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Degradation of Diclofenac by Advanced Oxidation and Reduction Processes: Kinetic Studies, Degradation Pathways and Toxicity Assessments

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ABSTRACT

Many pharmaceutical compounds and metabolites are found in surface and ground waters suggesting their ineffective removal by conventional wastewater treatment technologies. Advanced oxidation/reduction processes (AO/RPs), which utilize free radical reactions to directly degrade chemical contaminants, are alternatives to traditional water treatment. This study reports the absolute rate constants for reaction of diclofenac sodium and model compound (2, 6-dichloraniline) with the two major AO/RP radicals: the hydroxyl radical (•OH) and hydrated electron (e^-_{aq}). The bimolecular reaction rate constants (M^{-1} s^{-1}) for diclofenac for •OH was (9.29 ± 0.11) × 10^9, and for e^-_{aq} was (1.53 ± 0.03) ×10^9. To provide a better understanding of the decomposition of the intermediate radicals produced by hydroxyl radical reactions, transient absorption spectra are observed from 1 − 250 μs. In addition, preliminary degradation mechanisms and major products were elucidated using ^{60}Co γ-irradiation and LC-MS. The toxicity of products was evaluated using luminescent bacteria. These data are required for both evaluating the potential use of AO/RPs for the destruction of these compounds and for studies of their fate and transport in surface waters where radical chemistry may be important in assessing their lifetime.

1. Introduction

There is a rising concern with the occurrence and persistence of Pharmaceutical and Personal Care Products (PPCPs) in the aquatic environment, due to their potential impacts on the aqueous ecosystems and human health (Kumar and Xagoraraki 2010, Schwarzenbach et al. 2006). The worldwide consumption of medicines provides a continuous release of these substances or their metabolites to the environment. Conventional wastewater treatment systems such as filtration and activated sludge do not efficiently remove these PPCPs (Behera et al. 2011, Matamoros et al. 2009) and as a result they have been found in a wide range of environmental samples including surface water, groundwater and drinking water (Benotti et al. 2009, Kim et al. 2007, Kolpin et al. 2002, Makris and Snyder 2010). Therefore, advanced treatment technologies need to be evaluated and eventually employed (Yang et al. 2011), that are capable of either the complete removal of these chemicals from wastewater or at the very least the destruction of their biological activity (Snyder et al. 2003).

Recently studies indicate that the nanofiltration and reverse osmosis processes guarantee the rejection of PPCPs

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(Radjenovic et al. 2008). However, biofouling of membrane elements and disposal of retentate are considered major problems in these processes (Ben Abdelmelek et al. 2011, Snyder et al. 2007, Wintgens et al. 2006). Ozonation can destroy some of PPCPs in raw and/or clarified water; unfortunately, the competition between the PPCPs and organic material in the raw water may lead to rapid depletion of ozone, resulting in incomplete oxidation of PPCPs (Ikehata et al. 2006, Wert et al. 2009), in some cases, more toxic byproducts formed(Aguinaco et al. 2012). Formation of carcinogenic bromate ion is also a general concern during ozone water treatment where bromide ion is present in the water (von Gunten 2003).

Advanced oxidation/reduction processes (AO/RPs) are alternatives to traditional treatment and have recently received considerable attention for PPCPs removal. The formation of oxidizing hydroxyl radicals (•OH) and the reducing hydrated electrons (e^-_{aq}), can be utilized in the destruction of organic pollutants present in drinking or wastewater (Deng and Ezyske 2011). They are effective in the treatment of a variety of anthropogenic pollutants including PPCPs (Deng 2009, Li et al. 2012, Song et al. 2009). However, to provide a fundamental understanding of the applicability of these processes to degrade PPCPs, it is necessary to determine the bimolecular reaction rate constants, the reaction efficiency and degradation mechanisms, as well as the toxicity of the degradation products.

This study focused on diclofenac, a common non-steroidal anti-inflammatory drug (NSAID). It is often found as a persistent toxic waste and one of the most widely available drugs in the world. Approximately hundreds of tons of this prescription drug is sold annually worldwide (Buser et al. 1998). The average concentrations detected are in the low μg L^{-1} range in influents and effluents of municipal sewage treatment plants and surface waters in Austria, Pakistan, Germany and the United States (Al-Rifai et al. 2007, Kolpin et al. 2002, Scheurell et al. 2009, Stülten et al. 2008). Even at very low concentrations there are adverse effects in different organisms. In the livers, kidneys and gills of rainbow trout, the lowest observed effect concentration for cytopathology occurred at 1 μg L^{-1} (Triebskorn et al. 2004). An ecological effect resulted from diclofenac residues which caused the vulture population decline in Pakistan (Oaks et al. 2004). Therefore, it is critical to develop a fundamental understanding of the fate and oxidative and reductive degradation of diclofenac during treatment processes.

The objective of this study was to establish the absolute bimolecular reaction rate constants for reaction of the •OH and the hydrated electron (e^-_{aq}) with diclofenac in aqueous solution. Transient spectra from the reaction with the •OH were recorded from 1 – 250 μs to provide a better understanding of the nature of the radical intermediate species. Detailed studies of degradation pathways of diclofenac using steady-state ^{60}Co γ-irradiation were undertaken, and these suggest that •OH addition to the benzene ring and hydrated electron reduction of chlorine are responsible for a significant fraction of the observed degradation. Advanced reduction process more likely remove toxicity than the advanced oxidation processes.

2. Materials and Methods

2.1. Materials

Diclofenac, 2, 6-dichloraniline and catalase (bovine liver) were purchased from Sigma-Aldrich and used without any further purification. Methanol, 2-propanol, and acetic acid (Fisher Science) were of HPLC grade. All solutions were prepared in 5.0 mM phosphate buffer and adjusted to pH 7.0 with NaOH or H_3PO_4, as necessary.

2.2. Pulse radiolysis and γ-radiolysis

Pulse radiolysis experiments were performed at the United States Department of Energy, Notre Dame Radiation Laboratory using an 8-MeV Titan Beta model TBS-8/16-1S linear accelerator that produced 2 ns electron pulses which generate radical concentrations of 1-3 μM per pulse. All experimental data were taken by averaging 8 to 15 replicate pulses using the continuous flow mode of the instrument. Dosimetry was performed with N_2O-saturated, 1.00 x 10^{-2} M KSCN solutions monitored at $\lambda = 472$ nm.

The radiolysis of water is described in Eq 1:

$$H_2O \wedge\wedge\wedge -> e^-_{aq}(0.26) + H\cdot(0.06) + \cdot OH(0.27) + H_2(0.05) + H_2O_2(0.07) + H_3O^+(0.27) \quad (1)$$

Where the numbers in parentheses are *G* values (yields) in μmol J^{-1}. Reactions with the hydroxyl radical were achieved by using a nitrous oxide (N_2O) pre-saturated solution, which quantitatively converted solvated electrons and hydrogen atoms (H•) to the •OH radical. (Buxton et al. 1988)

$$e^-_{aq} + N_2O + H_2O \rightarrow N_2 + OH^- + \cdot OH \quad k_2 = 9.1 \times 10^9\ M^{-1}\ s^{-1} \quad (2)$$

$$H\cdot + N_2O \rightarrow \cdot OH + N_2 \quad k_3 = 2.1 \times 10^6\ M^{-1}\ s^{-1} \quad (3)$$

Reactions between the solvated electron and diclofenac were studied in N_2-saturated solutions buffered to pH 7.0. These solutions contained 0.10 M isopropanol to scavenge the hydroxyl radicals and hydrogen atoms, to convert them into relatively inert isopropanol radicals. (Buxton et al. 1988)

$$(CH_3)_2CHOH + \cdot OH \rightarrow (CH_3)_2C\cdot OH + H_2O \quad k_4 = 1.9 \times 10^9\ M^{-1}\ s^{-1} \quad (4)$$

$$(CH_3)_2CHOH + H\cdot \rightarrow (CH_3)_2C\cdot OH + H_2 \quad k_5 = 7.4 \times 10^7\ M^{-1}\ s^{-1} \quad (5)$$

A Shepherd® 109-86 Cobalt-60 source was used for γ radiolysis with samples of 1.0 mM diclofenac saturated with N_2O or N_2 saturated before irradiation. The dose rate was 7.72 krad min^{-1}, as measured by Fricke dosimetry.

2.3. HPLC and mass spectral analysis

The concentration of diclofenac was determined using an Agilent 1200 HPLC using the following conditions: column, Phenomenex Gemini C_{18} 250 × 4.6 mm i.d.; mobile phase consisting of 15 % CH_3OH, 15 % CH_3CN and 70 % 10 mM