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Ferrate promoted oxidative cleavage of sulfonamides: Kinetics and product formation under acidic conditions

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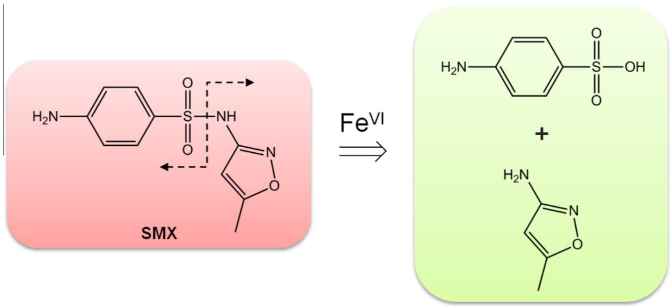
HIGHLIGHTS

- Decrease in rates with increasing pH under both acidic and basic conditions.
- Model considering species-specific reactions describes the trend in rates.
- Oxidative cleavage of S—N bond dominates in acidic medium.
- Hydroxylation appears to be major pathway in basic medium.
- Effective removal of the sulfonamide in presence of humic acid.

GRAPHICAL ABSTRACT



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ABSTRACT

Sulfonamide-based antibiotics are often detected in surface water and secondary wastewater effluent and pose an eminent threat for the development of antibiotic resistance bacteria and genes in aquatic environment. This paper presents the kinetics and stoichiometry of the oxidation of sulfonamides (sulfaguanidine, sulfisoxazole, sulfamethizole, sulfamethoxazole (SMX), sulfamethazine, and sulfadimethoxine) by ferrate(VI) (FeO_4^{2-}, Fe(VI)) in the acidic to basic pH range (2.0–9.6); apparent second-order rate constants (k_{app}, M^{-1} s^{-1}) decreased non-linearly with increase in pH. The specific rate constants for the individual Fe(VI) species ($H_3FeO_4^+$, H_2FeO_4, $HFeO_4^-$, and FeO_4^-) were determined using acid–base equilibria of Fe(VI) and sulfonamides. The reactivity order of Fe(VI) species with the neutral sulfonamide was $H_3FeO_4^+ > H_2FeO_4 > HFeO_4^-$, which generally explained the pH dependence behavior of rate constants. Detailed studies regarding the resultant oxidized products (OPs) using liquid chromatography–mass spectrometry/mass spectrometry were performed for oxidation of SMX at different molar ratios of Fe(VI) to SMX (i.e., 1.0–15) and at different pH's (i.e., 4.0, 7.0, and 9.0); oxidative degradative products include 3-amino-5-methylisoxazole, and hydroxyl-, hydroxylamine-, nitroso-, and nitro-derivatives of SMX. The possible reaction pathways comprise the S—N bond cleavage, ring-opening of isoxazole moiety, oxidation of aromatic amine, and the hydroxylation of the benzene ring; different OPs formed under acidic, neutral, and basic pH conditions are described. The value of k_{app}, 8.9×10^2 M^{-1} s^{-1} at pH 7.0 suggests the oxidative transformation of SMX in seconds by 1 mg L^{-1} K_2FeO_4 and interestingly, the removal of SMX could be achieved at neutral pH by Fe(VI) in the presence of humic acid.

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1. Introduction

Antibiotic-based pharmaceuticals have been reported in aquatic environment worldwide [1] and are responsible for adverse effects on human health and ecosystems due to their biological activity [2]. For example, mixtures of pharmaceuticals even at ng L^{-1} can inhibit cell proliferation [3]. Antibiotics can alter microbial activity and community composition of water-based organisms which lead to antibiotic resistant bacteria and genes in the aquatic environment [4]. Sulfonamides are one of the largest classes of antibiotics which have been widely used in animals and humans with occurrence of these molecules in the environment including wastewater treatment plant effluent, surface water, groundwater, sewage, and drinking water [5,6]. In order to reduce negative impacts of sulfonamide antibiotics in water bodies, it is imperative to treat them via an effective and sustainable treatment technology before their release into the environment.

Antibiotics can be removed by physical methods (e.g., nanofiltration, reverse osmosis, adsorption) [7]. Membrane processes, activated carbon adsorption, and the use of carbon nanotubes can be other options, which may be energy and/or material intensive [8,9]. The use of chemical oxidants is an alternate approach for treating antibiotics in water [10–12]. Chlorine has the potential to remove antibiotics, however, chlorination byproducts may be more toxic than the parent molecules themselves. Chlorine dioxide has also been investigated to oxidize antibiotics, but the transformation of antibiotics under typical ClO_2 disinfection doses may not eliminate the antibacterial activity [13]. Advanced oxidation processes (AOPs) have been successfully demonstrated to eliminate antibiotics from water [14–16]. Aforementioned processes may have limitations in terms of energy requirements.

Among various resources used in treating antibiotics, iron-based materials have garnered more attention in view of their special attributes such as earth-abundant and environmentally friendly nature. This paper pertains to the utility of high-valent iron compound, ferrate(VI) (FeO_4^{2-}, Fe(VI)), which has emerged as a novel oxidant to remove micropollutants in water [17–25]. While several studies have been conducted using Fe(VI), most of them have focused on evaluating the performance of Fe(VI) to remove various contaminants and only trifling effort has been dedicated to the mechanism of ferrate oxidation reactions. Furthermore, hardly any work has been carried out to understand the kinetics and products of the reactions over a wide pH range from acidic to basic [26,27]. The focus of the paper is on oxidation of sulfonamide antibiotics by Fe(VI) under varying pH conditions.

The present paper offers the kinetic measurements for the reactions of Fe(VI) with selected sulfonamides (sulfaguanidine (SFG), sulfisoxazole (SIX), sulfamethizole (SMIZ), sulfamethoxazole (SMX), sulfamethazine (SMAZ), and sulfadimethoxine (SDM)), which comprise a sulfonamide ($-SO_2NH_2-$) group, an aniline moiety, and a five-or six-membered heterocyclic component with the exception of SFG (Fig. 1). The present study fills the void for data under the acidic solutions; study on SFG over the entire pH range has not been performed previously. Importantly, this is the first study that demonstrates the cleavage of S—N bond in SMX by Fe(VI) to produce 3-amino-5-methylisoxazole; identified by high resolution liquid chromatography mass spectrometry/mass spectrometry (LC–MS/MS) technique.

Objectives of the study are: (i) to measure the kinetics of oxidation of selected sulfonamides by Fe(VI) over the acidic to basic pH range, (ii) to apply a kinetic model to explain the trend in rate constants with variation of pH in order to determine the species-specific rate constants, (iii) to compare the kinetics of Fe(VI) oxidation with other oxidants commonly deployed in treating water, (iv) to establish the identity of the oxidized products (OPs) emanating from most widely identifiable entity in water, SMX, at different molar ratios ([Fe(VI)]/[SMX]) and pH, and (v) to determine the influence of organic matter on the removal efficiency of SMX by Fe(VI) at neutral pH.

2. Material and methods

2.1. Reagents

Sulfonamides, sodium borate, and sodium hydrogen phosphate were obtained either from Sigma–Aldrich (St. Louis, MO, USA) or Fisher-Scientific (Austin, TX, USA) with purity higher than 97% and were used as received. High performance liquid chromatography (HPLC)-grade organic solvents of methanol and acetonitrile were purchased from Fisher-Scientific. Solid potassium ferrate (K_2FeO_4) of ~98% purity was chemically synthesized [28]. Fe(VI) solutions were prepared by adding solid K_2FeO_4 to 1 mM $Na_2B_4O_7 \cdot 10H_2O$/5 mM Na_2HPO_4 at pH 9.0; Fe(VI) is stable for conducting experiments in this media. Concentrations of Fe(VI) in the solution were quantified spectroscopically by measuring absorbance at a wavelength of 510 nm ($\varepsilon_{510nm} = 1150\ M^{-1}\ cm^{-1}$) using an UV–visible spectrophotometer (Agilent 8453, Santa Clara, CA, USA). Solutions were prepared using de-ionized water that had been passed through water purification system (18 MΩ cm Milli-Q Millipore, Waters Alliance, Milford, MA, USA). Solutions of sulfonamides were prepared by dissolving the solid compounds in the 10 mM Na_2HPO_4 buffer solution. Solubility of SMX, SIX, and SDM was enhanced by warming up to 50 °C. Once the solution was cooled down to room temperature, no crystals could be detected. The solution pH was adjusted by adding either phosphoric acid or NaOH.

2.2. Kinetic studies

Pseudo-order conditions were used to study the kinetics of the reactions between Fe(VI) and substrates (sulfonamides) wherein the concentrations of substrates were higher than Fe(VI) concentration. A stopped-flow spectrophotometer (SX-18 MV, Applied Photophysics, Surrey, UK) with a photomultiplier detector was used for the kinetic studies. Kinetic traces were collected at a wavelength of 510 nm and data collected from the stopped-flow spectrophotometer were analyzed using the nonlinear least-square algorithm of the SX-18MV Global Software (Applied Photophysics, Surrey, UK). Six replicate runs were performed to obtain averaged rate constant. The pseudo-first-order rate constants for the reactions were obtained by subtracting the observed rate constants from the rate constants determined for Fe(VI) decay with substrates at each studied pH (Sharma, [47]).

2.3. Stoichiometry and products studies

The stoichiometry experiments for the oxidation of SMX by Fe(VI) were carried out by mixing both solutions of 10 mL each, and the pH of the reaction mixtures was maintained at 4.0, 7.0, and 9.0. All the experiments were performed at room temperature. The concentration of SMX was maintained at 0.1 mM and the concentrations of Fe(VI) were varied to attain the ratio of Fe(VI) to SMX from 1:1 to 15:1. The Fe(VI) concentration was monitored using a spectrometer until no residual Fe(VI) was detected. The solutions were filtered using 0.45 μm nylon filters into HPLC vials. The concentration of the SMX in the resulting reaction mixtures was quantified by the use of an HPLC (Waters Alliance 2695, Milford, MA, USA) with a RP-C_{18} column (5 μm; 250 × 10 mm,