



Degradation of ketoprofen by sulfate radical-based advanced oxidation processes: Kinetics, mechanisms, and effects of natural water matrices



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HIGHLIGHTS

- Effective oxidation of KET was achieved by heat-activated persulfate.
- Natural water matrix significantly affected KET degradation.
- $\text{SO}_4^{\cdot-}$ plays dominant role in oxidizing KET.
- KET and its intermediates were finally mineralized to CO_2 and H_2O in PS oxidation system.

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ABSTRACT

Ketoprofen (KET) is a mostly used nonsteroidal anti-inflammatory drug that has been frequently detected in wastewater effluents and surface waters. In this study, we investigated the degradation of KET by sulfate radical ($\text{SO}_4^{\cdot-}$) based advanced oxidation processes (SR-AOPs) in aqueous solution. The degradation kinetics, mechanisms, and effects of natural water matrices on thermally activated persulfate (TAP) oxidation of KET were systematically investigated. Increasing the temperature and persulfate (PS) concentrations greatly enhanced the degradation of KET. KET degradation is pH-dependent with an optimum pH of 5.0. Reactions in the presence of radical quenchers revealed the dominant role of $\text{SO}_4^{\cdot-}$ in oxidizing KET. Water matrix significantly influenced the degradation of KET. The common inorganic anions present in natural waters exhibited inhibitory effect on KET degradation, and the inhibition followed the order of $\text{Cl}^- > \text{CO}_3^{2-} > \text{HCO}_3^- > \text{NO}_3^-$; however, no significant inhibition of KET degradation was observed in the presence of Ca^{2+} and Mg^{2+} cations. The presence of natural organic matter (NOM) suppressed KET degradation, and the suppression increased as NOM concentration increase. Products identification and mineralization experiments revealed that KET and its degradation intermediates were finally transformed into CO_2 and H_2O . The results of this study indicated that applying SR-AOPs for the remediation of KET contaminated water matrix is technically possible.

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1. Introduction

Pharmaceutical pollutants in the environment have received more attention due to their potential to cause adverse environmental and human health effects, so that their treatments have been addressed in many studies (Daughton and Ternes, 1999; Esplugas et al., 2007; Boxall et al., 2012). Nonsteroidal anti-

inflammatory drugs (NSAIDs) are an important group of pharmaceuticals, which have anti-inflammatory, analgesic and antipyretic activities. Because wastewater treatment plants (WWTP) are unable to effectively remove these pharmaceutical pollutants, these compounds are frequently detected in aquatic environment (Petrovic et al., 2005; Luo et al., 2014; Manzo et al., 2014).

Ketoprofen (2-(3-benzoylphenyl)-propanoic acid, KET) is one of the most commonly used NSAIDs, which has been extensively used for the treatment of pain, fever, and inflammation, and frequently detected in wastewater effluents and surface waters with concentrations ranging from ng L^{-1} up to $\mu\text{g L}^{-1}$ (Tixier et al., 2003; Kosjek

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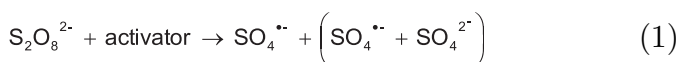
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et al., 2005). The potential negative effects, such as endocrine disrupting effect and oxidative stress of KET have been demonstrated in previous studies (Diniz et al., 2015; Ezechias et al., 2016). Because KET cannot be effectively removed by the conventional WWTP process, it is needed to develop cost-effective and environmental-friendly treatment techniques to eliminate the contamination of KET.

Advanced oxidation processes (AOPs), with the highly reactive hydroxyl or sulfate radicals as the main oxidative species, are promising for elimination of pharmaceutical pollutants in aquatic environment as it has been recently demonstrated (Huber et al., 2003; Klavarioti et al., 2009; Fatta-Kassinos et al., 2011). Compared to hydroxyl radical (HO•) based AOPs, sulfate radical (SO₄^{•-}) based AOPs offer several advantages (Waldemer et al., 2007). The standard reduction potential of SO₄^{•-} (E° = 2.5–3.1 V) is almost similar to that of HO• (E° = 1.9–2.7 V) (Zhang et al., 2015), so that SO₄^{•-} can act as a powerful oxidant to degrade organic contaminants. In addition, SO₄^{•-} is more stable and selective than HO• because SO₄^{•-} mainly reacts with organic compounds through electron transfer mechanism (Neta et al., 1977). It has been demonstrated that the consumption of SO₄^{•-} by non-target water constituents (e.g., natural organic matter) is much lower than that of HO•, which means that SO₄^{•-} based AOPs may be more efficient than HO• based AOPs in natural water matrices (Ghauch and Tuqan, 2012; Lutze et al., 2015).

Recently, SO₄^{•-}-based *in-situ* chemical oxidation (ISCO) technology has also received attention for water or soil remediation due to its high stability, high efficiency, and relatively low cost (Zhao et al., 2013; Monteagudo et al., 2015). SO₄^{•-} can be formed by activation of persulfate (PS) or peroxymonosulfate (PMS) by various approaches including heat (Johnson et al., 2008), UV (Monteagudo et al., 2015; Ghauch et al., 2017), transit-metal cations or metal oxides (Anipsitakis and Dionysiou, 2004; Ghauch et al., 2013; Ayoub and Ghauch, 2014; Naim and Ghauch, 2016), base (Furman et al., 2010), and carbon nanomaterials (Duan et al., 2015), as shown in Eq (1) (Matzek and Carter, 2016).



Among these activation methods, heat activation is particularly attractive for the treatment of emerging contaminants. Two sulfate radicals are produced through scission of the peroxide bond of persulfate with absorption of heat energy. The rate constant of sulfate radical formation ranges from $1 \times 10^{-7} \text{ s}^{-1}$ to $5.7 \times 10^{-5} \text{ s}^{-1}$ at temperature ranging from 25 °C to 70 °C (Liang et al., 2008a). Therefore, heat activation is a good method to achieve high efficiency of SO₄^{•-} formation. In addition, due to the simplicity of the system, thermally activated persulfate (TAP) can be employed to study the reaction mechanism between contaminants and SO₄^{•-}. Moreover, heat activated persulfate based ISCO technology can combine with the *in situ* thermal remediation (ISTR) technology to develop a promising *in situ* remediation method (Waldemer et al., 2007). To date, heat activated persulfate has been applied to decompose the recalcitrant contaminants, including chlorinated ethenes (Waldemer et al., 2007), naphthenic acids (Xu et al., 2016), herbicide (Ji et al., 2015a), as well as pharmaceuticals (Ghauch et al., 2012, 2015; Deng et al., 2013; Ji et al., 2015b; Gao et al., 2016; Ji et al., 2016).

In this study, in order to develop a reliable method to treat NSAIDs contaminated water, the degradation of KET was investigated using heat activated persulfate. A series of kinetic experiments were conducted to explore the effects of various factors including PS dosage, temperature, pH, natural organic matter, cations and anions. Liquid chromatography–tandem mass

spectrometry (LC–MS/MS) was used to identify the degradation intermediates. Detailed degradation mechanisms and transformation pathways for KET via TAP oxidation was proposed. Particularly, KET degradation efficiency in different natural water matrices was examined to evaluate the technical feasibility of heat-activated PS oxidation process on the treatment of KET contaminated water.

2. Materials and methods

2.1. Chemicals

KET (≥98%) was purchased from TCI Reagent Co. Ltd (Shanghai, China). Potassium persulfate (K₂S₂O₈, 99.5%) and humic acid used as a representative of natural organic matter (NOM, 90%) were obtained from Aladdin Chemistry Co. Ltd (Shanghai, China). Acetonitrile, methanol, and formic acid of HPLC grade were purchased from TEDIA (Fairfield, USA). Ethanol (EtOH) and tertiary butanol (TBA) in analytical grade were obtained from Guangzhou Chemical Reagent Factory (Guangzhou, China). Deionized (DI) water prepared from a Milli-pore Milli-Q system (>18 mΩ cm) was used for solution preparation. The stock solution (10 mM) of KET was respectively prepared in HPLC grade acetonitrile and stored at 4 °C.

2.2. Natural water sample collection and preparation

The water samples used in this study were obtained from four water sources: (1) river water was collected from the Pearl River in Guangzhou; (2) municipal wastewater effluent, which was obtained from an activated sludge sewage treatment plant (STP) in Guangzhou; (3) seawater was collected from the South China Sea in Huizhou; (4) the synthetic water, which was prepared using 10 mM phosphate buffer solution (PBS). The collected water samples were taken back to the laboratory within 12 h and stored at 4 °C for further use. Prior to analysis and use, all collected waters were filtered through a 0.45-μm filter to remove particulate matters. The corresponding physicochemical parameters of the water samples were characterized and listed in Table S1, Supplementary Data.

2.3. Experimental setup

2.3.1. Degradation kinetics

For all of the degradation kinetic experiments, 50-mL glass test vials sealed with Teflon-lined silicone septa were used as the batch reactors. Prior to initiate the reactions with the addition of PS, 10 μM of KET solution (20 mL) was introduced to the reactor and pre-heated in a thermostated water bath (Xianou Instrument Manufacture Co., Ltd., Nanjing) for 20 min to allow the solution to reach the desired temperature (40–70 °C). Acetonitrile introduced from the stock solution was dried via gentle nitrogen flow to avoid its effect on the reaction. Because the produced SO₄^{•-} can greatly influence the pH of the solution during thermal activation, PBS buffer was used to control the pH of the reaction solution in the current study. As suggested, the reactivity of phosphate species with SO₄^{•-} and HO• ($k = 1.2\text{--}7.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) is approximately three orders of magnitude lower than that of the organic compounds ($k > 10^9 \text{ M}^{-1} \text{ s}^{-1}$), hence the influence of phosphate species on PS oxidation is negligible (Ghauch et al., 2012). In the current study, the pH at the beginning and by the end of each experiment was almost constant. The effects of typical natural water constituents, including inorganic anions (HCO₃⁻, CO₃²⁻, Cl⁻, and NO₃⁻), cations (Ca²⁺ and Mg²⁺), and HA on heat activated PS oxidation of KET were also investigated. At designated time intervals, reactors were removed from the water bath, chilled in an ice bath for 5 min to

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