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## Treatment of Combined Sewer Overflows Using Ferrate (VI)

Rohan Gandhi, *The University of Western Ontario*

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A thesis submitted in partial fulfillment of the requirements for the Master of Engineering Science degree in Chemical and Biochemical Engineering

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**TREATMENT OF COMBINED SEWER OVERFLOWS USING FERRATE (VI)**

(Thesis format: Integrated Article)

by

Rohan Gandhi

Graduate Program in Engineering Science

Department of Chemical and Biochemical Engineering

A thesis submitted in partial fulfillment

of the requirements for the degree of

Master of Engineering Science

The School of Graduate and Postdoctoral Studies

The University of Western Ontario

London, Ontario, Canada

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## **Abstract**

Prevention of pollution from combined sewer overflows (CSOs) is currently a major concern due to their impact on aquatic and human environment. With the stringent regulations related to the CSOs treatment, it is necessary to develop an efficient, fast and low cost treatment technique that meets the applicable criteria. In this work, the comprehensive study was done to determine the efficiency of ferrate (VI) for the treatment of CSOs. At a Fe (VI) dose of 0.24 mg/l, TCOD, SCOD, TBOD<sub>5</sub>, SBOD<sub>5</sub>, TSS, VSS, TP, TN and soluble TN removal efficiencies of 71%, 75%, 69%, 68%, 72%, 83%, 64%, 38% and 36% respectively were achieved. Kinetic studies revealed that a contact time of only 15 minutes is sufficient to achieve secondary effluent criteria. An innovative technique of using primary sludge (PS) and thickened waste activated sludge (TWAS) as a source for the in-situ synthesis of ferrate was explored. A comparative study of treatment efficiencies achieved by Fe (VI) generated from different sources was done. At 0.1 mg/l dose of Fe (VI) synthesized from PS, TCOD, SCOD, TSS, VSS, TP and TN removal efficiencies of 60%, 62%, 63%, 67%, 30% and 25% respectively were achieved.

Keywords: Combined Sewer Overflows (CSOs), ferrate (VI), primary sludge (PS), thickened waste activated sludge (TWAS)

## **Co-authorship**

Chapter 3: Treatment of Combined Sewer Overflows using Ferrate (VI)

Authors: Rohan Gandhi, Ajay K. Ray, George Nakhla

Rohan Gandhi performed all the experimental work and data analysis under the guidance of Dr. Ajay K. Ray and Dr. George Nakhla. The draft of this manuscript was written by Rohan Gandhi. Modification of the draft was undertaken under the close supervision of Dr. George Nakhla and Dr. Ajay K. Ray. The final version was submitted to the Water Environment Research (WER) Journal.

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## Nomenclature

TCOD	Total Chemical Oxygen Demand	(mg/l)
SCOD	Soluble Chemical Oxygen Demand	(mg/l)
PCOD	Particulate Chemical Oxygen Demand	(mg/l)
TBOD <sub>5</sub>	Total Biochemical Oxygen Demand (5-day)	(mg/l)
SBOD <sub>5</sub>	Soluble Biochemical Oxygen Demand (5-day)	(mg/l)
TSS	Total Suspended Solids	(mg/l)
VSS	Volatile Suspended Solids	(mg/l)
TN	Total Nitrogen	(mg/l)
STN	Soluble Total Nitrogen	(mg/l)
TP	Total Phosphorous	(mg/l)
SON	Soluble Organic Nitrogen	(mg/l)
PS	Primary Sludge	
TWAS	Thickened Waste Activated Sludge	

## Abbreviations

dig.	digested
avg	average
gpm/sf	gallons per minute per square feet
nm	nanometer
µm	microns (micrometer)

# Chapter 1

## Introduction

### 1.1 Background

The growing population has led to a significant increase in the generation of wastewater, challenging the capacity of the collection system. Many municipalities are still served by combined sewers carrying the domestic sewage, industrial wastewater and stormwater runoff in the single pipe (Metcalf and Eddy, 2003). During a wet weather event, the hydraulic capacity of the combined sewer exceeds and the excess flow is discharged to the receiving waters as a combined sewer overflow (CSO) to prevent flooding and backup (Zukovs and Marsalek, 2004). Untreated wastewater when mixed with the receiving stream disturbs the aesthetics and can lead into major aquatic as well as human health damage (EPA, 2001). In order to keep the life cycle of environment intact, treatment of CSOs has become a major concern. To mitigate the impacts by CSOs, numerous efforts have been taken (Zukovs and Marsalek, 2004), such as:

- Separating the sewers, to fully isolate domestic sewage and stormwater runoff (EPA, 1999a).
- Constructing the storage tanks to retain CSOs, till the availability of WWTP to treat the loading (EPA, 1999b).
- Upgrading the sewage treatment plant capacity, to handle the excess loading (Zukovs and Marsalek, 2004).

Undertaking these CSO mitigation technologies have certain limitations, for example, land availability, and is also not economically viable. Concerns regarding these

limitations led to the development of few patented physical – chemical treatment processes like Actiflo (USFilter, Kruger Products, Cary, North Carolina), DensaDeg (Infilco Degremont, Inc., Richmond, Virginia) and CoMag (Siemens, inc., Alpharetta, Georgia). These are all high rate ballasted clarification treatment processes (EPA 2013). In Actiflo process, the colloids are destabilized by the addition of coagulants. Polymer is added to aid flocculation along with the microsand, a ballast material, which provides large surface area to prepare floc and aids sedimentation (Blumenschein et al., 2006; EPA, 2008; Landon et al., 2006). The TSS and BOD<sub>5</sub> removal by the 32.8 L/s hydraulic capacity, pilot Actiflo plant, located at Southeast Water Pollution Control Plant (SEWPCP) in San Francisco, California, were reported to be in the range of 70-80% and 50-65% respectively, for 80 mg/l FeCl<sub>3</sub> dose and 1 mg/l polymer dose. The retention time of 13 minutes was reported (Jolis and Ahmad, 2004). DensaDeg process, a combination of coagulation, weighted flocculation and Lamella settling uses thickened recirculated sludge as ballast. The DensaDeg system situated at the Water Pollution Control Station (WPCS) at the City of Akron, Ohio, handling the surface overflow rate (SOR) of 40 gpm/sf, removed 83 % TSS and 55% BOD<sub>5</sub> using 85 mg/l ferric chloride and 0.77 mg/l polymer dose (Frank and Smith III, 2006). The typical hydraulic retention time (HRT) of DensaDeg process is in the range of 15-22 min (EPA 2003). CoMag, based on the same concept of Actiflo and DensaDeg, uses magnetite as ballast for high rate sedimentation (McHale, 2011). This process has mainly been used for the enhanced removal of phosphorous from the secondary effluent (EPA, 2008) and is now being used for CSO treatment considering its high suspended solids removal efficiency (Backman and Irwin, 2012). The typical removal efficiencies of TSS, BOD<sub>5</sub> and TP achieved by CoMag

treatment plant are in the range of 70-90%, 40-50% and 85-95% respectively (Pratt et al., 2008; Hardy, 2008; Backman and Irwin, 2012). The HRT is in the range of 5-15 min depending on the plant capacity (Backman and Irwin, 2012) and has faster start up time as compared to Actiflo and DensaDeg (Dittami, 2008). Chemically Enhanced Primary Treatment (CEPT) technique is also being used for CSO treatment (Mouri et al., 2013; Haydar and Aziz, 2009). In this process, the pollutants are removed by coagulation and flocculation enhanced by the addition of chemicals. The CEPT process located at Ipiranga WWTP, Sao Paulo, Brazil observed 62%, 58%, 80% removal of COD, BOD<sub>5</sub> and TSS respectively for the flow rate of 50 L/s and the chemical doses of 50 mg/l ferric chloride and 0.5 mg/l soluble polymer (Bourke Jr., 2000).

All the above mentioned processes come with few limitations:

- Soluble organics and nitrogen from wastewater can't be removed (Plum et al., 1998; EPA, 2013), which possess a major threat to aquatic environment and can also affect human health.
- Many chemicals are required to be dosed in the system which is not favorable to the environment and necessitates more maintenance (EPA, 2003).
- Startup time required by Actiflo, DensaDeg and CoMag is high and is in the range of 15-30 minutes (EPA 2003; Metcalf and Eddy, 2003; Dittami, 2008), which can result into the discharge of the untreated wastewater to the receiving stream during the wet weather event.

All the concerns regarding these limitations can be alleviated by developing of a low cost oxidation and coagulation, CSO treatment process with no start up time and short contact

time. Looking at its numerous properties, and benefits reported by the researchers (Jiang and Lloyd, 2002; Sharma et al., 2005), ferrate (VI) promises to be the potential chemical that can meet these criteria.

Ferrate (VI) ( $\text{FeO}_4^{2-}$ ) is a strong oxidizing agent (Jiang et al., 2006; Tiwari et al., 2005) and also is a dual benefit chemical, as it performs oxidation and coagulation in single dose (Sharma et al., 2005; Lee et al., 2009). Fe (VI) gets reduced to Fe (III) ions or ferric hydroxide, known for their coagulating properties (Jiang et al., 2006; Lee et al., 2009).

There are numerous findings reported by researchers on the Fe (VI) performance as an oxidant, coagulant and disinfectant in treatment of water and wastewater. Ferrate (VI) successfully oxidized chlorinated phenols (Graham et al., 2004), arsenic (Lee et al., 2003), humic substances (Lim and Kim, 2010), cyanides (Flip et al., 2011), glucose, fructose, maltose, sucralose (Sharma et al., 2012), steroidal estrogens from dairy waste lagoon effluent (Remsberg et al., 2008) and ibuprofen (Sharma and Mishra, 2006). The use of ferrate (VI) for removal of heavy metals (Cu, Mn, Zn) (Lim and Kim, 2010), coagulation of colloidal particles (Jiang et al., 2001) and removal of color (Jiang and Wang, 2003) from water has been reported. Availability of literature on wastewater treatment using Fe (VI) is scarce, which can be related to the unstable nature of aqueous Fe (VI) (Jiang and Lloyd, 2002; Sharma et al.; 2005) and also to the high cost required for the preparation of solid Fe (VI) (Sharma et al., 2005). Ferrator, a patented onsite ferrate preparation and treatment reactor, was developed by Ferrate Treatment Technologies to address the concerns related to the instability of Fe (VI) (Ciampi and Daly, 2009). This reactor which synthesizes ferrate by wet oxidation method is being used for disinfection, color removal, destruction of emerging contaminants and odor control (Alig et al., 2011).



Onsite ferrate (VI) synthesis by electrochemical method has been reported by Jiang et al., (2009). The removal of 80% of TSS, 70 % of TCOD and 90% TP from wastewater was achieved at a dose of around 2 mg/l of Fe (VI) generated electrochemically (Stanford et al., 2010). The soluble organics removal was not investigated.

Ferrate (VI) can generally be synthesized by three oxidation methods, (1) dry oxidation, (2) wet oxidation and (3) electrochemical oxidation (Tiwari et al., 2005; Sharma et al., 2005). In dry oxidation synthesis method, ferric salt and an oxidant are heated at elevated temperature to produce Fe (VI) (Kopelev et al., 1992). This synthesis method is dangerous and is rarely used as high temperatures are required for production of Fe (VI). Wet oxidation method is the most commonly used technique for the production of Fe (VI) (Tiwari et al., 2005; Jiang and Lloyd, 2002). In this method, ferrous and ferric salts are oxidized in strong alkaline medium to produce ferrate (VI) (White and Franklin, 1998). The yield achieved is very low and the aqueous ferrate (VI) produced requires further separation techniques to prepare solid ferrate (VI) (Sharma et al., 2005). In electrochemical oxidation method, anode, made of iron or iron salt, is oxidized in a strong electrolyte using a desired anode potential to produce sodium or potassium ferrate (Jiang and Lloyd, 2002).

Wastewater sludges contain iron (Jenkins et al., 1981), as Iron (II) and Iron (III) salts are used as coagulants and precipitants for phosphorous and odor removal in many wastewater treatment plants (Jiang and Graham, 1998; Perkowski and Kos, 2002). The sludges have never been used as an iron source for the generation of ferrate (VI) and can be attributed to the unavailability of exact speciation of iron in municipal sludges and variability of sludge composition.

Based on the above, the objectives of the present work are:

- To evaluate the performance of Fe (VI) for the treatment of CSOs, monitoring the removal efficiencies of soluble organics and nutrients.
- To synthesize ferrate using primary sludge (PS) and Thickened waste activated sludge (TWAS) as an in-situ iron source and also by using ferrous sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), a pure iron source.
- To compare the treatment efficiencies of Fe (VI) generated from various iron source and to assess the performance with respect to the secondary effluent criteria proposed by US EPA.

## **1.2 Structure of the thesis**

The thesis is written in “Integrated-Article Format” and is divided into the following chapters:

Chapter 1 describes the research background and the structure of the thesis.

Chapter 2 presents the review of the existing work related to the research, identifying the research gaps.

Chapter 3 discusses the efficiency of commercial grade as well as laboratory synthesized ferrate (VI) for the treatment of CSOs.

Chapter 4 concludes the thesis by summarizing the conclusions of the research and pointing out the future research directions.

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## **Chapter 2**

### **Literature Review**

#### **2.1 Combined sewer overflows (CSOs)**

Collection of domestic sewage, industrial wastewater and rainwater runoff in a single pipe is termed as combined sewer system (Metcalf and Eddy, 2003). The concept of using combined sewer systems was initiated in Europe in 1840's (Field et al., 2003). North America incorporated this concept in late 19<sup>th</sup> century. Climate changes affect the collection and functionality of these systems (EPA, 2008a). During rainy seasons, combined sewer systems experience an increase in volume of flowing wastewater. Depending on the capacity, some of the combined sewer systems cannot handle the excess wastewater volume due to rainwater runoff. In order to prevent flooding and sewer backups due to the exceeding volume, some of this wastewater is diverted to the overflow pipe and is then discharged into nearby lakes, rivers and oceans. This discharge from combined sewer systems is termed as combined sewer overflows (CSOs) (Zukovs and Marsalek, 2004).

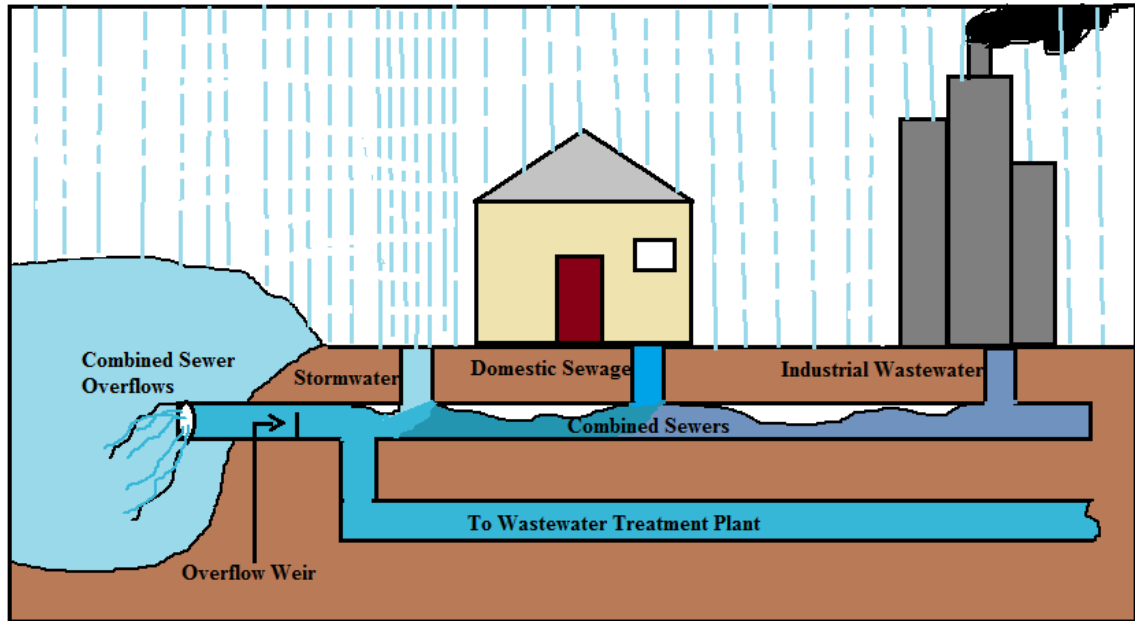


Figure 2.1: Combined Sewer Overflows

### 2.1.1 Impacts of CSOs

The CSOs are directly discharged into river streams, lakes or oceans. Wastewater carries number of bacteria and viruses which are harmful to the human environment (Metcalf and Eddy, 2003). Storm water before getting into the combined sewer collects chemicals, pesticides, oils and other wastes from the roadsides, parking lots, fields (EPA, 1994). Introduction of overflow to the receiving water disturbs the aquatic environment and also possess threat for human beings. CSOs act as a shock loading to environmental and biological surrounding. Table 2.1 (EPA 2001) summarizes pollutants and principal consequences of CSOs.

Table 2.1: Pollutants and their principal consequences (EPA 2001)

<b>Pollutants</b>	<b>Principal Consequences</b>
<b>Bacteria</b> <b>Viruses</b> <b>Protozoa</b>	Beach closures Shellfish bed closures Drinking water contamination Adverse public health effects
<b>Trash and floatables</b>	Aesthetic impairment Devaluation of property Odors Beach closures
<b>Organic compounds</b> <b>Metals</b> <b>Oil and grease</b> <b>Toxic pollutants</b>	Aquatic life impairment Adverse public health effects Fishing and shell fishing restrictions
<b>Biochemical oxygen demand (BOD<sub>5</sub>)</b>	Reduced oxygen levels and fish kills
<b>Solids deposits (sediments)</b>	Aquatic habitat impairment Shellfish bed closures
<b>Nutrients</b>	Eutrophication, algal blooms Aesthetic impairment
<b>Flow shear stress</b>	Stream erosion

### 2.1.2 Factors affecting the concentrations of pollutants in CSOs

The concentrations of pollutants depend on the quality of domestic wastewater, industrial wastewater and stream water runoff entering the combined sewer system. During rainfall or snowmelt event, perturbation occurs in the combined sewer system; settled particles get re-suspended into the flowing stream resulting into what is known as “first flush effect”. Pollutants concentrations are high during first flush effect. The first flush effect

can be observed for half an hour or more during heavy rainfall (EPA, 2004). The duration and the intensity of wet weather event also affect the concentrations of pollutants in CSOs (EPA, 2004).

Sierra legal report (2006) published that, from 20 cities examined, around 92 billion liters of raw sewage mixed with storm water was released into great lakes (which include Lake Superior, Lake Michigan, Lake Huron, Lake Erie and Lake Ontario) in one year via CSOs.

## **2.2 Regulations governing discharge of CSOs**

US Environmental Protection Agency (EPA) and Ontario Ministry of the Environment (MOE), sets up different treatment standards for different sewage treatment plants (Sierra legal report, 2006). According to Ministry of Environment (MOE) regulations for bypass treatment mentioned in procedure F-5-5, the removal efficiency of five day biochemical oxygen demand (BOD<sub>5</sub>) and total suspended solids (TSS) should be 30 % and 50 % respectively. According to the US EPA, CSO related bypass flows must receive primary clarification, solids and floatables removal and disinfection.

### **2.2.1 Laws**

Water management issues related laws can be passed by both federal and provincial governments, according to Canada's Constitution Act. Canadian Environmental Protection Act 1999 (CEPA) and the Fisheries Act are monitored by Environment Canada under Canadian Federal Laws. Toxic substances and Nutrients are regulated by CEPA. Fish habitat protection comes under Fisheries Act. Ontario Water Resources Act

(OWRA) and Environmental Protection Act (EPA) are governed by Ontario ministry under Ontario law. Ontario Ministry of Environment monitors the sources of water pollution through OWRA (Sierra legal report, 2006).

### **2.2.2 CSO Control Policy (EPA, 1994)**

Following are the key points of CSO control policy which makes sure that all the objectives of clean water act are fulfilled and the controls are cost effective

1. Clear levels of control needed to meet health and environmental criteria should be provided.
2. Municipalities should be given sufficient amount of freedom in order to come out with economic ways of abatement of pollutants caused due to CSO discharge and to satisfy all clean water act requirements.
3. Depending on the monetary capacity of municipalities, distributive approach should be given a green signal during the CSO controls implementation.
4. Provision should be made to review water quality standards and different issues surrounding it during the execution of CSO control plan.

In order to facilitate the implementation of CSO control policy EPA have published nine minimum controls (NMC) which can be helpful in responding to the CSO problems with very less construction costs and minimal engineering analysis. NMC forms the base to the implementation of long term control plan (LTCP).

Following are the nine minimum controls: (EPA, 2004)

1. There must be a smooth operation and regular checkup of the collection systems.

If collection system failure happens there can be a high risk of pollution, thus maintenance is a major preventative step in order to ensure the proper working of collection systems.

2. There should be an ultimate use of the storage tanks.

High usage of storage tanks can prevent higher discharge of untreated wastewater into the receiving stream thus helping in reducing the contamination.

3. Pretreatment programs should undergo a strict revisions and necessary changes.

4. Wastewater treatment plants capacity should be fully utilized.

All the WWTP's are designed in such a way that they can handle flows higher than their design capacities (peaking factor generally is 3). This can reduce a CSO discharge.

5. Care should be taken in order to avoid CSO discharge during no rainfall period (Dry weather period).

6. Preventive measures should be taken in order to reduce or monitor solid and floatable substances in CSO discharge.

7. Various programs should be established which can directly or indirectly help in pollution control.

8. Public should be made aware of the CSO, its impacts and danger related to it.

9. Monitoring should be done to characterize the CSO impacts and the efficiency of CSO controls.

In July 2004, EPA reported that for 94 percent of the active CSO permits, NMC execution was required. NMC made a base for the design of the long term control plan

(LTCP). LTCP included more detailed implementation. It included various aspects such as public participation, economic considerations, alternative techniques to control CSO, management plans, modeling and monitoring CSO discharge, increasing the treatment capacity of WWTP and post construction checkup. In Canada, the Federal laws have no obligations on CSO's until they meet all the requirements under Fisheries Act. Ontario Procedure F-5-5 lists following CSO control requirements: (Sierra legal report, 2006)

1. There should be no overflows during dry season unless and until there is major system failure.
2. There must be a smooth operation and regular maintenance of the systems.
3. Various programs regarding pollution control or prevention should be initiated.
4. Floatables in the combined sewer systems should be controlled.
5. There should be maximum storage of wastewater in tanks during heavy rainfalls.
6. Treatment plant utilization should be maximized during rain events.

### **2.3 CSO treatment techniques**

The simplest way to get rid of the Combined Sewer Overflow (CSO) crisis is to separate the sewers (EPA 1999a). This is not an economically viable option. Various treatment techniques are being used to treat CSOs.

#### **2.3.1 Wetlands**

Wetlands are shallow aquatic bodies which act as a filter for treatment of wastewater. Wetlands are also called as soil retention filters. Aquatic vegetation grown on these wetlands makes them retain permeability (Atlantic agriculture, 2005). Wetlands can be

used for primary treatment of CSOs. There are few ways in which wetland treatment technique can be applied:

1. CSOs can directly pass through the wetlands framework and then into receiving water.
2. CSOs can first be stored in storage tank. The outlet of the storage tank can be directly run into wetlands and then into receiving streams.
3. Wetlands can also be constructed in such a way that domestic wastewater, Industrial wastewater and storm water can directly be allowed to pass through them before getting into combined sewer systems. This can act as a pretreatment for wastewater plants.

In the wetland treatment technique, inlet wastewater source is situated above the constructed wetlands. Wetlands are made up of fine sand usually of diameter ranging from 0-2 mm (Uhl et al., 2005). This sand is covered with water which grows aquatic vegetation which helps in retaining permeability. The longer roots of these vegetation helps in producing oxygen at the bottom surface near soil layer, developing an environment favorable for aerobic bacteria. These bacteria help in degrading organic material from the influent stream. Suspended solids can be removed by the soil filter when waste water passes through the soil medium. The typical soil permeability for Free water surface constructed wetlands is  $10^{-6}$  -  $10^{-7}$  m/s (EPA, 1988). Nutrient removals can be achieved by adding carbon and ferric source to filter medium (Uhl et al., 2005). Meyer et al. (2013) reported the design criteria of constructed wetlands (CW) in France and Italy for CSO treatment. Table 2.2 represents the design criteria.



Table 2.2: Design criteria of constructed wetlands (CW) in France and Italy (Meyer et al., 2013)

<b>Criteria</b>	<b>CW France (full-scale Marcy-l'Etoile)</b>	<b>CW Italy (full-scale Gorla Maggiore)</b>
<b>Filter Bed</b>	2 alternated loaded, in Parallel for extreme events	4 alternated loaded, in parallel for extreme events
<b>Retention Layer Depth</b>	Flexible (0.1, 0.35, 0.6 or 0.8m each bed) , 2 m for connected beds	minimum 0.2 m
<b>Filtration Layer</b>	Minimum 0.5 m (one bed sand + zeolite, one bed pozzolana)	0.2 m (gravel 10 mm) + 0.4 m (gravel 2/6 mm)
<b>Saturated Layer</b>	flexible, minimum 0.2 m (0.3m gravel 10/20 mm, 0.1m gravel 3/8 mm)	0.2 m (gravel 40/80 mm)
<b>Outflow Limitation</b>	0.02 L/(m <sup>2</sup> .s)	0.004 L/m <sup>2</sup> .s
<b>Max. hydraulic loads</b>	40 - 80 m <sup>3</sup> /m <sup>2</sup> per year	35 - 40 m <sup>3</sup> /m <sup>2</sup> in annual average (max. 50 m <sup>3</sup> /m <sup>2</sup> per year)

The CW treatment performance for the combined sewer system in North America reported by Kadlec and Knight (1996) are mentioned in Table 2.3.

Table 2.3: North American Treatment operational performance (Kadlec and Knight, 1996)

<b>Parameter</b>	<b>Inlet Conc. (mg/l)</b>	<b>Outlet Conc. (mg/l)</b>	<b>% Removal</b>
<b>BOD<sub>5</sub></b>	30.3	8	74
<b>TSS</b>	45.6	13.5	70
<b>TP</b>	3.78	1.62	57

The use of wetlands for treatment of CSOs carry numerous advantages such as, it is cost effective, have low maintenance, require short startup time and creates an aesthetic environment for birds and aquatic habitat. Treatment of CSOs using wetlands have its own disadvantages, for example, it requires larger area, cannot sustain longer dry weather periods, clogging can take place resulting in the reduction of removal efficiencies in long run and more importantly it cannot remove soluble organics.

### **2.3.2 Settling tanks**

Additional settling tank just before the wastewater treatment plant can have multiple benefits (Kerbs et al. 1999). During the wet weather event, excess water from the combined sewer system can be stored in the settling tanks and when the wet weather flow decreases the stored wastewater can then pass into the WWTP. Thus settling tank can act as a storage tank and is also termed as retention time basin (Zukovs and Marsalek, 2004). In normal day to day activity it can act as a pretreatment settling tank in which suspended solids due to controlled flow and residence time can settle in the settling tank. Addition of coagulants to the tank and introducing stirring mechanisms can increase the settling of suspended solids and removal of various bacteria (EPA 1999b). The storage volume of retention basin is generally calculated using flow route modeling. The basin or tank shape generally should be circular or octagonal as they can be upgraded easily to self-clean settled solids and should have low inflow in order to avoid re suspension of settled solids. Brombach et al. (2008) specified the design criteria for retention basin in Germany for treatment of CSOs. These design criteria are noted in Table 2.4.

Table 2.4: Design criteria for retention basin (RB) in Germany (Brombach et al., 2008)

<b>Parameter</b>	<b>Value</b>
<b>Surface Overflow rate (SOR)</b>	>10m/h
<b>Inflow, critical</b>	(15 L/(s.ha))* impervious catchment area. For ecology sensitive receiving waters, (30 L/(s.ha))* impervious catchment area
<b>Sedimentation chamber</b>	Long and Narrow $10 < L/H < 15$ , $3 < L/W < 4.5$ , $2 < W/H < 4$
<b>Horizontal Flow Velocity</b>	< 5 cm/s
<b>Clarifier Overflow</b>	< 75 L/s.m
<b>Emptying CSO tank</b>	within 10-15 hours, to avoid odor and fouling

The 90 % reduction in the CSO discharge volume was noticed after the construction of 30 MG retention basin at Grand Rapids (EPA, 1999b). The well designed settling tank typically achieves the removal of TSS and BOD<sub>5</sub> in the range of 50-70% and 25-40% respectively (Metcalf and Eddy, 2003).

The settling tanks can survive long period without feed water and has low maintenance. With these positives, settling tanks have few drawbacks such as it requires high construction cost and moreover during the wet weather events, settling tanks can also overflow, leading to the discharge of untreated CSOs into the water streams.

### **2.3.3 Chemically Enhanced Primary Treatment (CEPT)**

Chemically Enhanced Primary Treatment (CEPT) is a process in which coagulants and flocculants are introduced into the untreated CSOs to enhance the removal of the pollutants (Haydar and Aziz, 2009; Chagnon and Harleman, 2004). Ferric chloride and

poly aluminium chloride are the most commonly used coagulants in CEPT (Harleman and Murcott, 1992). The introduction of coagulants into the CSOs destabilizes the charge on the suspended and colloidal particles thus speeding up the process of coalescence. The particles cling to each other forming larger particulate or flocs thus increasing the settling velocity, resulting into higher removal efficiencies (McLean, 2009). Figure 2.2 represents the schematic diagram of CEPT. In general, CEPT can handle surface overflow rates (SOR) of 10-30 gpm/sf. Typical removal efficiencies of TSS and BOD<sub>5</sub> achieved by CEPT are in the range of 70-90% and 35-50% respectively (McLean, 2009).

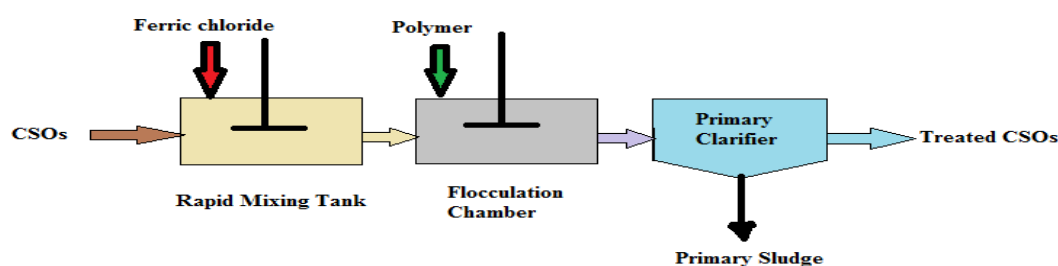


Figure 2.2: Schematic Diagram of Chemically Enhanced Primary Treatment

Morrissey and Harleman (1992) reported that, CEPT process set up at Point Loma, San Diego, for SOR of 4.5 m/h yielded 85% TSS removal, 55 % BOD<sub>5</sub> removal and 85% phosphorous removal. The ferric chloride dose of 25mg/l and polymer dose of 0.2 mg/l were used. The CEPT process located at Ipiranga WWTP, Sao Paulo, Brazil observed 62%, 58%, 80% removal of COD, BOD<sub>5</sub> and TSS respectively for the flow rate of 50L/s and the chemical doses of 50 mg/l ferric chloride and 0.5 mg/l soluble polymer (Bourke Jr., 2000). The high retention time, high amount of coagulant doses, large quantity of sludge, the incapability of the removal of soluble organic materials and high operational

and maintenance cost (Bourke Jr., 2000) are the few drawbacks of CEPT technique (Morrissey and Harleman, 1992).

### **2.3.4 High rate ballasted clarification treatment**

#### **2.3.4.1 Actiflo**

Actiflo (USFilter, Kruger Products, Cary, North Carolina) is a high rate ballasted clarification treatment process, a combination of coagulation, weighted flocculation and Lamella settling (Plum et al., 1998; Landon et al., 2006; Blumenschein et al., 2006). A coagulant, typically ferric chloride or poly-aluminium chloride is added to untreated CSO before entering the coagulation tank (see Figure 2.3). The flow enters the coagulation tank where suspended solids are destabilized and then overflows into the injection tank where polymer and microsand, a ballast material is added. The flow enters the maturation stage where flocculation takes place with the help of gentle mixing. The microsand serves as a seed for the floc formation. The ballasted floc then enters the settling tank in which floc settle due to gravity in the cone shaped chamber. The settling is enhanced by inclined tube settlers. The sludge scraper removes high volume of sludge. The microsand containing sludge is directed to a hydrocyclone which separates microsand from sludge and reintroduces microsand back into the injection tank (Frank and Smith III, 2006; Zhu et al., 2007; EPA, 2003; EPA, 2008). The typical hydraulic retention time (HRT) for coagulation tank, injection tank and maturatin tank is 2, 2 and 8 minutes respectively (Blumenschein et al., 2006). The microsand particles used are in general 45-150 microns in diameter (EPA, 2003) and have a specific gravity of 2.65 (Blumenschein et al., 2006;

Metcalf and Eddy, 2003). The Actiflo system can handle the overflow rate in the range of 40-60 gpm/sf (EPA, 2003; Blumenschein et al., 2006).

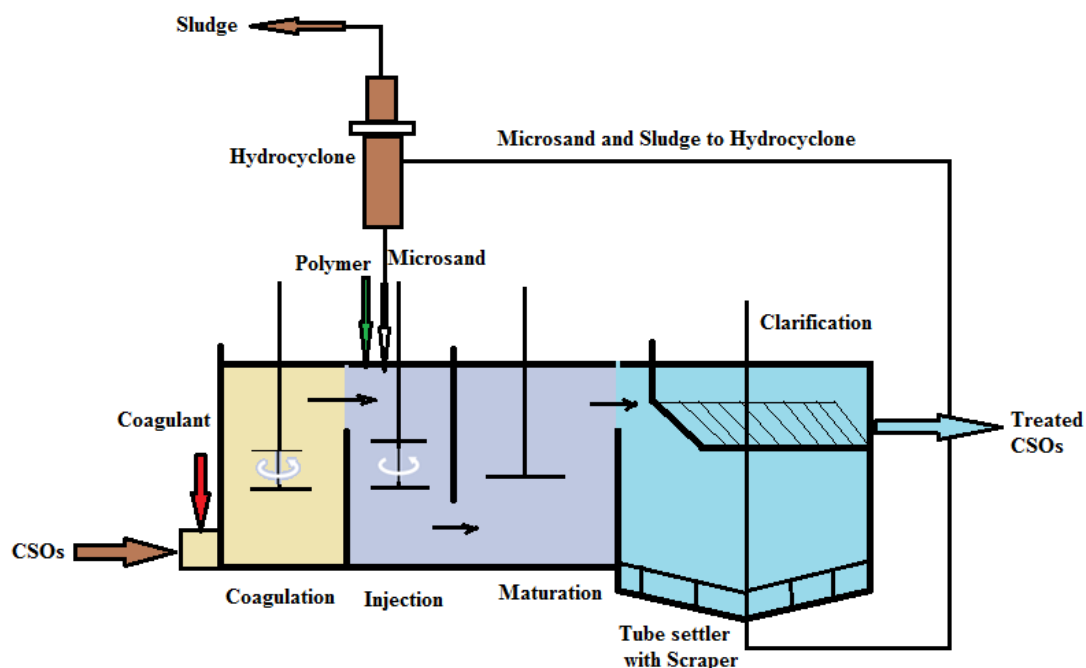


Figure 2.3: Actiflo Process Diagram (EPA, 2008)

A pilot Actiflo plant was set up at the Airport Wastewater Treatment Plant in Galveston, Texas to evaluate the performance. The TSS, COD and BOD<sub>5</sub> removal for the 150 m<sup>3</sup>/h CSOs were reported to be in the range of 80-94%, 65-83% and 48-75% respectively with the retention time of 7 minutes and startup time of 30 min (EPA, 2003). Ponist and Scheiter (2006) reported the HRT of 15 min and average removal of 88% TSS by the 12 MGD Ballasted High Rate Clarification Process set up in the City of Greenfield Indiana. A study was conducted by Jolis and Ahmad (2004) on the pilot Actiflo plant having an hydraulic capacity of 32.8 L/s, located at the Southeast Water Pollution Control Plant (SEWPCP) in San Francisco, California. The removal efficiency of 70-80% and 50-65%

of TSS and BOD<sub>5</sub> respectively and hydraulic retention time of 13 min was reported. The FeCl<sub>3</sub> dose of 80 mg/l and polymer dose of 1 mg/l was required. US Filter Actiflo demonstration facility at the West Point Wastewater Treatment Plant, Seattle, Washington, achieved 93-94% TSS removal, 60-71% COD removal and 75-91% TP removal at the surface overflow rate of 53.4 gpm/sf and for polymer and alum dose of 0.85 mg/l and 60 mg/l respectively. The total hydraulic retention time, dry startup time and wet start up time were reported as 6.5, 15 and 10 min respectively (Leng et al., 2002). Plum et al (1998) reported that the Actiflo method does not remove dissolved organic matter and nitrogen. The high startup time is the main disadvantage of the Actiflo system (EPA, 2003).

#### **2.3.4.2 DensaDeg**

The DensaDeg (Infilco Degremont, Inc., Richmond, Virginia) is a physical-chemical process made up of three units; coagulation, flocculation and clarification unit. The DensaDeg process works on the same principle as Actiflo, using thickened recirculated sludge as ballast material instead of microsand. The coagulant is added to the incoming CSO water in the coagulation unit, where it is rapidly mixed. This coagulated stream then enters the flocculation unit and is combined with the recirculated thickened sludge obtained from the clarification unit. The polymer addition is also done in this stage (see Figure 2.4). The flocculation unit comprises of turbine which promotes mixing and contact between the solids and recycled sludge forming denser flocs. This flocculated stream enters the clarification unit where solids settle out and sludge is thickened before getting recycled back to the flocculation unit. The treated water exits the system from the

top with the help of lamella tube assembly (EPA 2008; Jolis and Ahmad, 2004; Landon et al., 2006).

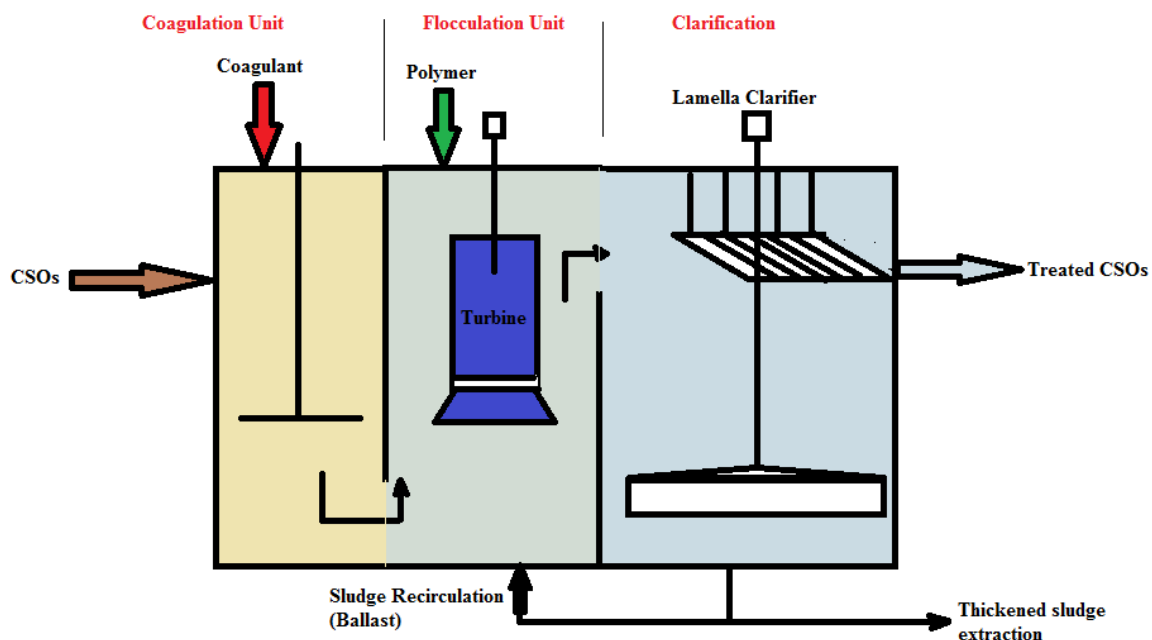


Figure 2.4: Schematic representation of DensaDeg process (EPA, 2008)

Densadeg 4D system set up at Village Creek WWTP Birmingham, Alabama achieved 45-60% and 80-95 % removal of COD and TSS respectively with the HRT of 15 min (EPA, 2003). The DensaDeg system handling the SOR of 40 gpm/sf piloted at the Water Pollution Control Station (WPCS) at the City of Akron, Ohio removed 83 % TSS and 55% BOD<sub>5</sub> using 85 mg/l ferric chloride and 0.77 mg/l polymer dose (Frank and Smith III, 2006). The pilot DensaDeg plant set up at city of Fort Worth, Texas, handling the SOR of 40-60 gpm/sf achieved BOD<sub>5</sub> removal in the range of 37-63%, TSS removal in the range of 81-90% and TP removal in the range of 88-95% when the ferric chloride and polymer doses used were in the range of 70-125 mg/l and 0.75-1 mg/l respectively. The



HRT observed was in the range of 15-22 min (EPA 2003; Sawey et al., 1999). Landon et al. (2006) pilot tested the DensaDeg system situated at Southerly Wastewater Treatment Plant. The system with the surface overflow rate of 40gpm/sf achieved 85% TSS removal with the use of 70 mg/l ferric chloride and 2.5 mg/l polymer dose. The hydraulic retention time observed was 14 min. Removal of soluble organics using DensaDeg process has never been reported. The high doses of metal salt required, the high startup time and the amount of sludge produced are the main disadvantages of the high rate clarification processes (EPA, 2003; Jolis and Ahmad, 2004).

#### **2.3.4.3 CoMag**

CoMag (Siemens, inc., Alpharetta, Georgia) is a high rate ballasted sedimentation process for enhanced removal of phosphorous (generally from secondary effluent) and suspended solids (EPA 2008). The CoMag technology is a combination of chemical coagulation and weighted flocculation with magnetite as ballast. Typical CoMag process is shown in Figure 2.5. The coagulant added to the influent CSOs get dispersed by mechanical mixing thus destabilizing the colloidal particles. The addition of polymer aggregates the particle forming the flocs. Magnetite has a specific gravity of 5.2 which helps in formation of denser flocs resulting in faster settling (Backman and Irwin, 2012; McHale, 2011). The magnetite is recovered from the sludge by magnetic drum and is reintroduced into mixing tank.

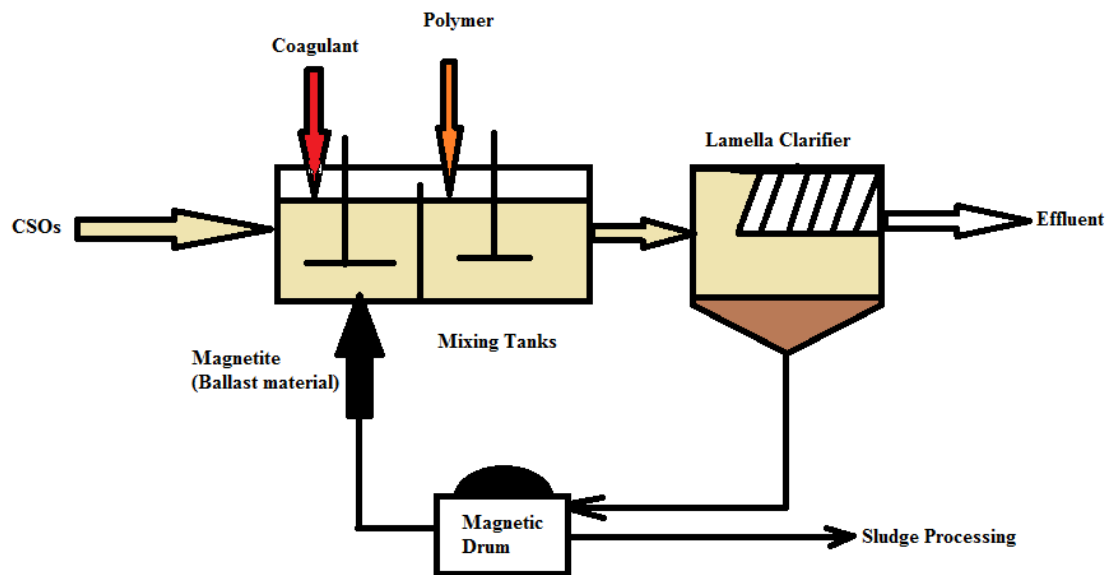


Figure 2.5: CoMag Process (Backman and Irwin, 2012)

The CoMag system is flexible to wide ranges of flows. It requires low maintenance and has rapid start up time typically 15 min (Dittami, 2008). CoMag plant can handle CSO surface overflow rate upto 50 gpm/sf. The typical removal efficiencies of TSS, BOD<sub>5</sub> and TP achieved are greater than 90%, 50% and 95% respectively. Typical HRT is 5-15 min depending on plant capacity (Backman and Irwin, 2012; McHale, 2011). The pilot CoMag plant setup at Westborough WWTP for tertiary treatment achieved 45% and 75% removal of BOD<sub>5</sub> and TSS respectively for the 30 mg/l and 3mg/l ferric chloride and polymer dose, respectively (Pratt et al., 2008; Hardy, 2008). CoMag is an emerging Technology and has no full scale installations for CSO treatment yet (EPA, 2013). Backman and Irwin (2012) reported that CoMag can be used only for the removal of particulate contaminants.

## 2.4 Ferrate (VI)

The most common oxidation states of iron that exists are +2 and +3. Iron being a transition metal, higher oxidation states such as +4, +5 and +6 can also be obtained (Sharma et al., 2005). All the oxidation states of iron above +3 are generally termed as Ferrate out of which Fe (VI) is well known because of its stability with respect to +4 and +5 oxidation states and also due to its occurrence (Tiwari et al., 2005). The aqueous solution of ferrate (VI) has a reddish violet color (Jiang and Lloyd, 2002). The molecular formula of ferrate (VI) ion is  $\text{FeO}_4^{2-}$  and has a tetrahedral structure (Macova et al., 2009; Jiang and Lloyd, 2002). Figure 2.6, shows the structure of ferrate (VI) in aqueous solution.

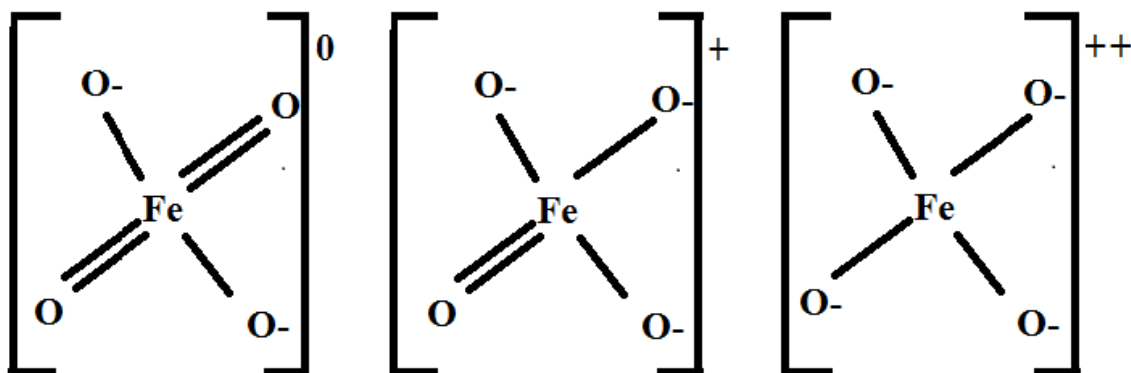


Figure 2.6: Structure of Ferrate (Norcross et al., 1997)

The redox potential of ferrate (VI) (2.2 V under acidic condition and 0.72 V under basic condition) is greater than other oxidizing agents (Jiang et al., 2006). During the oxidation of contaminants, Fe (VI) gets reduced to Fe (III) ions or ferric hydroxide known for their coagulating and flocculating properties, thus providing double benefit with a single

chemical (Jiang and Lloyd, 2002; Jiang et al., 2006; Lee et al., 2009; Sharma et al., 2005). The ferric hydroxide generated from the reduction of Fe (VI) aids the removal of metals, non-metals (Sharma, 2008). The removal of suspended particles, disinfection of microorganisms and oxidation of inorganic and organic compounds can be attained by single ferrate (VI) dose (Jiang and Lloyd, 2002; Jiang et al., 2005). The colloidal particles can be destabilized within 1 min using ferrate (VI) (Jiang and Lloyd, 2002). The very low dose of ferrate (VI) can achieve greater performance as compared to the other coagulants thus reducing the sludge production (White and Franklin, 1998; Jiang et al., 2012a). There are no carcinogenic or mutagenic by products formed after the Fe (VI) treatment making it a green chemical (Sharma et al., 2005; Tiwari et al., 2005). Fe (VI) is most stable at pH 9 (Graham et al., 2004; Sharma, 2002). Potassium Ferrate is the most stable and easily prepared derivative of Fe (VI) (Sharma, 2002; Lee et al., 2004).

#### **2.4.1 Applications of ferrate (VI)**

Ferrate (VI) has been studied widely as a potential chemical for treatment of water and wastewater (Jiang and Lloyd, 2002; Tiwari et al., 2005). There are numerous findings reported by researchers on the Fe (VI) performance as an oxidant, coagulant and disinfectant in treatment of water and wastewater. Fe (VI) performance as a disinfectant in water and wastewater was thoroughly reviewed by Sharma (2007). The 6 mg Fe (VI)/l killed 99.9% E.coli at pH 8.2 with contact time of 7 min (Jiang and Lloyd, 2002). A 10 mg Fe (VI)/l of dose achieved significant antimicrobials removal during water treatment (Sharma et al., 2008). Fe (VI) effectively removed chlorine resistant bacteria (Gombos et al., 2012). Sharma (2010) comprehensively reviewed the application of Fe (VI) as an oxidant for the removal of nitrogen containing organic and inorganic compounds. Ferrate

(VI) effectively oxidized phenolic endocrine disrupting chemicals (EDCs) and phenols, and second order kinetics was reported (Lee et al., 2005). N-nitrosodimethylamine (NDMA) was completely oxidized by 1.1 mg/l of Fe (VI) dose (Lee et al., 2008). Lee et al., (2009) attained 80% phosphate and 97% micropollutants (sulfamethoxazole, diclofenac and carbamazepine) removal by 7.5 mg Fe (VI)/l and 5 mg Fe (VI)/l, from secondary wastewater effluent. At pH 8, ferrate (VI) oxidized benzene, allylbenzene and phenol in the range of 18-47%, 85-100% and 32-55% respectively and maximum oxidation was observed at 3:1 molar ratio of ferrate (VI) to organics (Jiang et al., 2005). The removal efficiency of ciprofloxacin (CIP) was reported to be 80 % by mere 1 mg/l of Fe (VI) dose (Jiang et al., 2012b). Lee et al., (2004) reported that ferrate can reduce COD and BOD<sub>5</sub> of secondary wastewater effluent significantly. The ferrate (VI) dose of 15 mg/l attained almost 83% COD removal (COD was reduced from 40 mg/l to 7 mg/l) when applied to secondary wastewater treatment (Jiang et al., 2005). The ferrate (VI) dose of less than 10 mg/l achieved 93% Biochemical oxygen demand (BOD<sub>5</sub>) removal from domestic secondary effluent (Jiang and Lloyd, 2002). The full scale trials of online ferrate generation and application of ferrate (VI) were carried out at Halesham North Wastewater Treatment Plant of Southern Water Ltd., UK by Jiang et al., (2012a). The average removals of SS, phosphate, COD and BOD<sub>5</sub> reported were 64%, 44%, 46% and 40% respectively by 0.16 mg/l of Fe (VI) dose at pH above 9. The soluble organics removal was not investigated.

The applicability of Fe (VI) treatment as a tertiary treatment for removal of various EDCs, pharmaceutical products from secondary wastewater effluent was effectively demonstrated (Yang et al., 2012). Ferrate (VI) successfully oxidized alcohol (Norcross et

al., 1997), chlorinated phenols (Graham et al., 2004), arsenic (Lee et al., 2003), humic substances (Graham et al., 2010; Jiang and Wang, 2003; Lim and Kim, 2010), cyanides (Flip et al., 2011), glucose, fructose, maltose, sucralose (Sharma et al., 2012), steroidal estrogens from dairy waste lagoon effluent (Remsburg et al., 2008), Bisphenol A (Zhang et al., 2012), Benzotriazoles (Yang et al., 2011) and ibuprofen (Sharma and Mishra, 2006). The effective removal of heavy metals (Cu, Mn, Zn) (Lim and Kim, 2010), algae (Ma and Liu, 2002) and color (White and Franklin, 1998) using ferrate (VI) has been reported.

#### **2.4.2 Synthesis of ferrate (VI)**

Stahl in 1702, was the first to observe red purple color solution when he dissolved the molten residue, formed by heating of saltpaper and iron filings, into water (Jiang and Lloyd, 2002). The heating of iron ore and potash yielded a same color to Eckenberg and Becquerel in early 19<sup>th</sup> century (Jiang and Lloyd, 2002). The colored solution was later identified as potassium ferrate (Jiang and Lloyd, 2002; Macova et al., 2009). Fe (VI) was very rarely studied in 19<sup>th</sup> and early 20<sup>th</sup> century because of its highly unstable nature, difficult synthesis method and low yield (Tiwari et al., 2005). The enhanced oxidation properties and unique performance ability brought ferrate (VI) back into attention in late 20<sup>th</sup> century. There are three methods for synthesis of ferrate (VI) (Jiang Lloyd, 2002; Tiwari et al., 2005; Sharma et al., 2005; Yu and Licht, 2008):

##### **2.4.2.1 Electrochemical synthesis method**

In this method, the ferrate is produced by oxidizing an anode made up of iron or iron salts in a strong alkaline solution at a desired anode potential (Denvir and Pletcher, 1996;

Sharma et al., 2005). Following equations represents the preparation of Fe (VI) using electrochemical method (Jiang and Lloyd, 2002).

At anode:



At cathode:



Overall Reactions:



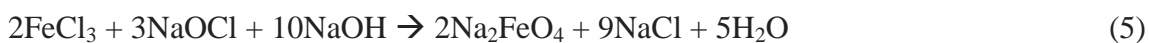
The efficiency of the ferrate produced depends on the current density, composition of anodes and also on the concentration of electrolytes (Jiang and Lloyd, 2002). More the carbon content, higher is the efficiency (Tiwari et al., 2005). A current efficiency of 35% was achieved at the optimum current density of 36 A/m<sup>2</sup>, 16M NaOH solution and 0.11% carbon content of steel (Alsheyab et al., 2010). The current yield achieved by raw iron, steel and cast iron were 15%, 27% and 50 % respectively, at 10 A/m<sup>2</sup> current density and 16.5 M NaOH (Tiwari et al., 2005). This method of preparation has been used widely for online generation of Fe (VI) since it uses nontoxic raw materials and produces pure dissolved Fe (VI) product (Jiang et al., 2009; Sharma et al., 2005). The yield obtained by this synthesis method is low and further preparation of solid Fe (VI) is difficult (Sharma et al., 2005; Lescuras –Darrou et al., 2002).

#### 2.4.2.2 Dry synthesis method

This method is also called thermal oxidation, since the iron oxide is fused with oxidants at high temperature and pressure (Sharma et al., 2005; Tiwari et al., 2005). This method is the oldest method used for the preparation of ferrate (VI) (Jiang and Lloyd, 2002). The ferric oxide was fused with sodium peroxide in the presence of oxygen and in a desired molar ratio at an elevated temperature (370 °C) produced sodium ferrate (VI) (Kopelev et al., 1992). The galvanizing wastes were fused with ferric oxide at 800 °C. The mixture was then reacted with sodium peroxide at high temperature to produce sodium ferrate (Jiang and Lloyd, 2002). The dry oxidation method comes with a safety concern due to high temperature and pressure conditions and also the yield of produced ferrate is low (Tiwari et al., 2005).

#### 2.4.2.3 Wet synthesis method

In this method, the ferric salts are made to oxidize using strong oxidants in presence of concentrated alkaline medium to produce ferrate (VI). Thompson et al., (1951) reacted ferric chloride with sodium hypochlorite in presence of sodium hydroxide to produce sodium ferrate. In order to prepare stable ferrate derivative, sodium ferrate was further reacted with potassium hydroxide (White and Franklin, 1998). Following are the reactions that generally occur in wet synthesis method:



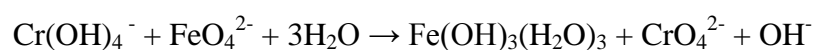


An on-site ferrate reactor was developed by Ferrate Treatment Technologies (FTT) based on the concept of wet synthesis and was named as Ferrator (Crampi and Daly, 2009). The raw materials used are ferric chloride, sodium hypochlorite, sodium hydroxide and potassium hydroxide. Ferrator is used for disinfection, destruction of emerging contaminants and odor control (Alig et al., 2011). The major drawback of this synthesis method is its low yield (10-15%) and numerous separation steps are required to obtain solid potassium ferrate making it an expensive procedure (Sharma et al., 2005, Tiwari et al., 2005).

### **2.4.3 Ferrate Analysis (Luo et al., 2011)**

#### **2.4.3.1 Volumetric titration method**

In this method, the samples containing Fe (VI) oxidizes the chromite salt.



The oxidized chromate is then titrated with standard ferrous salt solution in acidic medium. The sodium diphenylamine sulfonate is used as an indicator. The quantitative determination of Fe (VI) from submolar to molar level is possible with this method. The biggest disadvantage of this method is that the waste needs to be stored and treated before disposal as it produces chromium residual.

#### **2.4.3.2 UV-Visible spectroscopy**

The characteristic reddish purple color of Fe (VI) corresponds to the visible and infrared spectrum at about 500 and 800 nm. Denvir and Pletcher (1996) reported the absorption

spectrum of Fe (VI) at 505 nm while some researchers quoted it to be 510 nm (Sharma et al., 1998). The molar absorptivity of Fe (VI) was confirmed to be  $1150 \text{ M}^{-1}\text{cm}^{-1}$ .

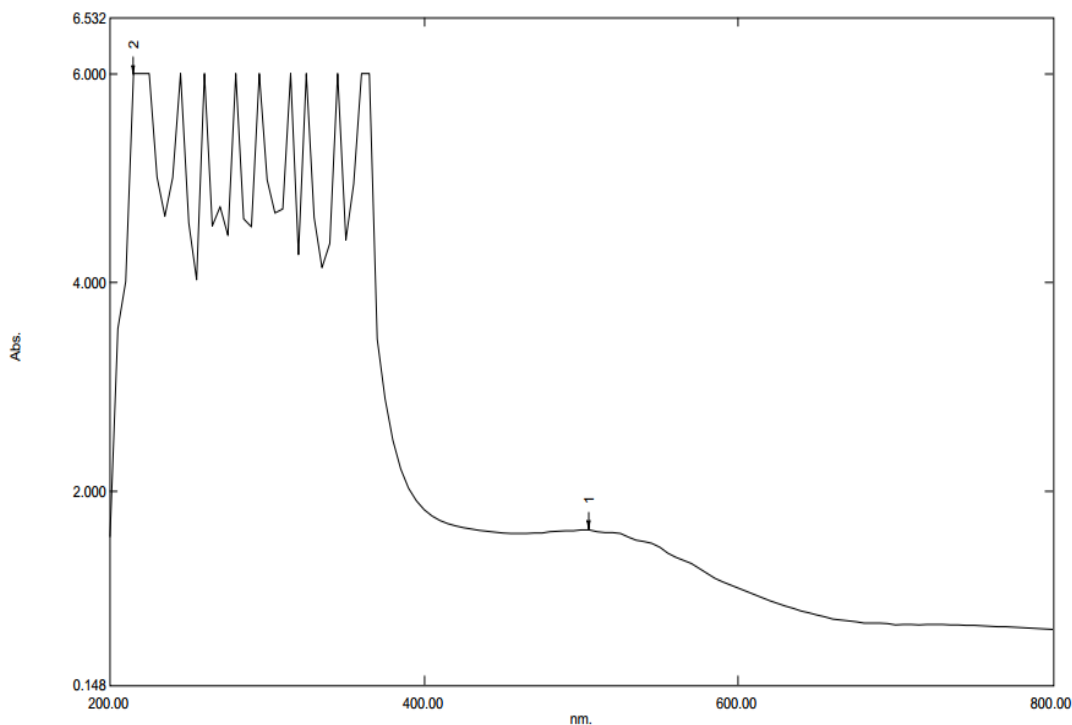


Figure 2.7: UV-Vis spectrum of Fe (VI) (Jiang and Lloyd, 2002)

## 2.5 Objectives of present research

Based on literature review, it was found that the commercial physical-chemical treatment techniques (Actiflo, DensaDeg and CoMag) used for the treatment of CSOs do not remove soluble organics. Apart from this, they use large quantities of coagulants and flocculants, and also the startup time required is high. Ferrate (VI) appeared to be a potential chemical that can treat CSOs in short contact time with a very low dose. From the literature it was noted that, only ferric salts have been used as an iron source for the synthesis of Fe (VI) using wet oxidation method, leaving the scope for evaluating

different iron sources for Fe (VI) synthesis. Moreover it was also noted that the Fe (VI) using wet oxidation method produces low yield aqueous Fe (VI) and the preparation of solid ferrate (VI) is very expensive as it requires many separation steps. The preparation of ferrate (VI) in-situ can help to solve the above mentioned issue. Iron is present in wastewater biosolids (Patterson and Kodukula, 1984), which are abundantly available at the WWTP.

Following are the questions which were attempted in this study

Can Fe (VI) be an effective chemical for treatment of CSO especially for the removal of soluble organics and nitrogen?

Can Fe (VI) be synthesized from different iron source other than ferric compounds especially wastewater biosolids (PS and TWAS) to evaluate the feasibility of in-situ generation?

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## Chapter 3

### Treatment of Combined Sewer Overflows using Ferrate (VI)

#### 3.1 Introduction

Combined Sewer Overflows (CSOs) treatment has become an immediate and urgent requirement due to the environmental threat it possess. Various physical-chemical treatment techniques like Actiflo, DensaDeg, CoMag and CEPT are available to treat CSOs. Actiflo (USFilter, Kruger Products, Cary, North Carolina) is a ballasted high rate clarification process, combining coagulation, flocculation and sedimentation process (Plum et al., 1998). A coagulant is added for destabilizing colloidal particles, followed by the addition of microsand which provides large surface area to prepare floc and then a polymer which aids flocculation and subsequent sedimentation is added (Landon et al., 2006). The Actiflo plant set up for the treatment of 100 m<sup>3</sup>/h CSOs at the intercepting sewer in Lyngby-Taarbaek municipality in the Capital Region of Denmark, achieved SS, COD and TP removal of 80%, 85% and 55% respectively (Plum et al., 1998). The typical hydraulic retention time (HRT) is 4-7 min (EPA, 2003). DensaDeg 4D (ONDEO Degremont, Inc., Richmond, Virginia) is a high rate ballasted clarification process that uses thickened recirculated sludge as ballast (Landon et al., 2006). Jolis and Ahmad in 2004 reported that the DensaDeg 4D pilot plant set up at Southeast Water Pollution Control Plant (SEWPCP) in San Francisco, California, achieved removal of 90% of SS and 60% of COD at an HRT of 20 min, and 80 mg/l and 1 mg/l ferric chloride and polymer dose, respectively. CoMag (Siemens, inc., Alpharetta, Georgia) uses magnetite as a ballasting agent along with regular coagulation and flocculation process (EPA,

2013). The CoMag treatment process (Screening, Grit Removal, CoMag, UV Disinfection) usually achieves BOD<sub>5</sub>, COD and TP removal efficiencies of 60%, 50% and 99% respectively, at an HRT of 5-15 min depending on plant capacity (Backman and Irwin, 2012). In chemically enhanced primary treatment (CEPT) chemicals are added to enhance coagulation and flocculation in order to effectively remove pollutants from wastewater (Haydar and Aziz, 2009). Jin et al., (2013) reported that the pilot plant set at an urban catchment in Tianjin, China attained 63%, 82 % and 81% of COD, TP and SS removal at 70mg/l dose of poly aluminium chloride (PAC).

The above mentioned physical-chemical treatment methods do not remove soluble organics and nitrogen from wastewater (Plum et al., 1998; EPA, 2013). Apart from this, many chemicals are required to be dosed in the system which can pose a threat to the environment and necessitates more maintenance (EPA, 2003). The typical startup time required by Actiflo, DensaDeg and CoMag is 15-30 minutes. The soluble organics present in CSO are a potential threat to aquatic environment and should be reduced. Development of a low cost oxidation and coagulation treatment process with no start up time and short contact time for the treatment of CSO can significantly mitigate adverse environmental impacts. Ferrate (VI) is the potential chemical that can meet these criteria.

Ferrate (VI) ( $\text{FeO}_4^{2-}$ ) is a strong oxidizing agent (Sharma, 2002; Jiang et al., 2006; Tiwari et al., 2005). Ferrate(VI) is quickly reduced to ferric or ferrous compound which acts as a coagulant thus providing double benefit with a single chemical (Sharma et al., 2005). There are numerous findings reported by researchers on the Fe (VI) treatment of water. The use of ferrate (VI) as a disinfectant in water and wastewater has been well reviewed by Sharma in 2007. Ferrate (VI) was used to oxidize endocrine disrupting compounds,



phenols (Lee et al., 2005), antimicrobials (Sharma et al. 2008), N- nitrosodimethylamine (NDMA) (Lee, 2008), alcohol (Norcross et al., 1997), ciprofloxacin (Jiang et al., 2012), glucose, fructose, maltose, sucralose (Sharma et al., 2012), benzotriazoles (Yang et al., 2011), recalcitrant compounds (EDTA and sulfamethoxazole) (Sharma et al., 2008) and ibuprofen (Sharma and Mishra, 2006). The use of ferrate (VI) for removal of toxic metals and non-metals (Bartzatt et al., 1992), coagulation of colloidal particles (Jiang et al., 2001) and removal of color (Jiang and Wang, 2003) from water has been addressed. The use of ferrate (VI) for the treatment of wastewater has been limited and can be attributed to the fact that Fe (VI) is very unstable and the cost required for the production of solid and stable ferrate (VI) is high. Alig et al., (2011) reported that the Ferrator, an on-site ferrate synthesis reactor, is used for disinfection, color removal, destruction of emerging contaminants and odor control. Stanford et al., (2010) reported the removal of 80% of TSS, 70 % of TCOD and 90% TP from wastewater at a dose of around 2 mg/l of Fe (VI) generated electrochemically. The removal of soluble organics was not investigated.

Ferrate (VI) can be synthesized by three methods, (1) dry synthesis, (2) wet synthesis and (3) electrochemical synthesis (Jiang and Lloyd, 2002; Sharma et al., 2005). Dry synthesis is a high temperature oxidation process. Ferric salt and an oxidant are heated at high temperature to produce Fe (VI). The ferric oxide when reacted with sodium peroxide in the presence of oxygen and in a desired reagent molar ratio at 370<sup>0</sup>C produces sodium ferrate (Kopelev et al., 1992). The dry oxidation method for synthesis of ferrate comes with a safety concern due to high temperature. In the wet synthesis method, ferrous and ferric salts are oxidized in strong alkaline medium to produce ferrate (VI). Ferric chloride is made to react with sodium hypochlorite in the presence of sodium hydroxide to

produce sodium ferrate (Thompson et al., 1951). White and Franklin in 1998 reported that Ferrate (VI) can be produced by reacting ferric hydroxide with potassium hydroxide with addition of chlorine. The major drawback of using the wet synthesis method is that the yield achieved is very low and the ferrate (VI) produced requires further purification (Sharma et al., 2005). The general principle of electrochemical synthesis of ferrate is to oxidize an anode, made of iron or iron salt, in a strong electrolyte using a desired anode potential to produce sodium or potassium ferrate (Jiang and Lloyd, 2002; Lescuras-Darrou et al., 2002). The electrochemical synthesis method has few limitations including low yield (Denvir and Pletcher, 1996).

Iron is present in wastewater sludges (Patterson and Kodukula, 1984; Jenkins et al., 1981). Iron (II) and Iron (III) salts are coagulants, precipitants and are also for odor removal in many water resources recovery facilities (Jiang and Graham, 1998; Perkowski and Kos, 2002). Iron occurs generally in two states, especially soluble ferrous iron and insoluble ferric iron (Vance, 1994). In sludge, iron is mostly present in amorphous form (Georgaki et al., 2004). The inavailability of exact speciation of iron in municipal sludges and variability of sludge composition have refrained researchers from using sludge as an iron source for generation of Fe (VI).

This chapter discusses the synthesis of Fe (VI) by oxidation of wastewater biosolids mainly primary sludge (PS) and thickened waste activated sludge (TWAS) using the wet synthesis method. It is important to note that PS and TWAS have never been reported as sources for Fe (VI) generation in the open literature.

The objectives of the present study were twofold: (1) to assess the treatment efficiency of Fe (VI) for soluble organics, nitrogen, and phosphorous found in CSOs; and (2) to synthesize ferrate (VI) using PS and TWAS to evaluate the feasibility of in-situ generation.

### 3.2 Materials and Methods

Iron (II) sulfate heptahydrate, sodium hypochlorite solution (NaOCl) and potassium hydroxide pellets (KOH) were obtained from Sigma Aldrich (Oakville, ON, Canada). The 1 M hydrochloric acid solution, 1M sodium hydroxide (NaOH) solution, 0.45  $\mu\text{m}$  polypropylene filters, 1.2  $\mu\text{m}$  syringe filters and whatman glass microfiber filters were obtained from VWR International (Mississauga, ON, Canada). The source of commercial grade ferrate (VI) was the potassium ferrate sample obtained from Regional Centre of Advanced Technologies and Materials (Olomouc, Czech Republic). The composition of 1g of sample was as follows: 21.3 %  $\text{K}_2\text{FeO}_4$ , 59.4%  $\text{KFeO}_2$ , 19.3% KOH or  $\text{K}_2\text{O}$ . Thus 1 g of sample contained 0.06 g of Fe (VI). The raw waste water (RWW), primary sludge (PS) and waste activated sludge (WAS) were collected from the Adelaide Pollution Control plant located in London (ON, Canada). The combined sewer overflow (CSO) water was prepared in lab by diluting RWW with distilled water in the ratio of 1:2. The waste activated sludge was settled and the supernatant was removed in order to thicken WAS. Total iron in PS and TWAS was determined after, PS and TWAS samples were digested. The pH of PS and TWAS samples were adjusted to 3 using HCl solution. The samples were then kept in a preheated oven at 105<sup>0</sup>C for 30 min. The samples were then filtered using 0.45  $\mu\text{m}$  polypropylene filters. The iron content in the samples was determined by inductively coupled plasma- optical emission spectrometer (ICP-OES,

Varian Vista Pro; CCD Simultaneous, Australia). In order to determine the soluble iron using ICP-OES, the PS and TWAS samples were filtered using 0.45  $\mu\text{m}$  polypropylene filters without digestion.

#### *Water Quality Analysis*

Total suspended solids (TSS), volatile suspended solids (VSS), total biochemical oxygen demand (TBOD<sub>5</sub>), and soluble biochemical oxygen demand (SBOD<sub>5</sub>) were analyzed according to the Standard Methods (APHA, 1998). HACH methods and testing kits (HACH Odyssey DR/2500) were used to measure total chemical oxygen demand (COD), soluble chemical oxygen demand (SCOD), total phosphorus (TP), total nitrogen (TN), soluble nitrogen (SN),  $\text{NH}_4$  and  $\text{PO}_4^{3-}$ . Samples were filtered using 0.45  $\mu\text{m}$  polypropylene filters in order to determine soluble parameters. Oakton pH meter was used to measure the pH of samples. The residual chlorine analysis was performed using the Thermo Scientific Orion AQUAfast II colorimeter. Table 3.1 represents the water quality parameters for the RWW.

Table 3.1: Raw waste water (RWW) characteristics

<b>Characteristics</b>	<b>RWW</b>
<b>TSS (mg/l)</b>	250 ± 80
<b>VSS (mg/l)</b>	200 ± 60
<b>TCOD (mg/l)</b>	314 ± 36
<b>SCOD (mg/l)</b>	124 ± 44
<b>TBOD<sub>5</sub> (mg/l)</b>	180 ± 26
<b>SBOD<sub>5</sub> (mg/l)</b>	75 ± 25
<b>TN (mg/l)</b>	28 ± 4
<b>STN (mg/l)</b>	19.2 ± 3
<b>NH<sub>4</sub> (mg/l)</b>	14.7 ± 1.5
<b>TP (mg/l)</b>	6.9 ± 1.1
<b>PO<sub>4</sub><sup>3-</sup> (mg/l)</b>	3.4 ± 1

### *Experimental procedures*

In order to determine the applicability of ferrate (VI) for the treatment of CSO, standard jar tests were performed. All the six beakers with 1-L capacity each were filled with laboratory prepared combined sewer overflow. The pH was adjusted to 7 using HCl or NaOH. The Fe (VI) was added as dry powder instead of stock solution, since Fe (VI) is very unstable and reacts with water quickly to form Fe (III) compound. One beaker was considered as blank while the other five beakers were dosed with 0.3 mg Fe (VI), 0.6 mg Fe (VI), 1.5 mg Fe (VI), 15 mg Fe (VI) and 30 mg Fe (VI). The mixture was then stirred at the speed of 100 rpm for 30 seconds, after which the mixing speed was reduced to 30 rpm for the next 30 min, in order to promote flocculation. Stirring was stopped and mixture was made to settle for 30 min before the collection of sample. Water quality analysis was carried out on the samples to determine the effectiveness of Fe (VI) for

treatment of CSOs. In order to check the consistency of the results, experiments were carried out three times.

#### *Dose Optimization*

The results obtained from the aforementioned experiments defined the effective range of Fe (VI). To determine the optimum dose of ferrate (VI), the jar test apparatus and procedure was kept the same as mentioned earlier. One beaker was considered blank and the other five beakers were spiked with 0.12 mg Fe (VI), 0.24 mg Fe (VI), 0.36 mg Fe (VI), 0.48 mg Fe (VI) and 0.6 mg Fe (VI). In order to determine the effect of pH on the treatment performance of Fe (VI) doses, tests were carried out at pH 6, 7, 8 and 9 maintaining the same aforementioned doses. The pH was adjusted by using HCl or NaOH solution. The final samples collected were analyzed for the aforementioned water quality parameters. The experiments were carried out multiple times to check the accuracy of the findings.

#### *Jar Test Kinetics*

Kinetic batch studies at neutral pH and the optimum dose of ferrate obtained from the aforementioned jar testing were conducted in a 4L completely mixed batch reactor. The mixture of ferrate (VI) and CSO was subjected to the initial stirring at 100 rpm for 1 minute. The stirring speed was reduced to 30 rpm for the next 4 min, after which stirring was stopped to settle the mixture. Mixed samples were collected every minute for first five minutes and then supernatant samples were collected every five minutes for the next 15 minutes. The final supernatant sample was collected 40 minutes after the initial start time.

### *Synthesis of Ferrate (VI)*

Ferrate (VI) was synthesized by the wet oxidation method. Ferrous sulfate heptahydrate was oxidized using sodium hypochlorite solution under strong alkaline conditions in order to produce potassium ferrate ( $K_2FeO_4$ ). Ferrate (VI) was measured spectrophotometrically at a wavelength of 505 nm (Denvir and Pletcher, 1996) using a UV-VIS spectrophotometer (UV-3600, Shimadzu).

### *Ferrate (VI) production from biosolids*

The PS and TWAS were used as an iron source to synthesize ferrate using the wet oxidation method. Table 3.2 shows the characteristics of PS and TWAS.

Table 3.2: Characteristics of PS and TWAS

	TSS (g/l)	VSS (g/l)	TCOD (g/l)	SCOD (g/l)	Total Fe (mg/l)	Soluble Fe (mg/l)
<b>Primary Sludge</b>	28.1 ± 1	22.4 ± 0.9	38 ± 0.9	9.4 ± 0.7	388 ± 24	38 ± 6
<b>TWAS</b>	14.7 ± 0.7	9.8 ± 0.6	13.5 ± 0.4	2.05 ± 0.15	192 ± 10	27 ± 4

Two different procedures were performed to synthesize ferrate (VI) using sludge.

- The digested PS and TWAS were treated with sodium hypochlorite solution in the presence of potassium hydroxide. Fifteen ml of 50 g/l sodium hypochlorite solution and 2 g of potassium hydroxide pellets were added to 5 ml of digested PS or TWAS without filtration. Fe (VI) concentration was measured using UV-VIS spectrophotometer.

- The digested PS and TWAS samples were filtered with 0.45  $\mu\text{m}$  polypropylene filters and then were subjected to the hypochlorite treatment under strong alkaline conditions. The 15 ml of 50 g/l sodium hypochlorite solution and 2 g of potassium hydroxide pellets were added to 5 ml of digested PS or TWAS filtrate. Fe (VI) concentration was measured using UV-VIS spectrophotometer.

To check the effectiveness, 10 ml solution of the liquid ferrate produced from different sources (ferrous sulfate heptahydrate, digested PS, digested TWAS, digested PS filtrate and digested TWAS filtrate) were dosed in the five beakers containing 1L CSO water respectively, with one beaker filled with CSO only as a blank in the above mentioned jar test. The samples were analyzed for the water quality parameters and the experiment was repeated multiple times to check the variability of the results.

### **3.3 Results and Discussions**

#### ***I. Assessment of the treatment efficiency of ferrate (VI) for soluble organics, nitrogen and phosphorous***

The applicability of ferrate (VI) for the treatment of CSOs at neutral pH was demonstrated using jar tests and the results obtained are presented in Figure 3.1. The removal efficiencies of TCOD, SCOD, TSS and VSS achieved by 0.3 mg Fe (VI)/l were 83%, 73%, 70% and 74% respectively, and those obtained by 0.6 mg Fe(VI)/l were 77%, 70% 78% and 95% respectively. These removal efficiencies obtained by 0.3 mg Fe (VI)/l and 0.6 mg Fe (VI)/l were found out to be much higher than those achieved by 1.5 mg Fe (VI)/l, 15 mg Fe (VI)/l and 30 mg Fe (VI)/l dose. The 15 mg Fe (VI)/l and 30 mg Fe (VI)/l turned out to be the over dose. The dose of 0.3 mg Fe (VI)/l showed high COD



removal and low SS removal as compared to 0.6 mg Fe (VI)/l due to more efficient reduction of SCOD.

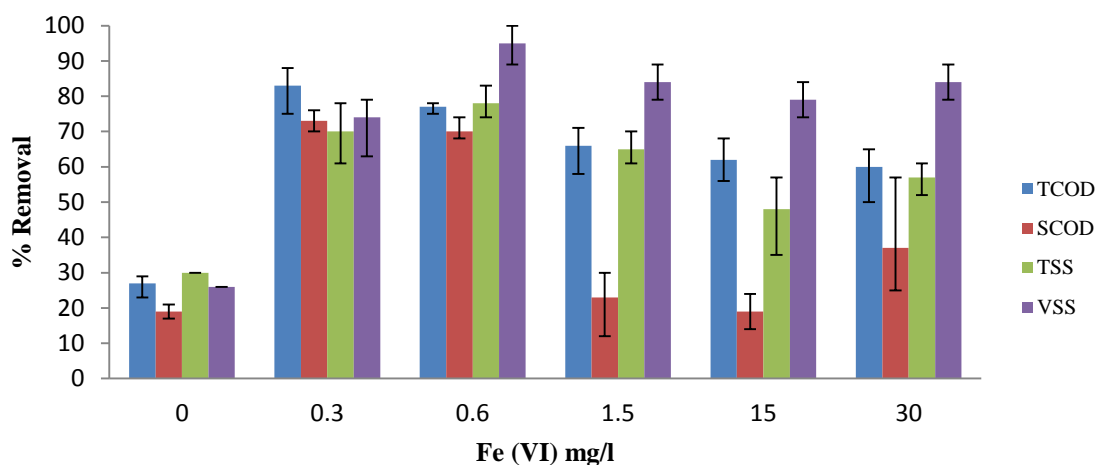


Figure 3.1: Treatment efficiency of different doses of Fe (VI) at neutral pH

### *Optimization*

The optimization of Fe (VI) dose required for the treatment of CSO was carried out with the range of dose figured out from the above mentioned results. The effect of pH on the efficiency of ferrate (VI) doses was also studied and the results are shown in Figure 3.2. The removal efficiencies of TCOD, SCOD, TSS, VSS, TP and TN obtained at pH 9 with a dose of 0.12 mg/l Fe (VI) were 81%, 81%, 57%, 67%, 52% and 28% respectively, and found to be higher than the efficiencies obtained by the same dose at pH 6, pH 7, and pH 8 respectively. The main reason for the high removal efficiency at pH 9 and at a very low dose of Fe (VI) can be attributed to the fact that Ferrate (VI) is more stable in alkaline medium. At pH 7 and a dose of 0.24 mg/l Fe (VI), the TCOD, SCOD, TSS, VSS, TP and TN removal efficiencies of 69%, 69%, 57%, 75%, 52% and 38%. The TCOD, SCOD,

TSS, VSS, TP and TN removal efficiencies obtained from 0.12 mg/l Fe (VI), 0.24 mg/l Fe (VI), 0.36 mg/l Fe (VI), 0.48 mg/l Fe (VI) and 0.60 mg/l Fe (VI) at pH 8 were almost equivalent to those achieved with the same doses at pH 7. The optimum pH was decided as 7 rather than pH 9, considering the fact that treated CSOs will be discharged in receiving water bodies.

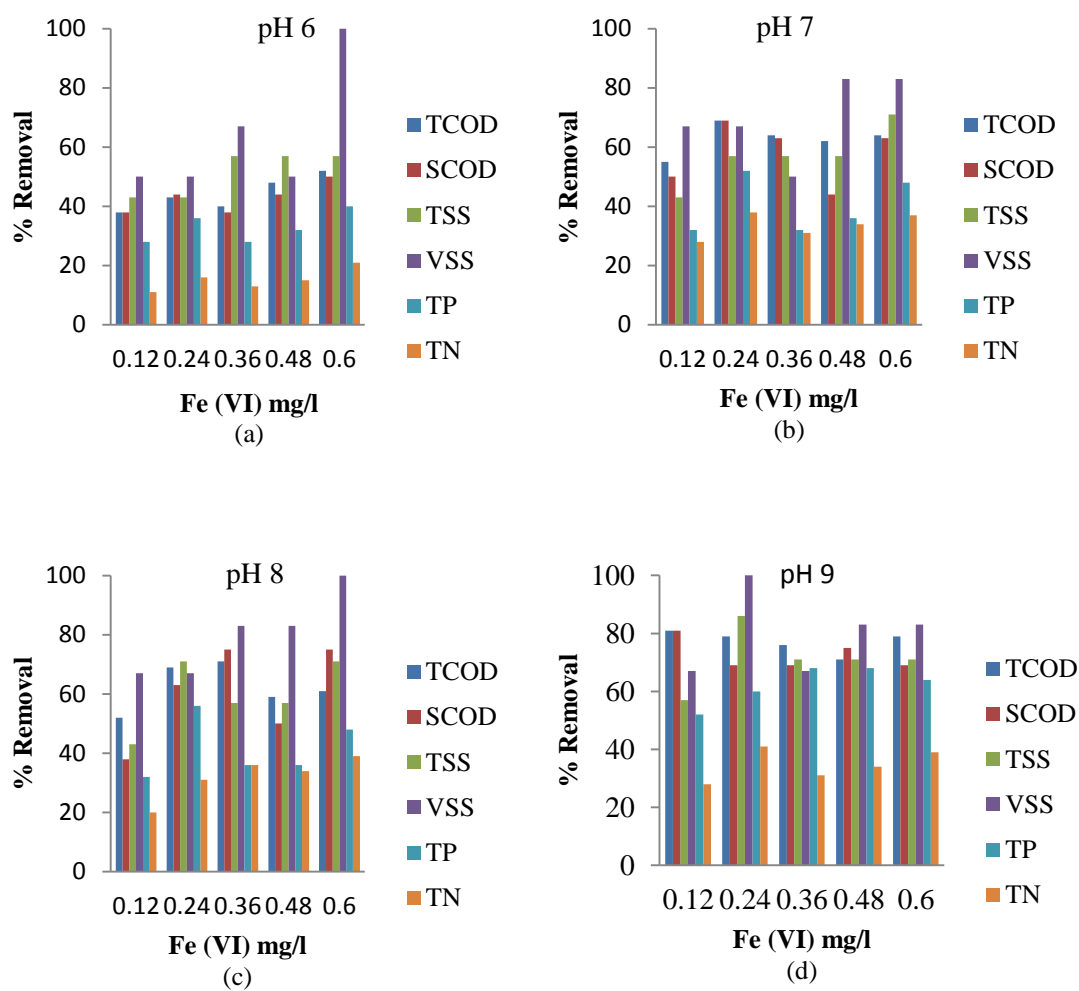


Figure 3.2: Effect of pH on the treatment performance of Fe (VI) doses, (a) pH 6; (b) pH 7; (c) pH 8; (d) pH 9

The removal efficiencies achieved by ferrate (VI) at pH 7 with respect to those achieved at pH 9 are compromised but not low. The optimum dose of 0.24 mg Fe (VI)/l at neutral pH was used for kinetic testing.

### *Kinetics*

The treated CSO water characteristics and the treatment efficiency obtained by the optimum dose of 0.24 mg Fe (VI)/l are represented in Table 3.3. The very low dose of ferrate (VI) achieved treated wastewater quality comparable to secondary effluent. The soluble organics, TP, TN and STN were removed effectively by Ferrate (VI). The optimum dose of Fe (VI) removed SCOD, SBOD<sub>5</sub>, TP, TN, STN and PO<sub>4</sub><sup>3-</sup> by 75%, 68%, 64%, 38%, 36% and 36% respectively. It must be asserted that the removal of soluble total nitrogen without any appreciable change in ammonia indicates that soluble organic nitrogen was oxidized primarily to nitrogen gas.

Table 3.3: Treatment Efficiency of Ferrate VI (0.24 mg/l dose)

	Untreated CSO (mg/l) *	Treated CSO (mg/l) <sup>a</sup>	Treatment Efficiency (%) <sup>a</sup>
<b>TCOD</b>	84	24±3	71±4
<b>SCOD</b>	32	8±1	75±3
<b>TBOD<sub>5</sub></b>	50.6	15.7±1.4	69±3
<b>SBOD<sub>5</sub></b>	17.9	5.5±0.4	68±5
<b>TSS</b>	70	20±10	72±15
<b>VSS</b>	60	10±10	83±17
<b>TP</b>	2.5	0.9±0.2	64±8
<b>TN</b>	9	5.6±0.6	38±6
<b>STN</b>	7.4	4.8±0.4	36±6
<b>PO<sub>4</sub><sup>3-</sup></b>	1.1	0.7±0.1	36±9
<b>NH<sub>4</sub></b>	4.8	4.4±0.1	9±1
<b>a.</b> Average ± SD (Three runs)			
*. Same CSO water was used for all the three runs			

The soluble organic nitrogen (SON= STN-NH<sub>4</sub>) correlated with SCOD statistically ( $R^2 = 0.9604$ ) as shown in Figure 3.3 with 0.084 mg SON/ mg SCOD.

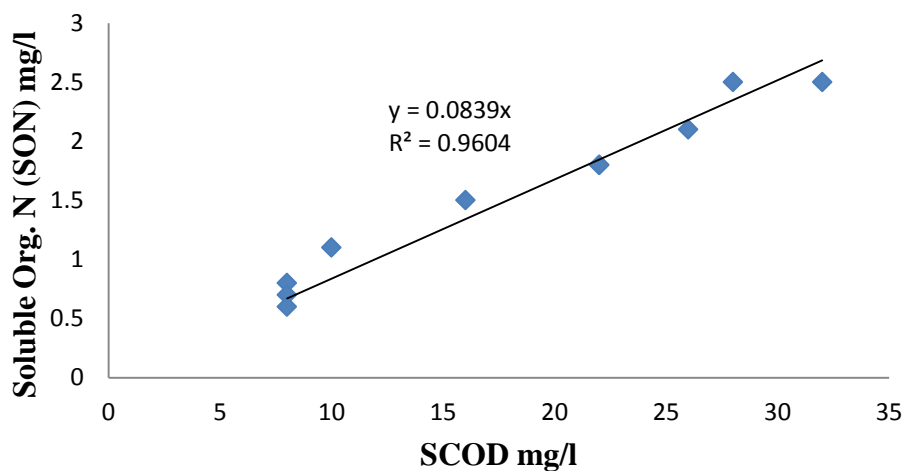


Figure 3.3: Plot of soluble organic nitrogen (SON) vs. soluble chemical oxygen demand (SCOD)

Figure 3.4a and 3.4b respectively depict the temporal variations of organics and nutrients (i.e. N and P) at a dose of 0.24 mg Fe (VI)/l. From the Figure 3.4-b, it can be noted that the NH<sub>4</sub> was almost unaffected by Fe (VI). It is interesting to note that the required contact time of Fe (VI) for treatment is as low as 15 min. The PCOD, SCOD, TP, TN, STN removal efficiencies of 65%, 75%, 56%, 34%, 32% respectively were attained by very low dose of ferrate (0.24 mg Fe (VI)/l) and in very short time (15 minutes). The TSS and VSS were reduced by 71% and 66% respectively, within 15 min by 0.24 mg Fe (VI)/l dose (not shown). It must be asserted that the 15 minute contact time included 5 minutes of mixing and 10 minutes of settling, and as apparent from Figure 3.4, more than 46%, 50%, 32%, 21%, and 19% of PCOD, SCOD, TP, TN, and STN removal were

actually achieved within 5 minutes. The high SCOD removal indicates that ferrate (VI) acts as a strong oxidant and the removal of PCOD implies that Fe (VI) can be an effective coagulant.

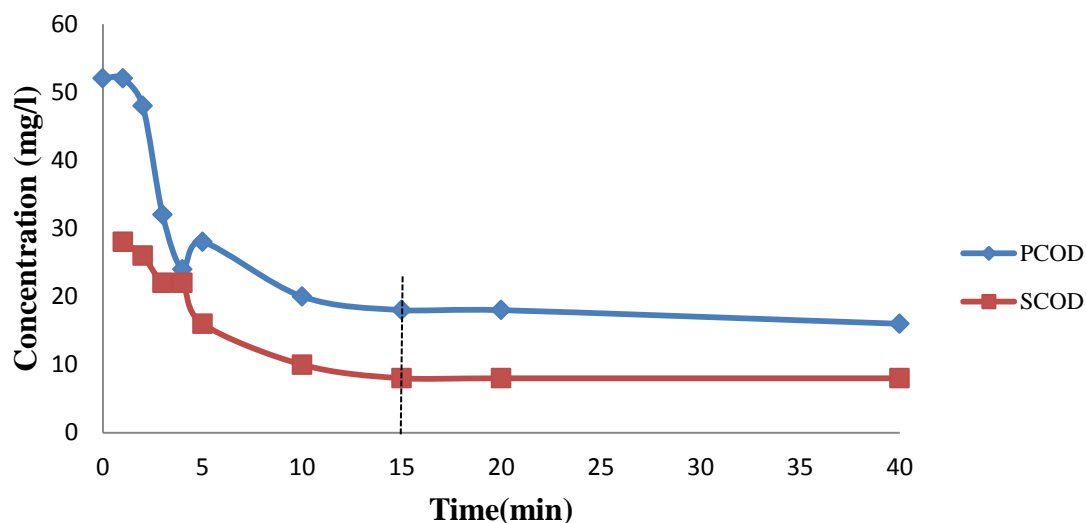


Figure 3.4-a: Effect of 0.24 mg/l ferrate (VI) dose on Concentration of PCOD and SCOD with respect to time.

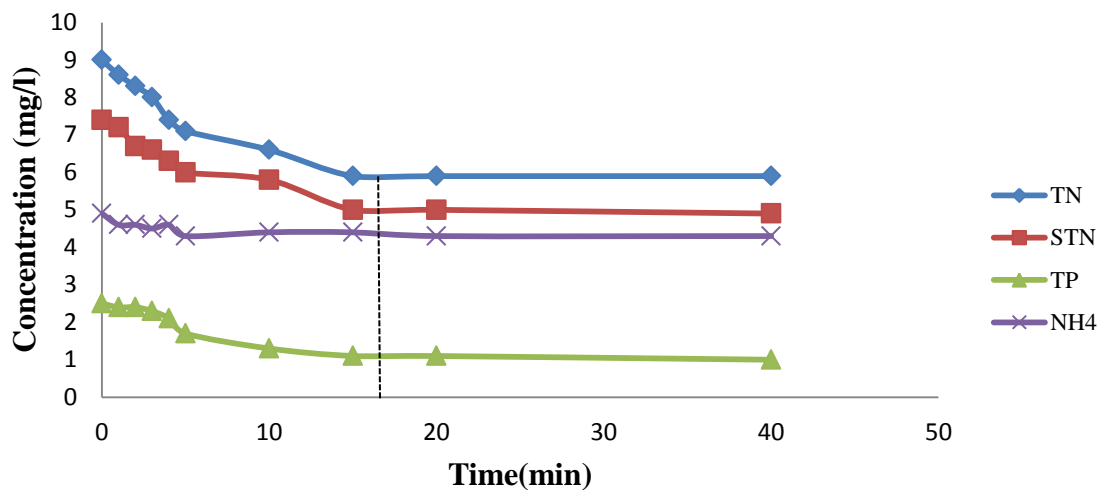


Figure 3.4-b: Effect of 0.24 mg/l ferrate (VI) dose on Concentration of TN, STN, TP and NH<sub>4</sub> with respect to time.

The second order model was found out to be the best fit for the reaction between water quality parameters and ferrate (VI). This can be due to reduction of ferrate into ferric ion which further acts as a coagulant. Sharma et al. (2008) reported that Fe (VI) oxidation of endocrine disruptors were modeled using second order reaction. The plot of  $1/\text{concentration}$  of PCOD and SCOD versus time is represented in Figure 3.5. The second order rate constant ( $k$ ), of oxidation reaction at neutral pH was  $0.0067 \text{ (mg/l)}^{-1}\text{min}^{-1}$  with  $R^2$  value of 0.9734 for SCOD. The  $k$ -value for PCOD was  $0.002 \text{ (mg/l)}^{-1}\text{min}^{-1}$  signaling that removal of SCOD by ferrate is faster than PCOD removal.

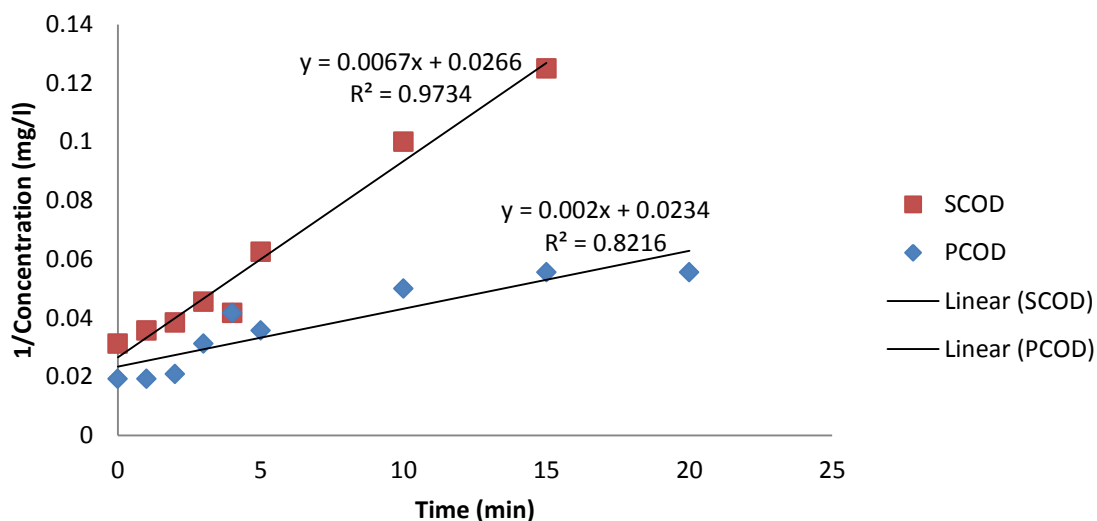


Figure 3.5: Plot of  $1/\text{Concentration}$  of PCOD and SCOD vs. time for the ferrate dose of  $0.24 \text{ mg/l}$ . (Kinetic study)

The rate constant,  $k$ , for the reaction of Fe (VI) with TCOD, TBOD<sub>5</sub>, SBOD<sub>5</sub>, TSS, VSS were  $0.0019 \text{ (mg/l)}^{-1}\text{min}^{-1}$ ,  $0.0032 \text{ (mg/l)}^{-1}\text{min}^{-1}$ ,  $0.0094 \text{ (mg/l)}^{-1}\text{min}^{-1}$ ,  $0.0015 \text{ (mg/l)}^{-1}\text{min}^{-1}$  and  $0.0034 \text{ (mg/l)}^{-1}\text{min}^{-1}$  respectively ( $R^2$  of 0.9652, 0.983, 0.9771, 0.8451 and 0.9048 respectively, not shown).

## ***II. Assessment of ferrate (VI) synthesis using wastewater biosolids***

The synthesis of Ferrate (VI) was carried out by wet oxidation method using ferrous sulfate heptahydrate as the iron source. Ferrous sulfate heptahydrate was added as a dry powder while sodium hypochlorite was added as 5% solution i.e. 50 g/l. The amount of ferrate (VI) produced using 2 grams of ferrous sulfate heptahydrate and 2.5 grams/50 ml of sodium hypochlorite (50 g/l) was 0.00245 g corresponding to only 0.61% of the theoretical quantity i.e. the yield was a mere 0.61%.

The wastewater biosolids were used as the iron source for the synthesis of ferrate (VI). Two synthesis methods as mentioned above in the materials and methods section were carried out. The amount of ferrate (VI) produced by digested PS, digested PS filtrate, digested TWAS and digested TWAS filtrate sources were measured by UV-VIS spectrophotometer and were 72 mg/l, 10 mg/l, 27 mg/l and 9 mg/l respectively. Jar tests on CSO treatment by biosolids synthesized Fe (VI) were conducted by adding 10 ml of the ferrate (VI) solutions to 1 L of CSO. The initial and the final concentrations of TCOD, SCOD, TSS and VSS for dose of 0.49 mg Fe (VI)/l, 0.72 mg Fe (VI)/l, 0.1 mg Fe (VI)/l, 0.27 mg Fe (VI)/l and 0.09 mg Fe (VI)/l synthesized from ferrous sulfate heptahydrate, digested PS, digested PS filtrate, digested TWAS and digested TWAS filtrate respectively, are shown in Figure 3.6. The addition of Ferrate (VI) synthesized from dig PS and dig TWAS to CSO accounted for the initial rise of TCOD, SCOD, TSS and VSS while the addition of Fe (VI) produced from dig PS filtrate and dig TWAS filtrate, increased the initial concentration of TCOD and SCOD in the CSO, without any change in TSS and VSS concentrations.

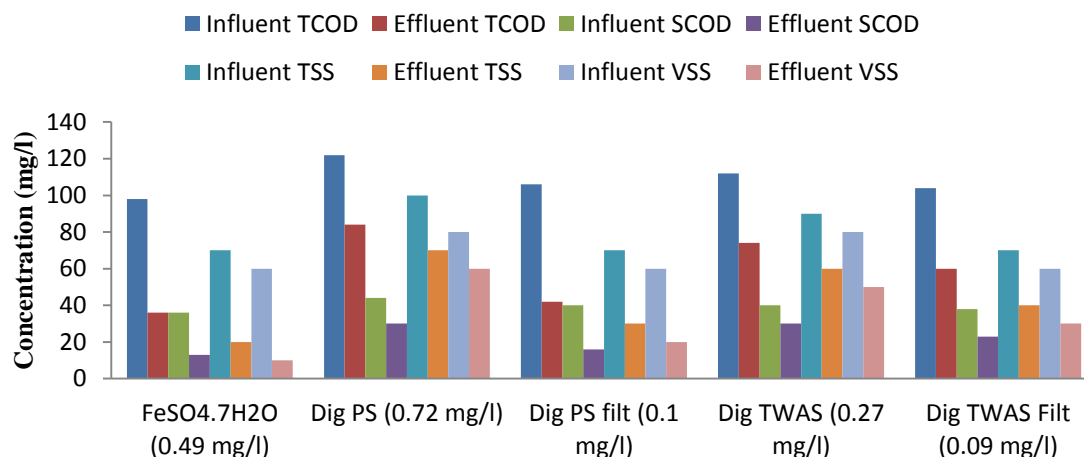


Figure 3.6: Influent and Effluent concentrations of water quality parameters obtained from ferrate doses prepared from different sources.

The concentrations of the unreacted NaOCl were found out to be 44 mg/l, 247 mg/l, 208 mg/l, 229 mg/l and 208 mg/l for the ferrate (VI) dose of 0.49 mg/l, 0.72 mg/l, 0.1 mg/l, 0.27 mg/l and 0.09 mg/l produced from FeSO<sub>4</sub>.7H<sub>2</sub>O, digested PS, digested PS filtrate, digested TWAS, and digested TWAS filtrate respectively. The treatment efficiencies achieved by 10 ml of each liquid ferrate solution per liter of CSO i.e. by the dose of 0.72 mg Fe (VI)/l, 0.1 mg Fe (VI)/l, 0.27 mg Fe (VI)/l, 0.09 mg Fe (VI)/l and 0.49 mg Fe (VI)/l synthesized from digested PS, digested PS filtrate, digested TWAS, digested TWAS filtrate and ferrous sulfate heptahydrate respectively, and their comparison with the treatment efficiency attained by the respective unreacted NaOCl dose of the prepared ferrate solutions are mentioned in Table 3.4. The removal efficiencies obtained by the control run without any chemical during the jar test are also listed in Table 4. The dose of 0.1 mg Fe (VI)/l synthesized by digested PS filtrate showed the higher treatment



efficiency than the 0.72 mg Fe (VI)/l, 0.27 mg Fe (VI)/l and 0.09 mg Fe (VI)/l doses synthesized by digested PS, digested TWAS and digested TWAS filtrate respectively.

Table 3.4: Comparative performance of ferrate (VI) produced from different source

	Synthesized Ferrate (VI) Source					Settled CSO
	Dig. PS <sup>a</sup>	Dig. PS Filtrate <sup>b</sup>	Dig. TWAS <sup>c</sup>	Dig. TWAS Filtrate <sup>b</sup>	FeSO <sub>4</sub> .7H <sub>2</sub> O <sup>d</sup>	
<b>Dose (mg/l)</b>	0.72 (247)	0.1 (208)	0.27 (229)	0.09 (208)	0.49 (44)	
<b>% TCOD Removal</b>	31 (42)	60 (43)	34 (44)	42 (43)	63 (40)	29
<b>%PCOD Removal</b>	31 (50)	61 (48)	39 (48)	44 (48)	63 (45)	34
<b>% SCOD Removal</b>	32 (28)	60 (33)	25 (36)	39 (33)	64 (31)	19
<b>% TSS Removal</b>	30 (38)	57 (38)	33 (25)	43 (38)	71 (25)	25
<b>% VSS Removal</b>	25 (33)	67 (17)	38 (33)	50 (17)	83 (33)	33
<b>%STN Removal</b>	17 (14)	28 (10)	20 (14)	26 (10)	33 (7)	3
<b>%NH<sub>4</sub> Removal</b>	6 (4)	8 (4)	8 (4)	6 (4)	8 (2)	
a. Values mentioned in brackets are the removal efficiencies obtained by control run of 247 mg NaOCl/l dose.						
b. Values mentioned in brackets are the removal efficiencies obtained by control run of 208 mg NaOCl/l dose.						
c. Values mentioned in brackets are the removal efficiencies obtained by control run of 229 mg NaOCl/l dose.						
d. Values mentioned in brackets are the removal efficiencies obtained by control run of 44 mg NaOCl/l dose.						

The highest removal efficiency achieved by 0.49 mg Fe (VI)/l dose produced by FeSO<sub>4</sub>.7H<sub>2</sub>O can be justified, as the pure iron source was used for the synthesis of ferrate (VI). The dose of 0.1mg Fe (VI)/l synthesized from digested PS filtrate performed almost similar to the dose of 0.49 mg Fe (VI)/l generated from FeSO<sub>4</sub>. 7H<sub>2</sub>O. It is hard to speculate the exact cause for this effect. One of the reasons can be the oxidation of various metals other than iron present in digested PS filtrate by sodium hypochlorite which further acted as a coagulant or oxidant in parallel with Fe (VI) thus providing better removal efficiency. The removal efficiencies achieved by the ferrate (VI) synthesized from digested sludge filtrate were better than those obtained from the ferrate (VI) synthesized from digested sludge. This indicates that the filtration of sludge caused

the changes in binding of metal thus increasing the availability of iron for oxidation. The TCOD, PCOD, SCOD, TSS, VSS and STN removal achieved by 0.1 mg Fe (VI)/l produced from digested PS filtrate were 40%, 27%, 82%, 50%, 294% and 180% respectively more, than the removal achieved by 208 mg/l dose of NaOCl. The removal efficiencies of TCOD, PCOD, SCOD, TSS, VSS and STN attained just by settling (no chemical addition) were 29%, 34%, 19%, 25%, 33% and 3% respectively. Table 4 data shows that the removal efficiencies achieved by Fe (VI) generated from digested PS and digested TWAS were inferior to the efficiencies achieved by control NaOCl dose. This infers that, practically we cannot use digested PS and digested TWAS for generation of Fe (VI).

In order to check the coagulation and oxidation effect of Fe (VI), the treated samples obtained after jar test were filtered through 0.45  $\mu\text{m}$  and 1.2  $\mu\text{m}$  syringe filters and were tested for COD. The difference between the results obtained was considered as coagulation effect since this fraction represents the colloidal matter. Table 3.5 represents the %COD removal attributed to coagulation achieved by ferrate (VI) synthesized from various sources. Overall coagulation contributed 42%, 53%, 39%, 48% and 32% of the COD removed by the 0.1 mg Fe (VI)/l, 0.72 mg Fe (VI)/l, 0.27 mg Fe (VI)/l, 0.09 mg Fe (VI)/l and 0.49 mg Fe (VI)/l doses synthesized by digested PS filtrate, digested PS, digested TWAS, digested TWAS filtrate and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  respectively.

Table 3.5: Contribution of the coagulation effect of Ferrate (VI) to COD removal

<b>Ferrate synthesis Source</b>	<b>Dose (mg Fe (VI)/l)</b>	<b>Coagulation (%)</b>
<b>Digested PS Filtrate</b>	0.1	42
<b>Digested PS</b>	0.72	53
<b>Digested TWAS Filtrate</b>	0.09	39
<b>Digested TWAS</b>	0.27	48
<b>FeSO<sub>4</sub>.7H<sub>2</sub>O</b>	0.49	32

As treatment of CSO ferrate (VI) synthesized by digested primary filtrate source demonstrated the best results, optimization of dose experiments were performed using jar tests at neutral pH and 0.1 mg Fe (VI)/l, 0.2 mg Fe (VI)/l, 0.3 mg Fe (VI)/l, 0.4 mg Fe (VI)/l and 0.5 mg Fe (VI)/l doses. The removal efficiencies of various water quality parameters for the range of Fe (VI) doses for the treatment of CSO are presented in Figure 3.7. The optimum dose was 0.1 mg Fe (VI)/l, which removed TCOD, SCOD, TSS, VSS, TP and TN by 60%, 62%, 63%, 67%, 30% and 25% respectively. The removal efficiency of TN and TP increased with increase in Fe (VI) dose.

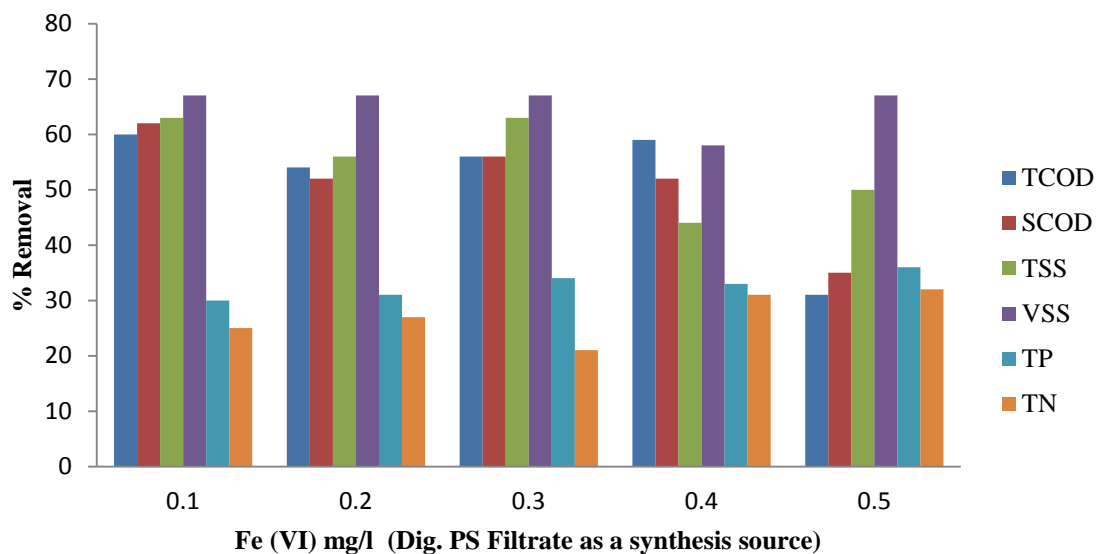


Figure 3.7: Treatment efficiency of different doses of Fe (VI) synthesized from digested PS filtrate.

### *Effluent guidelines*

The Ontario Ministry of Environment (MOE) law sets up different standards for different sewage treatment plants. The US EPA sets bypass treatment standards on case by case. The comparison between secondary treatment effluent criteria (USEPA and Ontario MOE) and the removal of water characteristics achieved by 0.49 mg Fe (VI)/l, 0.1 mg Fe (VI)/l, 0.09 mg Fe (VI)/l dose synthesized from  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , digested PS filtrate, digested TWAS filtrate respectively, are mentioned in Table 3.6. According to Ministry of Environment (MOE) regulations for bypass treatment mentioned in procedure F-5-5, the removal efficiency of five day biochemical oxygen demand ( $\text{BOD}_5$ ) and total suspended solids (TSS) should be 30 % and 50 % respectively. According to the US EPA, CSO related bypass flows must receive primary clarification, solids and floatables removal and disinfection.

Table 3.6: Comparison between the Secondary Treatment Effluent Criteria and the removal of water characteristics achieved by Fe (VI) synthesized from different iron sources (Metcalf and Eddy, 2003)

Characteristic of Discharge	Synthesized Ferrate (VI) Source			Ontario (Annual average Effluent guidelines)	United States
	FeSO <sub>4</sub> ·7H <sub>2</sub> O <sup>a</sup> (Dose: 0.49 mg/l)	Dig. PS Filtrate <sup>a</sup> (Dose: 0.1 mg/l)	Dig. TWAS Filtrate <sup>a</sup> (Dose: 0.09 mg/l)		
<b>5 day BOD<sub>5</sub></b>	23.9 ± 0.1 mg/l	25.3 ± 2.1 mg/l	36.6 ± 3.5 mg/l	25-30 mg/l	30 mg/l (30 day average) 45 mg/l (7 day average)
<b>TSS</b>	20 ± 10 mg/l	30 ± 10 mg/l	40 ± 10 mg/l	25-40 mg/l	30 mg/l (30 day average) 45 mg/l (7 day average)
<b>pH</b>	7 ± 0.2	7.2 ± 0.1	7.2 ± 0.2	----	within range of 6 to 9
<b>Removal</b>	61-63 % BOD <sub>5</sub> and 57-86% TSS	60-62 % BOD <sub>5</sub> and 43-71% TSS	41-47 % BOD <sub>5</sub> and 29-57 % TSS	----	85% BOD <sub>5</sub> and TSS
a. ± Average SD (Two runs)					

The treatment of CSO by Ferrate (VI) synthesized using FeSO<sub>4</sub>·7H<sub>2</sub>O and digested PS filtrate meets the Ontario MOE and US EPA, secondary effluent criteria and the bypass treatment removal guidelines. However CSO treatment using Fe (VI) generated from digested TWAS fails to meet these criteria. The low dose, short contact time, attainment of secondary effluent characteristics, no start up time, and the removal of soluble

organics, nitrogen and phosphorous are the most salient advantages of ferrate (VI) treatment.

### 3.4 Conclusions

Treatment of CSOs was performed using ferrate (VI) and the following conclusions can be drawn:

- At the optimum commercial Fe (VI) dose of 0.24 mg/l; TCOD, SCOD, TBOD<sub>5</sub>, SBOD<sub>5</sub>, TSS, VSS, TP, TN and STN removal efficiencies of 71%, 75%, 69%, 68%, 72%, 83%, 64%, 38% and 36% respectively were achieved.
- Contact time of ferrate (VI) was observed to be 15 min; in case of continuous mixing, the contact time of Fe (VI) can be expected to be in between 5-15 min.
- Soluble organics were removed and considerable reduction in total and soluble Nitrogen was achieved.

Synthesis of ferrate (VI) from PS and TWAS, using wet oxidation synthesis technique was carried out and the ferrate (VI) produced was used for the treatment of CSO with following conclusions:

- At Fe (VI) dose of 0.1 mg/l produced using digested PS filtrate, TCOD, SCOD, TSS, VSS, TP and TN removal efficiencies of 60%, 62%, 63%, 67%, 30% and 25% respectively.

- Treatment efficiencies achieved by 0.1 mg Fe (VI)/l synthesized from digested PS filtrate were comparable to those obtained from 0.49 mg Fe (VI)/l produced from  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (a pure iron source).
- Low removal efficiencies were observed for the treatment of CSO by ferrate (VI) produced from digested TWAS filtrate.
- High removal efficiency achieved by Fe (VI) prepared from filtered digested PS infers that Fe (VI) can be generated from filtered dewatering filtrate and may be more efficient and cost effective.
- Water quality characteristics of treated CSO obtained were comparable to the secondary effluent water characteristics proposed by Ontario MOE and USEPA.

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## Chapter 4

### Conclusions and Recommendations

#### 4.1 Conclusions

- Ferrate (VI) proved to be an efficient chemical for treatment of CSOs. Very low dose of commercial Fe (VI) i.e. 0.24 mg/l, achieved 75%, 68%, 64%, 38% and 36% removal of SCOD, SBOD<sub>5</sub>, TP, TN and STN respectively within a contact time of only 15 min.
- Ferrate (VI) was successfully synthesized from filtered digested biosolids, an in-situ iron source as well as from FeSO<sub>4</sub>·7H<sub>2</sub>O, a pure iron source.
- Ferrate (VI) synthesized from digested PS filtrate was found out to be more effective than the Fe (VI) generated from digested TWAS filtrate, digested PS, digested TWAS.
- At the optimum, filtered digested PS synthesized Fe (VI) dose of 0.1 mg/l; SCOD, TP and TN removal efficiencies of 62%, 30% and 25% respectively were achieved.
- Treatment efficiencies achieved by Fe (VI) synthesized from dig PS sludge were comparable to those achieved by Fe (VI) synthesized from FeSO<sub>4</sub>·7H<sub>2</sub>O.
- The removal efficiencies achieved by Fe (VI) produced from digested PS and digested TWAS were inferior to those achieved by respective control NaOCl dose. Thus, practically, digested PS and digested TWAS cannot be used for generation of Fe (VI).

- The treated CSOs water quality characteristics achieved by Fe (VI) treatment were comparable to the secondary effluent water characteristics proposed by Ontario MOE and USEPA.

The low dose, short contact time, attainment of secondary effluent characteristics, no start up time, and the removal of soluble organics, nitrogen and phosphorous are the most salient advantages of ferrate (VI) treatment.

#### **4.2 Recommendations**

Based on results presented, few issues need to be addressed. Following is the list of the future work that can be done to address these issues:

- The contact time of 15 minutes was calculated, which includes 5 minutes of mixing and 10 minutes of settling. With reference to figure 3.4, it can be pointed out that, in case of continuous mixing contact time of Ferrate (VI) can be expected to be less than 15 min. Thus, detailed kinetic study of Fe (VI) treatment needs to be done in order to find out the precise contact time of Fe (VI).
- Evaluation of Fe (VI) performance on the continuous CSO system, by setting up the pilot scale CSO treatment plant should be done in order to calculate the real time optimum Fe (VI) dose.
- The Fe (VI) synthesized from digested filtrate achieved high removal efficiency. This points out that, Fe (VI) can be generated from filtered dewatering filtrate and can be more efficient and cost effective. Thus, Fe (VI) synthesis should be tried using various in-situ iron sources.

- Treatment efficiencies achieved by 0.1 mg Fe (VI)/l synthesized from digested PS filtrate were comparable to those obtained from 0.49 mg Fe (VI)/l produced from  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (a pure iron source). Thus, characterization of the filtered biosolids synthesized Fe (VI) sample should be done in order to check the various compounds produced simultaneously with the Fe (VI), which can further act as an oxidant or coagulant.
- Impact of pH and oxidizing agents on the synthesis of ferrate (VI) should be studied in order to get pure and stable ferrate (VI).
- Modeling of the ferrate (VI) synthesis and treatment technology should be done.
- Cost analysis of Fe (VI) treatment method and its comparison with the established physical chemical treatment process should be carried out.

All these can lead to a more exhaustive study about the CSOs treatment using Fe (VI).

## Appendices

### Appendix A: Applicability of Fe (VI) for CSO treatment (Raw Data)

Table A1: Run 1 (Jar Test)

<b>Fe(VI) Dose(mg/l)</b>	<b>W1</b>	<b>W2</b>	<b>W3</b>	<b>W2- W1</b>	<b>W2- W3</b>	<b>Volume (ml)</b>	<b>TSS (mg/l)</b>	<b>VSS (mg/l)</b>
RWW	1.4466	1.4532	1.448	0.0066	0.0052	20	<b>330</b>	<b>260</b>
CSO	1.4417	1.444	1.4421	0.0023	0.0019	20	<b>115</b>	<b>95</b>
0	1.4524	1.454	1.4526	0.0016	0.0014	20	<b>80</b>	<b>70</b>
0.3	1.4439	1.4444	1.444	0.0005	0.0004	20	<b>25</b>	<b>20</b>
0.6	1.4471	1.4476	1.4474	0.0005	0.0002	20	<b>25</b>	<b>10</b>
1.5	1.45	1.4509	1.4507	0.0009	0.0002	20	<b>45</b>	<b>10</b>
15	1.4449	1.4458	1.4453	0.0009	0.0005	20	<b>45</b>	<b>25</b>
30	1.4508	1.4517	1.4513	0.0009	0.0004	20	<b>45</b>	<b>20</b>

<b>Fe (VI) Dose (mg/l)</b>		<b>TCOD (mg/l)</b>	<b>SCOD (mg/l)</b>	<b>TSS (mg/l)</b>	<b>VSS (mg/l)</b>
	RWW	350	168	330	260
	CSO	114	58	115	95
<b>0</b>	Jar Test 1	81	46	80	70
<b>0.3</b>	Jar Test 2	14	14	25	20
<b>0.6</b>	Jar Test 3	25	19	25	10
<b>1.5</b>	Jar Test 4	33	41	45	10
<b>15</b>	Jar Test 5	37	47	45	25
<b>30</b>	Jar Test 6	57	41	45	20

<b>Fe (VI) Dose (mg/l)</b>	<b>% Removal</b>			
	<b>TCOD</b>	<b>SCOD</b>	<b>TSS</b>	<b>VSS</b>
<b>0</b>	29	21	30	26
<b>0.3</b>	88	76	78	79
<b>0.6</b>	78	68	78	89
<b>1.5</b>	71	30	61	89
<b>15</b>	68	19	61	74
<b>30</b>	50	29	61	79



Table A2: Run 2 (Jar Test)

<b>Fe (VI) Dose (mg/l)</b>	<b>TCOD (mg/l)</b>	<b>SCOD (mg/l)</b>	<b>TSS (mg/l)</b>	<b>VSS (mg/l)</b>
	114	58	115	95
<b>0</b>	81	48	80	70
<b>0.3</b>	29	17	35	20
<b>0.6</b>	29	19	30	0
<b>1.5</b>	36	42	35	20
<b>15</b>	48	50	70	15
<b>30</b>	40	44	50	15

<b>Fe (VI) Dose (mg/l)</b>	<b>% Removal</b>			
	<b>TCOD</b>	<b>SCOD</b>	<b>TSS</b>	<b>VSS</b>
<b>0</b>	29	17	30	26
<b>0.3</b>	75	71	70	79
<b>0.6</b>	75	68	74	100
<b>1.5</b>	68	27	70	79
<b>15</b>	58	14	39	84
<b>30</b>	65	25	57	84

Table A3: Run 3 (Jar Test)

<b>Fe (VI) Dose (mg/l)</b>		<b>TCOD (mg/l)</b>	<b>SCOD (mg/l)</b>	<b>TSS (mg/l)</b>	<b>VSS (mg/l)</b>
	CSO	114	58	115	95
<b>0</b>	Jar Test 1	88	47	80	70
<b>0.3</b>	Jar Test 2	16	17	45	35
<b>0.6</b>	Jar Test 3	25	15	20	5
<b>1.5</b>	Jar Test 4	47	51	40	15
<b>15</b>	Jar Test 5	46	44	65	20
<b>30</b>	Jar Test 6	40	25	55	10

Fe (VI) Dose (mg/l)	% Removal			
	TCOD	SCOD	TSS	VSS
0	23	19	30	26
0.3	86	71	61	63
0.6	78	74	83	95
1.5	59	12	65	84
15	60	24	43	79
30	65	57	52	89

Table A4: Data used for Figure 3.1 (Average of all runs)

Fe (VI) Dose (mg/l)		TCOD (mg/l)	SCOD (mg/l)	TSS (mg/l)	VSS (mg/l)
	CSO	114	58	115	95
0	Jar Test 1	83	47	80	70
0.3	Jar Test 2	19	16	35	25
0.6	Jar Test 3	26	17	25	5
1.5	Jar Test 4	39	45	40	15
15	Jar Test 5	43	47	60	20
30	Jar Test 6	46	37	50	15

Fe (VI) Dose (mg/l)	% Removal			
	TCOD	SCOD	TSS	VSS
0	27	19	30	26
0.3	83	73	70	74
0.6	77	70	78	95
1.5	66	23	65	84
15	62	19	48	79
30	60	37	57	84

## Appendix B: Optimization of Fe (VI) dose (Data used for Figure 3.2)

Table B1: pH 6

Fe (VI)Dose (mg/l)	TSS (mg/l)	VSS (mg/l)	TCOD (mg/l)	SCOD (mg/l)	TN (mg/l)	TP(mg/l)
RWW	210	190	292	132	29	6.4
CSO	70	60	90	48	8.9	2.5
0	50	40	64	36	8.7	2.2
0.12	40	30	56	30	7.9	1.8
0.24	40	30	51	27	7.5	1.6
0.36	30	20	54	30	7.7	1.8
0.48	30	30	47	27	7.6	1.7
0.6	30	0	43	24	7	1.5

Fe (VI)Dose (mg/l)	% Removal					
	TSS	VSS	TCOD	SCOD	TN	TP
0	29	33	29	25	2	12
0.12	43	50	38	38	11	28
0.24	43	50	43	44	16	36
0.36	57	67	40	38	13	28
0.48	57	50	48	44	15	32
0.6	57	100	52	25	21	40

Table B2: pH 7

Fe (VI)Dose (mg/l)	TSS (mg/l)	VSS (mg/l)	TCOD (mg/l)	SCOD (mg/l)	TN (mg/l)	TP(mg/l)
CSO	70	60	90	48	8.9	2.5
0	50	50	67	33	8.7	2.3
0.12	40	20	41	24	6.4	1.7
0.24	30	20	28	15	5.5	1.2
0.36	30	30	32	18	6.1	1.7
0.48	30	10	34	27	5.9	1.6
0.6	20	10	32	18	5.6	1.3

Fe (VI)Dose (mg/l)	% Removal					
	TSS	VSS	TCOD	SCOD	TN	TP
0	29	16	26	31	2	8
0.12	43	67	54	50	28	32
0.24	57	67	69	69	38	52
0.36	57	50	64	63	31	32
0.48	57	83	62	44	34	36
0.6	71	83	64	63	37	48

Table B3: pH 8

Fe (VI)Dose (mg/l)	TSS (mg/l)	VSS (mg/l)	TCOD (mg/l)	SCOD (mg/l)	TN (mg/l)	TP(mg/l)
CSO	70	60	90	48	8.9	2.5
0	50	40	62	37	8.5	2.3
0.12	40	20	43	30	7.1	1.7
0.24	20	20	28	18	6.1	1.1
0.36	30	10	26	12	5.7	1.6
0.48	30	10	37	24	5.9	1.6
0.6	20	0	35	12	5.4	1.3

Fe (VI)Dose (mg/l)	% Removal					
	TSS	VSS	TCOD	SCOD	TN	TP
0	29	33	31	23	4	8
0.12	43	67	52	38	20	32
0.24	71	67	69	63	31	56
0.36	57	83	71	62.5	36	36
0.48	57	83	59	25	34	36
0.6	71	100	61	62.5	39	48

Table B4: pH 9

<b>Fe (VI)Dose (mg/l)</b>	<b>TSS (mg/l)</b>	<b>VSS (mg/l)</b>	<b>TCOD (mg/l)</b>	<b>SCOD (mg/l)</b>	<b>TN (mg/l)</b>	<b>TP(mg/l)</b>
CSO	70	60	90	48	8.9	2.5
0	50	40	62	39	8.8	2.2
0.12	30	20	17	9	6.4	1.2
0.24	10	0	19	15	5.2	1
0.36	20	20	22	15	6.1	0.8
0.48	20	10	26	12	5.9	0.8
0.6	20	10	19	15	5.4	0.9

<b>Fe (VI)Dose (mg/l)</b>	<b>% Removal</b>					
	<b>TSS</b>	<b>VSS</b>	<b>TCOD</b>	<b>SCOD</b>	<b>TN</b>	<b>TP</b>
0	29	33	31	19	1	12
0.12	57	67	81	81	28	52
0.24	86	100	79	69	41	60
0.36	71	67	76	69	31	68
0.48	71	83	71	75	34	68
0.6	71	83	79	69	39	64

**Appendix C: Kinetics (Data used for Figure 3.4)**

Table C1 (Neutral pH; Dose: 0.24 mg Fe (VI)/l)

<b>Time (min)</b>	<b>TSS (mg/l)</b>	<b>VSS (mg/l)</b>	<b>TCOD (mg/l)</b>	<b>SCOD (mg/l)</b>	<b>PCOD (mg/l)</b>	<b>TBOD (mg/l)</b>	<b>SBOD (mg/l)</b>	<b>PBOD (mg/l)</b>
RWW	190	170	284	90	194	163.6	50	113.6
CSO	70	60	84	32	52	50.6	17.9	32.7
1	60	60	80	28	52	50.1	17.4	32.7
2	50	50	74	26	48	44.4	15.2	29.2
3	40	40	54	22	32	32.6	14.1	18.5
4	50	30	46	22	24	29.7	14.5	15.2
5	30	40	44	16	28	26.9	10.2	16.7
10	40	20	30	10	20	19.3	6.9	12.4
15	30	20	26	8	18	15.4	5.3	10.1
20	20	20	26	8	18	16.2	4.9	11.3
40	30	20	24	8	16	15.7	5.5	10.2

<b>Time (min)</b>	<b>NH4 (mg/l)</b>	<b>TN (mg/l)</b>	<b>STN (mg/l)</b>	<b>org N (mg/l)</b>	<b>TP (mg/l)</b>	<b>PO43- (mg/l)</b>
RWW	13.8	26	18.7	4.9	6	3.4
CSO	4.9	9	7.4	2.5	2.5	1.1
1	4.6	8.6	7.2	2.5	2.4	1
2	4.6	8.3	6.7	2.1	2.4	1.1
3	4.5	8	6.6	1.8	2.3	1
4	4.6	7.4	6.3	1.8	2.1	1.1
5	4.3	7.1	6	1.5	1.7	1
10	4.4	6.6	5.8	1.1	1.3	0.9
15	4.4	5.9	5	0.8	1.1	0.8
20	4.3	5.9	5	0.7	1.1	0.9
40	4.3	5.9	4.9	0.6	1	0.8

Time (min)	% Removal							
	TCOD	SCOD	TBOD	SBOD	TSS	VSS	PCOD	PBOD
1	5	13	1	3	14	0	0	0
2	12	19	12	15	26	17	8	11
3	36	31	36	21	43	33	38	43
4	45	31	41	19	29	50	54	54
5	48	50	47	43	57	33	46	49
10	64	69	62	61	43	67	62	62
15	69	75	69	70	57	67	65	69
20	69	75	68	73	71	67	65	65
40	71	75	69	69	57	67	69	69

Time (min)	% Removal					
	NH4	TN	STN	org N	TP	PO43-
1	6	4	3	0	4	9
2	6	8	9	16	4	0
3	8	11	11	28	8	9
4	6	18	15	28	16	0
5	12	21	19	40	32	9
10	10	26	22	56	48	18
15	10	34	32	68	56	27
20	12	34	32	72	56	18
40	12	34	34	76	60	27

**Appendix D: Performance of Fe (VI) synthesized from various doses (Data used for Figure 3.6)**

	Ferrate Source	FeSO <sub>4</sub> .7H <sub>2</sub> O	Dig PS	Dig PS filt	Dig TWAS	Dig TWAS Filt
	<b>Dose (mg/l)</b>	0.49	0.72	0.1	0.27	0.09
TCOD (mg/l)	Influent TCOD	98	122	106	112	104
	Effluent TCOD	36	84	42	74	60
SCOD (mg/l)	Influent SCOD	36	44	40	40	38
	Effluent SCOD	13	30	16	30	23
TSS (mg/l)	Influent TSS	70	100	70	90	70
	Effluent TSS	20	70	30	60	40
VSS (mg/l)	Influent VSS	60	80	60	80	60
	Effluent VSS	10	60	20	50	30
TBOD <sub>5</sub> (mg/l)	Influent TBOD <sub>5</sub>	63	81.2	64.9	65.2	65.1
	Effluent SBOD <sub>5</sub>	23.9	50.7	25.3	51.6	36.6
SBOD <sub>5</sub> (mg/l)	Influent TBOD <sub>5</sub>	21.6	29.9	24.2	26.3	24.1
	Effluent SBOD <sub>5</sub>	8.3	21.7	8.1	18.6	13.2

**Appendix E: Performance of NaOCl doses (Control) (Data used for Table 3.4)**

	Dose (mg/l)	TCOD (mg/l)	SCOD (mg/l)	TSS (mg/l)	VSS (mg/l)	STN (mg/l)	NH <sub>4</sub> (mg/l)	PCOD (mg/l)
CSO		98	36	80	60	7.3	5	62
Blank		70	29	60	40	7.1	5	41
NaOCl (44)	44	59	25	60	40	6.8	4.9	34
NaOCl (208)	208	56	24	50	50	6.6	4.8	32
NaOCl (229)	229	55	23	60	40	6.3	4.8	32
NaOCl (247)	247	57	26	50	40	6.3	4.8	31



**Appendix F: Optimization of Fe (VI) synthesized from digested PS filtrate (Data used for Figure 3.7)**

Dose (mg/l)		TCOD (mg/l)	SCOD (mg/l)	TSS (mg/l)	VSS (mg/l)	TP (mg/l)	TN (mg/l)
0.1	Initial	110	52	80	60	3	10
	Final	44	20	30	20	2.1	7.5
0.2	Initial	113	54	80	60	3.2	10
	Final	52	26	35	20	2.2	7.3
0.3	Initial	119	55	80	60	3.2	11
	Final	52	24	30	20	2.1	8.7
0.4	Initial	122	58	80	60	3	10
	Final	50	28	45	25	2	6.9
0.5	Initial	130	65	80	60	3.3	11
	Final	90	42	40	20	2.1	7.5

Dose (mg/l)	% Removal					
	TCOD	SCOD	TSS	VSS	TP	TN
0.1	60	62	63	67	30	25
0.2	54	52	56	67	31	27
0.3	56	56	63	67	34	21
0.4	59	52	44	58	33	31
0.5	31	35	50	67	36	32

## Curriculum Vitae

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