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Short Communication

Kinetic assessment of the potassium ferrate(VI) oxidation of antibacterial drug sulfamethoxazole

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Abstract

Sulfamethoxazole (SMX), a worldwide-applied antibacterial drug, was recently found in surface waters and in secondary wastewater effluents, which may result in ecotoxical effects in the environment. Herein, removal of SMX by environmentally-friendly oxidant, potassium ferrate(VI) (K_2FeO_4), is sought by studying the kinetics of the reaction between Fe(VI) and SMX as a function of pH (6.93–9.50) and temperature (15–45 °C). The rate law for the oxidation of SMX by Fe(VI) is first-order with respect to each reactant. The observed second-order rate constant decreased non-linearly from $1.33 \pm 0.08 \times 10^3$ M^{-1} s^{-1} to $1.33 \pm 0.10 \times 10^0$ M^{-1} s^{-1} with an increase of pH from 7.00 to 9.50. This is related to protonation of Fe(VI) ($HFeO_4^- \Longleftrightarrow H^+ + FeO_4^{2-}$; $pK_{a,HFeO_4} = 7.23$) and sulfamethoxazole ($SH \Longleftrightarrow H^+ + S^-$; $pK_{a,SH} = 5.7$). The estimated rate constants were k_{11} ($HFeO_4^- + SH$) $= 3.0 \times 10^4$ M^{-1} s^{-1}, k_{12} ($HFeO_4^- + S^-$) $= 1.7 \times 10^2$ M^{-1} s^{-1}, and k_{13} ($FeO_4^{2-} + SH$) $= 1.2 \times 10^0$ M^{-1} s^{-1}. The energy of activation at pH 7.0 was found to be 1.86 ± 0.04 kJ mol^{-1}. If excess potassium ferrate(VI) concentration (10 μM) is used than the SMX in water, the half-life of the reaction using a rate constant obtained in our study would be approximately 2 min at pH 7. The reaction rates are pH dependent; thus, so are the half-lives of the reactions. The results suggest that K_2FeO_4 has the potential to serve as an oxidative treatment chemical for removing SMX in water.

Keywords: Potassium ferrate(VI); Oxidation; Kinetics; Sulfamethoxazole; Water treatment

1. Introduction

In recent years, there has been an increasing concern about the pharmaceuticals in the aquatic environment. Pharmaceuticals are produced with the aim of causing a biological effect and when applied to humans, many of their constituents are excreted unchanged through urine (Jones et al., 2001). Pharmaceuticals are also used as a preventive measure for veterinary purposes and as agricultural herbicides (Hirsch et al., 1999; Battaglin et al., 2000). Studies have reported pharmaceuticals in the environment, particularly antibiotics known as the sulfa drugs in the concentration ranging from 0.13 to 1.9 μg l^{-1} (Boreen et al., 2004; Carballa et al., 2004). Although sulfa drugs are present in low concentrations, which do not exceed any current water standards, their existence in the environment may result in ecotoxicolog-

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ical effects (Jones et al., 2001, 2002). Particularly, bacterial resistance effect at low concentration of drugs may be irreversible (Jorgensen and Halling-Sorensen, 2000).

Different treatment methods have been demonstrated to treat pharmaceuticals in drinking water (Ternes et al., 2002; Latch et al., 2003). Biodegradation of antibacterial drugs under aerobic conditions is limited (Ingerslev and Halling-Sorensen, 2000). Chlorination of sulfa drugs has been examined in detail to understand the kinetics, mechanisms, and pathways of the process (Uetrecht et al., 1993; Dodd and Huang, 2004). Significant transformation of drugs occurs during disinfection of municipal wastewater and drinking water using free chlorine. Recently, ozonation and filtration with granular activated carbon were shown as promises to remove pharmaceuticals (Ternes et al., 2002). Other advanced oxidation processes (AOPs) using O_3/H_2O_2 and UV/H_2O_2 have demonstrated degradation of pharmaceuticals (Zeiener and Frimmel, 2000; Vogna et al., 2004). The photocatalytic oxidation process can eliminate and mineralize pharmaceuticals in water (Doll and Frimmel, 2004). Recently, kinetics of the oxidation of pharmaceuticals with ozone and hydroxyl radicals (·OH) was studied in order to predict removal of pharmaceuticals (Huber et al., 2003). Another promising method is the use of potassium ferrate(VI) (K_2FeO_4) in treating pharmaceuticals in water.

Ferrate(VI) ($Fe^{VI}O_4^{2-}$, Fe(VI)) is a strong oxidant that can be seen from the reduction potentials of reactions (1) and (2) in acidic and alkaline solutions, respectively (Wood, 1958).

$$FeO_4^{2-} + 8H^+ + 3e^- \Longleftrightarrow Fe^{3+} + 4H_2O \quad E^0 = 2.20\ V \tag{1}$$

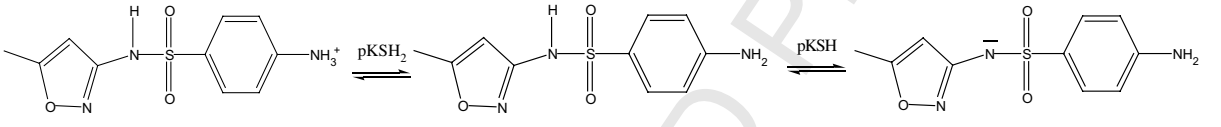
$$FeO_4^{2-} + 4H_2O + 3e^- \Longleftrightarrow Fe(OH)_3 + 5OH^- \quad E^0 = 0.70\ V \tag{2}$$

The spontaneous decomposition of Fe(VI) in water forms molecular oxygen (Eq. (3)).

$$FeO_4^{2-} + 5H_2O \rightarrow Fe^{3+} + 3/2O_2 + 10OH^- \tag{3}$$

A by-product of Fe(VI) is non-toxic, Fe(III), making Fe(VI) an environmentally friendly chemical for coagulation, disinfection, and oxidation for multipurpose treatment of water and wastewater (Jiang et al., 2001; Jiang and Lloyd, 2002; Sharma, 2002; Sharma et al., 2002; Lee et al., 2004). For the last few years, we have been studying the rates, stoichiometry, and products of the Fe(VI) oxidation of nitrogen- and sulfur-containing pollutants in the aquatic environment (Sharma et al., 2002). More recently, we have initiated the studies on the Fe(VI) oxidation of emerging contaminants in water (Eng et al., 2004; Hu et al., 2004). The aim of the research presented here is to assess the potential of Fe(VI) for oxidation of a specific sulfa-drug, sulfamethoxazole, in water.

Sulfamethoxazole (SMX) consists of two moieties, aniline and five member heterocyclic group, connected to both sides of the sulfonamide linkage (–NH–($S(O_2)$–) (Eq. (4)).



(4)

SMX has two dissociation constants, one corresponds to deprotonation of the aniline N and the other involves the protonation of sulfonamide NH (Pankratov et al., 2001). To assess the removal efficiency of SMX, it is critical to evaluate the rate constants for the oxidation of SMX with Fe(VI). The kinetics of the reaction between Fe(VI) and SMX were therefore determined as a function of pH (6.93–9.50) and temperature (15–45 °C). The results demonstrate that Fe(VI) can be applied to treat SMX in water.

2. Experimental

2.1. Materials

All chemicals (Sigma, Aldrich) were of reagent grade or better and were used without further purification. Solutions were prepared with water that had been distilled and then passed through an 18 MΩ Milli-Q water purification system. Potassium ferrate(VI) (K_2FeO_4) of high purity (98.6%) was prepared by the method of Thompson et al. (1951). The Fe(VI) solutions were prepared by addition of solid samples of K_2FeO_4 to 0.005 M Na_2HPO_4/0.001 M borate at pH 9.0, a pH at which the solutions are most stable (Carr et al., 1985). A molar absorption coefficient of $\varepsilon_{510nm} = 1150\ M^{-1}\ cm^{-1}$ was used for the calculation of $[FeO_4^{2-}]$ at pH 9.0 (Bielski and Thomas, 1987). Sulfamethoxazole

solutions were prepared in 0.01 M phosphate buffers to obtain the desired pH of the reaction mixtures.

2.2. Kinetics

A stopped-flow spectrophotometer (SX.18 MV, Applied Photophysics, UK) equipped with a photomultiplier (PM) detector was used to make the kinetic measurements. An HP8453 UV/Vis spectrophotometer was also used for the spectral studies. In the experiments, ferrate(VI) solutions were mixed in a 1:1 volume (100 μl) ratio with SMX at the desired pH. The pH of the mixed solution was controlled mostly by 0.01 M phosphate buffer solution of SMX. The pH of the phosphate solution was adjusted such that the mixture pH could be of desired value. The kinetic curves were collected by the PM detector and processed using the non-linear least-squares algorithm within the SX.18 MV software. The temperatures of the reaction media were controlled within ±0.1 °C with a Fischer Scientific Isotemp 3016 circulating water bath. The rate constants represent mean values of nine kinetic runs.

3. Results and discussion

3.1. Stoichiometry

The stoichiometric experiments were carried out by mixing equal volumes (5×10^{-3} l) of Fe(VI) and SMX together at pH 9.1. The concentration of SMX was kept at 1.0×10^{-4} M and Fe(VI) concentrations ranged from 5.0×10^{-5} M to 3.2×10^{-4} M. Ferrate(VI) concentrations were determined spectrophotometrically before and after mixing with SMX. The results obtained gave a stoichiometry of 1:1 (Fe(VI):SMX). In a separate experiment, the addition of potassium thiocyanate to the final reaction mixture gave a characteristic red ferric thiocyanate complex color. This suggests that the final product of Fe(VI) was Fe(III).

3.2. Rate law

The rate expression for the reaction of Fe(VI) with sulfamethoxazole can be expressed as

$$-\mathrm{d[Fe(VI)]}/\mathrm{d}t = k[\mathrm{Fe(VI)}]^m[\mathrm{SMX}]^n \quad (5)$$

where [Fe(VI)] and [SMX] are the concentrations of Fe(VI) and sulfamethoxazole, m and n are the orders of the reaction, and k is the overall reaction rate constant. The kinetic studies were carried out under pseudo-order conditions with SMX in excess i.e. [SMX] ≫ [Fe(VI)]. The concentrations of SMX in the experiments were more than 1×10^{-3} M, while the Fe(VI) concentrations were ranged from 0.75 to 1.00×10^{-4} M. Eq. (5) can thus be re-written under pseudo-order conditions as:

$$-\mathrm{d[Fe(VI)]}/\mathrm{d}t = k_1[\mathrm{Fe(VI)}]^m \quad (6)$$

where $k_1 = k[\mathrm{SMX}]^n$ (7)

Reactions were monitored by measuring the absorbance of Fe(VI) at 510 nm wavelength as a function of time. The reactions were completed within ten seconds and were followed for at least two half-lives. A successive integration model using the kinetic software for the absorbance of Fe(VI) as a function of time gave the best fit for an exponential value of 1, indicating the reaction is first-order with respect to Fe(VI). The k_1 values for the reaction were determined at various concentrations of SMX at pH 7.0 and 9.1. The plots of k_1 values versus [SMX] were linear with correlation coefficient, $r^2 = 0.99$ (Fig. 1). The k_1 values were corrected for the spontaneous Fe(VI) decay in buffer solutions at different pH values. A direct proportionality of the k_1 to the [SMX] suggests that the rate law for this reaction is first-order with respect to SMX. Since the stoichiometry of the reaction is 1:1, the observed rate law may be written in-terms of both Fe(VI) and SMX as

$$-\mathrm{d[Fe(VI)]}/\mathrm{d}t = -\mathrm{d[SMX]}/\mathrm{d}t = k[\mathrm{Fe(VI)}][\mathrm{SMX}] \quad (8)$$

The effect of temperature on the reaction of Fe(VI) with SMX was studied as a function of temperature (15–45 °C) at pH 7.0 (Table 1). The plot of log$k$ vs

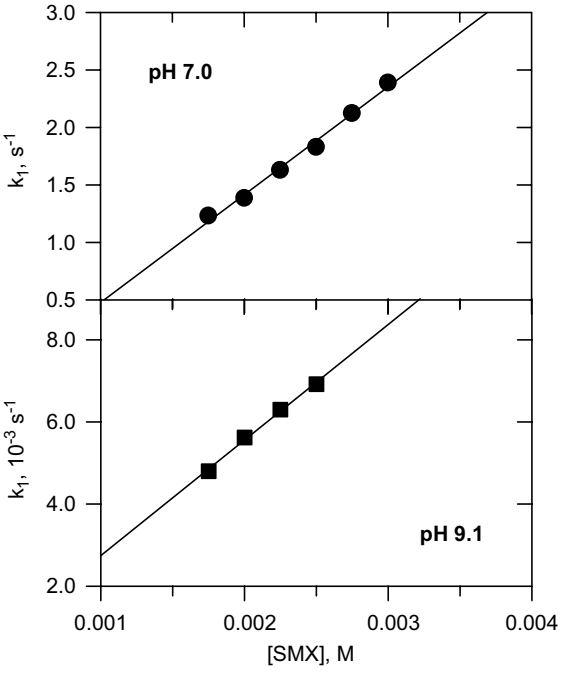


Fig. 1. Pseudo first-order rate constant, k_1 (s^{-1}) versus [SMX] at different pH and 25 °C.

Table 1
Temperature dependence of rate constant (k) for the oxidation of sulfamethoxazole (SMX) by ferrate(VI) at pH 7.0

Temperature, °C	k, 10^2 M^{-1} s^{-1}
15	8.29
25	8.46
35	8.57
45	8.95

$1/T$ was linear ($r^2 = 0.93$) and gave an activation energy of 1.86 ± 0.04 kJ mol^{-1}. This activation energy contains terms due to the effect of temperature on the dissociation of $HFeO_4^-$ and SMX.

3.3. pH dependence

The reaction rate constants for the reaction of Fe(VI) with SMX were determined as a function of pH and the rate of the reaction increases with a decrease in pH (Fig. 2). A change in k with pH can be described by considering the equilibrium of mono protonated Fe(VI) ($HFeO_4^-$) and SMX (SH)

$$HFeO_4^- \Longleftrightarrow H^+ + FeO_4^{2-}$$

$$pK_{a,HFeO_4} = 7.23 \quad \text{(Sharma et al., 2001)} \qquad (9)$$

$$SH \Longleftrightarrow H^+ + S^-$$

$$pK_{a,SH} = 5.7 \quad \text{(Boreen et al., 2004)} \qquad (10)$$

Two forms of mono protonated Fe(VI) react with two forms of SMX in the studied pH range (Fig. 3).

$$HFeO_4^- + SH \rightarrow Fe(OH)_3 + \text{Product(s)} \qquad (11)$$

$$HFeO_4^- + S^- \rightarrow Fe(OH)_3 + \text{Product(s)} \qquad (12)$$

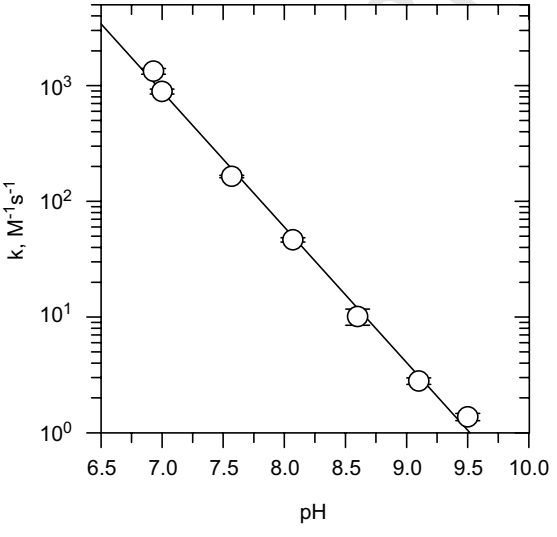


Fig. 2. The rate constant, k (M^{-1} s^{-1}) versus pH at 25 °C.

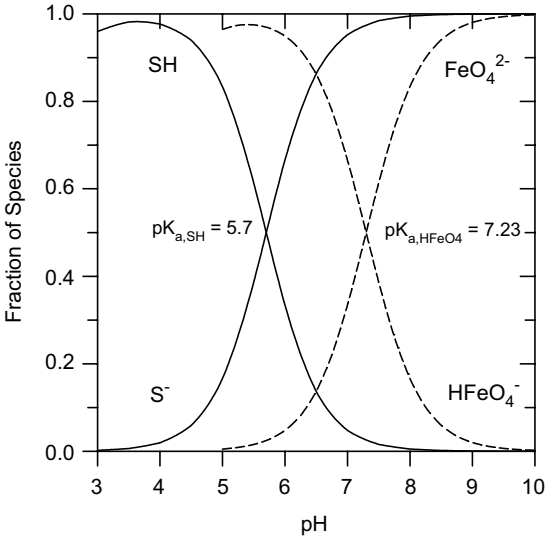


Fig. 3. Speciation of Fe(VI) and SMX.

$$FeO_4^{2-} + SH \rightarrow Fe(OH)_3 + \text{Product(s)} \qquad (13)$$

$$FeO_4^{2-} + S^- \rightarrow Fe(OH)_3 + \text{Product(s)} \qquad (14)$$

The rate of disappearance of Fe(VI) is given by

$$-d[Fe(VI)]/dt = k_{11}[HFeO_4^-][SH] + k_{12}[HFeO_4^-][S^-] + k_{13}[FeO_4^{2-}][SH] + k_{14}[FeO_4^{2-}][S^-] \qquad (15)$$

k can be derived into Eq. (16) considering equilibrium of Eqs. (9) and (10).

$$k = k_{11}\alpha(HFeO_4^-)\alpha(SH) + k_{12}\alpha(HFeO_4^-)\alpha(S^-) + k_{13}\alpha(FeO_4^{2-})\alpha(SH) + k_{14}\alpha(FeO_4^{2-})\alpha(S^-) \qquad (16)$$

where $\alpha(HFeO_4^-) = [H^+]/([H^+] + K_{a,HFeO_4})$; $\alpha(FeO_4^{2-}) = K_{a,HFeO_4}/([H^+] + K_{a,HFeO_4})$;

$\alpha(SH) = [H^+]/([H^+] + K_{a,SH})$; and

$\alpha(S^-) = K_{a,SH}/([H^+] + K_{a,SH})$.

Initially, mono protonated Fe(VI) species, $HFeO_4^-$ was considered the most reactive species to explain the pH dependence of the reaction, as was found in previous studies in our laboratory (Sharma et al., 1997, 1998, 1999, 2000, 2002). As shown in Fig. 4A, there is a linear relationship between the rate constants and fraction of $HFeO_4^-$ species (α_{HFeO_4}) at lower α_{HFeO_4} (i.e. higher pH), while deviation occurs in the linearity at higher α_{HFeO_4} (i.e. lower pH) (Fig. 4A). At a lower pH, the equilibrium of sulfamethoxazole (Eq. (10)) caused non-linearity in the relationship. This was evident from the linear relationship with respect to the fractions of both species, $HFeO_4^-$ and SH (Fig. 4B). Thus, both equilibrium are important in variation of k with pH in the oxidation of SMX by Fe(VI).

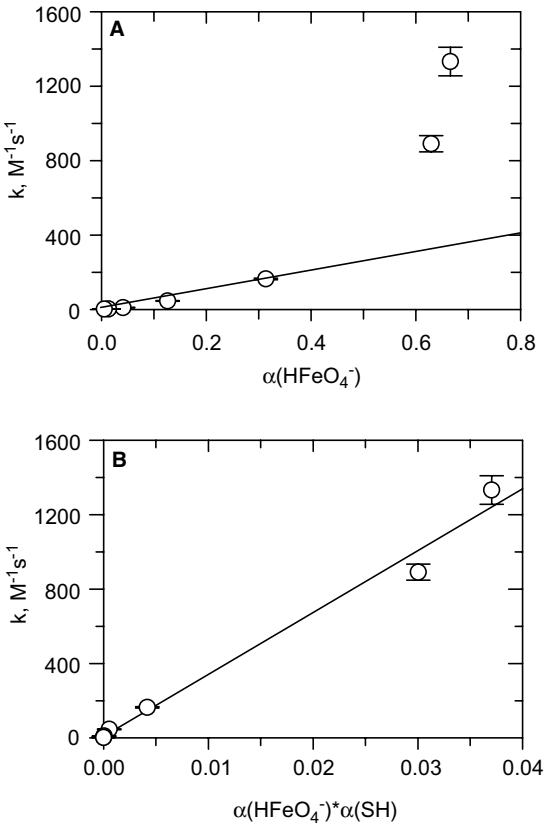
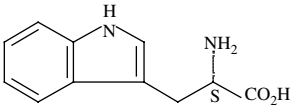
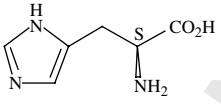
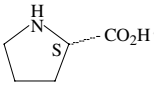
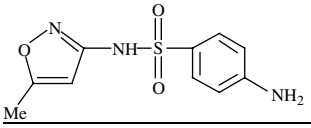


Fig. 4. Rate constant, k (M^{-1} s^{-1}) dependence the speciation of Fe(VI) and SMX.

The values of the individual rate constants of Eq. (16) were obtained by the non-linear regression of the data. Reaction (14) was not needed to fit the data and rate constants for other reactions were $k_{11} = 3.0 \times 10^4$ M^{-1} s^{-1}, $k_{12} = 1.7 \times 10^2$ M^{-1} s^{-1}, and $k_{13} = 1.2 \times 10^0$ M^{-1} s^{-1}. The estimated rate constants fit reasonably to the experimental data (Fig. 3 solid line). A faster reaction rate constant of the negatively charged protonated forms of Fe(VI) ($HFeO_4^-$) with the neutral SMX species (SH) than the negatively charged ionized species (S^-) was expected and is responsible for an increase in rates of oxidation of sulfamethoxazole by Fe(VI) with decreasing pH. Additionally, the $HFeO_4^-$ species also reacts faster than the FeO_4^{2-}. The fraction of $HFeO_4^-$ species increases with decrease in pH (Fig. 3) and thus also contributes to an increase in the rate with a decrease in pH. This is consistent with the faster rates for the spontaneous decomposition of Fe(VI) with a decrease in pH (Carr et al., 1985; Rush et al., 1996). The partial radical characters ($Fe^{VI} = O \leftrightarrow Fe^{V}-O^{\bullet}$) may be proton stabilized and increase the reactivity with sulfamethoxazole. It has also been stated that $HFeO_4^-$ has a larger spin density on the oxo ligands than FeO_4^{2-}, which increases the oxidation ability of protonated Fe(VI) (Shiota et al., 2003).

Reactivity of Fe(VI) with N-containing aromatic compounds at pH 9.0 are listed in Table 2. The order of reactivity is tryptophan > histidine > proline > sulfamethoxazole. The slowest rate of Fe(VI) with SMX relative to amino acids implies that sulfonamide group of SMX is not influencing the reactivity. In comparison,

Table 2
Reactivity of Fe(VI) with N-containing aromatic compounds at pH 9.0

Compound	k, 10^1 M^{-1} s^{-1}	Reference
Tryptophan 	25.5 ± 0.20	Sharma and Bielski, 1991
Histidine 	15.0 ± 0.20	Sharma and Bielski, 1991
Proline 	1.10 ± 0.10	Sharma and Bielski, 1991
Sulfamethoxazole 	0.28 ± 0.02	This Study

cysteine undergoes oxidation at the –SH group and gives the highest rate constant, $k = 750 \pm 49\ M^{-1}\ s^{-1}$, among amino acids (Sharma and Bielski, 1991). Previous work on the oxidation of amino acids, containing no sulfur group(s), showed that Fe(VI) preferentially attacked α-N and/or α-C–H of the side group rather than indole moiety of the amino acids (Sharma and Bielski, 1991). However, a recent study on the oxidation of N-containing ring compound by Fe(VI) gave ammonia as one of the oxidized product; suggesting opening of the ring in the oxidation process (Eng et al., 2004). The oxidation of SMX by Fe(VI) can thus take place at either aniline amino-nitrogen or sulfonyl amido-nitrogen. The 5-methylisoxazole moiety of SMX may also play a role in the reactivity with Fe(VI). An independent investigation of Fe(VI) reactivity with 3,5-dimethylisoxazole (CH_3–C_3(O–N)–CH_3) and 4-aminophenyl methyl sulfone (–SO_2–C_6H_4–NH_2) will unravel the site of attack in the oxidation of SMX by Fe(VI). Furthermore, a product analysis of SMX oxidation will give understanding of the mechanism of the degradation of SMX in water by Fe(VI).

4. Conclusions

The rate law for the oxidation of SMX by Fe(VI) is first-order with respect to each reactant. If one uses the excess Fe(VI) concentration (10 μM) than the SMX in water, the half-life of the reaction using a rate constant obtained in our study would be approximately 2 min at pH 7. The reaction rates are pH dependent; thus, so are the half-lives of the reactions. Overall, potassium ferrate(VI) exhibits good potential to be an oxidant for the removal of SMX in water.

Acknowledgements

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