Indian Journal of Biochemistry & Biophysics
Vol. 58, December 2021, pp. 532-542

Efficient use of Ferrate(VI) in the remediation of aqueous solutions contaminated with potential micropollutants: Simultaneous removal of triclosan and amoxicillin

Levia Lalthazuala[1], Lalhmunsiama[2], Diwakar Tiwari[1]* & Seung Mok Lee[3]

[1]Department of Chemistry; & [2]Department of Industrial Chemistry, School of Physical Sciences,
Mizoram University, Aizawl-796 004 Mizoram, India
[3]Department of Environmental Engineering, Catholic Kwandong University, Gangneung-25601 (Republic of Korea)

Received 14 December 2020; *revised 18 March 2021*

Ferrate(VI) is a safer oxidant compared to the often used oxidant in various wastewater treatment plants since the ferrate(VI) is devoid with the generation of harmful by-products. Hence, the present study is aimed to obtain laboratory experimental data for the treatment of water adulterated with emerging micro-pollutant (triclosan and amoxicillin) using the ferrate(VI). The parametric studies enabled us to deduce the kinetics of ferrate(VI) removal. The molar stoichiometry of ferrate(VI) and micro-pollutant was obtained as 2:1. Further, the mineralization of triclosan and amoxicillin is obtained which further enhances the applicability of ferrate(VI) in the waste water treatment. The simultaneous removal of these two pollutants (triclosan and amoxicillin) are extensively studied using the ferrate(VI). Moreover, the pH dependent degradation using ferrate(VI) is enabled to deduce the mechanism of removal. Additionally, the real matrix samples using the natural spring water (Tuikhur water) spiked with these micro-pollutants showed that the ferrate(VI) efficiency is almost unaffected at least in the removal of these two micro-pollutants. This showed the selectivity of the ferrate(VI) in the treatment process.

Keywords: Ferrate(VI), Mineralization, Pharmaceuticals, Real matrix samples, Selectivity, Simultaneous removal

Pharmaceutical products are chemical compounds that are extensively consumed by humans and animals for the treatment of various illnesses or even to enhance the quality of life[1]. The wide distribution of these compounds at low level in the water bodies is becoming a worldwide concern at present hence, are considered as potential and emerging contaminants of water bodies[2]. These compounds are primarily entering the terrestrial environment as a result of anthropogenic practices *viz*., landfill leaching, inefficient wastewater treatment plants (WWTPs), livestock farms, and their processing[3,4]. Further, it was reiterated that the presence of PPCPs trace level in water bodies has raised serious concern of the ecosystem's vulnerability[5]. PPCPs are grouped into different clusters depending on their implementations and properties. These compounds are employed either in mixture forms or as a specific product that is used to alter physiological processes, correct or repair them by a biochemical, pharmacological, or immunological intervention[6]. In a line, in the year 2000, EU and USEPA has identified such 33 priority chemicals which are further updated in 2007 and added several more chemicals including the diclofenac, iopamidol, musks, Ibuprofen, clofibric acid, triclosan *etc*. as future emerging and priority chemicals[7].

Triclosan is an antibacterial agent and it is extensively used as an additive in various personal care products, and also as an assortment of consumer items including toothpaste, soaps, plastic consumer goods, toys, hand wash as well as textiles[8,9]. However, a large amount of the used triclosan is washed down to the sewage treatment plants or surface water and other waterbodies[10,11].Triclosan is one of known potential endocrine disruptors, especially disrupting the metabolic processes or homeostasis of thyroid hormone[12,13]. Furthermore, the by-products such as methyl triclosan, biphenyl ethers and chlorinated phenols are highly toxic and has shown carcinogenic character with low biodegradability and bioaccumulation[14], which may lead to long term health risk as it has higher potential to accumulate in the biological system[15–19]. On the other hand, amoxicillin is one of the most common antibiotic that

---

*****Correspondence:
Phone: +91-9862323015 (Mob);
Fax: +91-389-2330834;
E-mail: diw_tiwari@yahoo.com

is often prescribed to the human as well to livestock to treat the respiratory disorders, stomach illnesses, urinary tract infections, skin bacterial infections, pharyngitis, and tonsillitis, as well as helicobacter pylori infection and duodenal ulcer disease[20–22]. However, due to excess release from several anthropogenic activities, it is considered as potential water contaminants[23,24]. The longer intake of amoxicillin causes rashes, vomiting, nausea and antibiotic-associated colitis as possible side effects in humans[25]. It further causes medication allergies, toxicological issues, and development of antibiotic-resistant bacteria[26,27].

Ferrate(VI) is regarded as a safer oxidant which is has multiple functions *viz*., coagulant or disinfectant in water treatment. As a strong oxidant, it is highly efficient in removing various pollutants existing in water, particularly organic pollutants, *viz*., anilines, phenols, olefins, and amines[28,29]. Ferrate(VI) is capable of killing bacteria and viruses; therefore, it can be used as disinfectant. Moreover, ferrate(VI) treatment showed a satisfactory performance since the by-product contained only negligible amount of halogenated disinfection by-products[30,31]. Therefore, unlike ozonation, a possible carcinogenic by-product is not produced by the ferrate(VI) treatment hence, is safer in the treatment technologies[32]. The ferrate(VI) treatment mechanism in aqueous solution at varied pH conditions and its application for treating various micro-pollutants are reported elsewhere [33–35]. The degradation kinetics of ferrate(VI) by organosulfur compound showed that 1 electron and 2 electrons reducing steps are associated in the oxidation of these compounds. The reduction of 1 electron takes place when ferrate(VI) is reduced to ferrate(V), and the reduction to iron (III) is accompanied by ferrate(V) as a result of 2 electrons reduction. In contrast, the reduction of 2 electron leads to reduction of Fe(VI) to Fe(IV), followed by iron (II)[36]. Ferrate(VI) is utilized in the elimination of parathion in aqueous media using the 15:1 (ferrate: parathion) molar ratio at pH 7.0 and temperature 25°C[37]. It was also revealed that when treating acetaminophen, a higher dose of ferrate(VI) in a neutral solution condition improves ferrate(VI) efficiency on acetaminophen degradation[38]. Under specific circumstances, sulfadiazine treatment by Fe(VI) attained removal efficiency up to 99.9% at pH 7[39].

Therefore, the current work aims to exploit ferrate(VI) for the removal of two emerging micro-pollutants *i.e*., triclosan and amoxicillin in its individual and simultaneous removal from aquatic environments using a batch reactor. Furthermore, degradation experiments performed with mineralization of these pollutants under various influencing factors enable us to deduce the mechanism of treatment. Additionally, the real matrix samples collected from various spring water sources are employed in the treatment of these contaminants to investigate the practical implications of ferrate(VI) in various treatment technologies.

Material and Methods

Materials

Triclosan ($C_{12}H_7Cl_3O_2$), diethyl ether, sodium chloride, glycine, hexane, syringe filters (0.22 µM pore size) are obtained from Himedia, India Ltd. India. Amoxicillin ($C_{16}H_{19}N_3O_5S$), is purchased from Sigma Aldrich, USA. Oxalic acid, disodium hydrogen phosphate, potassium hydroxide, iron(III) nitrate nonahydrate, hydrochloric acid, glass filtration fritted with funnel are bought from Merck India. Sodium nitrate, sodium nitrite and EDTA are procured from Loba Chemicals, India. Sodium hypochlorite is obtained from (Alfa Acer) Thermo Fisher Scientific India Pvt. Ltd. The purified water used in the entire experiments were purified using Sartorius water Purification System (model: Sartopore 2150, Germany). GF/C Whatman Filter Papers with a pore size of 0.45 µM were purchased from Whatman, USA. The UV-Visible Spectrophotometer (UV-1800, Shimadzu, Japan) is utilized for taking the absorbance data. TOC analyser was used for analysing the Non Purgeable Organic Carbon after degradation process. Further, the HPLC measurements are performed using the Waters 515 HPLC Pump with the Waters 2489 UV/Visible detector C18 column having dimensions of 4.6 × 250 mM.

Methods

Synthesis of potassium Ferrate(VI)

Potassium ferrate(VI) was obtained by the known wet chemical method as demonstrated elsewhere[40]. The ferrate(VI) purity was determined and found to be>90%[41]. The solid crystals of K_2FeO_4 are stored in a vacuum desiccator having NaOH pellets. It was always preferred to employ the freshly prepared ferrate(VI) in batch reactor operations.

Batch reactor method

Triclosan and amoxicillin solutions (1.0 mmol/L) were prepared in purified water by dissolving appropriate amounts of these compounds. Further, the successive dilution was conducted to obtain the required experimental concentrations of these pollutants. The pH of pollutant solution was maintained by adding of HCl/NaOH (0.1 mol/L). Further, the pollutant solution (100 mL) was taken in a reactor vessel and the correct amount of ferrate(VI) was added in the reactor vessel which was stirred constantly. The ferrate(VI) decomposition was measured with respect to the degradation of triclosan or amoxicillin. After the addition of ferrate(VI), the absorbance was measured using UV-Visible Spectrophotometer at 1 min interval of time. The lambda maximum was fixed at 510 nm. The overall reaction time is extended up to 20 min. In parallel, a blank self-degradation of ferrate(VI) at the same pH was also conducted by observing the absorbance at the wavelength 510 nm as to manually make the blank correction of ferrate(VI) concentration. The reactor vessel was further kept for a prolonged period of 2 h under the stirred conditions in order to complete the degradation reaction. These samples are then filtered using a 0.22 μM filter and the sample was further analysed using HPLC and TOC. Additionally, the simultaneous removal of triclosan and amoxicillin was also performed at two different concentrations of these pollutants at pH 10.0. The mixture of the triclosan and amoxicillin was obtained by mixing 0.05/0.1 mmol/L of each pollutant solution. The ferrate(VI) with a dose of 0.2 mmol/L used for treating these pollutants simultaneously. The samples after filtration were subjected for the HPLC and NPOC measurements.

The degradation of triclosan and amoxicillin were carried out in presence of $C_2H_5NO_2$, NaCl, $C_2H_2O_4$, $NaNO_2$, Na_2HPO_4, EDTA and $NaNO_3$. The concentrations of triclosan or amoxicillin, co-existing ions, and ferrate(VI) are taken at different molar ratios *i.e.*, (0.1:0.5:0.2) mmol/L at pH 10.0. These degradation experiments were extended upto 2 h and finally analysed using HPLC.

The Spring Waters (Tuikhur water) were collected from two locations. The water samples are stored in a polyethylene water container and subjected for its parametric analysis. A Multiphotometer (Model: HI98194, Hanna instrument, USA) is used for analyzing the content of phosphate, sulfate, nitrate and fluoride in these real water samples. Similarly, the atomic absorption spectrometer (AAS) (Model: AA-7000 Series, Shimadzu) was employed to obtain the metal contents *viz*., Zn, Mn, Ca, Pb, Cu, Fe and Ni. TOC analyzer was used to obtain the NPOC and inorganic carbon values of these water samples. The real water sample was further spiked with triclosan/or amoxicillin (0.02 to 0.5 mmol/L) at pH 10.0. The ferrate(VI) dose was maintained at 0.1 mmol/L to each sample and the solution mixture was stirred for 2 h. The treated samples were then filtered by the 0.22 μM syringe filters and subjected for the HPLC measurements to obtain the triclosan or amoxicillin concentrations

Results and Discussion

Effect of pollutant concentration

The effect of pollutant (triclosan/or amoxicillin) concentration was studied at various concentrations of triclosan or amoxicillin ranges between 0.02 mmol/L and 0.5 mmol/L at pH 10.0. The amount of ferrate(VI) used was 0.1 mmol/L. The degradation of ferrate(VI) with respect to pollutant concentrations was observed using a UV-Vis spectrophotometer. The decrease in ferrate(VI) concentration as a function time at various initial concentrations were obtained and displayed in (Fig. 1A & B). Degradation of ferrate(VI) was rapid during the initial period of time *i.e*., 8-10 min, thereby achieving almost a constant value in the latter period of reaction. It is further recorded that with an increase of triclosan/or amoxicillin concentration, the reduction rate of ferrate(VI) is increased sharply. Among these two emerging micro-pollutants, ferrate(VI) degradation was faster in triclosan solution than that of amoxicillin solution. Thus, we may be presumed that interaction of ferrate(VI) with triclosan in the OH and ether groups may faster than the ferrate(VI) interaction with amine and thioether moieties of amoxicillin[42,43]. Quantitatively, the ferrate(VI) concentration was reduced from 0.10 to 0.0411 mmol/L for triclosan and 0.10 to 0.0361 mmol/L for amoxicillin at the molar ratios of 1:1 for pollutant to ferrate(VI).

Further, the concentration of triclosan or amoxicillin is obtained using the HPLC measurements and the graph was plotted between the percentage removals of these pollutants as a function of initial concentrations of the pollutants and graphically shown in (Fig. 1C & D). It is to be observed that the percentage removal of triclosan varies from 87.49 to 18.15% while the concentration of triclosan increased from 0.02 to 0.50 mmol/L. Similarly, the removal of amoxicillin was considerably decreased from 94.45 to 18.16% for the same increase in the pollutant concentration. However, increasing the initial concentration of pollutant *i.e.,* 0.02 to 0.50

mmol/L, the extent of triclosan removed significantly increased from 0.175 mmol/L to 0.9 mmol/L, respectively. Similarly, the extent of amoxicillin removed was also increased from 0.0188 to 0.908 mmol/L for the increase in concentration from 0.02 to 0.5 mmol/L. This result is consistent with the previous report in which increasing the concentration of bisphenol A/or diclofenac greatly favoured the removal efficiency of ferrate(VI)[44]. Furthermore, the reactivity of FeO_4^- in aqueous solutions increases due to the electron-donating character of the alkyl group which further increases the removal efficiency of ferrate(VI) towards various micro-pollutants[45].

Kinetics of Ferrate(VI) Degradation

The kinetics of ferrate(VI) degradation was conducted extensively to obtain the stoichiometry of ferrate(VI) and micro-pollutant along with the order of reaction. A simple oxidation reaction could be given as:

$$Fe(VI) + Pollutant \rightarrow Fe(III) + Oxidized\ products + CO_2 \quad \ldots (1)$$

where Pollutant: Triclosan or Amoxicillin

The rate of ferrate(VI) decomposition is stated as:

$$-\frac{d[Fe(VI)]}{dt} = k_{app}[Fe(VI)]^m\,[TCSorAMX]^n \quad \ldots (2)$$

Or

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

$$k = k_{app}[Pollutant]^n \quad \ldots (4)$$

where k_{app} is overall rate constant and [Fe(VI)] and [Pollutant] are the ferrate(VI) and micro-pollutant concentrations, respectively. Further, '*m*' and '*n*' represent the order of reaction for each species whose values are estimated through the empirical fitting of the change in ferrate(VI) concentration and micro-pollutant concentration data. The optimization of 'm' values was proceeding by plotting the degradation data to both pseudo-first order (PFO)

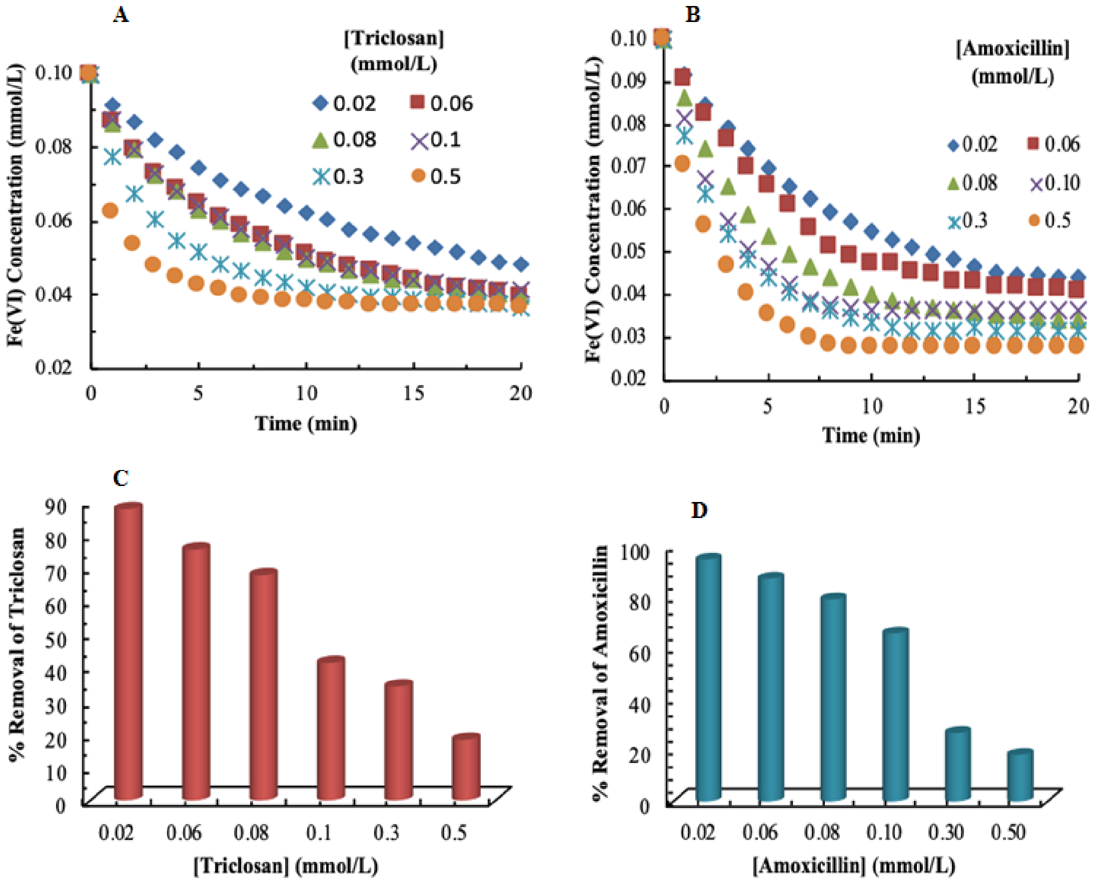

Fig. 1 — Ferrate(VI) degradation as a function of time with respect to (A) triclosan; and (B) amoxicillin. Percentage removal of (C) triclosan; and (D) amoxicillin at various concentrations [pH 10.0; initial concentration of Fe(VI): 0.1 mmol/L]

and pseudo-second order (PSO) equations. The result for PSO kinetics is shown in (Fig. 2A & B).

The kinetic data is apparently fitted well to the pseudo-second-order rate kinetics for both the pollutants *viz*., triclosan and amoxicillin. This suggests that the value of ‘m’ is 2. The rate constant values obtained using PSO for different concentrations of triclosan and amoxicillin at pH 10.0 are included in (Table 1). It is observed that PSO rate constant values increase as the concentrations of the pollutants increase and are relatively higher at 0.5 mM. The PSO rate constant values (k_2) increased from 648.31 to 2503.2 mM^{-1} min^{-1} for triclosan whereas, amoxicillin increased from 844.l to 3626.0 $mM^{-1}min^{-1}$.

Furthermore, the PSO rate constant values against the respective micro-pollutants (*i.e*., triclosan and amoxicillin) concentrations were used to estimate an optimum value of ‘n’ along with to calculate the k_{app}. Therefore, the figure was plotted between the concentrations of triclosan or amoxicillin against the measured values of k_2 and shown as in (Fig. 2C & D).

It is apparent from the figure that a good relation is obtained between the rate constant values and the concentration of triclosan or amoxicillin. This finding suggested that the value of ‘n’ obtained will be 1. Hence, the stoichiometric ratio of the ferrate(VI) to (triclosan or amoxicillin) must be 2:1. The apparent rate constant (k_{app}) was found to be 3583 $L^2/mmol^2/min$

Table 1 —Values of Pseudo-2nd-order rate constant obtained in the degradation of ferrate(VI) in presence of triclosan and amoxicillin at pH 10.0

Concentration of micro-pollutants (mmol/L)	Pseudo-second-order rate constant mM^{-1} min^{-1}			
	Triclosan		Amoxicillin	
	k_2	R^2	k_2	R^2
0.02	648.31	0.998	844.4	0.994
0.06	1044.2	1.000	1048	0.991
0.08	1128.3	0.999	1731	0.995
0.1	1083.8	0.999	2422	0.994
0.3	1837.1	0.996	2632	0.982
0.5	2503.2	0.997	3626	0.909

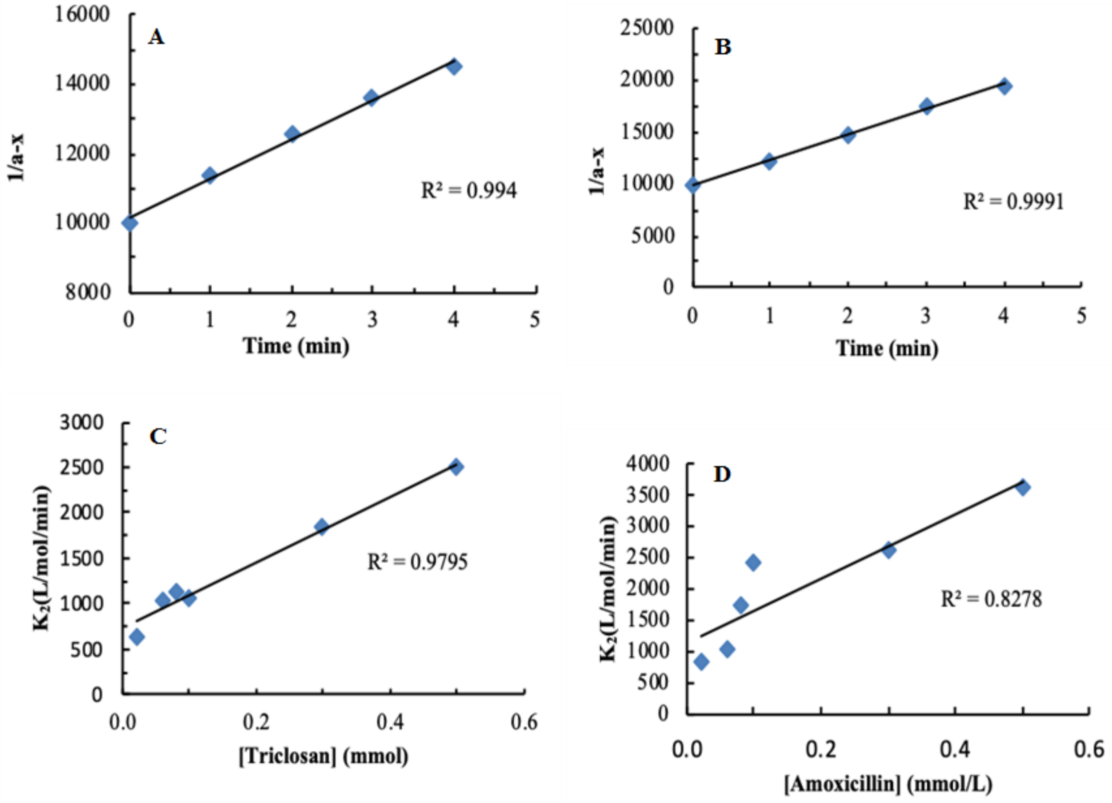

Fig. 2 — Plot of 1/(a-x) vs. time ‘t’ for the degradation of ferrate (VI) in presence of (A) triclosan; (B) amoxicillin at pH 10.0 [Ferrate(VI)]: 0.10 mmol/L; [Triclosan or Amoxicillin]: 0.10 mmol/L and ‘a’ and ‘x’ are initial and final concentration of pollutants at time ‘0’ and ‘t’ min, respectively. Variation of pseudo-second order rate constant (k_2) against the concentration of (C) triclosan; and (D) amoxicillin at pH 10.0 ([Triclosan/or Amoxicillin]: 0.1 mmol/L and [Fe(VI)]: 0.10 mmol/L)

for triclosan and 5137 $L^2/mmol^2/min$ for amoxicillin. These results showed that, in overall, the rate constant of amoxicillin is fairly higher than triclosan. These results are in line with the degradation efficiency of ferrate(VI) for amoxicillin and triclosan. Therefore, the very high value of overall rate constant indicated the potential applicability of ferrate(VI) for the complete degradation of these two pollutants in aquatic environment. It was observed that ferrate(VI) interacted with ampicillin, cloxacillin and penicillin G and had exhibited second-order rate kinetics at pH ranging from 6.0 to 9.5[46]. Other studies also showed that ferrate(VI) enabled the oxidation of triclosan and an apparent second-order rate constant was found to be 754.7 L/mol/sec at pH 7.0. The rate constant of the reaction of $HFeO_4^-$ species with anionic triclosan and neutral triclosan were close to the rate constant values obtained in this work[42].

Effect of pH in the degradation of triclosan or amoxicillin

The effect of pH was studied between pH 9.0 to 12.0 for triclosan and pH 7.0 to 10.0 for amoxicillin having a ferrate(VI) dose of 0.2 mmol/L and micro-pollutant concentrations of 0.1 mmol/L. The extent of degradation of ferrate(VI) as a function of time at various pH is obtained and shown in (Fig. 3A & B). The degradation of ferrate(VI) is greatly preferred at lower pH which apparently favoured the elimination of micro-pollutants. More quantitatively, the triclosan concentration was reduced from 0.1 mmol/L to 0.044 mmol/L at pH 9.0 while the amoxicillin degradation was carried out at pH 7.0 and it was reduced from 0.10 to 0.072 mmol/L.

Further, Figure 3C & D showed that lowering the pH from 12.0 to 9.0 had instigated an increase in triclosan removal from 22.7 to 93.1% indicating that increase in the basicity of the solution greatly affected the removal of triclosan. This is due to the fact that the protonated species of ferrate(VI) is more reactive and readily oxidizes the pollutant at lower pH conditions[47,48]. It was reported that oxidation of organic compounds occurred by the cleavage of ester bond through electrophilic attack by $HFeO_4^-$ species followed by single electron coupling reactions at the phenol moiety of triclosan[49]. Similar compounds like chlorophene (2-benzyl-4-chlorophenol) was degraded by ferrate(VI) and it was observed that chlorine and benzyl groups in benzene ring are shown to increase the reactivity of phenolic compound against

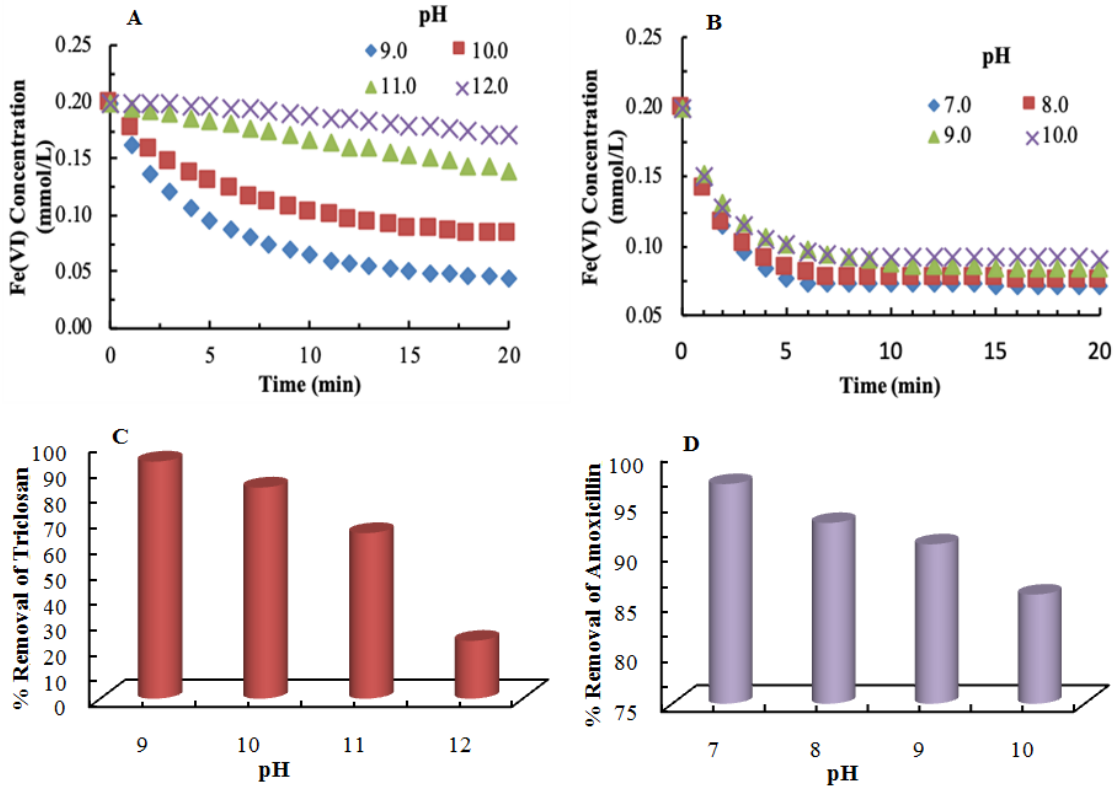

Fig. 3 — Extent removal of ferrate(VI) as a function of time in presence of (A) triclosan; and (B) Percentage removal of (C) triclosan; and (D) amoxicillin as a function of pH ([Triclosan/or Amoxicillin]: 0.1 mmol/L and [Fe(VI)]: 0.2 mmol/L)

ferrate(VI)[42,50]. On the other hand, the percentage elimination of amoxicillin was increased from 85.9 to 96.94% with the decrease in pH from 10.0 to 7.0 (*Cf* Fig. 3D). Amoxicillin is possessed with phenolic and amino groups, and, perhaps, ferrate(VI) is reacting simultaneously to the phenolic and amino groups, resulting in high percentage removal of amoxicillin[43]. Similar reports also showed that ferrate(VI) is quite efficient in oxidizing an array of water pollutants, including nitrogen and sulphur containing compounds, amines, phenols, pesticides, *etc*.[51–53]. Overall, decreasing the pH of the solution increases the ferrate(VI) reactivity which eventually enhances the removal efficiency.

Simultaneous removal of triclosan and amoxicillin

The triclosan and amoxicillin degraded simultaneously with the initial concentrations of 0.05 mmol/L and 0.1 mmol/L for triclosan and amoxicillin, respectively. The molar stoichiometric ratio was taken 2:1 between the ([FeVI]: [TCS+AMX]). The sample pH was maintained at pH 10.0. As shown in Figure 4, the percent removal of triclosan and amoxicillin was found to be 65.5% and 76.3%, respectively, at the pollutant concentrations of 0.05 mmol/L. However, increasing the pollutant concentration to 0.1 mmol/L, the percent removal of triclosan and amoxicillin achieved 32.37% and 52.83%, respectively. These results strongly imply that ferrate(VI) is effective even in simultaneous removal of pollutants from aquatic environments. Moreover, the treatment is relatively more favoured for the amoxicillin compared to the triclosan in mixed matrices. Further, the NPOC analysis showed that the percentage mineralization of the mixture of triclosan and amoxicillin was found to be 23.43 % and 15.73%. at the micro-pollutant concentration of 0.05 mmol/L and 0.1 mmol/L, respectively. Therefore, ferrate(VI) efficiently mineralizes, partially, the triclosan and amoxicillin using the limited amount of ferrate(VI). This further entails that a repeated operation with ferrate(VI) may enable mineralization of these pollutants completely.

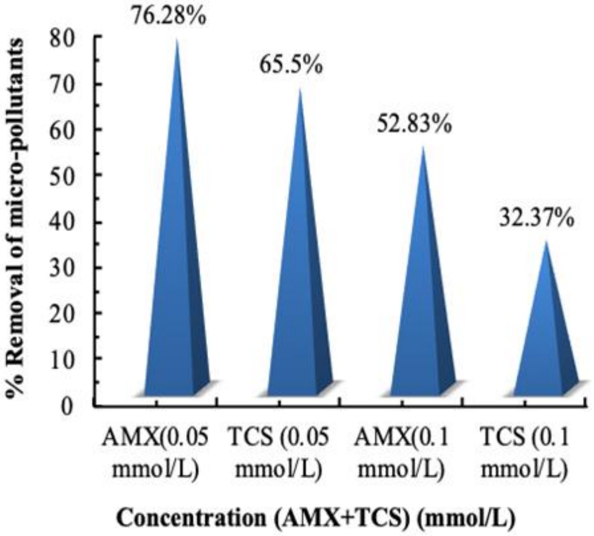

Fig. 4 — Simultaneous removal of amoxicillin and triclosan in mixture of these two pollutants having varied concentrations by ferrate(VI) ([Triclosan + Amoxicillin]: 0.05 mmol/L and 0.10 mmol/L; pH 10.0; [FeVI] : [TCS+AMX]: 2:1)

Mineralization of triclosan and amoxicillin

The mineralization of TCS/AMX by ferrate(VI)was studied using a total organic carbon analyzer. The information obtained is useful to assess an optimal use of ferrate(VI) technologies in real wastewater treatment methods. It was presumed that partially/completely oxidized TCS/AMX was mineralized to their final products, as determined by their total NPOC values. The triclosan and amoxicillin were treated for 2 h at fixed concentration of micro-pollutant (0.1 mmol/L) with ferrate(VI) (0.2 mmol/L) at pH ranges between 9.0 and 12.0 for triclosan and from pH 7.0 to 10.0 for amoxicillin. The NPOC values of the treated and untreated samples were obtained and hence, the percentage mineralization of these micropollutants were obtained at different pH and illustrated in (Fig. 5A & B). The percentage mineralization of these micropollutants are greatly favoured with decrease in solution pH. Quantitatively, decreasing the pH 12.0 to 9.0 has caused an increase in the percentage mineralization of triclosan from 22.71 to 93.12 %, respectively. Similarly, the amoxicillin was mineralized from 11.54 to 25.63% with a decrease in pH from 10.0 to 7.0, respectively. These results suggested that although the fractional amount of TCS/AMX are mineralized by a single dose of ferrate(VI) however, the repeated cycle of operations may enable the mineralization of these micro-pollutants completely.

Effect of co-existing ions

The occurrence of different co-existing ions could affect the efficacy of ferrate(VI) and eventually enable the selectivity of ferrate(VI) towards the target pollutants. This further relates the real/or complex matrix treatment of micro-pollutants. Therefore, a variety of co-existing ions *viz*., Na_2HPO_4, NaCl, $NaNO_2$, glycine, $NaNO_3$, EDTA, and oxalic acid are chosen for the study. The concentration of ferrate(VI), triclosan/or amoxicillin and co-existing ions were taken as 0.2 mmol/L, 0.1 mmol/L and 0.5 mmol/L, respectively. The percentage of elimination of these two micropollutants at pH 10.0 are shown in (Fig. 6A & B). Results indicated that these co-existing ions could not meaningfully affect the degradation of TCS or AMX except the presence of glycine and EDTA. This infers that ferrate(VI) preferably degrades the glycine and EDTA in a complex matrix. It was reported previously that ferrate(VI) reacted preferentially with $^{+}H_3N$-CH_2−COO^{-} species of glycine then could attack the C-N bond of the glycine molecule[54,55]. Similarly, EDTA is a chelating agent, the interaction of ferrate(VI) to EDTA make partial radical character of ferrate(VI) ($Fe^{VI} = O \leftrightarrow Fe^{V}–O^{\bullet}$) which may further inhibit the oxidation of other pollutants in aqueous media[56]. Additionally, upto a lower extent the oxalic acid affected the degradation efficiency of triclosan and amoxicillin.

Real matrix treatment

The introduction of ferrate(VI) technology in the elimination of micro-pollutants from the real matrix samples is an important aspect in implementing the technology for its possible implacability. Therefore, the real water samples were collected from two different spring water sources known as Tuikhur 1 and Tuikhur 2, located in Aizawl City, Mizoram, India. The physico-chemical parameters of these two water samples are listed in (Table 2). It consists of relatively high salinity along with the higher inorganic carbon values. This indicates that water samples are having higher values of carbonates and bicarbonates. The real water samples Tuikhur 1 and Tuikhur 2 are spiked with the triclosan and amoxicillin,

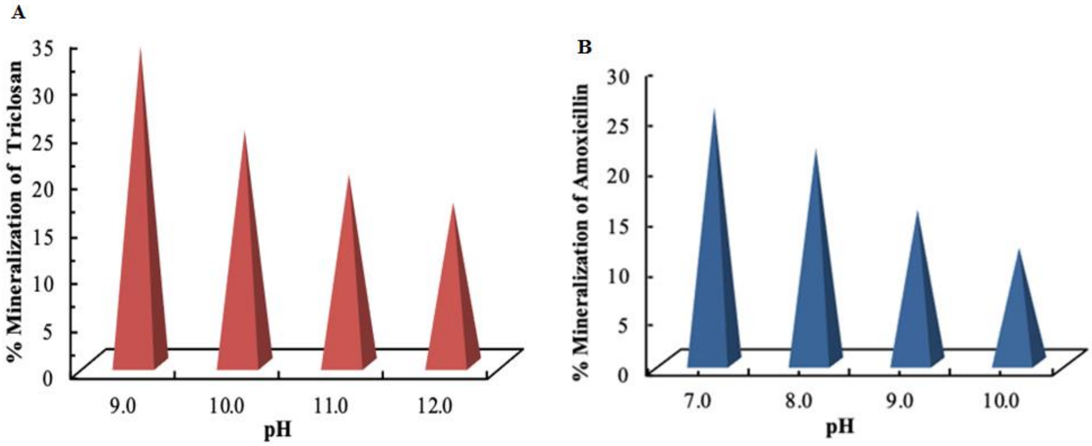

Fig. 5 — Percentage mineralization of (A) triclosan; and (B) amoxicillin as a function of pH ([Micro-pollutant]: 0.1 mmol/L and [Ferrate(VI): 0.2 mmo/L]

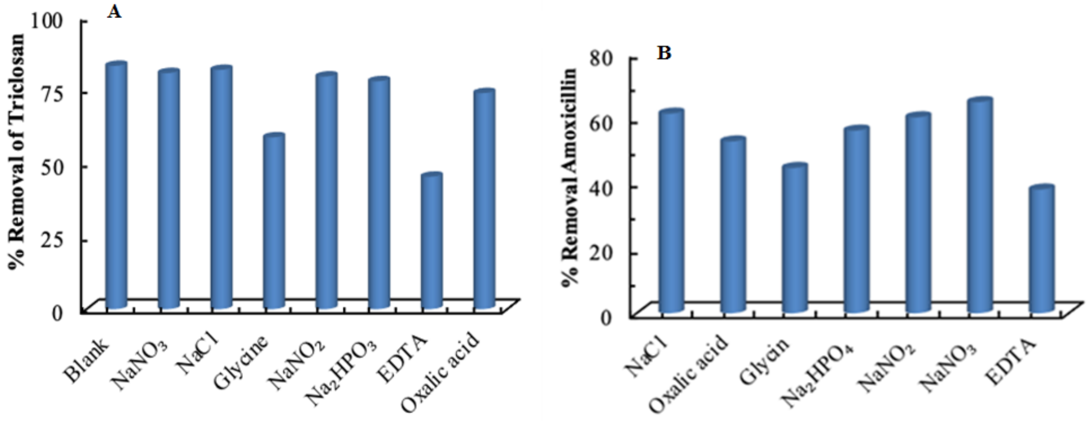

Fig. 6 — Oxidative degradation of (A) triclosan; and (B) amoxicillin in presence of several co-existing ions ([Amoxicillin]: 0.1 mM; [co-existing ions]: 0.5 mM; [Ferrate(VI)]: 0.2 mM; and at pH: 10.0)

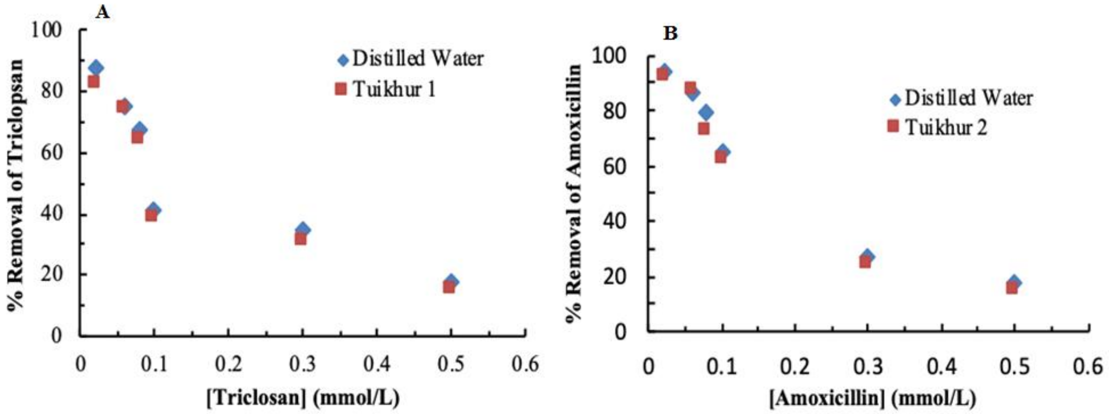

Fig. 7 — Percentage removal (A) Triclosan; and (B) Amoxicillin in real matrix samples along with the distilled water samples as a function of micro-pollutant concentrations ([Triclosan/or Amoxicillin]: 0.1 mmol/L, [Ferrate(VI)]: 0.1 mmol/L and at pH 10.0)

Table 2 — Water quality analysis of two different sources of Spring water known as Tuikhur 1 and Tuikhur 2

Parameters studied	Analytical Results	
	Tuikhur 1	Tuikhur 2
pH	6.97	7.32
TDS (mg/L)	102	96
Electrical Conductivity (µS/cm)	163	184
Oxi. Red. Potential(mV)	145	196
Salinity (mg/L)	94	82
Anions Studied	mg/L	mg/L
Sulphate	2	4
Phosphate	0.37	0.24
Fluoride	0.00(BDL)	0.00(BDL)
Nitrate	5.04	3.15
Elemental Analysis (AAS)	mg/L	mg/L
Ni	0.5124	0.7413
Fe	0.0124	0.0052
Cu	0.0014	0.0007
Pb	0.022	0.061
Ca	0.217	0.198
Mn	2.854	7.625
Zn	0.0094	0.0036
TOC Analysis	mg/L	mg/L
IC	7.96	6.21
NPOC	3.28	1.53

BDL – Below detection limit

respectively. The micro-pollutants concentrations ranged from 0.02 to 0.5 mmol/L at pH 10.0 and introduced a constant Fe(VI) dose of 0.1 mmol/L. The percentage elimination of these two pollutants along with the purified water treatment is shown as in (Fig. 7A & B). This indicated that the elimination of these two micro-pollutants are not affected using the real matrix samples. This further indicated the probable application of ferrate(VI) in the treatment of real matrix samples for the efficient and selective removal of triclosan and amoxicillin.

Conclusion

The efficacy of ferrate(VI) in the simultaneous removal of emerging micro-pollutants *viz.*, triclosan (TCS) and amoxicillin (AMX) was conducted at a wide range of pH and pollutant concentrations. The decrease in pH from 12.0 to 9.0 (for triclosan) and from 10.0 to 7.0 (for amoxicillin) greatly favoured the removal of these two micro-pollutants. The kinetic study conducted at pH 10.0 showed that the reaction followed a pseudo-second order reaction with a molar stoichiometric ratio of 2:1 for ferrate(VI) to micro-pollutants. Further, the simultaneous removal of these two micropollutants (each having 0.05 mmol/L) were conducted using the ferrate(VI) (0.1 mmol/L) and 65.5% and 76.3% of triclosan and amoxicillin, respectively were removed. Additionally, a significant amount of the micro-pollutants are mineralized in the individual as well in the simultaneous removal of these micro-pollutants using ferrate(VI). The presence of co-existing ions such as NaCl, $NaNO_2$, oxalic acid, $NaNO_3$, and Na_2HPO_4 could not affect the degradation of triclosan, while amoxicillin degradation was suppressed to some extent. On the other hand, the presence of EDTA and glycine greatly affected the degradation of triclosan and amoxicillin. The real matrix treatment using the Spring water (Tuikhur water) showed no significant change in the removal of these two micro-pollutants which indicated fairly good selectivity of ferrate(VI) in the remediation of water contaminated with triclosan or amoxicillin. Overall, the results indicated ferrate(VI) as a safer and selective oxidant to be employed for the advanced oxidation of micro-pollutants.

Acknowledgement

One of the author DT acknowledges the CSIR, New Delhi providing the financial assistance in the form of Extra Mural Research Grant vide No. 24(354)/18-EMR-II.

Conflict of interest

All authors declare no conflict of interest.

References

1 Lin T, Yu S & Chen W, Occurrence, removal and risk assessment of pharmaceutical and personal care products (PPCPs) in an advanced drinking water treatment plant (ADWTP) around Taihu Lake in China. *Chemosphere*, 152 (2016) 1.

2 Chaves M de JS, Barbosa SC, Malinowski M de M, Volpato D, Castro ÍB, Franco TCRDS & Primel EG, Pharmaceuticals and personal care products in a Brazilian wetland of international importance: Occurrence and environmental risk assessment. *Sci Total Environ*, 734 (2020) 139374.

3 Yang L, Zhou Y, Shi B, Meng J, He B, Yang H, Yoon SJ, Kim T, Bong-Oh K, Khim JS & Wang T, Anthropogenic impacts on the contamination of pharmaceuticals and personal care products (PPCPs) in the coastal environments of the Yellow and Bohai seas. *Environ Int*, 135 (2020) 105306.

4 Florence Borgia VJ, Thatheyus AJ & Murugesan AG, Impact of electroplating industry effluent on the electrophoretic protein pattern of serum in the freshwater fish *Cyprinus carpio*. *Indian J Biochem Biophys*, 56 (2019) 460.

5 Maruya KA, Dodder NG, Sengupta A, Smith DJ, Lyons JM, Heil AT & Drewes JE, Multimedia screening of contaminants of emerging concern (CECS) in coastal urban watersheds in southern California (USA). *Environ Toxicol Chem*, 35 (2016) 1986.

6 Kosma CI, Lambropoulou DA & Albanis TA, Investigation of PPCPs in wastewater treatment plants in Greece: Occurrence, removal and environmental risk assessment. *Sci Total Environ*, 466–467 (2014) 421.

7 Ebele AJ, Abou-Elwafa Abdallah M & Harrad S, Pharmaceuticals and personal care products (PPCPs) in the freshwater aquatic environment. *Emerg Contam*, 3 (2017) 1.

8 Sabaliunas D, Webb SF, Hauk A, Jacob M & Eckhoff WS, Environmental fate of Triclosan in the River Aire Basin, UK. *Water Res*, 37 (2003) 3145.

9 Sanches-Silva A, Sendón-García R, López-Hernández J & Paseiro-Losada P, Determination of triclosan in foodstuffs. *J Sep Sci*, 28 (2005) 65.

10 Zhao JL, Zhang QQ, Chen F, Wang L, Ying GG, Liu YS, Yang B, Li-Jun Z, Liu S, Hao-Chang S & Rui-Quan Z, Evaluation of triclosan and triclocarban at river basin scale using monitoring and modeling tools: Implications for controlling of urban domestic sewage discharge. *Water Res*, 47 (2013) 395.

11 McAvoy DC, Schatowitz B, Jacob M, Hauk A & Eckhoff WS, Measurement of triclosan in wastewater treatment systems. *Environ Toxicol Chem*, 21 (2002) 1323.

12 Allmyr M, Harden F, Leisa-Maree LT, Mueller JF, McLachlan MS, Adolfsson-Erici M & Sandborgh-Englund G, The influence of age and gender on triclosan concentrations in Australian human blood serum. *Sci Total Environ*, 393 (2008) 162.

13 Veldhoen N, Skirrow RC, Osachoff H, Wigmore H, Clapson DJ, Gunderson MP, Aggelen GV & Helbing CC, The bactericidal agent triclosan modulates thyroid hormone-associated gene expression and disrupts postembryonic anuran development. *Aquat Toxicol*, 80 (2006) 217.

14 Solá-Gutiérrez C, Schröder S, San-Román MF & Ortiz I, Critical review on the mechanistic photolytic and photocatalytic degradation of triclosan. *J Environ Manage*, 260 (2020) 110101.

15 Allmyr M, Adolfsson-Erici M, McLachlan M & Sandborgh-Englund G, Triclosan in Plasma and Milk from Swedish Nursing Mothers and Their Exposure *via* Personal Care Products. *Sci Total Environ*, 372 (2007) 87.

16 Fiss EM, Rule KL & Vikesland PJ, Formation of Chloroform and Other Chlorinated By products by Chlorination of Triclosan-Containing Antibacterial Products. *Environ Sci Technol*, 41 (2007) 2387.

17 Rule KL, Ebbett VR & Vikesland PJ, Formation of chloroform and chlorinated organics by free-chlorine-mediated oxidation of triclosan. *Environ Sci Technol*, 39 (2005) 3176.

18 Lindström A, Buerge IJ, Poiger T, Bergqvist PA, Müller MD & Buser HR, Occurrence and environmental behavior of the bactericide triclosan and its methyl derivative in surface waters and in wastewater. *Environ Sci Technol*, 36 (2002) 2322.

19 Sarma GVS, Rani SK, Chandra SK, Babu KB, Ramesh KV, Potential removal of phenol using modified laterite adsorbent. *Indian J Biochem Biophys*, 57 (2020) 613.

20 Ahmed M, Babu G & Shetty A, Development and validation of amoxicillin by RP-HPLC method in bulk drug and pharmaceutical dosage forms. *Int J Chem Tech Res*, 3 (2011) 1037.

21 Hrioua A, Loudiki A, Farahi A, Bakasse M, Lahrich S, Saqrane S & El Mhammedi MA, Recent advances in electrochemical sensors for amoxicillin detection in biological and environmental samples. *Bioelectrochemistry*, 137 (2021) 107687.

22 Deng B, Shi A, Li L & Kang Y, Pharmacokinetics of amoxicillin in human urine using online coupled capillary electrophoresis with electrogenerated chemiluminescence detection. *J Pharm Biomed Anal*, 48 (2008) 1249.

23 Elizalde-Velázquez A, Gómez-Oliván LM, Galar-Martínez M, Islas-Flores H & Dublán-García O, SanJuan-Reyes N, Amoxicillin in the Aquatic Environment, Its Fate and Environmental Risk. In: *Environmental Health Risk - Hazardous Factors to Living Species*, (Ed. by M Larramendy & S Soloneski, editors; InTech) 2016, 248.

24 Cunha BA, Antibiotic side effects. *Med Clin North Am*, 85 (2001) 149.

25 Pan X, Deng C, Zhang D, Wang J, Mu G & Chen Y, Toxic effects of amoxicillin on the photosystem II of *Synechocystis*

sp. characterized by a variety of *in vivo* chlorophyll fluorescence tests. *Aquat Toxicol*, 89 (2008) 207.

26 Thambavita D, Galappatthy P, Mannapperuma U, Jayakody L, Cristofoletti R, Abrahamsson B, Groot DW, Langguth P, Mehta M, Parr A, Polli JE, Shah VP & Dressman J, Biowaiver Monograph for Immediate-Release Solid Oral Dosage Forms: Amoxicillin Trihydrate. *J Pharm Sci*, 106 (2017) 2930.

27 Bai X, Zhao L, Liu Z, Li Y, Zhang T & Liu X, Synthesis and antibacterial activity evaluation of aminoguanidine or dihydrotriazine derivatives. *Indian J Biochem Biophys*, 56 (2019) 301.

28 Liu Y, Wang L, Huang Z, Wang X, Zhao X, Ren Y, Sun S, Xue M, Qi J & Ma J, Oxidation of odor compound indole in aqueous solution with Ferrate(VI): Kinetics, pathway, and the variation of assimilable organic carbon. *Chem Eng J*, 331 (2018) 31.

29 Zhou S, Shao Y, Gao NY, Zhu S, Li L, Deng J & Zhu M, Removal of Microcystis aeruginosa by potassium Ferrate(VI): Impacts on cells integrity, intracellular organic matter release and disinfection by-products formation. *Chem Eng J*, 251 (2014) 304.

30 Liu J, Lujan H, Dhungana B, Hockaday WC, Sayes CM, Cobb GP & Sharma VK, Ferrate(VI) pretreatment before disinfection: An effective approach to controlling unsaturated and aromatic halo-disinfection byproducts in chlorinated and chloraminated drinking waters. *Environ Int*, 138 (2020) 105641.

31 Hu L, Page MA, Sigstam T, Kohn T, Mariñas BJ & Strathmann TJ, Inactivation of bacteriophage MS2 with potassium ferrate(VI). *Environ Sci Technol*, 46 (2012) 12079.

32 Sun S, Liu Y, Ma J, Pang S, Huang Z, Gu J, Gao Y, Xue M, Yuan Y & Jiang J, Transformation of substituted anilines by ferrate(VI): Kinetics, pathways, and effect of dissolved organic matter. *Chem Eng J*, 332 (2018) 245.

33 Jiang Y, Goodwill JE, Tobiason JE & Reckhow DA, Impacts of ferrate oxidation on natural organic matter and disinfection by product precursors. *Water Res*, 96 (2016) 114.

34 Lee Y, Yoon J & von Gunten U, Kinetics of the oxidation of phenols and phenolic endocrine disruptors during water treatment with ferrate (Fe(VI)). *Environ Sci Technol*, 39 (2005) 8978.

35 Zhou Z & Jiang JQ, Treatment of selected pharmaceuticals by ferrate(VI): Performance, kinetic studies and identification of oxidation products. *J Pharm Biomed Anal*, 106 (2015) 37.

36 Sharma VK, Luther GW & Millero FJ, Mechanisms of oxidation of organosulfur compounds by ferrate(VI). *Chemosphere*, 82 (2011) 1083.

37 Liu H, Pan X, Chen J, Qi Y, Qu R & Wang Z, Kinetics and mechanism of the oxidative degradation of parathion by Ferrate(VI). *Chem Eng J*, 365 (2019) 142.

38 Wang H, Liu Y & Jiang JQ, Reaction kinetics and oxidation product formation in the degradation of acetaminophen by Ferrate(VI). *Chemosphere*, 155 (2016) 583.

39 Wang H, Wang S, Jiang JQ & Shu J, Removal of sulfadiazine by ferrate(VI) oxidation and montmorillonite adsorption—Synergistic effect and degradation pathways. *J Environ Chem Eng*, 7 (2019) 103225.

40 Tiwari D, Kim HU, Choi BJ, Lee SM, Kwon OH, Choi KM & Yang JK, Ferrate(VI): a green chemical for the oxidation of cyanide in aqueous/waste solutions. *J Environ Sci Health Part A Tox Hazard Subst Environ Eng*, 42 (2007) 803.

41 Lee Y, Cho M, Kim JY & Yoon J, Chemistry of ferrate (Fe(VI)) in aqueous solution and its applications as a green chemical. *J Ind Eng Chem*, 10 (2004) 161.

42 Yang B, Ying GG, Zhao JL, Zhang LJ, Fang YX & Nghiem LD, Oxidation of triclosan by ferrate: Reaction kinetics, products identification and toxicity evaluation. *J Hazard Mater*, 186 (2011) 227.

43 Sharma VK, Liu F, Tolan S, Sohn M, Kim H & Oturan MA, Oxidation of β-lactam antibiotics by ferrate(VI). *Chem Eng J*, 221 (2013) 446.

44 Sailo L, Tiwari D & Lee SM, Degradation of some micro-pollutants from aqueous solutions using Ferrate(VI): Physico-chemical studies. *Sep Sci Technol*, 52 (2017) 2756.

45 Sharma VK, Ferrate(VI) and ferrate(V) oxidation of organic compounds: Kinetics and mechanism. *Coord Chem Rev*, 257 (2013) 495.

46 Karlesa A, De Vera GAD, Dodd MC, Park J, Espino MPB & Lee Y, Ferrate(VI) Oxidation of β-Lactam Antibiotics: Reaction Kinetics, Antibacterial Activity Changes, and Transformation Products. *Environ Sci Technol*, 48 (2014) 10380.

47 Pachuau L, Lee SM & Tiwari D, Ferrate(VI) in wastewater treatment contaminated with metal(II)-iminodiacetic acid complexed species. *Chem Eng J*, 230 (2013) 14.

48 Sharma VK, Potassium ferrate(VI): an environmentally friendly oxidant. *Adv Environ Res*, 6 (2002) 143.

49 Chen J, Wu N, Xu X, Qu R, Li C, Pan X, Wei Z & Wang Z, Fe(VI)-Mediated Single-Electron Coupling Processes for the Removal of Chlorophene: A Combined Experimental and Computational Study. *Environ Sci Technol*, 52 (2018) 12592.

50 Chen J, Qi Y, Pan X, Wu N, Zuo J, Li C, Qu R, Wang Z & Chen Z, Mechanistic insights into the reactivity of Ferrate(VI) with phenolic compounds and the formation of coupling products. *Water Res*, 158 (2019) 338.

51 Elnakar H & Buchanan I, The role of mixing in potassium ferrate(VI) consumption kinetics and disinfection of bypass wastewater. *J Environ Manage*, 231 (2019) 515.

52 Feng M, Baum JC, Nesnas N, Lee Y, Huang CH & Sharma VK, Oxidation of Sulfonamide Antibiotics of Six-Membered Heterocyclic Moiety by Ferrate(VI): Kinetics and Mechanistic Insight into SO2 Extrusion. *Environ Sci Technol*, 53 (2019) 2695.

53 Zajíček P, Kolář M, Prucek R, Ranc V, Bednář P, Varma R, Sharma V & Zboril R, Oxidative degradation of triazine- and sulfonylurea-based herbicides using Fe(VI): The case study of atrazine and iodosulfuron with kinetics and degradation products. *Sep Purif Technol*, 156 (2015) 1041.

54 Sharma VK & Bielski BHJ, Reactivity of ferrate(VI) and ferrate(V) with amino acids. *Inorg Chem*, 30 (1991) 4306.

55 Noorhasan N, Patel B & Sharma VK, Ferrate(VI) oxidation of glycine and glycylglycine: kinetics and products. *Water Res*, 44 (2010) 927.

56 Noorhasan NN & Sharma VK, Kinetics of the reaction of aqueous iron(vi) (FeVIO42-) with ethylenediaminetetraacetic acid. *Dalton Trans*, 14 (2008) 1883.