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Sono-activated persulfate oxidation of diclofenac: Degradation, kinetics, pathway and contribution of the different radicals involved

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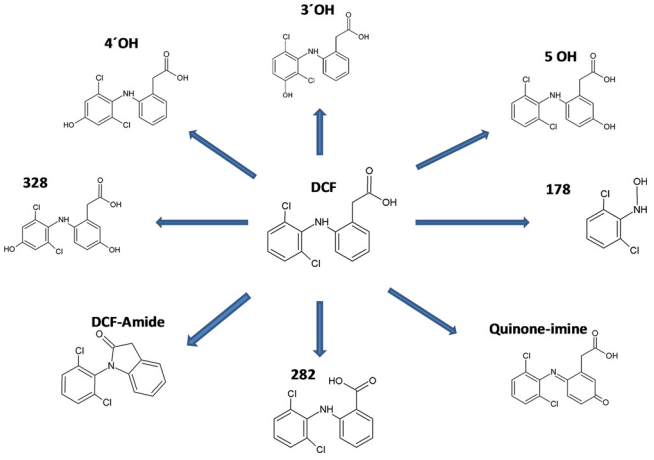
GRAPHICAL ABSTRACT



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ABSTRACT

Degradation of a diclofenac aqueous solution was performed using persulfate anions activated by ultrasound. The objective of this study was to analyze different parameters affecting the diclofenac (DCF) removal reaction by the ultrasonic persulfate (US/PS) process and to evaluate the role played by various intermediate oxidative species such as hydroxyl- and sulfate radicals, superoxide radical anion or singlet oxygen in the removal process as well as to determine a possible reaction pathway. The effects of pH, initial persulfate anion concentration, ultrasonic amplitude and temperature on DCF degradation were examined. Sulfate and hydroxyl radicals were involved in the main reaction pathway of diclofenac. Diclofenac amide and three hydroxy-diclofenac isomers (3´-hydroxy diclofenac, 4´-hydroxy diclofenac and 5-hydroxy diclofenac) were identified as reaction intermediates.

1. Introduction

In the last decades, various persistent pharmaceutical compounds were detected in aquatic environments such as effluents of Waste Water Treatment Plants (WWTPs), surface waters, ground waters or drinking waters [1–4]. These pollutants are very hard to degrade by the conventional activated sludge treatment [5] and may have adverse effects on different organisms [6,7]. Diclofenac (DCF) is one of the most widely

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used drugs in the world and one of the priority pharmaceuticals in the water environment [4,8]. Only between 21 and 40% DCF removal can be reached in WWTPs [9] which suggest the necessity of developing advanced technologies capable of its complete destruction.

Due to its high aqueous solubility, relatively high stability and low cost, persulfate can be used as a source of sulfate radicals ($SO_4\cdot^-$, E_o = 2.6 V) together with hydroxyl radicals (HO·, E_o = 2.8 V) as effective method for treating organic pollutants [10–13]. The conversion of persulfate into $SO_4\cdot^-$ and/or HO· can be achieved by using different activation systems including, heat [14], UV irradiation [15], transitional metals [16], electrochemistry [17], alkalinity [18], and ultrasound [13,19]. Recently, the persulfate-enhanced sonochemical degradation of organic compounds using low frequency ultrasound (20–100 kHz) has received attention [19–23]. However, only few studies have addressed the use of persulfate/ultrasound (US/PS) to degrade pharmaceuticals [1,13].

It is well-known that hydroxyl radicals, HO•, can be generated by treating water with ultrasound, additionally other reactive oxygen species such as $HO_2\cdot$, H· or $O_2\cdot^-$ can be generated [19,24–26]. In addition, persulfate activated with ultrasound generates mainly both HO· and $SO_4\cdot^-$ increasing the degradation efficiency for organic compounds [1,19,27].

With respect to diclofenac degradation, many oxidative treatment processes have been investigated utilising $CoFe_2O_4$ magnetic nanoparticles [29], temperature [2], UV-A/TiO_2 [30,31] and photocatalysis by TiO_2 [32–34], solar photo-Fenton [35,36], UV-C/H_2O_2 [37,38], ozone [39], heterogeneous-$FeCeO_x$ Fenton [40], UV-C/$S_2O_8^{2-}$ [38], single ultrasound [41], ultrasound intensified with TiO_2-SiO_2-SnO_2 [42] or $FeCeO_x$ [43], gamma-irradiation induced degradation [44] and sonoelectrochemical degradation [45]. Only one study used peroxymonosulfate activated by Co(II) [28]. However, to the best of our knowledge, there is no published study available regarding the removal of diclofenac using ultrasound activated persulfate (US/PS).

In this work, the US/PS reaction kinetics and the effect of different parameters such as the amplitude of ultrasound, pH, initial persulfate concentration and temperature were determined. The role which different reactive species (hydroxyl radical, HO·, sulfate radical, $SO_4\cdot^-$, superoxide radical anion, $O_2\cdot^-$, and singlet oxygen, $^1O_2$) play considering the removal of diclofenac in the US/PS system was investigated by scavenging these species using *tert*-butyl alcohol and methanol (HO· and $SO_4\cdot^-$ quenchers), 1,4-benzoquinone ($O_2\cdot^-$ quencher) and sodium azide ($^1O_2$ quencher) [13,46]. Finally, a possible reaction pathway was determined.

2. Experimental

2.1. Materials

Diclofenac sodium salt, $C_{14}H_{10}Cl_2NNaO_2$ (Fig. 1) (99.5%), methanol (99.8%), *tert*-butyl alcohol (99.7%), P-benzoquinone and sodium azide were obtained from Sigma-Aldrich, sodium persulfate ($Na_2S_2O_8$, 98%) was purchased from Panreac, hydrogen peroxide (30% w/v) was obtained from Merck. 5-hydroxy diclofenac (5-OH DCF), diclofenac amide (DCF amide) were bought from Toronto Research Chemicals (Toronto, Ontario, Canada), 3´-hydroxy diclofenac (3-OH DCF) and diclofenac-2,5-quinone imine (DCF quinone) were bought from TLC Pharmaceutical Standards Ltd (Aurora, Ontario, Canada) and ibuprofen D_3 was bought from Sigma-Aldrich (Darmstadt, Germany). All chemicals were used as received without further purification. The pH of the wastewater in each test was adjusted using 1 M PO_4H_3 and NaOH solutions. pH was maintained constant along the reaction by dosing NaOH when it was necessary.

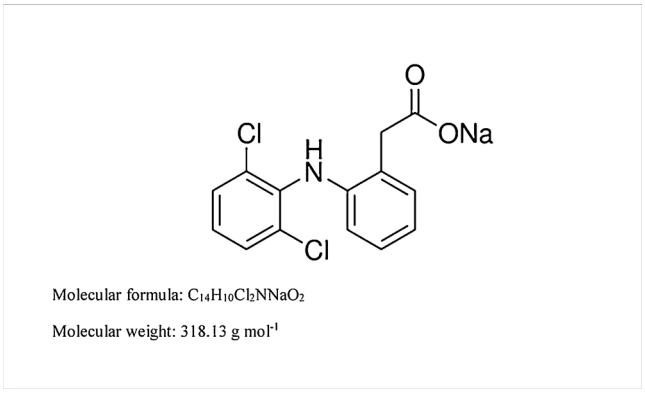

Fig. 1. Structure and properties of diclofenac.

To study the mechanisms of diclofenac removal, concentrations of 5 mg L^{-1} were chosen, mimicking typical production plants effluents and to gain fundamental insight into feasibility for removing diclofenac from municipal wastewater. Before a final decision on treating municipal wastewater is taken, another study should be conducted at much lower realistic concentrations of 1 µg/l (outside the scope of this paper). Total Organic Carbon (TOC) initial concentration was 2.64 mg L^{-1}.

2.2. Experimental runs

Fig. 2 illustrates the scheme of the experimental set-up (More information in Suplementary Material). For the duration of the tests, the samples were periodically taken from the reactor for later determination of the residual concentrations of diclofenac, TOC, H_2O_2 and dissolved O_2. The sampling volume was always below 5% of total volume to minimize the error.

Sulfate and hydroxyl radical scavenging was accomplished using 1 M *tert*-butyl alcohol or methanol ((scavenger/persulfate) molar relationship = 1600) to determine the contributions of the respective radicals on the degradation reaction. To quantify the effects of $O_2\cdot^-$ and $^1O_2$, 2 mM 1,4-benzoquinone and sodium azide ((scavenger/persulfate) molar relationship = 3.2) were used as scavenging agents, respectively. The persulfate/diclofenac molar relationship in this study was 40. The experiments were performed in triplicate to assess reproducibility of the results, and the medium values were used.

2.3. Analysis

Diclofenac concentrations were determined using high-performance liquid chromatography with UV detection (Agilent Technologies 1100 HPLC-UV). The mineralization of diclofenac in the treated wastewater was determined using a TOC analyzer (TOC-5050 Shimadzu, standard deviation < 0.2 mg L^{-1}). The residual $S_2O_8^{2-}$ concentration was measured according to the method of Liang et al. [47]. Residual hydrogen peroxide was determined spectrophotometrically at λ = 410 nm after adding titanium sulfate to form a hydrogen peroxide-Ti complex [48]. Quantification of hydroxyl radicals was carried out by fluorescence measurement using disodium salt of terephthalic acid (NaTA) [49]. The transformation products were identified by using ultra-high performance liquid chromatography coupled to high resolution mass spectrometry (UHPLC-HRMS) (More detailed analysis information in Supplementary material).

3. Results and discussion

3.1. Persulfate alone and combined with ultrasound. Synergistic effect

Fig. 3 compares diclofenac degradation with single ultrasound (US), persulfate alone (PS) and persulfate activated by ultrasound (US/PS). The experimental conditions were the following: ultrasonic amplitude 75% (3.5 W cm^{-2} acoustic intensity), $[DCF]_o$ = 5 mg L^{-1}, $[PS]_o$ = 120 mg L^{-1}, temperature = 30 °C, pH = 6, reaction time = 240 min. As can be seen, the efficiency of diclofenac removal by

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