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Article

Efficient Removal of Sulfamethoxazole in Aqueous Solutions Using Ferrate (VI): A Greener Treatment

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Abstract

The aim of this research is to assess the use of high purity potassium ferrate (VI) for the efficient removal of sulfamethoxazole (SMX), one of the potential micro-pollutant found in aqueous waste. In addition, various parametric studies have enabled us to deduce the mechanism in the degradation process. The pH and concentration of sulfamethoxazole enable the degradation of pollutants. Moreover, the time-dependent degradation nature of sulfamethoxazole showed that the degradation of ferrate (VI) in presence of sulfamethoxazole followed the pseudo-second order kinetics and the value of rate constant increased with an increase in the SMX concentration. The stoichiometry of SMX and ferrate (VI) was found to be 2 : 1 and the overall rate constant was estimated to be 4559 $L^2/mmol^2/min$. On the other hand, the increase in pH from 8.0 to 5.0 had catalyzed the degradation of SMX. Similarly, a significant percentage in mineralization of SMX increased with a decrease in pH and concentration. The presence of co-existing ions and SMS spiked real water samples was extensively analyzed in the removal of SMX using ferrate (VI) to simulate studies on real matrix implication of ferrate (VI) technology.

Keywords: *Ferrate (VI) technology, Sulfamethoxazole, Efficient treatment, Mineralization of pollutant, Real matrix treatment*

1. Introduction

Pharmaceuticals *viz*., analgesics, antibiotics, anti-inflammatory medicines, and steroids are known to be some of the emerging micro-pollutants that pose public and environmental health hazards due to their negative impact on biosystems[1-4]. Pharmaceutical compounds are substances which are used to alter, correct, or restore physiological functions through metabolic, pharmacological, or immunological action. In spite of the prevalence of such micro-pollutants in the marine environment at such low level (micro to nanogram per liter), the environmental risk of these micro-pollutants is severe and has significant effects on aquatic life[5].

Sulfamethoxazole (SMX) is an antibiotic drug which is often found in wastewater due to its low biodegradability and high usage by human beings and animals for prevention of various infectious diseases, including meningitis, urinary tract infection, respiratory system infection etc.[6-10]. Moreover, it is a known fact that more than 85% of the administered sulfamethoxazole is found in the urine or faeces excreta since it is not metabolized in the biological system[11]. Reverse osmosis[12], nanofiltration[13], adsorption by activated carbon or biochar [14-17], photolysis[18-20], and ozonation[21] are some of the methods often suggested for removing the SMX from wastewater, but their performance is stated to be varied and sometimes not achieve the required efficiency for complete elimination of these micro-pollutants. Additionally, oxidative removal (such as ozonation, chlorination) of micro-pollutants may result with more toxic intermediate compounds, which pose even a greater threat[22].

In treatment of various pharmaceutical pollutants present in aqueous solution, the conventional wastewater treatment plants are found to be inefficient for the removal of these persistent chemicals. Hence, there is need to develop more advanced treatment technologies for efficient removal or degradation of these pollutants from aqueous solutions. Ferrate (VI) is a formidable oxidant having redox potential of 2.20 and 0.72 V at pH of 1.0 and 14.0, respectively. It has multifunctional application in the wastewater treatment as it is a useful oxidant/disinfectant and also serves as an efficient coagulant to remove the non-degradable contaminants in aqueous solutions[23]. In addition, treatment with ferrate (VI) is not associated with generation of harmful by-products, thus, it is known to be an eco-friendly technology[24-28].

On reduction, ferrate ion (FeO_4^{2-}) gives ferric hydroxide and nascent oxygen in aqueous medium and the reaction is given as below:

$$4\ FeO_4^{2-} + 10\ H_2O \rightarrow 4\ Fe(OH)_3 + 8\ OH^- + 3\ O_2 \qquad (1)$$

The above-mentioned reaction mechanism facilitates the degradation

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of pollutants using the ferrate. The iron compound finally produces the non-toxic ferric ion, which forms oligomeric iron (III) hydroxides. Eventually, this process effectively cleans all suspended solids and particulate matter and at the same time allows the purification to occur simultaneously[29,30].

Therefore, in view of the potential of ferrate (VI), the present research assesses the synthesized ferrate (VI) for the efficient elimination of one of the most important pharmaceutical drugs *viz*., sulfamethoxazole from aqueous solution. The parametric studies enabled us to deduce the mechanism of the degradation process. Moreover, the mineralization of sulfamethoxazole is achieved along with the treatment of sulfamethoxazole spiked real water treatment using varied doses of ferrate (VI).

2. Material and Methods

Sulfamethoxazole, diethyl ether, and hexane were obtained from Sigma Aldrich Co., USA. Oxalic acid, disodium hydrogen phosphate, potassium hydroxide, iron (III) nitrate nonahydrate, hydrochloric acid, and the glass filtration with fritted funnel were obtained from Merck India Ltd., India. Sodium chloride, disodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$), glycine and syringe filter (pore size of 0.22 μm and 25 mm in diameter) were obtained from Himedia India Ltd, India. Ethylene diamine tetra acetic acid, sodium nitrate and sodium nitrite were obtained from Loba Chemicals, India. Purified sodium hypochlorite (NaClO; *Ca* 15%) was procured from Thermo Fisher Scientific India Pvt. Ltd. Sartorius water Purification System (model: Arium Mini Plus UV Lab., SterilePlus, Sartopore 2150, Germany; pore size of 0.45 μm + 0.2 μm) was utilized for purified water.

GF/C Whatman Filter Paper (diameter of 47 mm) was procured from Whatman, USA. The real water sample was obtained from Chite River, located at the outskirts of Aizawl city, India. The UV-Visible Spectrophotometer (UV-1800, Shimadzu, Japan) was used to measure the absorbance. The NPOC (non-purgeable organic carbon) data was collected using the TOC analyzer (total organic carbon; Shimadzu, Japan; Model: TOC-VCPH/CPN. HPLC instrument along with C18 column (4.6 × 250 mm) (model: Waters 515 HPLC pump, 2489 UV-Vis detector, USA) was used for quantitative analysis.

2.1. Preparation of potassium ferrate (VI)

Potassium ferrate (VI) was synthesized via wet oxidation process as demonstrated previously[31-34]. The synthesized potassium ferrate (VI) crystals were stored in a vacuum desiccator which is contained with excess potassium hydroxide pellets. The purity of potassium ferrate (VI) was checked using the known method as described previously[35] and was found to be > 90%[35].

2.2. Batch reactor method

The stock solution (0.5 mmol/L) of sulfamethoxazole was prepared by dissolving an appropriate amount of sulfamethoxazole in distilled water. The stock solution was then diluted to obtain the required concentrations of sulfamethoxazole. The pH of the solution was adjusted dropwise by adding 0.1 mol/L of hydrochloric acid or sodium hydroxide solutions from pH 5.0 to 8.0. The batch reactor experiments were performed by taking different concentrations of sulfamethoxazole solutions (0.02 to 0.2 mmol/L; 100 mL each) at a constant pH (i.e., at pH 6.0) for concentration studies and varied pH (from pH 5.0 to 8.0) at constant concentration of sulfamethoxazole (0.1 mmol/L) in a small reactor container. A known amount of freshly prepared ferrate (VI) (K_2FeO_4) was then added into the reactor vessel under stirring conditions. The ferrate (VI), which readily reduces in presence of sulfamethoxazole, signifies the oxidation property of sulfamethoxazole. The removal of ferrate (VI) was monitored by the change in absorbance of solution mixture as recorded by a UV-Vis Spectrophotometer at regular intervals within 20 minutes at wave length of 510 nm. The blank absorbance of self-decomposition of ferrate (VI) alone under the same pH conditions was also recorded at 510 nm, in order to nullify the blank correction with that of the absorbance in presence of sulfamethoxazole. The solution mixtures were further stirred for 2 h. and then filtered using a micro-syringe filter with a pore size of 0.22 μm. The filtered sample is divided in two fractions and one fraction was subjected to the TOC (total organic carbon) measurements, while the other fraction was subjected to the HPLC (high performance liquid chromatography) measurements.

The HPLC instrument was having a C18 column (4.6 × 250 mm) (Waters 515 HPLC pump and a UV-Vis detector of Waters 2489, USA). The volume of the sample injected into the system was 20 μL at a flow rate of 1.0 mL/min. The solvent used were acetonitrile and water, both of which have HPLC grade at a volumetric proportion of 45 : 55. This was the mobile phase and the sulfamethoxazole was detected at a wavelength of 259 nm. The peak area method was utilized to obtain the concentration of sulfamethoxazole and the removal of sulfamethoxazole was presented in terms of percentage removal. The results obtained are expressed as percentage removal of sulfamethoxazole as a function of sulfamethoxazole concentration and pH.

Similarly, the change in NPOC (non-purgeable organic carbon) value resembles that of mineralization of sulfamethoxazole from aqueous solutions. Consequently, the percentage mineralization of sulfamethoxazole, both as a function of sulfamethoxazole concentration and pH was obtained and presented.

The degradation of sulfamethoxazole by ferrate (VI), in presence of several co-existing ions *viz*., NaCl, $C_2H_5NO_2$, $C_2H_2O_4$, Na_2HPO_4, $NaNO_2$, $NaNO_3$ and EDTA was analyzed extensively. The concentration of sulfamethoxazole, ferrate (VI) and co-existing ions were taken 0.10, 0.20 and 0.50 mmol/L, respectively at pH 6.0. The quantity of sulfamethoxazole in the sample was then analyzed through HPLC measurements after filtering using a micro-syringe filter having a pore size of 0.22 μm.

The real water sample was collected from the Chite river, Aizawl, India. The samples were stored in polyethylene containers at room temperature and subjected to various parametric studies. The level of sulfate, phosphate, fluoride and nitrate in real water was obtained using a Multiparameter photometer (Hanna instrument, model: HI98194, USA) by utilizing their respective reagents. The elements *viz*., Ni, Fe, Cu, Pb,

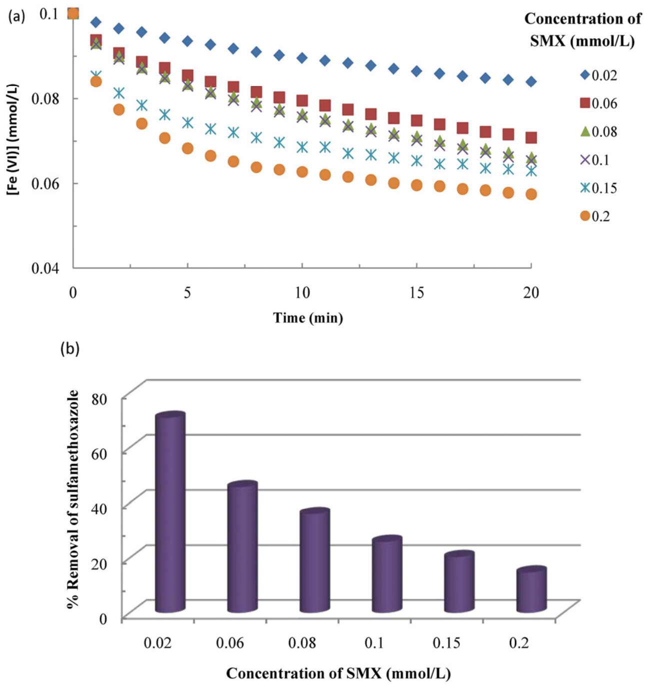

Figure 1. (a) Degradation of ferrate (VI) at various concentrations of sulfamethoxazole as a function of contact time at pH 6.0 [Fe(VI) concentration: 0.1 mmol/L], (b) Percentage removal of sulfamethoxazole as a function of SMX concentration using a constant dose of ferrate (VI) (0.1 mmol/L) at pH 6.0.

Ca, Mn, and Zn were analyzed using Atomic Absorption Spectroscopy (AAS; model: AA-7000 Series, Shimadzu, Japan). Similarly, the NPOC data was obtained using the TOC analyzer. The water from Chite river was spiked with various concentrations of sulfamethoxazole solutions (0.02 to 0.2 mml/L) at pH 6.0. These samples were then treated with known doses of ferrate (VI) (0.10 mmol/L). Further, the treated samples were filtered using the syringe filters (0.22 µm pore size) and then subjected to the HPLC analysis. The obtained HPLC data were then compared with the data obtained using distilled water.

3. Results and Discussion

3.1. Effect of sulfamethoxazole concentrations

The solutions having varied concentrations of sulfamethoxazole (0.02 to 0.20 mmol/L) was treated with a constant dose of ferrate (VI) 0.1 mmol/L at constant pH 6.0. This was done to achieve a ferrate (VI) to sulfamethoxazole molar ratio of 0.1 : 0.2 mmol/L from 0.1 : 0.02. The wide range of molar ratios made it possible to deduce the overall stoichiometric ratios of the degradation of sulfamethoxazole by ferrate (VI). The change in ferrate (VI) concentration in presence of sulfamethoxazole was observed via the UV-Visible spectrophotometer as a function of sulfamethoxazole concentrations and time of contact and the results are illustrated as in Figure 1(a). From the Figure 1(a) it is evident that the ferrate (VI) concentration was decreased significantly by increasing the concentration of sulfamethoxazole. This indicated that the ferrate (VI) facilitated the degradation of sulfamethoxazole. Moreover, a rapid degradation of ferrate (VI) was observed during the initial period of contact which attained a constant value at the lapse of time of *Ca* 10 mins. This confirms that ferrate (VI) causes the sulfamethoxazole to degrade efficiently. Further, quantitative study reveals that the concentration of ferrate (VI) was reduced from 0.1 mmol/L to 0.057 mmol/L at the end of 20 mins using 0.2 mmol/L of sulfamethoxazole.

Further, the removal of sulfamethoxazole through ferrate (VI) (0.1 mmol/L) treatment was analyzed using a wide range of sulfamethoxazole concentrations i.e., 0.02 to 0.2 mmol/L at a constant pH of 6.0. The results are illustrated as in Figure 1(b). Figure 1(b) clearly demonstrated that an increase in concentration of the pollutant, results to a decrease in the removal percentage. The data obtained are illustrated as in Figure 1(b). More specifically, increasing the concentration of sulfamethoxazole from 0.02 to 0.2 mmol/L resulted to a decrease in the percentage removal of SMX from 70.96 to 16.03%, respectively at pH 6. In other words, decreasing the concentration of sulfamethoxazole favored the degradation of SMX using a constant dose of ferrate (VI). This increase in percentage removal of SMX at lower concentration mainly due to the fact that a greater number of ferrate (VI) molecules are present to degrade the fewer number of SMX molecules. Conversely, an optimum amount of sulfamethoxazole was removed at higher concentration compared to lower concentrations. This indicates that although the percentage removal of SMX is higher at lower concentrations, the content of SMX removed was more at higher concentration of sulfamethoxazole.

3.2. Kinetics of ferrate (VI) removal

The data relating to the time dependence degradation of ferrate (VI) in presence of varied concentrations of sulfamethoxazole is utilized to deduce the kinetics of degradation. The kinetics applied is demonstrated as given below. The rate of removal of ferrate (VI) is given by:

$$-\frac{d[\mathrm{Fe(VI)}]}{dt} = k_{app}[\mathrm{Fe(VI)}]^m\,[\mathrm{SMX}]^n \qquad (2)$$

where k_{app} is the apparent rate constant of ferrate (VI) degradation in presence of sulfamethoxazole (SMX). In addition, at varied concentrations of SMX, the equation (2) is reduced to equation (3):

$$-\frac{d[\mathrm{Fe(VI)}]}{dt} = k[\mathrm{Fe(VI)}]^m \qquad (3)$$

where, $k = k_{app}[\mathrm{SMX}]^n \qquad (4)$

Therefore, the time dependent data in the removal of ferrate (VI) at varied SMX concentrations is introduced in equation (3) for the pseudo-first order and pseudo-second order for estimating an optimum value of 'm'. The results indicate that the kinetic data is well suited for the pseudo-second-order rate kinetics, signifying that the optimum value of 'm' is 2 for each sulfamethoxazole concentration [*Cf.* Figure 2(a)]. Further, the detailed pseudo-second order rate constant values are evaluated at varied concentrations of sulfamethoxazole and then pre-

Table 1. Pseudo-second Order Rate Constant Values Obtained for the Degradation of Ferrate (VI) in Presence of Sulfamethoxazole at pH 6.0

Concentration of sulfamethoxazole (mmol/L)	Rate constant (k_2) (L/mmol/min)	R^2
0.02	147.7	0.966
0.06	353.1	0.955
0.08	415.0	0.974
0.1	431.2	0.969
0.15	725.2	0.905
0.2	982.9	0.943

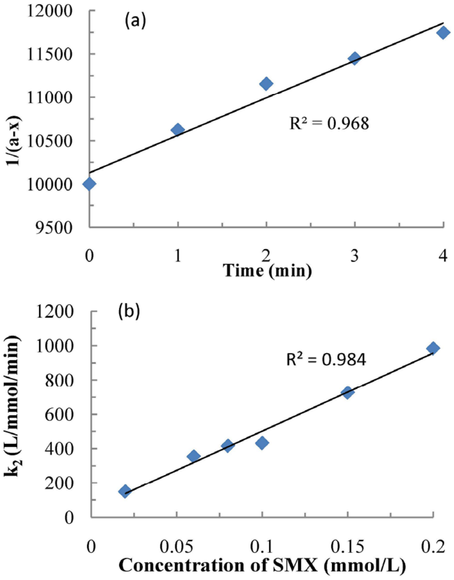

Figure 2. (a) Plot of 1/(a-x) vs time 't' in the degradation of sulfamethoxazole (SMX) by ferrate (VI) at pH 6.0 ([SMX]: 0.10 mmol/L; [Fe(VI)]: 0.10 mmol/L; 'a' and 'x' stands for the ferrate (VI) concentration at time '0' and time 't' min, respectively), (b) Variation of k_2 (pseudo-second-order rate constant) against the concentration of sulfamethoxazole concentration at pH 6.0.

sented in Table 1 along with the regression coefficient (R^2) values. The Table clearly indicated that an increase in the concentration of sulfamethoxazole (0.02 to 0.2 mmol/L) results to an increase in the pseudo-second order rate constant values (i.e., 147.7 to 982.9 L/mmol/min). The high value of pseudo-second order rate constant is due to the fact that ferrate (VI) possesses a fairly high ability to rapidly oxidize the sulfamethoxazole in aqueous solutions for degradation[32,36].

Further, the pseudo-second order rate constant values evaluated at various concentrations of sulfamethoxazole are used to obtain an optimum value of 'n'. This apparently provides the information about the molar stoichiometry between the ferrate (VI) and sulfamethoxazole in addition to the value of overall rate constant 'K_{app}' value. A plot of sulfamethoxazole concentration against the pseudo-second order rate constant values (k_2) at pH 6.0 is generated. A reasonably good linear line was obtained from the graph of sulfamethoxazole concentration against the pseudo-second order rate constant values (k_2) [*Cf.* Figure 2(b)], which clearly indicated that the value of 'n' is equal to '1'. Therefore, this clearly confirms the molar stoichiometry of sulfamethoxazole and ferrate (VI) as having a ratio of 2 : 1. Moreover, the value of k_{app} (overall rate constant) is found to be 4559 $L^2/mmol^2/min$ having the regression coefficient (R^2) value of 0.984. In aqueous media, efficient degradation of sulfamethoxazole by ferrate (VI) relatively implies a higher value of k_{app}[37,38].

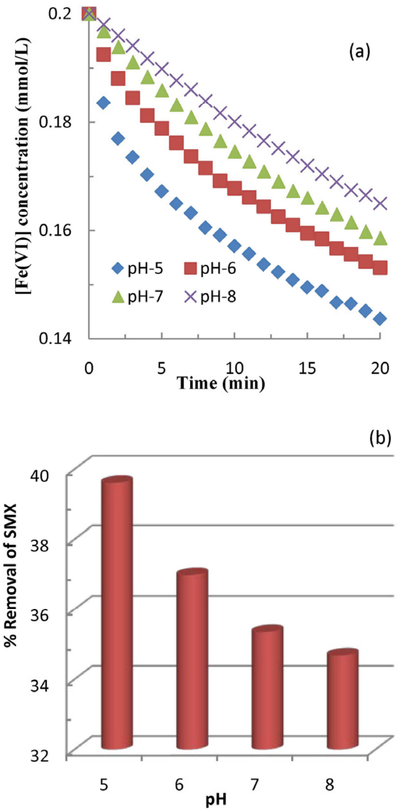

Figure 3. (a) Elimination of ferrate (VI) as a function of time and at different pH values ([Fe(VI): 0.20 mmol/L, [SMX]: 0.10 mmol/L); (b) Percentage removal of SMX as a function of pH at a fixed concentration of SMX i.e., 0.1 mmol/L ([Fe(VI)] : [SMX] = 2 : 1).

3.3. Effect of pH in removal of sulfamethoxazole

The pH of the solution is an important parameter in the degradation of sulfamethoxazole in aqueous solutions. It provides the insights of the reaction mechanism involved between the ferrate (VI) and sulfamethoxazole. The elimination of ferrate (VI) in presence of SMX as a function of pH is carried out. The molar stoichiometry which was found to be 2 : 1 for the ferrate (VI) to SMX, is employed for the pH dependence studies. Therefore, the ferrate and sulfamethoxazole concentrations were taken as 0.20 and 0.10 mmol/L, respectively. The elimination of ferrate (VI) as a function of time and at different pH values is shown as in Figure 3(a). It is evident from the Figure 3(a) that rapid and maximum elimination of ferrate (VI) was observed at lower pH values i.e., pH 5.0.

Further, the removal of sulfamethoxazole was also monitored using HPLC measurements at various pH values. The results are illustrated in Figure 3(b). From the Figure, it is evident that the percentage removal of sulfamethoxazole was decreased with an increase in pH. Quantitatively, with the decrease in pH of the solution from pH 8.0 to 5.0, the percentage elimination of SMX was increased from 34.67 to 39.7%. These results could be demonstrated with the species distribution and reactivities of species of ferrate (VI) at various pH values. Previous studies indicated that the protonated species of ferrate (VI) i.e., $HFeO_4^-$ are predominated at pH ~5.0[39]. Moreover, the spin density of the protonated species is high, hence, the species $HFeO_4^-$ possesses high reactivity towards the oxidation of sulfamethoxazole[32,40-42]. Moreover, the decrease in pH gives rise to the increase of protonated species of ferrate (VI). This implies that the rate of spontaneous decomposition of ferrate (VI) increases with a decrease in pH[43]. Additionally, the radical character of ferrate (VI) i.e., $Fe^{+6} = O \leftrightarrow Fe^{+5} - O \cdot$ stabilizes the proton which in turn, increases the reactivity of ferrate (VI) towards sulfamethoxazole. Sulfamethoxazole is, perhaps, oxidized either through the sulfonyl amido-nitrogen or aniline amino-nitrogen by the ferrate (VI). The moiety of 5-methylisoxazole in SMX is possibly involved in the degradation process. The SMX oxidation through the site attack by ferrate (VI) was revealed by a self-study of Fe (VI) reactivity using 3,5-dimethylisoxazole and 4-aminophenyl methyl[44]. Furthermore, alkyl groups are known to be electron-donating groups, which increases the reactivity of $HFeO_4^-$ in aqueous solutions. Similarly, the redox potential of Fe (VI) increases with decreasing pH, enhancing the reactivity of ferrate (VI) reactivity at lower pH values[25].

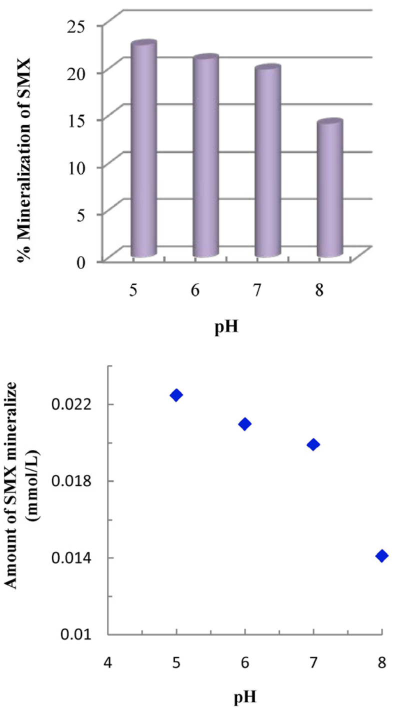

Figure 4. (a) Percentage mineralization of sulfamethoxazole as a function of pH, (b) Content of sulfamethoxazole mineralize as a function of pH at [SMX]: 0.1 mmol/L and [ferrate (VI)]: 0.2 mmol/L.

3.4. Mineralization of sulfamethoxazole

It is interesting to assess the amount of sulfamethoxazole mineralized by the ferrate (VI) treatment at varied pH conditions. Sulfamethoxazole (0.1 mmol/L) samples were treated for 2 h using a constant dose of ferrate (VI) (0.2 mmol/L) at various pH conditions (pH 5.0 to 8.0). The ferrate (VI) treated samples were subjected to the NPOC (non-purgeable organic carbon) contents. Hence, using the initial NPOC values, the percentage mineralization of sulfamethoxazole was obtained and presented as in Figure 4(a). It is evident from the Figure that the decrease in pH greatly favored the mineralization of sulfamethoxazole. Moreover, the amount of sulfamethoxazole removed at varied pH values are also obtained and shown as in Figure 4(b). Quantitatively, lowering the pH from 8.0 to 5.0 resulted to an increase in the percentage mineralization of sulfamethoxazole from 14.1 to 22.47%. These results are consistent with the previously obtained data regarding the removal of sulfamethoxazole using HPLC. However, the percentage removal of mineralization is slightly less compared to the total removal of sulfamethoxazole. This indicated that the sulfamethoxazole is partly mineralized by the ferrate (VI) treatment. It is further implied that a single dose of ferrate (VI) could mineralize a significant amount of sulfamethoxazole which may further be enhanced with the subsequent doses in reactor operations to achieve optimum efficiency.

3.5. Effect of co-existing ions

The presence of co-existing ions in the degradation of sulfamethoxazole by ferrate (VI) is studied to simulate the study for real matrix treatment. Moreover, the study may enable the assessment of preferential degradation of target pollutant in presence of various co-existing compounds. Therefore, the presence of several coexisting anions/cations *viz*., NaCl, glycine, Na_2HPO_4, EDTA, $NaNO_2$, oxalic acid and $NaNO_3$ is conducted in analysis of the degradation of sulfamethoxazole by ferrate (VI). The concentration of each of the ions was kept at 0.5 mmol/L, whereas the concentration of sulfamethoxazole and ferrate (VI) was taken as 0.1 and 0.2 mmol/L, respectively at pH 6.0. This implies that the coexisting ion concentration was taken to be five times higher than that of the sulfamethoxazole concentration. The ferrate (VI) treated samples were then subjected to measurement of sulfamethoxazole concentration using the HPLC. The results are presented in Figure 5. Figure 5 clearly indicate that the presence of NaCl, Na_2HPO_4 and $NaNO_3$ cannot significantly hinder the removal of sulfamethoxazole. However, on the other hand, the presence of EDTA and glycine greatly suppressed the percentage removal of sulfamethoxazole i.e., 13.7% and 11.11% respectively for EDTA and glycine. This is possibly due to the preferential oxidation of EDTA and glycine by the ferrate (VI) in the degradation process. Additionally, the presence of partially oxidized electrolytes $NaNO_2$ and oxalic acid showed slight suppression in the removal of sulfamethoxazole by ferrate (VI).

3.6. Real water treatment

The application of ferrate (VI) significantly depends on its effectiveness in the treatment of real matrix samples. Therefore, the real water sample was collected from the Chite River, which is located near Aizawl

Table 2. Various Physico-chemical Parametric Analysis of Riverwater (Chite, Aizawl, India)

Parameter studied	Analytical Result
pH	5.26
TDS (mg/L)	185
EC (μS/cm)	214
Oxi. Red. Potential (mV)	165
Salinity (mg/L)	216
Anions Studied	Result (mg/L)
Sulphate	3
Phosphate	1.18
Fluoride	0.00 (BDL)
Nitrate	2.33
Elements Studied	Result (ppm)
Ni	0.70
Fe	0.06
Cu	0.01
Pb	0.06
Ca	0.1
Mn	1.15
Zn	0.02
TOC Analysis	Result (ppm)
IC	5.02
NPOC	13.72

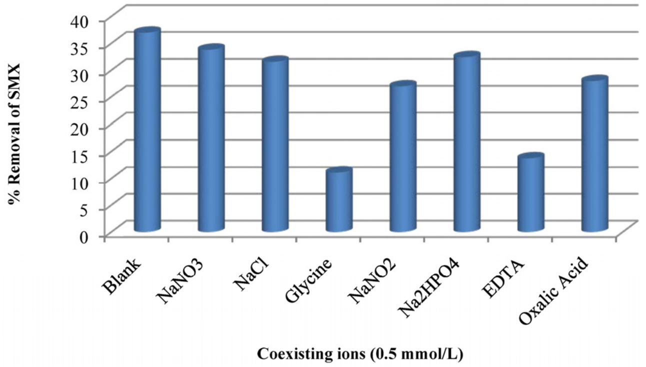

Figure 5. Oxidative degradation of co-existing ions ([SMX]: 0.1 mmol/L: concentration of co-existing ions: 0.5 mmol/L; and pH: 6.00.

City, India. The water quality was extensively analyzed for various physio-chemical parameters and the results are shown as in Table 2. The results indicated that the river water sample contained a relatively higher concentration of Mn, Ni and Ca, in addition to the high value of inorganic carbon. In addition, the water has a high level of salinity, which results to high conductivity. The river water was spiked with varied concentrations (0.02 to 0.2 mmol/L) of sulfamethoxazole and treated with a constant dose of ferrate (VI) 0.20 mmol/L at pH 6.0. The amount of sulfamethoxazole removed was analyzed using the HPLC measurements. Further, the percentage removal of sulfamethoxazole as a function of SMX concentration is obtained and the results are illustrated as in Figure 6. Figure 6 also compares the removal efficiency of ferrate (VI) for sulfamethoxazole in distilled water and in the real matrix water. The results clearly indicate that the removal of sulfamethoxazole by ferrate (VI) is efficient and is not affected in the real matrix analysis. This further implies that ferrate (VI) technology has the potential application in the real matrix treatment.

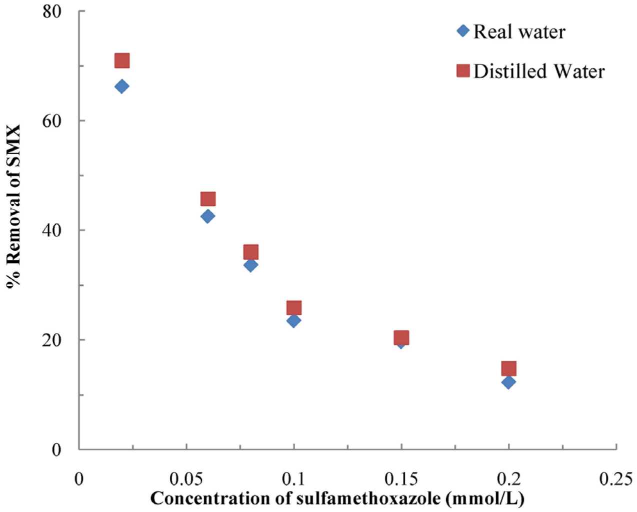

Figure 6. Percentage removal of sulfamethoxazole as a function of SMX concentration obtained in SMX spiked Chite river water and distilled water ([Fe(VI)]: 0.1 mmol/L, pH: 6.0).

4. Conclusion

High purity synthesized potassium ferrate (VI) was utilized for the efficient removal of sulfamethoxazole in aqueous solution under the batch reactor operations. The decrease in pH and concentration of sulfamethoxazole greatly increased the efficiency of sulfamethoxazole removal. The kinetic studies showed that each of the reactants followed a pseudo-second-order rate kinetics and the molar stoichiometry between the ferrate (VI) and sulfamethoxazole was found to be 2 : 1 and the overall rate constant was 4559 $L^2/mmol^2/min$. The presence of several co-existing ions does not significantly affect the removal efficiency of sulfamethoxazole except EDTA and glycine. The ferrate (VI) treatment allowed for the significant mineralization of the sulfamethoxazole and the TOC results showed that the decrease in pH greatly favored the sulfamethoxazole percentage removal. Additionally, the real matrix treatment (Chite river water) shows that the ferrate (VI) efficiency is not affected, at least, in regards to the removal of sulfamethoxazole. Thus, the study showed that ferrate (VI), as a strong oxidant, has the potential as a ‘green oxidant’ and possesses wider applications in the scaling up of the waste water treatment technology as a possible alternative in the advanced treatment process.

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