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Transformation of aqueous sulfonamides under horseradish peroxidase and characterization of sulfur dioxide extrusion products from sulfadiazine

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HIGHLIGHTS

- HRP can mediate high removal of most sulfonamides in the presence of H_2O_2.
- The coexistent sulfonamides might be acted as mediators for the enhancement of SMX removal.
- SDZ transformation involves the Smiles rearrangement and then oxidation and sulfur dioxide extrusion.

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ABSTRACT

The potential of horseradish peroxidase (HRP) to catalyze the removal of sulfonamides from water and the effects of different H_2O_2 and HRP concentrations were investigated. Six sulfonamides, each with a five- or six-membered heterocyclic group, including sulfamethoxazole (SMX), sulfathiazole (STZ), sulfapyridine (SPD), sulfadiazine (SDZ), sulfamerazine (SMR) and sulfamethoxypyridazine (SMP) were selected as target compounds. All sulfonamides exhibit a pseudo-first-order dependence of the concentration versus the reaction time. The decay rate (k, h^{-1}) of the six sulfonamides spiked individually exhibit a trend following the order of STZ > SMP, SPD > SMR > SDZ » SMX. When spiked together, the coexistent sulfonamides might act as mediators for the enhancement of SMX removal and as competitors for the decreased removal of most sulfonamides. Moreover, six transformation products of SDZ are identified by the Thermo Scientific LTQ Orbitrap Elite technique. SDZ transformation involves two steps: one is the Smiles re-arrangement of the structure, and the other is oxidation and sulfur dioxide extrusion. This study is the first to report the removal dynamics of sulfonamides in HRP-catalyzed reactions and the identified products of SDZ.

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1. Introduction

Sulfonamides represent a class of antimicrobial agents that are widely used for therapeutic and prophylactic purposes and as growth promoters for food producing animals (Sarmah et al., 2006). Since these compounds cannot be completely metabolized in the bodies of humans or animals, parts of them might be excreted as parent compounds, metabolites or conjugates (Garcia-Galan et al., 2008). These substances could escape degradation in sewage treatment plants (Gobel et al., 2005; Joss et al., 2006; Lindberg et al., 2005) and enter the aquatic environment (Miao et al., 2004; Peng et al., 2006). The occurrence of sulfonamide residues in sewage treatment plants, ground and surface waters has been widely reported, with most concentrations ranging from ng L^{-1} to μg L^{-1} (Gobel et al., 2005; Hirsch et al., 1999; Liang et al., 2013; Luo et al., 2011; Peng et al., 2006). Sulfonamides could cause acute toxicity to aquatic organisms (Yang et al., 2008), induce antibiotic resistance of

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native microorganisms (Onmaz et al., 2015) and, most importantly, stimulate the emergence of antimicrobial - resistant bacterial pathogens and related genes (Chen et al., 2013, 2016; Schmidt et al., 2015).

The clarification of environmental fate and pollution control of sulfonamides in aquatic environments is an emerging concern. Sulfonamides are recalcitrant chemicals in natural aquatic environments, with limited hydrolysis (Bialk-Bielinska et al., 2012) and photolysis (Boreen et al., 2004). Advanced oxidation techniques such as electro-Fenton (Dirany et al., 2012; Neafsey et al., 2010) and manganese oxide treatment (Gao et al., 2012) are reported to be efficient ways to treat sulfonamides. The biodegradation of sulfonamides is also efficiently done by the white-rot fungus *Trametes versicolor*, which might be attributed to its laccase activity (Garcia-Galan et al., 2011; Rodriguez-Rodriguez et al., 2012). Enzyme-catalyzed oxidation is a sustainable and eco-friendly process for treating contaminants (Weng et al., 2013). Laccase is a glycoprotein and multi-copper-containing oxidoreductase that can catalyze the monoelectronic oxidation of substrates at the expense of molecular oxygen (Riva, 2006). The transformation of sulfonamides in laccase-mediator systems (Rahmani et al., 2015; Weng et al., 2012, 2013) and their coupling to organic matter (Bialk et al., 2007; Bialk and Pedersen, 2008; Gulkowska et al., 2013) have been widely observed.

Peroxidase, in which a heme group serves as an active center, is another important oxidoreductase that can catalyze the oxidation of substrates in the presence of hydrogen peroxide (H_2O_2, CAS 7722-84-1). Among them, horseradish peroxidase (HRP, EC 1.11.1.7) from horseradish (*Armoracia rusticana*) roots has been extensively reported to be capable of removing phenolic compounds such as phenols (Colosi et al., 2006; Wagner and Nicell, 2002; Xu et al., 2005), halophenols (Arnoldsson et al., 2012; Colosi et al., 2006; Palomo and Bhandari, 2006; Wagner and Nicell, 2002), alkylphenols (Colosi et al., 2006), bisphenol A (Huang and Weber, 2005), lignosulfonates (Zhou et al., 2013), triclosan (Melo and Dezotti, 2013), as well as natural and synthetic hormones (Auriol et al., 2006, 2008; Colosi et al., 2006). Moreover, the combination of HRP and H_2O_2 has been proposed for the efficient removal of non-phenolic aromatic compounds (n-(3-indoleethyl) cyclic aliphatic amines) (Ling et al., 2008), organic acids (hydroxycinnamic acids, perfluorooctanoic acid, humic acid and fulvic acid) (Arrieta-Baez and Stark, 2006; Colosi et al., 2009; Cozzolino and Piccolo, 2002; Weber et al., 2005) and persistent organic pollutants (polychlorinated biphenyls and phenanthrene) (Colosi et al., 2007; Singh et al., 2000; Weber and Huang, 2003) and even the treatment of complex water matrices, such as azo dye and swine manure slurry (Govere et al., 2005, 2007; Kim et al., 2005; Ye et al., 2009). Based on the above studies, HRP-catalyzed enzymatic reaction of these compounds occurs mainly through oxidative coupling reactions, in which radicals are generated and coupled with each other to form polymeric products.

Except for the covalent cross-coupling of sulfamethazine with syringic and protocatechuic acids by peroxidase has been reported (Bialk et al., 2005), the environmental fate of sulfonamides under the reaction of HRP is currently unclear. Thus, in the present study, we intended to explore the potential of the HRP-catalyzed removal of sulfonamides from water. Here, the effects of H_2O_2 and HRP on sulfonamide removal were investigated. Studies were also performed to determine the time-dependent removal of multiple sulfonamides spiked together and individually. Moreover, the transformation products were identified by a combination of liquid chromatography–mass spectrometry (LC-MS) and Thermo Scientific LTQ Orbitrap Elite techniques.

2. Experimental section

2.1. Reagents and materials

All sulfonamide standards shown in Table 1, including sulfamethoxazole (SMX), sulfathiazole (STZ), sulfapyridine (SPD), sulfadiazine (SDZ), sulfamerazine (SMR) and sulfamethoxypyridazine (SMP) with purities greater than 98.5% were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Horseradish Peroxidase (HRP, lyophilized powder, 300 U mg^{-1}) was purchased from Xueman Biology, Inc. (Shanghai, China). HPLC-grade methanol and formic acid were obtained from Sigma-Aldrich Co. LLC. (St. Louis., MO, USA) and CNW Technologies GmbH (Düsseldorf, Germany), respectively. Purpurogallin of analytic grade was purchased from Sigma-Aldrich Co. LLC. (St. Louis., MO, USA). All other chemicals including pyrogallol, H_2O_2, phosphate buffer solution and Tris-HCl buffer solution were of analytical reagent grade and obtained from Guangzhou Chemical Reagent Factory (Guangzhou, China). All solutions and dilutions were prepared with ultrapure water (Resistivity = 18.2 MΩ cm) from a Milli-Q Plus water purification system (Millipore, Billerrica, MA, USA).

2.2. Enzyme assay

HRP activity was measured using a colorimetric assay with pyrogallol as a color-generating substrate, where the rate of color formation was proportional to enzyme activity. The formation of purpurogallin in the assay due to the catalytic action of HRP was monitored at a wavelength of 430 nm. The whole reaction system was 4 mL in 0.1 M phosphate buffer solution (pH 6) with 5 g L^{-1} pyrogallol and HRP activity at 1 U mL^{-1}. The reaction was initiated after the addition of 0.5 mM H_2O_2, and the absorbance was continuously monitored over time. One U of HRP activity is defined as the amount of enzyme required to mediate oxidation of pyrogallol at 20 s and is expressed in U per milliliter (U mL^{-1}).

2.3. Incubation studies

The HRP-catalyzed reaction was conducted in 10 mL brown bottles with Teflon/PDMS septa and screw caps from Agilent Technologies Inc. (Santa Clara, CA, USA) as batch reactors. As the solubilities of all target sulfonamides were in the range of 77–750 mg L^{-1} (Sarmah et al., 2006), a high concentration of each sulfonamide, ranging from 3 to 75 mg L^{-1}, were spiked into the enzyme-catalyzed reaction vessel (Bialk and Pedersen, 2008; Weng et al., 2012, 2013) (Gulkowska et al., 2013; Rahmani et al., 2015; Schwarz et al., 2010). In the present work, each sulfonamide was spiked at a concentration of 20 mg L^{-1} into each reactor, containing 1 U mL^{-1} HRP in 6 mL buffer solution. The reaction was initiated after the addition of 1 mM H_2O_2 and quenched at a specific time by the addition of methanol at a concentration of 80% (V/V). Then, the settling enzyme was filtered by a 0.22 μm syringe filter and 1 mL injector (INTMED Medical Appliance Co. LTD, Guangdong, China). The filtrate was then analyzed for sulfonamide quantification and product characterization.

To study the effects of varying reaction conditions, solutions of different HRP activity (0, 0.5, 1, 5 and 10 U mL^{-1}) and H_2O_2 concentration (0, 0.1, 0.5, 1 and 5 mM) were set individually in triplicate. Under optimized conditions, the six sulfonamides were spiked into the reactors individually or combined. The residual concentrations of sulfonamides were determined at 0.5, 1, 1.5, 2, 3, 5, 6, 8, 9, 10, 12, 15 and 21 h when spiked individually and at 1, 3, 5, 8, 12, 24, 48 and 72 h when spiked together.

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