Chemical Engineering Journal 331 (2018) 809–817

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

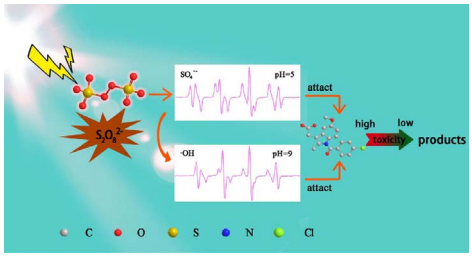
Removal of indomethacin using UV–vis/peroxydisulfate: Kinetics, toxicity, and transformation pathways

Ruobai Li[a], Jing Kong[a], Haijin Liu[b], Ping Chen[a], Yuehan Su[a], Guoguang Liu[a,*], Wenying Lv[a]

[a] School of Environmental Science and Engineering, Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou 510006, China

[b] School of Environment, Henan Normal University, Henan Key Laboratory for Environmental Pollution Control, Xinxiang 453007, China

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
UV–vis/peroxydisulfate
Sulfate radicals
ESR
Toxicity
Transformation pathway
Indomethacin

ABSTRACT

The extensive production and use of non-steroidal anti-inflammatory drugs (NSAIDs) has increased the volume of downstream residues that contaminate the environment, which pose great threats to ecosystems and human health. The decomposition of peroxydisulfate (PDS), which is activated by UV–vis to produce a potent oxidizing sulfate radical, comprises a new type of advanced oxidation technology. The degradation of indomethacin (IM) by the UV–vis activation of peroxydisulfate was investigated. The results demonstrated that IM degradation followed pseudo-first-order reaction kinetics. UV–vis irradiation led to the direct albeit slight photolysis of IM, whereas the addition of an oxidant significantly enhanced the removal efficiency. The IM degradation efficiency was increased when the pH was elevated from 5 to 7; however, the elimination of IM was reduced when the pH was elevated from 7 to 9 due to the conversion of $SO_4^{\cdot -}$ to $HO^{\cdot}$. A low concentration of Cl^- had a dual effect, while a high concentration led to a dramatic inhibitory effect. Fulvic acid (SRFA) inhibited the decomposition of IM through the light screening effect and the quenching of radicals. A quenching experiment revealed that $SO_4^{\cdot -}$ was the primary free radical, which is confirmed by electron spin resonance spectroscopy. The second-order rate constants of IM and $SO_4^{\cdot -}$ were also determined. The luminescent bacteria *Vibrio fischeri* was selected to assess the toxicity of the transformation products, which was further confirmed by quantitative structure-active relationship analysis. The cleavage of the bond between C on the benzene ring and N on the indole group, the hydroxylation of the benzene ring, and the decarboxylation of the aliphatic chain were the main pathways for the degradation of IM in the UV–vis/peroxydisulfate system.

1. Introduction

As an emerging class of environmental pollutants, pharmaceutical and personal care products (PPCPs) have attracted increasing attention due to their adverse effects on human health and ambient ecosystems [1]. Non-steroidal anti-inflammatory drugs (NSAIDs), as an important

* Corresponding author.
E-mail address: liugg615@163.com (G. Liu).

http://dx.doi.org/10.1016/j.cej.2017.09.025
Received 19 July 2017; Received in revised form 20 August 2017; Accepted 3 September 2017
Available online 07 September 2017

class of PPCPs, are widely used as an antipyretic and analgesic. NSAIDs are often detected in the effluent of sewage treatment plants, and their concentrations in surface water can attain even ng L^{-1} to μg L^{-1} levels [2]. This means that NSAIDs in sewage treatment plants are likely not completely removed, and are ultimately discharged into the ambient environment, which poses a significant threat to ecosystems. Therefore, the development of new technologies to avoid the permeation of NSAIDs into the environment is critical.

Advanced oxidation processes (AOPs) have shown to be promising and competitive technologies for the destruction of recalcitrant biodegradable organic compounds. AOPs are derived from a combination of technologies that generate highly oxidative species such as UV/H_2O_2, UV/O_3, UV/TiO_2, Fenton and electrochemical oxidation technologies [3–8]. Advanced oxidation based on sulfate radicals may be an alternative to traditional advanced oxidation techniques. Sulfate radicals can be readily generated through the thermal [9], transition metal (i.e., Fe^{2+}, Co^{2+}) [10–12], ultrasound irradiation [13], electrochemical process [14] and UV-light mediated decomposition of Peroxydisulfate (PDS) and peroxymonosulfate (PMS) [15,16]. The combination of persulfate with photocatalysis and metal-free catalysis for the generation of reactive radicals has also been reported [17–20]. The sulfate radicals ($SO_4^{\cdot -}$) can rapidly react with most organic and inorganic substances due to its high redox potential of (E° ($SO_4^{\cdot -}/SO_4^{2-}$) = 2.5–3.1 V), which is comparable to $HO^\cdot$ (E° ($HO^\cdot/H_2O$) = 1.9–2.7 V). The second-order reaction rate constant is in the range of from 10^7 to 10^{10} M^{-1} s^{-1} [21]. Similar to $HO^\cdot$, $SO_4^{\cdot -}$ may participate in reactions by three different routes: electron transfer, the addition of unsaturated double bonds, and hydrogen evolution reactions [22,23]. However, $SO_4^{\cdot -}$ is believed to be more selective than $HO^\cdot$ through single electron transfer [24]. Although $SO_4^{\cdot -}$ oxidation is more selective, most of the intermediates formed by the aromatic compounds that react with sulfate radicals are hydroxylated products, which are akin in performance to hydroxyl radicals [25,26].

Recent studies on PDS or PMS activation have focused on transition metal ion-mediated processes .Transition metal iron such as Co^{2+} or Cu^{2+} were found to be effective in activating $SO_4^{\cdot -}$ generation from PDS for contaminant degradation. Although heterogeneous oxide-mediated activators may reduce the population of harmful metal ions that reside in treated water [27,28], concerns arise from release of toxic metal ions. The adverse effects of residual metal ions on of human health are supposed to be properly assessed. In UV–vis/PDS processes, sulfate radicals are generated via the cleavage of peroxidic bonds without the involvement of mental ions (Eq. (1)). The combination of UV–vis and PDS or PMS to form an active oxidizing species is considered to be an environmentally compatible and feasible way [29]. Product identification combined with determination such as toxicity and total organic carbon (TOC) can be a complement to evaluate the overall efficiency of the treatment processes.

$$PMS/PDS \xrightarrow{hv} SO_4^{\cdot -} \quad (1)$$

Considering that IM is frequently detected in the aquatic environment, the core objectives of this paper are as follows: (1) Investigate the kinetics of IM degradation in the UV–vis/PDS system under different operating conditions; (2) Determine the second-order rate constant of IM with $SO_4^{\cdot -}$ through competitive kinetics; (3) Detect the radical species at different pH values through ESR; (4) Identify the reaction intermediates using mass spectrometry to investigate the IM conversion pathway by $SO_4^{\cdot -}$ oxidation.

2. Materials and methods

2.1. Chemicals

Indomethacin (IM, > 98%), benzoicacid (BA, ≥99%), and fulvic acid (SRFA, ≥90%) were purchased from Aladdin Industrial Corporation (Shanghai), potassium peroxydisulfate (PDS > 99%) was obtained from the reagent company, Sinopharm Chemical Reagent (Shanghai, China); dimethyl pyridine N-oxide (DMPO) was purchased from Sigma-Aldrich; sodium chloride, sodium thiosulfate, sodium hydroxide, ethanol, and tert-butyl alcohol, were purchased from Chengdu Kelon Reagent Co., Ltd.. All of the reagents listed above were of analytical grade and required no further purification. The acetonitrile purchased from Anaqua Chemicals Supply Co. Ltd. (USA) was of HPLC grade. Ultrapure water of 18.25 MΩ/cm from a Milli-Q apparatus (Smart2 Pure ultrapure water system integration, TKA, Germany) was employed in the preparation of all aqueous solutions.

2.2. Experimental procedures

A 600 mL sealed cylindrical borosilicate glass reactor equipped with a 350W Xenon lamp was used to conduct the photochemical experiments (Fig. S1). A 500 mL solution of IM (0.02 mM) was added to the reactor. The photo-reactor was water cooled such that the reaction temperature was maintained at 25 ± 2 °C. The pH of solution was adjusted with 0.01 mM H_2SO_4 and NaOH. The effects of Cl^- (0–10 mM) and SRFA (0–10 mg C L^{-1}) were investigated to evaluate the effects of typical natural water constituents on the oxidation of IM. The Xenon lamp was turned on and the reaction was initiated, once an appropriate quantity of peroxydisulfate was added. Most of the experiments were performed in triplicate to assure accurate data acquisition and the error bars in the figures represent standard deviations.

2.3. Analytical methods

2.3.1. HPLC and TOC analysis

Liquid samples were periodically extracted and analyzed. The IM was quantified by an Agilent 1100 series HPLC (Agilent, USA) system equipped with a diode array detector (SPD-M20A). The column was a Chromolith Performance XDB-C18 column (150 × 2.1 mm, 5 μm), and the injection volume was 4 μL. The mobile phase was a mixture of acetonitrile and 5 mM ammonium acetate in water (65:35, v/v) at a flow rate of 0.2 mL/min. under isocratic conditions, and the UV wavelength for detection was 228 nm. Total organic carbon (TOC) was measured using a TOC-VCPH analyzer (Shimadzu, Japan).

2.3.2. Identification of transformation products

The identification of the intermediate products was carried out using liquid chromatography with tandem mass spectrometry (HPLC–MS/MS), equipped with a Hypersil ODS column (250 × 4.6 mm, 5 μm). Full scans and product ion scans were conducted in order to determine the quasi-molecular ions, and elucidate the structures of major transformation products. Detailed operational conditions are presented in the Supplementary data, Text S1.

2.3.3. Toxicity analysis

The acute toxicity assay was carried out against *Vibrio fischeri* (*V. fischeri*) according to the Water Quality-Determination of the Acute Toxicity-Luminescent Bacteria Test (GB/T15441-1995). The QSAR analysis calculated by the Ecological Structure-Activity Relationship Model-ECOSAR program (ECOSAR, 2013) was conducted in order to predict the acute and chronic toxicities of IM and its transformation by-products to fish, Daphnia, and green algae [30]. Detailed information is provided in Text S2.

2.3.4. ESR measurements

The electron spin resonance (ESR) signals of DMPO spin-trapped radicals were measured to detect $SO_4^{\cdot -}$ and $HO^\cdot$ using a Bruker model ESR JES-FA200 spectrometer.

2.3.5. Determination of the light screening factor (S_λ)

The light screening factor (S_λ) of SRFA was calculated according to