the advanced treatment of drinking water and wastewater. This process mainly relies on the formation of highly reactive and non-selective $HO^{\cdot}$ which can be promptly generated from H_2O_2 by absorbing UV irradiation to oxidize a wide range of organic compounds [2,12]. More recently, UV/persulfate (PS, $S_2O_8^{2-}$) process has attracted significant scientific interest for the degradation of pharmaceutical through the production of sulfate radical ($SO_4^{\cdot -}$) [13,14]. Compared to the non-selective $OH^{\cdot}$ (1.8–2.8 V), $SO_4^{\cdot -}$ has a higher oxidizing power (2.5–3.1 V) and reacts with organic compounds via selective electron-transfer reactions [15]. Another AOP, the UV/chlorine process, is an emerging alternative to the UV/H_2O_2 system for the degradation of micropollutants [16,17]. It produces $HO^{\cdot}$ and reactive chlorine species

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(RCS) such as chlorine atoms ($Cl^{\cdot}$) and $Cl_2^{\cdot -}$ [16]. Also this process is found to be more efficient in generating RCS at acidic and neutral pH [18]. To date, less information is available to describe the degradation performance of CA by UV/PS, and there is no report about the use of UV/chlorine as AOP for CA removal.

In addition, in drinking water treatment processes (DWTPs), the pharmaceutical can potentially react with subsequent disinfectants (e.g. chlorine or chloramine) to form disinfection byproducts (DBPs) of health concern [19,20], such as halomethanes (HMs), haloacetic acids (HAAs) and N-nitrosodimethylamine (NDMA). The DBP formation of post-chlor(am)ination is related with the physicochemical properties of pharmaceutical and the poor treatability within WTP using traditional coagulation-sedimentation-filtration. Recently, some researchers began to investigate the impact of UV activated pre-oxidation process on DBP formation from the subsequent chlor(am)ination of pharmaceuticals. A study by Chu's group found chloroform and dichloroacetamide were formed during chlorination of chloramphenicols (CAPs), and their formation by post-chlorination were obviously increased and decreased by the pre-oxidation with UV/PS AOP [21,22]. They also found that UV/PS pre-oxidation slightly increased the formation of dichloroacetonitrile (DCAN) form CAP during chloramination [23]. However, little is known about how UV/PS pre-oxidation affect the formation of DBP from common pharmaceutical CA during downstream disinfection with chlor(am)ination. Another study indicated that UV/chlorine treatment slightly enhanced the DBP formation potential of chloral hydrate, haloketone and trichloronitromethane (TCNM) but reduced the formation of haloacetonitrile (HAN) during the post-chlorination because of molecular alteration of pharmaceuticals precursors [24]. To the best of our knowledge, limited reports have focused on the impact of UV/chlorine pre-oxidation on chlorinated DBP formation from CA, and especially, no information is available concerning the formation of DBP treated by UV/chlorine and subsequent chloramination.

The objective of the present study was to investigate and compare the degradation kinetics of CA by UV/PS and UV/chlorine AOP under varied conditions. Also the reaction rate constants and roles of reactive radicals were systematically investigated. Furthermore, when the two AOPs are used to decompose CA, many intermediate products will be simultaneously generated, which is likely to result in the changes in the speciation and quantities of DBP formed upon subsequent chlor(am)ination. Hence another objective of this study was to explore the impacts of two UV-AOP pre-treatment on the formation of DBP during subsequent chlor(am)ination of CA.

2. Materials and methods

2.1. Chemicals and reagents

CA (98%), sodium persulfate (99%), sodium bicarbonate ($NaHCO_3$, > 99.5%), sodium chloride (NaCl, > 99%), humic acid (HA, Cat. No. H108498) and sodium hypochlorite (NaClO, available chlorine 5%) were obtained from Aladdin Industrial Corporation (Shanghai, China). Benzoic acid (BA, > 99%), tertiary butanol (TBA, > 99.5%), nitrobenzene (NB, > 99%), ammonium chloride (NH_4Cl), sodium phosphate (Na_2HPO_4) and monobasic sodium phosphate (NaH_2PO_4) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Standard solutions of selected DBPs including HMs, HANs and halonitromethanes (HNMs) were obtained from Sigma-Aldrich (St Louis, Missouri, USA). All other reagents were of at least analytical grade and used without further purification. Ultrapure water was prepared using a Milli-Q Gradient water purification system (Millipore, Reference), and was used for preparing solution. Chlorine stock solutions (100 mM as Cl_2) were prepared by dilution of a 5% NaClO solution, which was standardized by a portable photometer (HACH, USA) daily before usage. The preparation steps of monochloramine (NH_2Cl) solution were carried out according to the method reported by Chu et al. [23].

2.2. Experimental procedure

A quasi collimated beam apparatus equipped with a 40 W low-pressure mercury lamp (254 nm, GPH 843T5 1/4 L) above quiescently stirred Petri dishes was employed for the UV/PS and UV/chlorine batch treatment tests. The UV lamp was warmed up at least 30 min before experiments. A calibration of the UV irradiance was simultaneously conducted according to the methods reported by Bolton and Linden [25]. UV irradiance used in this study was 0.1 mW cm^{-2} after calibration. For kinetic experiments, a 100 mL reaction solution containing 46.6 μM CA and 2 mM phosphate buffer was dosed with the PS (or chlorine) stock solution to achieve an initial PS (or chlorine) concentration of 0.25–1.0 mM and simultaneously exposed to UV irradiation. Samples were withdrawn at a specific time and quenched by ethanol (for PS termination) or sodium thiosulfate (for chlorine termination) before HPLC analysis. In present study, the solution pH, unless stated otherwise, was adjusted using 0.1 M H_2SO_4 or NaOH. Control tests of CA degradation by UV direct photolysis, PS oxidation alone and dark chlorination were also conducted in a similar manner, respectively.

To evaluate the impacts of the UV/PS and UV/chlorine pretreatments on subsequent chlor(am)ination DBP formation, an aliquot of Cl_2 or NH_2Cl was added to the treated samples after 60 min UV/PS or UV/chlorine treatment. The initial concentration of CA was 46.6 μM in each experiment and Cl_2 or NH_2Cl was dosed at a molar ratio (Cl_2 or NH_2Cl/CA molar concentration) of 20 in order to achieve enough residual chlorine or chloramine. For the sample treated by UV/chlorine AOP, additional chlorine was added considering the photolysis of chlorine, and the amount of free chlorine was in accordance with the molar ratio of disinfection dosage. In this study, chlorination or chloramination tests were performed in 40 mL brown glass volumetric bottles under headspace-free conditions in the dark at a controlled temperature (21.0 ± 0.5 °C). The reaction solution was buffered at 7.0 ± 0.2 (phosphate buffer). Chlor(am)ination proceeded for 24 h, before the disinfectant residual was quenched with a stoichiometric amount of ascorbic acid and subjected to DBP analysis [23]. All the experiments were conducted with at least duplicate measures, and the error bars in all the figures encompass the range for two replicate. The following formula was applied to calculate the DBP yield which is defined as the molar ratio of the produced DBP to the initial CA (Eq. (1)).

$$\text{DBP yield (\%)} = \frac{\text{Formed DBP molar concentration}}{\text{Initial CA molar concentration}} \times 100 \quad (1)$$

2.3. Analytical methods

Free chlorine and total chlorine concentration were quantitatively determined by the N, N-diethyl-p-phenylene diamine (DPD) colorimetric method [26]. Monochloramine was measured using the MonochlorF reagent (HACH, USA). The concentrations of CA were determined by high-performance liquid chromatography (HPLC) system (Shimadzu, Japan) equipped with a Shim-pack C_{18} column (250 mm × 4.6 mm, 5 μm), and a UV detector with the wavelength set at 230 nm. The mobile phase consisted of 60/40% (V/V) acetonitrile and 0.1% formic acid. Sample injection volumes were 20 μL with a flow rate of 1.0 mL min^{-1}. Solution pH was measured with a pH meter (Thermo Orion Co., 720A). Analysis of DBP concentrations, including HMs, HANs and HNMs were analyzed with a purge trap sample concentrator (eclipse4660, OI, USA) and gas chromatograph/mass spectrometry (QP2010, Shimadzu, Japan), based on US EPA method 524.2 [27]. The following details for DBPs analyses are available elsewhere [28]. The detection limit of the method was below 0.1 μg L^{-1}.