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Oxidative removal of diclofenac by chlorine dioxide: Reaction kinetics and mechanism

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HIGHLIGHTS

- The reaction kinetics of diclofenac oxidation via ClO_2 was investigated.
- The influences of pH and temperature on reactivities were elucidated.
- Quenching experiments were employed to establish a kinetics model.
- The degradation mechanism involved two tentative routes: ClO_2 oxidation and $O_2^{\cdot}$ oxidation.

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ABSTRACT

Diclofenac (DCF) is one of the most widely used anti-inflammatory drugs, which has been frequently detected in the aquatic environment. In this work, the detailed kinetics and mechanism of DCF degradation via ClO_2 under simulated water disinfection conditions were investigated. Experimental results demonstrated that DCF may be rapidly and completely oxidized with excess ClO_2. The reaction had first-order dependence with respect to DCF and ClO_2, and the largest apparent second-order rate constant, k_{app}, was $1.51(\pm0.017) \times 10^3\ M^{-1}\ s^{-1}$ at pH 7.0. Within the studied pH (5–10) and temperature (278–308 K) ranges, the small variation of k_{app} exhibited very slight pH and temperature dependence. The degradation of DCF was significantly inhibited (36.07(±0.36)%) through the addition of an $O_2^{\cdot-}$ scavenger (chloroform), but not by a $HO^{\cdot}$ scavenger (isopropanol). This indicated that $O_2^{\cdot-}$ played a key role during the DCF removal process. Based the obtained results, a kinetics model for DCF degradation by ClO_2 was established, which involved electron transfer from DCF to ClO_2 molecules to form $DCF^{\cdot}$ and subsequent $O_2^{\cdot-}$ radicals. A tentative mechanism that accounted for the kinetics model was proposed and validated, involving the two major pathways: direct oxidation by ClO_2 and indirect oxidation by $O_2^{\cdot-}$.

1. Introduction

Chlorine dioxide is a powerful one-electron oxidant (E_a = 0.936 V), known for its ability to oxidize organic [1] and inorganic pollutants [2]. ClO_2 is also known for its anti-bacterial [3] and anti-viral properties [4]. It is commonly employed in the pulp and paper industry [5], as well as in water treatment systems [6]. Previous studies have reported the oxidative degradation of several pharmaceutical contaminants via ClO_2 such as estrogenic 17α-ethinylestradiol, antibiotic sulfamethoxazole, roxithromycin, β-lactams and fluoroquinolones [7–9]. As a highly selective oxidant, ClO_2 has the advantages of comparable biocidal efficacy, along with less pH-dependence and the reduced potential of disinfectant by-products formation, in comparison to free chlorine [6,10]. In view of the increasing use of ClO_2 in domestic water treatment, it is of great interest to elucidate the specific reactions of ClO_2 with extensively consumed pharmaceutical drugs, which have been detected in groundwater, as some partially degraded products may be hazardous on release into the ecosystem [11,12].

Diclofenac (DCF, 2-[(2,6-dichlorophenyl) amino] phenylacetic acid), a non-steroidal anti-inflammatory drug, is one of the most frequently detected pharmaceuticals in the effluents emanating

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from hospitals and sewage treatment plants (STPs) [13], as well as in surface waters [14]. Since typically, only 20–30% of DCF loads are removed by conventional STPs, the remainder is subsequently introduced through STP-discharges into ambient surface waters, such as rivers and lakes [15,16]. Over the last several years, various advanced oxidation processes (AOPs) for the degradation of DCF have been studied under diverse experimental conditions, encompassing photocatalysis with TiO_2 [17] or Fenton reagents [18], ozonation [19] and sonolysis, either in isolation or when combined with UV–Vis irradiation in the presence of TiO_2 [20,21]. However, all of these AOPs, except for photo-Fenton processes, typically suffer from high operational costs and the only partial degradation of pharmaceuticals [22], a relatively high concentration of DCF was still detected in STP-effluents and ambient surface waters at level of up to 4.7 and 1.2 $\mu g\ L^{-1}$, respectively [19,23].

Several studies have revealed that the DCF residues in the environment pose threats to both human health and ecosystems. For example, the harmful effects of DCF on different organisms in realistic aquatic environments have been demonstrated [24]. DCF may also cause renal failure in the Indian Gyps vultures and gills alterations in rainbow trout, with these observed effects taking place at concentrations as low as 1 $\mu g\ L^{-1}$ [25,26]. According to Hernando et al. [27], based on the EC_{50} values reported in the literature, DCF may be considered as very toxic to bacteria ($EC_{50} < 1\ mg\ L^{-1}$) and to invertebrates and algae ($EC_{50} = 1–10\ mg\ L^{-1}$). In the year 2000, DCF was included into the EU priority list of compounds that are known to pose a significant risk to aquatic ecosystems [28]. As a result, novel and reactive disinfectant are required for the rapid and complete degradation of DCF during potable water treatment, while producing little or no toxic by-products.

From the foregoing, the structure of the DCF molecule contains phenyl ring, carboxyl and amine moieties and thus is likely to be susceptible to attack by oxidants such as ClO_2. A better understanding of the reaction kinetics and transformation pathways of DCF with ClO_2 will be useful to better predict the fate of DCF in water treatment. Furthermore, the simulation of actual water environments through variations of pH and temperature might ultimately validate the practical application of ClO_2. The primary objectives of this study were to both investigate the reaction kinetics of DCF oxidation and evaluate the influences of initial pH and temperature on this reactivity under simulated water disinfection conditions. A further step was to identify the major transformation pathways and degradation mechanism of the parent compound via quenching experiments, and through the establishment of a kinetics model.

2. Materials and methods

2.1. Standards and reagents

DCF, 2-[(2,6-dichlorophenyl) amino] benzeneacetic acid, sodium salt (98% purity), was purchased from J&K Chemical Co. Ltd. (Beijing, China). Sodium chlorite (90% purity), isopropanol (99.7%, AR) and chloroform (99.5%, AR) were obtained from Tianjin Guangfu Chemical Reagents Co. Ltd. (Tianjin, China). A pure solution of ClO_2 was generated from gaseous ClO_2 by slowly adding dilute H_2SO_4 to a $NaClO_2$ solution. Impurities such as chlorine were removed from the N_2 gas stream by a $NaClO_2$ scrubber and the gaseous ClO_2 was introduced into ultra-pure water and stored in a brown bottle at 4 °C in a dark refrigerator to slow decomposition [29]. Isopropanol and chloroform were used as hydroxyl radical (HO) and superoxide radical ($O_2^{\cdot-}$) scavengers, respectively. High performance liquid chromatography (HPLC)-grade methanol was obtained from Suqian Guoda Chemical Reagents Co. Ltd. (Jiangsu, China). Other employed reagents ($Na_2S_2O_3$, KI, phosphate, etc.) were of analytical grade and used without further purification. 18.2 MΩ cm of ultrapure water (Millipore, USA) was used throughout the experimental procedures and chromatographic analyses.

2.2. Experimental setup

Kinetics experiments involving DCF oxidation by ClO_2 were carried out in 250 mL circulating jacket beaker on a collector-type magnetic stirrer in the dark. To prevent the DCF from auto-oxidation/photolysis, the DCF reaction solution (250 mL) was freshly prepared by spiking 0.25 mL of its stock solution (3.00 mM) to attain a concentration of 3.00 μM. The pH of the tested aqueous solutions was adjusted to the desired level through the addition of either NaOH or phosphoric acid. Preliminary experiments to determine the reaction orders and rate constants were conducted with an initial DCF concentration (3.00 μM), and different volumes of ClO_2 stock solution (20–45 μL) were then added to initiate the reaction.

According to the factorial experiment design, the reactivity as a function of pH (5–10) and temperature (278–308 K) were systematically investigated. At preselected time intervals, 2.00 mL of the reaction liquid was transferred using an Eppendorf pipette, from the jacket beaker to the HPLC vial, which contained 50 μL of preloaded $Na_2S_2O_3$ (0.01 M), to immediately terminate the reaction [30,31]. Samples were further analyzed using HPLC to determine the remaining DCF concentration. All trials were performed in triplicate and mean values were quoted as results. The relative standard deviation (RSD) of three separate measurements was never higher than 20%.

2.3. Analytical methods

The concentrations of the DCF solutions were determined via a reversed-phase HPLC system, which consisted of two Waters 1525 Binary HPLC pumps and Waters 2998 Photodiode Array detector (Waters, Massachusetts, USA). Analytical column temperatures were controlled with a Model 1500 Column Heater (Waters, and product of Singapore). The analytical column was a 150 mm × 4.6 mm Waters C18 column, (particle size 5 μm). A Waters guard column (C18, 4.6 mm × 20 mm, particle size 5 μm) was employed to protect the analytical column (both purchased from Waters) , and the injection volume was 20 μL. The mobile phase was a mixture of 75% HPLC-grade methanol and 25% Milli-Q-water (containing 1% acetic acid) at a constant flow rate of 1.0 mL min^{-1}, with the detection wavelength set at 276 nm.

The high concentration of ClO_2 stock solution was standardized just prior to application by idometric titration with a standard sodium thiosulfate solution [32] and the low concentrations of ClO_2 reaction solutions were determined spectrophotometrically based on the molar absorption coefficient of ClO_2, $\varepsilon_{359\ nm} = 1230\ M^{-1}\ cm^{-1}$ at 359 nm [33]. The pH of the solution was measured using a Mettler Toledo Delta 320 pH, whereas, the reaction temperatures were simultaneously controlled by a HX-08 Cryostat (Shanghai Bilon Instruments Co. Ltd., China).

3. Results and discussion

3.1. Kinetic parameters for DCF-ClO_2 reaction

In the ClO_2 oxidation of organic contaminants, second order kinetics has generally been observed [10,11,34]. However, in some cases, the decay of ClO_2 might follow the mixed-order or second-order kinetics [35,36]. Initially, the experiments were conducted at pH 7.0 and 298 K to determine the rate law of the