EFFICIENT USE OF FERRATE(VI) IN THE DEGRADATION OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS FROM AQUEOUS SOLUTIONS

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LEVIA LALTHAZUALA
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Ph.D REGISTRATION NO. : MZU/Ph.D/1248 of 10.08.2018

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EFFICIENT USE OF FERRATE(VI) IN THE DEGRDATION OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS FROM AQUEOUS SOLUTIONS

BY

LEVIA LALTHAZUALA

Department of Chemistry

Under the supervision of

Prof. DIWAKAR TIWARI

Submitted

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MIZORAM UNIVERSITY
Department of Chemistry
(A DST-FIST Supported Department)
Tanhril, Aizawl, Mizoram. PIN: 796004

Prof. Diwakar Tiwari, Dean (SPS)

Thesis Certificate

This is hereby certified that the research work for the dissertation entitled ‘***Efficient use of Ferrate(VI) in the Degradation of Pharmaceuticals and Personal Care Products from Aqueous Solutions***’ submitted by ***Mr. Levia Lalthazuala*** to Mizoram University, Tanhril, Aizawl, for the award of the Degree of Doctor of Philosophy in Chemistry is *bona fide* record of the research work carried by under my supervision. The contents of this dissertation, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

Tanhril, Aizawl
Date : 30.09.2021

(DIWAKAR TIWARI)
Supervisor

Tanhril Campus, Aizawl 796 004
Fax : (0389) 233 0834
Phone : 9862323015
E-mail : diw_tiwari@yahoo.com

Declaration of the Candidate
Mizoram University
September, 2021

I, Levia Lalthazuala, hereby declare that the subject matter of this thesis is the record of work done by me, that the contents of this thesis did not form basis of the award of any previous degree to me or to the best of my knowledge to anybody else, and that the thesis has not been submitted by me for any research degree in any other University/Institute.

This is being submitted to the Mizoram University for the degree of Doctor of Philosophy in Chemistry.

(LEVIA LALTHAZUALA)
Candidate

(Prof. MUTHUKUMARAN, R.)	(Prof. DIWAKAR TIWARI)
Head	Supervisor

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(LEVIA LALTHAZUALA)

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CHAPTER 1

INTRODUCTION

1. INTRODUCTION

Water is essential for human and other living organisms (Yu *et al*., 2006). The need for fresh water has increased dramatically as the world's population, manufacturing industries and agricultural developments are all rising at a tremendous rate (Juardo *et al*., 2012). Moreover, the increased of human activities has caused for enhanced amounts of wastewater which is substantially discharged back into the water bodies. These wastewaters are seemingly contained with high levels of organic as well as inorganic compounds or even several complex substances that eventually affected the possible tolerance of the ecosystem.

Over the past few decades, the volume of global sewage disposal in aquatic environment was increased significantly. According to rough statistics on ocean emissions, 35 million tons of garbage are discarded into the water bodies per year across the globe (Zhang *et al*., 2020). Agricultural, commercial and urban activities use more than a third of the world's available sustainable freshwater. Thousands of synthetic and natural chemical products contaminate freshwater environments around the planet as a result of our daily activities. Every day, approximately 2 million tons of waste resulting from both manufacturing industries and human operations (for example, synthetic chemicals used in automotive and consumer products; dispersed farm pollution from fertilizer and pesticide application; and oil and fuel components from unintended spills) are discharged into the water bodies with insufficient or no treatment (Schwarzenbach *et al*., 2006; Dey *et al*., 2019) . The pollutants released into the water bodies are harmful to marine species and pose serious threats to aquatic environment (Bhatnagar and Sillanpää, 2010). Further, the presence of organic micropollutants in the ecosystem has captivated the attention of the public during the last decade, as there has been widespread concern regarding the adverse consequences of these environmental contaminants on living organisms (Cunningham *et al*., 2006; Kümmerer, 2009). Pharmaceuticals, personal care products (PCPs), plasticizers, antiseptics and pesticides are man-made compounds that are continually released into the atmosphere as a consequence of consumer practices, improper waste management, unintended seep outs, and intentional incorporation and are considered as emerging organic contaminants (EOCs) (Daughton, 2004).

Consequently, the quality of water is increasing deleteriously and has become a serious concern to the environment. This necessitated an emergent need of advanced wastewater treatment plants to efficiently decontaminate the pollutants from the wastewaters prior to its discharge into water bodies. Moreover, to conserve water supplies and maintain a balanced growth and allocation of water-derived benefits, there is a need for adequately financed facilities and effective governance structures at both the national and local levels. As a result, several initiatives are sprouting up all across the world to achieve this aim (UNESCO, 2012). In recent years, variety of methods for the treatment of urban/municipal and commercial wastewater has been developed. Physical, chemical, and biological procedures are the foundations of the current wastewater management systems (Sehar *et al*., 2013). But the real challenge emerges when it comes to treating low-quality water for discharge or reuse. Thus, wastewater management, reuse and reclamation are important components of the required strategy (Bouwer, 2000).

Several wastewater treatment systems are now in operation and there have been enormous advancements in the treatment systems, yet these modern water treatment facilities have shortcomings in many areas. Inspection was the first step in the wastewater treatment phase, preceded by biological/chemical treatment and innovative treatment approaches including disinfection. As a result, the treatment phase entails a number of time-consuming procedures that demand the use of a number of treatment chemicals. Perhaps the most significant disadvantage is involvement of environmental issues that arise from the procedures itself. The oxidants used in certain cases resulted in the release/discharge of harmful substances, creating an additional environmental burden. Chlorine, hypochlorite, and ozone are the common oxidants that are extensively utilized in wastewater treatment till date. These chemicals are widely used due to their abundance, perhaps, relative efficiency as oxidants and cost effectiveness. However, the chemicals and the by-products generated during the disinfection seemed to be harmful, hence their usage in such environmental remediation raise some health issues. For example, the usage and storage of ozone and chlorine in wastewater treatment, is said to be fraught with hazards due to the presence of extremely corrosive and poisonous gases. Furthermore, the development of toxic DBPs (disinfection by-products) such as bromate and trihalomethanes in the treatment of wastewater has been linked to the ozonation and chlorination processes (Haag and Hoigne, 1983; Jiang *et al*., 2007; Grünwald *et al*., 2002). Many of these by-products have the ability to be mutagens or carcinogens, making them potentially more dangerous and impossible to eliminate than the parent pollutants. Hypochlorite is also often considered harmful. It is used in smaller operations as a source of chlorine for water treatment due to its low-cost. It is generated from chlorine gas, which can easily break down into to chlorine when heated or mishandled chemically. A further disadvantage of current wastewater treatment systems is the existence of large amount of sludge, which contains a variety of harmful substances, making an additional problem in its elimination (Gracia-Lor *et al*., 2012). Additionally, several organic amines and sulfides released during wastewater treatment contribute to on-site scents that are problematic to humans, necessitating the development of modern H_2S management methods in urban sanitary sewage treatment plants and industrial waste treatment facilities. The health hazard caused by H_2S gas exposure even for short periods is also significantly threatening (Doujaiji *et al*., 2010). This kind of poisoning has been identified as the leading cause of mortality in sanitary sewer personnel. As a result, the growing demand for safe water, as well as the urgent need for reliable and successful wastewater treatment processes, has prompted a massive quest for more viable, environmentally friendly wastewater treatment chemicals to replace existing chemicals.

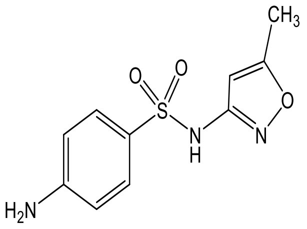
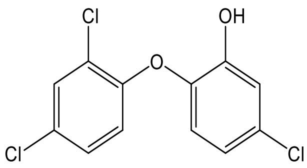
Ferrate (VI) is an exceptionally intriguing substitute green chemical that has earned considerable interest over the years due to its superior capabilities in wastewater treatment in comparison to other compounds (Zhou *et al*., 2012). It is also a strong oxidant that has a potential to act as a multi-functional agent in water treatment. A wide variety of its functions such as its ability to kill a large number of bacteria, partially decompose and/or oxidize organic and inorganic pollutants, remove suspended/colloidal particle materials, and dramatically lower phosphate concentrations in sewage treatment, has been well-documented (Jiang, 2014; Sharma *et al*., 2015). Further, recent studies have shown that ferrate (VI) can be used to remediate emerging micro-pollutants, (Dong *et al*., 2018; Kim *et al*., 2015; Manoli *et al*., 2017), odor compounds (Liu *et al*., 2018), and sludge (He *et al*., 2018) in wastewater treatment procedures with favorable results. In this regard, ferrate (VI) proves to be highly promising to meet the present demand of wastewater remediation as it outperforms many other commonly used oxidants.

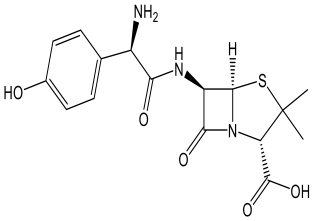
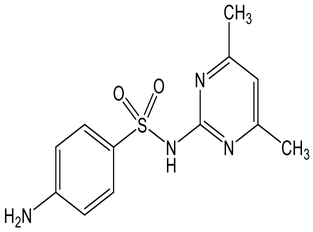
1.2. Fate of pollutants and their toxicity

Pharmaceutical are prescribed medications, whereas personal care products (PCPs) are non-prescribed medications that is used to enhance the quality of human life. Every year, the global production of PPCPs rises by 3%. Antibiotics, antipyretic and analgesics medications are the most often used pharmaceuticals. It was reported that the intake of non-prescription drugs (eg., ibuprofen) in UK was around 162 ton per annum and in Poland, it was 58 ton annually (Kwarciak-Kozłowska, 2019). The overall annual use of PPCPs has increased sharply over the last decade, with Brazil, South Africa, China, India, and Russia among the top consumers (Awfa *et al*., 2018; Tijani *et al*., 2016). In recent years, PPCPs have gotten a lot more recognition as emerging pollutants because of their potential risk to the marine ecosystem and human health (Liu *et al*., 2013; Wang *et al*., 2017).

PPCPs may be detected in the natural environment using high-sensitivity detection techniques. These chemical compounds are not fully removed and disposed in wastewater treatment due to their complicated composition and as a result, unchanged or intermediate metabolites can pollute ground and surface water, sewage sludge and soil (Ebele *et al*., 2017; Wang and Wang 2016; Kasprzyk-Hordern *et al.*, 2009; Boxall *et al*., 2012). According to studies, the PPCPs have been shown to be detectable in quantities ranging from from ng/L to mg/L in ground water, ng/L to g/L in surface water and it can reach upto μg/kg in soil or sewage sludge (Wang and Wang, 2016). Although the total PPCPs levels are minimal, their concentrations can last in the water or soil for months to years (Zhang *et al.*, 2012; Monteiro and Boxall, 2009). PPCPs are stable in the environment and, once absorbed, have the ability to bio-accumulate in cells, causing resistance to antibiotic, disruption of endocrine system, primary productivity inhibition, and other effects (Fent *et al.*, 2006). Thus, in our study we are selecting four PPCPs viz., sulfamethoxazole, sulfamethazine, triclosan and amoxicillin and there details are summarized in Table 1.1.

Table 1.1. List of selected PPCPs used for present investigation.

Sl. No.	**Pollutants**	**Structure**	**IUPAC**	**Application**	**Toxic-effect**
1.	Sulfameth-oxazole		4-Amino-*N*-(5-methylisoxazol-3-yi)-benzenesulfinamide	Antibiotics (human and veterinary medications), kill bacteria	Antibacterial resistance, allergic reactions, etc.
2.	Triclosan		5-chloro-2-(2,4-dichlorophenoxy)phenol	Disinfectants, kill unwanted germs and parasites	Endocrine disruption, antibacterial resistance, etc.

3.	Amoxicillin		(2*S*,5*R*,6*R*)-6-[[(2*R*)-2-amino-2-(4-hydroxyphenyl)acetyl]amino]-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid	Antibiotics (human and veterinary medications), kill bacteria	Antimicrobial resistance, affect cellular processes in marine organisms, etc.
4.	Sulfameth-azine		4-amino-*N*-(4,6-dimethylpyrimidin-2-yl)benzenesulfonamide	Antibiotics (human and veterinary medications), kill bacteria	Antibacterial resistance, allergic reactions, etc.

1.2.1. Sulfamethoxazole (SMX)

Sulfamethoxazole (SMX) is an antibiotic drug and is often detected in wastewater. It is a sulfonamide drug and is widely prescribed for various infectious diseases including meningitis, urinary tract infection, respiratory system infection etc. in human and animal (Baran *et al*., 2011; Gong and Chu, 2016; Shimizu *et al*., 2013; Trovó *et al*., 2009). Based on the US Geological Survey, sulfamethoxazole is one among the top 30 pharmaceuticals found in wastewater, which is having a half-life of 85 to 100 days or even longer (Zhu *et al*., 2017). Due to its persistence in nature, SMX was used to escape from the conventional treatment plants and is usually detected in the effluent of the treated wastewater accordingly entering into the water bodies. It was also reported that wastewater treatment facilities are unable to eliminate sulfamethoxazole completely because of its limited biodegradability (Ternes *et al*., 2004). In 1961, United States Food and Drug Administration have approved sulfamethoxazole to be used as an individual therapeutic agent. It is known fact that sulfamethoxazole is only partially metabolized in the body and *ca.* 45–70% of administered drug is eliminated through urine or feces (Cribb and Spielberg, 1992; Collado *et al*., 2013). Further, it was reported that the surface waters are contaminated with sulfamethoxazole, at a concentration level of ng/L, primarily due to the effluent of hospitals or pharmaceutical industries (Giang *et al*., 2015; Lin and Tsai, 2009).

Chronic toxicity was studied in marine ecosystem towards a complex algal and bacterial species (known as periphyton) and stated that sulfamethoxazole showed enhanced toxicity impact towards pheriphytic bacteria (Johansson *et al*., 2014). It was also revealed that sulfamethoxazole is harmful to microalgae because it induces the chloroplast translation process, which affects photosynthetic processes and affects cell wall formation (Välitalo *et al*., 2017).

1.2.2. Triclosan (TCS)

Triclosan is a common bactericide and antimicrobial drug. It is widely employed as a preservative chemical and often used as an added substance for various PPCPs (Pharmaceutical and Personal Care Products) formulations. It is also an additive for various consumer items such as detergents, toothpastes, plastics, cosmetics, kitchenware, antiseptic soaps, hand wash, carpets, textiles, toys, etc., (Reiss *et al.,* 2002; Sabaliunas *et al.,* 2003; Singer *et al*., 2003; Sanches-Silva *et al*., 2005; Solá-Gutiérrez *et al*., 2018). World consumption of triclosan is increased significantly, and a preliminary estimate suggests that European countries has consumed around 350 tons of triclosan per year (Pintado-Herrera *et al*., 2014; Halden and Paull, 2005; Young *et al.,* 2008). Moreover, the worldwide market for triclosan as an active ingredient in personal care items is estimated to be *ca.* 1500 tons (Chen *et al.,* 2011). Furthermore, about 96 percent of triclosan is estimated to be released through the sewage system and ultimately enters into the marine ecosystem (McAvoy *et al*., 2002). The extensive usage of triclosan in a number of PCPs has resulted in a massive discharge of triclosan into the wastewater treatment plants (WWTPs), which eventually enters to the surface waters (Pintado-Herrera *et al*., 2014; Halden and Paull, 2005). It was reported previously that triclosan is found in groundwater (0.03 μg/L Kabwe, Zambia) and rivers (3 to 68 ng/L, Jiaosu river, Taiwan) as well as sediments (0.4 to 85 ng/g, Minesota fresh water sediments, USA) (Sorensen *et al*., 2015; Peng *et al*., 2017; Yang *et al*, 2015). Triclosan is accumulated in marine and terrestrial ecosystems because of its hydrophobic nature and comparatively large value of log K_{ow} (octanol-water partition coefficients) i.e., 4.86. These possess risk to the health of living organisms in aquatic environment. Further, another reports showed that triclosan is detected in human samples as well (e.g., breast milk, urine and plasma) (Dann and Hontela, 2011).

Triclosan is partially removed by existing biological wastewater treatment plants (*ca.* 72-93 percent) (Ying and Kookana, 2007) hence, part of it is escaped from the treatment plants and enters into the water bodies, even into the drinking water and surface water at a concentration of 4.9 ng/L in the United States and 5.16 ng/L in India (Kolpin *et al*., 2002; Morrall *et al*., 2004; Singer *et al*., 2003; Nishi *et* *al*., 2008; Fair *et al*., 2009; Zhao *et al*., 2010; Ramaswamy *et al*., 2011). Triclosan is currently ranked as a serious and emerging water contaminant causing serious concern around the globe (von der Ohe *et al*., 2012; Kolpin *et al*., 2002). Additionally, triclosan is known to be an endocrine disruptors that alters the endocrine system (Gee *et al*., 2008). Several experiments have shown the metabolic impact of triclosan (Weatherly and Gosse, 2017). During birth, it lowers estrogen levels in the placenta. It also alters testosterone level, impairing sperm production and increased the body mass index while decreasing the constancy and viability of neural stem cells and modification of the endocrine system (Marques *et al*., 2017).

Triclosan is considered to be very toxic to marine animals, including the water flea daphnia magna, green algae, and fish (bluegill sunfish, fathead minnows and zebrafish) (Dann and Hontela, 2011; Chen *et al*., 2014). It was reported that the presence of triclosan in water greatly affects the earthworms (*Eisenia fetida*) and Japanese medaka fish (Lin *et al*., 2010; Nassef *et al*., 2010). It prevents bacterial development by suppressing lipid biosynthesis (Adolfsson-Erici *et al.,* 2002) and decreases the muscular activity of mice and the swimming motions of fish (Fritsch *et al*., 2013; Cherednichenko *et al.,* 2012). Humans are susceptible to microbial tolerance caused by triclosan (Dhillon *et al*., 2015). Several studies indicated that triclosan causes bacterial resistance and skin irritation (Brausch and Rand, 2011; Dayan, 2007). The byproducts such as methyl triclosan, biphenyl ethers and chlorinated phenols are highly toxic and has shown carcinogenic character with low biodegradability and bioaccumulation, which further leads to long term health hazard (Allmyr *et al*., 2008; Veldhoen *et al*., 2006; Zhao *et al*., 2017; McAvoy *et al*., 2002; Solá-Gutiérrez *et al*., 2020).

1.2.3. Amoxicillin (AMX)

Amoxicillin (AMX) is a beta-lactam antibiotic and is one of the most prescribed antibiotics in the penicillin family for both animal and human medications (Bound and Voulvoulis, 2006; Lissemore *et al*., 2006). It is employed to cure and avoid respiratory disorders, gastro-intestinal, urinary tract infections, skin bacterial infections, pharyngitis, tonsillitis, as well as helicobacter pylori infection and duodenal ulcer diseases. It is recommended for the management of chlamydia trachomatis infection due to its pharmacological and pharmacokinetic properties (Deng *et al*., 2008). It is highly resistant to bacteria such as *Escherichia coli*, *Neisseria gonorrhoeae*, *Haemophilus* influenza, *Streptococci*, *Pneumococci*, and certain *Staphylococci* strains (Fazelirad *et al*., 2015; Bebu *et al*., 2011).

Amoxicillin is having log K_{OW} (partition coefficient of octanol-water) of 0.87 and acid dissociation constants (pk_a) of 9.41 (Windholz, 1976; Carless, 1966). It is considered as a major water contaminants due to its pharmacological characteristics, ingestion rate, environmental toxicity, chemical composition, and solubility (Baghapour *et al*., 2014; Homem *et al*., 2013). Amoxicillin is hydrolyzed by varying the pH condition and the molecule is persistent in nature and not degraded completely in conventional treatment plants (Nägele and Moritz, 2005; Zia *et al*., 1977; Homem *et al*., 2013). As a result of this, amoxicillin and its hydrolyzed and metabolized byproducts are often detected in both urine and feces (Putra *et al*., 2009). It was reported that the oral ingestion of amoxicillin (500 mg) in human, excretes 86.8% of drug, which further causes a significant risk to many marine organisms (Sun *et al*., 2012; Pan *et al*., 2008; Jones *et al*., 2002). Amoxicillin compounds are seemingly harmful to the algae *Synechocystis* sp. by inhibiting the algae's photosynthesis process (Pan *et al*., 2008).

Amoxicillin concentrations in household wastewater vary from ng/L to mg/L *(*Zuccato *et al*., 2010; Andreozzi *et al*., 2005; Elmolla and Chaudhuri 2009; Putra *et al*., 2009). A report indicated that amoxicillin is detected at the ng/L levels in river water and hospital effluents in Australia (Watkinson *et al*., 2009). Amoxicillin causes unpleasant odors in the wastewater and could develop microbial resistance among a wide variety of pathogens. Hence, the resistant bacteria can further cause diseases, which is difficult to treat with regular antibiotics (Kanakaraju *et al*., 2015). Amoxicillin promotes the spread of bacteria immune to β- lactam antibiotics (Martinez, 2009). Presence of amoxicillin in aquatic environment contributes to bacterial tolerance and as a result, failure to treat infections with traditional antibiotics (Ding *et al*., 2012; Fatta *et al*., 2007). This implies the prevalence of resistant genes in drinking and surface water (Vaz-Moreira *et al*., 2014). As a result of these findings, it is imperative that amoxicillin have to be completely removed from the waste/effluent waters prior to discharge into the water bodies.

1.2.4. Sulfamethazine (SMZ)

Sulfamethazine is a sulfonamide drug and widely used antibiotic to treat variety of infectious diseases in humans and animals. It is prescribed for the treatment and prevention of influenza and also for feed additive in the dairy processing industries (Zhao *et al*., 2017; Lin and Wu, 2018; Wang *et al*., 2019)

Sulfamethazine is strongly hydrophilic substance and very poorly metabolized by microorganisms; about 90% of the administered sulfamethazine is excreted by humans and livestock, as a results the concentration of sulfamethazine in water bodies ranged from ng/L to µg/L (Wen *et al*., 2018; Tang and Wang, 2019; Lin and Wu, 2018). Furthermore, long term agricultural practices contributed significantly the presence of sulfamethazine on farmlands. As a consequence, the sulfamethazine is reintroduced into the ground and drinking waters, surface waters and ultimately the entire aquatic ecosystems through surface runoff (Dolliver and Gupta, 2008; Davis *et al*., 2006). On the other hand, sulfamethazine is not eliminated completely in the biological treatment plants because of its low biodegradability (Lin and Chen, 2018; Tzeng *et al*., 2016). In addition to other sulfonamides, it is also frequently detected in aquatic environment *viz.*, surface water, drinking water, ground water and effluent of wastewater treatment plant (Huang *et al*., 2012). It is distributed significantly in various environmental matrices due to its high mobility and solubility in water having the concentrations up to 20 mg/kg in animal waste, 323 ng/L in water and 15 g/kg in agricultural soils (Xu *et al*., 2007; Gaw *et al*., 2014; Kaczala and Blum, 2016; Larsbo *et al*., 2008). Additionally, sulfamethazine accumulates in soils and sediments or even enters the food chain, resulting the growth of antibiotic resistance. This further leads to significant reduction or lack of antibiotic drug efficacy against human pathogens (Heberer, 2002; Batt *et al*., 2006). In humans, sulfamethazine exhibits a trimodal form of polymorphic acetylation. In rats, it induced thyroid gland enlargement (goiter). In both mice and rats, it causes diffuse hypertrophy and hyperplasia (Peters *et al*., 1975; Littlefield *et al*., 1989; Littlefield *et al*., 1990). Sulfamethazine administration to rats under bioassay conditions is known to induce tumors altered thyroid hormone homeostasis. The reversible suppression of thyroid peroxidase function is the fundamental cause for these changes (Poirier *et al*., 1999). Sulfamethazine decreases reproduction in both males and females in a continuous breeding trial in mice, and had little effect on sperm parameters (Reel *et al*., 1992). Sulfamethazine exposure seemingly causes sister chromatid exchange in Chinese hamster cells in the absence of an exogenous metabolic mechanism (IARC, 2001). Further, it was reported that sulfonamide antibiotics inhibit the development of several Gram-negative as well as most of Gram-positive bacteria (Wan and Wang, 2016; Liu and Wang, 2013).

1.3. Overview of conventional wastewater treatment

According to historical documents and geological data, the first wastewater treatment plant was built *Ca* 1500 BC and these plants were mostly installed to civic and religious institutions (Wiesmann *et al*, 2006). Until the middle of the nineteenth century, towns were mostly devoid with waste disposal systems and wastes were dumped straight onto the streets. By the nineteenth century, human growth and urbanization necessitated the need for handling and management of wastes originated with various household and other activities. New methods were introduced to collect the wastewater in special canals and diverted safely to outside of the cities and discharged into the waterways. However, the untreated, polluted wastewaters are discharged into the water bodies including rivers, ponds, lakes, oceans etc. This resulted in the proliferation of pathogens, most notably cholera, which took thousands of lives. Later, with the advent of first microscope, bacterial colony was easily identified and paved the way for establishment of modern wastewater treatment plants as to protect the human health (Khodavirdipou *et al*., 2019). Further, because of the rapid growth of industries and urbanization, the local governments were necessitated to introduce the legitimate policy for safe disposal and dumping of wastewater. This initiated to conduct several trials to scale up the wastewater treatment plants both in the United Kingdom and the United States of America and the first technical-scale activated sludge plant was built in Sheffield, United Kingdom in 1920 (Zinicovscaia, 2016).

Rapid population growth and various socio-economic developments in the present era have led to significant increase of wastewater which is contained with a variety of chemical compounds and species. A rough estimate indicates that every day *ca*. two million tons of manufacturing and crop wastes are directly dumped in the water bodies (Schwarzenbach *et al*., 2010). Therefore, in order to handle the concerns related to the safe and secure wastewater management, almost every country is having regulatory bodies for proper control of waste disposal and monitoring of clean water supplies. Their responsibilities include the enforcement of regulations, the monitoring of drainage, and the maintenance of practices that affect the safety of drinking water (Schellenberg *et al*., 2020).

Natural water quality is determined by the wastewater treatment process as adopted in the treatment plant. However, the extended and advanced treatment is found to be more expensive. Currently, the conventional wastewater treatment is composed with three distinct stages: primary, secondary, and tertiary treatments. The number of stages is determined by the amount of pollutants eliminated and the processes employed to eliminate specific contaminants. Primary treatment involves removing dissolved solids and biological matter from drainage system using physical processes such as sampling and sedimentation. Secondary treatment converts the finely dissolved and dispersed organic matter into settle-able organic and inorganic solids that can be flocculated. The main purpose of this step is to remove suspended solids as well as colloidal and soluble contaminants that are escaped from primary treatment and to minimize COD and BOD levels by biological processes. This is usually accomplished by methods such as trickling filtration, oxidation ponds, oxidation ditches, and activated sludge. Tertiary treatment varies from traditional secondary treatment in terms of wastewater purification, which includes the elimination of large levels of heavy metals, nitrogen microbes, ammonia, viruses, and biodegradable organics. Apart from biological nutrient removal techniques, chemical flocculation, coagulation, and sedimentation are often used in association with activated carbon and filtration. Ion exchange and reverse osmosis are employed less often to remove or to decrease the concentration of dissolved solids (Zinicovscaia, 2016).

The traditional wastewater treatment plants are used to eliminate the variety of pollutants (including the chemical and microbial contaminants) from wastewater, which are detrimental to human health and the ecosystem. However, the efficacy of these plants are facing several challenges with the variety of emerging pollutants including the pharmaceuticals, personal care products, endocrine disrupting chemicals etc. (Mallevialle *et al.*, 1996; Langlais *et al.*, 1991). Moreover, the increasing public awareness regarding the consequences of water contamination, as well as the public demand for improved water safety, have prompted the introduction of even tougher regulation by lowering the maximum contaminant levels (MCLs) in water bodies. Similarly, the decreased or limited fresh water resources with rapid increase in industrialization and urbanization have led to pose tremendous problem on the fresh water distribution system. Industrial and municipal wastewater recycling, as well as the retrieval of potentially hazardous pollutants produced by industrial operations, becomes highly important.

Therefore, in view of the global demand and to overcome the emerging issues and to optimize the resources, a range of advanced treatment options are suggested and evaluated in recent past. This, perhaps, can resolve both existing and anticipated demands of fresh water. Several methods, including membrane filtration, UV irradiation and AOP (advanced oxidation processes) are promising to eliminate variety of micro-pollutants and shown enormous potential for its implication in effective wastewater management.

1.4. Methods in wastewater treatment

1.4.1. Adsorption

Adsorption is a process by which pollutants are transferred from a liquid phase to the solid phase surface. It is often categorized according to the nature of the interactions between the adsorbate molecules, or ions and the adsorbents. Physisorption is a kind of adsorption in which physical forces dominates over chemical bonding and the adsorbates are held to the adsorbent's surface by weaker physical forces such as van der Waal's forces. Adsorption equilibrium is rapidly established, and with the exception of a few molecular solids, the molecular structure of the solid does not change during physisorption (Butt *et al.*, 2010). On the other hand, chemisorption is dependent on the chemical forces produced when electrons are transferred or shared among the adsorbate and the adsorbent. The enthalpy of adsorption is much larger than that of physisorption. It is often slower than physisorption and temperature-dependent implying the existence of an activation energy barrier (Butt *et al*., 2010). Electrostatic adsorption occurs primarily as a result of attractive coulombic interactions between an electrically charged adsorbent surface and an oppositely charged adsorbate species. This is most often noticed in the adsorption of substances from aqueous solutions. In addition, exchange adsorption is a adsorption process which is selective, not necessarily reversible, and with a lower heat of adsorption than chemisorption (Helfferich, 1962). Adsorption processes are highly efficient when the soluble chemicals and the solid surface have similar chemical and physical characteristics. Commonly employed adsorbing materials include activated carbon, activated alumina, lignite coke, bentonite, zeolites etc. Among these materials, activated carbon has received greater attention. This is primarily because of its high sorption capacity, high specific surface area etc. It is noted that variety of activated carbons precursors to several biological materials are obtained and showed diverse applications in the remediation of aqueous solutions contaminated with variety of pollutants (Cossu *et al*., 2018).

1.4.2. Ozonation

Ozone is a powerful oxidizing agent and thus undergoes reactions with a diverse array of organic and inorganic substances. Substances may be ozonated either directly with ozone or indirectly by free radicals ($^\bullet OH$) produced by the spontaneous breakdown of ozone. The distinction is that ozone is a relatively selective oxidizing agent, while hydroxyl radicals interact with a variety of organic and inorganic molecules, resulting in the possibility of producing the large number of intermediate products, some of which are hazardous to the environment (Kwarciak-Kozłowska, 2018; Liu *et al*., 2015; Kaarsholm *et al*., 2016). Ozonation modifies the chemical composition of persistent organic molecules found in drinking water, wastewater, and sewage sludge, converting them to more readily assimilated molecules (Kwarciak-Kozłowska, 2018; Carballa *et al*., 2007; Kwarciak-Kozłowska and Krzywicka, 2016). Use of ozone in presence of bromine makes serious consequences, since the ozone converts the bromine to bromate and eventually formation of several bromated organic by-products which are highly hazardous and are having serious environmental concerns (Siddiqui *et al*., 1995; Westerhoff *et al*., 1998; Ozekin *et al*., 1998; Gunten *et al*., 1996; Singer *et a*l., 2003; Song *et al*., 1997). It was reported that bromate ions has a possible carcinogenic character (Buttler *et al*., 2005). Another drawback of using ozone is the difficulty in maintaining residual ozone in disinfection, which makes it impossible to prevent the regrowth of microorganisms which requires additional disinfectant like chlorine (Demir and Atguden, 2015). Additionally, the ozonation operation is expensive because of its synthesis and having relatively short half-life by which it needs to be synthesized on-site at all times.

1.4.3. Advanced Oxidation Processes (AOP)

AOPs are relatively newer process that include the photocatalytic/photochemical processes, Fenton/photo-Fenton processes, ozonation (O_3) in combination with hydrogen peroxide (H_2O_2), heterogeneous photocatalysis, titanium dioxide (TiO_2), ultrasound, ultraviolet light, and/or intense electron beam irradiation, electrochemical oxidation, electrocatalysis, sonolysis, pulsed plasma etc. (Miklos *et al.*, 2018). Among these methods, O_3/H_2O_2, O_3/UV, H_2O_2/UV, and heterogeneous photocatalytic reactions have the potential for water and wastewater detoxification. AOPs depends on the formation of hydroxyl radicals (•OH), a highly reactive species and a potent oxidizer. Additionally, radical species like hydrogen peroxide radicals, superoxide radicals, singlet oxygen radicals, and hydroperoxyl radicals are formed under AOP conditions (Oulton *et al.*, 2010).

1.4.3.1. Fenton oxidation

The Fenton oxidation process uses iron salts and hydrogen peroxide in an acidic environment to generate highly oxidizing hydroxyl radicals. However, the precipitation of iron oxide generates excess amount of sludge. Additionally, it requires minimal dose of H_2O_2 in the oxidation process which limits the standard Fenton treatment. The homogeneous Fenton reaction utilizes Fe(II) or Fe(III) and is quite successful in removing PPCPs; however, the operating pH range is very low, and the process is associated with excess amount of sludge generated as in the form of ferric hydroxide. Therefore, in order to overcome the disadvantages of homogeneous Fenton catalysis process, it is modified by using the heterogeneous catalysts like Fe_2O_3, $[Fe(OH)_2]^+$, α-FeOOH, ferrous polycation, and $[Fe(H_2O)]^{2+}$, etc. (Tayo *et al.*, 2018). This prevents the ferric ions from leaching and ultimate formation of hydroxide precipitation and can further operates at higher pH conditions as well. The modified Fenton-based processes include photo-Fenton and solar-Fenton, which uses light photons, ultraviolet radiations, or solar irradiations to enhance the production of hydroxyl radicals. Experimental investigations show that the use of solar photo-Fenton process in the treatment of municipal wastewater was successful in degrading emergent pollutants at low iron concentrations (Klamerth *et al.*, 2010). The only drawback of Fenton-based methods is the possibility of producing harmful by-products, which need to be thoroughly analyzed.

1.4.3.2. Heterogeneous photocatalytic processes

Heterogeneous photocatalysis is a newer method for treating wastewater. It is a reasonably inexpensive process that results in the full mineralization of organic substances to CO_2. The oxidation processes occur at room temperature, and the photocatalyst utilized are inexpensive (Lee *et al*., 2016; Khataee and Kasiri 2010). Catalysts in the form of metal oxides such as ZnO, SnO_2, and TiO_2; sulfates, telluride and selenium minerals such as ZnS, CdS, and CdSe are the primary semiconductors utilized in heterogeneous photocatalysis. On the surface of a semiconductor, electrons and holes engage in redox reactions that results in the production of of O_2^- (superoxide anion radicals) and •OH (hydroxyl radicals) (Awfa *et al*., 2018). TiO_2 has the greatest activity of all semiconductors utilized in photocatalysis processes. TiO_2 is quickly activated by ultraviolet light and it is insoluble in most of the reaction settings, photochemically stable, and nontoxic (Lee *et al*., 2016; Khataee and Kasiri, 2010; Banerjee *et al*., 2006; Bohdziewicz *et al*., 2016). Tio_2 doped with Ag and Au nanoparticles is fairly effective in the treatment of several micropollutants present in water (Lalliansanga *et al*., 2020; Tiwari *et al*., 2020).

1.4.3.3. Ozone – Ultraviolet radiation

Ozonation in combination with UV (O_3/UV) is an effective catalytic technique for degrading refractory waste water contaminants. The ozone photolysis enabled to generate •OH radical which are generated when O• reacts with water (Emam, 2012). The synergistic impact of O_3 with UV light is that it enhances the ozone breakdown to hydroxyl radicals directly and indirectly. Ozone shows maximum absorption at 253.7 nm (Hearn, 2002). The utilization of O_3/UV in effective oxidation of aromatic and aliphatic chlorinated organic pollutants, pesticides and natural organic matter was reported previously (Beltran *et al*., 1994; Glaze 1987; Peyton *et al*., 1982). The combination of ozone with UV synergizes the degradation process as compared to the ozonation alone. Early of 1980s, it is marketed for the commercial remediation of groundwater containing PCE (perchloroethylene) and TCE (trichloroethylene) (Cooper *et al*., 1993). The use of

O_3/UV process is reported to be less cost-effective than the O_3/H_2O_2 and H_2O_2/UV processes. Moreover, the main disadvantage is that in presence of colored substances or high turbidity, the transmittance of UV light is significantly reduced, thereby decreased efficiency of process was obtained. Similarly, the absorbance of UV light was obstructed by the powder catalyst material (Mierzwa *et al*., 2012).

1.4.3.4. Hydrogen peroxide – Ultraviolet radiation

The mechanism underlying the use of UV and H_2O_2 is based on the *in situ* production of hydroxyl radicals, which readily oxidizes pollutants (Molina *et al*., 1977). The UV light prompted to decompose the H_2O_2 resulted with generation of two hydroxyl radicals per unit of absorbed energy (Glaze *et al*., 1987). The hydroxyl radicals reacted with organic pollutants or participate in the H_2O_2 decomposition cycle (Crittenden *et al*., 1999). Moreover, the direct UV photo-oxidation enhances the overall decomposition of pollutants in the H_2O_2/UV system. The H_2O_2/UV system, like the O_3/UV, is efficient in oxidizing the persistent organic pollutants in aqueous solutions. Previously, Beltran and co-workers investigated the oxidation of atrazine in water by H_2O_2 and ultraviolet light. The results indicated that > 99% of the atrazine was degraded just less than 15 mins of contact (Beltran *et al*., 1994). The drawback is quite similar as of O_3/UV process since the excessive turbidity or high nitrate level in the solution caused to block the UV light penetration in the reactor. Similarly, the existence of residual hydrogen peroxide in water is required to be removed from the reaction mixture in the later stage of process (Brienza and Katsoyiannis, 2017).

1.4.3.5. Ozone – hydrogen peroxide

Ozonation in combination with H_2O_2 is the other possible way for effective catalytic method for degradation of dissolved organic impurities in wastewater. The O_3/H_2O_2 mechanism is most frequently referred to as peroxone which involves radical chain reaction based on decomposition of ozone as initiated by the hydroperoxide anion (HO_2^-) (Rekhate and Srivastava, 2020). Interaction between O_3 and H_2O_2 enhances the formation of •OH radicals. The O_3/H_2O_2 process is mostly employed in water treatment to oxidize micropollutants, remove pesticides, and control chemicals that impart flavor and odor (Karimi *et al.*, 1997; Ferguson *et al.*, 1990). The recommended H_2O_2 to O_3 ratio is typically between 0.3 and 0.6. In previous reports, removal of color from three paper and pulp mill effluent streams was investigated. It was found that the O_3/H_2O_2 operation could remove color up to 85% from the caustic extract stream, up to 90% in the acidic stream, and up to 50% from the final effluent (Zhou and Smith, 2002). O_3/H_2O_2 produces less •OH radicals, resulting in lower degradation rates and become less effective compared to other advance oxidation processes. Moreover, ozone produces toxic by-products like bromate ion which poses serious environmental concerns (Brienza and Katsoyiannis, 2017).

1.5. Ferrate (VI)

Ferrate (VI) is the higher oxidation state of iron. Ferrate (VI) is possessed with strong oxidizing capacity and received greater attention in several areas of scientific studies *viz*., i) A multifunctional chemical for environmental remediation and serve as disinfectant, coagulant, oxidant etc.; ii) Hypervalent iron source for some biomolecules; iii) Green synthesis oxidant for selective organic synthesis; and iv) Cathode material for super iron battery.

In the natural environment, iron is often present as the metallic iron (Fe^0), ferrous (Fe^{2+}) and ferric (Fe^{3+}) states. However, greater oxidation states of iron *viz.*, +4, +5, +6, and +8 exists under specific conditions. These higher oxidation states are collectively referred as ferrates. Out of these, +6 state is relatively stable and found easy to synthesize as compared to other oxidation states of iron (Audette and Quail, 1972; Bielski 1991; Thompson *et al.*, 1951). Therefore, during past few decades, there has been increased interest towards the possible uses of +6 state of iron, and various researches are conducted using ferrate (VI) (Lee *et al.*, 2003; Xu *et al.*, 2007; Sharma *et al.*, 2006; Yuan *et al.*, 2008).

Literature reveals that ferrate (VI) was first observed by Stahl in 1715 when the combination of saltpeter and iron filings was exploded in an experiment and the molten was dissolved in water. This was resulted with a colorful solution (dark purple) which was recognized as higher oxidation state of iron possibly the potassium ferrate (K_2FeO_4). Later, in 1834, Eckenber and Becquerel observed a same hue when red potash (potassium hydroxide) and iron ores were heated (Delaude *et al*., 1995). Similarly, Fermy postulated in 1840 that the deep purple color occurred is primarily due to the higher-valent iron species, although its formula was believed to be FeO_3 (Delaude *et al*., 1995). Later, more effective synthesis and analytic procedures for ferrate (VI) were developed with the systematic work conducted by the Schreyer and his colleagues (Ockerman and Schreyer, 1951; Thompson *et al*., 1951). The chemistry and applications of ferrate (VI) were more thoroughly investigated in the late 1950s. Ferrate (VI) is synthesized by the three synthetic routes i.e., (i) Dry oxidation; (ii) Wet oxidation; and (iii) Electrochemical oxidation of iron.

1.5.1. Structure and speciation of ferrate (VI)

The X-ray powder pattern suggested that, the potassium ferrate (VI) (K_2FeO_4) in its +6 oxidation state, the central iron atom is bonded covalently by four equivalent oxygen atoms (Hoppe *et al*., 1982). An isotopic oxygen exchange experiment in aqueous solution demonstrated that the four oxygen atoms are kinetically equivalent, which verified the tetrahedral structure of ferrate (VI) (Goff and Murmann, 1971). Figure 1.1 depicts three resonating hybrid configurations of ferrate (VI) ions, such that structures '2' and '3' are postulated as the primary structures of ferrate (VI) (Norcross *et al*., 2011).

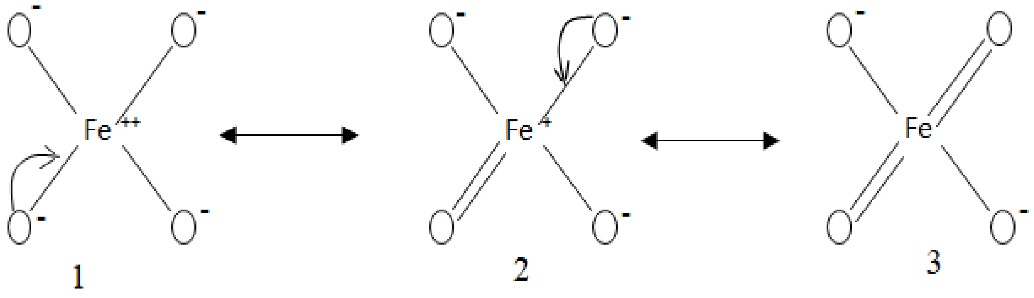


Figure 1.1: Three resonating hybrid configurations of ferrate (VI) ions (Norcross *et al.*, 2011).

On the basis of spectroscopic and kinetic investigations, four different species of ferrate (VI) are identified having the three acid dissociation constant values (pk_a) (Rush *et al.*, 1996). The three acid dissociation constants are reported as 1.6, 3.5 and 7.3 (Shrama *et al.*, 2001). Based on these pk_a values, the speciation studies are conducted and the percentage species distribution of ferrate (VI) as a function of pH is obtained (*Cf* Figure 1.2). Figure 1.2 illustrates that FeO_4^{2-} and $HFeO_4^-$ are the dominating species in alkaline and neutral pH conditions and ferrate (VI) in these forms is relatively stable in terms of spontaneous disintegration from ferrate (VI) to iron (III) (Tiwari *et al.*, 2007; Lee and Gai, 1993).

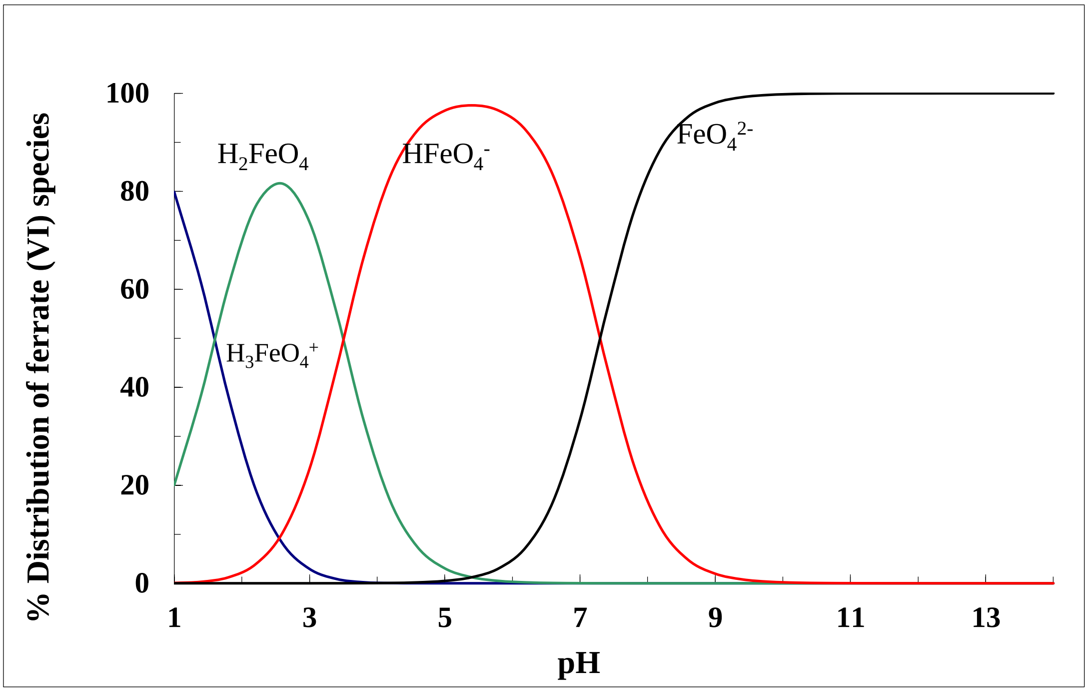


Figure 1.2. Species distribution of ferrate (VI) in aqueous solution (Tiwari *et al.* 2007).

1.5.2. Quantification and characterization of ferrate (VI): UV/Vis Spectroscopic studies

Qualitative and quantitative estimation of ferrate (VI) is reported previously (Tiwari and Lee, 2011). Ferarte (VI) gives red-violet color in aqueous solutions and a characteristic absorption maximum occurs at the wavelength of 510 nm (Jiang, 2014). Additionally, aqueous ferrate (VI) solution is relatively stable in phosphate for hours within pH 9.0 to 10.5. Therefore, the spectral investigations at this pH are rather simple to perform. In phosphate buffer solution (pH 9.2), the UV-Vis absorbance spectrum of ferrate (VI) with respect to ferrate (VI) concentrations was reported previously as shown in Figure 1.3 (Lee *et al.*, 2004). The FeO_4^{2-} species is stated to possess the molar extinction constant of 1150 $M^{-1}cm^{-1}$ at pH 9.0 (Lee *et al.*, 2004; Bielski *et al.*, 1987; Sharma *et al.*, 2001). This enables to quantify the ferrate (VI) (Sharma, 2002).

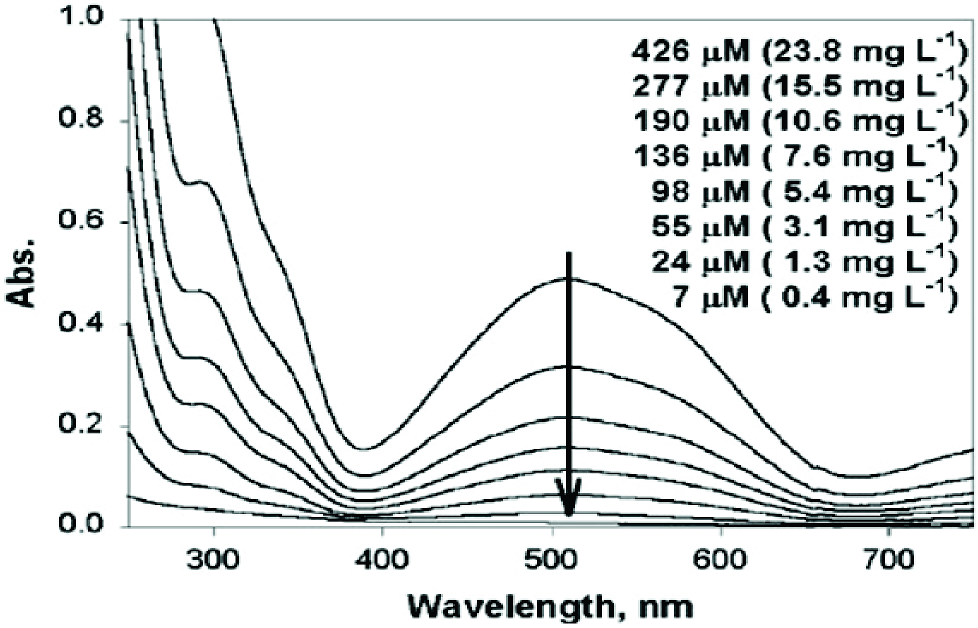


Figure 1.3. UV-vis absorption spectra of ferrate (VI) with respect to concentration in aqueous solution [Phosphate buffer: 25.0 mM; pH: 9.2] (Lee *et al.*, 2004)

1.5.3. Stability and decomposition of ferrate (VI)

The ferrate (VI) stability in aqueous solution is highly dependent on a number of factors which includes pH, temperature, ferrate (VI) concentration and the presence of coexisting ions. (Johnson and Sharma, 1999). The ferrate (VI) solution having higher concentrations is relatively less stable compared to the dilute solutions (Schreyer and Ockerman, 1951). Previously it was reported that the ferrate (VI) solution having 0.025 M concentration retained 89 percent of its original concentration at the end of 60 mins, however, if the concentration is raised to 0.03 M, it degrades completely within 60 mins (Tiwari and Lee, 2011). Similarly, 79.5% of the 0.01 M K_2FeO_4 solution was decomposed within 2.5 hrs however, 0.0019 M ferrate (VI) solution degrades only 37.4% within 3.5 hours at 25 ^{0}C (Wagner *et al.*, 1952). The K_2FeO_4 stability was enhanced from hours to week in 10 M KOH solution if CO^{2+}or Ni^{2+} impurity is not present (Stuart and Ghosh, 1999). On the other hand, the nitrate salts of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Zn^{2+}, Fe^{3+}, Cu^{2+} and other salts such as Na_2MoO_4, Na_2WO_4, Na_2SiO_3, Na_2SiF_6, $Na_2P_2O_7$, K_3PO_4, $K_2B_4O_9$, KIO_4

and $K_2Zn(OH)_4$ have shown no effect on K_2FeO_4 stability (Licht *et al.*, 1999). In presence of FeOOH, NaCl, KNO_3 and KCl, the ferrate (VI) stability was investigated in a 0.5 M K_2FeO_4 solution. Initially, rapid decomposition of ferrate (VI) was observed however, as the concentration of ferrate (VI) lowered, it became stable in presence of KNO_3 and KCl (Schreyer and Ockerman, 1951). Ferrate (VI) decomposition in phosphate buffer is significantly suppressed (Scheryer and Okerman, 1951). The spontaneous degradation of ferrate (VI) in aqueous solutions was found to be greatly enhanced when the solution pH was decreased from pH 10.0 to 5.0 (*Cf* Figure 1.4). Figure 1.4 illustrated that at pH 5.0, the ferrate (VI) was completely decomposed just after 7 mins of time, whereas at pH 9.0 and 10.0, it remained stable even after 20 mins of time (Tiwari *et al.*, 2007). Other reports indicated that the potassium ferrate concentration was reduced moderately when it was in 6 M KOH solution, but quickly reduced when it was prepared in 3 M KOH (Tiwari and Lee, 2011).

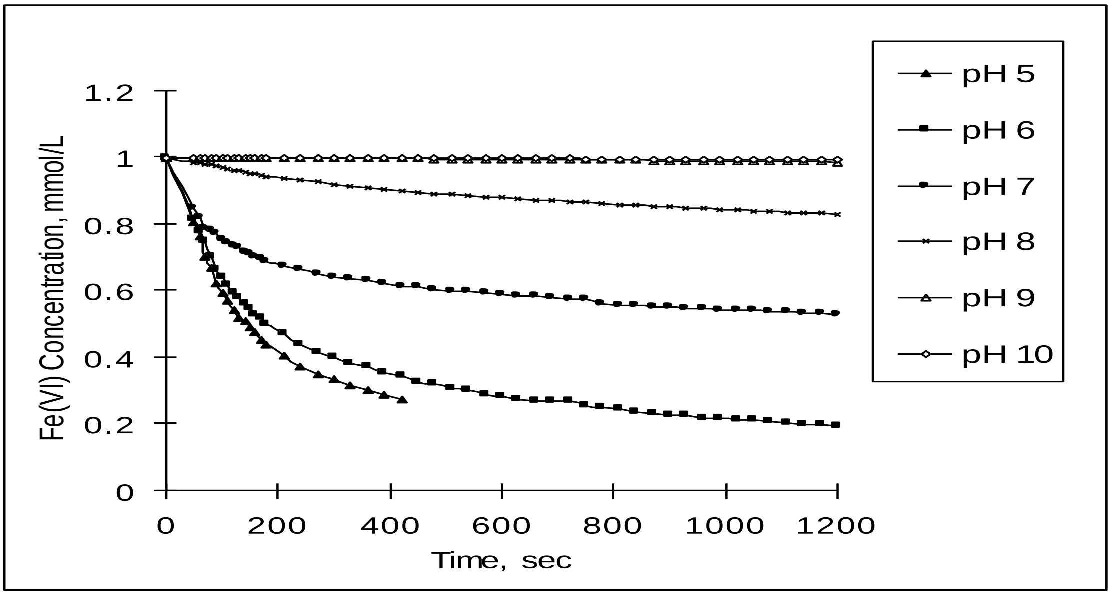


Figure 1.4. variation of Second-order rate constants for Fe (VI) to Fe(III) decay in 5 mM acetate/phosphate buffers (Tiwari *et al.*, 2007)

Ferrate (VI) salts in aqueous solutions undergoes with spontaneous degradation produces ferric hydroxide along with oxygen which is evolved (Equation 1.1) (Bielski, 1992):

$$4K_2FeO_4 + 10H_2O \rightarrow 4Fe(OH)_3 + 8KOH + 3O_2 \qquad \ldots (1.1)$$

Further, the rate of ferrate (VI) decomposition is greatly influenced by solution pH. At pH values > 9.0-10.0, the decomposition rate is minimum, however, as pH values are lowered below to pH 9.0, the rate of degradation is increased significantly (Karim *et al.*, 2020). The kinetics of ferrate (VI) spontaneous degradation followed first order above pH 10.0, and second-order below pH 9.0 (Lee and Gai, 1993). As a result, the equilibrium and kinetic models for ferrate (VI) decomposition are as follows (Equations 1.2-1.7) (Rush *et al.*, 1996):

$$2H_3FeO_4^{+} \leftrightarrow [H_4Fe_2O_7]^{2+} + H_2O \qquad k_2 = 3.5\text{x}10^5\ M^{-1}\ s^{-1} \qquad \ldots(1.2)$$

$$[H_4Fe_2O_7]^{2+} + 2H^{+} + 6H_2O \rightarrow Fe_2(OH)_2(H_2O)_8^{4+} + 3/2\ O_2 \quad \text{(Fast step)} \qquad \ldots(1.3)$$

$$H_3FeO^{4+} + H_2FeO_4 \leftrightarrow [\text{diferrate}] \qquad k_4 \approx 3.5\text{x}105\ M^{-1}\ s^{-1} \qquad \ldots(1.4)$$

$$2H_2FeO_4 \leftrightarrow [\text{diferrate}] \qquad k_5 = 1.5\text{x}104\ M^{-1}\ s^{-1} \qquad \ldots(1.5)$$

$$H_2FeO_4 + HFeO^{4-} \leftrightarrow [\text{diferrate}] \qquad k_6 \approx 1.5\text{x}104\ M^{-1}\ s^{-1} \qquad \ldots(1.6)$$

$$2HFeO^{4-} \leftrightarrow [Fe_2O_7]^{2-} + H_2O \qquad k_7 = 2.5\text{x}102\ M^{-1}\ s^{-1} \qquad \ldots (1.7)$$

It is evident from the above reactions that except for reaction (1.3), the forward reactions (1.2) to (1.7) are slow steps and hence, considered to be the rate determining steps. The rate constants for self-decomposition of ferrate (VI) are then computed, which are considered to be second-order reactions. The rate constants for the decomposition of Fe (VI) to Fe (III) in deionized water at various pH are also shown in Figure 1.5.

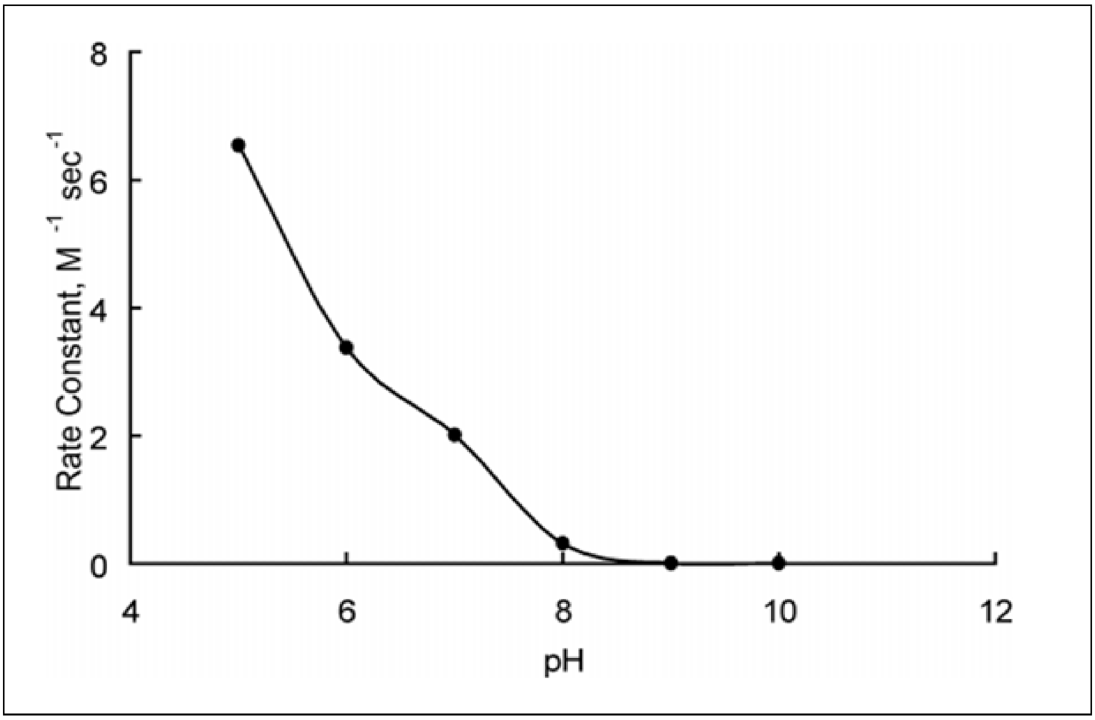


Figure 1.5. Second-order rate constants for Fe(VI) to Fe(III) decay in deionized water [Initial Fe(VI) concentration: 0.1 mM] (Tiwari *et al*., 2007).

1.5.4. Ferrate (VI): A multipurpose green chemical in wastewater treatment

Ferrate (VI) is a multifunctional chemical and is employed for oxidation, disinfection, coagulation etc. Moreover, the by-product formed in wastewater treatment process is iron (III) which is environmentally safe. Therefore, the use of ferrate (VI) in wastewater treatment processes received a greater attention (Lee and Tiwari, 2009). Ferrate (VI) is a formidable oxidant having redox potential of 2.20 V at pH 1.0 and 0.72 at pH 14.0 (Sharma, 2002). It was observed that the use of ferrate (VI) in wastewater treatment acts as an effective/efficient oxidant/disinfectant in the first step and in the second step, the product iron (III), serves as an efficient coagulant that coagulates the non-degradable contaminants from aqueous solutions (Acosta-Rangel *et al*., 2020). Ferrate (VI) has a higher redox potential than ozone in acidic conditions. Also, ferrate (VI) is having higher potential over to the commonly used oxidants/disinfectants *viz.*, hydrogen peroxide, chlorine, hypochlorite, perchlorate, ozone etc. in water and wastewater treatments (Table 1.2). Ferrate (VI) decomposes into iron (III) with the release of oxygen and ferric ions (Iron (III)) as a by-product, making it highly reactive (Equation 1.1). This reaction is significant in water treatment since it gives a mechanism for ferrate (VI) to self-eliminate in aqueous solution. The end product of iron in all oxidation process gives rise to harmless ferric ions thus, forming hydroxide oligomers. Settling and flocculate suspended the particulate matters. Several investigations have shown that ferrate (VI) is a potential oxidizing agent and found efficient in eliminating a variety of organic contaminants, including hydrazine compounds (Okabe *et al*., 2003), amino-acids (Rush and Bielski, 1995, 1993), chlorine oxyanions (Okabe *et al*., 2003), thiourea (*Æ*søy *et al*., 2002), 1,2-Diols (Lee and Gai, 1993), nitrogen containing organic compounds (Sharma, 2010; Johnson and Hornstein 1996), phenol (Liu *et al*., 2013), compounds of nitrosamines (Bartzatt and Nagel, 1991), carboxylic compounds (Bielski *et al*., 1994), aliphatic sulphur (Sharma *et al*., 2011), thiosulphate (Read *et al.*, 2001), recalcitrant organics (Sharma *et al*., 2008b), alcohol, etc. (Lee and Gai, 1993; Rao *et al*., 1988). Furthermore, ferrate (VI) revealed its effectiveness to oxidize several major pollutants that found in water bodies, including bisphenol A, estrogens, and pharmaceuticals (Lee *et al*., 2005, 2008, 2009; Sharma *et al*., 2006a, 2008a, 2009a,b; Anquandah and Sharma 2009; Zhou and Jiang, 2015; Barışçı *et al*., 2015; Han *et al*., 2015; Chiu *et al*., 2016). Ferrate (VI) is also effective in the removal/degradation of various inorganic pollutants, such as hydrogen sulphide, ammonia, and cyanide in addition to organic impurities (Sharma *et al.*, 1998a,b; Tiwari, 2007; Sailo *et al*., 2015, Pachuau *et al*., 2013). Ferrate (VI) is also an excellent disinfectant in the treatment of wastewater (Cho *et al*., 2006; Sharma, 2007; Jiang *et al.*, 2007). It was reported that more than 99.9% of all *coliforms* can be destroyed by ferrate (VI) (Sharma *et al*., 2005a). Similarly, at lower concentrations and shorter contact durations, ferrate (VI) was found to be more efficient than hypochlorite in deactivating the *Escherichia coli* (*E.coli*) (Jiang *et al*., 2007).

Ferrate (VI) treatment significantly reduces the turbidity, the content of various metals in their free and complexed forms, humic acid, nutrients and radionuclides (Stupin and Ozernoi, 1995; Sharma *et al*., 2005a,b; Potts and Churchwell, 2009; Liu and Liang 2008; Lee *et al*., 2003, 2009; Joshi *et al*., 2008;

Jiang *et al.*, 2006; Graham *et al.*, 2010; Jiang *et al.*, 2001; Jiang and Sharma, 2008; Jiang *et al.*, 2009; Jiang and Lloyd, 2002; Tiwari *et al.*, 2008). Ferrate (VI) was also shown to be a promising antifouling agent. It is also useful in controlling odor management e.g., unpleasant odors generated by sulfides and ammonia (de Luca *et al.*, 1996). Ferrate (VI) is reported to be ecologically safe and showing its effectiveness in managing biofilm development in condenser systems (Fagan and Waite, 1983), implying its utility as a biocide in biofouling management.

Apart from being a powerful oxidant, coagulant, disinfectant and antifouling agent, ferrate (VI) is referred to as a 'Green Chemical' due to generation of non-toxic byproduct i.e., Fe (III), which has less or negligible impact on the environment. This eco-friendly property of ferrate (VI) makes it an extremely viable alternative option to environmental benign chemicals/oxidants to be employed in water treatment technologies. Additionally, in order to remove non-biodegradable pollutants such as metallic species, the conventional wastewater treatment plants require adsorbent/coagulant doses. However, a single dosage of ferrate (VI) destroys degradable contaminants while eliminating non-degradable pollutants by coagulation through ferric ions produced as by-product. In this aspects, ferrate (VI) shows no reactivity towards bromide ion unlike ozone, such that in the treatment of water that contains bromide, no carcinogenic bromate ion is generated (Zhou *et al.*, 2009). Furthermore, ferrate (VI) oxidation is relatively faster than permanganate or chromate oxidation makes it rather efficient in the treatment methods (Delaude and Laszlo, 1996).

Table 1.2. Redox potentials of commonly used oxidizing agents (Tiwari and Lee, 2011)

Oxidant	Reaction	Potential (V)
Ferrate (VI)	$FeO_4^{2-} + 8H^+ + 3e^- \leftrightarrow Fe^{3+} + 4H_2O$ $FeO_4^{2-} + 8H_2O + 3e^- \leftrightarrow Fe(OH)_3 + 8H_2O$	2.20 0.70
Hypochlorite	$HClO + H^+ + 2e^- \leftrightarrow Cl^- + H_2O$	1.48
Chlorine dioxide	$ClO_2(aq) + e^- \leftrightarrow ClO_2^-$	0.95
Perchlorate	$ClO_4^- + 8H^+ + 8e^- \leftrightarrow Cl^- + 4H_2O$	1.38
Ozone	$O_3 + 2H^+ + 2e^- \leftrightarrow O_2 + 2H_2O$	2.07
Hydrogen peroxide	$H_2O_2 + 2H^+ + 2e^- \leftrightarrow 2H_2O$	1.77
Dissolved oxygen	$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$	1.22
Permanganate	$MnO_4^- + 4H^+ + 3e^- \leftrightarrow MnO_2 + 2H_2O$ $MnO_4^- + 8H^+ + 5e^- \leftrightarrow Mn^{2+} + 4H_2O$	1.67 1.50
Chromate	$Cr_2O_7^{2-} + 14H^+ + 6e^- \leftrightarrow 2Cr^{3+} + 7H_2O$	1.33
Chlorine	$Cl_2(g) + 2e^- \leftrightarrow 2Cl^-$ $ClO^- + H_2O + 2e^- \leftrightarrow Cl^- + 2OH^-$	1.35 0.84

1.6. Review of literature

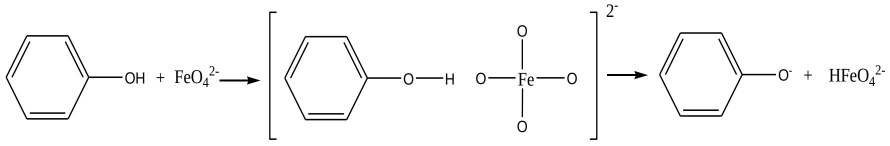
The utility of ferrate (VI) in wastewater treatment is widely documented previously (Sharma *et al*., 2005b; Tiwari *et al*., 2005; Lee and Tiwari, 2009; Tiwari *et al*., 2017; Rai *et al*., 2018; Hu *et al*., 2020; Alsheyab *et al*., 2009; Sharma, 2013, McBeath *et al*., 2021; Talaiekhozani *et al*., 2017; Mácová *et al*., 2009) . In addition to the degradation of organic and even inorganic contaminants from waste water, it has shown an excellent ability to eliminate a broad array of bacteria and viruses encountered during the treatment of water and wastewater. The use of ferrate (VI) in the treatment of wastewater is studied, and studies showed that the ferrate (VI) treatment decreases the color more by 50%, reduces COD by 30%, and disinfect bacteria by 10% as compared to the use of aluminum sulphate or ferric sulphate (Jiang *et al*., 2007).

Literature survey reveals that ferrate (VI) is found efficient in oxidizing the variety of organic molecules, including phenol, allylbenzene, chlorobenzene, benzene etc. (Waite and Gilbert, 1978; Song and Ma 2013; Bielski *et al*., 1994). Numerous reports showed the oxidation of organic compounds, including methanol, formic acid, formaldehyde, glycolaldehyde (Carr *et al*., 1985), aniline (Sharma *et al*., 2002), 1,4-thioxane (Read *et al*., 1998b), benzenesulfonate (Johnson and Read, 1996), thiourea (Sharma *et al*., 1999a), 2-mercaptoethansulphonate (Read *et al*., 1998a) and cysteine (Sharma *et al*., 2012). The decomposition of these compounds by ferrate (VI) was found to be quite rapid, and the degradation rate was further increased by increasing the ferrate (VI) dosage. Further, the oxidation of these organic compounds was involved with one- and two-electron transfer mechanisms. The reduction of ferrate (VI) to ferrate (V) is proceeded by one electron process by reacting with hydrated electron (e_{aq}^{-}) (reaction (1.8)) (Bielski and Thomas, 1987). Further, it is shown that ferrate (VI) interacted with organic compounds through the process of one-electron reduction (one electron transfer) (reaction (1.9)) and it transformed to ferrate (V) which are reconfirmed by pulse radiolysis and rapid spectroscopic data (Bielski, 1991; Bielski and Thomas, 1987; Rush and Bielski, 1986).

$$FeO_4^{2-} + e_{aq}^{-} \rightarrow FeO_4^{3-} \qquad \ldots (1.8)$$

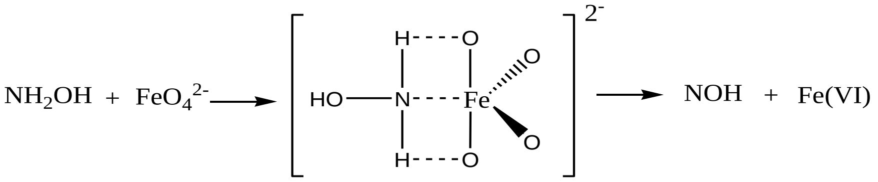
$$FeO_4^{2-} + R\dot{C}OH \rightarrow HFeO_4^{2-} + RCO \qquad \ldots (1.9)$$

The formation of phenoxy radicals via the hydrogen abstraction process was demonstrated in the one electron transfer reaction with ferrate (VI) and phenol (Rush and Bielski, 1995). Moreover, the EPR studies showed that the ferrate (VI) oxidizes the phenol via an intermediate radical species i.e., phenoxy radical (reaction (1.10)) (Huang *et al*., 2001).



… (1.10)

Similarly, a two-electron transfer process was suggested to oxidize a variety of nitrogen-containing substances (Johnson and Hornstein, 1994, 1996, 2003). The hydroxylamine oxidation was proposed to proceed through a concerted two-hydrogen abstraction mechanism involving the production of an adduct between the reactants of both N and Fe atoms (reaction (1.11)). This assumption is based on their multiple experimental data, which include product analysis, kinetic and reaction stoichiometry. The outcomes of one-electron processes, such as thioacetamide, thiourea, phenol, esters, amino acids and ascorbates, as well as two-electron processes such as hydroxylamines, 1,4-thioxane, thiol compounds, methionine, alcohols, benzene sulfinate, thiosulfate, methylhydrazine, hydrazine etc. (Lee *et al.*, 2004).



… (1.11)

Several organic contaminants such as aniline, acetaldehyde, iminodiacetic acid, N-methyliminodiacetic acid, trimethylaldehyde, ethyl alcohol, methylamine, phenol, dimethylsulphoxide, ethylene glycol, p-Hydroquinone, methyl alcohol, p-nitroaniline, nitriloacetic acid, thiodietanol, thioxane etc. were degraded by ferrate (VI) through second order rate kinetics in aqueous medium and there rate constants are optimized at different pH values. It was observed that the FeO_4^{2-} and $HFeO_4^{-}$ species are mainly involved in the reaction mechanism at moderately high pH values. The reaction rate constants are found to be moderately high with short half-life periods indicating that a rapid and efficient oxidation reaction is occurred using the ferrate (VI) (Tiwari and Lee, 2011). The effect of pH and pollutant concentrations in the treatment of aqueous waste polluted with potassium hydrogen phthalate (KHP) by ferrate (VI) was extensively investigated. It was observed that 76.13% of

KHP was eliminated at pH 8.0 having ferrate (VI) to KHP molar ratio of (0.1:0.03 mmol/L). The overall rate constant was reported to be 83.40 L/mol/min. Further the TOC data showed that mineralization of KHP was increased by decreasing the solution pH and KHP concentration (Tiwari *et al.*, 2017a). Similar reports were aslo observed in the degradation of bisphenol A, diclofenac sodium, 17 α-ethynylestradiol and 4-tertocylphenol. In these systems the removal percentage was increased with decreasing concentration and pH of the solution (Tiwari *et al.*, 2017b; Sailo and Lee, 2017).

Ferrate (VI) is promising to oxidize a variety of inorganic water contaminants including ammonia (Sharma *et al.*, 1998a), cyanide (Sharma *et al.*, 1998b), hydroxylamine (Johnson and Hornstein, 2003), hydrazine (Johnson and Hornstein, 1994), superoxide ion, hydrogen peroxide (Rush *et al.*, 1996). Ferrate (VI) is effective and potential in oxidizing complex compounds including, Cu(II)-EDTA (Tiwari *et al.*, 2008), Cd(II)-EDTA or Cu(II)-NTA (Sailo *et al.*, 2015), Cu-CN, Ni-CN or Ni-Cu-CN (Lee and Tiwari, 2009), Zn(II)-IDA or Cu(II)-IDA (Pachuau *et al.*, 2013). One and two electron processes are proposed in the oxidative mechanism between the ferrate (VI) and inorganic compounds. Compounds such as sulfite, cyanides and iodides have shown a one-electron mechanism, but oxy compounds of sulphur, nitrogen, selenium and arsenic have shown a two-electron mechanism while reacted with ferrate (VI). Similarly, azide, ammonia, hydrazine, sulfide, superoxide, cyanide, iodide and oxy-compounds of arsenite, selenium, sulphur and nitrogen all have seconds-order kinetics when reacting with ferrate (VI) (Johnson and Read, 1996; Johnson and Hornstein 2003, 1994; Sharma *et al.*, 2002, 2005a; Lee *et al.*, 2003; Joshi *et al.*, 2008; Sharma, 2010a,b). In general, the reaction rate equation for the reaction of ferrate (VI) with organic compounds is illustrated using the equation (1.12):

$$-\frac{d[Fe(VI)]}{dt} = k_p[Fe(VI)][P] \qquad \ldots(1.12)$$

where k_p is the rate constant for second-order reaction. The rate equations (1.13 and 1.14) are shown in ferrate (VI) reactions with selenite, zinc (II)-cyanide and cadmium(II)-cyanide (Yngard *et al.*, 2007, 2008; Johnson and Bernard 1992). Equation (1.13). It was demonstrated that the half-order reaction was occurred with respect to the Zn(II)-cyanide and Cd(II)-cyanide concentrations. In contrast to this, the second-order rate law for ferrate(VI) reaction with various cyanides ($Ni(CN)^{3-}$, $Cu(CN)_4^{3-}$, SCN^-, and CN^-) is reported previously (Yngard *et al.*, 2007; Sharma *et al.*, 1998b, 2002, 2005a; Lee and Tiwari, 2009).

$$-\frac{d[Fe(VI)]}{dt} = k_p[Fe(VI)][M(CN)_4^{2-}]^{1/2} \qquad \ldots(1.13)$$

where M = Cd(II) and Zn(II)

The reaction between selenite and ferrate (VI) was found to be first and second-order reaction based on the concentration of selenite in the rate law (equation (1.14)) (Johnson and Bernard, 1992).

$$-\frac{d[Fe(VI)]}{dt} = \mathrm{k}_p[\mathrm{Fe(VI)}][SeO_3^{2-}] + k_2\,[\mathrm{Fe(VI)}][SeO_3^{2-}]^2 \quad \ldots(1.14)$$

where k_2 is the rate constant of third-order reaction. Similarly, thioacetamide and thiourea was degraded with ferrate (VI), and it was suggested that thioacetamide and thiourea were transformed to sulphate at pH 9.0. Ferrate (VI), thiourea and thioacetamide stoichiometric ratios were estimated to be 1:0.380±02 (Sharma *et al.*, 1999). Additionally, the molar stoichiometry of ferrate (VI) and various pollutants, rate of degradation with apparent rate constant values along with the products generated are compiled and reported elsewhere (Sharma, 2010; Tiwari and Lee, 2011).

Ferrate (VI) disinfection abilities were first assessed to remove two pure laboratory bacterial cultures i.e., Recombinant and Non-recombinant *Pseudomonas*. (Murmann and Robinson, 1974). Ferrate (VI) dosage of 0-50 mg/L was adequate to kill completely the bacteria in all the tested samples. In addition, the reaction between deoxyribonucleosides and ferrate (VI) had caused to the breaking of DNA chain through a process where base loss was accompanied by β-elimination (Basu *et al.*, 1987; Stevenson and Davies 1995). The findings revealed that ferrate (VI) inactivated *E. Coli* in an irreversible manner. At pH 8.2, a maximum dose of 6.0 mg/L of ferrate (VI) had killed 99.9 percent of *E. coli* within time 7 mins of contact. However, a longer period of contact i.e., 18 mins enabled to eliminate completely the *E. coli* even using a lower dose of ferrate (VI) 2.4 mg/L (Gilbert *et al*., 1976). The results further indicated that pH < 8.0 showed seemingly high disinfection ability of FeO_4^{2-}. Similarly, ferrate (VI) (8 mg/L) enabled to eliminate 99.9% of total *coliforms* and 97% of total pathogenic bacteria in a secondary effluent waters (Waite 1979; Jiang *et al*., 2006). Furthermore, it was reported that 99% of *f2 Coliphage* was inactivated within 5.7 mins by using ferrate (VI) dose of 1.0 mg/L at pH 6.9; nevertheless, at pH 7.8, in order to obtain 99.9% inactivation, an interaction period of 30 minutes with ferrate (VI) dose of 10 mg/L was required (Jiang *et al.*, 2007; Schink and Waite, 1980). The study of disinfection by sodium ferrate (VI) on spore-forming bacteria showed that sulfite-reducing *clostridia* were successfully destroyed while aerobic spore-formers were decreased up to 3-log units (White and Franklin, 1998).

Literature reveals that the use of ferrate (VI) in wastewater treatment generates iron (III) which is an effective coagulant or adsorbent and possesses fair ability to remove several radionuclides or even toxic heavy metals present in water bodies (Sharma *et al*., 2017; Yates *et al*., 2014; Potts and Churchwell, 2009). The ferrate (VI) is useful materials to remove several α and β emitting radionuclides $^{237+239}Np(V)$, $^{238+233}U(VI)$, $^{239}Pu(IV)$, $^{243}Am(III)$, etc. Thus, apart from the removal of typical colloidal particles, the radioactive waste can be treated using ferrate (VI) and the hazardous radionuclides be separated from the waste water (Petrov *et al*., 2016). The radioactive waste from uranium ore mines which includes ^{238}U, ^{232}Th, ^{226}Ra etc. along with the various radionuclides *viz.*, ^{137}Cs, ^{239}Pu, ^{90}Sr etc., were removed by ferrate (VI) (Emerson and Powell, 2015). The jar test results showed that potassium ferrate is a useful chemical to detoxify the wastewater that contained with plutonium and americium (Potts and Churchwell, 2009). Furthermore, several laboratory experiments were conducted to remove various radionuclides *viz*., Np(V), Sr(II), Th(IV), Eu(VI) and U(VI) using potassium ferrate over a wide range of pH ~5.0 to 11.0 (Perfil'ev *et al*., 2013; Petrov *et al.,* 2016; Volkova *et al*., 2011).

Ferrate (VI) is a potential coagulation/flocculation capability hence, coagulates efficiently various heavy metal toxic ions. Furthermore, Fe^{3+} as iron (III) hydroxide is found to be a promising adsorbent, and capable of removing free metallic contaminants by adsorption. The arsenic (III) oxidized to arsenic(V), and arsenic (V) was successfully removed by reduced iron (III) with the coagulation process (Lee *et al.*, 2003). TO oxidize three moles of arsenic (III), two moles of ferrate (VI) were needed (Equation 1.15). At pH 8.4 to 9.0, arsenic (III) oxidation followed a second order rate law, and within few seconds, the whole oxidation process was completed.

$$2Fe(VI) + 3As(III) \rightarrow 2Fe(III) + 3As(V) \qquad \ldots (1.15)$$

Furthermore, even a lower dosage of ferrate (VI) combined with a supplemental dose of iron (III) is quite effective in removing arsenic from river water (Lee *et al.*, 2003). Similarly, potassium ferrate (VI) is promising in the removal of various cations viz., Hg(II), Cr(II), Cd(II), Pb(II), Cu(II) and Mn(II) by adsorption/coagulation using a minimal dosage of ferrate (VI) 10-100 mg/L (Bartzatt *et al.*, 1992).

The ferrate (VI) was utilized in the treatment of metal complexed species in aqueous solutions. The mechanism reveals that in the first step, ferrate (VI) decomplexes the complexed species and oxidizes the degradable species and in the second step, the reduced iron (III) coagulates or adsorbs the non-degradable metal cations (Sailo *et al.*, 2015; Tiwari *et al.*, 2007; Tiwari *et al.*, 2014). The Cu(II)-EDTA decomplexation favored acidic medium i.e., 100% complexed species were decomplexed at pH 6.5, whereas only 35% of decomplexation was observed at pH 9.9. However, overall Cu(II) removal was quick at higher pH values, which is explained with the fact that the coagulation/adsorption capacity of Fe(III) is significantly high at higher pH values (Tiwari *et al.*, 2007). The elimination of Cd(II)-NTA by ferrate (VI) was studied at wide pH range i.e., pH 8.0 – 12.0 in aqueous medium (Yu *et al.*, 2012). At pH 8, a quick ferrate (VI) reduction was occurred however, the reduction was significantly slow at higher pH values. The decrease in pH favored greatly the removal of Cd(II). The decrease in decomplexation at higher pH was mainly due to the low mineralization of NTA.

According to TOC data, up to 23% of NTA was mineralized at pH 8.0. ICP measurements also showed that increasing ferrate (VI) dosages from 0.1 to 0.2 mmol/L resulted in an increase in Cd(II) elimination from 14.9 to 23.8 % (Sailo *et al*., 2015). Ferrate (VI) experiment was also performed in simulated wastewater polluted with Ni(II)-IDA and Cd(II)-IDA metal complexes. A varying concentration (i.e., 0.3 to 10.0 mmol/L) of metal complex species was treated with a fixed amount of ferrate (VI) (i.e., 1.0 mmol/L). The results indicated that a rapid and effective decomplexation/removal was obtained at wide range of pH 8.0 to 12.0. It was observed that by lowering the solution pH from 10.0 to 8.0, the ferrate (VI) efficiency was significantly increased. However, 100% removal of Cd(II) was obtained at pH 12.0 (Tiwari *et al*., 2014). The effectiveness, efficiency, and potential of ferrate (VI) as in the treatment of aqueous waste contained with complex species of Cu(II)/IDA and Zn(II)/IDA are extensively studied for various parametric studies and deduced a plausible mechanism involved in the ferrate (VI) treatment process (Pachuau *et al*., 2013; Tiwari *et al*., 2014; Sailo *et al*., 2015).

PPCPs and EDCs removal from the waste or surface waters is an emerging area of research because of its growing concern in recent past (Reyes *et al*., 2021). Several researchers have studied the use of ferrate (VI) to degrade PPCPs as well as EDCs, as such ferrate can remove 97.5% of bisphenol A, (Han *et al*., 2015), 40% of ibuprofen (Sharma and Mishra, 2006), 99.9% of both flurbiprofen and naproxen (Barışçı et al., 2015), 70% of Ciprofloxacin (Zhou and Jiang, 2015) and 99% of diclofenac (Chiu *et al*., 2016) from aqueous solutions as studied in laboratory experimentations. Ferrate (VI) encapsulated in 3D printed PVA (polyvinyl alcohol) capsules and it was examined for its capacity to oxidize a variety of micro-pollutants present in actual wastewaters. It was reported that >80% removal of micro-polluatnts were achieved specially in the removal variety of micro-pollutants *viz*., clarithromycin, azithromycin, valsartan, diclofenac, atenolol, and carbamazepine from aqueous solutions. Also, the encapsulation of ferrate (VI) provides not only the storage of ferrate (VI) but also quick availability for its prompt applications (Czölderová *et al*., 2018). Researchers have also compared the efficacy of utilizing UV and ferrate (VI) independently with that of the simultaneous use of UV/ferrate

(VI) to eliminate formaldehyde from water. The effects of temperature, ferrate (VI) concentration and pH on formaldehyde elimination is extensively studied. The results indicated that increasing the temperature from 25 to 50 ^{o}C enhances formaldehyde elimination from 69 to 97% just within 35 mins of treatment. Further, the combination of UV and ferrate (VI) enhances formaldehyde elimination performance and it degrades 100% within the same period of time. However, further increase in temperature showed a detrimental impact on the removal efficiency (Talaiekhozani *et al*., 2016). Similarly, ferrate (VI) with UV radiation is employed in the removal of 1,9-dimethyl-methyleneblue zinc chloride from waste water (Talaiekhozani *et al.*, 2020). Zboril *et al.*, utilized the Fe(0) nanoparticles with ferrate (VI)/(III) composite to remove the various chemical warfare agents (Zboril *et al*., 2012).

Thus, keeping in view the potentials of ferrate (VI), the present thesis encompasses the possible implications of ferrate (VI) in the treatment of emerging micro-pollutants (particularly the pharmaceutical drugs) from aqueous wastes. The various physico-chemical parametric studies enabled to deduce the mechanism involved in the degradation process. Moreover, the real matrix implications are added values of studies for possible real matrix implications of ferrate (VI).

1.7. Scope of the present investigation

Water treatment includes two essential unit processes: oxidation/disinfection and coagulation. In the treatment of water and wastewater, a variety of oxidants and coagulants are used. Aluminum sulphate, ferric chloride and ferric sulphate are the most oftenly used coagulants, whereas halogen-based oxidants like sodium hypochlorite, chlorine dioxide and chlorine, as well as oxygen-based oxidants like hydrogen peroxide and ozone, are employed as disinfectants/oxidants. Coagulation diffuses colloidal pollutants and aggregates them into bigger clumps that can be filtered and sedimented. Oxidants are used to eliminate chemical pollutants and to control hazardous microbes in water. Despite their widespread usage, these chemicals have limits, and their usage has raised environmental concerns owing to excessive sludge, harmful disinfection byproducts, and onsite stench etc. These constraints, in conjunction with rising levels of water pollution, a scarcity of safe water, and increased demands for stringent regulation of wastewater and drinking water, prompted the quest for a more efficient, profitable, and ecologically acceptable oxidant and coagulant.

Ferrate (VI) is a prospective and perfect alternative chemical due to its high oxidizing capability, efficacy in disinfection, coagulation, and ecologically friendly in nature. Although several researchers have demonstrated its achievement in removing/degrading a variety of waste water pollutants, little study was conducted upon potential applicability on pharmaceutical compounds in aqueous solution. Ferrate (VI) is considered to be a promising oxidizing agent for removing pharmaceutical compounds from aqueous waste and it is intended to decompose harmful pharmaceutical waste in a manner similar to that of other organic pollutants. Thus, the proposed research aims to increase awareness of the suitability of ferrate (VI) in water treatment technique in relation to the presence of PPCPs in simulated wastewater samples and to investigate the usefulness of ferrate (VI) as a green oxidant alternative to the existing water treatment technology. As a result, the objectives of the current research is to improve knowledge about the use of ferrate (VI), specifically in the degradation of PPCPs such as triclosan (TCS), amoxicillin (AMX), sulfamethazine (SMZ), and sulfamethoxazole (SMX) from aqueous solutions under various parametric studies.

CHAPTER 2

METHODOLOGY

2. METHODOLOGY

2.1. Materials and Instrumentations

2.1.1. Chemicals and Apparatus

All chemicals and reagents acquired are of analytical grade and are utilized without further purification. Table 2.1 contains a complete list of all compounds. Syringe filters (pore size of 0.22 µm and 25 mm in diameter) were obtained from Himedia Pvt. Ltd India. GF/C Whatman Filter Paper (diameter of 47 mm) was procured from Whatman, USA. Glass filtration and a fritted funnel were procured from Merck Pvt. Ltd., India.

Table 2.1. Details of various chemicals utilized in present investigation.

Sl. No.	Chemicals used	IUPAC Name	Formula	Company	CAS No./ID
1.	Triclosan	5-chloro-2-(2,4-dichlorophenoxy)phenol	$C_{12}H_7Cl_3O_2$	Himedia,India	3380-34-5
2.	Amoxicillin	(2*S*,5*R*,6*R*)-6-[[(2*R*)-2-amino-2-(4-hydroxyphenyl)acetyl]amino]-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid	$C_{16}H_{19}N_3O_5S$	Sigma Aldrich,USA	26787-78-0
3.	Sulfamethoxa-zole	4-amino-N-(5-methyl-1,2-oxazol-3-yl)benzene-1-sulfonamide	$C_{10}H_{11}N_3O_3S$	Sigma Aldrich, USA	723-46-6

4.	Sulfamethazine	4-amino-N-(4,6-dimethylpyrimidin-2-yl)benzene-1-sulfonamide	$C_{12}H_{14}N_4O_2S$	Sigma Aldrich,USA	57-68-1
5.	Sodium chloride	Sodium chloride	$NaCl$	Himedia,India	7440-23-5
6.	Ethylenediaamine- tetraacetic acid	2,2',2",2"'-(Ethane-1,2-diyldinitrilo)tetraacetic acid	$C_{10}H_{16}N_2O_8$	Qualigens Fine Chemicals,India	60-00-4
7.	Glycine	2-Aminoethanoic acid	$C_2H_5NO_2$	Himedia,India	56-40-6
8.	Oxalic acid	Etahnedioic acid	$C_2H_2O_4$	Merck	144-62-7
9.	Sodium nitrite	sodium nitrite	$NaNO_2$	Loba Chemicals, India	7632-00-0
10.	Disodium hydrogen phosphate anhydrous	Sodium hydrogen phosphate	Na_2HPO_4	Merck	7558-79-4
11.	Sodium nitrate	Sodium nitrate	$NaNO_3$	Loba Chemicals, India	7631-99-4
12.	Hexane	Hexane	C_6H_{14}	Sigma Aldrich, USA	110-54-3

13.	Diethyl ether	Ethoxyethane	$(C_2H_5)_2O$	Sigma Aldrich, USA	60-29-7
14.	Potassium hydroxide	Potassium hydroxide	KOH	Merck	1310-58-3
15.	Ferric nitrate nonahydrate	Iron (III) nitrate	$Fe(NO_3)_3$	Merck	7782-61-8
16.	Hydrochloric acid	Chlorane	HCl	Merck	7647-01-0
17.	Disodium tetraborate	Disodium tetraborate decahydrate	$Na_2.B_4O_5.(OH)_4.8H_2O$	Himedia,India	1330-43-4
18.	Sodium hypochlorite (*Ca.* 15%)	Sodium hypochlorite	NaClO	Thermo Fisher Scientific India	7681-52-9
19.	Sodium hydroxide	Sodium hydroxide	NaOH	Himedia,India	1310-73-2

Sartorius water Purifier (model: Sartopore 2150, Arium Mini Plus UV Lab., Sterile Plus, Germany) was utilized for purifying water. Phosphate buffer solutions were prepared by dissolving appropriate amounts of disodium tetraborate (0.001 M) along with disodium phosphate (0.005 M) in distilled water. Sample Stock solutions (1.0 mM) of different pharmaceuticals and personal care products (PPCPs) viz., sulfamethoxazole, sulfamethazine, triclosan and amoxicillin were prepared using the purified water. Standard buffer solutions having pH 4.01, 7.01 & 12.01 were used to calibrate the pH meter. 0.1 M NaOH and/or HCl solutions were prepared in purified water to adjust the pH of PPCPs or otherwise phosphate buffer was used.

The real water samples were collected from Chite River and three spring water (Tuikhur) from Aizawl city, Mizoram, India. pH Meter (HI2002, Hanna Instruments, USA) was employed for measuring the pH of all the samples, Multiphotometer (Hanna Instruments, USA; Model: HI98194) were used for analyzing various water parameters from the collected real water samples. Further, Atomic Absorption Spectrometer (AAS) (Model: AA-7000 Series, Shimadzu) was employed to obtain the metal contents. The UV-Vis Spectrophotometer (Shimadzu, UV-1800, Japan) is used for measuring the absorbance of solutions. The NPOC (Non-Purgeable Organic Carbon) data was collected by utilizing the TOC analyzer (Total Organic Carbon; Model: TOC-VCPH/CPN; Shimadzu, Japan). HPLC instrument along with C_{18} column (4.6 x 250 mm) (model: Waters 515 HPLC pump, 2489 UV-Vis detector, USA) was used for quantitative analysis of various pollutants.

2.1.2. Ultra Violet-Visible spectrophotometer

The UV-Vis Spectrophotometer was utilized for determining the concentration of ferrate (VI) by measuring the absorbance of ferrate (VI) solutions. In electronic spectroscopy, the excitation of electrons from ground level to higher energy level was involved. The absorption of intensity of light at a specific wavelength of incident light was measured using a UV-Vis spectrometer. The radiation of visible and ultraviolet light is sufficient to promote outer electrons to higher energy state. In certain cases, UV-Vis spectroscopy is used to study the solution of complexes, molecules and inorganic ions. The UV-Vis spectra have a wide range of applications that are helpful for quantitative measurements but limited for sample identification. By evaluating absorption at a certain wavelength, the concentration of a sample or analyte in solution obtained utilizing the Beer-Lambert's law.

Electronic excitation occurs between 200 and 800 nm in the visible and ultra violet spectrums and the transfer of electrons to higher energy molecular orbitals take place in this region. This method is also known as electronic spectroscopy, as it involves in electronic excitation from ground or zero energy level to higher energy level. The spectrum has sharp absorption peaks, each of which correlates to the excitation of an electron from one electronic stage to the next. On the other hand, due to the fact that electronic excitation is often accompanied by the continuing vibratory and rotatory motion of molecules, hence, sharp peaks are not detected, instead, wide absorption bands are obtained (Castner, 2005). The molecules that contain σ-electrons or π-electrons are excited to the higher levels of anti-bonding molecular orbitals by absorbing energy in the form of visible or ultraviolet light. The longer the wavelength of light it absorbs, the easier the electrons to be excited (i.e., the smaller the energy difference between the HOMO and the LUMO).

A spectrophotometer is an instrument that measures the percentage transmittance of photons of a certain intensity and frequency spectrum that passes through a sample. As a result, the instrument compares the intensity of light before and after passing through the sample.

Ultraviolet-visible spectrometer is instrumented with the light source, monochromator, detector, amplification, and storage devices. The best sources of light are hydrogen-deuterium discharge and tungsten filament lamps, both of which release a high amount of red radiation. The main light source split into two equal-intensity beams. Until it is separated into two beams, incoming light is dispersed by a rotating prism and then chosen via slits in such a manner that the prism's movement permits a succession of steadily increasing wavelengths to pass through the slits. The chosen beam is monochromatic, and then separated into two equal-intensity beams. A dispersion grating may also be used to convert polychromatic radiation into a monochromatic beam of light. It is impossible to separate or collimate very narrow band widths since the dispersion of a single beam or grating is too confined. As a result, light from the first dispersion is sent to the second dispersion through a slit. Light moves into the exit slit after the second dispersion. The key benefit of the second dispersion is that the emitted beam of the band width enlarges, and the light flowing through the exit slit is almost monochromatic and almost any of the stray light is eliminated.

2.1.3. Atomic Absorption Spectrophotometer (AAS)

Atomic Absorption Spectroscopy (AAS) is used for the quantitative estimation of total metal quantities *viz.*, Cu, Fe, Pb, Mn, Zn, Ni, etc. The technique of flame atomic absorption is widely used to identify metals and metalloids in environmental samples. It is simple, accurate, quick, and widely used technique with an appropriate degree of accuracy. The method is based on the principle that ground state atomic metal absorbs light at various wavelengths, allowing absorption spectrometry to determine an analyte's concentration in the complex matrix. In short, promotion of electrons to higher energy orbital in the atomizer can happen for a short duration due to the absorption of definite amount of energy of radiation at a particular wavelength. This wavelength is related to a specific electron transition in a specific element. In addition, each wavelength represents a single atom, and the line width absorption is just a few picometers (pm), which gives the technique efficient and selective. A detector measures the flux of radiation with and without a sample in the atomizer, and the ratio of the two quantities (the absorbance) is transformed into the analyte concentration using the Beer-Lambert’s law.

Walsh proposed the use of cathode lamps to generate the corresponding wavelength emissions (Walsh, 1955) and to produce neutral atoms by using flame, which would absorb emission as traversing through its path. In a solution, metal ions are transformed by a flame to an atomic state. The flame atomic absorption technique requires aspirated or aerosolized liquid sample to be combined with combustible gases, such as acetylene and nitrous oxide. The mixture is combusted in a flame where high temperature is maintained i.e., *Ca.* 2100 and 2800 ^{o}C. Upon combustion, the atoms of target element are brought down to unexcited free or ground state atoms, which absorb light at element-specific wavelengths that are precise low band width i.e., 0.01-0.1 nm. A beam of light from a cathode lamp with known elemental composition is transmitted through the flames to provide element-specific wavelengths. A photomultiplier which multiplies the signal to extent of measurable quantity, for instance, measures the extent of intensity of light reduced caused by analyte absorption, and this is correlated to the element quantity present in the sample.

The hardware for flame atomic absorption is divided into six components, each with two main functions: producing signal processing and atomic signals. Signal processing is an expanding additional capability that is added or mounted externally to the instrument. A cathode lamp is one of the instrumental components, since it requires a steady light source to generate the element's specific characteristic peaks. Each element requires a separate cathode lamp, despite the fact that certain lamps may evaluate three or four separate components if the cathode includes all of them. When adjusting a lamp, it must be positioned appropriately to enable a maximum amount of light to flow into the flame, where the analyte is atomized and via the monochromator. The atomic cell serves two primary functions: it nebulizes the sample solution into a fine aerosol and it dissociates the analyte components into their free ground state gaseous forms. Every analyte does not pass through the flame, some of it was discarded. The light beam passes through the sample as it travels through the flame towards the monochromator. By spectral dispersion, the monochromator isolates the particular spectral line produced by the light source and position it on a photomultiplier sensor, which converts the signal of light into an electrical signal. An amplifier is used to process the electrical signal. The signal can be shown in the required format or can be added to a data station for printing.

2.1.4. Total Organic Carbon (TOC) Analyzer

A TOC analyzer is an analytical tool used for assessing the content of total organic carbon and is considered to be more quantitative than the commonly used methods viz., chemical oxygen demand (COD) or biochemical oxygen demand (BOD). A normal TOC study analyses both total carbon (TC) and inorganic carbon (IC), with the latter describing the amount of dissolved carbon dioxide and carbonic acid salts. TOC is computed by deducting inorganic carbon (IC) from overall carbon (TOC=TC-IC). The organic carbon is of two types: POC (purgeable organic carbon) and NPOC (non-purgeable organic carbon). Further, NPOC is further classified as particulate organic carbon and liquid organic carbon. The TOC analyzer measures the IC component first and the remaining carbon is then measured as total carbon (TC). This process includes the purging of an acidified sample using nitrogen or pollution-free air. This process is also more accurately known as non-purgeable organic carbon (NPOC).

TOC calculations are divided into two ways: differential methods and direct methods. TC and IC can be measured separately using the differential approach by evaluating them separately. By subtracting IC from TC, the total organic carbon (TOC) is determined. This approach is appropriate for samples in which IC is less than TOC, or equivalent in size. In the direct process, IC is first eliminated from the sample by purifying the sample with distilled gas, and then TOC is measured using the TC measurement method, as TC equals TOC. Since chloroform, cyclohexane, toluene and benzene which are considered as purgeable organic carbon can be partially removed by gas stripping from the sample. Thus, direct method can also be termed as NPOC. It is also suitable for drinking water, ground water and surface water since it contains fewer TOC than IC and a negligible amount of POC.

The TOC Analyzer used in this study is based on the catalytic combustion at 680 °C oxidation/NDIR process, which is highly responsive and reliable of analyzing parameters such as TC, IC, TOC, and NPOC with measuring ranges and detection limits of TC: 4 ng/L to 25000 mg/L and IC: 4 ng/L to 30000 mg/L. Absolute combustion of samples is achieved using the 680 °C combustion catalytic oxidation process, with a combustion tube having platinum as catalyst. The sample is heated at 680 °C in excess of oxygen in combustion tube. Since this process is based on the simple theory of oxidation through heating and combustion, no pretreatment or post-treatment with oxidizing agents is required, which improves operability. A non-dispersive infrared (NDIR) gas analyzer is used to detect the carbon dioxide produced by oxidation.

2.1.5. High performance liquid chromatography (HPLC)

The HPLC instrument was utilized to determine the concentration of PPCPs present in water. HPLC requires a liquid mobile phase to transport a solid sample/ liquid sample immersed in an appropriate solvent through a chromatographic column. Separation is determined by interactions between the stationary phase and the solute, such as liquid–liquid partitioning, size exclusion, ion exchange, liquid–solid adsorption and, as well as by interactions between the solute and the mobile phase. An HPLC usually has two columns: a guard column for protection and an analytical column for separation. The analytical column is protected from contamination by the guard column, which is mounted prior to it. The most popular HPLC columns are made of stainless steel and have lengths varying from 30 mm to 300 mm with an internal diameters varying from 2.1 mm to 4.6 mm. These columns are made up of transparent silica particles that are 3–10 mm in diameter and are having irregular or rectangular in shape. These columns are filled with porous silica particles ranging from 3 to 10 mm in size and having a spherical or irregular appearance. Column efficiencies ranged from 40,000 to 60,000 theoretical plates/m. It was presumed that 25 cm column of 50,000 plates/m has a theoretical plate and a peak volume of 12,500 if V_{max}/V_{min} is roughly 50. The stationary phase of liquid-liquid chromatography is a liquid film deposited on a packaging material composed of 3 to 10-micron porous silica particles. It is possible that the partial solubility of the stationary phase allows to "bleed" the stationary phase out of the column over time. To overcome such difficulties, the silica particles and the stationary phase are covalently bonded to each other with the help of organochlorosilane $Si(CH_3)_2RCl$, R being the alkyl substituent.

The most frequently encountered type of HPLC is the reverse phase chromatography which employs non-polar molecules as stationary phase and polar molecules as mobile phase. An organochlorosilane with an R category of n-octyldecyl for (C_{18}) or n-octyl (C_8) hydrocarbon chain is used in the most typical nonpolar stationary phase. The majority of reverse phase separations are performed using a polar mobile phase composed of a buffered aqueous solution. Due to the hydrolysis of the silica substrate in alkaline solutions, the pH of the mobile phase must be kept less than 7.5. Polarity dictates the order of solute elution in HPLC. In the polar stationary phase, the least polar solute spends relatively less time and is the first to elute from the column in a typical phase separation. The mobile phase is used to monitor retention times such that a lesser polar mobile phase results in a longer retention time. If, for example, a separation is weak due to rapid elution of the solutes, shifting to a less polar mobile phase results in longer retention times, which will provide a greater chance of achieving an adequate separation. When two solutes are sufficiently resolved, shifting to a mobile phase with more polar can result in an admissible separation with a lesser analysis time. The order of elution is reversed in a reverse phase partition, and the more polar solute eluting first. Increasing the mobile phase polarity can results in longer retention times, but reducing the polarity in mobile phase give rise to shorter retention time. When a separation employs a single fixed-composition of mobile phase, it is referred to as isocratic elution. However, it is often challenging to find a single mobile phase composition that is compatible with all solutes.

The average operational pressure of an HPLC is so high that injection of the sample in the same way as in gas chromatography is unlikely. Other than that, a loop injector is used to insert the sample. Interchangeable sampling loops are accessible in quantities varying from 0.5 mL to 2 mL. The sampling loop is separated from the mobile phase and exposed to the environment in the load position. To put the sample in the sampling loop, a syringe with a capacity of two times more than that of the loop is required. Any excess sample that is not needed to fill the sample loop is discarded via the waste line. The injector is used to turn to the inject position after loading the sample. The mobile phase flows across the sampling loop in this position, and the sample is swept onto the column. Further, the UV detector can detect each compound at a certain but specific wavelength.

2.2. Analytical methods

2.2.1. Preparation of potassium ferrate (VI)

Potassium ferrate (VI) (K_2FeO_4) was synthesized using the wet chemical oxidation process as stated previously (Tiwari *et al*., 2007; Lee *et al*., 2005). High percentage of sodium hypochlorite (NaClO) solution (12-14 percent) is being used to oxidize the iron (III) to ferrate (VI). The precise preparation procedure is as follows: A 300 mL chilled solution of sodium hypochlorite was taken in a beaker and 90 g of potassium hydroxide pellets was added to this solution under stirred condition and the resultant mixture was further cooled in refrigerator. The excess undissolved potassium hydroxide was filtered using GF/C filter paper and a clear yellow highly alkaline sodium hypochlorite solution was collected. The solution was again cooled and filtered. Further, 20 g of pulverized ferric nitrate was gradually added to this solution with continuous and intense stirring over a period of approximately 2 hrs, under cold conditions (8 ^{o}C) using ice bath. Once the ferric nitrate was fully added, the mixture was stirred constantly for another 30 mins. Cold condition and strong alkaline environment favored the oxidation or conversion of iron (III) to ferrate (VI). A rapid change in color from yellow brown to dark purple indicates the formation of ferrate (VI). Further, about 50 g of potassium hydroxide pellets was slowly introduced to the solution and keeping the mixture temperature *Ca.* 15 ^{o}C. The solution mixture was again kept in the refrigerator for *Ca.* 40 mins. The resultant slurry having dark purple color was filtered through GF/C filter paper (pore size of approximately 10-15 µm) using a glass filtration assembly. The filtrate was discarded and solid was washed with 100 mL of 3 M potassium hydroxide (chilled cold solution). This allowed to dissolve the ferrate (VI) and collected as filtrate in the filtration flask. The filtrate was taken in a flask and then added 100 mL of chilled saturated solution of potassium hydroxide. The potassium ferrate is precipitated easily and was filtered again using GF/C filter paper. The filtrate was eliminated, and the solid was again flushed with a cold 3 M potassium hydroxide solution (50 mL) and the filtrate was again collected. The ferrate (VI) was again precipitated using chilled cold saturated potassium hydroxide solution. Similarly, re-precipitation was performed at least two more times to eliminate any remaining impurities and thereby improve the purity of ferrate (VI). Lastly, the solid was washed with (10 mL) of n-hexane followed by diethyl ether (10 mL). The end product was carefully collected (*Cf* Figure 2.1); it was nearly black in color and was placed in a vacuum desiccator which was previously filled with potassium hydroxide pellets.

Figure 2.1. Synthesized dark purple solid of potassium ferrate (K_2FeO_4)

2.2.2. Determination of the purity of the synthesized potassium ferrate (VI)

The spectrophotometer was used to determine the purity of synthesized potassium ferrate. The molar extinction coefficient of potassium ferrate (VI) solution at pH 9.2 (phosphate buffer) and at 510 nm was stated to be 1150 M^{-1} cm^{-1} (Sharma *et al.*, 1998). It was reported that ferrate (VI) is relatively stable in phosphate buffer (Tiwari *et al.*, 2011). Therefore, the phosphate buffer was utilized for preparing aqueous solution of ferrate (VI). 0.0198 g (1.0 mM) of potassium ferrate (VI) was dissolved in 100 mL of phosphate buffer (pH 9.2). Immediately the absorbance of this solution was measured using the UV-Vis Spectrophotometer at the wavelength 510 nm. The UV-Visible spectrometer was previously adjusted with blank zero-base correction using the same phosphate buffer (pH 9.2) and at the same wavelength i.e., 510 nm. The absorbance value observed was used to measure the ferrate (VI) concentration using the Beer- Lambert's law as equation (2.1).

$$A = \varepsilon.b.C \qquad \ldots (2.1)$$

where, A = absorbance of the light absorbing ferrate (VI) solution

ε = molar extinction coefficient of ferrate (VI)

b = path length of sample cell.

C = molar concentration of ferrate (VI) (M)

Using equation (2.1) the actual concentration of potassium ferrate is obtained. Further, the purity of potassium ferrate was obtained using the equation (2.2):

$$Purity\ \%\ offerrate(VI) = \frac{Obtained\ conc.\ \times 100}{Initial\ conc.taken\ (1\times10^{-3}\ M)} \qquad \ldots(2.2)$$

The purity of ferrate (VI) was always found greater than 95%.

2.2.3. Batch reactor method

Sulfamethoxazole, sulfamethazine, triclosan and amoxicillin solutions (1.0 mM) 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 micro-pollutants viz., sulfamethoxazole (0.02 to 0.2 mM), sulfamethazine (0.02 to 0.2 mM), triclosan (0.02 to 0.5 mM) and amoxicillin (0.02 to 0.5 mM). The pH of each solution is controlled by using 0.1 M of NaOH or HCl solutions by a drop wise addition. In a reactor vessel, batch reactor operations were carried out varying the concentration of these micro-pollutants and the solution pH was fixed i.e., pH 6.0 (for sulfamethoxazole and sulfamethazine) and pH 10.0 for (triclosan and amoxicillin). On the other hand, the batch reactions were carried out varying pH values from pH 5.0 to 8.0 (for sulfamethoxazole and sulfamethazine), pH 7.0 to 10.0 (for triclosan) and pH 9.0 to 12.0 (for amoxicillin) at a fixed concentration of these micro-pollutants (0.1 mM) for pH dependent studies. A constant amount of solid potassium ferrate (equivalent to 0.1 mM) was added in reaction mixture and continuously stirred. The decomposition of ferrate (VI) in a reactor implies the degradation of the micro-pollutants. The absorbance of the solution mixture was calculated and reported using UV-Vis Spectrophotometer at a regular time interval of 1 min for a total time period of 20 mins at wavelength 510 nm. The absorbance of self- decomposition of ferrate (VI) at the same pH and solution was also taken at 510 nm to nullify the blank corrections by comparing the absorbance in presence of micro-pollutants. After the treated sample was detained for another 2 hrs, reaction mixture was filtered using syringe filter. One portion of the filtered sample was used for TOC measurements, and the other part was used for each of micro-pollutants measurements using HPLC. 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/or 0.1 mM of each pollutant solution. Ferrate (VI) with a dose of 0.2 mM was used for treating these pollutants simultaneously. The samples, after filtration were subjected for the HPLC and NPOC measurements.

For HPLC measurements, 20 μL of the sample was pumped into the column using acetonitrile and water (HPLC grade) as mobile phase. The wavelength and the flow rate of mobile phase were set as 275 nm and 1 $mLmin^{-1}$, respectively. An appropriate volume of each micro-pollutant was dissolved in water (HPLC grade) to prepare their respective standard solutions, and the area of the peak obtained was used to achieve the exact percentage elimination of micro-pollutants. The results were then represented as a function of concentration and pH in terms of percentage removal of micro-pollutants. TOC calculation was used to determine micro-pollutants mineralization, which is then recorded in terms of percentage elimination using the initial TOC values of micro-pollutants. Furthermore, the disparity in TOC values between the initial and treated samples was used to measure the amount of each micro-pollutant eliminated, and the results are shown as a function of pH and initial pollutant concentration.

The degradation of micro-pollutants by ferrate (VI) is also performed in presence of various co-existing ions such as NaCl, $C_2H_5NO_2$, $NaNO_3$, $C_2H_2O_4$, $NaNO_2$, Na_2HPO_4 and EDTA. The concentrations of micro-pollutants, ferrate (VI), and co-existing ions are taken in a fixed molar ratio of 0.1: 0.2: 0.5 and at pH 6.0.

The samples were stirred for 2 hrs, then filtered and subjected for measurements using HPLC.

The real water samples (spring and river water) were collected from four locations in Aizawl City, Mizoram, India. Various parametric studies were performed for these water samples. The real water samples were further spiked with sulfamethoxazole/or sulfamethazine solutions (0.02 to 0.2 mM) at pH 6.0 and triclosan/or amoxicillin solutions (0.02 to 0.5 mM) at pH 10.0. The ferrate (VI) dose was maintained at 0.1 mM to each sample and the solution mixture was stirred for 2 hrs. The treated samples were then filtered by 0.22 µm syringe filters and subjected for the HPLC measurements to obtain the concentrations of these compounds.

2.2.4. Degradation of organic species using ferrate (VI): UV-Visible measurements

The synthesized potassium ferrate was employed to treat different PPCPs such as sulfamethoxazole, sulfamethazine, triclosan and amoxicillin in aqueous solutions. The degradation of these compounds in presence of ferrate (VI) was examined indirectly by observing the change in ferrate (VI) concentration with the help of UV-Visible spectrophotometer. The absorbance of the sample solution was then measured using a UV-Vis spectrophotometer (at 510 nm) at regular intervals of time (i.e., every 1 min) for 20 mins of contact. In parallel, a blank self-degradation of potassium ferrate at same pH and concentration was also prepared (i.e., without the pollutant) and the absorbance of solution is recorded at the same wavelength i.e., 510 nm. The absorbance was employed for the blank correction. The corrected absorbance data was converted for the ferrate (VI) concentration and utilized for kinetic studies i.e., the time dependence data was computed for the pseudo-first and pseudo-second order rate laws to their standard form. Separate experiments were carried out with each PPCPs at various pH values and concentrations.

2.2.5. Degradation of organic species using ferrate (VI): TOC measurements

After obtaining the UV-Visible measurements, the solution mixture was further stirred for 2 hrs under stirred conditions. This enabled to complete the degradation reaction. The solution mixture was filtered using a 0.22 μm syringe filter and the filtrate was divided into two parts. The first fraction was subjected for the TOC measurement and other fraction was subjected for the PPCPs concentration using HPLC measurement.

The total organic carbon content of the ferrate (VI) treated sample solutions along with the untreated PPCPs samples were subjected for the TOC measurements using a TOC analyzer (Shimadzu, TOC-VCPH/CPN). The TOC values of these two samples i.e., treated and untreated PPCPs samples provide the percentage removal of TOC or entail the percentage mineralization of PPCPs with ferrate (VI) treatment. Therefore, the percentage mineralization of PPCPs was obtained at various concentrations of PPCPs and at various pH values.

2.2.6. Removal of pharmaceutical and personal care products (PPCPs): HPLC measurements

The removal of pharmaceutical and personal care products (PPCPs) by the ferrate (VI) treatment was investigated by using HPLC data. The instrument was calibrated using standard solutions of various PPCPs concentrations dissolved in HPLC grade water and the calibration curve was plotted and the R^2 values were found to be nearly equal to 1. The blank solutions of each PPCPs i.e., the untreated samples and ferrate (VI) treated samples were subjected for the HPLC measurements. Further, the parameters used in the HPLC analysis of each PPCPs are represented in Table 2.2.

Table 2.2. Parameters used in HPLC analysis

Name of the pollutants	Mobile phase	Wavelength (nm)	Injection volume (µL)	Flow rate (mL/min)	Retention time (min)
Sulfamethoxazole (SMX)	Acetonitrile : water (55 : 45)	259	20.0	1.0	4.7
Sulfamethazine (SMZ)	Acetonitrile : water (55 : 45)	275	20.0	1.0	3.7
Triclosan (TCS)	Acetonitrile : water (90 : 10)	280	20.0	1.0	3.8
Amoxicillin (AMX)	Acetonitrile : water (90:10)	228	20.0	1.0	2.9

The peak obtained at the retention time indicated the presence of particular analyte (i.e., individual PPCPs) and it was directly proportional to the analyte concentrations. The peak area was measured using the Empower2 software and the concentration of particular PPCP was estimated. Further, the percentage elimination of each PPCPs was obtained using the blank concentration of PPCPs at various pH values and concentration.

2.2.7. Effect of co-existing ions

The impact of co-existing ions in the degradation of PPCPs by ferrate (VI) was performed to simulate the study for real matrix treatment. Moreover, the study may enable to assess the preferential degradation of target pollutant in presence of various co-existing ions. Therefore, the degradation of PPCPs by ferrate (VI) was conducted in presence of several electrolytes *viz.*, Sodium chloride (NaCl), glycine ($C_2H_5NO_2$), Oxalic acid ($C_2H_2O_4$), disodium hydrogen phosphate (Na_2HPO_4), sodium nitrite ($NaNO_2$), sodium nitrate ($NaNO_3$) and ethylenediaminetetraacitic acid (EDTA) provide a molar ratio of PPCPs to coexisting ion of 1:5. A known quantity of potassium ferrate was introduced in the reaction mixture to obtain a potassium ferrate concentration of 0.2 mM, i.e., the stoichiometric ratios of PPCPs, electrolyte, and ferrate (VI) is 1:5:2. The solution mixture was stirred for 2 hrs and then filtered with using a syringe filter (0.22 μm). The filtrate was divided into two parts. The first part was subjected for the PPCPs concentration measurements using HPLC. Further, using the blank concentration of PPCPs, the percentage removal of PPCPs was obtained. On the other hand, the second portion of filtrate was employed for the TOC measurements. Similarly, using the blank TOC data, the percentage mineralization of PPCPs was obtained. The pH of the solution was adjusted by a drop-wise addition of 0.1 M HCl/or NaOH solutions. The concentration of each of the ions was kept at 0.5 mM whereas the concentration of PPCPs was taken as 0.1 mM.

2.2.8. Real water Samples

The real water samples obtained from four distinct sources (river and spring water) in Aizawl City, Mizoram, India, and were utilized for real matrix experiment. The water samples were stored in a polyethylene water container and subjected for its parametric analysis. Multiparameter instrument was utilized to measure various water quality parameters *viz*., pH, conductivity, resistivity, salinity, oxidation-reduction potential, total dissolved solids, phosphate, sulfate, nitrate and fluoride. The water samples were also analyzed by atomic absorption spectrometer (AAS) 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 sulfamethoxazole, sulfamethazine, triclosan and amoxicillin solutions at various concentrations at pH 10.0. The ferrate (VI) dose was maintained at 0.1 mM to each sample and the solution mixture was stirred for 2 hrs. The treated samples were then filtered by the 0.22 μm syringe filters and subjected for the HPLC measurements. The results obtained were then compared with those obtained using distilled water to observe the efficiency of ferrate (VI).

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CHAPTER 3

RESULTS AND DISCUSSIONS

3. RESULTS AND DISCUSSIONS

3.1. Effect of micropollutant concentration in the removal of micropollutants

3.1.1. Sulfamethoxazole removal

The reduction of ferrate (VI) as a function of time is obtained for varied concentrations of micro-pollutants. Various concentrations of sulfamethoxazole (0.02 to 0.20 mM) were treated with a constant ferrate (VI) concentration i.e., 0.10 mM at constant pH 6.0. This enabled to study the wide range of ferrate (VI) to sulfamethoxazole molar ratios (i.e., from 1:0.2 to 1:2). This wide range of molar ratios further enabled to deduce the overall stoichiometric ratios of the decomposition of sulfamethoxazole by ferrate (VI) also to obtain the overall rate constant in the degradation of micro-pollutants by ferrate (VI). The change in ferrate (VI) concentration by the interaction of sulfamethoxazole was monitored by using the UV-Visible spectrophotometer as a function of sulfamethoxazole concentrations and time of contact and the results are shown in Figure 3.1 (a). It is evident from the Figure 3.1 (a) that the concentration of ferrate (VI) was decreased significantly by increasing the concentration of sulfamethoxazole. This implies that the ferrate (VI) was enabled to decompose the sulfamethoxazole. Moreover, a rapid decrease in ferrate (VI) concentration was observed during the initial period of contact, which reached to almost a steady state after *Ca* 10 mins of contact. This confirms that ferrate (VI) is efficient for the degradation of sulfamethoxazole in aqueous solutions. Further, quantitatively, the study reveals that the concentration of ferrate (VI) was reduced from 0.10 to 0.057 mM at the end of 20 mins for the 0.2 mM of sulfamethoxazole. It was reported previously that ferrate (VI) decomposes into iron (III) via the following reductive mechanism (Zhang *et al*., 2012; Pachuau *et al*., 2013).

$$2FeO_4^{2-} + 3H_2O \rightarrow 2\,Fe(OH)_3 + 5[O] \quad \ldots(3.1)$$

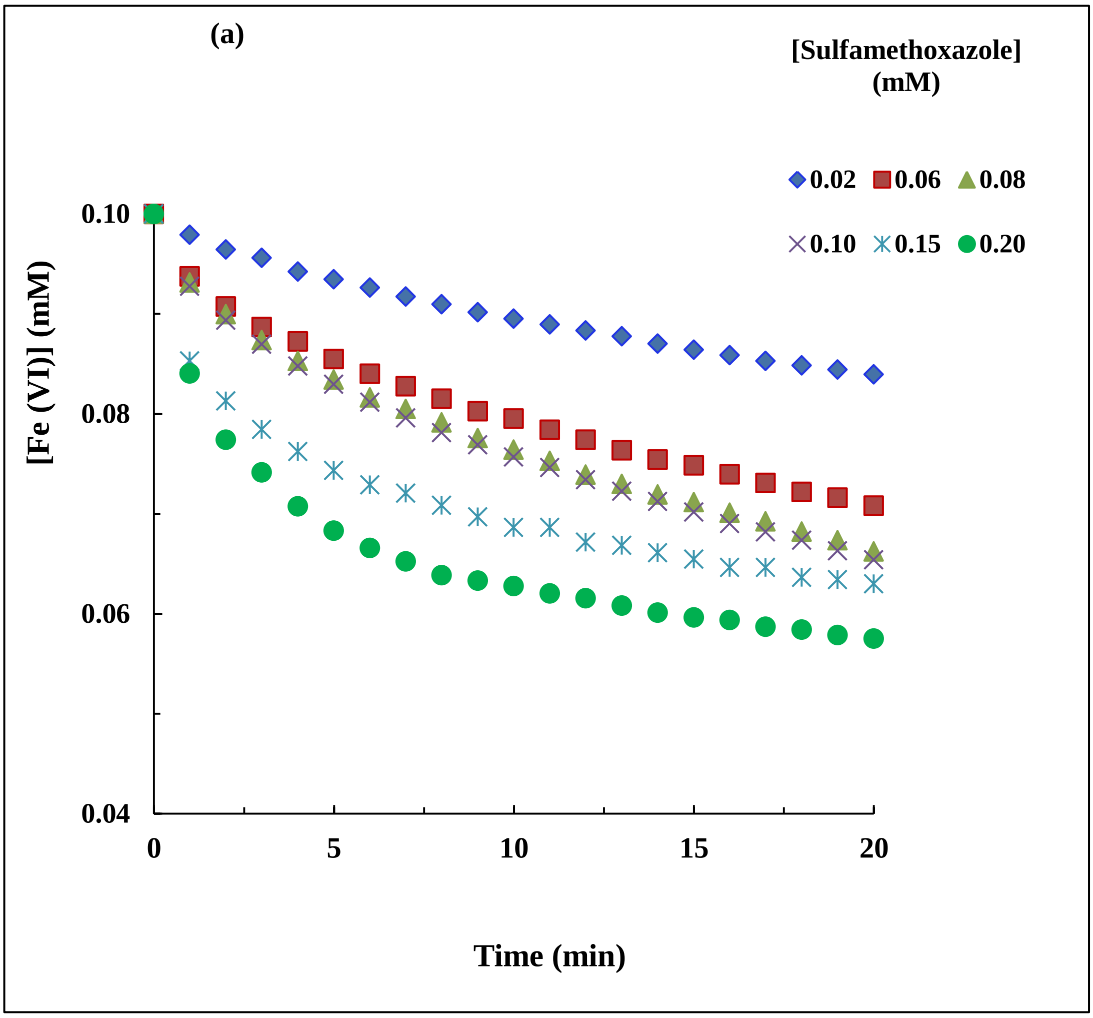
$$[O] + H_2O \rightarrow 2\,\bullet OH \quad \ldots(3.2)$$

$$2\,\bullet OH \rightarrow H_2O_2 \quad \ldots(3.3)$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad \ldots(3.4)$$

The hydroxyl radical produced in the reaction process is a powerful oxidizing agent which is likely to oxidize organic contaminants in aqueous solutions, (Han *et al.*, 2013). Hence, this further enhances the rate of degradation sulfamethoxazole by ferrate (VI). It was also assumed that the sulfamethoxazole degradation was initiated by the free oxygen atom of ferrate (VI) species, which then allowed the transfer of electrons from the ferrate (VI) species to the isoxazole, and thus, further promotes the ring-opening reaction of sulfamethoxazole (Yu *et al.*, 2017).

Further, the removal of sulfamethoxazole by ferrate (VI) was analyzed at a wide range of sulfamethoxazole concentrations (0.02 to 0.2 mM) having constant dose of ferrate (VI) and at pH 6.0. The removal of sulfamethoxazole was analyzed by the HPLC measurements. The HPLC results are included in Table 3.1 also the percentage removal of sulfamethoxazole as a function of sulfamethoxazole concentration is shown in Figure 3.1 (b). Moreover, the HPLC representative figure for the removal of sulfamethoxazole is shown in Figure 3.2. The figure 3.2 clearly showed that distinct peak of sulfamethoxazole is appeared at the retention time of 4.7 mins and the ferrate (VI) treated sample showed a significant decrease in peak area. Using the peak areas, the percentage removal of sulfamethoxazole was obtained at different concentrations of sulfamethoxazole and shown in Table 3.5. Table 3.5 clearly depicts that with an increase in sulfamethoxazole concentration, the removal percentage of sulfamethoxazole was decreased sharply. More specifically, increasing the sulfamethoxazole concentration from 0.02 to 0.20 mM caused to decrease the percentage elimination of sulfamethoxazole from 71.0% to 15.0%, respectively at pH 6. The higher percentage elimination of sulfamethoxazole at lower concentrations is mainly due to the fact that a relatively more amount of ferrate (VI) is present to degrade the lesser extent of sulfamethoxazole. In the study of similar compounds like 4-tert-octylphenol, bisphenol A, dilcofenac sodium and 17α-ethynylestradiol, it was reported that, their removal percentage was also decreased with an increase in pollutant concentration (Tiwari *et al.*, 2017; Sailo *et al.*, 2017). Moreover, it is evident that although the percentage removal of sulfamethoxazole at higher pollutant concentration is less however, the extent of sulfamethoxazole removal is higher at an increased concentration of sulfamethoxazole.



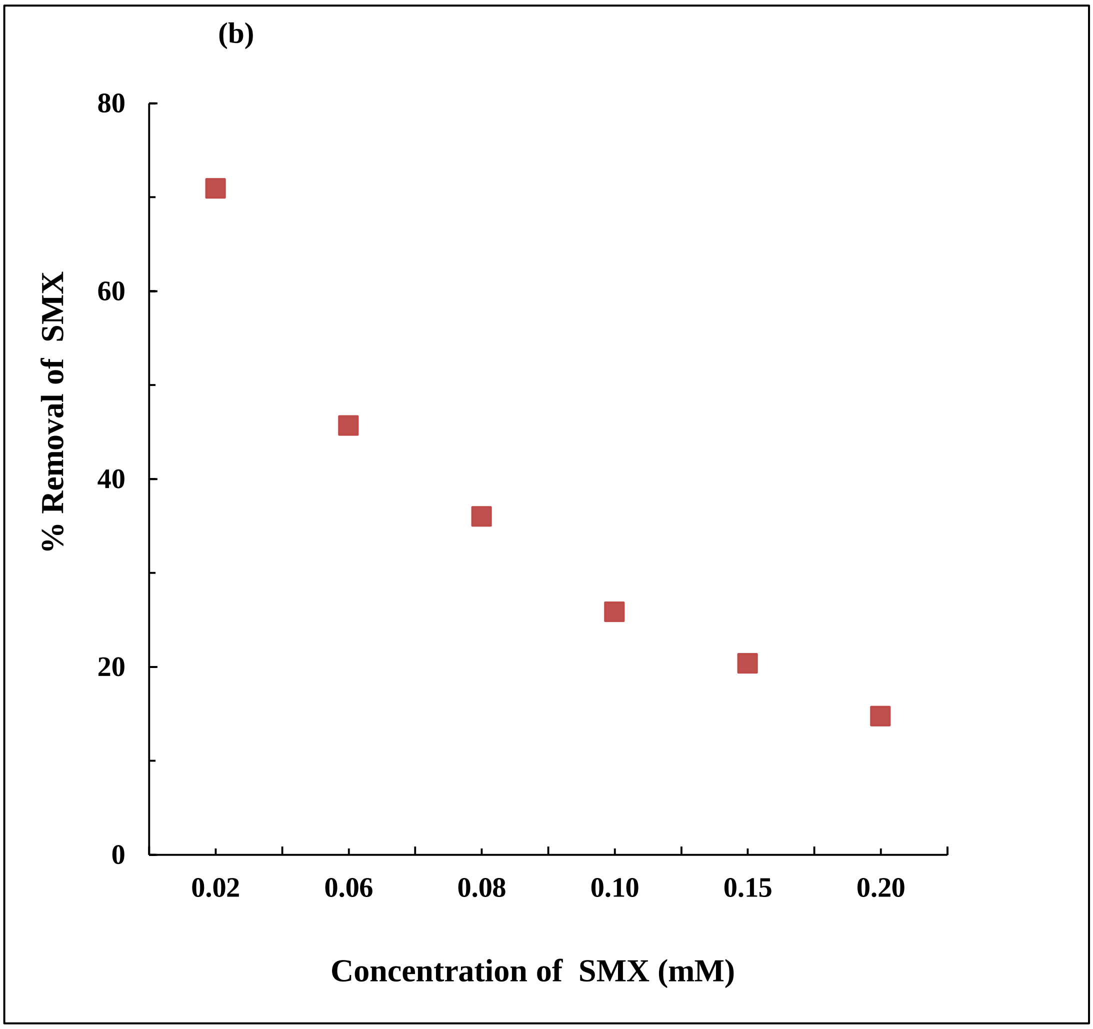


Figure 3.1. (a) Degradation of ferrate (VI) at varying concentrations of sulfamethoxazole as a function of contact time at pH 6.0 [Fe(VI)]: 0.1 mM; **(b)** Percentage elimination of sulfamethoxazole by ferrate(VI) as a function of sulfamethoxazole concentration (pH 6.0; [Fe(VI)]: 0.1 mM).

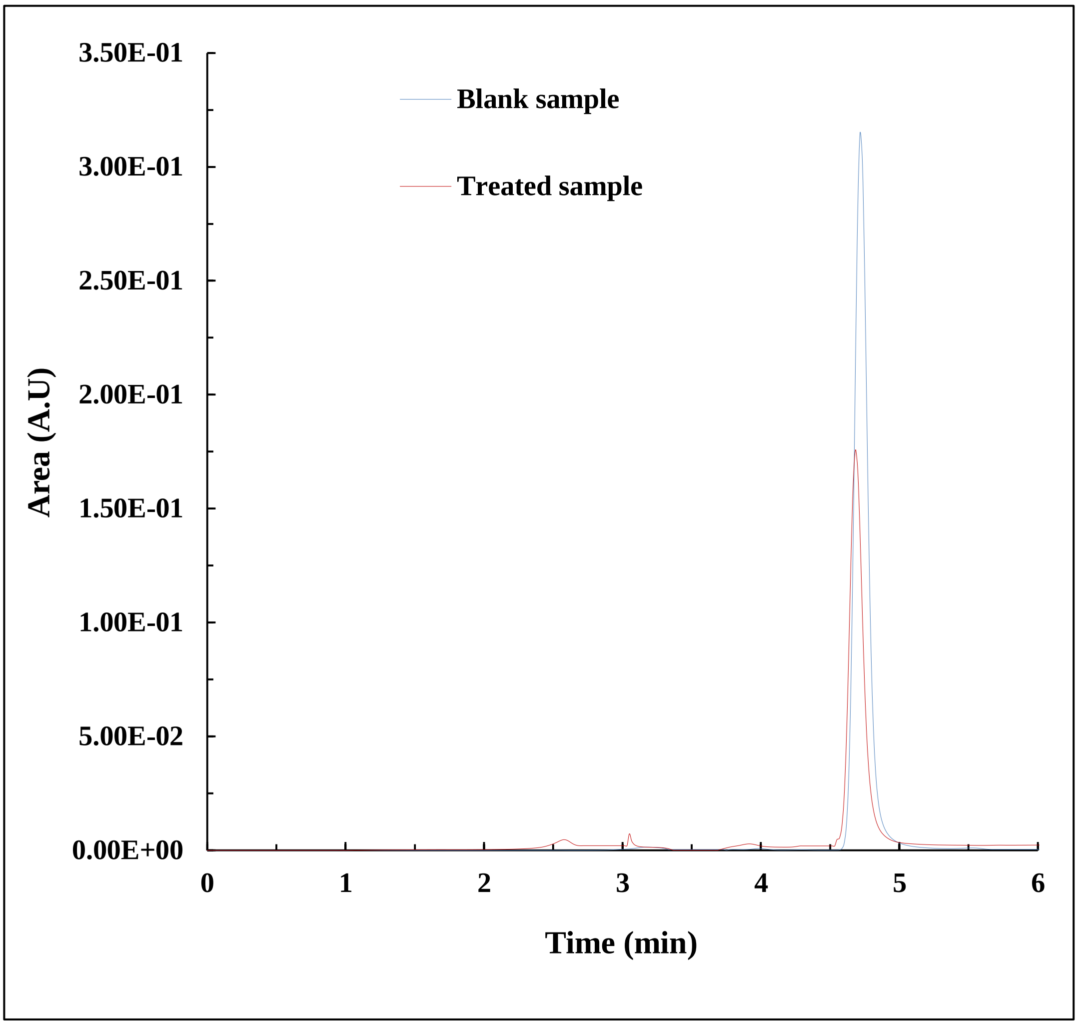


Figure 3.2. Degradation of sulfamethoxazole (SMX) at ferrate (VI); SMX ratio 1:1 (pH 6.0).

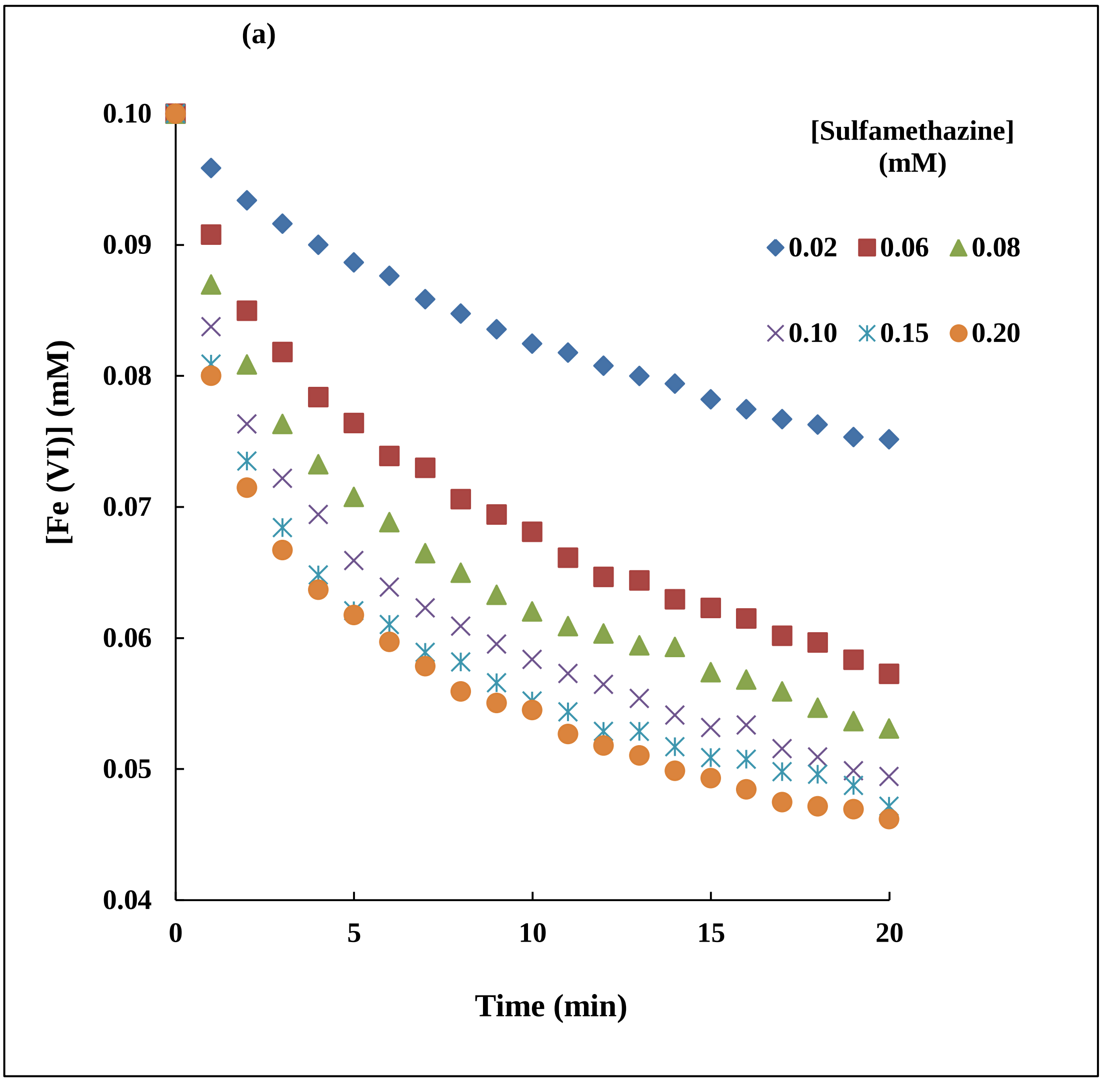
Table 3.1. Percentage removal of sulfamethoxazole by ferrate (VI) with respect to concentration at pH 6.0 (HPLC measurements).

Concentration of sulfamethoxazole (mM)	Retention time (min)	Area (µV*sec)		%Removal of sulfamethoxazole
		Blank sample	Treated sample	
0.02	4.7	848522	246382	70.9
0.06	4.7	2071994	1125145	45.7
0.08	4.7	2728935	1746265	36.0
0.10	4.7	3353163	2485657	25.8
0.15	4.7	4859277	3869414	20.3
0.20	4.7	6272233	5345413	14.7

3.1.2. Sulfamethazine removal

Sulfamethazine (SMZ) having concentrations from 0.02 mM to 0.2 mM is treated with ferrate (VI) (0.1 mM) at pH 6.0. The concentration of sulfamethazine is varied to obtain varied ferrate (VI) to sulfamethazine molar ratios (i.e., from 1: 0.2 to 1:2). The time dependent variations in ferrate (VI) concentration in presence of sulfamethazine are continuously recorded using UV-visible spectrophotometer. The results are graphically presented as in Figure 3.3 (a). It is noticed that the reduction of ferrate (VI) is considerably increased at higher concentrations of sulfamethazine. Quantitatively, at 1:1 molar ratio, the concentration of ferrate (VI) was decreased from 0.1 mM to 0.05 mM. This indicated that the rate of degradation of sulfamethazine is favored at higher concentration of sulfamethazine. Furthermore, it is noted that the degradation of ferrate (VI) is reasonably faster during the initial period of interaction, but it reaches almost a constant value at around 10 mins of contact. This reveals that a rapid degradation of sulfamethazine is occurred by the ferrate (VI) hence, ferrate (VI) was found to be an effective/efficient oxidant in the degradation of sulfamethazine in aqueous medium. Quantitatively, the concentration of ferrate (VI) was decreased from 0.1 mM to 0.05 mM in presence of 0.1 mM sulfamethazine and at pH 6.0.

Furthermore, the elimination of sulfamethazine by ferrate (VI) was investigated at a broad range of sulfamethazine concentrations (0.02 to 0.2 mM) at constant concentration of ferrate (VI). In other words, the ferrate (VI) : sulfamethazine molar ratios are varied from 1:0.2 to 1:2. The HPLC measurements were performed to examine the concentration of sulfamethazine. The peak area of ferrate (VI) treated sample and the blank sample of sulfamethazine was compared and hence the percentage removal of sulfamethazine was obtained and shown graphically in figure 3.3 (b). Moreover, the HPLC representative graph for the elimination of sulfamethazine was obtained and shown in Figure 3.4. The figure 3.4 shows that a distinct peak of sulfamethazine was occurred at the retention time of 3.7 mins and a significant decrease in peak resembles with the ferrate (VI) treated sample. Using the peak areas of these peaks, the percentage removal of sulfamethazine at various concentrations of sulfamethazine was obtained and returned in table 3.2. It is evident from the table 3.2 that the increase in sulfamethazine concentrations from 0.02 to 0.2 mM, the percentage elimination of sulfamethazine is decreased from 79.9 to 15.0%, respectively having the ferrate (VI) concentration of 0.1 mM. This reduction is attributed to the assumption that a comparatively higher amount of ferrate (VI) molecules are available at a lower concentration of sulfamethazine to break down the lesser extent of sulfamethazine molecules. However, an apparent increase in the content of sulfamethazine elimination was therefore achieved by increasing concentration of sulfamethazine. This showed that, though the percentage removal of sulfamethazine is higher at lower concentration, however, the increase in sulfamethazine concentration favored the extent elimination of sulfamethazine by ferrate (VI). It was reported previously that ferrate (VI) is a potential oxidant to remove several sulfonamides including sulfamethazine, sulfamethizole and sulfadiazine from aqueous media. These compounds were almost completely degraded within a period of 5 mins using a molar ratio ferrate (VI): sulfonamides of 6:1 at pH 3.0 (Acosta-Rangel *et al.*, 2020). The comparative study of oxidation of 4-aminobenzene sulfonamides using Fe(0)/sulfite, Fe(II)/sulfite, Fe(III)/sulfite and Fe(VI)/sulfite systems shows that Fe(VI)/sulfite system exhibits most effective degradation of pollutant since it degrades completely the pollutant from aqueous media at pH 3.0 (Acosta-Rangel *et al.*, 2019). In case of similar compound such as sulfamethoxazole, it was reported that AOP using TiO_2 and WO_3 nanoparticles enabled complete degradation within 90 mins at pH 3.0 and pH 4.0 under UV and halogen irradiation source (Beheshti *et al.*, 2019). Thus, these studies reveal that ferrate (VI) is efficient oxidizing agent to degrade variety of micro-pollutants in aqueous solution.



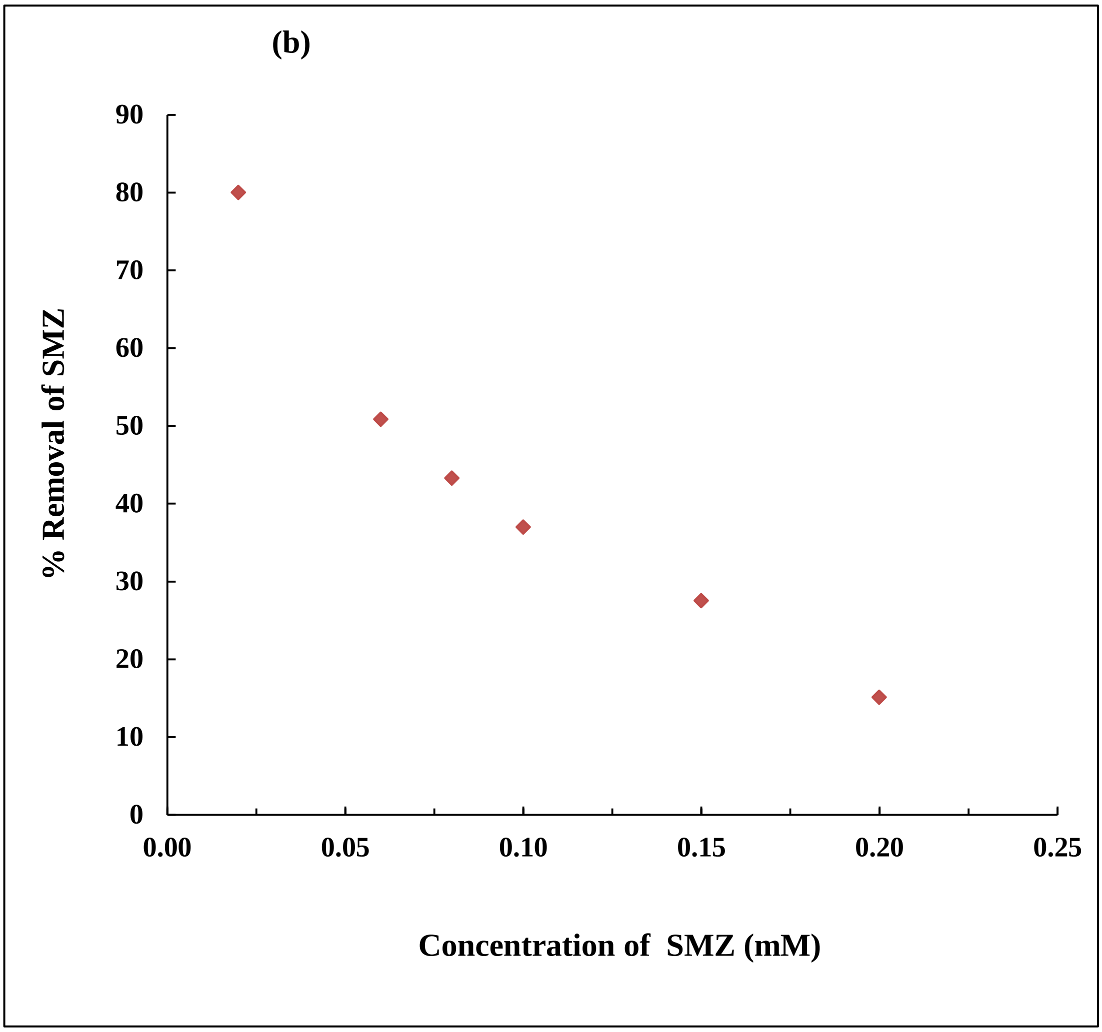


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Figure 3.3. (a) Removal of ferrate (VI) concentration with respect to varied concentrations of sulfamethazine at pH 6.0 and **(b)** Percentage removal of SMZ as a function of SMZ concentrations (pH 6.0; [Fe(VI)]: 0.1 mM).

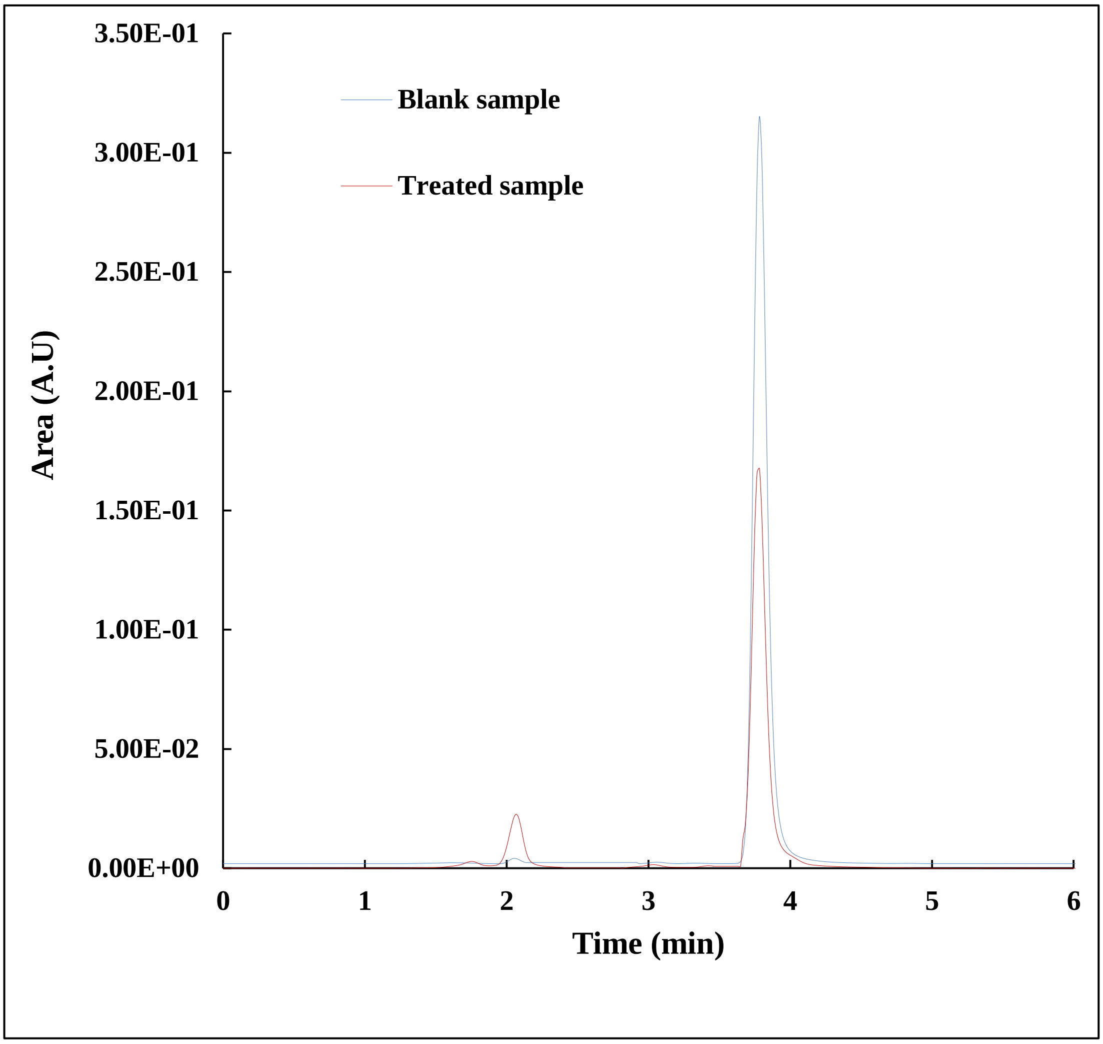


Figure 3.4. Degradation of sulfamethazine (SMZ) at Fe(VI): SMZ 1:1 ratio (pH 6.0).

Table 3.2. Percentage removal of sulfamethazine by ferrate (VI) at varied concentrations of sulfamethazine at pH 6.0 (HPLC measurements).

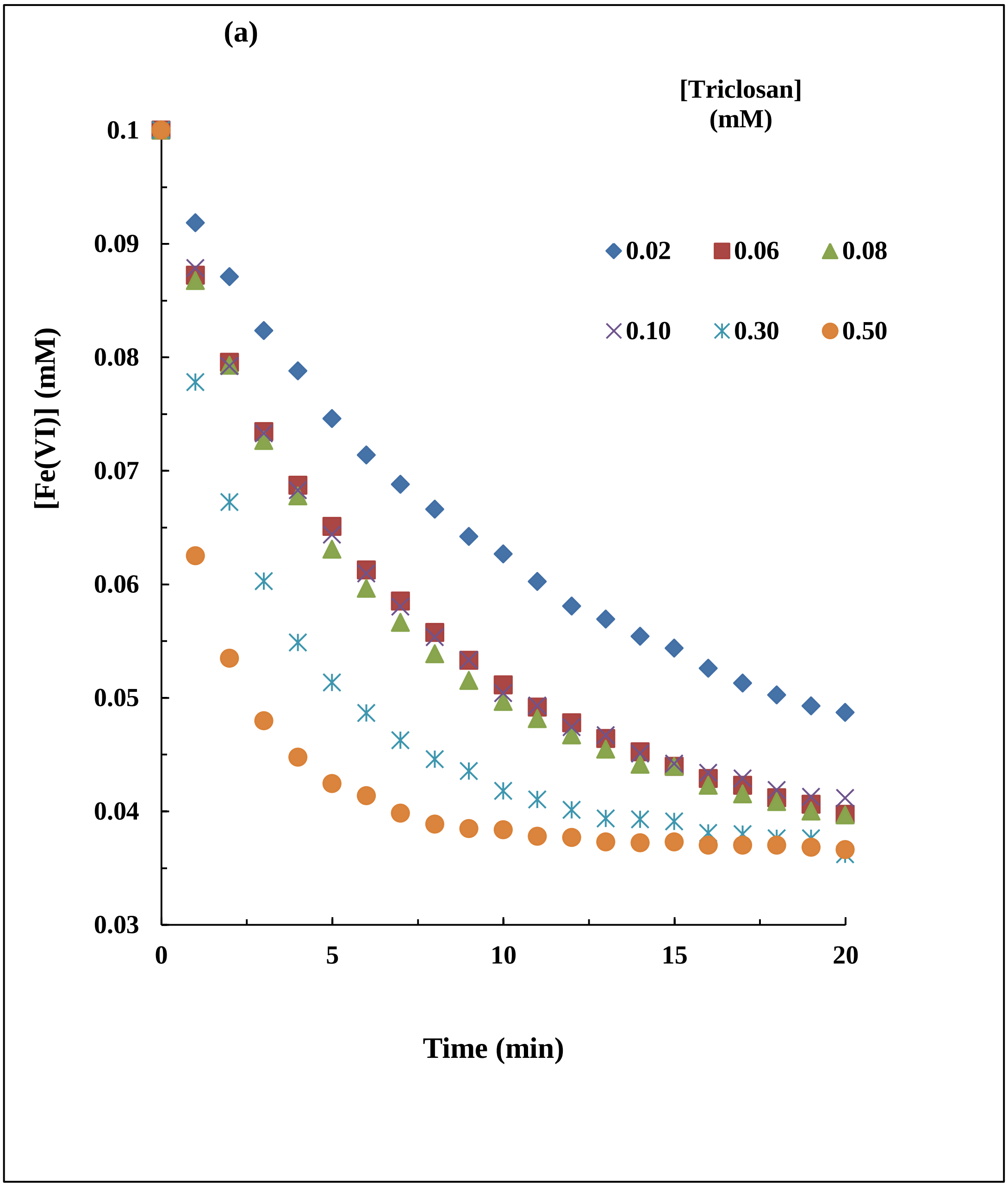
Concentration of sulfamethazine (mM)	Retention time (min)	Area (µV*sec)		% Removal of sulfamethazine
		Blank sample	Treated sample	
0.02	3.7	407081	81517	79.9
0.06	3.7	1346485	662140	50.8
0.08	3.7	1774757	1007265	43.2
0.10	3.7	2225217	1402795	36.9
0.15	3.7	3537589	2564921	27.4
0.20	3.7	43789369	37197370	15.0

3.1.3. Triclosan removal

The effect of concentration of triclosan was analyzed by increasing the initial concentration of triclosan from 0.02 to 0.5 mM at pH 10.0 using the ferrate (VI) dose of 0.1 mM. The degradation of ferrate (VI) with respect to triclosan concentrations was observed for 20 mins using a UV-Vis spectrophotometer. Therefore, the change in ferrate (VI) concentrations as a function of triclosan concentration is obtained and shown in Figure 3.5 (a). It is clearly indicated from figure 3.5 (a) that the ferrate (VI) reduction is rapid during the initial period of time i.e., 8-10 mins, thereby achieving almost a constant value in the latter period of reaction. It was further recorded that with an increase in triclosan concentration (from 0.02 to 0.5 mM), the reduction rate of ferrate (VI) was increased significantly. Quantitatively, the concentration of ferrate (VI) was decreased from 0.10 to 0.0411 mM at the concentration of ferrate

(VI) of 0.1 mM. The increase in ferrate (VI) degradation at higher concentration of triclosan is due to the fact that at higher concentration of triclosan, relatively lesser extent of ferrate (VI) is present as to degrade the higher amount of triclosan. Further, the degradation of triclosan by the ferrate was assumed through the interaction of hydroxyl radicals with the ether group of triclosan which resulted in rapid degradation of triclosan (Yang *et al*., 2011).

Additionally, the concentration of triclosan was analyzed by using the HPLC measurements. The HPLC data for percentage removal of triclosan as a function of its concentrations are shown in Table 3.3 and illustrated graphically in Figure 3.5 (b). The HPLC representative chromatogram at 1:1 molar ratio of ferrate (V): triclosan is also shown in Figure 3.6. The figure 3.6 shows distinct peak of triclosan (ferrate (VI) treated peak and the blank peak) at the retention time of 3.8 mins. The area of the two peaks i.e., ferrate (VI) treated triclosan and blank triclosan were utilized and the percentage removal of triclosan was obtained at varied concentrations of triclosan and returned in Table 3.3. It is evident from the Table that increasing the concentration of triclosan from 0.02 to 0.50 mM had caused to decrease the percentage removal of triclosan from 87.4% to 18.1%, respectively. On the other hand, however, on increasing the initial concentration of triclosan i.e., from 0.02 to 0.50 mM, the extent of triclosan removed was increased from 0.175 to 0.9 mM, respectively. This result is consistent with the previous report in which increasing the concentration of bisphenol A/or diclofenac greatly favored the removal efficiency of ferrate (VI) (Sailo *et al*., 2017). Furthermore, the reactivity of FeO_4^- in aqueous solutions was increased significantly due to the electron-donating character of the alkyl group which further increased the removal efficiency of ferrate (VI) towards various micropollutants (Sharma, 2013). Moreover, the oxidation of triclosan was enhanced by an acidic condition, however; the presence of hydrogen peroxide and natural organic matter hindered the triclosan elimination (Li *et al*., 2016). These studies enabled that ferrate (VI) is efficient in the removal of triclosan from aqueous solutions.


(a)
[Triclosan]
(mM)
◆0.02
■0.06
▲0.08
×0.10
⁎0.30
●0.50
[Fe(VI)] (mM)
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0
5
10
15
20
Time (min)

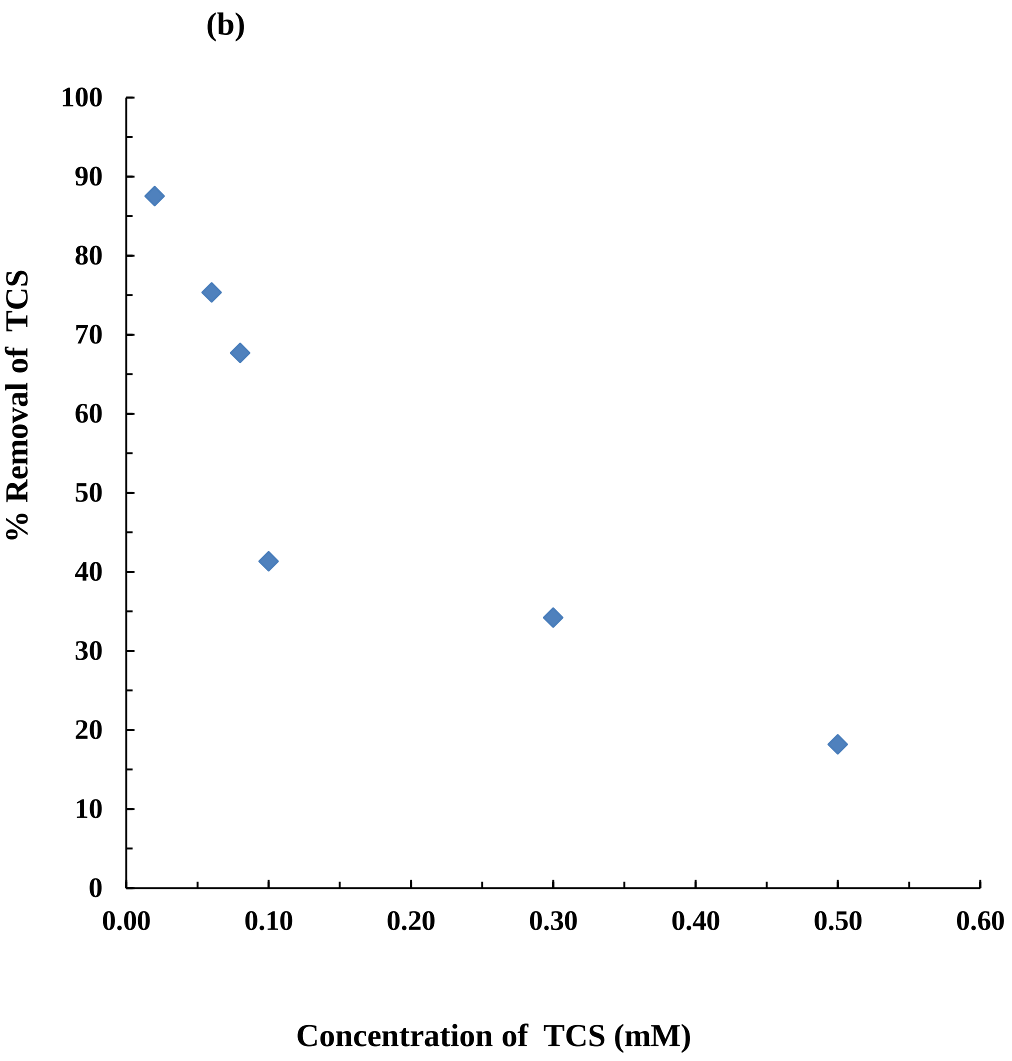


Figure 3.5. (a) Ferrate (VI) degradation as a function of time with respect to triclosan and **(b)** percentage elimination of triclosan as a function of triclosan concentrations [pH 10.0; initial concentration of Fe(VI): 0.1 mM]

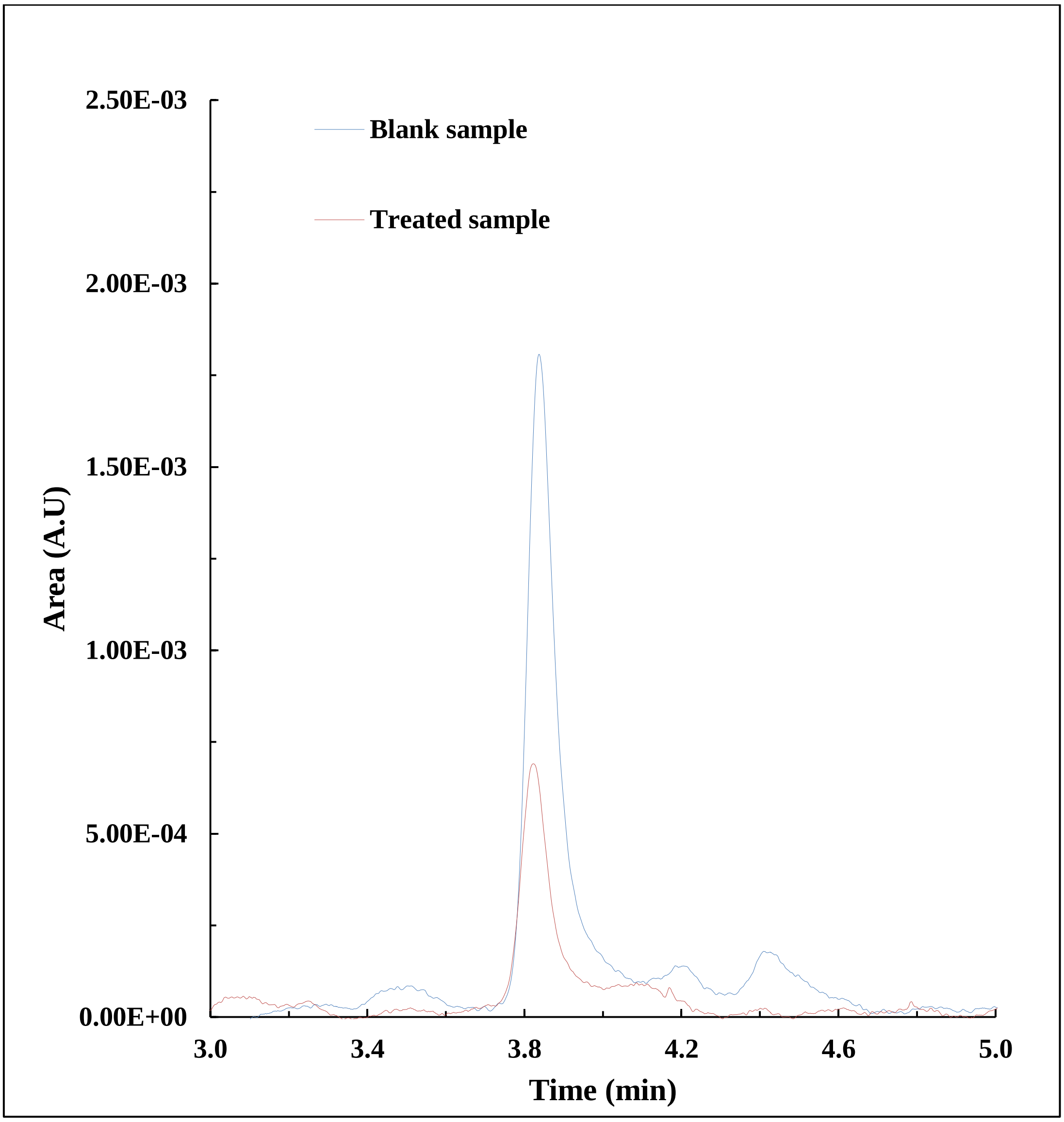


Figure 3.6. Degradation of triclosan (TCS) at Fe(VI):TCS 1:1 ratio (pH 10.0).

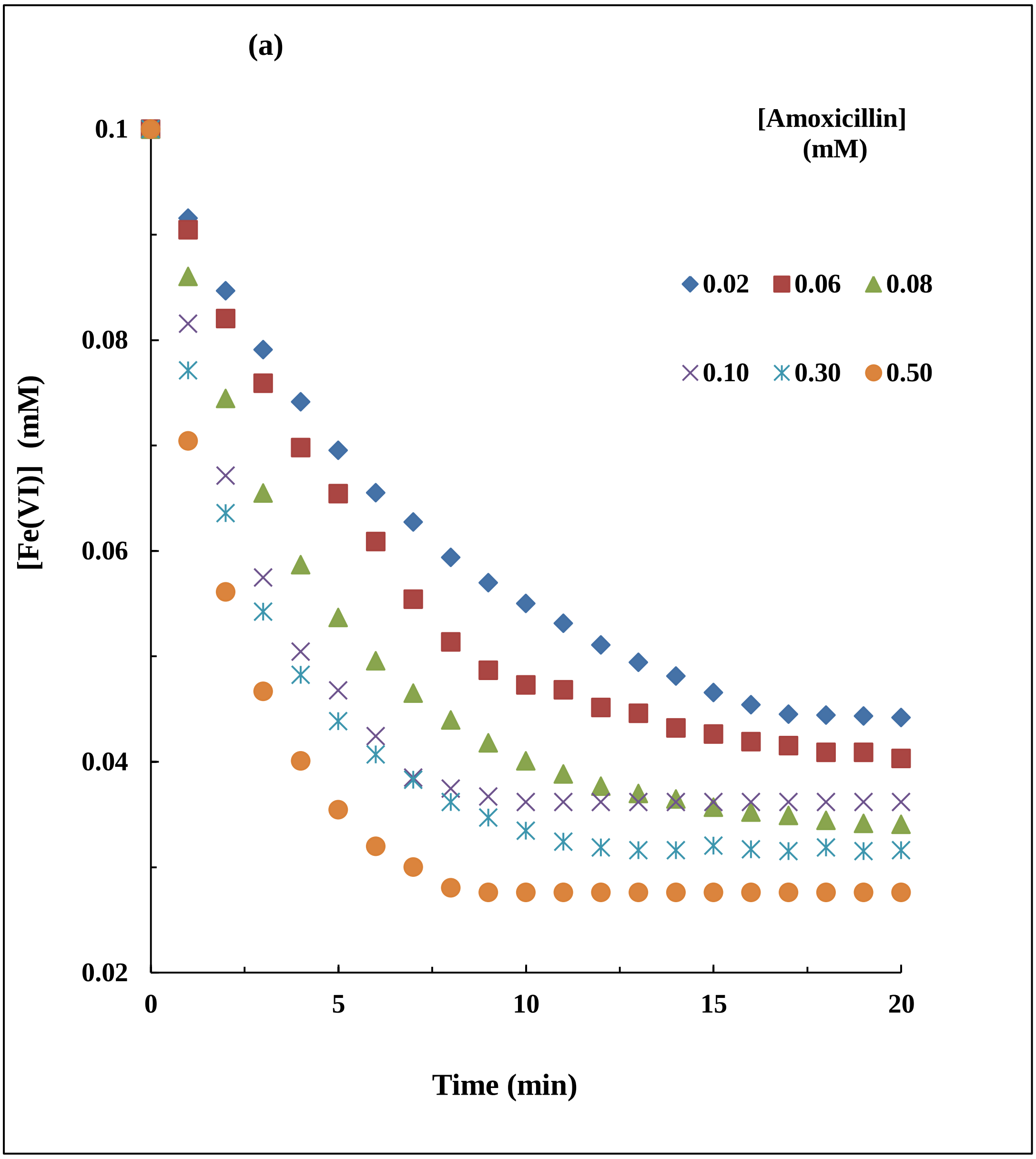
Table 3.3. Percentage removal of triclosan by ferrate (VI) with respect to various concentrations of triclosan at pH 10.0 (HPLC measurements).

Concentration of triclosan (mM)	Retention time (min)	Area (μV*sec)		% Removal of triclosan
		Blank sample	Treated sample	
0.02	3.8	1631	204	87.4
0.06	3.8	2131	426	80.0
0.08	3.8	2610	644	75.3
0.10	3.8	3046	1788	45.3
0.30	3.8	5989	3941	34.2
0.50	3.8	9201	7531	18.1

3.1.4. Amoxicillin removal

Amoxicillin is treated at varied concentrations i.e., from 0.02 to 0.5 mM at pH 10.0 and at constant dose of ferrate (VI) 0.1 mM. This enabled to vary the molar ratios of ferrate (VI) to amoxicillin from 1:0.2 to 1:5. The degradation of ferrate (VI) with respect to amoxicillin concentrations was obtained using a UV-Vis spectrophotometer. Therefore, the change in ferrate (VI) concentrations as a function of amoxicillin concentration with respect to time is obtained and displayed in Figure 3.7 (a). Figure clearly reveals that the removal of ferrate (VI) is rapid during the initial period of contact i.e., 8-10 mins, thereby achieved almost a constant value in the latter period of interaction. It was further recorded that with an increase of amoxicillin concentration i.e., 0.02 to 0.5 mM, the reduction rate of ferrate (VI) was increased sharply. Quantitatively, the concentration of ferrate (VI) was decreased from 0.1 to 0.0361 mM at the amoxicillin concentration of 0.1 mM.

Further, the concentration of amoxicillin is obtained using the HPLC measurements. A representative HPLC chromatogram is shown for the 1:1 molar ratio of amoxicillin and ferrate (VI). It is noted that a distinct peak of amoxicillin is obtained at the retention time 12.19 mins (*Cf* Figure 3.8). The peak areas of blank solution of amoxicillin along with the ferrate (VI) treated samples were utilized to obtain the percent elimination of amoxicillin at various concentrations of amoxicillin at pH 10.0. The results are returned in Table 3.8 and in Figure 3.7 (b). It is evident from the figure 3.7 (b) that increasing the concentration of amoxicillin from 0.02 to 0.50 mM had caused to decrease the percentage removal of amoxicillin from 94.4% to 18.1%, respectively. On the other hand, however, increasing the initial concentration of amoxicillin i.e., from 0.02 to 0.50 mM, the extent of amoxicillin removed was increased from 0.0188 to 0.908 mM, respectively. The recent studies revealed that ferrate (VI) could remove completely the variety of antibiotics from secondary wastewater effluents including triclosan, estrogen, carbamazepine, antibiotics containing aniline moieties, progestogens and compounds (PPCPs and EDCs) that contain phenolic groups (Yang *et al*., 2012). Moreover, the other studies showed that ferrate (VI) is efficient in oxidizing the amoxicillin at neutral pH 7.0 conditions (Sharma *et al.*, 2013).

(a)
[Amoxicillin] (mM)
0.02
0.06
0.08
0.10
0.30
0.50
[Fe(VI)] (mM)
0.1
0.08
0.06
0.04
0.02
0
5
10
15
20
Time (min)

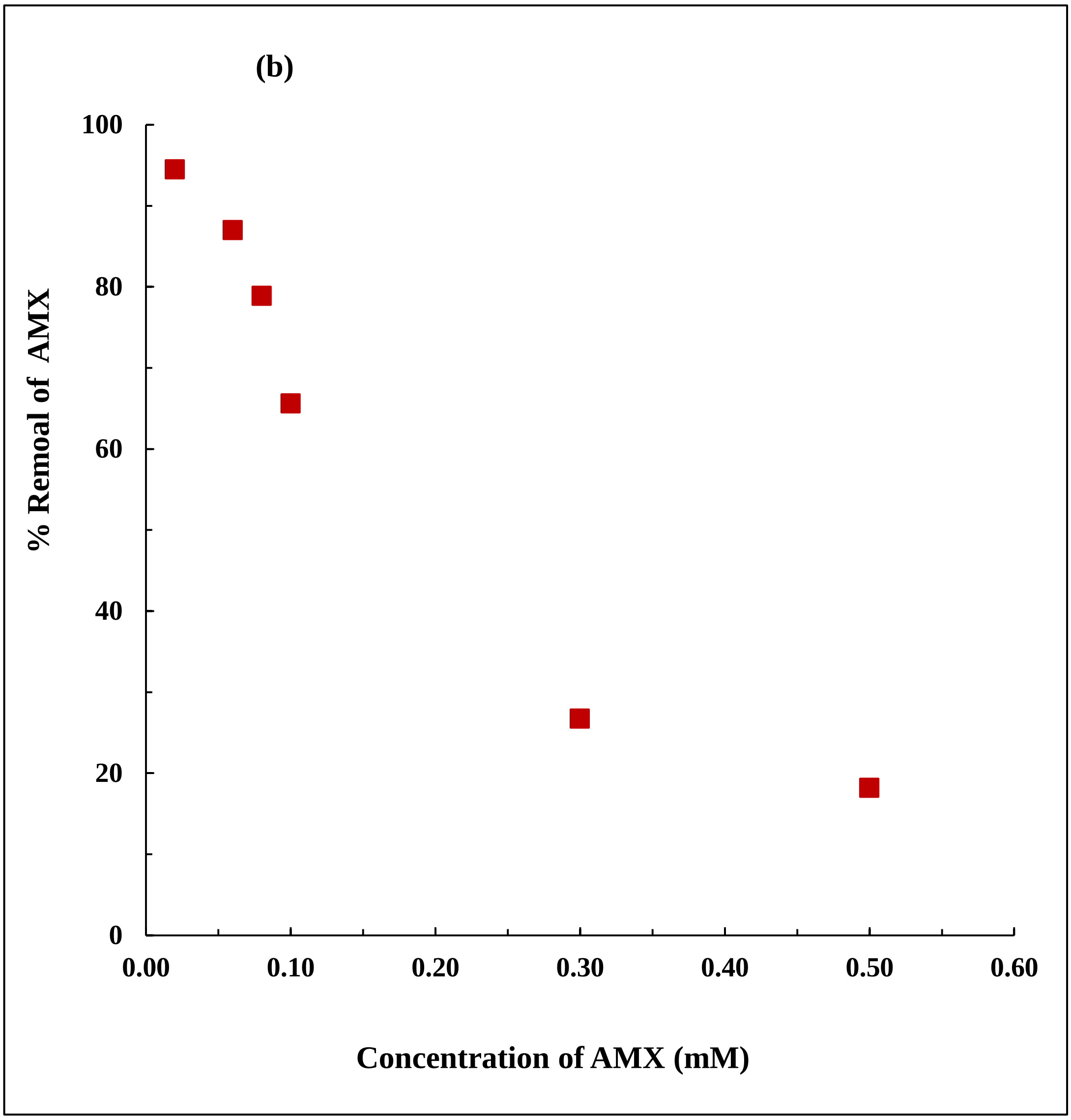


Figure 3.7. (a) Removal of ferrate (VI) as a function of time with respect to amoxicillin and **(b)** percentage elimination of AMX as a function of AMX concentrations [pH 10.0; initial concentration of Fe(VI): 0.1 mM]

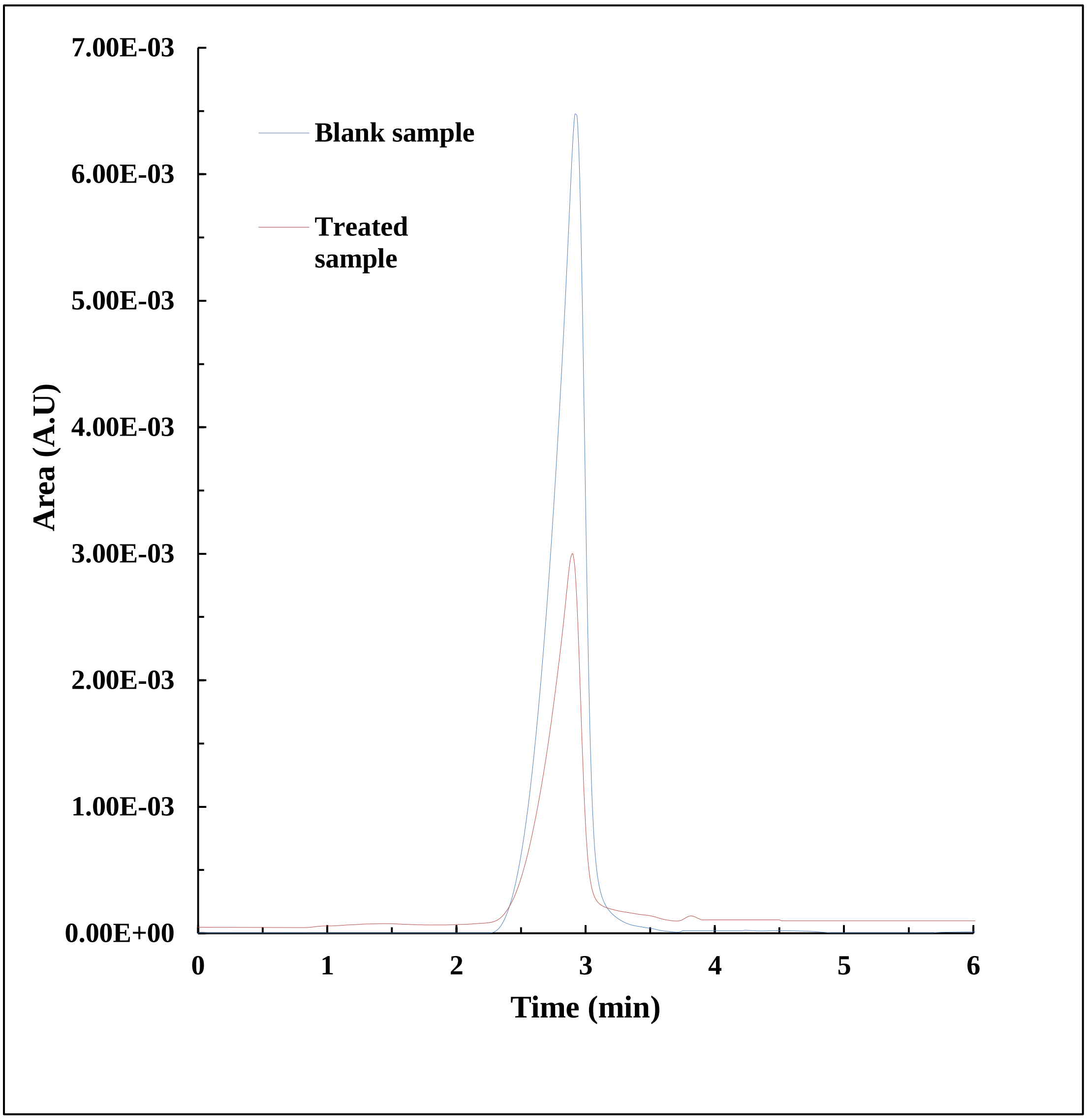


Figure 3.8. Degradation of amoxicillin at Fe(VI):AMX 1:1 ratio (amoxicillin and ferrate (VI) concentrations: 0.1 mM; and pH 10.0).

Table 3.4. Percentage removal of amoxicillin by ferrate (VI) with respect to various concentrations of amoxicillin and at pH 10.0 (HPLC measurements).

Concentration of triclosan (mM)	Retention time (min)	Area (μV*sec)		% Removal of triclosan
		Blank sample	Treated sample	
0.02	2.9	6309	350	94.4
0.06	2.9	12107	1578	86.9
0.08	2.9	29854	6309	78.8
0.10	2.9	35188	16107	54.5
0.30	2.9	51642	37838	26.7
0.50	2.9	72736	59524	18.1

3.2. Kinetic studies

3.2.1. Degradation kinetics of ferrate (VI) as a function of micropollutant concentrations

The kinetic study on the degradation of ferrate (VI) was conducted extensively in order to obtain the order of reaction along with the apparent rate constant values. This further enables the molar stoichiometry involved between the micropollutant and ferrate (VI). A simple oxidation/reduction reaction is written as:

$$\text{Fe(VI)} + \text{Micropollutant} \rightarrow \text{Fe(III)} + \text{Oxidized by-products} + CO_2 \qquad \ldots(3.5)$$

where Micropollutant: sulfamethoxazole, sulfamethazine, triclosan or amoxicillin

Hence, the ferrate (VI) reduction rate equation is given as:

$$\frac{-d[Fe(VI)]}{dt} = k_{app}\,[Fe(VI)]^m\,[Micropollutant]^n \qquad \ldots(3.6)$$

or $$\frac{-d[Fe(VI)]}{dt} = k_{app}\,[Fe(VI)]^m \qquad \ldots(3.7)$$

where, $$k = k_{app}\,[Micropollutant]^n \qquad \ldots(3.8)$$

where k_{app} is the overall rate constant and [Fe(VI)] and [Micropollutant] are the ferrate(VI) and micropollutant concentrations, respectively. Further, 'm' and 'n' represents the order of reaction for each reactant involved in the reaction. The value of 'm' is optimized through the empirical fitting of the change in ferrate (VI) concentrations for pseudo-first-order (Equation 3.5) or pseudo-second-order rate kinetics (Equation 3.6). Therefore, the rate constant values (k) are obtained at various concentrations of micropollutants. Further, using the 'k' values at different concentrations of micropollutant, the overall or apparent rate constant value (k_{app}) is obtained for each micropollutant separately using the Equation (3.4).

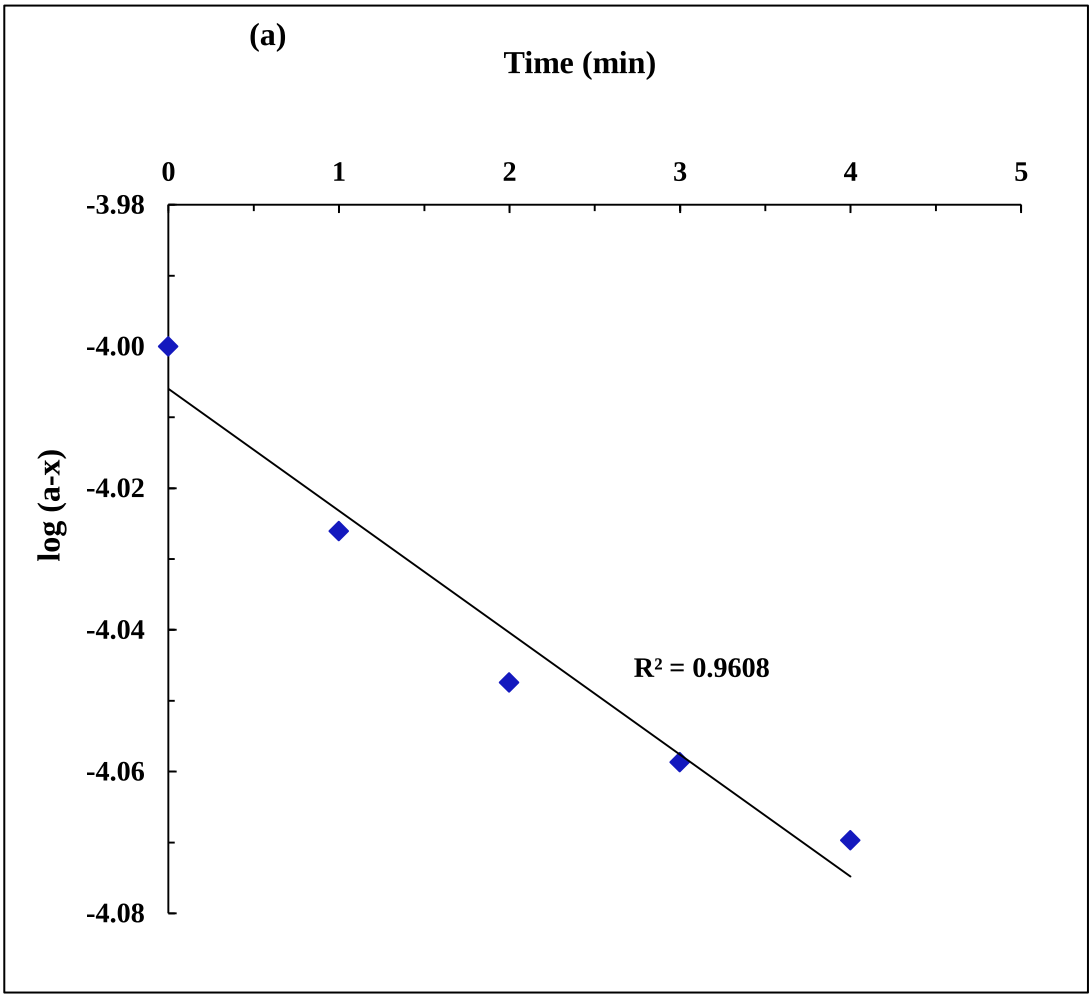
$$\ln(\mathrm{a} - \mathrm{x}) = \ln(\mathrm{a}) - k_1 \mathrm{t} \qquad \ldots(3.9)$$

$$1/(a - \mathrm{x}) = 1/\mathrm{a} + k_2\,\mathrm{t} \qquad \ldots(3.10)$$

where 'a' is the initial concentration of ferrate (VI) and 'x' is the concentration of ferrate (VI) reacted with micropollutant within time 't'. Hence, (a-x) is the remaining concentration of ferrate(VI) at time 't'. The k_1 and k_2 are the rate constants for the pseudo-first and pseudo-second order rate constants for the degradation of ferrate (VI) in presence of micropollutant.

3.2.1.1. Degradation kinetics of ferrate (VI) with respect to sulfamethoxazole (SMX)

The time dependence degradation of ferrate(VI) in presence of sulfamethoxazole was further utilized to plot both for pseudo-first order kinetics i.e., log(a-x) *vs* 't' (Equation 3.9) and pseudo-second order kinetic equations i.e., 1/(a-x) *vs* 't' (Equation 3.10) so as to optimize the value of 'm' as either 1 or 2. The fitting of the time dependence data at different concentrations of sulfamethoxazole was carried out for both the rate equations i.e., pseudo-first order and pseudo-second order equations (*Cf* Figure 3.9 (a - b) e.g., 1:1 molar stoichiometric data) and the results are returned in Table 3.5. It is evident from the Table 3.5 that the time dependence data is fitted-well to the pseudo-second order rate kinetics since the R^2 values for pseudo-second order kinetics is suitably fitted well as compared to the pseudo-first order equation. This infers that the value of '*m*' is 2 for the degradation of ferrate (VI) in presence of sulfamethoxazole. Moreover, it is evident from the table 3.5 that increasing the concentration of sulfamethoxazole from 0.02 to 0.20 mM, the pseudo-second order rate constant of ferrate (VI) is increased from 147.7 to 982.9 $mM^{-1}.min^{-1}$, respectively. The high value of rate constant is due to the fact that ferrate(VI) possesses fairly high reactivity to oxidize rapidly the sulfamethoxazole in aqueous solutions (Yang *et al.*, 2010; Tiwari *et al.*, 2008). Moreover, since the degradation kinetics was carried out relatively at lower pH value (i.e, pH ~6.0), the reactivity of ferrate (VI) was much increased.



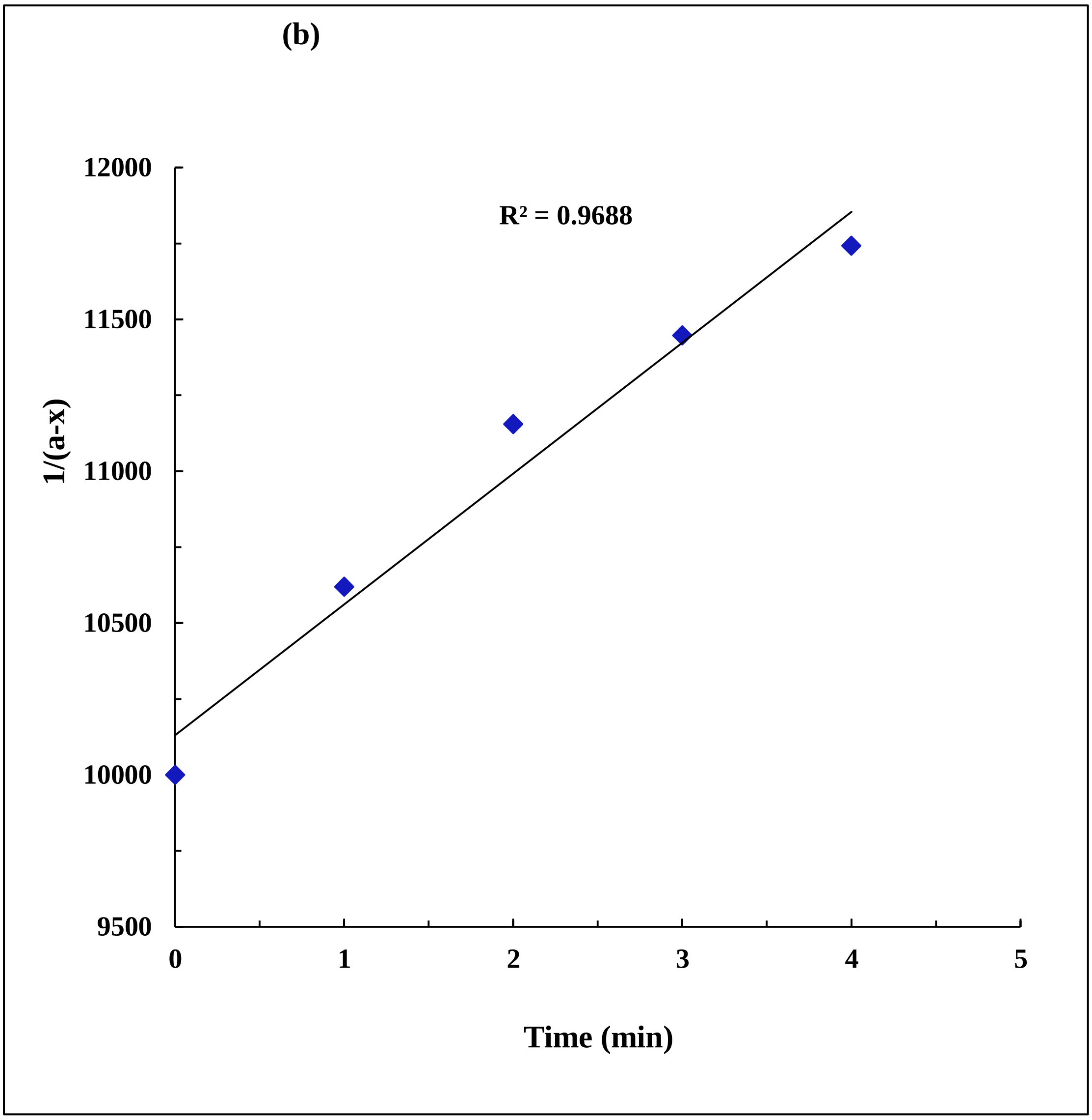


Figure 3.9. Plots of **(a)** log(a-x) *vs* time ‘t' and **(b)** 1/(a-x) vs time ‘t' in the decomposition of sulfamethoxazole (SMX) by Fe(VI) at pH 6.0 ([Fe(VI)]: 0.10 mM; [SMX]: 0.10 mM.

Table 3.5. Rate constant values of pseudo-first order and pseudo-second order reaction for ferrate (VI) degradation in presence of sulfamethoxazole at pH 6.0.

Concentration of Sulfamethoxazole (mM)	**Pseudo-first Order Rate Constant (x10^{-2}) (min^{-1})**		**Pseudo-second Order Reaction Rate Constant (mM^{-1}.min^{-1})**	
	k_1	**R^2**	**k_2**	**R^2**
0.02	1.4287	0.965	147.7	0.966
0.06	3.2932	0.948	353.1	0.955
0.08	3.8230	0.967	415	0.974
0.10	3.9612	0.961	431.2	0.969
0.15	6.8872	0.883	725.2	0.905
0.20	8.1756	0.919	982.9	0.943

Further, the pseudo-second order rate constant values obtained at various concentrations of sulfamethoxazole is utilized to obtain an optimum value of *'n'*. This apparently provides the information about the molar stoichiometry occurred between the sulfamethoxazole and ferrate (VI) as well as the value of 'k_{app}' (overall rate constant). A graph is plotted between the sulfamethoxazole concentrations and the rate constant values (k_2) at pH 6.0. A reasonable linear relationship is obtained between the value of k_2 against the concentrations of sulfamethoxazole (*Cf* Figure 3.10). This indicates that the value of '*n*' is appropriate to '1'. Therefore, this infers that the stoichiometry of ferrate (VI) to sulfamethoxazole is 2:1. Moreover, the value of 'k_{app}' is obtained by the slope of line (*Cf* Figure 3.10) and found to be 4559 (mM)$^{-2}$.min^{-1} having the regression coefficient (R^2) of 0.984. In previous studies showed that the ferrate (VI) is efficient in degrading various pollutants in aqueous media as possessed relatively high 'k_{app}' values (Sailo *et al.*, 2017; Sharma *et al.*, 2017). Recent studies indicated that the degradation of some sulfonamides *viz.*, sulfadiazine (SDZ), sulfamethazine (SMZ) and sulfamethizole (SML) followed second-order rate kinetics and the rate constant values ranged from 50 to 227 x 10^2 $M^{-1}s^{-1}$ at pH 3.0 (Acosta-Rangel *et al.*, 2020).

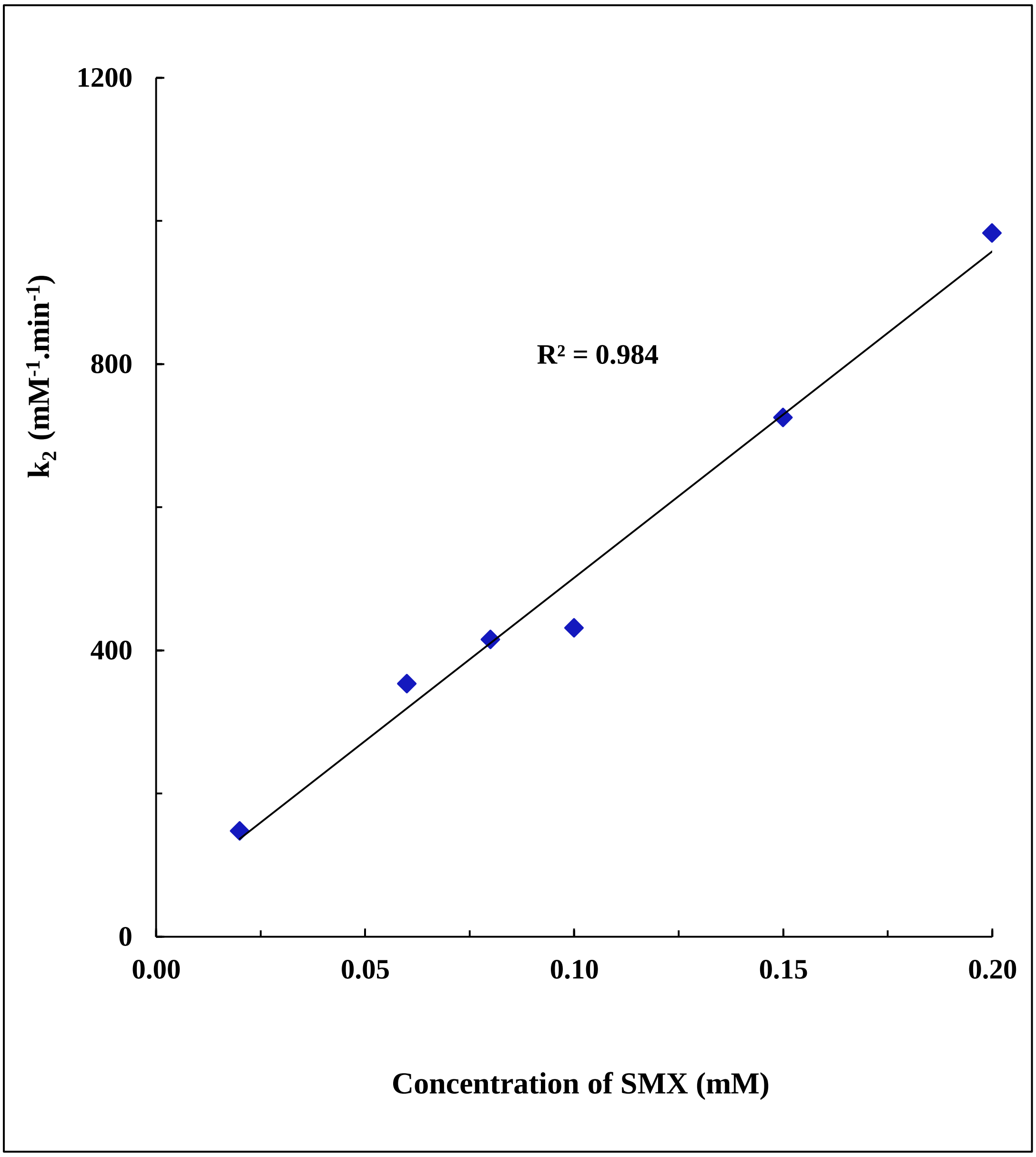
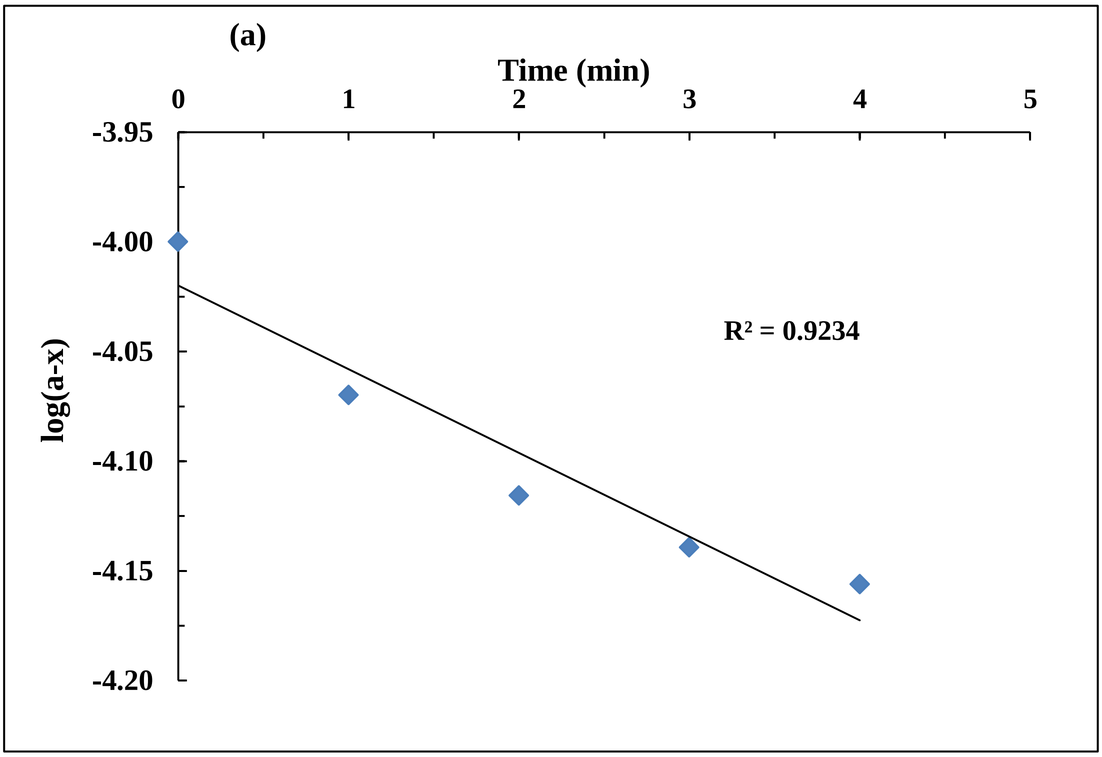


Figure 3.10. Variation of k_2 (pseudo-second-order rate constant) against the concentration of sulfamethoxazole concentration at pH 6.0.

3.2.1.2 Degradation kinetics of ferrate (VI) with respect to sulfamethazine (SMZ)

The presence of sulfamethazine in the degradation of ferrate (VI) is studied. The time dependent reduction of ferrate (VI) at varied concentrations of sulfamethazine (0.02 to 0.2 mM) is carried out at pH 6.0 using the ferrate concentration of 0.1 mM. Further, the rate expression for decomposition of ferrate (VI) is represented in equation (3.5). The pseudo-first order kinetics i.e., log(a-x) *vs* ‘t’(Equation 3.9) and pseudo-second order kinetics i.e., 1/(a-x) *vs* ‘t’ (Equation 3.10) is utilized to plot the rate time dependence degradation of ferrate (VI) in presence of sulfamethazine. This further provides the value of ‘*m*’ which is either 1 or 2 based on kinetic data fittings. The results of the fitted data of pseudo-first order and pseudo-second order equations are shown in Figure 3.11 (a - b) (e.g., for 1:1 molar ratio of ferrate (VI) and sulfamethazine). It is evident from the results that the kinetic data is fitted well to the pseudo-second order equation compared to the pseudo-first order kinetics since the regression coefficient (R^2) values for pseudo-second order kinetics is reasonably high (*Cf* Table 3.6). This implies that the reaction followed pseudo-second order kinetics with respect to each of the sulfamethazine concentration (*Cf* Figure 3.11 (b)), and thus the value of ‘*m*' was obtained as 2. The rate constant values of pseudo-first order and pseudo-second order kinetics at pH 6.0 along with the regression coefficient are shown in table 3.6. It also showed from table 3.6 that the values obtained for pseudo-first order and pseudo-second order rate constant values. It is evident from the table that increasing the concentration of sulfamethazine i.e., from 0.02 to 0.2 mM had caused to increase the rate constant values. Quantitatively, increasing the concentration of sulfamethazine from 0.2 to 0.2 mM; the rate constant was increased from 2.58 x 10^{-2} to 10.82 x 10^{-2} min^{-1} (pseudo-first order) and from 271.2 to 1383.1 $mM^{-1}.min^{-1}$ (pseudo-second order) at pH 6.0.



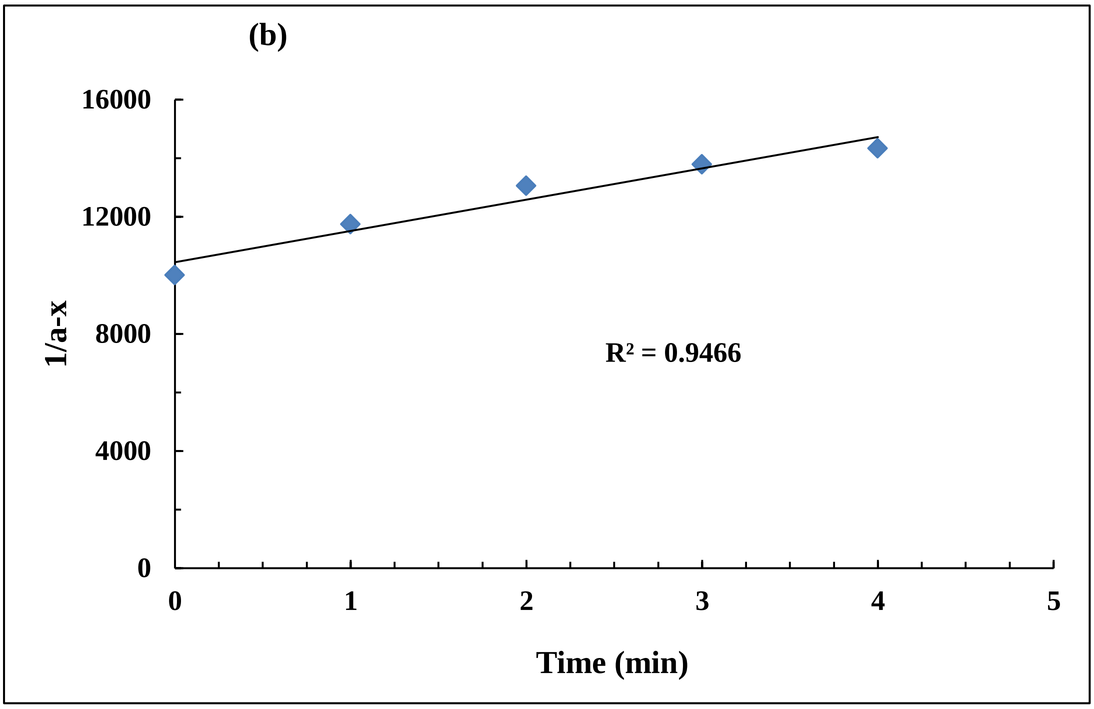


Figure 3.11. Plot of **(a)** log(a-x) vs time ‘t' and **(b)** 1/(a-x) vs time ‘t' in the decomposition of sulfamethazine (SMZ) by Fe(VI) at pH 6.0 ([Fe(VI)]: 0.10 mM; [SMZ]: 0.10 mM.

Table 3.6. Rate constant values of pseudo-first order and pseudo-second order reaction for ferrate(VI) degradation in the presence of sulfamethazine at pH 6.0 [Ferrate (VI) concentration: 0.1 mM].

Concentration of Sulfamethazine (mM)	**Pseudo-first Order Rate Constant (x10^{-2}) (min^{-1})**		**Pseudo-second Order Reaction Rate Constant ($mM^{-1}.min^{-1}$)**	
	k_1	**R^2**	**k_2**	**R^2**
0.02	2.579	0.977	271.18	0.980
0.06	5.919	0.969	670.85	0.979
0.08	7.531	0.953	887.82	0.970
0.10	8.797	0.923	1069.3	0.947
0.15	10.340	0.931	1305.6	0.959
0.20	10.824	0.917	1383.1	0.947

Further, the obtained rate constant (k_2) values of pseudo-second order reaction at various concentrations of sulfamethazine at pH 6.0 are then used to calculate the value of '*n*' along with the apparent value of 'k_{app}'. Figure 3.12 shows a plot of the sulfamethazine concentrations against the calculated value of 'k_2'. It is evident from Figure 3.12 that reasonably a good linear relationship is attained between the concentration of sulfamethazine and the values of k_2. This indicated that the value of 'n' is '1'. Hence, the stoichiometric ratio of ferrate(VI) to sulfamethazine is 2:1. Furthermore, the apparent or overall rate constant k_{app} value is calculated as 6128.0 $(mM)^{-2}.min^{-1}$ with R^2 values of 0.903. Relatively large k_{app} value indicated that the ferrate (VI) is efficient in the degradation of sulfamethazine in aqueous medium (Sailo *et al.*, 2017). It was also reported that the oxidation of sulfonamide antibiotics by ferrate (VI) follows second-order rate law at pH between 6.5 to 10.0 and there species specific rate constant values ranged from $(1.2 \pm 0.1) \times 10^3 - (2.2 \pm 0.2) \times 10^4\ M^{-1}\ s^{-1}$ for $HFeO_4^-$, and from $(1.1 \pm 0.1) \times 10^2$ to $(1.0 \pm 0.1) \times 10^3\ M^{-1}s^{-1}$

for FeO_4^{2-} among which sulfamethizole (SMIZ) and sulfamethoxypyridazine (SMP) possessed highest reactivity towards $HFeO_4^-$ and FeO_4^{2-} respectively. On the other hand, sulfathiazole (STZ) reacted slowly with $HFeO_4^-$ and FeO_4^{2-} (Kim et al., 2015; Feng et al., 2019).

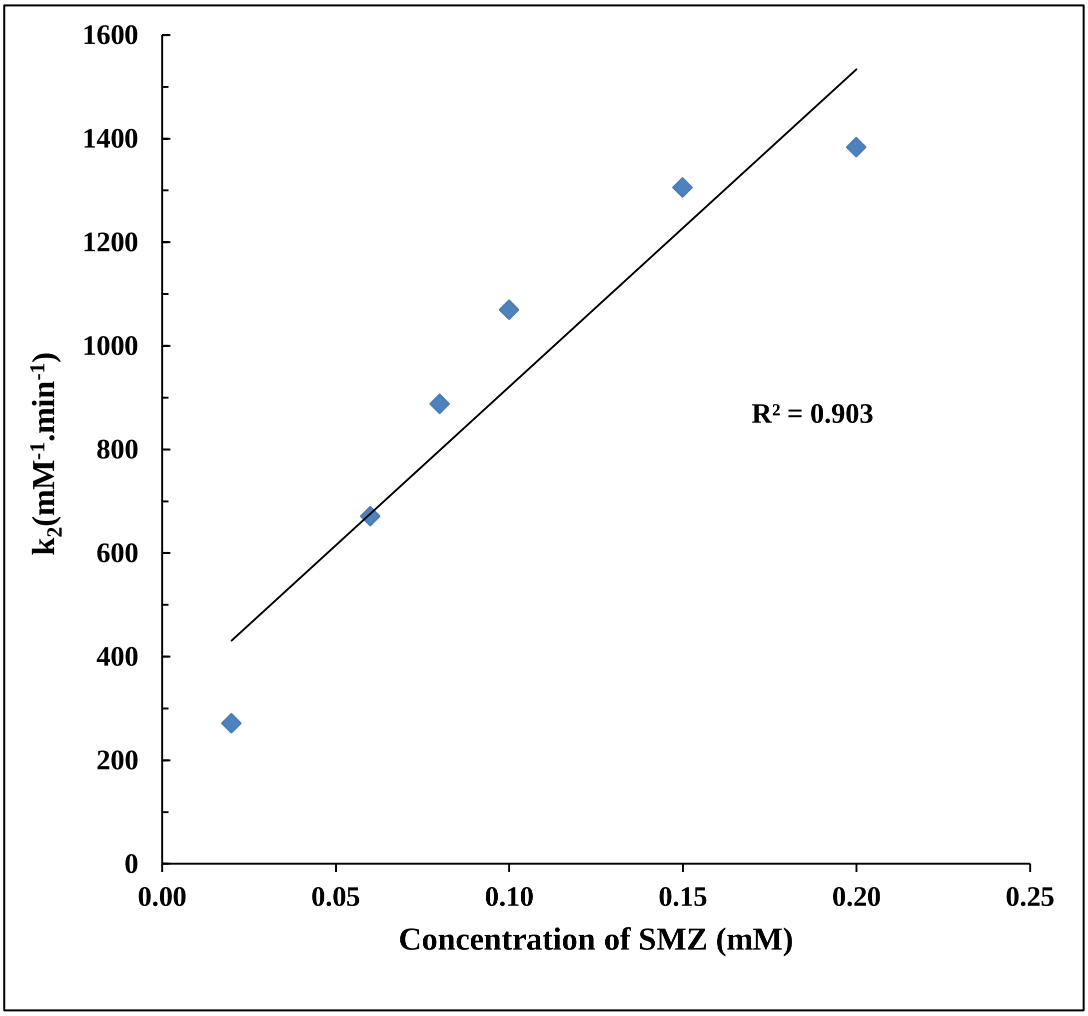


Figure 3.12. Variation of k_2 (pseudo-second-order rate constant) against the concentration of sulfamethazine concentration at pH 6.0 [Ferrate (VI) concentration: 0.1 mM].

3.2.1.3. Degradation kinetics of ferrate (VI) with respect to triclosan (TCS)

The kinetics of triclosan degradation was calculated using the time dependence change in ferrate(VI) concentration data in presence of various concentrations of triclosan (0.02 to 0.5 mM) at pH 10.0 and using the constant concentration of ferrate (VI) of 0.1 mM. The rate expression of ferrate (VI) reduction is shown in equation (3.5). Therefore, in order to optimize the order of reaction at least for the reduction of ferrate (VI) (i.e., *'m'* = 1 or 2); the time dependence change in ferrate (VI) concentration was utilized to plot the pseudo-first order equation (log(a-x) *vs* 't') and pseudo-second order equation (1/(a-x) *vs* 't') (*Cf* Figure 3.13 (a - b)). The fittings of the time dependence data seem to be fitted well with the pseudo-second-order kinetics (Figure 3.13 (b)). These suggest that *'m'* has a value of 2. The optimized values of rate constant of pseudo-first order constants (k_1) and pseudo-second order constants (k_2) at various concentrations of triclosan (0.02 to 0.5 mM) at pH 10.0 are given in table 3.7. It is observed from the Table 3.7 that increasing the triclosan concentrations had caused to increase the rate constant values. Quantitatively, the k_1 values were increased from 5.57 x10^{-2} to 15.25 x10^{-2} min^{-1} and the k_2 values were increased from 648.3 to 2503.2 mM^{-1}.min^{-1} as the concentration of triclosan was raised from 0.02 to 0.5 mM, respectively. Similar, results were obtained for the oxidation of potassium hydrogen phthalate (KHP)) using the ferrate (VI) and the overall rate constant k_{app} was found to be 8.1347 L/mol/min (Tiwari *et al.*, 2017). These results showed that ferrate (VI) is useful oxidizing agent and efficiently oxidizing the recalcitrant in aqueous media.

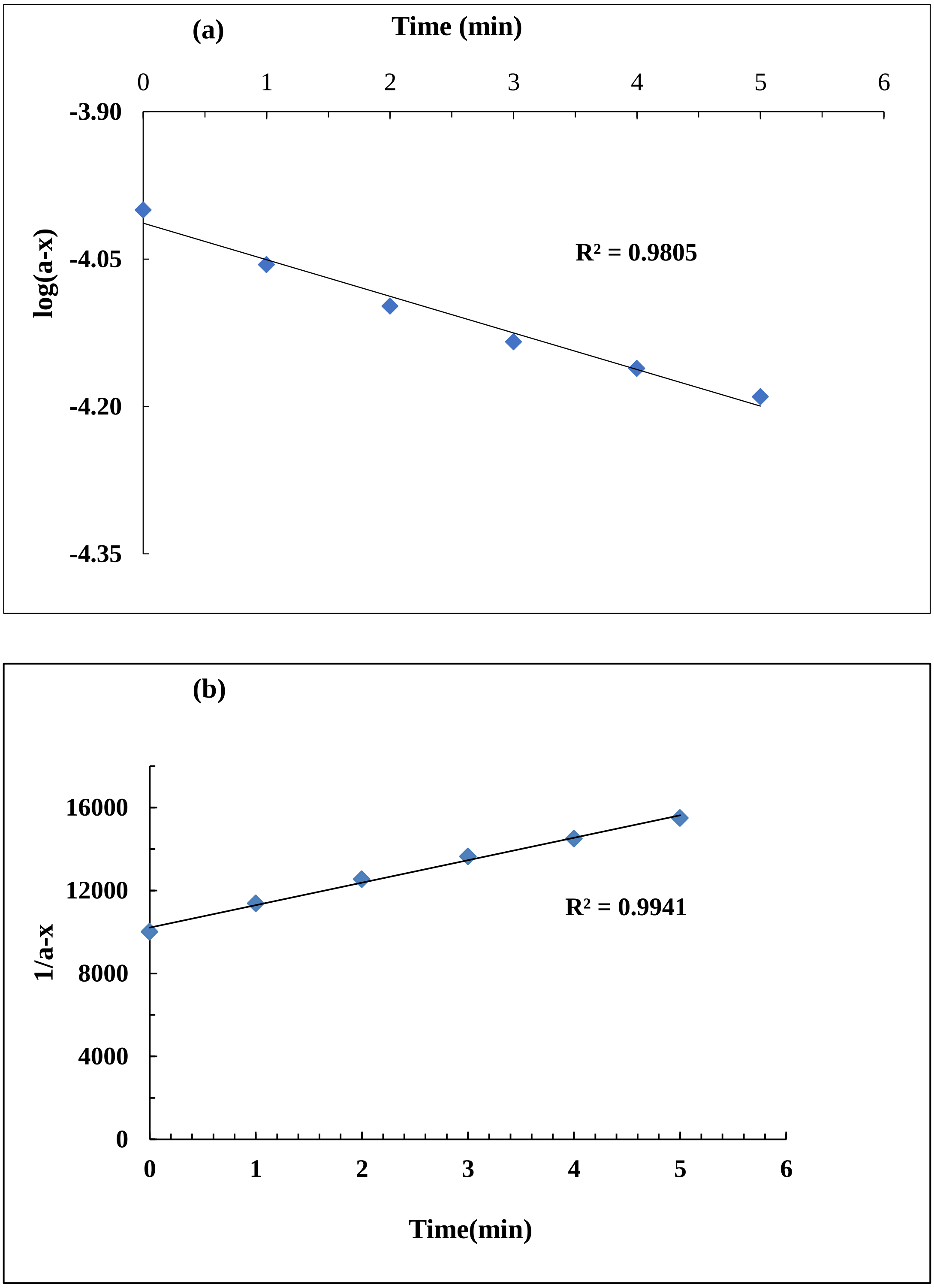


Figure 3.13. Plot of **(a)** log(a-x) vs time ‘t' and **(b)** 1/(a-x) vs time ‘t' in the decomposition of triclosan (TCS) by Fe(VI) at pH 10.0 ([Fe(VI)]: 0.10 mM; [TCS]: 0.10 mM.

Table 3.7. Rate constant values of pseudo-first order and pseudo-second order reaction for ferrate(VI) degradation in the presence of triclosan at pH 10.0 [Ferrate (VI) concentration: 0.1 mM].

Concentration of Triclosan (mM)	**Pseudo-first Order Rate Constant (10^{-2}) (min^{-1})**		**Pseudo-second Order Reaction Rate Constant ($mM^{-1}.min^{-1}$)**	
	k_1	**R^2**	**k_2**	**R^2**
0.02	5.573	0.989	648.31	0.994
0.06	8.291	0.975	1044.2	0.991
0.08	8.014	0.982	1128.3	0.995
0.1	8.567	0.857	1083.8	0.994
0.3	12.689	0.947	1837.1	0.982
0.5	15.246	0.829	2503.2	0.909

Furthermore, the triclosan concentrations and the k_2 values were used to estimate an optimum value of '*n*' along with the 'k_{app}'. Therefore, the graph was plotted between triclosan concentrations against the obtained 'k_2' values and is shown in Figure 3.14. It is evident from the Figure 3.14 that a good linearity is obtained between the rate constant values against the concentration of triclosan. This clearly suggested that '*n'* has a value of '1'. Hence, the possible molar stoichiometry of the ferrate (VI) to triclosan is 2:1. Further, the k_{app} value (apparent rate constant) was obtained to be 3583 $(mM)^{-2}.min^{-1}$. Relatively high value of overall rate constant indicated the potential applicability of ferrate (VI) in the elimination of triclosan from aqueous solutions. Oher studies also revealed that ferrate (VI) was enabled to oxidize the triclosan having an apparent second-order rate equation with rate constant value of 754.7 M^{-1} s^{-1} at pH 7.0. The rate constant of the reaction of $HFeO_4^-$ species with anionic triclosan and neutral triclosan were found to be 6.7(±1.9) × 10^2 and 7.6(±0.6) × 10^3 M^{-1} s^{-1}, respectively (Yang *et al.*, 2011). The oxidation of bisphenol

A and diclofenac sodium by ferrate (VI) followed pseudo-second order kinetics in which the k_{app} values ranged from 8.35×10^2 to 7.62×10^2 L/mol/min (Sailo *et al.*, 2017).

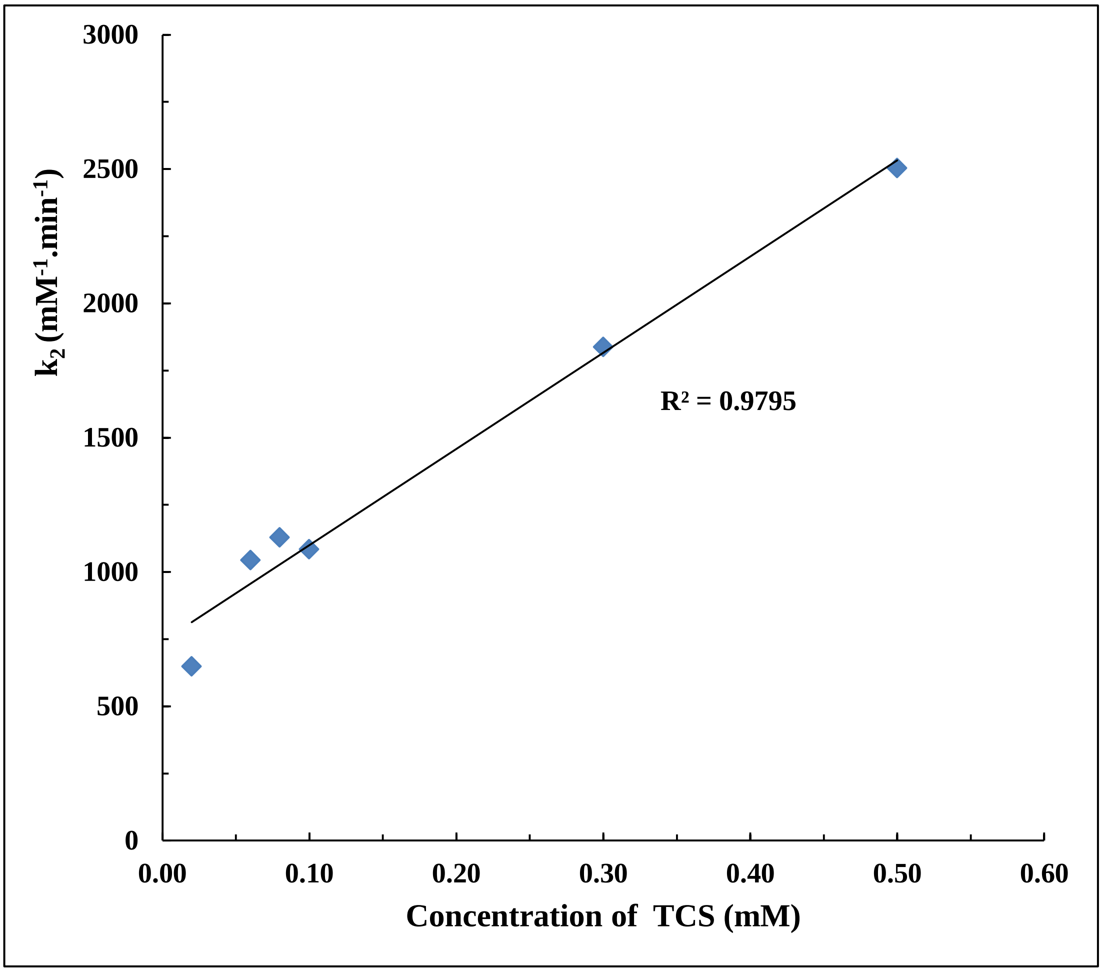
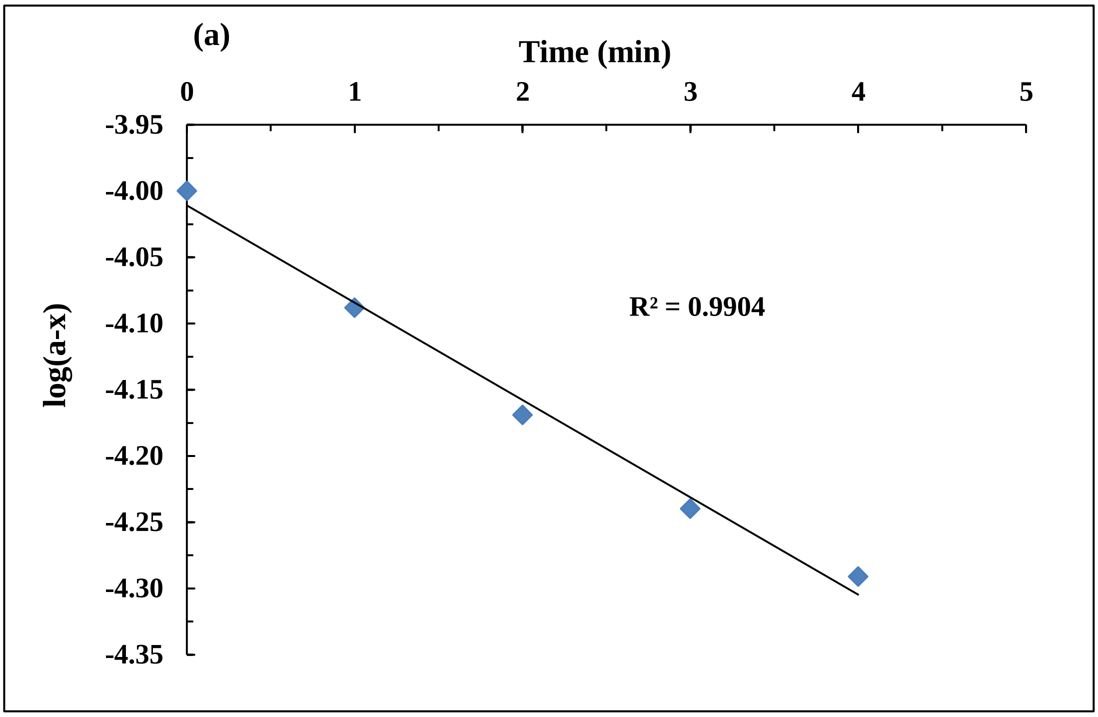


Figure 3.14. Variation of k_2 (pseudo-second-order rate constants) against the concentration of triclosan concentration at pH 10.0 [Ferrate (VI) concentration: 0.1 mM].

3.2.1.4. Degradation kinetics of ferrate (VI) with respect to amoxicillin (AMX)

Further, similar to the previous batch reactor operations, the kinetics of ferrate (VI) reduction with respect to amoxicillin was obtained for the pseudo-first order and pseudo-second order equations at varied concentrations of amoxicillin (0.02 to 0.5 mM) with a fixed dose of ferrate (VI) 0.1 mM and at pH 10.0. The results are graphically illustrated in Figure 3.15 (a - b). The data indicated that the results are well fitted to the pseudo-second order equation which signified that the optimum value of *'m'* is 2 for each amoxicillin concentrations (*Cf* Figure 3.15 (b)). Further, the detailed values of pseudo-first order and pseudo-second order rate constants are evaluated at varied concentrations of amoxicillin and returned in Table 3.8 along with the R^2 values. Table 3.8 clearly showed that increasing the amoxicillin concentration (0.02 to 0.5 mM) had caused to increase the rate constant values of pseudo-first order reaction from 7.14 $x10^{-2}$ to 21.88 $x10^{-2}$ $M^{-1}s^{-1}$ and pseudo-second order reaction from 844.4 to 3626 $mM^{-1}.min^{-1}$, respectively. The similar results were also reported previously in the oxidation of bisphenol A and diclofenac sodium by ferrate (VI) at pH ranging from 7.0 to 12.0 (Sailo *et al*., 2017). High value of overall rate constant in the degradation of pollutants, inferred that ferrate (VI) possesses high oxidizing capacity towards variety of contaminants and therefore rapidly oxidizes the pollutants in aqueous media.



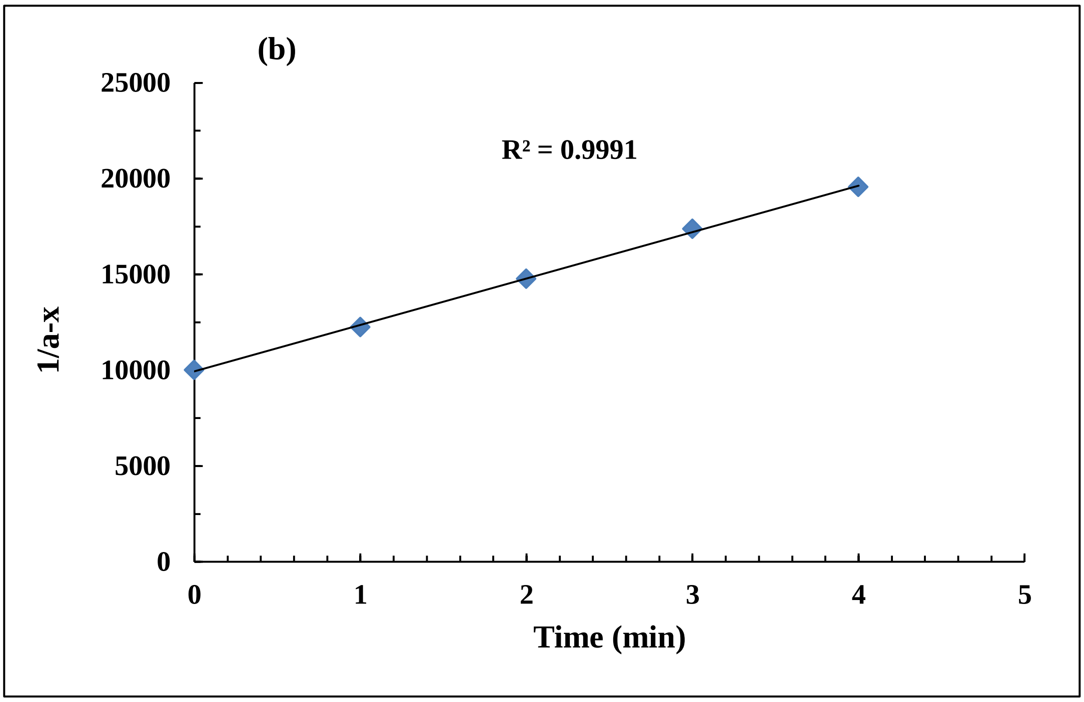


Figure 3.15. Plot of **(a)** log(a-x) vs time ‘t' and **(b)** 1/(a-x) vs time ‘t' in the decomposition of amoxicillin (AMX) by Fe(VI) at pH 10.0 ([Fe(VI)]: 0.10 mM; [AMX]: 0.10 mM.

Table 3.8. Rate constant values of pseudo-first order and pseudo-second order reaction for ferrate(VI) degradation in the presence of amoxicillin at pH 10.0 [Ferrate (VI) concentration: 0.1 mM].

Concentration of Amoxicillin (mM)	**Pseudo-first Order Rate Constant (x10^{-2}) (min^{-1})**		**Pseudo-second Order Reaction Rate Constant (mM^{-1}.min^{-1})**	
	k_1	**R^2**	**k_2**	**R^2**
0.02	7.139	0.994	844	0.998
0.06	8.751	0.970	1048	1.000
0.08	13.127	0.950	1731	0.999
0.1	16.812	0.900	2422	0.999
0.3	18.733	0.976	2632	0.996
0.5	21.879	0.969	3626	0.997

Moreover, the rate constant values of the pseudo-second order reactions evaluated at varied concentrations of amoxicillin were used for obtaining an optimum value of *'n'*. A graph is plotted between the amoxicillin concentrations and the rate constant values (k_2) of pseudo-second order reaction (*Cf* Figure 3.16). A reasonable linear relationship was obtained between the k_2 and amoxicillin concentrations, which further indicated the optimum value of '*n*' is 1. Therefore, this clearly confirmed the possible stoichiometry of ferrate (VI) to amoxicillin is 2:1. Moreover, the value of k_{app} was obtained from the slope of line (*Cf* figure 3.8) and was found to be 5137.0 (mM)$^{-2}$.min^{-1} having the regression coefficient (R^2) value of 0.8278. This high value of overall rate constant implies the potential of ferrate (VI) in the elimination of pollutants from aqueous solutions. Another study also showed that ferrate (VI) when interacted with β-lactum antibiotics exhibited second-order rate law at pH ranging from 6.0 to 9.5 and the 'k_{app}' values are found to be 418 M^{-1}s^{-1} (ampicillin), 116 M^{-1}s^{-1} (cloxacillin) 114 M^{-1}s^{-1} (penicillin G), 418 M^{-1}s^{-1} (amoxicillin) and 686 M^{-1}s^{-1} (cephalexin) (Karlesa *et al.*, 2014).

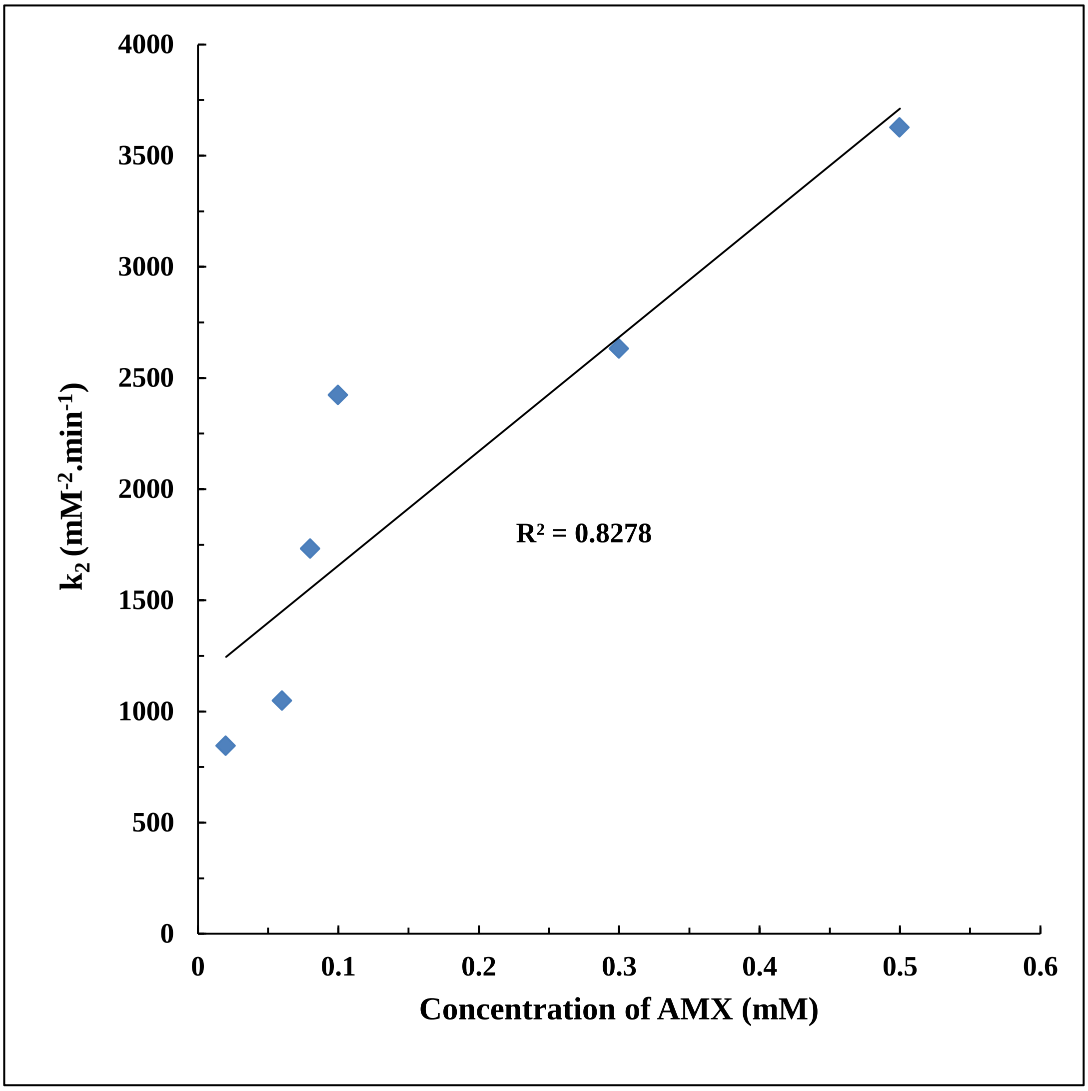


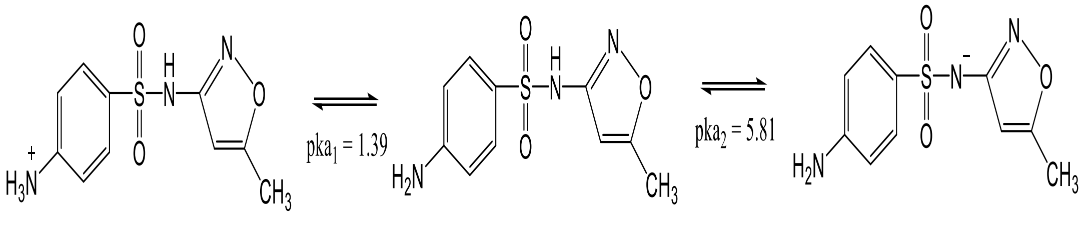
Figure 3.16. Variation of k_2 (pseudo-second-order rate constant) against the concentration of amoxicillin concentration at pH 10.0 [Ferrate (VI) concentration: 0.1 mM].

3.3. Speciation studies

The species of micropollutants are greatly varied with the solution pH which is based on the acid dissociation constants of micropollutants. Moreover, the species played a significant role in the degradation mechanism of these pollutants. Therefore, the species distribution of these micropollutants are extensively studied using the known acid dissociations constants of these micropollutants.

3.3.1. Speciation of sulfamethoxazole

The acid dissociation constant values (pk$_a$ values) influence the species distribution of sulfamethoxazole at different pH levels. The pk$_{a1}$ and pk$_{a2}$ values of sulfamethoxazole are 1.39 and 5.81, respectively (Simon *et al*, 2011). Therefore, the sulfamethoxazole possessed with three species as SMX, SMX^{-1} and SMX^{2-}. Further, using the known pK$_a$ values the speciation studies are conducted and the results are presented graphically in Figure 3.17. The figure exhibited that sulfamethoxazole is mainly comprised of anionic species (SMX$^-$ or SMX^{2-}) with a wide pH range i.e., pH 2.6 to 10.0. Moreover, pH ≥ 5.81 is mostly contained with SMX^{2-} di-ionic species. The neutral species of sulfamethoxazole is dominant only pH ≤ 1.39. The acid-base equilibria of SMX is shown below (Avisar *et al.*, 2010):



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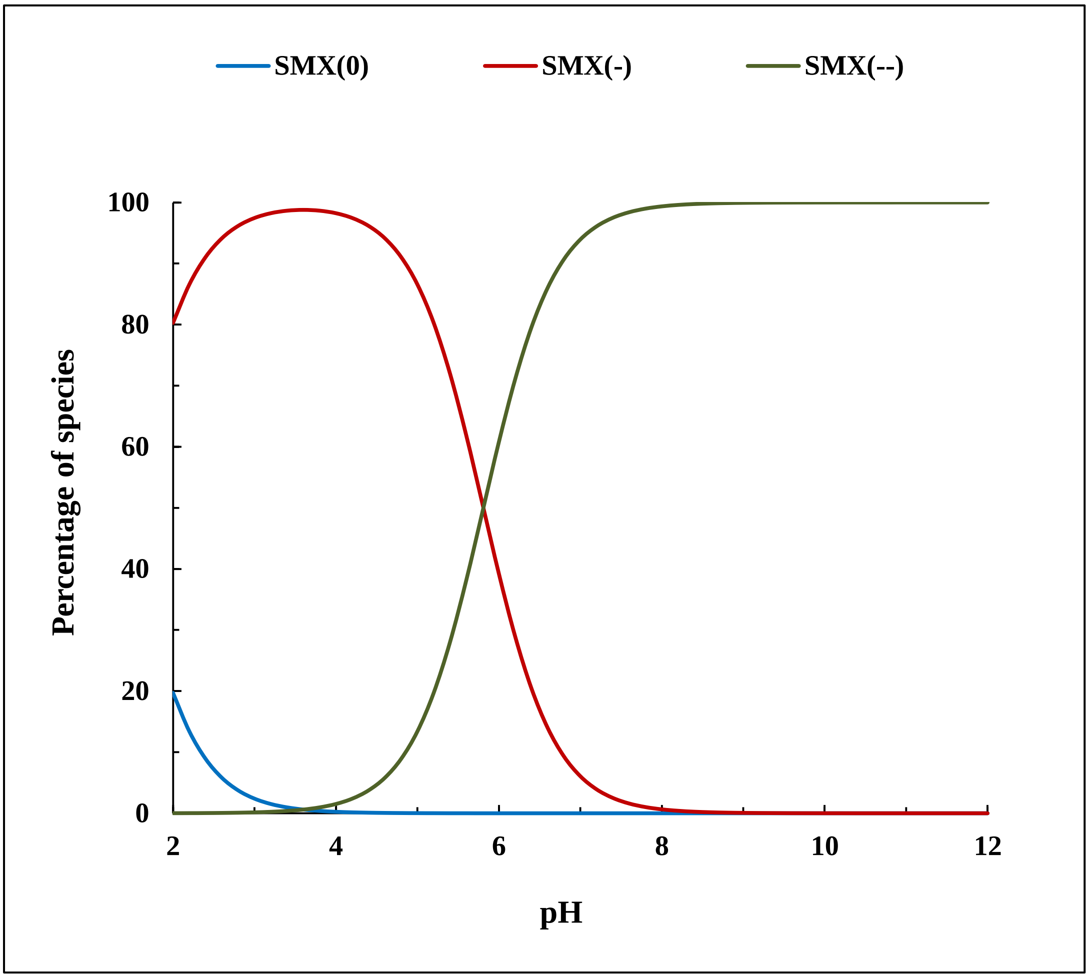
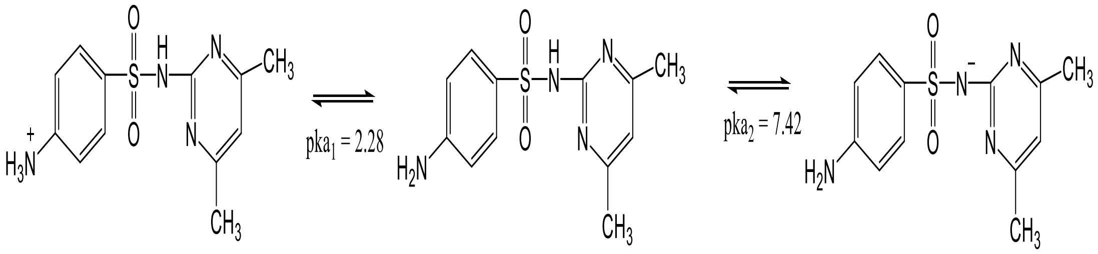


Figure 3.17. Distribution of various species of sulfamethoxazole (SMX) as a function of pH.

3.1.3.2. Speciation of sulfamethazine

The species distribution of sulfamethazine (SMZ) at various pH is obtained utilizing the acid dissociation constant values (pk_a) sulfamethazine. The pk_{a1} and pk_{a2} values of SMZ are 2.28 and 7.42, respectively (Liu et al., 2017). The species distribution of SMZ are obtained at various pH values and illustrated in *Cf* Figure 3.18. It is observed that SMZ exists as neutral species at pH ≤ 2.28. Moreover, the anionic species of (SMZ$^-$) is dominated within a pH range of 3.0 to 7.0. Further, the di-ionic species of sulfamethazine (SMZ^{2-}) is dominated at pH ≥ 8.0. The acid-base equilibria of SMZ is shown below (Wegst-Uhrich *et al.,* 2014):



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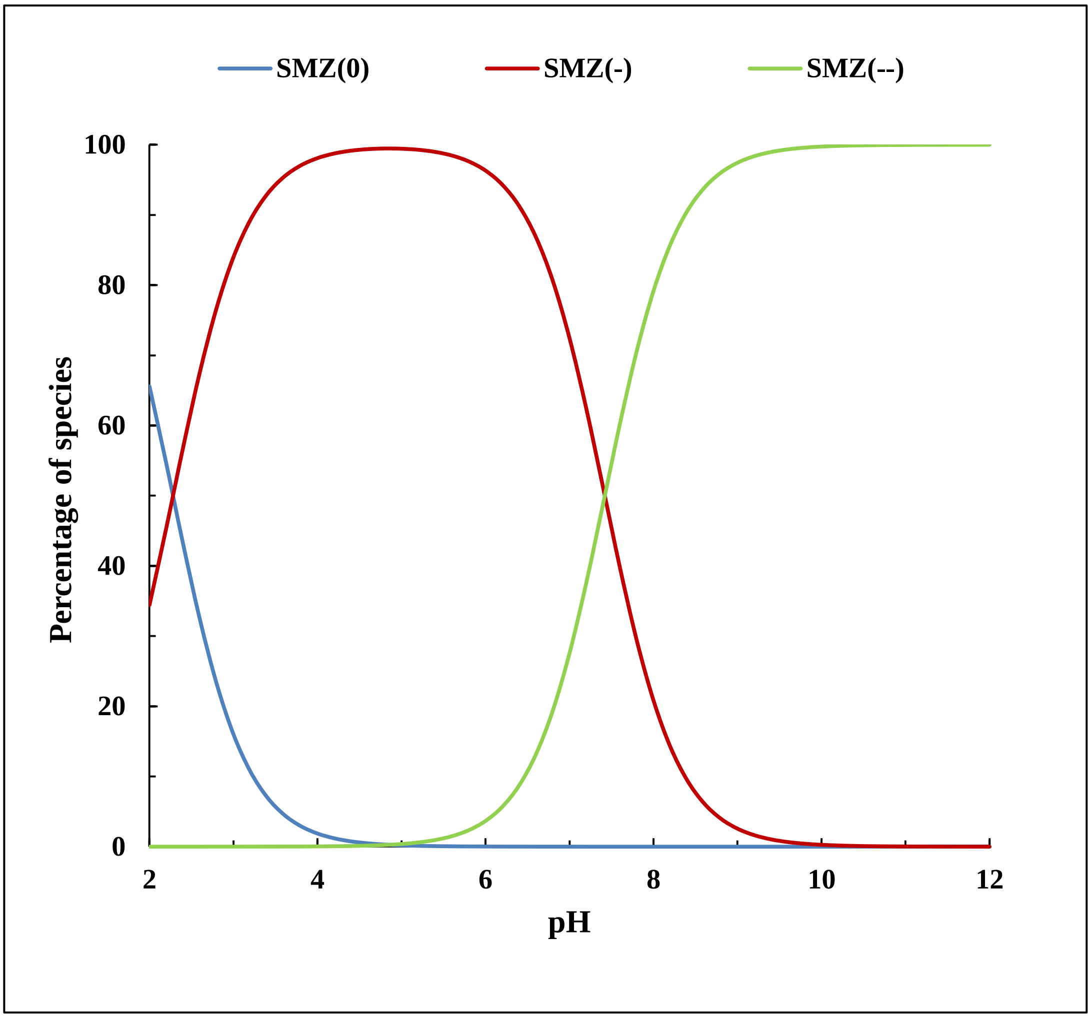
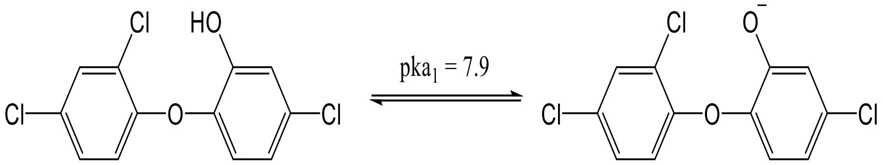


Figure 3.18. Distribution of various species of sulfamethazine (SMZ) as a function of pH.

3.1.3.3. Speciation of triclosan

Triclosan (TCS) is a monoprotic acid having the pk_{a1} value of 7.9 (Solá-Gutiérrez *et al.*, 2020). Further, using the pk_{a1} value, the species distribution of triclosan is obtained and the results are shown in Figure 3.19. Figure clearly demonstrated that TCS is mainly consisting of neutral species (TCS^0) at pH ≤ 7.9. However, increasing the pH>7.9, it turned to the anionic species (TCS^-). The below equation gives the acid-base equilibria of triclosan (Rowett *et al.*, 2016):



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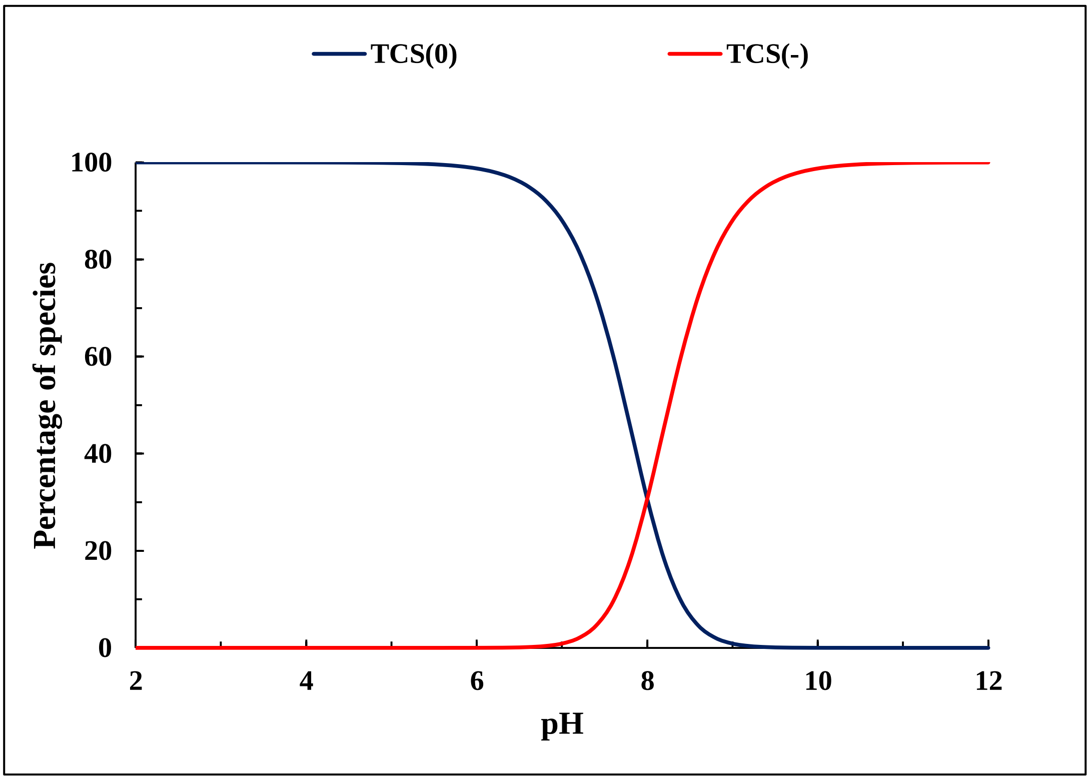
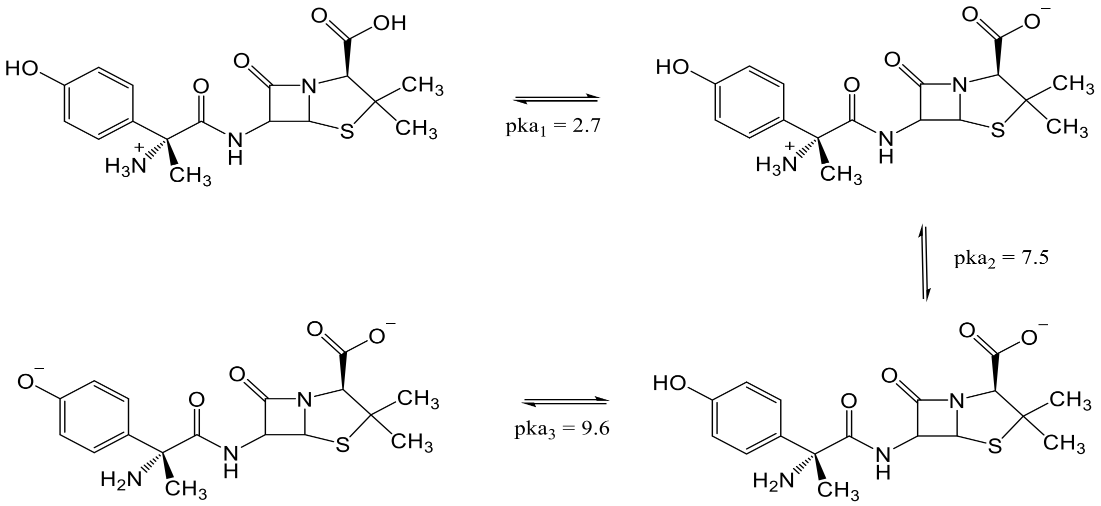


Figure 3.19. Species distribution of triclosan (TCS) as a function of pH

3.1.3.4. Speciation of amoxicillin

The amoxicillin (AMX) is having three pk_a values i.e., pk_{a1}, pk_{a2} and pk_{a3} as 7.0, 7.5 and 9.6 respectively (Çağlar Yılmaz *et al.*, 2020). Various species of amoxicillin are obtained at different values of pH and results are shown in Figure 3.20. The figure demonstrated that at pH $\leq$ 2.7 the AMX exits as neutral species. However, within the pH region 2.7 - 7.5, the amoxicillin exists as anionic species $(AMX)^-$, and in between pH 7.5 to 9.6, it exists the di-ionic species of AMX^{2-}. Further increasing the pH (pH $\geq$ pH 9.6), the AMX is dominated with the species AMX^{3-}. The acid-base equilibria of AMX is demonstrated below (Elmolla & Chaudhuri, 2010):



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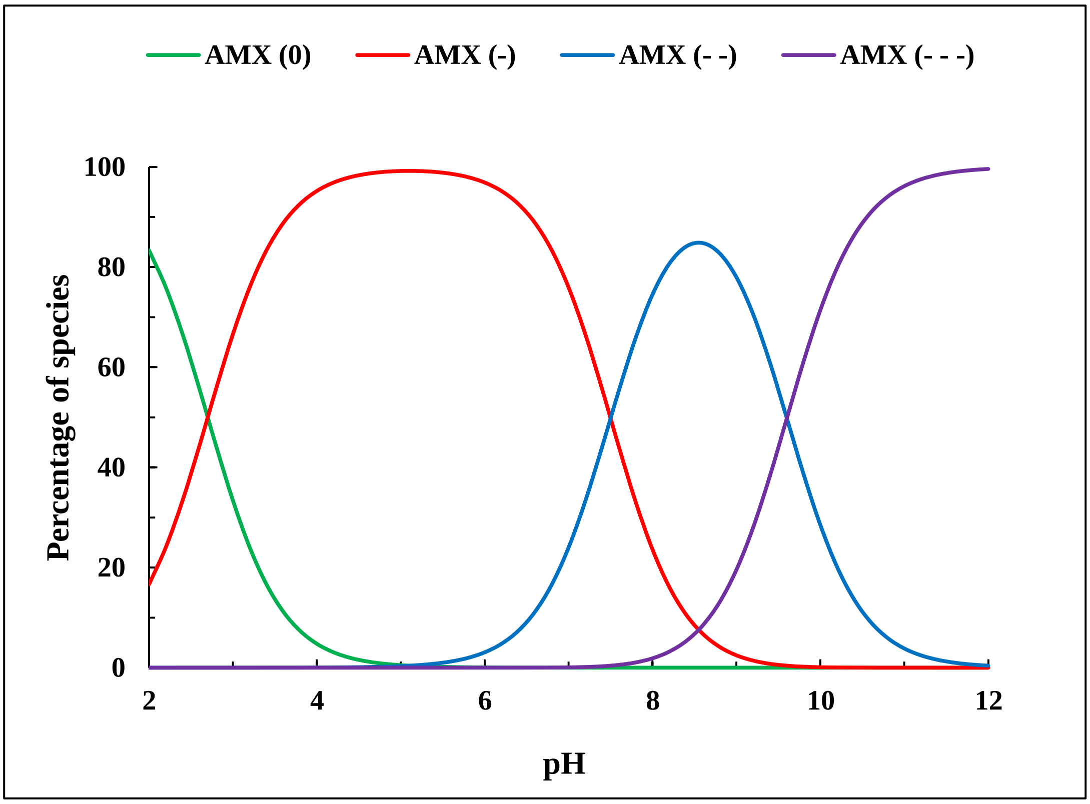


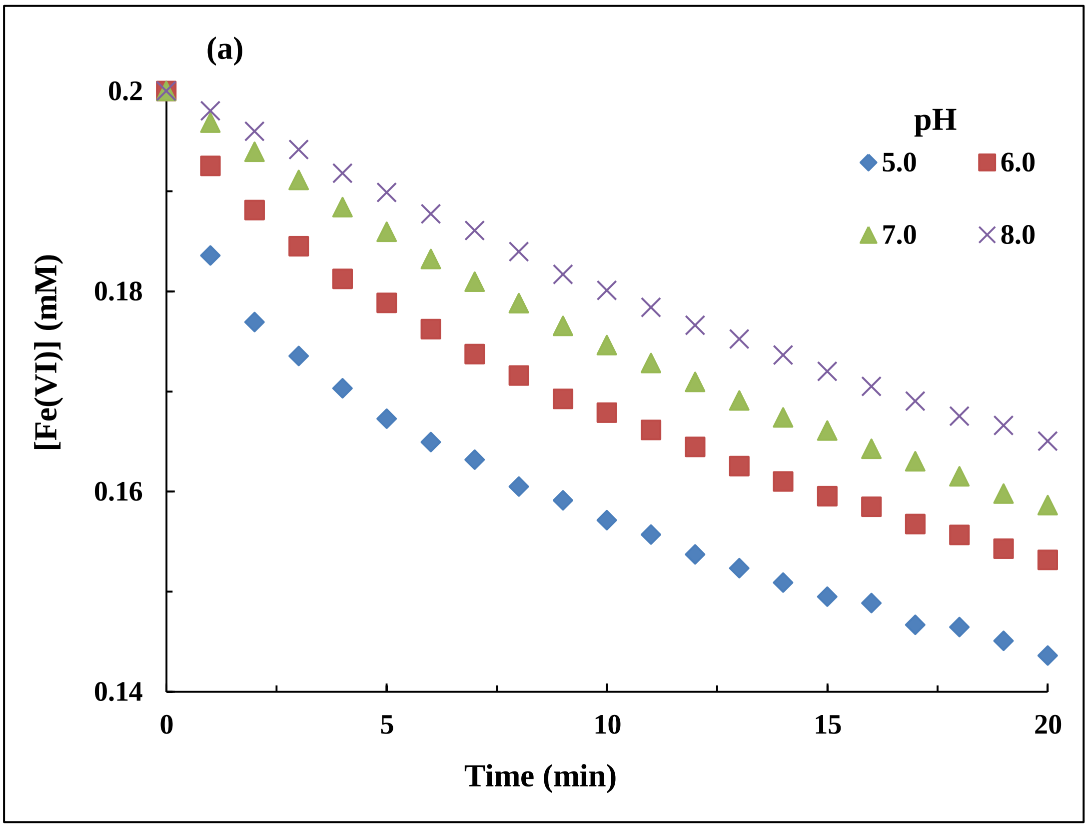
Figure 3.20. Distribution of various species of amoxicillin (AMX) as a function of pH.

3.4. Effect of pH in the Oxidative Degradation of Micropollutants

3.4.1. Sulfamethoxazole removal

The pH of the solution is an important parameter that affects significantly the degradation of sulfamethoxazole in aqueous solutions. It provides the insights of the reaction mechanism which is involved in the degradation process. The elimination of ferrate (VI) in presence of sulfamethoxazole is carried out at varied pH values. 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 (VI) and sulfamethoxazole concentrations were taken as 0.20 and 0.10 mM, respectively. The elimination of ferrate (VI) as a function of time at different pH values are shown in Figure 3.21(a). It is evident from the Figure 3.21(a) that very rapid elimination of ferrate (VI) was occurred at lower pH value i.e., pH 5.0 which was gradually slowed down with increase in pH (from 5.0 to 8.0). Quantitatively, the amount of ferrate (VI) was decreased from 0.20 mM to 0.14 mM in just 20 mins of contact at pH 5.0. However, at pH 8.0 the ferrate (VI) concentration was reduced from 0.20 mM to 0.16 mM in 20 mins of contact. This inferred clearly that the degradation of pollutant is seemingly high at lower pH values.

Further, the removal of sulfamethoxazole was obtained with the HPLC data obtained at various pH values i.e., pH 5.0 to 8.0. The area of the ferrate (VI) treated samples and the blank samples of sulfamethoxazole were obtained in the HPLC measurements. Hence, the percentage removal of sulfamethoxazole as a function of solution pH was obtained and illustrated in Table 3.9 and Figure 3.21(b). It is evident from Table 3.9 that the percentage removal of sulfamethoxazole was decreased with an increase in pH. Quantitatively, with the decrease in pH from pH 8.0 to 5.0, the percentage elimination of sulfamethoxazole was increased from 34.7% to 39.7%. These results can be explained with the species distribution and reactivity of ferrate (VI) species at various pH values. The previous studies indicated that the protonated species of ferrate (VI) i.e., $HFeO_4^-$ are predominated at pH ~5.0 (Tiwari *et al*., 2008). Moreover, the spin density of the protonated species is higher than deprotonated form of ferrate (VI) i.e., FeO_4^{2-}. Hence, the species $HFeO_4^-$ possesses high reactivity towards the oxidation of sulfamethoxazole (Rush *et al*., 1996; Sharma *et al*., 2006a; Shiota *et al*., 2003; Yang *et al*., 2010). Further, sulfamethoxazole which is a diprotic acid having pk_a values 1.39 and 5.81. As the speciation studies conducted separately showed that pH >5.7, the anionic species of SMX were dominated, and ferrate (VI) also existed in its anionic form. The reactivity of ferrate (VI) is relatively less at higher pH values hence, caused for decrease in oxidation of sulfamethoxazole. Moreover, the rate of spontaneous decomposition of ferrate (VI) increases with decrease in pH (Rush *et al*., 1996). Additionally, the radical character of ferrate (VI) i.e., $Fe^{+6}= O \leftrightarrow Fe^{+5}-O^{\cdot}$ stabilizes the protons which 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 the possible ferrate (VI) reactivity towards 3,5-dimethylisoxazole and 4-aminophenyl methyl (Sharma *et al*., 2006b). Furthermore, alkyl groups are known to be an electron-donating group, which increases the reactivity of $HFeO_4^-$ in aqueous solutions. Similarly, the redox potential of ferrate (VI) increases with decrease in pH, enhancing the reactivity of ferrate (VI) at lower pH values (Sharma, 2013).



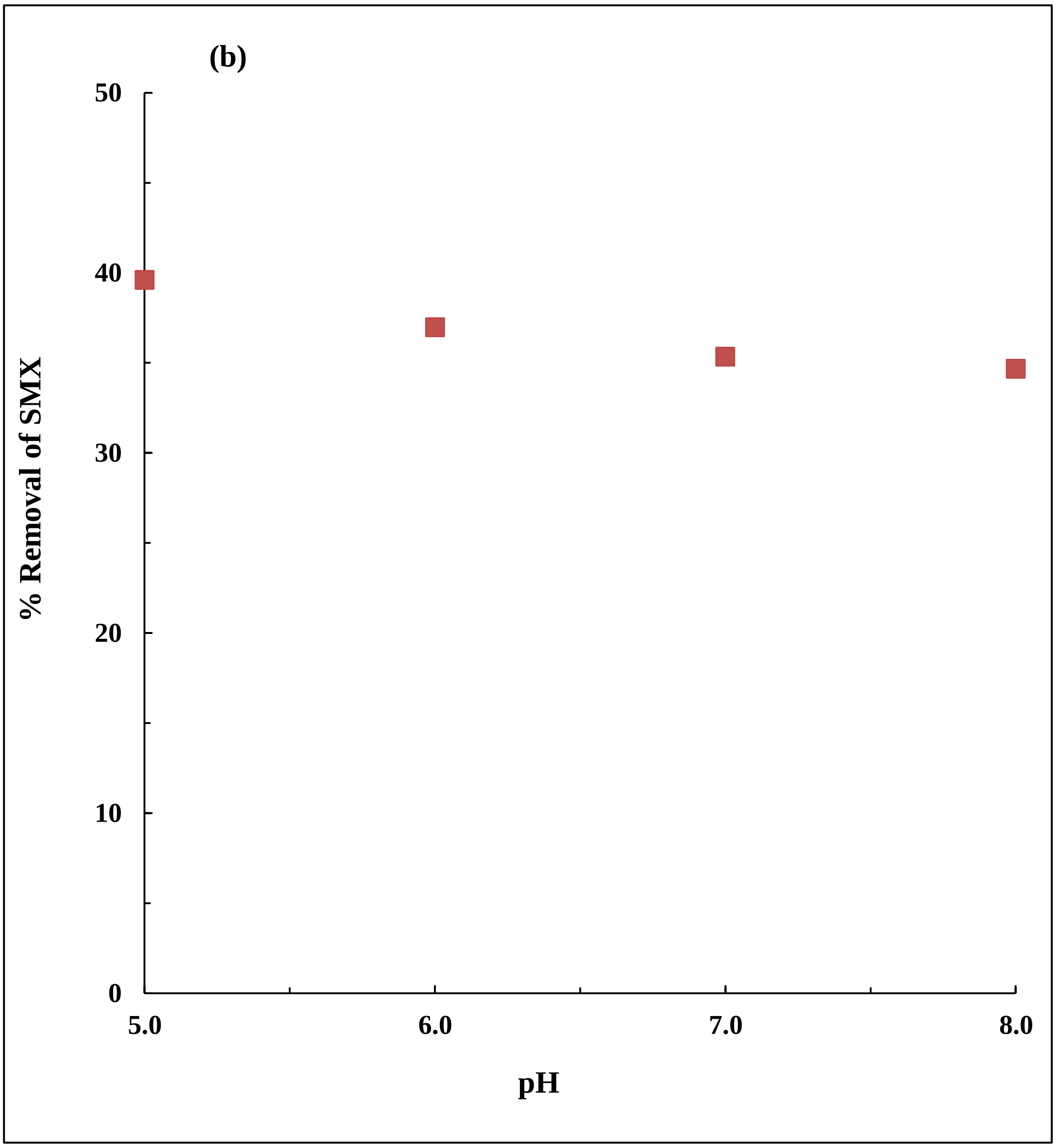


Figure 3.21. (a) Elimination of ferrate (VI) as a function of time and at different pH values ([Fe(VI): 0.20 mM; [SMX]: 0.10 mM); **(b)** Percentage removal of SMX with respect to pH at a fixed concentration of SMX i.e., 0.1 mM([Fe(VI)]:[SMX] = 2:1).

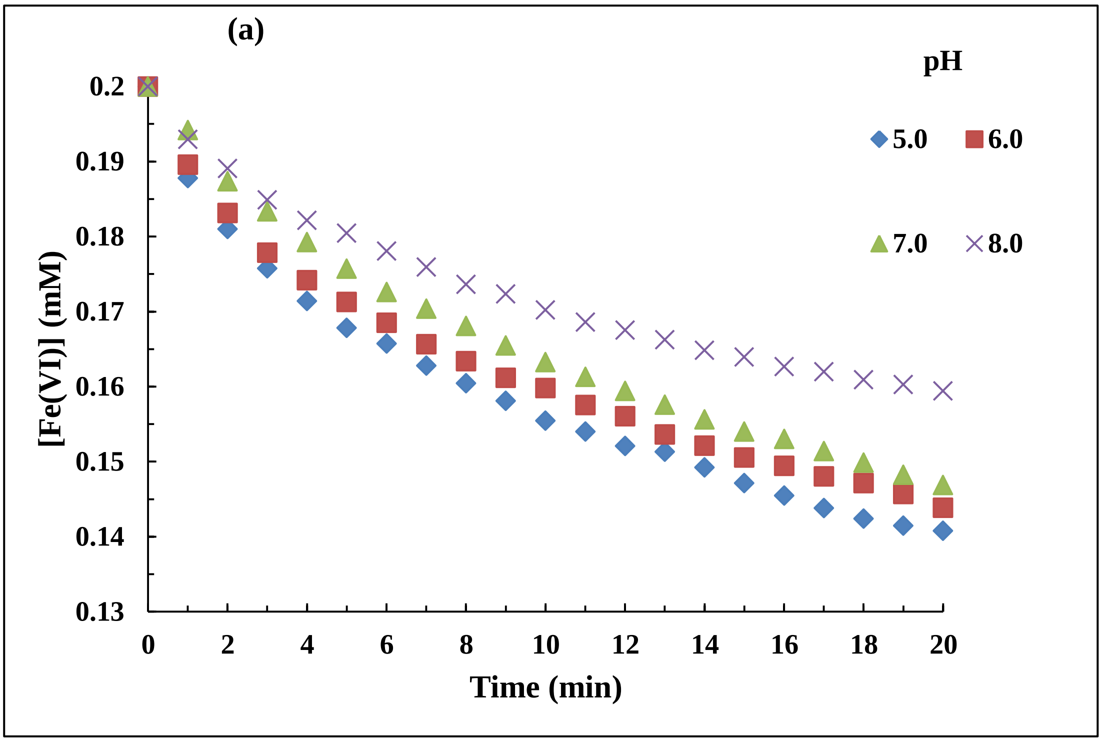
Table 3.9. Percent removal of sulfamethoxazole by ferrate (VI) with respect to pH at a fixed concentration of 0.1 mmol/L (HPLC measurments).

pH	**Retention Time (min)**	**Area (µV*sec)**		**% Removal of sulfamethoxazole**
		Blank sample	**Treated sample**	
5.0	4.7	3335490	2014342	39.6
6.0	4.7	3353163	2113165	36.9
7.0	4.7	3514338	2272371	35.3
8.0	4.7	3388727	2213541	34.6

3.4.2. Sulfamethazine removal

The pH dependent degradation of sulfamethazine by ferrate (VI) was studied since this provides possible mechanism of oxidation process involved with ferrate (VI)-mediated pollutant degradation (Tiwari *et al.*, 2006). Moreover, it is important to optimize the optimal pH for degradation of pollutants in aqueous media. The pH dependence studies are conducted using the ferrate (VI) and sulfamethazine molar ratio of 2:1. Therefore, a fixed dose of ferrate (VI) concentration (0.2 mM) is employed for degrading the sulfamethazine having concentration of 0.1 mM and solution pH is varied from pH 5.0 to 8.0. The degradation efficacy of ferrate (VI) in presence of sulfamethazine at various pH is shown as in Figure 3.22 (a). It is observed that the degradation of ferrate (VI) in presence of sulfamethazine is greatly favored as the solution pH is increased. The degradation of ferrate (VI) is relatively slower at pH 8.0; however, at pH 5.0, the concentration of ferrate (VI) was reduced from 0.2 to 0.14 mM within just 20 min of contact.

The degradation of sulfamethazine is further investigated by obtaining the percentage removal of sulfamethazine using the HPLC measurements. The area of ferrate (VI) treated sulfamethazine samples and untreated/blank samples of sulfamethazine were obtained and hence, the percentage removal of sulfamethazine was obtained and shown in Table 3.10 and Figure 3.22 (b). Table 3.10 showed that the sulfamethazine removal efficiency was increased from 41.2% to 51.3% while the solution pH is decreased from 8.0 to 5.0. This is mainly because; ferrate (VI) is predominantly present in its pronated species $HFeO_4^-$ form at neutral to acidic pH values. However, the deprotonated species FeO_4^{2-} is predominant in basic medium (Shiota *et al*., 2003). On the other hand, the speciation studies of SMZ showed that (*Cf* Figure 3.18) the fully dissociated anionic species $(SMZ)^{2-}$ is predominant at pH 8.0. The dissociated molecule of SMZ is relatively stable in aqueous media and hindered the degradation of SMZ. However, at lower pH values, the protonated species of ferrate (VI) was highly reactive and caused for the enhanced removal of SMZ. Moreover, the protonated species of ferrate (VI) possessed with high spin density compared to the deprotonated species, which increases its oxidizing capability. Hence, this enabled to enhance the degradation of SMZ at lower pH values. It was further assumed that the degradation of sulfamethazine was occurred through the cleavage of C–S and S–N bonds in sulfamethazine due to hydroxylation by ferrate (VI). Moreover, degradation is likely to occur with the oxidation of aniline moiety (NH_2 substituent) of sulfamethazine by ferrate (VI) species of $HFeO_4^-$ (Sun *et al*., 2018).



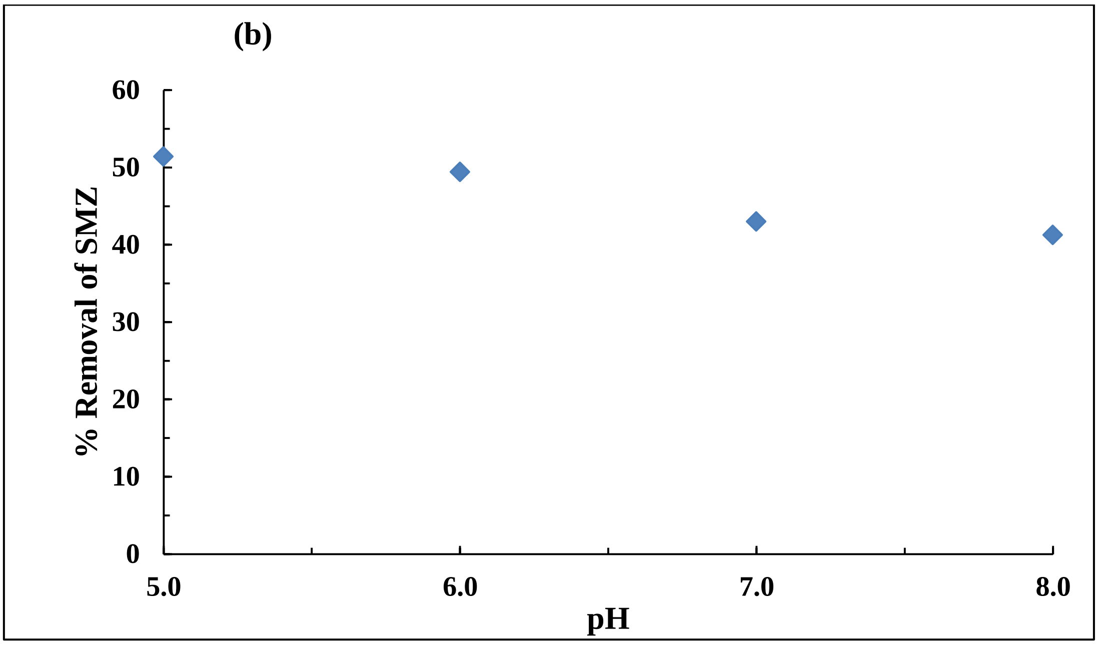


Figure 3.22. (a) Degradation of ferrate (VI) concentration (0.2 mM) as a function of pH at constant concentration of SMZ (0.1 mM) **(b)** Percentage removal of SMZ as a function of pH; [SMZ]: 0.1mM, [Fe(VI)]: 0.2 mM.

Table 3.10. Percent removal of sulfamethazine by ferrate (VI) with respect to pH at a fixed concentration of 0.1 mM (HPLC measurements).

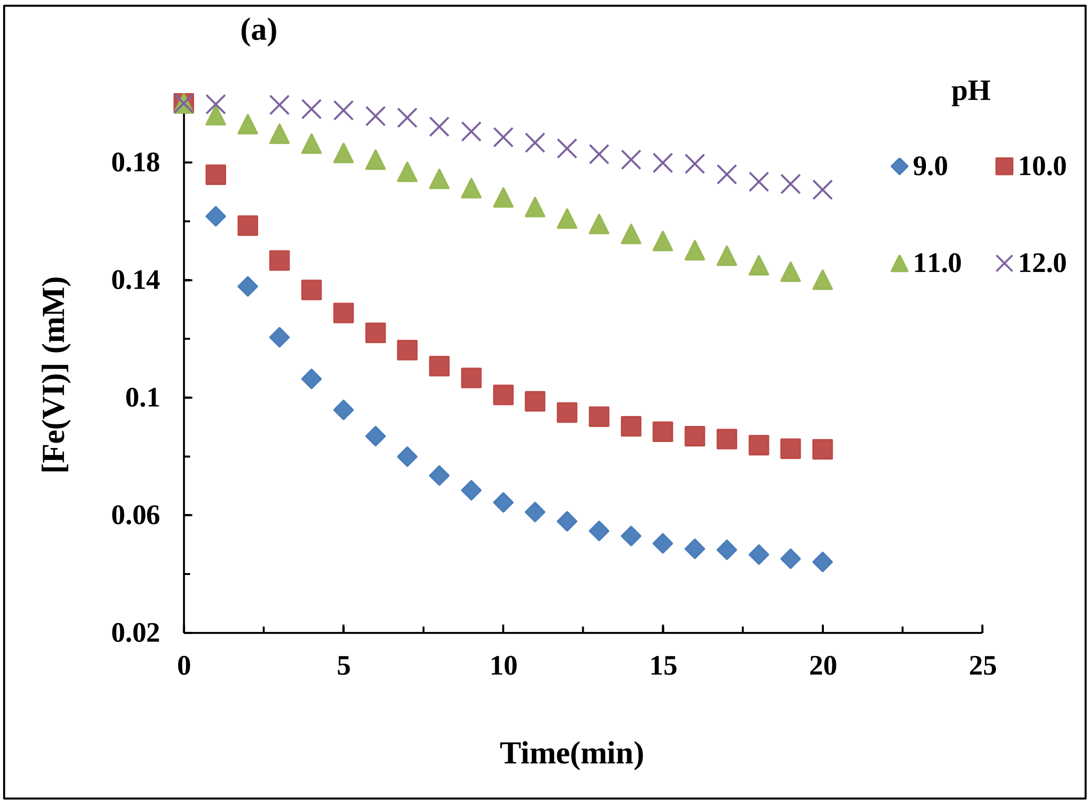
pH	Retention Time (min)	Area (µV*sec)		% Removal of sulfamethazine
		Blank sample	**Treated sample**	
5.0	3.7	2109728	1025758	51.3
6.0	3.7	2225217	1126416	49.3
7.0	3.7	2123813	1211042	42.9
8.0	3.7	2173433	1277357	41.2

3.4.3. Triclosan removal

The effect of pH was studied between pH 9.0 to 12.0 for triclosan having a ferrate (VI) dose of 0.2 mM and triclosan concentrations of 0.1 mM. The degradation of ferrate (VI) as a function of time with respect to pH is obtained and shown in Figure 3.23 (a). It is evident from the Figure 3.23 (a) that lowering the pH greatly favored the removal of ferrate (VI) which apparently favored the elimination of triclosan. More quantitatively, the ferrate (VI) concentration is removed from 0.1 mM to 0.021 mM at pH 9.0.

Further, the removal efficiency of triclosan by ferrate (VI) is obtained by measuring the area of both the ferrate (VI) treated and untreated samples of triclosan using HPLC measurements. Hence, the percentage removal of triclosan is obtained and shown in Table 3.11 and Figure 3.23 (b). It is evident from the Table 3.11 that lowering the pH from 12.0 to 9.0 had caused to increase the removal of triclosan from 22.7% to 93.1%, respectively. The results indicated that ferrate (VI) is potential oxidant and enabled to remove very high percentage of triclosan from aqueous solutions.

Further, the results indicated that increase of solution pH has caused to hinder the removal of triclosan which is due to the fact that the reactivity of ferrate (VI) is decreased significantly at higher pH values. Moreover, the protonated species of ferrate (VI) is more reactive and oxidizes readily the pollutant at lower pH conditions (Pachuau *et al.*, 2013; Sharma 2002). It was reported previously 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 (Chen *et al.*, 2018). Similar compounds like chlorophene (2-benzyl-4-chlorophenol) was degraded by ferrate (VI) such that the presence of chlorine and benzyl groups in the benzene ring are shown to increase the reactivity of phenolic compound against ferrate (VI) (Chen *et al.*, 2019; Yang *et al.*, 2011).



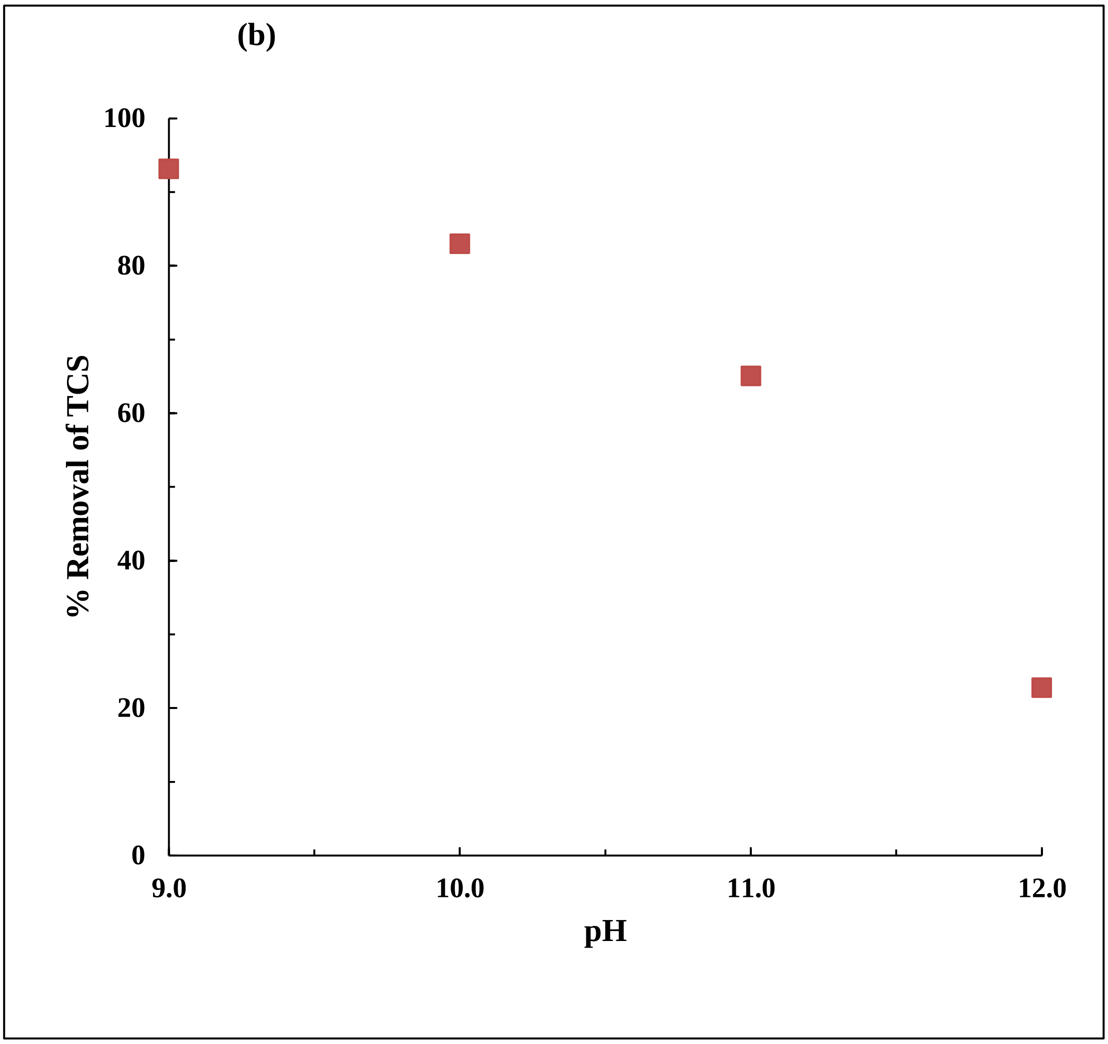


Figure 3.23 (a) Extent removal of ferrate (VI) with respect to time in presence of triclosan and **(b)** percentage removal of triclosan as a function of pH ([Triclosan]: 0.1 mM and [Fe(VI)]: 0.2 mM).

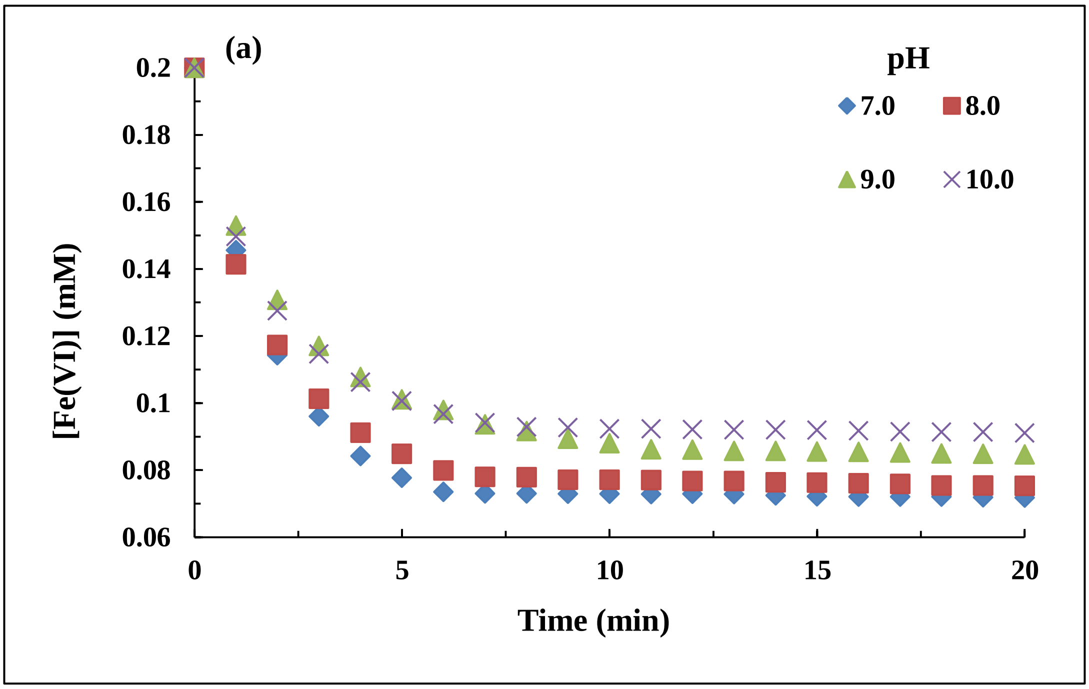
Table 3.11. Percent removal of triclosan by ferrate(VI) with respect to pH at a fixed concentration of 0.1 mM (HPLC measurements).

pH	Retention time (min)	Area (µV*sec)		% Removal of triclosan
		Blank sample	Treated sample	
9	3.8	2820	194	93.1
10	3.8	3046	520	82.9
11	3.8	1950	682	65.0
12	3.8	1752	1354	22.7

3.4.4. Amoxicillin removal

The effect of pH was studied between pH 7.0 to 10.0 for amoxicillin having a ferrate dose of 0.2 mM and amoxicillin concentrations of 0.1 mM. The degradation of ferrate (VI) in presence of amoxicillin as a function of time and pH is obtained and shown in Figure 3.24 (a). It was observed that lowering the pH greatly favored the removal of ferrate (VI) which apparently favored the elimination of amoxicillin. More quantitatively, with decrease in pH, the degradation of ferrate (VI) in presence of amoxicillin increased and at pH 7.0, it was observed that the concentration of ferrate (VI) was decreased from 0. 20 to 0.07 mM at ferrate (VI) to AMX molar ratio of 2:1.

Further, the removal percentage of amoxicillin was analyzed by using HPLC measurements. It was observed that on increasing the pH from 7.0 to 10.0, the percent removal of amoxicillin was decreased (*Cf* Table 3.12 and Figure 3.24 (b)). Quantitatively, lowering the pH from 10.0 to 7.0 caused to increase the percentage removal of amoxicillin from 85.9 to 96.9%, respectively. Similarly, the concentration of amoxicillin was removed from 0.10 to 0.07 mM at pH 7.0. The decrease in removal with increase in pH is due to the fact that at higher pH, AMX exists as anions either in the form of $(AMX)^{2-}$ or $(AMX)^{3-}$ (*Cf* Figure 3.12), which is relatively stable species and ferrate (VI) also possessed with reduced reactivity at higher pH values. This caused for relatively degradation of amoxicillin at pH 10.0. However, at lower pH values i.e., pH 7.0, the highly reactive protonated species of ferrate (VI) ($HFeO_4^-$) caused to enhance the elimination of amoxicillin. Moreover, on decreasing the pH, amoxicillin 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 (Sharma *et al*., 2013). Similar reports also showed that ferrate (VI) is quite efficient in oxidizing an array of aqueous contaminants, including nitrogen and sulfur containing compounds, amines, phenols, pesticides, pharmaceuticals and personal care products (Elnakar and Buchanan, 2019; Feng *et al*., 2019; Zajíček *et al*., 2015).



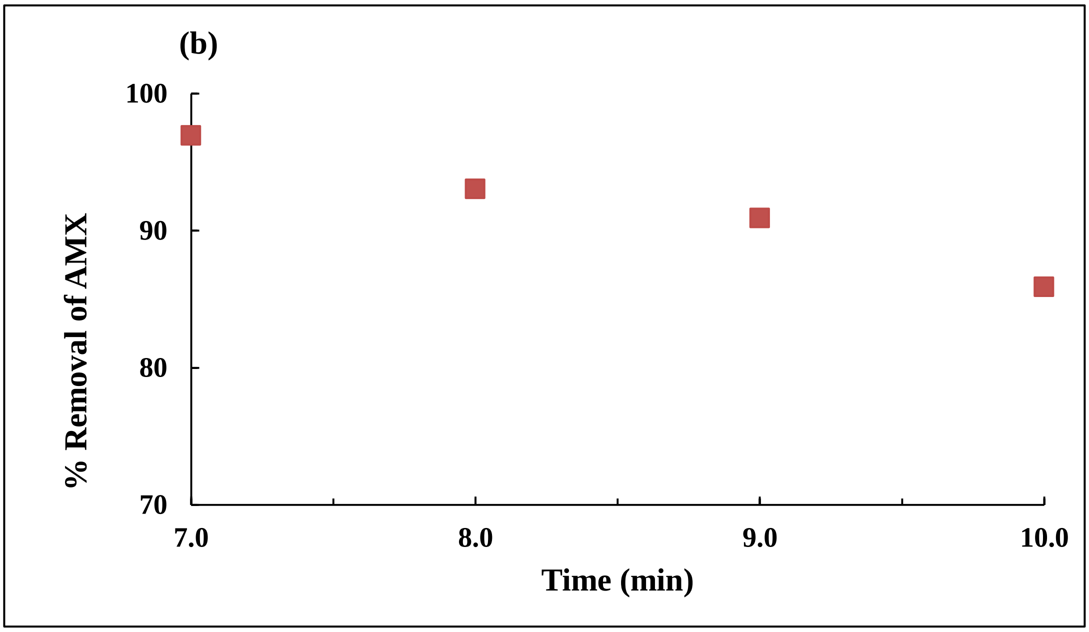


Figure 3.24 (a) Extent removal of ferrate (VI) with respect to time in presence of amoxicillin and **(b)** percentage removal of amoxicillin as a function of pH ([amoxicillin]: 0.1 mM and [Fe(VI)]: 0.2 mM).

Table 3.12. Percent removal of Amoxicillin by ferrate (VI) with respect to pH at a fixed concentration of 0.1 mM (HPLC measurments).

pH	Retention time (min)	Area (µV*sec)		% Removal of amoxicillin
		Blank sample	Treated sample	
7.0	2.9	36487	1114	96.9
8.0	2.9	38746	2687	93.0
9.0	2.9	37669	3416	90.9
10.0	2.9	35188	4958	85.9

3.4.5. Mechanism of Micro-pollutants Degradation

The interactions between organic contaminants and ferrate (VI) involves direct attack by the ferrate (VI) followed by the formation of reactive ·OH radical. Firstly, the direct attack by ferrate (VI) involves the delocalization of electrons from the ferrate (VI) species which led to the transfer of electrons between ferrate (VI) and pollutant molecules in the form of one electron or two electron transfer mechanism which results in the oxidation of pollutant molecule. Secondly, the formation of ·OH radical which was formed during the reaction intermediates also enhances the degradation of pollutants (Pachuau *et al.*, 2013). Thus, in case of compounds like sulfonamides (SMX and SMZ), ferrate(VI) readily attacks on the N-O bond and S–N bond which caused the oxidative cleavage and further facilitates the ring-opening reaction and then enhances the degradation of these organic pollutants (Yu *et al.*, 2017). In case of triclosan, the attacks on –OH and –CO groups occurred and breaks these bonds and eventually enables the degradation of triclosan by ferrate (VI) (Yang *et al.*, 2011). Moreover, ferrate (VI) attacks the –NH group and phenolic group of amoxicillin through the mechanism of electron transfer process and degrade the molecules into simpler compounds (Sharma *et al.*, 2013). The other possible pathway of these micro-pollutants removal may be adsorption or co-precipitation on Fe (III) produced from reduction of ferrate (VI).

3.5. Effect of Co-existing ions

3.5.1. Sulfamethoxazole

The presence of co-existing ions in the degradation of sulfamethoxazole by ferrate (VI) was studied to simulate the study for real matrix treatment. Moreover, the study enables to assess the preferential degradation of target pollutant in presence of various co-existing species. Therefore, the presence of several coexisting anions/cations *viz*., NaCl, glycine, Na_2HPO_4, EDTA, $NaNO_2$, oxalic acid and $NaNO_3$ was conducted in the degradation of sulfamethoxazole by ferrate (VI). The concentration of each of the ions was kept at 0.5 mM whereas the concentration of sulfamethoxazole and ferrate (VI) was taken as 0.1 and 0.2 mM, respectively at pH 6.0. This implies that the co-existing ion concentration was taken five times higher than the sulfamethoxazole concentration. The ferrate (VI) treated samples were then subjected for the measurement of sulfamethoxazole concentration using the HPLC. The results are presented in Table 3.13 and graphically in Figure 3.25. Table 3.13 clearly indicated that the presence of NaCl, Na_2HPO_4 and $NaNO_3$ could not hinder significantly the removal of sulfamethoxazole. However, the presence of EDTA and glycine greatly suppressed the removal of sulfamethoxazole from 36.9% to 13.7% and 11.1%, respectively. 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 electrolyte $NaNO_2$ and oxalic acid showed slight suppression in the removal of sulfamethoxazole by ferrate (VI).

Table 3.13. Percentage removal of sulfamethoxazole by ferrate (VI) as a function of different electrolytes at pH 6.0 (HPLC measurements) (Blank removal = 36.9% removal).

Electrolytes present	**Retention time (min)**	**Area (µV*sec)**		**% Removal of sulfamethoxazole**
		Blank sample	**Treated sample**	
$NaNO_3$	4.7	3353163	2219419	33.8
NaCl	4.7	3353163	2294793	31.5
Glycine	4.7	3353163	2980544	11.1
$NaNO_2$	4.7	3353163	2447582	27.0
Na_2HPO_4	4.7	3353163	2265434	32.4
EDTA	4.7	3353163	2892687	13.7
Oxalic Acid	4.7	3353163	2414216	28.0

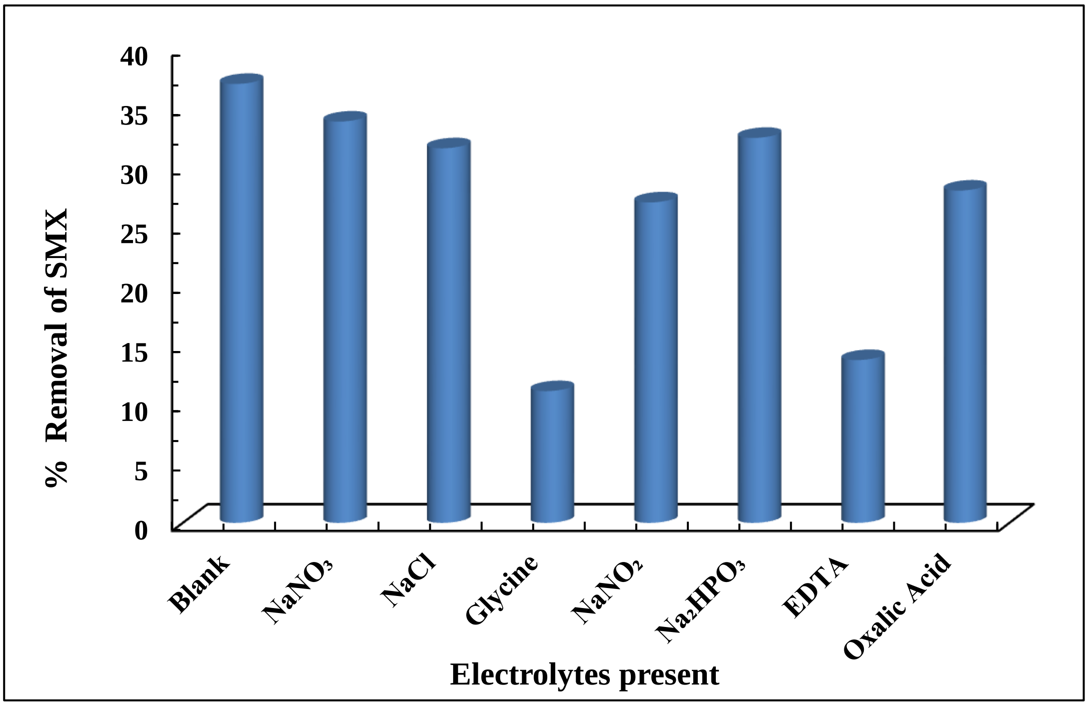


Figure 3.25. Oxidative degradation of sulfamethoxazole in presence of several co-existing ions ([Fe(VI)]: 0.2 mM; [SMX]: 0.1 mM; [Co-existing ions]: 0.5 mM; and pH: 6.0]).

3.5.2. Sulfamethazine

The oxidative removal of sulfamethazine is assessed in presence of several co-existing ions using ferrate (VI) at a ferrate (VI) dose of 0.2 mM and pH 6.0. Co-ions *viz.*, oxalic acid, glycine, NaCl, EDTA, $NaNO_2$, Na_2HPO_4 and $NaNO_3$ are used. The concentration of each of the selected ions was employed as 0.5 mM, while the concentration of sulfamethazine was taken as 0.1 mM. Thus, the actual molar ratio of ferrate (VI) to sulfamethazine to co-ions was 2: 1: 5. Depending upon the nature of co-ion, the degradation or removal of sulfamethazine is varied. The HPLC results are shown in Table 3.14 and graphically in Figure 3.26. As shown in Figure 3.26 or Table 3.14, the presence of electrolytes such as NaCl, Na_2HPO_4, $NaNO_3$, oxalic acid and $NaNO_2$ on the degradation of sulfamethazine by ferrate (VI) was not affected significantly. However, the decomposition of sulfamethazine was greatly affected in presence of glycine and EDTA. The percentage elimination of sulfamethazine in presence of EDTA and glycine is found to be 14.5 % and 15.8 % which was significantly low as compared to that of the blank i.e., 49.3 % removal in absence of co-ions. The less removal of sulfamethazine in presence of EDTA and glycine is possibly due to competitive oxidation of sulfamethazine by ferrate (VI). Hence, ferrate (VI) preferentially degraded the organic impurity present in aqueous wastes. On the other hand, the radical scavenging is less possible since EDTA is efficient in scavenging the h^+ in the semiconductors specially the TiO_2 (Tiwari *et al*., 2019; Jia *et al*., 2017). Moreover, previously, it was reported that the reductive pathways of ferrate (VI) is demonstrated as (Pachuau *et al*., 2013; sailo *et al*., 2015):

$$2FeO_4^{2-} + 3H_2O \rightarrow 2\,Fe(OH)_3 + 5[O] + 4e^- \qquad \text{….(3.11)}$$

$$[O] + H_2O \rightarrow 2\,{\bullet}OH \qquad \text{….(3.12)}$$

Therefore, the *in-situ* hydroxyl radical generated take part in the degradation of pollutants in the aqueous medium.

Table 3.14. Percentage removal of sulfamethazine by ferrate (VI) as a function of different electrolytes at pH 6.0 (HPLC measurements) (Blank removal = 49.3% removal).

Electrolytes present	**Retention time (min)**	**Area (μV*sec)**		**% Removal of sulfamethazine**
		Blank sample	**Treated sample**	
$NaNO_3$	3.7	2225217	1328789	40.2
NaCl	3.7	2225217	1406008	36.8
Glycine	3.7	2225217	1872193	15.8
$NaNO_2$	3.7	2225217	1404393	36.8
Na_2HPO_4	3.7	2225217	1251980	43.7
EDTA	3.7	2225217	1901824	14.5
Oxalic Acid	3.7	2225217	1343191	39.6

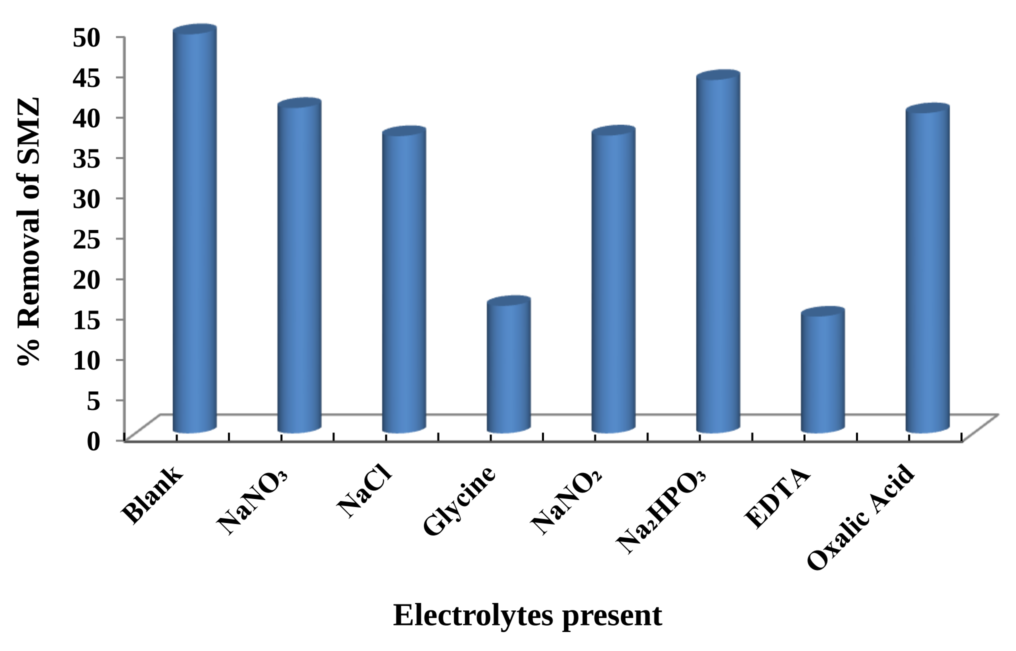


Figure 3.26. Oxidative degradation sulfamethazine in presence of various co-existing ions ([SMZ]: 0.1 mM: [Co-existing ions]: 0.5 mM; [Fe(VI)]: 0.2 mM; and pH: 6.0]).

3.5.3. Triclosan

The presence of different co-existing ions could affect the efficacy of ferrate (VI) and eventually enables to obtain the selectivity of ferrate (VI) towards the target pollutants. This further, relates the real/or complex matrix treatment of micro-pollutants. Therefore, 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 degradation of triclosan is conducted in five-fold presence of these co-existing ions by ferrate (VI). The concentration of ferrate (VI), triclosan and co-existing ions were taken as 0.2 mM, 0.1 mM and 0.5 mM, respectively. The HPLC results in terms of percentage elimination of triclosan at pH 10.0 are shown in Table 3.15 and graphically in Figure 3.27. Results indicated that these ions (NaCl, Na_2HPO_4 and $NaNO_3$) could not significantly affect the degradation of triclosan except the presence of glycine and EDTA. Quantitatively, EDTA and glycine greatly suppressed the removal of triclosan from 82.9% to 45.1% and 58.5%, respectively. This inferred that ferrate (VI) preferentially degraded the glycine and EDTA in a complex matrix. It was reported previously that ferrate (VI) reacted preferentially with $^{+}H_3N\text{-}CH_2\text{–}COO^{-}$ species of glycine then could attack the C-N bond of the glycine molecule (Sharma and Bielski 1991; Noorhasan *et al.*, 2010). Also, EDTA is a chelating agent, when ferrate (VI) interacts with EDTA, it forms a partial radical ($Fe^{VI} = O \leftrightarrow Fe^{V}\text{–}O^{\bullet}$), which prevented the oxidation of other contaminants in aqueous solutions (Noorhasan and Sharma, 2008). Additionally, up to lower extent the oxalic acid affected the degradation efficiency of triclosan.

Table 3.15. Percentage removal of triclosan by ferrate (VI) as a function of different electrolytes at pH 10.0 (HPLC measurements) (Blank removal = 82.9% removal).

Electrolytes present	**Retention time (min)**	**Area (µV*sec)**		**% Removal of triclosan**
		Blank sample	**Treated sample**	
NaCl	3.8	3046	562	81.5
Oxalic acid	3.8	3046	803	73.6
Glycine	3.8	3046	1263	58.5
Na_2HPO_4	3.8	3046	680	77.6
$NaNO_2$	3.8	3046	631	79.2
$NaNO_3$	3.8	3046	595	80.4
EDTA	3.8	3046	1672	45.1

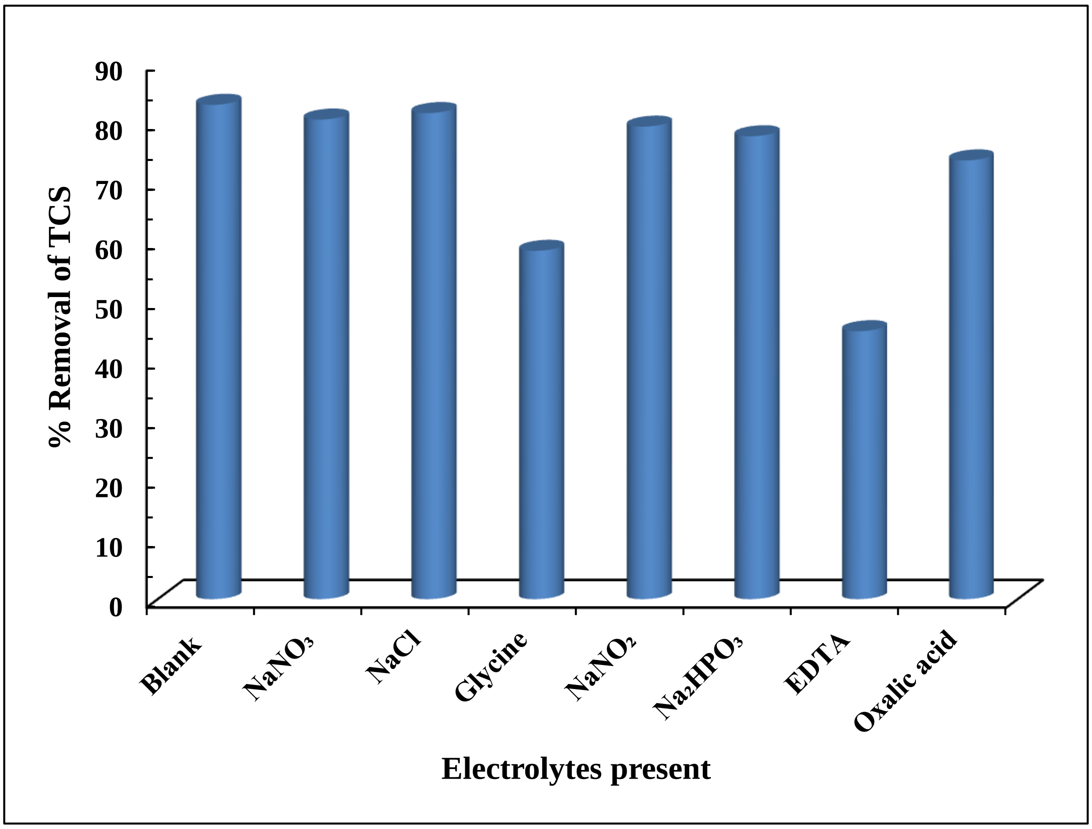


Figure 3.27. Oxidative degradation of triclosan in presence of co-existing ions ([Triclosan]: 0.1 mM; [Co-existing ions]: 0.5 mM; [Ferrate (VI)]: 0.2 mM; and at pH: 10.0).

3.5.4. Amoxicillin

Similarly, the presence of co-existing ions in the degradation of amoxicillin by ferrate (VI) is studied to simulate the study for real matrix treatment. This further, relates the real/or complex matrix treatment of micropollutants. Therefore, variety of co-existing ions viz., Na_2HPO_4, NaCl, $NaNO_2$, glycine, $NaNO_3$, EDTA, and oxalic acid are chosen in the degradation of amoxicillin by ferrate (VI). The degradation of amoxicillin is conducted in five-fold presence of these co-existing ions by ferrate(VI). The concentration of ferrate (VI), amoxicillin and co-existing ions were taken as 0.2 mM, 0.1 mM and 0.5 mM, respectively. The pH of the solutions was maintained at pH 10.0. The ferrate (VI) treated and the untreated samples were then subjected for the measurement of amoxicillin concentration using the HPLC measurements. The results are shown in Table 3.16 and illustrated graphically in Figure 3.28. Table 3.16 clearly indicated that the presence of NaCl, Na_2HPO_4 and $NaNO_3$ could not hinder significantly the removal of amoxicillin. Furthermore, due to their partial oxidizing properties, the presence of oxalic acid and $NaNO_2$ showed some impact in the removal of amoxicillin. On the other hand, the presence of EDTA and glycine greatly suppressed the removal of amoxicillin. It was observed that the percentage elimination of amoxicillin in presence of EDTA and glycine was found to be 44.5% and 37.9% which are comparatively much lower than the blank removal i.e., 85.9%. This suggests that in a complex matrix, ferrate (VI) preferentially degraded the glycine and EDTA. It was also reported previously that ferrate (VI) reacted preferentially with $^{+}H_3N\text{-}CH_2{-}COO^{-}$ species of glycine then could attack the C-N bond of the glycine molecule (Sharma and Bielski 1991; Noorhasan *et al.*, 2010). 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 solutions (Noorhasan and Sharma, 2008).

Table 3.16. Percentage removal of amoxicillin by ferrate (VI) in presence of several electrolytes at pH 10.0 (HPLC measurements) (Blank removal = 85.9%).

Electrolytes	Retention time (min)	Area (µV*sec)		% Removal of amoxicillin
		Blank sample	Treated sample	
NaCl	2.9	35188	8224	76.6
Oxalic acid	2.9	35188	10632	69.7
Glycine	2.9	35188	19497	44.5
Na_2HPO_4	2.9	35188	11463	67.4
$NaNO_2$	2.9	35188	11025	68.6
$NaNO_3$	2.9	35188	7380	79.0
EDTA	2.9	35188	21823	37.9

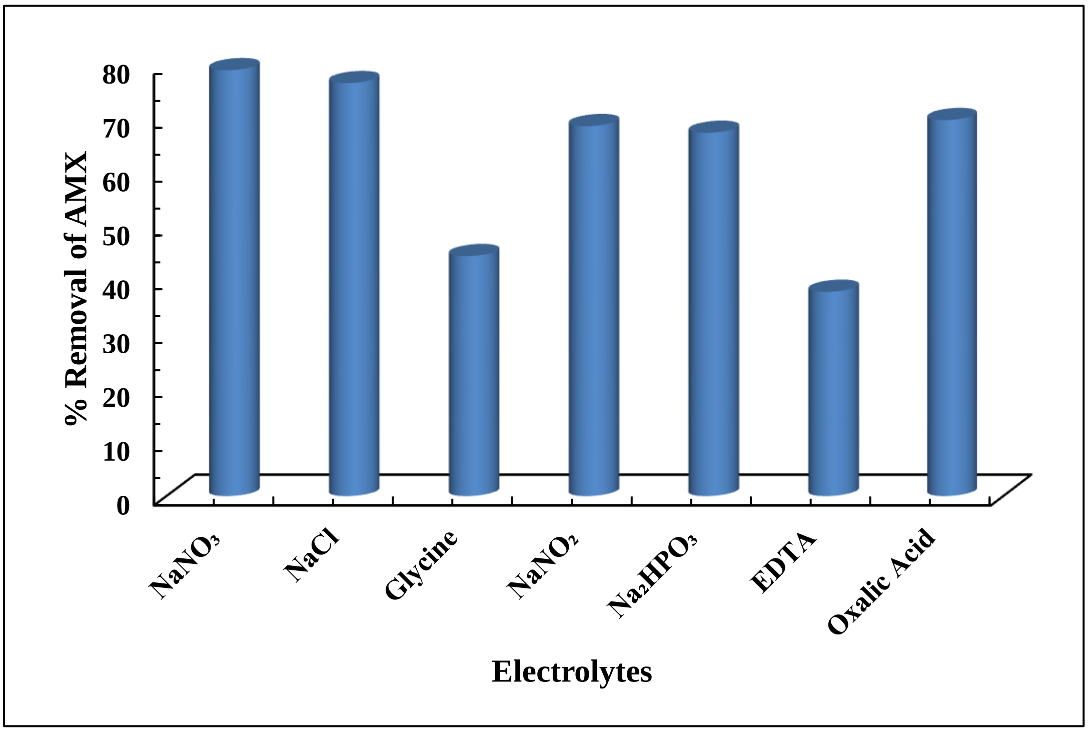
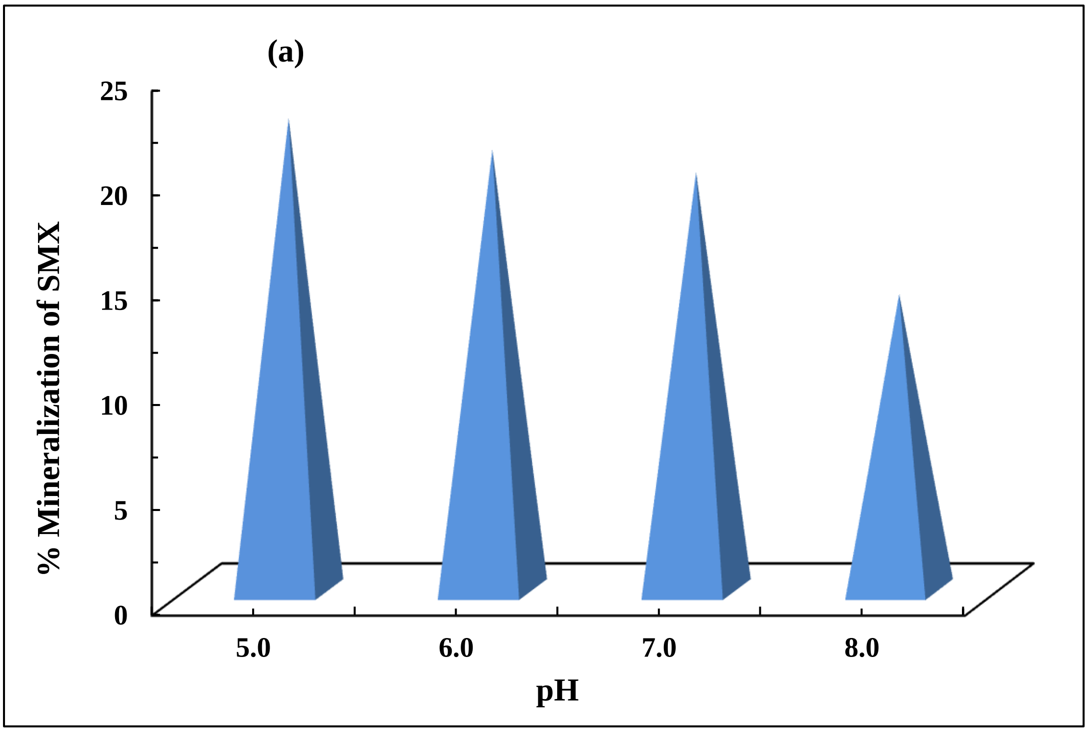


Figure 3.28. Oxidative degradation of amoxicillin in presence of several co-existing ions ([Amoxicillin]: 0.1 mM; [co-existing ions]: 0.5 mM; [Ferrate (VI)]: 0.2 mM; and at pH: 10.0).

3. 6. .Mineralization of Micro Pollutants

3. 6.1. Sulfamethoxazole

It is interesting to assess the amount of sulfamethoxazole mineralized by the ferrate (VI) treatment at varied pH conditions. Sulfamethoxazole (0.1 mM) was treated with ferrate (VI) (0.2 mM) for a period of 2 hrs at various pH conditions (pH 5.0 to 8.0). The ferrate (VI) treated samples were subjected to measure the NPOC (Non-Purgeable Organic Carbon) contents. Hence, using the initial NPOC values of blank samples, the percentage mineralization of sulfamethoxazole was obtained and returned in Figure 3.29 (a). It is evident from the figure that the decrease in pH greatly favored the mineralization of sulfamethoxazole. Moreover, the content of sulfamethoxazole removed at varied pH values are also obtained and shown in Figure 3.29 (b). Quantitatively, lowering the pH from 8.0 to 5.0 had caused to increase the percentage mineralization of sulfamethoxazole from 14.1 to 22.47 %. These results are in a line to the previously obtained results for the removal of sulfamethoxazole using HPLC. However, the percentage mineralization of SMX is somewhat less than its removal. 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 an optimum efficiency. It was reported previously that increase in ferrate (VI) doses resulted with enhanced mineralization of BPA (bisphenol A). However, an increase in ferrate (VI) dosages from 0.05 mM to 0.5 mM had caused to decrease the dissolved organic carbon from 60% to 20% in presence of BPA (0.1 mM) (Li *et al.*, 2008). Similarly, increasing the pH from 8.0 to 12.0, the percent mineralization of various metal-organo complex species were decreased from 24.2% to 18.8% (for Cd(II)-EDTA), 64.5% to 32.1% (for Cu(II)-EDTA) and 25.3% to 17.3% (for CU(II)-NTA), respectively at 1:1 molar ratios of ferrate (VI) and metal-ligand complex (Sailo *et al.*, 2015).



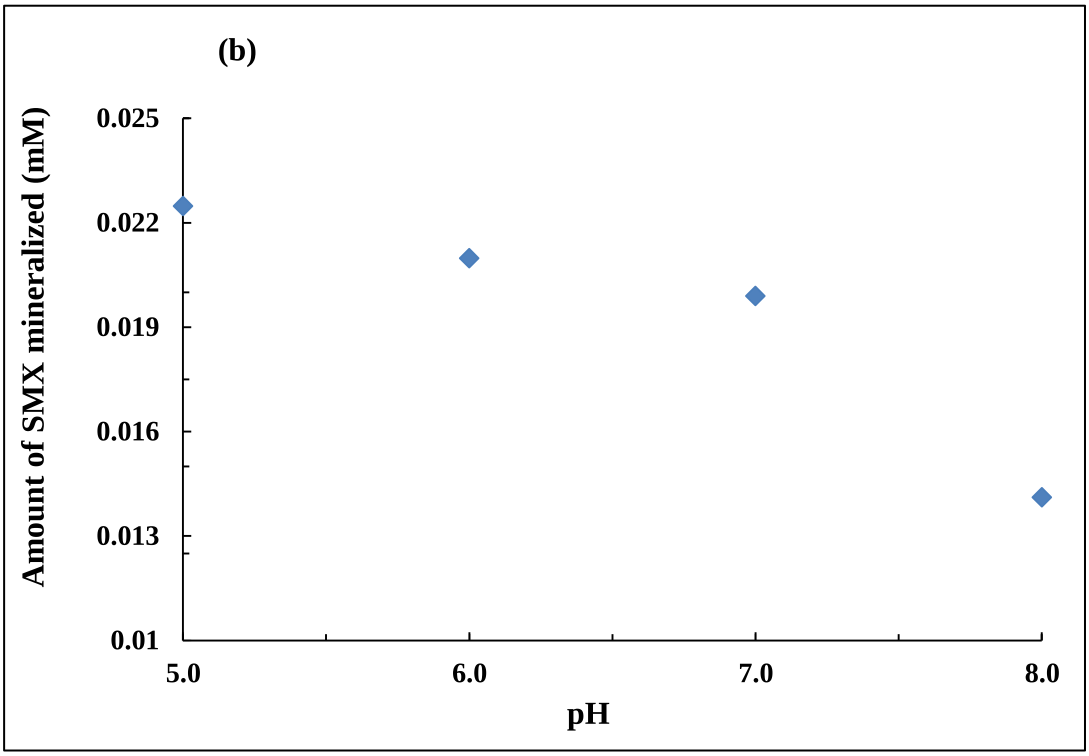


Figure 3.29. **(a)** Percentage mineralization of sulfamethoxazole as a function of pH; **(b)** Content of sulfamethoxazole mineralized as a function of pH ([SMX]: 0.1 mM and [Ferrate (VI)]: 0.2 mM).

3.6.2. Sulfamethazine

A total organic carbon analyzer is used to evaluate the mineralization of sulfamethazine by ferrate (VI). In this study, 0.1 mM of sulfamethazine solution is treated with 0.2 mM of ferrate (VI) for a total period of 2 hrs. The experiments are performed at various pH values i.e., from pH 5.0 to 8.0. Once, the reaction time was completed, the solution was filtered and then taken for total organic carbon analysis along with untreated sulfamethazine samples (i.e., the blank samples). The NPOC values are utilized to obtain the percentage mineralization of sulfamethazine. The results are graphically illustrated in Figure 3.30 (a). Figure depicted that decreasing the pH of reaction mixture greatly favored the mineralization of sulfamethazine. More quantitatively, decreasing the solution pH from pH 8.0 to 5.0 caused to increase the percentage mineralization of sulfamethazine from 8.4% to 22.7% at the ferrate (VI) to sulfamethazine molar ratio of 2:1. The actual amount of sulfamethazine mineralized with respect to solution pH is further illustrated in Figure 3.30 (b). Figure showed that the oxidation of sulfamethazine by ferrate (VI) is favored at lower pH values. This confirms that the reactivity of ferrate (VI) in aqueous solution is higher at lower pH conditions. These results are comparable to the HPLC results obtained separately. However, the TOC data showed that, although partial mineralization of sulfamethazine is achieved however, a significant percentage of sulfamethazine is mineralized using a small amount of ferrate (VI). The results are also consistent with earlier research that increasing the pH from 8.0 to pH 11.0, trichloroethylene exhibited maximum degradation at pH 8.0 which then further decreased as the solution pH was increased (Graham *et al*., 2004).

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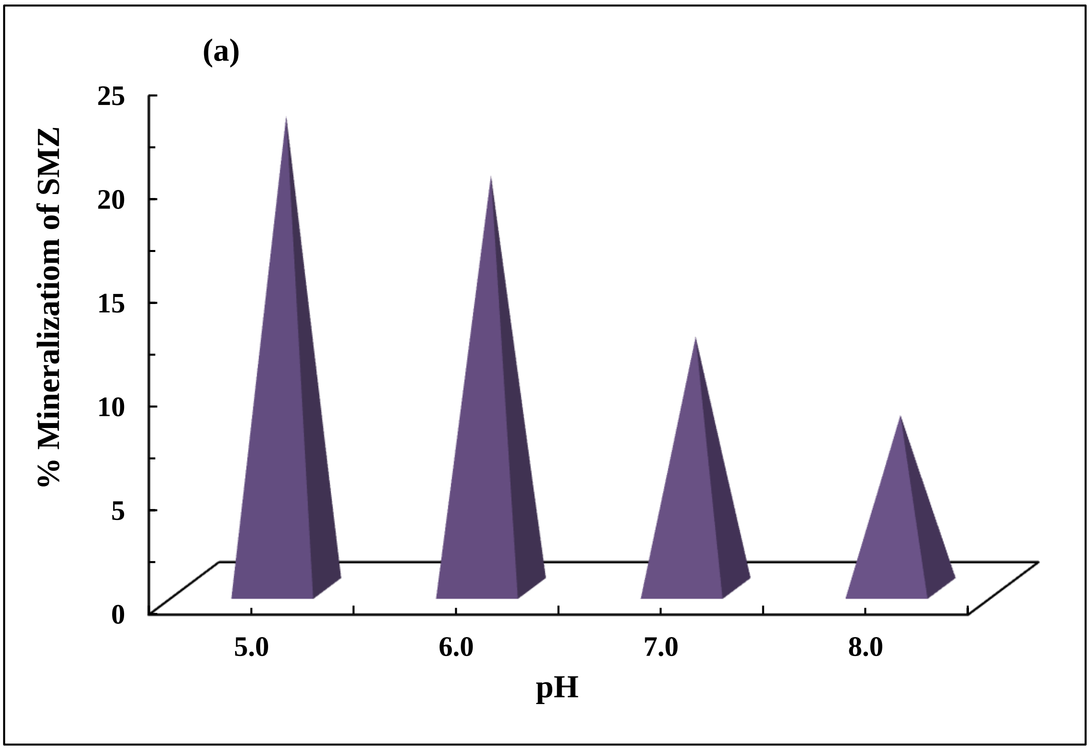


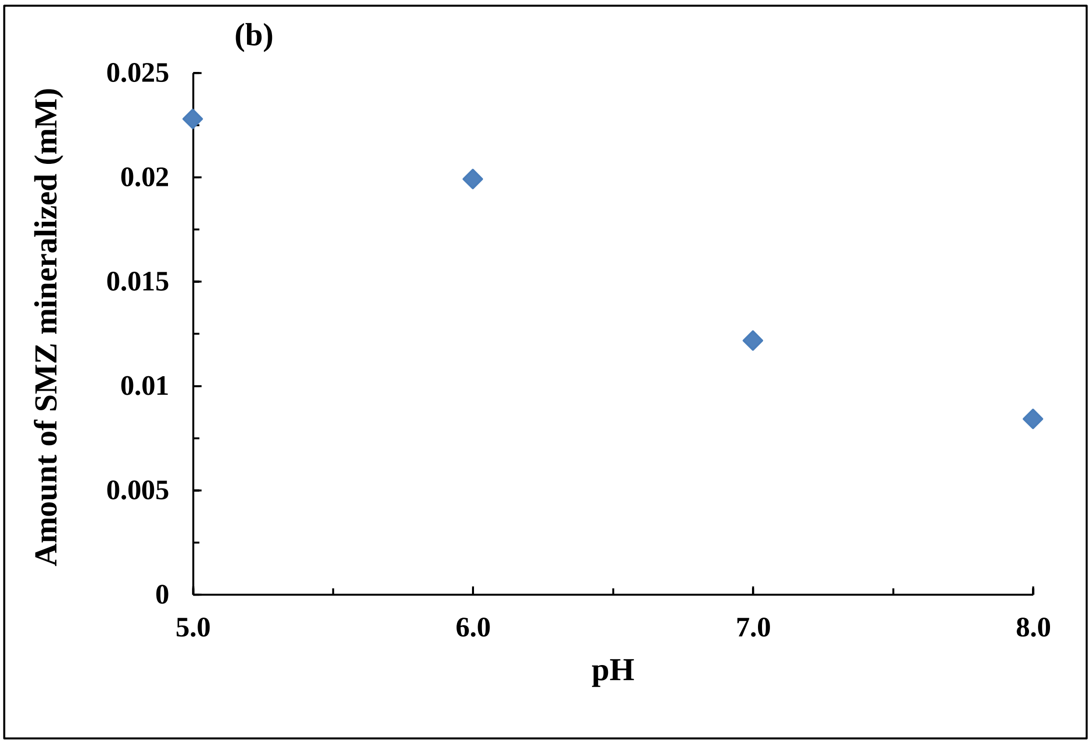


Figure 3.30. (a) Percentage mineralization of SMZ at various pH values; and (b) Extent of sulfamethazine mineralized as a function of pH ([SMX]: 0.1mM; [Ferrate (VI)]: 0.2 mM).

3.6.3. Triclosan

The mineralization of triclosan by ferrate (VI) was studied using a total organic carbon analyzer. The mineralization of pollutants to its end products is a useful parameter to achieve in the ferrate (VI) utilization. Therefore, the changes in total non-purgeable organic carbon values are obtained to correlate results for possible mineralization in ferrate (VI) treatment for triclosan. The triclosan was treated for 2 hours at fixed concentration of triclosan (0.1 mM) and ferrate (VI) (0.2 mM) at varied pH conditions i.e., from pH 9.0 to 12.0. The NPOC values of the treated and untreated samples were obtained and hence, the percentage of mineralization of triclosan was obtained as a function of pH and illustrated in Figure 3.31 (a). It is evident from the figure that the percentage mineralization of triclosan was greatly favored at lower pH value. Moreover, the extent of triclosan removed at varied pH values are shown in Figure 3.31 (b). Quantitatively, decreasing the pH from 12.0 to 9.0 enabled to increase the percentage mineralization of triclosan from 17.1% to 33.6%, respectively. These results indicated that although triclosan was partially mineralized with single dose of ferrate (VI) however, with the repeated cycle of operations may enable to mineralize it completely or to greater extent. The higher extent of triclosan mineralization at lower pH values is because of the reactivity of ferrate (VI) which is significantly high at lower pH values (Tiwari *et al.*, 2007). The mineralization of cetylpyridinium chloride (CPC) by ferrate (VI) was reported previously that in the first stage of reaction with ferrate (VI), the organic carbon chain of CPC was almost mineralized to its inorganic carbon (Eng *et al.*, 2006).

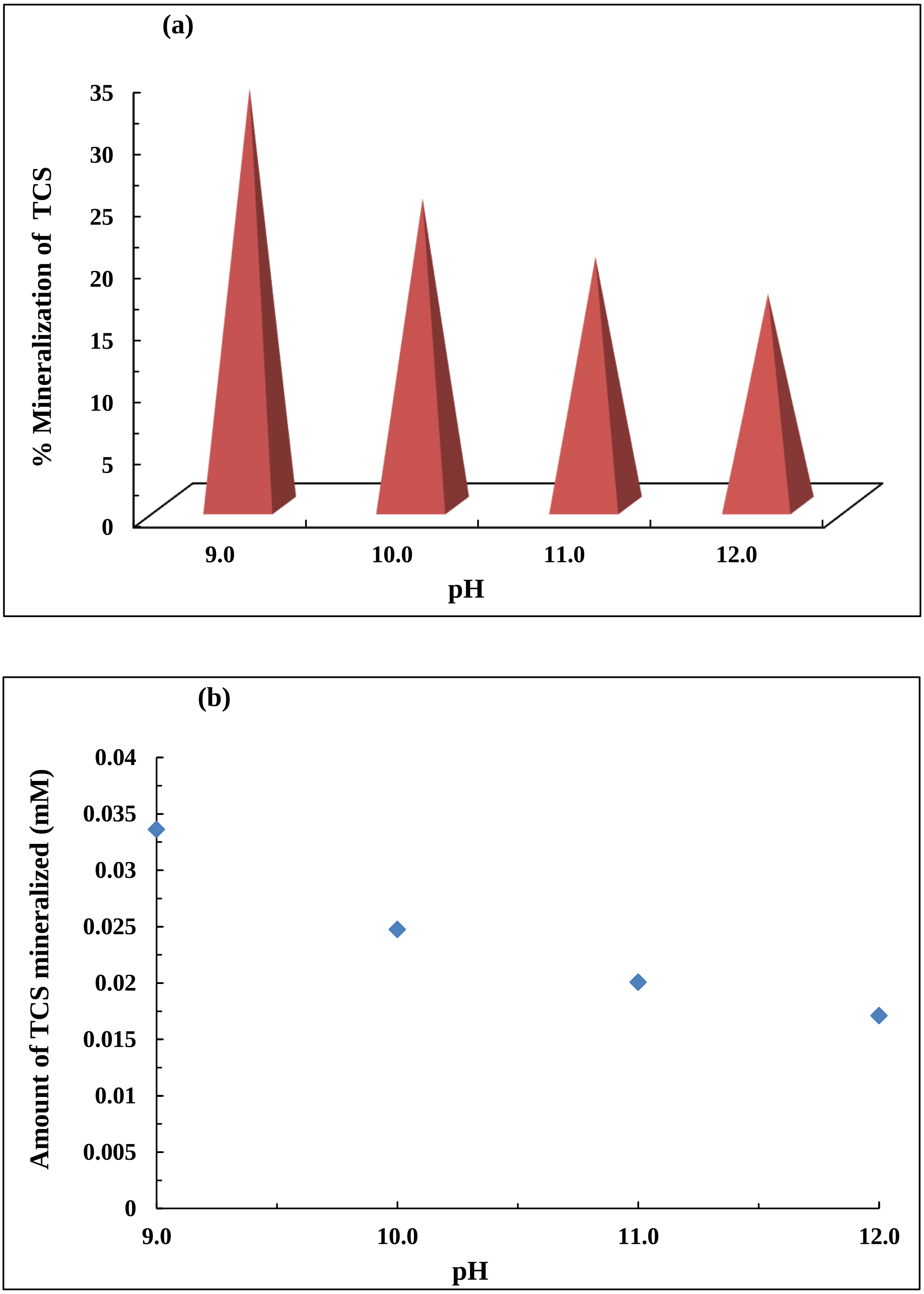


Figure 3.31. (a) Percentage mineralization of triclosan at various pH values; and **(b)** Extent of triclosan mineralized as a function of pH ([Triclosan]: 0.1 mM and [Ferrate (VI)]: 0.2 mM).

3.6.4. Amoxicillin

Similarly, the mineralization of amoxicillin by ferrate (VI) was carried out. The amoxicillin and ferrate (VI) concentrations were taken as 0.1 mM and 0.2 mM at various pH conditions i.e., pH 7.0 to 10.0. The samples were treated for a period of 2. The treated samples along with the blank were subjected for the NPOC values and hence, the percentage mineralization of AMX was obtained at various pH values and illustrated in Figure 3.32 (a). It is evident from the figure 3.32 (a) that the decrease in pH favored greatly the percent mineralization of amoxicillin. Further, the extent of amoxicillin mineralized at varied pH values are also obtained and shown in Figure 3.32 (b). Quantitatively, decreasing the pH from 10.0 to 7.0, caused to an increase in percentage mineralization of amoxicillin from 11.5% to 25.6%, respectively. The other organic pollutants such as trichloroethylene and naphthalene were reported to be completely mineralized by ferrate (VI) (DeLuca *et al.*, 1983). Similarly, the TOC removal of 4-tert-octylphenol by ferrate (VI) treatment was increased from 13.9% to 30.5% as the solution pH was decreased from 12.0 to 7.0 at 1:1 molar ratio of pollutant to ferrate (VI) (Tiwari *et al.*, 2017).

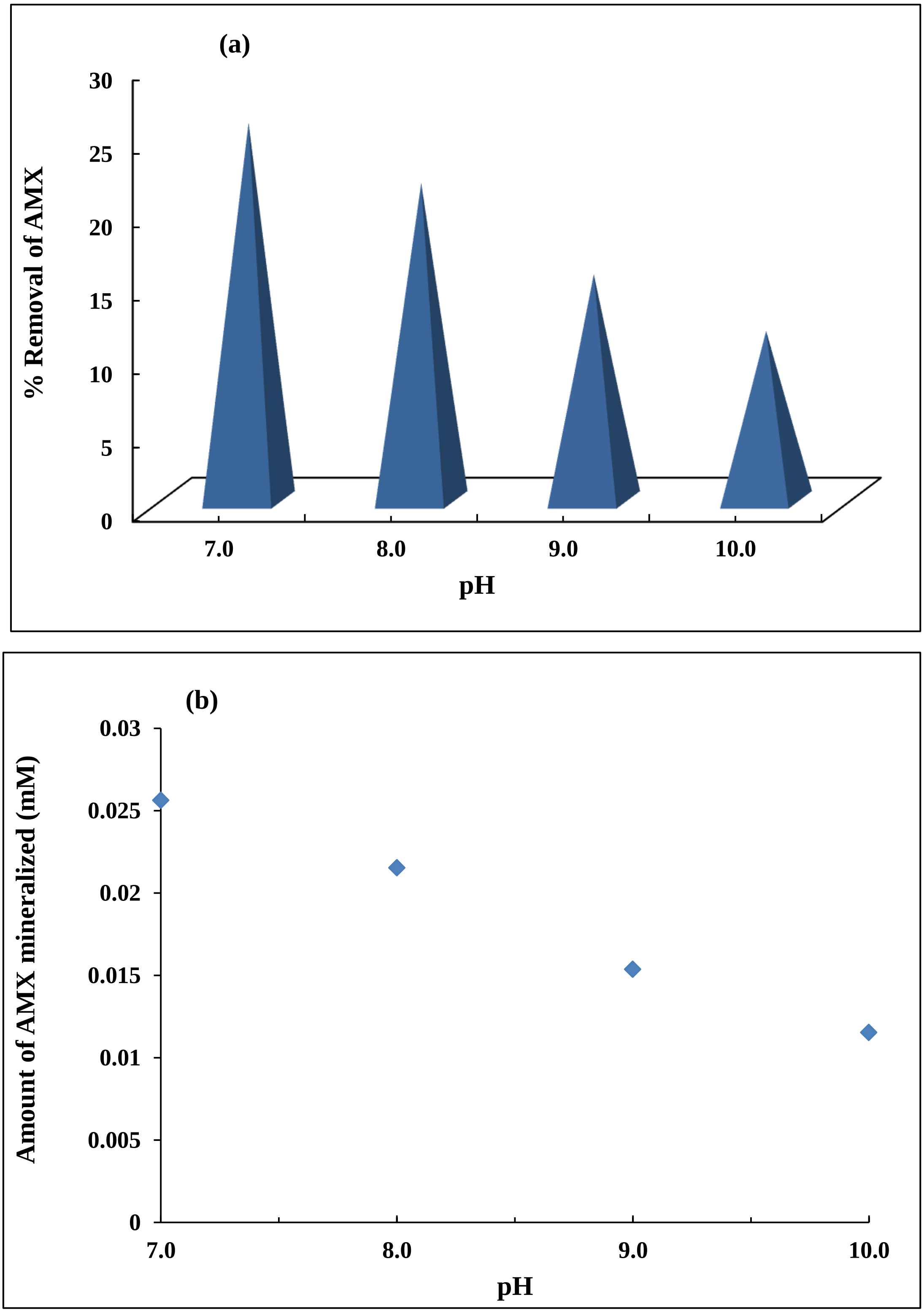


Figure 3.32. (a) Percentage mineralization of amoxicillin at various pH values; and **(b)** Extent of amoxicillin mineralized as a function of pH ([Amoxicillin]: 0.1 mM and [Ferrate (VI): 0.2 mM].

3. 7. Real matrix treatment

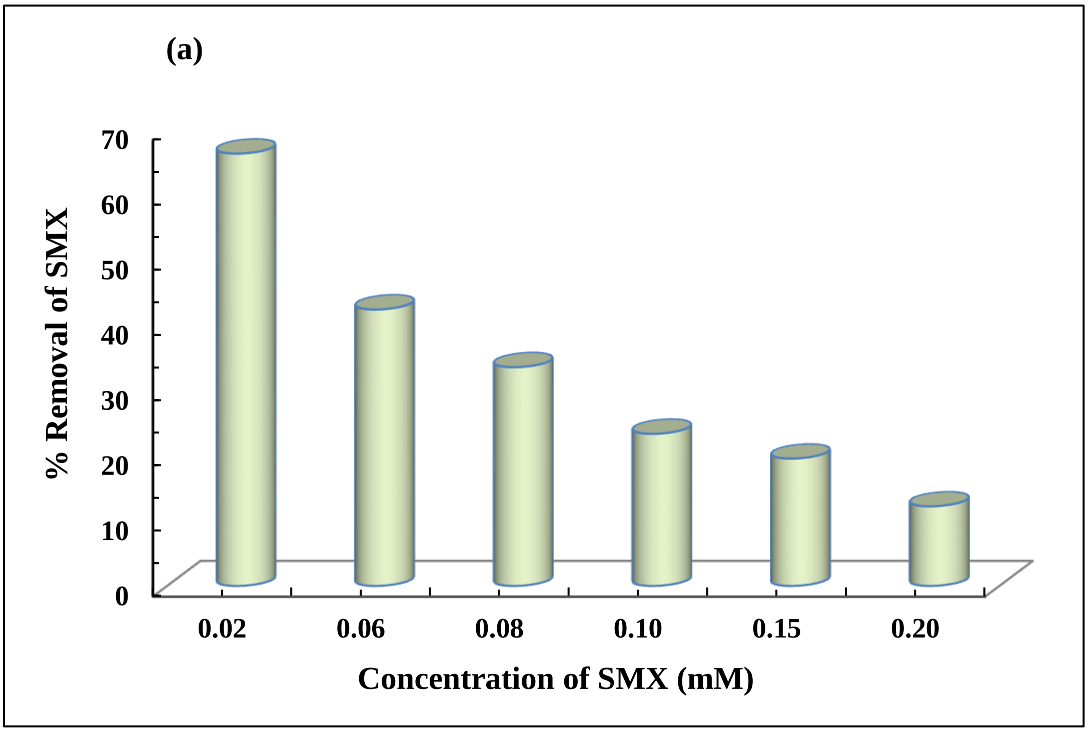
3.7.1. Sulfamethoxazole

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, as located near Aizawl City, India. The water quality was extensively analyzed for various physico-chemical parameters using multi-parameter photometer. Similarly, the dissolved metal contents were analyzed using the atomic absorption spectrophotometer (AAS) and the non-purgeable organic and inorganic carbon contents were obtained with TOC analyzer. The results are shown in Table 3.5. The results indicated that the river water sample contained relatively high concentration of Mn, Ni and Ca along with the high value of organic and inorganic carbon. The presence of inorganic carbon indicated the presence of carbonates and bicarbonates. Similarly, the water is also having high salinity which causes high conductivity of the water. The river water was spiked with varied concentrations (0.02 to 0.2 mM) of sulfamethoxazole and treated with a constant concentration of ferrate (VI) 0.20 mM 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 sulfamethoxazole concentration is obtained and illustrated in Figure 3.33 (a-b). The data is presented with the blank (i.e., the removal of sulfamethoxazole in distilled water) treatment. This eventually compares the efficiency of ferrate (VI) treatment in the real matrix treatment. The results clearly indicated that the removal of sulfamethoxazole by ferrate (VI) was almost unaffected in the real matrix treatment since the percentage removal of sulfamethoxazole in real water sample was not significantly altered at all studied concentrations of sulfamethoxazole. This further, showed the greater applicability of ferrate (VI) in the treatment of waste water contaminated with sulfamethoxazole.

Table 3.17. Various physico-chemical parametric analysis of river water (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	3.00
Phosphate	1.18
Fluoride	BDL
Nitrate	2.33
Elements Studied	**Result (mg/L)**
Ni	0.70
Fe	0.06
Cu	0.01
Pb	0.06
Ca	0.10
Mn	1.15
Zn	0.02
TOC Analysis	**Result (mg/L)**
IC	5.02
NPOC	13.7

BDL - Below detection limit



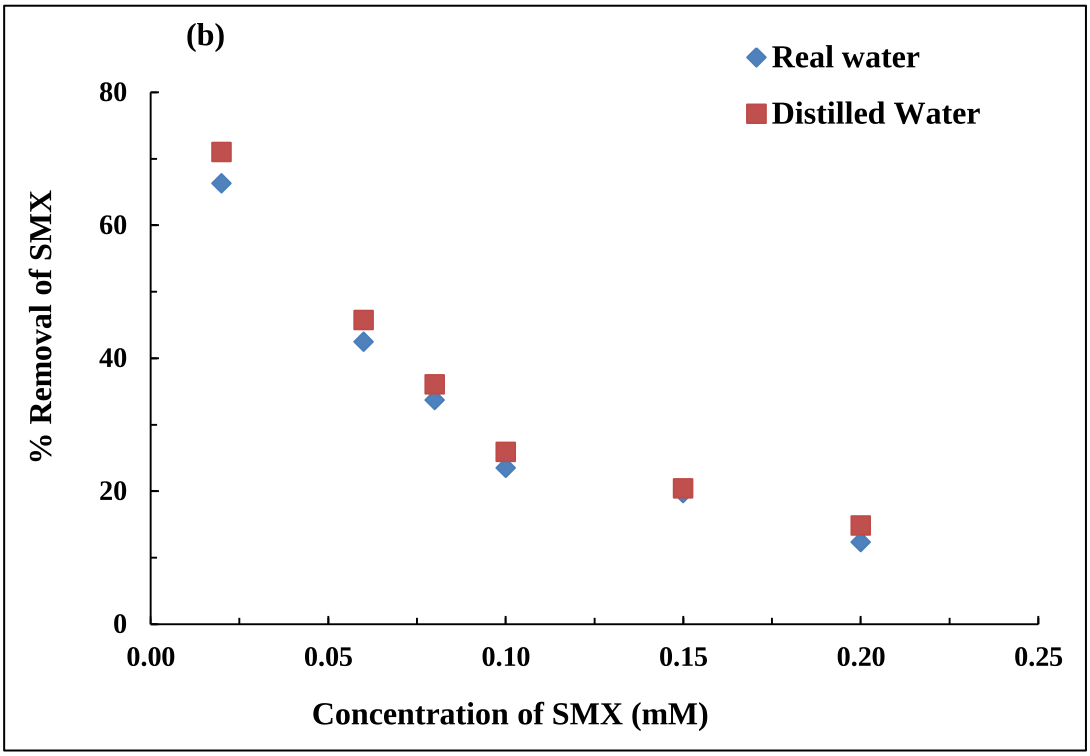


Figure 3.33. **(a)** Percentage removal of sulfamethoxazole in real water samples; and **(b)** in comparison with distilled water as a function of sulfamethoxazole concentrations ([Fe(VI)]: 0.1 mM; pH: 6.0).

3.7.2. Sulfamethazine

The oxidative degradation of sulfamethazine in real water sample was carried out using the ferrate (VI). The spring (Tuikhur) water sample was collected from Electric Veng, Aizawl City, Mizoram, India. Various physico-chemical parameters of real water were obtained and shown in Table 3.18. It is evident from the table that the real water sample is insignificantly contained with heavy metals including calcium. However, the water sample is having high value of inorganic as well non-purgeable carbons. The non-purgeable organic carbon is relatively high. Similarly, the water sample is having high salinity and TDS. Further, the real water sample was spiked with known concentrations of sulfamethazine (0.02 to 0.2 mM) and the solution pH was adjusted to pH 6.0. The oxidative degradation of sulfamethazine was conducted using a known concentration of ferrate (VI) i.e., 0.1 mM. The samples were stirred for 2 h and then filtered. The filtrate was subjected for sulfamethazine concentration using the HPLC. The percentage removal of sulfamethazine was obtained with the blank sample (*Cf* Figure 3.34(a)). Further, the results are compared with the treatment of sulfamethazine in distilled water as shown in Figure 3.34 (b). It is evident from the figure that the removal of sulfamethazine by ferrate (VI) was not significantly affected as treated in spring water samples. This indicated that ferrate (VI) is efficient and potential oxidant in the degradation of sulfamethazine even in the spring water samples.

Table 3.18. Physico-chemical Parametric Analysis of spring water (Tuikhur) located in Electric Veng, Aizawl City, Mizoram, India.

Parameter studied	**Analytical Result**
pH	7.62
TDS (mg/L)	96.0
EC (µS/cm)	187
Oxi. Red. Potential(mV)	124
Salinity (mg/L)	52.0
Anions Studied	**Result (mg/L)**
Sulphate	1.05
Phosphate	0.05
Fluoride	BDL
Nitrate	3.27
Elements studied (AAS)	**Result (mg/L)**
Ni	0.021
Fe	0.031
Cu	BDL
Pb	0.007
Ca	0.423
Mn	0.067
Zn	0.001
TOC Analysis	**Result (mg/L)**
IC	2.16
NPOC	10.4

BDL – Below detection limit

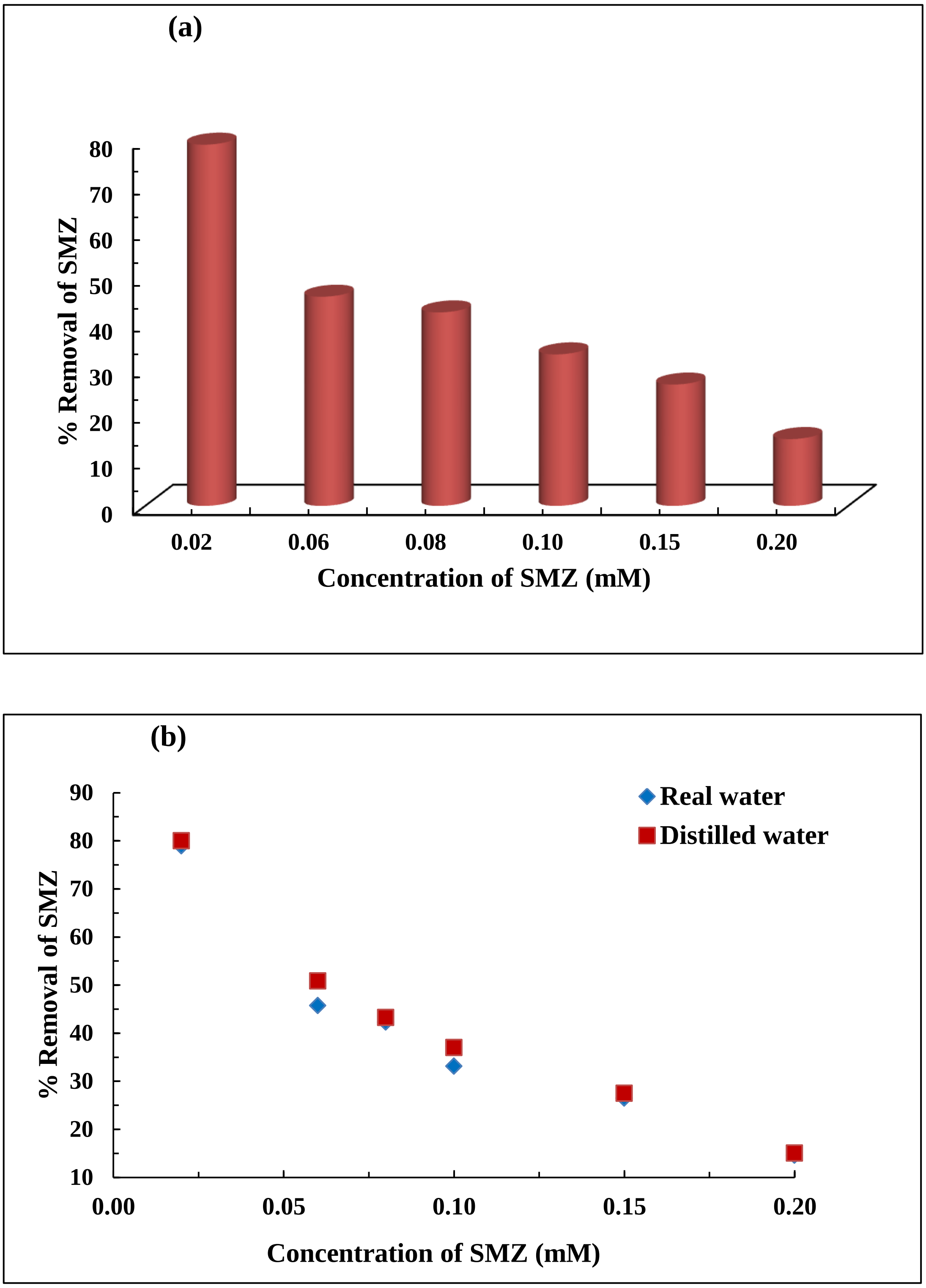


Figure 3.34. (a) Percentage removal of sulfamethazine in real water samples; and **(b)** in comparison with distilled water samples as a function of sulfamethazine concentrations ([Fe(VI)]: 0.1 mM; pH: 6.0).

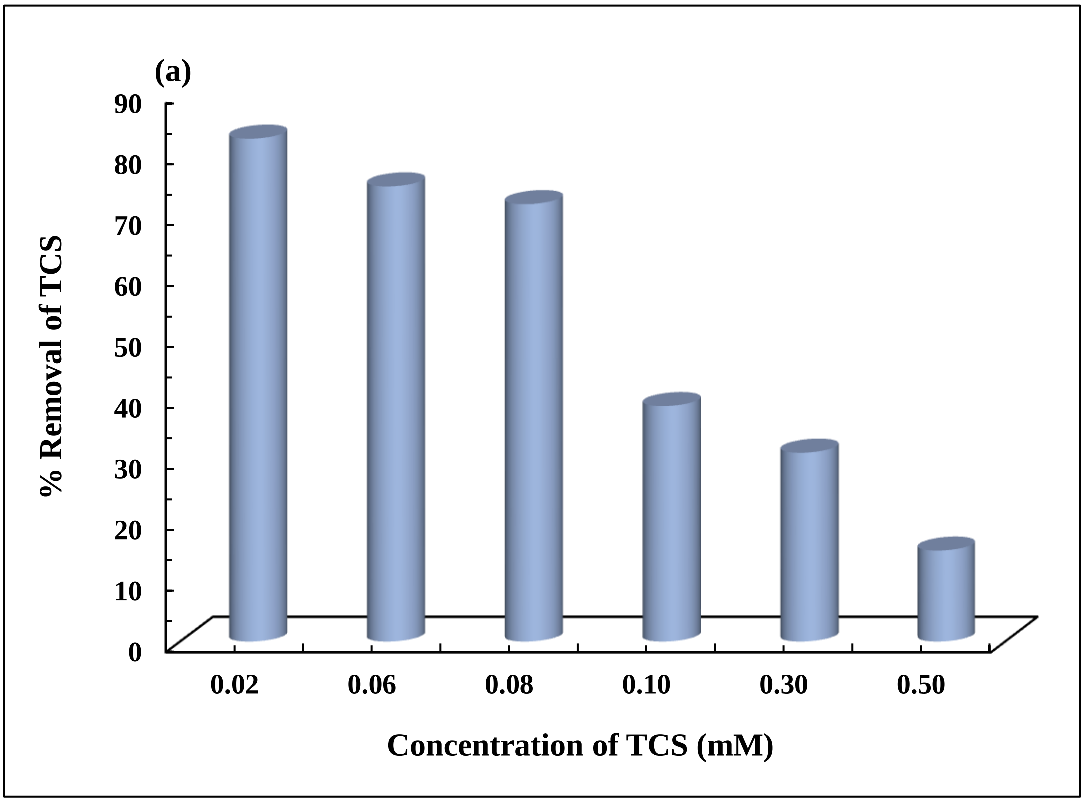
3.7.3. Triclosan

Similarly, the triclosan is treated with ferrate (VI) in the real water samples. The spring water sample was collected from spring water (Tuikhur), located in Ramhlun South, Aizawl City, Mizoram, India. The physico-chemical parameters of the water sample were obtained and shown in Table 3.19. It is noted that the water sample is contained with relatively high salinity along with the high value of inorganic carbon contents. This indicates that water sample is, perhaps, having high value of carbonates and bicarbonates. It is also noted that the real water sample is not contained with heavy metals. The spring water sample was spiked with the triclosan. The triclosan concentrations were taken from 0.02 to 0.5 mM at pH 10.0 and the ferrate (VI) dose was employed as 0.1 mM. The percentage elimination of triclosan is obtained in spring water sample and compared with the purified water treatment (*Cf* Figure 3.35 (a - b)). The results indicated that the removal of triclosan was not affected in the real matrix samples. This eventually indicated the potential of ferrate (VI) in the treatment of triclosan even in spring water real matrix samples.

Table 3.19. Water quality analysis of spring water (Tuikhur) from Ramhlun South, Aizawl City, (Mizoram), India.

Parameter studied	**Analytical Result**
pH	7.32
Tds(mg/L)	96.0
EC (µS/cm)	184
Oxi. Red. Potential(mV)	196
Salinity (mg/L)	82.0
Anions Studied	**Result (mg/L)**
Sulphate	4.00
Phosphate	0.240
Fluoride	BDL
Nitrate	3.15
Elements studied (AAS)	**Result (mg/L)**
Ni	0.741
Fe	0.005
Cu	BDL
Pb	0.061
Ca	0.198
Mn	7.62
Zn	0.003
TOC Analysis	**Result (mg/L)**
IC	6.21
NPOC	1.53

BDL – Below detection limit



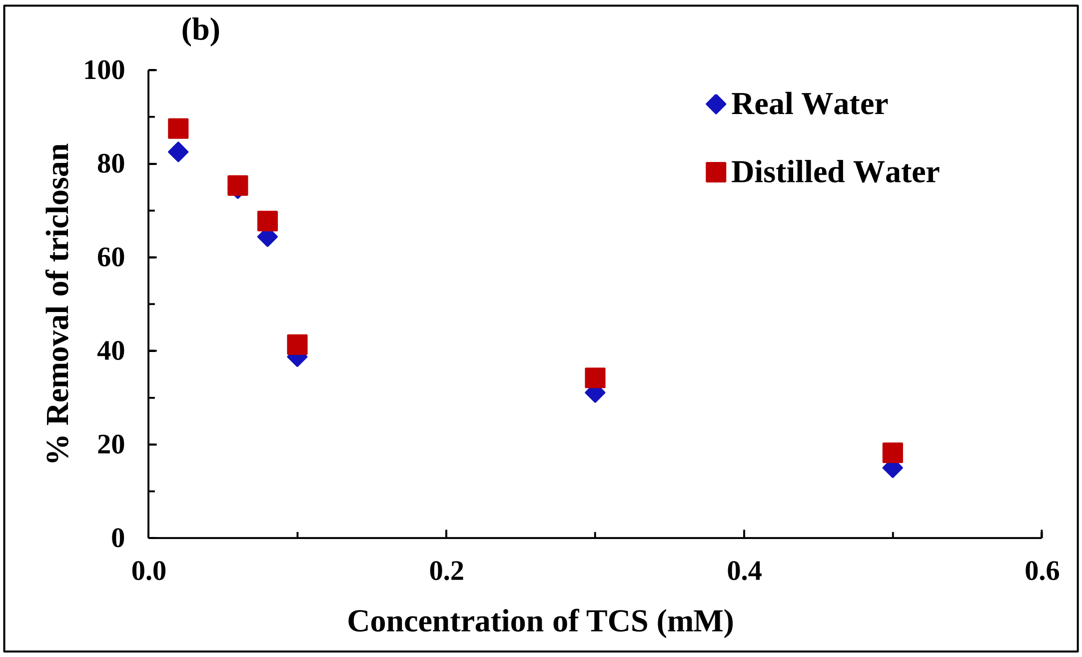


Figure 3.35. Percentage removal of triclosan **(a)** in real water samples; and **(b)** in comparison with distilled water as a function of triclosan concentrations ([Fe(VI)]: 0.1 mM; pH: 10.0).

3.7.4. Amoxicillin

The spring water sample was collected from spring (Tuikhur) located in Republic Veng, Aizawl City, Mizoram, India. Further, the spring water sample was extensively studied for various physico-chemical parametric studies. The results are shown in table 3.35. The elemental analysis showed that the water sample is contained with slightly high content of manganese. The sample is also having high salinity along with the higher inorganic carbon contents. The organic carbon content is relatively low in the sample. The high value of salinity resulted with enhanced salinity and conductivity of sample. The real water sample was spiked with the amoxicillin. The amoxicillin concentrations were ranged from 0.02 to 0.5 mM at pH 10.0. These samples were treated with a constant dose of ferrate (VI) i.e., 0.1 mM. The percentage removal of amoxicillin in real water along with in the purified water was obtained and shown in Figure (3.36 (a - b)). The results indicated that the elimination of amoxicillin was not affected in the real matrix samples as compared to the purified water sample. This further indicated the potential use of ferrate (VI) in the treatment of amoxicillin even in the real matrix samples.

Table 3.20. Various physico-chemical parametric studies of spring water sample collected from Republic Veng, Aizawl City, Mizoram, India.

Parameter studied	**Analytical Result**
pH	6.97
Tds(mg/L)	102
EC (µS/cm)	163
Oxi. Red. Potential(mV)	145
Salinity (mg/L)	94.0
Anions Studied	**Result (mg/L)**
Sulphate	2.00
Phosphate	0.37
Fluoride	BDL
Nitrate	5.04
Elements studied (AAS)	**Result (mg/L)**
Ni	0.512
Fe	0.012
Cu	0.001
Pb	0.022
Ca	0.217
Mn	2.85
Zn	0.009
TOC Analysis	**Result (mg/L)**
IC	7.96
NPOC	3.28

BDL – Below detection limit

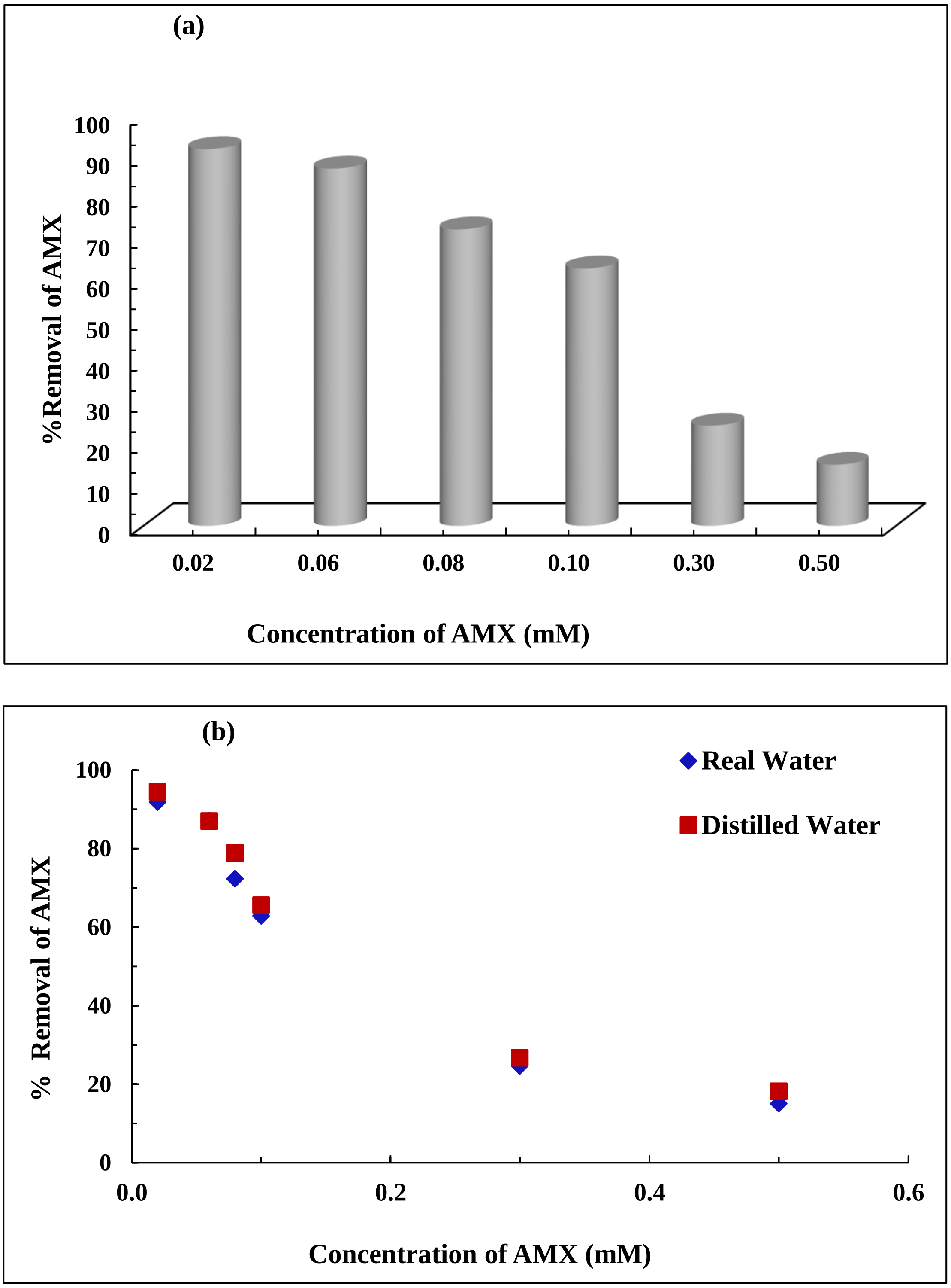


Figure 3.36. Percentage removal of amoxicillin **(a)** in real water sample; and **(b)** in comparison with distilled water as a function of amoxicillin concentrations ([Fe(VI)]: 0.1 mM; pH: 10.0).

3.8. Simultaneous degradation of Micropollutants

The ferrate (VI) efficiency was assessed in the simultaneous removal of triclosan and amoxicillin in aqueous solutions. The micropollutant samples having combined concentrations of triclosan and amoxicillin as 0.05 mM and 0.1 mM. The molar stoichiometric ratio was taken 2:1 between the ([Fe (VI)] : [TCS+AMX]). The sample pH was maintained at pH 10.0 and treated for a period of 2 hrs with ferrate (VI). Further, the percentage removal of these two pollutants was obtained and results are illustrated in Figure 3.37. These results indicated that at the micro-pollutant concentrations of 0.05 mM, the percent removal of triclosan and amoxicillin was found to be 65.5% and 76.3%, respectively. However, increasing the pollutant concentration to 0.1 mM, the percentage removal of triclosan and amoxicillin was observed to be 32.3% and 52.8%, respectively. The results showed that the ferrate (VI) is efficient even in simultaneous removal of these two pollutants. Moreover, the treatment is relatively more favored 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 23.4% at the micropollutant concentration of 0.05 mM. However, increasing the mixed pollutant concentration to 0.1 mM the respective percentage mineralization of triclosan and amoxicillin was found to be 15.7%. This showed that the ferrate (VI) mineralizes, partially, the triclosan and amoxicillin using the limited dose of ferrate (VI). This further entails that a repeated operations with ferrate (VI) may enable a complete mineralization of these micropollutants from aqueous wastes.

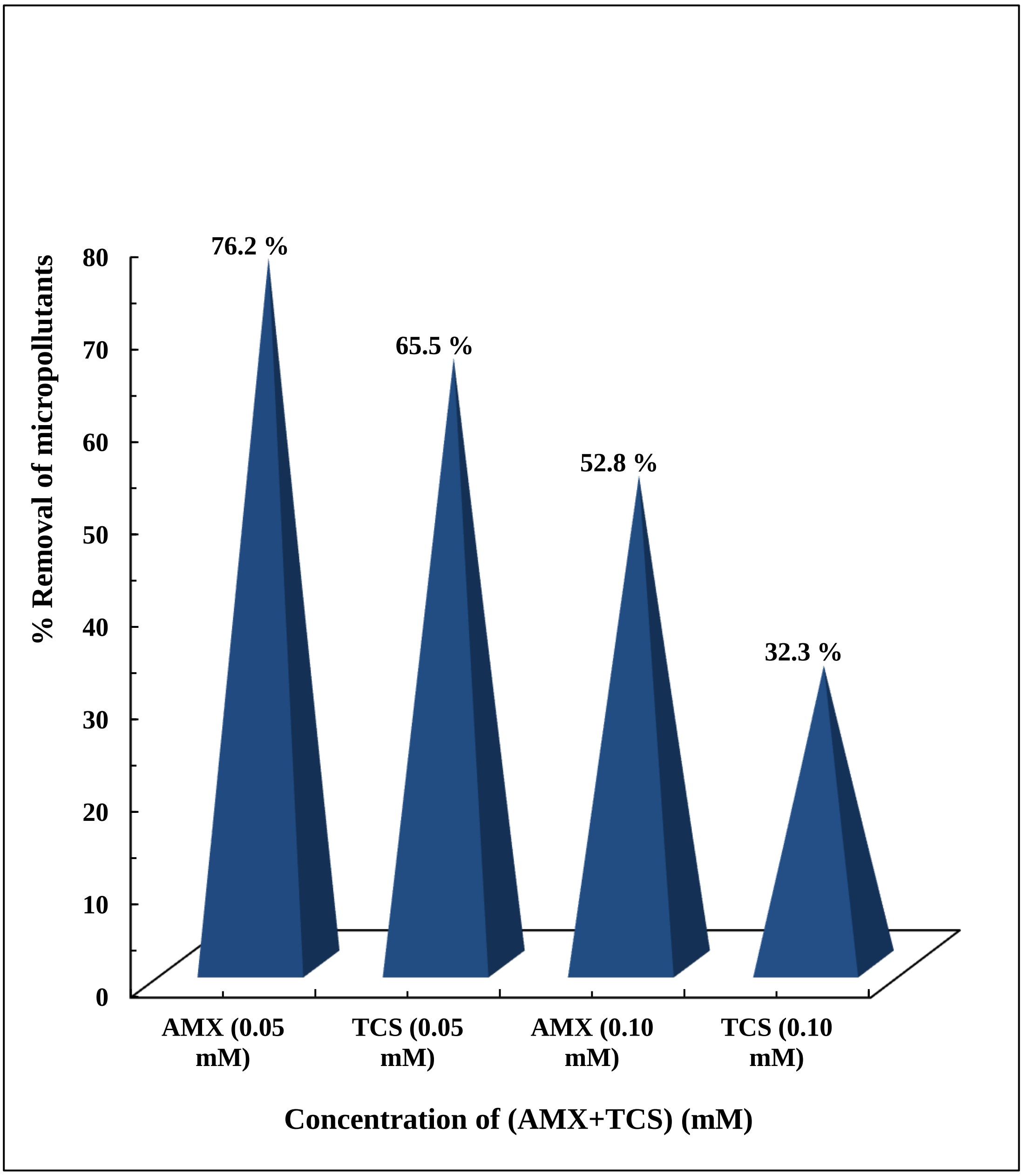


Figure 3.37. Simultaneous removal of amoxicillin and triclosan in mixtures of these two micro-pollutants having varied concentrations by ferrate (VI) ([Triclosan + Amoxicillin]: 0.05 mM and 0.10 mM; pH 10.0; [FeVI] : [TCS+AMX]: 2:1).

CHAPTER 4

CONCLUSIONS

4. CONCLUSIONS

Potassium ferrate (K_2FeO_4) was synthesized in the laboratory through the method of wet oxidation process. The purity of the synthesized ferrate (VI) was analyzed spectrophotometrically and found to be more than 95% pure. The highly reactive ferrate (VI) was employed in order to evaluate its effectiveness and applicability towards the degradation of micro-pollutants particularly pharmaceutical and personal care products (PPCPs) viz., sulfamethoxazole, sulfamethazine, triclosan and amoxicillin from aqueous solutions. The batch reactor experiments were performed on various parametric studies in order to assess the efficiency of ferrate (VI). The PPCPs were treated at varied pH (5.0-12.0) and concentrations (0.02 to 0.5 mM). The overall rate constant values were evaluated for each pollutant using the time dependence degradation of ferrate (VI). The kinetic results eventually reveal an optimum stoichiometry of ferrate (VI) to individual PPCPs which was found to be 2:1. It was observed that ferrate (VI) reactivity is highly dependent on pH towards the degradation of these PPCPs. A fast degradation of ferrate (VI) in presence of PPCPs was observed. Therefore, it was further revealed that rate of reaction increased with increase in concentration of pollutants. The overall rate constant (k_{app}) of various PPCPs at 0.1 mM was estimated as 5137 $(mM)^{-2}.min^{-1}$ for amoxicillin at pH 10.0, 3583 $(mM)^{-2}.min^{-1}$ for triclosan at pH 10.0, 4559 $(mM)^{-2}.min^{-1}$ for sulfamethoxazole at pH 6.0 and 6128 $(mM)^{-2}.min^{-1}$ for sulfamethazine at pH 6.0.

Furthermore, the ferrate (VI) treated and the untreated PPCPs samples were analyzed with HPLC measurements for PPCPs quantification. The results were obtained in terms of percent removal of PPCPs as a function of pH i.e., pH 5.0 to 8.0 (for sulfamethoxazole and sulfamethazine), pH 7.0 to 10.0 (for amoxicillin) and pH 9.0 to 12.0 (for triclosan) and concentrations of PPCPs from 0.02 to 0.2 mM (for sulfamethoxazole and sulfamethazine) and 0.02 to 0.5 mM (for triclosan and amoxicillin). The results showed that high percentage removal of pollutants was observed with decrease in pH and concentrations of PPCPs solution. It was observed that at ferrate (VI) : PPCPs molar ratio of 1:1, the removal percentage was found to be 25.8% for sulfamethoxazole (at pH 6.0), 36.9% for sulfamethazine (at pH 6.0), 41.3% for triclosan (pH 10.0) and 54.59% for amoxicillin (at pH 10.0). Moreover, it was also observed that at pH 10.0 and at ferrate (VI) : PPCPs molar ratio of 2:1, the percent removal was found to be 82.9% for triclosan, 85.9% for amoxicillin and at pH 6.0 having similar molar ratio (i.e., 2:1), the percent removal of sulfamethoxazole and sulfamethazine was found to be 36.97% and 49.37%, respectively.

Mineralization was achieved with the help of total organic carbon (TOC) analyzer, which enables to estimate PPCPs mineralization with a single dose of ferrate (VI). A partial but significant amount of PPCPs was mineralized and it was observed that at molar ratio of Fe (VI) : PPCPs (2 :1), 22.4% of SMX and 22.7% of SMZ was mineralized at pH 5.0 and 33.6% of TCS at pH 9.0 and 25.6% of AMX was mineralized at PH 7.0. Further, since the reactivity of ferrate (VI) was significantly increased at lower pH values hence, enabled to increase significantly the percentage mineralization of PPCPs at lower pH values in aqueous solutions. Through these results indicated that using a single dose of ferrate(VI) caused to mineralize partially these micro-pollutants, however, expecting a successive cycle of operations may enable to mineralize these micropollutant completely. Moreover, at low pH condition, the redox potential of ferrate (VI) is considerably higher hence, the reactivity of ferrate (VI) was increased significantly at lower pH values

The effect of co-existing ions in the degradation of PPCPs by ferrate (VI) was studied which enabled to assess the preferential degradation of target pollutants in presence of variety of co-existing species. Therefore, the presence of several coexisting anions/cations *viz*., NaCl, Na_2HPO_4, $NaNO_2$, $NaNO_3$, oxalic acid, glycine and ethylene diamine tetraacetic acid is investigated in the degradation of PPCPs using ferrate (VI). The concentrations of ferrate (VI), PPCPs and co-existing ions were taken as 0.2 mM, 0.1 mM and 0.5 mM, respectively. Results indicated that the presence of NaCl, Na_2HPO_4 and $NaNO_3$ could not hinder significantly the removal percentage of sulfamethoxazole. However, on the other hand, the presence of EDTA and glycine greatly suppressed the removal of sulfamethoxazole from 36.9% (blank) to 13.7% and 11.1%, respectively for EDTA and glycine. Similarly, the decomposition of sulfamethazine was greatly affected in presence glycine and EDTA. The percentage elimination of sulfamethazine in presence EDTA and glycine was found to be 14.5% and 15.8% as compared to that of the blank of 49.3%. The percentage removal of triclosan was found to be 82.9%, 58.5%, and 45.1% respectively for the blank, glycine and EDTA. Similarly, the amoxicillin removal was also hampered in presence of glycine and EDTA. Quantitatively, the amoxicillin removal was decreased from 74.5% (blank) to 44.5% (for glycine) and 37.9% (for EDTA). The presence of partially oxidized electrolytes $NaNO_2$ and oxalic acid showed slight suppression in the removal of PPCPs by ferrate (VI) for all these micropollutants. Interestingly, the other co-existing ions negligibly impacted the removal of these PPCPs by ferrate (VI), which clearly depicted the potential of ferrate (VI) in the degradation of these PPCPs from aqueous solutions. The simultaneous removal conducted at two different concentrations of triclosan and amoxicillin (i.e., 0.05 mM and 0.1 mM) by ferrate (VI) (0.2 mM) at pH 10.0 showed that 65.5% removal of triclosan and 76.3% removal of amoxicillin was achieved at the concentration of 0.05 mM and 32.3% removal of triclosan and 52.8% removal of amoxicillin was achieved at the concentration of 0.10 mM.

The ferrate (VI) applicability in the wastewater treatment strategies is largely depends on its oxidative efficiency, effectiveness and performance in the real water matrix. Therefore, the real water samples were collected from four different sources of water (river water and spring waters). These water samples were extensively studied for various parametric analysis. It was noted that water samples were contained with high level of salinity hence, relatively higher conductivity was observed for these water sampels. Moreover, the TOC analysis showed that the river water (Chite River) contained with high value of non-purgeable organic carbon and low value of inorganic carbon while that of spring water (Tuikhur) contained with relatively high inorganic carbon and low value of non-purgeable organic carbon. In general the samples were contained with high value of calcium. Further, the real water samples were spiked with varied concentrations of sulfamethoxazole (0.02 to 0.2 mM), sulfamethazine (0.02 to 0.2 mM) , triclosan (0.02 to 0.5 mM) and amoxicillin (0.02 to 0.05 mM) and treated with a constant concentration of ferrate (VI) (0.20 mM) at a fixed pH 10.0. Further, it is interesting to note the removal efficieny of these micro-pollutants by ferrate (VI) treatment was almost similar as compared to the ferrate (VI) treatment conducted in distilled water samples. These results implied that ferrate (VI) is efficient and possessed with adequate selectivity in the removal of PPCPs in real water sample treatment.

Therefore, it was concluded that, ferrate (VI) is efficient and selective oxidant in the degradation of micro-polluants from aqueous solutions. Further, the implication of ferrate (VI) is devoid with the generation of toxic or harmful by-products in the wastewater treatments hence, it is known to be useful ‘GREENER TREATMENT’. The batch reactor input data is useful for scaling up the treatment technology in the efficient and selective treatment of wastewaters.

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BIO-DATA

1. NAME : Levia Lalthazuala

2. DATE OF BIRTH : 17th April, 1991.

3. FATHER'S NAME : C. Lalrinchhana

4. PERMANENT ADDRESS : E-41, Zohnuai, Lunglei, 796701.

5. EDUCATIONAL QUALIFICATIONS :

Qualification	Year of Passing	Board/University	Subjects	% of Marks	Division
HSLC	2007	Mizoram Board of School Education	English, Mizo, Mathematics, Science, Social sciences	68	First
HSSLC	2010	Mizoram Board of School Education	English, Biology, Physics, Chemistry, Mathematics	58.8	second
B.Sc (Chemisty)	2015	Mizoram University	Chemistry, Physics, Maths	60.83	First
M.Sc (Chemistry)	2017	Mizoram University	Inorganic Chemistry, Physical Chemistry (specialization), Organic Chemistry, Analytical Chemistry	71.59	First

PARTICULARS OF THE CANDIDATE

NAME OF THE CANDIDATE : Levia Lalthazuala

DEGREE : Doctor of Philosophy (Ph.D)

DEPARTMENT : Department of Chemistry

TITLE OF THESIS : Efficient use of Ferrate(VI) in the Degradation of Pharmaceuticals and Personal Care Products from Aqueous Solutions.

DATE OF ADMISSION : 10th August, 2018

APPROVAL OF RESEARCH PROPOSAL :

1. BOS : 23th April, 2019

2. SCHOOL BOARD : 8th May, 2019

3. MZU REGN. NO. : 2568 of 2011

4. Ph.D REGISTRATION NO.

& DATE : MZU/Ph.D/1248 of 10.08.2018

5. EXTENSION : NIL

Head

Department of Chemistry

List of Publications

A. Journals

1. **Levia Lalthazuala**, Diwakar Tiwari, Seung Mok Lee. Efficient Removal of Sulfamethoxazole in Aqueous Solutions Using Ferrate(VI): A Greener Treatment. ***Applied Chemical Engineering***, *33(3*) (2021) 340-341.

2. Levia Lalthazuala, Lalhmunsiama, Diwakar Tiwari, Seung-Mok Lee. Efficient use of ferrate(VI) in the remediation of aqueous solutions contaminated with potential micro-pollutants: Simultaneous removal of triclosan and amoxicillin. ***Indian Journal of Biochemistry and Biophysics***, 58 (2021) 532-542.

3. Lalhmunsiama, **Levia Lalthazuala**, Diwakar Tiwari. Ferrate(VI) as Efficient Oxidant for Elimination of Sulfamethazine in Aqueous Wastes: Real Matrix Implications. ***Environmental Engineering Research***, 27(5) (2022) 210256

B. Conference/Seminar

1. Presented “Surface Funcionalized Activated Sericite: A Sustainable Adsorbent for the Removal of Diclofenac Sodium and Clofibric Acid from Aqueous Solutions” at Internatonal Conference on Chemistry & Environmental Sustainability (ICCES-2019) on 19th to 22nd February, 2019 which was organized by Department of Chemistry, Mizoram university Aizawl, Mizoram, India.

2. Presented “Efficient Removal of Tetracycline in Aqueous Solution Using Ferrate(VI): A Greener Treatment” at National Conference on Functional Materilas and Applications- 2019 (NCFMA- 2019) on 22nd to 23rd November 2019, organized by Department of BS&HSS (Physics), National Institute of Technology, Aizawl , Mizoram, India.

3. Presented “Efficient Removal of Triclosan in Aqueous Solution Using Ferrate(VI): A Greener Treatment” at the 2nd Annual Convention of North East (India) Academy of Science and Technology (NEAST) & International Seminar on Recent Advances in Science and Technology (ISRAST) , 16th -18th November 2020, Organized NEAST, Mizoram University, Aizawl, Mizoram, India.

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Article

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

Levia Lalthazuala, Diwakar Tiwari†, Seung-Mok Lee*,† and Suk Soon Choi**

Department of Chemistry School of Physical Sciences, Mizoram University, Aizawl-796004, India
**Department of Environmental Engineering, Catholic Kwandong University, Gangneung 25601, Republic of Korea*
***Department of Biological and Environmental Engineering, Semyung University, Jecheon 27136, Republic of Korea*
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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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† Corresponding Author: D. Tiwari: Mizoram University, Department of Chemistry School of Physical Sciences, Aizawl-796004, India; S.-M. Lee: Catholic Kwandong University, Department of Environmental Engineering, Gangneung 25601, Republic of Korea
Tel: D. Tiwari: +91-9862323015; S.-M. Lee: +82-10-8891-7635
e-mail: D. Tiwari: diw_tiwari@yahoo.com; S.-M. Lee: leesm@cku.ac.kr

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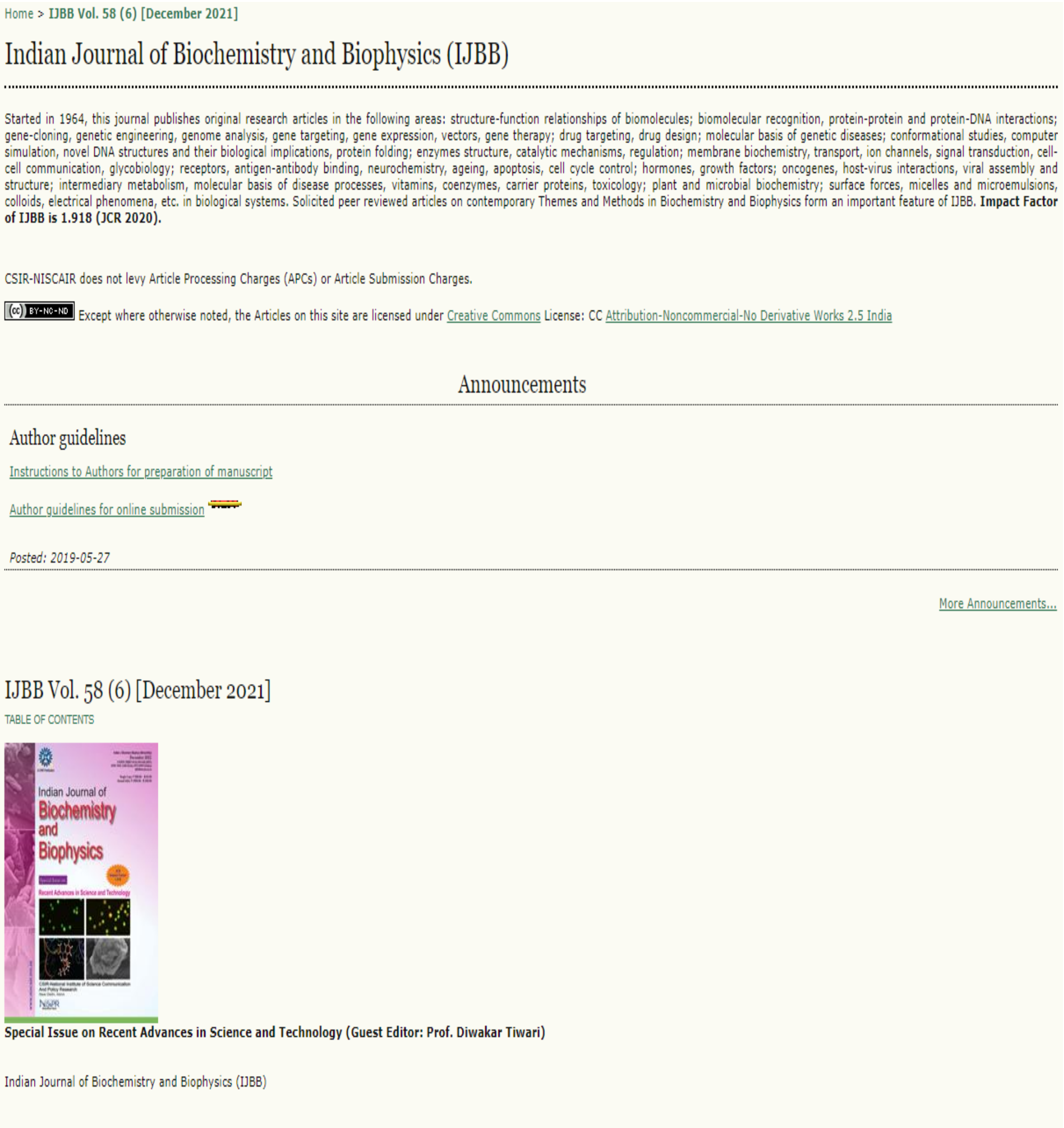

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Efficient use of Ferrate(VI) in the remediation of aqueous solutions contaminated with potential micropollutants: Simultaneous removal of triclosan and amoxicillin

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)

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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

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

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Ferrate (VI) as efficient oxidant for elimination of sulfamethazine in aqueous wastes: Real matrix implications

Lalhmunsiama[1], **Levia Lalthazuala**[2], **Diwakar Tiwari**[2†]

[1]*Department of Industrial Chemistry, School of Physical Sciences, Mizoram University, Aizawl-796004, India*
[2]*Department of Chemistry, School of Physical Sciences, Mizoram University, Aizawl-796004, India*

ABSTRACT

The presence of antibiotics in aquatic environments has become a serious concern since they develop the antibiotic/multi-drug-resistant bacteria which further affect to living beings. The study intended to assess the freshly synthesized ferrate (VI) in the degradation of an important emerging micro-pollutant i.e., sulfamethazine (SMZ). Moreover, the real matrix implications are extensively conducted for implication of ferrate (VI) technology as safer and viable options. Batch reactor studies enabled the molar ratio of ferrate (VI) to sulfamethazine is 2:1 with overall rate constant 6,128 $mM^{-2}.min^{-1}$. Percentage elimination of sulfamethazine was observed *Ca.* 80% at initial sulfamethazine concentration 0.02 mM and ferrate (VI) dose 0.1 mM. Presence of several co-ions NaCl, Na_2HPO_4, $NaNO_3$, oxalic acid and $NaNO_2$ showed insignificant effect on elimination of sulfamethazine; whereas the efficiency of ferrate (VI) was lowered due to glycine and EDTA. Mineralization of sulfamethazine is significantly increased at lower pH value (pH 5.0). Further, the removal of sulfamethazine in the real water matrix showed that the elimination efficiency of sulfamethazine is almost unaffected as compared to the distilled water treatment. This implied that ferrate (VI) is a viable and greener option for treatment of emerging water pollutants to enhance the efficiency of existing wastewater treatment plants.

Keywords: Emerging water pollutants, Ferrate (VI) treatment, Mineralization, Oxidative removal, Real matrix treatment, Sulfamethazine

1. Introduction

The presence of antibiotics in the aquatic environment has become a special concern due to their potential adverse effects in human and other living organisms. Even trace amounts of antibiotics present in aqueous media possibly will develop antibiotic/multi-drug-resistant bacteria which is a serious threat to modern medicine [1, 2]. Sulfonamides are the most common antibiotics which are widely used in poultry breeding and livestock for treating various diseases in order to increase the animal products. The extensive usage of sulfonamides by humans or animals caused them to enter into the aquatic environment since these antibiotics are only partially metabolized [3]. Moreover, the wastewater released from pharmaceutical manufacturing industries causes additional environmental concerns [4]. It has been reported that the soil fertilized with manure containing sulfonamide served as a long term source of antibiotic into aquatic environments [5]. Upon entering the soil the antibiotic enters the trophic chain through surface and ground water which significantly enhances the tolerance of bacteria towards the antibiotics [6, 7].

Sulfamethazine [4-amino-*N*-(4,6-dimethylpyrimidin-2-yl)benzene sulfonamide] is a sulfonamide with sulfanilamide and para-amino groups and it is a commonly prescribed as sulfonamide drug. These along with other sulfonamides are often detected in aquatic environments including the drinking water, surface water, groundwater, and wastewater treatment plant effluent. Due to its low cost and efficient antibiotic impact, sulfamethazine is commonly used as a feed additive in the dairy processing industry and also utilized for the treatment and prevention of influenza [8, 9]. Hence, the extensive uses of it, the level of sulfamethazine exposure in aquatic ecosystems is significantly increased and reports have shown the concentration of sulfamethazine varies from $ng.L^{-1}$ to $\mu g.L^{-1}$ [10]. Sulfamethazine is strongly hydrophilic substance and it is poorly metabolized by microorganisms [11]; further, it is reported that sulfonamide antibiotics possibly inhibits the development of several *Gram-negative* as well as most of *Gram-positive* bacteria [12, 13].

The exposure of sulfamethazine in wastewater treatment plant effluent or even in treated drinking water indicates that it is not

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† Corresponding author
E-mail: diw_tiwari@yahoo.com
Tel: +91-9862323015 Fax: +91-389-2330834
ORCID: 0000-0002-9177-9704

ABSTRACT

EFFICIENT USE OF FERRATE(VI) IN THE DEGRADATION OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS FROM AQUEOUS SOLUTIONS

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LEVIA LALTHAZUALA
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ABSTRACT

EFFICIENT USE OF FERRATE(VI) IN THE DEGRDATION OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS FROM AQUEOUS SOLUTIONS

BY
LEVIA LALTHAZUALA
Department of Chemistry

Under the supervision of
Prof. DIWAKAR TIWARI

Submitted
In partial fulfillment of the requirement of the Degree of Doctor of Philosophy in Chemistry of Mizoram University, Aizawl.

Abstract

Water is essential for human and other living organisms. The need for fresh water has increased dramatically as the world's population, manufacturing industries and agricultural developments are all rising at a tremendous rate. Over the past few decades, the volume of global sewage disposal in aquatic environment was increased significantly. According to rough statistics on ocean emissions, 35 million tons of garbage is discarded into the water bodies per year across the globe. Moreover, the increased of human activities has caused for enhanced amounts of wastewater which is substantially discharged back into the water bodies. These wastewaters are seemingly contained with high levels of organic as well as inorganic compounds or even several complex substances that eventually affected the possible tolerance of the ecosystem. Further, the presence of organic micropollutants in the ecosystem has captivated the attention of the public during the last decade, as there has been widespread concern regarding the adverse consequences of these environmental contaminants on living organisms.

The contamination of surface/ground waters by pharmaceutical and personal care products products (PPCPs) has become a very serious environmental and public problem because of the fact that these pollutants are non-biodegradable and tend to accumulate within the bio-system, causing various biological disorders. PPCPs 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. The wide distribution of these compounds at low level in the water bodies is becoming worldwide concern at present hence, are considered as potential and emerging contaminants of water bodies. These compounds are primarily entering the terrestrial environment as a result of anthropogenic practices such as inefficient wastewater treatment plants (WWTPs), livestock farms, landfill leaching, and their processing. Further, it was reiterated that the presence of PPCPs trace level in water bodies has raised a threat to the aquatic life, human health and the environment. 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. Additionally, the growing global shortages of clean water and the adverse serious consequences on the environment caused by the polluted wastewater necessitate the treatment and reduction of such wastewaters. It has become mandatory through the stringent environmental regulations and norms that these wastewaters collected from municipalities and communities is to be treated adequately as to meet the prescribed and stringent water quality standards prior to dispose it into the natural ecosystem. Various oxidants such as hypochlorite, chlorine, ozone, and hydrogen peroxide etc. have often been used for the treatment of these chemicals; however, they are either ineffective or releases hazardous byproducts which can negatively impact the environment. Similarly, the use of hypochloride/chlorine for the oxidation of cyanide often produces harmful intermediates accompanied by aromatic organic chlorides, which becomes hazardous if discharged directly into the environment. Therefore, it is necessary use chemicals that possess better efficiency, eco-friendly and that releases of no harmful byproducts.

Ferrate (VI) is a promising oxidant in the removal of pharmaceutical chemicals present in aqueous waste. It is a multifunctional chemical and is employed for oxidation, disinfection, coagulation etc. Ferrate (VI) is able to degrade toxic pharmaceutical waste following similar degradation pathway of other organic contaminants. Moreover, the by-product formed in wastewater treatment process is iron (III) which is environmentally safe. Thus, the use of ferrate (VI) in wastewater treatment processes received a greater attention.

Therefore, keeping in view, the present investigation deals with the synthesis of high purity potassium ferrate (VI) (K_2FeO_4) through the method of wet oxidation process. The purity of the synthesized ferrate (VI) was analyzed spectrophotometrically and found to be more than 95% pure. The highly reactive ferrate (VI) was employed in order to evaluate its effectiveness and applicability towards the degradation of micro-pollutants particularly pharmaceutical and personal care products (PPCPs) viz., sulfamethoxazole, sulfamethazine, triclosan and amoxicillin from aqueous solutions. The batch reactor experiments were performed on various parametric studies in order to assess the efficiency of ferrate (VI). The PPCPs were treated at varied pH (5.0-

12.0) and concentrations (0.02 to 0.5 mM). The overall rate constant values were evaluated for each pollutant using the time dependence degradation of ferrate (VI). The kinetic results eventually reveal an optimum stoichiometry of ferrate (VI) to individual PPCPs which was found to be 2:1. It was observed that ferrate (VI) reactivity is highly dependent on pH and concentrations towards the degradation of these PPCPs. Therefore, it was further revealed that rate of reaction increased with increase in concentration of pollutants. The overall rate constant (k_{app}) of various PPCPs at 0.1 mM was estimated as 5137 $(mM)^{-2}.min^{-1}$ for amoxicillin at pH 10.0, 3583 $(mM)^{-2}.min^{-1}$ for triclosan at pH 10.0, 4559 $(mM)^{-2}.min^{-1}$ for sulfamethoxazole at pH 6.0 and 6128 $(mM)^{-2}.min^{-1}$ for sulfamethazine at pH 6.0.

The HPLC measurements for PPCPs quantification for the ferrate (VI) treated and the untreated samples showed that high percentage removal of pollutants was observed with decrease in pH and concentrations of PPCPs solution. It was observed that at ferrate (VI) : PPCPs molar ratio of 1:1, the removal percentage was found to be 25.87% for sulfamethoxazole (at pH 6.0), 36.95% for sulfamethazine (at pH 6.0), 41.3% for triclosan (pH 10.0) and 54.59% for amoxicillin (at pH 10.0). Moreover, it was also observed that at pH 10.0 and at ferrate (VI) : PPCPs molar ratio of 2:1, the percent removal was found to be 82.92% for triclosan, 85.9% for amoxicillin and at pH 6.0 having similar molar ratio (i.e., 2:1), the percent removal of sulfamethoxazole and sulfamethazine was found to be 36.97% and 49.37%, respectively. Mineralization was achieved with the help of total organic carbon (TOC) analyzer, which enables to estimate PPCPs mineralization with a single dose of ferrate (VI). A partial but significant amount of PPCPs was mineralized and it was observed that at molar ratio of Fe (VI) : PPCPs (2 :1), 22.47 % of SMX and 22.78 % of SMZ was mineralized at pH 5.0 and 33.61% of TCS at pH 9.0 and 25.63% of AMX was mineralized at PH 7.0.

The effect of co-existing ions in the degradation of PPCPs by ferrate (VI) was studied in presence several coexisting anions/cations *viz*., NaCl, Na_2HPO_4, $NaNO_2$, $NaNO_3$, oxalic acid, glycine and ethylene diamine tetraacetic. The molar ratios of ferrate (VI), PPCPs and co-existing ions were taken as 2 : 1 : 5 , respectively. Results indicated that the presence of NaCl, Na_2HPO_4 and $NaNO_3$ could not hinder significantly the removal percentage of sulfamethoxazole. However, the presence of EDTA and glycine greatly suppressed the removal of sulfamethoxazole from 36.97% (blank) to 13.7% and 11.11%, respectively for EDTA and glycine. Similarly, the decomposition of sulfamethazine was greatly affected in presence glycine and EDTA. The percentage elimination of sulfamethazine in presence EDTA and glycine was found to be 14.53% and 15.86% as compared to that of the blank of 49.37%. The percentage removal of triclosan was found to be 82.9%, 58.5%, and 45.1% respectively for the blank, glycine and EDTA. Similarly, the amoxicillin removal was decreased from 74.54 % (blank) to 44.59% (for glycine) and 37.98 % (for EDTA). The presence of partially oxidized electrolytes $NaNO_2$ and oxalic acid showed slight suppression in the removal of PPCPs by ferrate (VI) for all these micro-pollutants. Interestingly, the other co-existing ions negligibly impacted the removal of these PPCPs by ferrate (VI), which clearly depicted the potential of ferrate (VI) in the degradation of these PPCPs from aqueous solutions. The simultaneous removal conducted at two different concentrations of triclosan and amoxicillin by ferrate (VI) at pH 10.0 showed that 65.5% removal of triclosan and 76.3% removal of amoxicillin was achieved at the concentration of 0.05 mM and 32.37% removal of triclosan and 52.83% removal of amoxicillin was achieved at the concentration of 0.10 mM.

The ferrate (VI) applicability in the wastewater treatment was and performance in the real water matrix. Therefore, the real water samples were collected from four different sources of water (river water and spring waters). The various parametric analysis of the water samples showed that it contained with high level of salinity hence, relatively higher conductivity was observed for these water samples. Moreover, the TOC analysis showed that the river water (Chite River) contained with high value of non-purgeable organic carbon and low value of inorganic carbon while that of spring water (Tuikhur) contained with relatively high inorganic carbon and low value of non-purgeable organic carbon. In general the samples were contained with high value of calcium. Further, the real water samples were spiked with varied concentrations of sulfamethoxazole, sulfamethazine, triclosan and amoxicillin and treated with a constant concentration of ferrate (VI) (0.20 mM) at a fixed pH 10.0. Further, it was noted that the removal efficieny of these micro-pollutants by ferrate (VI) treatment was almost similar as compared to the ferrate (VI) treatment conducted in distilled water samples. These results implied that ferrate (VI) is efficient and possessed with adequate selectivity in the removal of PPCPs in real water sample treatment. Further, the implication of ferrate (VI) is devoid with the generation of toxic or harmful by-products in the wastewater treatments hence, it is known to be useful ‘GREENER TREATMENT’.