Ferrate as a New Treatment Chemical for Removal of Effluent Organic Matter (EfOM) and Emerging Micro-Pollutants in Treated Municipal Wastewater for Water Reuse

Nanzhu Li
Montclair State University

Follow this and additional works at: https://digitalcommons.montclair.edu/etd

Part of the Environmental Sciences Commons

Recommended Citation
https://digitalcommons.montclair.edu/etd/37

This Dissertation is brought to you for free and open access by Montclair State University Digital Commons. It has been accepted for inclusion in Theses, Dissertations and Culminating Projects by an authorized administrator of Montclair State University Digital Commons. For more information, please contact digitalcommons@montclair.edu.
FERRATE AS A NEW TREATMENT CHEMICAL FOR REMOVAL OF EFFLUENT ORGANIC MATTER (EFOM) AND EMERGING MICRO-POLLUTANTS IN TREATED MUNICIPAL WASTEWATER FOR WATER REUSE

A DISSERTATION

Submitted to the Faculty of
Montclair State University in partial fulfillment
of the requirement
for the degree of Doctor of Philosophy

by
NANZHU LI

Montclair State University
Upper Montclair, NJ
2017

Dissertation Chair: Dr. Yang Deng
MONTCLAIR STATE UNIVERSITY
THE GRADUATE SCHOOL
DISSERTATION APPROVAL

We hereby approve the Dissertation

FERRATE AS A NEW TREATMENT CHEMICAL FOR REMOVAL OF EFFLUENT ORGANIC MATTER (EFOM) AND EMERGING MICRO-POLLUTANTS IN TREATED MUNICIPAL WASTEWATER FOR WATER REUSE

of

Nanzhu Li

Candidate for the Degree:

Doctor of Philosophy

Department of Earth & Environmental Studies

Certified by:

Dr. Joan C. Ficke
Dean of The Graduate School

Date

1/18/17

Dissertation Committee:

Dr. Yang Deng
Dissertation Chair

Dr. Huan Feng

Dr. Dibyendu Sarkar

Dr. Yueqiang Liu
Abstract

Rapidly expanding population, escalating water consumption, and dwindling water resources make water shortage a crisis on a global level, particularly in arid and semi-arid areas or where water sources are highly contaminated. Water reuse, accomplished by a variety of water reclamation technologies, is a strategically sound approach to this crisis. In practice, secondary effluent that is the treated wastewater discharged from municipal wastewater treatment plants (WWTPs) is a preferred reclaimed water source due to its high quality and stable quantity. However, various pollutants, effluent organic matters (EfOM) and emerging contaminants in particular, are still present in secondary effluent. They should be effectively removed before the reclaimed water is safely used.

In this dissertation study, ferrate (Fe(VI)) is proposed as a new treatment agent for treatment of secondary effluent, with an emphasis of removing EfOM and emerging contaminants. Fe(VI) is an environmentally friendly treatment agent with multiple treatment mechanisms including oxidation, coagulation, adsorption, precipitation and disinfection. Bench-scale studies were performed to investigate ferrate(VI) treatment of secondary effluent for the purpose of water reclamation. Special attention was paid to EfOM and a model emerging contaminant, i.e. mefenamic acid (MEF), which represent two challenging traditional and emerging contaminants in secondary effluent, respectively. Initial efforts were made to preliminarily evaluate the treatment performance of ferrate(VI) for the removal of different secondary effluent contaminants under different operating conditions. Thereafter, ferrate(VI) reactions with EfOM and
MEF were mechanistically investigated. All the aforementioned experiments were carried out in a batch mode. Afterwards, the treatment performance of ferrate(VI) treatment of secondary effluent was studied in a continuous-flow reactor, which is more commonly selected in engineering practices. Besides removal of the common wastewater contaminant, focus would be specially on coagulative behaviors of ferrate(VI) resultant particles, which could not be studied in a batch mode due to a different hydraulic flow state. Moreover, preliminary cost analysis was made to compare ferrate(VI) treatment and ozonation (a common chemical oxidation option in water reuse) for water reclamation. Finally, implications of ferrate(VI) for environmental management were discussed and future research suggestion was identified.
Acknowledgements

I would like to express my sincere respect and gratitude to my advisor, Dr. Yang Deng. He is always available for my questions on research and life during my PhD study. He showed me how to be a good scientist and critical thinking.

Special thanks also go to my committee members Dr. Dibyendu Sarkar (Stevens Institute of Technology), Dr. Huan Feng (Montclair State University), and Dr. Yueqiang Liu (Weston Solutions, Inc.) for their guidance and contributions on my research.

I would like to thank the funding and financial support from New Jersey Water Resources Research Institute (NJWRRI) and Montclair State University Graduate Assistantship. The work cannot be completed without the facility resource from the Department of Earth and Environmental Studies and Department of Chemistry and Biochemistry.

I am grateful to Lei Zheng, Dr. Chanil Jung, Dr. Dongyu Lyu, Dr. Yali Song and Dr. Xin Huang for their assist on my laboratory work. I want to thank Dr. Laying Wu, Dr. Xiaona Li and Dr. Kevin Olsen for their guidance on instrumental analysis. A special appreciation goes to Dr. Jinshan Gao from Chemistry Department for discussion and collaboration in the research project. I would like to thank all EAES colleagues, faculties and staffs who shared the adventure in the past five years.

Last but not least, I want to thank my parents, husband, family members and friends who have been support me in the past years for this long journey.
# Table of Contents

CHAPTER 1 BACKGROUND AND SIGNIFICANCE .................................................. 1  
1.1 Problem Statement and Research Needs .................................................. 1  
1.2 EfOM and emerging contaminants in water reuse ..................................... 5  
1.3 Ferrate chemistry and its application in water and wastewater treatment ....... 6  
1.4 Nature and Scope of Research ................................................................. 11  
1.5 References ............................................................................................... 13  

CHAPTER 2 RATIONALE, OBJECTIVES, AND HYPOTHESIS ......................... 23  
2.1 Rationales .............................................................................................. 23  
2.2 Objectives and hypothesis ...................................................................... 25  
2.3 References ............................................................................................... 27  

CHAPTER 3 PRELIMINARY STUDIES ON FERRATE(VI) TREATMENT OF  
SECONDARY EFFLUENT .................................................................................. 28  
3.1 Introduction .............................................................................................. 28  
3.2 Materials and Methods .......................................................................... 30  
3.3 Results and Discussion .......................................................................... 33  
3.4 Conclusions ............................................................................................ 48  
3.5 References ............................................................................................... 50  

CHAPTER 4 FERRATE(VI) REACTIONS WITH EFFLUENT ORGANIC MATTER 53  
4.1 Introduction .............................................................................................. 53  
4.2 Materials and Methods .......................................................................... 55  
4.3 Results and Discussion .......................................................................... 57  
4.4 Conclusions ............................................................................................ 77  
4.5 References ............................................................................................... 79  

CHAPTER 5 FERRATE(VI) OXIDATION OF MEFENAMIC ACID (MEF) IN  
WATER: KINETICS AND REACTION MECHANISMS ..................................... 81  
5.1 Introduction .............................................................................................. 81
LIST OF TABLES

Table 3-1 Conversion of DOD and Fe(VI) mass concentrations

Table 3-2 Basic parameters of secondary effluent

Table 5-1 Structures and physiochemical properties of mefenamic acid

Table 5-2 MEF removal efficiencies at different Fe(VI) doses in PBS and SE matrixes

Table 5-3 Comparison of different oxidative processes for the degradation of MEF

Table 5-4 Rate constant k and R² in different kinetics models for Fe(VI) decomposition due to the reactions with MEF and Ops

Table 5-5 Fragments (m/z) and chemical formula of OPs identified by multiple-stage tandem MS

Table 6-1 Basic water quality parameters of secondary effluent

Table 7-1 Cost comparison between Fe(VI) treatment and ozonation + FeCl₃ for treatment of secondary effluent
LIST OF FIGURES

Fig. 1-1 Chemical structure of ferrate(VI) anion

Fig. 2-1 Conceptual scheme of ferrate(VI) application for water reuse

Fig. 3-1 Preliminary tests for ferrate(VI) treatment of secondary effluent: (a) jar tests; and 
(b) secondary effluent after ferrate(VI) treatment and an overnight settling (ferrate(VI)-
induced sludge settled at the bottom).

Fig. 3-2 COD removal under different DOD and initial pH (COD$_0$ = 33.0 mg/L for pH 
8.0 and 34.4 mg/L for pH 5.0)

Fig. 3-3 UV$_{254}$ removal under different DOD and initial pH (initial UV$_{254}$ = 0.115 cm$^{-1}$ 
for pH 8.0 and 0.130 cm$^{-1}$ for pH 5.0)

Fig. 3-4 TP removal under different DOD and initial pH (TP$_0$ = 4.84 mg/L for pH 8.0 and 
5.19 mg/L for pH 5.0)

Fig. 3-5 Log removal of bacteria indicators during ferrate(VI) treatment of secondary 
effluent: (a) DOD = 0.1; and (b) DOD = 3.0 (pH = 8.0, initial total coliform = $2.46 \times 10^5$
MPN/100 mL, $E.Coli.$ = $3.29 \times 10^4$ MPN/100 mL)

Fig. 3-6 Removal of E3 and OTC during ferrate(VI) treatment of secondary effluent: (a) 
pH 8.0; and (b) pH 5.0 (initial E3 = 3.83 mg/L; and initial OTC = 2.00 mg/L)

Fig. 4-1 Residual ferrate(VI) at different reaction times (pH = 7.5): (a) ferrate(VI) decay 
at different initial ferrate(VI) doses in secondary effluent; and (b) comparison of 
ferrate(VI) decay in secondary effluent and DI water (5.00 mg/L Fe(VI))
Fig. 4-2 Experimental data vs. model data for ferrate(VI) decomposition kinetics (pH = 7.5): (a) 1st order reaction; and (b) 2nd order reaction

Fig. 4-3 2nd order reaction rate constant (k) at different ferrate(VI) doses

Fig. 4-4 Turbidity and EfOM at different chemical doses during Fe(VI) or Fe(III) treatment of the secondary effluent at the initial pH of 7.5: (a) turbidity; and (b) removal efficiencies of COD and UV254 (initial pH = 7.5; initial COD = 31.7-33.1 mg/L; initial UV254 = 0.135 – 0.142 cm⁻¹)

Fig. 4-5 MW fractions of Fe(VI) and Fe(III)-treated secondary effluent in terms of UV254: (a) Fe(VI) treatment; and (b) Fe(III) treatment (initial pH = 7.5)

Fig. 4-6 UV absorbance of the untreated, Fe(VI)-treated and Fe(III)-treated secondary effluents (initial pH = 7.5; chemical dose = 15.0 mg/L)

Fig. 4-7(a) Fluorescence excitation-emission matrix (EEM) images of untreated secondary effluent (X-axis is the excitation wavelength and Y-axis is the emission wavelength: regions I and II, proteins at Ex/Em of < 250 nm/< 380 nm; region III, fulvic acid-like materials at Ex/Em of < 250 nm/> 380 nm; region IV, soluble microbial byproduct-like materials at Ex/Em of 250-280 nm/< 380 nm; and region V, humic acid-like organics at Ex/Em of > 250 nm/> 380 nm.

Fig. 4-7(b) Fluorescence excitation-emission matrix (EEM) images of untreated and Fe(VI) treated secondary effluent (initial pH = 7.5)
**Fig. 4-7(c)** Fluorescence excitation-emission matrix (EEM) images of untreated and Fe(III) treated secondary effluent (initial pH = 7.5)

**Fig. 5-1** MEF removal rate under different initial ferrate(VI) dose in buffer and secondary effluent

**Fig. 5-2** Kinetics of overall ferrate(VI) decomposition and ferrate(VI) decomposition due to self-decay and reactions with MEF and its OPs: (a) [Fe(VI)]:[MEF] = 3:1; (b) [Fe(VI)]:[MEF] = 4:1; (c) [Fe(VI)]:[MEF] = 5:1; and (d) [Fe(VI)]:[MEF] = 6:1. (pH =7.5, initial MEF = 0.018 mM, i.e. 4.3 mg/L, and [Fe(VI)] = 0.054, 0.072, 0.090, and 0.108 mM, corresponding to 3.0, 4.0, 5.0 and 6.0 mg/L, respectively).

**Fig. 5-3** k vs. [Fe(VI)]:[MEF] (pH =7.5, initial MEF = 0.018 mM) The rate constant k2’ has a negative correlation again the initial Fe (VI):MEF ratio

**Fig. 5-4** Structure identification and functional group determination of MEF OPs after ferrate(VI) oxidation

**Fig. 5-5** Multiple-stage tandem mass spectrometry studies of m/z 138 ion in the positive mode. EIC: extracted ion chromatography of m/z 138; MS1: m/z 138 is the parent ion of interest; MS2: CID of m/z 138 ion; MS3: CID of m/z 120 ion.

**Fig. 5-6** Multiple-stage tandem mass spectrometry studies of m/z 256 ion in the positive mode. EIC: extracted ion chromatography of m/z 256; MS1: m/z 256 is the parent ion of interest; MS2: CID of m/z 256 ion; MS3: CID of m/z 238 ion; MS4: CID of m/z 223 ion.
Fig. 5-7 Multiple-stage tandem mass spectrometry studies of m/z 138 ion in the positive mode. EIC: extracted ion chromatography of m/z 138; MS1: m/z 138 is the parent ion of interest; MS2: CID of m/z 138 ion; MS3: CID of m/z 120 ion.

Fig. 5-8 Multiple-stage tandem mass spectrometry studies of m/z 256 ion in the positive mode. EIC: extracted ion chromatography of m/z 256; MS1: m/z 256 is the parent ion of interest; MS2: CID of m/z 256 ion; MS3: CID of m/z 238 ion; MS4: CID of m/z 223 ion.

Fig. 5-9 Proposed pathway of MEF degradation with Fe(VI)

Fig. 6-1 Scheme of the continuous flow reactor design (CSTR (inlet zone) + PFR (reaction zone + sludge zone + outlet zone)

Fig. 6-2 The secondary effluent reservoir (left) and Fe(VI) stock solution container (right)

Fig. 6-3 Flow patterns in the continuous flow reactor using a food-grade dye

Fig. 6-4 Residua turbidity at different contact times with different Fe(VI) doses during ferrate(VI) treatment of secondary effluent (initial pH = 7.23)

Fig. 6-5 TEM images of suspended Fe(VI)-induced particles in the reaction and settling zone during Fe(VI) treatment of secondary effluent (initial pH = 7.23, Fe(VI) = 5.00 mg/L, and contact time = 120 min)
**Fig. 6-6** Zeta potentials of suspended particles in the reaction and settling zone during Fe(VI) treatment of secondary effluent (initial pH = 7.23; relative standard deviations are below 5%, not shown in the figure)

**Fig. 6-7** Numbers of suspended particles in secondary effluent during Fe(VI) treatment of secondary effluent (initial pH = 7.23; 5.00 mg/L Fe(VI); relative standard deviations are below 5%, not shown in the figure)

**Fig. 6-8** Size distributions of suspended particles in secondary effluent during Fe(VI) treatment of secondary effluent (initial pH = 7.23; 5.00 mg/L Fe(VI))

**Fig. 6-9** Total Fe in the reaction and settling zone with different Fe(VI) doses during ferrate(VI) treatment of secondary effluent (initial pH = 7.23)

**Fig. 6-10** Particulate Fe in the reaction and settling zone with different Fe(VI) doses during ferrate(VI) treatment of secondary effluent (initial pH = 7.23)

**Fig. 6-11** Total P in the reaction and settling zone with different Fe(VI) doses during ferrate(VI) treatment of secondary effluent (initial pH = 7.23)

**Fig. 6-12** Dissolved P in the reaction and settling zone with different Fe(VI) doses during ferrate(VI) treatment of secondary effluent (initial pH = 7.23)

**Fig. 6-13** COD removal with different Fe(VI) doses during ferrate(VI) treatment of secondary effluent (initial pH = 7.23, COD$_0$ = 21.0 mg/L, and reaction time = 2 hr)
CHAPTER 1 BACKGROUND AND SIGNIFICANCE

1.1 Problem Statement and Research Needs

Current municipal water management involving wholesale transfers of water among geographic areas often leads to a reliance on water conveyance and disposal with a low efficiency of water and energy use (Englehardt et al. 2015). Meanwhile, rapidly expanding population, escalating water consumption, and dwindling water resources have severely aggravated the water shortage problem on a global scale, particularly in arid and water-stressed countries and regions. The both situations are making water reuse to meet current and future water demands (USEPA 2012, Watkinson et al. 2007). Presently, United States Environmental Protection Agency (USEPA) and sixteen state and territorial environmental agencies (e.g. New Jersey Department of Environmental Protection, NJDEP) have issued their guidance to highly encourage water reuse through implementation of a variety of water reclamation technologies (USEPA, 2012). Among various reclaimed water sources, secondary effluent from municipal wastewater treatment plants (WWTPs), i.e. biologically treated municipal wastewater, represents a stable non-seasonal one. It is preferred as a reclaimed water source due to 1) it generally meets 87 of the 93 numerical primary and secondary U.S. drinking water standards without further treatment (Englehardt et al. 2001); and 2) the U.S. population generates ~ 121 million m³ sewage every day, of which 1/3 can be reused but only 7-8% is practically reclaimed (NRC 2012, Intelligence 2010, Miller 2011), leaving a tremendous potential for expanding the use of reclaimed water in the future((GWI) 2010).
entering into potable water supplies through indirect or direct reuse or non-potable urban, industrial, and agricultural scenarios, or fouling downstream reverse osmosis (RO) systems (the most common water reclamation practice in the United States) in water reclamation. For example, EfOM significantly contributes to organic fouling of RO membranes in advanced wastewater treatment plants (Lee et al. 2006, Ang and Elimelech 2007).

A portfolio of treatment options, including engineered and managed natural treatment processes, have been developed and applied to mitigate chemical and microbial contaminants for water reclamation. However, existing treatment options are limited in two aspects. Firstly, they often suffer from various technical or economic restrictions. RO filtration requires intensive energy and generates a large volume of potentially toxic concentrates, which need to be appropriately disposed of (NRC 2012). Furthermore, membrane fouling caused by certain wastewater matrix constituents can reduce permeate flux, increase energy consumption, and lead to frequent chemical cleaning and even membrane replacement. Activated carbon adsorption is restricted by a high cost and complex regeneration. Advanced oxidation processes (AOPs) are energy-intensive, in which hydroxyl radicals unselectively react with target pollutants and co-existing chemicals, thereby largely wasting chemical oxidants (Dickenson et al. 2009). Ozone has a low solubility that limits its treatment efficiency, in addition to high cost, safety concerns, and the production of disinfection byproducts (DBPs) such as bromate. Secondly, the presence of multiple contaminants in secondary effluent requires a complex treatment train composed of several treatment options. Each treatment in the system
focuses on specific contaminants, thereby making the design and operation more complex and costly. Therefore, there is an urgent demand to develop new, effective, low-cost, and sustainable water reuse technologies.
1.2 EfOM and emerging contaminants in water reuse

EfOM in secondary effluent is a complicate organic mixture, particulate and dissolved, with a broad molecular weight (MW) range between $10^3$ and $10^6$ Da. The complex mixture is primarily comprised of extracellular polymeric substances (EPS), soluble microbial products (SMP), and natural organic matter (NOM) derived from drinking water sources (Laspidou and Rittmann 2002). SMP is originally from the biomass utilized in the bio-treatment units within WWTPs. NOM in secondary effluent derives from the NOM in natural water, which is not removed from drinking water and eventually enters into sewer systems. Although NOM is part of EfOM, EfOM has its unique physical and chemical properties such as low specific ultraviolet absorbance (SUVA), rich hydrophilic organic matter, high fluorescence index (FI) values, as well as abundant polysaccharide and protein-like compounds.

The presence of EfOM in secondary effluent has profound impacts on water reclamation: 1) many countries and states’ guidelines limit the maximum organic content in reclaimed water (e.g. BOD$_5$ ≤ 10 mg/L in urban unrestricted reclaimed water in New Jersey) 2) EfOM as a principal sink of ferrate(VI) exerts a major fraction of chemical dose; 3) EfOM significantly contributes to the RO membrane fouling in water reclamation (RO is a widely used water reclamation technology) (Ang and Elimelech 2007, Tang et al. 2011); 4) EfOM serves as DBP precursors; 5) EfOM can bind metals in wastewater to increase their solubility and bioavailability; and 6) it is a microbial substrate to enhance biomass re-growth in water distribution networks (Shon et al. 2006).
On the other hand, emerging contaminants are synthetic or naturally occurring chemicals or microorganisms that are not commonly monitored in the environment but have the potential to enter into the environment and cause known or suspected adverse ecological and/or human health effects (Terzić et al. 2008, Wintgens et al. 2008, Bolong et al. 2009, Daughton 2004). Examples of emerging contaminants recently found in untreated and treated wastewater include PPCPs, endocrine disrupting compounds (EDCs), brominated flame retardants, perfluorinated compounds (PFCs), and new DBPs (e.g. NDMA). It should be noted that traditional WWTPs are not designed specifically for the removal of these unregulated micro-pollutants. Consequently, many emerging contaminants largely flow through WWTPs and enter into effluents. They are persistent, unregulated, and of great concern in the environment even at traceable levels (Terzić et al. 2008). The unwanted emerging contaminants should be substantially removed for water reuse in order to obtain safe reclaimed water. Although activated carbon adsorption and RO or nanomembrane filtration have been reported to effectively remove certain emerging contaminants, the former one only transfers the undesirable contaminants from one phase to another, and the latter one still keep these contaminants in membrane concentrates. In contrast, chemical oxidation potentially provides an ultimate solution through chemical degradation of them into less harmful organic compounds and even nontoxic water and carbon dioxide (Englehardt et al. 2015).

1.3 Ferrate chemistry and its application in water and wastewater treatment

Ferrate(VI), i.e. the oxyanion FeO₄²⁻ containing iron in + 6 oxidation state, is recognized as an *environmentally friendly* water treatment agent due to its multiple
treatment mechanisms, the formation of non-toxic final products, and little production of undesirable DBPs (Sharma 2002, Jiang 2007, Lee et al. 2004). It has a tetrahedral structure and the four Fe-O bonds are equivalent with covalent character (Fig. 1-1) (Hoppe et al. 1982). Although the Fe(VI) studies for water treatment began in the 1970s (Waite and Gilbert 1978, Waite 1979, Gilbert et al. 1976), ferrate(VI) has recently captured a renewed interest in environmental applications. Once added to water, Fe(VI) is reduced to intermediate high valence iron species – more reactive Fe(V) and Fe(IV) - and eventually to stable Fe(III) and even Fe(II) (Jiang 2007, Sharma et al. 2008, Jiang and Lloyd 2002). Under typical water and wastewater treatment conditions, Fe(III) immediately precipitates from water to initiate a unique in-situ coagulation (Graham et al. 2010). Besides chemical oxidation and coagulation, many other treatment mechanisms concurrently proceed due to the production of Fe(III), including disinfection, adsorption and precipitation. Therefore, in a single dose, Fe(VI) can replace multiple treatment units and function as oxidant, coagulant, adsorbent, and disinfectant (Waite 2012a).

Particularly, ferrate(VI) is a unique oxidant with a reduction potential up to +2.2 V (Cyr and Bielski 1991, Lee et al. 2005a, Wood 1958). Its reactivity and stability are acutely pH dependent, because Fe(VI) exists in four individual protonated forms (H₃FeO₄⁺, H₂FeO₄, HFeO₄⁻, and FeO₄²⁻) with pK₁ = 1.6 (Rush et al. 1996), pK₂ = 3.5 (Rush et al. 1996, Carr et al. 1985), and pK₃ = 7.3(Rush et al. 1996). Fe(VI) is unstable at an acidic-neutral condition but relatively stable at an alkaline environment. For example, the half-life of Fe(VI) is around 3 min at pH 7.1, but 2 hours at pH 9.2 (Li et al. 2005). Another property of Fe(VI)-driven oxidation is selectivity. Similar to other selective
oxidants, ferrate(VI) preferentially reacts with electron-rich organic moieties (ERMs), such as activated aromatic compounds (e.g., phenol, aniline, and polycyclic aromatics), organosulfur compounds, and deprotonated amines (Lee and von Gunten 2010, Yang et al. 2012). Selective nature of Fe(VI) oxidation, to some degree, restricts its application, but Fe(VI) is more efficient than nonselective OH- for transforming ERM-containing pollutants, because less Fe(VI) is wasted by non-pollutants such as water and water matrix constituents (Lee and von Gunten 2010).

knowledge in ferrate(VI) chemistry remains largely underdeveloped with little understanding on mechanisms and little information for optimizing treatment sized systems. Therefore, more efforts are highly needed to advance ferrate chemistry for specific applications.
Fig. 1-1 Chemical structure of ferrate(VI) anion
1.4 Nature and Scope of Research

Simultaneous removal of multiple contaminants present in secondary effluent at a reasonable cost is a great challenge in the water reuse industry. In particular, EfOM and emerging contaminants are of great concern due to their chemical and biochemical persistence. This dissertation focuses on revolutionizing water reuse through development of ferrate(VI)-based technologies with at least four major benefits: (1) multiple mechanisms allow the Fe(VI) treatment to simultaneously and effectively addresses different contaminants; (2) a single treatment achieves different treatment goals, thus simplifying design and operation, saving costs, and reducing the physical footprint requirement; (3) ferrate(VI) is a safe oxidant without the production of DBPs, advantageous over other oxidants (e.g. O3 and chlorine dioxide); and (4) recent advances in ferrate(VI) production significantly reduce its manufacture costs ($2/lb) and on-site ferrate(VI) generators have become commercially available in the water treatment market (Waite 2012b), making ferrate(VI) a potentially affordable water reclamation technology.

In this dissertation research, bench-scale studies were performed to investigate ferrate(VI) treatment of secondary effluent for the purpose of water reclamation. Special attention was paid to EfOM and a model emerging contaminant, i.e. mfenamic acid (MEF), which represent two challenging traditional and emerging contaminants in secondary effluent, respectively. Initial efforts were made to preliminarily evaluate the treatment performance of ferrate(VI) for the removal of different secondary effluent contaminants under different operating conditions. Thereafter, ferrate(VI) reactions with EfOM and MEF were mechanistically investigated. All the aforementioned experiments
were carried out in a batch mode. Afterwards, the treatment performance of ferrate(VI) treatment of secondary effluent was studied in a continuous-flow reactor, which is more commonly applied than a batch reactor in engineering practices. Besides removal of the common wastewater contaminant, focus would be specially on coagulative behaviors of ferrate(VI) resultant particles, which could not be studied in a batch mode due to a different hydraulic flow state. Moreover, preliminary cost analysis was made to compare ferrate(VI) treatment and ozonation (a common chemical oxidation option in water reuse) for water reclamation. Finally, implications of ferrate(VI) for environmental management were discussed and future research suggestion was identified.
1.5 References


Wood, R.H. (1958) The heat, free energy and entropy of the ferrate (VI) ion. Journal of the American Chemical Society 80(9), 2038-2041.


CHAPTER 2 RATIONALE, OBJECTIVES, AND HYPOTHESIS

2.1 Rationales

Ferrate(VI) has a potential to serve as a new treatment agent to develop a new-generation water reuse technology due to at least three reasons. Firstly, multiple treatment mechanisms allow for the removal of different contaminants in secondary effluent (Fig. 2-1). Specifically, chemical oxidation can decompose EfOM and certain emerging contaminants; disinfection can inactivate pathogenic microorganisms; coagulation can remove particulate and colloidal particles, thus reducing TSS; precipitation can transform unwanted dissolved inorganic species (e.g. phosphate) into particulates, which is subsequently removed in a downstream solid-liquid separation; and adsorption due to the produced iron particles can adsorb certain dissolved or particulate pollutants (e.g. heavy metals). Secondly, ferrate(VI) is a safe oxidant compared with other oxidants such as chlorine and ozone in terms of the DBP production. It is well known that chlorine reacts with NOM and EfOM to produce different DBP species (e.g. two EPA regulated DBPs - trihalomethanes and haloacetic acids), while ozone can oxidize bromide to bromate (another EPA regulated DBP) (Sedlak and von Gunten 2011). The contaminants are produced after treatment and can reach end users through water distribution systems. Thirdly, the final product of ferrate(VI) treatment is iron sludge. Similar to water treatment residual (WTR) from drinking water treatment plants, the ferrate(VI)-based iron sludge has a potential to be used for land application, as long as it passes certain chemical leaching tests. If this is the case, this will greatly save landfill space and waste disposal costs.
Fig. 2-1 Conceptual scheme of ferrate(VI) application for water reuse
2.2 Objectives and hypothesis

The long-term goal of this study is to develop new, technically viable, and cost effective water reuse technologies to address both traditional and emerging contaminants in secondary effluent. The overall objective of this dissertation research is to provide a scientific basis for ferrate(VI) reactions with contaminants in biologically treated secondary effluent, with a purpose of the development of ferrate(VI)-based water reclamation technologies for water reuse. Particularly, the reaction mechanisms of Fe(VI) with EfOM and a model emerging pollutant, i.e. MEF, will be investigated. The central hypothesis is that ferrate(VI) is capable of effectively and simultaneously removing different traditional and emerging contaminants in secondary effluent for water reuse through multiple treatment mechanisms, thereby providing a new, technically reliable and low-cost water reclamation technology. To achieve the overall objective, four specific objectives were pursued, including:

1. To evaluate the technical feasibility of ferrate(VI) as a new treatment agent for treatment of secondary effluent.
2. To understand the interactions between EfOM and Fe(VI) as well as characterize chemical oxidation products of EfOM;
3. To investigate reaction kinetics and mechanisms of ferrate(VI) oxidation of mefenamic acid (a model emerging contaminant) in water;
4. To evaluate the performance of ferrate(VI)-based secondary effluent treatment in a continuous flow reactor.
In this dissertation research, four tasks were designed to achieve the four aforementioned specific objectives. The first three tasks were performed in a batch reactor, while the fourth task was carried out in a continuous-flow reactor. The first task preliminarily examined the treatment feasibility of ferrate(VI) for different contaminants in a secondary effluent as well as evaluate the effects of solution pH and chemical dose on the treatment results. The second task targeted at ferrate(VI) degradation of EfOM (a traditional contaminant). The degradation products of EfOM after ferrate(VI) treatment was particularly characterized to understand the reaction mechanisms of ferrate(VI) oxidation of EfOM. In the third task, ferrate(VI) interactions with MEF (a model emerging contaminant) were investigated. Ferrate(VI) decomposition kinetics were studied. And the oxidation byproducts of MEF were identified to reveal the reaction pathways. In the fourth task, the treatment performance of ferrate(VI) in a continuous-flow reactor (a much more commonly applied reactor type in engineering practices) was evaluated. In particular, the coagulation driven by ferrate(VI)-induced particles was investigated, because the iron floc-driven coagulation and ensuing settling could not be readily studied in a batch reactor in which the solution was under a complete mixing state. Finally, preliminary cost analysis was made to compare ferrate(VI)-based technologies with ozonation that is a common chemical oxidation practice in water reuse. Based on these major findings in the aforementioned four tasks, the implication of this dissertation research in environmental management was discussed, and future research needs were identified.
2.3 References

CHAPTER 3 PRELIMINARY STUDIES ON FERRATE(VI)
TREATMENT OF SECONDARY EFFlUENT

3.1 Introduction

Ferrate(VI) is an emerging, safe, and multi-treatment agent for water and wastewater treatment (Sharma 2002, Jiang 2007, Ghernaout and Naceur 2011). It is being primarily used as an environmentally friendly oxidant due to its powerful oxidative capacity and little production of DBPs (Ghernaout and Naceur 2011, Alsheyab et al. 2009). Besides chemical oxidation and disinfection, ferrate(VI) can initiate coagulation, precipitation, and adsorption due to the in-situ production of Fe(III) in water. The multiple treatment mechanisms allow ferrate(VI) to simultaneously remove different contaminants from water and wastewater. With this unique property, ferrate(VI) is an attractive option for water reuse using secondary effluent because a variety of contaminants are present in biologically treated municipal wastewater. However, the information regarding ferrate(VI) removal of secondary effluent contaminants is very limited.

Although several hundreds of publications are available to report ferrate(VI) for different environmental applications (Waite 2012b), the most of them focus only on a single pollutant or a specific group of compounds. Comprehensive evaluations of ferrate(VI) for various contaminants in a specific water matrix are very few. However, such an evaluation is important to water reclamation with ferrate(VI), because this can examine whether the removals of different contaminants of concern from secondary
effluent can occur under the operating conditions related to wastewater treatment (e.g. ferrate(VI) dose and solution pH). Another limitation in previous studies is the usage of phosphate buffered solution. Phosphate was widely used in ferrate(VI) studies because it, besides pH control, can complex the Fe(III) from Fe(VI) reduction and prevent the formation of iron precipitates and sludge. It facilitates the studies on ferrate(VI) oxidation, because ferrate(VI) can be directly monitored using spectrophotometry at 510 nm in the absence of particulate matters and the effect of iron sludge adsorption is not considered. However, such a high phosphate concentration (typically a few to a few tens of mM) is not present in a real secondary effluent. Application of phosphate in laboratory tests may lead to the deviation of experimental data from data obtained in engineering practices. For example, it has been noticed that ferrate(VI) decomposition rates can be accelerated with an increasing phosphate concentration (Jiang et al. 2015). Another drawback for the phosphate buffer solution is that ferrate(VI) precipitation of phosphate and other dissolved species cannot be studied, because few iron precipitates are produced due to the complexing effect of phosphate.

The objective of this chapter is to preliminarily evaluate ferrate(VI) removal of different contaminants in secondary effluent. Phosphate or other buffer chemicals were not used, in case that these externally added chemicals influenced ferrate(VI) decomposition and treatment. Two factors were tested in this study, including pH and ferrate(VI) doses.
3.2 Materials and Methods

_Chemicals and Reagents._ Secondary effluent samples were collected from the secondary clarifier of the Joint Meeting of Essex & Union Counties in Elizabeth, New Jersey, which is a municipal WWTP using activated sludge process. Once collected, the samples were transported to Montclair State University’s water treatment laboratory and stored in a refrigerator at 4°C until use. Potassium ferrate (K$_2$FeO$_4$, 96% purity) and all other chemicals (reagent grade) were purchased from Sigma-Aldrich (St. Louis, MO, US) or Fisher-Scientific (Pittsburgh, PA, US).

_Fe(VI) treatment tests._ Ferrate(VI) treatment tests were performed in 600 mL glass beakers with 200 mL secondary effluent on a four paddle programmable jar tester (Phipps & Bird - 7790-950) (Fig. 3-1). Estriol (E3) and oxytetracycline (OTC) were spiked into the secondary effluent as model micro-pollutants. The treatment was initiated through the addition of an appropriate weight of K$_2$FeO$_4$ to the secondary effluent. Initial pH was adjusted to a designated level using 1 N NaOH or H$_2$SO$_4$ solution. In the first oxidation phase, the solution was rapidly mixed at 150 rpm until all ferrate(VI) depleted. Thereafter, the solution was gently stirred at 30 rpm to achieve the following coagulation. In the coagulation phase, the iron flocs were formed. After 2-hr sedimentation, the supernatant of treated effluent sample was collected. Solution pH was not controlled during the treatment.

In this study, dimensionless oxidant dose (DOD) was used to quantify ferrate(VI) dose. DOD is defined as chemical equivalent ratio of the added oxidant to the initial COD (COD$_0$) as Eq.(3-1) (Jung et al. (in press)).
\[ DOD = \frac{\text{chemical equivalent of oxidant}}{\text{chemical equivalent of } COD_0} \]  

Equivalents of Fe(VI) and COD\(_0\) can be computed as follows.

\[ \text{Equivalent of Fe(VI) added} = \frac{Fe(VI)}{18.6} \]  

\[ \text{Equivalent of COD}_0 = \frac{COD_0}{8} \]

Here, 18.6 and 8.00 are the equivalent weights (mg/meq) of Fe(VI) and COD, respectively. Fe(VI) is ferrate(VI) mass concentration (mg/L as Fe). Considering that COD\(_0\) is different from one secondary effluent sample to another, the use of DOD would facilitate comparison of the treatment performances of an oxidation treatment technology for different secondary effluent samples. Theoretically, the added oxidant just eliminates all the COD at DOD = 1.00 as long as the four conditions are met: 1) the oxidant can completely oxidize target pollutants; 2) electron transfer is the only chemical oxidation mechanism; 3) co-existing chemical species do not compete with target pollutants for the oxidant; and 4) the oxidant does not self-decay. The conversion of DOD and Fe(VI) mass concentrations in this study is summarized in Table 3-1.

**Table 3-1** Conversion of DOD and Fe(VI) mass concentrations

<table>
<thead>
<tr>
<th>Fe(VI) (mg/L as Fe)</th>
<th>DOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>7.7</td>
<td>0.10</td>
</tr>
<tr>
<td>19.2</td>
<td>0.25</td>
</tr>
<tr>
<td>38.4</td>
<td>0.50</td>
</tr>
<tr>
<td>76.8</td>
<td>1.00</td>
</tr>
<tr>
<td>153.6</td>
<td>2.00</td>
</tr>
</tbody>
</table>
Analytical methods. Solution pH was measured with a pH meter (Thermo Scientific Orion 5-Star Plus). All the contaminants excluding bacteria indicators were analyzed prior to the filtration with 0.45µm syringe membrane filters (Millipore, nylon, 17 mm diameter). COD was measured colorimetrically following digestion (0.4–40 mg/L range, HACH). UV$_{254}$ absorbance was measured using a UV-Vis spectrophotometer (HACH, DR 5000). Total phosphorus concentration was measured using PhosVer® 3 Phosphate Reagent Powder Pills (HACH). E3 and OTC were measured using high performance liquid chromatography (HPLC) (Li 2006). Total coliform and E.Coli. were measured using IDEXX Colilert-18 test kits that are an EPA approved method for simultaneous detection of total coliform and E.Coli. in water and wastewater. All the experiments were run in triplicates.
3.3 Results and Discussion

3.3.1 Quality of secondary effluent

Quality of secondary effluent is shown in Table 3-2. The sample was an effluent from an activated sludge process, which is the most common secondary treatment practice in the United States (Tchobanoglous et al. 2003). As seen, the solution pH was at a slightly alkaline condition. The sample contained EfOM with a COD range within 33.0-34.4 mg/L. Total phosphorus (TP) varied between 4.84 and 5.19 mg/L as P. Two bacteria
indicators were measured, including total coliform ($2.46 \times 10^5$ MPN/100 mL) and *E. Coli.* ($3.29 \times 10^4$ MPN/100 mL).

**Table 3-2.** Basic parameters of secondary effluent

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.31-7.61</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>33.0-34.4</td>
</tr>
<tr>
<td>UV$_{254}$ (cm$^{-1}$)</td>
<td>0.115-0.130</td>
</tr>
<tr>
<td>TP (mg/L as P)</td>
<td>4.84-5.19</td>
</tr>
<tr>
<td>NO$_3$-N (mg/L)</td>
<td>4.1</td>
</tr>
<tr>
<td>NH$_3$-N (mg/L)</td>
<td>20.2</td>
</tr>
<tr>
<td>Total coliform (MPN/100 mL)</td>
<td>$2.46 \times 10^5$</td>
</tr>
<tr>
<td><em>E. coli</em> (MPN/100 mL)</td>
<td>$3.29 \times 10^4$</td>
</tr>
</tbody>
</table>

### 3.3.2 Treatment results

The removal of EfOM indicated as COD and UV$_{254}$ absorbance is presented in Fig. 3-2 and 3-3, respectively. As seen in Fig. 3-2, COD removal exhibited a biphasic pattern. In the first phase, COD removal dramatically increased to 38% at pH 8.0 and 57% at pH 5.0, respectively, as the DOD increased to 0.5 and 1.0. This finding suggests that ferrate(VI) rapidly reacted with EfOM through chemical oxidation and degraded oxygen demanding materials. However, as the DOD further went up to 2.0, the increase in COD removal was almost marginal, regardless of pH, suggesting that remaining organic matters were recalcitrant to ferrate(VI) oxidation. As shown in Fig. 3-3, UV$_{254}$ removals went up to 42% and 38% at pH 8.0 and 5.0, respectively, with the increasing DOD from 0.0 to 0.5. At the two pH levels, the profiles of UV$_{254}$ removal with DOD were not obviously different at the low DOD range. As DOD further increased to 1.0, the
UV$_{254}$ removals reached to 49% and 60% at pH 8.0 and 5.0, respectively. However, the increase of UV$_{254}$ removal did not augmented as DOD further increased.

Different from unselective free radical oxidation in advanced oxidation processes, ferrate(VI)-driven oxidation is selective. Ferrate(VI) is more reactive with electron-rich moieties (ERMs) (Lee and von Gunten 2010, Yang et al. 2012), which are the functional groups that release electron density to neighboring atoms from themselves via resonance or inductive effects. However, ferrate(VI) poorly reacts with electron withdrawing moieties (EWMs) that have an opposite effect, drawing electron density from neighboring atoms to themselves. In this study, the similarity in the removal profiles of COD and UV$_{254}$ (UV$_{254}$ indicates the abundance of aromatic structures and double bonds) with DOD reflects the preferential reactivity of ferrate(VI). For example, at pH 5.0, as DOD increased from 0.5 to 1.0, COD removal was increased from 40% to 58%, while the UV$_{254}$ removal went up from 38% to 60%. The slightly increased removal in COD or UV$_{254}$ at a high DOD range indicates that ERMs available to Fe(VI) oxidation became less as the oxidation proceeded and residual organic molecules became more recalcitrant. Moreover, the higher EfOM removal observed at an acidic condition suggest that HFeO$_4^-$, the dominant ferrate(VI) species below pH 7.3, was more reactive with EfOM than FeO$_4^{2-}$ that is a prevailing ferrate(VI) species above pH 7.3.
Fig. 3-2 COD removal under different DOD and initial pH (COD$_0$ = 33.0 mg/L for pH 8.0 and 34.4 mg/L for pH 5.0)

Fig. 3-3 UV$_{254}$ removal under different DOD and initial pH (initial UV$_{254}$ = 0.115 cm$^{-1}$ for pH 8.0 and 0.130 cm$^{-1}$ for pH 5.0)
The removal efficiencies of TP at different chemical doses and pH are shown in Fig. 3-4. As DOD increased from 0.0 to 1.0, the TP removals were substantially increased to 98% and 99% at pH 8.0 and 5.0, respectively. Within the chemical dose range, TP removal was greater at pH 8.0 than at pH 5.0 at an specific dose. For example, at DOD = 0.5, the TP removal at pH 8.0 was 79%, which was higher than 55% at pH 5.0. Generally speaking, phosphate can be removed from water through the formation of Fe-P precipitates and the adsorption to iron hydroxides (Tchobanoglous et al. 2003, Crittenden et al. 2012). Iron has the lowest solubility around pH 8.0 (Stumm 1992). The observation on the pH effect on TP removal is likely due to higher iron solubility at pH 5.0 that disfavors the formation of Fe-P precipitates and/or iron hydroxides. Of note, the TP removal was roughly linearly correlated with ferrate(VI) dose at a low DOD range of 0.0-0.5 (i.e. 0.00-38.4 mg/L Fe(VI)): TP removed = 0.23 Fe(VI), $R^2 = 0.76$, for pH 8.0; TP removed = 0.20 Fe(VI), $R^2 = 0.98$, for pH 5.0. Here, TP removed is the mass concentration of removed TP (mg/L as P); and Fe(VI) is the mass concentration of ferrate(VI) (mg/L as Fe).

Typically, raw wastewater contains 5.0 – 20.0 mg/L total P (TP), particulate or dissolved, of which a majority is reactive P (orthophosphate), and the rest is nonreactive P (acid hydrolysable and organic P) not readily removed by conventional secondary treatment (Tchobanoglous et al., 2003). Unfortunately, the conventional secondary treatment only removes 1.0-2.0 mg/L TP. Consequently, a majority of phosphorous remains in secondary effluent. Although P may be beneficial for some water reuse purpose (e.g. agricultural reuse), it is problematic in many reuse scenarios. Firstly, excess
P can cause severe eutrophication when reclaimed water is for environmental reuse and the receiving water bodies are environmentally sensitive (e.g. wetland restoration). For example, the State of Florida requires TP in the reclaimed water for environmental reuse below 1.0 mg/L (US EPA, 2012). Secondly, when reverse osmosis filtration (the most common water reclamation technology) is applied, P can cause inorganic membrane fouling due to the formation of calcium phosphate as well as bio-fouling because P as a nutrient can support microbial growth. The most common P removal practices employ enhanced biological phosphorus removal (EBPR) and/or chemical precipitation. However, these methods only remove reactive P, but are ineffective for nonreactive P. Here, ferrate(VI) treatment provides a promising alterative for the traditional options. Although ferrate(VI) application typically targets at other pollutants in water reclamation, the P removal provides a secondary benefit for ferrate(VI) treatment.

When Fe(VI) was reduced to Fe(III), the *in-situ* formed Fe(III) had a potential to remove phosphate from water. Two mechanisms might be involved. The first one is the direct precipitation between Fe(III) and phosphate to produce solid ferric phosphate. This mechanism has been long recognized as the major pathway to remove orthophosphate from wastewater with ferric salt addition, in which Fe(III) is dosed in a single step (Crittenden et al., 2012). And the other mechanism is the adsorption of phosphate to the produced iron hydroxide, which is gradually produced with the Fe(VI) reduction. Adsorption of phosphate to iron oxides is ascribed to surface complexation theory (Stumm 1992). The relevant reactions include the complexation between phosphate and surface iron ions as well as the protonation reactions of adsorbed phosphate.
Consequently, three surface phosphate complexes are likely formed, including ≡Fe-O-PO$_3$H$_2$, ≡Fe-O-PO$_3$H, and ≡Fe-O-PO$_3$$^{2-}$. Thermodynamic and spectrophonic experimental observations support that these are inner-sphere surface complexation reactions (Persson et al. 1996).
Fig. 3-4 TP removal under different DOD and initial pH (TP₀ = 4.84 mg/L for pH 8.0 and 5.19 mg/L for pH 5.0)
The log removal of bacterial indicators during ferrate(VI) treatment of secondary effluent at pH 8.0 is shown in Fig. 3-5(a) and (b). Fe(VI) dose was selected at its low and high levels (DOD = 0.1 and 3.0, i.e. 7.7 and 153.6 mg/L, respectively). The initial total coliform and E.Coli. concentrations were $2.46 \times 10^5$ and $3.29 \times 10^4$ MPN/100 mL, respectively. Here the log removal is defined as below (Tchobanoglous et al. 2003, Crittenden et al. 2012).

$$\text{Log removal} = -\log\left(\frac{\text{remaining bacteria concentration}}{\text{initial bacteria concentration}}\right) = -\log(1 - \frac{\text{inactivated bacteria concentration}}{\text{initial bacteria concentration}}) \quad (3-4)$$

Log removal has been widely used to evaluate the treatment performance of a disinfection process. As shown in Fig. 3-5(a), the log removal of total coliform increased to 0.96 within the first minute. Thereafter, the log removal slightly increased to 1.20 (i.e. 93.7% inactivation) at 10 min. Meanwhile, the log removal of E.Coli. rapidly reached 1.61 within the first minute and then gradually went up to 2.52 (i.e. 99.7% inactivation) at 10 min. As DOD was increased to 3.0, the log removals of total coliform and E.Coli. were promptly increased to 2.37 (i.e. 99.6% inactivation) and 2.34 (i.e. 99.5 inactivation), respectively. Afterwards, there was not an obvious variation for the removal of total coliform or E.Coli. Higher inactivation efficiencies were achieved at higher chemical doses, because a higher ferrate(VI) dose could achieve a greater oxidant exposure, which is commonly used as a major operating parameter to control a disinfection process.

The concentration of E. coli was reduced by ferrate(VI) to 100 MPN/100 mL at 10-min disinfection at DOD=0.1 (7.7 mg/L as Fe). This result meets with the non-food crop and processed food crops agricultural reuse criteria, restricted impoundment criteria, and industrial reuse criteria in Texas (Type II) and Virginia (Level 2). Previous studies
show that ferrate(VI) is capable of inactivating indicator organisms (Cho et al., 2006; Gombos et al., 2012; Jiang et al., 2006; Jiang et al., 2007), viruses (Schink and Waite, 1980), and bacteriophages (Hu et al., 2012; Kazama et al., 1994). These studies have demonstrated that ferrate disrupts cell membranes and that it may cause some genome damage in bacteriophage (Hu et al., 2012). Therefore, ferrate(VI)-induced cell damage is a plausible reason to inactivate *E. Coli*. The damage may be caused by ferrate(VI) oxidation of certain substances on cell membrane or DNA, such as sulphydryl and sulfur bonds in peptides.
Fig. 3-5 Log removal of bacteria indicators during ferrate(VI) treatment of secondary effluent: (a) DOD = 0.1; and (b) DOD = 3.0 (pH = 8.0, initial total coliform = $2.46 \times 10^5$ MPN/100 mL, *E.Coli.* = $3.29 \times 10^4$ MPN/100 mL)
Ferrate(VI) removals of two selected emerging contaminants, i.e. E3 and OTC, at pH 8.0 and 5.0 are shown in Fig. 3-6 (initial E3 = 3.83 mg/L; and initial OTC = 2.00 mg/L). DOD varied between 0.0 and 1.0. At DOD = 0.1 (i.e. 7.7 mg/L Fe(VI)), the removal efficiencies of E3 and OTC reached 94% and 97% at pH 8.0 and 98% and 99% at pH 5.0, respectively. For either contaminant, the slightly higher removal efficiency at pH 5.0 was due to the higher reactivity of ferrate(VI) at an acidic condition than at an alkaline environment. As DOD was increased to 0.25 or greater, the removal reached over 99%, regardless of solution pH. These findings demonstrated the high reactivity of ferrate(VI) toward E3 and OTC. In water, two ferrate(VI) species, i.e. HFeO$_4^-$ and FeO$_4^{2-}$, have a potential to react with E3 or OTC in its dissociated and undissociated states. For example, it is found that HFeO$_4^-$ is more reactive for E3 in the both dissociated and undissociated states, while dissociated E3 is more reactive in the reactions with Fe(VI) than undissolved E3 (Li and Gao 2009).

The primary goal of the set of experiments was to examine the treatment feasibility of ferrate(VI) for removal of certain micro-pollutants in secondary effluent, but not to fundamentally investigate the interactions between ferrate(VI) and the target micro-pollutants. These findings in Fig.3-6 were due to two reasons: 1) the both compounds were highly reactive toward ferrate(VI) oxidation; and 2) the ferrate(VI) doses were sufficiently high to effectively remove the compounds. The lowest ferrate(VI) dose was DOD = 0.1 (i.e. 138.5 µM Fe(VI)), while E3 was 3.83 mg/ (i.e. 13.3 µM) and OTC was 2.00 mg/L (i.e. 4.35 µM). Hence, [Fe(VI)]:[E3] = 10.4:1 and [Fe(VI)]:[E3] = 31.9:1. Of note, the lowest ferrate(VI) dose (138.5 µM, i.e. 7.70 mg/LFe(VI)) fell within a typical
ferrate(VI) dose range for wastewater treatment. Therefore, the promising findings showed that ferrate(VI) appeared to be effective for elimination of these unwanted micro-pollutants as long as it is capable of degrading them. The study regarding the reactivity of ferrate(VI) toward different functional groups was out of scope in this task. But a recent study (Yang et al., 2012) provides a deep insight into what endocrine disrupting compounds and PPCPs ferrate(VI) can chemically oxidize in a secondary effluent matrix. A further study on ferrate(VI) degradation of a model micro-pollutant (MEF) would be investigated in Chapter 5.

Oxidation results of traceable micro-pollutants obtained from bench scale tests using deionized water are likely discounted in a real wastewater matrix because other water matrix constituents, which have much higher concentrations than these micro-pollutants, may scavenge the oxidant to “protect” the traceable micro-pollutants of concern. Such a water matrix constituent in secondary effluent is EfOM. EfOM is present in a secondary effluent with a typical COD at a few tens of mg/L. However, the preliminary tests showed that ferrate(VI), even at a low dose, was sufficient to effectively remove E3 or OTC, regardless of solution pH. Therefore, ferrate(VI) oxidation appeared to be a potentially powerful process to address wastewater-derived emerging contaminants in secondary effluent.
Fig. 3-6 Removal of E3 and OTC during ferrate(VI) treatment of secondary effluent: (a) pH 8.0; and (b) pH 5.0 (initial E3 = 3.83 mg/L; and initial OTC = 2.00 mg/L)
To better understand the treatment potential of ferrate(VI) technology, results from the preliminary experiments are compared with the guidelines for water reuse. For EfOM, BOD$_5$, rather than COD, has been used in different guidelines. For example, BOD$_5 \leq 30$ mg/L for restricted urban reuse, environmental reuse, or industrial reuse (US EPA, 2012). In this study, the lowest ferrate dose of 7.00 mg/L (DOD = 0.10) reduced COD to 25.3 mg/L at pH 8.0 and 24.3 mg/L at pH 5.0. Because BOD$_5$ is part of COD, which indicates the 5-day biochemical degradable fraction of chemical oxygen demand, the lowest ferrate(VI) dose sufficiently meets with the reuse guideline levels. TP is also required for water reuse in some U.S. states. For example, TP $\leq 1$ mg/L for environmental reuse in Florida, North Carolina, and Washington (US EPA, 2012). Preliminary results in this study show that a ferrate(VI) dose of 19.2 mg/L (DOD = 0.25) is capable of removing TP below 1.00 mg/L from 4.84 mg/L, showing that ferrate(VI) is an effective treatment for phosphorus in water reclamation. On the other hand, emerging micro-pollutants are not regulated in water reuse. However, the almost complete removal of E3 and OTC by ferrate(VI) suggests that ferrate(VI) technology is a reliable barrier for these traceable contaminants in water.
3.4 Conclusions

Preliminary tests were performed to evaluate the treatability of ferrate(VI) for different contaminants in secondary effluent. The major findings in this study are summarized as below.

1) Ferrate(VI) can chemically oxidize EfOM, thereby reducing COD and UV<sub>254</sub>. The substantial reduction in UV<sub>254</sub> suggests that ferrate(VI) favorably reacts with UV-absorbing moieties in EfOM molecules, which are associated with aromatic structures and double bonds. The treatment characteristic is likely related to the selectivity of ferrate(VI) oxidation, because Fe(VI) more tends to react with ERMs.

2) Ferrate(VI) also effectively removes phosphorus in secondary effluent through transformation of dissolved P into particulate P.

3) Ferrate(VI) is an effective disinfecting agent. In this dissertation, it achieved a 1.20 log inactivation for total coliform and a 2.52 log removal for *E. Coli.* within 10 min at a dose of 7.7 mg/L Fe(VI).

4) Ferrate(VI) removal of certain micro-pollutants is rapid and sufficient. E3 and OTC in this study was removed by 98% at a low ferrate(VI) dose of 7.7 mg/L.

5) Ferrate(VI)-driven oxidation was pH dependent. Generally, higher removal of COD, UV<sub>254</sub>, bacteria indictors, E3 and OTC was achieved at an acidic pH condition than at an alkaline environment, because HFeO<sub>4</sub><sup>-</sup> (the dominant ferrate(VI) species at pH < 7.30) was more reactive than FeO<sub>4</sub><sup>2-</sup> (the dominant ferrate(VI) species at pH > 7.30).
These findings suggest that ferrate(VI) is a promising agent to directly treat secondary effluent for water reuse. It can concurrently and efficiently remove different pollutants, including EfOM, P, bacteria indicators, and emerging micro-pollutants, in a single dose. Solution pH and ferrate(VI) dose are two important operating parameters affecting the treatment results.
3.5 References


CHAPTER 4 FERRATE(VI) REACTIONS WITH EFFLUENT ORGANIC MATTER

4.1 Introduction

EfOM is a mixture of complex organic components (Liu and Fang 2002). Its composition and negative impacts on water reclamation have been discussed in Chapter 1. As a major water matrix constituent, it inevitably reacts with ferrate(VI) that is added into secondary effluent. The interactions between ferrate(VI) and EfOM include ferrates(VI) consumption due to Fe(VI) reactions with EfOM as well as the EfOM degradation. It is technically difficult to investigate the effect of EfOM alone on ferrate(VI) decomposition because EfOM cannot be extracted from secondary effluent and EfOM with a high purity grade, unlike NOM, is not commercially available. The ferrate(VI) decomposition in secondary effluent is an overall effect of ferrate(VI) self-decay and reactions with certain reducing agents, of which EfOM was a major component. Studies on ferrate(VI) treatment of secondary effluent were reported previously, but the information on ferrate decomposition kinetics in a secondary effluent matrix is very limited (Lee and von Gunten 2010). Lee and von Gunten (2010) compared the decomposition of four oxidants (40-45 µM) in a secondary effluent at pH 8.0. Results showed that all the oxidants followed a 2nd order reaction pattern. Among the four oxidants, ferrate(VI) decomposition was the slowest. The oxidation exposure of the four oxidants followed the order: ferrate(VI) (4.5 × 10⁻² M) ≈ chlorine dioxide > chlorine (3.6 × 10⁻² M⁻¹ s⁻¹) > ozone (6.0 × 10⁻⁴ M⁻¹ s⁻¹). Ferrate(VI) stability is beneficial because this
may maintain a greater oxidant exposure for better oxidation of target pollutants. Moreover, ferrate(VI) decomposition was very distinct from the decay of the other three oxidants, which exhibited a biphasic behavior – a rapid decay at the onset followed by a slow decomposition. In contrast, ferrate(VI) concentration decreased smoothly over the reaction time.

A variety of treatment methods for reduction of EfOM in secondary effluent have been intensively studied, including chemical coagulation, activated carbon adsorption and advanced oxidation processes (Shon et al. 2006, Michael-Kordatou et al. 2015). Coagulation can largely remove particulate matters in secondary effluent, thereby being an effective method for the alleviation of particulate organic matter. However, the treatment capability of coagulation or dissolved EfOM is very limited. Therefore, it is often used as a pre-treatment prior to other treatments (e.g. activated carbon adsorption or RO filtration). Activated carbon adsorption has proven to remove significant quantities of dissolved EfOM from secondary effluent (Michael-Kordatou et al. 2015, Gur-Reznik et al. 2008). For example, Gur-Reznik et al. (2008) removed 80-90% dissolved EfOM from secondary effluent using granular activated carbon for mitigation of the downstream RO fouling. Activated carbon favorably removes hydrophobic and biodegradable EfOM and low-medium MW EfOM molecules with low SUVA (Shon et al. 2004). However, activated carbon is particularly costly. Moreover, economical regeneration methods of spent carbon need to be considered in practices to save operating costs. AOPs are another option for removal of EfOM. Various AOPs are available for the application purpose, such as the Fenton treatment, ozone-based AOPs (e.g. O₃/H₂O₂ and O₃/UV), UV-based
AOPs (e.g. TiO$_2$/UV), and emerging sulfate radical–based AOPs (e.g. heated activated persulfate). Hydroxyl or sulfate radicals are among the strongest oxidizing agents with a reduction potential over 2.80 V. They can rapidly degrade EfOM molecules and even mineralize certain EfOM into water and carbon dioxide. A DOC removal of 20 - 90% has been reported for free radical oxidation of EfOM during AOPs (Ito et al. 1998, Shon et al. 2003). However, AOPs are typically energy-intensive. And the free radicals are less efficiently utilized because they unselectively react with many non-target constituents in water to cause a chemical waste.

The objective of this study is to elucidate the interactions of ferrate(VI) and EfOM in a secondary effluent matrix. Ferrate(VI) decomposition kinetics in a secondary effluent was firstly studied. Afterwards, EfOM degradation products after ferrate(VI) treatment were characterized to understand the reactivity of EfOM toward ferrate(VI) oxidation.

4.2 Materials and Methods

*Chemicals and Reagents.* Potassium ferrate (K$_2$FeO$_4$, 96% purity) and all other chemicals (reagent grade) were purchased from Sigma-Aldrich (St. Louis, MO, US) or Fisher-Scientific (Pittsburgh, PA, US). Secondary effluent was collected from a secondary clarifier prior to disinfection at a local municipal wastewater treatment plant using activated sludge treatment (Elizabeth, NJ). Once collected, the sample was delivered to Montclair State University’s water treatment laboratory and stored at 4ºC in a refrigerator until use. A concentrated ferrate(VI) stock solution (200 mg/L Fe(VI)) was prepared by dissolving an appropriate mass of K$_2$FeO$_4$ in deionized water. The pH of this
stock solution was around 9.0 at which Fe(VI) was relatively stable. The Fe(VI) concentration was confirmed with the ABTS method (Lee et al. 2005b). A concentrated ferric stock solution (1,000 mg/L Fe(III)) was prepared by dissolving an appropriate amount of ferric chloride salt in deionized water. The Fe(VI) and Fe(III) stock solutions were freshly prepared prior to use.

*Fe(VI) and Fe(III) treatment tests.* Ferrate(VI) treatment tests were performed in 600 mL glass beakers with 200 mL secondary effluent on a six-paddle programmable jar tester (Phipps & Bird - 7790-950). The treatment was initiated through the addition of an aliquot of K$_2$FeO$_4$ from the stock solution to the secondary effluent. Within the first 3 minutes, the solution was rapidly mixed at 150 rpm to completely disperse the added ferrate(VI). The solution was gently stirred at 30 rpm in the following 60 minutes during which Fe(VI) was completely decomposed. A low mixing speed during the slow mixing also prevented the produced iron flocs from destruction. For the kinetics tests, 2 mL of sample was collected at designated sampling times and then filtered through 0.45 μm membrane for measurement of residual ferrate(VI). Thereafter, a 60-min settling cycle started to allow for sedimentation of the large iron flocs. Finally, 100 mL supernatant was collected for analysis. Control tests were performed with Fe(III) under the identical conditions to understand the behavior of Fe(III)-based coagulation alone in the removal of EfOM. The initial solution pH was 7.5. During the treatment, pH was not controlled but monitored over time. The final pH was not beyond 8.10.

*Analytical methods.* Solution pH was measured with a pH meter (Thermo Scientific Orion 5-Star Plus). Turbidity was determined with a portable turbidity meter
(HACH, 2100Q). EfOM in the supernatant samples was analyzed prior to the filtration with 0.45µm syringe membrane filters (Millipore, nylon, 17 mm diameter). COD was measured colorimetrically using a set of COD test kits (0.4–40 mg/L ultralow range, HACH). UV\textsubscript{254} absorbance was measured using a UV-Vis spectrophotometer (HACH, DR 5000). EfOM was sequentially fractionated using a stirred cell (Millipore, Model 8200) in terms of their molecular weight (MW) with 10 and 1 kDa UF membranes. Two litters of Milli-Q water (18.2 MΩ/cm) passed through the UF membrane filters before use. Fluorescence excitation-emission matrix (EEM) analyses were conducted with a LS-55 fluorescence spectrometer (Perkin-Elmer, Norwalk, Connecticut, USA) under the excitation wavelength of $\lambda_{\text{ex}} = 200–460$ nm at 5 nm increments across an emission range of $\lambda_{\text{em}} = 240–590$ nm at 2 nm intervals. Excitation and emission slit widths were set to 2.5 nm with a photomultiplier tube voltage of 800 V. All the experiments were run in triplicates. Their relative standard deviations were below 5% (not shown in figures).

### 4.3 Results and Discussion

#### 4.3.1 Ferrate(VI) decomposition kinetics in secondary effluent

Ferrate(VI) decomposition kinetics data at different ferrate(VI) doses is show in Fig. 4-1(a). The ferrate(VI) decomposition exhibited a biphasic reaction pattern, having a dramatic decrease at the initial phase followed by a subsequent slow decay. The reaction times for Fe(VI) decrease by 90% were 400, 450, 600, and 650 s for 5.00, 10.00, 15.00, and 20.00 mg/L Fe(VI) (i.e., 0.09, 0.18, 0.27 and 0.36 mM), respectively. Two kinetics models, i.e. 1\textsuperscript{st} order and 2\textsuperscript{nd} order reaction equations, were fitted with experimental data, as shown in Fig. 4-2(a) and (b). At any specific ferrate(VI) dose,
Fe(VI) decomposition well followed a 2nd order reaction pattern ($R^2 > 0.98$) rather than a 1st order reaction pattern. Very clearly, as shown in Fig. 4-2(a), the experimental data did not exhibit a linear relationship between $\ln(C/C_0)$ and time for the 1st order fitting. The observed 2nd order rate constants ($k$) at 0.09, 0.18, 0.27 and 0.36 mM Fe(VI) (i.e. 5.00, 10.00, 15.00 and 25.00 mg/L Fe(VI)) were 0.2239, 0.1030, 0.0475, and 0.0314 mM$^{-1}$ s$^{-1}$, respectively.

Generally speaking, ferrate(VI) decomposition is due to two pathways: (1) 2nd order reaction for homogenous self-decomposition; and (2) 1st order reaction for ferrate(VI) reactions with different water matrix constituents (Lee et al. 2004). Comparison of ferrate(VI) decay in secondary effluent and DI water is shown in Fig. 4-1(b) (Fe(VI) = 5.00 mg/L). Although ferrate(VI) might react with different reducing agents in the secondary effluent, the major ferrate(VI) sink, excluding self-decomposition, was EfOM because its concentration was much greater than others (e.g. nitrite). In Fig. 4-1(b), ferrate(VI) decay in DI water showed Fe(VI) consumption due to self-decomposition alone (the diamond symbols), while the ferrate(VI) decomposition in secondary effluent represented Fe(VI) consumption due to both self-decomposition and the reactions with reducing agent (the majority was EfOM) (the square symbols). Therefore, the difference between two curves was primarily caused by Fe(VI) reaction with EfOM. As shown, the EfOM accounted for a significant fraction of Fe(VI) decomposition, particularly in the initial phase. For example, at a ferrate(VI) dose of 5.00 mg/L, the Fe(VI) consumptions due to self-decomposition and reactions with EfOM were 0.70 and 2.45 mg/L, respectively, within the 1st min. This finding suggests that EfOM rapidly reacted with
ferrate(VI) at the onset of treatment. Thereafter, the Fe(VI) consumption due to EfOM was not obviously increased with time, suggesting that ferrate(VI) decomposition was not greatly influenced by EfOM in the following phase. The data of k against ferrate(VI) dose is presented in Fig. 4-3. As seen, k considerably dropped from 0.2239 to 0.0314 mM$^{-1}$ s$^{-1}$ with the increasing ferrate(VI) dose from 0.09 to 0.36 mM. The correlation between the 2$^{nd}$ order rate constant and ferrate(VI)_dose was not linear. As the ferrate(VI) dose went up, the extent of the decrease in the rate constant was reduced. The kinetics parameter including reaction order, rate constant, and the relationship between k and ferrate(VI) dose are important to determine Fe(VI) lifetime and exposure in a secondary effluent matrix.
Fig. 4-1 Residual ferrate(VI) at different reaction times (pH = 7.5): (a) ferrate(VI) decay at different initial ferrate(VI) doses in secondary effluent; and (b) comparison of ferrate(VI) decay in secondary effluent and DI water (5.00 mg/L Fe(VI)).
Fig. 4-2 Experimental data vs. model data for ferrate(VI) decomposition kinetics (pH = 7.5): (a) 1\textsuperscript{st} order reaction; and (b) 2\textsuperscript{nd} order reaction.
Fig. 4-3 2nd order reaction rate constant (k) at different ferrate(VI) doses
4.3.2 Ferrate(VI) reaction with effluent organic matter (EfOM) in secondary effluent

Turbidity and EfOM of Fe(VI) or Fe(III)-treated secondary effluents at different chemical doses are presented in Fig. 4-4 (a) and (b), respectively. As seen in Fig. 4-4 (a), the secondary effluent turbidity was initially decreased from 6.53 to 2.58 NTU as the Fe(VI) dose increased from 0.00 to 1.00 mg/L, and then gradually increased to 13.1 NTU when the Fe(VI) dose further increased to 15.00 mg/L. In contrast, the turbidity in Fe(III)-treated secondary effluent consistently dropped from 6.53 to 0.87 NTU with the increasing Fe(III) dose from 0.00 to 15.00 mg/L. For any specific Fe(VI) dose, the Fe(III) treatment achieved lower effluent turbidity than Fe(VI) treatment. The finding suggests that coagulation and flocculation with Fe(III) produced flocs with the better settleability than Fe(VI)-induced coagulation and flocculation. The mechanisms behind the observation would be explored in Chapter 6.

The removal and transformation of EfOM with Fe(VI) or Fe(III) are presented in Fig.4-4 (b). COD removal significantly went up from 0 to 12% as Fe(VI) dose increased from 0.00 to 1.00 mg/L, and then slightly augmented to 15% when Fe(VI) further increased to 15.0 mg/L. In contrast, for the Fe(III) treatment, the COD removal slightly increased from 9% to 18% as the Fe(III) dose from 1.0 to 15.0 mg/L. For the COD removal, Fe(VI) performed better than Fe(III) only at a low chemical dose (1.00 mg/L), but provided an inferior treatment at a higher chemical dose (1.0-15.0 mg/L), thereby indicating that the capability of Fe(VI) for COD removal was limited.
However, the different patterns of the \( \text{UV}_{254} \) reduction were noticed between the Fe(VI) and Fe(III) treatment. \( \text{UV}_{254} \) is a measurement of the amount of ultraviolet light absorbed by aqueous constituents (e.g. natural organic matter or phenolic compounds), especially aromatic organic compounds, in water. As the ferrate(VI) dose was increased from 0.0 to 15.0 mg/L, the effluent \( \text{UV}_{254} \) removal was dramatically increased to 49% and 23% in the Fe(VI) and Fe(III)-treated secondary effluents, respectively.

The different behaviors of Fe(VI) and Fe(III) in removal of COD and \( \text{UV}_{254} \) were due to their different treatment mechanisms. In a typical Fe(VI) treatment system, Fe(VI) decomposes via self-decomposition and reactions with water constituents (e.g. EfOM) (Lee et al. 2004). Fe(VI) oxidation has proven to be very selective, so that ferrate(VI) preferentially attacks organic compounds with ERMs (Lee and von Gunten 2010, Yang et al. 2012). Accompanied with Fe(VI) reduction, Fe(III) is produced to initiate an \textit{in-situ} coagulation (Graham et al. 2010). Both chemical oxidation and coagulation are capable of potentially removing EfOM. Graham et al. (2010) attempted to quantify the roles of Fe(VI) oxidation and coagulation in the removal of humic acid (HA) through comparison of the HA removals with Fe(VI) in the absence and presence of phosphate, which could complex Fe(III) and prevent the formation of iron particles. However, the quantitative information might not be accurate because phosphate can significantly alter the ferrate stability in water, thereby changing the ferrate exposure. It is technically difficult to separate the extents of organics removal due to oxidation and coagulation during the Fe(VI) treatment (Graham et al. 2010).
On the other hand, Fe(III) removed EfOM only through coagulative mechanism. It should be noted that the coagulation performances with Fe(VI) and Fe(III) in secondary effluent have been demonstrated to be greatly different (Jiang et al. 2015, Goodwill et al. 2015). Fe(III)-induced flocs tended to rapidly settle, while a majority of Fe(VI) resultant particles remained suspended probably because of the formation of more stable iron particles. In Fig.4-4(b), the stoichiometric relationship between COD removal and the added Fe(III) in the Fe(III) treatment could be described as follows.

\[
\text{COD removal} \% = 0.016 \text{Fe(III)} \quad (R^2 = 0.96)
\]

(4-1)

The finding suggests that the Fe(III) coagulation efficiency was almost linearly increased with Fe(III) dose. On the other hand, for Fe(VI) treatment, significant COD removal occurring at 1.00 mg/L Fe(VI) was principally due to Fe(VI) oxidation, because coagulation with iron was almost ineffective for organics removal at such a low dose (Tchobanoglous et al. 2003). Generally, COD coagulation efficiency with Fe(III) is theoretically increased with an increasing iron dose. However, the increase in COD removal over 1.00 - 15.00 mg/L Fe(VI) was almost marginal, indicating that Fe(VI)-induced coagulation was poor for removal of the secondary effluent COD. The UV\textsubscript{254} reduction by Fe(III) was caused by direct Fe(III) coagulation through adsorption of UV-absorbing compounds, while a better removal with Fe(VI) was achieved by the both oxidative and coagulative mechanisms. Although the both effects were not separated in this study, UV\textsubscript{254} removal due to Fe(VI) oxidation was likely dominant because the removal efficiency of Fe(VI)-induced coagulation for EfOM was very limited as discussed above.
Fig. 4-4 Turbidity and EfOM at different chemical doses during Fe(VI) or Fe(III) treatment of the secondary effluent at the initial pH of 7.5: (a) turbidity; and (b) removal efficiencies of COD and UV$_{254}$ (initial pH = 7.5; initial COD = 31.7-33.1 mg/L; initial UV$_{254}$ = 0.135 – 0.142 cm$^{-1}$)
Molecular weight (MW) fractions of EfOM in Fe(VI) and Fe(III)-treated secondary effluents in terms of UV$_{254}$ are shown in Fig. 4-5 (a) and (b), respectively. EfOM compounds in untreated and treated samples were isolated into three groups, i.e. high (> 10 k Da), medium (10-1 k Da), and low (< 1k Da) MW fractions. For the untreated sample, the UV$_{254}$ levels of high, medium and low MW molecules were 0.026, 0.026 and 0.082 cm$^{-1}$, respectively. These findings suggested that low MW molecules prevailed among the EfOM compounds, which accounted for 61% of the overall UV$_{254}$. As seen in Fig. 4-5 (a), UV$_{254}$ in both high and medium MW groups gradually dropped with the increasing Fe(VI) dose, suggesting that Fe(VI) treatment favorably removed high and medium MW molecules rather than the low MW group. A significant UV$_{254}$ reduction in the two groups was noticed at a low Fe(VI) dose at which coagulation efficiency was insignificant owing to a too low Fe(III) dose (the Fe(VI) reduction product). Therefore, chemical oxidation in the Fe(VI) treatment played an essential role in the removal of UV$_{254}$ due to the two groups of compounds. In contrast, UV$_{254}$ removal for the low MW EfOM molecules exhibited a different pattern with Fe(VI) dose. It slightly increased from the original 0.082 to 0.088 cm$^{-1}$ at 1.00 mg/L Fe(VI), and then substantially dropped to 0.052 cm$^{-1}$ as Fe(VI) increased to 15.00 mg/L. The UV$_{254}$ increase observed at the low Fe(VI) dose was likely because part of high and medium MW molecules were chemically transformed into low MW molecules after Fe(VI) oxidation. The ensuing decrease in UV$_{254}$ with increasing Fe(VI) dose indicated the reactivity of ferrate(VI) towards these low MW EfOM molecules was high. Consequently, the fraction of low MW molecules after the 15.00 mg/L Fe(VI) treatment
was increased to 73%. Results of the control tests with Fe(III) are presented in Fig. 4-5 (b). Generally, the high and medium MW molecules were slightly removed with an increasing Fe(III) dose. For example, UV$_{254}$ due to high MW fraction was decreased from 0.026 to 0.014 cm$^{-1}$ as the increasing Fe(III) was increased from 0.0 to 15.0 mg/L. However, the removal of UV$_{254}$ from the low MW group was very slight (7% removal) over the tested Fe(III) range. Therefore, Fe(III)-driven coagulation was almost ineffective for alleviating UV$_{254}$ from low MW EfOM molecules.
Fig. 4-5 MW fractions of Fe(VI) and Fe(III)-treated secondary effluent in terms of UV$_{254}$: (a) Fe(VI) treatment; and (b) Fe(III) treatment (initial pH = 7.5)
UV absorbance spectra (200-400 nm) of the untreated, Fe(VI)-treated and Fe(III)-treated secondary effluents are presented in Fig. 4-6. The three spectra were characterized with a shoulder at 200-230 nm and a gradual decrease (tailing) over 230-400 nm. The first band referred to Bz band was centered at 203 nm primarily due to the vibrational perturbations in the π-electron system, while the band centered at 253 nm (ET band) was a distinctive feature of the electronic spectra of aromatic compounds (Korshin et al. 1997). The shoulder and tailing spectra were obvious in the untreated secondary effluent, but became less pronounced after Fe(VI) or Fe(III) treatment. Therefore, either treatment could somewhat remove the associated chromospheres. However, the two treatments had different removal efficiencies over different wavelength ranges. Fe(III) and Fe(VI) appeared to preferentially alleviate the absorption in the Bz and ET bands, respectively, suggesting that Fe(VI) or Fe(III) selectively removed polar functional groups such as hydroxyl, carbonyl, carboxyl and ester groups. UV_{253}/UV_{203} is an indicator of the presence of activated aromatic rings in EfOM. The original UV_{253}/UV_{203} was 0.163 in untreated secondary effluent, but dropped to 0.103 and 0.139 after Fe(VI) and Fe(III) treatment, respectively, again validating that the both treatments favorably targeted at the destruction of aromatic rings. The lower UV_{253}/UV_{203} achieved by Fe(VI) was likely because these aromatic structures were better removed through Fe(VI)-driven oxidation than Fe(III) coagulation.

The aforementioned findings indicate that ferrate(VI) tends to lower the aromatic degrees primarily via chemical oxidation. The reactions between EfOM and Fe(VI) can lead to additional consumption of ferrate(VI) in advanced wastewater treatment practices
to reduce the degree of ferrate(VI) exposure. Therefore, the impact of EfOM on Fe(VI) exposure needs to be evaluated to accurately determine the ferrate(VI) dose for target pollutants during applications. Meanwhile, although ferrate(VI) does not preferentially remove secondary effluent COD, it appears to be effective for the removal of UV$_{254}$, implying that ferrate(VI) is a potential tool for controlling DBP formation in downstream disinfection, because UV$_{254}$ is a widely accepted surrogate to measure the DBP precursors in water (Crittenden et al. 2012).
**Fig. 4-6** UV absorbance of the untreated, Fe(VI)-treated and Fe(III)-treated secondary effluents (initial pH = 7.5; chemical dose = 15.0 mg/L)
Fluorescence EEM spectra of untreated secondary effluent, Fe(VI)-treated secondary effluent and Fe(III)-treated secondary effluent are presented in Fig. 4-7 (a), (b), and (c), respectively. Fluorescence EEM spectra is an effective tool to provide qualitative information on chemical compositions of dissolved organic matter, such as NOM and EfOM (Chen et al. 2012, Bro 1997, Lee and Hur 2016). Generally, the fluorescence EEM spectra can be divided into five unique Ex–Em regions that represent different dissolved organic matter (DOM) types (Chen et al. 2003): 1) regions I and II, proteins (e.g. tyrosine) at Ex/Em of < 250 nm/< 380 nm; 2) region III, fulvic acid-like materials at Ex/Em of < 250 nm/> 380 nm; 3) region IV, soluble microbial byproduct-like materials at Ex/Em of 250-280 nm/< 380 nm; and 4) region V, humic acid-like organics at Ex/Em of > 250 nm/> 380 nm.

The fluorescence EEM image of untreated secondary effluent is shown in Fig. 4-7(a). Obviously, two EEM peaks were observed in the regions III and V, representing the presence of fulvic acid-like and humic acid-like DOM, respectively. Because the two DOM types are hydrophobic organic matter, the secondary effluent EfOM was characterized with hydrophobic organic compounds. Of note, both of the two hydrophobic compounds are characterized with abundant UV-absorbing moieties (Tchobanoglous et al. 2003, Zhao et al. 2013). As ferrate(VI) dose was gradually increased, the EEM spectra in all the five regions were weakened, to the different degrees (Fig. 4-(b)). In particular, the EEM peak in the region V was almost eliminated at 5.00 mg/L Fe(VI), and the EEM peak in the region V was dramatically reduced at 15.00 mg/L. In contrast, for the Fe(III) treatment, only the EEM peak in the region III was somewhat
alleviated as the Fe(III) dose was increased from 0.00 to 15.00 mg/L (Fig. 4-(c)). However, the region V peak was not significantly altered. This finding suggests that the capability of Fe(III) for the removal of UV-quenching hydrophobic matters was limited. Fe(III) coagulation only mitigated fulvic acid-like substances, but did not obviously remove the humic-like organic matter. In contrast, ferrate(VI) treatment was very effective for the removal of both fulvic-like and humic-like substances because of the dual mechanisms, i.e. chemical oxidation and coagulation. The finding was in agreement with the aforementioned observation that ferrate(VI) could better remove UV$_{254}$ absorbance from secondary effluent, considering that the both hydrophobic organic matters contributed to UV$_{254}$ absorbance due to their strong UV-quenching properties. The finding is also similar to the observation from a recent study (Song et al. 2016) to investigate ferrate(VI) treatment of NOM in a drinking water source. Song et al. (2016) also found that ferrate(VI) favorably removed hydrophobic DOM rather than hydrophilic constituents. They ascribed the unique treatability of ferrate(VI) to the selectivity of ferrate(VI) oxidation. Namely, ferrate(VI) better reacts with aromatic rings and double bonds in the hydrophobic groups.
Fig. 4-7(a) Fluorescence excitation-emission matrix (EEM) images of untreated secondary effluent (X-axis is the excitation wavelength and Y-axis is the emission wavelength: regions I and II, proteins at Ex/Em of < 250 nm/< 380 nm; region III, fulvic acid-like materials at Ex/Em of < 250 nm/> 380 nm; region IV, soluble microbial byproduct-like materials at Ex/Em of 250-280 nm/< 380 nm; and region V, humic acid-like organics at Ex/Em of > 250 nm/> 380 nm.
Fig. 4-7(b) Fluorescence excitation-emission matrix (EEM) images of untreated and Fe(VI) treated secondary effluent (initial pH = 7.5)
4.4 Conclusions

Ferrate(VI) application for wastewater reclamation targets at certain pollutants in secondary effluent (e.g. emerging micro-pollutants, phosphorus and pathogens). However, it unavoidably reacts with other water matrix constituents. One such example is EfOM. The major findings in this study include:

1) Ferrate(VI) decomposition in a secondary effluent matrix follows a 2\textsuperscript{nd} order reaction with respect to Fe(VI) concentration. The rate constant exponentially decreases with the increasing ferrate(VI) dose.
2) Ferrate(VI) is more effective for reduction of UV$_{254}$ than Fe(III) in secondary effluent, but not better than Fe(III) in the removal of COD.

3) At a low dose, Fe(VI) preferentially decomposes high (> 10 k Da) and medium (10-1 k Da) MW molecules into low MW compounds (< 1 k Da) in terms of UV$_{254}$, thereby causing an increased low MW fraction. As chemical dose further increases, the UV$_{254}$ absorbance of all the MW groups are somewhat decreased.

4) Fluorescence EEM spectra results reveal that ferrate(VI) treatment effectively removes hydrophobic DOM, including fulvic-like and humic-like substances. In contrast, Fe(III) coagulation only obviously alleviates fulvic-like dissolved organic compounds.

5) Although both chemical oxidation and coagulation in ferrate(VI) treatment could potentially contribute to EfOM removal, ferrate(VI)-driven oxidation seemed to play a more essential role in the EfOM transformation under the tested conditions.
4.5 References


CHAPTER 5 FERRATE(VI) OXIDATION OF MEFENAMIC ACID (MEF) IN WATER: KINETICS AND REACTION MECHANISMS

5.1 Introduction

Emerging contaminants are traceable synthetic or naturally occurring chemicals or microorganisms that are not commonly monitored in the environment but have the potential to enter into the environment and cause known or suspected adverse ecological and/or human health effects. Examples of emerging contaminants recently identified in untreated and treated wastewater include pharmaceuticals and personal care products (PPCPs), endocrine disrupting compounds (EDCs), brominated flame retardants, perfluorinated compounds (PFCs), and new disinfection byproducts (e.g. NDMA). Most of them are biochemically and chemically persistent, unregulated, and of ecological or health concern even at traceable levels (Choi et al., 2006; Ying et al., 2003).

Unfortunately, traditional water and wastewater treatment plants were not specially designed for these emerging contaminants. Many emerging contaminants have been reported to largely flow through these treatment facilities without a sufficient removal. Therefore, advanced treatment methods are required to eliminate or alleviate these micropollutants before reclaimed water is safely reused.

Since the mid-1990s PPCPs have attracted public attention in water industries as an emerging contaminant type due to their potentially adverse environmental and health impacts. Because pharmaceutically active compounds are commonly used and most of them are not completely metabolized, many pharmaceuticals end up in natural water
bodies through sewers and treatment systems. Since the 1990s, a variety of PPCPs at low concentrations have been identified in surface water, groundwater and drinking water in the world (Doerr-MacEwen and Haight, 2006).

Ferrate(VI) has proven to be very effective for degradation of certain emerging PPCPs in a buffered deionized (DI) water matrix, hospital wastewater (Wilde et al., 2013) and municipal wastewater effluent. In this dissertation study, mefenamic acid (MEF) is selected as a representative emerging PPCP. Structure and basic physical/chemical properties of MEF are summarized in Table 5-1. It served as a model micro-pollutants due to the following reasons. Firstly, MEF has been widely used as a common non-steroidal anti-inflammatory drug (NSAID) for treatment of pain such as menstrual pain. Secondly, it has been frequently identified in natural and engineered water systems. Marketed as Ponstel in the United States and known as Ponstan in UK, MEF has been detected at trace levels in the effluent of WWTPs in many countries such as Switzerland, UK and Japan (Tauxe-Wuersch et al. 2005; Roberts and Thomas, 2006; Nakada et al. 2005). Thirdly, it has negative impacts on human and ecological health. Jones et al. (2002) reported that the ratio of its predicted environmental concentration (PEC) to its no-effect concentration (PNEC) is greater than one (1.03) based on aquatic toxicity data. Tauxe-Wuersch et al. (2005) found that the PEC/PNEC of MEF is ten times greater than that of ibuprofen, another commonly used pain killer, thereby indicating that the aquatic toxicity of MEF is significant. Finally, very few efforts have been made to remove MEF from secondary effluent for water reuse (Nakada et al. 2007; Gimeno et al. 2010; Chang et al. 2012; Khalaf et al. 2013; Colombo et al. 2016; Chen et al. 2016a, 2016b). Yang et
al. (2012) has examined ferrate(VI) removal efficiencies of 68 emerging contaminants including MEF in water. However, the kinetics information and reaction mechanisms were not studied. Therefore, there is an urgent research need for a better understanding of ferrate(VI) degradation of MEF in a secondary effluent matrix.
Table 5-1. Structure and physiochemical properties of mefenamic acid

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular weight</th>
<th>Water solubility (mg/L)</th>
<th>pKa</th>
<th>LogKow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mefenamic acid</td>
<td>241</td>
<td>15.4</td>
<td>4.2</td>
<td>5.12</td>
</tr>
</tbody>
</table>

(Chang et al. 2012)

5.2 Materials and methods

MEF (analytical grade, ≥99%), anhydrous, sodium phosphate dibasic (Na₂HPO₄) and sodium phosphate monobasic (NaH₂PO₄) were purchased from Sigma-Aldrich (St. Louis, Missouri, USA). All the buffer solutions were prepared with 18.2 MΩ purified DI water (Millipore Milli-Q water purification system). HPLC grade methanol and acetonitrile were purchased from EMD Merk (Gibbstown, NJ, USA).

The experiments to evaluate the ferrate(VI) capability for removing MEF were first carried out in 100 mL beaker. The reactors were installed in a shaking bed at a rapid mixing speed (100 rpm) to ensure a complete mixing state during the reaction. The MEF solution (1.0 mg/L) was prepared in phosphate buffer solution (10 μM) or a secondary
effluent. Of note, phosphate was selected only for the purpose of pH buffer. Although ferrate(VI) might remove part of phosphate from water, the mechanisms are associated with precipitation due to the formation of Fe(III) from ferrate(VI) and/or adsorption to the Fe(III) oxide particles. Therefore, the possible reactions did not influence Fe(VI) oxidation of MEF. Furthermore, P was not a chemical species of interest in this study. In fact, phosphate buffer were commonly used in the previous studies on ferrate(VI) oxidation of organic compounds in water. Therefore, phosphate buffer was used in this task. The secondary effluent was the effluent from a secondary settling tank prior to disinfection in the WWTP in Verona, NJ. Solution pH was adjusted pH 7.5 with 1.0 mM NaOH or H₂SO₄. Ferrate(VI) dose was varied from 0.1 to 2.0 mg/L as Fe. The oxidation treatment was initiated through the addition of an appropriate weight of K₂FeO₄. Reaction proceeded for two hours within which all the ferrate(VI) was depleted through the visual inspection (purple color vanished) and the ABTS method (Lee et al. 2005b). Fifty milliliters of Fe(VI)-treated samples were collected and then filtered through 0.45 um membrane filters prior to analysis. The concentration of MEF was determined using the HPLC method (Werner et al. 2005). A Supelcosil LC-18 column (25cm×4.6mm, 5μm) was used. The mobile phase was a mixed solution composed of acetonitrile and water (60:40, v/v). Prior to use, pH of the mobile phase solution was adjusted to 3.9 with acetic acid. Flow rate was controlled at 1.2 mL/min. MEF samples were analyzed with a PDA Plus-300 nm detector (Thermo) with a retention time at 6.1 min. Kinetics tests of ferrate(VI) degradation of MEF were conducted in 10 μM phosphate buffer at pH 7.5. The initial concentration of MEF was fixed at 4.3 mg/L (0.0178 M). Four
different molar ratios of Fe(VI) to MEF were tested, including 3:1, 4:1, 5:1 and 6:1. At different sampling times, appropriate volumes of samples were collected into 25 ml centrifuge tube for Fe(VI) analysis. Residual concentration of Fe(VI) was quantified using ABTS method (Lee et al. 2005). To accurately measure residual MEF, the collected sample was mixed with 0.5 mL 100 mM sodium thiosulfate solution that could quench any residual Fe(VI). Results showed that MEF degradation was too rapid to be accurately measured.

In order to determine MEF degradation pathways, a Thermo-Fisher Scientific linear quadrupole ion trap (LTQ-XL) mass spectrometer equipped with an electrospray ionization (ESI) source and HPLC was used to identify chemically transformation products (OPs) of MEF for better understating of its degradation pathway. The treatment tests were carried out in 10 µM pH 7.5 phosphate buffer solution using the method as described previously. Ferrate dose was 10.0 mg/L as Fe and the initial MEF was 10.0 mg/L. Although the initial MEF concentration was over the typical MEF occurrence level in a treated wastewater, the high level of MEF did not influence Fe(VI) degradation of MEF molecules in water and could produce a strong signal in HPLC/MS analysis for the identification of OPs. Once the reaction was completed, 5 mL sample was collected and then filtered through 0.45 µm membrane filters for analysis. The chemical OPs were separated by HPLC equipped with a C18 column followed by a multiple-stage tandem mass spectrometry (MS², MS³, and MS⁴) of ions of interest. The structure and/or functionalities of OPs were proposed based on the obtained fragmentation patterns of multiple-stage tandem mass spectrometry.
5.3 Results and Discussion

5.3.1 Ferrate(VI) degradation of MEF in phosphate buffered solution (PBS) and secondary effluent matrixes

MEF removal efficiencies at different ferrate(VI) doses are summarized in Table 5-2 and shown in Fig. 5-1. Generally, the removal was increased with the increase in ferrate(VI) dose. The removal efficiency had a positively linear relationship with ferrate(VI) dose in a phosphate buffered solution (PBS) or a secondary effluent.

\[
\text{MEF removal} = 0.332 \text{Fe(VI)}, \quad R^2 = 0.96 \quad (5-1)
\]

\[
\text{MEF removal} = 0.217 \text{Fe(VI)}, \quad R^2 = 0.99 \quad (5-2)
\]

Here, MEF removal is MEF removal efficiency (%); and Fe(VI) is the ferrate(VI) mass concentration. At the highest ferrate(VI) dose (i.e. 2.0 mg/L), the maximum removal efficiencies of MEF were 61% and 44% at PBS and secondary effluent, respectively. The discounted removal in secondary effluent was ascribed to the matrix effect of secondary effluent. Various reducing agents present in secondary effluent potentially competed with MEF for ferrate(VI). The resulted ferrate(VI) consumption could cause a decreased MEF degradation.

It is of interest to compare ferrate(VI) oxidation with other oxidative processes for the degradation of MEF in water, as presented in Table 5-3. Among the different oxidative processes, O₃/UV (an AOP) had the highest removal efficiency for MEF (70%) in terms of the removal efficiency, followed by ferrate(VI) oxidation (61% removal in PBS). Ferrate(VI) exhibited better removal than other two AOPs (photo-Fenton process and H₂O₂/UV) and ozonation in terms of the MEF degradation efficiency. It is of interest
to compare ferrate(VI) and ozone for the degradation of MEF, because the both oxidants share some unique oxidative characteristics. For example, the two oxidants are selective and preferentially oxidize ERMs. Here the molar ratio of oxidized MEF to an oxidant dose is used as an indicator. Ferrate(VI) had 0.071 mM MEF removed/1.0 mM Fe(VI), slightly below 0.088 mM removed/1.0 mM O₃. This finding indicates that ferrate(VI) appeared to be slightly less efficient for the MEF degradation than ozone.

Table 5-2 MEF removal efficiencies at different Fe(VI) doses in PBS and secondary effluent matrixes

<table>
<thead>
<tr>
<th>Fe(VI) dose (mg/L)</th>
<th>Fe(VI) dose (mmol/L)</th>
<th>MEF removal in PBS (%)</th>
<th>MEF removal in SE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.002</td>
<td>6%</td>
<td>2%</td>
</tr>
<tr>
<td>0.5</td>
<td>0.009</td>
<td>23%</td>
<td>7%</td>
</tr>
<tr>
<td>1.0</td>
<td>0.018</td>
<td>40%</td>
<td>22%</td>
</tr>
<tr>
<td>2.0</td>
<td>0.036</td>
<td>61%</td>
<td>44%</td>
</tr>
</tbody>
</table>

Table 5-3 Comparison of different oxidative processes for the degradation of MEF

<table>
<thead>
<tr>
<th>Oxidation processes</th>
<th>Oxidant dose</th>
<th>Initial MEF concentration</th>
<th>pH</th>
<th>Time (min)</th>
<th>Degradation of MEF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>photo-Fenton</td>
<td>10 mmol/L</td>
<td>-</td>
<td>6.5</td>
<td>60</td>
<td>54.61 (Colombo et al. 2016)</td>
</tr>
<tr>
<td>H₂O₂/UV</td>
<td>10 mmol/L</td>
<td>-</td>
<td>2.5</td>
<td>60</td>
<td>41.47 (Colombo et al. 2016)</td>
</tr>
<tr>
<td>Ozonation</td>
<td>0.015 mmol/L (0.7 mg/L)</td>
<td>0.002 mmol/L (0.54 mg/L)</td>
<td>7.0</td>
<td>40</td>
<td>57.5 (Chang et al. 2012)</td>
</tr>
<tr>
<td>O₃/UV</td>
<td>0.015 mmol/L (0.7 mg/L)</td>
<td>0.002 mmol/L (0.54 mg/L)</td>
<td>7.0</td>
<td>40</td>
<td>~70 (Chang et al. 2012)</td>
</tr>
<tr>
<td>Fe(VI)</td>
<td>0.036 mmol/L (2.0 mg/L)</td>
<td>0.004 mmol/L (1.0 mg/L)</td>
<td>7.5</td>
<td>&gt; 60</td>
<td>61 (PBS) 44 (secondary effluent) (this study)</td>
</tr>
</tbody>
</table>
**Fig 5-1** MEF removal rate under different initial ferrate(VI) dose in buffer and secondary effluent
5.3.2 Kinetics studies of Fe(VI) degradation of MEF

Kinetic tests were carried out at pH 7.5 in 10 μM phosphate buffer solution. The overall Fe(VI) decomposition is through two pathways: 1) self-decomposition; and 2) reactions with MEF or its OPs. Therefore, the overall ferrate(VI) decomposition kinetics equation can be written as:

\[
\frac{d[Fe(VI)]}{dt} = -k_1[Fe(VI)]^2 - \sum_{i=2}^{n} k_i[Fe(VI)]^{a_i}[C_i]^{b_i}
\]  

(5-3)

Here, \(-k_1[Fe(VI)]^2\) is Fe(VI) self-decomposition (a 2\textsuperscript{nd} order reaction with respect to [Fe(VI)], in which \(k_1\) is a rate constant; \(-\sum_{i=2}^{n} k_i[Fe(VI)]^{a_i}[C_i]^{b_i}\) is the rate of Fe(VI) loss due to the reactions with MEF and its OPs; \(i=2, MEF\); \(i=3, 4,…n\) for different chemical oxidation products of MEF; \(a_i\) is the reaction order with Fe(VI) for the ferrate((VI) \(i\); and \(b_i\) is the reaction order with Fe(VI) for the chemical compound \(i\).

Kinetic data of overall Fe(VI) decomposition and its consumption due to MEF and its OPs are shown in Fig. 5-2. Kinetic data of the overall Fe(VI) decomposition and Fe(VI) self-decomposition can be measured in a PBS solution in the presence and absence of MEF, respectively, corresponding to the red and blue symbols and lines in Fig. 5-2. At any specific sampling time, the difference between the two residual ferrate(VI) concentrations in the absence and presence of MEF was the kinetic data of Fe(VI) reactions with MEF and its OPs (the purple symbols and lines in Fig. 5-2). And the ferrate(VI) consumption could be obtained from the difference between the added ferrate(VI) dose and residual ferrate(VI) concentration (the green symbols in Fig. 5-2). Therefore, the blue and red symbols represent experimentally measured data, while the purple and green symbols are the processed data from experimental results. As seen, at all
the different [Fe(VI)]:[MEF] ratios, a majority of ferrate(VI) loss was due to the reactions with MEF and its OPs, rather than self-decomposition. Within 60 s, the residual Fe(VI) rapidly dropped to 1.0 mg/L or below. It is found that the second item in Eq. (5-3) can be empirically expressed as a kinetic reaction with respect to [Fe(VI)], as follows.

\[
\frac{d[Fe(VI)]}{dt} \bigg|_{MEF&OPS} = - \sum_{i=2}^{n} k_i [Fe(VI)]^{a_i} [C_i]^{b_i} = -k[Fe(VI)]^a \quad (5-4)
\]

Here, k is the rate constant; and a is the reaction order with respect to [Fe(VI)].

Experimental data of Fe(VI) decomposition due to the reactions with MEF and its OPs were fitted with the kinetic models of 1st and 2nd order reactions with respect to [Fe(VI)], separately. Key kinetics parameters are summarized in Table 5-4. Clearly, the ferrate(VI) decomposition due to MEF and OPs better followed a 2nd order reaction pattern (R^2 > 0.93) than a 1st order reaction behavior (R^2 = 0.72-0.81). Since there is insufficient MEF kinetic data from literature, it is not possible to compare the rate constant from our research to others. However, the pattern of ferrate(VI) decomposition in present of MEF shows similarity with MEF degradation with ozone (Chang et al. 2012). Furthermore, a plot of k and [Fe(VI)]:[MEF] is shown in Fig. 5-3. The rate constant k decreased from 0.0209 to 0.0067 mM\(^{-1} \cdot s^{-1}\) as [Fe(VI)]:[MEF] increased from 3 to 6. The data enable us to determine the kinetics behaviors for Fe(VI) decomposition in ferrate(VI) treatment of MEF in water and obtain key kinetics parameters, but cannot provide mechanistic information on the MEF degradation by Fe(VI).
[Fe(VI)]:[MEF]=3:1

(a)

[Fe(VI)]:[MEF]=4:1

(b)
Fig. 5-2 Kinetics of overall ferrate(VI) decomposition and ferrate(VI) decomposition due to self-decay and reactions with MEF and its OPs: (a) \([\text{Fe(VI)}]:[\text{MEF}]=3:1\); (b) \([\text{Fe(VI)}]:[\text{MEF}]=4:1\); (c) \([\text{Fe(VI)}]:[\text{MEF}]=5:1\); and (d) \([\text{Fe(VI)}]:[\text{MEF}]=6:1\). (pH =7.5, initial MEF = 0.018 mM, i.e. 4.3 mg/L, and \([\text{Fe(VI)}] = 0.054, 0.072, 0.090, \text{ and } 0.108 \text{ mM, corresponding to } 3.0, 4.0, 5.0 \text{ and } 6.0 \text{ mg/L, respectively} ) \).
Table 5-4 Rate constant $k$ and $R^2$ in different kinetics models for Fe(VI) decomposition due to the reactions with MEF and OPs

<table>
<thead>
<tr>
<th>[Fe(VI)]:[MEF]</th>
<th>$1^{st}$ order</th>
<th></th>
<th>$2^{nd}$ order</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_2$ (s$^{-1}$)</td>
<td>$R^2$</td>
<td>$k_2$ (mM$^{-1}$ s$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>3</td>
<td>0.0297</td>
<td>0.81</td>
<td>0.0209</td>
<td>0.98</td>
</tr>
<tr>
<td>4</td>
<td>0.0281</td>
<td>0.76</td>
<td>0.0144</td>
<td>0.93</td>
</tr>
<tr>
<td>5</td>
<td>0.0222</td>
<td>0.75</td>
<td>0.0076</td>
<td>0.94</td>
</tr>
<tr>
<td>6</td>
<td>0.0229</td>
<td>0.72</td>
<td>0.0067</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Fig. 5-3 $k$ vs. [Fe(VI)]:[MEF] (pH = 7.5, initial MEF = 0.018 mM) The rate constant $k_2'$ has a negative correlation against the initial Fe (VI):MEF ratio.
5.3.3 Reaction pathways of ferrate(VI) degradation of MEF

HPLC-LTQ was used to identify chemical OPs produced from ferrate(VI) decomposition of MEF in water. The advanced analytical technique enabled the determination of multiple leveled MS fragmentation. Five major chromatogram peaks were noticed at \( m/z \) 138, 256, 258, 290, and 511 under a positive mode, respectively (Table 5-5). Multiple-stage tandem mass spectrometry of the five fragments are shown in Fig. 5-5, 5-6, 5-7 and 5-8. Two of the five observed peaks (i.e. \( m/z = 256 \) and 258) were also reported in other studies to investigate photo-degradation of MEF (Chen el al, 2016a and Chen el al. 2016b). In the photo-degradation of MEF, the principle oxidants were reactive oxygen species (ROS) such as \(^\cdot\)OH, \( O_2 \) and \(^\cdot\)O\(_2\)⁻.

**Table 5-5** Fragments (\( m/z \)) and chemical formula of OPs identified by multiple-stage tandem MS

<table>
<thead>
<tr>
<th>( m/z )</th>
<th>Chemical formula</th>
<th>( MS^2 )</th>
<th>( MS^3 )</th>
<th>( MS^4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>138.17</td>
<td>C(_7)H(_7)NO(_2)</td>
<td>120</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td>256.17</td>
<td>C(<em>{15})H(</em>{13})NO(_3)</td>
<td>239, 238, 223</td>
<td>210, 223</td>
<td>206, 195, 167</td>
</tr>
<tr>
<td>258.21</td>
<td>C(<em>{15})H(</em>{15})NO(_3)</td>
<td>240</td>
<td>212,225</td>
<td>197</td>
</tr>
<tr>
<td>290.11</td>
<td>C(<em>{15})H(</em>{14})NO(_5)</td>
<td>272</td>
<td>244, 243, 254</td>
<td>215, 228</td>
</tr>
<tr>
<td>511.20</td>
<td>C(<em>{30})H(</em>{25})N(_2)O(_6)</td>
<td>493,489, 293, 270</td>
<td>475, 252,</td>
<td>447,226</td>
</tr>
</tbody>
</table>

The MS spectrum of OP-138 indicates the breakage of MEF occurred at the N-C bond. In \( MS^2 \) and \( MS^3 \) fragmentation spectrum of OP-138, major fragments ions with \( m/z \) 120 (-18) and 92 (-28) corresponded to the loss of \( H_2O \) and C=O carbonyl group,
respectively (Fig. 5-4). OP-138 had a much smaller m/z than those of all the peaks observed by Chen et al. (2016 a and b), suggesting that ROS produced from photo-degradation was not capable of breaking down MEF into very small MW fragments that ferrate(VI) could.

The OP-256 and OP-258 observed in this study were also reported by Chen et al. (2016a and b). For OP-256, three fragment ions at m/z 239 (-13), 238 (-18) and 223(-18, -15) were detected in the MS² spectrum, which corresponded to loss of –OH, -H₂O and –CH₃, respectively. In addition, -CO and –CH₃ groups could be deduced according to the MS³ spectrum of OP-256. The further MS⁴ spectrum of OP-256 revealed that three more moieties (one hydroxyl group and two carbonyl groups) were included in OP-256, which had the m/z of 206, 195 and 167, respectively. These fragments could be formed due to loss of –OH, -CO and two –CO, respectively (Fig. 5-6). Similar fragments with m/z 210 and m/z 195 were discovered in MS² fragments by Chen et al. (2016 a and b). Of note, the multi-stage tandem MS provided the information regarding the functionalities and their possible locations of OP-256, but the information was not sufficient to identify the detailed structure of OP-256. Under our MS² spectrum, the major fragments were ions with m/z 238, m/z 239 and m/z 223, corresponding to the loss of –OH, -H₂O and –CH₃, respectively. Next, the fragments from m/z 238 in MS³ spectrum included two smaller pieces, i.e. m/z 223 (-15) and m/z 210 (-28), which indicates that the loss of a –CH₃ and a -CO occurred for OP-256. The further MS⁴ cleavage of m/z 223 shows that the m/z 195 and 167 were due to the loss of a –CO and two –CO. Based on these finding, it is
plausible that Fe(VI) oxidation led to the addition of one oxygen atom and a carbon from one of the methyl group of MEF, producing –C=O to replace -CH₃.

Moreover, another common transformation compound OP-258 was identified from these studies of Chen et al. (2016 a and b), which suggests the similarity of Fe(VI)-driven oxidation process and UV-photolysis. As shown in Fig. 5-7, the fragment with a m/z at 258 clearly indicates that one oxygen atom was attached on MEF. This carbonization could take place at either para- or meta-position of the nitrogen atom (Fig 5-7). As seen in the fragments from the MS³ spectrum, the major MS² molecule with m/z 240 was further cleaved into smaller fragments with m/z 225 (-15) and m/z 212 (-28), which indicated the loss of a -CH₃ and –CO. The MS⁴ spectrum shows that the m/z 197 was due to one –CO loss from m/z 225. The proposed OP-258 structure in this study is similar to that proposed by Chen et al. (2016 a and b), likely because both Fe(VI) oxidation and UV photo-degradation could result in the carbonization of MEF. In other studies to degrade microcystin-LR (MC-LR), similar chemical oxidation products were also reported from Fe(VI) and photocatalytic oxidation processes (Jiang et al. 2014; Zong et al. 2013; Antoniou et al. 2008).

However, two other major OPs were identified after Fe(VI) degradation of MEF in this study, i.e. OP-290 and OP-511, which were not reported after photo-degradation. OP-290 was detected at MS², whose fragments m/z 244 (-28), m/z 243 (-29) and m/z 254 (-18) were identified from the MS³ fragment ion with m/z 272. These molecule losses were probably due to the cleavage of –CO, -COH and –H₂O. Further MS⁴ fragment ions from m/z 243 indicate that one more –CO and one more –CH₃ were included in OP-290. The
difference between OP-290 and MEF suggests that two additional C=O and one –OH could be attached on MEF after Fe(VI) oxidation (Fig 5-8). This finding is in agreement with the observations in the Fe(VI)-driven oxidation studies from other groups (Yang et al. 2011; Anquandah et al. 2013; Jiang et al. 2014, Karlesa et al. 2014). Jiang et al. (2014) proposed the formation of a number of products associated with mono-, di- and trihydroxylation of aromatic rings from MC-LR in Fe(VI) oxidation of MC-LR. Anquandah et al. (2013) suggested that Fe(VI) oxidation of propranolol involved the cleavage of an aromatic ring by two oxygen atoms. However, Karlesa et al. (2014) proposed the either one or two additional oxygen atoms would attack the thioether moiety rather than the only one aromatic ring when ferrate(VI) was applied to oxidize beta-lactam antibiotic, likely because thioether ring was less stable than aromatic rings. In addition, a similar coupling reaction was proposed because of the existing of OP-511. OP-511 could be a dimer ion of OP-256 as a further oxidation product. The reaction mechanism was discussed by Wilde (2013) for Fe(VI) degradation of atenolol in water.

Degradation pathways of MEF during ferrate(VI) oxidation is proposed in this study (Fig. 5-9). It is known that Fe(VI) favorably attacks ERM s such as secondary amine or Sulphur group in the molecule (Yang et al. 2011). Therefore, the breakage of N-C bonding occurs to form OP-138 (Pathway I), which is similar to the ether bond breaking in the study of Yang et al. (2011) and Wilde et al. (2013). In addition, Raphael et al. (2000) and Ma et al. (2012) found that the energy of N-C bond was low, making it more vulnerable. The pathway II proposed involves with the reactions such as hydroxylation, ketonization, and coupling. According to the MS$^3$ and MS$^4$ fragments, a –
OH attack could occur on one methyl carbon to produce intermediate OP-256. Further oxidation could result in the formation of OP-256 isomers. This is in agreement with one of the MEF pathways during UV photo-degradation of MEF (Chen et al. 2016a and b). The plausible coupling reaction is proposed based on the by identification of OP-511. Similar mechanism have been discussed by Yang et al. (2011) and Wilde et al. (2013) that investigated ferrate(VI) degradation of triclosan and atenolol, respectively.

The electrophilic attack on the aromatic ring makes delocalization of positive charges from the nitrogen atom to the aromatic ring. This enabled the electron deficiency on the aromatic ring, thus making the para or meta position was readily attacked by oxygen atom to produce OP-258 (Pathway III). OP-290 formed in the fourth proposed pathway gets involved with the trihydroxylation of aromatic rings, which was proposed by Jiang et al. (2014) that studied ferrate(VI) degradation of MC-LR in water.

To sum up, ferrate(VI) degradation of MEF experienced different reaction pathways. Partially similar to the UV photolysis, it produced OP-256 through hydroxylation and ketonization. However, more reaction mechanisms occurred simultaneously, suggesting that ferrate(VI) oxidation was more powerful than UV photolysis. For example, ferrate(VI) was able to break the N-C bonding to produce smaller fragments i.e. OP-138. And mono-, di- or trihydroxylation occurred to form OP-258 and OP-290 when aromatic rings were attacked by oxygen atoms.
Fig. 5-4 Structure identification and functional group determination of MEF OPs after ferrate(VI) oxidation
Fig. 5-5 Multiple-stage tandem mass spectrometry studies of m/z 138 ion in the positive mode. EIC: extracted ion chromatography of m/z 138; MS1: m/z 138 is the parent ion of interest; MS2: CID of m/z 138 ion; MS3: CID of m/z 120 ion
Fig. 5-6 Multiple-stage tandem mass spectrometry studies of m/z 256 ion in the positive mode. EIC: extracted ion chromatography of m/z 256; MS1: m/z 256 is the parent ion of interest; MS2: CID of m/z 256 ion; MS3: CID of m/z 238 ion; MS4: CID of m/z 223 ion.
Fig. 5-7 Multiple-stage tandem mass spectrometry studies of m/z 258 ion in the positive mode. EIC: extracted ion chromatography of m/z 258; MS1: m/z 258 is the parent ion of interest; MS2: CID of m/z 258 ion; MS3: CID of m/z 240 ion; MS4: CID of m/z 225 ion.
Fig. 5-8 Multiple-stage tandem mass spectrometry studies of m/z 290 ion in the positive mode. EIC: extracted ion chromatography of m/z 290; MS1: m/z 290 is the parent ion of interest; MS2: CID of m/z 290 ion; MS3: CID of m/z 272 ion; MS4: CID of m/z 243 ion.
Fig. 5-9 Proposed pathways of MEF degradation with Fe(VI)
5.4 Conclusions

The major findings in this chapter are summarized as below.

1) The MEF degradation efficiency exhibited a linear correlation with ferrate(VI) dose in both PBS and secondary effluent. A ferrate(VI) dose of 2.0 mg/L Fe(VI) could remove 61% and 44% MEF at an initial concentration of 1.0 mg/L in PBS and secondary effluent matrixes, respectively. The lower removal efficiency observed in the secondary effluent was due to the matrix effect of secondary effluent. MEF was not mineralized by ferrate(VI) completely. The reduction of MEF is more due to chemical transformation.

2) Ferrate(VI) decomposition due to the reaction with MEF and its OPs followed a 2\textsuperscript{nd} order reaction pattern. The rate constant was linearly decreased with the increasing molar ration of Fe(VI) to MEF (i.e. [Fe(VI)]:[MEF]).

3) HPLC-LTQ technique was used to reveal the reaction mechanisms of ferrate(VI) degradation of MEF in water. Five major oxidation products (OPs) and four different reaction pathways are proposed to explain the complex reaction mechanisms. As a variety of complex products were generated and their impact to water quality is unknown at this point, a future research regarding toxicity of the OPs are strongly recommended.
5.5 References


Zong, W.; Sun, F.; Sun, X. Oxidation by-products formation of microcystin-LR exposed to UV/H₂O₂: Toward the generative mechanism and biological toxicity. Water Res. 2013, 47, 3211−3219
CHAPTER 6 PERFORMANCE OF FERRATE(VI) FOR TREATMENT OF SECONDARY EFFLUENT IN A CONTINUOUS-FLOW REACTOR

6.1 Introduction

Batch reactors are typically restricted to laboratory-scale investigation or small flow water treatment. In engineering practice, however, continuous-flow reactors are used more commonly in full-scale treatment facilities because of the large volumes of water processed. The reactors are operated on a continuous basis with flow into and out of the reactor.

Proper reactor types are crucial for treatment because a reactor is where both mixing and reactions occur. Two major continuous-flow reactors are continuous stirred-tank reactor (CSTR) and plug-flow reactor (PFR). In CSTR, solution is completely uniform without concentration gradients, and any chemical added to the solution is instantly and uniformly distributed throughout the reactor. In contrast, in PFR, solution is ideally mixed in the lateral direction but not mixed longitudinally. Selection of a proper reactor type depends heavily upon kinetics. Under an ideal flow condition, PFR is more (for 1st or 2nd-order reactions) efficient than, or at least equally (for zero-order reaction) efficient with, CSTR, because the concentration of the chemical added sharply drops due to dilution in CSTR, but gradually decreases to maintain a relatively high level within PFR. That is, to achieve the same treatment efficiency, the reactor size required for PFR is less than, or at least equal to, the volume of a corresponding CSTR. Or PFR can
accomplish higher removal rates than, or at least equal to, the treatment achieved by CSTR with identical reactor sizes. Besides, in engineering practice, PFR is a preferred option for chemical oxidation processes (e.g., UV/H$_2$O$_2$ and O$_3$). However, the information regarding the performance of ferrate(VI) for removal of wastewater contaminants in a PFR is highly limited.

Another interesting question on ferrate(VI) application in a PFR is the properties of the produced iron precipitates accompanied with Fe(VI) reduction. Different from the oxidants (e.g. ozone) subject to a homogenous reduction, ferrate(VI) is reduced to Fe(III) at an equimolar amount (Jiang 2007, Sharma et al. 2008, Jiang and Lloyd 2002, Carr et al. 1985, Carr 2008, Lee et al. 2014). The formation of Fe(III) is a continuous process, rather than a one-step addition of Fe(III). At a typical wastewater treatment condition, the produced Fe(III) rapidly precipitates in water. Traditionally, it is believed that the formation of Fe(III) can initiate a unique in-situ coagulation that is capable of removing suspended particles in water. The iron precipitates are a complex mixture when ferrate(VI) is applied for treatment of secondary effluent, at least composed of certain iron hydroxide species and Fe-P minerals.

Previous studies were performed to characterize these Fe(VI)-induced particles produced from ferrate(VI) reduction, and compared them with Fe(III) resultant iron oxide particles in a traditional coagulation process (Graham et al. 2010, Prucek et al. 2013, Goodwill et al. 2015, Tien and Graham 2011, Prucek et al. 2015). Graham et al. (2010) applied a photometric dispersion analyzer (PDA) instrument to study the flocs from Fe(VI) in a humic acid solution. PDA is an instrument to monitor rapidly changing
particle suspensions with an optical technique that analyses the light transmitted through a flowing suspension (Graham et al. 2010). Although ferrate achieved the comparable, or better, floc formation to ferric chloride, a less DOC removal was observed in the ferrate(VI) treatment. Tien and Graham (2011) evaluated the effect of a disperse phase on the floc formation through the addition of kaolin (colloidal particles) to a Fe(VI)-humic acid solution system. They found that the magnitude of floc formation with ferrate was inferior to that with ferric chloride. Moreover, the iron floc growth rate in the ferrate(VI) group was slower than that in the control group with ferric chloride. This observation may be because of a slow Fe(VI) reduction rate that led to a gradual production of Fe(III). Very recently, Goodwill et al. (2015) compared ferrate(VI) and ferric resultant particles produced in carbonate or phosphate buffered solutions and a real natural water (reservoir). The particles from two different iron sources exhibited similar surface charges, but had different size distributions in the buffered deionized water solutions. Scanning electron microscope (SEM) revealed that the ferrate(VI) resultant particles looked smoother and more granular. From X-ray photoelectron spectroscopy (XPS) analysis Fe$_2$O$_3$ was observed in the ferrate(VI)-induced particles, which was not detected in ferric chloride resultant particles. In the reservoir water, more nanoparticles with negative surface charges were produced from the Fe(VI) addition than from ferric addition. It is surprising that a large number of these particles remained suspended, similar to stable colloids in natural water. Furthermore, Prucek et al. (2013, 2015) studied ferrate(VI)-resultant particles in water and found that they were characterized with a unique core ($\gamma$-Fe$_2$O$_3$)-shell ($\gamma$-FeOOH) structure.
A question is raised. Do the Fe(VI)-induced particles sufficiently settle in a PFR? If the iron precipitates produced from ferrate(VI) coagulation tend to settle in a PFR, the PRR performs like a horizontal flow sedimentation tank, in which a large of iron precipitates may settle down at the bottom, thus facilitating the removal of suspended particles in wastewater and reducing the particulate loadings of downstream solid-liquid separation processes (e.g. sand filter or membrane filtration units). However, if the particles have a poor settling property, the Fe(VI)-induced particles increase the original turbidity through the formation of additional iron particles, which requires an efficient downstream solid-liquid separation process. Batch reactors cannot provide useful information to answer this question, because the formation of settleable floc are tightly associated with some factors that cannot be easily controlled in a batch mode, such as hydraulic conditions.

Therefore, the objective of this chapter is to determine the treatment performance of ferrate(VI) in a PFR and characterize the produced iron particles. Particularly, turbidity, P, organic content in wastewater, and the settling properties of the produced particles were studied.

6.2 Materials and methods

All the reagents used were at least analytical grade, except as noted. Potassium ferrate (K$_2$FeO$_4$) (> 96%) was purchased from Sigma–Aldrich. Secondary effluent was the effluent from a secondary clarifier prior to disinfection at a local municipal wastewater treatment plant (Verona, New Jersey). The sample was delivered to Montclair State University’s water treatment laboratory and stored at 4°C in a refrigerator until use.
A 300 mg/L Fe(VI) stock solution was prepared by dissolving an appropriate mass of K$_2$FeO$_4$ in deionized water. The stock solution pH was over 9.0 under which Fe(VI) was relatively stable. The Fe(VI) concentration in the stock solution was confirmed with the ABTS method (Lee et al. 2005b). The stock solution was freshly prepared every day.

**Continuous flow reactor.** A customized continuous-flow reactor was designed and built as shown in Fig. 6-1. As seen, the reactor is composed of a CSTR (inlet zone) and a PFR (reaction and settling zone, sludge zone and outlet zone). Secondary effluent and Fe(VI) stock solution were continuously fed into the inlet zone through two peristaltic pumps from a secondary effluent reservoir and a Fe(VI) stock solution container (Fig. 6-2), respectively. The inlet is a chamber with a size of 4.78 ×4.45×13.97 cm (L×W×D), which was installed on a magnetic stirrer. Secondary effluent and Fe(VI) stock solution were sufficiently and instantly mixed in the inlet zone under a complete mixing (100 rpm). The inlet served as a rapid mixer in WWTPs to ensure a rapid mixing between Fe(VI) and secondary effluent. It should be noted that no iron precipitates settled down in the inlet zone due to the mixing, though the reactions of Fe(VI) with secondary effluent constituents were initiated. The inlet is separated from the following PFR with a slotted plate, which ensures that water uniformly enters into the reaction and sludge zones.

The ensuing upper section include the reaction and settling zone as shown in Fig. 6-1, in which the added Fe(VI) continued its reactions with secondary effluent and the iron precipitates were continuously produced. Ideally, water was under a plug-flow state here (that is, there was not any horizontal mixing). Therefore, concentrations of the chemicals (e.g. Fe(VI) and wastewater contaminants) were decreased with the increasing
distance and contact time. Particles were primarily subject to two movements. Firstly, they move horizontally with the flowing water. Secondly, they also move down vertically (i.e. settle) because their gravity was greater than buoyant force. If the settling velocity was sufficiently large, some particles settled down to the bottom before they flew through the outlet. It is assumed that the iron particles settling to the bottom did not re-suspend. Therefore, the zone below the reaction and settling zone is called the sludge zone, where the iron sludge is stored. A slotted plate separates the reaction/settling and sludge zones with the following outlet zone as shown in Fig. 6-1. The water entering into the outlet zone overflowed from the reactor through an outlet. As the water flow (arrow lines in Fig. 6-1) showed, the water entering into the outlet zone could be completely withdrawn to the outlet. Therefore, the slotted plate was a crucial design to avoid the iron particles in the sludge zone from re-suspending and escaping from the reactor.

To visualize the flow patterns in the continuous flow reactor, a food-grade dye was added into the feeding water, as shown in Fig. 6-3. A sludge zone (no dye) was observed in the section 3 cm above the bottom.

**Continuous flow treatment experiments.** The treatment was initiated in the inlet zone in which secondary effluent and Fe(VI) stock solution were completely mixed. The total flow rate (the sum of secondary effluent and Fe(VI) stock feeding rates) was fixed to ensure a 2-hr retention time in the reactor. The feeding rate of the secondary effluent was adjusted at 58.65, 58.15 and 57.65 ml/min. And the pumping rate of Fe(VI) stock solution was varied at 0.5, 1 and 1.5 ml/min to achieve 2.50, 5.00 and 7.50 mg/L Fe(VI), respectively. During the treatment, solution pH was not controlled. Over the different
distances, four 5 mL aliquot samples were collected at 1.75~7 cm below the water table for analysis. The different distances corresponded to different reaction times, as shown in Eq. 6-1.

\[ t = \frac{L}{v} \]  

(6-1)

Here, \( t \) is the contact time; \( L \) is distance; and \( v \) is the water speed.

**Analyses.** Solution pH was measured by a pH meter (Thermo Scientific Orion 5-Star Plus). Ferrate(VI) was determined using the ABTS method (Lee et al. 2005b). In order to determine the settling properties of iron particles, turbidity and particulate iron were measured. In this study, particulate iron was operationally defined as Fe present in these iron oxide particles that could not pass through a 0.45 µm membrane filter. Turbidity, particle size, size distribution, zeta potential, particle count, and total iron were measured using the unfiltered samples. Turbidity was quantified using a portable turbidity meter (HACH, 2100Q). Zeta potentials (ZPs) were determined using a Nano Zetasizer (Malvern, ZEN 3690) without any sample dilution. The measurement ranges were as follows: Z-average sizes, 0.3 nm–10 microns; and ZPs for 3.8 nm - 100 micron particles. Particle sizes and size distributions were measured using a Dynamic Imaging Particle Analyzer (FlowCAM® VS Series). Iron was determined with an inductively coupled plasma-mass spectroscopy (ICP-MS Thermo X-Series II, XO 472). Total iron was measured after the unfiltered samples were completely digested (EPA Method 3005A). Dissolved iron was measured after the samples were filtered through 0.45µm syringe membrane filters (Thermo Scientific, cellulose acetate (CA), 30 mm diameter).
Morphology of Fe(VI)-induced particles were determined with a Hitachi H-7500 transmission electron microscope (TEM). All the experiments were run in duplicates.

**Fig. 6-1** Scheme of the continuous flow reactor design (CSTR (inlet zone) + PFR (reaction zone + sludge zone + outlet zone)
Fig. 6-2 The secondary effluent reservoir (left) and Fe(VI) stock solution container (right)

Fig. 6-3 Flow patterns in the continuous flow reactor using a food-grade dye
6.3 Results and Discussion

6.3.1 Quality of secondary effluent

Basic water quality parameters of the secondary effluent sample are shown in Table 6-1. Solution was slightly alkaline (pH 7.23). In this study, turbidity (16.7 NTU), particle size (1,005 nm), particle count (5,762/mL), and zeta potential (-9.37 mV) were used to characterize particles in the sample. Turbidity (16.7 NTU) was selected as an aggregate parameter to measure colloidal particles, rather than TSS, because turbidity was more sensitive at a low amount of particles. Moreover, turbidity is more commonly used for potable and reclaimed water. The suspended particles had a hydrodynamic size of 1,005 nm, indicating that their size was in a micro-particle scale, but close to a nano range. The zeta potential of -8.97 mV suggests that these micro-particles had slightly negatively charges. Although the zeta potential did not fall within a range (> 20.0 mV or < -20.0 mV) that extremely stabilizes colloidal particles in water, it appeared to sufficiently keep these micro-particles suspended in secondary effluent.

The secondary effluent had a typical dissolved organic content (COD = 16.0 mg/L). $\text{UV}_{254}$ at 0.123 cm$^{-1}$ indicates the abundant presence of aromatic structures and/or double bonds in EfOM, which preferentially react with ferrate(VI) as demonstrated in Chapter 4. TP was 3.851 mg/L, 98% of which was reactive P. The level was significantly below TP present in sewage because New Jersey WWTPs typically remove P from wastewater using a chemical precipitation method.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.23</td>
<td>Dissolved P (mg/L)</td>
<td>3.762</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>16.7</td>
<td>Particulate P (mg/L)</td>
<td>0.089</td>
</tr>
<tr>
<td>Hydrodynamic size (nm)</td>
<td>1,005</td>
<td>COD (mg/L)</td>
<td>21.0</td>
</tr>
<tr>
<td>Particle # (particles/mL)</td>
<td>1.32×10^4</td>
<td>UV_254 (cm⁻¹)</td>
<td>0.123</td>
</tr>
<tr>
<td>Zeta potential (mV)</td>
<td>-9.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Fe (mg/L)</td>
<td>0.270</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total P (mg/L)</td>
<td>3.851</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 6-1** Basic water quality parameters of secondary effluent

6.3.2 Turbidity, morphology, and zeta potential of Fe(VI)-induced particles

Turbidity of Fe(VI) treated secondary effluent at different contact times with different Fe(VI) doses is shown in **Fig. 6-4**. The initial turbidity was 6.87 NTU due to the presence of TSS in untreated secondary effluent. However, the turbidity was increased to 16.70, 30.07, and 34.23 NTU at 2.50, 5.00, and 7.50 mg/L Fe(VI) at 10 min, respectively. Thereafter, the turbidity almost stabilized until 120 min, regardless of the Fe(VI) dose. It should be noted that the detention time in the inlet zone was around 10 min, in which the solution was under a complete mixing state and the turbidity was constant. The turbidity in **Fig. 6-4** was almost the earliest contact time for the following PF reactor. The above finding suggests that Fe(VI) addition created a large number of particles, of which most were non-settatable.
TEM images of the suspended particles in the reaction and settling zone are shown in Fig. 6-5(a) and (b). It is found that Fe(VI) reduction caused the formation of numerous nanoparticles. The nanoscale particles had spherical shapes and uniform sizes approximately ranging within 30-70 nm. Many nanoscale particles tended to aggregate and produce a few micrometer flocs. As demonstrated from Fig. 6-4, these aggregates had a poor settling velocity to significantly increase the water turbidity. Zeta potentials of these suspended Fe(VI)-induced iron nanoparticles in the reaction and settling zone were measured under different experimental conditions (Fig. 6-6). The zeta potentials were slightly increased from the initial -9.37 mV to -8.23, -8.45 and -7.88 mV at 2.50, 5.00, and 7.50 mg/L Fe(VI) at 120 min, respectively. The zeta potentials allowed these particles under a relatively stable state.

![Fig. 6-4](image)

**Fig. 6-4** Residual turbidity at different contact times with different Fe(VI) doses during ferrate(VI) treatment of secondary effluent (initial pH = 7.23)
Fig. 6-5 TEM images of suspended Fe(VI)-induced particles in the reaction and settling zone during Fe(VI) treatment of secondary effluent (initial pH = 7.23, Fe(VI) = 5.00 mg/L, and contact time = 120 min)
Fig. 6-6 Zeta potentials of suspended particles in the reaction and settling zone during Fe(VI) treatment of secondary effluent (initial pH = 7.23; relative standard deviations are below 5%, not shown in the figure)
6.3.3 Particle counting and size of Fe(VI)-induced particles

To further understand formation and coagulative behaviors of Fe(VI)-induced particles, the numbers of suspended particles were counted using the Dynamic Imaging Particle Analysis technique, which captures the images of particles in water using a non-invasive approach. Numbers of suspended particles in secondary effluent at different contact times are shown in Fig. 6-7 (5.00 mg/L Fe(VI)). The particle number of untreated secondary effluent was $1.32 \times 10^4$ particles/mL, which was primarily caused by TSS. Of interest, the profile of particle number with time was composed of two phases. In the 1st phase (0-300 min), the number was linearly increased to $1.14 \times 10^5$ particles/mL as the contact time reached 30 min ($\text{Particle \#} = 3210 \times t + 21830$, $R^2 = 0.95$). In the 2nd phase, the particle number linearly dropped to $7.91 \times 10^4$ particles/mL with the increasing contact time to 120 min ($\text{Particle \#} = -380 \times t + 123545$, $R^2 = 0.95$). The variation of particle number was primarily due to the competition between the formation and aggregation rates of new Fe(VI)-induced particles. As demonstrated previously, Fe(VI) gradually decomposed due to self-decomposition and reactions with certain reducing agents to continuously produce Fe(III), which immediately formed precipitates (nanoparticles in Fig. 6-5) to contribute to the increase in the particle number. In contrast, the produced Fe(VI)-induced nanoparticle tended to aggregate to form larger particles, thereby reducing the particle number. In the 1st phase, the formation rate of new Fe(VI)-induced particles appeared to be greater than the aggregation rate, because a majority of Fe(VI) decayed within the first 30 min as demonstrated before. This led to an increase in the net number of particles. Afterwards, the formation rate of Fe(III) was substantially reduced
so that the aggregation predominated in the system, which caused an decreasing net particle number with time.

Size distributions of suspended particles in secondary effluent during Fe(VI) treatment are shown in Fig. 6-8. At any specific contact time, the particle size was almost normally distributed. Although the particle numbers varied with contact time, the size distribution curves were very similar: the peaks were observed around 0.5 µm; and the most of particles had a size below 5.0 µm. These findings, in addition to the observation in Fig. 6-4, indicate that the size distribution and turbidity were almost consistent within 120 min and were not influenced by the varied particle number.
Numbers of suspended particles in secondary effluent during Fe(VI) treatment of secondary effluent (initial pH = 7.23; 5.00 mg/L Fe(VI); relative standard deviations are below 5%, not shown in the figure)

Size distributions of suspended particles in secondary effluent during Fe(VI) treatment of secondary effluent (initial pH = 7.23; 5.00 mg/L Fe(VI))
6.3.4 Settleability of Fe(VI)-induced particles

To better evaluate the settleability properties of Fe(VI)-induced particles under different experimental conditions, the particulate iron content in treated secondary effluent was studied. In this study, the concentrations of total and dissolved Fe in secondary effluent were measured. Because particulate Fe = total Fe – dissolved Fe, the particulate Fe could be accordingly determined. Concentrations of total and particulate Fe in treated secondary effluent at different contact times are shown in Fig. 6-9 and 6-10, respectively. It is found that a majority of total Fe existed in the form of solid, because Fe(III), once formed from Fe(VI) reduction, tended to precipitate at the study pH range.

As seen in Fig. 6-10, at 2.50 mg/L Fe(VI), the particulate Fe was increased to 2.296 mg/L at 10 min, representing the level of total Fe-containing particles at 10 min. Thereafter, the particulate Fe gradually decreased to 1.394 mg/L, suggested that 45% particulate Fe settled down. At 5.00 and 7.50 mg/L Fe(VI), the particulate increased to 4.509 and 4.268 mg/L at 10 min and reached 4.869 and 4.307 mg/L at 120 min, respectively. The fractions of particulate Fe that was removed through sedimentation at 120 min were 3% and 43% for 5.00 and 7.50 mg/L, respectively.
Fig. 6-9 Total Fe in the reaction and settling zone with different Fe(VI) doses during ferrate(VI) treatment of secondary effluent (initial pH = 7.23)

Fig. 6-10 Particulate Fe in the reaction and settling zone with different Fe(VI) doses during ferrate(VI) treatment of secondary effluent (initial pH = 7.23)
6.3.5 P in Fe(VI) treated secondary effluent

Total and dissolved P were also measured during Fe(VI) treatment of secondary effluent, as shown in Fig. 6-11 and 6-12, respectively. Experimental analysis showed that the reactive phosphorus (i.e. orthophosphate) accounted for 98% of total P, while the remaining 2% was nonreactive (poly or organic phosphorus). And almost all the P existed in a dissolved state. As seen in Fig. 6-11, over 120 min, TP in the secondary effluent in the reaction and settling zone was not obviously altered at 2.50 mg/L, while TP at 5.00 and 7.50 mg/L Fe(VI) slightly dropped to 3.209 and 3.129 mg/L, respectively, both corresponding to a 85% TP removal through sedimentation. The finding suggests that a majority of TP flew through the continuous-flow reactor and existed in the effluent.

At Fig. 6-12, dissolved P dropped to 3.308, 2.330, and 1.917 mg/L at 2.50, 5.00, and 7.50 mg/L at 10 min, respectively, indicating that 12%, 38%, and 49% dissolved P were transformed to a particulate state. As the treatment proceeded until 120 min, dissolved P further decreased to 2.982, 2.222, and 1.57 mg/L, respectively, indicating that 21%, 41%, and 58% of dissolved P became particulate P. Of extreme interest, the ratio of the transformed dissolved P to Fe(VI) dose was 0.30 mg dissolved P removed /mg Fe (i.e. 0.54 mM dissolved P removed/1.00 mM Fe), regardless of the ferrate(VI) dose. Generally speaking, dissolved orthophosphate can be transformed to a particulate state by Fe(III) through two possible pathways, i.e. the direct precipitation between Fe(III) and phosphate (Eq.(6-2)) and adsorption of P to iron hydroxides through surface complexation.

\[
\text{Fe(III) + PO}_4^{3-} = \text{FePO}_4 \downarrow
\]  \hspace{1cm} (6-2)
The first mechanism requires a theoretic molar ratio of dissolved P removed to Fe at 1:1. Moreover, the second mechanism would provide additional P removal. Therefore, the overall theoretic molar ratio should be greater than 1:1. However, the observed ratio in this study was 0.54:1.00, likely because Fe(III) produced from Fe(VI) reduction is also subject to other competition reactions, such as hydrolysis. It is technically difficult to separate contributions of the two different mechanisms in this study.
Fig. 6-11 Total P in the reaction and settling zone with different Fe(VI) doses during ferrate(VI) treatment of secondary effluent (initial pH = 7.23)

Fig. 6-12 Dissolved P in the reaction and settling zone with different Fe(VI) doses during ferrate(VI) treatment of secondary effluent (initial pH = 7.23)
6.3.6 EfOM in Fe(VI) treated secondary effluent

Measurement of COD in the presence of ferrate(VI) is technically difficult, because ferrate(VI) (an oxidant) can underestimate the solution COD after the sample is added to the HACH COD test kits (Deng 2007). Therefore, only the COD data in effluent is discussed here. COD removal efficiencies in effluent at different ferrate(VI) doses are shown in Fig. 6-13. The COD removals were 22%, 40%, and 38% at 2.50, 5.00, and 7.500 mg/L, respectively. It should be noted that the COD removal was dramatically increased at a low ferrate(VI) range (0.00-5.00 mg/L), but almost stabilized at a high ferrate(VI) dose (> 5.00 mg/L). The trend was in agreement with the finding from batch tests in Chapter 4, again validating that ferrate(VI) could effectively alleviate EfOM in secondary effluent. However, the observed COD removal was greater than the COD removal achieved in Chapter 4. One or more of the following reasons may contribute to the disparate observations. Firstly, a lower pH (pH 7.23, the original pH) in this chapter was applied than that in Chapter 4 (pH 7.50). It is well known that ferrate(VI) is more reactive at a lower pH. Therefore, it is not surprising that more COD was removed in the PFR flow reactor. Secondly, the two secondary effluent samples had different initial COD (21.0 mg/L in this study vs. 31.7-33.1 mg/L in Chapter 4). Thirdly, chemical compositions might be different between the two batches of secondary effluent samples, e.g. the nature of EfOM (e.g. MW distribution) and the concentrations of potentially competing reducing species.
Fig. 6-13 COD removal with different Fe(VI) doses during ferrate(VI) treatment of secondary effluent (initial pH = 7.23, COD$_0$ = 21.0 mg/L, and reaction time = 2 hr)
6.4 Conclusions

The major conclusions of this chapter are described as follows.

1) Ferrate(VI) reduction in secondary effluent produces numerous nanoscale iron particles in a continuous-flow reactor. These nanoparticles tend to aggregate to microscale particles.

2) A majority of these micro-particles remained suspended due to negative surface charge, thereby increasing effluent turbidity.

3) Number of Fe(VI)-induced particles is initially increased because a large number of Fe(III) is in-situ produced to form new iron oxide particles at the initial phase. Thereafter, as the Fe(III) production rate decreases and the particle aggregation rate prevails in the system, the particle number gradually drops in the ensuing phase. However, the variation in particle number does not significantly alter water turbidity.

4) Sizes of Fe(VI)-induced particles at different contact times are almost normally distributed with their size peaks around 0.5 µm.

5) In this study, 0.30 mg/L dissolved P is transformed to a particulate state by 1.00 mg/L Fe(VI), regardless of Fe(VI) dose. The transformation is likely due to chemical precipitation and/or adsorption to iron precipitates.

6) COD was removed be 5.00 mg/L Fe(VI) by 40% in this study, validating that EfOM could be largely removed by ferrate(VI).
6.5 References


CHAPTER 7 ENVIRONMENTAL IMPLICATIONS

7.1 Preliminary cost analysis

Cost is a key factor for a technology application. Although a few hundreds of publications on ferrate(VI) studies for environmental applications have been available, economic information regarding ferrate(VI) treatment is extremely limited (Waite 2012a). An effort of this dissertation is to preliminarily explore costs associated with ferrate(VI) treatment of secondary effluent. The expenses associated with capital and operating/maintenance (O&M) costs need to be considered. In order to have a clear picture on the costs for ferrate(VI) treatment, the estimated expenses would be compared with those from existing treatments that provide an equivalent treatment in water reuse. Ferrate(VI) serves as a multi-treatment agent. The primary function of ferrate(VI) for water reclamation is chemical oxidation for the degradation of EfOM and emerging contaminants. Among existing chemical oxidation technologies for water reuse, ozonation plays a very similar role because: 1) ozonation is also a selective oxidant that favorably reacts with ERM (Lee and von Gunten 2010, AWWA 1991); 2) ozone and ferrate(VI) have similar reduction potentials (2.07 V for O₃ vs. 2.20 V for ferrate(VI)); and 3) the COD removal efficiencies achieved by ozone are very similar to those by ferrate(VI) in this study (Tripathi et al. 2011, Domenjoud et al. 2011). Therefore, ozonation is selected in this dissertation as the existing chemical oxidation process for the comparison.

The secondary purpose of ferrate(VI) treatment of secondary effluent is the alleviation of phosphate. In practices, the most commonly used method for the phosphate
elimination is chemical precipitation with a coagulant (e.g. ferric chloride) 
(Tchobanoglous et al. 2003, Wilfert et al. 2015). This technology is particularly 
commonly applied at WWTPs in New Jersey, United States. Ferric chloride can 
transform dissolve phosphate into a solid phase that can be subsequently removed 
through a solid-liquid separation process such as sand filtration. It shares a similar 
treatment mechanism with ferrate(VI) for the removal of phosphate from secondary 
effluent. Therefore, ferric chloride-driven coagulation is selected as the existing treatment 
option for phosphate removal for the comparison purpose.

Cost analysis for the two treatment options (Option1: ferrate(VI) treatment alone; 
Option 2: ozonation combined with ferric chloride precipitation) are made below. The 
treatment performance data of ferrate(VI) is obtained from the continuous-flow reactor in 
Chapter 6. It is assumed that ferrate(VI) can provide an equivalent treatment of ozonation 
combined with ferric chloride precipitation. Ferrate(VI) treatment and O₃ + FeCl₃ are 
compared in terms of the expenses (capital and O&M costs) spent for treatment of 1,000 
gallons of secondary effluent. Data on chemical price, equipment, and treatment 
performance of ozonation and ferric chloride precipitation are obtained from literature. 
All the costs are expressed as dollars in 2016. The inflation rate is 1.6% which is an 
average one in the United States over 2006-2016.

Cost estimation for Option 1- ferrate(VI) treatment. Our continuous- flow reactor 
tests showed that ferrate(VI) at 5.0 mg/L Fe(VI) could reduce COD from 21 mg/L to 12.6 
mg/L with a decrease by 8.4 mg/L COD, corresponding to 40% COD removal. EPA has 
recently estimated the cost of ferrate(VI) treatment using a set of Ferrator® (on-site
ferrate(VI) generator) systems (Cashman et al. 2014). The annual cost including electricity usage, chemical inputs, incidental repairs, and amortized capital investment (15-yr lifetime) is $833,300/yr (dollars in 2014) for a capacity of 10 MGD at a dose of 5.00 mg/L Fe(VI). The unit cost is $0.23/1000 gal treated water (dollars in 2014). The corresponding value in 2016 is $0.24/1000 gal, which is calculated as below.

\[ PV = \frac{FV}{(1 + r)^Y} \quad \text{(Eq. 7-1)} \]

Where PV is the present value (= starting principal), FV is the future value, r the inflation rate (1.6%), and Y is the number of years for investment.

Cost estimation for Option 2- ozonation treatment and ferric chloride precipitation. Ozonation can provide a very similar treatment result for EfOM. Domenjoud et al. (2011) reported that 5.00 mg/L O\(_3\) could reduce a secondary effluent COD approximately by 14%, corresponding to a COD reduction by 11.0 mg/L (COD\(_o\) = 78.4 mg/L). Amortized costs for ozonation at 5.00 mg/L O\(_3\) in water treatment was estimated at $3.48/1000 gal (dollars in 1998). The corresponding value in 2016 is $4.13/1000 gal.

Ferric chloride can be added during primary or secondary wastewater treatment in engineering practices. The produced precipitates can be removed together with TSS in a primary or secondary settling tank. Therefore, any special mixing equipment or reactor is not required to achieve the precipitation. In this dissertation, only chemical cost (the major O&M cost) is considered.

The average price of ferric chloride (100% grade) was $325/US ton in the United States chemical market in 2006 (ICIS 2006, Van Savage 2001), corresponding to
$381/US ton (dollars in 2016). One US ton is 907.19 kg. So the unit price for FeCl$_3$ is $0.0012/g as Fe. When chemical dose is 5.0 mg/L Fe(III), the treatment cost of ferric precipitation is $0.02/1000 gal.

*Cost comparison.* Cost estimates for the two treatment options (i.e. ferrate(VI) treatment and ozonation combined with ferric chloride precipitation) for water reclamation are summarized in Table 7-1. Unit costs for ferrate(VI) treatment and O$_3$ + FeCl$_3$ are $0.25/1000$ gal and $4.15/1000$ gal, respectively. Therefore, ferrate(VI) treatment is a much cost-effective option, accounting for approximately 6% of ozonation + ferric chloride precipitation. Although costs in practices are largely influenced by many site-specific factors (e.g. material and transportation costs), the preliminary cost analyses indicates the economic competitiveness of ferrate(VI) treatment in water reclamation.

The majority of ferrate(VI) treatment cost is the price of ferrate(VI) generators. A ferrate(VI) generator unit costs approximately $836,127 (2016 dollar) with a capacity of 10 MGD (Cashman et al. 2014). On the other hand, ozonation contributes to 99.5% expense of the second option. Ozonation is a costly wastewater treatment technology. The major costs during ozonation come from ozone generators, oxygen feed gas, compressors, and energy consumption (EPA 1999). Furthermore, the transfer efficiency of O$_3$ generation from oxygen gas is a critical economic consideration. This requires a deep and tightly covered contact chambers for the reactions, which leads to a high capital costs in design, materials and construction.
Table 7-1 Cost comparison between Fe(VI) treatment and ozonation + FeCl₃ for treatment of secondary effluent

<table>
<thead>
<tr>
<th>Treatment option</th>
<th>Treatment unit</th>
<th>Cost ($/1000 gal)¹,²</th>
<th>Total cost ($/1000 gal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ferrate(VI)</td>
<td>0.24</td>
<td>0.24</td>
</tr>
<tr>
<td>2</td>
<td>Ozonation</td>
<td>4.13</td>
<td>4.15</td>
</tr>
<tr>
<td></td>
<td>FeCl₃ precipitation</td>
<td>0.02</td>
<td></td>
</tr>
</tbody>
</table>

¹Cost is the expense spent for treatment of 1000-gallon secondary effluent; ²Price is expressed in dollars in 2016.

Recently, an EPA project (Cashman et al. 2014) compared ferrate(VI) technology with two other treatment trains, including traditional water treatment processes (coagulation + sedimentation + filtration + chlorination) plus granular activated carbon (GAC) adsorption and for drinking water treatment. Cost analysis showed that ferrate(VI) technology was the least costly among the candidate treatment options, which is in consistence with the finding in this study. However, it should be noted that transportation, treatment, and disposal of ferrate(VI)-induced sludge was not considered in this preliminary cost analysis.

7.2 Implications in Environmental Management

This dissertation research made an effort to explore a new water reclamation process with an environmentally friendly treatment agent – ferrate(VI). Results from this study suggests that ferrate(VI) has a potential to revolutionize water reclamation technologies and bring about profound impacts on environmental management.
7.2.1 Implication to water reuse industry

Although the demand for safe water is increasing with the increasing population, growing agricultural and industrial needs, and increasingly serious pollution, there is not an obvious increase in reliable water supply to match the growing demand. As a result of overused water resources and changed climate patterns, available fresh water is decreasing. Undoubtedly, water reuse serves as a sound approach to closing the gap between the demand and supply and supporting the sustainable development of our society. It should be noted that the market for water reuse technologies reached $29 billion in 2010 and increased to $57 billion in 2015. Development of new-generation water reuse technologies is crucial to water reuse industry. Ferrate(VI)-based treatment represents a new direction due to its technical and economic competitiveness.

Findings from this dissertation provides a scientific basis for industrialization of ferrate(VI)-based treatment process for water reuse industry. Data acquired from this study is critically important to engineering design for the ferrate(VI) application at least in the following aspects.

1) Data from the experiments to evaluate the treatability of ferrate(VI) for different wastewater contaminants demonstrate the multiple treatment functions of ferrate(VI). It may be of extreme interest to the industry because: a) it can achieve different treatment goals (e.g. disinfection, precipitation of phosphate, elimination of emerging contaminants, and EfOM degradation) in a single reactor, thereby simplifying the engineering design and operation; b) it requires a much smaller space to accommodate a reactor, rather than a
treatment train composed of different treatment units, which typically need a large space for the reactor installation. This may be of significance to water reclamation facilities in remote areas where less labor is needed to operate and maintain the treatment systems, as well as in urban areas where land space has a high priority in engineering investment.

2) Kinetics data of ferrate(VI) decomposition in a secondary effluent matrix enables the appropriate sizing of a ferrate(VI) reactor. In this study, ferrate(VI) was observed to follow a 2\(^{nd}\) order reaction pattern, and key kinetics data were determined. The data can be used to determine ferrate(VI) oxidant exposure and life time in a reactor, which is important to correctly size a ferrate(VI) reactor in engineering design.

3) Ferrate(VI) removals of EfOM and P were investigated and the effects of operating factors were evaluated. The knowledge is useful when ferrate(VI) is used prior to RO filtration during water reclamation. Membrane filtration is currently commanding 70% water reuse market share. Both EfOM and P significantly contribute to RO fouling, which is a key barrier to RO technologies, reducing permeate flux, increasing energy consumption, and leading to frequent chemical cleaning and even membrane replacement. EfOM and P can serve as substrate and nutrient to enhance microbial growth on membranes, respectively. They also contribute to organic and inorganic membrane fouling, respectively (Vrouwenvelder et al. 2010). For example, phosphate can precipitate calcium that deposits on RO membrane to reduce
water reflux (Tang et al. 2011, Ning and Troyer 2007). Ferrate(VI) application is capable of alleviating such membrane fouling through mitigation of EfOM and P in the RO influent.

4) Data on ferrate(VI) decomposition of MEF again validates that ferrate(VI) oxidation is a powerful tool to screen unregulated emerging contaminants from treated wastewater. Identification of MEF degradation byproducts also reveals that ferrate(VI)-driven oxidation has a different degradation pattern from other chemical oxidation processes. This finding suggests that ferrate(VI) may be an alternative for some emerging compounds, which are persistent to traditional chemical oxidants.

5) Cost analysis provides water reuse industry a picture on affordable expenses for ferrate(VI) applications for water reclamation. The quantitative information, though preliminary, clearly indicates that ferrate(VI) is more cost competitive than traditional ozonation and chemical precipitation technologies. Based on the preliminary cost analyses in this dissertation, ferrate(VI) treatment saves $3.91/1000 gal than ozonation combined with ferric precipitation. Therefore, for a 10 MGD water reclamation facility (a small treatment capacity), ferrate(VI) treatment can reduce capital and O&M costs by $14.3 million (dollars in 2016) annually. Unquestionably, the economic advantage allows the new treatment option more competitive in the water reuse market and encourages more major intended end users, e.g. water
managers/planners, engineers, and water reclamation facilities, to accept and apply the affordable treatment.

### 7.2.2 Environmental Benefits

Ferrate(VI)-based technologies for water reuse are beneficial for environmental quality from two aspects. Firstly, ferrate(VI) treatment directly removes different pollutants from reclaimed water and significantly alleviates these pollutant loadings into the environment (for example, the pollutants in reclaimed are mitigated when it is reused for agricultural irrigation and wetland restoration), thus safeguarding ecological health. This dissertation has demonstrated that ferrate(VI) is capable of effectively removing several pollutants of particular concern, such as phosphorus (a nutrient to cause algal blooming), pathogens, dissolved organic matter, and emerging contaminants. The reduction of these unwanted microbes, organic substances and nutrients can protect the health of ecological systems and alleviate the effects of these stressors on vulnerable wildlife populations.

Secondly, ferrate(VI) treatment has a potential to bring about less environmental impact than other technologies that provide similar treatment effects. Life cycle assessment (LCA) was recently made to compare ferrate(VI) and other oxidation technologies for water disinfection (Cashman et al. 2014). This study compared ferrate(VI)-based water treatment technology with conventional water treatment scenario (coagulation + sedimentation + filtration + chlorination) in addition to granular activated carbon adsorption in a representative moderate-sized water treatment facility. Results show that ferrate(VI) reduced global warming potential, smog formation, energy demand,
fossil depletion, acidification, human health criteria impacts, ozone depletion impacts, metal depletion results, human health non-cancer results, human health cancer results, and ecotoxicity results are decreased by 7%, 10%, 8%, 4%, 5%, 9%, 15%, 15%, 36%, 11%, and 12%, respectively (Cashman et al. 2014). It is also expected that ferrate(VI) in water reuse similarly has less negative influence on the environment and provides a more environmentally friendly water reuse treatment option.

7.2.3 Social benefits

As a result of the shortage of clean fresh water resources, the public and policy makers have paid more attention to water reclamation. United States EPA and many state level agencies (e.g. NJ Department of Environmental Protection) have issued their guidance to highly encourage water reuse. The efforts from this dissertation research will have multiple social impacts.

1) Water supply reliability. As a technically reliable and cost competitive water reclamation treatment option, ferrate(VI) technology enables locally produced sewage as a water reuse source and thus mitigates the dependence upon water conveyance from remote sources. This benefit is of significance for the U.S. arid states such as California, Nevada, Arizona, and Texas.

2) Local economic influence. Safe and reliable water can stimulate the economy by providing local business with the assurance of water supplies for agricultural, manufacturing, recreational, or other activities. This will strongly support the creation of more job opportunities.
3) **Life quality and public health.** The aforementioned different environmental benefits from the environmentally friendly water reuse technology improve public health and allow for increasing more recreational spaces, thereby creating more livable and resilient communities.

4) **Sustainability awareness.** Water reuse represents a sustainable approach to addressing water shortage issues in arid and water-stressed areas. Success implementation of new and green water reclamation projects will help expand the public awareness and understanding of sustainability in their normal living.

5) **Aesthetics.** Safe recycled water can be used to irrigate parks, golf courses and other recreational facilities (e.g. fountains and lakes) to create aesthetic values.

### 7.3 Limitations of Ferrate(VI) Technology

Although ferrate(VI) treatment brings about many benefits, making it advantageous over many existing treatment options, its application is restricted, more or less, in the following five aspects. To overcome these issues will enable the emerging treatment technology to be widely applied in engineering practices. Firstly, commercial ferrate(VI) suppliers are very limited. To the best of knowledge, there is only one ferrate(VI) manufacturer, i.e. the Ferrate Treatment Technology (FTT), LLC (Orlando, FL), in the U.S. market. The on-site ferrate(VI) generator from FTT is called Ferrator, which produces sodium ferrate solution via the wet chemistry method. Although it can continuously produce ferrate solution on site, the ferrate(VI) solution is alkaline, under which ferrate(VI) remains stable. Addition of the ferrate solution may cause a pH increase in the treated water and wastewater. Secondly, ferrate(VI) treatment produces
iron sludge as a final product. The sludge should be removed using a solid-liquid separation method and then appropriately disposed of. The additional treatment and disposal increases the complexity of ferrate(VI) treatment and the overall costs. Thirdly, ferrate(VI) reactivity is highly pH sensitive. Ferrate(VI) oxidation is much more reactive at an acidic condition than at an alkaline condition. Therefore, ferrate(VI) treatment is very effective for the removal of many organic pollutants at a low pH. However, the treatment may be substantially discounted at an alkaline environment. In practices, this may be problematic when water or wastewater has an original pH within an alkaline range. Fourthly, ferrate(VI) is highly unstable at an acidic condition. Ferrate(VI) can rapidly self-decompose at an acidic condition, thereby reducing ferrate(VI) oxidant exposure. The quick self-decomposition can compete with target pollutants for available ferrate(VI) to reduce the expected treatment efficiency. Fifthly, ferrate(VI) self-decomposition in water can release OH\(^-\) and increase pH. The extent of pH increase depends on the amount of produced OH\(^-\) and solution chemistry (e.g. acidity). The pH increase may be substantial at a high ferrate(VI) dose and for a water with a low pH buffer capacity. If this is the case, pH adjustment has to be used to satisfy the pH requirement in effluent.

7.4 Overall Conclusions

Ferrate(VI) treatment as a new-generation water reclamation technology has a potential to revolutionize the water reuse industry. A principal advantage of ferrate(VI) treatment is to achieve multiple treatment goals with a single reactor and thus bring about many attractive benefits, such as simple system design and operation, low investment,
and small physical footprint. This dissertation, in addition to literature, demonstrates the capability of ferrate(VI) for mitigation and elimination of sewage organic matter, total suspended particles, phosphorus, pathogenic microorganism, and unregulated micro-pollutants from treated wastewater. The treatment performance relies heavily upon two operating factors, i.e. ferrate(VI) dose and solution pH. Their effects on the treatment performance need to be carefully evaluated when ferrate(VI) treatment is used in full scale applications.

The major expected mechanism from ferrate(VI) is chemical oxidation. In many previous studies, ferrate(VI) has been long used as a chemical oxidant alone. It is capable of chemically transforming EfOM in secondary effluent. Although its capability to mineralize these organic compounds is limited, Fe(VI) preferentially attacks aromatic structures and double bonds to significantly lower UV$_{254}$. This can reduce the formation potential of DBPs because strong UV-absorbing EfOM compounds characterized with high UV$_{254}$ absorbance generally serve as major DBP precursors. The production and presence of DBPs in reclaimed water are recognized as a great challenge in water reuse, because the toxic byproducts pose a threat to public health and reduce the safety of reclaimed water. The other benefit is to mitigate EfOM-caused fouling for RO membrane filtration if ferrate(VI) is combined with RO in water reclamation practices (RO treatment accounts for 70% of the U.S. water reuse market). EfOM can organically foul RO membrane materials and also enhance the growth of biofilms on RO membrane as a substrate. On the other hand, ferrate(VI)-driven oxidation can simultaneously oxidize unregulated wastewater-driven micro-pollutants such as pharmaceutical and personal care
products. Over the two past decades, hundreds of them have been identified in treated wastewater due to their persistence and the poor treatment capability of conventional wastewater treatment. The reactivity of these micro-pollutants toward ferrate(VI) allows ferrate(VI) treatment to be a powerful tool to address the emerging challenge in water reuse. However, the degradation products of these compounds should be carefully identified. Their toxicity should be determined and compared with their parent compounds to examine whether more harmful compounds are produced after ferrate(VI) oxidation.

Generally, higher chemical dose and lower pH achieve better degradation of target compounds. A high dose brings more Fe(VI) into water to react with pollutants. A threshold likely exists beyond which the pollutant removal increases slightly with the increasing ferrate(VI) dose. In this dissertation research, such a trend was observed for ferrate(VI) removal of EfOM in terms of COD or UV$_{254}$ absorbance. At an acidic condition, ferrate(VI) is much more reactive but more unstable. Therefore, ferrate(VI) is competed by the reactions with target pollutants and ferrate(VI) self-decomposition.

Coagulation and precipitation also occur after the in-situ formation of Fe(III) from Fe(VI) reduction. Of interest, the expected TSS removal is not observed in the results from batch or continuous-flow experiments. Moreover, the nanoscale iron particles quickly aggregate to form micro-scale particles that remain suspended, significantly increasing effluent turbidity. Meanwhile, Fe(III) from Fe(VI) reduction can transform dissolved phosphorus in secondary effluent into a solid phase. However, a majority of these Fe-P solids still remain suspended. These findings are different from the widely
accepted viewpoint – ferrate(VI) also functions as a coagulant. Therefore, the Fe(VI)-induced particles with a poor settling property require an ensuing solid-liquid separation process (e.g. sand filtration) to remove TSS and P.

Costs of ferrate(VI) treatment are low when compared with the expenses of other treatment practices. Ferrate(VI) application was extremely restricted by the ferrate(VI) manufacture. However, the barrier is being removed with the advances in ferrate(VI) synthesis. Similar to ozone, ferrate(VI) needs to be generated on site due to its chemical instability. Recently, such on-site ferrate(VI) generators have been commercially available to produce sodium ferrate solution through a wet chemistry method. Other methods such as electrochemical methods are being explored to produce a large amount of ferrate(VI) to meet full-scale applications. Capital cost on the generators and O&M costs associated with electricity are less than those of ozone or energy intensive advanced oxidation processes. As a result, the affordable costs enable ferrate(VI) technology more acceptable and competitive than existing treatment options.

7.5 Future Research

Future research needs in ferrate(VI) treatment for water reuse are recommended as follows.

1) *Effect of water sources.* Quality of secondary effluent may vary with different sources. In this study, the effluent from activated sludge treatment, the most common secondary treatment option in the United States, was used. It is likely that the treatment performance of ferrate(VI) is changed with the varying compositions and nature of pollutants and water matrix constituents in secondary
effluent. Besides the activated sludge process, many other treatments such as trickling filters and rotating biological contactors are also broadly applied in the United States. Nature of EfOM and chemical composition (e.g. the nitrite concentration) from different treatments are likely different. Effect of the different secondary biological treatments on the following ferrate(VI) treatment should be evaluated.

2) *Effect of temperature.* All the experiments in this study were completed at a room temperature (25°C). If ferrate(VI) is truly applied in practices, the treatment will proceed under a widely varied temperature range in different seasons. However, the information on the effect of temperature on ferrate(VI) oxidation or coagulation is extremely limited. The impact of temperature should be elucidated prior to full-scale applications.

3) *Identification the toxicity of MEF oxidation products.* Oxidation products from Fe(VI) reactions with MEF are identified and the reaction pathways are proposed. However, it remains unclear whether these OPs are less or more harmful than the parent compound. The toxicity information is essential to determine whether ferrate(VI) is selected for addressing the MEF pollution.

4) *Lifecycle assessment.* Lifecycle assessment is needed for ferrate(VI) treatment of secondary effluent to quantitatively understand the impacts of ferrate(VI) in water reclamation. To the best of knowledge, only one study was performed to conduct lifecycle assessment of ferrate(VI) for drinking water. But such an analysis for water reuse is unavailable. Information of lifecycle assessment regarding
ferrate(VI) application for water treatment is of importance for comprehensive comparison of ferrate(VI) and other treatment candidates for water reclamation.

5) **Solid-liquid separation.** A solid-liquid separation process need to be selected and optimized for removing suspended iron particles after Fe(VI) treatment. In the current treatment market, different separation processes are available, such as rapid sand filtration, microfiltration, and centrifugation. Investigations are needed to compare the treatment performance and costs of different separation processes and select the optimal candidate.
7.6 References


