

Efficient Elimination of Tetracycline by Ferrate (VI): Real Water Implications

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Abstract

The detection of antibiotics in treated wastewater is a global concern as it enters water bodies and causes the development of antibiotic resistance genes in humans and marine life. The study specifically aims to explore the potential of ferrate (VI) in eliminating tetracycline (TCL). The degradation of TCL is optimized with parametric studies, *viz.*, the effect of pH and concentration, which provide insights into TCL elimination. The increase in pH (from 7.0 to 10.0) favors the percentage removal of TCL; however, the increase in TCL concentrations from 0.02 to 0.3 mmol/L caused a decrease in percentage TCL removal from 97.4 to 29.1%, respectively, at pH 10.0. The time-dependent elimination of TCL using ferrate (VI) followed pseudosecond-order rate kinetics, and an apparent rate constant (k_{app}) was found at 1978.8 L²/mol²/min. Coexisting ions, *i.e.*, NaNO₃, Na₂HPO₄, NaCl, and oxalic acid, negligibly affect the oxidation of TCL by ferrate (VI). However, EDTA and glycine significantly inhibited the elimination of TCL using ferrate (VI). The mineralization of TCL using ferrate (VI) was favored at higher pH, and it increased from 18.57 to 32.52% when the solution pH increased from pH 7.0 to 10.0. Additionally, the real water samples containing a relatively high level of inorganic carbon spiked with TCL revealed that ferrate (VI) performance in the removal of TCL was unaffected, which further inferred the potential of ferrate (VI) in real implications.

Keywords: Persistent antibiotics, Elimination of tetracycline, Mineralization of pollutant, Real matrix samples, Potential of ferrate (VI)

1. Introduction

Antibiotics from all classes are often detected on the ground surface and even in drinking waters around the globe. They frequently escape from existing wastewater treatment plants due to the partial degradation of these pollutants. Additionally, the relaxed legislation, administrative oversights, and unregulated release of pharmaceutical compounds pose serious human health concerns. Moreover, antibiotics in water bodies and their continuous usage cause gene mutations among bacteria, viruses, and fungi that develop antibacterial resistance genes in humans. Therefore, eliminating antibiotics from wastewater is essential before their release into the aquatic environment[1,2].

Tetracycline (TCL) is an extensively used antibiotic to prevent and cure infectious diseases in humans and animals. Due to its reasonable cost and strong antibacterial properties, TCL is a widely prescribed antibiotic. It is prescribed for treating cholera and pneumonia, including several medicinal therapies. TCL is prescribed for several in-

fectious animal diseases, including poultry, swine, sheep, etc.[3-6].

TCL is partially metabolized in the biosystem and releases a significant amount of TCL into wastewater through urine and feces. Moreover, due to its low biodegradability and persistence in nature, TCL is not eliminated efficiently in conventional treatment plants[7]. The occurrence of TCL in treated wastewater suggests that conventional treatment methods are insufficient and need advanced treatment to remove persistent chemicals[7,8]. Several treatment methods have been demonstrated for removing antibiotics from water bodies, including chlorination, activated carbon filtration, microfiltration, ultrafiltration, and advanced oxidation processes such as ozonation, Fenton reaction, photocatalysis, and ultraviolet (UV) radiation[9-15]. However, apart from their removal performance and efficiency, these approaches have limitations, including high sludge production, time consumption, and sometimes toxic byproduct formation[16].

On the other hand, ferrate (VI) is perhaps a suitable alternative oxidant due to its strong oxidizing capacity with a redox potential of 2.20 V, relatively higher than the redox potential of a common oxidant such as permanganate (1.67 V) and ozone (2.07)[17]. Moreover, it is an environmentally friendly oxidant and has received greater attention [18,19]. In aqueous environments, ferrate (VI) exists in four different species, *viz.*, FeO₄²⁻, HFeO₄⁻, H₂FeO₄, and H₃FeO₄⁺. At moderate and alkaline pH, the dominant ferrate (VI) species are HFeO₄⁻ and FeO₄²⁻, respectively; nevertheless, the oxidizing ability and strength of ferrate

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(VI) diminishes with an increase in solution pH[20-22]. Ferrate (VI) shows multifunctional properties and has been applied in diverse research areas[23]. The adaptable and multifaceted strong oxidant ferrate (VI) has shown widespread applications in wastewater treatment [24-27]. As a microbial disinfectant, ferrate (VI) kills chlorine-resistant bacteria and total *coliforms* efficiently by more than a 3-log scale compared to hypochlorite[28]. Ferrate (VI) eliminates pharmaceuticals such as β -blockers, β -lactams, sulfonamides, and fluoroquinolones in an aqueous medium[29-32]. Similarly, a single dose of ferrate (VI) 0.01 mM degrades more than 87% and 94%, respectively, of triclosan and amoxicillin at pH 10.0[33]. Diclofenac is readily degraded by ferrate (VI) at pH 9.0. Ferrate (VI) (24 $\mu\text{mol/L}$) degrades approximately 65% of diclofenac (0.8 $\mu\text{mol/L}$) in an aqueous medium[34].

The challenges of using common oxidants in wastewater treatment are the efficiency of oxidants toward persistent chemicals and the presence of various contaminants in waterbodies, which hampers the efficiency of oxidants. Therefore, the present investigation aims to assess the applicability of ferrate (VI) in treating water contaminated with persistent TCL at various concentrations. Furthermore, parametric studies aid the applicability of ferrate (VI) in the treatment of water contaminated with TCL.

2. Materials and methods

2.1. Chemical & analysis

All reagents and chemicals were of analytical grade and used without additional purification. Tetracycline hydrochloride ($\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8\text{HCl}$), hexane (C_6H_{14}), and diethyl ether ($(\text{C}_2\text{H}_5)_2\text{O}$) were purchased from Sigma Aldrich (St. Louis, United States). Sodium chloride (NaCl), methanol, disodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7(\text{OH})_4 \cdot 8\text{H}_2\text{O}$), sodium hydroxide (NaOH), acetonitrile, and glycine ($\text{C}_2\text{H}_5\text{NO}_2$) were purchased from Himedia (Maharashtra, India). Ethylenediamine-tetraacetic acid ($\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$) was a product of Qualigens Fine Chemicals (Maharashtra, India). Potassium hydroxide (KOH), ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3$), hydrochloric acid (HCl), oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$), and disodium hydrogen phosphate anhydrous (Na_2HPO_4) were Merck (Darmstadt, Germany) products. Sodium nitrite (NaNO_2) and sodium nitrate (NaNO_3) were procured from Loba Chemicals (Maharashtra, India). Sodium hypochlorite (NaClO) was purchased from Thermo Fisher Scientific (Waltham, United States).

Syringe filters (0.22 μm pore size) were the product of Himedia (Maharashtra, India). GF/C filter paper was acquired from Whatman (Maidstone, United Kingdom). Glass filtration with a fritted funnel was purchased from Merck (Darmstadt, Germany). A Sartorius water purifier (Sartopore 2150, Sterile Plus, Arium Mini Plus UV Lab., Germany) was used for water purification. The real water sample was collected from spring water from Aizawl city, Mizoram, India.

A pH meter (Hanna Instruments, HI2002, USA) was used to determine the pH of the water samples, and a multiphotometer (Hanna Instruments, HI98194, USA) was employed to analyze the various water quality parameters of the collected water samples. A UV-visible spectrophotometer (UV-1800, Shimadzu, Japan) was used to measure

the absorbance of the solutions. A total organic carbon (TOC) analyzer was utilized to collect the nonpurgeable organic carbon (NPOC) data (TOC-VCPH/CPN, Shimadzu, Japan). An atomic absorption spectrometer (AAS, AA-7000, Shimadzu, Japan) was used to measure the concentrations of metal ions in a spring water sample.

HPLC instrument along with C_{18} column (4.6×250 mm, 2489 UV-Vis detector, Waters 515 HPLC pump, USA) was employed to detect micro-pollutant. The mobile phase includes the acetonitrile, methanol, and oxalic acid (v/v ratio of 15:25:60) in the HPLC measurements. A 20 μL injection volume delivers at the flow rate of 1 mL/min in the HPLC instrument and measures the TCL concentrations at the wavelength of 365 nm.

2.2. Experimental methods

The wet chemical method synthesizes high-purity ferrate (VI) in its potassium salt (K_2FeO_4), as demonstrated previously[35,36]. A 300 mL chilled sodium hypochlorite solution was placed in a beaker in an ice bath. Slowly, 90 g of potassium hydroxide pellets were added to the hypochlorite solution under constant stirring. The solution mixture was placed in the refrigerator for 2 hrs. Furthermore, the undissolved potassium hydroxide was filtered using GF/C filter paper, and a clear yellow, highly alkaline sodium hypochlorite solution was obtained. Twenty grams of pulverized ferric nitrate was gradually added to the alkaline sodium hypochlorite solution with continuous and intense stirring for approximately 2 hrs under cold conditions (8 $^\circ\text{C}$) using an ice bath. The solution mixture was stirred constantly for another 30 min. A rapid change in color from yellow-brown to dark purple indicated the formation of ferrate (VI). Fifty grams of potassium hydroxide pellets were slowly added into the solution, keeping the mixture temperature at ~ 15 $^\circ\text{C}$. The solution mixture was again kept in the refrigerator for 40 min. The resultant slurry contained dark purple and was carefully filtered through GF/C filter paper. The filtrate was discarded, and the solid was washed with 100 mL of 3 M potassium hydroxide (chilled cold solution). This allowed the ferrate (VI) to be dissolved and collected as filtrate in the flask. The filtrate was placed in a flask, and 100 mL of chilled saturated potassium hydroxide solution was added. The potassium ferrate was precipitated easily and filtered again using GF/C filter paper. The filtrate was eliminated, the solid was flushed with a cold 3 M potassium hydroxide solution (50 mL), and the filtrate was again collected. The ferrate (VI) was again precipitated using a chilled cold saturated potassium hydroxide solution. Similarly, reprecipitation two more times eliminated the impurities and resulted in high-purity ferrate (VI). Finally, the solid was washed with 10 mL of n-hexane, followed by diethyl ether (10 mL). The final product was carefully collected and placed in a vacuum desiccator containing potassium hydroxide pellets. The solid was dried in a desiccator and subjected to further experiments.

Batch reactor operations use freshly prepared ferrate (VI). The efficiency of ferrate (VI) is optimized as a function of TCL concentration and the pH of the solution. Purified water was used to prepare a stock solution of TCL (0.50 mmol/L) and diluted as per the experimental requirements. A set of TCL concentrations ranging from 0.02 to 0.30

mmol/L was placed in the reactor at pH 10.0. Furthermore, in each pollutant solution, a constant amount of ferrate (VI) (0.10 mmol/L) was added under stirring conditions. Once ferrate (VI) was added to the pollutant solution (100 mL), ferrate (VI) removal was recorded as a function of time using a UV-Vis spectrophotometer at 510 nm. The absorbance data were collected for 20 mins at a time interval of 1 min. In parallel, ferrate (VI) self-decomposition was recorded using a blank solution by measuring the absorbance at the same wavelength with the same interval of time. This enables the required correction in ferrate (VI) concentrations due to the self-decomposition of ferrate at the same pH. The reactor vessel was then stirred for another 2 hrs to complete the degradation process. The samples were filtered through a 0.22 μm pore size syringe filter before being delivered for TOC and high-performance liquid chromatography (HPLC) analyses. Similar measurements performed at pH 7.0, 8.0, 9.0, and 10.0 revealed insights into TCL removal at each pH using ferrate (VI). The varied molar ratios of ferrate (VI) to TCL also provide an apparent stoichiometry involved in the degradation process.

The efficiency of ferrate (VI) examines the selectivity in TCL elimination in the presence of several coexisting ions/compounds (EDTA, Na_2HPO_4 , NaNO_2 , $\text{C}_2\text{H}_2\text{O}_4$, NaNO_3 , $\text{C}_2\text{H}_5\text{NO}_2$, and NaCl) at pH 10.0. The TCL, coexisting ions, and ferrate (VI) concentrations were taken as 0.10 mmol/L, 0.50 mmol/L, and 0.20 mmol/L, respectively. The reaction mixture was stirred for 2 hrs.

The spring water was spiked with known concentrations of TCL (from 0.02 to 0.03 mmol/L) at pH 10.0 and treated with a constant ferrate (VI) concentration of 0.10 mmol/L. The reaction mixture was agitated for 2 hrs, filtered with a syringe filter, and subjected to HPLC measurements to determine the TCL bulk concentrations. Spring water was collected from Bawngkawn south, Aizawl, Mizoram, India (GPS location; Latitude: 23.751507°, Longitude: 92.727747°). A multi-photometer measures sulfate, phosphate, and fluoride concentrations. Moreover, AAS measures the zinc, manganese, calcium, lead, copper, iron, and nickel concentrations in spring water. A TOC analyzer measured the inorganic and NPOC contents of spring water.

3. Results and discussion

3.1. Effect of tetracycline concentrations

A fixed concentration of ferrate (VI) 0.10 mmol/L was employed for the degradation of TCL at different concentrations (from 0.02 to 0.30 mmol/L) and at a constant pH of 10.0. This eventually enables obtaining a wide range of molar ratios of TCL to ferrate (VI), i.e., from 0.20:1 to 3.00:1 mmol/L. Figure 1(a) represents the change in ferrate (VI) concentrations as a function of time and at various concentrations of TCL. Ferrate (VI) degradation increases with increasing TCL concentration and attains a maximum degradation at a TCL concentration of 0.30 mmol/L (Figure 1(a)). Figure 1(a) also depicts that rapid ferrate (VI) degradation occurred during the initial time, and just within 10 mins of contact, ferrate (VI) achieved a constant concentration. This suggests that ferrate (VI) is very efficient in the degradation process and degrades a major portion of the TCL content during the initial

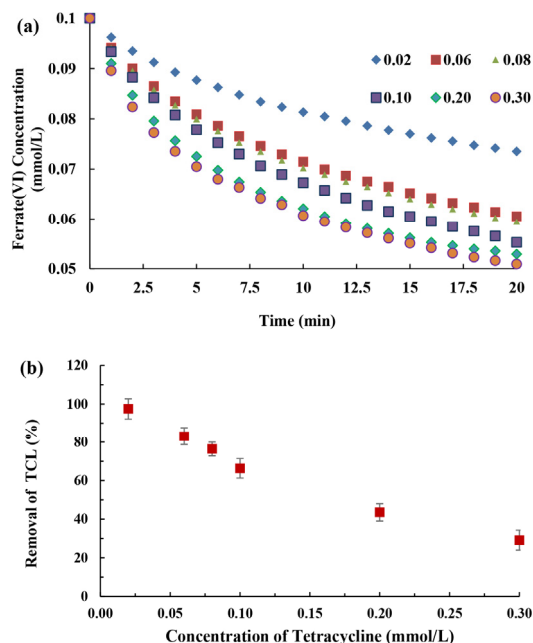


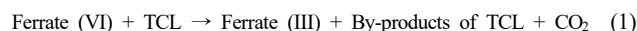
Figure 1. (a) Ferrate (VI) decomposition at various concentrations of TCL with respect to time at pH 10.0 using ferrate (VI) concentration of 0.10 mmol/L; (b) Percent elimination of TCL with respect to tetracycline concentrations at pH 10.0.

contact period.

Figure 1(b) shows the percentage removal of TCL in the ferrate (VI) treatment at various TCL concentrations. It is evident that an increase in TCL dilution from 0.30 to 0.02 mmol/L significantly favored the percentage elimination of TCL, from 29.12 to 97.42%. In other words, an increase in TCL concentrations decreased the percentage removal of TCL using a constant dose of ferrate (VI). A higher percentage elimination of TCL at lower concentrations is explicable with the relatively lesser number of TCL molecules present in the solution that is degraded with the same amount of ferrate (VI). Even the percentage removal of TCL is relatively low at higher concentrations of TCL; however, the extent of TCL removal is relatively high at higher concentrations[35,36].

3.2. Kinetics of ferrate (VI) elimination for TCL

The kinetic studies reveal the reaction order and apparent rate constant values in the removal of ferrate (VI) at varied TCL concentrations. These results also provide the molar stoichiometric ratios of ferrate (VI) and TCL in reactor operations. A simple redox reaction demonstrates the oxidation of TCL by ferrate (VI):



Hence, the rate equation for ferrate (VI) removal is represented as:

$$\frac{-d[\text{Ferrate(VI)}]}{dt} = k[\text{Ferrate(VI)}]^m [\text{TCL}]^n \quad (2)$$

Table 1. Rate Constant Values for PFO and PSO Reaction at pH 10.0 for the Decomposition of Ferrate (VI) as a Function of TCL Concentration

Concentration of TCL (mmol/L)	PFO			PSO		
	Rate Constant (1/min)	RSD (%)	R ²	Rate Constant (L/mmol · min)	RSD (%)	R ²
0.02	2.64×10^{-2}	3.01	0.955	278.67	2.91	0.957
0.06	4.28×10^{-2}	4.83	0.978	467.17	3.76	0.982
0.08	4.56×10^{-2}	4.78	0.977	497.17	4.17	0.981
0.10	5.11×10^{-2}	3.06	0.980	566.56	3.32	0.984
0.20	6.72×10^{-2}	4.71	0.981	770.58	3.98	0.987
0.30	7.41×10^{-2}	3.84	0.971	864.16	4.41	0.980

$$\text{or } \frac{-d[\text{Ferrate(VI)}]}{dt} = k_{app} [\text{Ferrate(VI)}]^m \quad (3)$$

$$\text{where, } k_{app} = k [\text{TCL}]^n \quad (4)$$

where k_{app} represents the overall rate constant, while [TCL] and [Ferrate (VI)] are the concentrations of TCL and ferrate (VI), respectively. The order of the reactants involved in the reaction is denoted as 'm' and 'n'. Optimization of the 'm' value in the reaction was obtained by an empirical fitting of the time-dependent ferrate (VI) concentrations to the known PFO (pseudo-first-order) or PSO (pseudo-second-order) rate models[29]. Hence, the k_1 or k_2 (where k_1 and k_2 are rate constants for PFO and PSO models, respectively) values were estimated at various TCL concentrations. The k_1 values were obtained by plotting time against the $\log(a-x)$, whereas k_2 by plotting time against the $1/(a-x)$ values for various concentrations of TCL at pH 6.0. Furthermore, the k_{app} value is deduced using the k_1 or k_2 values at varied TCL concentrations.

The time-dependent ferrate (VI) elimination at varied concentrations of TCL was employed for fitting PFO and PSO kinetic models. Results indicated that the data agreed better with the PSO model than the PFO model (Table 1). The relative standard deviation (RSD) obtained for each k value is relatively low, and they all fall below 5%. Overall, the results in Table 1 confirmed that in the removal of ferrate (VI) in the presence of TCL, the 'm' value is 2. Additionally, an increase in TCL concentrations from 0.02 to 0.30 mmol/L favoured the PSO rate constant from 278.67 to 864.16 L/mmol · min, respectively. The higher rate constant value is attributed to the strong reactivity of ferrate (VI) in oxidizing TCL in aqueous solutions[33,17].

Further, the PSO rate constant values at various TCL concentrations optimizes the 'n' value in equation 4. This eventually provides the molar stoichiometry of TCL with ferrate (VI) along with the " k_{app} " value. A plot between TCL concentrations against the PSO rate constant values finds an excellent linear relationship between the two variables. This demonstrates that the 'n' value is equal to 1. Hence, the stoichiometric ratio of ferrate (VI) to TCL is 2:1. Moreover, the value of ' k_{app} ' is evaluated from the slope of the line and found to be $1,978.8 \text{ L}^2/\text{mol}^2 \cdot \text{min}$ ($R^2: 0.932$). It was previously demonstrated that ferrate (VI) efficiently oxidizes several contaminants in an aqueous medium with relatively high ' k_{app} ' values[38-40]. Recently, it was reported that the degradation of sulfamethazine (SMZ), sulfamethoxazole (SML), and

sulfadiazine (SDZ) followed PSO kinetics with rate constant values ranging from 0.50 to $2.27 \times 10^4 \text{ L/mol} \cdot \text{sec}$ at pH 3.0[41]. The ferrate (VI) degrades diclofenac with a rate constant of 0.022 sec^{-1} at pH 9.0, and that of bisphenol-A shows a rate constant of $7.62 \times 10^2 \text{ min}^{-1}$ at pH 7.0[34,38].

3.3. pH dependence elimination of TCL

The elimination of TCL by ferrates is assessed at various pH (from 7.0 to 10.0) conditions. The concentrations of TCL and ferrate were 0.10 and 0.20 mmol/L, respectively. Figure 2(a) shows the time-dependent elimination of ferrate (VI) in the presence of TCL under different pH conditions. Figure 2(a) further infers that ferrate (VI) elimination is highly pH dependent, and the elimination of ferrate (VI) is relatively faster during the initial period of contact at all pH values.

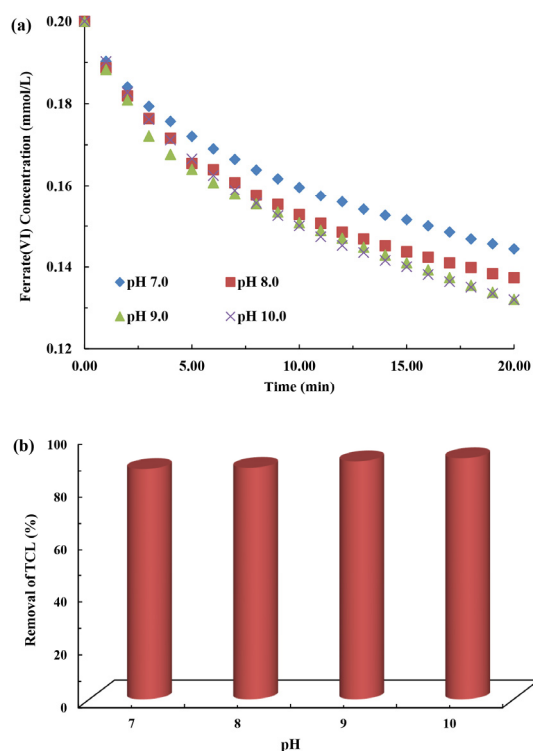


Figure 2. (a) Ferrate (VI) degradation at various pH of tetracycline solution with respect to time; (b) Percent elimination of tetracycline with respect to pH of TCL solution; [Ferrate (VI)]: 0.20 mmol/L; [TCL]: 0.10 mmol/L.)

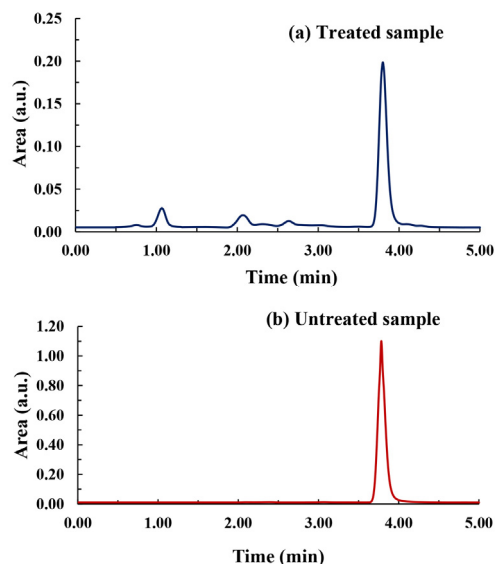


Figure 3. (a) HPLC chromatograms of ferrate (VI) treated TCL sample; (b) Untreated TCL sample; [Ferrate (VI)]: 0.20 mmol/L; [TCL]: 0.10 mmol/L; pH: 10.0.

On the other hand, the elimination efficiency of TCL by ferrate (VI) is shown in Figure 2(b). The increase in pH from 7.0 to 10.0 favored the elimination of TCL from 87.6 to 91.6%, respectively. The HPLC representative graph of TCL removal at pH 10.0 is clearly shown in Figure 3(a&b). The ferrate (VI)-treated sample of TCL showed additional peaks at lower retention times, indicating the formation of some degraded compounds of TCL. However, the untreated sample of TCL showed a distinct single chromatographic peak at a retention time of 3.8 min. The results infer that ferrate (VI) eliminates a very high percentage of TCL in the aqueous medium. The maximum percentage removal of TCL occurs at pH 10.0. Speciation studies reveal that TCL is present in its dissociated species at pH > 9.8 since TCL has a pK_a value of 9.8[42]. Thus, at pH 10.0, the dissociated species of TCL are readily oxidized by the reactive and stable FeO_4^{2-} species.

3.4. Effect of co-existing ions and compounds

The ferrate (VI) efficiency in eliminating TCL was studied in the presence of various coexisting ions and compounds (Na_2HPO_4 , NaCl, glycine, oxalic acid, $NaNO_2$, $NaNO_3$, and EDTA). The TCL, coexisting ions/compounds, and ferrate (VI) concentrations are taken as 0.10 mmol/L, 0.50 mmol/L, and 0.20 mmol/L, respectively, at pH 10.0. Figure 4 shows that the removal of TCL is negligibly affected in the presence of $NaNO_3$, Na_2HPO_4 , NaCl, and oxalic acid. However, the presence of EDTA and glycine affected the elimination of TCL. The elimination of TCL decreased from 91.65% to 47.92% and 52.05% in the presence of EDTA and glycine, respectively. The decrease in the percentage removal of TCL in the presence of these compounds is mainly due to the preferential degradation of EDTA or glycine by ferrate (VI) over TCL. It was observed previously that ferrate (VI) interacted favorably with $^+H_3N-CH_2COO^-$ and $H_2N-CH_2COO^-$ species of glycine, allowing it to attack the glycine molecule of the C-N bond

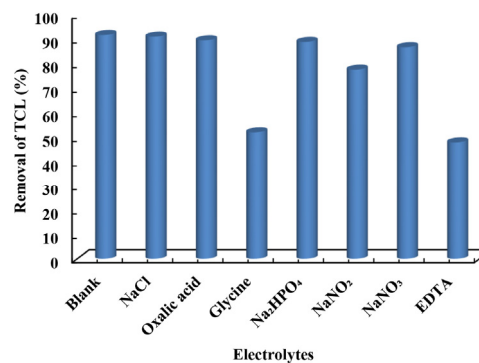


Figure 4. Elimination efficiency of TCL by ferrate (VI) with respect to various electrolytes.

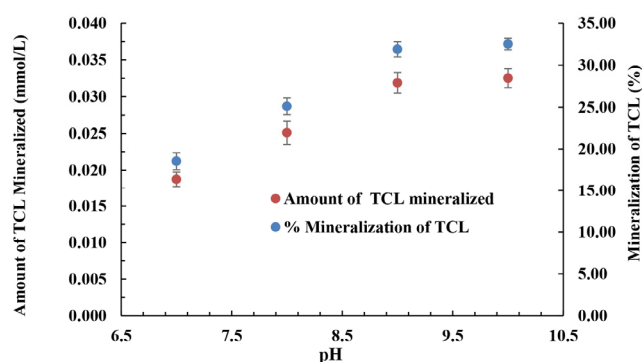


Figure 5. Actual amount of TCL mineralized as function of pH, and mineralization of TCL (%) by ferrate (VI).

[43,44]. Moreover, EDTA reacts with ferrate (VI), giving rise to partial radical formation ($Fe^{VI} = O \leftrightarrow Fe^V - O^*$), which further prevents the degradation of contaminants in aqueous solutions[45]. Additionally, $NaNO_2$ is a partially oxidized species; hence, it slightly affected the elimination efficacy of ferrate (VI) for TCL degradation.

3.5. Mineralization of TCL

The TCL is mineralized in ferrate (VI) treatment, and the mineralization of TCL was obtained with the ferrate (VI) treated TCL samples. The percentage of TCL mineralization, along with the extent of TCL mineralization as a function of pH, is shown in Figure 5. Figure 5 shows that by increasing the solution pH from 7.0 to 10.0, the percentage mineralization of TCL is increased from 18.57% to 32.52%. This implies that TCL mineralization is more favoured at higher pH values. Results show that a considerable amount of TCL was mineralized with a single dose of ferrate (VI). These results are consistent with TCL elimination obtained by the HPLC measurements. It was reported previously that a fixed amount of ferrate (VI) (0.10 mmol/L) could effectively mineralize bisphenol-A from 11% to 25% while decreasing the pH from 12.0 to 7.0[38].

3.6. Real matrix treatment

The practical application of ferrate (VI) in the removal of TCL was conducted using a spring water sample. The spring water is analyzed

Table 2. Water Quality Parameters of Spring Water, Bawngkawn South, Aizawl, Mizoram, India

Parameters	Values
TDS (mg/L)	106
Salinity (mg/L)	98
Oxidation-Reduction Potential(mV)	168
EC ($\mu\text{S}/\text{cm}$)	173
pH	7.85

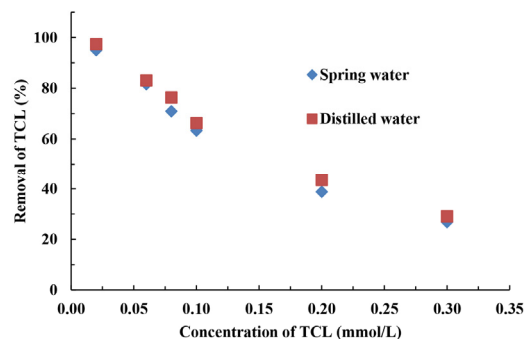
Chemical constituents	Concentration (mg/L)
Phosphate	0.25
Sulphate	3.40
Nitrate	3.02
Fluoride	BDL
Cu	0.001
Fe	0.021
Ni	0.421
Mn	0.765
Zn	0.082
Pb	0.002
Ca	0.128
NPOC	2.60
IC	7.53

BDL – Below detection limit

for various water quality parameters; the results are shown in Table 2. The water sample contains a high level of inorganic carbon (7.53 mg/L), which is attributed to the high value of carbonates or bicarbonates of calcium. Moreover, the amount of organic carbon or NPOC is due to the presence of humic substances in the water. However, the water sample contains low concentrations of total Ni, Mn, and Ca and negligible amounts of Cu, Fe, Zn, and Pb. Additionally, the sample contains a relatively higher phosphate concentration; however, the sulfates and nitrates are at a low level. The water sample was spiked with varying concentrations of TCL (from 0.02 to 0.3 mmol/L), and these TCL samples were treated with ferrate (VI) (0.1 mmol/L) at pH 10.0. The results are shown in Figure 6, and the percentage of TCL removal is compared with the results obtained previously with distilled water (Figure 5). The results indicated that ferrate (VI) efficiently eliminates the TCL even in spring water samples since no significant difference is observed compared to the purified water results. Overall, the studies demonstrated that ferrate (VI) is an effective and potential oxidant in eliminating TCL.

4. Conclusion

The high-purity synthesized potassium ferrate showed potential for the degradation of TCL in aqueous medium. The increase in solution pH (from 7.0 to 10.0) and decrease in TCL concentrations favored the percentage elimination of TCL. A considerably high percentage elimi-

**Figure 6. Percentage elimination of TCL as a function of Target concentration in spring water and distilled water.**

nation of TCL (97.4%) was achieved at pH 10.0, taking ferrate (VI) and TCL concentrations of 0.1 and 0.02 mmol/L, respectively. In the presence of TCL, ferrate (VI) removal followed pseudosecond-order rate kinetics. An apparent molar stoichiometry of 2:1 was obtained for ferrate (VI) to TCL in the degradation kinetics. The overall rate constant (k_{app}) was estimated to be $1,978.8 \text{ L}^2/\text{mmol}^2 \cdot \text{min}$. EDTA and glycine suppressed the percentage removal of TCL by ferrate (VI); however, the presence of NaCl, Na_2HPO_4 , NaNO_3 , oxalic acid, and NaNO_2 negligibly affected the removal of TCL. Nevertheless, ferrate (VI) mineralized the TCL significantly, and mineralization was favored at higher pH values, increasing from 18.57 to 32.52% when the solution pH increased from pH 7.0 to 10.0. Similarly, ferrate (VI) efficiently removes TCL in spring water samples. The studies indicated that ferrate (VI) is relatively efficient in eliminating emerging water contaminants from the aquatic environment.

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