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Transformation kinetics of biochemically active compounds in low-pressure UV Photolysis and UV/H_2O_2 advanced oxidation processes

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ABSTRACT

Factors controlling photolysis and UV/H_2O_2 photooxidation rates of the biochemically active compounds (BACs) sulfamethoxazole, sulfamethazine, sulfadiazine, trimethoprim, bisphenol A, and diclofenac were determined. Experiments were conducted with a quasi-collimated beam apparatus equipped with low-pressure UV lamps. The effects of pH, H_2O_2 concentration, and background water matrix (ultrapure water, lake water, wastewater treatment plant effluent) on BAC transformation rates were evaluated. For the sulfa drugs, solution pH affected direct photolysis rates but had little effect on the hydroxyl radical oxidation rate. For sulfamethoxazole, the neutral form photolyzed more easily than the anionic form while the reverse was the case for sulfamethazine and sulfadiazine. For trimethoprim, the hydroxyl radical oxidation rate was higher for the cationic form (pH 3.6) than for the neutral form (pH 7.85). Quantum yields and second order rate constants describing the reaction between the hydroxyl radical and BACs were determined and used together with background water quality data to predict fluence-based BAC transformation rate constants (k'). For both the lake water and wastewater treatment plant effluent matrices, predicted k' values were generally in good agreement with experimentally determined k' values. At typical UV/H_2O_2 treatment conditions (fluence = 540 mJ cm^{-2}, H_2O_2 dose = 6 mg L^{-1}), BAC transformation percentages in North Carolina lake water ranged from 43% for trimethoprim to 98% for diclofenac. In wastewater treatment plant effluent, BAC transformation percentages were lower (31–97%) at the same treatment conditions because the hydroxyl radical scavenging rate was higher.

1. Introduction

The presence of biochemically active compounds (BACs) such as endocrine disrupting chemicals (EDCs) and antimicrobial compounds in the aquatic environment continues to be an issue of concern. BACs are commonly detected in surface and ground water, and concentrations of some BACs can reach low μg L^{-1} levels (e.g., Alexy and Kümmerer, 2006; Petrovic et al., 2004). While EDC concentrations in some surface water bodies are sufficiently high to cause gender bending in fish (e.g., Kidd et al., 2007), it is still debated whether the evolution of antibiotic-resistant bacteria is facilitated at such

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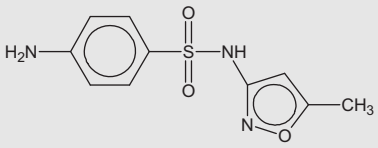
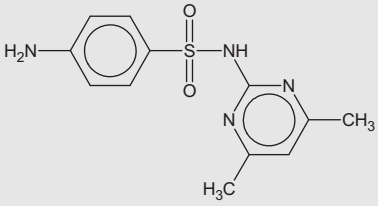
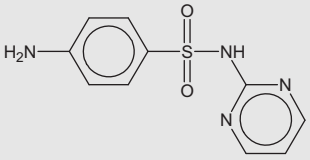
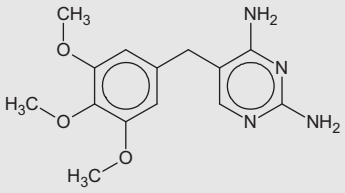
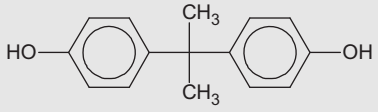
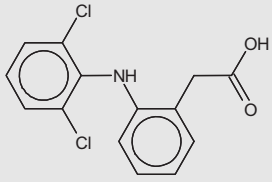
Table 1 – Molecular structures and characteristics of targeted compounds.

BAC	Chemical structure	Properties
Sulfamethoxazole (SMX)		Sulfonamide (antibiotic) Molecular weight = 253.3 Da $pK_{a,1}$ = 1.74[a] $pK_{a,2}$ = 5.65[b]
Sulfamethazine (SMZ)		Sulfonamide (antibiotic) Molecular weight = 278.3 Da $pK_{a,1}$ = 2.26[a] $pK_{a,2}$ = 7.65[b]
Sulfadiazine (SDZ)		Sulfonamide (antibiotic) Molecular weight = 280.2 Da $pK_{a,1}$ = 2.02[a] $pK_{a,2}$ = 6.43[b]
Trimethoprim (TMP)		DHFR inhibitor (antibiotic) Molecular weight = 290.3 Da $pK_{a,1}$ = 3.23[c] $pK_{a,2}$ = 6.76[c]
Bisphenol A (BPA)		Endocrine disrupting chemical Molecular weight = 228.3 Da $pK_{a,1}$ = 9.78[d] $pK_{a,2}$ = 10.53[d]
Diclofenac (DCL)		Analgesic Molecular weight = 296.15 Da pK_a = 4.15[e]

a Lin et al., 1997a.
b Lin et al., 1997b.
c Qiang and Adams, 2004.
d Calculated from SPARC v.4.5 (http://ibmlc2.chem.uga.edu/sparc/).
e Database of experimental values in EPI SUITE v.4 (http://www.epa.gov/opptintr/exposure/pubs/episuitedl.htm).

concentrations. Also, the effects of chronic human exposure to different pharmaceuticals at trace levels in drinking water are not known (Snyder et al., 2005). Wastewater treatment plants (WWTPs) represent one important entry point for BACs into the environment (e.g. Göbel et al., 2005), and BACs are not effectively removed by conventional drinking water processes (Adams et al., 2002; Westerhoff et al., 2005).

The use of UV disinfection processes has increased dramatically in drinking water and wastewater treatment. While the transformation of organic compounds by direct photolysis at disinfection doses is limited (Adams et al., 2002; Canonica et al., 2008), advanced oxidation processes (AOPs) present a potentially effective treatment alternative for micropollutants. Several studies have evaluated UV/H_2O_2