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Review

Oxidative transformations of environmental pharmaceuticals by Cl_2, ClO_2, O_3, and Fe(VI): Kinetics assessment

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ABSTRACT

Several pharmaceuticals have been detected globally in surface water and drinking water, which indicate their insufficient removal from water and wastewater using conventional treatment methods. This paper reviews the kinetics of oxidative transformations of pharmaceuticals (antibiotics, lipid regulators, antipyretics, anticonvulsants, and beta-blockers) by Cl_2, ClO_2, O_3, and ferrate(VI) ($Fe^{VI}O_4^{2-}$, Fe(VI)) under treatment conditions. In the chlorination of sulfonamide antibiotics, HOCl is the major reactive Cl_2 species whereas in the oxidation by Fe(VI), $HFeO_4^-$ is the dominant reactive species. Both oxidation processes can oxidize sulfonamides in seconds at a neutral pH ($t_{1/2} \leqslant 220$ s; 1 mg L^{-1} HOCl or K_2FeO_4). The reactivity of O_3 with pharmaceuticals is generally higher than that of HOCl ($k_{app,pH\ 7}$ (O_3) = 1–10^7 M^{-1} s^{-1}; $k_{app,pH\ 7}$ (HOCl) = 10^{-2}–10^5 M^{-1} s^{-1}). Ozone selectively oxidizes pharmaceuticals and reacts mainly with activated aromatic systems and non-protonated amines. Oxidative transformation of most pharmaceuticals by O_3 occurs in seconds ($t_{1/2} \leqslant 100$ s; 1 mg L^{-1} O_3) while half-lives for oxidations by HOCl differ by at least two orders of magnitude. Ozone appears to be efficient in oxidizing pharmaceuticals in aquatic environments. The limited work on Fe(VI) shows that it can also potentially transform pharmaceuticals in treatment processes.

Contents

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1. Introduction

Micropollutants in the aquatic environment are of great concern because of their influence on freshwater systems (Schwarzenbach et al., 2006). Increased levels of micropollutants in surface and groundwaters may cause long term effects on aquatic ecology and on human health. Among emerging micropollutants, pharmaceuticals in the aquatic environment have drawn attention in the last decade (Halling-Sorensen et al., 1998; Cunningham et al., 2006; Khetan and Collins, 2007). Pharmaceuticals are designed to treat and prevent diseases and their sale has increased by 62% over five years (2000–2004) in the United States (Khetan and Collins, 2007). Because of growth and an inverting age structure of the population, increased use of pharmaceuticals is expected in the future.

The intake of pharmaceuticals leads to the adsorption, distribution, metabolism, and ultimately excretion of the original or modified drugs from the body. Significant proportions of molecules are excreted in unmetabolized form or as active metabolites through urine, which may or may not be treated (Halling-Sorensen et al., 1998; Ternes et al., 2004). Additionally, unused medicines and drug-containing waste from manufacturing facilities may also contribute to environmental contamination. The fates of human and veterinary pharmaceuticals after excretion are different (Halling-Sorensen et al., 1998). Excreted human drugs pass through sewage treatment plants (STP) before entering streams or rivers. Comparatively, veterinary pharmaceuticals do not undergo STP treatment and may directly enter soil and groundwater. Animal manure containing these pharmaceuticals is usually applied to soil directly and may cause contamination of surface water and groundwater by runoff after rainfall. STP are not designed to treat pharmaceuticals, hence plant treatment processes do not adequately remove these compounds (Miao et al., 2004; Ternes et al., 2004). A wide range of biologically active compounds including antibiotics, painkillers, anticonvulsants, lipid regulators, beta-blockers, cytostatic drugs, and antihistamines have been detected in the range of ng L^{-1} to μg L^{-1} in STP effluents and in surface waters (Kolpin et al., 2002; Andreozzi et al., 2003; Snyder et al., 2003; Anderson et al., 2004; Miao et al., 2004; Ternes et al., 2004; Jiang et al., 2005; Westerhoff et al., 2006; Batt et al., 2007; Watkinson et al., 2007). Unfortunately, mixtures of pharmaceuticals even at ng L^{-1} can inhibit cell proliferation (Pomati et al., 2006).

In general, drinking water utilities abstract water from various sources such as ground water, rivers, streams, springs, or lakes in a watershed; small communities generally receive water from aquifers, while large metropolitan areas receive water from surface sources. In most cases, source waters require treatment before use in order to meet national quality standards for regulated compounds. Pharmaceutical compounds are not currently regulated but their treatment is desired. Pharmaceuticals can be treated by membrane filtration (nanofiltration or reverse osmosis) or filtration over activated carbon (Benner et al., 2008). The adsorption or retention capacity of these methods decreases with operation time due to buildup of organic matter, which causes clogging of filters (Schwarzenbach et al., 2006). Moreover, membrane processes and activated carbon adsorption are energy and/or material intensive for application to wastewater treatment. Inherent tests of antibiotics proved an occurrence of ultimate biodegradation of Penicillin G (Gartiser et al., 2007). In this study, certain ultimate biodegradation of amoxicillin, imipenem, and nystatin was observed (Gartiser et al., 2007). In testing of biological degradation of pharmaceuticals in municipal wastewater treatment, more than 90% transformation occurred for ibuprofen, paracetamol, 17β-estradiol, and estrone (Joss et al., 2006). UV light irradiation techniques for the disinfection of drinking water and purification of wastewater (Hijnen et al., 2006) can induce transformation of pharmaceuticals (Andreozzi et al., 2003; Boreen et al., 2004). Advanced oxidation processes such as O_3/H_2O_2, UV/H_2O_2, Fenton/photo-Fenton, and UV/TiO_2 have also been studied to degrade pharmaceuticals and results are recently reviewed (Ikehata et al., 2006; Esplugas et al., 2007).

Table 1
Redox potentials for the oxidants/disinfectants used in water treatment

Oxidant	Reaction	E^o (V)
Ferrate(VI)	$FeO_4^{2-} + 8H^+ + 3e^- \Leftrightarrow Fe^{3+} + 4H_2O$	2.20
	$FeO_4^{2-} + 4H_2O + 3e^- \Leftrightarrow Fe(OH)_3 + 5OH^-$	0.70
Ozone	$O_3 + 2H^+ + 2e^- \Leftrightarrow O_2 + H_2O$	2.08
	$O_3 + H_2O + 2e^- \Leftrightarrow O_2 + 2OH^-$	1.24
Hypochlorite	$HClO^- + H^+ + 2e^- \Leftrightarrow Cl^- + H_2O$	1.48
	$ClO^- + H_2O + 2e^- \Leftrightarrow Cl^- + 2OH^-$	0.84
Chlorine	$Cl_2(g) + 2e^- \Leftrightarrow 2Cl^-$	1.36
Chlorine dioxide	$ClO_2(aq) + e^- \Longleftrightarrow ClO_2^-$	0.95

The use of chemical oxidants before or after biological treatment may be a feasible approach for treating water. Chemicals selectively oxidize pharmaceuticals to readily biodegradable and less toxic compounds. In treatment systems, Cl_2, HOCl, ClO_2, and O_3 are frequently applied for oxidative treatments because of their high reduction potentials (Dodd et al., 2006; Ikehata et al., 2006; Esplugas et al., 2007) (Table 1). In recent years, the use of ferrate(VI) ($Fe(VI), FeO_4^{2-}$) has also been proposed (Jiang, 2007; Sharma, 2007). In acid solution, the redox potential of Fe(VI) is the highest of oxidants commonly used in water treatment (Table 1) (Jiang and Lloyd, 2002; Sharma, 2002). However, O_3 is a more powerful oxidant in basic solution compared to other oxidants (Table 1). This study gives an overview of the aqueous chemistry of different oxidants and their reaction kinetics with pharmaceuticals. The structures of pharmaceuticals are presented in the Supplementary material (Figs. S1–S9). The rates of the reactions are discussed based on reactive functional groups. The summary of rate constants will provide information on the dose consumption of an oxidant if matrix component of water compete for applied oxidant in treatment processes.

2. Aqueous chemistry of oxidants

2.1. Chlorine

The reactivity of compounds with Cl_2 depends on the speciation of Cl_2 as a function of pH (Fig. 1). HOCl and OCl^- are both present in the pH range of 6–9. HOCl is the major reactive Cl_2 species in oxidation processes. The kinetics of the Cl_2 reaction with compounds is first-order in the $[HOCl]_{Total}$ and first-order in the total concentration of compound, i.e. overall second-order. The reactivities of HOCl and OCl^- for a particular compound vary significantly; therefore, the second-order rate constants (k) vary with pH in chlorination reactions (Deborde and Gunten, 2008). The reactivity of Cl_2 with inorganic molecules is generally derived from an initial electrophilic attack of HOCl. The k for organic compounds varies from <0.1 to 10^9 M^{-1} s^{-1} and possible pathways of reactions include oxidation, addition, and electrophilic substitutions (Deborde and Gunten, 2008).

2.2. Chlorine dioxide

Chlorine dioxide is a stable free radical, a powerful oxidant, and does not produce trihalomethanes. Chlorine dioxide decomposes slowly in neutral aqueous solution (Odeh et al., 2002). However, its decay is accelerated in basic solution and kinetic studies have shown three concurrent pathways: pathway 1 is first-order in