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Chemically enhanced primary treatment processes for wastewater resource redirection and its impact on downstream processes

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Graduate Program in Civil and Environmental Engineering
A thesis submitted in partial fulfillment of the requirements for the degree in Master of Science
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Abstract

There is a recent focus within the global wastewater industry on the steps being taken by treatment facilities to move towards net zero, or in some cases, energy positive operation. As part of maximizing energy recovery from the incoming wastewater, there has been increased attention upon the energy contained in the wastewater, and maximizing the redirection of more carbon captured through the primary treatment process rather than conventional removal through carbon oxidation. The chemically enhanced primary treatment (CEPT) process is a promising method for carbon redirection and improving the performance and efficiency of wastewater treatment processes. This research was conducted to optimize the CEPT performance regarding simultaneous carbon and nutrients redirection in both bench-scale and full-scale operations. In order to improve the CEPT process, the performance of ferric chloride and seven types of polymers were evaluated by jar tests. Results indicated that 15 mg/L ferric chloride and 0.5 mg/L poly aluminum chloride (PACL) showed the best performance which was determined by a simplified comparison matrix regarding removal efficiencies. The best coagulant and flocculant combination determined by this study achieved total chemical oxygen demand (tCOD), soluble chemical oxygen demand (sCOD), total suspended solids (TSS) and total phosphorus (TP) removal efficiencies of 76%, 58%, 89%, and 84%, respectively, in a full-scale primary clarifier operation. Furthermore, the relationship between influent characteristics and removal rates under varying operating conditions were investigated. The impact of CEPT on the downstream liquid and solid train processes were also investigated. The study on the

impact of CEPT on the downstream liquid train processes showed that PACl addition has improved the sludge volume index (SVI) in the activated sludge process, and lowered TSS and TP concentrations in secondary clarifier effluent. Furthermore, the addition of PACl did not affect the BOD₅ and the ammonia concentration of the effluent from the secondary clarifier. However, the sludge produced from CEPT dosed with ferric chloride and PACl (test clarifier sludge) showed a lower methane production rate compared to the sludge produced from CEPT dosed with ferric chloride (control clarifier sludge).

Keywords

Chemically enhanced primary treatment (CEPT), carbon redirection, polymer, municipal wastewater, optimization, phosphorus removal, bio-methane potential (BMP), downstream process

Co-Authorship Statement

Chapter three is submitted for publication under the co-authorship of Tianchen Dong

Wudneh Ayele Shewa, Kyle Murray and Martha Dagneu

Chapter four will be submitted for publication under the co-authorship of Tianchen

Dong, Wudneh Ayele Shewa, Wenjuan Mu and Martha Dagneu

Acknowledgements

First and foremost, I would like to express my immense gratitude to the most supportive person in my school life, my supervisor Dr. Martha Dagnev for her support, guidance, advice, understanding, and belief in me. It is she who motivated me and enlightened me to think critically and reach higher level every time. This research cannot be completed without her guidance and help.

Second, I would like to thank Dr. Wudneh Ayele Shewa in my group for keeping helping me in writing and learning, and he had spent a lot of his time with patience to teach me and help me in my project, which is highly appreciated.

Next, I would like to sincerely thank Randy Robinson, Kyle Murray and all the other fabulous people in the City of London that went out of their way to help me in every way possible. The hospitality and generosity that I received were invaluable.

Additionally, I would like to thank all of the people at Western University that made my stay here enjoyable. To my group mates: Shuang Pan, Lin Sun, Wenjian Mu and Panagiota Stamatopoulou, the time we have spent in the lab is my unforgettable memory. To my friends at the gym, the time that I got to spend away from the lab with you guys, definitely help to keep me real, energetic and work in social life.

Last, but not least, I would like to extend my gratitude towards to the most important and influential people in my life, my parents, Lin Dong and Yandong Hao, for their love, encouragement and wisdom to help me accomplish my degree.

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List of Abbreviations and Symbol

AD	anaerobic digestion
Anammox	anaerobic ammonia oxidation
BMP	bio-methane potential
BOD	biochemical oxygen demand
BOD5	5-day Biochemical oxygen demand (mg/L)
CEPT	chemically enhanced primary treatment
CO ₂	carbon dioxide
COD	chemical oxygen demand (mg/L)
tCOD	total chemical oxygen demand (mg/L)
sCOD	soluble chemical oxygen demand (mg/L)
CST	capillary suction time
ECP	extracellular polymer
F/M	food/microorganism
MLSS	mixed liquid suspended solids
SS	suspended solids (mg/L)
SVI	sludge volume index
TP	total phosphorus (mg/L)
TS	total solids (mg/L)
TSS	total suspended solids (mg/L)
O ₂	Oxygen
O & M	Operation and maintenance
PACl	poly aluminum chloride
PAM	Polyacrylamide
VFA	volatile fatty acid (mg/L)
d	diameter of particle
g	acceleration due to gravity
V _c	terminal Velocity of Particle
ρ _s	density of the particle
ρ	density of fluid
μ	dynamic viscosity

Chapter 1

1. Introduction

1.1 Rationale

Energy consumption by wastewater treatment plants has been increased as plants are using more advanced treatment processes to meet the increased effluent quality requirements and in response to increased flows. To help solve these problems, domestic wastewater has been considered more as a resource of energy, water and nutrients than as a waste (Asano et al., 2007). The goal of this research was motivated by increased attention on the potential energy contained in the raw wastewater. The most direct, commonly used and most useful source of energy in wastewater is the chemical energy of its organic fraction as measured by the total chemical oxygen demand (tCOD) which indicates the amount of oxygen (O_2) required to oxidize the organic material to carbon dioxide (CO_2) and water (H_2O) (McCarty et al., 2011). One kg of tCOD in the raw wastewater can produce around 12-15 MJ of chemical energy (Eddy et al., 2013). Thus redirecting these carbon sources, from the energy consuming liquid train process to the energy generating solid train processes, is beneficial. Although some carbon redirection technologies have existed for a long time, from physico-chemical to biological processes (Jimenez, 2017), limited research has been done on optimizing the carbon redirection processes.

Chemically enhanced primary treatment (CEPT) is one of the existing treatment methods for carbon redirection. CEPT is a process in which the chemicals (generally metal salts or polymers) are added in the primary clarifier. The added chemicals can conglomerate the suspended solids particles through the processes of coagulation and flocculation (Zhou et al., 2004). The formed flocs via the mechanism of coagulation and flocculation have high sedimentation velocity resulting in the improvement of the treatment performance parameters, such as total suspended solids (TSS), tCOD, soluble chemical oxygen demand (sCOD) and total phosphorus (TP) (Sarparastzadeh et al., 2007). The CEPT process displays advantages in reducing energy requirements, and the removal of biological and toxic chemical pollutants (Haydar and Aziz, 2009; Wang 2004; Johnson et al., 2008). In addition, the CEPT process can be easily applied in the existing overloaded treatment plants and can also be used in the wet weather conditions to improve their efficiency in removing suspended solids (Chagnon and Herleman, 2002; Haydar and Aziz, 2009).

Despite these advantages, studies addressing the potential and optimization of CEPT technology for simultaneous carbon redirection, wet weather flow and phosphorus removal are limited. Most studies so far have focused on using CEPT to remove more TSS and phosphorus. Although the concept of using CEPT for carbon redirection raised researchers' attention, almost no studies have focused on significant carbon removal by adding various coagulants and flocculants, and few have further investigated the sludge biodegradability when substantial carbon and nutrients are concentrated chemically into the sludge. Besides, the impact of substantial carbon removal during the primary treatment on the downstream carbon oxidation and nitrification liquid train process is still unknown. Therefore, these research gaps will be addressed in this thesis.

1.2 Objectives

This research was conducted to: (1) optimize the CEPT technology in simultaneous carbon redirection and phosphorus redirection, and (2) characterize its impact on the downstream liquid and solid train processes. Firstly, the performance of a ferric coagulant and flocculant (polymer) combination was examined through jar testing to determine the best combination and dosage. Then, the selected chemicals were applied in the full-scale CEPT process to demonstrate their performance regarding TSS, tCOD, sCOD, and TP removal efficiencies. Additionally, the influence of various influent characteristics on the removal rates based on a full-scale CEPT operation was investigated. Secondly, the methane production from CEPT sludge was evaluated by anaerobic digestion and Bio-methane potential (BMP) tests in order to characterize the effect of the addition of polymer on the methane generation. Finally, the downstream liquid train process, including the aeration process and the final clarifier, was assessed to check the influence of CEPT on TSS, 5-day biochemical oxygen demand (BOD₅), TP and ammonia removal efficiencies and sludge volume index (SVI) of the activated sludge.

1.3 Thesis Format and Organization

This thesis is written in the integrated-article format according to the specifications provided by the School of Graduate and Postdoctoral Studies at Western University.

Chapter 1 presents an overview of the thesis and the rationale behind evaluating the CEPT technology as a promising method for carbon redirection. It briefly introduces the background of this study and states specific research objectives. Chapter 2 provides a comprehensive literature review of the background, principles and applications of the

CEPT process. In addition, the latest research conducted on the CEPT process is summarized in this chapter. Furthermore, characteristics of CEPT sludge and its impact on anaerobic digestion are described. Finally, the research gap in CEPT is highlighted. Chapter 3 is a research article entitled “Optimizing CEPT processes for simultaneous carbon redirection and phosphorus removal”. The objective of this work was to select the best combination of coagulant and flocculant by lab-scale jar tests and then to apply this combination to the full-scale operation. Further, the influence of influent characteristics on the removal rates is articulated. Chapter 4 further evaluates the impact of CEPT on the downstream process including the anaerobic digestion, aeration process, and final clarifier. Finally, Chapter 5 summarizes the main findings of this study and makes several recommendations for future research.

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Wang, D. J. (2004). Experimental study and discussion on coagulation-sedimentation process in strengthen treatment of municipal wastewater. *Environ. Prot. Sci*, **30**: 36-38.

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Chapter 2

2. Literature Review

2.1 Carbon redirection background

The wastewater industry has been undergoing significant transformation, changing from energy-consuming treatment to energy-generating treatment, to achieve energy neutral and/or positive operations. Currently, the wastewater industry is focusing more on how to manage and extract energy contained in organic matters from the wastewater rather than merely treating wastewater. The organic carbon is the most valuable component in wastewater to generate energy. Therefore, the control and redirection of this organic matter for recovery and energy production from the wastewater can be the key for sustainable and energy-friendly wastewater treatment.

The potential energy available in the raw wastewater usually exceeds the energy demand of wastewater treatment processes (Metcalf and Eddy, 2014). There are four main dominant forms of wastewater energy: chemical, thermal, kinetic and potential energy. However, the most direct, commonly utilized and useful energy source in wastewater is the chemical energy of its organic portion which is often represented by chemical oxygen demand (COD), indicating the amount of oxygen (O_2) required to oxidize the organic material to carbon dioxide (CO_2) and water (H_2O). Furthermore, 1 kg COD in the raw wastewater influent is identified as having 12-15 MJ chemical energy content (Metcalf and Eddy, 2014). The biodegradable fraction of organic matter in wastewater can be divided into two components which are readily and slowly biodegradable organics. Since most of the raw wastewater consists of slowly biodegradable COD, mainly in the form of colloidal and particle COD portions, the main potential of energy recovery is to capture these colloids and particulate matter and

limit their oxidation. The slowly biodegradable organics are much easier to be captured compared to readily biodegradable organics which are biologically more unstable and more accessible to oxidize rapidly in biological processes.

Although carbon removal and redirection technologies have existed for decades, the current emphasis on low-energy operations has prompted the industry to reconsider its carbon management. These technologies, from physico-chemical to biological processes, maximize the capture of organic matter from mainstream processing and provide beneficial recycling and reusing strategies for low-energy, sustainable operations. One of the existing technologies for carbon redirection is chemically enhanced primary treatment (CEPT).

2.2 CEPT process background

2.2.1 CEPT History

The earliest practice of CEPT probably occurred as early as 1870 in England. It is also stated that CEPT was widely used in the late 1890s and early 1900s in the United States before the development of the biological treatment (Metcalf and Eddy, 2014). Moreover, it was pointed out that CEPT had a recurrence in the 1930s in the USA (Metcalf and Eddy, 2014). Over years chemicals used in CEPT were developing. A low dosage of chemical application is preferred, such as ferric chloride with a supplemental anionic polymer. This process was named as “the Dow Process for Phosphorus Removal.” The experiments using a lower dosage combination of metal salts with polymers were firstly conducted in bench-scale, and then the results of bench-scale were used in full-scale tests at Grayling and Lake Odessa, Michigan (Wukash, 1968, Dow Chemical Company, 1967a, and Dow Chemical Company, 1967b).

The results of the Dow process were also confirmed by the researches in Canada who conducted full-scale tests in Toronto, Windsor and Sarnia. (Heike et al., 1980). Alum was tested in treating wastewater in Tampa, Florida, and it showed 83% of SS and 44% of BOD removal (Wilson et al., 1975). Afterwards, additional research was focused on the performance evaluation of polymers.

2.2.1 CEPT Application

CEPT is a technology that has been promoted and advanced mainly through industrial and research areas in an effort to develop and improve an innovative and cost-friendly municipal wastewater treatment technology (Ho et al., 2008, Haydar & Aziz., 2009). The general mechanism behind the CEPT technology is to improve the rate and efficiency of the gravitational settling, which is accomplished by adding a relatively low dosage of metal salts, such as iron or aluminum salts, as a coagulant, sometimes combined with polymers .

In the past, CEPT was applied as a principal process and/or in conjunction with the activated carbon process for wastewater treatment. With the advent of the activated sludge process, the use of CEPT processes has declined in North America and are only used to (1) enhance plant performance during wet weather flow, or (2) to enhance phosphorus removal for plants with a strict phosphorus effluent limit. Under these circumstances, an upgrade of conventional treatment requires minimal investment associated with the installation of a dosing system to a conventional primary treatment (Figure 2-1).

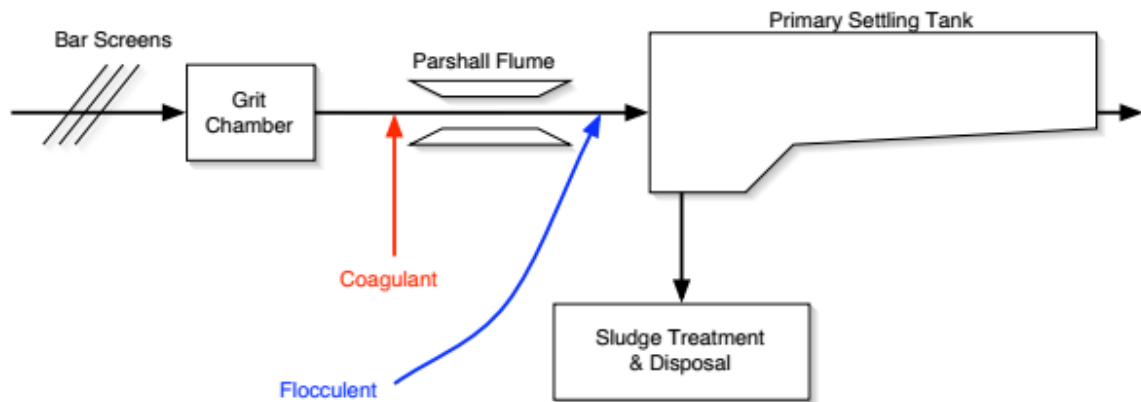


Figure 2-1: Schematic of conventional primary treatment and CEPT (Chagnon and Harleman, 2002).

Table 2-1 summarizes CEPT applications around the world. CEPT has begun to gain popularity in the developing countries and also developed countries in coastal cities such as San Diego and Hong Kong where new carbon removal regulations are in place. In this case, the CEPT process is being considered as a cost- effective and easily implemented method over conventional processes. In 1992, the National Research Council collected data from 100 plants comparing CEPT versus conventional primary plus secondary treatment processes (Table 2-2). Chagnon and Harleman (2002) performed capital and operation cost evaluation. (Table 2-3). These findings suggest that the CEPT option, while cheaper, had relatively lower performance. Hence in this study, the interest is not to use the CEPT as a standalone unit process, but, along with conventional processes, as a way of enhancing simultaneous carbon redirection and phosphorus and TSS removal.

Table 2-1: Selected CEPTs in the world

Plants name	City	Flow (m ³ /d)
Stonecutters Island Sewage Treatment Works	Hong Kong, China	1.7 million
Bailonggang Wastewater Treatment Plant	Shanghai, China	1.2 million
Hyperion Wastewater Treatment Plant	Los Angeles, USA	1.1 million
Gaobeidian Wastewater Treatment Plant	Beijing, China	1.0 million
Hunts point Wastewater Treatment Plant	New York, USA	0.8 million
Boda Wastewater Treatment Plant	Anyang, Korea	0.3 million
ETIG Wastewater Treatment Plant	Rio de Janeiro, Brazil	44000
Qingshan Lake Wastewater Treatment Plant	Huangshi, China	40000
Vaxuall Wastewater Treatment Plant	London, Canada	13530
Damanhour Wastewater Treatment Plant	Tanta, Egypt	12000

Table 2-2: Comparison of removal efficiency (National Research Council, 1992).

	TSS (%)	BOD (%)
Conventional primary + Biological Secondary Treatment	91	85
Chemically Enhanced Primary Treatment	85	57

Table 2-3: Comparison of treatment cost (Chagnon and Harleman, 2002)

	Construction Costs ¹ (US \$ M per m ³ /s)	O&M Costs ² (US \$ M per year per m ³ /s)
Primary Treatment (no disinfection)	1.5	0.2
CEPT & Disinfection	1.3	0.5
Primary & Activated sludge & Disinfection	5.0	1.0

1. Construction costs are based on the maximum plant flow capacity.
2. Operation and maintenance costs are based on the average yearly flow (assumed to be 1/2 the max. plant capacity).

2.3. Coagulation and Flocculation

In most colloidal systems, the colloidal are maintained in suspension as a result of the electrostatic forces of the colloids themselves. Since most of naturally occurring colloids are negatively charged and like charges are repulsive, the colloids remain in

suspension because of the action of repulsive forces. In water, the negative colloidal particle will attract the opposite charge from the surrounding water to its surface ions and create a compact layer (Figure 2-2). The compact layer of counter-ions is frequently termed the fixed layer and outside the fixed layer is the diffused layer. The two layers represent the region surrounding the particle where there is an electrostatic potential due to the particle, as illustrated in Figure 2-2. The zeta potential is the electrostatic potential at the shear surface, as shown in Figure 2-2, this potential is usually related to the stability of a colloidal suspension. The colloidal stability depends on the relative magnitude of the forces of attraction due to van der Waals forces, which are effective only in the immediate neighborhood of the colloidal particle. The forces of repulsion are due to the electrostatic forces of the colloidal dispersion which is measured by zeta potential

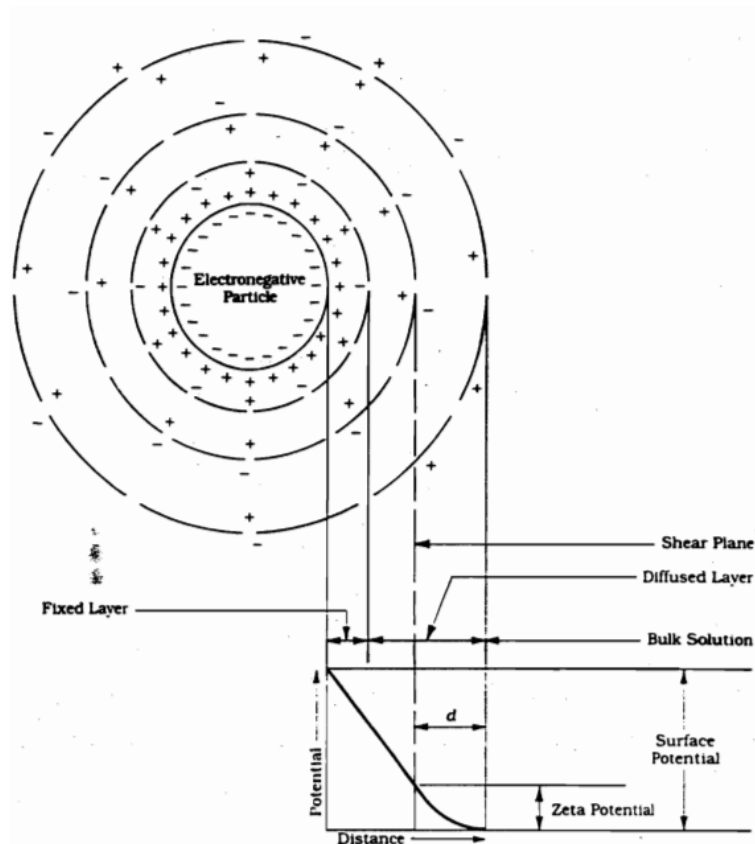


Figure 2-2: A negative colloidal particle with its electrostatic field (Priesing, 1962)

CEPT is the process in which chemicals with or without polymers are added before the primary clarifier in order to enhance settling. The processes of forming larger particles or flocs in wastewater can be divided into three successive processes which are coagulation, flocculation, and sedimentation. These larger conglomerates, which have bigger density and weight, can improve the performance of the sedimentation process as the large particles can settle faster. In its simplest form, the mechanism inside this process can be explained by Stokes law of settling (Equation 2.1).

$$V_s = \frac{g(\rho_s - \rho)d^2}{18\mu} \dots\dots\dots (2.1)$$

Where:

V_s = Terminal Velocity of Particle (m/s)

g = Acceleration due to gravity (m/s²)

ρ_s = Density of the particle (kg/m³)

ρ = Density of fluid (kg/m³)

d = Diameter of particle (m)

μ = Dynamic viscosity (kg/m/s)

Equation 2.1 shows that the settling velocity is proportional to the particle density and the square of particle diameter. This equation assumes that the size of the particle remains the same during the settling process and is applicable for particles < 0.2 mm and laminar flow condition. In practice, small particles will collide with other particles and get bigger as they are settling down to the bottom of the tank.

Coagulation is the addition and rapid mixing of a coagulant, the resulting destabilization of the colloidal and fine suspended solids, and the initial aggregation of the colloidal and fine suspended solids (Reynolds and Richards, 1996). During coagulation, particles can be destabilized either through the action of sweep coagulation, charge neutralization, and/or interparticle bridging.

Sweep coagulation happens when a large amount of metal salts is added to wastewater, which causes the formation of metal hydroxide which can settle quickly.

Charge neutralization is regarded as the second destabilization process in which negatively charged products are counteracted by the addition of a positively charged coagulant. These positively charged coagulants include metal salts, such as ferric chloride and aluminum chloride and cationic polymers. These cationic coagulants will first compress the positively charged diffusive layer around the negatively charged wastewater particles, causing the Van der Waals' forces of attraction between cationic coagulant and negatively charged particles to be more prominent than the repulsive force, thus resulting in the particles getting together and becoming larger flocs. This effect can be magnified by the ability of cationic coagulants to absorb particles in wastewater, resulting in flocs of larger size. So, the settling velocity of these particles increases. Furthermore, it is recommended that cationic coagulants be added to the wastewater during the rapid mixing to trigger this process. This is why the cationic dosing system is always placed in the location where the wastewater has a high degree of turbulence.

The third particle destabilization process is **interparticle bridging** that occurs with the addition of polymer coagulant. During this process, a 'bridge' will be established by a large polymer between the gap separating two similar charged particles. Thus, flocs can

be formed by the polymer bridge between the wastewater particles. Figure 2-2 displays the six reactions of interparticle bridging in floc formation that is essential in flocculation (Murcott and Harleman, 2000).

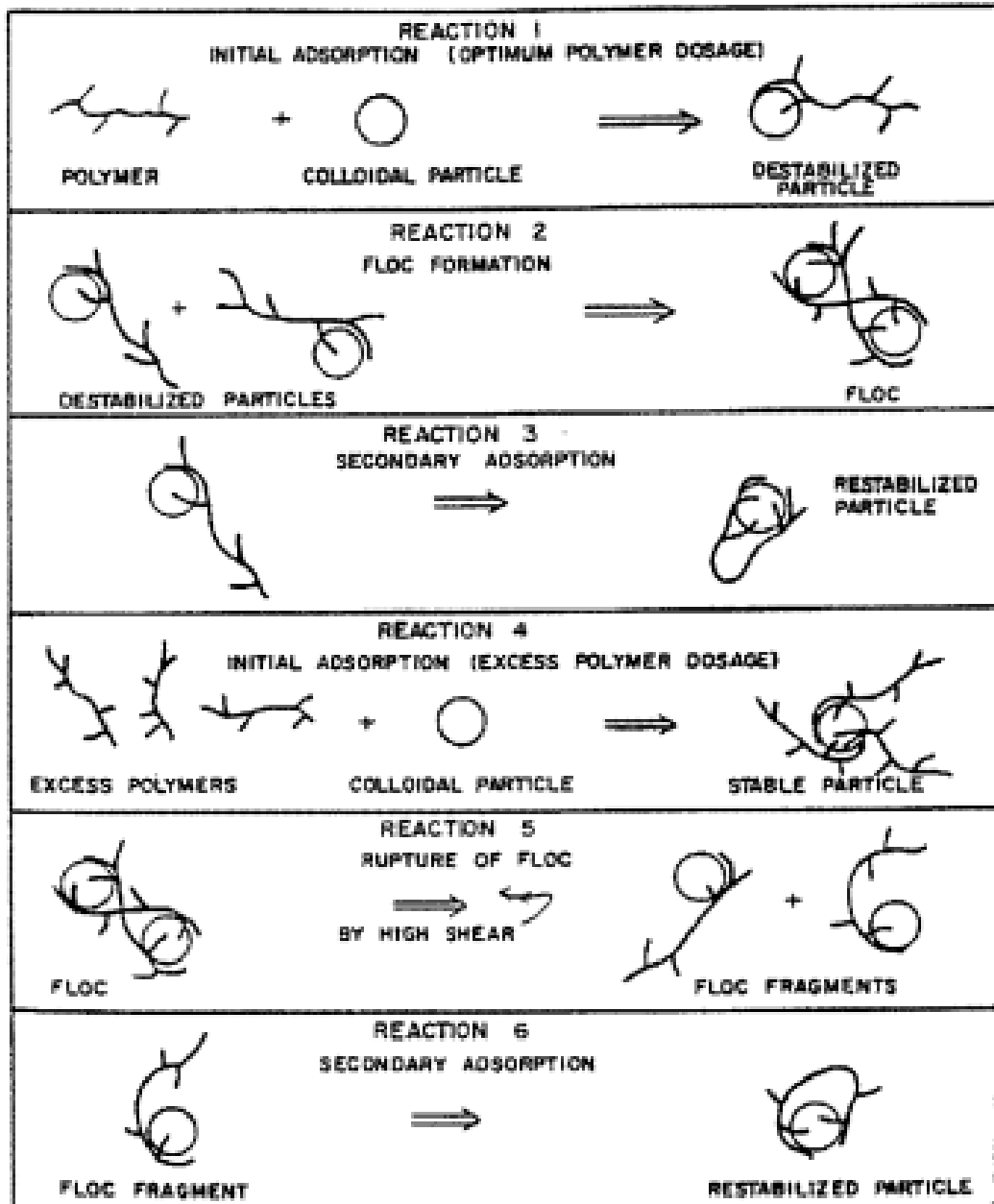


Figure 2-3: Schematic of interparticle bridging (Melia, 1970)

Flocculation, also referred to as particle transportation, is defined as the process to form large particles or flocs by the aggregation of coagulated particles. Although the

coagulation process needs fast mixing, the flocculation process should be undertaken in the condition of gentle and slower mixing. The primary purpose of flocculation is to promote collision among destabilized particles resulting in the formation of larger wastewater particle products. Three mechanisms are very significant behind the collision; - they are Brownian motion (perikinetic flocculation), shear force (orthokinetic flocculation) and differential settlement (a particular case of orthokinetic flocculation) (Atkinson et al., 2005). For the particles whose size is less than 1 μm , the Brownian motion is of primary importance in aggregating particles, which is due to the thermal energy of the fluid. For the particles whose size is greater than 1 μm , a shear force which is induced by mixing is the main force to create collisions between particles. For the differential settlement, which is the process caused by external forces such as gravity on the particles, heavier particles are settling faster, and further collisions will happen between the larger particles and smaller particles during settling. What should be noted is that the mixing rate and time should be well controlled during both coagulation and flocculation, because rapid mixing can break up the flocs which are already formed (Gotovac, 1999, Morrissey, 1990).

In addition to bridging, electrostatic patch mechanisms can induce flocculation. In electrostatic patch, positively charged polymers connect to the negatively charged cell surface and form patches on the cell surface, where the surface charge is inversed from negative to positive. Positively charged patches on one cell can connect to a negatively charged patch on another cell and flocs can be formed. Short and highly charged polymers often cause flocculation by the electrostatic patch mechanism (Bolto and Gregory, 2007).

2.4. Coagulants and flocculants used in CEPT processes

2.4.1. Coagulants

Metal salts are usually used as coagulants. The coagulants are made by replacing atoms of acids with metal atoms or electropositive radicals. These metal salts will dissociate into ions when they are added to the wastewater. They have the role of enhancing the coagulation of suspended solids in the wastewater. Some of the popularly applied coagulants are listed in Table 2-4.

Table 2-4: Widely used coagulants

Coagulants	Composition
Alum	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$
Aluminum chloride	AlCl_3
Polyaluminum chloride	PAC
Ferric chloride	FeCl_3
Ferrous chloride	FeCl_2
Ferric sulfate	$\text{Fe}_2(\text{SO}_4)_3$
Ferrous sulfate	FeSO_4
Lime	$\text{Ca}(\text{OH})_2$

Alum is a widely used coagulant in potable water treatment because of its lower cost and ease of application (Mouri et al., 2013). However, the performance of alum is unstable and will be affected by different factors, such as temperature, pH, concentration and mixing rate (Mouri et al., 2013). AlCl_3 is better than alum in precipitating out the organic matter in wastewater. The drawbacks for AlCl_3 are the excess sludge production and higher cost (Droste and Ronald, 1997). The application of ferric and ferrous salts depends on the nature of the wastewater. If organic nitrogenous, textile, or fermentation wastes are present, ferric salts and ferrous salts can

hardly form flocs (Rudolfs and Willem, 1996). Lime is also a widely used coagulant because it is cheap, and due to its ease of manufacture features. The addition of lime will produce the precipitate of $Mg(OH)_2$ if the wastewater contains Mg^{2+} ions. The advantage of lime is that the pH of wastewater can be increased to avoid acidic conditions. It should also be noted that lime addition will cause a high volume of sludge generation (Metcalf and Eddy, 1991).

2.4.2 Flocculants

Flocculants, such as polymers and polyelectrolytes, serve as coagulant aid. They have a long chain of organic molecules which can provide ionized sites to which ions in wastewater can attach. In the polymerization process, different monomers or single units are combined to generate the polymer molecules. Besides the complex formation, the polymer can be used in a small dosage which is cost-effective and easy to handle. The broad application of polymers can be attributed to the advantages: (1) The dosage of coagulant can be reduced by using polymers, (2) The sludge production can be decreased during wastewater treatment, (3) Microorganisms easily digest sludge produced by the primary clarifier, (4) pH is easy to control and (5) Chemical residuals in treated water can be minimized (Bratby, 2016). Polymers can be natural or synthetic. Natural polymer, such as starch or gelatin, existed for a long time but was seldom used. Most of the widely used polymers are synthetic polymers. Polymers can be differentiated in various ways, such as molecular weight, charge, form, or charge density (Figure 2-3).

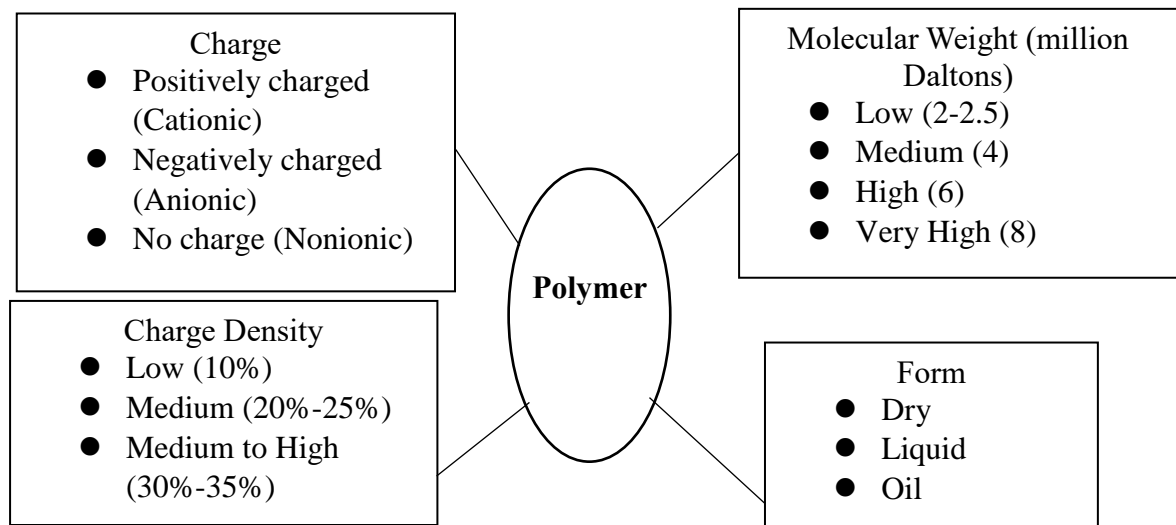


Figure 2-4: Classification of Polymers.

2.5. CEPT performance evaluation

2.5.1 Methods for evaluation

For the wastewater treatment plants, especially those that are adapting CEPT technology, bench-scale testing is regarded as a time-effective and economical method to provide reliable information which can be applied to the real primary clarifier operational progress. Although pilot research and full-scale studies are always conducted with the bench-scale studies, bench-scale studies exhibit more flexibility and advantages than starting the pilot or full-scale studies because they can be conducted in the laboratory with jar test equipment and necessary coagulants and flocculants. The time needed for the jar test is just a few hours. The priority purposes of jar tests are to discover the best coagulant and flocculant type and dosage and the optimal removal rate of tCOD, TSS and TP, and optimize the mixing intensity and time (Hudson et al., 1981, He et al., 2016). The results of jar tests can be applied and evaluated in the real primary clarifier operation.

2.5.2 Total suspended solids (TSS) removal

One of the main purposes of using CEPT is to improve the TSS removal rate. Table 2-5 has summarized the TSS removal rates of different studies. It can be seen that CEPT has high efficiency in removing TSS (70% to 95% removal efficiency). The most widely used coagulant is ferric chloride, and the corresponding dosage for ferric chloride to use in wastewater treatment depends on the wastewater types and its raw TSS concentration. Different kinds of polymers are also used with coagulants, such as PAC and anionic PAM. The dosage of a polymer is relatively low when it is used with a coagulant. Furthermore, it can be concluded that the polymer addition can greatly enhance TSS removal efficiency (Amuda et al., 2006).

Table 2-5: Total suspended solids (TSS) removal summary

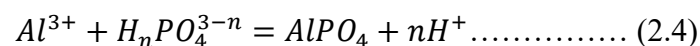
References	Coagulant		Polymer		TSS (mg/L)			References
	Name	Dosage (mg/L)	Name/type	Dosage (mg/L)	Influent	Effluent	Removal eff (%)	
Sarparastzadeh et al. (2007)	Aluminum sulfate	80	N/A	N/A	77.5	24	69	Sarparastzadeh et al. (2007)
	Ferric chloride	70	N/A	N/A	77.5	40.3	48	
Haydar & Aziz. (2009)	Aluminum sulfate	200-240	N/A	N/A	568-2130	N/A	94.3-97.1	Haydar & Aziz. (2009)
Amuda et al. (2006)	Ferric sulfate	500	Poly acrylamide polyelectrolyte	25	1620	97.2	94	Amuda et al. (2006)
	Ferric sulfate	500	N/A	N/A	1620	421.2	74	
Yu & Bourke (2000)	Ferric chloride	50	Anionic PAM	0.5	N/A	N/A	85	Yu & Bourke (2000)
Wang et al. (2009)	N/A	N/A	PAC	100	N/A	N/A	76	Wang et al. (2009)
He et al. (2016)	N/A	N/A	PAC	35	N/A	N/A	90	He et al. (2016)
Poon & Chu (1999)	Ferric chloride	30	Polyacrylamide	0.5	N/A	N/A	60-80	Poon & Chu (1999)
Johnson et al. (2008)	Ferric chloride	40	Anionic polymer	0.5	N/A	N/A	83	Johnson et al. (2008)
Aiyuk et al. (2004)	Ferric chloride	50	Anionic polymer	10	N/A	N/A	85	Aiyuk et al. (2004)
Ghafari et al. (2009)	Aluminum	9500	N/A	N/A	80	7.92	90.1	Ghafari et al. (2009)
	N/A	N/A	PAC	2000	80	7.84	90.2	

2.5.3 Phosphorous removal

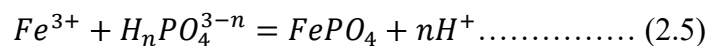
Another primary objective of adapting CEPT is to remove more phosphorus. Table 2-6 summarizes some researches which are related to TP removal. TP removal efficiency is excellent under the condition of adding coagulant and flocculant. Almost 70% to 95% of phosphorous is removed by CEPT. Amuda et al. (2006) evaluated the impact of polymer on TP removal and showed that small dosage (25 mg/L) of polymer addition compared to the dosage of coagulant (500 mg/L) can significantly enhance the TP removal efficiency from 75% by using coagulant alone to 96% by polymer addition.

The removal of phosphorus includes the incorporation of phosphate into TSS and the subsequent removal of those solids. Phosphorus can be incorporated into either biological solid, such as microorganisms, or chemical precipitates. The basic reactions involved in the precipitation of phosphorus with aluminum and iron are as follows:

Phosphate precipitation with aluminum:



Phosphate precipitation with ferric:



Organic phosphorus and poly phosphorus are removed by complex reactions and by adsorption onto particles in the primary treatment. (Metcalf and Eddy, 2014).

Table 2-6: Phosphorous removal summary

Coagulant		Polymer		TP (mg/L)			References
Name	Dosage (mg/L)	Name/type	Dosage (mg/L)	Influent	Effluent	Removal eff (%)	
Aluminum sulfate	80	N/A	N/A	15.8	5.4	66	Sarparastzadeh et al. (2007)
Ferric chloride	70	N/A	N/A	15.8	4.3	73	
Ferric sulfate	500	N/A	N/A	89.5	22.4	75	
Ferric sulfate	500	Poly acrylamide polyelectrolyte	25	89.5	3.6	96	Amuda et al. (2006)
Aluminum	300	Anionic PAM	1	N/A	N/A	90	Mohmoud. (2009)
Aluminum	140	N/A	N/A	N/A	N/A	78	Wang et al. (2009)
N/A	N/A	PACl	100	N/A	N/A	76	
N/A	N/A	PACl	35	N/A	N/A	40	He et al. (2016)
Ferric chloride	30	Polyacrylamide	0.5	N/A	N/A	40	Poon & Chu (1999)
Ferric chloride	50	Anionic polymer	10	N/A	N/A	80	Aiyuk et al. (2004)
Ferric chloride	16	N/A	N/A	N/A	N/A	96	Lin et al. (2017)
N/A	N/A	PACl	20	N/A	N/A	97	
N/A	N/A	PACl	30	N/A	N/A	90	Hatton & Sampson. (1985)
N/A	N/A	PACl	16	N/A	N/A	97.2	Lin et al. (2018)

2.6. Characteristics of CEPT sludge

2.6.1 Sludge characteristics

The sludge generated from different processes of WWTP is usually in the form of a liquid or a semisolid, which generally has from 0.25% to 12% solids by weight, depending on the operations and processes which have been used. Table 2-7 has listed typical chemical composition of untreated sludge and digested biosolids. The sludge is so far the largest in volume, and its corresponding processing, reuse and disposal ways are perhaps the most complicated problems which are faced by the engineer in the wastewater treatment (Metcalf and Eddy, 2014).

Table 2-1: Typical chemical composition of untreated sludge and digested biosolids (Metcalf and Eddy, 2014).

Item	Untreated primary sludge	Digested primary sludge	Untreated activated sludge
Total dry solid (TS), %	5-9	2-5	0.8
Volatile solids (% of TS)	50-80	30-60	59-88
Nitrogen (N, % of TS)	1.5-4	1.6-3.0	2.4-5.0
Phosphorus (% of TS)	0.8-2.8	1.5-4.0	2.8-1.1
Energy content, (kJ /kg TS)	23000-29000	9000-14000	19000-23000

To treat and reuse the sludge from the wastewater treatment process in a most effective way, it is significant to study the characteristics of the sludge which will be treated.

Furthermore, the sludge characteristics always depend on the source of the sludge, the amount of aging that has been taken place, and the method of processing to which they are subjected. The conventional primary sludge is usually gray and slimy with an extremely offensive odor, and it can be readily digested in an anaerobic environment (Metcalf and Eddy, 2014). CEPT sludge is usually dark in color with an objectionable odor, and significant gas might be produced. While chemical sludge is somewhat slimy, the hydrate of iron or aluminum in it makes it gelatinous. The density of sludge will increase by long residence times in storage (Metcalf and Eddy, 2014).

2.6.2 Anaerobic Digestibility

Sludge anaerobic digestibility is always measured by conducting bench scale anaerobic digestion tests . The test involves quantifying the amount of methane gas produced by adding a known quantity of primary sludge to an anaerobic digester containing a known amount of anaerobic biomass. Anaerobic digestion (AD) is defined as a process by which both organic and inorganic matter is decomposed in the environment without oxygen. In the process of converting 40% to 60% of organic solids in the sludge, CO₂, CH₄ and a large number of by-products are produced during anaerobic digestion, and the remaining organic matter is in a chemically stable form (Frnazini et al., 1992). The process of anaerobic digestion is an old process which can be dated back to the 1850's, but is still widely used around the world, especially in large wastewater treatment plants.

Anaerobic digestion includes four stages in which microorganisms will break down biodegradable material without oxygen. The four stages of anaerobic digestion are 1)

Hydrolysis, 2) Acidogenesis, 3) Acetogenesis and 4) Methanogenesis (Figure 2-4). The detailed explanation of these four steps is described below (Scragg, 2005):

- **Hydrolysis:** Liquefaction of complex organic compounds to simpler forms by hydrolytic bacteria. The main end products consist of soluble sugars, amino acids, peptides and long-chain fatty acids.
- **Acidogenesis:** Metabolization of the end products of hydrolysis by Acidogenic bacteria. The major end products are short-chain volatile organic acids (propionic, butyric, acetic and formic acids), CO₂ and H₂.
- **Acetogenesis:** Reduction of carbon dioxide and catabolization of short-chain fatty acids produced during the process of acidogenesis by syntrophic acetogenic and homoacetogenic bacteria. CO₂, H₂, and acetate are the principal end materials of this process.
- **Methanogenesis:** Reduction of CO₂ and cleaved acetate by Methanogens. This process will finally produce CH₄, CO₂ and trace gases.

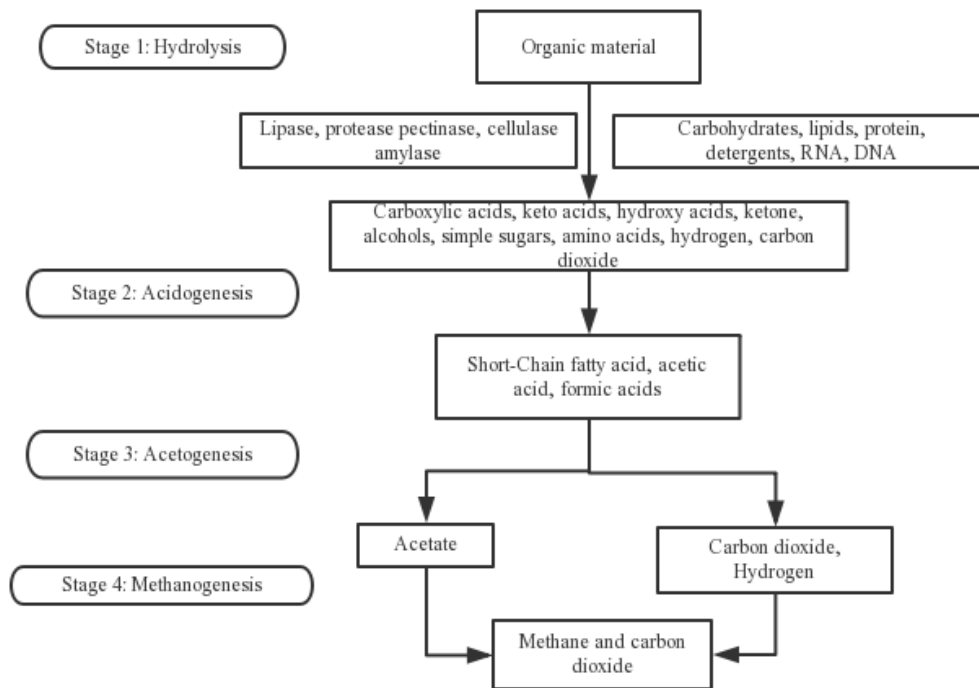


Figure 2-5: Schematic Representation of Anaerobic Digestion (Scragg, 2005).

Environmental factors such as the amount of nutrients for microorganisms, the concentrations of different toxicants, temperature, pH, alkalinity and moisture content in the substrate affect the anaerobic digestion process (Davidsson, 2007). The two widely used temperatures for the operation of anaerobic digestion are mesophilic (in the range of 15 to 45 °C with the optimum temperature of 35°C) and thermophilic temperature (in the range of 45 to 75 °C with the optimal temperature of 55°C) (Vindis et al., 2009). Anaerobic digestibility tests are typically conducted at 35°C temperature.

2.6.3 Sludge dewaterability

Dewaterability is a mechanical or physical means that affects the ability to reduce the water (moisture) content of sludge, thus decreasing sludge volume. Some methods can

be applied for sludge dewatering, such as vacuum filtration, solid bowl centrifugation, imperforate basket centrifugation, belt filter pressing, recessed plate filter pressing, sludge drying beds and sludge lagoons (Metcalf and Eddy, 2014). The chemicals contained in the sludge and the presence of microbial extracellular polymer (ECP) in the sludge can influence the dewaterability of sludge (Houghton et al., 2001). Good dewaterability is helpful in many different ways, including the following: volume reduction can allow for lower trucking costs in its disposal, moisture content reduction is an advantage for the next process which requires a higher solids concentration, and it will be much easier to treat when it is thickened.

The sludge volume index (SVI) can be used to check the dewaterability of different sludge. It is defined as “the volume in mL occupied by 1g activated sludge after settling the aerated liquor for 20 minutes”. This describes the ability of sludge to settle and compact (APHA, 2015). The typical range for an SVI at a conventional activated sludge plant should be between 50 and 150. When the SVI is too low (less than 50), this situation usually indicates that the sludge is dense and has relatively rapid settling characteristics. This is most likely because of an old, over-oxidized sludge typically seen in an extended aeration facility. If the SVI is very high, the sludge settles very slowly and compacts poorly in the settle ability test. The MLSS looks light and fluffy and not very dense. The reason behind that is probably because the wastewater plant is undergoing startup or filamentous sludge bulking (Jenkins et al., 2005, Clifton, 1988).

Although the SVI measurement method was introduced a long time ago, few studies have studied the impact of CEPT on the dewaterability of downstream activated sludge quality by using SVI. Thus, the influence of CEPT on SVI will be addressed in this thesis.

2.7. The impact of CEPT process on the downstream aeration process

The aeration process in wastewater treatment plants is a biological process primarily used for carbon oxidation, nitrification and/or denitrification. The application of CEPT has an impact on denitrification because of its effect on the COD/N ratio. Previous studies have shown that a significant removal of tCOD in the CEPT process impacts the denitrification process negatively because of insufficient COD available for the denitrification process (Van Nieuwenhuijzen et al. 2000). Recent studies have indicated that total nitrogen removal can be achieved with minimal or no carbon using second generation nitrogen removal processes, such as anammox processes (Zeng et al., 2016). For conventional carbon oxidation and nitrification plants, information is not available on the impact of removing a large percentage of tCOD, sCOD, TSS and TP during the downstream activated sludge process. Therefore, one of the objectives of this thesis is to study the impact of CEPT on the downstream process.

2.8 Research gaps

As discussed above, studies addressing the potential and optimization of CEPT technology for simultaneous carbon redirection, wet weather flow and phosphorus removal are needed. Most studies so far have focused on using CEPT to remove more TSS and phosphorus. Although the concept of using CEPT for carbon redirection raised researchers' attention, almost no studies have focused on significant carbon removal by adding various coagulants and flocculants, and few have further investigated the sludge biodegradability when substantial carbon and nutrients are concentrated chemically into the sludge. Besides, the impact of substantial carbon removal during the primary treatment on the downstream carbon oxidation and nitrification liquid train process is still unknown. Therefore, these research gaps will be addressed in this thesis.

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Chapter 3¹

3. Optimizing chemically enhanced primary treatment processes for simultaneous carbon redirection and phosphorus removal

3.1 Introduction

One of the most prominent and practical topics which concerns all facets of the wastewater industry is the necessity for low-energy and sustainable technologies. Recent developments in wastewater treatment have also heightened the need for carbon redirection from primary treatment units to transfer more carbon to anaerobic digestion or incinerators for maximizing energy recovery and generation. One of the existing technologies being considered for carbon redirection is chemically enhanced primary treatment (CEPT) (Jimenez et al. 2017). CEPT refers to the process whereby chemicals are added to primary influent to promote coagulation and/or flocculation in primary clarifiers, resulting in improved removals via precipitation of particulate/dissolved solids as well as the carbon and nutrients associated with those solids (Neupane et al., 2008). Historically, metal salts, such as ferric chloride and alum, were considered as coagulants to be added to primary influent to enhance the removal of phosphorus. CEPT with inorganic coagulants have been shown to improve phosphate removal rates from 75% to 95% by using metal salts (Tchobanoglous, 2014). Wang et al. (2009) also showed that dosing alum can effectively remove 78% of phosphate through primary treatment. Therefore, metal salts addition has been demonstrated to have a significant

¹ Chapter 3 submitted to Bioresource Technology for publication.

impact on phosphorus removal performance for primary clarification when compared to a conventional clarifier, which typically only achieves removals of approximately 30%. Further, the chemical addition causes the particulate matter to form larger flocs, increasing the settling rate and thus reducing the required residence time for primary treatment, which translates into the ability to treat higher wastewater flows in wet weather or overflow conditions without compromising primary treatment performance (Wang et al., 2009). Odegaard (1998) conducted research on the impact of polymer to supplement metal salt addition for a CEPT process. This research showed a promising increase in the floc settling rate allowing similar performance at higher surface overflow rates than when the metal salts were used alone. The results of bench-scale testing show that total suspended solids (TSS) removal rate can be increased to around 90% by adding coagulant and flocculants (Aiyuk et al., 2004, He et al., 2016, Ghafari et al., 2009). Furthermore, the results of a survey of 100 wastewater treatment plants in the United States suggests that, based on the results comparing full-scale CEPT applications to conventional primary clarification under similar operating conditions, CEPT results in a 30% increase in TSS removed through primary treatment (National Research Council, 1992).

Currently, many wastewater treatment plants are being upgraded for the purposes of resource recovery, which lead both industry professionals and researchers to consider the role which the CEPT process can play. Compared with conventional primary treatment, CEPT shows superior efficiencies in removing suspended solids and

phosphorus (Lin et al., 2017). As organic carbon is a potential energy-rich component of wastewater, a key consideration for sustainable, energy self-sufficient wastewater treatment is the removal and management of the carbon in the influent wastewater. Therefore, the removal rate of total chemical oxygen demand (tCOD) and soluble chemical oxygen demand (sCOD) will be more important in the processes of CEPT. Furthermore, although there are some recent studies that discuss the potential of using CEPT in carbon redirection, there is a notable lack of research being undertaken that focuses on optimizing CEPT for simultaneous carbon and nutrient redirection by removing more tCOD, sCOD and TP.

If a large amount of carbon can be redirected by CEPT compared to traditional primary treatment, a larger portion of pollutants are concurrently removed via CEPT sludge rather than requiring removal through downstream biological or chemical treatment processes. Additionally, the pollutants concentrated in CEPT sludge, such as organic carbon and nutrients, can be regarded as valuable resources to increase anaerobic digester gas production or promote autogenous combustion in sludge incineration. The other advantages of CEPT include reduction of the footprint of primary settling processes as it permits operation at high surface overflow rates, while also reducing the footprint and operating cost of subsequent biological treatment processes due to the decreased organic loadings contained in primary effluent. Despite these advantages, previous studies concerning CEPT have only focused on the selection of coagulants and flocculants (Mahmoud, 2009, Neupane et al., 2008, Shi et al., 2007) for wet weather

flow conditions and phosphorus removal. Studies which holistically address the potential for optimization of CEPT technology for simultaneous carbon redirection, wet weather flow and phosphorus removal are limited. Thus, the objectives of this study are to (1) investigate effectiveness of several polymers with ranging characteristics on simultaneous carbon and nutrient removal (2) monitor and characterize full scale CEPT performance under optimal and suboptimal polymer dosing operations and (3) evaluate influence of influent characteristics on removal rates under varying operating conditions.

3.2 Material and methods

The study was conducted using bench scale units to address the above objectives prior to evaluation at full-scale. The bench scale study was conducted systematically to identify the best coagulant- polymer combination for achieving simultaneous carbon redirection and P removal. The study evaluated the effectiveness of seven different types of polymers in combination with ferric chloride by assessing the removals of tCOD, sCOD, total phosphorus (TP) and TSS. After the optimal combination was identified, it was further implemented on a full-scale primary clarifier in a side-by-side comparative evaluation using a similar full-scale conventional clarifier as a control. The primary influent and effluent was characterized and the long-term performance of each clarifier, as well as the impact of the primary influent characteristics on their performance, was evaluated.

3.2.1 Full Scale site layout and sampling

Full scale tests were conducted at the Vauxhall Pollution Control Plant (PCP) (London, Ontario). The plant has two sections, designated as Sections 1 and 2, treating two third and one third of the total flow respectively (Figure 3-1). According to the 2016 annual report, the annual average daily flow of the Vauxhall PCP is 13,500 m³/day (City of London, 2017). The plant makes use of ferric chloride for phosphorus removal and occasionally uses Alcomer[®]120L polymer (hereafter called Alcomer) to enhance the plant's performance during wet weather flow conditions. The CEPT optimization experiment was conducted on the section designated as Section 2 and Section 1 was monitored as a control clarifier (Figure 3-1). During the test period, the flow going to each section was manipulated to maintain similar surface overflow rate and detention time between the test clarifiers and the control (Table 3-1). Ferric chloride addition for phosphorus removal was resumed for Section 1 (herein referred to as the control clarifier) while a selected polymer in combination with ferric chloride was added to Section 2 influent (herein referred as the test clarifier) for simultaneous carbon redirection and phosphorus removal. The influent and effluent of the primary clarifiers of both sections (Section 1 and section 2) were collected twice per week for wastewater quality analysis, which included total chemical oxygen demand (tCOD), soluble chemical oxygen demand (sCOD), total phosphorus (TP) and total suspended solids (TSS). The operating parameters and characteristics of the raw wastewater are shown in Table 3-1.



Figure 3-1: Lay out of Vauxhall WWTP.

Table 3-1: Clarifier operating parameters and wastewater characteristics.

Operating parameters	Control clarifier	Test clarifier
Flow (MLD)	9	4.5
Detention time (hours)	1.7	1.8
Surface overflow rate (m ³ /m ² /d)	32	30
TSS, mg/L		354*
BOD, mg/L		228*
TP, mg/L		6.3*

*24-hour composite samples, average year

3.2.2 Bench scale Jar testing and Polymer selection

The jar test experiments were performed using Phipps and Bird PB-900 six-paddle flocculation stirrer and the contents of the jars were mixed simultaneously. One liter of raw wastewater was placed into each of the jars and a fixed dosage of ferric chloride (15 mg/L), an optimal dosing rate for phosphorus removal (Appendix-A), was added to each jar. After the addition of ferric chloride, the wastewater was briefly stirred at 100 rpm for 1 minute and increasing dosages of polymer solution (0.25 to 2 mg/L) was added in each jar as quickly in succession as possible; then slowly stirred at 20 rpm for another 2 minutes. The wastewater mixture was then allowed to settle for 30 minutes and then a sample of supernatant was withdrawn for analysis.

As part of the jar testing methodology, special emphasis was given to the method of coagulant and flocculant addition to mimic the dosing conditions typically found at full-scale wastewater treatment facilities (Aguilar et al., 2005, Feo et al., 2008). In actual wastewater treatment plants, standard design practice is to inject coagulant at a location where there is a high degree of turbulence in order to stimulate the process of coagulation. Because of the negative impact of rapid mixing on the flocculation process, causing a break-up of already formed flocs, flocculants are typically added in a more quiescent location. Concomitant to this, the coagulant was added during rapid mixing followed by flocculant addition during slow mixing.

A total of 126 tests were performed using seven different polymers, each applied at concentration of 0.25, 0.5, 0.75, 1, 1.5 and 2 mg/L and conducted in triplicate. Prior to the test, stock solutions of ferric chloride and the seven different polymers were prepared and stored at 21°C in sealed plastic bottles. Table 3-2 provides a summary of the polymers used for this study. The polymers were selected based on their wide range of characteristics and their potential impact on carbon redirection.

Table 3-2: Comparison of different polymers.

Polymer name	Type	Composition
Polyacrylamide	Nonionic	(C ₃ H ₅ NO) _n
Polyacrylamide	Anionic	(C ₃ H ₅ NO) _n
Polyacrylamide	Cationic	[-CH ₂ -CH(CONH ₂)] _n -
Poly aluminum chloride	-	(Al ₂ (OH) ₃ Cl ₃) _n
BASF 8848FS (B1)	Cationic	Unknown, proprietary
BASF 8858FS (B2)	Cationic	Unknown, proprietary
Alcomer	Anionic	Anionic, acrylamide-based copolymer

3.2.3 Wet chemistry and statistical analysis

The wet chemistry analysis including total and soluble COD (HACH method 8000) and TP (HACH method 10127) was performed according to HACH method. Total

suspended solids (TSS) was measured as per the standard methods (APHA et al., 2005). Analysis of field samples was carried out within 24 hours after their collection to minimize any changes in the wastewater characteristics. Samples collected during jar testing were analyzed immediately after collection. The assessment of normality of the data and mean comparison was made using the Anderson-Darling Test and t-test, respectively (Ghasemi and Zahediasl, 2012). MINITAB 18 (Minitab Inc., State College, PA), a statistical software program, was used to determine the skewness, kurtosis, Anderson-Darling p -values and t critical value.

3.3. Results and Discussion

3.3.1 An evaluation of polymer type on simultaneous carbon redirection and TP removal

A total of seven different polymers were selected and the carbon and nutrients removal efficiency of these polymers were investigated, aiming to select an optimal polymer type and its corresponding dosage. The evaluation was conducted using jar testing with a fixed coagulant (ferric chloride) dose of 15 mg/L and varying doses of polymers. The details of the comparison are described in the subsequent sections.

Figures 3-2a to 3-2d illustrate the performance of different types and concentration of polymers in terms of tCOD, sCOD, TSS and TP removals. Overall the tCOD removal ranged from 22 ± 2 to $94\pm 2\%$ (Figure 2a). The results indicated an optimal polymer dose of < 1 mg/L with corresponding tCOD removals ranging from 68 ± 0.8 to $94\pm 2\%$. The

highest removal achieved ($94\pm 2\%$) is demonstrated when applying poly aluminum chloride (PACl) at a dose of 0.5mg/L: the removal rate was found to be 20 to 68% higher than the removal efficiencies of the other 6 polymers (Figure 3-2a). COD is a bulk parameter and typically its enhanced removal by coagulant aids is expected to involve both patch charge neutralization and bridging. Previous studies showed that the dominant mechanism for high molecular PAMs is bridging (Ebeling et al., 2005) while PACl showed strong bridging and patch charge neutralization capability (Bratby, 2016) thus the best performance. The best tCOD removal rate for nonionic PAM, cationic B1, cationic PAM, anionic PAM were measured to be $71\pm 0.8\%$, $68\pm 0.8\%$, $74\pm 2.1\%$ and $68\pm 0.7\%$, respectively. This demonstrates that the charge associated with the PAM had no substantial impact on the tCOD removal thus confirming the patch charge neutralization capability of PAMs is rather minimal. For the Alcomer and B2, the highest removal rates were $43\pm 0.7\%$ and $26\pm 0.7\%$, which demonstrate that the cationic polyelectrolyte and high molecular weight polymer (Alcomer) achieve a poor tCOD removal efficiency. Previous studies demonstrated that PACl, even when used alone as a coagulant, can achieve good removals because of its excellent bridging and charge neutralization ability (Ghafari et al., 2009, Lin et al., 2017 and Lin et al., 2018). These studies have reported tCOD removal rates ranging from 40% to 80% at different dosages of PACl from 20 mg/L to 2000 mg/L. The results observed during the jar testing completed under the current study indicate that if PACl can be used with ferric chloride, not only are tCOD removal rates greatly enhanced, but that the concentration of PACl can be decreased to a dose as low as 0.5 mg/L while still achieving high removals,

suggesting that PACl addition is a cost-effective method to improve the primary clarifier performance relative to tCOD removal.

A second parameter that was investigated in relation to carbon redirection is sCOD, Figure 3-3b shows the percent sCOD removals upon the addition of various polymers. The results show lower sCOD removals ranging from 2 ± 0.7 to $30\pm 3.1\%$ for all polymers, with the exception of the nonionic PAM polymer, which showed a higher $70\pm 2.5\%$ removal at a dosing rate of 0.5 mg/L. The lowest removals observed (2 ± 0.7 and $10\pm 0.5\%$) correspond to the cationic polymer B2 and Alcomer. These results are noted to be consistent with tCOD performance. The sCOD removal rate could either be the result of removal of the true soluble fraction or the fraction of colloidal COD present after filtering the sample using a 0.45 micron filter. In order for sCOD to be removed, it would be converted to insoluble forms, by complexation and formation of insoluble precipitates, by adsorption to solid materials, or by a combination of these processes (Edzwald, 1993). From Figure 3-2b, it can be seen that the nonionic polymer is the only polymer that achieved a notable increase in removal when compared to the remaining six polymers tested, which are either positively or negatively charged.

This phenomenon may be explained by the fact that soluble COD is not preferably adsorbed on the floc which is formed during the coagulant process with charged polymers, whereas nonionic PAM, which does not contain a charge, assists in the conversion of soluble COD to particulate forms which enhances removal. The results

of the current study, which demonstrates lower relative sCOD removals achieved by the other six polymers, are in agreement with similar studies conducted by Haydar and Aziz (2009) which demonstrated that only a small portion (ranging from 7% to 28%) of sCOD can be removed by the adsorption of sCOD on Al(OH)₃ floc during the process of coagulation.

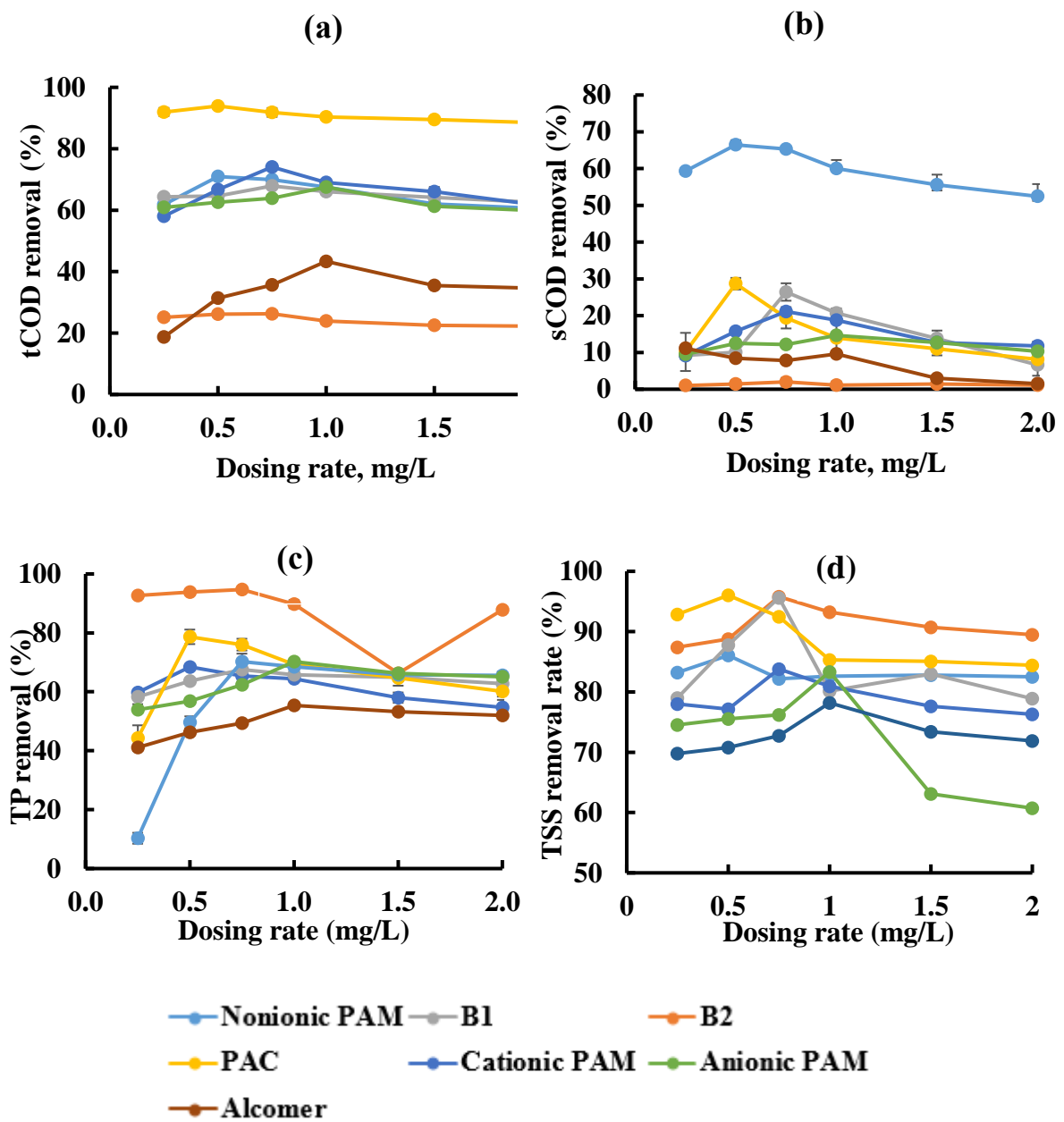


Figure 3-2: Percent removal by individual polymers with 15 mg/L Ferric chloride (values are averages of triplicates): (a) tCOD (b) sCOD (c) TP and (d) TSS.

Figure 3-2c shows the TP removal achieved through Ferric chloride (15mg/L) coupled polymer dosing. The cationic polymer, B2, was found to be the best polymer to be used with ferric chloride for removing TP based on a removal rate of $95\pm 1.1\%$ at a polymer dosage of 0.75 mg/L. The TP removal performance of other cationic, anionic or nonionic polymers is in the range of $50\pm 2.4\%$ to $70\pm 2.5\%$, with the exception of PACl, which removed $80\pm 4.9\%$ of TP accounting to phosphate removal by charge neutralization and organic phosphorous and poly phosphorus by bridging. These results again demonstrate that the charge neutralization mechanism of PAM was not the dominant mechanism. This can be concluded on the basis of equal removal rates from both anionic PAM ($70.2\pm 2.1\%$) and cationic PAM ($70.2\pm 5.4\%$). Most of the TP is removed by ferric and polymer ion co-precipitation (Hauduc et al., 2015, Ratnaweera et al., 1992). However, B2 (Cationic Polyelectrolyte) displayed a much better performance for removing TP, which demonstrates that the liquid grade cationic polyelectrolyte used is superior for TP removal to all varieties of PAM tested. Further research regarding the impact of the characteristics of B2, such as its molecular weight, charge density and viscosity on its bridging and patch charge neutralization capability need to be done to establish this argument.

Figure 3-2d graphically illustrates the observed TSS removals associated with various polymers added as coagulant aid. Typically, the capability of polymers to remove TSS is an indicator of their potential use for wet weather flow conditions. Interestingly, all the polymers achieved removals that exceed 70%. This is a contrast to the results of

tCOD, sCOD and TP removal efficiencies. Three of the polymers, including PACl, B1 and B2, have higher (>90%) and comparable TSS removal rates (Figure 3-3d). However, the dosage needed to achieve these removals with PACl (0.5 mg/L) is lower than the other two polymers (0.75 mg/L) (Figure 3-2d). Therefore, PACl was considered best polymer from a performance and cost standpoint for the removal of TSS. The ability of PACl to achieve a high level of removal despite a lower dosage compared to other polymers may be explained by it has both charge neutralization and bridging ability. Molecular weight and intrinsic viscosity are the most important factors in the coagulation and flocculation process, owing to the size and bridging ability of the molecules for aggregation (Wei et al., 2009). In addition, the ratio of the Al³⁺ and the positive charge are elevated during the manufacturing process of PACl, which effectively brings about its excellent abilities of charge neutralization and bridging ability for flocculation (Yan et al., 2009).

3.3.2 Selection of best performing polymer

The summary of the results obtained from the jar test analysis is shown in Table 3-3. It is apparent from this table that selecting the best performing polymer is not straightforward because no single polymer provides the best observed removal efficiency for each of the parameter considered. By using a simplified comparison matrix introduced by Feo et al. (2007), where equal weights are given to all performance evaluation parameters, (Table 3-4), PACl (average index = 1.916) is the best polymer.

Therefore, using 0.5 mg/L PACl combined with 15 mg/L of ferric chloride can remove as high as 94% of tCOD, 29% of sCOD, 79% of TP and 96% of TSS through CEPT. Although the sCOD removal efficiency of PAC is not the highest compared to the nonionic PAM (Figure 3-4), it exhibits an outstanding performance in removing tCOD, TP and TSS. In addition to better performance, the cost of PACL (200-350 USD/ton) was much lower than PAM (1000-1800 USD/ton) making it is the most economic polymer.

Table 3-3: Comparison of different polymers.

Polymer type	Optimum dosage (mg/L)	Removal efficiency (%)			
		tCOD	sCOD	TP	TSS
Nonionic PAM	0.5	71	66	68	86
Anionic PAM	1	67	15	70	83
Cationic PAM	0.75	74	21	70	84
PACL	0.5	94	29	78	96
B1	0.75	68	26	67	96
B2	0.75	26	2	95	96
Alcomer	1	43	10	55	78
	Min = 0.5	Max = 94	Max = 66	Max = 95	Max = 96

Table 3-4: Alternative matrix of polymers using equilibrate weight distribution.

S.No	Polymer type	Criteria ¹				Average Index ²
		tCOD removal	TP removal	TSS removal	Dosage	
1	PACl	2.000	1.662	2.000	2.000	1.916
2	Nonionic PAM	1.512	1.445	1.794	2.000	1.688
3	B1	1.446	1.426	1.992	1.333	1.549

4	Cationic PAM	1.578	1.483	1.746	1.333	1.535
5	B2	0.560	2.000	1.996	1.333	1.472
6	Anionic PAM	1.438	1.483	1.735	1.000	1.414
7	Alcomer	0.922	1.170	1.629	1.000	1.180

¹ Each criteria is attributed an equal weight of 2.

² Average index is the average of the 4 weighted values for each alternative.

3.3.3 Full scale carbon redirection, TP removal and wet weather flow performance

Full scale carbon redirection, TP removal and wet weather flow performance characterization was conducted at the Vauxhall PCP using both a test and control clarifier, which provides 105 and 277 m² of surface area. During the study period, these clarifiers operated at a surface overflow rate of 30 and 32 m³/m²/d, respectively. Prior to this experiment, the plant has been dosing 15 mg/L ferric chloride for phosphorus removal and uses Alcomer on an as needed basis to enhance the plant's performance during wet weather flows. The full scale test was conducted in three phases: (1) Phase-1: in addition to ferric chloride, Alcomer at 1 mg/L was added on continuous basis to assess the effectiveness of the plants existing polymer for carbon redirection and TP removal (2) Phase-2: compare the test and control clarifier performance subjected to only ferric chloride dosing (3) Phase-3: compare the test clarifier, which received a dose of ferric chloride followed by an optimized polymer (PACl) versus the control clarifier that receives only ferric chloride.

The TSS, tCOD, sCOD and TP removal efficiency for both the test and control full scale primary clarifiers during phase-1 are depicted in Figures 3-3 (a) – (d). The average TSS, COD, sCOD and TP removal efficiencies for the control were $68\pm 12\%$, $40\pm 20\%$, $20\pm 14\%$ and $33\pm 20\%$ and for the test clarifier with polymer addition were $84\pm 9\%$, $47\pm 16\%$, $21\pm 13\%$ and $41\pm 18\%$, respectively. For most of the parameters, the test clarifier demonstrated marginal improvement except for TSS, where a statistically significant (16%) improvement in removal was demonstrated. This confirms that the usage of polymer during wet weather flow conditions could be used to enhance removals. However, it should be noted that the enhancement in TP removal was not comparable with other studies that reported higher removal rates of around 80% (Mohmoud 2009; Lin et al. 2017). It is theorized that the reason the Alcomer does not achieve a higher performance improvement may be because of the polymer itself or the performance of two primary clarifiers having an inherent difference requiring further data collection and statistical analysis. Thus, the addition of Alcomer to the test primary clarifier was stopped in order to compare the performance of the two primary clarifiers under similar conditions.

The light green-shaded areas in Figures 3-3(a) to (d) represent the period when Alcomer was not added to the test primary clarifier (phase-2). The two primary clarifiers exhibited similar performance however another observation to emerge from the data comparison between phase-2 and phase-1 was the increase in the primary clarifier removal rate of TSS, COD, sCOD and TP during phase-2: during the period in which

polymer dosing was suspended, primary removals increased from an average of $68 \pm 12\%$, $40 \pm 20\%$, $20 \pm 14\%$ and $33 \pm 20\%$ during phase-1 to $74 \pm 19\%$, $74 \pm 10\%$, $34 \pm 16\%$ and $51 \pm 10\%$ during phase 2. This increase may be explained due to the weather conditions during phase-1 testing; several snow melt events occurred on February during which approximately 35 mm of rain was received (Appendix-B). This resulted in elevated influent flows, which increased the operating surface overflow rate higher than those during phase-2. Operation under these conditions and the lower temperature likely explains some of the reduced removals observed during phase-1.

In summary, the results from phase-2 demonstrate that the treatment efficiency of Section 1 and Section 2 clarifiers operated under identical condition were not similar ($P < 0.05$). Subsequently, addition of polymer was reinitiated, this time using the selected optimal polymer (PACl) in the test clarifier for over 2 months period and a promising result was found (Figures 3-3 (a) to (d)). The comparison data shows a clear benefit of PACl in the removal of carbon and nutrient from the primary effluent. The full-scale monitoring results show the PACl added to the primary clarifier in the test clarifier achieved removals of $89 \pm 2\%$ TSS, $76 \pm 4\%$ tCOD, $58 \pm 7\%$ sCOD and $84 \pm 5\%$ TP. On the other hand, the control primary clarifier which is fed with only ferric chloride removed $77 \pm 5\%$ TSS, $62 \pm 12\%$ tCOD, $35 \pm 10\%$ sCOD and $67 \pm 12\%$ TP. A comparison of the two results between the full-scale test and control primary clarifiers reveal that the PACl combined with ferric chloride performed significantly better than ferric chloride on its

own ($P < 0.05$), which is in agreement with the jar test result. Thus, it can be concluded that the PACl addition does greatly increase the performance of primary clarifier.

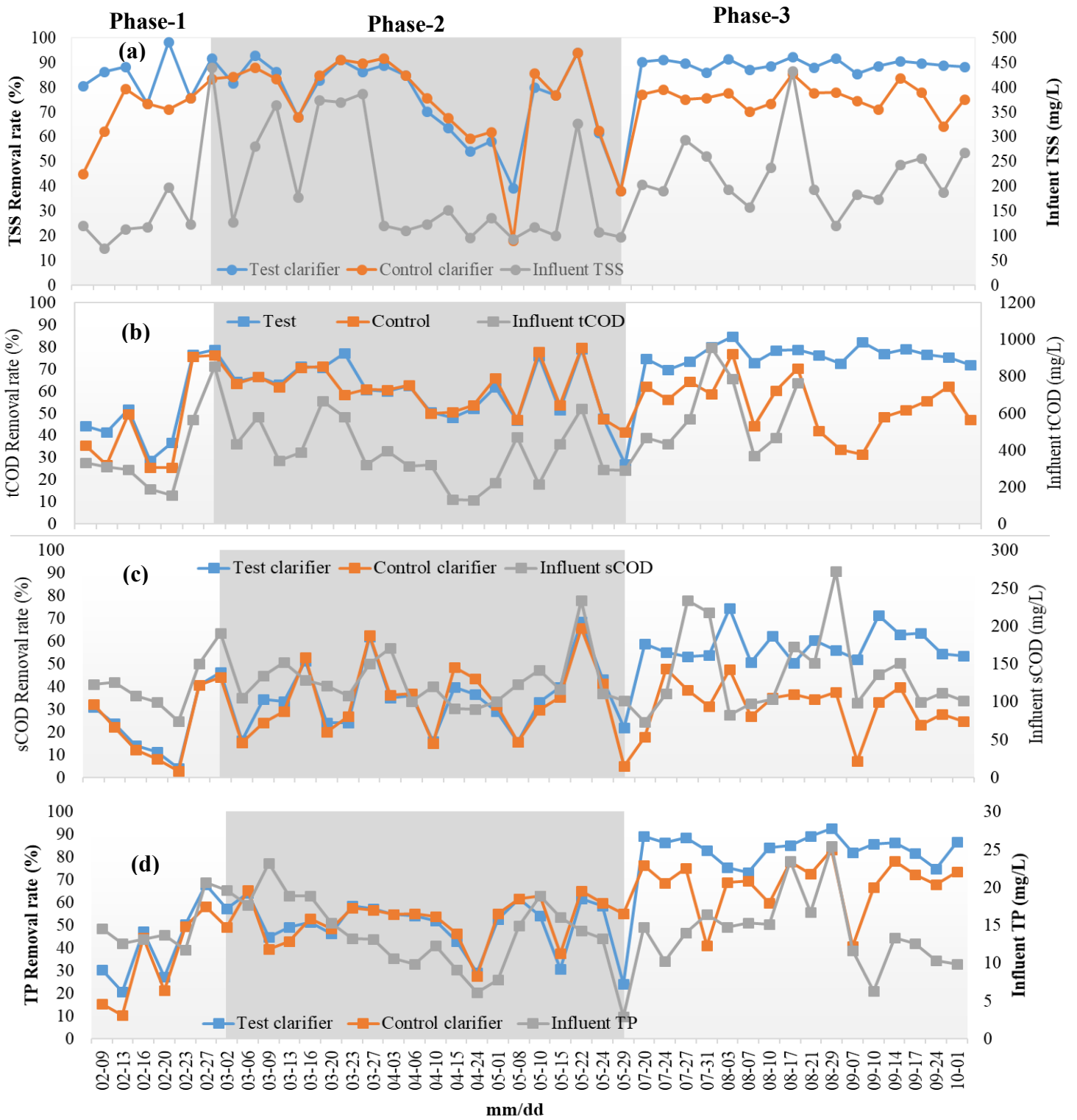


Figure 3-3: Removal efficiency (a) TSS (b) tCOD (c) sCOD and (d) TP removal

The improvements observed are not only limited to TSS removal, which in practice is the design parameter for most full-scale applications of CEPT for overflow conditions, but enhanced removals of COD, sCOD and TP were also observed, which will provide significant benefit through the redirection of additional carbon and phosphorus to primary sludge. The full-scale monitoring results presented in Figure 3-3 demonstrate that there is potential to optimize the CEPT process, providing a significant benefit for facilities looking to optimize phosphorus removal and increase carbon capture in primary sludge for redirection, reducing the aeration requirements by limiting the carbon that must be oxidized through secondary treatment. As discussed previously, carbon redirection has the potential to significantly increase digester gas production rates for facilities equipped with anaerobic digesters. On the other hand, facilities that utilize incineration for solids disposal can derive benefit from increasing the calorific content of sludge processed, reducing supplemental fuel requirements or assisting in achieving autogenous sludge conditions. However, it is anticipated that capture of additional nutrients in the primary sludge beyond those examined under the current study will occur, and thus additional study is required to assess the potential impacts of receiving sludge arising from PACl addition within anaerobic digestion systems.

3.3.4 Influence of influent characteristics on removal rates

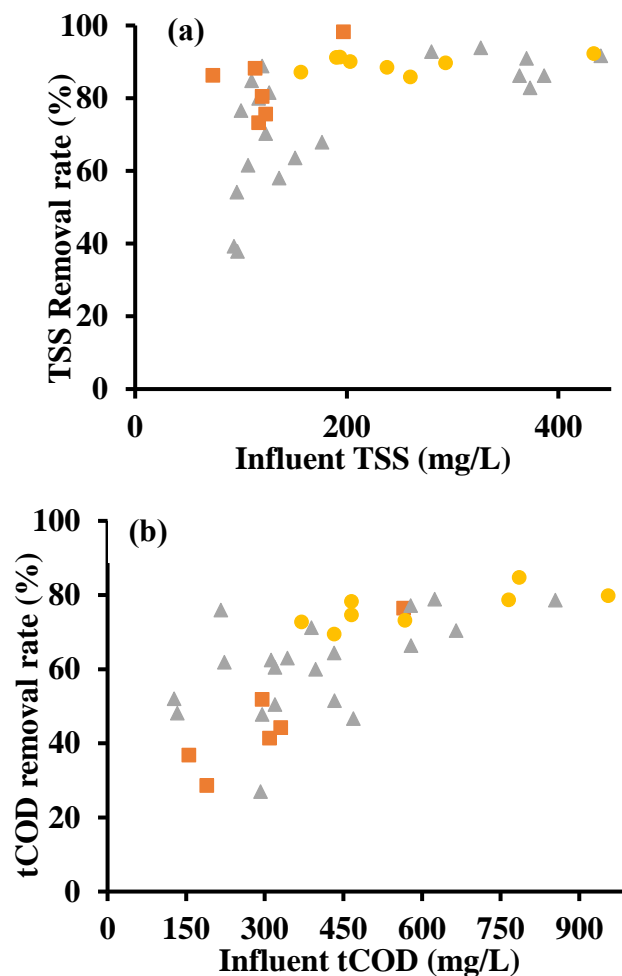
The relationship between raw wastewater concentration (TSS, tCOD, sCOD and TP) and corresponding removal rates for the test clarifier was plotted to determine if there was any correlation. To discern if the type of chemical dosing impacted the removal

rate relative to influent characteristics, Figures 3-4 (a) – (d) were generated, which include data for phases-1, -2 and -3 where: Alcomer + ferric chloride; ferric chloride; and PACl + ferric chloride, were added to the test clarifier, respectively.

From the plots of raw TSS concentration vs the observed removal rate (Figure 3-4(a)), there was no significant correlation ($r^2 < 0.3$) observed under all test scenarios (Phase 1, Phase 2 and Phase 3). This result is consistent with past research, Exall and Marsalek, (2013) that reported that performance of PACl on the removal of TSS will not depend on the initial TSS concentration.

For the relationship of tCOD, sCOD and TP concentration relative to the corresponding removal rate, an interesting phenomenon was found, whereby the removal rates increase with the increase of the respective influent wastewater concentration only during phase 1 when Alcomer was used ($r^2 = 0.8$ to 0.9). However, this relationship between removal rates and influent concentrations of tCOD ($r^2 = 0.5$), sCOD ($r^2 = 0.2$) and TP ($r^2 < 0.1$) was not observed when PACl (Phase 3) was used as a polymer (Figures 3-4(b), 3-4(c) and 3-4(d)). This finding clearly demonstrates that COD and TP concentrations may influence the respective removal rates for Alcomer, but not PACl. This might be attributed to the difference in the removal mechanisms of the two polymers. The dominant removal mechanism for Alcomer is bridging and that of PACl is polymer both charge neutralization and bridging. It should be noted that no dependency on influent characteristics for PACl could indicate that the polymer

behaves similarly when applied to wastewater of varying characteristics thus results can be applicable to other sites. A comparative evaluation between the TP/TSS ratio as a parameter to evaluate the TP removal efficiency across all three phases was also conducted. As depicted in Figure 3-4(e), for PACl addition (Phase 3), TP/TSS ratio and TP removal are negatively correlated ($r^2 = 0.6$) and in the other two scenarios (Phase 1 and Phase 2) TP removal is independent of TP/TSS ratio ($r^2 < 0.1$). Therefore, at higher TSS concentrations, TP removal is adversely affected when PACl is added which is in agreement with studies conducted by Szabo et al. (2008) that observed less efficient phosphorus removal at higher TSS concentrations.



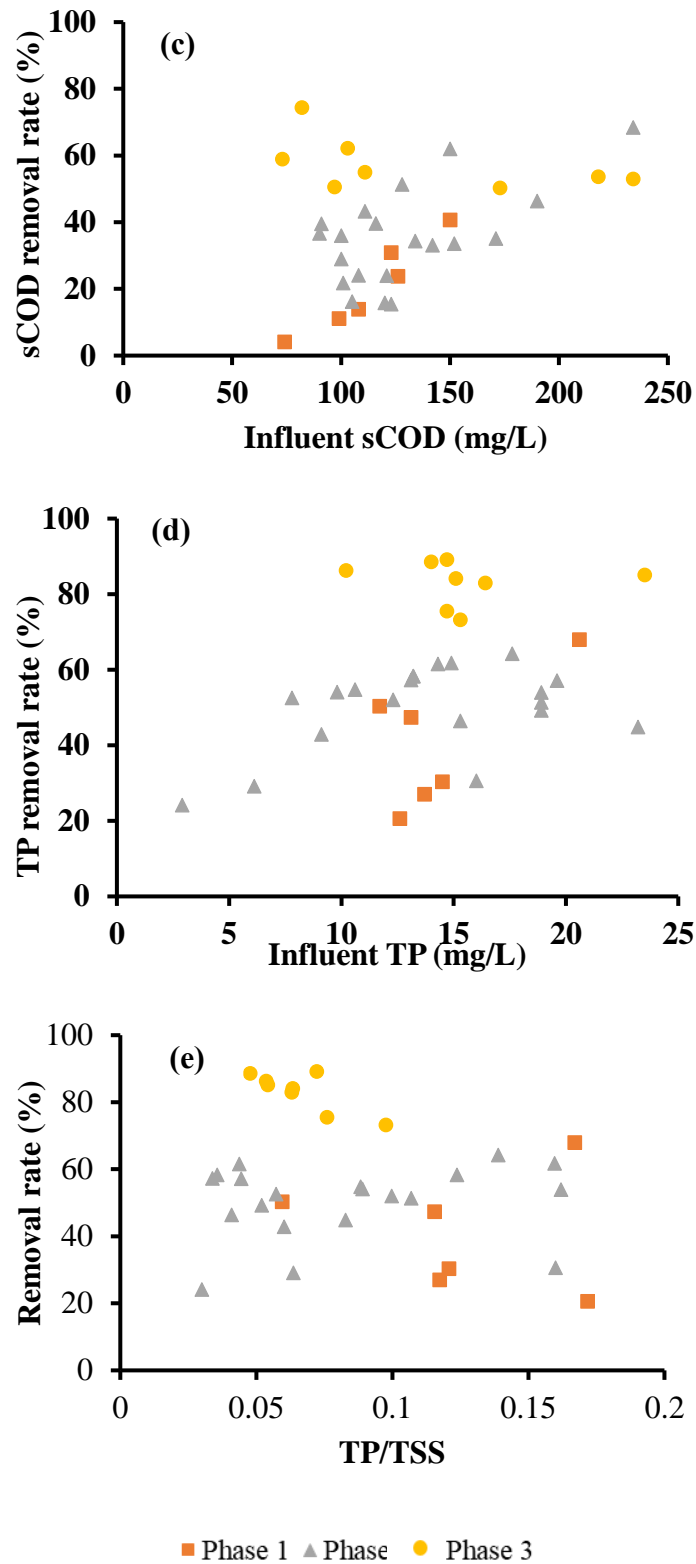


Figure 3-4: Effect of influent characteristics on removal rate (a) TSS, (b) total COD, (c) soluble COD, (d) TP concentration and (e) TP/TSS ratio.

Furthermore, when Alcomer was added, the removal rate of sCOD increases when the tCOD concentration in the influent wastewater increases. Again, the tCOD concentration has no impact on the sCOD removal efficiency when PACl was added (Figure 3-5).

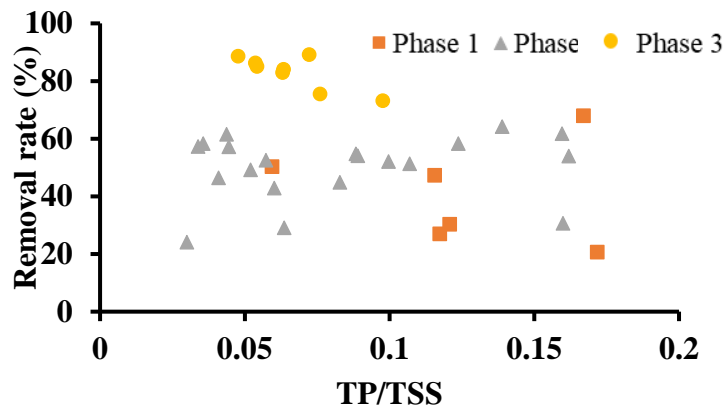


Figure 3-5: Effect of total COD on soluble COD removal.

3.3.5 Influence of influent characteristics on removal rates during summer versus winter season

In this section the impact of influent characteristics on removal rates were further characterized by comparing the summer versus winter data of the test clarifier during alcomer polymer addition. The results were consistent with observations made in section 3.3.4 except for sCOD removal where higher removals were observed during summer season. For example, at sCOD concentration of 100 mg/L the corresponding removal rate during winter was 10% whereas the removal increased to 30-50% during summer season. This difference may be attributed to the presence of a larger colloidal fraction during summer season (Leal et al., 2011, Halalsheh et al., 2005). This also explained the discrepancy between the jar tests versus full scale sCOD removal data for PACl where the jar test that was conducted during winter showed 20% removal whereas

an average removal of 60% was demonstrated during full scale testing that was conducted during summer/fall season.

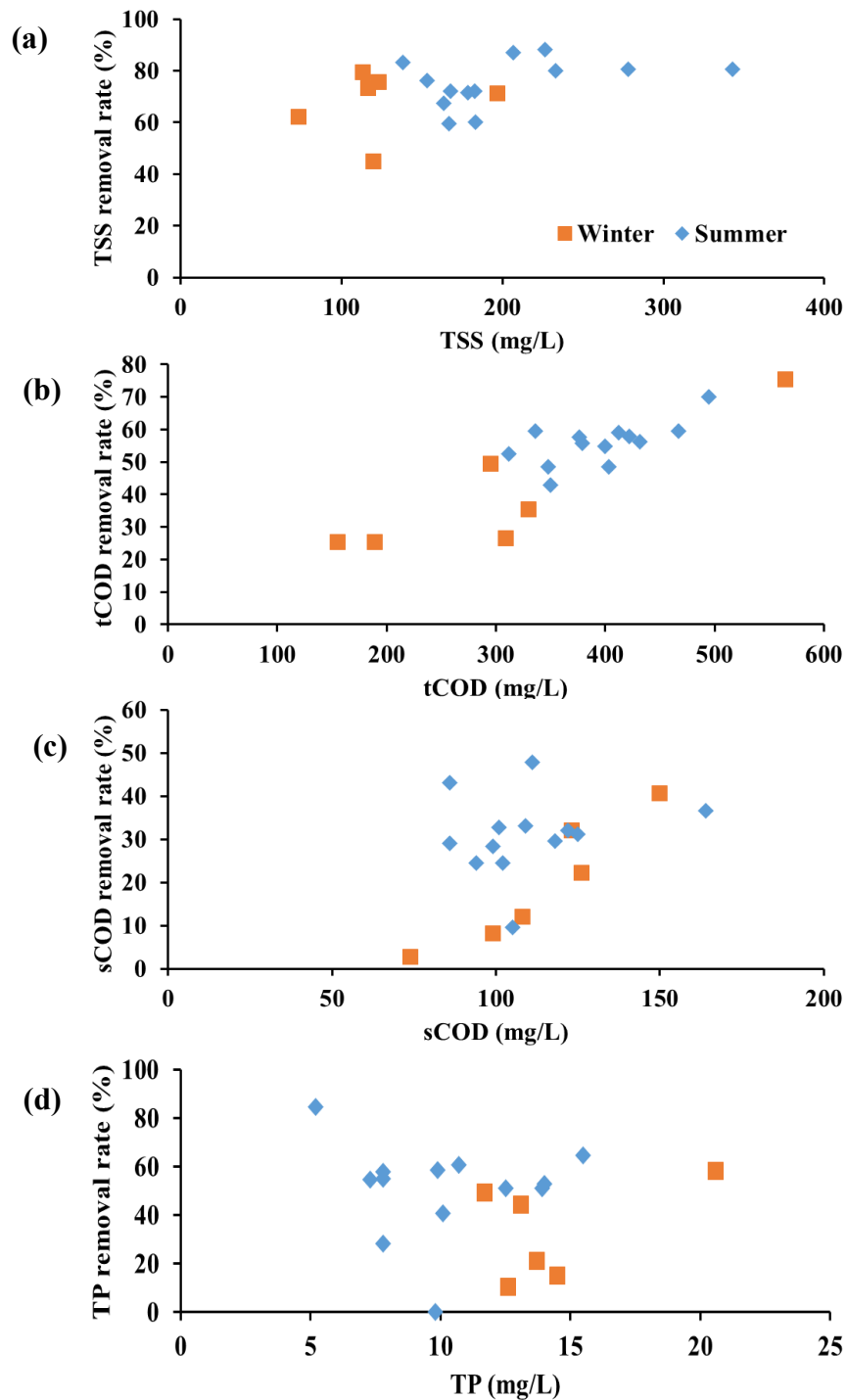


Figure 3-6: Effect of influent characteristics on removal rate during winter versus summer season (a) TSS concentration, (b) total COD, (c) soluble COD and (d) TP

3.4 Conclusions

This study has demonstrated that the optimized CEPT has successfully achieved both carbon redirection and nutrients removal in full scale application. The effect of polymer addition on CEPT was investigated at different operating conditions. Key findings can be summarized as follows.

- Through the jar test of ferric chloride and 7 polymers, 15 mg/L ferric chloride and 0.5 mg/L PACL was selected as the best coagulant and flocculant combination determined by a simplified comparison matrix.
- The application of 15 mg/L ferric chloride and 0.5 mg/L PACL in full-scale primary clarifier operation had a demonstrated removal efficiency of 76% tCOD, 58% sCOD, 89% TSS and 84% TP.
- Removal rate of TSS was independent of influent TSS concentrations in all scenarios.
- The removal of tCOD, sCOD and TP had a positive relationship with their corresponding concentration when the polymer Alcomer was used, whereas no correlation between removal and concentration was observed with PACl.
- Soluble COD removal appeared to be season dependent where the removals were lower during winter season which could be attributed to lower colloidal fraction during winter season.

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Chapter 4

4. The impact of CEPT on the downstream processes

4.1 Introduction

The application of chemical coagulants and flocculants such as ferric chloride, polyaluminum chloride or alum is increasing in the chemically enhanced primary treatment (CEPT) process as a practical method of achieving simultaneous carbon redirection, TP removal and TSS removal. While all these are required qualities in terms of resource recovery, its impact on the downstream liquid train (aeration process) and/or downstream anaerobic digestion process needs to be further studied.

There are several previous studies that looked at the application of CEPT process and the impact of tCOD/N ratio in the downstream denitrification process (Eddy et al., 2013, Van Nieuwenhuijzen et al., 2000, Sobieszuk and Szewczyk, 2006). If a large amount of tCOD is removed by the addition of chemicals in the primary clarifier, nitrogen removal will be decreased due to the lack of COD carbon source (Van Nieuwenhuijzen et al., 2000). From the electron balance of nitrogen reaction, the minimum requirement of tCOD for nitrification and denitrification is 1.71 g tCOD/gN. Furthermore, the microorganism in wastewater also needs carbon to grow. Therefore, the actual demand for tCOD/N ratio is 6 to 10 g tCOD/gN (Golterman, 1985, Sobieszuk and Szewczyk, 2006, Roy et al., 2010). In order to make up the deficit in carbon for the downstream biological denitrification, some novel, low tCOD/N-tolerant nitrogen technologies, such as Anammox or nitrogen removal over nitrite have been introduced in the

wastewater treatment processes (Kartal et al., 2010). If the Anammox can be applied, a tCOD/N ratio which is as low as < 1 g tCOD/gN is shown to be sufficient for the removal of nitrogen (Joss et al., 2009, Wett et al., 2000, Zeng et al., 2016). The application of a low tCOD/N-tolerant process like Anammox can significantly be advantageous for energy saving and space requirement in the future development of the wastewater treatment process (WWTP). However, the effects of the CEPT process on conventional aeration processes and more specifically on the aeration tank sludge quality such as its sludge volume index (SVI) and on the effluent quality such as TP and TSS concentration are unclear.

With the improved removal of CEPT compared to the conventional primary treatment, a large number of organic matter, phosphorous and solids are concentrated in the sludge (solid train) instead of flowing into downstream processes referred to as the liquid train. Several studies have been done on the effectiveness of the CEPT process; however, there has been limited work on the characteristics of the CEPT product such as the gas production of CEPT sludge.

Some studies have suggested that the sludge produced by the coagulation and flocculation in CEPT with ferric or alum is less degradable than the sludge generated by the conventional primary treatment, which is measured by the biogas or the methane production (Dental and Gossett, 1988; Guan, 2005; Hsu and Pipe, 1973). Cabirol et al. (2003) investigated the effect of aluminum and sulphate compounds on the specific methane activity, which showed that aluminum and sulphate inhibit methanogenic and

acetogenic bacteria, resulting in a 50% to 72% and 48% to 65% decrease in the specific methanogenic activity bacteria, respectively. If the combined aluminum-sulphate coagulant is used in CEPT, a higher inhibition on the specific methanogenic activity was displayed (Cabiol et al., 2003). Lin et al. (2017) examined the inhibition effect caused by ferric chloride and poly aluminum chloride (PACl) and showed that the ferric chloride at dosages of 10 to 30 mg/L has little effect on the sludge hydrolysis and volatile fatty acid (VFA) production. On the other hand, 8 mg/L PACl does have an apparently inhibitory impact on the organic hydrolysis of the sludge. However, Kim and Chuang (2015) reported that both ferric chloride and PACl have an inhibitory impact on the VFA production, even at a small dosage. Moreover, the inhibitory effect on VFA production will be more severe when the dosage of PACl is over 102 mg/L (Kim and Chuang, 2015). Contrary to these observations, Kooijman et al. (2017) showed that the addition of coagulant and flocculant could increase the hydrolysis rate, resulting in a higher biomethane potential (BMP), because of the substantial removal of readily degradable biomass by coagulation and flocculation. Kooijman et al. (2017) checked the dewaterability of the CEPT sludge and the results depicted that coagulated and flocculated sludge has a lower CST value compared to the sludge without chemical addition, which is probably due to the lower fraction of small particles in the CEPT sludge (Kooijman et al., 2017).

A review of the literature showed that although some work has been done on the impact of CEPT processes on the downstream solid and liquid train, there is still (1) a lack of

critical examination regarding the influence of CEPT process on the aeration process and final effluent, and (2) for the solids train, there remain some conflicts concerning whether the coagulant and flocculant have a positive or negative effect on the performance of sludge fermentation or the methane production. Therefore, the objectives of this study were to (1) investigate the impact of PACl on the anaerobic biodegradability of sludge and (2) evaluate the addition of PACl on the downstream sludge settling characteristics and effluent quality of the activated sludge process.

4.2 Material and Methods

4.2.1 Anaerobic digestion and Biomethane potential (BMP) test setup

In this study, anaerobic digestion of CEPT sludge 1) from the control primary clarifier (dosed with ferric chloride (15 mg/L)) and 2) from the test primary clarifier (dosed with ferric chloride (15mg/L) and PACl (0.5 mg/L)) of Vauxhall WWTP was performed to evaluate the impact of PACl addition in primary clarifiers.

The anaerobic digestion experiments were conducted in an orbital shaker (Thermo scientific Model Max Q 4000) (Figure 4-2) for testing the anaerobic digestibility of the sludge. In addition, bio-methane potential (BMP) tests (Figure 4.3) were conducted in parallel to evaluate the methane production potential. All anaerobic digestion experiments and BMP tests were conducted with 500 mL serum bottles (working volume of 400 mL) using an inoculum obtained from a secondary anaerobic digester of Guelph's (Ontario, Canada) municipal wastewater treatment facility. The serum bottles

in the orbital shaker were agitated at 150 rpm throughout the duration of the study. Both the orbital shaker and the BMP reactors were set at 38.5 °C.

The test was conducted using food to microorganism (F/M) ratios of 0.1, 0.25, 0.5 and 0.75 calculated as per Equation 4-1. The proportion between the substrate and seed sludge was calculated according to the F/M ratio. A control with the only inoculum was included to make a baseline for the biogas produced by the inoculum in the BMP tests. All experiments were conducted in duplicates.

$$\frac{F}{M} = \frac{VSS_{substrate} * V_{substrate}}{VSS_{seed} * V_{seed}} \quad (4-1)$$

Where F represents substrate concentration (mg/L), M represents microorganism concentration (mg/L), VSS is the volatile suspended solids (mg/L) of substrate or seed, and V (L) is the volume of substrate or seed added.



Figure 4-1: The set-up of anaerobic digestion batch test.

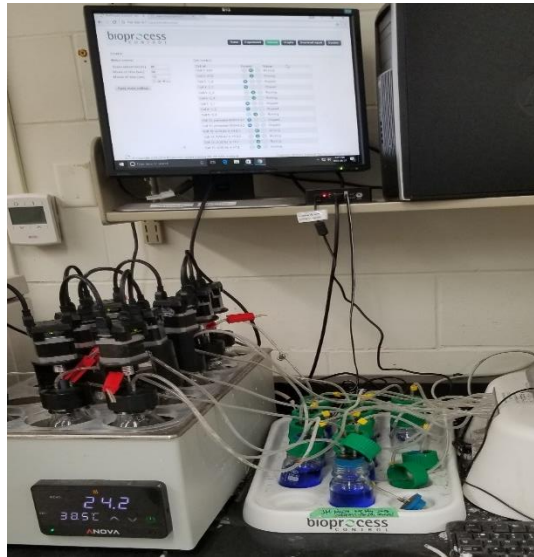


Figure 4-2: The set-up of anaerobic digestion batch test.

4.2.2 Analytical schedule and methods

Sludge samples were taken from the outlet of each batch serum bottle and analyzed for pH, TSS, VSS, tCOD, sCOD, TP and PO_4^{3-} at 0th, 1st, 4th, 8th and 15th day. The gas produced by the biomethane potential (BMP) test bottles was scrubbed with a 3M NaOH solution to remove CO_2 . The produced methane was measured over time by Bioprocess Control (Lund, Sweden), which is an automated methane potential system.

Sludge volume index (SVI) and mixed liquid suspended solids (MLSS) of the activated sludge and secondary clarifier effluent wastewater quality parameters (ammonia, total suspended solids (TSS), 5-day biochemical oxygen demand (BOD_5) and total phosphorus (TP)) of both downstream processes were obtained from the City of London. For the anaerobic digestion experiments, TSS and volatile suspended solids (VSS) were measured using standard methods (APHA et al., 2005); and total chemical oxygen

demand (tCOD), soluble chemical oxygen demand (sCOD), TP and phosphate were determined by using HACH analyzer kits (HACH, USA).

4.2.3 Statistical method

The assessment of the difference between different datasets was made using a *t*-test, MINITAB 18 (Minitab Ink., State College, PA), a statistical software which was used to determine the *t* critical value through the *t*-test.

4.3 Results and Discussion

4.3.1 Biomethane potential (BMP) and anaerobic digestion tests

During the BMP tests, the methane production profile per gram COD fed of the primary sludge of control and test clarifiers was plotted (Figure 4-3). The methane production of sludges was quite different during the first two days. The produced methane of all samples was considerably higher than the methane generated by the raw seed sludge over the whole period, showing that both sludge samples generated by the CEPT process are not toxic to the anaerobic biomass. Comparing the digestibility of the control and test clarifier sludge, sludge samples with only ferric chloride displayed a higher methane production rate compared to the methane production of the sludge samples with both ferric chloride and PACl at F/M ratio 0.1, 0.25 and 0.5. Although the addition of PACl resulted in a high removal of tCOD and sCOD compared to the addition of ferric alone, (which can be concentrated to the sludge), the methane production with the addition of PACl was 20% to 30% lower than the sludge which is

generated by the sludge with only ferric chloride. This result may be because of the toxicity of PACl which can inhibit the methane production. This phenomenon is also reported by Kim and Chuang (2014) who state that even a small dosage of PACl will cause the decrease in the VFA concentration and further reduce the methane production. Moreover, suspended solids are assembled by polymeric chain which is formed by $\text{FePO}_4/\text{AlPO}_4$ and $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ after the addition of ferric chloride and PACl. The formed clusters are aggregated to form large flocs and settled to the bottom as CEPT sludge (Lin et al., 2017). The aggregated sludge flocs would create a “cage” effect which can limit bacteria and enzymes to access the particulate organic inside the floc, leading to the reduced degradability and degradation kinetics of the CEPT sludge from the test clarifier (Dentel and Gossett, 1982; Gossett et al., 1978). Thus, the number of solid organics in the floc formed by the addition of PACl is limited to be hydrolyzed into the supernatant. However, for the floc formed by the ferric chloride addition, the reduction reaction from Fe (III) to Fe (II) occurs rapidly under anaerobic conditions (Nielsen, 1996). Thus, the transformation of Fe during anaerobic digestion can accelerate the disintegration of sludge flocs. Because of the reduction of sludge flocs, hydrolytic bacteria and enzymes can assess a much greater surface area of the solid organics, and consequently, there will be no inhibitory impact caused by ferric chloride on the hydrolysis of organics in CEPT sludge from the control clarifier (Lin et al., 2017).

At the same time, it can be seen from the comparison of different F/M ratios (Figure 4-3), that if the F/M ratio increases, the corresponding methane production would

decrease, which means that in the case of higher F/M, metabolic imbalance will happen because the substrates have exceeded the needs of the microbes (Hadiyanto et al., 2015). The appearance of this imbalance may be due to the possibility of contact with the substrate, and it is smaller when the number of microbes is much less than the substrate. Moreover, higher substrate concentration will result in excessive diffusion to the cell which causes the microbes to rupture (Hadiyanto et al., 2015). On the other hand, the high F/M ratios became less advantaged as the values of methane generation are divided by a larger number of COD each time (Kolsoy and Sanin, 2010).

However, after a short “fall behind” period, the methane production from test sludge at $F/M = 0.75$ caught up and showed similar methane production with those of control sludge. That could be because the high F/M ratio has limited biomass, and excessive acids products which will inhibit the methane production for both sludges.

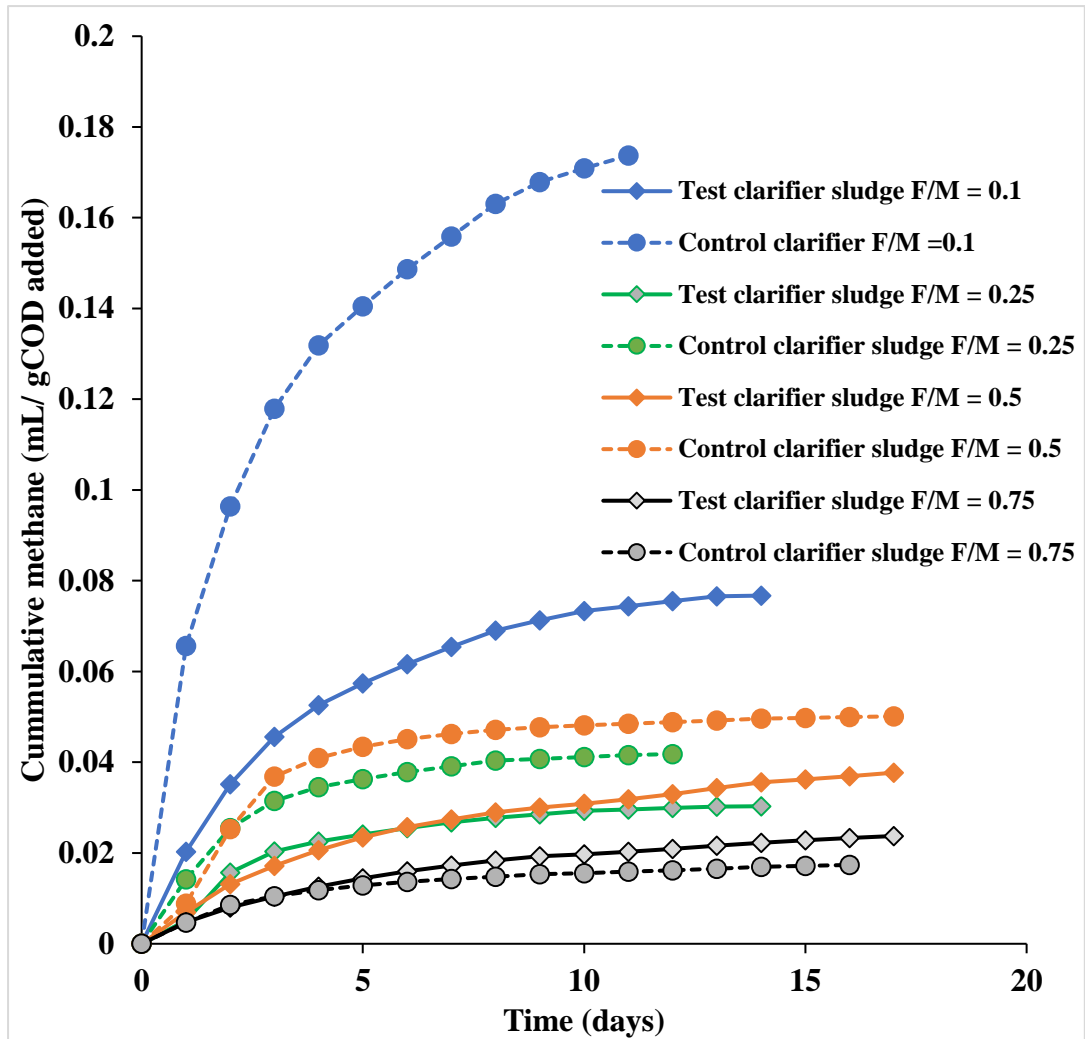


Figure 4-3: Methane production during BMP tests.

4.3.2 The impact of CEPT on the downstream process

4.3.2.1 The impact of CEPT on the activated sludge process

The sludge volume index (SVI) data for the aeration process is shown in Figure 4-4.

The average SVI for the test section is $85 \pm 15 \text{ mg/L}$ which is significantly ($P \text{ value} = 0.01$)

higher and better than that of the control section ($74 \pm 7 \text{ mg/L}$). Although both are in the

normal range (50-150 mg/L), the sludge from the control section is dense and has rapid

settling characteristics when the SVI is less than 80 mg/L, which is always attributed to

an old and over-oxidized sludge in an extended aeration facility (Jenkins et al., 2004).

Furthermore, the sludge with low SVI would settle rapidly, resulting in less contact time for the colloidal fraction to become bigger, so the supernatant above the settled sludge blanket has a cloudy appearance. Therefore, the TSS concentration in the effluent may be high in the control section. According to Metcalf and Eddy (2014), a value of 100 mg/L is considered as a good settling sludge, so the influent with ferric chloride and PACl improve the sludge quality of its downstream process. The average mixed liquid suspended solids (MLSS) of the control and test sections were depicted in Figure 4-4. The MLSS for the two sections were not statistically different (P value=0.6); they were 1796 ± 119 mg/L for the control and 1775 ± 134 mg/L for the test section. This is because the MLSS of the two sections is constantly maintained through controlling the waste activated sludge flow (Personal communication: City of London WWTP operators). Therefore, it is difficult to investigate the impact of PACl addition in the CEPT process on MLSS.

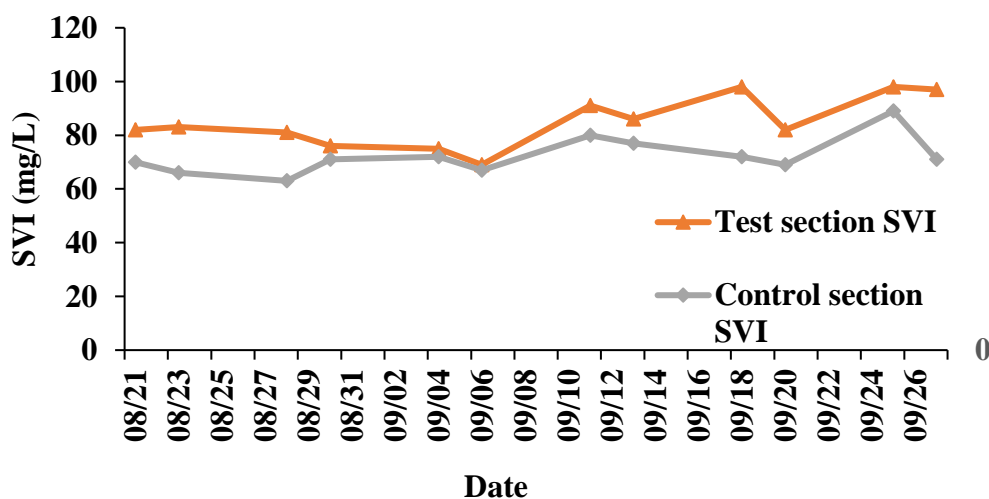


Figure 4-4: SVI for control section and test section.

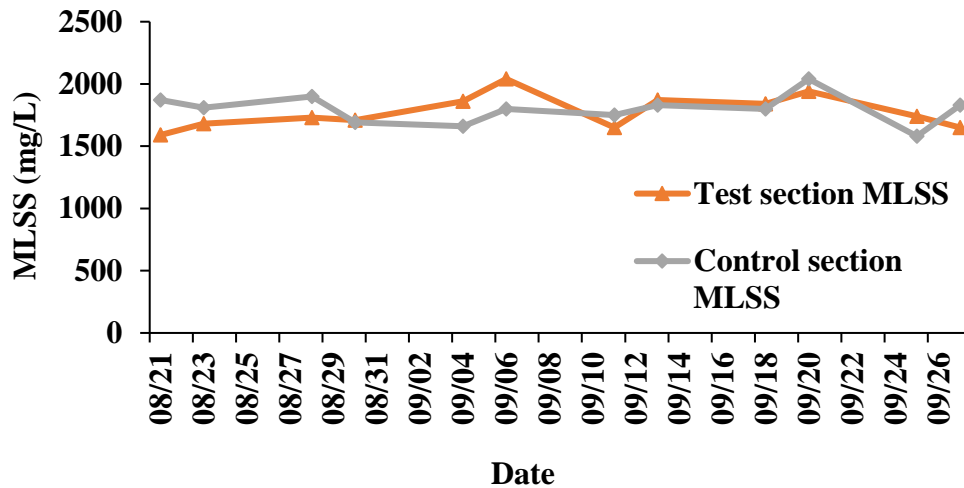


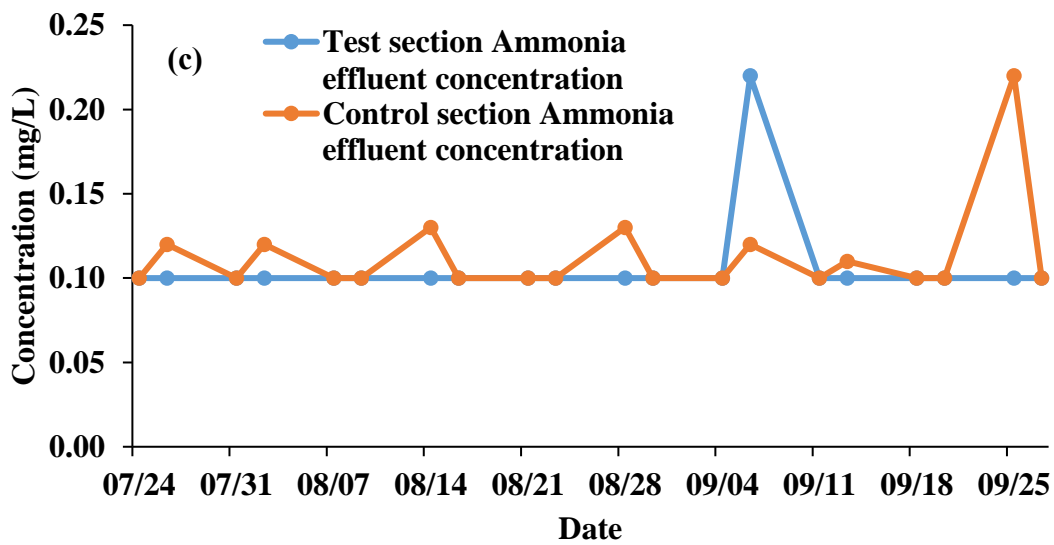
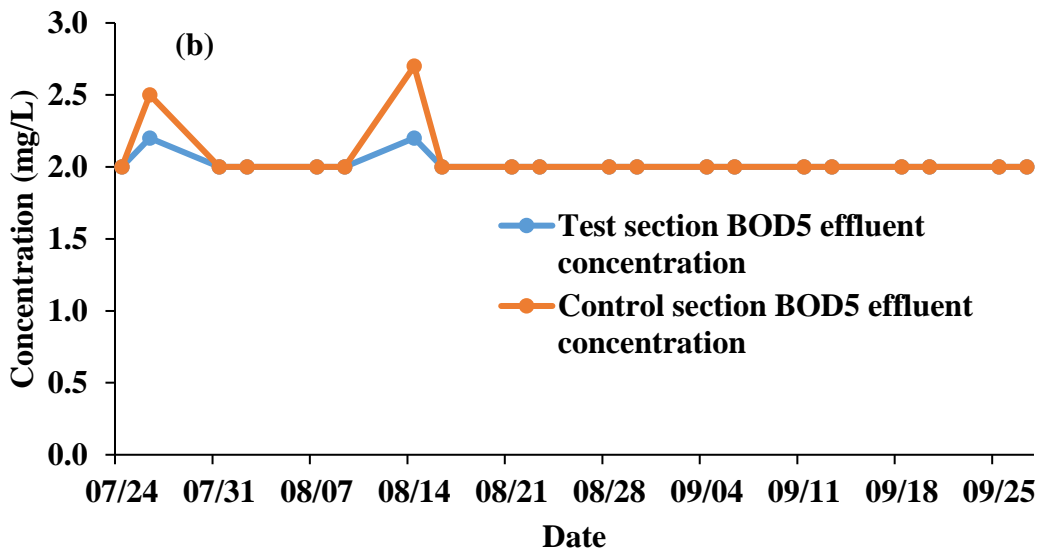
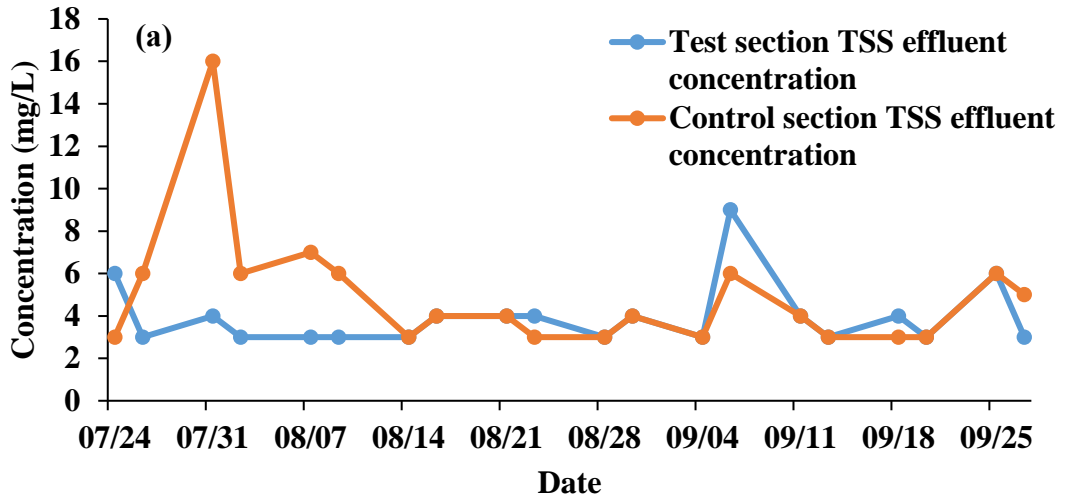
Figure 4-5: MLSS for control section and test section.

4.3.2.2 The impact of CEPT on the effluent of secondary clarifier

The concentrations of TSS, BOD₅, ammonia, and TP from the effluent of final clarifiers of the control and test sections are shown in figures 4-5 (a), (b), (c) and (d). The average TSS concentrations for control and test sections are 4.9±1.3 mg/L and 3.9±0.8 mg/L, respectively. The TSS concentrations from both sections have met the effluent quality standard (15 mg/L) for Vauxhall WWTP. The test section showed stable and significantly lower effluent TSS (3.9±0.8 mg/L) than the control section effluent TSS concentration (P value = 0.2) possibly due to the good sludge quality in the activated sludge process which showed a better SVI value. The good activated sludge quality, in turn, could be attributed to the addition of PACl in the test primary clarifier. In comparison, the TSS concentration in the effluent of the control section would exceed the effluent limit sometimes. For the effluent concentration of BOD₅, the performance of 2 sections were quite similar (P value = 0.18), which are 2.06±0.02 mg/L and 2.02±0.02 mg/L respectively and the effluent quality regarding the BOD₅ concentration is far below the approved limit which is 20 mg/L.

In terms of ammonia removal efficiency (Figure 4-5 (c)), the concentrations of two sections exhibited the same result which is 0.11 ± 0.1 mg/L. Although on Sep 6th and Sep 25th, the ammonia concentration for the test section and control section had suddenly increased, this is because of the higher ammonia concentration than usual. As it is stated in section 4-1, the actual demand for tCOD/N ratio should be 6 to 10 g tCOD/gN for nitrogen removal in the aeration process (Golterman, 1985; Sobieszuk and Szewczyk, 2006; Roy et al., 2010), and the actual average of tCOD/gN ratio for the test and control sections are 6.7 and 11.7, respectively. Therefore, although the CEPT in the test section had removed around 80% of tCOD before the activated sludge process, the rest of the tCOD in the effluent of the primary clarifier is still enough for the nitrogen removal in the downstream.

As can be seen in Figure 4-6 (d), the average TP concentrations of the control section (0.43 ± 0.03 mg/L) was significantly higher than test section (0.29 ± 0.04 mg/L) (p value = 0.22). The TP concentration in the control section exceeds the effluent standard limit (0.75 mg/L) on some occasions (Figure 4-6 (d)). Therefore, it can be envisaged that the PACl addition in the primary clarifier of the test section improved the phosphorus removal.



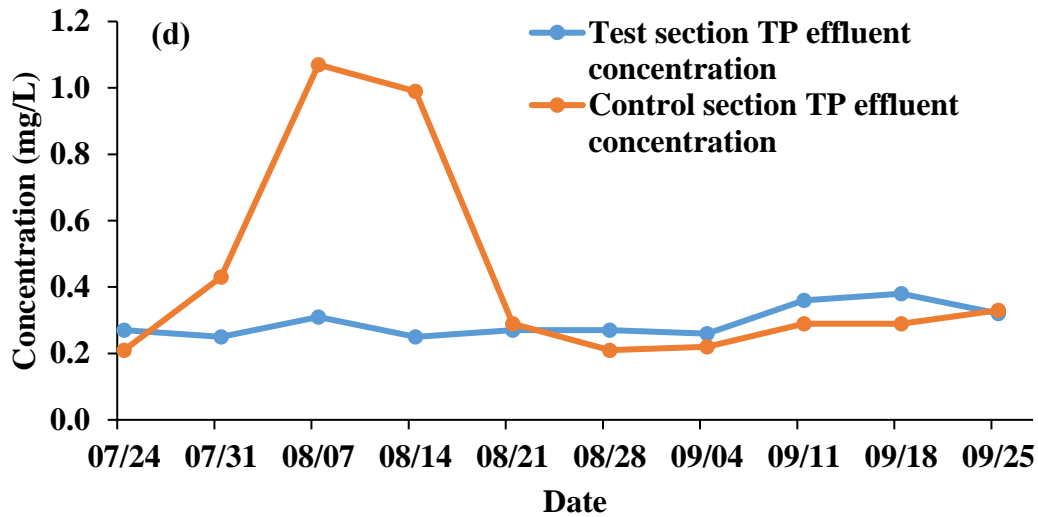


Figure 4-6: Secondary clarifier effluent characteristics of control and test sections (a) TSS concentration. (b) BOD5 concentration. (c) Ammonia concentration (d) TP concentration.

4.4 Conclusion

This study has demonstrated the performance of CEPT sludge at different F/M ratios, the impact of polymer addition on the activated sludge processes, and the effluent quality of the secondary clarifier. The significant findings can be summarized as follows:

- The methane production per gram of added tCOD of control clarifier is higher than test clarifier sludge at F/M ratios 0.1, 0.25 and 0.5. Therefore, the addition of 0.5 mg/L of PACl has an inhibitory effect on the methane production.
- The generated methane per gram of tCOD added is negatively related with the F/M ratio. The higher the F/M ratio, the lower methane production per gram of added tCOD.
- The addition of PACl in the test clarifier has improved the SVI of the sludge in the activated sludge process.

- The TSS and TP concentrations in the effluent of the secondary clarifier of the test section are 20% and 33% lower than that of the control section.
- Effluent BOD₅ and ammonia concentration of the downstream process is not affected by the addition of PACl as the primary clarifier.

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Chapter 5

5. Conclusion and future research direction

This chapter presents the key findings based on the current work and lays out recommendations for future research.

5.1 Conclusion

The following conclusions can be made from this study.

- A combination of 15 mg/L ferric chloride and 0.5 mg/L PACl was selected as the best combination of coagulant and flocculant for CEPT.
- The 15 mg/L ferric and 0.5 mg/L PACl dose applied in the full-scale primary clarifier operation demonstrated 79% tCOD, 58% sCOD, 89% TSS and 84 % TP removal efficiencies. Thus, the optimized performance of the primary clarifier achieved carbon redirection and nutrients removal simultaneously.
- TSS removal efficiency is independent of the raw influent TSS concentration in all different scenarios.
- The removal efficiencies of tCOD, sCOD and TP have a positive relationship with the corresponding concentration when Alcomer was adapted, whereas no correlation was found between the removal efficiency and concentration when PACl was used.
- The sludge produced from CEPT dosed with ferric chloride and PACl showed less methane production rate compared to the sludge produced from CEPT dosed with ferric chloride

- The addition of PACl in the primary clarifier can improve the SVI of the sludge in the activated sludge process and reduce the TP concentration in the effluent of the secondary clarifier. The TSS concentration is also improved by the better SVI in the test section. BOD₅ concentrations in the effluent are similar between 2 sections.

5.2 Future research direction

The following recommendations for future research can be made to complement and extend the current study.

- The impact of PACl on the fractionation of effluent of the primary clarifier should be investigated to fully understand the impact of PACl on the primary clarifier.
- It is recommended that research be conducted to study how to increase the methane production from the sludge produced from CEPT dosed with ferric chloride and PACl.
- Phosphorus recovery from CEPT sludge can be studied for nutrient recovery.
- Further work needs to be done to establish the argument that PACl added in the CEPT process is toxic and/or inhibitory for the biomethane producing microbial community.

Appendix A:

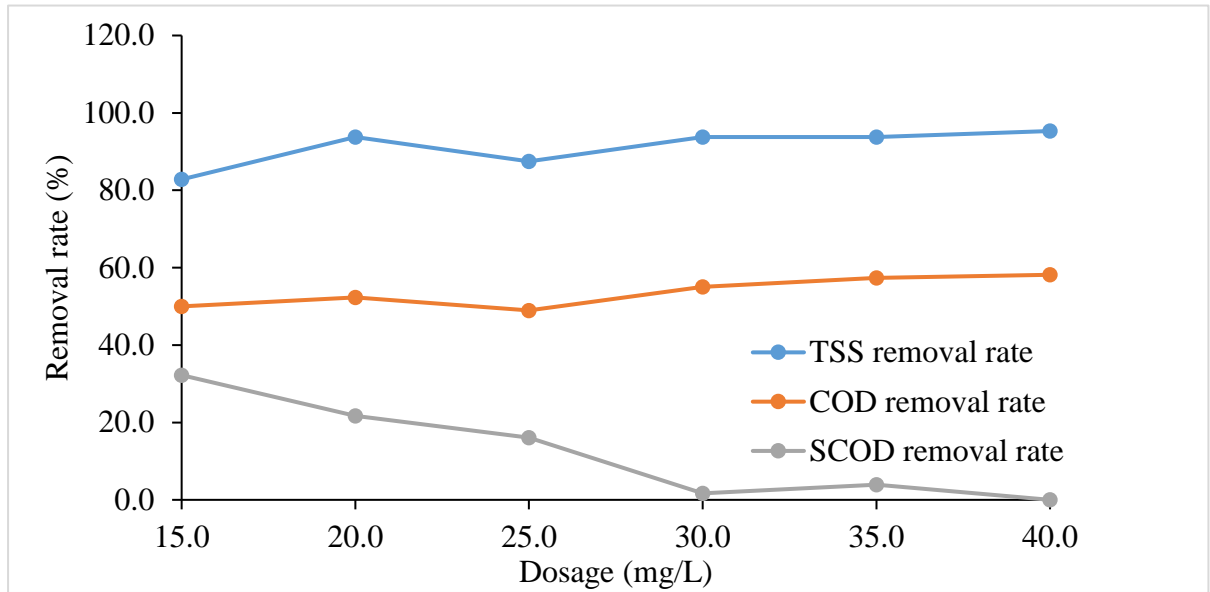


Figure A: Removal efficiencies of TSS, tCOD, sCOD with only ferric chloride addition

Appendix B:

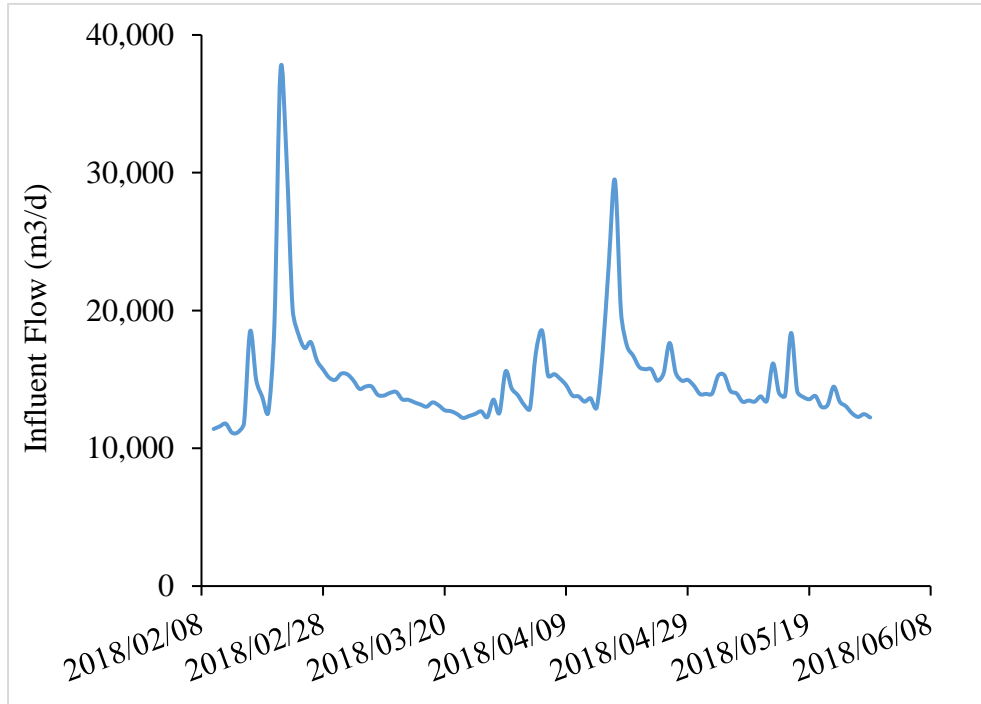


Figure B1: Wastewater flow profile

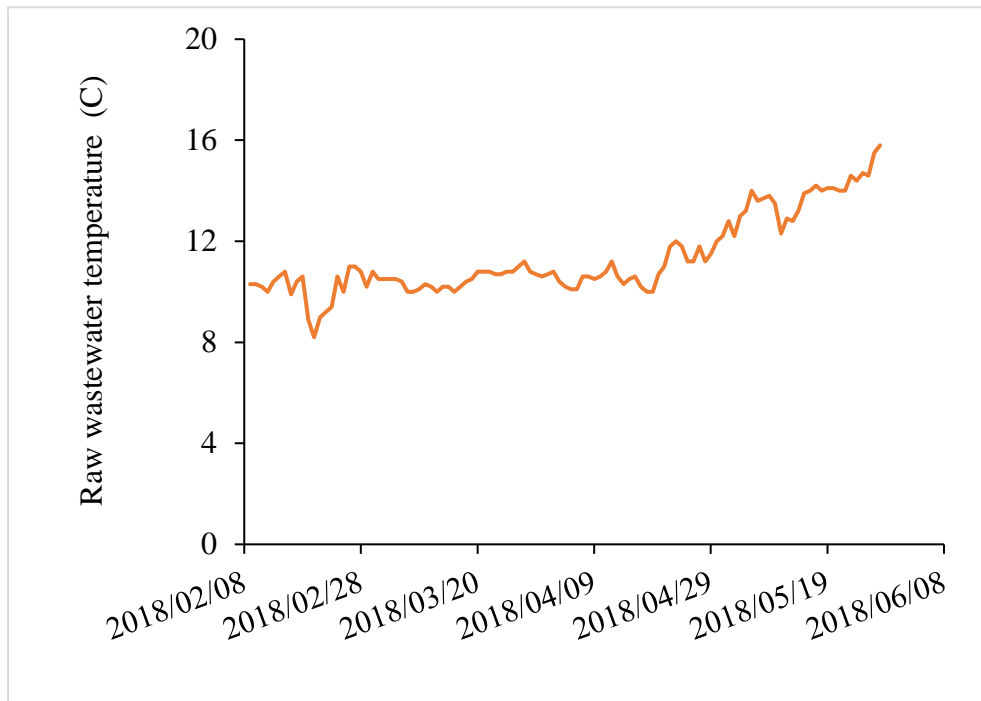


Figure B2: Wastewater temperature profile

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