



Thermo activated persulfate oxidation of antibiotic sulfamethoxazole and structurally related compounds



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ARTICLE INFO

Article history:

Received 1 July 2015

Received in revised form

1 September 2015

Accepted 2 September 2015

Available online 9 September 2015

Keywords:

Thermo activated persulfate oxidation

Sulfate radical

Sulfonamides

Reaction products

Transformation mechanisms

ABSTRACT

The widespread occurrence of sulfonamides (e.g., sulfamethoxazole) in natural environment has raised growing concerns due to their potential to induce antibiotic-resistant genes. In this study, the degradation of SMX and related sulfonamides by thermo activated persulfate (PS) oxidation was investigated. Experimental results demonstrated that SMX degradation followed pseudo-first-order reaction kinetics. The pseudo-first-order rate constant (k_{obs}) was increased markedly with increasing temperature and pH. The presence of bicarbonate manifested promoting effect on SMX degradation while fulvic acid reduced it. Radical scavenging tests revealed that the predominant oxidizing species was $SO_4^{\cdot-}$ at neutral pH. Aniline moiety in SMX molecule was confirmed to be the primary reactive site for $SO_4^{\cdot-}$ attack by comparison with substructural analogues. Reaction products were enriched by solid phase extraction (SPE) and analyzed by liquid chromatography-electrospray ionization-triple quadrupole mass spectrometry (LC-ESI-MS/MS). A total of 7 products derived from hydroxylation, sulfonamide S–N bond cleavage, aniline moiety oxidation and coupling reaction were identified, and transformation pathways of SMX oxidation were proposed. Degradation of sulfonamides was appreciably influenced by the heterocyclic ring present in the molecules. Results reveal that thermo activated PS oxidation could be an efficient approach for remediation of water contaminated by SMX and related sulfonamides.

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1. Introduction

Recently, groundwater contamination by micropollutants such as antibiotics has raised increasing concerns (Barnes et al., 2008; Barber et al., 2009; Avisar et al., 2009). Wastewater treatment plant effluents, land application of biosolids, and municipal landfill leaching are sources responsible for the occurrence of antibiotics in groundwater (Jones et al., 2005; Sarmah et al., 2006; Eggen et al., 2010; Lapworth et al., 2012; Michael et al., 2013). Due to the lack of light, low oxygen level and microorganism activity in subsurface environment, natural attenuation processes such as photolysis and biodegradation have limited impact on the dissipation of these contaminants (Kümmerer, 2009a; Lapworth et al., 2012). Although adsorption to naturally occurring clay and minerals as well as abiotic transformation under iron-reducing soil may result in the attenuation of antibiotics (Tolls, 2001; Mohatt et al., 2011), such processes generally occur slowly and have limited influence on the

fate of these contaminants (Kümmerer, 2009a; Lapworth et al., 2012). The widespread occurrence of antibiotics in the groundwater may directly influence the ecosystem by proliferation of antibiotic-resistant genes (Kümmerer, 2009b; Rizzo et al., 2013). Human population may also be affected when exposure to antibiotics-contaminated groundwater (e.g., when the groundwater was used as drinking water source) (Benotti et al., 2009; Watkinson et al., 2009). Although environmental concentrations of antibiotics are typically at nanogram per liter to microgram per liter level, their long-term and subtle chronic effects cannot be ignored (Crane et al., 2006; Kümmerer, 2009b). In addition, the mixture of antibiotics and other pharmaceuticals at environmentally realistic levels may exhibit synergic effect (Richards et al., 2004; Pomati et al., 2006). Thus, cost-effective and environmentally-friendly treatment and/or remediation technologies are highly desirable to minimize these risks.

Activated persulfate oxidation is a promising *in situ* chemical oxidation (ISCO) technology widely used in remediation of contaminated groundwater and soil (Tistonaki et al., 2010; Zhang et al., 2014). This technology is based on the formation of highly

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reactive sulfate radical ($\text{SO}_4^{\bullet-}$, $E^0 = 2.5\text{--}3.1$ V depending on pH) after persulfate (PS) or peroxymonosulfate (PMS) activation by heat, transit metals, UV light, and base (Tistonaki et al., 2010; Zhang et al., 2014; Neta et al., 1988). $\text{SO}_4^{\bullet-}$ is a single electron oxidant that reacts with a variety of organic compounds with second-order-rate constants ranging from 10^6 to 10^9 $\text{M}^{-1} \text{s}^{-1}$ (Neta et al., 1977, 1988). Unlike hydroxyl radical ($\text{HO}\bullet$), $\text{SO}_4^{\bullet-}$ is more selective, and reacts with organic compounds mainly through electron-transfer mechanism (Neta et al., 1977, 1988). Of various activation methods, thermo activation is of particular attention due to its high efficiency (Huang et al., 2002; Liang et al., 2003; Waldemer et al., 2007) although it usually requires high costs for equipment and operation. Nevertheless, in combination with *in situ* thermal remediation (ISTR) technology makes this technology an attractive option (Tistonaki et al., 2010). In addition, thermo activated PS oxidation is usually applied to study the degradation mechanisms of contaminants due to the simplicity of the system (Antoniu et al., 2010a).

In the present study, we attempted to evaluate the feasibility to employ thermo activated PS to degrade sulfamethoxazole (SMX) and other sulfonamides. These antibiotics were frequently detected in groundwater due to their extensive use and antibacterial nature (Barnes et al., 2008; Barber et al., 2009; Avisar et al., 2009; Lapworth et al., 2012). SMX is commonly prescribed as a synergist with trimethoprim (TMP) to treat diseases and infections caused by both Gram-positive and Gram-negative aerobic bacteria and as a feed additive to promote growth of animals (Walsh, 2003). Previous studies have demonstrated that SMX could be effectively destructed by sulfate radical-based advanced oxidation processes (SR-AOPs) such as Fe^0/PS (Ghauch et al., 2013), $\text{Fe(II)}/\text{PS}$ (Ji et al., 2014), microwave/PS (Qi et al., 2014) and $\text{Co(II)}/\text{PMS}$ (Mahdi Ahmed et al., 2012). However, the reactive sites in SMX molecule were unidentified, and the underlying mechanisms of SMX reaction with $\text{SO}_4^{\bullet-}$ warrant further study. In addition, how the molecular structures of SMX and other sulfonamides affect their degradation in $\text{SO}_4^{\bullet-}$ -mediated oxidation process is largely unknown.

In the present study, we reported that the aniline moiety of SMX could be preferentially attacked by $\text{SO}_4^{\bullet-}$, generating a radical cation $\text{SMX}^{\bullet+}$, which underwent further reactions via several pathways including aniline moiety oxidation, sulfonamide S–N bond cleavage, hydroxylation and coupling reaction, leading to the formation of a series of intermediate products. These findings may give new insights into the mechanisms of sulfonamides oxidation by SR-AOPs because sulfonamides all contain the aniline moiety connected with a heterocyclic ring via a sulfonamide bridge. However, the degradation of sulfonamides by thermo activated PS oxidation was also strongly influenced by the nature of heterocyclic rings, a fact that was potentially important, but previously unrecognized.

2. Material and methods

2.1. Chemicals and materials

Chemicals, suppliers, and purities are listed in the Supplementary data, Text S1. The molecular structures of SMX and related compounds are showed in Table S1.

2.2. Experimental setup

Batch kinetic studies (with 30 μM SMX and 2 mM PS) were conducted in 33 mL screw-cap vials with Teflon septa at predetermined temperature (i.e., 30–60 °C) controlled by a thermostatic water bath (Xianou Instrument Manufacture Co., Ltd, Nanjing). Control experiments with target compounds alone were performed under same conditions and showed no loss of the chemicals, indicating SMX and structurally related compounds are

hydrolysis-resistant and thermally stable. Solution pH was adjusted by 0.1 M H_2SO_4 or NaOH to desired value. No buffer was used to rule out any reactions between these additives and $\text{SO}_4^{\bullet-}$. The effects of Suwannee River fulvic acid (SRFA, 0–25 mg L^{-1}) and bicarbonate (HCO_3^- , 0–20 mM) as natural water constituents were evaluated. Aliquots (1.0 mL) were withdrawn at predetermined time points and chilled in an ice bath for 10 min to stop the reaction and then kept in a 4 °C refrigerator until further treatment and analysis. All the experiments were carried out in duplicates or triplicates, and the data were averaged. The standard deviations were usually within 5–10% unless otherwise stated. Formation of AMI and hydroxylated sulfanilic acid (OH-SAA) over time course was quantified by HPLC analysis. For quantification, higher initial concentrations of SMX (136 μM) and PS (9 mM) were employed, and reaction samples were analyzed directly without any enriching steps.

2.3. Analytical methods

2.3.1. HPLC analysis

SMX and structurally related compounds were analyzed by a Hitachi L-2000 high performance liquid chromatography (Hitachi, Japan) equipped with an L-2455 diode array detector. Detailed operation conditions were provided in Supplementary data, Table S1. Quantification of the target compounds was based on multipoint standard calibration curves.

2.3.2. Solid phase extraction

Transformation products of SMX were enriched by solid phase extraction (SPE) using Waters Oasis hydrophilic-lipophilic balance (HLB) cartridges. Detailed experimental procedures are given in Text S2, Supplementary data.

2.3.3. HPLC-MS/MS analysis

Transformation products were identified using liquid chromatography with tandem mass spectrometry (HPLC-MS/MS), consisting of an Agilent 1200 series HPLC and a 6410B triple quadrupole mass spectrometer (Agilent Technologies, USA). Separation was accomplished using an Agilent ZORBAX Eclipse Plus C18 column (3.5 μm , 2.1 mm I.D. \times 150 mm). Full scans and product ion scans were conducted to determine the quasi-molecular ions and elucidate the structures of major transformation products. Detailed operational conditions are presented in the Supplementary data, Text S3.

2.3.4. pH measurement

Solution pH was measured by a combined glass electrode (E-201-C, Leici) connected to a PHS-3CW microprocessor pH/mV meter (BANTE instrument).

3. Results and discussion

3.1. Reaction kinetics

A series of experiments were conducted to investigate the operational variables and solution conditions that affect reaction rates of SMX in thermo activated PS oxidation process. In all the cases, SMX degradation followed pseudo-first-order kinetics. The pseudo-first-order rate constant, k_{obs} , was obtained by linear regression of $\ln [\text{SMX}]$ to time at each condition (Eq. (1)).

$$\ln \left(\frac{[\text{SMX}]_t}{[\text{SMX}]_0} \right) = -k_{\text{obs}} t \quad (1)$$

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