5-2020

Ferrate(VI) for Wastewater Treatment : Phosphorus Removal

Lei Zheng
Montclair State University

Recommended Citation

Zheng, Lei, "Ferrate(VI) for Wastewater Treatment : Phosphorus Removal" (2020). *Theses, Dissertations and Culminating Projects*. 544.
https://digitalcommons.montclair.edu/etd/544

FERRATE(VI) FOR WASTEWATER TREATMENT: PHOSPHORUS REMOVAL

A DISSERTATION

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

by

LEI ZHENG

Montclair State University
Upper Montclair, NJ

May 2020

Dissertation Chair: Dr. Yang Deng

MONTCLAIR STATE UNIVERSITY

THE GRADUATE SCHOOL

DISSERTATION APPROVAL

We hereby approve the Dissertation

FERRATE (VI) FOR WASTEWATER TREATMENT: PHOSPHORUS REMOVAL

of

Lei Zheng

Candidate for the Degree:

Doctor of Philosophy

Graduate Program:
Environmental Management

Certified by:

[redacted]

Dr. M. Scott Herness
Vice Provost for Research and
Dean of The Graduate School

April 27, 2020
Date

Dissertation Committee:

[redacted]

Dr. Yang Deng
Dissertation Chair

[redacted]

Dr. Huan Feng

[redacted]

Dr. Jinshan Gao

[redacted]

Dr. Yueqiang Liu

Abstract

FERRATE(VI) FOR WASTEWATER TREATMENT: PHOSPHORUS REMOVAL

by Lei Zheng

Phosphorus (P) is a major nutrient present in municipal wastewater. Without proper treatment and management, residual P in treated wastewater finally enters into natural receiving water bodies. Nutrient pollution resulting from excessive P, together with the other nutrient, i.e. nitrogen (N), is a leading cause of eutrophication, a ubiquitous U.S. water quality issue. An overgrowth of algae during eutrophication brings extremely adverse impacts on the water quality. The algal bloom can rapidly deplete dissolved oxygen, lead to the death of aquatic life, increase water turbidity, and cause taste and odor issues. Moreover, some harmful algal boom can produce toxins to give rise to various illnesses in human and animals. The aforementioned challenges are of particular concern when eutrophication occurs in drinking water sources. Although existing wastewater treatment technologies can remove P, to different extents, they are restricted by technical difficult to achieve a very low P concentration and/or poor removal capability for organic P in wastewater. On the other hand, the regulations on the P discharge from municipal wastewater treatment facilities are increasingly stringent, particularly for highly nutrient sensitive water bodies. Therefore, there is an urgent research demand to develop innovative, reliable, and efficient treatment technologies for elimination of phosphorus in municipal wastewater.

The primary objective of this dissertation is to evaluate the treatment performance of ferrate(VI) for removal of different phosphorus species at different wastewater treatment stages and elucidate the underlying reaction mechanisms. Two treatment scenarios were tested, i.e. chemically enhanced primary treatment (CEPT) and advanced wastewater treatment. The central hypothesis is that ferrate(VI) is capable of effectively removing inorganic phosphate through precipitation and/or adsorption due to the formation of iron (hdyr)oxides and alleviating organic phosphorus via chemical oxidation and precipitation/adsorption mechanisms. Laboratory sale tests were carried out to sequentially implement four tasks for achieving the objective.

In Task 1, ferrate(VI) treatment was applied to CEPT with a particular focus on the removal of phosphorus in wastewater. Results show that ferrate(VI) enabled CEPT could effectively remove total phosphorus by up to 87%. The most majority of phosphorus removed was particulate phosphorus. The removal was primarily ascribed by gravity-driven sedimentation. In contrast, ferrate(VI) CEPT poorly removed organic phosphorus present in municipal wastewater. Accompanied by the alleviation of phosphorus, ferrate(VI) addition improved the removal of particles and particulate organic matter in wastewater. In Task 2, ferrate(VI) removal of orthophosphate was investigated in a secondary effluent matrix at an advanced treatment scenario. Results show that ferrate(VI) could effectively alleviate phosphate (a majority of inorganic phosphorus) from secondary effluent primarily due to the adsorption mechanisms. Ferrate(VI) resultant particles comprised both amorphous and crystalline (hematite) iron (hydr)oxides. Effluent organic matter (EfOM) could inhibit the phosphate removal. Task 3 aimed to remove organic phosphorus for advanced wastewater treatment. Ferrate(VI) exhibited an excellent capability for abating of organic phosphorus in in secondary effluent. The presence of phosphate could suppress ferrate(VI) removal of organic phosphorus. In order to understand the underlying mechanisms, the reactions between ferrate(VI) and six organic phosphorus model compounds were separately investigated. Results show that ferrate(VI) degraded the model compounds into daughter P-containing molecules, followed by adsorption of the transformation compounds by the resultant iron (hdyr)oxide particles. Ferrate(VI) oxidation insufficiently decomposed the organic phosphorus into inorganic phosphorus. Of note, the treatment performance of ferrate(VI) for removal of phosphorus during the CEPT or advanced treatment relied heavily on ferrate(VI) dose and pH. In Task 4, a preliminary cost analysis was made. Although ferrate(VI) addition was more costly than traditional phosphorus removals with ferric slats, ferrate(VI) treatment brings many unmatched benefits such as the removal of organic phosphors. Finally, the impacts of ferrate(VI) technologies on urban water management, environment, and society were discussed, and future research directions were identified.

This dissertation research clearly demonstrates that ferrate(VI) treatment is a promising technology for elimination of different phosphorus species in municipal wastewater and abatement of other wastewater contaminants. Besides mitigation of phosphorus, organic matter, and particles in wastewater, ferrate(VI) has proven highly effective for degradation of micro-pollutants and inactivation of pathogens in water and wastewater. In this dissertation research, ferrate(VI) can be resiliently applied for CEPT or advanced treatment for improving wastewater quality. At the first scenario, the ferrate(VI) enabled technology can enhance the performance of traditional secondary wastewater treatment facilities. It can also be a standalone wastewater treatment process for many developing countries with the primary treatment only. At the second scenario, ferrate(VI) treatment as a post-treatment step is expected to dramatically improve water quality through the removal of persistent contaminants such as organic phosphorus and emerging contaminants. Implementation of ferrate(VI) technologies for wastewater treatment has profound impacts on the wastewater industry, environment, and society.

Keywords: Ferrate(VI), Wastewater treatment, Phosphorus, Adsorption, Coagulation, Oxidation

Acknowledgments

I want to give my sincerely thanks to all my committee members for their support in my Ph. D. life! Especially to my advisor, Dr. Yang Deng, who taught me how to be a professional scientist and researcher with patience, respect and brilliant mind, pushing me forward step by step. He is an excellent mentor in my academic life and an extremely important friend in my personal life. I am very glad to meet him in my life!

I do appreciate my other committee members, Dr. Huan Feng, Dr. Jinshan Gao and Dr. Yueqiang Liu, who helped and mentored me friendly and professionally throughout the dissertation research. Their efforts are highly valuable to me. Meanwhile, I also want to thank my former committee member, Dr. Dibyendu Sarkar. I cannot reach here without his help.

Special thanks to Dr. Xiaona Li, Dr. Kevin Olsen, Dr. Laying Wu, and Dr. Matthew Gorring, for their professional supports whenever I need for sample tests. They are friendly and willing to help at any time. Without them, I would not be able to finish my experiments.

I would like to appreciate all my colleagues and friends during my Ph. D. life. Thank you, Dr. Nanzhu Li and Dr. Chanil Jung, for their help of making me comfortable when stepping into Ph. D life at the very beginning. Thank you, my colleagues, Panpan Gao, Lisitai Yang and Junkui Cui, for your help and support at the end of my Ph. D. life. I am so proud to meet you all in my life!

Last but not least, I want to give my parents my sincere appreciation! Thanks so much for their unconditional support and understanding!

To my parents who has been supporting me unconditionally

and

My future lovely wife and children.

Table of Contents

List of Figures

Chapter 1 Introduction and Objectives

1.1 Phosphorus Element

Phosphorus (P), with an element symbol of P, has the atomic number of 15 in the periodic table of the elements. Because P is highly reactive, free elemental P does not exist in nature. Among different elements, P ranks No. 11 in the Earth's crust and No. 13 in seawater in terms of abundance (Smil, 2000). The unique element plays a critically important role to support the life on the Earth and human activities.

P is an essential element for supporting all the living organisms in the world. For example, both deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) are nucleic acids and genetic materials of every life on the Earth. DNA stores all the genetic information, which organisms need to develop, function, and reproduce, to be transferred to the next generations. On the other hand, RNA guides protein synthesis to perform specific functions. P as a key structural element behaves like a bridge between mononucleotide units in DNA and RNA. In another example, adenosine diphosphate (ADP) combined with a phosphate forms adenosine triphosphate (ATP), which can release the stored energy through hydrolysis to drive many biochemical processes in living cells (Smil, 2000). In addition, P is a major element for the bones and teeth of vertebrate animals (E. N. M. C. T. T. Martin, 1998). Hydroxyapatite ($Ca_{10}(PO4)_6(OH)_2$, a P-containing organic chemical, contributes to almost 60% of bone and 70% of teeth on the basis of mass (E. N. M. C. T. T. Martin, 1998; Smil, 2000). Therefore, P is indispensable for all the life on the Earth.

A variety of human activities also need phosphorus. P is substantially consumed for agriculture, which is the practice of farming, from the crop growing in the soil to the rearing of animals, for providing the human with food, cotton, wool, and other products. P is a key element for the growth of both plants and animals. Currently, over 90% of human-mined phosphorus goes to agriculture as fertilizers (Yuan et al., 2018). Phosphorus also has an important role in the building and construction field. Asphalt is a mixture of bituminous with sands or gravels for paving and roofing. In order to make asphalt stronger and more durable, polyphosphoric acid (PPA), a P-containing polymer, is often added to modify the properties of asphalt (Baumgardner, Masson, Hardee, Menapace, & Williams, 2005). Moreover, P is a major element in the detergents used in the car wash and automatic dishwashing industry. Besides, P can be used as an inhibitor to control lead release in water distribution systems (Edwards & McNeill, 2002; Hozalski, Esbri-Amador, & Chen, 2005).

1.2 Phosphorus Cycle

The phosphorus cycle, different from the cycles of other elements such as carbon, nitrogen, and sulfur on the Earth, is poorly understood. However, the phosphorus cycle has gained much attention (Smil, 2000; Yuan et al., 2018). Rather than other common elements, P is not relatively active to form a stable gaseous chemical species. Therefore, the phosphorus cycle does not have significant interactions via the atmosphere, even though little P can exist in the atmosphere as an element in dusts and aerosols (the quantity is low as compared to the amount in other reservoirs). In contrast, lithosphere, oceans, riverine systems, and biota are major pools of P on the Earth. Ruttenberg (2003) proposes that the global phosphorus cycle comprises four major components between these pools, as follows.

1) The uplifting tectonic process makes phosphorus-rich mineral rocks exposed to various weathering forces.
2) After the formation of soil, the erosion and chemical weathering bring dissolved and particulate phosphorus to the riverine system.

3) Dissolved and particulate P in the riverine system either becomes part of river sediment or enters into the oceans.
4) Phosphorus becomes part of the sediments in the ocean.

1.2.1 Phosphorus Cycle in the Terrestrial Environment

In the terrestrial environment, P mainly exists in the Earth's crust, surface soil, and biota. Apatite ($Ca_{10}(PO_4)_6(OH, F, Cl)_2$) is the most abundant primary phosphorus mineral, which can be exposed to various weathering processes. Physical weathering, such as freeze-thaw and exfoliation, can break apatite into fine minerals, but they are unavailable for uptake and assimilation of terrestrial plants. Afterwards, chemical weathering, e.g., corrosion with acids derived from microbial activities (Ruttenberg, 2003), solubilizes these small minerals for direct utilization for plants. Besides, part of P can exist in soil. For example, it is reported that P retention in soil plays a significant role in the fate and transport of phosphorus, because soluble P is easily bonded with different soil components, particularly iron and aluminum oxyhydroxides (Lajtha & Harrison, 1995). As a result, soluble P is uptaken by plants or bonded in soil.

Once entering into plants via roots, P is subject to different biochemical transformations to form various organic P (e.g., DNA, RNA, and ATP), which play a critical role in photosynthesis and metabolism. After the plant death, the litterfall, primarily in the form of organic phosphorus, returns to the topsoil, which is gradually released as phosphate through self-decomposition and biochemical oxidation initiated by bacterial and fungal communities (Bucher, 2007). The phosphorus is barely lost due to the high recycle efficiency of plants (Lajtha & Harrison, 1995; Ruttenberg, 2003; Vitousek et al., 1997).

On the other hand, the phosphorus in soil can be present in different phases. As aforementioned, iron and aluminum oxyhydroxides can bind phosphate, due to their large specific surface area, abundant active moieties, and high binding capacity (Filippelli, 2002). Meanwhile, soluble P can exist in pore water in soil or sorb to the surface of soil particles, which can serve as a source of phosphorus loss during the following soil erosion. After well developed, P in the soil may reach a balance that the rate of phosphorus loss equals to the rate of newly generated phosphorus from apatite weathering (Filippelli, 2008). In the cycle, P exists primarily in refractory minerals and organic phosphorus (Ruttenberg, 2003; Walker & Syers, 1976).

1.2.2 Phosphorus Cycle in the Riverine Environment

Riverine phosphorus, particulate or dissolved, mainly derives from soil erosion and surface runoff. Particulate P accounts for more than 90% of total riverine phosphorus (Ruttenberg, 2003). As an active element, dissolved phosphate can be easily captured by metal oxyhydroxides and transformed to a solid phase. The particulate P is barely released at normal river conditions. It becomes either part of river sediments or the source of oceanic phosphorus, without participation in biological processes in the riverine system. Chemical forms of particulate P vary, depending on such factors as soil development, river conditions, and land use. Ruttenberg (2003) states that approximately 20-40% of the P associated with particles is organic phosphorus.

Dissolved phosphorus in the riverine system is more complicated than its particulate counterpart, because of its strong reactivity toward particles (Withers & Jarvie, 2008) and participation in the biotic cycle in the riverine system. The interactions between dissolved phosphorus and particles in the riverine system mainly include sorption and precipitation. Suspended particles, such as clays (House, Jickells, Edwards, Praska, & Denison, 1998) and metal oxides and hydroxides (Withers & Jarvie, 2008), can adsorb dissolved phosphorus either onto particle surface or into solid phase through diffusion. Many mechanisms govern this process, such as ligand-exchange and electrostatic attraction, which is influenced by many factors such as pH, redox conditions, and the presence of particle-organic matter complexes (Froelich, 1988; Kadlec, Flaig, & Gale, 1999; Withers & Jarvie, 2008; Zhou, Tang, & Wang, 2005). Dissolved phosphorus interacts with minerals in the river to form precipitation, facilitating the fixation of P in sediment. Neal et al. (2002) reports that dissolved phosphorus can co-precipitate with calcite in water columns. Meanwhile, aluminum and iron in the river water can precipitate dissolved phosphorus by forming unsolvable chemicals, such as aluminum and iron(III) phosphate. Moreover, dissolved phosphorus is a key element in the biotic cycle in the riverine system. Phytoplankton assimilate dissolved phosphorus through photosynthesis, converting inorganic P to organic P and enabling phosphorus to enter into the food web in the riverine system. Previous studies suggest that around 10-15% dissolved phosphorus is assigned to phytoplankton communities (Withers & Jarvie, 2008). After the death of biota, bacteria and fungi in the riverine system decompose organic matters and release phosphorus back to water, making phosphorus available again for phytoplankton assimilation. Meanwhile, bacteria and fungi can change pH and redox conditions on the water-sediment surface, resulting in phosphorus adsorption on or desorption from the sediment (McDowell, 2003).

1.2.3 Phosphorus Cycle in the Oceanic Environment

After the transportation via the riverine system, phosphorus reaches oceans. Atmospheric deposits, such as aerosols and mineral dusts, also contribute to oceanic phosphorus, particularly for the remote ocean (Paytan & McLaughlin, 2007). Most of the particulate phosphorus deposits in the estuarine and coastal shelf environments (Paytan & McLaughlin, 2007), which will be geologically uplifted. On the other hand, part of adsorbed phosphorus to soil particles may desorb back to the sea water when physical and chemical conditions of the water (e.g., pH and salinity) change, contributing to phosphorus in the open ocean. Dissolved inorganic phosphorus can participate in the biological processes in the coastal environment, supporting the food web for the coastal ecosystem. Part of dissolved organic P can be trapped through flocculation and then settle to the sediment, while the other dissolved organic phosphorus can be photo-hydrolyzed and then transform to phosphate. Paytan and McLaughlin (2007) report that around 99% of particulate P and 25% of dissolved P enter into the coastal environment. Similar to phosphorus in the riverine system, some particulate phosphorus settle in the sediments. Part of dissolved phosphorus degrades to phosphate by bacteria and fungi, participating in primary production. Death of biota brings organic phosphorus back to microorganisms for closing the phosphorus cycle.

To sum up, the global phosphorus cycle begins from the weathering of phosphorus-enriched minerals, sustains in the biosphere, and ends with deposition in the sediments. It takes approximately 10^7-10^8 years to complete a cycle due to the inclusion of geological uplifting (Smil, 2000). Considering that the human civilization has a much shorter history (less than 10,000 years), phosphorus, which flows one direction, is acknowledged as a non-renewable resource.

1.3 Eutrophication

1.3.1 Definition

Eutrophication is the over richness of nutrients in natural water bodies to cause the excessive growth of plants and algae. Two major nutrients include nitrogen and phosphorus. Le Moal et al. (2019) suggests that eutrophication is an imbalance in quantity, relative proportion or chemical forms of nitrogen and phosphorus in aqueous ecosystems. Eutrophication can occur in lakes, streams, estuaries, and coastal environments. Previous investigations suggest that nitrogen is the limiting nutrient for eutrophication in estuaries and coastal areas, while phosphorus is for eutrophication in freshwater ecosystems (Howarth & Marino, 2006; Schindler et al., 2008; Yuan et al., 2018). Besides the quantities of these nutrients, other conditions of aqueous ecosystems can affect eutrophication, including hydraulic residence time, temperature, and light (Le Moal et al., 2019). Due to the acceleration of nutrient loss from human activities, aqueous ecosystems receive excessive input of nitrogen and phosphorus in a short time period, causing overproduction of plants and algae. Anthropogenic eutrophication caused by human activities has similar mechanisms with natural eutrophication. However, they occur on quite different time scales and bring totally different environmental and social impacts (Le Moal et al., 2019).

1.3.2 Adverse Effects

Anthropogenic eutrophication brings multiple adverse impacts on aqueous ecosystems. As a result of the substantial input of nutrients, the fast growth of phytoplankton and algae species is triggered. Consequently, water turbidity increases and water transparency declines, preventing sunlight from penetrating to deep water. Lack of sunlight causes the shift of biodiversity in aqueous ecosystems. Meanwhile, the decomposition of excessive phytomass significantly consumes dissolved oxygen, resulting in hypoxia or dead zones, which kill fishes and decrease biodiversity in the aqueous ecosystem. To the extreme condition, eutrophication may turn into harmful algal blooms (HABs) that can produce toxins. Eutrophication-induced HABs caused serious drinking water crises in the cities near Lake Tai in 2008 and Lake Erie in 2014 (Jetoo, Grover, & Krantzberg, 2015; B. Qin et al., 2010; Yuan et al., 2018). Eventually, the anaerobic condition leads to the formation of offensive taste and odors. Therefore, the degradation of water quality can bring adverse effects on the fishery industry, pose a potential threat to public health due to the production of toxin in recreational water or drinking water sources, and affect tourism resources.

1.3.3 The Extent Development of Eutrophication

The extent of eutrophication in the past decades becomes increasingly severe. After the World War II, the expansion of the world economy and population, in addition to the wide use of phosphate detergents, led to the occurrence of an increasing number of eutrophication events (Ashley, Cordell, & Mavinic, 2011). In the 1950s, the eutrophication in the Great Lakes of North America caused the negative environmental consequences due to phosphorus enrichment in freshwater (Yuan et al., 2018). Later on, the initiation of phosphorus detergent ban and requirements of industrial and domestic pollution treatment dramatically reduced phosphorus discharge from wastewater treatment plants, resulting in gradual abatement of eutrophication (Le Moal et al., 2019). However, the recurrence of eutrophication at multiple locations, such as the Chesapeake Bay and the Gulf of Mexico, again attracted public attention to the nutrient contribution from non-point pollution sources, especially in agriculture and urbanized areas. In the past two decades, the number of eutrophication-caused hypoxic areas has increased approximately by 300%. More importantly, the occurrence of HABs has become worse in size, frequency, diversity and geographical extent (Diaz & Rosenberg, 2008; Le Moal et al., 2019).

1.3.4 Phosphorus Sources to Eutrophication

Excessive phosphorus comes from both point and nonpoint pollution sources. Point sources are single pollution ones that can be identifiable, such as discharge from wastewater treatment plants and combined sewer overflow (CSO). Nonpoint sources are diffuse sources that are not identifiable and usually happen over a large area without attributing to a single source. Nonpoint sources mainly include various runoffs and groundwater, such as urban runoff, farmland runoff, and groundwater flow. Withers and Jarvie (2008) summarized probable human-induced phosphorus sources (**Table 1**). As shown, non-point sources discharge various types of phosphorus, and the discharges occur episodically with a high dependency on rainfall besides land surface conditions, the frequency and intensity of rainfalls can substantially affect phosphorus discharge amount from non-point sources. In contrast, point sources discharge concentrated phosphorus continuously with very low dependency on rainfall. Generally, except agricultural runoff, other non-point sources have relatively low total phosphorus ranges and mean concentrations in comparison with point sources. Among the different types, wastewater treatment plants and farmland discharges are the major phosphorus sources of point and non-point routes, respectively.

Currently, both point and non-point sources are monitored under relevant regulations, but this cannot prevent the occurrence of new issues. As two major components of non-point sources, livestock wastewater and agricultural runoff are well managed. As mentioned previously, human diet preference change to meat boosts the development of the livestock industry, which is becoming more and more centralized for better management and lower cost. Since 1995, United States Environmental Protection Agency (USEPA) has started to regulate concentrated animal feeding operations (CAFOs) and required CAFOs under the National Pollutant Discharge Elimination System (NPDES), which uses permits to control phosphorus discharge (Litke, 1999). Meanwhile, USEPA encourages the management of agricultural runoff by the development of local best management practices (BMPs), which are funded through Section 319 of the Clean Water Act (Litke, 1999). The primary functions of BMPs are to minimize the generation of runoff, prevent the transportation of runoff pollutants, and safeguard water quality. However, complicated and voluntary BMPs are highly restricted by local hydrological and environmental conditions, so that the performance of BMPs is highly site specific.

More attention has also been paid to the treatment and reuse of agricultural wastewater using the technologies such as constructed wetlands, bioreactors, reed bed system and harvest for re-irrigation, which can significantly reduce runoffs and nutrient release to surface water bodies (Jiménez, 2005; Kern & Idler, 1999; Vymazal, 2010). Although non-point source pollutions are considered as the major source of phosphorus, their discharge and frequency are relatively low and episodic. Moreover, the application of BMPs as well as the treatment and reuse of agricultural wastewater can reliably mitigate the impact of phosphorus release from agricultural runoff. Thus, phosphorus release from point sources, particularly wastewater treatment plants, is considered as a major way for phosphorus pollution to the environment.

1.4 Phosphorus in Municipal Wastewater

1.4.1 Phosphorus Sources to Municipal Wastewater

Globally, approximately 20-30% of mined P ends up in sewer systems based on various estimations (Brunner, 2010; Kazuaki Shimamura, Homma, Watanabe, & Tanaka, 2003). The P primarily originate from either municipal or industrial wastewater. Typically, industrial wastewater contains highly concentrated phosphorus compounds, so that special treatment processes are needed for onsite purification, rather than direct discharge into municipal wastewater treatment plants. Municipal wastewater has a relatively low phosphorus concentration. Based on the literature data, P in municipal wastewater originates principally from PPCPs, detergents, drinking water supply, human excreta, and food waste (Comber, Gardner, Georges, Blackwood, & Gilmour, 2013).

Comber et al. (2013) pointed out that cocamidopropyl PG-dimonium chloride phosphate and sodium diethylenetriamine pentamethylene phosphate are two commonly used forms of P in personal care products, such as hair shampoo, conditioner, show gel, hand soaps, and body lotions. Meanwhile, tetra sodium pyrophosphate, dicalcium phosphate, pentasodium triphosphate, and disodium phosphate are contained in most toothpaste brands and contribute 22 mg phosphorus per person per day to sewer systems, based on the assumption that every person consumes 5 g toothpaste everyday (Comber et al., 2013).

About 5% of mined P is worldwide used for detergents in which pentasodium triphosphate is a major chemical form (P. A. Gilbert & De Jong, 1978). Since the occurrence of eutrophication in the Great Lakes of North America in the 1950s, detergent ban has dramatically reduced the use of P in household detergents. However, the use of phosphorus in automatic dishwashing area is not restricted by the detergent ban, because of the difficulty to find a cost-effective detergent alternative. It is estimated that automatic dishwashing phosphorus contributes about 175 mg-P per person per day to sewer systems (Comber et al., 2013).

Phosphate is used in water supply systems as a corrosion inhibitor to prevent the unintended leaching of lead and copper from water distribution pipes (Edwards & McNeill, 2002; Hozalski et al., 2005). The addition of orthophosphate forms a protective coating of insoluble mineral scale, which serves as a liner for preventing dissolution of unwanted heavy metals from the pipe materials. Water crisis happened in Flint, Michigan in 2014 due to the leaching of lead from water pipes into drinking water, making over 100,000 local residents exposed to potential lead poisoning. However, only part of the dosed orthophosphate finally becomes the coating on the inside surface of pipes, while the remaining P in water can potentially contribute phosphorus into municipal wastewater after the use. Contribution of P from a residual water system to the sewage is estimated to be 130 mg-P per person per day, while a greater contribution is expected from office, industrial, and commercial areas (Comber et al., 2013).

Human needs a certain amount of phosphorus for daily requirements, but extra intake of phosphorus is excreted through feces and urine. The excreted quantity of P depends heavily on the diet and ages of different persons. Urine and feces are estimated to contribute 900 mg-P per person per day and 500 mg-P per person per day, respectively (Comber et al., 2013). The overall contribution from this source is expected to rise with time due to the increase of the world population and because more people will become connected to sewer systems.

Finally, P in wastewater can come from food waste. Kitchen sinks and toilets are two common locations to dispose of food waste, which can introduce P into municipal wastewater. Carbonated drinks, milk, cereals, gravy, puddings, and fruit drinks are the main food waste disposed into sewer systems, according to the recent report of Waste Resources Action Program (WRAP) (Comber et al., 2013). It is estimated that 30 mg-P per person per day is added into sewers through food waste in developed countries (Comber et al., 2013).

1.4.2 Different Phosphorus Species

In municipal wastewater, phosphorus species can be grouped into three major categories, including orthophosphate, polyphosphates, and organic phosphates, according to a well-known phosphorus extraction method established by the American Public Health Association (APHA). Each type of phosphorus can be present in either particulate or dissolved form (Parsons & Smith, 2008). This speciation method has been widely used in the literature related to the measurement and treatment of phosphorus in wastewater (Dueñas, Alonso, Rey, & Ferrer, 2003; Pastor, Marti, Bouzas, & Seco, 2008; K. Shimamura, Ishikawa, Mizuoka, & Hirasawa, 2008; Zeng, Yuan, Shi, & Qiu, 2010). **Figure 1-1** shows how to differentiate phosphorus species in details.

Phosphorus species can be differentiated into dissolved and particulate forms. Dissolved P is the phosphorus in water passing through 0.45 μm microfiltration filters, while particulate P is retained by 0.45 μm filters. Based on their reactivity, phosphorus species can also be differentiated through hydrolysis and oxidative digestion processes. Reactive phosphorus refers to the orthophosphates that respond to the colorimetric tests without hydrolysis and oxidative digestion. Orthophosphates are a group of phosphorus species that have phosphoric acid in the chemical forms, including H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}, which are bioavailable (Zeng et al., 2010). Acid-hydrolyzable phosphorus (AHP) is the condensed phosphates that can be transformed into reactive phosphorus through acid digestion. These species contain two or more phosphorus atoms sharing an oxygen atom in their molecules and are very stable in water over a wide range of pH and temperatures (Rao, Gómez-García, & Kornberg, 2009). However, such species can be easily transformed into orthophosphates by bacterial enzymes (Kuroda et al., 2002). Organic phosphorus is determined by the difference of total phosphorus and acid-hydrolyzable phosphorus through further vigorous digestion processes. Organic compounds that contribute organic phosphorus to wastewater include nucleic acids, phospholipids, phosphoramides, sugar phosphates, and amino phosphoric. Typically, organic phosphorus does not account for a major proportion in the total phosphorus in municipal wastewater, but its faction may be significant in microorganism-rich wastewater.

1.4.3 Phosphorus Removal

Total phosphorus in municipal wastewater typically varies between 5 and 20 mg-P/L, of which 50% is in the form of orthophosphates, while the remaining ones include polyphosphoric (35%) and organic phosphorus (15%) (Dueñas et al., 2003). Dueñas et al. (2003) investigated phosphorus removal in wastewater treatment plants (**Figure 1-2**). As seen, most of the particulate phosphorus in the influent can be removed after the clarifiers. After the primary sedimentation, about 5-10% of the total phosphorus is removed (Smil, 2000). Without any phosphorus-focused treatments, conventional secondary treatment (e.g., the activated sludge process) can only remove 1-2 mg-P/L. Therefore, there is still a large amount of phosphorus in the effluent, which is much higher than one mg-P/L. Thus, specific phosphorus treatments are needed during the wastewater treatment to meet federal and local phosphorus discharge standards.

1.5 Phosphorus Removal Technologies in Municipal Wastewater Treatment

The removal of phosphorus from municipal wastewater can be achieved through physico-chemical processes, biological treatments, or combination of the both (Yeoman, Stephenson, Lester, & Perry, 1988). It should be noted that each treatment option has its advantages and disadvantages.

1.5.1 Physico-chemical Methods

Physico-chemical methods have been commonly used for phosphorus removal over many decades due to the technical reliability and effectiveness. Specifically, the treatment category includes precipitation, adsorption, and ion exchange (Bunce, Ndam, Ofiteru, Moore, & Graham, 2018).

1.5.1.1 Precipitation

Chemical precipitation process mainly targets at the removal of inorganic phosphorus (mostly phosphates) by adding a coagulant to mix with wastewater, forming solid residuals, and solid-liquid separation by settling or filtration. The widely used coagulants are calcium, aluminum and iron-based salts (Bunce et al., 2018).

Calcium is usually added as lime $Ca(OH)_2$. Initially, lime reacts with the natural alkalinity in wastewater to form calcium carbonate (Eq.1-1). With the addition of lime, the pH of wastewater continuously increases. Calcium ions can precipitate phosphates to form hydroxylapatite at pH over 10 (Eq. 1-2).

$Ca(HCO_3)^2 + Ca(OH)_2 \leftrightarrow 2CaCO_3 \downarrow + 2H_2O$ (1-1)

$10\ Ca^{2+} + 6\ PO_4^{3-} + 2\ OH^- \leftrightarrow Ca_{10}(PO_4)\cdot 6(OH)_2 \downarrow$ (1-2)

Since lime first reacts with alkalinity in wastewater, the required dose of lime for phosphorus removal is more than the concentration required to stoichiometrically precipitate all phosphates in the wastewater. Therefore, the lime dose relies on the concentrations of both alkalinity and phosphate. Moreover, neutralization is needed after the treatment. The commonly used pH adjustment method is injection of carbon dioxide (i.e. recarbonation). Owen (1953) found that the addition of lime could remove phosphorus in sewage samples by up to 99% in the laboratory studies, but by only 77% in a plant-scale test.

Alum (aluminum sulfate) is also a widely used multivalent salt for precipitating phosphates to form aluminum phosphates as Eq. 1-3.

$Al^{3+} + H_nPO_4^{3-n} \leftrightarrow AlPO_4 + nH^+$ (1-3)

This reaction can be affected by many factors, such as the competition between hydroxyl and phosphates ions, alkalinity, and pH. Alum dose depends on the phosphate concentration in wastewater. In the most cases, it can remove 90% or greater of total phosphorus in wastewater. The removal efficiency typically decreases as the phosphate concentration decreases. Banu, Do, and Yeom (2008) applied alum to remove phosphorus in a secondary effluent with a low alkalinity. The optimal removal was achieved at 80 mg/L alum, beyond which a further increase in the alum dose led to a decreasing removal efficiency.

Iron salts are also commonly used for phosphorus precipitation. The widely used chemicals include ferric chloride, ferric sulfate, and ferrous sulfate. The benefits of iron salts for phosphorus removal include a low cost and a short treatment time in comparison with alum (Ramasahayam, Guzman, Gunawan, & Viswanathan, 2014). The basic reaction is as follows:

$Fe^{3+} + H_nPO_4^{3-n} \leftrightarrow FePO_4 + nH^+$ (1-4)

Different from alum, iron salts react slowly with alkalinity in wastewater and decrease pH. Therefore, the addition of coagulant aids such as lime is commonly used to raise the pH to enhance the performance.

Magnesium salt is a novel agent for removing phosphorus from wastewater. Besides phosphorus, the addition of magnesium ions can remove ammonia nitrogen to produce struvite ($MgNH_4PO_4 \cdot 6H_2O$) as follows.

$Mg^{2+}(aq) + NH^{4+}(aq) + HPO_4^{3-}(aq) + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O\downarrow + H^+$ (1-5)

H. M. Huang, Song, and Xu (2011) reprot that the formation of struvite can be influenced by many factors, including pH, the $Mg^{2+}:PO_4^{3-}:NH^{4+}$ molar ratio, the extent of super-saturation, temperature, and the presence of co-existing metal ions capable of reacting with phosphate to form insoluble compounds.

Chemical agents can be dosed at three locations (**Figure 1-3**): before the primary settling tanks; before the biological treatment tank (co-precipitation); and in the secondary effluent (post-precipitation) (Cornel & Schaum, 2009). Dosing salts before the primary settlement tank is also called chemically enhance primary treatment (CEPT), in which chemical salts are added to initiate coagulation and flocculation processes, facilitating aggregation of suspended particles. Along with phosphorus removal by up to 90%, CEPT can improve the removal of biological oxygen demand (BOD) and suspended solid (SS). In the second situation, co-precipitation process can provide a complementary treatment for biological wastewater treatment originally designed for the removal of dissolved BOD. The addition of coagulant salts can enable the concurrent occurrence of coagulation-flocculation and adsorption for removal of other wastewater pollutants such as phosphorus. However, the addition of chemical salts should not influence microbial community for the biological wastewater treatment. In practice, alum and iron salt are the commonly selected coagulants. In the third scenario, the post-precipitation is an advanced treatment process to remove nutrient by adding coagulant salts. This process may provide the highest phosphorus removal efficiency (> 95%). Because microorganisms in a biological treatment step may release phosphorus into effluent, post- precipitation typically has a better P removal than co-precipitation.

Physico-chemical precipitation methods may be restricted due to two disadvantages. First, the phosphorus-rich sludge produced, particularly aluminum and iron sludge, is technically difficult to be used for phosphorus recovery (Le Corre, Valsami-Jones, Hobbs, & Parsons, 2009). Second, the physico-chemical approach has proven effective for orthophosphates in wastewater, but poorly removes poly- and organic phosphorus. Bunce et al. (2018) reported that conventional gravity settling could achieve 1mg/L phosphorus in the effluent, but the conventional design rarely accomplished a lower phosphorus concentration in the treated wastewater, unless more sophisticated separation techniques are used.

1.5.1.2 Adsorption

Adsorption is another option to remove wastewater phosphorus using adsorbent materials (Bunce et al., 2018; Drizo, Forget, Chapuis, & Comeau, 2006; Gustafsson, Renman, Renman, & Poll, 2008; Herrmann, Nordqvist, Hedström, & Viklander, 2014; Shilton et al., 2006). Adsorbents for P removal may originate from natural products (e.g., apatite, bauxite or limestone), industrial waste products (e.g., flyash, ochre, steel slag, and water treatment residuals) or man-made products (e.g., Filtralite^{TM}) (Bunce et al., 2018). Phosphorus in wastewater is sorped onto the surface of or inside the adsorbents (Brix, Arias, & del Bubba, 2001). Therefore, the P removal performance depends on physical and chemical properties of adsorbents, solution chemistry, and operation conditions (e.g., the adsorbent dose). For example, Renman and Renman (2010) used Polonite for removal of 91% phosphate in municipal wastewater. In another example, oyster shells as the source of lime were mixed with clay to immobilize more than 90% of phosphorus from wastewater (Chen, Cai, Clark, & Yu, 2013).

1.5.1.3 Ion Exchange

Ion exchange (IX) is a well-established treatment process for municipal and industrial water treatment, such as desalination of sea water (Awual & Jyo, 2011). However, IX is less studied for removal of wastewater phosphorus than the two aforementioned technologies. B. D. Martin, Parsons, and Jefferson (2009) report that phosphate ions can reversibly interchange between wastewater and solid ion exchanger, making desorption possible during the phosphorus removal. Further investigations reveal that the pre-treatment of ion exchangers can improve phosphate removal efficiency (Bunce et al., 2018; B. D. Martin et al., 2009; Seo et al., 2013). However, three issues challenge the IX treatment. First, many wastewater matrix constituents, such as sulfate, chloride, and sewage organic matter, can compete with phosphate for the active sites on ion exchangers, so that the use efficiency is low. Second, application of ion exchangers for wastewater treatment is prohibitive due to the high cost of ion exchangers. Third, the regenerant produced from regeneration of ion exchangers requires appropriate treatment and management.

1.5.2 Biological Methods

1.5.2.1 Enhanced Biological Phosphorus Removal (EPBR)

Enhanced biological phosphorus removal (EPBR) (**Figure 1-4**), consisting of an anaerobic tank and an aeration tank, has been widely studied over the past decades. EPBR is considered to be an environmentally sustainable and cost-effective alternative for chemical treatment (Acevedo et al., 2012; Bunce et al., 2018; Nguyen, Ngo, & Guo, 2013). During the EPBR, microorganisms uptake phosphorus in wastewater and transform it into biomass that is removed in the downstream treatment as waste sludge. Among the different microorganism species in an activated sludge system, phosphorus-accumulating organisms (PAO) can uptake more phosphorus than others. At the anaerobic conditions, PAO hydrolyzes the internally stored polyphosphate to generate ATP for energy. The breakdown of polyphosphate releases orthophosphate into wastewater (Smolders, van der Meij, van Loosdrecht, & Heijnen, 1994). In contrast, at an aerobic environment, PAO utilizes phosphate in wastewater to form polyphosphate stored in cells. The difference between uptaken and released phosphate at the two different conditions is the removed phosphorus from the wastewater. The performance of biological removal of phosphorus is directly related to the proportion of PAO present in the microorganism communities (Bunce et al., 2018). EBPR can be incorporated into membrane bioreactors (MBR), granular sludge reactors, and sequencing batch biofilm reactors (SBRs) for removing 70-97% phosphorus in wastewater (Bunce et al., 2018). The potential drawbacks of EBPR include: 1) the treatment efficiency of EBPR may highly fluctuate; 2) highly skilled operators are needed for reliable performance; and 3) the underlying mechanisms remain poorly understood, making the system optimization difficult (Seviour, Mino, & Onuki, 2003).

1.5.2.2 Algal Phosphorus Removal

Phosphorus is an essential nutrient for algal growth. Therefore, algae are capable of uptaking excessive phosphorus beyond their growth requirements (Larsdotter, 2006; Powell, Shilton, Chisti, & Pratt, 2009). Algae-based systems for treatment of wastewater have been well established (Martínez, Sánchez, Jiménez, El Yousfi, & Muñoz, 2000; Shi, Podola, & Melkonian, 2007). During the treatment, algae can capture excessive orthophosphate and store it as polyphosphate granules for future use at a phosphorus deficient environment (Bunce et al., 2018). Larsdotter (2006) reported that when orthophosphate was unavailable, algae might convert organic phosphorus to orthophosphate on the cell surface using the enzyme phosphatase. Although algae systems have shown promising results for phosphorus removal from wastewater (de Godos, González, Becares, García-Encina, & Muñoz, 2009), this technology remains in a lab-scale study. Larger scales tests are required to demonstrate robust and reliable treatment performance.

1.6 Ferrate(VI) Technology

1.6.1 Ferrate(VI) chemistry and its application to water and wastewater treatment

Ferrate(VI), i.e. FeO_4^{2-}, is the oxyanion containing iron in +6 oxidation state (**Figure 1-5**). It has a tetrahedral structure in which four F-O bonds are equivalent with covalent character (Hoppe, Schlemper, & Murmann, 1982). The first ferrate(VI) synthesis was reported in 1702 (Stahl, 1715). Later on, ferrate(VI) was mostly studied by chemists (Schreyer & Ockerman, 1951; Thompson, Ockerman, & Schreyer, 1951; Wagner, Gump, & Hart, 1952; Williams & Riley, 1969; Wood, 1958). The ability of ferrate(VI), mostly as a chemical oxidant, for water and wastewater treatment was explored in the 1970s (M. Gilbert, Waite, & Hare, 1976; T.D. Waite, 1979; T.D. Waite & Gilbert, 1978). Since then, ferrate(VI) for removal of different water contaminants has been increasingly studied (J. Q. Jiang, 2007; J. Q. Jiang & Lloyd, 2002; Y. Lee, Cho, Kim, & Yoon, 2004; Sharma, Chen, & Zboril, 2015; Sharma, Zboril, & Varma, 2015).

The most frequently used ferrate(VI) salts include potassium ferrate(VI) (K_2FeO_4) and sodium ferrate(VI) (Na_2FeO_4). Once dosed to water, Fe(VI) in ferrate(VI) gains electrons to be reduced to intermediate high valence iron species – more reactive Fe(V) and Fe(IV) - and eventually to stable Fe(III) (J. Q. Jiang, 2007; J. Q. Jiang & Lloyd, 2002; Y. Lee, Kissner, & von Gunten, 2014; Sharma, Yngard, Cabelli, & Baum, 2008). The reduction of Fe(VI) to Fe(III) is achieved through three major pathways, including ferrate(VI) reaction with water, traditionally recognized as ferrate(VI) self-decay; chemical oxidation of water matrix constituents (e.g. natural organic matter (NOM)); and chemical oxidation of target pollutants, e.g. mircopollutants (Deng, Jung, Liang, Goodey, & Waite, 2018). The overall self-decomposition reaction of ferrate(VI) is as follows.

$$2FeO_4^{2-} + 5\ H_2O \rightarrow 2Fe^{3+} + 1.5O_2 + 10\ OH^- \qquad (1\text{-}6)$$

With the decreasing Fe(VI) concentration, an equivalent amount of iron precipitate is gradually formed. At typical water and wastewater treatment related conditions, the *in-situ* produced Fe(III) may initiate coagulation for destabilization of colloidal particles (Lv, Zheng, Zhang, & Deng, 2018), precipitate soluble contaminants (e.g. toxic metals) (Robert Prucek et al., 2015), and adsorb inorganic and organic pollutants due to the formation of iron (hdyr)oxides from Fe(III) hydrolysis (T. Yang et al., 2018). Of note, some Fe(III) may remain in a soluble state in water, depending on the solution chemistry and water treatment conditions (Cui, Zheng, & Deng, 2018; Goodwill, Jiang, Reckhow, Gikonyo, & Tobiason, 2015). After the treatment, the final product is ferrate(VI) treatment residuals, primarily comprising iron (hydr)oxide solids (Graham, Khoi, & Jiang, 2010).

Ferrate(VI)-driven oxidation. Fe(VI) was mostly investigated as a chemical oxidant with unique properties as discussed below. First, its reactivity and stability are acutely pH dependent. Ferrate(VI) in water exists in four individual protonated forms ($H_3FeO_4^+$, H_2FeO_4, $HFeO_4^-$, and FeO_4^{2-}) with $pK_1 = 1.6$ (Rush, Zhao, & Bielski, 1996), $pK_2 = 3.5$ (Carr et al., 1985; Rush et al., 1996), and $pK_3 = 7.3$ (Rush et al., 1996) or 7.8 (Carr et al., 1985). Under a typical water treatment pH condition (pH 6-8), the reduction potential of Fe(VI) ranges between +2.2 V ($HFeO_4^-$) at an acidic condition and +0.7 V (FeO_4^{2-}) in alkaline solution (Cyr & Bielski, 1991; Y. Lee, Yoon, & Von Gunten, 2005; Wood, 1958). Moreover, Fe(VI) is unstable at an acidic-neutral condition but relatively stable at higher pH. For example, the half-life of Fe(VI) is reported to be ~ 3 min at pH 7.1, but increases to 2 hrs at pH 9.2 (Li, Li, & Graham, 2005). Second, ferrate(VI) oxidation is selective. Similar to many other selective oxidants (e.g. ozone), ferrate(VI) preferentially reacts with electron-rich organic moieties (ERM), such as activated aromatic compounds (e.g., phenol, aniline, and polycyclic aromatics), organosulfur compounds, and deprotonated amines (Y. Lee & von Gunten, 2010; B. Yang et al., 2012). It also favorably attacks olefins. Although the selective nature may restrict its application to removal of certain organic pollutants, ferrate(VI) is more efficient than nonselective oxidants (e.g., $OH\cdot$) for transforming ERM-containing pollutants, because less ferrate(VI) is wasted (Y. Lee & von Gunten, 2010).

Ferrate(VI) coagulation. In contrast, insufficient attention has been paid to ferrate(VI)-driven coagulation. Ferrate(VI) was reported to perform better than ferric salts in the coagulation performance or enhance particle removals in the following coagulation. Jiang et al (J. Q. Jiang, Lloyd, & Grigore, 2001) found that ferrate(VI) was advantageous over ferric sulfate (2-12 mg/L Fe) during treatment of an upland colored water. The ferrate(VI) coagulation removed almost all the turbidity at pH 7.5. Ma and Liu (Ma & Liu, 2002a, 2002b) reported that the pre-oxidation with ferrate(VI) improved an ensuing coagulation for removal of algal cells. Goodwill et al (Goodwill, Jiang, Reckhow, & Tobiason, 2016) also reported that ferrate(VI) pre-oxidation improved the turbidity removal for a downstream dual-media filter in the treatment of two U.S. Northeast surface waters.

However, other studies reported that ferrate(VI) could not offer better coagulation than ferric salts. Tien and Graham (Tien & Graham, 2011) compared coagulations with ferrate(VI) and Fe(III) in a kaolin suspension solution in the absence of NOM. They used a photometric dispersion analyzer (PDA) instrument to observe changing particle suspensions. The PDA technique analyses the light transmitted through a flowing suspension (Graham et al., 2010). They found that sweep coagulation occurred with ferrate(VI) or Fe(III) (2.8-11.2 mg/L Fe) at pH 6.0 - 8.0. Moreover, the magnitude of floc formation with Fe(III) was superior to that with ferrate(VI). The same group (Graham et al., 2010) also studied the formation of ferrate(VI)-induced floc in a humic acid solution without particles. They reported that ferrate(VI) accomplished comparable, or better, floc formation to Fe(III). The group (Yu, Yang, & Graham, 2016) recently carried out another study to compare coagulation behaviors of ferrate(V) and Fe(III) in an artificial raw water with PDA. In this study, flocculation index (FI) was used to indicate the change of floc size with time as an indicator of floc growth. Results show that FI of Fe(III) coagulation was higher than that of Fe(VI) at 0.02 – 0.30 mM as Fe. Lv et al. (Lv et al., 2018) further compared ferrate(VI) and ferric salts in coagulation of kaolin particles in a simulated natural water. They noticed that lower minimum effective iron doses (MEIDs) were observed for ferrate(VI) coagulation than for direct Fe(III) coagulation at pH 6.5 and 7.5 (DOC = 2.00 mg/L).

Mechanisms of ferrate(VI)-driven coagulation appears to depend on solution chemistry conditions and operating conditions (e.g., pH and ferrate(VI) dose). Charge neutralization and sweep coagulation were reported to be responsible for the particle removals in literature (Deng et al., 2017; Lv et al., 2018; H. Zhang, Zheng, Li, Pi, & Deng, 2020).

In recent years, ferrate(VI)-induced particles, particularly nano or micro-sized ones, in water have gained much attention (Goodwill et al., 2015; Radina P Kralchevska et al., 2016; Lv et al., 2018; T. Yang et al., 2018; Zheng & Deng, 2016). Goodwill et al. (Goodwill et al., 2015) reported that ferrate(VI) and ferric resultant particles had different size distributions and morphologies in laboratory buffered water and reservoir water at pH 6.2. The ferrate(VI) resultant particles contained crystalline Fe_2O_3, which was not found in the Fe(III) resultant particles. Prucek et al. (R. Prucek et al., 2013; Robert Prucek et al., 2015) found that the ferrate(VI) resultant iron (hydr)oxide particles possessed a unique two layer structure comprising the core (γ-Fe_2O_3) and shell (γ-FeOOH). Cui et al.(Cui et al., 2018) investigated the size distribution and coagulation of particles after ferrate(VI) treatment. In the study, ferrate(VI) dose was believed to play a key role in the particle characteristics. As the ferrate(VI) dose was increased, the fractions of soluble and colloidal iron went up, but the portion of large-sized particulates decreased. Zheng and Deng (Zheng & Deng, 2016) also evaluated settleability of ferrate(VI)-induced particles in a biologically treated municipal wastewater. Of surprise, a vast majority of ferrate(VI) particles remained suspended in the secondary effluent, suggesting the poor aggregation of these small particulate matters.

Potential of ferrate(VI) for water and wastewater treatment. Ferrate(VI) is preferred as a promising agent for water and wastewater treatment due to multiple treatment mechanisms, safety without production of known disinfection byproducts (DBPs) at typical water treatment conditions, formation of non-toxic final products (i.e. iron sludge), and selective oxidation capability (X.; Huang & Deng, 2014; Xin Huang et al., 2016; Y. Jiang, Goodwill, Tobiason, & Reckhow, 2016; Sharma, Chen, et al., 2015; Sharma, Zboril, et al., 2015). The unique traits allows ferrate(VI) to achieve multiple treatment functions within a reactor at one step (T. D. Waite, 2012; H. Zhang et al., 2020).

A large number of studies have demonstrated the effectiveness of ferrate(VI) for removal of a broad range of water matrix constituents and contaminants in aqueous solution, including NOM (Graham et al., 2010; J. Q. Jiang & Wang, 2003; Lim & Kim, 2009; Qu, Liu, Liu, & Lei, 2003; Song, Deng, & Jung, 2016), sewage organic substances (Alsheyab, Jiang, & Stanford, 2010; Eng, Sharma, & Ray, 2006; J. Q. Jiang, 2007; J. Q. Jiang & Lloyd, 2002; J. Q. Jiang, Panagouopoulos, Bauer, & Pearce, 2006; J. Q. Jiang, Stanford, & Alsheyab, 2009; J. Q. Jiang, Stanford, & Mollazeinal, 2012; Sharma, Zboril, et al., 2015; Yngard, Sharma, Filip, & Zboril, 2008), phosphorus, organic pollutants, toxic inorganic substances (e.g. arsenic and cyanides) (Costarramone, Kneip, & Castetbon, 2004; Fan, Brown, & Huang, 2002; Y. Lee, Um, & Yoon, 2003; Lim & Kim, 2010; R. Prucek et al., 2013; Sharma, 2010; T. Yang et al., 2018), algae (Deng et al., 2017; Radina P Kralchevska et al., 2016; Ma & Liu, 2002a), pathogen and pathogen indicators/surrogates (Hu et al., 2012; Jessen, Randall, Reinhart, & Daly, 2008; J. Q. Jiang, Wang, & Panagoulopoulos, 2006, 2007; Manoli et al., 2019; Schink & Waite, 1980), as well as emerging pollutants such as PPCPs, EDCs (Anquandah, Sharma, Knight, Batchu, & Gardinali, 2011; Anquandah et al., 2013; Feng et al., 2019; Luo, Feng, Sharma, & Huang, 2019), NDMA precursors (C. Lee, Lee, Schmidt, Yoon, & Von Gunten, 2008), and microcystins (de Luca, Pegorer, & de Luca, 2010; Deng et al., 2017). Bench- and pilot--scale experiments have been conducted to test Fe(VI) for treatment of drinking water (Cashman et al., 2014; Deng et al., 2017; J. Q. Jiang et al., 2001; J. Q. Jiang, Wang, et al., 2006; Lim & Kim, 2009; Qu et al., 2003; H. Zhang et al., 2020), sewage (Alsheyab et al., 2010; Bandala et al., 2009; Cekerevac, Nikolic-Bujanovic, Mirkovic, & Popovic, 2010; E. Gombos et al., 2013; J. Q. Jiang, Panagouopoulos, et al., 2006; J. Q. Jiang et al., 2012; J. Q. Jiang, Wang, et al., 2006; J. Q. Jiang et al., 2007; T.D. Waite, 1979), industrial wastewater(Ciabatti, Tognotti, & Lombardi, 2010), ballast water (Gillis, Walters, Yeargain, & Reinhart, 2005; Jessen et al., 2008), landfill leachate (Batarseh, Reinhart, & Daly, 2007; Gravesen, 2013), and biosolids (X. H. Zhang et al., 2012).

Ferrate(VI) application to water and wastewater was extremely restricted, because synthesis of a dry or powder high-purity ferrate product, with sufficient stability to be shipped and handled, is prohibitively expensive (> $130/kg) (T. D. Waite, 2012). However, recent advances in ferrate(VI) production can commercially produce ferrate(VI) solution on site, thereby significantly reducing the cost to < $10/kg (< 8% of previous costs) (J. Q. Jiang et al., 2009; J. Q. Jiang et al., 2012; T. D. Waite, 2012). Such advances have opened new opportunities for making ferrate(VI) treatment feasible.

1.6.2 Ferrate(VI) and Phosphorus in Wastewater Treatment

Currently, chemical precipitation using Fe or Al slats is the most popular method to remove P from wastewater. Compared with Al salts, Fe salts are usually preferred due to a lower cost. In the near future, Fe will play an essential role in the next-generation wastewater treatment plants that will adopt an A-B process, i.e., a high loaded biological treatment (A stage) followed by a bio-oxidation or B stage for N recovery (Wilfert, Kumar, Korving, Witkamp, & van Loosdrecht, 2015). In the A stage, Fe addition is the most cost-efficient option for reduction of colloidal and particulate COD and elimination of P.

Ferrate(VI) with multiple functions has a potential to effectively remove total phosphorus in wastewater.

In-situ produced Fe(III) from ferrate(VI) has the potential to bond with phosphate ions and form precipitates. Or ferric oxide nanoparticles can absorb phosphorus from wastewater. last ferrate(VI) may oxidize organic phosphorus to transform the molecule so that organic phosphorus can be absorbed and removed. However, by far, there is only a few publications mention ferrate(VI)'s capabilities of phosphorus removal from aqueous solutions.

Y. Lee, Zimmermann, Kieu, and von Gunten (2009) report that a ferrate(VI) dose of 7.5 mg Fe/L could remove around 80% of phosphate in water, exhibiting a similar treatment efficiency like Fe(II) but a slightly better performance than Fe(III). The difference was ascribed to the reason that ferrate(VI) resultant particles had a higher specific surface. Erzsébet Gombos et al. (2013) report in a similar way that ferrate(VI) treatment of secondary effluent could achieve a total phosphorus removal by 97.3%. Kwon, Kim, Park, Kim, and Cho (2014) and Gandhi, Ray, Sharma, and Nakhla (2014) also report total phosphorus removal using ferrate(VI). However, all the studies did not further explore the underlying reaction mechanisms for ferrate(VI) removal of phosphorus. Rather, Radina P. Kralchevska et al. (2016) investigated the mechanisms for ferrate(VI) reactions with phosphate ions in aqueous solutions. This study revealed that after ferrate(VI) treatment phosphate could be adsorbed onto the surface of ferrate(VI) resultant oxide/oxyhydroxide nanoparticles. The removal efficiency could be 100% at a sufficiently high ferrate(VI) dose.

It should be noted that the most studies focused on the removal of phosphate, but much less efforts were made to investigate alleviation of polyphosphate and organic phosphorus in wastewater. C. Qin et al. (2015) highlights that in order to meet a strict phosphorus discharge limit (< 0.1 mg /L total phosphorus), a high removal efficiency for phosphate is insufficient, because organic phosphorus accounts for a substantial fraction in the treated effluent. Unfortunately, conventional phosphorus treatment methods poorly remove organic phosphorus.

1.7 Objectives and Hypothesis

The long-term goal of this study is to develop innovative wastewater treatment technologies for more effectively, efficiently, and economically removing phosphorus present in municipal wastewater. The primary objective of this dissertation is to evaluate the treatment performance of ferrate(VI) for removal of different phosphorus species at different wastewater treatment stages and elucidate the underlying reaction mechanisms. The central hypothesis is that ferrate(VI) is capable of effectively removing inorganic phosphate through precipitation and/or adsorption due to the formation of iron (hdyr)oxides and alleviating organic phosphorus via chemical oxidation and precipitation/adsorption mechanisms. To achieve the overall objective, the following four specific objectives were pursued:

Objective I: To investigate ferrate(VI) for chemically enhanced primary treatment for removal of phosphorus during the primary treatment and elucidate the fundamental reaction mechanisms.

Objective II: To evaluate the performance of ferrate(VI) removal of inorganic phosphorus in secondary effluent during the advanced wastewater treatment and explore the reaction pathways.

Objective III: To evaluate the performance of ferrate(VI) removal of organic phosphorus in secondary effluent during the advanced wastewater treatment and explore the reaction pathways.

Objective IV: To comprehensively assess the implications of the innovative ferrate(VI) technologies for water resources management, environment, and society.

Table 1-1 Anthropogenic Phosphorus Sources (Withers & Jarvie, 2008)

Source type/source	Delivery		Chemical composition	TP	
	Discharge	Rainfall dependency		Range (mg/L)	Mean (mg/L)
Wastewater					
STW/industry	Continuous	Low	Concentrated	0.2-17.1	6.63
CSOs	Episodic	High	Concentrated	n.d	n.d
Septic tanks	Episodic to semi-continuous	Low	Vatiable	1.0-22.0	10.2
Impervious surfaces					
Road/track runoff	Episodic	High	Variable (High SS)	0.11-16	2.39
Farmyards	Episodic to semi-continuous	Low-High	Vatiable	0.02-247	30.8
Pervious Surfaces					
Field surface runoff	Episodic	High	Variable (High SS)	0.17-6.8	1.29
Field tile drains	Episodic to semi-continuous	Low-High	Vatiable	0.02-6.2	0.76
Field sub-surface runoff	Episodic	High	Dilute	n.d	n.d

STW, Sewage Treatment Works; CSOs, Combined Sewer Overflows; SS, Suspended Solid; n.d, no data.

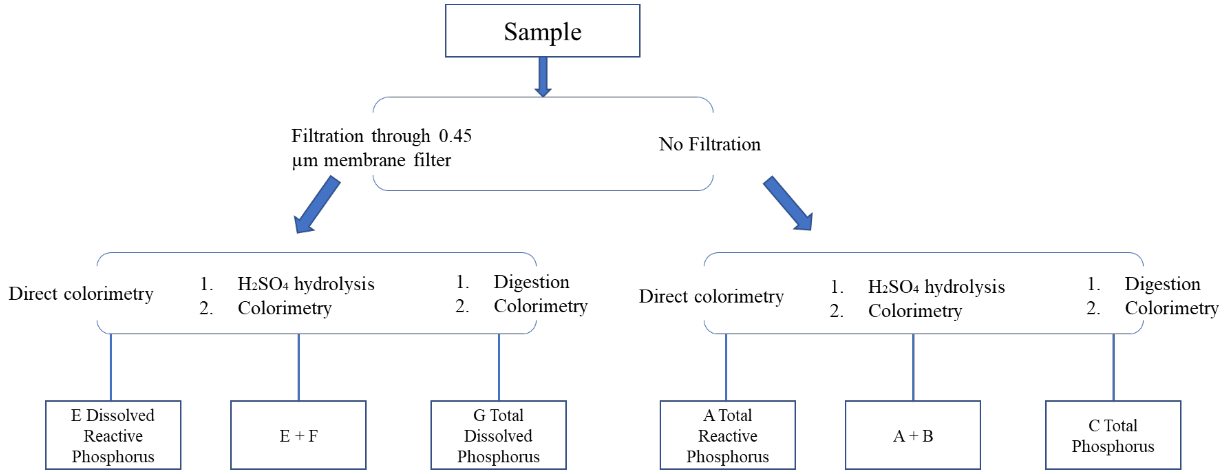


Figure 1-1 Phosphorus Speciation Method (APHA 2006)

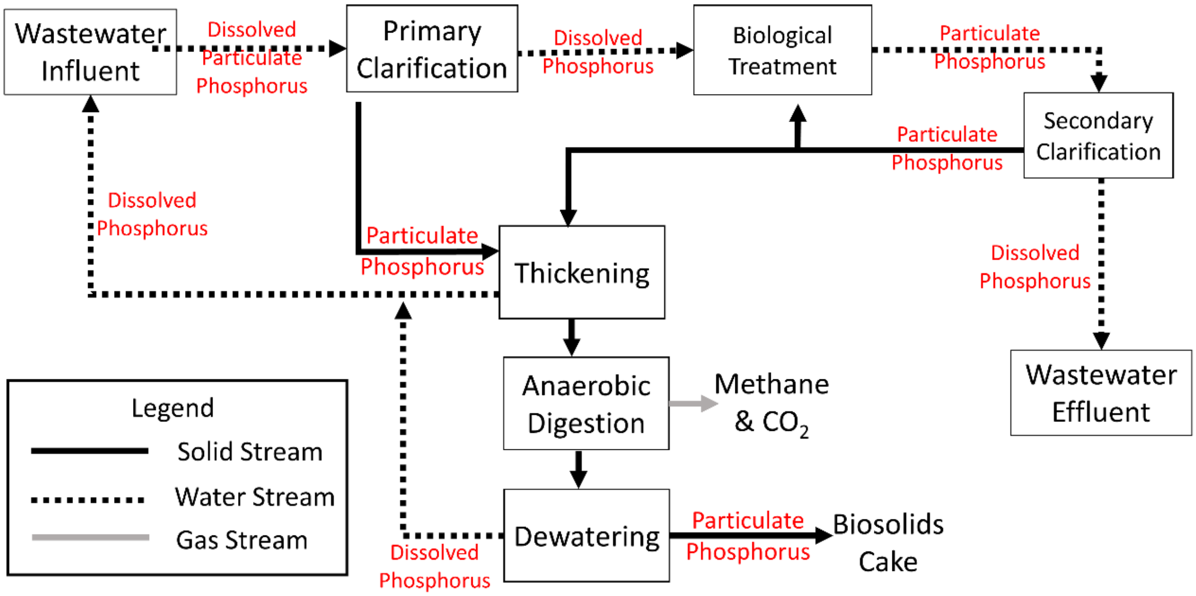


Figure 1-2 Phosphorus Removal in Municipal Wastewater Treatment Plants (Dueñas et al., 2003)

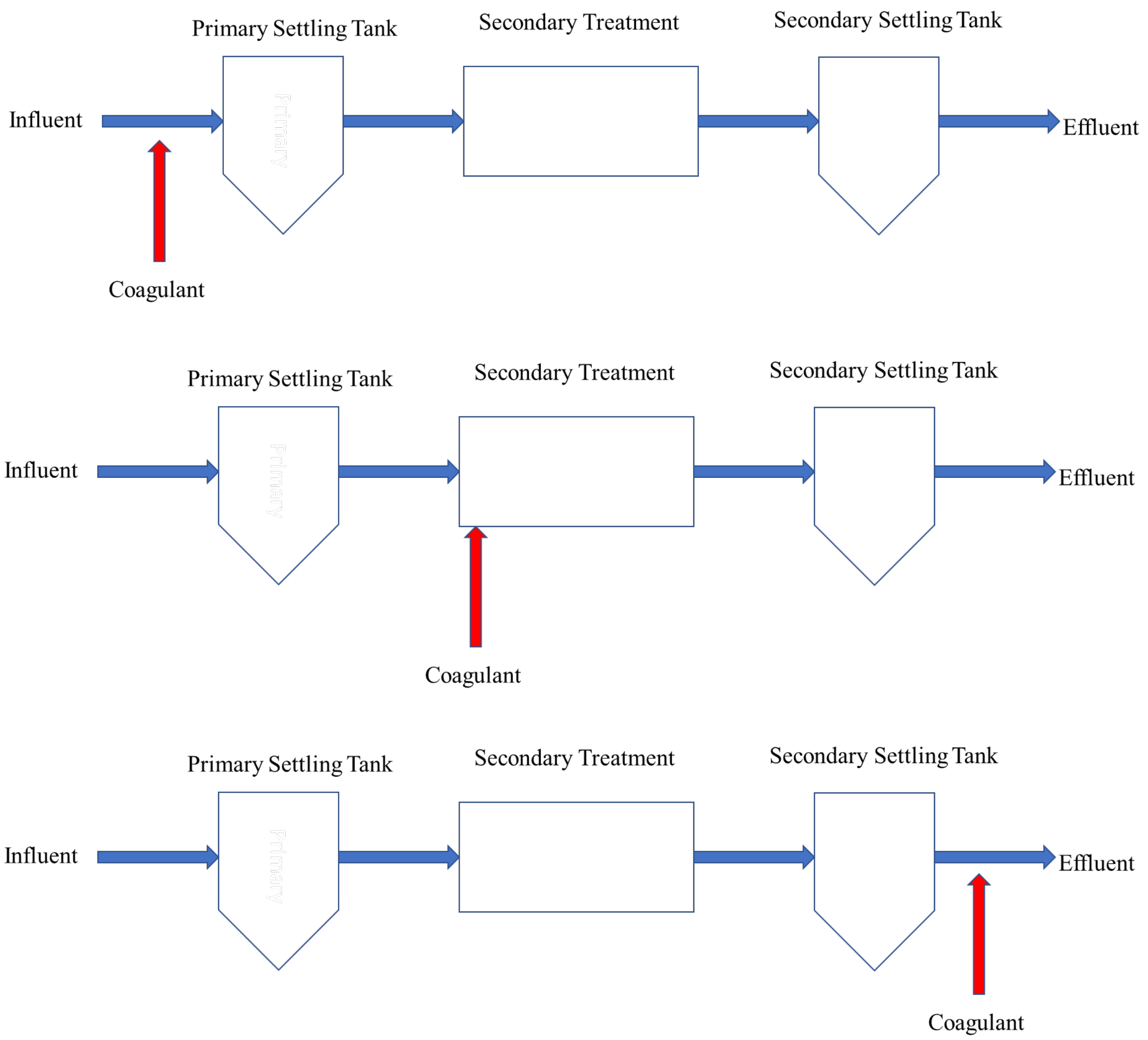


Figure 1-3 Three Strategies to Perform Phosphorus Precipitation

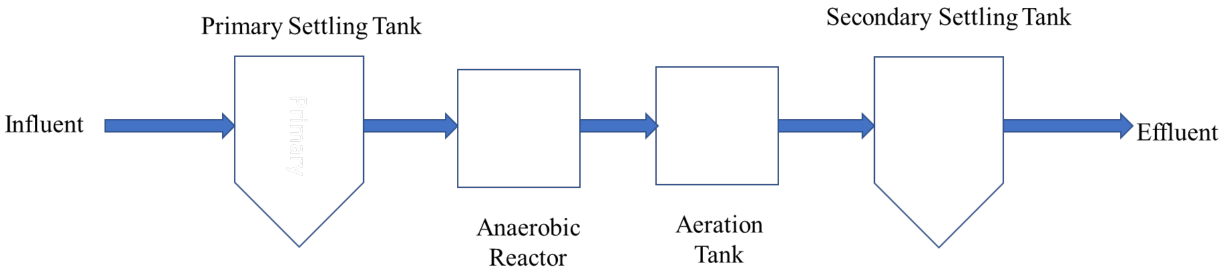


Figure 1-4 Enhanced Biological Phosphorus Removal Process

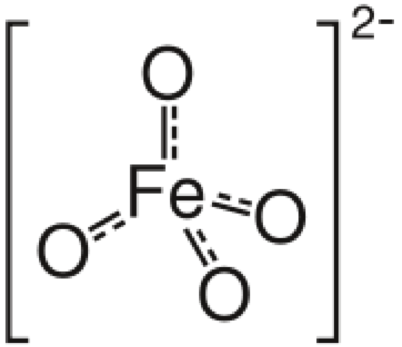


Figure 1-5 Chemical structure of ferrate(VI) (FeO_4^{2-})

1.8 References

Acevedo, B., Oehmen, A., Carvalho, G., Seco, A., Borrás, L., & Barat, R. (2012). Metabolic shift of polyphosphate-accumulating organisms with different levels of polyphosphate storage. *Water Research, 46*(6), 1889-1900. doi:https://doi.org/10.1016/j.watres.2012.01.003

Alsheyab, M., Jiang, J. Q., & Stanford, C. (2010). Engineering Aspects of Electrochemical Generation of Ferrate: A Step Towards Its Full Scale Application for Water and Wastewater Treatment. *Water Air and Soil Pollution, 210*(1-4), 203-210. doi:10.1007/s11270-009-0242-2

Anquandah, G. A. K., Sharma, V. K., Knight, D. A., Batchu, S. R., & Gardinali, P. R. (2011). Oxidation of Trimethoprim by Ferrate(VI): Kinetics, Products, and Antibacterial Activity. *Environmental Science & Technology, 45*(24), 10575-10581. doi:10.1021/es202237g

Anquandah, G. A. K., Sharma, V. K., Panditi, V. R., Gardinali, P. R., Kim, H., & Oturan, M. A. (2013). Ferrate(VI) oxidation of propranolol: Kinetics and products. *Chemosphere, 91*(1), 105-109. doi:10.1016/j.chemosphere.2012.12.001

Ashley, K., Cordell, D., & Mavinic, D. (2011). A brief history of phosphorus: From the philosopher's stone to nutrient recovery and reuse. *Chemosphere, 84*(6), 737-746. doi:https://doi.org/10.1016/j.chemosphere.2011.03.001

Awual, M. R., & Jyo, A. (2011). Assessing of phosphorus removal by polymeric anion exchangers. *Desalination, 281*, 111-117. doi:https://doi.org/10.1016/j.desal.2011.07.047

Bandala, E. R., Miranda, J., Beltran, M., Vaca, M., Lopez, R., & Torres, L. G. (2009). Wastewater disinfection and organic matter removal using ferrate(VI) oxidation. *Journal of Water and Health, 7*(3), 507-513. doi:10.2166/wh.2009.003

Banu, R. J., Do, K. U., & Yeom, I. T. (2008). Phosphorus removal in low alkalinity secondary effluent using alum. *International Journal of Environmental Science & Technology, 5*(1), 93-98. doi:10.1007/BF03326001

Batarseh, E. S., Reinhart, D. R., & Daly, L. (2007). Liquid sodium ferrate and Fenton's reagent for treatment of mature landfill leachate. *Journal of Environmental Engineering, 133*(11), 1042-1050.

Baumgardner, G. L., Masson, J., Hardee, J. R., Menapace, A. M., & Williams, A. G. (2005). Polyphosphoric acid modified asphalt: proposed mechanisms. *Journal of the Association of Asphalt Paving Technologists, 74*, 283-305.

Brix, H., Arias, C. A., & del Bubba, M. (2001). Media selection for sustainable phosphorus removal in subsurface flow constructed wetlands. *Water Science and Technology, 44*(11-12), 47-54. doi:10.2166/wst.2001.0808

Brunner, P. H. (2010). Substance Flow Analysis as a Decision Support Tool for Phosphorus Management. *Journal of Industrial Ecology, 14*(6), 870-873. doi:10.1111/j.1530-9290.2010.00300.x

Bucher, M. (2007). Functional biology of plant phosphate uptake at root and mycorrhiza interfaces. *New Phytologist, 173*(1), 11-26. doi:10.1111/j.1469-8137.2006.01935.x

Bunce, J. T., Ndam, E., Ofiteru, I. D., Moore, A., & Graham, D. W. (2018). A Review of Phosphorus Removal Technologies and Their Applicability to Small-Scale Domestic

Wastewater Treatment Systems. *Frontiers in Environmental Science, 6*(8). doi:10.3389/fenvs.2018.00008

Carr, J. D., Kelter, P. B., Tabatabai, A., Splichal, D., Erickson, J., & McLaughlin, C. (1985). *Properties of ferrate(VI) in aqueous solution: an alternate oxidant in wastewater treatment.* Paper presented at the Proceedings of Conference on Water Chlorination Chem. Environment Impact Health Eff.(Jolley, RL ed.). Lewis Publisher, Chelsea, Michigan.

Cashman, S., Gaglione, A., Mosley, J., Weiss, L., Hawkins, T., Ashbolt, N., . . . Arden, S. (2014). Environmental and Cost Life Cycle Assessment of Disinfection Options for Municipal Wastewater Treatment. *Office of Research and Development. National Homeland Security Research Center*.

Cekerevac, M. I., Nikolic-Bujanovic, L. N., Mirkovic, M. B., & Popovic, N. H. (2010). APPLICATION OF ELECTROCHEMICALLY SYNTHESIZED FERRATE(VI) IN THE PURIFICATION OF WASTEWATER FROM COAL SEPARATION PLANT. *Hemijska Industrija, 64*(5), 423-430. doi:10.2298/hemind100325047c

Chen, J., Cai, Y., Clark, M., & Yu, Y. (2013). Equilibrium and Kinetic Studies of Phosphate Removal from Solution onto a Hydrothermally Modified Oyster Shell Material. *PLOS ONE, 8*(4), e60243. doi:10.1371/journal.pone.0060243

Ciabatti, I., Tognotti, F., & Lombardi, L. (2010). Treatment and reuse of dyeing effluents by potassium ferrate. *Desalination, 250*(1), 222-228. doi:10.1016/j.desal.2009.06.019

Comber, S., Gardner, M., Georges, K., Blackwood, D., & Gilmour, D. (2013). Domestic source of phosphorus to sewage treatment works. *Environmental Technology, 34*(10), 1349-1358. doi:10.1080/09593330.2012.747003

Cornel, P., & Schaum, C. (2009). Phosphorus recovery from wastewater: needs, technologies and costs. *Water Science and Technology, 59*(6), 1069-1076. doi:10.2166/wst.2009.045

Costarramone, N., Kneip, A., & Castetbon, A. (2004). Ferrate(VI) oxidation of cyanide in water. *Environmental Technology, 25*(8), 945-955. doi:10.1080/09593330.2004.9619388

Cui, J., Zheng, L., & Deng, Y. (2018). Emergency Water Treatment with Ferrate(VI) in Response to Natural Disasters. *Environmental Science: Water Research & Technology, 4*, 359-368

Cyr, J. E., & Bielski, B. H. (1991). The reduction of ferrate(VI) to ferrate (V) by ascorbate. *Free Radical Biology and Medicine, 11*(2), 157-160.

de Godos, I., González, C., Becares, E., García-Encina, P. A., & Muñoz, R. (2009). Simultaneous nutrients and carbon removal during pretreated swine slurry degradation in a tubular biofilm photobioreactor. *Applied Microbiology and Biotechnology, 82*(1), 187-194. doi:10.1007/s00253-008-1825-3

de Luca, S. J., Pegorer, M. G., & de Luca, M. A. (2010). Aqueous oxidation of microcystin-LR by ferrate(VI). *Engenharia Sanitaria E Ambiental, 15*(1), 5-10. doi:10.1590/s1413-41522010000100001

Deng, Y., Jung, C., Liang, Y., Goodey, N., & Waite, T. D. (2018). Ferrate(VI) decomposition in water in the absence and presence of natural organic matter (NOM). *Chemical Engineering Journal, 334*, 2335-2342.

Deng, Y., Wu, M., Zhang, H., Zheng, L., Acosta, Y., & Hsu, T.-T. D. (2017). Addressing harmful algal blooms (HABs) impacts with ferrate(VI): Simultaneous removal of algal cells and toxins for drinking water treatment. *Chemosphere, 186*, 757-761.

Diaz, R. J., & Rosenberg, R. (2008). Spreading Dead Zones and Consequences for Marine Ecosystems. *Science, 321*(5891), 926. doi:10.1126/science.1156401

Drizo, A., Forget, C., Chapuis, R. P., & Comeau, Y. (2006). Phosphorus removal by electric arc furnace steel slag and serpentinite. *Water Research, 40*(8), 1547-1554. doi:https://doi.org/10.1016/j.watres.2006.02.001

Dueñas, J. F., Alonso, J. R., Rey, À. F., & Ferrer, A. S. (2003). Characterisation of phosphorous forms in wastewater treatment plants. *Journal of Hazardous Materials, 97*(1), 193-205. doi:https://doi.org/10.1016/S0304-3894(02)00260-1

Edwards, M., & McNeill, L. S. (2002). Effect of phosphate inhibitors on lead release from pipes. *Journal-American Water Works Association, 94*(1), 79-90.

Eng, Y. Y., Sharma, V. K., & Ray, A. K. (2006). Ferrate(VI): Green chemistry oxidant for degradation of cationic surfactant. *Chemosphere, 63*(10), 1785-1790. doi:10.1016/j.chemosphere.2005.08.062

Fan, M. H., Brown, R. C., & Huang, C. P. (2002). Preliminary studies of the oxidation of arsenic(III) by potassium ferrate. *International Journal of Environment and Pollution, 18*(1), 91-96. doi:10.1504/ijep.2002.000698

Feng, M., Baum, J. C., Nesnas, N., Lee, Y., Huang, C.-H., & Sharma, V. K. (2019). Oxidation of sulfonamide antibiotics of six-membered heterocyclic moiety by ferrate(VI): Kinetics and mechanistic insight into SO2 extrusion. *Environmental Science & Technology, 53*(5), 2695-2704.

Filippelli, G. M. (2002). The Global Phosphorus Cycle. *Reviews in Mineralogy and Geochemistry, 48*(1), 391-425. doi:10.2138/rmg.2002.48.10

Filippelli, G. M. (2008). The Global Phosphorus Cycle: Past, Present, and Future. *Elements, 4*(2), 89-95. doi:10.2113/GSELEMENTS.4.2.89

Froelich, P. N. (1988). Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism1. *Limnology and Oceanography, 33*(4part2), 649-668. doi:10.4319/lo.1988.33.4part2.0649

Gandhi, R., Ray, A. K., Sharma, V. K., & Nakhla, G. (2014). Treatment of Combined Sewer Overflows Using Ferrate(VI). *Water Environment Research, 86*(11), 2202-2211. doi:10.2175/106143014x14062131178475

Gilbert, M., Waite, T. D., & Hare, C. (1976). An Investigation of the Applicability of Ferrate Ion for Disinfection. *Journal of American Water Works Association, 68*(9), 495-497.

Gilbert, P. A., & De Jong, A. L. (1978). The Use of Phosphate in Detergents and Possible Replacements for Phosphate. *Ciba Foundation Symposium 57 - Phosphorus in the Enviroment: Its Chemistry and Biochemistry*. doi:doi:10.1002/9780470720387.ch14

10.1002/9780470720387.ch14

Gillis, N., Walters, L., Yeargain, M., & Reinhart, D. (2005). Effectiveness of Ferrate (FeO4-2) as a ballast water disinfectant. *Integrative and Comparative Biology, 45*(6), 1137-1137. Retrieved from <Go to ISI>://WOS:000235337601206

Gombos, E., Barkacs, K., Felfoldi, T., Vertes, C., Mako, M., Palko, G., & Zaray, G. (2013). Removal of organic matters in wastewater treatment by ferrate(VI)-technology. *Microchemical Journal, 107*, 115-120. doi:10.1016/j.microc.2012.05.019

Gombos, E., Barkács, K., Felföldi, T., Vértes, C., Makó, M., Palkó, G., & Záray, G. (2013). Removal of organic matters in wastewater treatment by ferrate(VI)-technology. *Microchemical Journal, 107*, 115-120. doi:https://doi.org/10.1016/j.microc.2012.05.019

Goodwill, J. E., Jiang, Y., Reckhow, D. A., Gikonyo, J., & Tobiason, J. E. (2015). Characterization of Particles from Ferrate Preoxidation. *Environmental Science & Technology, 49*(8), 4955-4962.

Goodwill, J. E., Jiang, Y., Reckhow, D. A., & Tobiason, J. E. (2016). Laboratory Assessment of Ferrate for Drinking Water Treatment. *Journal: American Water Works Association, 108*(3).

Graham, N. J. D., Khoi, T. T., & Jiang, J. Q. (2010). Oxidation and coagulation of humic substances by potassium ferrate. *Water Science and Technology, 62*(4), 929-936. doi:10.2166/wst.2010.369

Gravesen, C. (2013). Fe(VI) as a new chemical agent for treatment of landfill leachate. *Master Thesis, Montclair State University*.

Gustafsson, J. P., Renman, A., Renman, G., & Poll, K. (2008). Phosphate removal by mineral-based sorbents used in filters for small-scale wastewater treatment. *Water Research, 42*(1), 189-197. doi:https://doi.org/10.1016/j.watres.2007.06.058

Herrmann, I., Nordqvist, K., Hedström, A., & Viklander, M. (2014). Effect of temperature on the performance of laboratory-scale phosphorus-removing filter beds in on-site wastewater treatment. *Chemosphere, 117*, 360-366. doi:https://doi.org/10.1016/j.chemosphere.2014.07.069

Hoppe, M. L., Schlemper, E. O., & Murmann, R. K. (1982). Structure of dipotassium ferrate(VI). *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry, 38*(8), 2237-2239.

House, W. A., Jickells, T. D., Edwards, A. C., Praska, K. E., & Denison, F. H. (1998). Reactions of phosphorus with sediments in fresh and marine waters. *Soil Use and Management, 14*(s4), 139-146. doi:10.1111/j.1475-2743.1998.tb00632.x

Howarth, R. W., & Marino, R. (2006). Nitrogen as the limiting nutrient for eutrophication in coastal marine ecosystems: Evolving views over three decades. *Limnology and Oceanography, 51*(1part2), 364-376. doi:10.4319/lo.2006.51.1_part_2.0364

Hozalski, R. M., Esbri-Amador, E., & Chen, C. F. (2005). Comparison of stannous chloride and phosphate for lead corrosion control. *Journal-American Water Works Association, 97*(3), 89-103.

Hu, L. H., Page, M. A., Sigstam, T., Kohn, T., Marinas, B. J., & Strathmann, T. J. (2012). Inactivation of Bacteriophage MS2 with Potassium Ferrate(VI). *Environmental Science & Technology, 46*(21), 12079-12087. doi:10.1021/es3031962

Huang, H. M., Song, Q. W., & Xu, C. L. (2011). The Mechanism and Influence Factors of Struvite Precipitation for the Removal of Ammonium Nitrogen. *Advanced Materials Research, 189-193*, 2613-2620. doi:10.4028/www.scientific.net/AMR.189-193.2613

Huang, X., & Deng, Y. (2014). *Bromate Formation during Ferrate (Fe(VI)) Oxidation of Bromide-containing Water*. Paper presented at the 2014 Annual Conference (ACE) - American Water Works Association, Boston, MA.

Huang, X., Deng, Y., Liu, S., Song, Y., Li, N., & Zhou, J. (2016). Formation of bromate during ferrate(VI) oxidation of bromide in water. *Chemosphere, 155*, 528-533.

Jessen, A., Randall, A., Reinhart, D., & Daly, L. (2008). Effectiveness and Kinetics of Ferrate as a Disinfectant for Ballast Water. *Water Environment Research, 80*(6), 561-569. doi:10.2175/193864708x267423

Jetoo, S., Grover, I. V., & Krantzberg, G. (2015). The Toledo Drinking Water Advisory: Suggested Application of the Water Safety Planning Approach. *Sustainability, 7*(8). doi:10.3390/su7089787

Jiang, J. Q. (2007). Research progress in the use of ferrate(VI) for the environmental remediation. *Journal of Hazardous Materials, 146*(3), 617-623. doi:10.1016/j.jhazmat.2007.04.075

Jiang, J. Q., & Lloyd, B. (2002). Progress in the development and use of ferrate(VI) salt as an oxidant and coagulant for water and wastewater treatment. *Water Research, 36*(6), 1397-1408. doi:10.1016/s0043-1354(01)00358-x

Jiang, J. Q., Lloyd, B., & Grigore, L. (2001). Preparation and evaluation of potassium ferrate as an oxidant and coagulant for potable water treatment. *Environmental Engineering Science, 18*(5), 323-328. doi:10.1089/10928750152726041

Jiang, J. Q., Panagouopoulos, A., Bauer, M., & Pearce, P. (2006). The application of potassium ferrate for sewage treatment. *Journal of Environmental Management, 79*(2), 215-220. doi:10.1016/j.jenvman.2005.06.009

Jiang, J. Q., Stanford, C., & Alsheyab, M. (2009). The online generation and application of ferrate(VI) for sewage treatment-A pilot scale trial. *Separation and Purification Technology, 68*(2), 227-231. doi:10.1016/j.seppur.2009.05.007

Jiang, J. Q., Stanford, C., & Mollazeinal, A. (2012). THE APPLICATION OF FERRATE FOR SEWAGE TREATMENT: PILOT- TO FULL-SCALE TRIALS. *Global Nest Journal, 14*(1), 93-99. Retrieved from <Go to ISI>://WOS:000304741400014

Jiang, J. Q., & Wang, S. (2003). Enhanced coagulation with potassium ferrate(VI) for removing humic substances. *Environmental Engineering Science, 20*(6), 627-633. doi:10.1089/109287503770736140

Jiang, J. Q., Wang, S., & Panagoulopoulos, A. (2006). The exploration of potassium ferrate(VI) as a disinfectant/coagulant in water and wastewater treatment. *Chemosphere, 63*(2), 212-219. doi:10.1016/j.chemosphere.2005.08.020

Jiang, J. Q., Wang, S., & Panagoulopoulos, A. (2007). The role of potassium ferrate(VI) in the inactivation of Escherichia coli and in the reduction of COD for water remediation. *Desalination, 210*(1-3), 266-273. doi:10.1016/j.desal.2006.05.051

Jiang, Y., Goodwill, J. E., Tobiason, J. E., & Reckhow, D. A. (2016). Bromide oxidation by ferrate(VI): The formation of active bromine and bromate. *Water Research, 96*, 188-197.

Jiménez, B. (2005). Treatment technology and standards for agricultural wastewater reuse: a case study in Mexico. *Irrigation and Drainage, 54*(S1), S23-S33. doi:10.1002/ird.183

Kadlec, R. H., Flaig, E., & Gale, P. M. (1999). Phosphorus Retention in Streams and Wetlands: A Review AU - Reddy, K. R. *Critical Reviews in Environmental Science and Technology, 29*(1), 83-146. doi:10.1080/10643389991259182

Kern, J., & Idler, C. (1999). Treatment of domestic and agricultural wastewater by reed bed systems. *Ecological Engineering, 12*(1), 13-25. doi:https://doi.org/10.1016/S0925-8574(98)00051-2

Kralchevska, R. P., Prucek, R., Kolařík, J., Tuček, J., Machala, L., Filip, J., . . . Zbořil, R. (2016). Remarkable efficiency of phosphate removal: Ferrate(VI)-induced in situ sorption on core-shell nanoparticles. *Water Research, 103*, 83-91.

Kralchevska, R. P., Prucek, R., Kolařík, J., Tuček, J., Machala, L., Filip, J., . . . Zbořil, R. (2016). Remarkable efficiency of phosphate removal: Ferrate(VI)-induced in situ sorption on core-shell nanoparticles. *Water Research, 103*, 83-91. doi:https://doi.org/10.1016/j.watres.2016.07.021

Kuroda, A., Takiguchi, N., Gotanda, T., Nomura, K., Kato, J., Ikeda, T., & Ohtake, H. (2002). A simple method to release polyphosphate from activated sludge for phosphorus reuse and recycling. *Biotechnology and Bioengineering, 78*(3), 333-338. doi:10.1002/bit.10205

Kwon, J. H., Kim, I. K., Park, K. Y., Kim, Y. D., & Cho, Y. H. (2014). Removal of phosphorus and coliforms from secondary effluent using ferrate(VI). *Ksce Journal of Civil Engineering, 18*(1), 81-85. doi:10.1007/s12205-013-0024-7

Lajtha, K., & Harrison, A. F. (1995). *Strategies of phosphorus acquisition and conservation by plant species and communities. In Phosphorus in the Global Environment. SCOPE 54, chap. 8 (ed. H. Tiessen).* Wiley, New York.

Larsdotter, K. (2006). Wastewater treatment with microalgae-a literature review. *Vatten, 62*(1), 31.

Le Corre, K. S., Valsami-Jones, E., Hobbs, P., & Parsons, S. A. (2009). Phosphorus Recovery from Wastewater by Struvite Crystallization: A Review. *Critical Reviews in Environmental Science and Technology, 39*(6), 433-477. doi:10.1080/10643380701640573

Le Moal, M., Gascuel-Odoux, C., Ménesguen, A., Souchon, Y., Étrillard, C., Levain, A., . . . Pinay, G. (2019). Eutrophication: A new wine in an old bottle? *Science of The Total Environment, 651*, 1-11. doi:https://doi.org/10.1016/j.scitotenv.2018.09.139

Lee, C., Lee, Y., Schmidt, C., Yoon, J., & Von Gunten, U. (2008). Oxidation of suspected N-nitrosodimethylamine (NDMA) precursors by ferrate(VI): Kinetics and effect on the NDMA formation potential of natural waters. *Water Research, 42*(1-2), 433-441. doi:10.1016/j.watres.2007.07.035

Lee, Y., Cho, M., Kim, J. Y., & Yoon, J. (2004). Chemistry of ferrate (Fe (VI)) in aqueous solution and its applications as a green chemical. *JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY-SEOUL-, 10*(1), 161-171.

Lee, Y., Kissner, R., & von Gunten, U. (2014). Reaction of ferrate(VI) with ABTS and self-decay of ferrate(VI): Kinetics and mechanisms. *Environmental Science & Technology, 48*(9), 5154-5162.

Lee, Y., Um, I. H., & Yoon, J. (2003). Arsenic(III) oxidation by iron(VI) (ferrate) and subsequent removal of arsenic(V) by iron(III) coagulation. *Environmental Science & Technology, 37*(24), 5750-5756. doi:10.1021/es034203+

Lee, Y., & von Gunten, U. (2010). Oxidative transformation of micropollutants during municipal wastewater treatment: Comparison of kinetic aspects of selective (chlorine, chlorine dioxide, ferrate(VI), and ozone) and non-selective oxidants (hydroxyl radical). *Water Research, 44*(2), 555-566. doi:10.1016/j.watres.2009.11.045

Lee, Y., Yoon, J., & Von Gunten, U. (2005). Kinetics of the oxidation of phenols and phenolic endocrine disruptors during water treatment with ferrate (Fe(VI)). *Environmental Science & Technology, 39*(22), 8978-8984. doi:10.1021/es051198w

Lee, Y., Zimmermann, S. G., Kieu, A. T., & von Gunten, U. (2009). Ferrate (Fe(VI)) Application for Municipal Wastewater Treatment: A Novel Process for Simultaneous

Micropollutant Oxidation and Phosphate Removal. *Environmental Science & Technology, 43*(10), 3831-3838. doi:10.1021/es803588k

Li, C., Li, X. Z., & Graham, N. (2005). A study of the preparation and reactivity of potassium ferrate. *Chemosphere, 61*(4), 537-543. doi:10.1016/j.chemosphere.2005.02.027

Lim, M., & Kim, M. J. (2009). Removal of Natural Organic Matter from River Water Using Potassium Ferrate(VI). *Water Air and Soil Pollution, 200*(1-4), 181-189. doi:10.1007/s11270-008-9902-x

Lim, M., & Kim, M. J. (2010). Effectiveness of Potassium Ferrate (K2FeO4) for Simultaneous Removal of Heavy Metals and Natural Organic Matters from River Water. *Water Air and Soil Pollution, 211*(1-4), 313-322. doi:10.1007/s11270-009-0302-7

Litke, D. W. (1999). *Review of Phosphorus Control Measures in the United States and Their Effects on Water Quality* (Water-Resources Investigations Report 99–4007). Retrieved from

Luo, C., Feng, M., Sharma, V. K., & Huang, C.-H. (2019). Oxidation of pharmaceuticals by ferrate(VI) in hydrolyzed urine: Effects of major inorganic constituents. *Environmental Science & Technology, 53*(9), 5272-5281.

Lv, D., Zheng, L., Zhang, H., & Deng, Y. (2018). Coagulation of colloidal particles with ferrate(VI). *Environmental Science: Water Research & Technology.*

Ma, J., & Liu, W. (2002a). Effectiveness and mechanism of potassium ferrate(VI) preoxidation for algae removal by coagulation. *Water Research, 36*(4), 871-878. doi:10.1016/s0043-1354(01)00282-2

Ma, J., & Liu, W. (2002b). Effectiveness of ferrate(VI) preoxidation in enhancing the coagulation of surface waters. *Water Research, 36*(20), 4959-4962. Retrieved from <Go to ISI>://WOS:000179091500003

Manoli, K., Maffettone, R., Sharma, V. K., Santoro, D., Ray, A. K., Passalacqua, K. D., . . . Sarathy, S. (2019). Inactivation of Murine Norovirus and Fecal Coliforms by Ferrate(VI) in Secondary Effluent Wastewater. *Environmental Science & Technology*.

Martin, B. D., Parsons, S. A., & Jefferson, B. (2009). Removal and recovery of phosphate from municipal wastewaters using a polymeric anion exchanger bound with hydrated ferric oxide nanoparticles. *Water Science and Technology, 60*(10), 2637-2645. doi:10.2166/wst.2009.686

Martin, E. N. M. C. T. T. (1998). *Human anatomy & physiology*: Menlo Park, Calif. ; Harlow : Benjamin Cummings, ©1998.

Martínez, M. E., Sánchez, S., Jiménez, J. M., El Yousfi, F., & Muñoz, L. (2000). Nitrogen and phosphorus removal from urban wastewater by the microalga Scenedesmus obliquus. *Bioresource Technology, 73*(3), 263-272. doi:https://doi.org/10.1016/S0960-8524(99)00121-2

McDowell, R. W. (2003). Sediment Phosphorus Chemistry and Microbial Biomass along a Lowland New Zealand Stream. *Aquatic Geochemistry, 9*(1), 19-40. doi:10.1023/B:AQUA.0000005620.15485.6d

Montalvo, S. J., Guerrero, L. E., Milán, Z., & Borja, R. (2011). Nitrogen and phosphorus removal using a novel integrated system of natural zeolite and lime. *Journal of Environmental Science and Health, Part A, 46*(12), 1385-1391. doi:10.1080/10934529.2011.606709

Neal, C., Jarvie, H. P., Williams, R. J., Neal, M., Wickham, H., & Hill, L. (2002). Phosphorus□calcium carbonate saturation relationships in a lowland chalk river impacted by sewage inputs and phosphorus remediation: an assessment of phosphorus self-cleansing mechanisms in natural waters. *Science of The Total Environment, 282-283*, 295-310. doi:https://doi.org/10.1016/S0048-9697(01)00920-2

Nguyen, T. T., Ngo, H. H., & Guo, W. (2013). Pilot scale study on a new membrane bioreactor hybrid system in municipal wastewater treatment. *Bioresource Technology, 141*, 8-12. doi:https://doi.org/10.1016/j.biortech.2013.03.125

Owen, R. (1953). Removal of Phosphorus from Sewage Plant Effluent with Lime. *Sewage and Industrial Wastes, 25*(5), 548-556. Retrieved from http://www.jstor.org/stable/25032172

Parsons, S. A., & Smith, J. A. (2008). Phosphorus Removal and Recovery from Municipal Wastewaters. *Elements, 4*(2), 109-112. doi:10.2113/GSELEMENTS.4.2.109

Pastor, L., Marti, N., Bouzas, A., & Seco, A. (2008). Sewage sludge management for phosphorus recovery as struvite in EBPR wastewater treatment plants. *Bioresource Technology, 99*(11), 4817-4824. doi:https://doi.org/10.1016/j.biortech.2007.09.054

Paytan, A., & McLaughlin, K. (2007). The Oceanic Phosphorus Cycle. *Chemical Reviews, 107*(2), 563-576. doi:10.1021/cr0503613

Powell, N., Shilton, A., Chisti, Y., & Pratt, S. (2009). Towards a luxury uptake process via microalgae – Defining the polyphosphate dynamics. *Water Research, 43*(17), 4207-4213. doi:https://doi.org/10.1016/j.watres.2009.06.011

Prucek, R., Tucek, J., Kolarik, J., Filip, J., Marusak, Z., Sharma, V. K., & Zboril, R. (2013). Ferrate(VI)-Induced Arsenite and Arsenate Removal by In Situ Structural Incorporation into Magnetic Iron(III) Oxide Nanoparticles. *Environmental Science & Technology, 47*(7), 3283-3292. doi:10.1021/es3042719

Prucek, R., Tucek, J., Kolařík, J., Hušková, I., Filip, J., Varma, R. S., . . . Zboril, R. (2015). Ferrate(VI)-Prompted Removal of Metals in Aqueous Media: Mechanistic Delineation of Enhanced Efficiency via Metal Entrenchment in Magnetic Oxides. *Environmental Science & Technology, 49*(4), 2319-2327.

Qin, B., Zhu, G., Gao, G., Zhang, Y., Li, W., Paerl, H. W., & Carmichael, W. W. (2010). A Drinking Water Crisis in Lake Taihu, China: Linkage to Climatic Variability and Lake Management. *Environmental Management, 45*(1), 105-112. doi:10.1007/s00267-009-9393-6

Qin, C., Liu, H., Liu, L., Smith, S., Sedlak, D. L., & Gu, A. Z. (2015). Bioavailability and characterization of dissolved organic nitrogen and dissolved organic phosphorus in wastewater effluents. *Science of The Total Environment, 511*, 47-53. doi:https://doi.org/10.1016/j.scitotenv.2014.11.005

Qu, J. H., Liu, H. J., Liu, S. X., & Lei, P. J. (2003). Reduction of fulvic acid in drinking water by ferrate. *Journal of Environmental Engineering-Asce, 129*(1), 17-24. doi:10.1061/(asce)0733-9372(2003)129:1(17)

Ramasahayam, S. K., Guzman, L., Gunawan, G., & Viswanathan, T. (2014). A Comprehensive Review of Phosphorus Removal Technologies and Processes. *Journal of Macromolecular Science, Part A, 51*(6), 538-545. doi:10.1080/10601325.2014.906271

Rao, N. N., Gómez-García, M. R., & Kornberg, A. (2009). Inorganic Polyphosphate: Essential for Growth and Survival. *Annual Review of Biochemistry, 78*(1), 605-647. doi:10.1146/annurev.biochem.77.083007.093039

Renman, A., & Renman, G. (2010). Long-term phosphate removal by the calcium-silicate material Polonite in wastewater filtration systems. *Chemosphere, 79*(6), 659-664. doi:https://doi.org/10.1016/j.chemosphere.2010.02.035

Rush, J. D., Zhao, Z., & Bielski, B. H. (1996). Reaction of ferrate(VI)/ferrate (V) with hydrogen peroxide and superoxide anion--a stopped-flow and premix pulse radiolysis study. *Free radical research, 24*(3), 187-198.

Ruttenberg, K. C. (2003). 8.13 - The Global Phosphorus Cycle. In H. D. Holland & K. K. Turekian (Eds.), *Treatise on Geochemistry* (pp. 585-643). Oxford: Pergamon.

Schindler, D. W., Hecky, R. E., Findlay, D. L., Stainton, M. P., Parker, B. R., Paterson, M. J., . . . Kasian, S. E. M. (2008). Eutrophication of lakes cannot be controlled by reducing nitrogen input: Results of a 37-year whole-ecosystem experiment. *Proceedings of the National Academy of Sciences, 105*(32), 11254. doi:10.1073/pnas.0805108105

Schink, T., & Waite, T. D. (1980). Inactivation of f2 virus with ferrate(VI). *Water Research, 14*(12), 1705-1717.

Schreyer, J., & Ockerman, L. (1951). Stability of Ferrate(VI) ion in aqueous solution. *Analytical Chemistry, 23*(9), 1312-1314.

Seo, Y. I., Hong, K. H., Kim, S. H., Chang, D., Lee, K. H., & Kim, Y. D. (2013). Phosphorus removal from wastewater by ionic exchange using a surface-modified Al alloy filter. *Journal of Industrial and Engineering Chemistry, 19*(3), 744-747. doi:https://doi.org/10.1016/j.jiec.2012.11.008

Seviour, R. J., Mino, T., & Onuki, M. (2003). The microbiology of biological phosphorus removal in activated sludge systems. *FEMS Microbiology Reviews, 27*(1), 99-127. doi:10.1016/S0168-6445(03)00021-4

Sharma, V. K. (2010). Oxidation of Inorganic Compounds by Ferrate(VI) and Ferrate(V): One-Electron and Two-Electron Transfer Steps. *Environmental Science & Technology, 44*(13), 5148-5152. doi:10.1021/es1005187

Sharma, V. K., Chen, L., & Zboril, R. (2015). Review on high valent FeVI (ferrate): a sustainable green oxidant in organic chemistry and transformation of pharmaceuticals. *ACS Sustainable Chemistry & Engineering, 4*(1), 18-34.

Sharma, V. K., Yngard, R. A., Cabelli, D. E., & Baum, J. C. (2008). Ferrate(VI) and ferrate(V) oxidation of cyanide, thiocyanate, and copper(I) cyanide. *Radiation Physics and Chemistry, 77*(6), 761-767. doi:10.1016/j.r,idphyscliezii.2007.11.004

Sharma, V. K., Zboril, R., & Varma, R. S. (2015). Ferrates: Greener oxidants with multimodal action in water treatment technologies. *Accounts of chemical research, 48*(2), 182-191.

Shi, J., Podola, B., & Melkonian, M. (2007). Removal of nitrogen and phosphorus from wastewater using microalgae immobilized on twin layers: an experimental study. *Journal of Applied Phycology, 19*(5), 417-423. doi:10.1007/s10811-006-9148-1

Shilton, A. N., Elmetri, I., Drizo, A., Pratt, S., Haverkamp, R. G., & Bilby, S. C. (2006). Phosphorus removal by an ‘active’ slag filter–a decade of full scale experience. *Water Research, 40*(1), 113-118. doi:https://doi.org/10.1016/j.watres.2005.11.002

Shimamura, K., Homma, Y., Watanabe, A., & Tanaka, T. (2003). Research on MAP Recovery Conditions using a Fluidized-bed Crystallized Phosphorous Removal System. *Journal of Water and Environment Technology, 1*(1), 73-78. doi:10.2965/jwet.2003.73

Shimamura, K., Ishikawa, H., Mizuoka, A., & Hirasawa, I. (2008). Development of a process for the recovery of phosphorus resource from digested sludge by crystallization technology. *Water Science and Technology, 57*(3), 451-456. doi:10.2166/wst.2008.065

Smil, V. (2000). PHOSPHORUS IN THE ENVIRONMENT: Natural Flows and Human Interferences. *Annual Review of Energy and the Environment, 25*(1), 53-88. doi:10.1146/annurev.energy.25.1.53

Smolders, G. J. F., van der Meij, J., van Loosdrecht, M. C. M., & Heijnen, J. J. (1994). Model of the anaerobic metabolism of the biological phosphorus removal process: Stoichiometry and pH influence. *Biotechnology and Bioengineering, 43*(6), 461-470. doi:10.1002/bit.260430605

Song, Y., Deng, Y., & Jung, C. (2016). Mitigation and degradation of natural organic matters (NOMs) during ferrate(VI) application for drinking water treatment. *Chemosphere, 146*, 145-153.

Stahl, G. E. (1715). *Opusculum chymico-physico-medicum*.

Thompson, G., Ockerman, L., & Schreyer, J. (1951). Preparation and purification of potassium ferrate. VI. *Journal of the American Chemical Society, 73*(3), 1379-1381.

Tien, K., & Graham, N. (2011). *Evaluating the Coagulation Performance of Ferrate: Coagulation of Kaolin Suspension.* Paper presented at the Minamata International SympoSIum ON Environment And Energy Technology, Kumamoto, Japan.

Vitousek, P. M., Chadwick, O. A., Crews, T. E., Fownes, J. H., Hendricks, D. M., & Herbert, D. (1997). Soil and Ecosystem Development Across the Hawaiian Islands. *GSA Today, 7*(9), 1-8.

Vymazal, J. (2010). Constructed Wetlands for Wastewater Treatment. *Water, 2*(3). doi:10.3390/w2030530

Wagner, W., Gump, J., & Hart, E. (1952). Factors affecting stability of aqueous potassium ferrate(VI) solutions. *Analytical Chemistry, 24*(9), 1497-1498.

Waite, T. D. (1979). Feasibility of Wastewater Treatment with Ferrate. *Journal of the Environmental Engineering Division, 105*(6), 1023-1034.

Waite, T. D. (2012). On-Site Production of Ferrate for Water and Wastewater Purification. *American Laboratory, 44*(10), 26-28. Retrieved from <Go to ISI>://WOS:000312286700006

Waite, T. D., & Gilbert, M. (1978). Oxidative destruction of phenol and other organic water residuals by iron(VI) ferrate. *Journal Name: J. - Water Pollut. Control Fed.; (United States); Journal Volume: 50:3*, Medium: X; Size: Pages: 543-551.

Walker, T. W., & Syers, J. K. (1976). The fate of phosphorus during pedogenesis. *Geoderma, 15*(1), 1-19. doi:https://doi.org/10.1016/0016-7061(76)90066-5

Wilfert, P., Kumar, P. S., Korving, L., Witkamp, G. J., & van Loosdrecht, M. C. M. (2015). The Relevance of Phosphorus and Iron Chemistry to the Recovery of Phosphorus from Wastewater: A Review. *Environmental Science & Technology, 49*(16), 9400-9414. doi:10.1021/acs.est.5b00150

Williams, D. H., & Riley, J. (1969). Chemistry of the Oxidant, Ferrate, Its Interaction With Specific Organics Found in Waste Water.

Withers, P. J. A., & Jarvie, H. P. (2008). Delivery and cycling of phosphorus in rivers: A review. *Science of The Total Environment, 400*(1), 379-395. doi:https://doi.org/10.1016/j.scitotenv.2008.08.002

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.

Yang, B., Ying, G. G., Zhao, J. L., Liu, S., Zhou, L. J., & Chen, F. (2012). Removal of selected endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products

(PPCPs) during ferrate(VI) treatment of secondary wastewater effluents. *Water Research, 46*(7), 2194-2204. doi:10.1016/j.watres.2012.01.047

Yang, T., Wang, L., Liu, Y., Jiang, J., Huang, Z., Pang, S.-Y., . . . Ma, J. (2018). Removal of organoarsenic with ferrate and ferrate resultant nanoparticles: oxidation and adsorption. *Environmental Science & Technology, 52*(22), 13325-13335.

Yeoman, S., Stephenson, T., Lester, J. N., & Perry, R. (1988). The removal of phosphorus during wastewater treatment: A review. *Environmental Pollution, 49*(3), 183-233. doi:https://doi.org/10.1016/0269-7491(88)90209-6

Yngard, R. A., Sharma, V. K., Filip, J., & Zboril, R. (2008). Ferrate(VI) oxidation of weak-acid dissociable cyanides. *Environmental Science & Technology, 42*(8), 3005-3010. doi:10.1021/es0720816

Yu, W., Yang, Y., & Graham, N. (2016). Evaluation of ferrate as a coagulant aid/oxidant pretreatment for mitigating submerged ultrafiltration membrane fouling in drinking water treatment. *Chemical Engineering Journal, 298*, 234-242.

Yuan, Z., Jiang, S., Sheng, H., Liu, X., Hua, H., Liu, X., & Zhang, Y. (2018). Human Perturbation of the Global Phosphorus Cycle: Changes and Consequences. *Environmental Science & Technology, 52*(5), 2438-2450. doi:10.1021/acs.est.7b03910

Zeng, S., Yuan, X., Shi, X., & Qiu, Y. (2010). Effect of inoculum/substrate ratio on methane yield and orthophosphate release from anaerobic digestion of Microcystis spp. *Journal of Hazardous Materials, 178*(1), 89-93. doi:https://doi.org/10.1016/j.jhazmat.2010.01.047

Zhang, H., Zheng, L., Li, Z., Pi, K., & Deng, Y. (2020). One-step Ferrate(VI) treatment as a core process for alternative drinking water treatment. *Chemosphere, 242*, 125134.

Zhang, X. H., Lei, H. Y., Chen, K., Liu, Z., Wu, H., & Liang, H. Y. (2012). Effect of potassium ferrate (K2FeO4) on sludge dewaterability under different pH conditionse. *Chemical Engineering Journal, 210*, 467-474. doi:10.1016/j.cej.2012.09.013

Zheng, L., & Deng, Y. (2016). Settleability and characteristics of ferrate(VI)-induced particles in advanced wastewater treatment. *Water Research, 93*, 172-178.

Zhou, A., Tang, H., & Wang, D. (2005). Phosphorus adsorption on natural sediments: Modeling and effects of pH and sediment composition. *Water Research, 39*(7), 1245-1254. doi:https://doi.org/10.1016/j.watres.2005.01.026

Chapter 2 Chemically Enhanced Primary Treatment (CEPT) With Ferrate(VI)

2.1 Introduction and Objectives

2.1.1 Chemically enhanced primary treatment

Primary treatment is in the initial stage at a municipal wastewater treatment facility, typically comprising pretreatment (e.g. bar racks, grit chambers, and equalization basins) and gravity-driven primary sedimentation basins (Deng, 2015; Tchobanoglous et al., 2014). Pretreatment aims to remove large objects (e.g. rags and logs), inert materials (e.g. sands), dampen the variations of inflow rates for the protection of downstream treatment equipment. The ensuing primary sedimentation basins primarily target at the removal of settable or floatable pollutants, rather than soluble ones (Tchobanoglous et al., 2014). The primary settling is characterized by Type II sedimentation, in which the size and settling velocity of particles are increased due to the occurrence of particle flocculation (Davis & Cornwell, 2008). After a typical primary treatment, approximately 60% total suspended solids (TSS) and 35% 5-day biochemical oxygen demand (BOD_5) are reduced. However, soluble pollutants are poorly removed (Davis & Cornwell, 2008).

In order to improve the treatment efficiency of the primary treatment, the conventional primary treatment can be enhanced through the introduction of specific chemical compounds (e.g. metal salts and organic polymers) (Chagnon & Harleman, 2005). The so-called chemically enhanced primary treatment (CEPT) was early practiced in England in 1870 and in the United States from the 1890s to early 1900s prior to the development of biological wastewater treatment (Parker, Barnard, Daigger, Tekippe, & Wahlberg, 2001). Thereafter, the CEPT technology has evolved for addressing different issues such as the reduction of wastewater phosphorus for controlling the occurrence of eutrophication in receiving water bodies (Parker et al., 2001) and coupling with biological treatment for maximizing the downstream nitrification (Horstkotte, Niles, Parker, & Caldwell, 1974). Different chemical agents have been employed with the development of CEPT. Lime was early used for CEPT to result in a high primary effluent pH. Acid production and CO_2 production in ensuing biological treatment (e.g. an activated sludge process) sufficiently reduce pH to a neutral pH condition (Parker et al., 2001). Interest was later transitioned to coagulants widely used for coagulation in drinking water treatment, such as ferric chloride, alum, and polymers (Johnson et al., 2008; Neupane, Riffat, Murthy, Peric, & Wilson, 2008; Ødegaard, 1998; Poon & Chu, 1999; Wang, Li, Keller, & Xu, 2009). Recently, new chemicals have been tested, such as recovered coagulant sludge produced from drinking water treatment (Xu, Yan, Wang, & Li, 2009; Xu, Yan, Wang, & Wang, 2009).

Chemical addition promotes the aggregation of suspended particulates in wastewater via the processes of coagulation and flocculation, thereby increasing the settling velocity of these particles and enhancing the removals of TSS, particulate organic matter, and nutrient (Olive, 2002). Olive (2002) reported that CEPT could improve the TSS removal from 60% to 85%, BOD_5 removal from 35% to 57%, and P reduction from 20% to 80%, in comparison with the conventional primary treatment. On the other hand, after the conventional primary treatment is replaced with CEPT, the size of primary settling tanks can be significantly reduced for a constant wastewater inflow rate, or the surface overflow rate can be increased when the reactor size is maintained (Neupane et al., 2008).

Besides the improvement of the performance at a traditional biological secondary treatment facility, CEPT is a possible alternative for secondary treatment, which can effectively remove dissolved and colloidal BOD_5 and further reduce TSS, for many regions in developing countries, in which only primary treatment facilities are available, but costly secondary treatment cannot be afforded (Harleman & Murcott, 2001b; Olive, 2002). Although CEPT removes less BOD_5 than biological secondary treatment, it may provide a comparable TSS removal and a much better phosphate reduction. The P removal is ascribed to addition of the metallic (e.g. iron) salts capable of precipitating phosphate in wastewater. Furthermore, CEPT may produce less sludge required for further disposal than biological secondary treatment, and can be easily implemented over existing infrastructure and operated at a much lower cost than secondary treatment (Harleman & Murcott, 2001a, 2001b).

Iron-based metallic coagulants have been successfully employed for CEPT. One such example is ferric chloride. It is of great interest whether other iron-base coagulants can also serve for CEPT to provide an equivalent or better treatment efficiency, such as ferrate(VI). Ferrate(VI), FeO_4^{2-}, is the oxyanion containing iron in its +6 oxidation state (Virender K Sharma, Zboril, & Varma, 2015). Once dosed to water, ferrate(VI) tends to gain electrons, thereby being a strong chemical oxidant with a reduction potential of up to 2.20 V (Yunho Lee, Min Cho, Jee Yeon Kim, & Jeyong Yoon, 2004). Fe(VI) can be reduced to Fe(III) via self-decomposition and reactions with reductants in water (Deng, Jung, Liang, Goodey, & Waite, 2018; Y. Song, Y. Deng, & C. Jung, 2016). The *in-situ* formation of Fe(III) can subsequently initiate coagulation for the removal of colloids in water (Graham, Khoi, & Jiang, 2010; Lv, Zheng, Zhang, & Deng, 2018; Tien & Graham, 2011) and eliminate phosphate in wastewater through precipitation and/or adsorption (Radina P Kralchevska et al., 2016; Yunho Lee, Zimmermann, Kieu, & von Gunten, 2009). The multiple treatment mechanisms of ferrate(VI) enables it to be potentially advantageous over ferric chloride, because it is capable of removing multiple pollutants of concern in raw municipal wastewater. For example, coagulation can remove suspended particles, chemical oxidation can inactivate pathogens and degrade dissolved organic matter as well as emerging micropollutants, and precipitation/adsorption can abate phosphorus in wastewater.

2.1.2 Objectives

The objective of this chapter was to evaluate the treatment performance of and elucidate mechanisms of ferrate(VI) for chemically enhanced primary treatment of municipal wastewater for removal of phosphorus and other wastewater pollutants including TSS, BOD_5, and COD. To achieve the objective, the following three questions would be investigated:

1) What is the performance of ferrate(VI) enabled CEPT for removal of various phosphorus species in municipal wastewater?
2) What are the reaction mechanisms behind the phosphorus removal during the ferrate(VI) enabled CEPT?
3) How does ferrate(VI) enabled CEPT alter other quality indicators in municipal wastewater?

2.2 Material and Method

2.2.1 Wastewater samples and reagents

All the reagents used were at least analytical grade, except as noted. Potassium ferrate (K_2FeO_4) (> 96%) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Untreated municipal wastewater was collected from a local sewage treatment plant (Verona, NJ, USA). The treatment facility received 9,464 m^3/day wastewater from residual areas. The raw wastewater was sampled after the grit chambers and before a primary sedimentation tank. Once collected, the sample was delivered to the Montclair State University's Water Treatment and reuse Laboratory and then stored at 4°C in a refrigerator until use. Quality parameters of the untreated municipal wastewater are as follows: pH 7.43, total suspended solids (TSS) = 108.9 mg/L, 5-day biochemical oxygen demand (BOD_5) = 209 mg/L, total chemical oxygen demand (TCOD) = 293 mg/L, dissolved COD (DCOD) = 85 mg/L, particulate COD (PCOD) = 208 mg/L, total phosphorus (TP) = 12.920 mg/L, particulate phosphorus (PP) = 9.021 mg/L, dissolved phosphorus (DP) = 3.899 mg/L, dissolved inorganic phosphorus (DIP) = 3.541 mg/L, dissolved organic phosphorus (DOP) = 358 μg/L, total nitrogen (TN) = 39.47 mg/L, dissolved nitrogen (DN) = 31.05 mg/L . Concentrated ferrate(VI) (200 mg/L as Fe) stock solution was prepared by dissolving appropriate weights of K_2FeO_4 in ultrapure water produced from a Milli-Q water purification system (Milli-Q Direct 8). Fe(VI) in the ferrate(VI) stock solution was confirmed with the ABTS method (Y. Lee, Yoon, & von Gunten, 2005). The stock solution was prepared immediately before the treatment tests.

2.2.2 CEPT Experiments

CEPT tests were carried out in 1 L glass beakers containing 800 mL well-mixed untreated municipal wastewater on a four-paddle programmable jar tester (Phipps and Bird - 7790-950) at room temperature (20 ± 1 °C) and under atmospheric pressure. Initial solution pH was adjusted to 6.0 or 7.5 with 1 N NaOH or 0.5 M H_2SO_4 solution. The treatment was initiated once an appropriate volume of ferrate(VI) stock solution was dosed. For the CEPT with Fe(VI), the iron dose was 1.0, 3.0, 5.0, 7.0, or 9.0 mg/L. Within the first minute, the solution was rapidly mixed at a velocity gradient of 241 s^{-1} to completely disperse the added iron. During the following 59 minutes, the solution was gently stirred at a velocity gradient of 21 s^{-1} for the growth of flocs. During the treatment, pH was not controlled or additionally buffered, but monitored. Following the slow mixing, gravity-driven sedimentation proceeded for 2 hours to simulate the primary sedimentation at a municipal wastewater treatment facility. Subsequently, supernatant samples were collected for analysis. Control tests were carried out with the identical experimental procedure, except that any iron salt was not dosed. Results from the control group indicated the treatment effect of conventional primary treatment.

2.2.3 Sample Analyses

Ferrate(VI) was spectrophotometrically measured using the ABTS method (Y. Lee et al., 2005). Solution pH was measured by a pH meter (Thermo Scientific Orion 5-Star Plus). Unfiltered wastewater samples were used for the measurements of different total organic indicators, total P, and total N. Dissolved organic parameters, P, and N were measured after the wastewater was filtered through 0.45-μm syringe membrane filters (Thermo Scientific, cellulose acetate (CA), 30 mm diameter). COD was measured calorimetrically following digestion (20–1,500 mg/L range, HACH, Loveland, CO, USA). The measurements of TSS and BOD_5 followed the U.S. Environmental Protection Agency (EPA)-approved Standard Methods 160.2 and 5210 B, respectively. Total P was determined with an inductively coupled plasma-mass spectroscopy (ICP-MS Thermo X-Series II, XO 472). Acid hydrolysable P was measured using the HACH TNT reagent set and indicated the concentration of inorganic P in water. The concertation of organic P was the difference between total and inorganic phosphorus. Particle sizes, size distributions, and zeta potentials (ZPs) were determined using a Nano Zetasizer (Malvern, ZEN 3690) without any sample dilution. All the experiments were run in triplicates. All the analytical results reported represent the mean of the three replicate samples. Error bars in the figures indicate one standard deviation of these replicate measurements.

2.3 Results

2.3.1 Phosphorus

Initial pH 6.0. Concentrations of different P species in the supernatant after ferrate(VI) CEPT at an initial pH of 6.0 are shown in **Figure 2-1 (a)-(c)**. As seen in **Figure 2-1(a)**, TP narrowly varied between 9.50 and 10.10 mg/L PO_4^{3-} at 0.0-9.0 mg/L Fe(VI), indicating that TP was not significantly removed under the studied conditions. Specifically, we measured TIP and

TOP, separately. As Fe(VI) dose was increased from 0.0 to 9.0 mg/L, TIP almost remained at 8.60-8.65 mg/L PO_4^{3-}, while TOP slightly decreased from 1.45 to 1.20 mg/L PO_4^{3-}.

In order to further understand the variation between dissolved and particulate P, we measured IP and OP in dissolved and particulate states, as illustrated in **Figure 2-1(b)** and **(c)**, respectively. As shown, for the untreated wastewater, DP and PP were 8.35 and 1.75 mg/L PO_4^{3-}, respectively, indicating that the vast majority of P was in a soluble state (83% of TP). Of note, with the increasing ferrate(VI) dose, DIP almost linearly decreased from 7.93 to 1.21 mg/L PO_4^{3-} (residual DIP = 7.93 – 0.80 Fe(VI), $R^2 = 0.98$), while PIP linearly increased from 0.73 to 7.39 mg/L PO_4^{3-} (residual PIP = 0.73 + 0.79 Fe(VI), $R^2 = 0.98$). Of note, the two model equations representing the decrease of DIP and the increase of PIP, respectively, share a very similar slope approximately at 0.80, thereby leading to a very stable residual TIP at the Fe(VI) dose of 0.0-9.0 mg/L as shown in **Figure 2-1(a)**.

In contrast, we noticed that very limited removal was achieved for organic P at different ferrate(VI) doses, regardless of the dissolved or particulate state. When Fe(VI) dose was increased from 0.0 to 9.0 mg/L, DOP and POP slightly declined from 0.43 to 0.32 mg/L PO_4^{3-} and from 1.03 to 0.89 mg/L PO_4^{3-}, respectively, corresponding to the removal of 26% DOP and 14% POP. Although organic P was slightly removed with the increase of ferrate(VI) dose, the total P in the wastewater was stable after CEPT, irrespective of ferrate(VI) dose, because OP accounted for a very small fraction of TP.

Initial pH 7.5. Concentrations of different P species in the supernatant after CEPT with ferrate(VI) at an initial pH of 7.5 are shown in **Figure 2-2 (a)-(c)**. It should be noted that the patterns of different P species with ferrate(VI) dose was very different between the initial pH 6.0 and 7.5. At the initial pH of 7.5, TP consistently decreased from 10.85 to 5.75 mg/L PO_4^{3-} with the increasing Fe(VI) dose from 0.0 to 9.0 mg/L, corresponding to a removal of 47%. The reduction of TP was ascribed to the decrease of both inorganic and organic P. Specifically, as Fe(VI) dose was increased from 0.0 to 9.0 mg/L, TIP consistently declined from 9.35 to 5.20 mg/L PO_4^{3-} with a 52% reduction. In contrast, TOP dropped from 1.50 to 0.55 mg/L PO_4^{3-} with the increase of Fe(VI) dose from 0.0 to 5.0 mg/L, corresponding to a 63% removal; however, a further increase of the Fe(VI) dose to 9.0 mg/L did not translate into any significant improvement in the TOP removal.

IP and OP in dissolved and particulate states were measured in order to explore the variation of these different P species at different ferrate(VI) doses, as illustrated in **Figure 2-2(a)** and **(b)**. For the untreated wastewater, DP and PP were 9.50 and 1.35 mg/L PO_4^{3-}, respectively, again indicating that the vast majority of P was dissolved (88% of TP). As Fe(VI) dose was increased from 0.0 to 9.0 mg/L, DIP went down from 8.55 to 0.79 mg/L PO_4^{3-}. On the other hand, residual PIP increased from 0.80 to 3.95 mg/L PO_4^{3-} with the increasing Fe(VI) dose from 0.0 to 3.0 mg/L. As Fe(VI) dose was further increased to 9.0 mg/L, PIP was marginally raised to 4.41 mg/L PO_4^{3-}. Dramatically different from the DIP and PIP removal behaviors at the initial pH of 6.0, the removal of DIP and PIP did not exhibit any linear pattern with ferrate(VI) dose.

Organic P, irrespective of a dissolved or particulate state, was appreciably removed at the initial pH of 7.5 as the Fe(VI) dose was increased, different from the little OP removal at the initial pH of 6.0. As shown in **Figure 2-2 (b)**, DOP was decreased from 0.95 to 0.40 mg/L PO_4^{3-} with the increase of Fe(VI) dose from 0.0 to 3.0 mg/L, corresponding to a 58% removal. However, the further increase of Fe(VI) dose to 9.0 mg/L did not evidently increase or decrease residual DOP. As seen in **Figure 2-2 (c)**, Fe(VI) from 0.0 to 9.0 mg/L constantly reduced the residual POP from 0.55 to 0.06 mg/L mg/L PO_4^{3-} with an 89% removal.

Overall, CEPT with ferrate(VI) better removed wastewater P at a weakly basic condition than in a weakly acidic solution. Our results show that the overall removal of TP (up to 47%) was achieved at the initial pH of 7.5, advantageous over the TP removal (≤3%) at the initial pH of 6.0, in this study. To gain a comprehensive picture of variation of wastewater quality after CEPT with ferrate(VI), we measured other water quality indicators, including final solution pH, particulate matter, and organic matter.

2.3.2 Final solution pH

Final solution pH after CEPT at different ferrate(VI) doses is shown in **Figure 2-3**. Initial wastewater pH was adjusted to 6.0 or 7.5. It should be noted that the final solution pH in the control (without ferrate(VI) addition) was slightly increased to 6.44 and 7.68 at the initial pH of 6.0 and 7.5, respectively. As ferrate(VI) dose was increased to 9.0 mg/L, final solution pH was slightly increased to 6.67 and 8.08 at the initial pH of 6.0 and 7.5, respectively. The extent of pH increase was marginal under the studied conditions (the pH increase < 0.6 over 0.0-9.0 mg/L Fe (VI)). The pH increase with the increasing ferrate(VI) dose is ascribed to the release of hydroxyl ions (OH^-) during ferrate(VI) self-decomposition in water. The overall reaction of ferrate(VI) self-decay in water is as follows (Goff & Murmann, 1971):

$$2FeO_4^{2-} + 5H_2O = 2Fe(OH)_3 + 4OH^- + 1.5O_2\uparrow \qquad (2\text{-}1)$$

2.3.3 Particulate matter (PM)

Photos of PM present in untreated and treated wastewater are shown in **Figure 2-4**. Cloudiness was evidently observed in the untreated wastewater (**Figure 2-4(a)**), suggesting the presence of much suspended PM originally present in the untreated wastewater. For either initial pH, the supernatant became less cloudy with the increasing ferrate(VI) dose from 0.0 to 9.0

mg/L. At any specific ferrate(VI) dose, the supernatant seemed to be more transparent in the wastewater treated at the initial pH of 7.5 (**Figure 2-4(c)**) than 6.0 ((**Figure 2-4(b)**)).

In order to quantitatively determine the PM removal during the CEPT, two water quality indicators, i.e. turbidity and TSS, were measured before and after ferrate(VI) treatment at different conditions, as shown in **Figure 2-5** and **2-6**, respectively. As seen in **Figure 2-5**, residual turbidity in the supernatant after CEPT decreased from 32.5 NTU at 0.0 mg/L Fe(VI) to 22.3 NTU and 11.2 NTU at 9.0 mg/L Fe(VI) at pH of 6.0 and 7.5. respectively. At any specific ferrate(VI) dose, the greater residual turbidity was observed in the sample treated at the initial pH of 6.0 than 7.5.

Residual TSS after CEPT at different ferrate(VI) doses is illustrated in **Figure 2-6**. For the initial pH of 6.0, residual TSS consistently increased from 37.29 mg/L at 0.0 mg/L Fe(VI) to 59.67 mg/L at 9.0 mg/L. In contrast, at the initial pH 7.5, TSS increased from 43.75 to 53.50 mg/L as the Fe(VI) dose increased from 0.0 to 1.0 mg/L, and then gradually declined to 20.63 mg/L as Fe(VI) dose was further increased to 9.0 mg/L. The different observations in the patterns of residual turbidity and TSS with ferrate(VI) doses implied occurrence of complex chemical and/or physical changes in the system, which will be discussed later.

2.3.4 Organic Matter

Residual total, dissolved, and particulate COD after CEPT are shown in **Figure 2-7 (a)**, **(b)**, and **(c)**, respectively. At the initial pH of 6.0, TCOD was marginally removed over 0.0-9.0 mg/L Fe(VI) with the maximum reduction of TCOD from 185.6 to 170.5 mg/L with 8% removal only at 9.0 mg/L Fe(VI) (**Figure 2-7(a)**). The slight TCOD removal was due to the minor removal of PCOD from 110.0 to 96.0 mg/L (**Figure 2-7(c)**), while DCOD remained around 75.6 mg/L, regardless of ferrate(VI) dose.

In contrast, at the initial pH of 7.5, TCOD was consistently decreased from 190.5 to 123.0 mg/L as Fe(VI) dose was increased from 0.0 to 9.0 mg/L with a 35% removal (**Figure 2-7(a)**), exhibiting a much better capability for alleviating organic matter in wastewater. As illustrated in **Figure 2-7(b)**, DCOD narrowly varied between 77.0 and 84.5 mg/L over 0.0-9.0 mg/L Fe(VI), indicating an insignificant removal of dissolved organic matter in wastewater. On the other hand, PCOD was constantly decreased from 106.5 mg/L at 0.0 mg/L Fe(VI) to 43.0 mg/L at 9.0 mg/L Fe(VI), highlighting that the overall COD removal was principally ascribed to the mitigation of particulate organic matter during CEPT with ferrate(VI). To sum up, the removal of organic matter in wastewater using CEPT with ferrate(VI) relies upon solution pH. The reduction of COD, regardless of dissolved or particulate COD, was minor at a weakly acidic condition. However, the removal becomes pronounced as the pH was increased to a weakly alkaline condition primarily due to the removal of particulate organic matter.

Fractions of COD due to dissolved and particulate organic matter in the overall COD with ferrate(VI) doses at the initial pH of 6.0 and 7.5 are shown in **Figure 2-8 (a)** and **(b)**, respectively. For the initial pH of 6.0 (**Figure 2-8(a)**), the fractions of DCOD and PCOD narrowly varied at 39%-44% and 56%-61%, respectively, indicating that: 1) dissolved and particulate organic matter both significantly contributed to COD at all the studied conditions, of which the latter accounted for a slightly greater fraction in the overall COD; and 2) the relative contributions of dissolved and particulate organic matter to the overall COD somewhat stabilized, independent of ferrate(VI) dose. These findings are not surprising, because residual DCOD and PCOD were not evidently altered over the studied ferrate(VI) dose at the initial pH of 6.5, as mentioned above.

Nonetheless, at the initial pH of 7.5, as Fe(VI) dose was increased from 0.0 to 9.0 mg/L, the fraction of DCOD grew up from 44% to 65%, while the PCOD portion declined from 56% to 35% (**Figure 2-8(b)**). The observation is due to the fact that CEPT with ferrate(VI) more readily removed PCOD than DCOD as shown in **Figure 2-7 (b)** and **(c)**.

In order to examine the evolution of wastewater biodegradability after CEPT, BOD_5 of ferrate(VI) treated wastewater was measured, as illustrated in **Figure 2-9 (a)**. As shown, BOD_5 went down from 130.7 mg/L at 0.0 mg/L Fe(VI) to 61.6 and 40.0 mg/L at 9.0 mg/L Fe(VI) at the initial pH of 6.0 and 7.5, respectively. At any specific ferrate(VI) dose over 3.0-9.0 mg/L, residual BOD_5 at the initial pH of 7.5 was lower than that at the initial pH 6.0. Furthermore, we determined BOD_5/COD, a well-recognized indicative of wastewater biodegradability, at different pH and ferrate(VI) doses (**Figure 2-9(b)**). For the initial pH of 6.0 and 7.5, BOD_5/COD was gradually decreased from the initial 0.70 to 0.36 and 0.32, respectively, as Fe(VI) dose was increased to 9.0 mg/L, indicating that CEPT with ferrate(VI) decrease the biodegradability. The reduction of BOD_5/COD with ferrate(VI) dose was primarily because the extent of BOD_5 removal was greater than the degree of COD decrease with the increasing ferrate(VI) dose, as shown in **Figure 2-7(a)** and **2-9(a)**.

2.4 Discussion

This study represented the first investigation on ferrate(VI) application to CEPT in municipal wastewater treatment. Results from the above experiments would be in-depth discussed in two aspects, i.e. the removal of phosphorus in untreated wastewater and the impacts on other wastewater quality indicators. Implications to the wastewater treatment industry would be finally discussed.

2.4.1 P Removal during CEPT with Ferrate(VI)

Ferrate(VI) removal of IP and OP in wastewater. Based on the residual concentrations of different P in the supernatant at different treatment conditions (**Figure 2-1** and **2-2**), we noticed a poor removal of TP at pH 6.0, regardless of ferrate(VI) dose. The ferrate(VI)-based CEPT could not change the DOP and TOP concentrations, indicating the ineffectiveness of ferrate(VI) for removal of organic phosphorus at the primary wastewater treatment conditions. In contrast, as ferrate(VI) dose increased, the residual DP concentration dramatically declined, but the almost equimolar PP increased, so that the net effect in the TP removal was marginal. The plausible reason is that the removed DP was transformed or attached to particulates that had poor settleability and finally remained in the supernatant.

However, when pH increased to 7.5, dissolved or particulate organic phosphorus was somewhat removed with the increasing ferrate(VI) dose, suggesting that ferrate(VI) can alleviate OP at a weakly acidic condition. For inorganic phosphorus, the increase in the ferrate(VI) could translate into the removal of DIP, but slightly increased the PIP. It should be noted that the extent of DIP removal was greater than that of PIP at pH 7.5, so that the overall residual IP was decreased with the ferrate(VI) dose as shown in **Figure 2-2(a)**.

Overall, when the removal of P occurs during ferrate(VI) CEPT, the major mechanism is sedimentation in which particulate matter settles down to the bottom of the reactor by gravity, because P, different from degradable organic matter, cannot be eliminated from the system. Based on the results from the control groups, the particulate IP or OP could not effectively settle down by itself. Therefore, ferrate(VI) removal of P in the untreated wastewater can proceed via the following different pathways. For dissolved IP, Fe(III) produced from ferrate(VI) reduction can precipitate phosphate (the major form of DIP) and/or form iron (hydr)oxides that subsequently adsorb phosphate (the further mechanistic investigation for ferrate(VI) reactions with orthophosphate would be performed in Chapter 3). For particulate IP and OP, the production of Fe(III) and the formation of iron (hydr)oxides increase the size and/or density of particles, so that they can settle down in water. For dissolved OP, the removal may be due to 1) transformation into IP through ferrate(VI) oxidation followed by the removal of IP; and/or 2) direct adsorption to particles that later settle down. Whether ferrate(VI) can significantly oxidize P-containing organic matter in wastewater or not would be further investigated in Chapter 4.

Evolution of particle size after ferrate(VI) treatment. In order to understand the size evolution of particles during and after the CEPT, we used the dynamic light scattering (DLS) technique to examine the change of particle size (**Figure 2-10 (a)-(d)**). The measurements were made at two sampling time: 1) immediately after ferrate(VI) treatment (i.e. before settling); and 2) immediately after settling. The ferrate(VI) dose was fixed at 9.0 mg/L as Fe, while pH was 6.0 or 7.5. As shown, all the particle sizes were almost normally distributed.

At pH 6.0, for the control group, the particle sizes before settling varied at a narrower and lower size range than those before settling, indicating that the original settleable particles in wastewater had smaller sizes, while non-settleable particles were larger but had lower densities. After ferrate(VI) treatment and before settling, we noticed that the particle size range became narrower and lower than that in the control. The peak size was around 292 nm, suggesting that these particles were in a range of colloidal particles. After the following sedimentation, the particle size range was a little higher, but the peak particle size was still below 400 μm, suggesting that these particles remain in a colloidal state. It should be noted that very little particulate P was removed at pH 6.0 and numerous particulate IP particles were suspended in water under the studied conditions (**Figure 2-1**), indicating the poor settleability of these particles. Therefore, at pH 6.0, ferrate(VI) addition produced many small particles associated with phosphate, which remained in water to cause a poor P removal. We also measured zeta potential of these particles before settling. The zeta potential was -15.1 mV, lower than the zeta potential (-14.2 mV) of these original particles. This finding suggests that more negatively charged surface due to the formation of ferrate(VI) resultant particles stabilizes the particles in wastewater and thus inhibits the P removal due to particle sedimentation.

In contrast, at pH 7.5, the particle size before settling was increased with a peak around 531 nm, greater than the peak sizes of these particles formed at pH 6.0, implying that a weakly alkaline pH favors the growth of particles. After settling, the particle sizes slightly declined, but became a litter broader.

Mass distributions of P and Fe after ferrate(VI) treatment. Phosphorus, different from degradable organic matter, cannot be eliminated in the entire system during the CEPT with ferrate(VI). Therefore, the total P mass remains constant over the treatment. However, P can be transformed among the different species. Regardless of inorganic and organic P, the removal of P from wastewater means that P does not exist in the supernatant after primary settling. Namely, the removed P settles down to the bottom of the reactor. After ferrate(VI) treatment and before the sedimentation, TP in the system can be categorized into dissolved P and particulate P, of which the latter can be further split into P in settleable particulates (PP_s) and P in non-settleable P (PP_{ns}), as follows.

$$PP = PP_s + PP_{ns} \qquad (2\text{-}2)$$

Of note, the criterion for determination of “settleable” and “non-settleable” particulate matters are arbitrary. In this study, settleable particles are defined as the ones that settle down after 2-hr sedimentation following the CEPT, while non-settleable particles are ones that remain in the supernatant after the 2-hr sedimentation.

In order to further obtain quantitative information on the P and Fe distributions, we measured the concentrations of P and Fe in dissolved, settleable, and non-settleable states before and after settling, as **Figure 2-11 (a)** and **(b)**, respectively. Generally, the P and Fe distributions share a similar pattern. Dissolved P and Fe accounted for a small fraction. On the other hand, between settleable and non-settleable states, settleable P and Fe concentrations were greater at pH 7.5 than pH 6.0, in agreement with our findings in the size distribution. Moreover, the similar mass distribution patterns of Fe and P highlight that the fate of P is highly related to the dosed iron during the CEPT.

2.4.2 Other Wastewater Quality Indicators

Besides phosphorus, other wastewater quality indicators can also be influenced after ferrate(VI) dose. Although ferrate(VI) self-decomposition can potentially increase water pH due to the release of hydroxyl ions, we did not notice a marked change of water pH over the treatment. The finding suggests that the typical acidity in the municipal wastewater sufficiently maintained the water pH after ferrate(VI) dosing under the studied conditions.

We also noticed that turbidity after settling declined with the increasing ferrate(VI) dose. Lower turbidity was observed at pH 7.5 than at pH 6.0 under identical treatment conditions, which is in consistence with the effects of pH on the particle size and P/Fe mass distributions. Moreover, the other parameter associated with particulate matter is TSS. The decrease of TSS with ferrate(VI) was observed at pH 7.5. But a slight increase of TSS was noticed with the increasing ferrate(VI) at pH 6.0. The disparity of residual turbidity and TSS at pH 6.0 is likely caused by the different measurement methods of the two indicators. Turbidity is defined as the reduction in clarity of water caused by the scattering of visible light by particles (Crittenden, Trussell, Hand, Howe, & Tchobanoglous, 2012), while TSS is the portion of the total solids retained on a filter with a specified pore size, measured after being dried at a specified temperature (105°C) (Tchobanoglous et al., 2014). Turbidity is an optical parameter that mass cannot directly affect, but TSS is computed based on the mass of particles. Integration of iron, with a high atomic weight, into particulate matter in wastewater can potentially increase the particle density and mass. Therefore, it is not surprising to observe the increase in total suspended solids with the increasing ferrate(VI) dose.

Ferrate(VI) removal of organic matter in wastewater is ascribed to settling of particulate organics, rather than the degradation of dissolved organic matter. This can be validated by the evidence that particulate COD declined but dissolved COD was almost constant with the increasing ferrate(VI) dose. It is unexpected that dissolved organic matter was not significantly degraded by ferrate(VI), because ferrate(VI) has a high oxidizing capacity. Generally, once ferrate(VI) is dosed to water, Fe(VI) can be consumed through two pathways. First, ferrate(VI) is subject to self-decomposition. Self-decay rate of ferrate(VI) is dramatically increased with the pH decrease (Virender K Sharma et al., 2015). Second, ferrate(VI) reacts with reducing agents in water, such as dissolved organic compounds. The aforementioned findings suggest that ferrate(VI) might have been substantially lost due to self-decomposition without reactions with dissolved organic compounds. The role of self-decomposition is particularly dominant at pH 6.0, at which 9.0 mg/L Fe(VI) can completely decay within a few seconds.

2.4.3 Implication for the wastewater industry

Ferrate(VI) exhibited the potential for chemically enhanced primary treatment. Under the optimal conditions, it can effectively remove inorganic and organic phosphorus, together with

TSS and COD. The effective removals for different wastewater parameters are principally attributed to the sedimentation mechanisms, because the ferrate(VI) introduction can enhance the settleability of particulate matter. The findings are of significance to the wastewater industry in two aspects.

1) For these developed countries that require a secondary treatment as the minimum wastewater treatment, the adoption of ferrate(VI) in primary treatment can significantly reduce the pollutant loadings to ensuing biological treatment. For example, the highest removals of P, COD, and TSS removals after the ferrate(VI) CEPT in this study were greater than those typically reported in the traditional primary treatment. The alleviated loading can improve the treatment efficiency and/or reduce the required biomass concentrations in the downstream treatment. The latter can bring two benefits. The first is the less dioxygen input. Given that oxygen supply is the major component of the operating costs in a wastewater treatment plant, this is expected to lower the overall wastewater treatment costs. Second, quantify of waste biomass, which needs costly management and disposal, is reduced.
2) Many developing countries only require a primary treatment for wastewater management due to the economical restriction. The poorly treated water, after discharged into the environment, poses a serious threat to human and environmental health. Ferrate(VI) technologies provide an innovative treatment alternative for enhanced wastewater treatment. Compared with traditional primary treatment, ferrate(VI) methods can considerably remove P to minimize the occurrence of algal blooms in receiving water bodies. Moreover, ferrate(VI) is a potent disinfectant. If ferrate(VI) is adopted in primary

treatment, additional chlorination for inactivation of water-borne pathogens is not needed, thus reducing the treatment costs and system complexity.

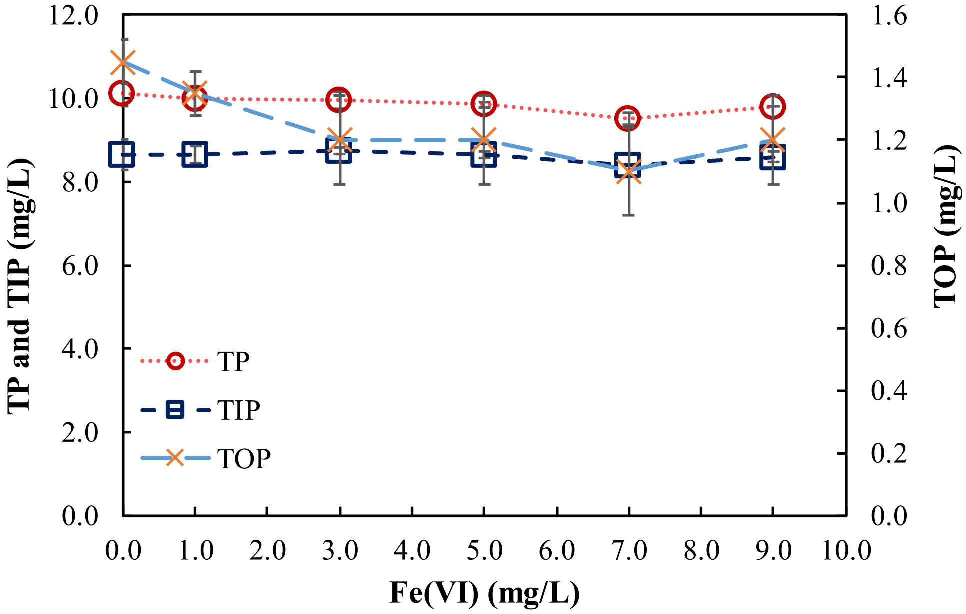
3) Although ferrate(VI) can produce additional particles, settleable or non-settleable, an additional liquid-solid separation unit is not required. The settleable particles can be removed within the primary settling tanks, while the non-settleable particles can be most likely removed in the following biological treatment unit and/or in a secondary settling tank.

2.5 Conclusion

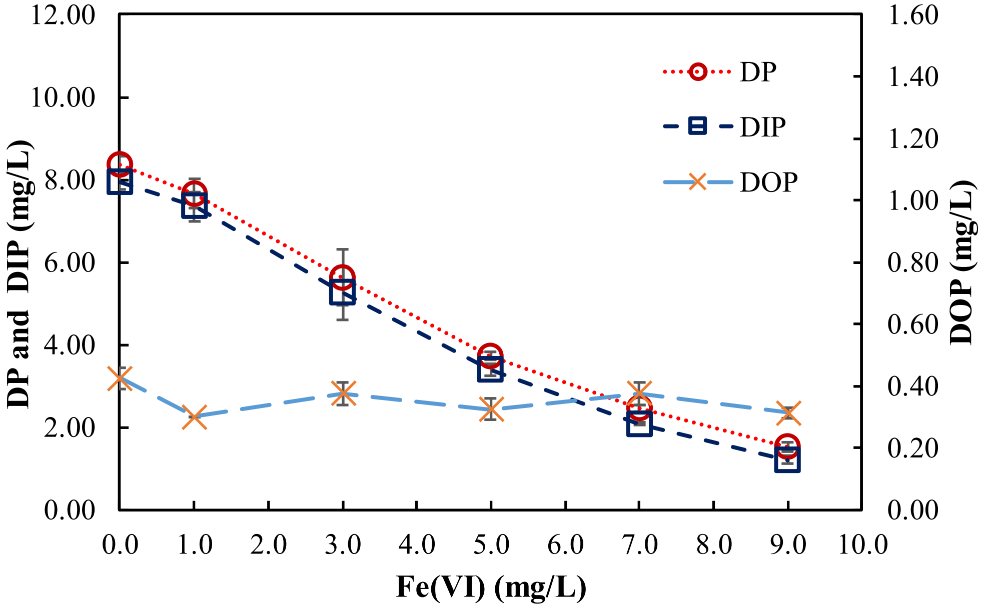
This study aimed to evaluate the feasibility of ferrate(VI) for chemically enhanced primary treatment of municipal wastewater. Particular attention was paid to the removal of phosphorus in wastewater. The treatment mechanisms behind the observations were also explored. Major conclusions can be made as follows.

1) Ferrate(VI) CEPT is an effective treatment method to early remove total phosphorus in wastewater with a removal of total phosphorus as high as by 87%.
2) Removal of phosphorus by ferrate(VI) CEPT is influenced by ferrate(VI) dose and pH. Generally, higher ferrate(VI) dose and a weakly alkaline pH favor the phosphorus removal.
3) The phosphorus removal by ferrate(VI) is ascribed to the sedimentation mechanism. Therefore, the formation of settleable particles is key. Fe(III) produced from ferrate(VI) and subsequently formed iron oxide can capture dissolved phosphate, the vast majority of P in wastewater.

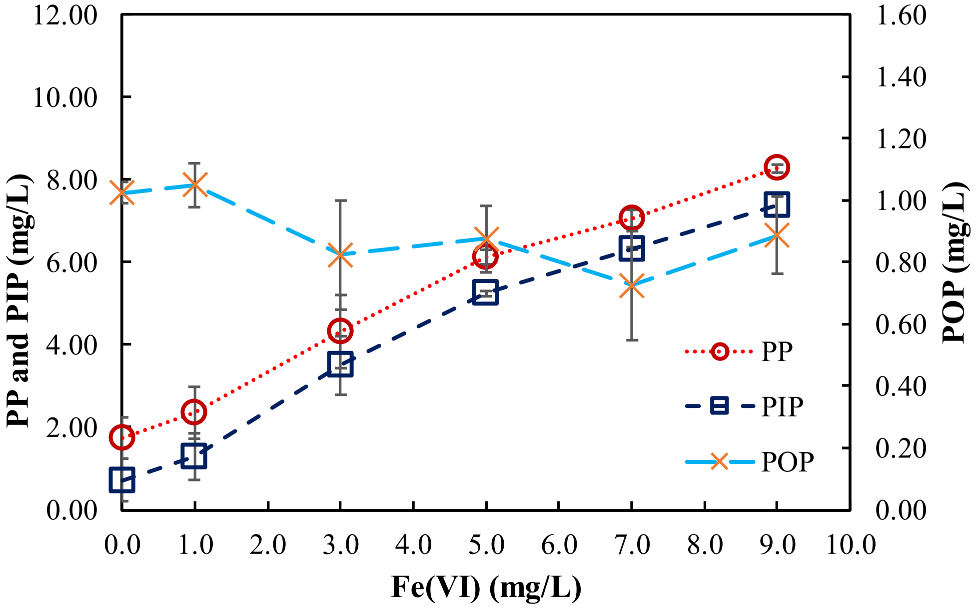
4) Ferrate(VI) addition to wastewater can also remove particles originally present in wastewater as well as particulate organic matter, thereby improving the quality of treated wastewater


TP and TIP (mg/L)
TOP (mg/L)
Fe(VI) (mg/L)
12.0
10.0
8.0
6.0
4.0
2.0
0.0
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
TP
TIP
TOP

(a)

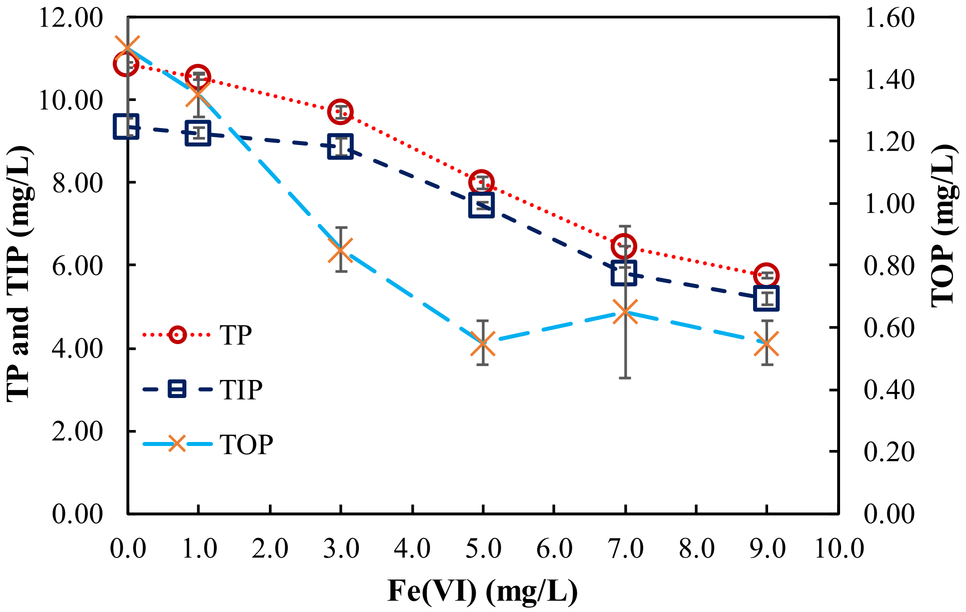

DP and DIP (mg/L)
DOP (mg/L)
Fe(VI) (mg/L)
12.00
10.00
8.00
6.00
4.00
2.00
0.00
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
DP
DIP
DOP

(b)

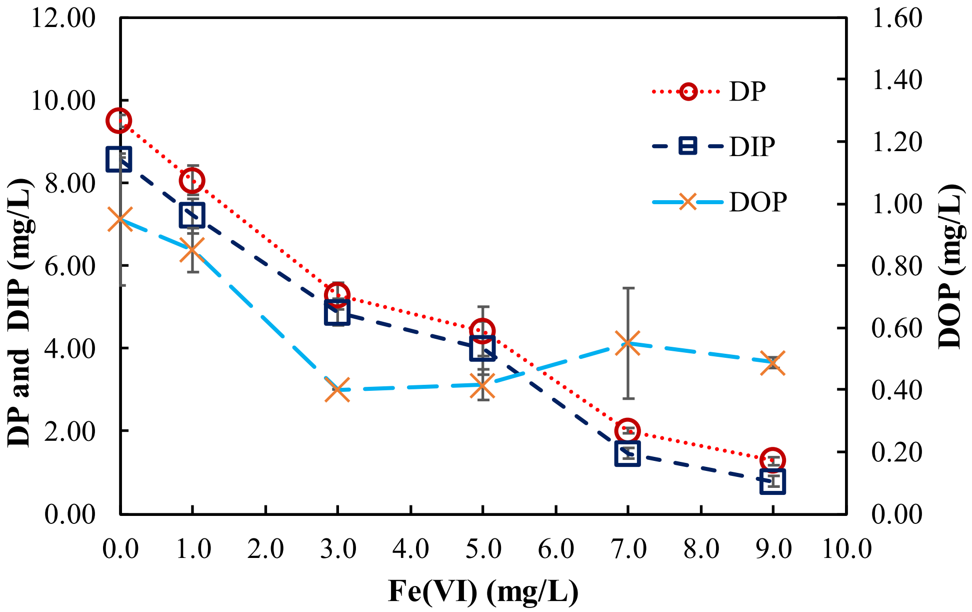


(c)

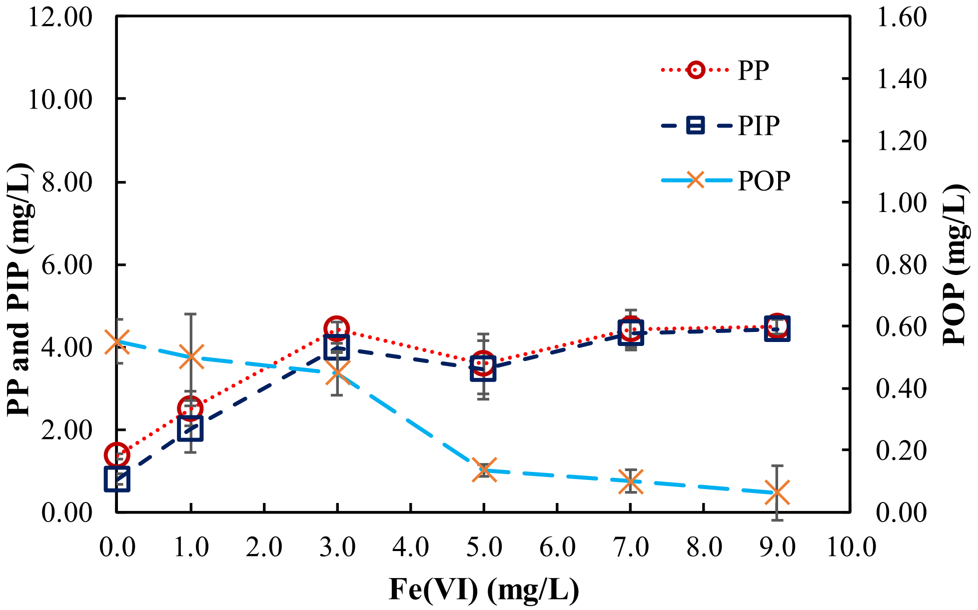
Figure 2-1 Concentrations of different P species in the supernatant after CEPT with ferrate(VI) at an initial pH of 6.0: (a) total P; (b) dissolved P; and (c) particulate P (P is expressed as mg/L PO_4^{3-}; and Fe(VI) dose = 0.0 - 9.0 mg/L as Fe)


12.00
10.00
8.00
6.00
4.00
2.00
0.00
TP and TIP (mg/L)
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
TOP (mg/L)
TP
TIP
TOP
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
Fe(VI) (mg/L)

(a)


12.00
10.00
8.00
6.00
4.00
2.00
0.00
DP and DIP (mg/L)
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
DOP (mg/L)
DP
DIP
DOP
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
Fe(VI) (mg/L)

(b)



(c)

Figure 2-2 Concentrations of different P species in the supernatant after CEPT with ferrate(VI) at an initial pH of 7.5: (a) total P; (b) dissolved P; and (c) particulate P (P is expressed as mg/L PO_4^{3-}; and Fe(VI) dose = 0.0 - 9.0 mg/L as Fe)

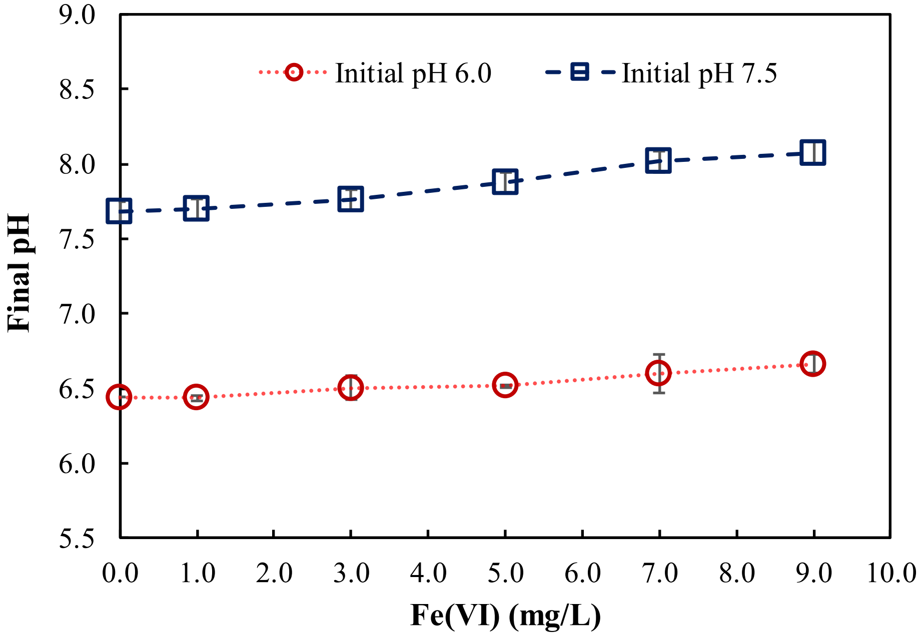
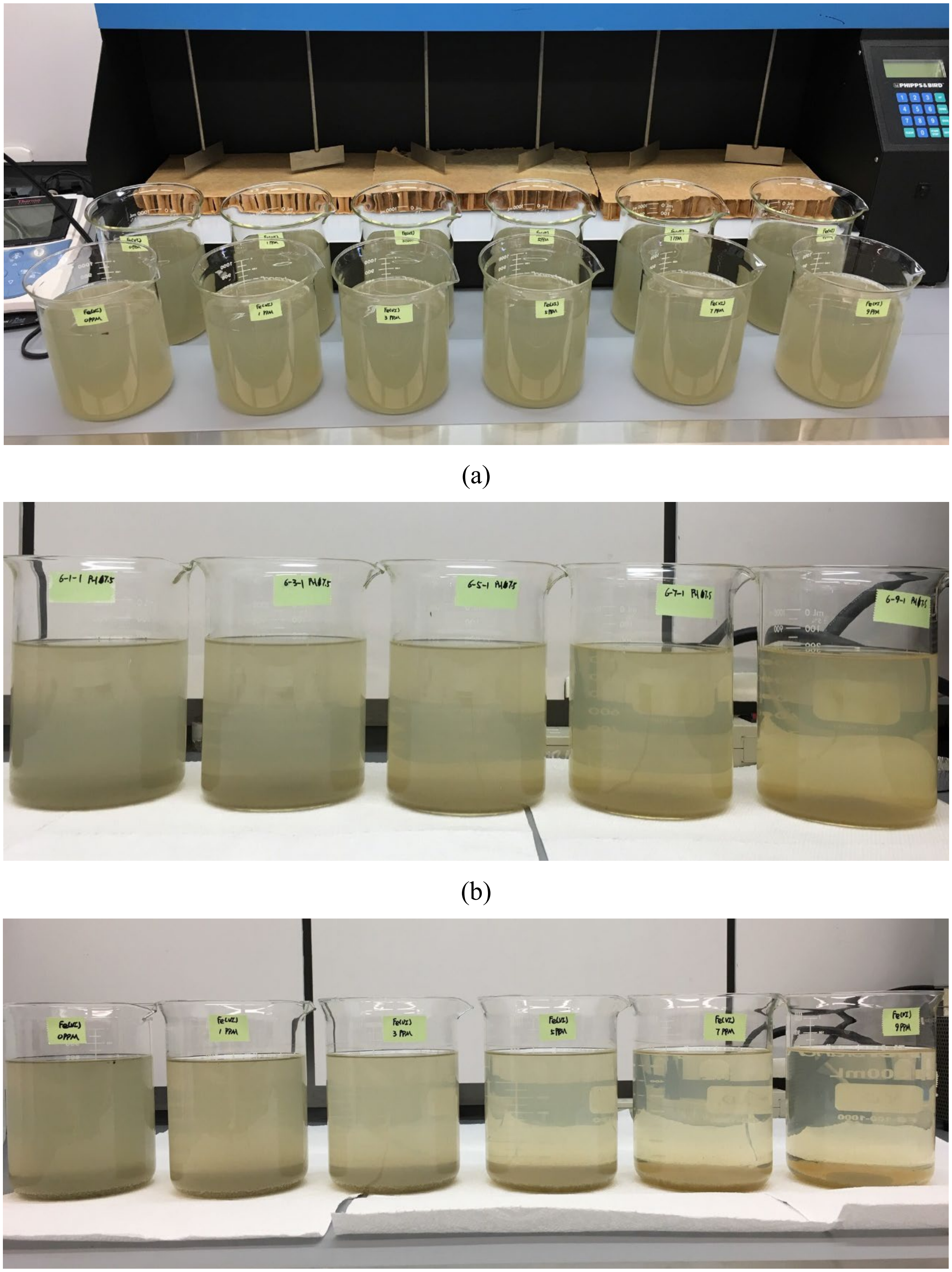


Figure 2-3 Final solution pH after CEPT with ferrate(VI) (initial pH = 6.0 and 7.5; and Fe(VI) = 0.0 -9.0 mg/L)



(a)

(b)

(c)

Figure 2-4 Visualization of PM in wastewater before and after ferrate(VI) treatment: (a) untreated wastewater; (b) CEPT at the initial pH of 6.0; and (c) CEPT at the initial pH 7.5 (Fe(VI) dose: 0.0, 1.0, 3.0, 5.0, 7.0, 9.0 mg/L as Fe from left to right)

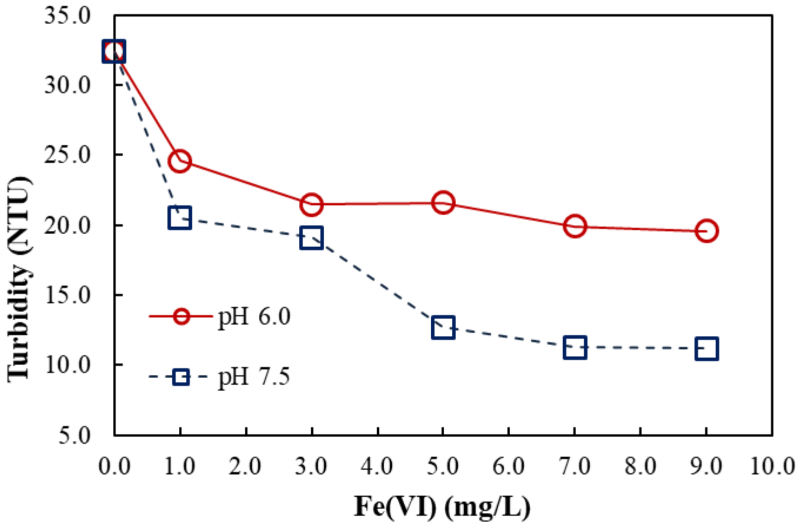


Figure 2-5 Residual turbidity after CEPT at different Fe(VI) doses (initial pH = 6.0 and 7.5; and Fe(VI) = 0.0 -9.0 mg/L)

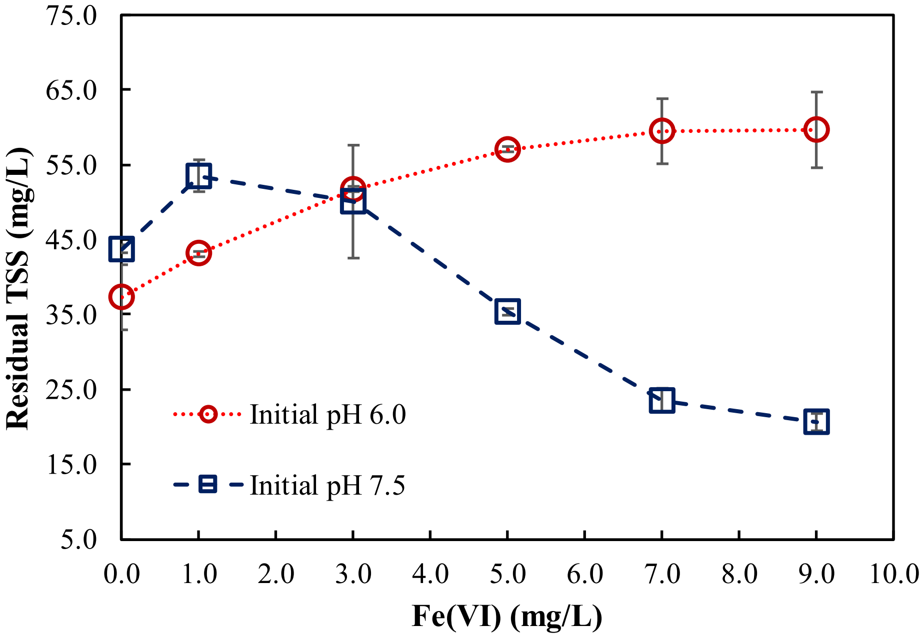
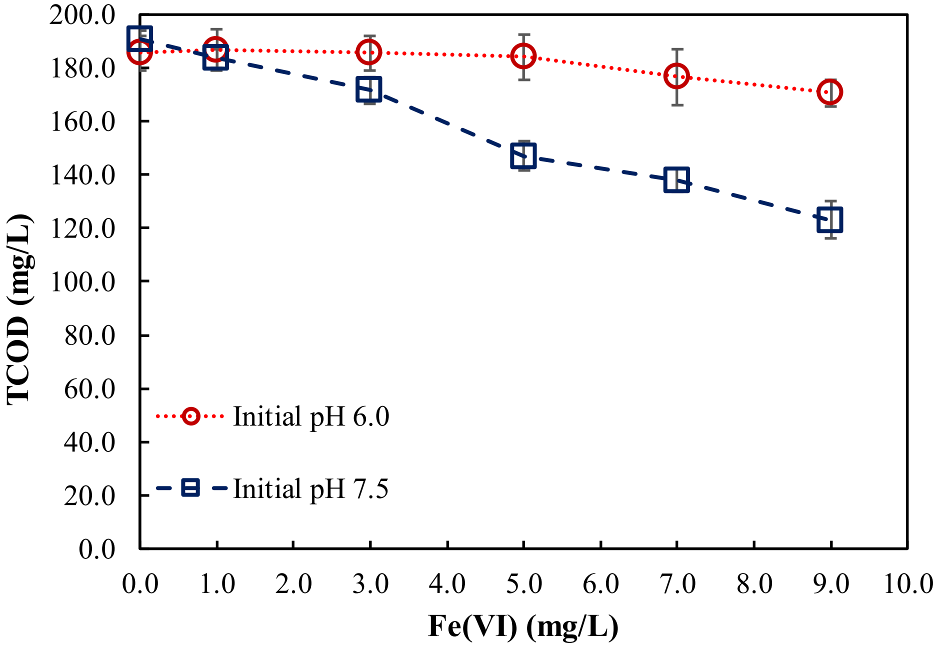
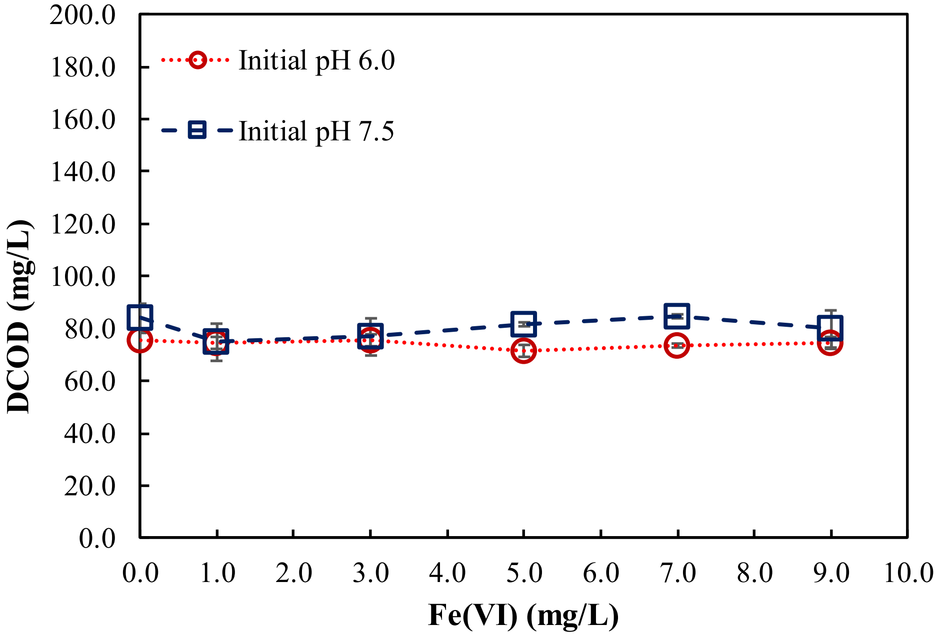


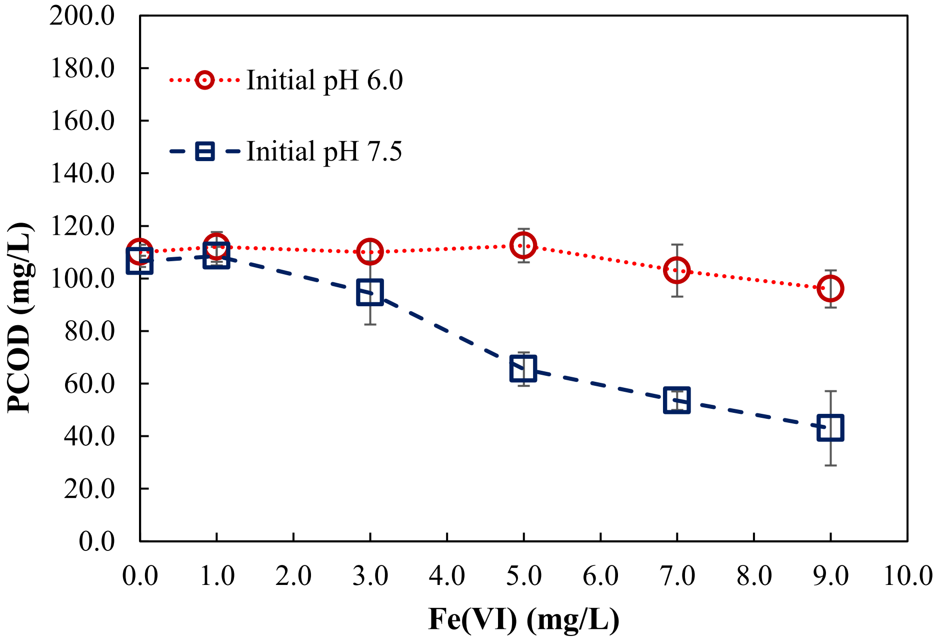
Figure 2-6 Residual TSS after CEPT at different Fe(VI) doses (initial pH = 6.0 and 7.5; and Fe(VI) = 0.0 -9.0 mg/L)


200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
TCOD (mg/L)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
Fe(VI) (mg/L)
Initial pH 6.0
Initial pH 7.5

(a)

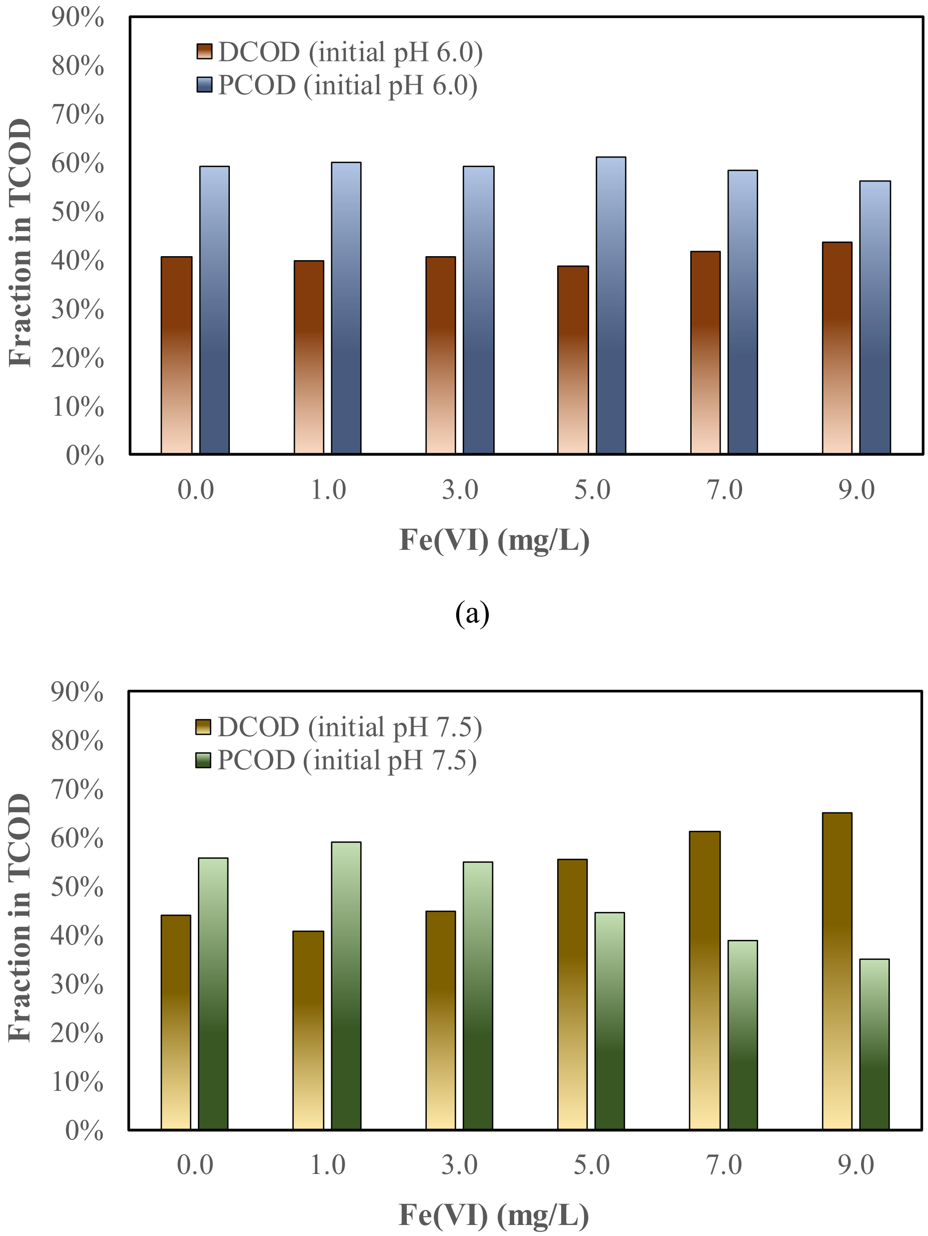

200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
DCOD (mg/L)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
Fe(VI) (mg/L)
Initial pH 6.0
Initial pH 7.5

(b)



(c)

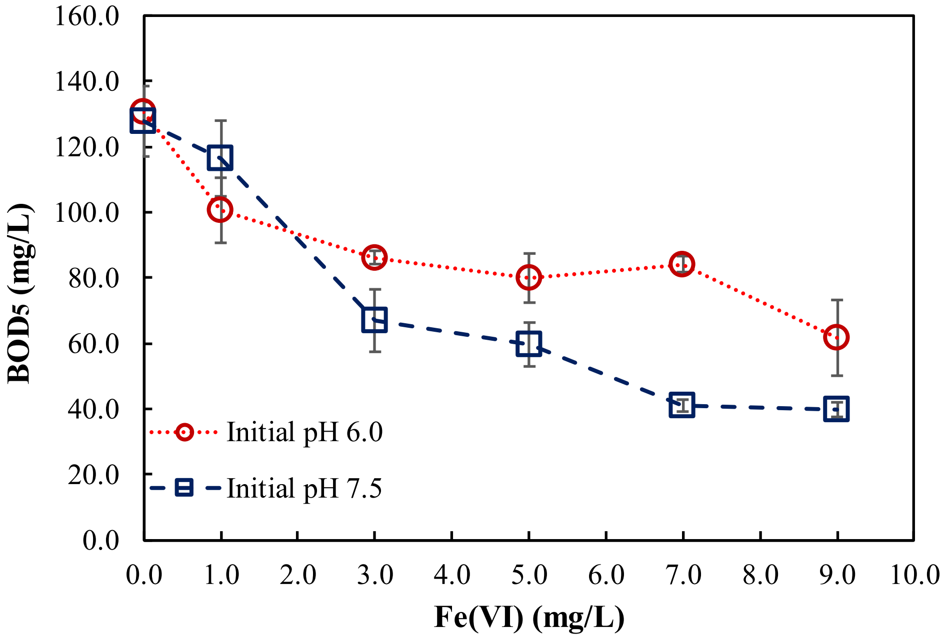
Figure 2-7 Residual COD after CEPT at different Fe(VI) doses: (a) TCOD; (b) DCOD; and (c) PCOD (initial pH = 6.0 and 7.5; and Fe(VI) = 0.0 -9.0 mg/L)



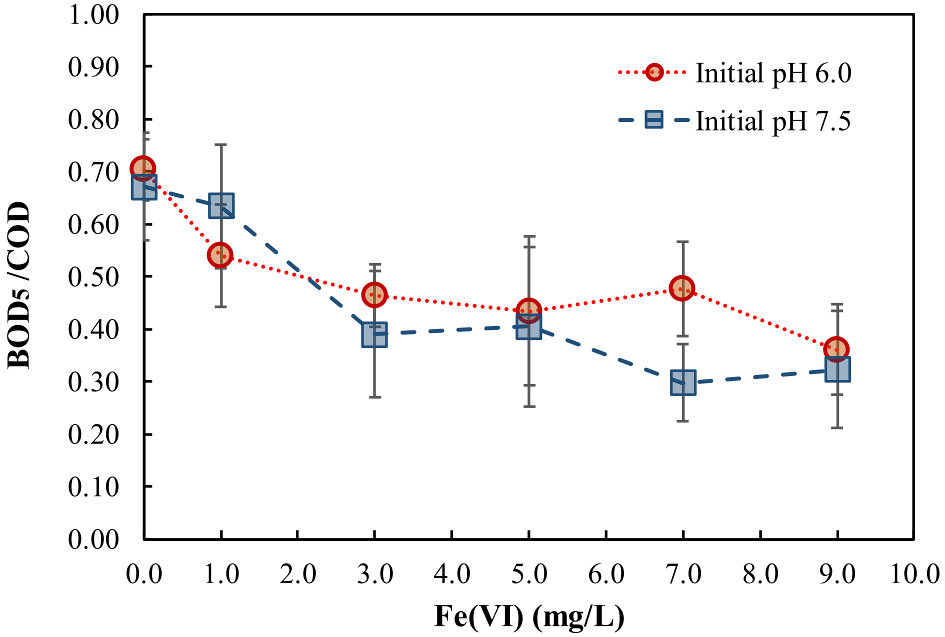
(a)

(b)

Figure 2-8 Fractions of dissolved and particulate COD after CEPT at different Fe(VI) doses: (a) initial pH of 6.0; and (b) initial pH 7.5 (Fe(VI) = 0.0 -9.0 mg/L)

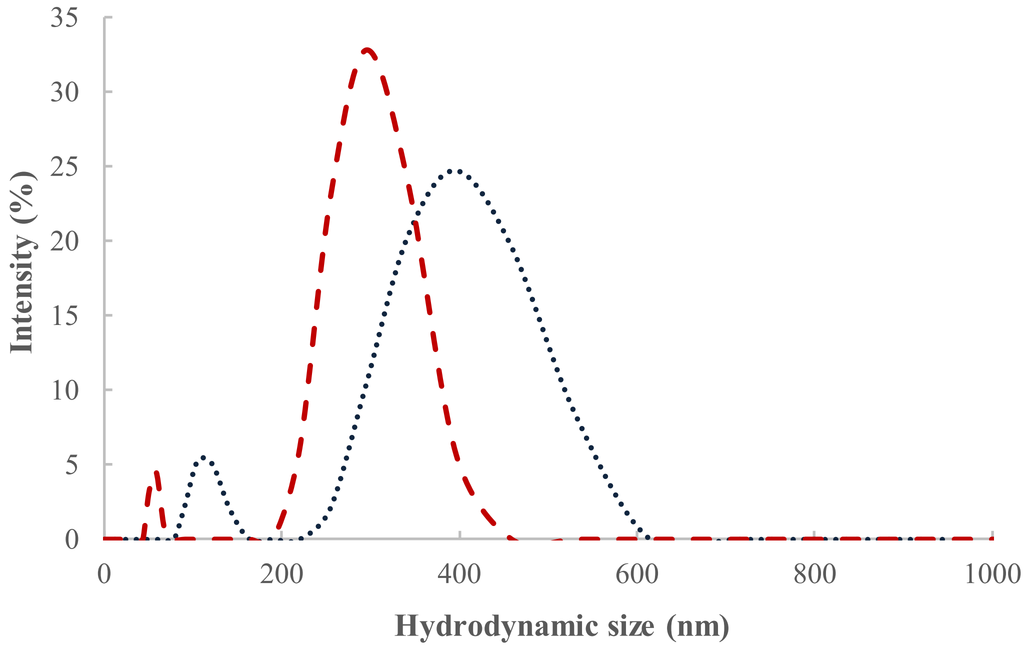


(a)

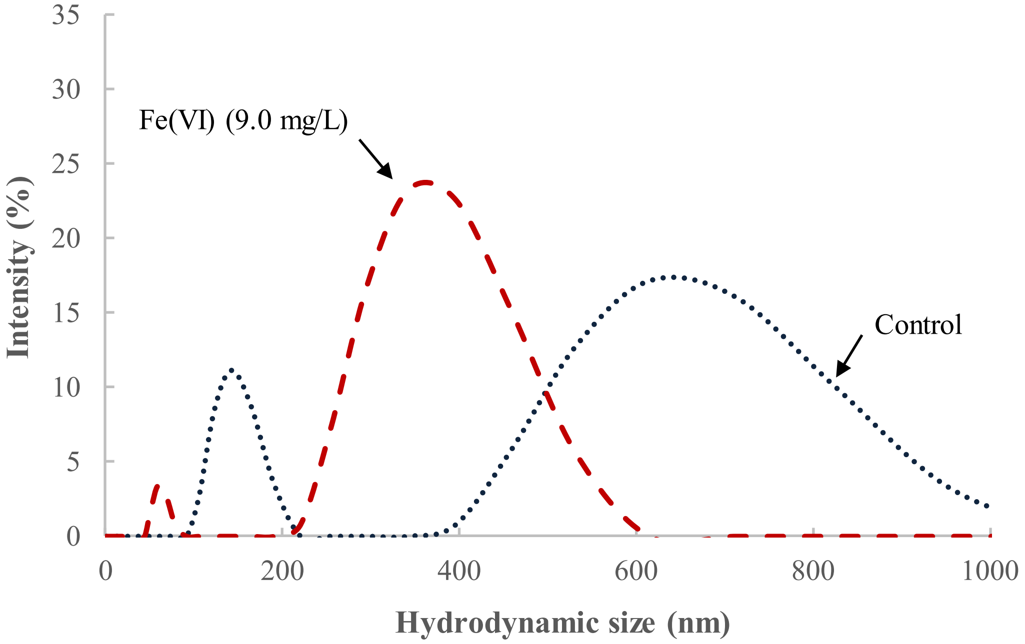


(b)

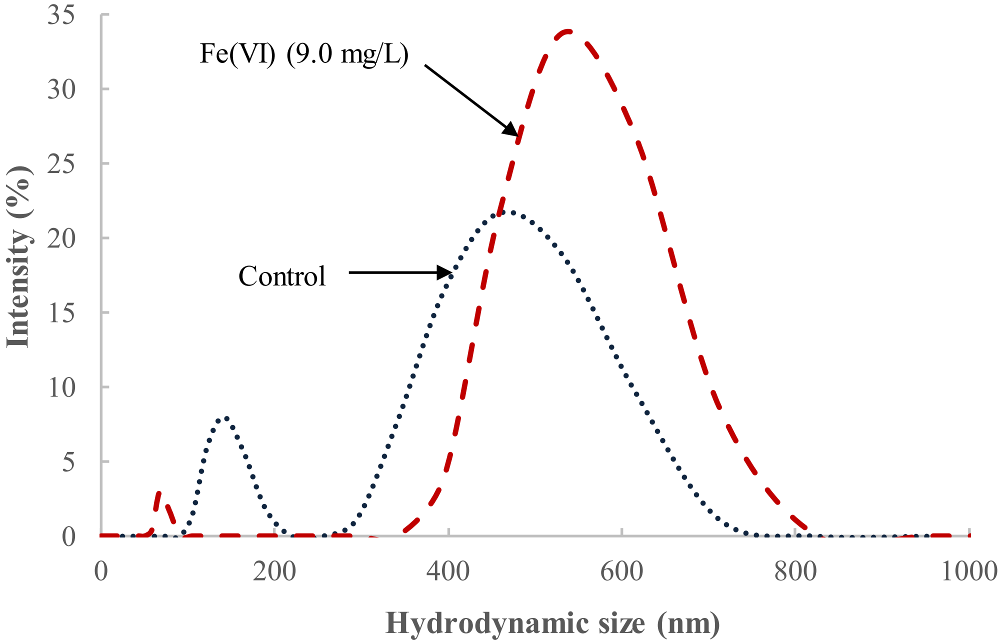
Figure 2-9 Evolution of wastewater biodegradability after CEPT at different Fe(VI) doses: (a) BOD_5; and (b) BOD_5/COD (initial pH = 6.0 and 7.5; and Fe(VI) = 0.0 -9.0 mg/L)



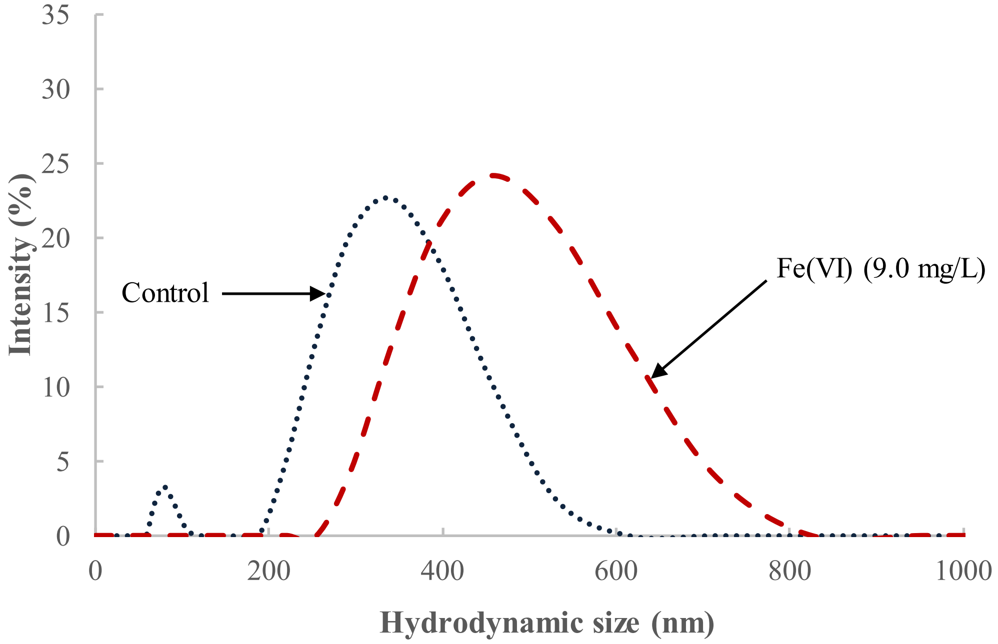
(a) Initial pH 6.0, before settling



(b) Initial pH 6.0, after settling

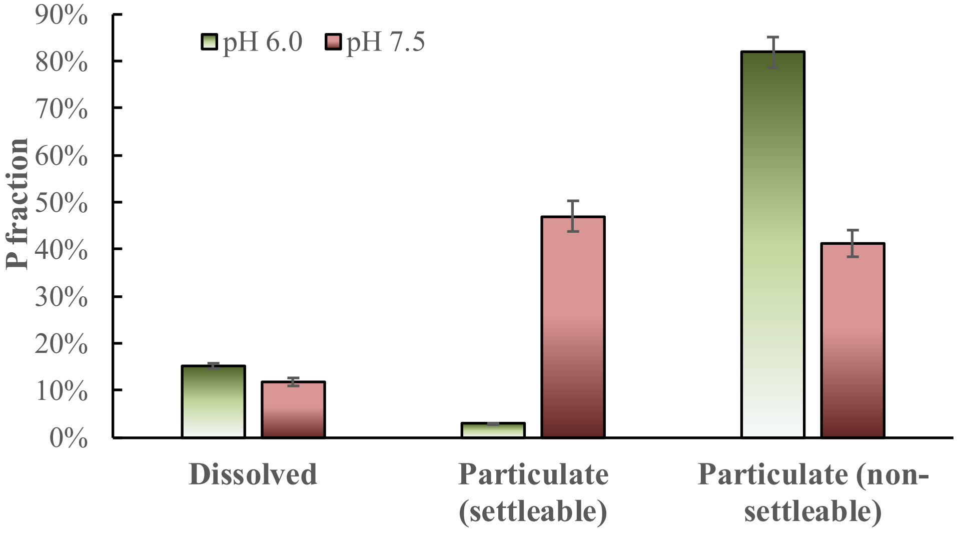


(c) Initial pH 7.5, before settling

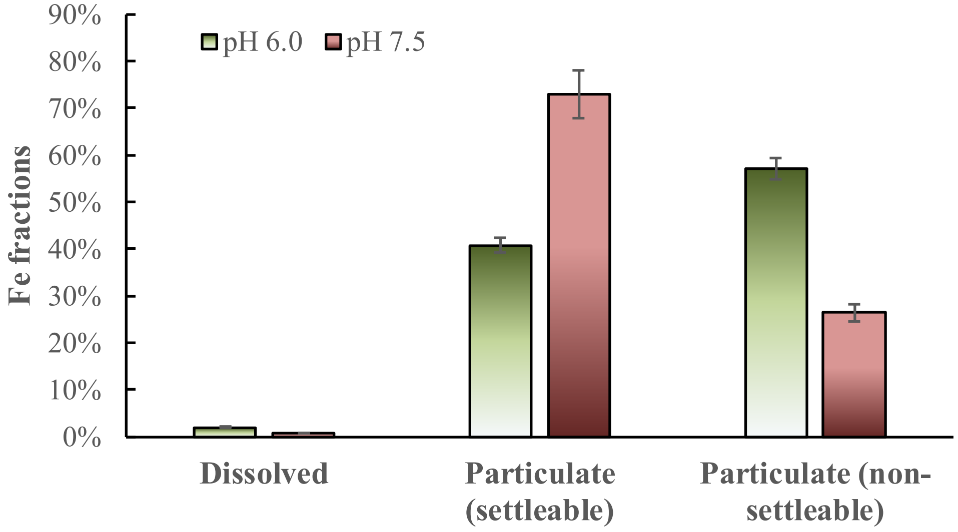


(d) Initial pH 7.5, after settling

Figure 2-10 Hydrodynamic size of particles at 1-hr mixing and at ensuing 2-hr settling after CEPT: (a) initial pH 6.0, after 1-hr mixing; (b) initial pH 6.0, after 2-hr settling; (c) initial pH 7.5, after 1-hr mixing (i.e., before settling); and (d) initial pH 7.5, after 2-hr settling (no Fe(VI) dosing for the control group; and Fe(VI) = 1.0 or 9.0 mg/L)



(a) p



(b) Fe

Figure 2-11 Fractions of different P and Fe states (dissolved, particulate (settleable), and particulate (non-settleable)) after CEPT with Fe(VI): (a) P; and (b) Fe (9.0 mg/L Fe(VI))

2.6 References

Anquandah, G. A. K., Sharma, V. K., Knight, D. A., Batchu, S. R., & Gardinali, P. R. (2011). Oxidation of Trimethoprim by Ferrate(VI): Kinetics, Products, and Antibacterial Activity. *Environmental Science & Technology, 45*(24), 10575-10581. Retrieved from <Go to ISI>://WOS:000298118300044. doi:10.1021/es202237g

Anquandah, G. A. K., Sharma, V. K., Panditi, V. R., Gardinali, P. R., Kim, H., & Oturan, M. A. (2013). Ferrate(VI) oxidation of propranolol: Kinetics and products. *Chemosphere, 91*(1), 105-109. Retrieved from <Go to ISI>://WOS:000315615700017. doi:10.1016/j.chemosphere.2012.12.001

Chagnon, F. J., & Harleman, D. R. (2005). Chemically Enhanced Primary Treatment of Wastewater. *Water Encyclopedia, 1*, 659-660.

Costarramone, N., Kneip, A., & Castetbon, A. (2004). Ferrate(VI) oxidation of cyanide in water. *Environmental Technology, 25*(8), 945-955. Retrieved from <Go to ISI>://WOS:000223974100011.

Crittenden, J. C., Trussell, R. R., Hand, D. W., Howe, K. J., & Tchobanoglous, G. (2012). *MWH's Water Treatment: Principles and Design*: John Wiley & Sons.

Davis, M. L., & Cornwell, D. A. (2008). *Introduction to environmental engineering* (Vol. 4): McGraw-Hill New York.

Deng, Y. (2015). Engineering in Environmental Management In D. Sarkar, R. Datta, A. Mukherjee, & R. Hannigan (Eds.), *An Integrated Approach to Environmental Management* (pp. 151-172): Wiley.

Deng, Y., Jung, C., Liang, Y., Goodey, N., & Waite, T. D. (2018). Ferrate(VI) decomposition in water in the absence and presence of natural organic matter (NOM). *Chemical Engineering Journal, 334*, 2335-2342.

Fan, M. H., Brown, R. C., & Huang, C. P. (2002). Preliminary studies of the oxidation of arsenic(III) by potassium ferrate. *International Journal of Environment and Pollution, 18*(1), 91-96. Retrieved from <Go to ISI>://WOS:000178438200008. doi:10.1504/ijep.2002.000698

Ghernaout, D., Ghernaout, B., & Naceur, M. W. (2011). Embodying the chemical water treatment in the green chemistry—A review. *Desalination, 271*(1), 1-10. Retrieved from http://www.sciencedirect.com/science/article/pii/S0011916411000439

https://www.sciencedirect.com/science/article/pii/S0011916411000439?via%3Dihub. doi:https://doi.org/10.1016/j.desal.2011.01.032

Goff, H., & Murmann, R. K. (1971). Mechanism of isotopic oxygen exchange and reduction of ferrate(VI) ion (FeO42-). *Journal of the American Chemical Society, 93*(23), 6058-6065. Retrieved from https://doi.org/10.1021/ja00752a016. doi:10.1021/ja00752a016

Graham, N. J. D., Khoi, T. T., & Jiang, J. Q. (2010). Oxidation and coagulation of humic substances by potassium ferrate. *Water Science and Technology, 62*(4), 929-936. Retrieved from <Go to ISI>://WOS:000281602000025. doi:10.2166/wst.2010.369

Harleman, D., & Murcott, S. (2001a). CEPT: challenging the status quo.

Harleman, D., & Murcott, S. (2001b). An innovative approach to urban wastewater treatment in the developing world. *WATER 21*, 44-48.

Horstkotte, G., Niles, D., Parker, D., & Caldwell, D. (1974). Full-scale testing of a water reclamation system. *Journal (Water Pollution Control Federation)*, 181-197.

Hu, L. H., Page, M. A., Sigstam, T., Kohn, T., Marinas, B. J., & Strathmann, T. J. (2012). Inactivation of Bacteriophage MS2 with Potassium Ferrate(VI). *Environmental Science & Technology, 46*(21), 12079-12087. Retrieved from <Go to ISI>://WOS:000310665000072. doi:10.1021/es3031962

Jessen, A., Randall, A., Reinhart, D., & Daly, L. (2008). Effectiveness and Kinetics of Ferrate as a Disinfectant for Ballast Water. *Water Environment Research, 80*(6), 561-569. Retrieved from <Go to ISI>://WOS:000261127500010. doi:10.2175/193864708x267423

Jiang, J. Q. (2007). Research progress in the use of ferrate(VI) for the environmental remediation. *Journal of Hazardous Materials, 146*(3), 617-623. Retrieved from <Go to ISI>://WOS:000248524500030. doi:10.1016/j.jhazmat.2007.04.075

Jiang, J. Q., & Lloyd, B. (2002). Progress in the development and use of ferrate(VI) salt as an oxidant and coagulant for water and wastewater treatment. *Water Research, 36*(6), 1397-1408. Retrieved from <Go to ISI>://WOS:000174719300001. doi:10.1016/s0043-1354(01)00358-x

Jiang, J. Q., Wang, S., & Panagoulopoulos, A. (2006). The exploration of potassium ferrate(VI) as a disinfectant/coagulant in water and wastewater treatment. *Chemosphere, 63*(2), 212-219. Retrieved from <Go to ISI>://WOS:000236989600004. doi:10.1016/j.chemosphere.2005.08.020

Jiang, J. Q., Wang, S., & Panagoulopoulos, A. (2007). The role of potassium ferrate(VI) in the inactivation of Escherichia coli and in the reduction of COD for water remediation. *Desalination, 210*(1-3), 266-273. Retrieved from <Go to ISI>://WOS:000247159700027. doi:10.1016/j.desal.2006.05.051

Johnson, P. D., Girinathannair, P., Ohlinger, K. N., Ritchie, S., Teuber, L., & Kirby, J. (2008). Enhanced removal of heavy metals in primary treatment using coagulation and flocculation. *Water Environment Research, 80*(5), 472-479.

Kooti, M., Tarassoli, A., Javadi, H., & Jorfi, M. (2008). A Facile Conversion of Alcohols to Esters Mediated by Potassium Ferrate. *E-Journal of Chemistry, 5*(4), 718-722. Retrieved from <Go to ISI>://WOS:000267204100007

http://downloads.hindawi.com/journals/jchem/2008/589834.pdf. doi:10.1155/2008/589834

Kralchevska, R. P., Prucek, R., Kolarik, J., Tucek, J., Machala, L., Filip, J., . . . Zboril, R. (2016). Remarkable efficiency of phosphate removal: Ferrate(VI)-induced in situ sorption on core-shell nanoparticles. *Water Research, 103*, 83-91. Retrieved from <Go to ISI>://WOS:000383292100010

https://ac.els-cdn.com/S0043135416305255/1-s2.0-S0043135416305255-main.pdf?_tid=5ed5a05b-6d08-4f09-9638-e660062e3be3&acdnat=1538079174_93d2653bae956e534292a03c8b9b00e6. doi:10.1016/j.watres.2016.07.021

Kralchevska, R. P., Prucek, R., Kolařík, J., Tuček, J., Machala, L., Filip, J., . . . Zbořil, R. (2016). Remarkable efficiency of phosphate removal: Ferrate(VI)-induced in situ sorption on core-shell nanoparticles. *Water Research, 103*, 83-91.

Lee, Y., Cho, M., Kim, J. Y., & Yoon, J. (2004). Chemistry of ferrate (Fe (VI)) in aqueous solution and its applications as a green chemical. *JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY-SEOUL-, 10*(1), 161-171.

Lee, Y., Cho, M., Kim, J. Y., & Yoon, J. (2004). Chemistry of ferrate (Fe(VI)) in aqueous solution and its applications as a green chemical. *Journal of Industrial and Engineering Chemistry, 10*(1), 161-171. Retrieved from <Go to ISI>://WOS:000188469500021.

Lee, Y., Kissner, R., & von Gunten, U. (2014). Reaction of Ferrate(VI) with ABTS and Self-Decay of Ferrate(VI): Kinetics and Mechanisms. *Environmental Science & Technology, 48*(9), 5154-5162. Retrieved from <Go to ISI>://WOS:000335720100062

https://pubs.acs.org/doi/pdfplus/10.1021/es500804g. doi:10.1021/es500804g

Lee, Y., Um, I. H., & Yoon, J. (2003). Arsenic(III) oxidation by iron(VI) (ferrate) and subsequent removal of arsenic(V) by iron(III) coagulation. *Environmental Science & Technology, 37*(24), 5750-5756. Retrieved from <Go to ISI>://WOS:000187248000038. doi:10.1021/es034203+

Lee, Y., & von Gunten, U. (2010). Oxidative transformation of micropollutants during municipal wastewater treatment: Comparison of kinetic aspects of selective (chlorine, chlorine dioxide, ferrate(VI), and ozone) and non-selective oxidants (hydroxyl radical). *Water Research, 44*(2), 555-566. Retrieved from <Go to ISI>://WOS:000275353900016. doi:10.1016/j.watres.2009.11.045

Lee, Y., Yoon, J., & von Gunten, U. (2005). Spectrophotometric determination of ferrate (Fe(Vl)) in water by ABTS. *Water Research, 39*(10), 1946-1953. Retrieved from <Go to ISI>://WOS:000230241200002. doi:10.1016/j.watres.2005.03.005

Lee, Y., Zimmermann, S. G., Kieu, A. T., & von Gunten, U. (2009). Ferrate (Fe (VI)) application for municipal wastewater treatment: a novel process for simultaneous micropollutant oxidation and phosphate removal. *Environmental Science & Technology, 43*(10), 3831-3838.

Lim, M., & Kim, M. J. (2010). Effectiveness of Potassium Ferrate (K2FeO4) for Simultaneous Removal of Heavy Metals and Natural Organic Matters from River Water. *Water Air and Soil Pollution, 211*(1-4), 313-322. Retrieved from <Go to ISI>://WOS:000282159200027. doi:10.1007/s11270-009-0302-7

Lv, D., Zheng, L., Zhang, H., & Deng, Y. (2018). Coagulation of colloidal particles with ferrate(VI). *Environmental Science: Water Research & Technology*.

Neupane, D. R., Riffat, R., Murthy, S. N., Peric, M. R., & Wilson, T. E. (2008). Influence of source characteristics, chemicals, and flocculation on chemically enhanced primary treatment. *Water Environment Research, 80*(4), 331-338.

Ødegaard, H. (1998). Optimised particle separation in the primary step of wastewater treatment. *Water Science and Technology, 37*(10), 43-53.

Olive, N. (2002). *Design of a chemically enhanced primary treatment plant for the city of Alfenas, Minas, Gerais, Brazil.* Massachusetts Institute of Technology,

Parker, D. S., Barnard, J., Daigger, G. T., Tekippe, R. J., & Wahlberg, E. J. (2001). The future of chemically enhanced primary treatment: evolution not revolution. *WATER 21*, 49-56.

Poon, C., & Chu, C. (1999). The use of ferric chloride and anionic polymer in the chemically assisted primary sedimentation process. *Chemosphere, 39*(10), 1573-1582.

Prucek, R., Tucek, J., Kolarik, J., Filip, J., Marusak, Z., Sharma, V. K., & Zboril, R. (2013). Ferrate(VI)-Induced Arsenite and Arsenate Removal by In Situ Structural Incorporation into Magnetic Iron(III) Oxide Nanoparticles. *Environmental Science & Technology, 47*(7), 3283-3292. Retrieved from <Go to ISI>://WOS:000317173100036. doi:10.1021/es3042719

Sharma, V. K. (2002). Ferrate(V) oxidation of pollutants: a premix pulse radiolysis study. *Radiation Physics and Chemistry, 65*(4-5), 349-355. Retrieved from <Go to ISI>://WOS:000179423200008. doi:10.1016/s0969-806x(02)00335-3

Sharma, V. K. (2008). Oxidative transformations of environmental pharmaceuticals by Cl(2), ClO(2), O(3), and Fe(VI): Kinetics assessment. *Chemosphere, 73*(9), 1379-1386. Retrieved from <Go to ISI>://WOS:000261249300001

https://ac.els-cdn.com/S0045653508010898/1-s2.0-S0045653508010898-main.pdf?_tid=e71c4bbe-af82-47e0-88fd-3c6c7b2f5f48&acdnat=1538078217_3f5e12c16ddfe6e7c870982586380b9a. doi:10.1016/j.chemosphere.2008.08.033

Sharma, V. K. (2010). Oxidation of nitrogen-containing pollutants by novel ferrate(VI) technology: A review. *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering, 45*(6), 645-667. Retrieved from <Go to ISI>://WOS:000275852200001. doi:10.1080/10934521003648784

Sharma, V. K., Burnett, C. R., O'Connor, D. B., & Cabelli, D. (2002). Iron(VI) and iron(V) oxidation of thiocyanate. *Environmental Science & Technology, 36*(19), 4182-4186. Retrieved from <Go to ISI>://WOS:000178351800040

https://pubs.acs.org/doi/abs/10.1021/es020570u. doi:10.1021/es020570u

Sharma, V. K., Zboril, R., & Varma, R. S. (2015). Ferrates: Greener oxidants with multimodal action in water treatment technologies. *Accounts of chemical research, 48*(2), 182-191.

Song, Y., Deng, Y., & Jung, C. (2016). Mitigation and degradation of natural organic matters (NOMs) during ferrate(VI) application for drinking water treatment. *Chemosphere, 146*, 145-153.

Song, Y. L., Deng, Y., & Jung, C. I. (2016). Mitigation and degradation of natural organic matters (NOMs) during ferrate(VI) application for drinking water treatment. *Chemosphere, 146*, 145-153. Retrieved from <Go to ISI>://WOS:000369457000017

https://ac.els-cdn.com/S0045653515304562/1-s2.0-S0045653515304562-main.pdf?_tid=878e27dd-6420-43dc-b89b-031404e3770d&acdnat=1538079220_9a2d1e8a37953b7bfadc08879ce65d0b. doi:10.1016/j.chemosphere.2015.12.001

Tchobanoglous, G., Stensel, H., Tsuchihashi, R., Burton, F., Abu-Orf, M., Bowden, G., & Pfrang, W. (2014). Wastewater Engineering: Treatment and Resource Recovery, ; Metcalf and Eddy I AECOM. In: McGraw-Hill Book Company: New York, NY.

Tien, K., & Graham, N. (2011). *Evaluating the Coagulation Performance of Ferrate: Coagulation of Kaolin Suspension.* Paper presented at the Minamata International SympoSIum ON Environment And Energy Technology, Kumamoto, Japan.

Waite, T. D. (2012). On-Site Production of Ferrate for Water and Wastewater Purification. *American Laboratory, 44*(10), 26-28. Retrieved from <Go to ISI>://WOS:000312286700006.

Wang, H., Li, F., Keller, A. A., & Xu, R. (2009). Chemically enhanced primary treatment (CEPT) for removal of carbon and nutrients from municipal wastewater treatment plants: a case study of Shanghai. *Water Science and Technology, 60*(7), 1803-1809.

Xu, G., Yan, Z., Wang, N., & Li, G. (2009). Ferric coagulant recovered from coagulation sludge and its recycle in chemically enhanced primary treatment. *Water Science and Technology, 60*(1), 211-219.

Xu, G., Yan, Z., Wang, Y., & Wang, N. (2009). Recycle of Alum recovered from water treatment sludge in chemically enhanced primary treatment. *Journal of hazardous materials, 161*(2-3), 663-669.

Chapter 3 Phosphate Removal from Secondary Effluent Using Ferrate(VI) Treatment

3.1 Introduction and Objectives

3.1.1 Phosphate and Eutrophication

Phosphorus is an essential element to sustain life. In the aqueous environment, phosphate is the primary form of phosphorus that can be readily uptaken by plants and other organisms. Concentrations of available phosphate, together with nitrogen, in an aqueous environment limits its primary production. However, an exceedingly high phosphate concentration can lead to eutrophication, which can cause harmful algal blooms (HABs) to deplete dissolved oxygen and increase mortality of biota in the aqueous ecosystems (Maier, Nimmo-Smith, Glegg, Tappin, & Worsfold, 2009; Withers, Neal, Jarvie, & Doody, 2014; Worsfold, McKelvie, & Monbet, 2016). As a result, water quality is severely degraded due to the production of taste and odor compounds, the release of toxic algal toxins, and the increase of turbidity. The environmental quality degradation poses a serious threat to public health, particularly when the water serves as a drinking water source. For example, eutrophication-derived HABs caused a drinking water crisis in the cities adjacent to the Lake Tai (China) in 2008 and the Lake Erie (USA) in 2014 (Jetoo, Grover, & Krantzberg, 2015; B. Qin et al., 2010; Yuan et al., 2018). Currently, eutrophication has become a major global issue for the freshwater systems (Falkowski et al., 2000; Thompson & Cotner, 2018). For the eutrophication events, phosphate from different sources has been recognized as a major cause (Darch, Blackwell, Hawkins, Haygarth, & Chadwick, 2014; Macklon et al., 1997; Meinikmann, Hupfer, & Lewandowski, 2015).

Phosphate is widely involved in different human activities. It can enter into the aquatic environment through point or non-point pollution sources. Treated wastewater serves as a major point pollution source. Approximately 20-30% of globally mined phosphorus was estimated to finally end up with the sewer system globally (Brunner, 2010; Shimamura, Homma, Watanabe, & Tanaka, 2003). Personal care products, detergents, phosphorus from water supply system, human excreta and food waste are the primary sources of phosphate in the municipal wastewater (Comber, Gardner, Georges, Blackwood, & Gilmour, 2013). In the recent years, more stringent phosphorus discharge limits have become effective for municipal wastewater treatment plants, especially in a highly environmentally sensitive area, such as the Chesapeake Bay where 0.3 mg/L total phosphorus was required for the treated wastewater effluent (Clark et al., 2010; C. Qin et al., 2015). The high standards challenge the existing wastewater treatment options. Therefore, innovative, reliable, cost-effective, and environmentally friendly treatment technologies are required for alleviation of phosphate in treated wastewater.

3.1.2 Phosphate in Water

Phosphate is the has a relative simple chemical structure in comparison with a variety of organic phosphorus. It most commonly means orthophosphate ($PO_4{}^{3-}$) (the most common phosphorus oxoanion), but it is generally used for any hydrated or substituted form of the ion (Darch et al., 2014). As discussed in the Chapter 1, phosphate has two types in an aqueous solution in terms of size, i.e. particulate and soluble forms. The particulate phase can include either adsorbed phosphate ion or the precipitation where phosphate ion is incorporated into the chemical structure (e.g. $CaPO_4$ and $FePO_4$). In a soluble form, phosphate ions can have four different species with three pKa, as shown below (Loganathan, Vigneswaran, Kandasamy, & Bolan, 2014).

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4{}^-,\ pK_{a1} = 2.15; \qquad (3\text{-}1)$$

$$H_2PO_4{}^- \rightleftharpoons H^+ + HPO_4{}^{2-},\ pK_{a2} = 7.2; \qquad (3\text{-}2)$$

$$HPO_4{}^{2-} \rightleftharpoons H^+ + PO_4{}^{3-},\ pK_{a3} = 12.33; \qquad (3\text{-}3)$$

3.1.3 Objectives

The objective of this chapter was to examine the treatment performance of ferrate(VI) for alleviation of phosphate present in secondary effluent and elucidate underlying reaction mechanisms. The working hypothesis is that ferrate(VI) is capable of effectively removing phosphate in secondary effluent via adsorption and/or precipitation processes. To achieve the objective, two following questions would be answered.

1) How and why do operating factors and typical wastewater matrix constituents influence ferrate(VI) removal of phosphate in secondary effluent?
2) What are the underlying mechanisms behind the phosphate removal?

3.2 Materials and Methods

3.2.1 Wastewater samples and reagents

All the reagents used were at least analytical grade, except as noted. Potassium ferrate (K_2FeO_4) (> 96%), sodium bicarbonate ($NaHCO_3$), sodium nitrate ($NaNO_3$), disodium phosphate (Na_2HPO_4), and ammonia chloride (NH_4Cl) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Secondary effluent was collected from a local municipal sewage treatment plant (Verona, New Jersey, USA). The treatment facility received 9,464 m^3/day wastewater from residual areas. The secondary effluent was sampled after a secondary clarifier and before disinfection. Once collected, the sample was delivered to the Montclair State University's Innovative Water Treatment and Reuse Laboratory, filtered with 0.45 µm membrane filters (GE Healthcare Whatman™ Nylon Membrane), and then stored at 4ºC in a refrigerator until use. Quality parameters of the secondary effluent are as follows: pH 7.48, dissolved total phosphorus (DTP) = 2.12 mg/L as P, dissolved inorganic phosphorus (DIP) = 2.08 mg/L as P, total organic phosphorus (TOP) = 42 µg/L as P, UV_{254} absorbance = 0.161 cm^{-1}, dissolved organic carbon

(DOC) = 40.0 mg/L, turbidity = 2.33 NTU, nitrate-nitrogen (NO_3^--N) = 2.6 mg/L, ammonia-nitrogen (NH_3-N) = 10.4 mg/L, and alkalinity = 200 mg/L as $CaCO_3$. Concentrated ferrate(VI) (200 mg/L Fe(VI)) and phosphate (250 mg/L as P) stock solutions were prepared by dissolving appropriate weights of K_2FeO_4 and Na_2HPO_4 in ultrapure water produced from a Milli-Q water purification system (Milli-Q Direct 8), respectively. Fe(VI) in the ferrate(VI) stock solution was confirmed with the ABTS method (Y. Lee, Yoon, & von Gunten, 2005). P concentration was measured using an inductively coupled plasma-mass spectroscopy (ICP-MS Thermo X-Series II, XO 472). The stock solution was prepared immediately before the treatment tests.

3.2.2 Treatment of secondary effluent with ferrate(VI)

Laboratory scale batch tests were carried out in 500 mL glass beakers containing 400 mL well-mixed secondary effluent on a four-paddle programmable jar tester (Phipps and Bird - 7790-950) at room temperature (20 ± 1 °C) and under atmospheric pressure. If needed, the secondary effluent pH was adjusted to a designated level with 0.1 M sulfuric acid or sodium hydroxide. The treatment was initiated once an appropriate volume of ferrate stock solution was dosed. Within the first minute, the solution was rapidly mixed at a velocity gradient of 241 s^{-1} to completely disperse the added iron. During the following 59 minutes, the solution was gently stirred at a velocity gradient of 21 s^{-1} for the growth of flocs. During the treatment, pH was monitored, but not controlled or intendedly buffered. Following the slow mixing, the treated wastewater was filtered using 0.45 µm membrane filters (GE Healthcare Whatman™ Nylon Membrane) for removing particulate matter, and the filtrates were collected for further analysis. Control tests were carried out with the identical experimental procedure, except that ferrate(VI) was not dosed.

In the tests to evaluate the effect of ferrate(VI) dose, ferrate(VI) dose was varied from 0.0, 1.0, 3.0, 5.0, 7.0, 9.0, to 11.0 mg/L. In the experiments to assess the effect of initial pH, ferrate(VI) dose was fixed at 5.0 mg/L Fe, while initial pH was varied at 5.5, 6.0, 6.5, 7.0, 7.5, and 8.0. For the experiments to evaluate effects of alkalinity (250-500 mg/L as $CaCO_3$), nitrate (NO_3^-) (2.6-30.0 mg/L NO_3-N), and ammonia (NH_3) (10-60 mg/L NH_3-N), $NaHCO_3$, $NaNO_3$, and NH_4Cl were dosed to achieve their respective designated concentrations, respectively, at 5.0 mg/L Fe(VI) and pH 6.5. Because effluent organic matter (EfOM) is commercially unavailable, the effect of EfOM cannot be assessed using the aforementioned experimental design. Instead, distilled water was added to the secondary effluent at an appropriate volumetric ratio to dilute the initial DOC of 40.0 mg/L to a designated level. Although the concentrations of alkalinity, nitrate, and ammonia were different between the undiluted and diluted secondary effluent, they did not significantly influence the experimental results for evaluating the effect of EfOM, because experimental results show that the three matrix constituents had very limited influence on the phosphate removal.

3.2.3 Removal Mechanisms

Treatment tests were carried out in 500 mL glass beakers containing 400 mL phosphate-containing water (1.000 mg/L P) on a four-paddle programmable jar tester (Phipps and Bird - 7790-950) at room temperature (20 ± 1 °C) and under atmospheric pressure. In order to eliminate the possible influence of wastewater matrix constituents, the solution was prepared with distilled water. The initial pH was adjusted to 6.5 and 7.5 using 0.1 M NaOH and 0.1 M HCl. Ferrate(VI) dose was fixed at 5.0 mg/L as Fe. The experiments protocols followed the procedure of Section 3.2.2, except that solution pH was manually maintained at a designated pH with 0.1 M NaOH and 0.1 M HCl.

3.2.5 Sample Analyses

Ferrate(VI) was spectrophotometrically measured using the ABTS method (Y. Lee et al., 2005). Solution pH was measured by a pH meter (Thermo Scientific Orion 5-Star Plus). Various secondary effluent parameters were measured after filtration through 0.45-μm syringe membrane filters (Thermo Scientific, cellulose acetate (CA), 30 mm diameter). EfOM was quantified using DOC, which was measured with a total organic carbon (TOC) analyzer (TOC-LCPH, Shimadzu Corp., Kyoto, Japan). Measurements of alkalinity, NO_3^--N, and NH_3-N followed the U.S. Environmental Protection Agency (EPA) approved Standard Methods 2320B, 1685, and 4500F, respectively. Total phosphate was determined with an inductively coupled plasma-mass spectroscopy (ICP-MS Thermo X-Series II, XO 472). Acid hydrolyzable P was measured with the HACH TNT reagent sets to determine inorganic P concentration in water. The morphology of the retained particles was examined by a transmission electron microscope (TEM, Hitachi H-7500) and a scanning electron microscope (SEM, Hitachi S-3400N). To quantify the amorphous iron in the produced iron oxides, a citrate–ascorbate iron extraction method was used with minor modification. Briefly, 0.2 M Na-citrate and 0.05 M ascorbic acid (pH 6.0) were added to the well-mixed immediately after the coagulation and flocculation tests (3.0 mg/L Fe(VI)) with a reagent to solution weight ratio of 60 : 1. The suspensions were shaken on a horizontal shaker for 16 h and then centrifuged at 11 000 rcf for 30 min. The extractable dissolved iron in the suspensions was collected for analysis of amorphous iron by inductively coupled plasma-mass spectroscopy (ICP-MS Thermo X-Series II, XO 472). The data allowed for the determination of the mass fraction of amorphous Fe in the total Fe (i.e. 3.0 mg/L Fe) in the ferrate(VI) resultant oxide particles. The crystal structure of amorphous and crystal iron oxide was investigated on a Bruker D8 Advance X-ray diffractometer (XRD) with Cu-Kα radiation in the 2θ range of 10-

75°. The function group was investigated using Fourier Transform Infrared (FTIR, Nicolet 4700). All the experiments were, at a minimum, run in triplicates. All the analytical results reported represent the mean of the replicate samples. Error bars in the figures indicate one standard deviation of these measurements.

3.3 Results and Discussion

3.3.1 Treatment performance of ferrate(VI) for removal of phosphate in secondary effluent

3.3.1.1 Effects of operating factors

Initial effects were made to evaluate effects of two operating factors, i.e. ferrate(VI) dose and initial pH, on residual phosphate and ferrate(VI) utilization efficiency during ferrate(VI) treatment of secondary effluent. Ferrate(VI) utilization efficiency is defined as the molar ratio of the removed phosphate to the dosed ferrate(VI), as follows.

$$\mathrm{Fe(VI)\ utilization\ efficiency} = \frac{\mathrm{Removed\ phosphate\ (mol\ as\ P)}}{\mathrm{Dosed\ Fe(VI)(mol\ as\ Fe)}} \qquad (3\text{-}9)$$

Here ferrate(VI) utilization efficiency is used as a parameter to indicate how much phosphate can be removed by a unit of ferrate(VI).

Ferrate(VI) dose. Effect of ferrate(VI) dose on residual phosphate and ferrate(VI) utilization efficiency during ferrate(VI) treatment of secondary effluent is presented in **Figure 3-1** (initial DIP = 2.08 mg/L as P and Fe(VI) dose = 0.0 - 11.0 mg/L). Residual DIP in the control was 2.01 mg/L P, slightly below the initial 2.08 mg/L P. In contrast, the residual DIP sharply declined from 1.60 mg/L at 1.0 mg/L Fe(VI) to 0.46 mg/L P at 5.0 mg/L Fe(VI), and then was marginally decreased to 0.29 mg/L P as Fe(VI) was further increased to 11.0 mg/L. Meanwhile, the Fe(VI) utilization efficiency constantly declined from 0.87 to 0.36 mol P/mol Fe with increasing Fe(VI) dose from 1.0 to 11.0 mg/L. These findings suggest that a higher ferrate(VI) dose can achieve more P removal but has a lower utilization efficiency. In the following treatment experiments, 5.0 mg/L Fe(VI) was selected because the P removal became trivial beyond 5.0 mg/L Fe(VI).

Initial pH. Effect of the initial pH on residual phosphate and ferrate(VI) utilization efficiency during ferrate(VI) treatment of secondary effluent is shown in **Figure 3-2** (Fe(VI) = 5.0 mg/L). Residual DIP declined from 0.68 mg/L P at pH 5.5 to 0.43 mg/L P at pH 6.5, and then slightly increased to 0.54 mg/L P as pH went up to 7.5. As pH was further raised to 8.0, the residual P was not significantly changed. Meanwhile, the ferrate(VI) utilization efficiency was narrowly varied within 0.51 – 0.60 mol P/mol Fe. The findings clearly indicate that the minimum residual P (0.43 mg/L P) and the maximum ferrate(VI) utilization efficiency (0.60 mol P/mol Fe) were achieved at pH 6.5 with a corresponding P removal of 80%. Therefore, the initial pH of 6.5 was used for the ensuing treatment experiments.

3.3.1.2 Effect of wastewater matrix constituents

Effects of four common wastewater matrix constituents, including alkalinity (the major chemical is bicarbonate at the study pH condition), NO_3^-, NH_4^+, and effluent organic matter were subsequently investigated, as shown in **Figure 3-3(a), (b), (c),** and **(d)**, respectively. As seen in **Figure 3-3(a)**, residual phosphate was increased from 0.45 to 0.61 mg/L P, while the corresponding P removal efficiency was decreased from 78% to 71%, as alkalinity increased from 200 to 250 mg/L as $CaCO_3$. However, the residual P in treated wastewater did not evidently change over the alkalinity of 250 – 500 mg/L $CaCO_3$. Effect of NO_3^- on the residual phosphate is illustrated in **Figure 3-3(b)**. When NO_3^--N was increased from 2.6 to 30.0 mg/L, the residual phosphate narrowly varied between 0.45 and 0.57 mg/L P, and the phosphate removal ranged within 73% - 78%, indicating a minor impact of nitrate on the phosphate removal by ferrate(VI). Role of NH_3 on the phosphate removal is presented in **Figure 3-3(c)**. With the increase of NH_3-

N from 10.6 to 60.0 mg/L, the residual phosphate slightly remained at 0.78-0.79 mg/L P, indicating that ammonia cannot obviously influence ferrate(VI) removal of phosphate from secondary effluent. Overall, alkalinity, nitrate, and ammonia in secondary effluent exhibited no or little impacts on the abatement of phosphate in secondary effluent with ferrate(VI).

However, the effect of EfOM on the phosphate removal was significant. As shown in **Figure 3-3(d)**, residual phosphate stabilized at 0.47 – 0.53 mg/L P as EfOM increased from 2.5 to 10.0 mg/L DOC. However, when DOC was increased to 40.0 mg/L, residual phosphate significantly increased to 1.37 mg/L P. These findings suggest that ferrate(VI) removal of phosphate in a secondary effluent matrix can be suppressed at a high EfOM range, but the inhibiting effect became minor at a low EfOM concentration.

3.3.2 Mechanistic Studies

To explore underlying mechanisms of ferrate(VI) reactions with phosphate in water, ferrate(VI) treatment of phosphate was performed in distilled water. After ferrate(VI)-treated samples at different pH were filtered with 0.45 μm membrane, residual phosphate and iron concentrations are shown in **Figure 3-4**. As seen, the residual phosphate declined from the initial 1.000 to 0.026 mg/L P at pH 6.5, but to 0.950 mg/L P at pH 7.5, indicating that the lower pH significantly improved the removal of P. Meanwhile, a similar pattern with pH was observed for residual iron. At a Fe(VI) dose of 5.0 mg/L, the residual Fe was 0.001 mg/L at pH 6.5, but remained as high as 4.247 mg/L at pH 7.5. Based on chemical equilibrium computation with the Visual Minteq, residual iron at the studied conditions were nearly zero. Therefore, the residual Fe observed in the filtrate most likely represents iron present in small-sized ferrate(VI) resultant particles that passed through 0.45 μm membrane filters. From **Figure 3-4**, we cannot determine whether the considerable residual P after ferrate(VI) treatment at pH 7.5 was truly soluble or associated with these small-sized iron particles. Of note, orthophosphoric acid has a pK_{a2} of 7.20, so the majority of its derived ions was anionic $H_2PO_4^-$ and HPO_4^{2-} at pH 6.5 and 7.5, respectively. The higher pH of 7.5 enabled a less positively or more negatively charged surface area of iron (hydr)oxides with a typical point zero of charge at pH 6.5-8.5 (Stumm, 1992a) , thereby disfavoring the access of phosphate to iron (hydr)oxide particles. Based on the aforementioned observations, we can concluded that: 1) at pH 6.5, the most phosphate were associated with the resultant iron particles that could be almost completely screened by the filtration; and 2) at pH 7.5, a vast majority of iron particles were sufficiently small to go through the membrane, while phosphate appeared to be on/in these fine particles and/or soluble in water.

Direct characterization of ferrate(VI) resultant particles after ferrate(VI) treatment of phosphate. In order to further understand the phosphate removal, the following material analysis focused on the reactions at pH 6.5, at which phosphate was more effectively removed. Surface elemental analyses were made for the ferrate(VI) resultant particles (**Figure 3-5**). Results evidently show that abundant Fe, P, and O co-existed on the solid phase. Fe and P were uniformly distributed on the solid surface. Morphology of these particles are illustrated in **Figure 3-6**. The SEM image (**Figure 3-6(a)**) reveals that the particles were somewhat angular and their sizes broadly ranged from a few tens of nanometers to several micrometers. The morphology is different from that of these particles from ferrate(VI) decomposition in the absence of phosphate in a previous study (Goodwill, Jiang, Reckhow, Gikonyo, & Tobiason, 2015), in which ferrate(VI) resultant particles were more rounded and less angular, and their sizes were relatively uniform around several micrometers. The TEM image in **Figure 3-6(b)** more clearly presents the morphology of the nano-sized portion of these particles, the size of which was adequately small to pass through the ensuing filtration. As shown, these particles were roughly spherical with the particle sizes of less than 20 nm. They aggregated to form a net structure.

FTIR spectra of the ferrate(VI) resultant particles after ferrate(VI) treatment of phosphate are presented in **Figure 3-7**. Very broad peaks were observed over the wavenumber of 500-4000 cm^{-1}, suggesting a poor crystalline structure. The broad peak at 2800-3600 cm^{-1} and sharp peak at 1600-1700 cm^{-1} are attributed to water -OH stretching and bending vibrations, respectively, suggesting the presence of crystalline H_2O on these samples (Pironon & Barrès, 1992). The sharp and strong peak at 900-1300 cm^{-1} indicates the stretching vibration of P-O in PO_4^{3-} (Boonchom & Puttawong, 2010; Derrick, Stulik, & Landry, 2000). The presence of P is in agreement with the observation from the EDS analysis. On the other hand, XRD patterns of the ferrate(VI) resultant particles after the treatment of phosphate are shown in **Figure 3-8**. The particle sample was mostly X-ray amorphous, making the interpretation difficult.

Characterization of crystalline fraction of these particles produced from ferrate(VI) treatment of phosphate. Although the aforementioned analyses revealed the amorphous properties of ferrate(VI) resultant particles produced after ferrate(VI) reactions with phosphate, previous studies highlighted occurrence of both amorphous and crystalline iron (hydr)oxides after ferrate(VI) reduction in the absence of phosphate in water (Lv, Zheng, Zhang, & Deng, 2018). Therefore, it is likely that amorphous and crystalline iron oxides simultaneously existed in the ferrate(VI) resultant particles after ferrate(VI) reactions with phosphate in distilled water. Here we used a citrate-ascorbate extraction method for dissolution of the amorphous fraction of the ferrate(VI) resultant particles. After the extraction, the remaining particles were the crystalline portion. The extraction method was early proposed for dissolving poorly crystalline iron oxides (primarily ferrihydrite) in soils and mineral mixtures (Reyes & Torrent, 1997), and later became a widely accepted method for separation of amorphous and crystalline fractions of iron (hydr)oxide in environmental sample analyses (Ginn, Meile, Wilmoth, Tang, & Thompson, 2017; Lv et al., 2018).

Surface elemental analyses of the crystalline fraction of the ferrate(VI) resultant particles are shown in **Figure 3-9**. Surprisingly, P was not obviously found, though Fe and O remained among the most abundant elements. This finding reveals that the most P removed was associated with the amorphous fraction in ferrate(VI) resultant particles. SEM and TEM analyses were also made to determine the morphology of the crystalline particles, as shown in **Figure 3-10 (a)** and **(b)**, respectively. The SEM image show that the crystalline particles exhibited a sheet structure with very uniform sizes of several micrometers. The TEM image reflects that besides the large-sized particles shown in **Figure 3-10(a)**, nano-sized aggregates (around 100 nm) composed of very small and uniformly sized nanoparticles (< 10-20 nm) existed. Spectra of FTIR for these crystalline particles are shown in **Figure 3-11**. The peak at 570 cm^{-1} is attributable to Fe-O stretching vibration (Okada et al., 2005). Of note, the peak at 900-1300 cm^{-1}, representing the stretching vibration of P-O in PO_4^{3-}, was not observed, thereby ruling out the presence of $FePO_4$. Therefore, the precipitation reaction of Fe(III) produced from Fe(VI) reduction with phosphate appeared not to be a major reaction pathway of the phosphate removal for ferrate(VI) removal of phosphate. XRD patterns of these crystalline particle are presented in **Figure 3-12**. The measured data well matched the XRD pattern of hematite (α-Fe_2O_3) based on the database of The International Centre for Diffraction Data (ICDD) and the findings previously reported from literature (Schimanke & Martin, 2000; Zainuri, 2017). The finding suggests that the majority of crystalline fraction of particles produced from the ferrate(VI) treatment of phosphate was hematite, while the formation of ferric phosphate was not supported from the characterization tests.

Moreover, fractions of different iron types in the ferrate(VI) resultant particles from ferrate(VI) removal of phosphate are shown in **Figure 3-13**. Three types of iron were investigated, including amorphous iron in particulate matters (> 0.45 μm), crystalline iron in particulate matters (> 0.45 μm), and total iron in small-sized particles (≤ 0.45 μm) or in a soluble state. At 5.0 mg/L Fe(VI) for removal of phosphate (1.00 g/L P), the amorphous, crystalline, and small-sized/soluble iron accounted for 49%, 40%, and 11%, respectively. This finding is in agreement with the aforementioned observation that both crystalline and amorphous iron oxides existed in the final iron sludge.

3.3.2 Discussion

Mechanisms for phosphate removal. Based on the findings from this study, removal of phosphate with ferrate(VI) exhibits different reaction mechanisms with phosphate removal with common iron-based coagulants (e.g. ferric and ferrous salts). Ferric salts such as ferric chloride are a chemical reagent widely used for abatement of phosphate present in municipal wastewater. Although the detailed mechanistic information regarding ferric removal of phosphate in water is not fully understood, adsorption and precipitation reactions have been regarded as two key processes for the phosphate removal (Frossard, Bauer, & Lothe, 1997; Huang & Shenker, 2004; Luedecke, Hermanowicz, & Jenkins, 1988; Smith, Takács, Murthy, Daigger, & Szabó, 2008; Wilfert, Kumar, Korving, Witkamp, & van Loosdrecht, 2015). Several previous studies support that the adsorption of phosphate onto iron oxides is the major mechanism when ferric salts are applied (Luedecke et al., 1988; Smith et al., 2008; Szabó et al., 2008). Iron oxides are a general term for the insoluble iron based (hydr)oxides, which can be rapidly formed through ferric hydrolysis (Cornell & Schwertmann, 2003). The adsorption of phosphate occurs when surface hydroxyls on iron oxides serve as a Lewis acid and exchange with phosphate ions in water (Cornell & Schwertmann, 2003; Thistleton, Berry, Pearce, & Parsons, 2002; Wilfert et al., 2015). This leads to the formation of surface complexes on the iron oxides. The other possible reaction pathway is the formation of insoluble iron-phosphate precipitates after ferric dosing (Tchobanoglous et al., 2014). Although $FePO_4$ is traditionally acknowledged as the major precipitation product, the structure of final iron-phosphate products is indeed complex (Tchobanoglous et al., 2014). In a realistic water and wastewater treatment, the adsorption and precipitation reactions may simultaneously occur during ferric removal of phosphate in water (Thistleton et al., 2002).

Different from ferric elimination of phosphate in water, this study reveals that adsorption of phosphate to ferrate(VI) resultant iron (hydr)oxide is a dominant mechanism for ferrate(VI) removal of orthophosphate. The conclusion is made based on the experiment evidence – absence of insoluble iron-phosphate precipitates in the final solid products. We found that amorphous and crystalline iron particles were both produced from ferrate(VI) reactions with phosphate. The citrate-ascorbate extraction could dissolve the amorphous iron fraction, but could not remove iron-phosphate precipitates, if they truly formed. After the extraction, we did not observe P in the remaining crystalline fraction based on the EDS analysis. Moreover, the FTIR spectrum did not indicate the presence of Fe-P bounds in the remaining insoluble particles. Furthermore, the XRD patterns suggests that hematite only, no iron-phosphate minerals, existed in the final solid products. These findings rule out the principle role of the precipitation mechanism for ferrate(VI) removal of phosphate in water.

Adsorption of phosphate to iron (hydr)oxides was extensively studied. The phosphate binding to the surface of iron (hydr)oxides is primarily attributed to formation of inner-sphere surface complexes, as follows (Butkus, Grasso, Schulthess, & Wijnja, 1998; Stumm, 1992b).

$$\equiv FeOH + PO_4^{3-} + H^+ =\equiv FePO_4^{2-} + H_2O \qquad (3\text{-}11)$$

$$\equiv FeOH + PO_4^{3-} + 2H^+ =\equiv FeHO_4^{-} + H_2O \qquad (3\text{-}11)$$

$$\equiv FeOH + PO_4^{3-} + 3H^+ =\equiv FeH_2PO_4 + H_2O \qquad (3\text{-}12)$$

Where $\equiv FeOH$ represents a surface hydroxyl group on the iron oxide surface. Of note, there are two possible reasons for the fact that phosphate was not abundantly associated with crystalline iron particles after the citrate-ascorbate extraction. Firstly, amorphous iron (hdyr)oxides typically have a greater adsorption capacity than their crystalline counterparts (Wang et al., 2013). Therefore, phosphate was more associated with amorphous iron oxides. Secondly, adsorption of phosphate to hematite (the crystalline iron oxide formed in this study) in water was reported (Elzinga & Sparks, 2007; Gimsing & Borggaard, 2007; Kuo & Lotse, 1973). The absence of P on the crystalline iron fraction may be because the phosphate adsorbed to hematite desorbed during the extraction.

Concurrent formation of both amorphous and crystalline iron (hydr)oxide is of interest. Formation of crystalline iron (hydr)oxide only from ferrate(VI) decomposition in water was previously reported (Goodwill et al., 2015; Radina P Kralchevska et al., 2016). However, a recent study indicates that the ratio of amorphous Fe to crystalline Fe was 2.3:1.0 when ferrate(VI) was applied for coagulation of colloidal particles in water (pH 7.5, 3.0 mg/L Fe(VI), and 2.00 mg/L DOC) (Lv et al., 2018), highlighting that the both iron types were concurrently present in ferrate(VI) resultant particles. In this study, the FTIR spectra, XRD patterns, and citrate-ascorbate extraction all indicate that amorphous and crystalline iron were present in the final iron (hydr)oxide products after ferrate(VI) treatment of phosphate. It is not surprising that amorphous iron (hdyr)oxide was produced during ferrate(VI) treatment, because ferric ions were *in-situ* produced from ferrate(VI) reduction in the ferrate(VI) –phosphate system and amorphous iron (hdyr)oxide is a principal product of ferric hydrolysis during ferric-based coagulation (Crittenden, Trussell, Hand, Howe, & Tchobanoglous, 2012). However, the underlying mechanisms for the formation of crystalline iron oxides are unknown. Although the crystallization of amorphous iron hydroxides is a thermodynamically favorable process, the time required for the aging process is typically long, beyond the time length of the treatment experiments in this study. Production of crystalline iron oxide in this dissertation research might be ascribed to OH^- continuously released from ferrate(VI) self-decomposition (Eq. 3-13) (Goodwill et al., 2015). The OH^- locally produced adjacent to iron can accelerate the aging process to generate crystalline iron oxides (Cornell, Giovanoli, & Schneider, 1989).

$$2FeO_4^{2-} + 5H_2O = 2Fe(OH)_3 + 4OH^- + 1.5O_2\uparrow \qquad (3\text{-}13)$$

In this study, the produced crystalline iron oxide was hematite, in agreement with the finding of Goodwill et al. (2015). However, other crystalline iron oxide types were reported from ferrate(VI) decomposition. For example, core-shell structured nanoparticles were found (Radina P Kralchevska et al., 2016), in which maghemite (γ-Fe_2O_3) was in the center covered by a layer of lepidocrocite (γ-FeOOH). Mechanisms for formation of the different iron oxide minerals in these ferrate(VI) systems are unclear. A likely reason is that different experimental conditions were used in these studies.

Roles of operating factors and wastewater matrix constituents. Performance of phosphate removal relies heavily upon ferrate(VI) dose and solution pH. The increased phosphate removal with a higher ferrate(VI) dose is ascribed to the increasing quantity of iron (hydr)oxide, which can provide more active adsorption sites. On the other hand, solution pH would influence the species of phosphate in water and zeta potentials of ferrate(VI) resultant particles. As discussed above, at the studied pH (6.5 and 7.5), the major phosphate species are anionic. With the increasing pH, the surface charge of ferrate(VI) resultant particles became less positive or more negative, so that anionic phosphate more difficultly accesses to the solid surface. It should be noted that the aforementioned electrostatic interaction only leads to a physical adsorption, but can serve as the first step towards the inner-sphere surface complexation (chemical adsorption) (Stumm, 1992a), which is widely accepted as the major reaction mechanism for adsorption of phosphate to iron oxide.

Among the wastewater matrix constituents, EfOM exhibited an inhibiting effect in ferrate(VI) removal of phosphate. The finding may be ascribed to the following reasons. Firstly, part of EfOM molecules can be also bound to the surface of iron (hydr)oxides (Shon, Vigneswaran, & Snyder, 2006). These compounds can compete with phosphate for the active adsorption sites on the iron oxide adsorbents, thereby suppressing the phosphate adsorption and removal. Secondly, once adsorbed on the iron oxide particles, the EfOM molecules, similar to natural organic matter (Lv et al., 2018), can further reduce zeta potential on the ferrate(VI) induced particles, making adsorption of negatively charged phosphate more difficult.

Implication to wastewater treatment industry. Findings of this chapter have profound impacts for wastewater treatment industry.

1) Ferrate(VI) is a technically efficient agent for elimination of phosphate in secondary effluent. The removal performance depends on ferrate(VI) dose and pH. Most wastewater constituents appear not to significantly influence the treatment, except EfOM that exhibited a

negative effect on the phosphate removal at a sufficiently high EfOM level. Therefore, special attention should be paid to the two operating factors and EfOM in practical use for achieving a treatment goal. Particularly, if the inhibiting role of EfOM, especially at a high EfOM concentration, needs to be mitigated, additional treatment, such as activated carbon adsorption, may be required for alleviation of EfOM before ferrate(VI) dosing.

2) Adsorption is a dominant reaction pathway for ferrate(VI) removal of phosphate. The underlying mechanism is the inner-sphere surface complexation, which can lead to a strong binding. Therefore, desorption of phosphate from the iron sludge to secondary effluent is not a concern. Therefore, the ferrate(VI) treatment can provide a reliable phosphate removal from wastewater. However, the strong association makes a challenge if the removed phosphorus needs to be recovered after wastewater treatment.

3) Liquid-solid separation is required as a downstream treatment step because the produced iron (hydr)oxide particles must be removed for separation of phosphate from secondary effluent as well as for abatement of the particle-induced total suspended solids. The size growth and settleability of the iron (hydr)oxide particles at different treatment conditions need to be further investigated. The information is key to determine what types of liquid-solid separation technologies (e.g. gravity-driven sedimentation basins, rapid or slow sand filters, membrane filtration, or centrifuge separation) can serve as an effective and efficient liquid-solid separation method. Our previous studies reveal that ferrate(VI) induced particle did not completely settle down within 72 hours after ferrate(VI) treatment of secondary effluent, while many micro-scale particles remained suspended and their sizes slowly grew up with time (Zheng & Deng, 2016). However, the particle settleability would be expectedly improved after the operating factors (e.g. ferrate(VI) dose and pH) were optimized.

3.4 Conclusion

This study aimed to study the treatment performance and reaction mechanisms of ferrate(VI) removal of phosphate in a secondary effluent matrix. The treatment option was expected to serve as a novel advanced wastewater treatment. Based on the findings form this study, major conclusions are made as follows.

1) Ferrate(VI) is capable of effectively alleviating phosphate (the vast majority of inorganic phosphorus) from secondary effluent. The treatment performance relies on ferrate(VI) dose and water pH. Generally, higher ferrate(VI) dose and lower pH (6.5-7.5) favor the phosphate removal. Of the different wastewater matrix constituents, EfOM may markedly inhibit ferrate(VI) removal of phosphate, particularly within a high EfOM concentration range.
2) Iron sludge produced after ferrate(VI) treatment of phosphate comprise both amorphous and crystalline iron (hydr)oxides. The major crystalline form is hematite.
3) Adsorption is the dominant mechanism for ferrate(VI) removal of phosphate. Given that inner-sphere surface complexation is the major reaction pathway for iron oxide adsorption of phosphate from water, the binding is strong and unexpected phosphate desorption should be minor.
4) Liquid-solid separation is required as an ensuing treatment subsequent to ferrate(VI) reactions with phosphate, due to the production of insoluble iron sludge from ferrate(VI) removal of phosphate. Although the liquid-solid separation was not investigated in this chapter, the knowledge on this aspect is of importance. Properties (e.g. size, density, and settleability) of these ferrate(VI) resultant particles deserve an in-depth study in future.

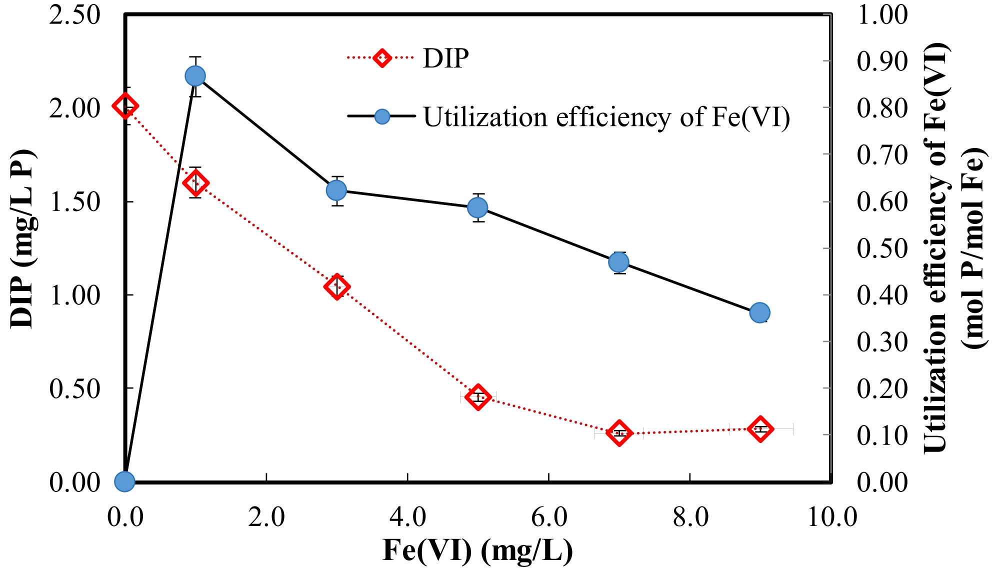


Figure 3-1 Effect of ferrate(VI) dose on residual phosphate and Fe(VI) utilization efficiency during ferrate(VI) treatment of secondary effluent (Initial DIP = 2.08 mg/L as P; Fe(VI) dose = 0.0 - 11.0 mg/L; and pH was not controlled or internationally buffered)

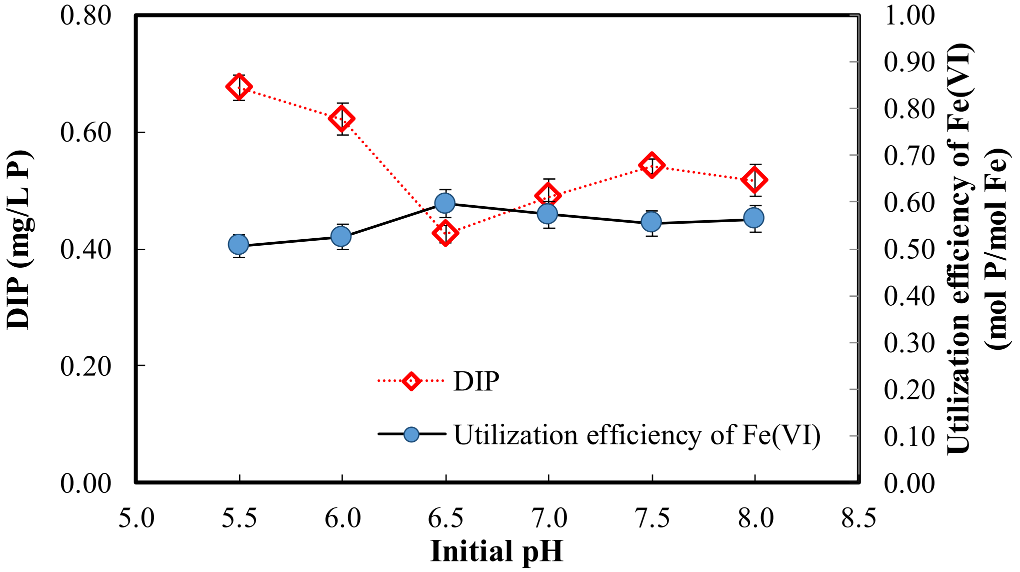
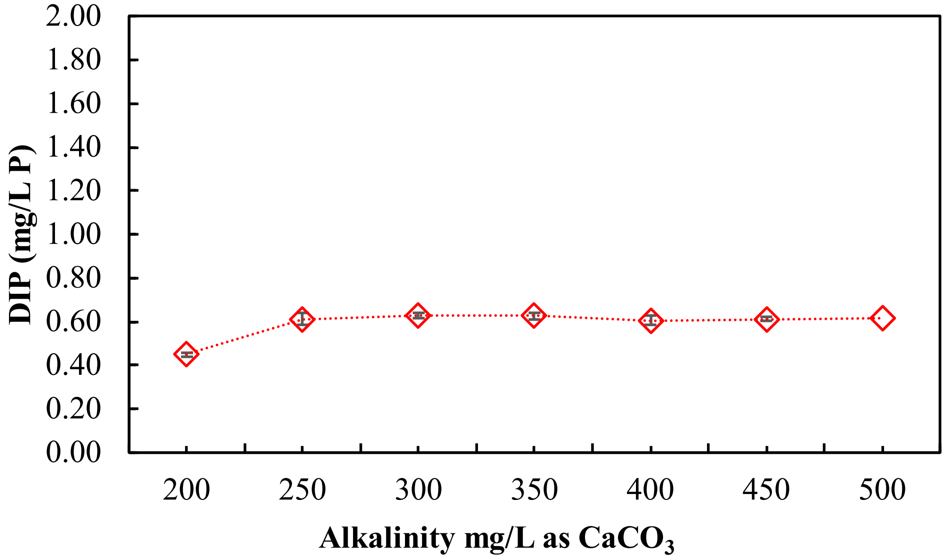
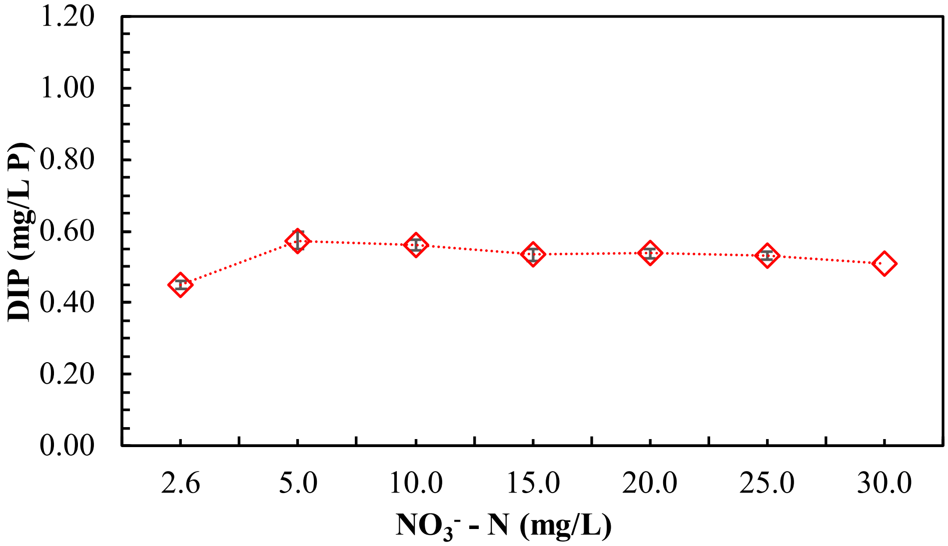


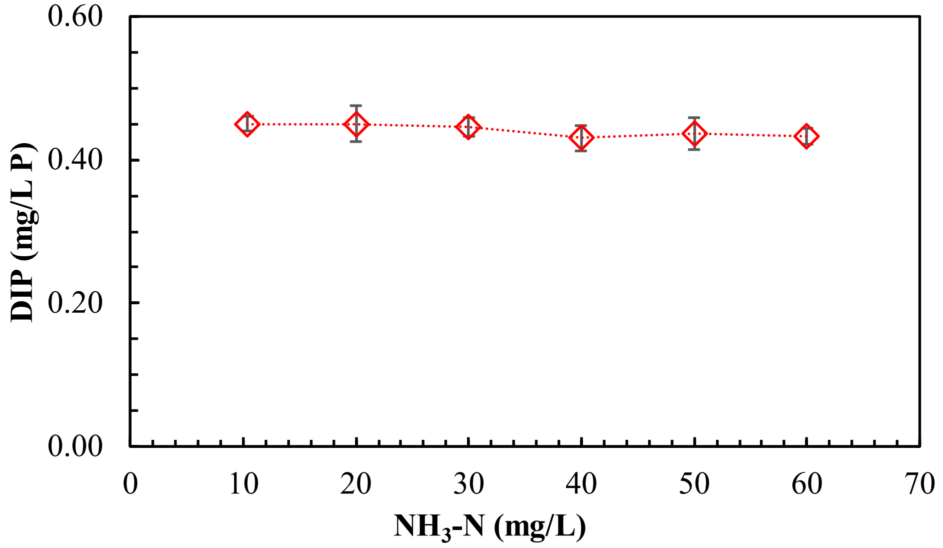
Figure 3-2 Effect of initial pH on residual phosphate and Fe(VI) utilization efficiency during ferrate(VI) treatment of secondary effluent (Initial DIP = 2.08 mg/L as P; initial pH: 5.5, 6.0, 6.5, 7.0, 7.5, and 8.0; Fe(VI) dose = 5.0 mg/L; and pH was not controlled or internationally buffered)


2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
DIP (mg/L P)
200
250
300
350
400
450
500
Alkalinity mg/L as $CaCO_3$

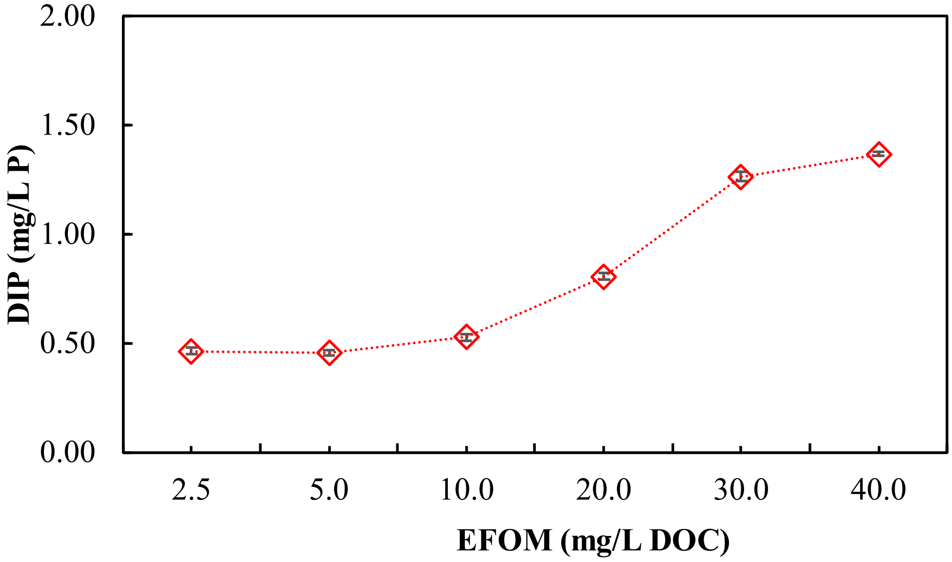
(a)


1.20
1.00
0.80
0.60
0.40
0.20
0.00
DIP (mg/L P)
2.6
5.0
10.0
15.0
20.0
25.0
30.0
NO_3^- - N (mg/L)

(b)



(c)



(d)

Figure 3-3 Effects of different wastewater matrix constituents on residual phosphate during ferrate(VI) treatment of secondary effluent (Fe(VI) dose = 5.0 mg/L, initial DIP = 2.08 mg/L P): (a) alkalinity: 200-500 mg/L as CaCO3; (b) NO_3^--N: 2.6-30.0 mg/L; c) NH_3-N: 10.6-60 mg/L; and d) EfOM: 2.5-40 mg/L)

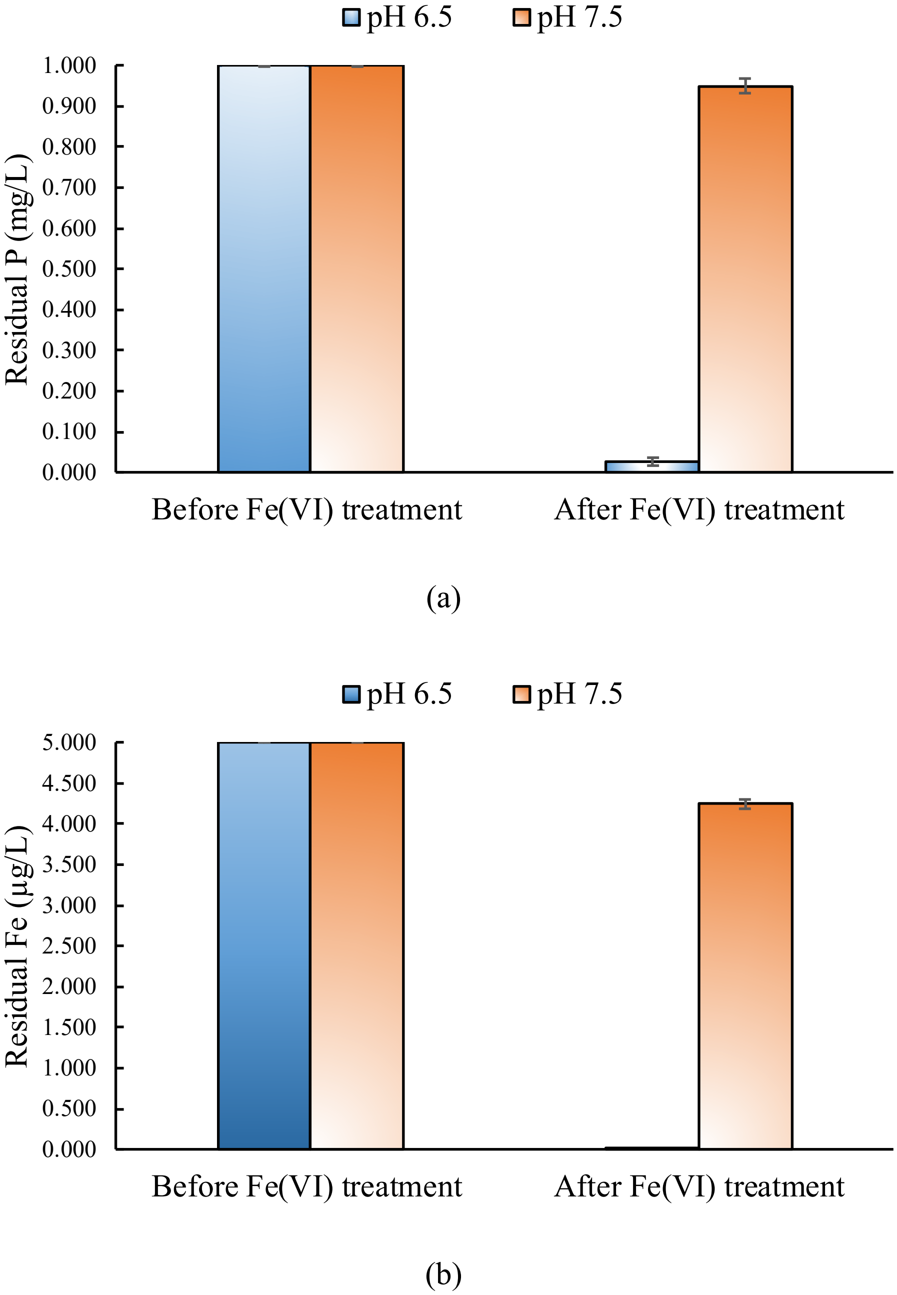
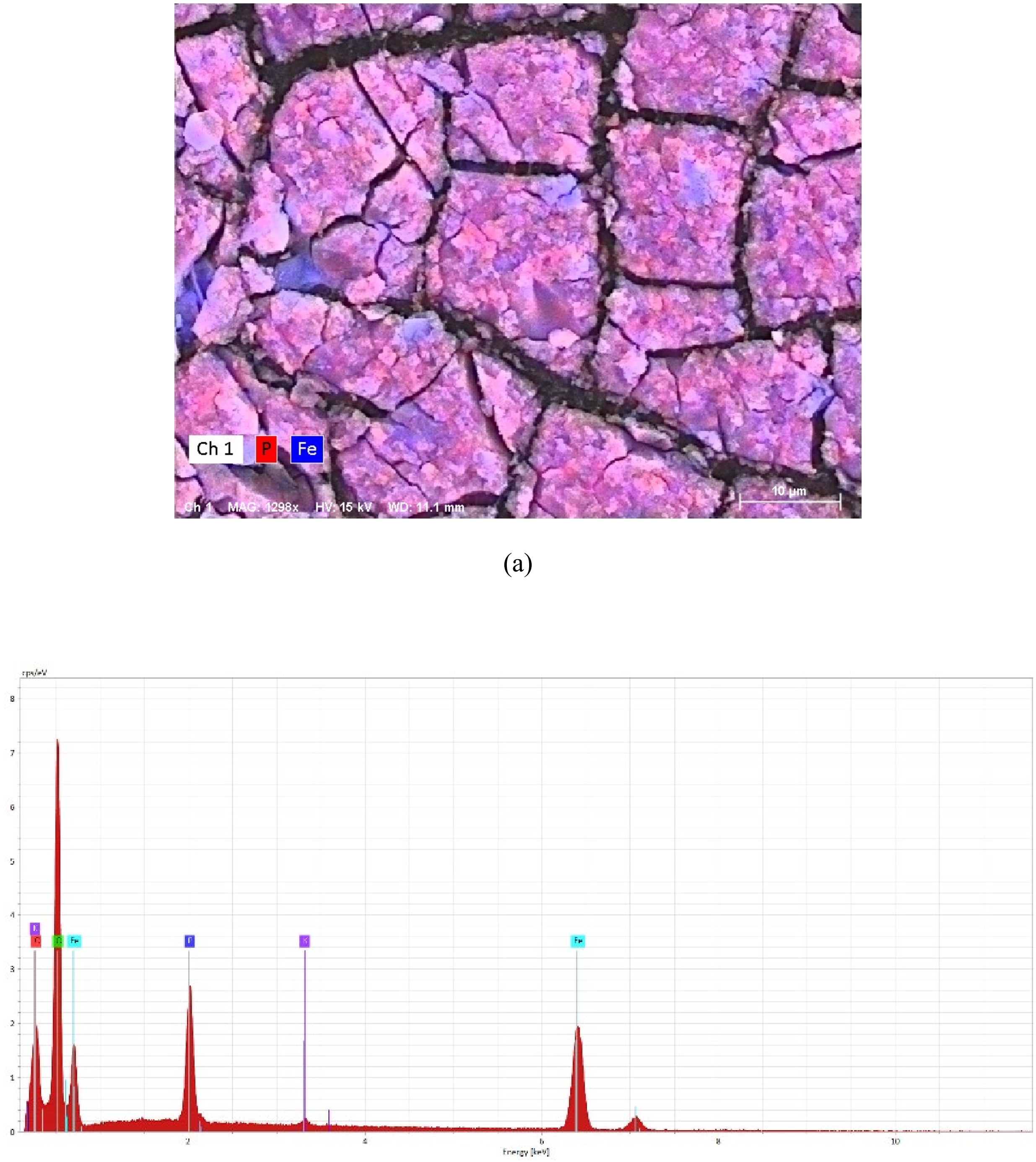


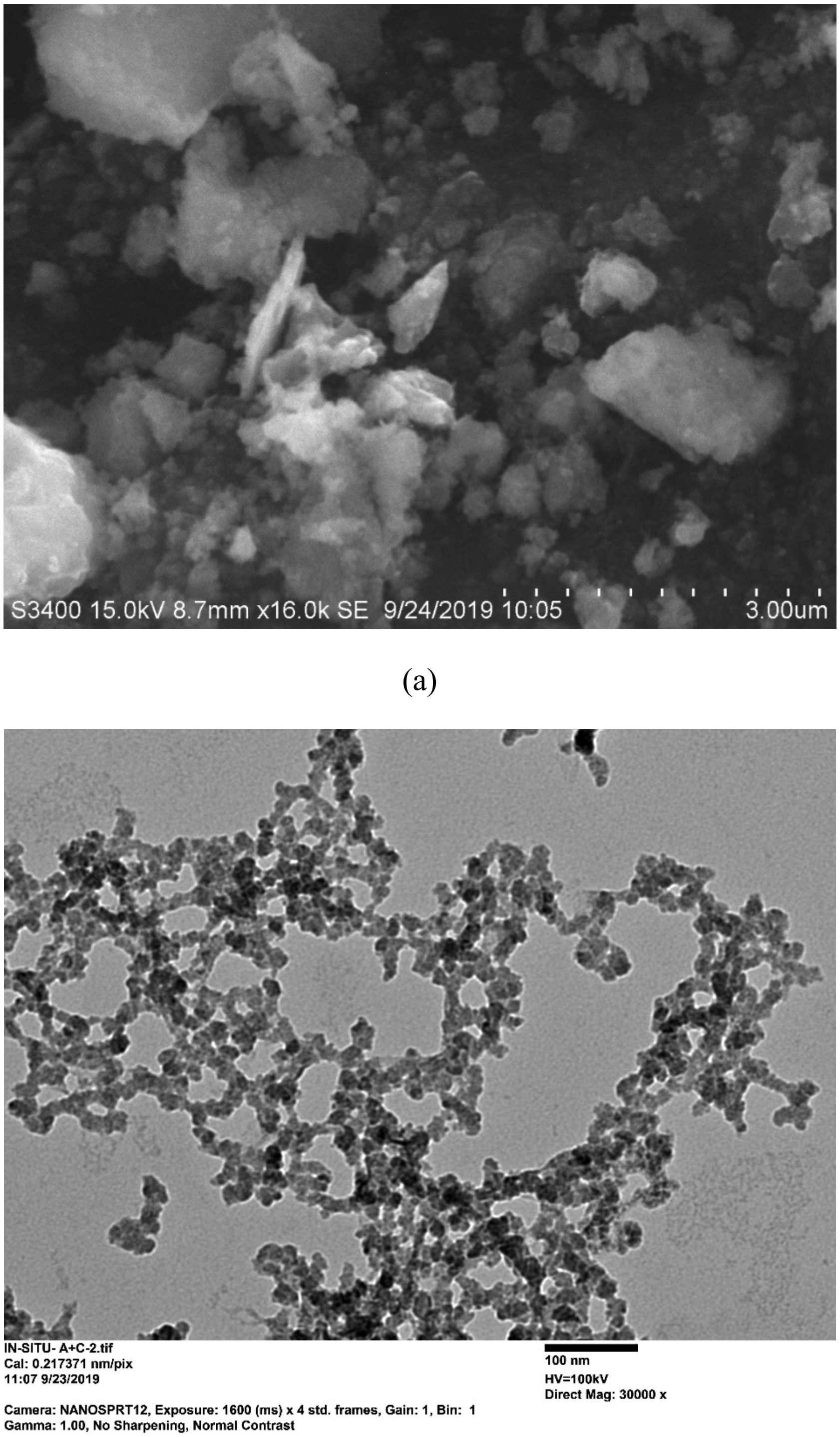
Figure 3-4 Residual phosphate and iron after ferrate(VI) treatment of phosphate in distilled water (Fe(VI)=5.0 mg/L; initial phosphate =1.000 mg/L P; initial pH= 6.5 or 7.5; and P and Fe were measured after 0.45μm membrane filtration)



(a)

(b)

Figure 3-5 Surface element analysis of ferrate(VI) resultant particle after ferrate(VI) treatment of phosphate in distilled water (Fe(VI)=5.0 mg/L; initial phosphate =1.000 mg/L P; initial pH= 6.5)



(a)

(b)

Figure 3-6 Morphology of ferrate(VI) resultant particle after ferrate(VI) treatment of phosphate in distilled water: (a) SEM image; and (b) TEM image (Fe(VI)=5.0 mg/L; initial phosphate =1.000 mg/L P; and initial pH= 6.5)

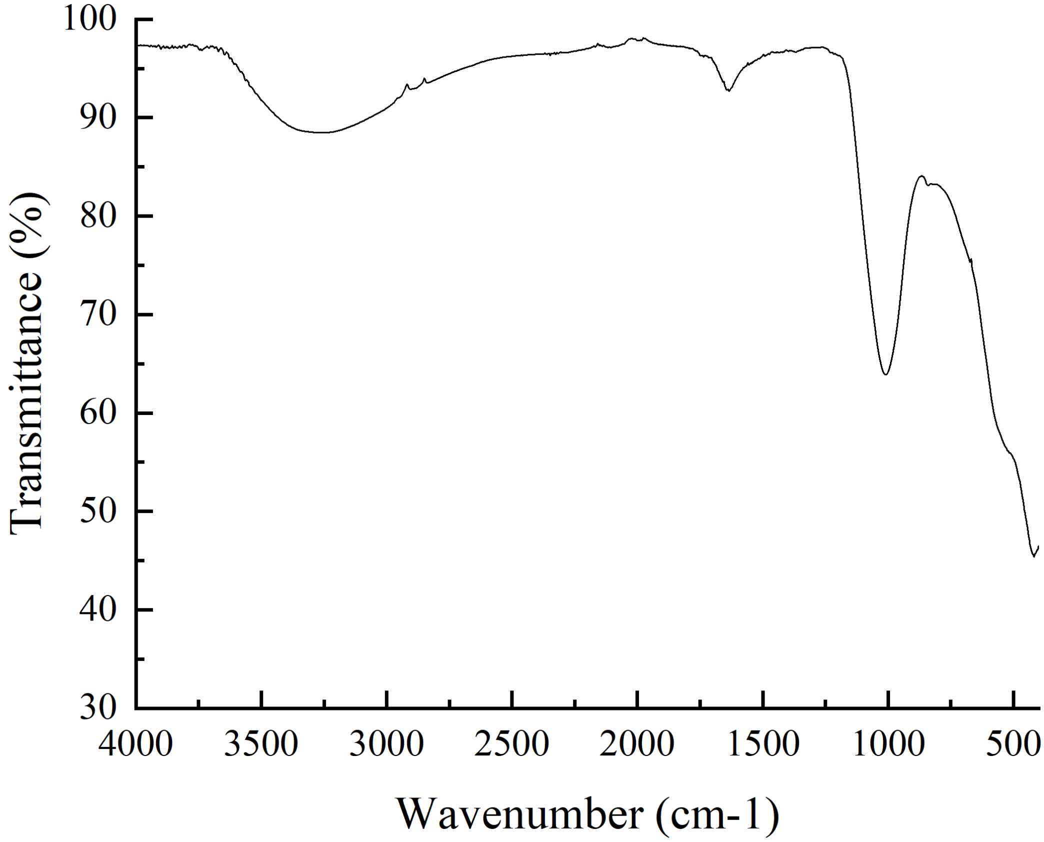


Figure 3-7 FTIR spectrum of ferrate(VI) resultant particle after ferrate(VI) treatment of phosphate in distilled water (Fe(VI)=5.0 mg/L; initial phosphate =1.000 mg/L P; and initial pH= 6.5)

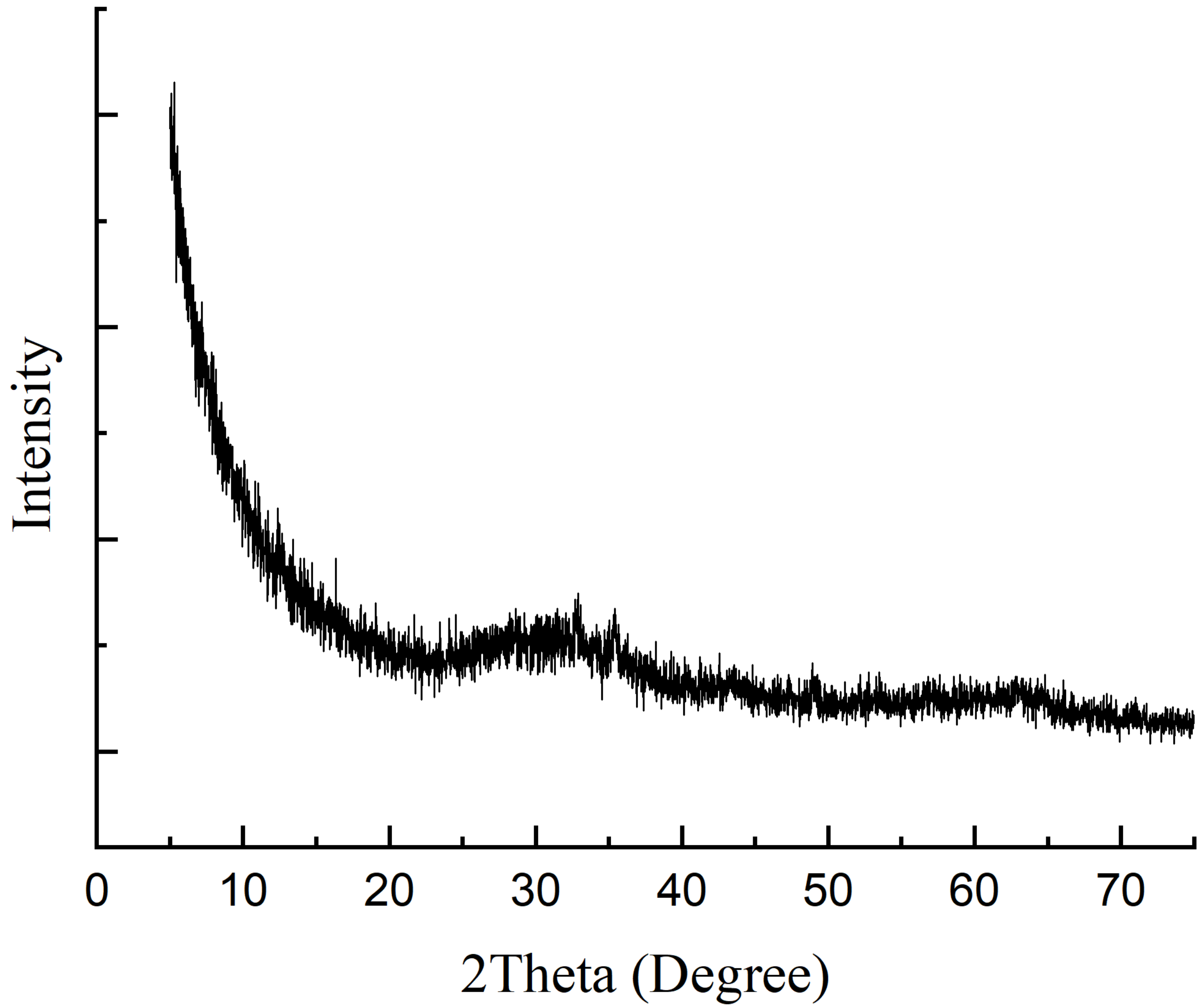
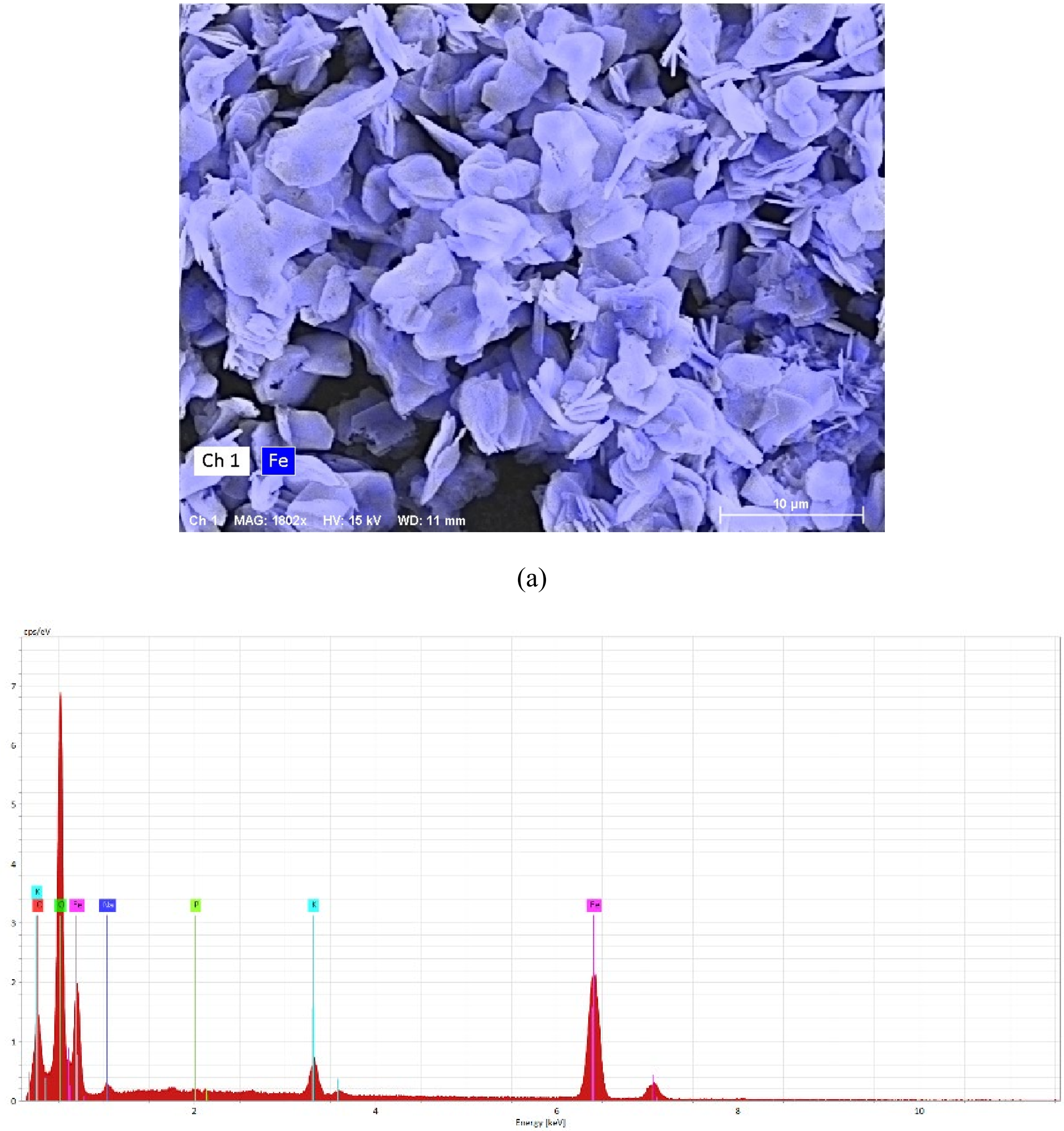


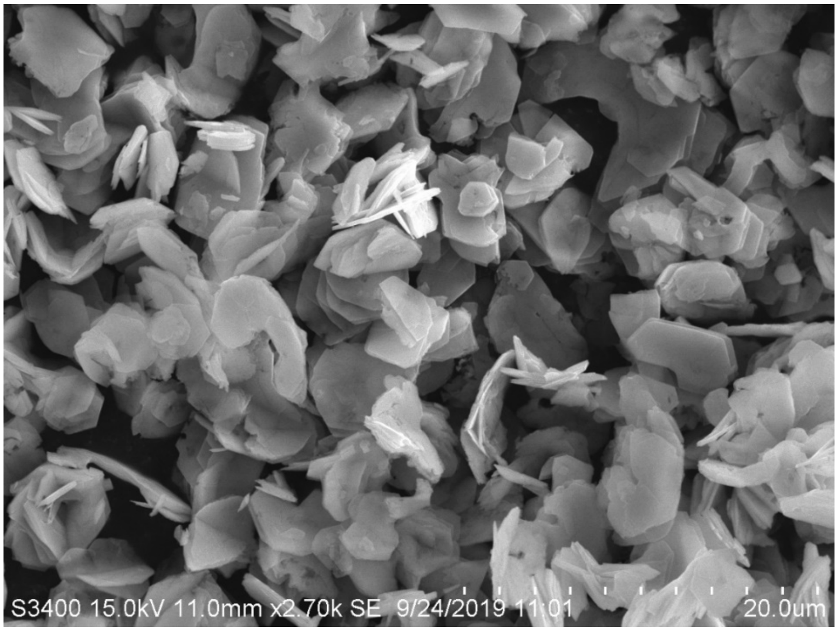
Figure 3-8 XRD spectrum of ferrate(VI) resultant particle after ferrate(VI) treatment of phosphate in distilled water (Fe(VI)=5.0 mg/L; initial phosphate =1.000 mg/L P; and initial pH= 6.5)



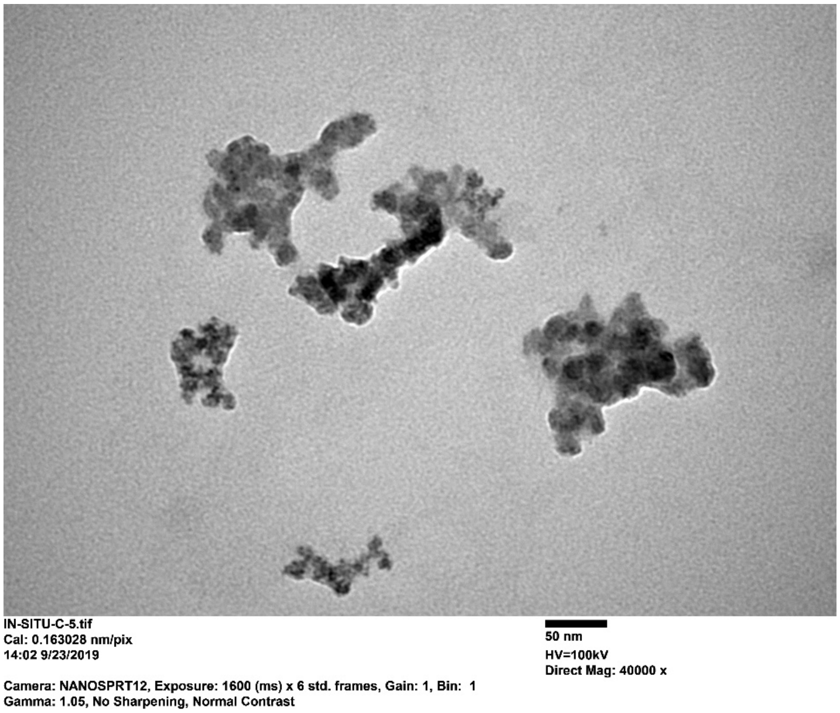
(a)

(b)

Figure 3-9 Surface element analysis of the crystalline fraction of ferrate(VI) resultant particle after ferrate(VI) treatment of phosphate in distilled water (Fe(VI)=5.0 mg/L; initial phosphate =1.000 mg/L P; initial pH= 6.5)



(a)



(b)

Figure 3-10 Morphology of the crystalline fraction in the ferrate(VI) resultant solid samples produced after ferrate(VI) treatment of phosphate in distilled water: (a) SEM; and (b) TEM (Fe(VI)=5.0 mg/L; initial phosphate =1.000 mg/L P; initial pH= 6.5)

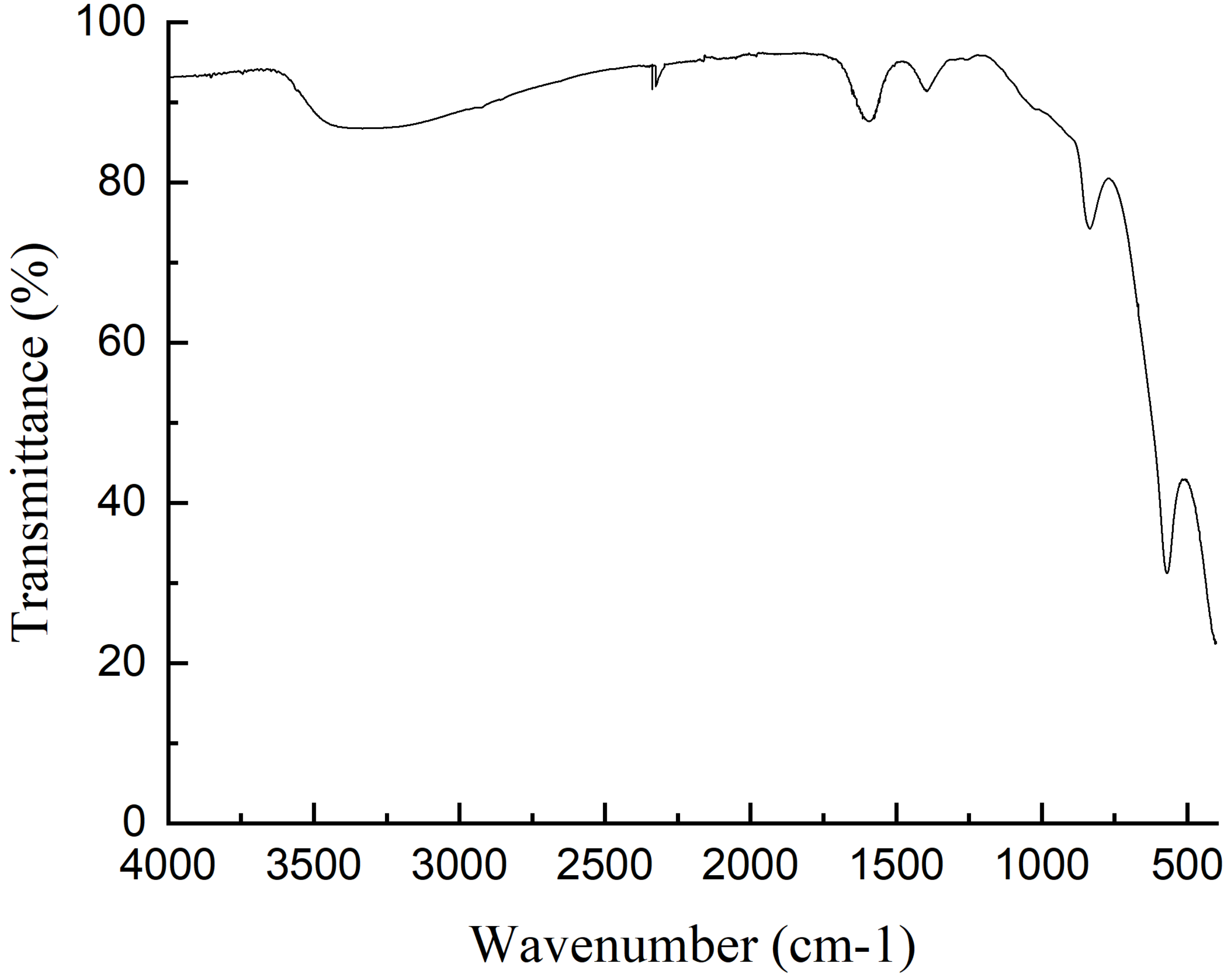


Figure 3-11 FTIR spectrum of the crystalline fraction in the ferrate(VI) resultant solid samples produced after ferrate(VI) treatment of phosphate in distilled (Fe(VI)=5.0 mg/L; initial phosphate =1.000 mg/L P; initial pH= 6.5)

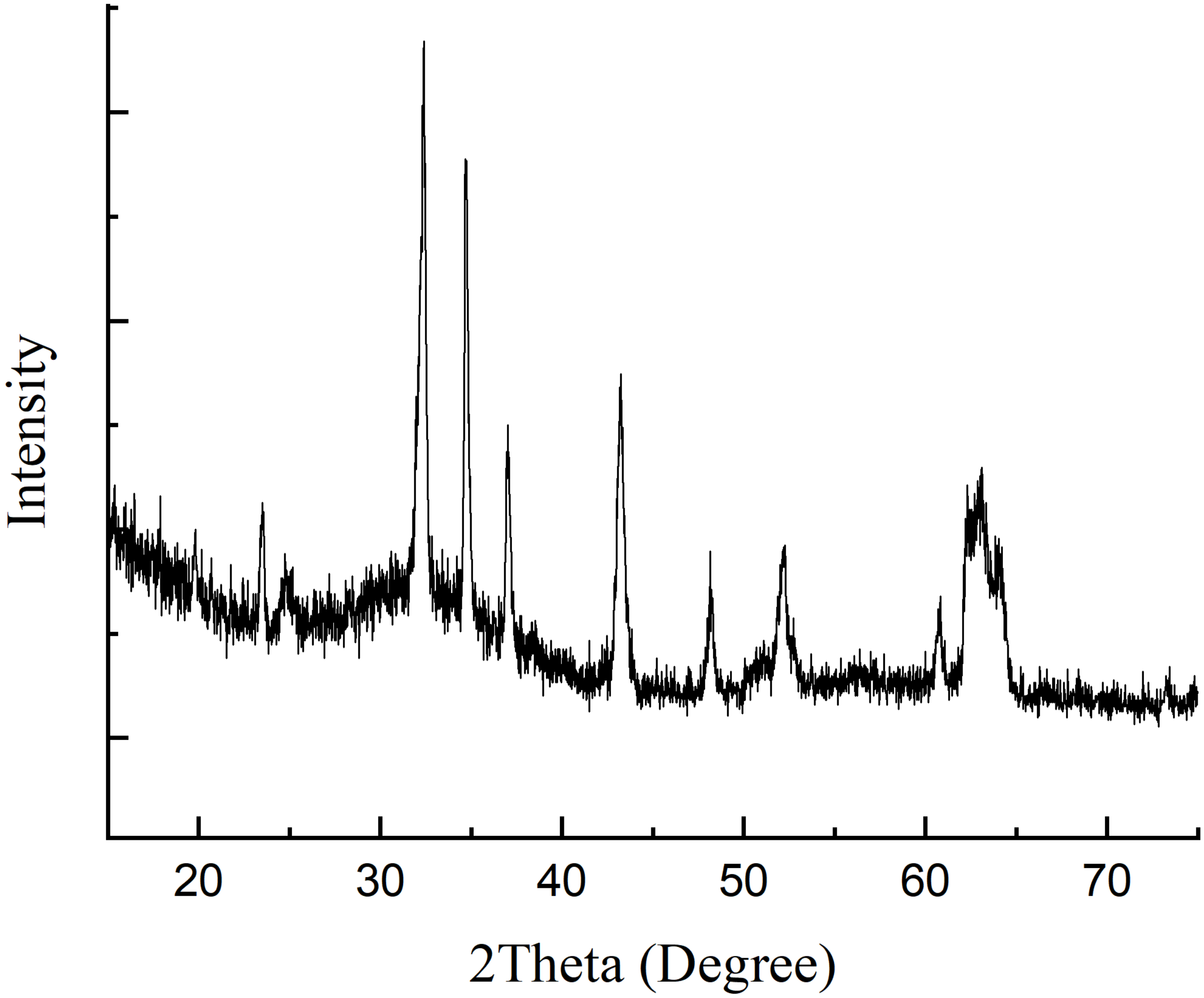


Figure 3-12 XRD patterns of the crystalline fraction in the ferrate(VI) resultant solid samples produced after ferrate(VI) treatment of phosphate in distilled water (Fe(VI)=5.0 mg/L; initial phosphate =1.000 mg/L P; initial pH= 6.5)

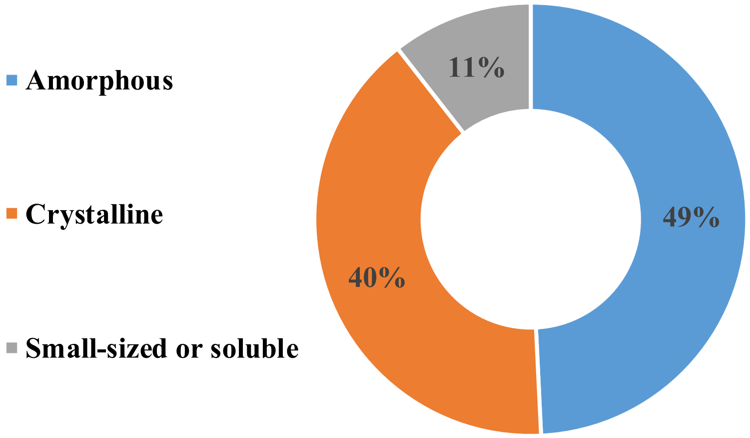


Figure 3-13 Fractions of different iron species in the ferrate(VI) resultant solid samples produced after ferrate(VI) treatment of phosphate in distilled water: (Fe(VI)=5.0 mg/L; initial phosphate =1.000 mg/L P; initial pH= 6.5; amorphous and crystalline iron existed in the iron (hydr)oxide particles with the sizes over 0.45 µm, while small-sized or soluble iron existed in the filtrate after 45 µm membrane filtration)

3.5 References

Acevedo, B., Oehmen, A., Carvalho, G., Seco, A., Borrás, L., & Barat, R. (2012). Metabolic shift of polyphosphate-accumulating organisms with different levels of polyphosphate storage. *Water Research, 46*(6), 1889-1900. Retrieved from http://www.sciencedirect.com/science/article/pii/S0043135412000097. doi:https://doi.org/10.1016/j.watres.2012.01.003

Anquandah, G. A. K., Sharma, V. K., Knight, D. A., Batchu, S. R., & Gardinali, P. R. (2011). Oxidation of Trimethoprim by Ferrate(VI): Kinetics, Products, and Antibacterial Activity. *Environmental Science & Technology, 45*(24), 10575-10581. Retrieved from <Go to ISI>://WOS:000298118300044. doi:10.1021/es202237g

Anquandah, G. A. K., Sharma, V. K., Panditi, V. R., Gardinali, P. R., Kim, H., & Oturan, M. A. (2013). Ferrate(VI) oxidation of propranolol: Kinetics and products. *Chemosphere, 91*(1), 105-109. Retrieved from <Go to ISI>://WOS:000315615700017. doi:10.1016/j.chemosphere.2012.12.001

Boonchom, B., & Puttawong, S. (2010). Thermodynamics and kinetics of the dehydration reaction of FePO4 center dot 2H(2)O. *Physica B-Condensed Matter, 405*(9), 2350-2355. Retrieved from <Go to ISI>://WOS:000277719500042. doi:10.1016/j.physb.2010.02.046

Brunner, P. H. (2010). Substance Flow Analysis as a Decision Support Tool for Phosphorus Management. *Journal of Industrial Ecology, 14*(6), 870-873. Retrieved from https://doi.org/10.1111/j.1530-9290.2010.00300.x

https://onlinelibrary.wiley.com/doi/abs/10.1111/j.1530-9290.2010.00300.x. doi:10.1111/j.1530-9290.2010.00300.x

Bunce, J. T., Ndam, E., Ofiteru, I. D., Moore, A., & Graham, D. W. (2018). A Review of Phosphorus Removal Technologies and Their Applicability to Small-Scale Domestic Wastewater Treatment Systems. *Frontiers in Environmental Science, 6*(8). Retrieved from https://www.frontiersin.org/article/10.3389/fenvs.2018.00008

https://fjfsdata01prod.blob.core.windows.net/articles/files/290291/pubmed-zip/.versions/1/.package-entries/fenvs-06-00008/fenvs-06-00008.pdf?sv=2015-12-11&sr=b&sig=ZL%2FHUO27EoXwbiyJzM0dBroedfS05dQLV7jLVcPANGQ%3D&se=2019-06-02T14%3A08%3A07Z&sp=r&rscd=attachment%3B%20filename%2A%3DUTF-8%27%27fenvs-06-00008.pdf. doi:10.3389/fenvs.2018.00008

Butkus, M. A., Grasso, D., Schulthess, C. P., & Wijnja, H. (1998). Surface complexation modeling of phosphate adsorption by water treatment residual. *Journal of Environmental Quality, 27*(5), 1055-1063.

Clark, D. L., Hunt, G., Kasch, M. S., Lemonds, P. J., Moen, G. M., & Neethling, J. B. (2010). *Nutrient Management: Regulatory Approaches to Protect Water Quality: Volume 1 – Review of Existing Practices*. Retrieved from https://doi.org/10.2166/9781780403465 doi:10.2166/9781780403465

Comber, S., Gardner, M., Georges, K., Blackwood, D., & Gilmour, D. (2013). Domestic source of phosphorus to sewage treatment works. *Environmental Technology, 34*(10), 1349-1358. Retrieved from https://doi.org/10.1080/09593330.2012.747003

https://www.tandfonline.com/doi/abs/10.1080/09593330.2012.747003. doi:10.1080/09593330.2012.747003

Cornell, R. M., Giovanoli, R., & Schneider, W. (1989). Review of the hydrolysis of iron (III) and the crystallization of amorphous iron (III) hydroxide hydrate. *Journal of Chemical Technology and Biotechnology, 46*(2), 115-134.

Cornell, R. M., & Schwertmann, U. (2003). *The iron oxides: structure, properties, reactions, occurrences and uses*: John Wiley & Sons.

Costarramone, N., Kneip, A., & Castetbon, A. (2004). Ferrate(VI) oxidation of cyanide in water. *Environmental Technology, 25*(8), 945-955. Retrieved from <Go to ISI>://WOS:000223974100011.

Crittenden, J. C., Trussell, R. R., Hand, D. W., Howe, K. J., & Tchobanoglous, G. (2012). *MWH's Water Treatment: Principles and Design*: John Wiley & Sons.

Darch, T., Blackwell, M. S. A., Hawkins, J. M. B., Haygarth, P. M., & Chadwick, D. (2014). A Meta-Analysis of Organic and Inorganic Phosphorus in Organic Fertilizers, Soils, and Water: Implications for Water Quality. *Critical Reviews in Environmental Science and Technology, 44*(19), 2172-2202. Retrieved from https://doi.org/10.1080/10643389.2013.790752

https://www.tandfonline.com/doi/abs/10.1080/10643389.2013.790752.

doi:10.1080/10643389.2013.790752

Derrick, M. R., Stulik, D., & Landry, J. M. (2000). *Infrared spectroscopy in conservation science*: Getty Publications.

Dueñas, J. F., Alonso, J. R., Rey, À. F., & Ferrer, A. S. (2003). Characterisation of phosphorous forms in wastewater treatment plants. *Journal of Hazardous Materials, 97*(1), 193-205. Retrieved from http://www.sciencedirect.com/science/article/pii/S0304389402002601. doi:https://doi.org/10.1016/S0304-3894(02)00260-1

Elzinga, E. J., & Sparks, D. L. (2007). Phosphate adsorption onto hematite: An in situ ATR-FTIR investigation of the effects of pH and loading level on the mode of phosphate surface complexation. *Journal of Colloid and Interface Science, 308*(1), 53-70.

Falkowski, P., Scholes, R. J., Boyle, E., Canadell, J., Canfield, D., Elser, J., . . . Steffen, W. (2000). The Global Carbon Cycle: A Test of Our Knowledge of Earth as a System. *Science, 290*(5490), 291. Retrieved from http://science.sciencemag.org/content/290/5490/291.abstract

https://science.sciencemag.org/content/sci/290/5490/291.full.pdf.

doi:10.1126/science.290.5490.291

Fan, M. H., Brown, R. C., & Huang, C. P. (2002). Preliminary studies of the oxidation of arsenic(III) by potassium ferrate. *International Journal of Environment and Pollution, 18*(1), 91-96. Retrieved from <Go to ISI>://WOS:000178438200008. doi:10.1504/ijep.2002.000698

Frossard, E., Bauer, J. P., & Lothe, F. (1997). Evidence of vivianite in FeSO4-flocculated sludges. *Water Research, 31*(10), 2449-2454. Retrieved from

Gandhi, R., Ray, A. K., Sharma, V. K., & Nakhla, G. (2014). Treatment of Combined Sewer Overflows Using Ferrate(VI). *Water Environment Research, 86*(11), 2202-2211. Retrieved from <Go to ISI>://WOS:000343915000006. doi:10.2175/106143014x14062131178475

Ghernaout, D., Ghernaout, B., & Naceur, M. W. (2011). Embodying the chemical water treatment in the green chemistry—A review. *Desalination, 271*(1), 1-10. Retrieved from http://www.sciencedirect.com/science/article/pii/S0011916411000439 https://www.sciencedirect.com/science/article/pii/S0011916411000439?via%3Dihub. doi:https://doi.org/10.1016/j.desal.2011.01.032

Gimsing, A. L., & Borggaard, O. K. (2007). Phosphate and glyphosate adsorption by hematite and ferrihydrite and comparison with other variable-charge minerals. *Clays and Clay Minerals, 55*(1), 108-114.

Ginn, B., Meile, C., Wilmoth, J., Tang, Y., & Thompson, A. (2017). Rapid iron reduction rates are stimulated by high-amplitude redox fluctuations in a tropical forest soil. *Environmental Science & Technology, 51*(6), 3250-3259.

Gombos, E., Barkács, K., Felföldi, T., Vértes, C., Makó, M., Palkó, G., & Záray, G. (2013). Removal of organic matters in wastewater treatment by ferrate(VI)-technology. *Microchemical Journal, 107*, 115-120. Retrieved from http://www.sciencedirect.com/science/article/pii/S0026265X12001373. doi:https://doi.org/10.1016/j.microc.2012.05.019

Goodwill, J. E., Jiang, Y., Reckhow, D. A., Gikonyo, J., & Tobiason, J. E. (2015). Characterization of Particles from Ferrate Preoxidation. *Environmental Science & Technology, 49*(8), 4955-4962.

Hu, L. H., Page, M. A., Sigstam, T., Kohn, T., Marinas, B. J., & Strathmann, T. J. (2012). Inactivation of Bacteriophage MS2 with Potassium Ferrate(VI). *Environmental Science & Technology, 46*(21), 12079-12087. Retrieved from <Go to ISI>://WOS:000310665000072. doi:10.1021/es3031962

Huang, X.-L., & Shenker, M. (2004). Water-Soluble and Solid-State Speciation of Phosphorus in Stabilized Sewage Sludge. *Journal of Environmental Quality, 33*(5), 1895-1903. Retrieved from http://dx.doi.org/10.2134/jeq2004.1895. doi:10.2134/jeq2004.1895

Jessen, A., Randall, A., Reinhart, D., & Daly, L. (2008). Effectiveness and Kinetics of Ferrate as a Disinfectant for Ballast Water. *Water Environment Research, 80*(6), 561-569. Retrieved from <Go to ISI>://WOS:000261127500010. doi:10.2175/193864708x267423

Jetoo, S., Grover, I. V., & Krantzberg, G. (2015). The Toledo Drinking Water Advisory: Suggested Application of the Water Safety Planning Approach. *Sustainability, 7*(8). Retrieved from https://res.mdpi.com/sustainability/sustainability-07-09787/article_deploy/sustainability-07-09787-v2.pdf?filename=&attachment=1. doi:10.3390/su7089787

Jiang, J. Q. (2007). Research progress in the use of ferrate(VI) for the environmental remediation. *Journal of Hazardous Materials, 146*(3), 617-623. Retrieved from <Go to ISI>://WOS:000248524500030. doi:10.1016/j.jhazmat.2007.04.075

Jiang, J. Q., & Lloyd, B. (2002). Progress in the development and use of ferrate(VI) salt as an oxidant and coagulant for water and wastewater treatment. *Water Research, 36*(6), 1397-1408. Retrieved from <Go to ISI>://WOS:000174719300001. doi:10.1016/s0043-1354(01)00358-x

Jiang, J. Q., Wang, S., & Panagoulopoulos, A. (2006). The exploration of potassium ferrate(VI) as a disinfectant/coagulant in water and wastewater treatment. *Chemosphere, 63*(2), 212-219. Retrieved from <Go to ISI>://WOS:000236989600004. doi:10.1016/j.chemosphere.2005.08.020

Jiang, J. Q., Wang, S., & Panagoulopoulos, A. (2007). The role of potassium ferrate(VI) in the inactivation of Escherichia coli and in the reduction of COD for water remediation. *Desalination, 210*(1-3), 266-273. Retrieved from <Go to ISI>://WOS:000247159700027. doi:10.1016/j.desal.2006.05.051

Kooti, M., Tarassoli, A., Javadi, H., & Jorfi, M. (2008). A Facile Conversion of Alcohols to Esters Mediated by Potassium Ferrate. *E-Journal of Chemistry, 5*(4), 718-722. Retrieved from <Go to ISI>://WOS:000267204100007

http://downloads.hindawi.com/journals/jchem/2008/589834.pdf. doi:10.1155/2008/589834

Kralchevska, R. P., Prucek, R., Kolařík, J., Tuček, J., Machala, L., Filip, J., . . . Zbořil, R. (2016). Remarkable efficiency of phosphate removal: Ferrate(VI)-induced in situ sorption on core-shell nanoparticles. *Water Research, 103*, 83-91.

Kralchevska, R. P., Prucek, R., Kolařík, J., Tuček, J., Machala, L., Filip, J., . . . Zbořil, R. (2016). Remarkable efficiency of phosphate removal: Ferrate(VI)-induced in situ sorption on core-shell nanoparticles. *Water Research, 103*, 83-91. Retrieved from http://www.sciencedirect.com/science/article/pii/S0043135416305255. doi:https://doi.org/10.1016/j.watres.2016.07.021

Kuo, S., & Lotse, E. (1973). Kinetics of phosphate adsorption and desorption by hematite and gibbsite1. *Soil Science, 116*(6), 400-406.

Kwon, J. H., Kim, I. K., Park, K. Y., Kim, Y. D., & Cho, Y. H. (2014). Removal of phosphorus and coliforms from secondary effluent using ferrate(VI). *Ksce Journal of Civil Engineering, 18*(1), 81-85. Retrieved from <Go to ISI>://WOS:000329104300011

https://link.springer.com/content/pdf/10.1007%2Fs12205-013-0024-7.pdf. doi:10.1007/s12205-013-0024-7

Lee, Y., Cho, M., Kim, J. Y., & Yoon, J. (2004). Chemistry of ferrate (Fe(VI)) in aqueous solution and its applications as a green chemical. *Journal of Industrial and Engineering Chemistry, 10*(1), 161-171. Retrieved from <Go to ISI>://WOS:000188469500021.

Lee, Y., Kissner, R., & von Gunten, U. (2014). Reaction of Ferrate(VI) with ABTS and Self-Decay of Ferrate(VI): Kinetics and Mechanisms. *Environmental Science & Technology, 48*(9), 5154-5162. Retrieved from <Go to ISI>://WOS:000335720100062

https://pubs.acs.org/doi/pdfplus/10.1021/es500804g. doi:10.1021/es500804g

Lee, Y., Um, I. H., & Yoon, J. (2003). Arsenic(III) oxidation by iron(VI) (ferrate) and subsequent removal of arsenic(V) by iron(III) coagulation. *Environmental Science & Technology, 37*(24), 5750-5756. Retrieved from <Go to ISI>://WOS:000187248000038. doi:10.1021/es034203+

Lee, Y., & von Gunten, U. (2010). Oxidative transformation of micropollutants during municipal wastewater treatment: Comparison of kinetic aspects of selective (chlorine, chlorine dioxide, ferrate(VI), and ozone) and non-selective oxidants (hydroxyl radical). *Water Research, 44*(2), 555-566. Retrieved from <Go to ISI>://WOS:000275353900016. doi:10.1016/j.watres.2009.11.045

Lee, Y., Yoon, J., & von Gunten, U. (2005). Spectrophotometric determination of ferrate (Fe(Vl)) in water by ABTS. *Water Research, 39*(10), 1946-1953. Retrieved from <Go to ISI>://WOS:000230241200002. doi:10.1016/j.watres.2005.03.005

Lee, Y., Zimmermann, S. G., Kieu, A. T., & von Gunten, U. (2009). Ferrate (Fe(VI)) Application for Municipal Wastewater Treatment: A Novel Process for Simultaneous Micropollutant Oxidation and Phosphate Removal. *Environmental Science & Technology, 43*(10), 3831-3838. Retrieved from https://doi.org/10.1021/es803588k. doi:10.1021/es803588k

Lim, M., & Kim, M. J. (2010). Effectiveness of Potassium Ferrate (K2FeO4) for Simultaneous Removal of Heavy Metals and Natural Organic Matters from River Water. *Water Air and*

Soil Pollution, 211(1-4), 313-322. Retrieved from <Go to ISI>://WOS:000282159200027. doi:10.1007/s11270-009-0302-7

Loganathan, P., Vigneswaran, S., Kandasamy, J., & Bolan, N. S. (2014). Removal and Recovery of Phosphate From Water Using Sorption. *Critical Reviews in Environmental Science and Technology, 44*(8), 847-907. Retrieved from https://doi.org/10.1080/10643389.2012.741311

https://www.tandfonline.com/doi/abs/10.1080/10643389.2012.741311. doi:10.1080/10643389.2012.741311

Luedecke, C., Hermanowicz, S. W., & Jenkins, D. (1988). PRECIPITATION OF FERRIC PHOSPHATE IN ACTIVATED SLUDGE: A CHEMICAL MODEL AND ITS VERIFICATION. In L. Lijklema, K. R. Imhoff, K. J. Ives, D. Jenkins, R. G. Ludwig, M. Suzuki, D. F. Toerien, A. B. Wheatland, A. Milburn, & E. J. Izod (Eds.), *Water Pollution Research and Control Brighton* (pp. 325-337): Pergamon.

Lv, D. Y., Zheng, L., Zhang, H. Q., & Deng, Y. (2018). Coagulation of colloidal particles with ferrate(vi). *Environmental Science-Water Research & Technology, 4*(5), 701-710. Retrieved from <Go to ISI>://WOS:000431434000009

Macklon, A. E. S., Grayston, S. J., Shand, C. A., Sim, A., Sellars, S., & Ord, B. G. (1997). Uptake and transport of phosphorus by Agrostis capillaris seedlings from rapidly hydrolysed organic sources extracted from32 P-labelled bacterial cultures. *Plant and Soil, 190*(1), 163-167. Retrieved from https://doi.org/10.1023/A:1004294617461

Maier, G., Nimmo-Smith, R. J., Glegg, G. A., Tappin, A. D., & Worsfold, P. J. (2009). Estuarine eutrophication in the UK: current incidence and future trends. *Aquatic Conservation:*

Marine and Freshwater Ecosystems, 19(1), 43-56. Retrieved from https://doi.org/10.1002/aqc.982

https://onlinelibrary.wiley.com/doi/abs/10.1002/aqc.982. doi:10.1002/aqc.982

Meinikmann, K., Hupfer, M., & Lewandowski, J. (2015). Phosphorus in groundwater discharge – A potential source for lake eutrophication. *Journal of Hydrology, 524*, 214-226. Retrieved from http://www.sciencedirect.com/science/article/pii/S0022169415001432

Nguyen, T. T., Ngo, H. H., & Guo, W. (2013). Pilot scale study on a new membrane bioreactor hybrid system in municipal wastewater treatment. *Bioresource Technology, 141*, 8-12. Retrieved from http://www.sciencedirect.com/science/article/pii/S0960852413004938. doi:https://doi.org/10.1016/j.biortech.2013.03.125

Okada, S., Yamamoto, T., Okazaki, Y., Yamaki, J.-i., Tokunaga, M., & Nishida, T. (2005). Cathode properties of amorphous and crystalline FePO4. *Journal of Power Sources, 146*(1-2), 570-574.

Pironon, J., & Barrès, O. (1992). Influence of brine-hydrocarbon interactions on FT-IR microspectroscopic analyses of intracrystalline liquid inclusions. *Geochimica Et Cosmochimica Acta, 56*(1), 169-174.

Prucek, R., Tucek, J., Kolarik, J., Filip, J., Marusak, Z., Sharma, V. K., & Zboril, R. (2013). Ferrate(VI)-Induced Arsenite and Arsenate Removal by In Situ Structural Incorporation into Magnetic Iron(III) Oxide Nanoparticles. *Environmental Science & Technology, 47*(7), 3283-3292. Retrieved from <Go to ISI>://WOS:000317173100036. doi:10.1021/es3042719

Qin, B., Zhu, G., Gao, G., Zhang, Y., Li, W., Paerl, H. W., & Carmichael, W. W. (2010). A Drinking Water Crisis in Lake Taihu, China: Linkage to Climatic Variability and Lake

Management. *Environmental Management, 45*(1), 105-112. Retrieved from https://doi.org/10.1007/s00267-009-9393-6

https://link.springer.com/content/pdf/10.1007%2Fs00267-009-9393-6.pdf. doi:10.1007/s00267-009-9393-6

Qin, C., Liu, H., Liu, L., Smith, S., Sedlak, D. L., & Gu, A. Z. (2015). Bioavailability and characterization of dissolved organic nitrogen and dissolved organic phosphorus in wastewater effluents. *Science of The Total Environment, 511*, 47-53. Retrieved from http://www.sciencedirect.com/science/article/pii/S0048969714015873. doi:https://doi.org/10.1016/j.scitotenv.2014.11.005

Reyes, I., & Torrent, J. (1997). Citrate-ascorbate as a highly selective extractant for poorly crystalline iron oxides. *Soil Science Society of America Journal, 61*(6), 1647-1654. Retrieved from <Go to ISI>://WOS:A1997YK30100015.

Schimanke, G., & Martin, M. (2000). In situ XRD study of the phase transition of nanocrystalline maghemite (gamma-Fe2O3) to hematite (alpha-Fe2O3). *Solid State Ionics, 136*, 1235-1240. Retrieved from <Go to ISI>://WOS:000165996600182. doi:10.1016/s0167-2738(00)00593-2

Seviour, R. J., Mino, T., & Onuki, M. (2003). The microbiology of biological phosphorus removal in activated sludge systems. *FEMS Microbiology Reviews, 27*(1), 99-127. Retrieved from https://doi.org/10.1016/S0168-6445(03)00021-4

Sharma, V. K. (2002). Ferrate(V) oxidation of pollutants: a premix pulse radiolysis study. *Radiation Physics and Chemistry, 65*(4-5), 349-355. Retrieved from <Go to ISI>://WOS:000179423200008. doi:10.1016/s0969-806x(02)00335-3

Sharma, V. K. (2008). Oxidative transformations of environmental pharmaceuticals by Cl(2), ClO(2), O(3), and Fe(VI): Kinetics assessment. *Chemosphere, 73*(9), 1379-1386. Retrieved from <Go to ISI>://WOS:000261249300001

https://ac.els-cdn.com/S0045653508010898/1-s2.0-S0045653508010898-main.pdf?_tid=e71c4bbe-af82-47e0-88fd-3c6c7b2f5f48&acdnat=1538078217_3f5e12c16ddfe6e7c870982586380b9a. doi:10.1016/j.chemosphere.2008.08.033

Sharma, V. K. (2010). Oxidation of nitrogen-containing pollutants by novel ferrate(VI) technology: A review. *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering, 45*(6), 645-667. Retrieved from <Go to ISI>://WOS:000275852200001. doi:10.1080/10934521003648784

Sharma, V. K., Burnett, C. R., O'Connor, D. B., & Cabelli, D. (2002). Iron(VI) and iron(V) oxidation of thiocyanate. *Environmental Science & Technology, 36*(19), 4182-4186. Retrieved from <Go to ISI>://WOS:000178351800040

https://pubs.acs.org/doi/abs/10.1021/es020570u. doi:10.1021/es020570u

Shimamura, K., Homma, Y., Watanabe, A., & Tanaka, T. (2003). Research on MAP Recovery Conditions using a Fluidized-bed Crystallized Phosphorous Removal System. *Journal of Water and Environment Technology, 1*(1), 73-78. Retrieved from https://www.jstage.jst.go.jp/article/jwet/1/1/1_1_73/_pdf. doi:10.2965/jwet.2003.73

Shon, H., Vigneswaran, S., & Snyder, S. A. (2006). Effluent organic matter (EfOM) in wastewater: constituents, effects, and treatment. *Critical reviews in environmental science and technology, 36*(4), 327-374.

Smith, S., Takács, I., Murthy, S., Daigger, G. T., & Szabó, A. (2008). Phosphate Complexation Model and Its Implications for Chemical Phosphorus Removal. *Water Environment Research, 80*(5), 428-438. Retrieved from https://doi.org/10.1002/j.1554-7531.2008.tb00349.x

https://onlinelibrary.wiley.com/doi/abs/10.1002/j.1554-7531.2008.tb00349.x?sid=nlm%3Apubmed. doi:10.1002/j.1554-7531.2008.tb00349.x

Smolders, G. J. F., van der Meij, J., van Loosdrecht, M. C. M., & Heijnen, J. J. (1994). Model of the anaerobic metabolism of the biological phosphorus removal process: Stoichiometry and pH influence. *Biotechnology and Bioengineering, 43*(6), 461-470. Retrieved from https://doi.org/10.1002/bit.260430605

https://onlinelibrary.wiley.com/doi/abs/10.1002/bit.260430605. doi:10.1002/bit.260430605

Song, Y. L., Deng, Y., & Jung, C. I. (2016). Mitigation and degradation of natural organic matters (NOMs) during ferrate(VI) application for drinking water treatment. *Chemosphere, 146*, 145-153. Retrieved from <Go to ISI>://WOS:000369457000017

https://ac.els-cdn.com/S0045653515304562/1-s2.0-S0045653515304562-main.pdf?_tid=878e27dd-6420-43dc-b89b-031404e3770d&acdnat=1538079220_9a2d1e8a37953b7bfadc08879ce65d0b. doi:10.1016/j.chemosphere.2015.12.001

Stumm, W. (1992a). Chemistry of the solid-water interface. In: Wiley, New York.

Stumm, W. (1992b). *Chemistry of the solid-water interface: processes at the mineral-water and particle-water interface in natural systems*: John Wiley & Son Inc.

Szabó, A., Takács, I., Murthy, S., Daigger, G. T., Licskó, I., & Smith, S. (2008). Significance of Design and Operational Variables in Chemical Phosphorus Removal. *Water Environment Research, 80*(5), 407-416. Retrieved from https://doi.org/10.2175/106143008X268498

https://onlinelibrary.wiley.com/doi/abs/10.2175/106143008X268498?sid=nlm%3Apubmed. doi:10.2175/106143008X268498

Talaiekhozani, A., Talaei, M. R., & Rezania, S. (2017). An overview on production and application of ferrate(VI) for chemical oxidation, coagulation and disinfection of water and wastewater. *Journal of Environmental Chemical Engineering, 5*(2), 1828-1842. Retrieved from http://www.sciencedirect.com/science/article/pii/S2213343717301161

https://www.sciencedirect.com/science/article/pii/S2213343717301161?via%3Dihub. doi:https://doi.org/10.1016/j.jece.2017.03.025

Tchobanoglous, G., Stensel, H., Tsuchihashi, R., Burton, F., Abu-Orf, M., Bowden, G., & Pfrang, W. (2014). Wastewater Engineering: Treatment and Resource Recovery, ; Metcalf and Eddy I AECOM. In: McGraw-Hill Book Company: New York, NY.

Thistleton, J., Berry, T. A., Pearce, P., & Parsons, S. A. (2002). Mechanisms of Chemical Phosphorus Removal II: Iron (III) Salts. *Process Safety and Environmental Protection, 80*(5), 265-269. Retrieved from

Thompson, S. K., & Cotner, J. B. (2018). Bioavailability of Dissolved Organic Phosphorus in Temperate Lakes. *Frontiers in Environmental Science, 6*, 62. Retrieved from https://www.frontiersin.org/article/10.3389/fenvs.2018.00062.

Waite, T. D. (2012). On-Site Production of Ferrate for Water and Wastewater Purification. *American Laboratory, 44*(10), 26-28. Retrieved from <Go to ISI>://WOS:000312286700006.

Wang, Xiaoming, Liu, Fan, Tan, Wenfeng, Li, Wei, Feng, Xionghan, & Sparks, D. L. (2013). Characteristics of Phosphate Adsorption-Desorption Onto Ferrihydrite: Comparison With Well-Crystalline Fe (Hydr)Oxides. *Soil Science, 178*(1), 1-11. Retrieved from https://journals.lww.com/soilsci/Fulltext/2013/01000/Characteristics_of_Phosphate_Adsorption_Desorption.1.aspx. doi:10.1097/SS.0b013e31828683f8

Wilfert, P., Kumar, P. S., Korving, L., Witkamp, G. J., & van Loosdrecht, M. C. M. (2015). The Relevance of Phosphorus and Iron Chemistry to the Recovery of Phosphorus from Wastewater: A Review. *Environmental Science & Technology, 49*(16), 9400-9414. Retrieved from <Go to ISI>://WOS:000359891700003

https://pubs.acs.org/doi/pdfplus/10.1021/acs.est.5b00150. doi:10.1021/acs.est.5b00150

Withers, J. A. P., Neal, C., Jarvie, P. H., & Doody, G. D. (2014). Agriculture and Eutrophication: Where Do We Go from Here? *Sustainability, 6*(9). Retrieved from https://res.mdpi.com/d_attachment/sustainability/sustainability-06-05853/article_deploy/sustainability-06-05853.pdf. doi:10.3390/su6095853

Worsfold, P., McKelvie, I., & Monbet, P. (2016). Determination of phosphorus in natural waters: A historical review. *Analytica Chimica Acta, 918*, 8-20. Retrieved from http://www.sciencedirect.com/science/article/pii/S0003267016302860

https://www.sciencedirect.com/science/article/pii/S0003267016302860?via%3Dihub.

doi:https://doi.org/10.1016/j.aca.2016.02.047

Yeoman, S., Stephenson, T., Lester, J. N., & Perry, R. (1988). The removal of phosphorus during wastewater treatment: A review. *Environmental Pollution, 49*(3), 183-233. Retrieved from http://www.sciencedirect.com/science/article/pii/0269749188902096. doi:https://doi.org/10.1016/0269-7491(88)90209-6

Yuan, Z., Jiang, S., Sheng, H., Liu, X., Hua, H., Liu, X., & Zhang, Y. (2018). Human Perturbation of the Global Phosphorus Cycle: Changes and Consequences. *Environmental Science & Technology, 52*(5), 2438-2450. Retrieved from https://doi.org/10.1021/acs.est.7b03910

https://pubs.acs.org/doi/10.1021/acs.est.7b03910. doi:10.1021/acs.est.7b03910

Zainuri, M. (2017). *Hematite from Natural Iron Stones as Microwave Absorbing Material on X-Band Frequency Ranges.* Paper presented at the IOP Conference Series: Materials Science and Engineering.

Zheng, L., & Deng, Y. (2016). Settleability and characteristics of ferrate(VI)-induced particles in advanced wastewater treatment. *Water Research, 93*, 172-178.

Chapter 4 Removal of Organic Phosphorus from Secondary Effluent with Ferrate(VI)

4.1 Introduction and Objectives

4.1.1 Eutrophication and Organic Phosphorus

Eutrophication in natural water systems is a process to describe the excessive growth of algal biomass because of excessive input of nutrients, including nitrogen and phosphorus (Schindler et al., 2008; Thompson & Cotner, 2018). The increasing nitrogen and phosphorus fluxes into the freshwater system are primarily caused by human activities through various point and non-point pollution sources. The undesirable algal bloom can significantly degrade water quality, thereby posing a serious threat to natural water systems in the world (Falkowski et al., 2000; Thompson & Cotner, 2018). Of note, the excessive input of phosphorus has been frequently reported to trigger the overgrowth of phytoplankton and algae species, even at a concentration as low as 0.01 mg/L as P (Smil, 2000). As discussed in Chapter 1, eutrophication can seriously degrade the quality of aquatic ecosystem and pose a threat to public health, particularly when the polluted water serves as a drinking water source.

Phosphorus is a major nutrient to cause eutrophication in natural water bodies. The inorganic phosphate, as investigated in Chapter 2 and 3, accounts for a major fraction in phosphorus present in municipal wastewater (Darch, Blackwell, Hawkins, Haygarth, & Chadwick, 2014; Macklon et al., 1997). However, the recent attention has been directed to organic phosphorus. Although its fraction in the total phosphorus of raw municipal wastewater is very low, organic phosphorus is typically recalcitrant to conventional wastewater treatment, so that its portion in treated wastewater cannot be overlooked. Thompson and Cotner (2018) pointed out that the availability of dissolved organic phosphorus to aquatic organisms might be associated with the occurrence of eutrophication. Organic phosphorus refers to chemical species having carbon and phosphorus atoms in the same molecule (Baldwin, 2013). Wetzel (2001) states that organic phosphorus occupies 25-50% of the total phosphorus in freshwater systems. Recent studies have showed that certain forms of organic phosphorus can act as a phosphorus source for aquatic organisms when phosphate is limited or absent in freshwater systems (Björkman & Karl, 2003; Cotner & Wetzel, 1992; Li & Brett, 2013; Nausch & Nausch, 2007). Although organic phosphorus is not directly available to plants and organisms in the most cases, they can release phosphatase enzymes to hydrolyze organic phosphorus and then transform it into phosphate for uptake (Cotner & Wetzel, 1992; Dyhrman et al., 2006; Lu, Yang, Zhang, & Wu, 2014; Sañudo-Wilhelmy, 2006; Toor, Condron, Di, Cameron, & Cade-Menun, 2003). The role of organic phosphorus, in comparison with its inorganic counterparts, in eutrophication occurring in freshwater has been underestimated. In fact, the presence of organic phosphorus can potentially cause eutrophication in freshwater even in the absence of phosphate.

4.1.2 Organic Phosphorus in Freshwater

There are five classes of organic phosphorus that have been well identified and characterized in the freshwater systems, including nucleic acids, other nucleotides, inositol phosphates, phospholipids, and phosphonates (Baldwin, 2013). Nucleic acids include deoxyribonucleic acid (DNA) and ribonucleic acid (RNA), which are found in all living things. They have been recognized as the common forms of dissolved organic phosphorus (Baldwin, 2013). Algae and bacteria are the leading sources of DNA and RNA in freshwater (Ishii, Kawabata, Nakano, Min, & Takata, 1998; Siuda & GÃƒÂ¼de, 1996). The other nucleotides refer to organic phosphorus like adenosine 5’-triphosphate (ATP) and adenosine 5’-monophosphate (AMP), which are involved in cellular activities in organisms (Baldwin, 2013). Organic phosphorus as nucleotides in the freshwater systems has a relatively low concentration. Organisms appear to be their origins, while their peak production is related to algal blooms in freshwater (Nawrocki & Karl, 1989). Inositol phosphates include a central inositol group which is bound to one of the six phosphate groups by phosphomonoester bonds (Turner, Papházy, Haygarth, & McKelvie, 2002). Inositol phosphates are produced from biological synthesis within plants. Phospholipids have phosphate mono or di-ester groups in the polar region of the molecule. They are the main component of cell membranes (Baldwin, 2013). Because the amphiphilic characteristic of phospholipids makes them insoluble, they tend to stay on the interface of water and air. Therefore, they typically exist in the particulate form. The direct C-P bond is the major characteristic of phosphonates. Phosphonates have been widely used in human commercial products, such as metal chelates, concrete admixtures, and herbicides. However, phosphonates is less abundant in freshwater than in the marine systems (Baldwin, 2013; Cheesman, Turner, & Ramesh Reddy, 2012; Dong, Yang, Liu, & Liu, 2012).

4.1.3 Organic Phosphorus during Municipal Wastewater Treatment

Organic phosphorus in the dissolved and particulate forms typically accounts for a small fraction (~15%) of the total phosphorus in untreated municipal wastewater based on the report of Dueñas, Alonso, Rey, and Ferrer (2003). Unfortunately, conventional secondary wastewater treatment only abates part of particulate organic phosphorus through sedimentation, but barely removes dissolved organic phosphorus. In the recent years, more stringent phosphorus discharge limits have been effective for wastewater treatment plants, especially the ones adjacent to the environmentally sensitive areas. For example, total phosphorus in the treated wastewater effluent discharged to the Chesapeake Bay cannot be over 0.3 mg/L (Clark et al., 2010; C. Qin et al., 2015). Although recent studies demonstrate that existing phosphorus treatment technologies can substantially remove inorganic phosphorus in municipal wastewater to a very low level, they poorly alleviate organic phosphorus, which represents 26-81% of total phosphorus in the treated wastewater (A. Z. Gu, Liu, Neethling, Stensel, & Murthy, 2011; April Z Gu et al., 2014; Haizhou Liu, Jeong, Gray, Smith, & Sedlak, 2012; Pagilla, Urgun-Demirtas, & Ramani, 2006; C. Qin et al., 2015). Therefore, there is an urgent research need to develop an innovative, green, and cost-effective advanced phosphorus removal technology to remove organic phosphorus in the treated wastewater.

4.1.4 Objectives

This study aimed to evaluate the treatment performance of ferrate(VI) for alleviation of recalcitrant organic phosphorus in biologically treated municipal wastewater and elucidate the underlying treatment mechanisms. The working hypothesis is that ferrate(VI) is capable of destructing certain P-containing organic compounds via chemical oxidation and then removing the phosphorus through adsorption. To achieve the objective, three following tasks would be answered.

1) What is the treatment efficiency of ferrate(VI) removal of recalcitrant organic phosphorus from secondary effluent? And how do the operating factors influence the treatment results?
2) How do water matrix constituents affect the removal efficiency of organic phosphorus?
3) What are the reaction mechanisms behind the removal?

4.2 Materials and Methods

4.2.1 Wastewater samples and reagents

All the reagents used were at least analytical grade, except as noted. Potassium ferrate (K_2FeO_4) (> 96%), sodium bicarbonate ($NaHCO_3$), sodium nitrate ($NaNO_3$), disodium phosphate (Na_2HPO_4), ammonia chloride (NH_4Cl), ribonucleic acid (RNA), deoxyribonucleic acid (DNA) sodium salt, adenosine-5'-triphosphate (ATP) disodium salt hydrate, uridine-5'-diphosphate disodium salt (UDP), guanosine-5'-diphosphate (GDP) disodium salt (GDP), and adenosine-5'-monophosphate (AMP) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Secondary effluent was collected from a local municipal sewage treatment plant (Verona, NJ, USA). The treatment facility received 9,464 m^3/day wastewater from residual areas. The secondary effluent was sampled after a secondary clarifier and before disinfection. Once collected, the sample was delivered to Montclair State University's Innovative Water Treatment and Reuse Laboratory, filtered with 0.45 μm membrane filters (GE Healthcare Whatman™ Nylon Membrane), and then stored at 4°C in a refrigerator until use. Quality parameters of the secondary effluent are as follows: pH 7.48, dissolved total phosphorus (DTP) = 2.12 mg/L as P, dissolved inorganic phosphorus (DIP) = 2.08 mg/L as P, total organic phosphorus (TOP) = 42 μg/L as P, UV_{254} absorbance = 0.161 cm^{-1}, dissolved organic carbon (DOC) = 40.0 mg/L, turbidity = 2.33 NTU, nitrate-nitrogen (NO_3^--N) = 2.6 mg/L, ammonia-nitrogen (NH_3-N) = 10.4 mg/L, and alkalinity = 200 mg/L as $CaCO_3$. Concentrated ferrate(VI) (200 mg/L Fe(VI)) stock solution was prepared by dissolving appropriate weights of K_2FeO_4 in ultrapure water produced from a Milli-Q water purification system (Milli-Q Direct 8). Fe(VI) in the ferrate(VI) stock solution was confirmed with the ABTS method (Y. Lee, Yoon, & von Gunten, 2005). Organic phosphorus model compound-containing solutions were prepared through dissolution of appropriate weights of model compounds in ultrapure water to ensure the initial OP at 500 μg/L. The initial OP concentration was confirmed using an inductively coupled plasma-mass spectroscopy (ICP-MS Thermo X-Series II, XO 472). The solutions were prepared immediately before the treatment tests.

4.2.2 Ferrate(VI) removal of OP in secondary effluent

Laboratory-scale batch tests were carried out in 500 mL glass beakers containing 400 mL well-mixed secondary effluent on a four-paddle programmable jar tester (Phipps and Bird - 7790-950) at room temperature (20 ± 1 °C) and under atmospheric pressure. If needed, the secondary effluent pH was adjusted to a designated level with 0.1 M sulfuric acid or sodium hydroxide. The treatment was initiated once an appropriate volume of ferrate stock solution was dosed. Within the first minute, the solution was rapidly mixed at a velocity gradient of 241 s^{-1} to completely disperse the added iron. During the following 59 minutes, the solution was gently stirred at a velocity gradient of 21 s^{-1} for the growth of flocs. During the treatment, pH was monitored, but not controlled or intendedly buffered. Following the slow mixing, the treated wastewater was filtered using 0.45 µm membrane filters (GE Healthcare Whatman™ Nylon Membrane) for removing particulate matter, and the filtrates were collected for further analysis. Control tests were carried out with the identical experimental procedure, except that ferrate(VI) was not dosed.

In the tests to evaluate the effect of ferrate(VI) dose, ferrate(VI) dose was varied from 0.0, 1.0, 3.0, 5.0, 7.0, 9.0, to 11.0 mg/L. In the experiments to assess the effect of initial pH, ferrate(VI) dose was fixed at 5.0 mg/L Fe, while initial pH was varied at 5.5, 6.0, 6.5, 7.0, 7.5, and 8.0. For the experiments to evaluate effects of wastewater matrix constituents, alkalinity (250-500 mg/L as $CaCO_3$), nitrate (NO_3^-) (2.6-30.0 mg/L NO_3-N), ammonia (NH_3) (10-60 mg/L NH_3-N), and disodium phosphate (Na_2HPO_4) (2.08-5.22 mg/L as P) were dosed to achieve their respective designated concentrations. Treatment tests were carried out at 5.0 mg/L Fe(VI) and pH 6.5.

4.2.3 Ferrate(VI) treatment of OP model compounds

In-situ ferrate(VI) treatment tests for removal of individual OP model compounds were carried out with the procedure similar to the treatment tests for secondary effluent, except that: 1) an OP solution, rather than secondary effluent, was treated; and 2) pH was manually controlled at a designated pH using 0.1 M sulfuric acid and sodium hydroxide. On the other hand, *ex-situ* ferrate(VI) treatment tests in the OP solution was performed using a similar *in-situ* treatment procedure. The only modification is that ferrate(VI) was dosed first and then mixed for 1 hour before the OP model compound was introduced. *In-situ* and *ex-situ* treatment tests would evaluate the combined effect of ferrate(VI) oxidation and iron oxide adsorption and effect of iron oxide adsorption only, respectively. After the *in-situ* or *ex-situ* treatment, samples were filtered through 0.45 μm membrane filters (GE Healthcare Whatman™ Nylon Membrane) for removing particulate matter, and the filtrate would be collected for analyses. In the tests for determination of size distributions of ferrate(VI) resultant particles, the samples after treatment, comprising water and iron (hdyr)oxides, was sequentially filtered through 0.45 μm microfiltration (GE Healthcare Whatman™ Nylon Membrane), 0.1 μm microfiltration (Thermo Scientific, cellulose acetate (CA)), and 30 kDa ultrafiltration (UF) membranes (EMD Millipore, regenerated cellulose). Approximately 50 mL filtrate after each filtration was collected for analyses. Particles filtered by 0.45 μm microfiltration were operationally defined as large-sized particles. Solids passing 0.45 μm microfiltration filters but filtered by 0.1 μm microfiltration were colloidal particles. Particles passing 0.1 μm microfiltration filters but filtered by 30 kDa UF membrane were nano-sized particles. And the chemicals passing 30 KDa MF filters were regarded as soluble substances. A similar fractionation method was applied elsewhere (Goodwill, Jiang, Reckhow, Gikonyo, & Tobiason, 2015) to study the size of iron particles in ferrate(VI) decomposition in natural waters.

4.2.4 Sample Analyses

Ferrate(VI) was spectrophotometrically measured using the ABTS method (Y. Lee et al., 2005). Solution pH was measured by a pH meter (Thermo Scientific Orion 5-Star Plus). Various secondary effluent parameters were measured after filtration through 0.45-µm syringe membrane filters (Thermo Scientific, cellulose acetate (CA), 30 mm diameter). EfOM was quantified using DOC, which was measured with a total organic carbon (TOC) analyzer (TOC-LCPH, Shimadzu Corp., Kyoto, Japan). Measurements of alkalinity, NO_3^--N, and NH_3-N followed the U.S. Environmental Protection Agency (EPA) approved Standard Methods 2320B, 1685, and 4500F, respectively. Total phosphate was determined with an inductively coupled plasma-mass spectroscopy (ICP-MS Thermo X-Series II, XO 472). Acid hydrolyzable P was measured with the HACH TNT reagent sets to indicate inorganic P in water. OP was the difference between total P and inorganic P. The morphology of the retained particles was examined by a transmission electron microscope (TEM, Hitachi H-7500) and a scanning electron microscope (SEM, Hitachi S-3400N). To quantify the amorphous iron in the produced iron oxides, a citrate–ascorbate iron extraction method was used with minor modification. Briefly, 0.2 M Na-citrate and 0.05 M ascorbic acid (pH 6.0) were added to the well-mixed samples immediately after the coagulation and flocculation (3.0 mg/L Fe(VI)) with a reagent to solution weight ratio of 60 : 1. The suspensions were shaken on a horizontal shaker for 16 h and then centrifuged at 11 000 rcf for 30 min. The extractable dissolved iron in the suspensions was collected for analysis of amorphous iron. The data allowed for the determination of the mass fraction of amorphous Fe in the total Fe (i.e. 3.0 mg/L Fe) in the ferrate(VI) resultant oxide particles. The daughter products of model OPs were identified using a liquid chromatography–mass spectrometry system (LC-MS 2020, Shimadzu Corp., Kyoto, Japan), which was equipped with a Supelcosil LC-18 column (25cm×4.6mm, 5µm). Mobile phase A consisted of 100 % acetonitrile, while mobile phase B consisted of 7.5 mM of ammonium acetate and adjusted to pH=7.5 with 0.1 mol/L acetate acid and ammonium hydroxide. Flow rate was controlled at 0.5 mL/min with a retention time of 10 mins in total. The ratio of mobile phase A and B was fixed at 35% and 65% through the analysis. The injection volume was 20 µL and the peaks were detected at 254 nm.

All the experiments were run, at a minimum, in triplicates. All the analytical results reported represent the mean of the replicate samples. Error bars in the figures indicate one standard deviation of these measurements.

4.3 Results and Discussion

4.3.1 Treatment performance of ferrate(VI) for removal of OP in secondary effluent

Treatment feasibility of ferrate(VI) removal of OP in secondary effluent was first investigated. Residual OP and OP removal efficiency were used as two parameters to determine the treatment performance. Effects of operating factors and selected wastewater matrix constituents on the OP removal were sequentially evaluated.

4.3.1.1 Effects of operating factors

Ferrate(VI) dose. Residual DOP and DOP removal efficiency after ferrate(VI) treatment of secondary effluent at different Fe(VI) doses are shown in **Figure 4-1** (DOP= 114 µg/L as P; Fe(VI) = 0.0 – 9.0 mg/L). As seen, as Fe(VI) dose was increased from 0.0 to 3.0 mg/L, residual DOP sharply declined from 114 to 29 µg/L, while the DOP removal efficiency dramatically increased from 0% to 75%. As Fe(VI) dose was further increased to 9.0 mg/L, residual DOP almost stabilized at 29-31 µg/L with a corresponding DOP removal efficiency ranging within

75%-80%. In the following experiments, Fe(VI) dose was selected at 5.0 mg/L. These findings clearly demonstrate that ferrate(VI) could effectively alleviate DOP present in secondary effluent.

Initial pH. Residual DOP and DOP removal efficiency after ferrate(VI) treatment of secondary effluent at different initial pH are shown in **Figure 4-2** (DOP= 114 µg/L as P; Fe(VI) = 5.0 mg/L; and initial pH = 5.5-8.0). Residual DOP dramatically decreased from 78 µg/L at pH 5.5 to 59 µg/L at pH 6.5, while the removal efficiency was increased from 31% to 49%. As pH further increased to 8.0, residual DOP was not obviously altered. These observations evidently show that pH disfavor the OP removal with the pH decreased at an acidic solution condition. However, the effect of pH on the OP removal was insignificant at a weakly acidic to weakly alkaline condition (pH 6.5-8.0). In the following experiments, solution pH was selected at 6.5.

4.3.1.2 Effect of wastewater matrix constituents

Effects of common wastewater matrix constituents, including alkalinity, NO_3^-, NH_4^+, and PO_4^{3-}, were subsequently investigated, as shown in **Figure 4-3(a), (b), (c),** and **(d)**, respectively. As seen in **Figure 3-3(a)**, residual DOP slightly declined from 59 µg/L (48% removal) at an alkalinity of 250 mg/L $CaCO_3$ to 47 µg/L (59% removal) at an alkalinity of 250 mg/L $CaCO_3$, and then narrowly varied between 44 and 47 µg/L, corresponding to the removal within 59% - 69%, over an alkalinity range of 250 - 500 mg/L $CaCO_3$, indicating that alkalinity did not greatly affect the OP removal. Effect of NO_3^- on the residual OP is illustrated in **Figure 4-3(b)**. When NO_3^--N was increased from 2.6 to 5.0 mg/L, the residual DOP dropped from 59 to 48 µg/L, corresponding to the increase of the DOP removal efficiency from 48% to 58%. At 5.0-30.0 mg/L NO_3^--N, residual DOP ranged within 42-48 NO_3^--N µg/L, also indicating that nitrate had a minor influence on ferrate(VI) removal of organic phosphorus in secondary effluent. And the effect of NH_3 on residual DOP is presented in **Figure 4-3(c)**. Over 10.6 – 60.0 NH_3-N, the residual DOP varied slightly within 48-59 μg/L, corresponding to the overall DOP removal of 48%-58%, suggesting that ammonia had a limited influence on ferrate(VI) removal of OP in secondary effluent. Overall, these observations indicate that the impacts of alkalinity, nitrate, and ammonia on the organic phosphorus removal during ferrate(VI) treatment of secondary effluent are insignificant.

In contrast, a significant inhibiting effect of inorganic orthophosphate on ferrate(VI) removal of DOP was observed, as shown in **Figure 4-3(d)**. As seen, as phosphate increased from the original 2.08 to 5.22 mg/L as P (i.e. 16.00 mg/L PO_4^{3-}), residual DOP increased from 59 to 112 μg/L, with the corresponding removal efficiency dramatically declined from 48% to 1%, indicating that the OP removal was suppressed with the increasing phosphate concentration.

4.3.2 Mechanistic studies of ferrate(VI) removal of DOP

OP exists in EfOM molecules that are an integral part of wastewater matrix constituents in biologically treated municipal wastewater. It is well known that NOM and its different fractions (e.g. humic acid and fulvic acid) can be extracted from natural water, or representative NOM compounds are commercially available for scientific studies. However, there are no standardized methods to extract EfOM from secondary effluent, and commercial EfOM products are unavailable. Therefore, it is technically difficult to investigate the fundamental reactions between ferrate(VI) and P-containing organic compounds in a real secondary effluent. In order to overcome the technical barriers, we selected six individual P-containing organic compounds as OP model compounds in secondary effluent for the ferrate(VI) treatment tests. They include RNA, DNA, ATP, UDP, GDP, and AMP. These model compounds were used as surrogate compounds for P-containing compounds in EfOM. To eliminate the influences of other wastewater matrix constituents, all the treatment experiments were carried out in distilled water. For each specific OP model compound, its initial OP concertation was fixed at 500 µg/L. And solution pH was manually controlled during the reactions.

Ferrate(VI) removals of individual OP model compounds. Residual P concentrations after ferrate(VI) treatment of RNA, DNA, ATP, UDP, GDP, and AMP are shown in **Figure 4-5 (a), (b), (c), (d), (e)**and **(f)**, respectively (Fe(VI) = 5.0 mg/L; P = 500 µg/L). For each model compound, *in-situ* and *ex-situ* ferrate(VI) treatments were performed at pH 6.5 or 7.5. *In-situ* treatment means that ferrate(VI) was dosed to the P-containing water, in which ferrate(VI)-driven oxidation and adsorption due to ferrate(VI) resultant particles might both contribute to the OP removal. On the other hand, in an *ex-situ* treatment, ferrate(VI) was dosed to distilled water and then depleted before a specific OP model was introduced, which reflected the OP adsorption effect only. Of note, part of or whole OP molecules may be subject to change of chemical structure due to chemical oxidation during an *in-situ* treatment, while the structure of the OP molecules remained intact over the *ex-situ* treatment because of the lack of chemical degradation reactions.

As shown in **Figure 4-4**, the residual P concentrations of the six OP model compounds all slightly declined (< 20%) in comparison to their respective initial levels at either pH during *ex-situ* ferrate(VI) treatment. The finding evidently demonstrates that there was a poor adsorption of ferrate(VI) resultant particles for the six model compounds. Therefore, direct adsorption due to the formation of iron (hydr)oxide did not serve as a principal mechanism for mitigation of these model compounds.

During the *in-situ* treatment, any model compound was very little removed at pH 7.5, indicating that the joint utilization of chemical oxidation and adsorption could not effectively remove these compounds at the studied conditions. However, residual P significantly declined at pH 6.5 after the *in-situ* treatment, except for GDP that slightly dropped from 500 to 467 µg/L with a minor removal of 7%. The residual P in RNA, DNA, ATP, UDP, and AMP decreased from the initial 500 µg/L to 20, 2, 15, 40, and 79 µg/L, respectively. Based on the above results, we can conclude that the effective removals of RNA, DNA, ATP, UDP, and AMP are primarily ascribed to the co-occurrence of ferrate(VI)-driven chemical oxidation and adsorption at a weakly acidic condition.

Size fractions of P and Fe after ferrate(VI) treatment. In order to further understand the size fractions of P and Fe after the *in-situ* treatment, the treated samples were subject to sequential filtration with 0.45 µm microfiltration, 0.1 µm microfiltration, and 300 kDa ultrafiltration. Concentrations of residual P and Fe in the filtrate after each filtration were measured. Total P and Fe in the ferrate(VI) treated samples were also analyzed after sample digestion. In this study, particulate matters with the sizes of > 0.45 µm, 0.45-0.1 µm, and 0.1 µm – 300 kDa were categorized into large-sized, colloidal, and nano-sized particles, respectively. P and Fe measured in the filtrate after < 300 kDa ultrafiltration derived from soluble substances. The size fractionation methods were successfully adopted for investigation of the size distribution patterns of these ferrate(VI) resultant particles, which were produced after ferrate(VI) treatment of natural water or sewage polluted source water, in previous studies (Cui, Zheng, & Deng, 2018; Goodwill et al., 2015).

Size distributions of P and Fe after ferrate(VI) treatment of RNA, DNA, ATP, AMP, GDP, and UDP at pH 7.5 are shown in **Figure 4-5**. At pH 7.5, P and Fe shared the similar size distribution patterns. Two observations are of importance. First, for any specific model compound, soluble P and Fe were insignificant, suggesting that P was not indeed dissolved in the treated water. Second, the majority of P and Fe were present in the nano-sized particles, implying that the most P adsorbed to or was incorporated into ferrate(VI) resultant particles. Because part of or whole parent compounds may be degraded by ferrate(VI) oxidation, we cannot conclude whether the P associated with the nano-sized particles originated from the parent compounds, daughter compounds, or even inorganic phosphate, which might be produced from ferrate(VI) oxidation of OP molecules, based on the above observations.

Size distributions of P and Fe after ferrate(VI) treatment at pH 6.5 are also shown in **Figure 4-5**. Very different size distribution patterns of Fe and P are observed. The vast majority P and Fe in the RNA, DNA, ATP, UDP, and AMP treatment groups existed in the large-sized particles of > 0.45 μm, while the most Fe and P were present in the colloidal particles of 0.45- 0.1 μm in the GDP group. Based on these findings, we can acquire important information in the four aspects. First, the very low concentrations of the soluble P indicate that residual P was not truly dissolved after the treatment. Second, the poor removal of GDP with ferrate(VI) at pH 6.5 (**Figure 4-4**) is because the most GDP was associated with colloidal particles (0.45 μm – 0.1 μm). These fine particles could pass 0.45 μm membrane filtration, so that the nominal "dissolved" P was high, as shown in **Figure 4-4**. Third, the similar size distributions of P and Fe imply that P was associated with ferrate(VI) resultant particles with different sizes. Four, the sizes of these particles produced at lower pH were greater than those at higher pH, which favored the downstream filtration that could remove the P associated with the particles. This finding is likely related to the performance of iron-driven coagulation. Typically, better coagulation and flocculation occur at an acidic pH level with the formation of larger and denser iron flocs (Crittenden, Trussell, Hand, Howe, & Tchobanoglous, 2012).

From this set of experiments, we noticed that the RNA and DNA used contained very low fractions of OP in terms of mass. To achieve 500 µg/L OP for the above experiments, too much RNA or DNA needed to be dosed into water, which had a much greater DOC than the realistic DOC in secondary effluent. That is, RNA and DNA had a very high mass ratio of C to P. Given that the concentrations of RNA and DNA should be trivial in a real secondary effluent, the RNA and DNA were not investigated in the following experiments.

Surface elemental analyses of ferrate(VI) resultant particles. SEM and EDS analyses were made for the particles produced from *in-situ* ferrate(VI) treatment of ATP, UDP, GDP, and AMP at pH 6.5, as shown in **Figure 4-6**, **4-7**, **4-8**, and **4-9**, respectively. Results show that abundant Fe and P existed in these particles for all the four groups. This finding is in agreement with the above observation that both P and Fe shared the similar distribution pattern.

Identification of degradation products in treated water. In order to understand the reactions of ferrate(VI) and OP model compounds, the degradation products of the model compounds after ferrate(VI) oxidation were identified using LC/MS. Because GDP could not be well removed by ferrate(VI), only the samples from ferrate(VI) treatment of ATP, UDP, and AMP were tested. *In-situ* ferrate(VI) treatment tests were performed at pH 6.5. LC/MS data of the parent and major daughter compounds after ferrate(VI) treatment of ATP, UDP, and AMP are shown in **Figure 4-10**, **4-11**, and **4-12**, respectively. After treatment of any selected model compound, a major daughter compound with a P-containing chain was identified. Of interest, the daughter compound of ATP or AMP was a fragment after the breakdown of the C-N bond between two ring structures in the parent compound. Ferrate(VI) reactivity toward different organic molecules was extensively investigated (V. K. Sharma, 2010; Yang et al., 2012). The ferrate(VI) induced degradation may be involved with electron transfer, hydrogen atom transfer, hydride ion or covalently bonded ferrate intermediates depending upon the nature of the compound (D. G. Lee & Gai, 1993). Particularly, similar to ozone, ferrate (V) preferentially attacks electron-rich function groups on an organic molecule (Yang et al., 2012). The C-N bonds of two ring structures on the parent compounds was attacked due to the electron rich property. The cleavage occurs due to the low bond energy and easy activation through the resonance from the two ring structures. Cleavage of C-N bond by ferrate(VI) oxidation was also previously reported elsewhere (Deng, Wu, Wang, Liu, & Wang, 2019; Sun et al., 2018).

Ferrate(VI) oxidation of UDP seems a little more complex. The identified daughter compound had a m/z of 350. Its plausible chemical structure is shown in **Figure 4-11**. The two reactions might have occurred, including: 1) the scission of the C-N bond between two ring structures, similar to the destruction patterns of ATP and AMP; and 2) two –OH groups appeared to transform to –COOH. A similar reaction was recently reported elsewhere (Han et al., 2018). The latter reaction pathway might proceed as follows. Ferrate(VI) firstly oxidized alcohols to carbonyl groups in a manner reported previously (Delaude & Laszlo, 1996; Y. R. Song & Ma, 2013). Afterward, the carbonyls transformed to carboxylic moieties through hydroxylation.

4.3.3 Discussion

Mechanisms for OP removal with ferrate(VI). Ferrate(VI) oxidation may entirely or partially degrade OP compounds into daughter P-containing compounds or into inorganic P. Following ferrate(VI) treatment, the P originally present in these OP model compounds would have three possible fates, including: 1) parent compounds in water or on the ferrate(VI) resultant particles; 2) daughter OP compounds in water or on the ferrate(VI) resultant particles; and 3) inorganic phosphorus in water or associated with the ferrate(VI) resultant particles. Further analyses of the fate of P after ferrate(VI) treatment is of importance to understanding the reaction mechanisms for OP in secondary effluent. Below are the detailed discussion on ferrate(VI) removal of the selected OP model compounds.

Results from *ex-situ* ferrate(VI) treatment show the poor removal of these OP model compounds through adsorption only with the ferrate(VI) resultant particles. Therefore, it is unlikely that these parent compounds could be mostly captured by the produced iron (hydr)oxides. Meanwhile, we did not find these parent compounds in water after ferrate(VI) treatment. Therefore, the selected OP compounds were almost all degraded by ferrate(VI) oxidation.

On the other hand, inorganic P (e.g., orthophosphate and polyphosphate) was undetectable in the aqueous phase after ferrate(VI) treatment. It is most unlikely that polyphosphate, if truly produced from the OP degradation, could adsorb to iron (hydr)oxide, because polyphosphate is poorly removed by adsorption with iron oxides (Tchobanoglous et al., 2014). The extraction method, which was described in detail in Chapter 3, was used to examine whether any orthophosphate was adsorbed to the ferrate(VI) resultant particles. Results show the absence of orthophosphate on the iron sludge. The aforementioned findings suggest that ferrate(VI) cannot sufficiently degrade these OP model compounds into inorganic phosphorus. It is well known that ferrate(VI) preferentially transforms dissolved organic matter, rather than completely oxidize them into inorganic species (Y. L. Song et al., 2016; Yang et al., 2012). This was evidenced by the fact that ferrate(VI) oxidation could readily alleviate chemical oxidation demand (COD) but poorly abate dissolved organic carbon (DOC) when it was used for degradation of NOM in natural water sources (Y. L. Song et al., 2016). This finding is primarily ascribed to the nature of ferrate(VI). Although it has a high redox potential of up to 2.20 V, ferrate(VI) oxidation is highly selective. The oxidative anion tends to react with electron-rich moieties, but very slowly reacts with electron-poor moieties. Meanwhile, ferrate(VI) is subject to its self-decomposition in water, which can make ferrate(VI) to gradually decay until ferrate(VI) depletion.

Based on the mass balance analysis, only daughter P-containing compounds existed in the treatment systems. The degradation of the parent compounds can be validated by the identification of decomposition products in solutions after the treatment using the mass spectrometry technique. Results in the ferrate(VI) treatment of the selected OP model compounds clearly indicate that the most of P was associated with the finally produced iron (hydr)oxides. Therefore, the P is plausibly present in the degradation products of the OP model compounds after ferrate(VI) treatment. Overall, the major plausible reaction mechanisms for ferrate(VI) removal of the selected OP compounds are as follows. Ferrate(VI) first attacks certain functional groups on the OP parent compounds for production of various P-containing compounds. The chemical oxidation most likely occurs on electron-rich moieties. With the nature of different degradation products, some sorb to the produced iron (hydr)oxides, while the others remain in water in a soluble state. Adsorption of P-containing organic compounds to various iron oxides have been documented elsewhere (Johnson & Loeppert, 2006; Lü et al., 2017; Ruttenberg & Sulak, 2011; Yan et al., 2016).

It should be noted that the aforementioned reaction pathways for ferrate(VI) oxidation and ensuing adsorption for removal of OP are proposed based on the experimental evidence with selected OP model compounds. Organic phosphorus in EfOM may have been contributed from many other individual organic compounds in secondary effluent. Further studies are needed for in-depth understanding of ferrate(VI) reactions with other OP species in EfOM.

Operating factors and coexisting wastewater matrix constituents. Ferrate(VI) removal of OP, similar to ferrate(VI) alleviation of phosphate in water, can be greatly influenced by ferrate(VI) dose and solution pH. Better OP removal was achieved at higher ferrate(VI) during treatment of secondary effluent, because more Fe(VI) is available for degradation of OP compounds and more iron (hydr)oxide particles are produced for adsorption of OP degradation products. On the other hand, lower pH at 5.5-6.5 favored OP removal likely due to the greater ferrate(VI) reactivity. Ferrate(VI) reactivity is acutely increased with the pH decrease (D. Ghernaout & Naceur, 2011; V. K. Sharma, 2002b; Virender K Sharma, Chen, & Zboril, 2015). The extremely strong Fe(VI) at such an acidic condition may greatly degrade OP into inorganic phosphate before removal of P through adsorption. However, in a realistic municipal wastewater treatment, solution pH mostly varies within a nearly neutral pH range (6.5-8.5). In the treatment tests with real secondary effluent, very slight difference was observed for the DOP removals over pH 6.5 – 8.0. However, in the ferrate(VI) treatment tests for model OP compounds, better removal was observed at pH 6.5 than at pH 7.5. As discussed above, the difference was caused due to the different size distribution patterns of ferrate(VI) resultant particles produced at different pH. Generally, more large-sized particles were produced at pH 6.5, so that these particles to which OP compounds adsorb were readily removed in the downstream filtration, thereby having a lower residual OP.

Different from many other wastewater matrix constituents without a marked effect on ferrate(VI) removal of OP, phosphate exhibited a significant inhibiting effect. As discussed in Chapter 3, adsorption of phosphate to ferrate(VI) resultant particles is the dominant mechanism for ferrate(VI) removal of reactive phosphate in secondary effluent. Therefore, more phosphate is expected to be captured by the ferrate(VI) induced particles when more phosphate is present in secondary effluent. The ferrate(VI) treatment tests for removal of model OP compounds also reveal that adsorption of P-containing degradation compounds to ferrate(VI) resultant particles plays an essential role for the OP alleviation. Therefore, there is a competition between phosphate and OP compounds for active adsorption sites on iron (hydr)oxides. More adsorption sites would be occupied at higher initial phosphate concentration, so that less OP compounds are adsorbed. Ruttenberg and Sulak (2011) found that phosphate had a greater affinity with various iron oxides than many organic phosphorus compounds.

Implication to the wastewater industry. Findings from this chapter have unique implications for the wastewater industry in the following aspects.

1) This study finds a new pathway to prevent recalcitrant wastewater–derived OP from entering into natural receiving water bodies. Addition of common coagulants, such as ferric chloride and aluminum sulfate, has been used as a widely accepted method for elimination of phosphate from biologically treated municipal wastewater due to their effectiveness and low costs. Although the coagulation can well remove reactive phosphate, it has proven ineffective for mitigation of OP. Encouraging results from this study shows that ferrate(VI) is a promising treatment agent for capturing OP in secondary effluent. This is of significance, particularly for these natural water bodies that are highly environmentally sensitive to nutrient loadings (e.g., the Chesapeake Bay in the United States).
2) Ferrate(VI) removal of OP can be significantly influenced by ferrate(VI) dose, water pH, and the presence of phosphate. The first two are operating factors. while the last one represents a wastewater matrix constituent. For different secondary effluents, the specific optimal ferrate(VI) dose and pH need to be determined. It should be noted that the original secondary effluent pH may not be the optimal level. If additional pH adjustment is required before and after the treatment, the costs are increased due to the use of

acid/base as well as additional pH adjustment equipment and pipelines. Accordingly, the system design, operation, and maintenance would become more complex. If this is the case, what ferrate(VI) dose and pH are realistically adopted depends on the comparison at different operational conditions in terms of treatment efficiencies and treatment expenses.

3) This study reveals that OP adsorption to ferrate(VI) resultants plays a vital role in the ferrate(VI) removal of wastewater OP. Therefore, the controlling of particle sizes during the treatment operation is essential to selection of appropriate downstream liquid-solid separation techniques, because different liquid-solid separation methods are effective for different particle size ranges. Generally, larger particles are more readily and less costly separated. Therefore, the size growth of particles during ferrate(VI) treatment through appropriate engineering designs and operation control (e.g., control of pH and chemical mixing gradients) deserves a further investigation in future.

4.4 Conclusion

In this study, the treatment performance of ferrate(VI) removal of OP in secondary effluent was evaluated. Effects of two operating factors (i.e., ferrate(VI) dose and water pH) and four coexisting wastewater matrix constituents (i.e., alkalinity, nitrate, ammonia, and phosphate) were particularly evaluated. In order to elucidate the underlying reaction mechanisms, ferrate(VI) reactions with six OP model compounds were investigated. Major conclusions from this study are summarized as follows.

1) Ferrate(VI) treatment is a technically effective method for mitigation of organic phosphorus in biologically treated municipal wastewater. The treatment efficiency is influenced by ferrate(VI) dose and pH.

2) Among different wastewater matrix constituents, alkalinity, nitrate, and ammonia have very limited influence on ferrate(VI) removal of OP. In contrast, inorganic phosphate can suppress the OP removal. The inhibiting effect is ascribed to competitive adsorption of phosphate with OP compounds for active adsorption sites on the ferrate(VI) resultant particles.

3) Based on the studies with OP model compounds, ferrate(VI) oxidation and ensuing adsorption with ferrate(VI) resultant particles are the major OP removal mechanisms. Specifically, ferrate(VI) firstly degrades these parent OP compounds into daughter P-containing compounds, followed by adsorption of these daughter compounds by the resultant iron (hdyr)oxide particles. Of note, inorganic phosphate is not observed after ferrate(VI) treatment of OP model compounds, suggesting that ferrate(VI) insufficiently degrades OP into inorganic P. However, the conclusions are made only based on the selected model compounds. Given that OP derives from various EfOM molecules, novel experimental approaches need to be developed for exploration of the mechanisms for ferrate(VI) removal of aggregate OP in secondary effluent.

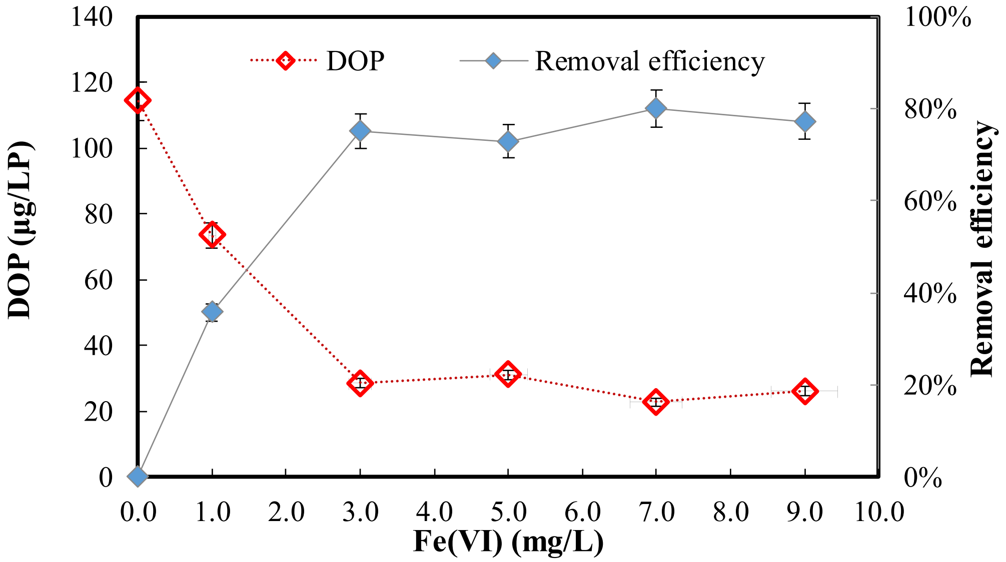


Figure 4-1 Residual DOP and DOP removal efficiency after ferrate(VI) treatment of secondary effluent at different Fe(VI) doses (DOP= 114 µg/L as P; Fe(VI) = 0.0 – 9.0 mg/L)

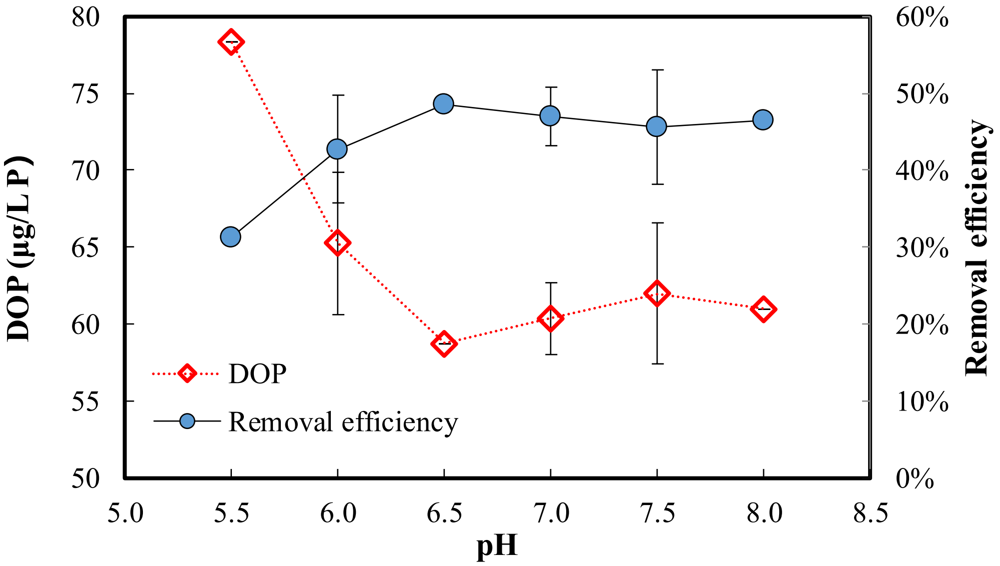
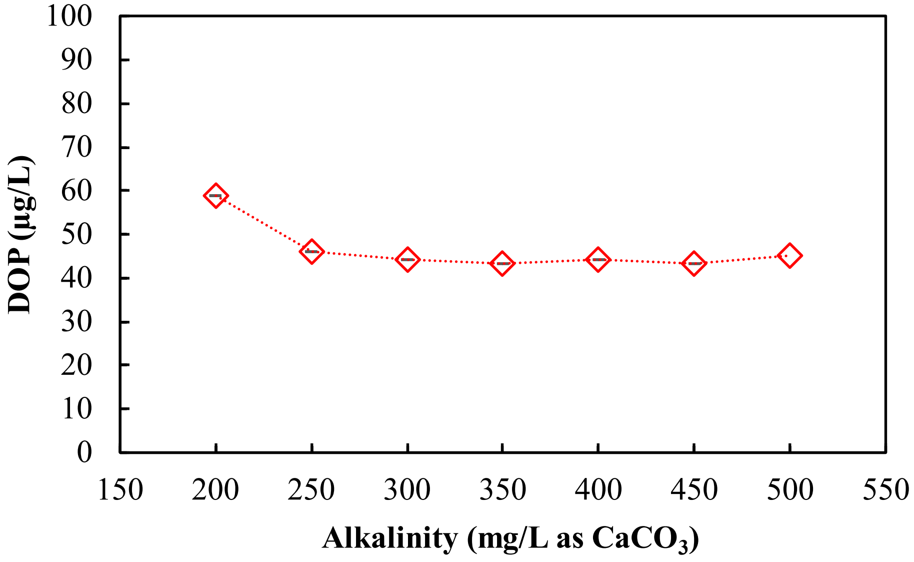
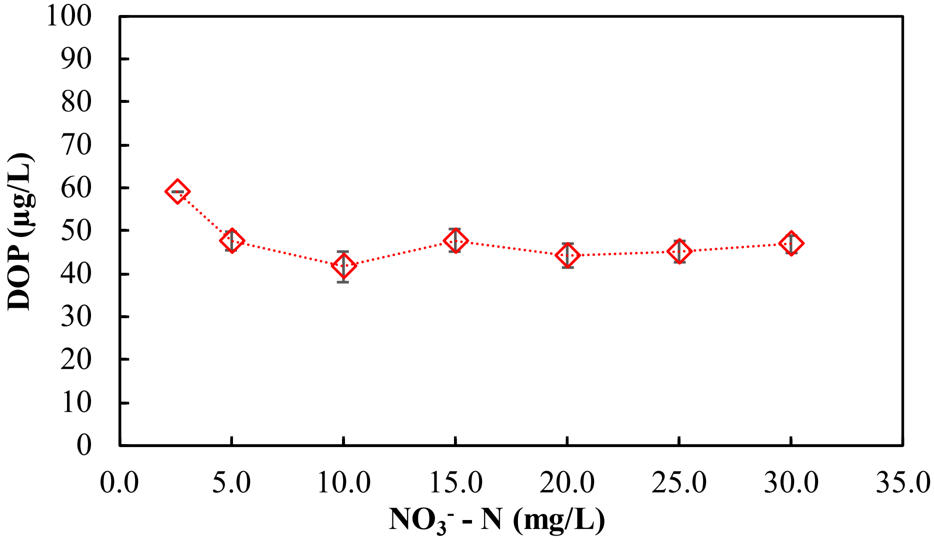


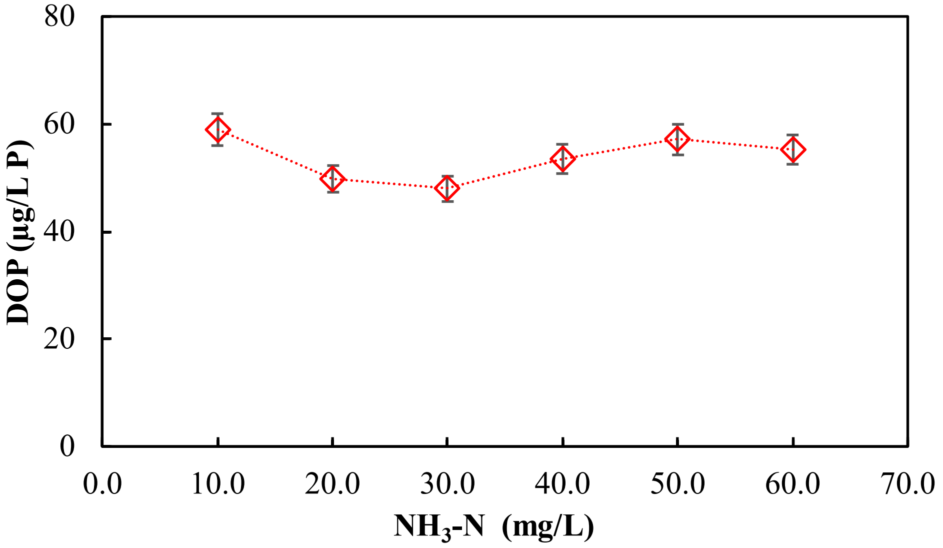
Figure 4-2 Residual DOP and DOP removal efficiency after ferrate(VI) treatment of secondary effluent at different initial pH (DOP= 114 µg/L as P; Fe(VI) = 5.0 mg/L; and initial pH = 5.5-8.0)


DOP (µg/L)
100
90
80
70
60
50
40
30
20
10
0
150
200
250
300
350
400
450
500
550
Alkalinity (mg/L as CaCO3)

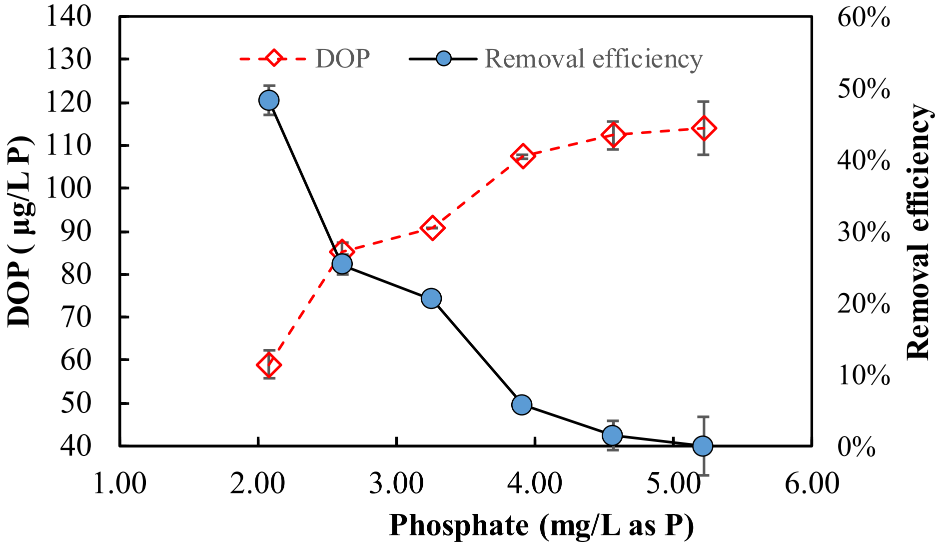
(a)


DOP (µg/L)
100
90
80
70
60
50
40
30
20
10
0
0.0
5.0
10.0
15.0
20.0
25.0
30.0
35.0
NO3- - N (mg/L)

(b)

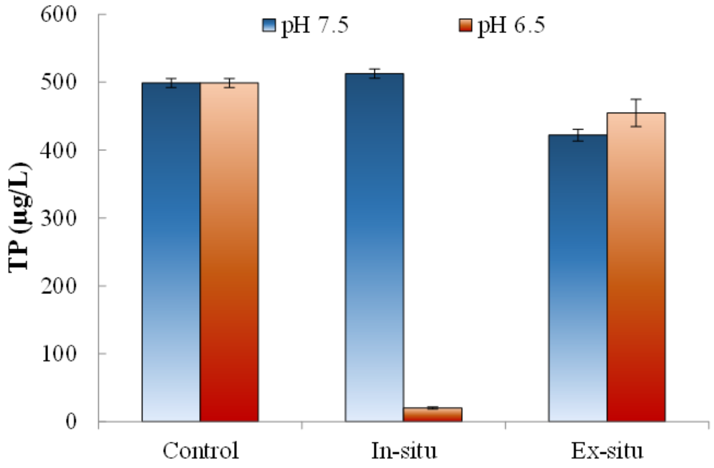


(c)

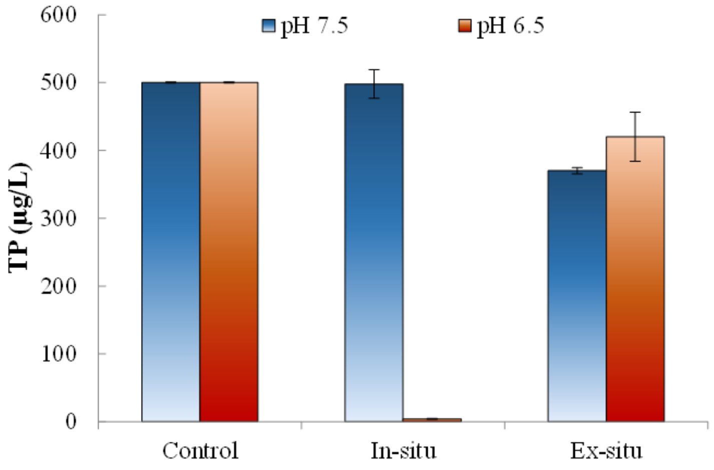


(d)

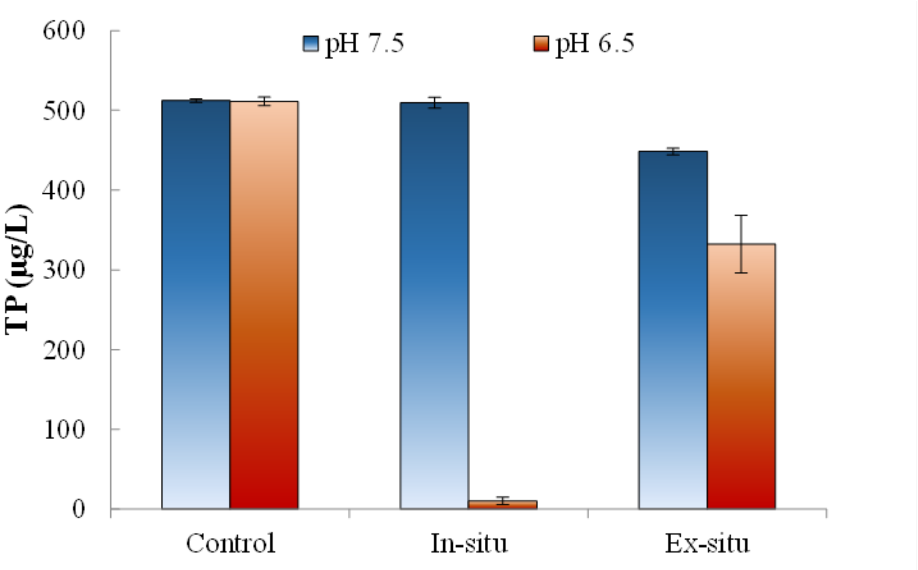
Figure 4–3 Effects of different wastewater matrix constituents on residual DOP during ferrate(VI) treatment of secondary effluent (Fe(VI) dose = 5.0 mg/L; initial DOP = 114 µg/L P; and initial pH = 6.5): (a) alkalinity: 200-500 mg/L as $CaCO_3$; (b) NO_3^--N: 2.6-30.0 mg/L; c) NH_3-N: 10.6-60 mg/L; and d) phosphate: 2.08-5.22 mg/L as P)



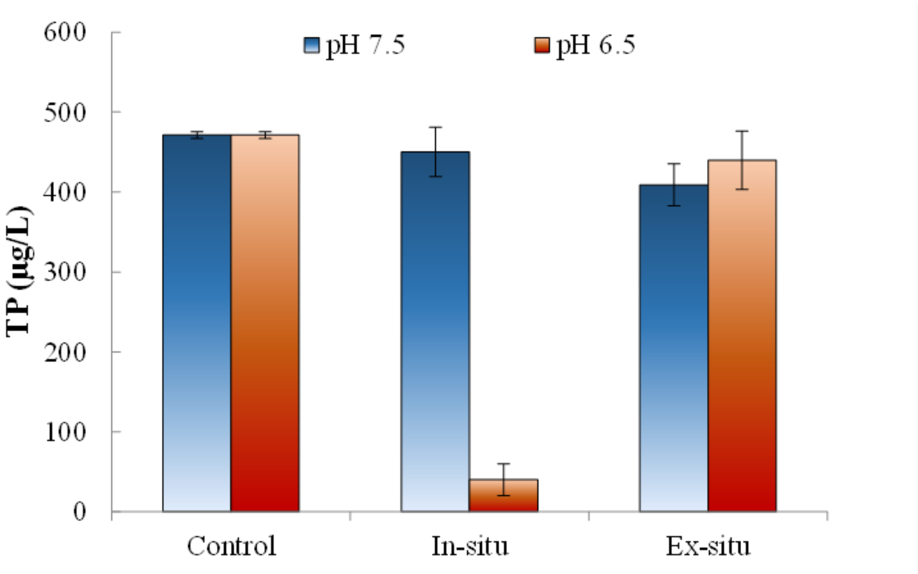
(a) Ribonucleic Acid (RNA)



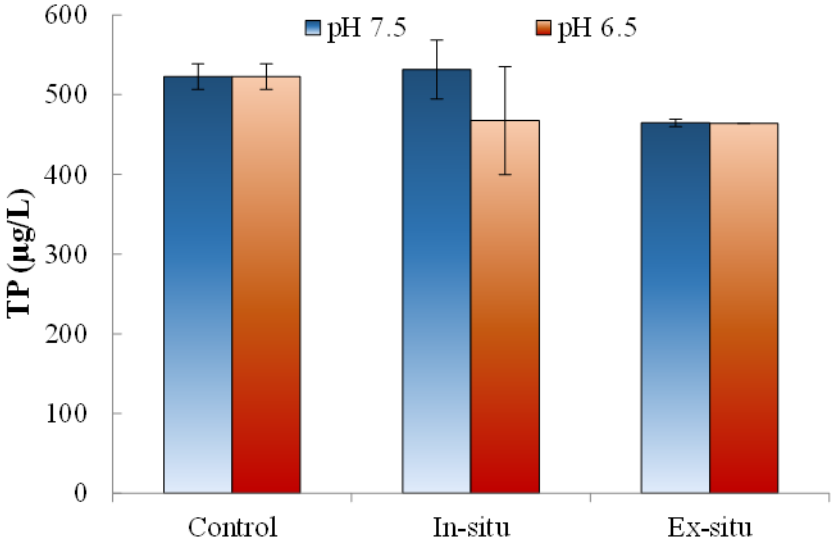
(b) Deoxyribonucleic Acid Sodium Salt (DNA)



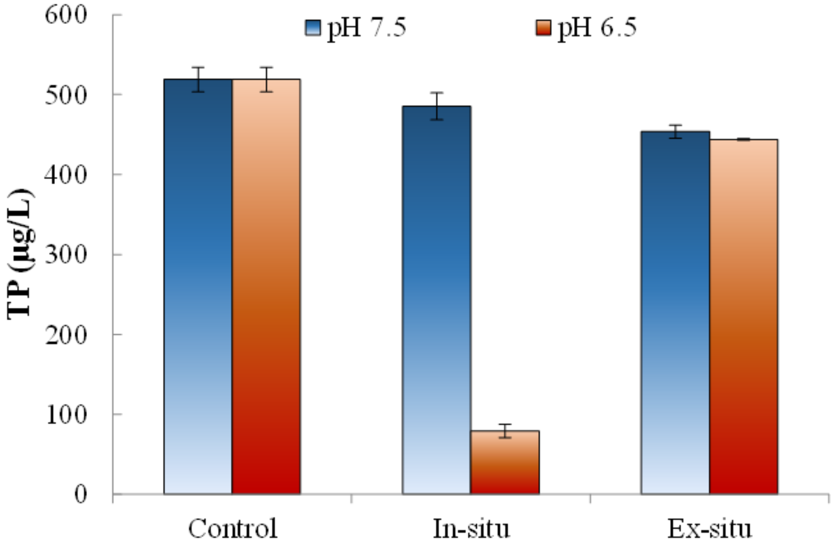
(c) Adenosine-5’-triphosphate Disodium Salt Hydrate



(d) Uridine-5’-diphosphate Disodium Salt

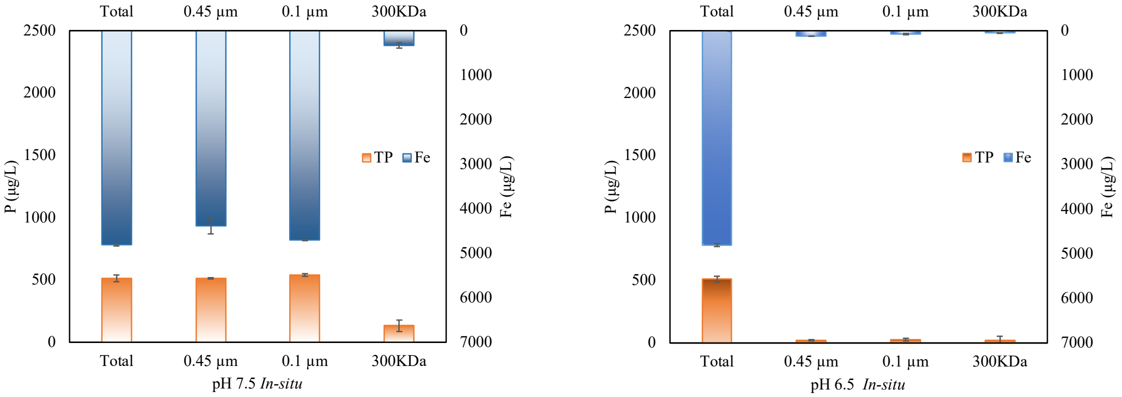


(e) Guanosine-5’-diphosphate Disodium Salt

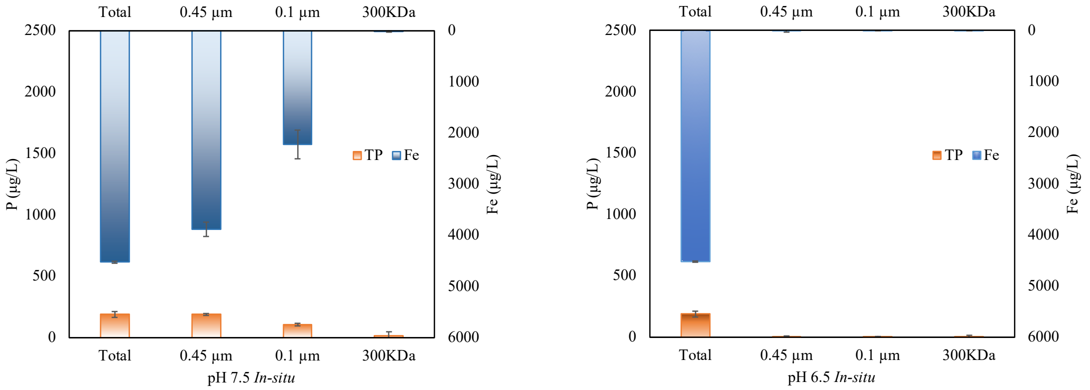


(f) Adenosine-5’-monophosphate

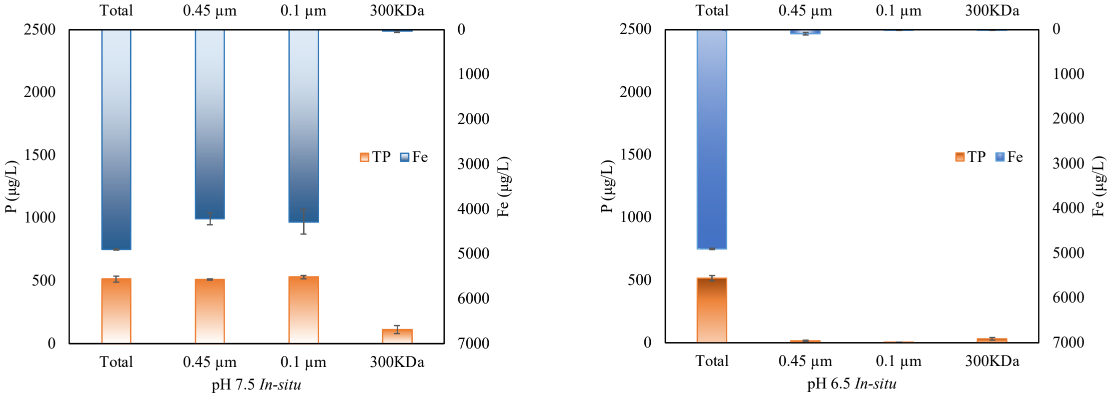
Figure 4-4 Ferrate(VI) removal of different model OP compounds at different conditions (TP=500 µg/L P; Fe(VI) = 5.0 mg/L; pH = 6.5 or 7.5; Control: no ferrate(VI) addition; *in-situ* treatment: direct ferrate(VI) addition to OP-containing solution; and *ex-situ* treatment: ferrate(VI) decay followed by OP addition)



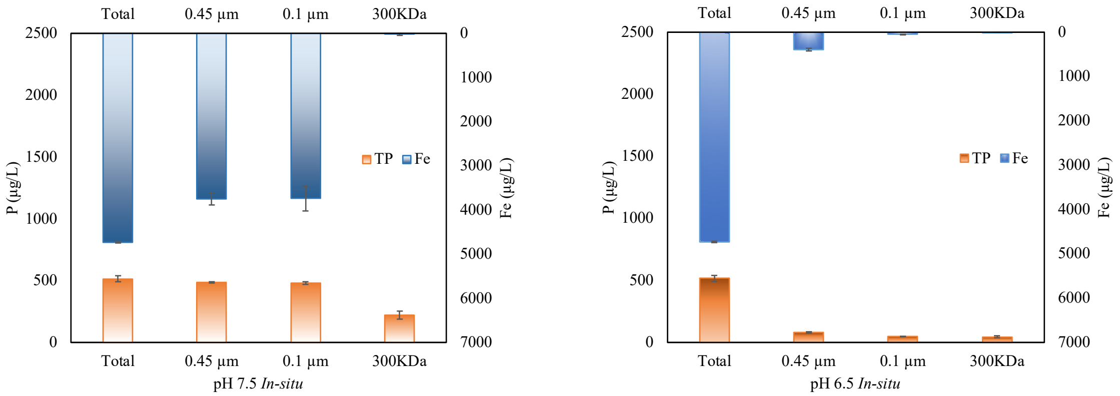
(a) RNA



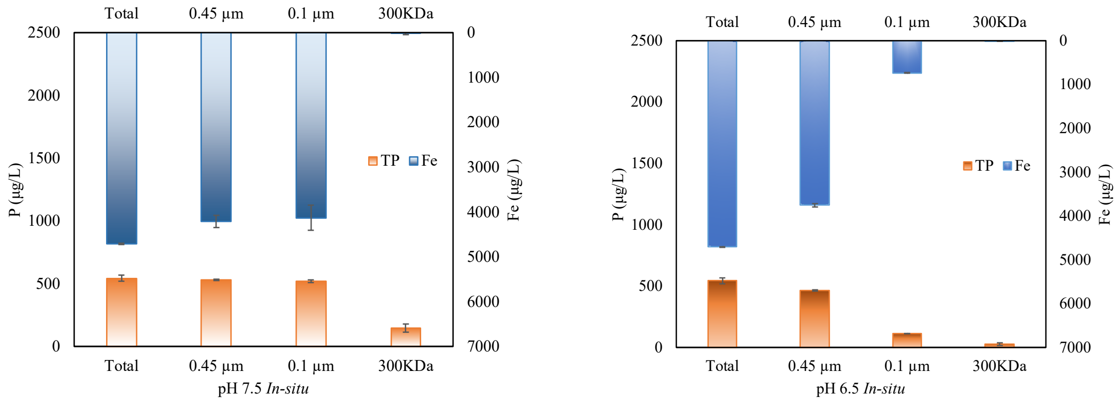
(b) DNA



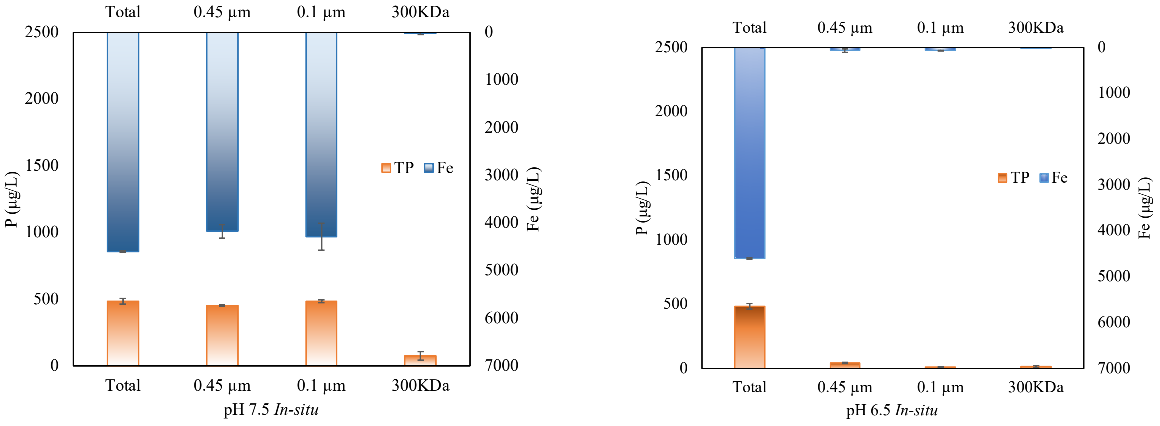
(c) ATP



(d) AMP

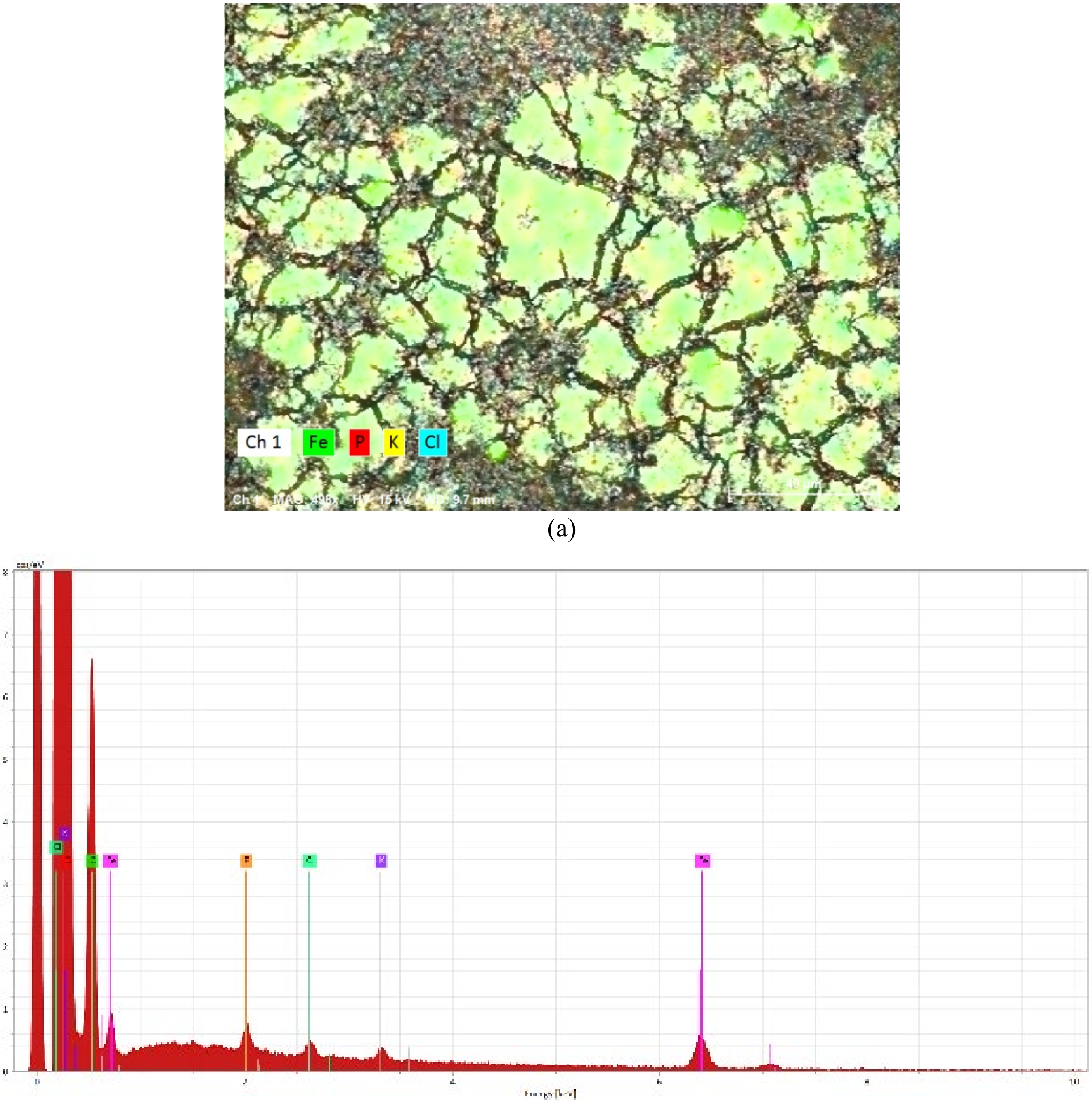


(e) GDP



(f) UDP

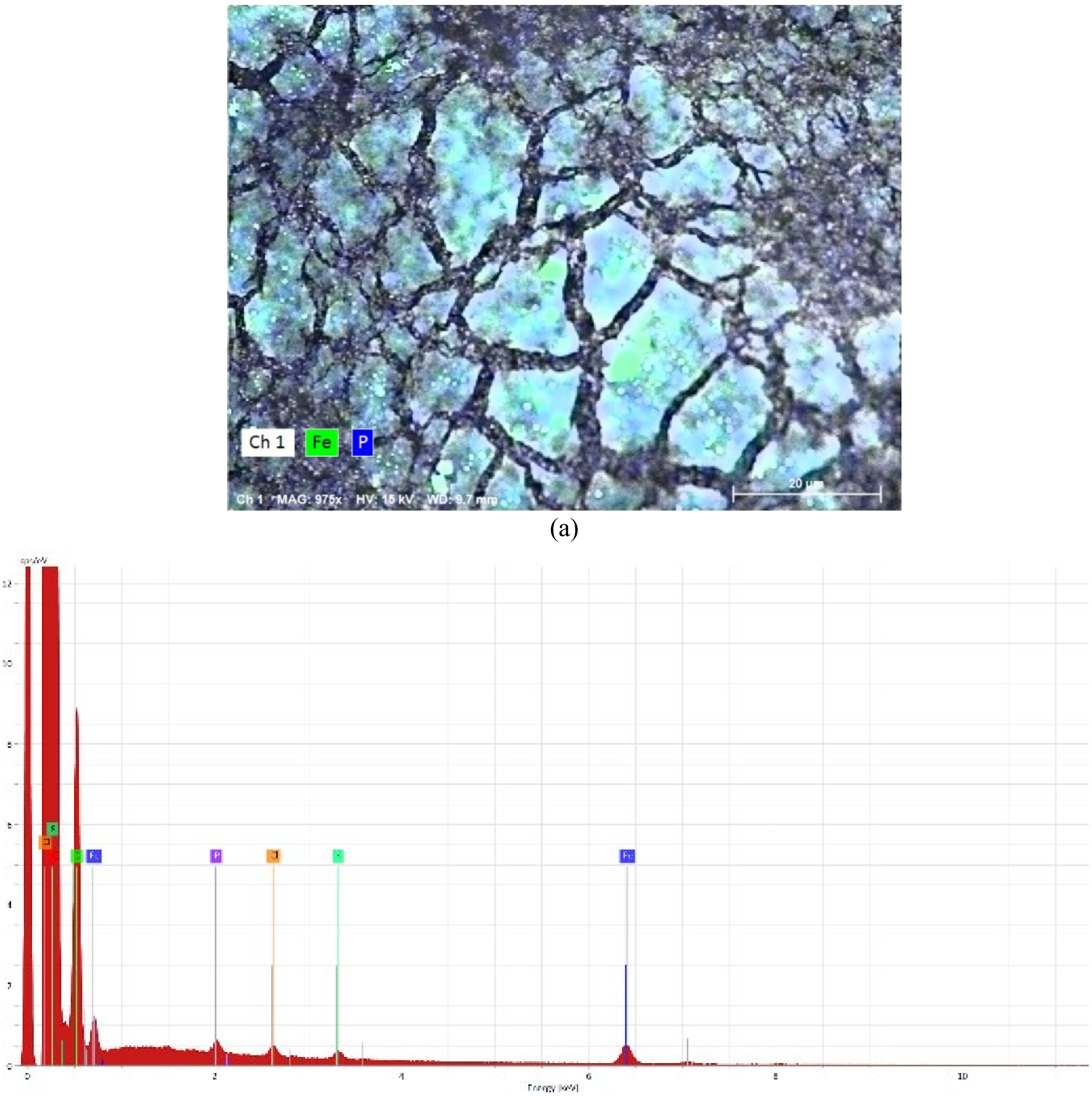
Figure 4-5 Size distribution of P and Fe after *in-situ* ferrate(VI) treatment of different OP model compounds: a) DNA; b) RNA; c) ATP; d) AMP; e) GDP; and f) UDP (initial OP =1000 µg/L as P; Fe(VI)=5.0 mg/L; and pH was maintained at 6.5)



(a)

(b)

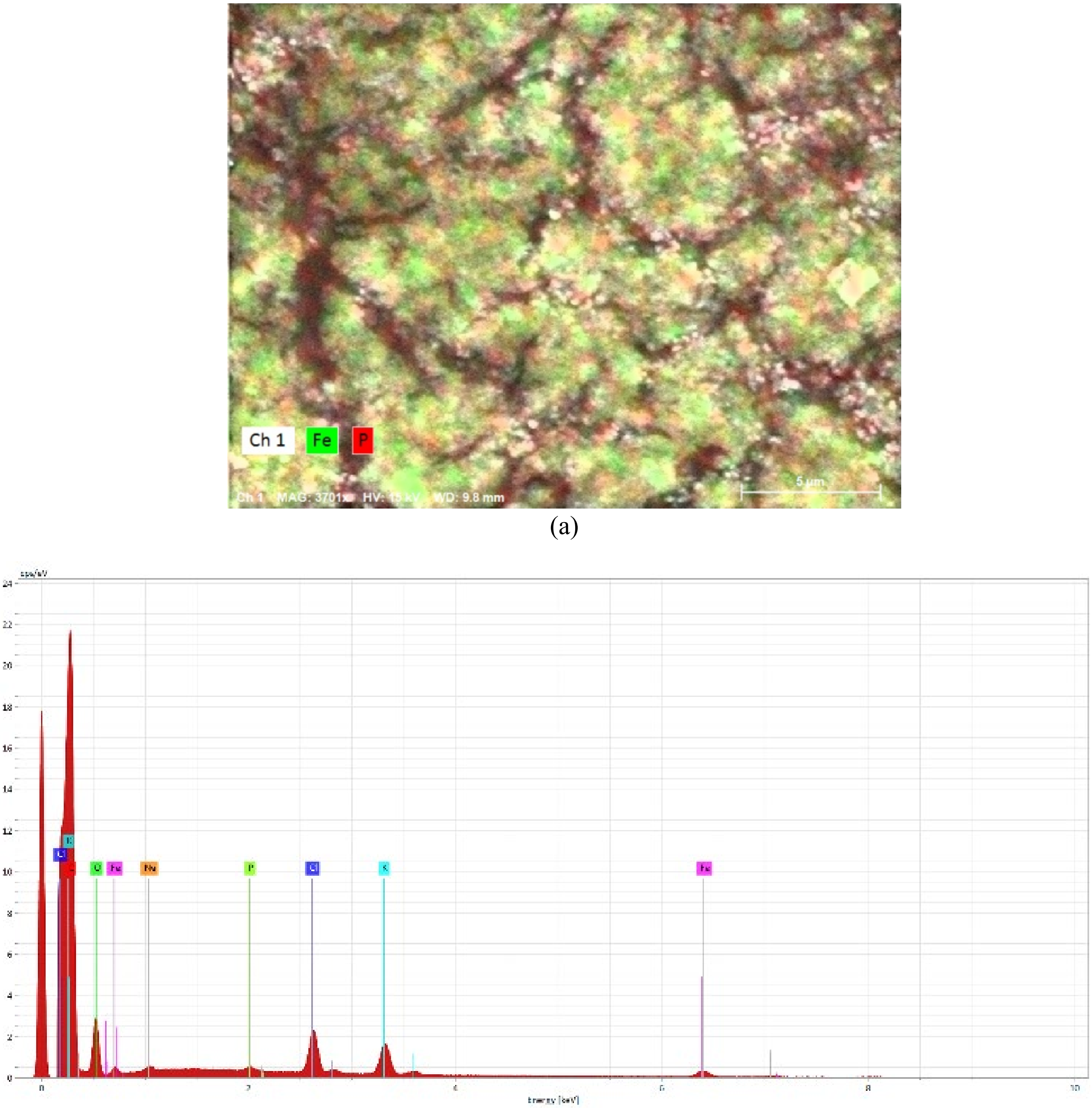
Figure 4-6 Surface element analysis of ferrate(VI) resultant particles after ferrate(VI) treatment of ATP in distilled water (P=500 µg/L; Fe(VI) = 5.0 mg/L; pH = 6.5; the top image: Fe and P mapping on the particle surface; and the bottom image: intensities of different detected elements)



(a)

(b)

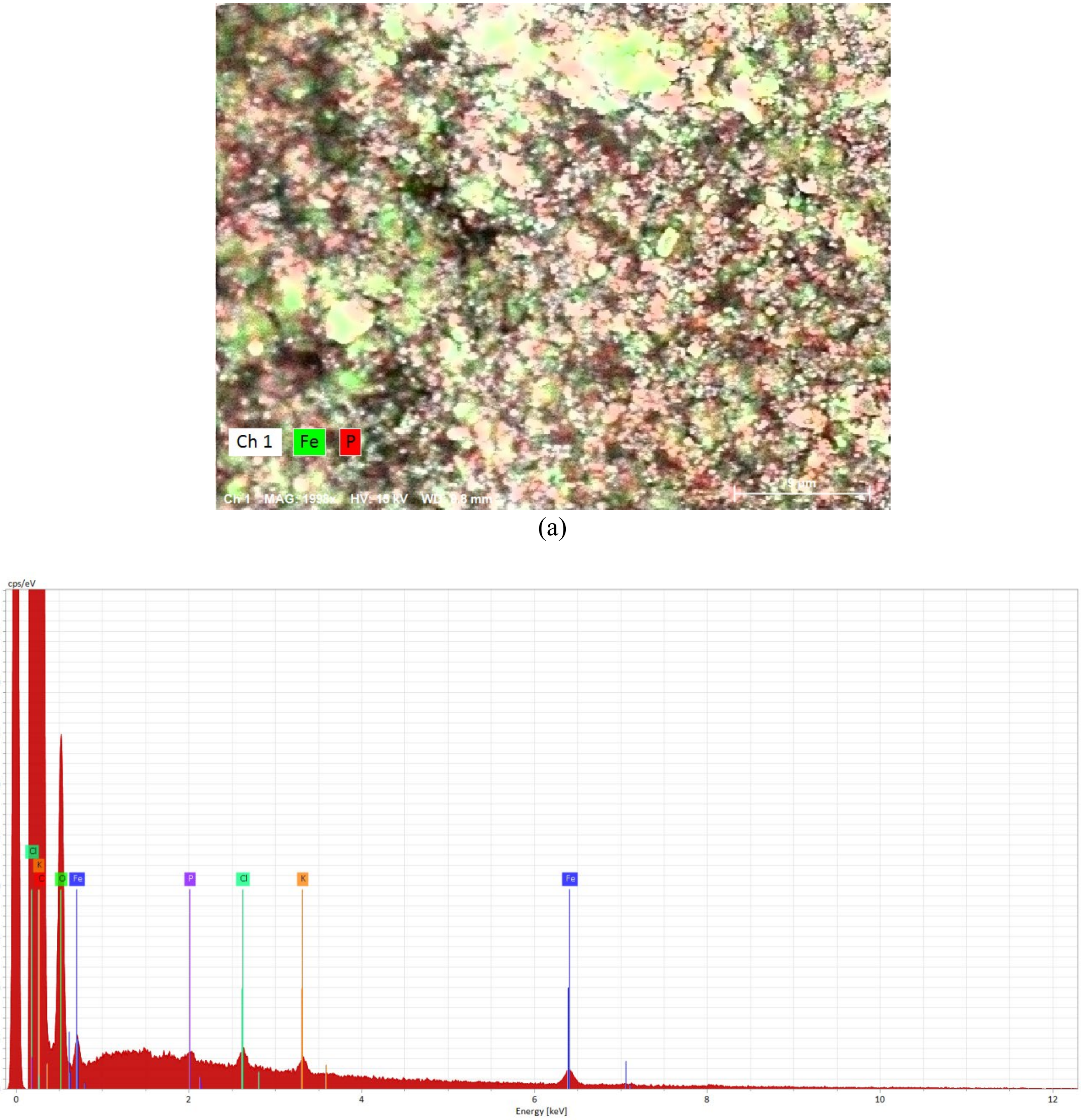
Figure 4-7 Surface element analysis of ferrate(VI) resultant particles after ferrate(VI) treatment of UDP in distilled water (P=500 µg/L; Fe(VI) = 5.0 mg/L; pH = 6.5; the top image: Fe and P mapping on the particle surface; and the bottom image: intensities of different detected elements)



(a)

(b)

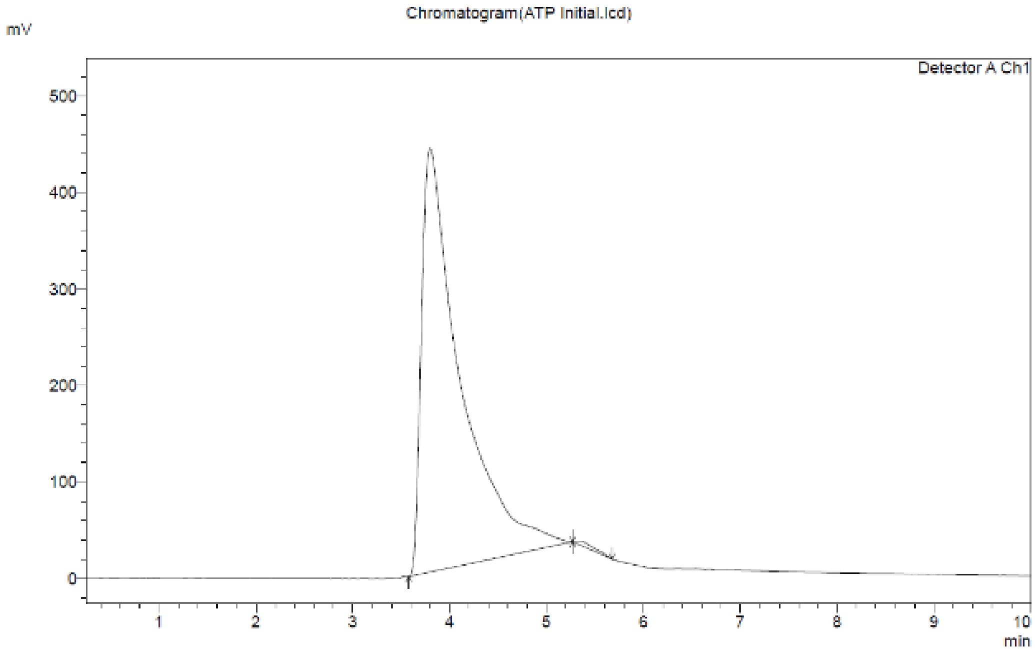
Figure 4-8 Surface element analysis of ferrate(VI) resultant particles after ferrate(VI) treatment of GDP in distilled water (P=500 µg/L; Fe(VI) = 5.0 mg/L; pH = 6.5; the top image: Fe and P mapping on the particle surface; and the bottom image: intensities of different detected elements)



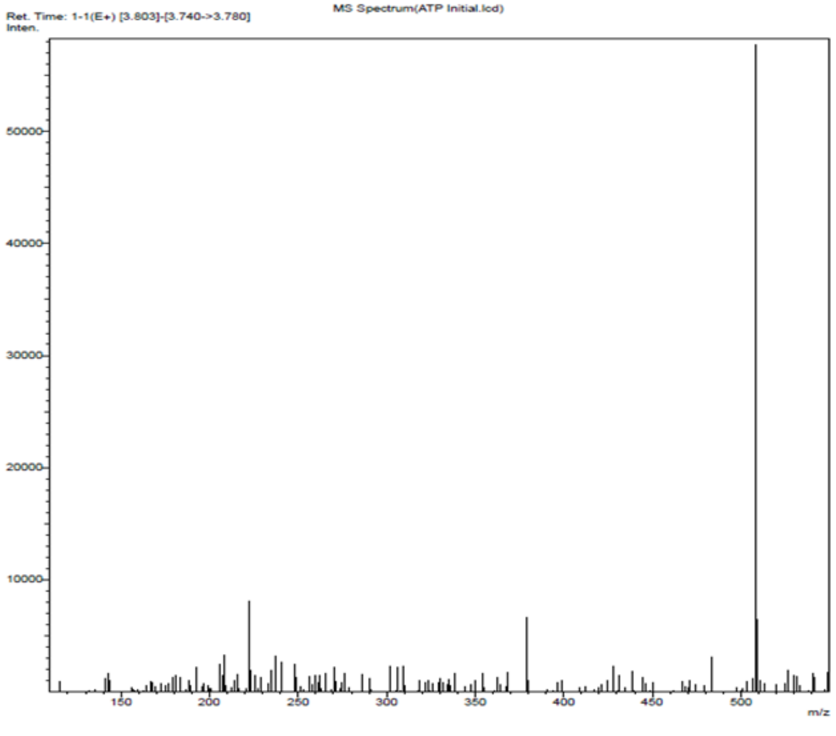
(a)

(b)

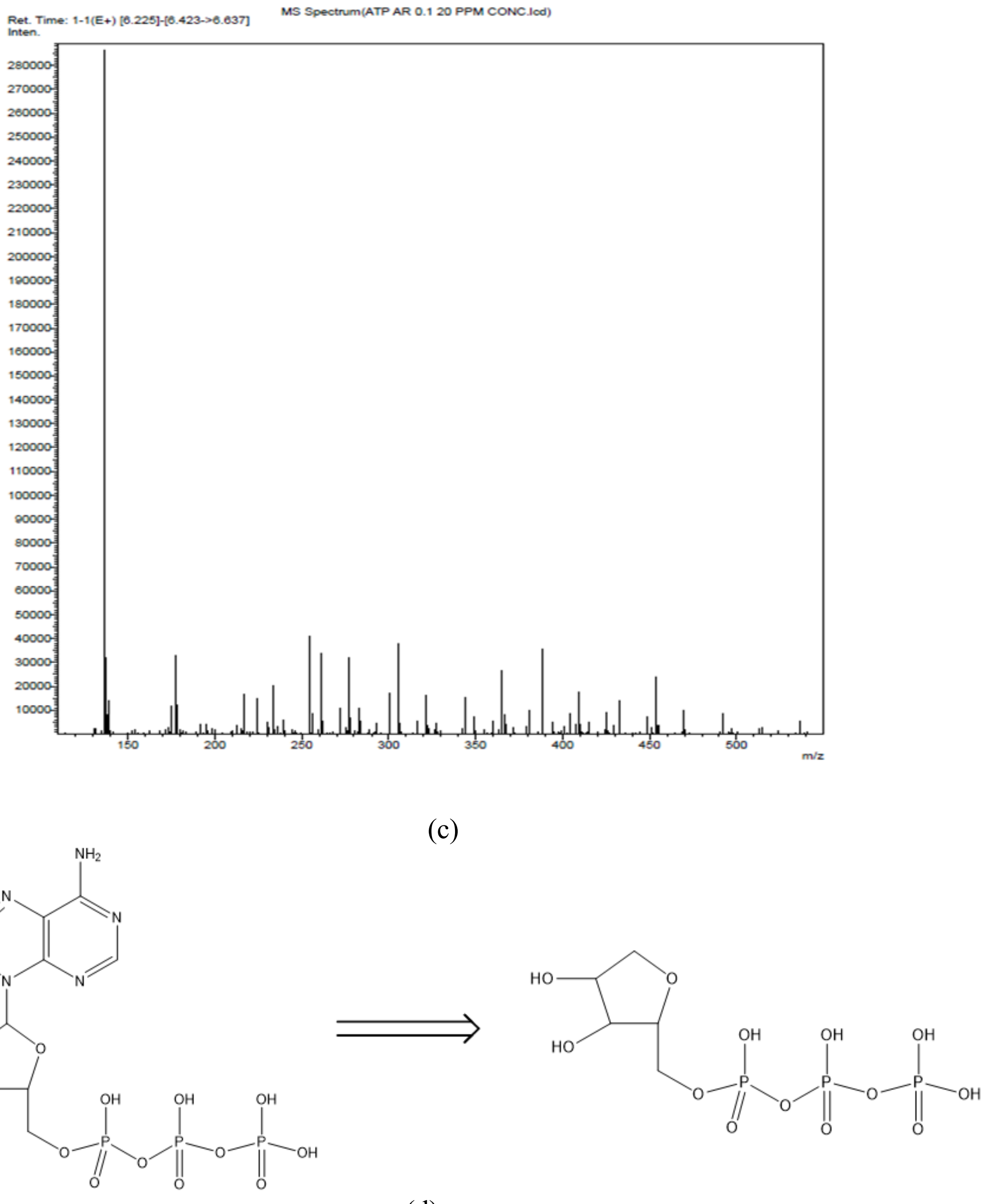
Figure 4-9 Surface element analysis of ferrate(VI) resultant particles after ferrate(VI) treatment of AMP in distilled water (P=500 µg/L; Fe(VI) = 5.0 mg/L; pH = 6.5; the top image: Fe and P mapping on the particle surface; and the bottom image: intensities of different detected elements)


Chromatogram(ATP Initial.lcd)
mV
Detector A Ch1
500
400
300
200
100
0
1
2
3
4
5
6
7
8
9
10
min

(a)


MS Spectrum(ATP Initial.lcd)
Ret. Time: 1-1(E+) [3.803]-[3.740->3.780]
Inten.
50000
40000
30000
20000
10000
150
200
250
300
350
400
450
500
m/z

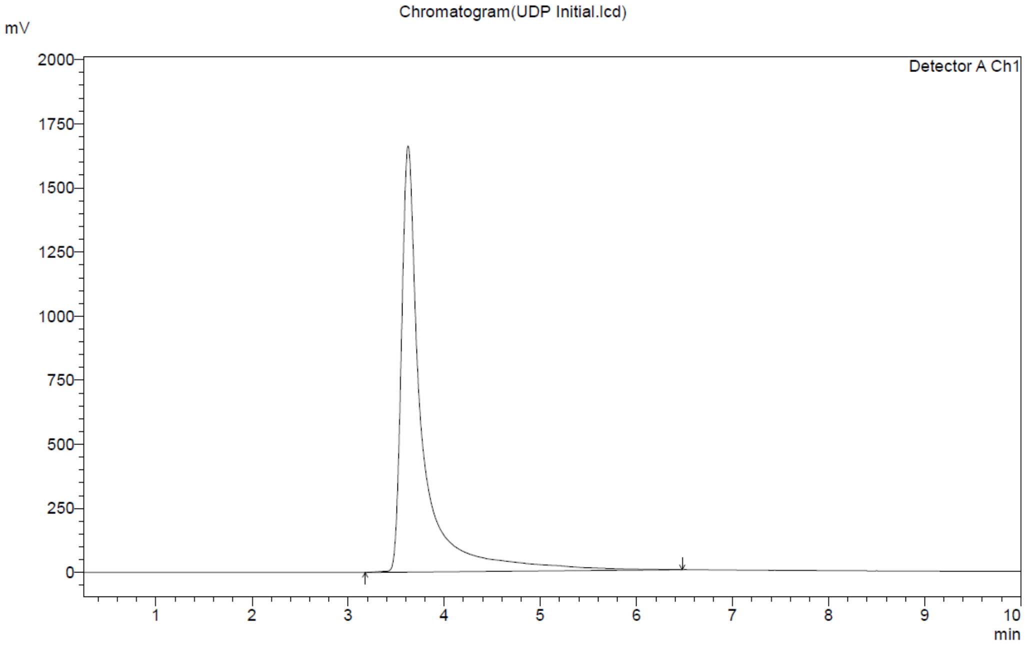
(b)



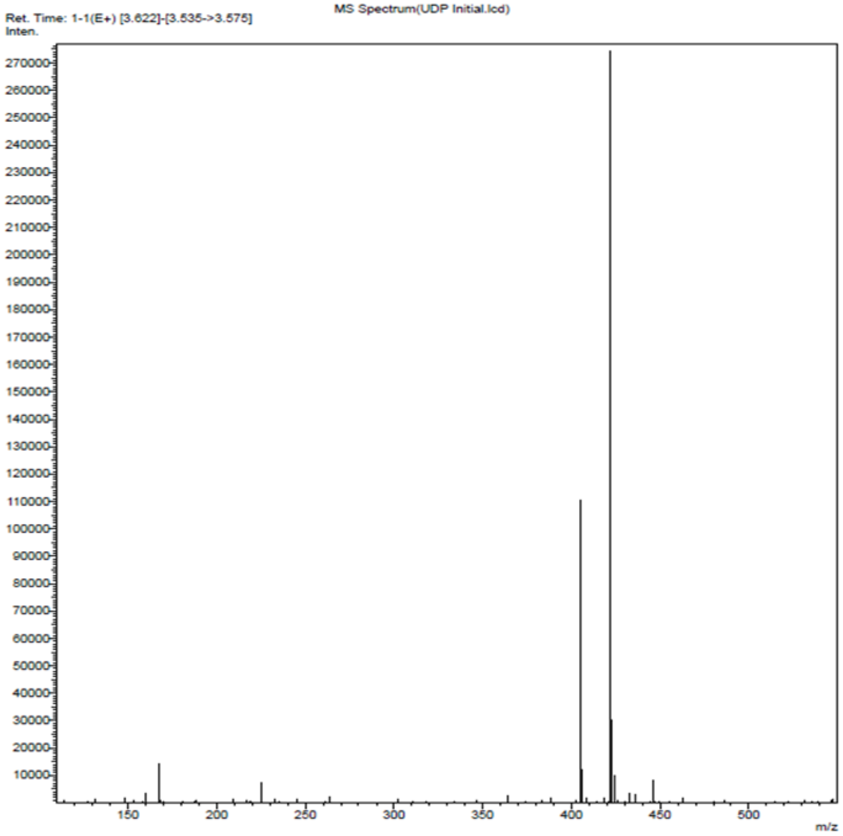
(c)

(d)

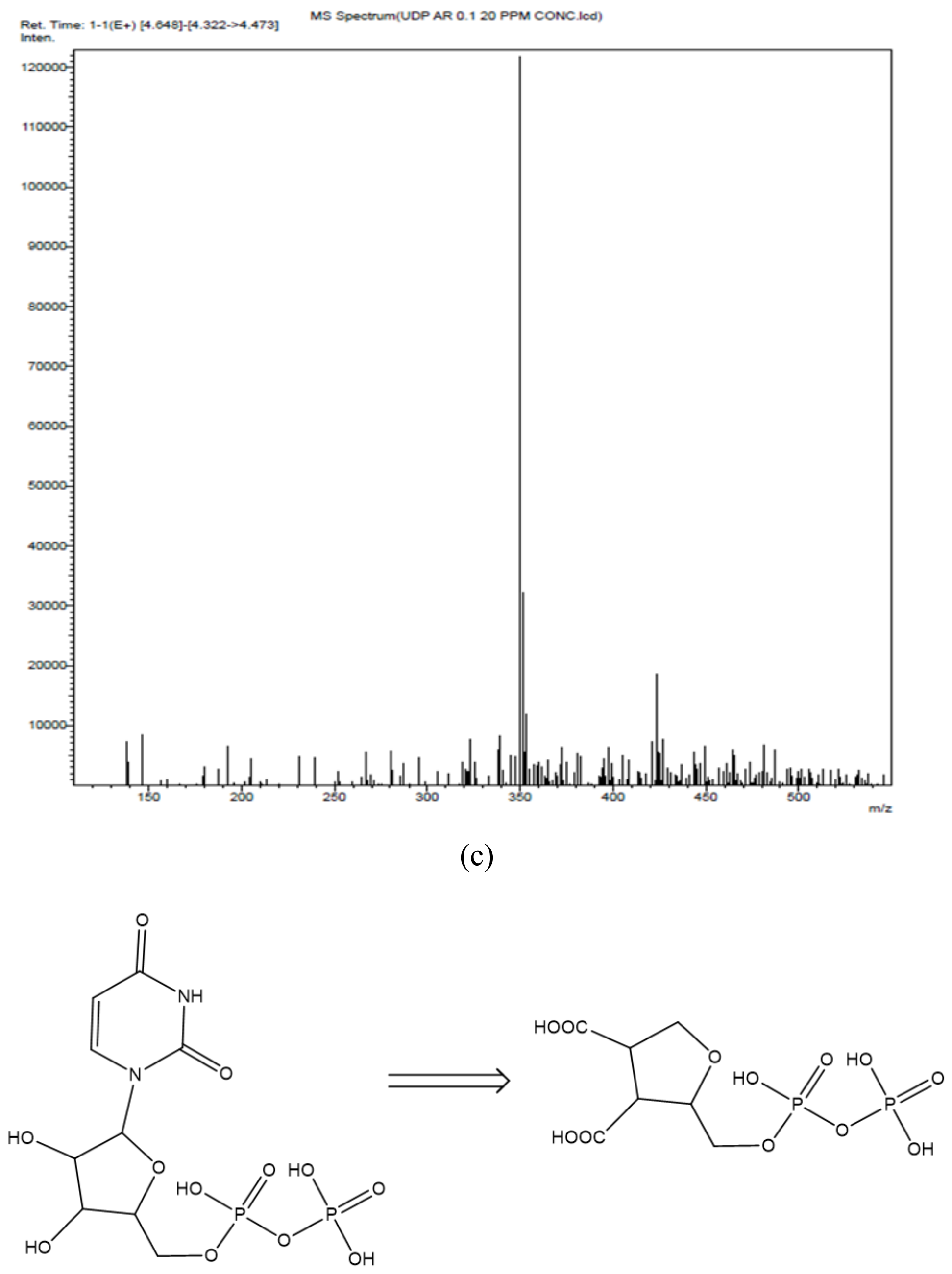
Figure 4-10 Ferrate(VI) oxidation of ATP (P=500 µg/L; Fe(VI) = 5.0 mg/L; and pH = 6.5) a) liquid chromatography of ATP; b) mass spectroscopy of ATP; c) mass spectroscopy of degradation products; and d) proposed degradation pathway)


Chromatogram(UDP Initial.lcd)
mV
Detector A Ch1
2000
1750
1500
1250
1000
750
500
250
0
1
2
3
4
5
6
7
8
9
10
min

(a)


Ret. Time: 1-1(E+) [3.622]-[3.535->3.575]
Inten.
MS Spectrum(UDP Initial.lcd)
270000
260000
250000
240000
230000
220000
210000
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
150
200
250
300
350
400
450
500
m/z

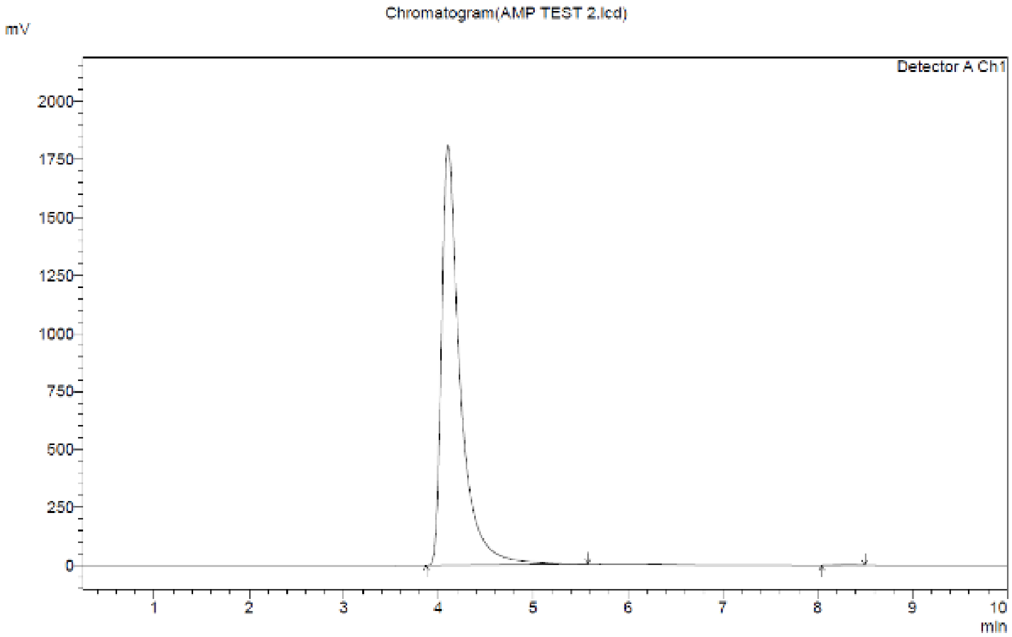
(b)



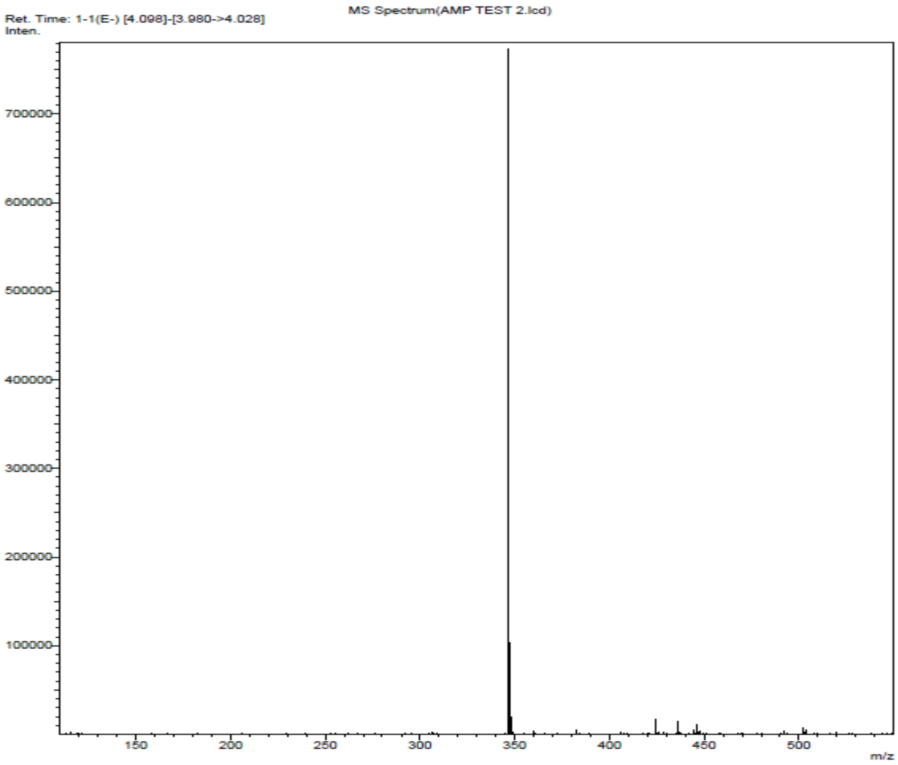
(c)

(d)

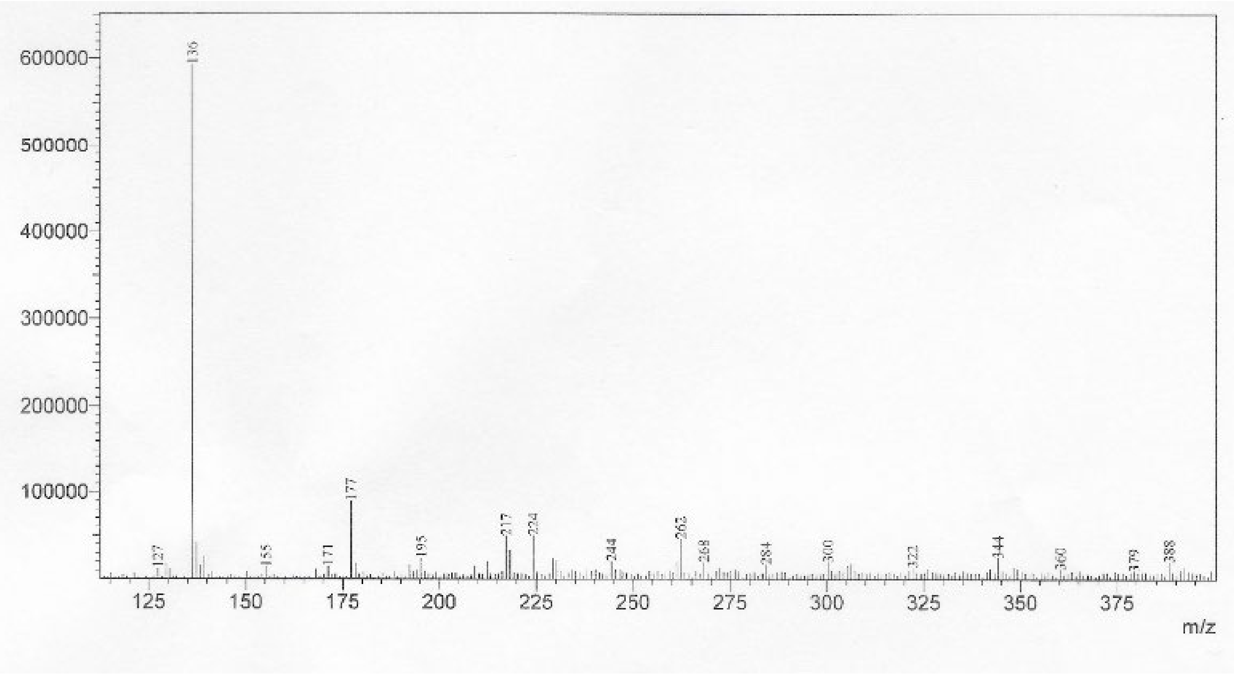
Figure 4-11 Ferrate(VI) oxidation of UDP (P=500 µg/L; Fe(VI) = 5.0 mg/L; and pH = 6.5) a) liquid chromatography of UDP; b) mass spectroscopy of UDP; c) mass spectroscopy of degradation products; and d) proposed degradation pathway)


Chromatogram(AMP TEST 2.lcd)
mV
Detector A Ch1
2000
1750
1500
1250
1000
750
500
250
0
1
2
3
4
5
6
7
8
9
10
min

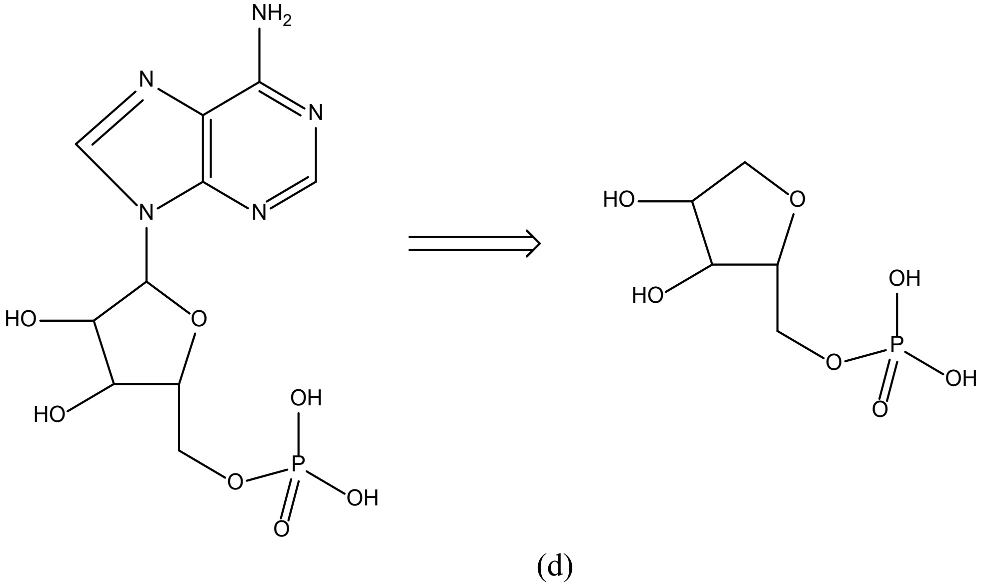
(a)


MS Spectrum(AMP TEST 2.lcd)
Ret. Time: 1-1(E-) [4.098]-[3.980->4.028]
Inten.
700000
600000
500000
400000
300000
200000
100000
150
200
250
300
350
400
450
500
m/z

(b)



(c)



(d)

Figure 4-12 Ferrate(VI) oxidation of AMP (P=500 µg/L; Fe(VI) = 5.0 mg/L; and pH = 6.5) a) liquid chromatography of AMP; b) mass spectroscopy of AMP; c) mass spectroscopy of degradation products; and d) proposed degradation pathway)

4.5 References

Anquandah, G. A. K., Sharma, V. K., Knight, D. A., Batchu, S. R., & Gardinali, P. R. (2011). Oxidation of Trimethoprim by Ferrate(VI): Kinetics, Products, and Antibacterial Activity. *Environmental Science & Technology, 45*(24), 10575-10581. doi:10.1021/es202237g

Anquandah, G. A. K., Sharma, V. K., Panditi, V. R., Gardinali, P. R., Kim, H., & Oturan, M. A. (2013). Ferrate(VI) oxidation of propranolol: Kinetics and products. *Chemosphere, 91*(1), 105-109. doi:10.1016/j.chemosphere.2012.12.001

Baldwin, D. S. (2013). Organic phosphorus in the aquatic environment. *Environmental Chemistry, 10*(6), 439-454. Retrieved from https://doi.org/10.1071/EN13151

Björkman, K. M., & Karl, D. M. (2003). Bioavailability of dissolved organic phosphorus in the euphotic zone at Station ALOHA, North Pacific Subtropical Gyre. *Limnology and Oceanography, 48*(3), 1049-1057. doi:10.4319/lo.2003.48.3.1049

Cheesman, A. W., Turner, B. L., & Ramesh Reddy, K. (2012). Soil Phosphorus Forms along a Strong Nutrient Gradient in a Tropical Ombrotrophic Wetland. *Soil Science Society of America Journal, 76*, 1496-1506. doi:10.2136/sssaj2011.0365

Clark, D. L., Hunt, G., Kasch, M. S., Lemonds, P. J., Moen, G. M., & Neethling, J. B. (2010). *Nutrient Management: Regulatory Approaches to Protect Water Quality: Volume 1 – Review of Existing Practices*. doi:10.2166/9781780403465

Costarramone, N., Kneip, A., & Castetbon, A. (2004). Ferrate(VI) oxidation of cyanide in water. *Environmental Technology, 25*(8), 945-955. doi:10.1080/09593330.2004.9619388

Cotner, J. J. B., & Wetzel, R. G. (1992). Uptake of dissolved inorganic and organic bphosphorus compounds by phytoplankton and bacterioplankton. *Limnology and Oceanography, 37*(2), 232-243. doi:10.4319/lo.1992.37.2.0232

Crittenden, J. C., Trussell, R. R., Hand, D. W., Howe, K. J., & Tchobanoglous, G. (2012). *MWH's Water Treatment: Principles and Design*: John Wiley & Sons.

Cui, J., Zheng, L., & Deng, Y. (2018). Emergency Water Treatment with Ferrate(VI) in Response to Natural Disasters. *Environmental Science: Water Research & Technology, 4*, 359-368

Darch, T., Blackwell, M. S. A., Hawkins, J. M. B., Haygarth, P. M., & Chadwick, D. (2014). A Meta-Analysis of Organic and Inorganic Phosphorus in Organic Fertilizers, Soils, and Water: Implications for Water Quality. *Critical Reviews in Environmental Science and Technology, 44*(19), 2172-2202. doi:10.1080/10643389.2013.790752

Delaude, L., & Laszlo, P. (1996). A Novel Oxidizing Reagent Based on Potassium Ferrate(VI)1. *The Journal of Organic Chemistry, 61*(18), 6360-6370. doi:10.1021/jo960633p

Deng, J., Wu, H. D., Wang, S. J., Liu, Y. B., & Wang, H. Y. (2019). Removal of sulfapyridine by ferrate(VI): efficiency, influencing factors and oxidation pathway. *Environmental Technology, 40*(12), 1585-1591. doi:10.1080/09593330.2018.1426642

Dong, L., Yang, Z., Liu, X., & Liu, G. (2012). Investigation into organic phosphorus species in sediments of Baiyangdian Lake in China measured by fractionation and 31P NMR. *Environmental Monitoring and Assessment, 184*(9), 5829-5839. doi:10.1007/s10661-012-2550-z

Dueñas, J. F., Alonso, J. R., Rey, À. F., & Ferrer, A. S. (2003). Characterisation of phosphorous forms in wastewater treatment plants. *Journal of Hazardous Materials, 97*(1), 193-205. doi:https://doi.org/10.1016/S0304-3894(02)00260-1

Dyhrman, S. T., Chappell, P. D., Haley, S. T., Moffett, J. W., Orchard, E. D., Waterbury, J. B., & Webb, E. A. (2006). Phosphonate utilization by the globally important marine diazotroph Trichodesmium. *Nature, 439*(7072), 68-71. doi:10.1038/nature04203

Falkowski, P., Scholes, R. J., Boyle, E., Canadell, J., Canfield, D., Elser, J., . . . Steffen, W. (2000). The Global Carbon Cycle: A Test of Our Knowledge of Earth as a System. *Science, 290*(5490), 291. doi:10.1126/science.290.5490.291

Fan, M. H., Brown, R. C., & Huang, C. P. (2002). Preliminary studies of the oxidation of arsenic(III) by potassium ferrate. *International Journal of Environment and Pollution, 18*(1), 91-96. doi:10.1504/ijep.2002.000698

Gandhi, R., Ray, A. K., Sharma, V. K., & Nakhla, G. (2014). Treatment of Combined Sewer Overflows Using Ferrate(VI). *Water Environment Research, 86*(11), 2202-2211. doi:10.2175/106143014x14062131178475

Ghernaout, D., Ghernaout, B., & Naceur, M. W. (2011). Embodying the chemical water treatment in the green chemistry—A review. *Desalination, 271*(1), 1-10. doi:https://doi.org/10.1016/j.desal.2011.01.032

Ghernaout, D., & Naceur, M. W. (2011). Ferrate(VI): In situ generation and water treatment - A review. *Desalination and Water Treatment, 30*(1-3), 319-332. doi:10.5004/dwt.2011.2217

Gombos, E., Barkács, K., Felföldi, T., Vértes, C., Makó, M., Palkó, G., & Záray, G. (2013). Removal of organic matters in wastewater treatment by ferrate(VI)-technology. *Microchemical Journal, 107*, 115-120. doi:https://doi.org/10.1016/j.microc.2012.05.019

Goodwill, J. E., Jiang, Y., Reckhow, D. A., Gikonyo, J., & Tobiason, J. E. (2015). Characterization of Particles from Ferrate Preoxidation. *Environmental Science & Technology, 49*(8), 4955-4962.

Gu, A. Z., Liu, L., Neethling, J. B., Stensel, H. D., & Murthy, S. (2011). Treatability and fate of various phosphorus fractions in different wastewater treatment processesA. Z. Gu et al.Treatability and fate of various phosphorus fractions in different wastewater treatment processes. *Water Science and Technology, 63*(4), 804-810. doi:10.2166/wst.2011.312

Gu, A. Z., Liu, L., Onnis-Hayden, A., Smith, S., Gray, H., Houweling, D., & Takács, I. (2014). Phosphorus Fractionation and Removal in Wastewater Treatment: Implications for Minimizing Effluent Phosphorus.

Han, Q., Dong, W. Y., Wang, H. J., Liu, T. Z., Tian, Y., & Song, X. (2018). Degradation of tetrabromobisphenol A by ferrate(VI) oxidation: Performance, inorganic and organic products, pathway and toxicity control. *Chemosphere, 198*, 92-102. doi:10.1016/j.chemosphere.2018.01.117

Hu, L. H., Page, M. A., Sigstam, T., Kohn, T., Marinas, B. J., & Strathmann, T. J. (2012). Inactivation of Bacteriophage MS2 with Potassium Ferrate(VI). *Environmental Science & Technology, 46*(21), 12079-12087. doi:10.1021/es3031962

Ishii, N., Kawabata, Z. i., Nakano, S.-i., Min, M.-G., & Takata, R. (1998). Microbial interactions responsible for dissolved DNA production in a hypereutrophic pond. *Hydrobiologia, 380*(1), 67-76. doi:10.1023/A:1003475000195

Jessen, A., Randall, A., Reinhart, D., & Daly, L. (2008). Effectiveness and Kinetics of Ferrate as a Disinfectant for Ballast Water. *Water Environment Research, 80*(6), 561-569. doi:10.2175/193864708x267423

Jetoo, S., Grover, I. V., & Krantzberg, G. (2015). The Toledo Drinking Water Advisory: Suggested Application of the Water Safety Planning Approach. *Sustainability, 7*(8). doi:10.3390/su7089787

Jiang, J. Q. (2007). Research progress in the use of ferrate(VI) for the environmental remediation. *Journal of Hazardous Materials, 146*(3), 617-623. doi:10.1016/j.jhazmat.2007.04.075

Jiang, J. Q., & Lloyd, B. (2002). Progress in the development and use of ferrate(VI) salt as an oxidant and coagulant for water and wastewater treatment. *Water Research, 36*(6), 1397-1408. doi:10.1016/s0043-1354(01)00358-x

Jiang, J. Q., Wang, S., & Panagoulopoulos, A. (2006). The exploration of potassium ferrate(VI) as a disinfectant/coagulant in water and wastewater treatment. *Chemosphere, 63*(2), 212-219. doi:10.1016/j.chemosphere.2005.08.020

Jiang, J. Q., Wang, S., & Panagoulopoulos, A. (2007). The role of potassium ferrate(VI) in the inactivation of Escherichia coli and in the reduction of COD for water remediation. *Desalination, 210*(1-3), 266-273. doi:10.1016/j.desal.2006.05.051

Johnson, S. E., & Loeppert, R. H. (2006). Role of organic acids in phosphate mobilization from iron oxide. *Soil Science Society of America Journal, 70*(1), 222-234.

Kooti, M., Tarassoli, A., Javadi, H., & Jorfi, M. (2008). A Facile Conversion of Alcohols to Esters Mediated by Potassium Ferrate. *E-Journal of Chemistry, 5*(4), 718-722. doi:10.1155/2008/589834

Kralchevska, R. P., Prucek, R., Kolařík, J., Tuček, J., Machala, L., Filip, J., . . . Zbořil, R. (2016). Remarkable efficiency of phosphate removal: Ferrate(VI)-induced in situ sorption on core-shell nanoparticles. *Water Research, 103*, 83-91. doi:https://doi.org/10.1016/j.watres.2016.07.021

Kwon, J. H., Kim, I. K., Park, K. Y., Kim, Y. D., & Cho, Y. H. (2014). Removal of phosphorus and coliforms from secondary effluent using ferrate(VI). *Ksce Journal of Civil Engineering, 18*(1), 81-85. doi:10.1007/s12205-013-0024-7

Lee, D. G., & Gai, H. (1993). Kinetics and mechanism of the oxidation of alcohols by ferrate ion. *Canadian journal of chemistry, 71*(9), 1394-1400.

Lee, Y., Cho, M., Kim, J. Y., & Yoon, J. (2004). Chemistry of ferrate (Fe(VI)) in aqueous solution and its applications as a green chemical. *Journal of Industrial and Engineering Chemistry, 10*(1), 161-171. Retrieved from <Go to ISI>://WOS:000188469500021

Lee, Y., Kissner, R., & von Gunten, U. (2014). Reaction of Ferrate(VI) with ABTS and Self-Decay of Ferrate(VI): Kinetics and Mechanisms. *Environmental Science & Technology, 48*(9), 5154-5162. doi:10.1021/es500804g

Lee, Y., Um, I. H., & Yoon, J. (2003). Arsenic(III) oxidation by iron(VI) (ferrate) and subsequent removal of arsenic(V) by iron(III) coagulation. *Environmental Science & Technology, 37*(24), 5750-5756. doi:10.1021/es034203+

Lee, Y., & von Gunten, U. (2010). Oxidative transformation of micropollutants during municipal wastewater treatment: Comparison of kinetic aspects of selective (chlorine, chlorine dioxide, ferrate(VI), and ozone) and non-selective oxidants (hydroxyl radical). *Water Research, 44*(2), 555-566. doi:10.1016/j.watres.2009.11.045

Lee, Y., Yoon, J., & von Gunten, U. (2005). Spectrophotometric determination of ferrate (Fe(Vl)) in water by ABTS. *Water Research, 39*(10), 1946-1953. doi:10.1016/j.watres.2005.03.005

Lee, Y., Zimmermann, S. G., Kieu, A. T., & von Gunten, U. (2009). Ferrate (Fe(VI)) Application for Municipal Wastewater Treatment: A Novel Process for Simultaneous Micropollutant Oxidation and Phosphate Removal. *Environmental Science & Technology, 43*(10), 3831-3838. doi:10.1021/es803588k

Li, B., & Brett, M. T. (2013). The influence of dissolved phosphorus molecular form on recalcitrance and bioavailability. *Environmental Pollution, 182*, 37-44. doi:https://doi.org/10.1016/j.envpol.2013.06.024

Lim, M., & Kim, M. J. (2010). Effectiveness of Potassium Ferrate (K2FeO4) for Simultaneous Removal of Heavy Metals and Natural Organic Matters from River Water. *Water Air and Soil Pollution, 211*(1-4), 313-322. doi:10.1007/s11270-009-0302-7

Liu, H., Jeong, J., Gray, H., Smith, S., & Sedlak, D. L. (2012). Algal Uptake of Hydrophobic and Hydrophilic Dissolved Organic Nitrogen in Effluent from Biological Nutrient Removal Municipal Wastewater Treatment Systems. *Environmental Science & Technology, 46*(2), 713-721. doi:10.1021/es203085y

Liu, H., Pan, X., Chen, J., Qi, Y., Qu, R., & Wang, Z. (2019). Kinetics and mechanism of the oxidative degradation of parathion by Ferrate(VI). *Chemical Engineering Journal, 365*, 142-152. doi:https://doi.org/10.1016/j.cej.2019.02.040

Liu, L., Smith, D., Bracken, M., Neethling, J., Stensel, H., Murthy, S., . . . Gu, A. (2011). Occurrence and implication of dissolved organic phosphorus (DOP) in tertiary wastewater effluents. *Water Environment Research Foundation*.

Lü, C., Yan, D., He, J., Zhou, B., Li, L., & Zheng, Q. (2017). Environmental geochemistry significance of organic phosphorus: An insight from its adsorption on iron oxides. *Applied Geochemistry, 84*, 52-60.

Lu, H., Yang, L., Zhang, S., & Wu, Y. (2014). The Behavior of Organic Phosphorus under Non-Point Source Wastewater in the Presence of Phototrophic Periphyton. *PLOS ONE, 9*(1), e85910. doi:10.1371/journal.pone.0085910

Macklon, A. E. S., Grayston, S. J., Shand, C. A., Sim, A., Sellars, S., & Ord, B. G. (1997). Uptake and transport of phosphorus by Agrostis capillaris seedlings from rapidly hydrolysed organic sources extracted from32 P-labelled bacterial cultures. *Plant and Soil, 190*(1), 163-167. doi:10.1023/A:1004294617461

Nausch, M., & Nausch, G. (2007). Bioavailable dissolved organic phosphorus and phosphorus use by heterotrophic bacteria. *Aquatic Biology, 1*(2), 151-160. Retrieved from https://www.int-res.com/abstracts/ab/v1/n2/p151-160/

Nawrocki, M. P., & Karl, D. M. (1989). Dissolved ATP turnover in the Bransfield Strait, Antarctica during a spring bloom. *Marine Ecology Progress Series, 57*(1), 35-44. Retrieved from http://www.jstor.org/stable/24836041

Pagilla, K. R., Urgun-Demirtas, M., & Ramani, R. (2006). Low effluent nutrient technologies for wastewater treatment. *Water Science and Technology, 53*(3), 165-172. doi:10.2166/wst.2006.089

Prucek, R., Tucek, J., Kolarik, J., Filip, J., Marusak, Z., Sharma, V. K., & Zboril, R. (2013). Ferrate(VI)-Induced Arsenite and Arsenate Removal by In Situ Structural Incorporation into Magnetic Iron(III) Oxide Nanoparticles. *Environmental Science & Technology, 47*(7), 3283-3292. doi:10.1021/es3042719

Qin, B., Zhu, G., Gao, G., Zhang, Y., Li, W., Paerl, H. W., & Carmichael, W. W. (2010). A Drinking Water Crisis in Lake Taihu, China: Linkage to Climatic Variability and Lake Management. *Environmental Management, 45*(1), 105-112. doi:10.1007/s00267-009-9393-6

Qin, C., Liu, H., Liu, L., Smith, S., Sedlak, D. L., & Gu, A. Z. (2015). Bioavailability and characterization of dissolved organic nitrogen and dissolved organic phosphorus in wastewater effluents. *Science of The Total Environment, 511*, 47-53. doi:https://doi.org/10.1016/j.scitotenv.2014.11.005

Ruttenberg, K. C., & Sulak, D. J. (2011). Sorption and desorption of dissolved organic phosphorus onto iron (oxyhydr)oxides in seawater. *Geochimica et Cosmochimica Acta, 75*(15), 4095-4112. doi:https://doi.org/10.1016/j.gca.2010.10.033

Sañudo-Wilhelmy, S. A. (2006). A phosphate alternative. *Nature, 439*(7072), 25-26. doi:10.1038/439025a

Schindler, D. W., Hecky, R. E., Findlay, D. L., Stainton, M. P., Parker, B. R., Paterson, M. J., . . . Kasian, S. E. M. (2008). Eutrophication of lakes cannot be controlled by reducing nitrogen input: Results of a 37-year whole-ecosystem experiment. *Proceedings of the National Academy of Sciences, 105*(32), 11254. doi:10.1073/pnas.0805108105

Sharma, V. K. (2002a). Ferrate(V) oxidation of pollutants: a premix pulse radiolysis study. *Radiation Physics and Chemistry, 65*(4-5), 349-355. doi:10.1016/s0969-806x(02)00335-3

Sharma, V. K. (2002b). Potassium ferrate(VI): an environmentally friendly oxidant. *Advances in Environmental Research, 6*(2), 143-156. doi:10.1016/s1093-0191(01)00119-8

Sharma, V. K. (2008). Oxidative transformations of environmental pharmaceuticals by Cl(2), ClO(2), O(3), and Fe(VI): Kinetics assessment. *Chemosphere, 73*(9), 1379-1386. doi:10.1016/j.chemosphere.2008.08.033

Sharma, V. K. (2010). Oxidation of nitrogen-containing pollutants by novel ferrate(VI) technology: A review. *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering, 45*(6), 645-667. doi:10.1080/10934521003648784

Sharma, V. K., Burnett, C. R., O'Connor, D. B., & Cabelli, D. (2002). Iron(VI) and iron(V) oxidation of thiocyanate. *Environmental Science & Technology, 36*(19), 4182-4186. doi:10.1021/es020570u

Sharma, V. K., Chen, L., & Zboril, R. (2015). Review on high valent FeVI (ferrate): a sustainable green oxidant in organic chemistry and transformation of pharmaceuticals. *ACS Sustainable Chemistry & Engineering, 4*(1), 18-34.

Siuda, W., & GÃƒÂ¼de, H. (1996). Determination of dissolved deoxyribonucleic acid concentration in lake water. *Aquatic Microbial Ecology, 11*(2), 193-202. Retrieved from https://www.int-res.com/abstracts/ame/v11/n2/p193-202/

Smil, V. (2000). PHOSPHORUS IN THE ENVIRONMENT: Natural Flows and Human Interferences. *Annual Review of Energy and the Environment, 25*(1), 53-88. doi:10.1146/annurev.energy.25.1.53

Song, Y. L., Deng, Y., & Jung, C. I. (2016). Mitigation and degradation of natural organic matters (NOMs) during ferrate(VI) application for drinking water treatment. *Chemosphere, 146*, 145-153. doi:10.1016/j.chemosphere.2015.12.001

Song, Y. R., & Ma, J. W. (2013). A Review of Ferrates (VI) Oxidation of Organic Compounds. *Advanced Materials Research, 774-776*, 556-559. doi:10.4028/www.scientific.net/AMR.774-776.556

Sun, S. F., Jiang, J., Pang, S. Y., Ma, J., Xue, M., Li, J., . . . Yuan, Y. X. (2018). Oxidation of theophylline by Ferrate(VI) and formation of disinfection byproducts during subsequent chlorination. *Separation and Purification Technology, 201*, 283-290. doi:10.1016/j.seppur.2018.03.014

Talaiekhozani, A., Talaei, M. R., & Rezania, S. (2017). An overview on production and application of ferrate(VI) for chemical oxidation, coagulation and disinfection of water and wastewater. *Journal of Environmental Chemical Engineering, 5*(2), 1828-1842. doi:https://doi.org/10.1016/j.jece.2017.03.025

Tchobanoglous, G., Stensel, H., Tsuchihashi, R., Burton, F., Abu-Orf, M., Bowden, G., & Pfrang, W. (2014). Wastewater Engineering: Treatment and Resource Recovery, ; Metcalf and Eddy I AECOM. In: McGraw-Hill Book Company: New York, NY.

Thompson, S. K., & Cotner, J. B. (2018). Bioavailability of Dissolved Organic Phosphorus in Temperate Lakes. *Frontiers in Environmental Science, 6*, 62. Retrieved from https://www.frontiersin.org/article/10.3389/fenvs.2018.00062

Toor, G. S., Condron, L. M., Di, H. J., Cameron, K. C., & Cade-Menun, B. J. (2003). Characterization of organic phosphorus in leachate from a grassland soil. *Soil Biology and Biochemistry, 35*(10), 1317-1323. doi:https://doi.org/10.1016/S0038-0717(03)00202-5

Turner, B. L., Papházy, M. J., Haygarth, P. M., & McKelvie, I. D. (2002). Inositol phosphates in the environment. *Philosophical transactions of the Royal Society of London. Series B, Biological sciences, 357*(1420), 449-469. doi:10.1098/rstb.2001.0837

Waite, T. D. (2012). On-Site Production of Ferrate for Water and Wastewater Purification. *American Laboratory, 44*(10), 26-28. Retrieved from <Go to ISI>://WOS:000312286700006

Wetzel, R. G. (2001). *Limnology: Lake and River Ecosystems* (3rd Edition ed.). San Diego, CA: Gulf Professional Publishing.

Yan, J., Jiang, T., Yao, Y., Lu, S., Wang, Q., & Wei, S. (2016). Preliminary investigation of phosphorus adsorption onto two types of iron oxide-organic matter complexes. *Journal of Environmental Sciences, 42*, 152-162. doi:https://doi.org/10.1016/j.jes.2015.08.008

Yang, B., Ying, G. G., Zhao, J. L., Liu, S., Zhou, L. J., & Chen, F. (2012). Removal of selected endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) during ferrate(VI) treatment of secondary wastewater effluents. *Water Research, 46*(7), 2194-2204. doi:10.1016/j.watres.2012.01.047

Yuan, Z., Jiang, S., Sheng, H., Liu, X., Hua, H., Liu, X., & Zhang, Y. (2018). Human Perturbation of the Global Phosphorus Cycle: Changes and Consequences. *Environmental Science & Technology, 52*(5), 2438-2450. doi:10.1021/acs.est.7b03910

Chapter 5 Conclusions

5.1 Economic Analysis

Cost is another essential factor affecting the acceptance of an innovative technology in the market. However, it is unsuitable to perform techno-economic assessment (TEA) for ferrate(VI) treatment technologies and compare them with exiting treatment options, considering that the emerging treatment technologies still remain at the early stage. However, a preliminary cost analysis could be made to estimate the expenses for chemical reagents during ferrate(VI) treatment of biologically treated municipal wastewater.

Ferrate(VI) application was extremely restricted because the synthesis of a dry or powder high-purity ferrate product, with sufficient stability to be transported, handled, and stored, was prohibitively expensive (> \$130/kg) (Waite, 2012). However, recent advances in ferrate(VI) production can substantially produce ferrate(VI) stock solution on site, thereby making the application feasible (Cashman et al., 2014; Jiang, Stanford, & Alsheyab, 2009; Jiang, Stanford, & Mollazeinal, 2012; Waite, 2012). Such advances have opened new opportunities for applications of ferrate(VI) to new areas, such as wastewater treatment. At an annual inflation rate of 3%, ferrate(VI) has an estimated price at \$0.49/kg as Fe (the present value in 2020) (Cui, Zheng, & Deng, 2018). On the other hand, the common ferric chloride has a price around at \$0.19/kg (the present value in 2020) (ICIS, 2006). We can notice that the expense of ferrate(VI) treatment was 2.57 times as that of ferric treatment in terms of chemical agents when ferrate(VI) and ferric salts are used at the identical doses. Although the ferrate(VI) treatment appears more costly, it would bring more treatment benefits as discussed later. Here we made a preliminary cost analysis for ferrate(VI) application. When ferrate(VI) is used for treatment of phosphorus in secondary effluent at a dose of 5.0 mg/L as Fe, the estimated cost for ferrate(VI) consumption was approximately < $\$0.10/10^3$ gal.

5.2 Implication in Environmental Management

Wastewater treatment plays a key role in water resources management, particularly at an urban setting. This project aimed to improve the quality of untreated or treated wastewater, of which the latter one may be discharged into the environment or reused for an intended purpose, particularly in the removal of phosphorus. These findings from this project have profound impacts on the aspects on urban water management, environment, and society, as discussed below.

5.2.1 Implication to Water Management

Wastewater treatment is one key component in an urban or agricultural water cycle. Engineering technologies and designs are applied to improve wastewater quality for different purposes. This study clearly demonstrates that ferrate(VI) is a promising treatment agent for alleviation of organic and inorganic wastewater phosphorus in the dissolved and particulate forms, together with other wastewater contaminants at different wastewater treatment stages. Specific discussion on the implication to water management is as follows.

1) Ferrate(VI) treatment can serve as a CEPT in wastewater treatment. Secondary wastewater treatment is typically the minimum wastewater treatment requirement in many developed countries, such as the United States and Singapore. Within a typical secondary or even tertiary wastewater treatment facility, ferrate(VI) can early remove phosphorus in the primary treatment step, before the wastewater enters into a biological wastewater treatment unit. Meanwhile, the CEPT can alleviate many particulate pollutants, such as TSS and particulate COD. Therefore, the ferrate(VI) CEPT can significantly mitigate the loading for the ensuing

biological treatment (e.g. activated sludge basins or trickling filters), thereby enhancing the wastewater treatment.

Application of CEPT for low-income or developing countries is another scenario, where primary wastewater treatment serves as a dominant wastewater option. Undoubtedly, the quality of treated wastewater after the primary sedimentation tank is poor, because the major treatment mechanism in the primary treatment is settling driven by gravity. Consequently, the major pollutants to be removed in primary sedimentation tanks are particulate matters, rather than soluble contaminants (e.g., dissolved COD, N, P, and trace emerging contaminants). In contrast, adoption of a CEPT with ferrate(VI) is expected to significantly improve the effluent quality due to multiple functions of ferrate(VI). Besides TSS, ferrate(VI) can remove phosphorus and decompose emerging contaminants. Moreover, ferrate(VI) inactivation of water-borne pathogens can be a substitute of traditional wastewater disinfection (e.g., chlorination or ozonation). This will greatly decrease the complexity of system design and operation, while improving the quality of treated wastewater.

2) Ferrate(VI) treatment provides a new advanced wastewater treatment to the wastewater industry. The innovative option can concurrently remove inorganic and organic phosphorus, thus achieving a very low effluent P. This is of significance for the wastewater industry that always stay current and proactive for the increasingly stringent wastewater discharge regulations on different wastewater parameters, such as phosphorus. Although addition of iron or aluminum coagulants at wastewater treatment plants, as a traditional P removal method, can effectively remove phosphate in wastewater, the treatment poorly removes organic phosphorus. Consequently, the traditional method cannot meet with the low P discharge requirement in many environmentally sensitive water bodies, e.g. the Cheapskate Bay. In contrast, one benefit from

ferrate(VI) treatment is the effective removal of organic phosphorus, accompanied by the mitigation of phosphate. The better P removal performance is ascribed to concurrence of chemical oxidation and adsorption over the ferrate(VI) treatment.

Besides phosphorus, ferrate(VI) has been well demonstrated to remove many other wastewater contaminants, such as trace emerging contaminants and pathogenic microorganisms. Of note, in the realistic advanced wastewater treatment, alleviation of emerging contaminants (e.g. antibiotics) is frequently achieved by activated carbon adsorption or chemical oxidation (e.g., ozonation and UV/hydrogen peroxide), while inactivation of pathogens is accomplished by chlorination, ozonation, or UV disinfection. However, when ferrate(VI) is adopted for P removal, emerging contaminants and water-borne pathogens can be simultaneously removed. Therefore, the treatment units originally designed for organics removal and disinfection may not be needed. This will save treatment costs and decrease the system complexity.

3) Ferrate(VI) treatment is beneficial to water reuse in an urban water cycle. Planned water reuse is a common option in urban water management in the arid and semi-arid regions, such as the western United States. Pollutants present in treated wastewater should be sufficiently removed before intended reuse. In the U.S. Northeast, although large-scale wastewater reclamation projects are barely implemented due to the abundant precipitation, the unexpected “de facto” water reuse often occurs, at which the intake of a drinking water treatment plant is in proximity to the discharge outlet of an upstream municipal wastewater treatment facility. Therefore, a technically viable treatment technology is required to significantly improve the quality of treated wastewater, which later serves as the source water of a wastewater reclamation facility or a potable water treatment plant.

4) Despite the aforementioned advantages, ferrate(VI) treatment brings potential challenges to the wastewater treatment facility. Similar to the traditional coagulant addition, ferrate(VI) dosing finally leads to production of iron sludge, which may require appropriate management and disposal. Of note, when ferrate(VI) is applied to CEPT, the liquid-solid separation is not an issue in the most cases, because the iron sludge can readily settle down in the primary sedimentation basins. However, when ferrate(VI) is used for advanced wastewater treatment, a following liquid-solid separation must be used for removal of these unwanted particles. Size and density of these ferrate(VI) resultant particles rely on the treatment operation and solution chemistry, as evidenced by the findings from this dissertation research and our previous studies (Zheng & Deng, 2016). In order to address the issue, a strategy for the wastewater industry is to promote the formation of larger and denser particles through controlling of the operation conditions and solution chemistry parameters.

5.2.2 Environmental Benefits

Environmental benefits of the ferrate(VI) treatment technologies are embodied in two aspects, including 1) the improvement of environmental quality and 2) the environmental friendless of the technology.

Improving environmental quality. Ferrate(VI) alleviation of phosphorus, both inorganic and organic, in wastewater would minimize the occurrence of eutrophication in natural receiving water bodies, given that phosphorus is one of the two primary nutrients. Eutrophication is one of the most common water pollution events in the United States and many other countries. This can directly cause algal blooms, which can deplete dissolved oxygen, produce taste and odor compounds, increase water turbidity, and release toxic algal toxins. A serious algal blooming event may lead to the shutdown of neighboring potable water treatment plants due to the contamination of water sources. Wastewater discharge is a principal point pollution source for the input of phosphorus and nitrogen. Therefore, mitigation of wastewater nutrients within the wastewater treatment plants is a strategically sound approach to preventing the occurrence of eutrophication.

Meanwhile, ferrate(VI) has proven very effective for degradation of harmful emerging contaminants through chemical oxidation, such as pharmaceuticals and personal care products, endocrine disrupting chemicals, and algal toxins. These contaminants, even at trace concentrations, may have adverse effects on human and environmental health. Therefore, ferrate(VI) treatment capable of removing phosphorus and many other wastewater derived pollutants can safeguarde the environmental quality.

Environmentally friendly technologies. Ferrate(VI) is recognized as a “green” water treatment technology (Sharma, Zboril, & Varma, 2015). Ferrate(VI) itself does not produce harmful products. Rather, the final product is non-toxic iron (hdyr)oxide (sludge). Binding of many contaminants (e.g. phosphate and arsenic) on the ferrate(VI) resultant particles is strong and irreversible, so that desorption is minimal. Meanwhile, ferrate(VI) oxidation, different from many other chemical oxidation (e.g., ozonation), barely produces undesirable disinfection byproducts (e.g. carcinogenic bromate) in treated water. Therefore, ferrate(VI) is a safe treatment agent.

Furthermore, very minimal environmental impacts are expected during ferrate(VI) treatment. Cashman (2014) compared ferrate(VI) and many other treatment technologies in water disinfection in an U.S. Environmental Protection Agency-supported project. Their life cycle assessment (LCA) shows that ferrate(VI) technology has fewer negative impacts on the environment than conventional disinfection options in terms of global warming, smog formation, energy reduction, fossil depletion, acidification, ozone depletion, metal depletion and human health.

5.2.3 Social Benefits

Innovative, effective, and efficient wastewater treatment technologies can also bring about social benefits, considering that clean and safe water is vital to our community. At a minimum, four social benefits are expected from the inventive ferrate(VI) treatment technologies for wastewater treatment.

1) *Enhancing clean water supply*. Wastewater is recognized as a resource in the modern viewpoint of environmental engineering. It, as part of our water cycle, will be finally recycled for drinking water supply. One example is direct potable reuse (DPR). In DPR, wastewater becomes part of raw water directly after water reclamation or indirect potable reuse (IPR) in which treated wastewater enters into an environmental buffer (e.g., wetlands) before used in drinking water treatment plants. The other example is the unplanned "de facto" reuse scenario, in which treated wastewater from a wastewater treatment plant is part of raw water in the downstream water treatment plant. At the either situation, if ferrate(VI) treatment is adopted as an advanced treatment, it will significantly improve the water quality and enhance the water reuse, regardless of planned or unintentionally reuse.

2) *Boosting local economy*. A less polluted water environment can create many new opportunities for the local community, such as convenient water transportation, lively recreation activities, and rising real estate. Meanwhile, sufficient ad safe water supply will promote human health and reduce the occurrence of water-borne diseases. The ecological and public health can stimulate the community economy by attracting more people and new business. Therefore, more employment opportunities will be accordingly created.

3). *Promoting the awareness of sustainability*. Ferrate(VI) is a potentially environmentally friendly technology. Adoption of ferrate(VI) for water and wastewater treatment with less negative impacts than conventional technologies will expand public awareness in the concept of sustainability. The emerging “green” treatment method can be used as a modern technology model for sustainability education of our next generation.

4) *Beautifying communities*. Water is a key component in landscaping design. It can be used for irrigation to support the plant growth and be part of the landscaping (e.g. foundations, wetlands, lakes, and streams). Sufficient and clean water will strongly support the beautification and various recreation activities (e.g. boating, fishing, and swimming) at local communities. Therefore, the innovation in wastewater treatment will help create a beautiful community.

5.3 Overall Conclusions

This dissertation aimed to evaluate the treatment performance for ferrate(VI) removal of phosphorus in municipal wastewater and elucidate the underlying mechanisms. Laboratory-scale tests were sequentially carried out to test ferrate(VI) application in primary and advanced treatments. Results from the CEPT tests show that ferrate(VI) can substantially remove phosphate in raw wastewater. The ferrate(VI) enabled CEPT is particularly effective for enhanced mitigation of particulate matters and particulate-associated phosphorus and organic matter. The enhancement is primarily ascribed to the improved sedimentation of particles due to the attachment of ferrate(VI) resultant particles on the suspended solids in wastewater.

Ferrate(VI) treatment is also effective for removal of residual phosphorus, inorganic and organic, in biologically treated municipal wastewater. The treatment performance relies on two operating factors, i.e. ferrate(VI) dose and pH. Alkalinity, nitrate, and ammonia appear to have a limited influence on the removal of both inorganic and organic phosphorus. However, EfOM can significantly inhibit ferrate(VI) removal of inorganic phosphate, while inorganic phosphate in wastewater can greatly suppress the alleviation of organic phosphorus. Mechanistic studies reveal that the abatement of phosphate is primarily attributed to the adsorption of phosphate to ferrate(VI) resultant particles, a mixture of amorphous and crystalline iron (hydr)oxides. Of particular, the most phosphate is captured on the amorphous fraction of the mixed iron (hydr)oxides. On the other hand, the mechanisms for ferrate(VI) removal of organic phosphorus is more complex. For the selected model compounds, ferrate(VI) oxidation first degrades them into simple daughter compounds, of which some are subsequently adsorbed to the ferrate(VI) resultant particles, while others remain in water.

Experimental results in the treatment performance and mechanisms show the potential of ferrate(VI) as a promising treatment agent for abatement of wastewater phosphorus. Besides the alleviation of phosphorus, ferrate(VI) is expected to remove many other chemical and microbial contaminants with production of little byproducts and minimal environmental impacts. Therefore, though ferrate(VI) is more expensive than the traditional phosphorus removal methods with ferric coagulant, it can bring about unmatched benefits that traditional technologies cannot provide.

5.4 Future Research

This dissertation research is the first step toward ferrate(VI) technologies for removal of phosphorus in municipal wastewater. Although encouraging results are obtained, the technology needs to be further developed in future. Four following directions are identified as follows for the future research.

1) How much phosphorus needs to be removed from wastewater? Although P is a wastewater pollutant, it may be beneficial. For example, wastewater P after primary

treatment may be needed for microbial growth in the ensuing activated sludge treatment. And P in treated secondary effluent may be useful if the wastewater will be later used for agricultural irrigation, because P is a nutrient for the growth of crops. Accurate control of the P removal efficiency is needed for ferrate(VI) application to wastewater treatment and reuse. As shown before, the treatment performance is influenced not only by ferrate(VI) dose and pH, but also by wastewater matrix constituents. However, species and concentrations of wastewater matrix constituents are different from one secondary effluent to another. Therefore, further studies are needed to investigate the impacts from wastewater matrix. Particularly, many municipal wastewater treatment plants receive industrial wastewater, which may bring more uncertainty on the performance of ferrate(VI) treatment due to the introduction of industrial wastewater pollutants (e.g. toxic heavy metals).

2) Wastewater treatment plants are operated over the entire years. Therefore, the treatment should be viable at different temperatures. Effect of temperature on ferrate(VI) removal of wastewater phosphorus was not investigated in this study. Theoretically, temperature may influence the reaction through the change of the reaction rates and adsorption capacity of iron oxides. Therefore, the role of reaction temperature within a typical wastewater treatment range deserves an in-depth study.
3) Although phosphorus is a wastewater pollutant, it is a valuable chemical due to its limited resources on the Earth. Recovery of phosphorus has recently become a direction for sustainable management of our municipal wastewater. After ferrate(VI) induced sludge is collected, whether P associated with the iron (hdyr)oxide can be efficiently recovered remains interesting. However, the strong binding between Fe

and P can seriously challenge the existing P recovery methods. Therefore, development of innovative P recovery methods from the iron sludge is urgently demanded.

4) Development of cost and energy-efficient technologies with minimal environmental impacts is highly attractive for removal of wastewater phosphorus. However, it is unsuitable now to carry out TEA and LCA for the innovative ferrate(VI) technologies, given that the emerging treatment process is still at its early stage. With the advances in the ferrate(VI) chemistry and technology, TEA and LCA need to be carried out at a more-developed phase to compare ferrate(VI) treatment and existing technologies.

5.5 References

Cashman, S., Gaglione, A., Mosley, J., Weiss, L., Hawkins, T., Ashbolt, N., . . . Arden, S. (2014). Environmental and Cost Life Cycle Assessment of Disinfection Options for Municipal Wastewater Treatment. *Office of Research and Development. National Homeland Security Research Center.*

Cui, J., Zheng, L., & Deng, Y. (2018). Emergency Water Treatment with Ferrate(VI) in Response to Natural Disasters. *Environmental Science: Water Research & Technology, 4*, 359-368

ICIS. (2006). List of chemical prices.

Jiang, J. Q., Stanford, C., & Alsheyab, M. (2009). The online generation and application of ferrate(VI) for sewage treatment-A pilot scale trial. *Separation and Purification Technology, 68*(2), 227-231. Retrieved from <Go to ISI>://WOS:000268648200015. doi:10.1016/j.seppur.2009.05.007

Jiang, J. Q., Stanford, C., & Mollazeinal, A. (2012). THE APPLICATION OF FERRATE FOR SEWAGE TREATMENT: PILOT- TO FULL-SCALE TRIALS. *Global Nest Journal, 14*(1), 93-99. Retrieved from <Go to ISI>://WOS:000304741400014.

Sharma, V. K., Zboril, R., & Varma, R. S. (2015). Ferrates: Greener oxidants with multimodal action in water treatment technologies. *Accounts of chemical research, 48*(2), 182-191.

Waite, T. D. (2012). On-Site Production of Ferrate for Water and Wastewater Purification. *American Laboratory, 44*(10), 26-28. Retrieved from <Go to ISI>://WOS:000312286700006.

Zheng, L., & Deng, Y. (2016). Settleability and characteristics of ferrate(VI)-induced particles in advanced wastewater treatment. *Water Research, 93*, 172-178.

This page intentionally left blank.