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Chemically enhanced primary treatment: Modelling and Resources Recovery

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Abstract

The chemically enhanced primary treatment (CEPT) process is gaining momentum for carbon redirection, thereby lowering the downstream liquid train load and maximizing energy recovery from the primary sludge. CEPT technique enhances coagulation and flocculation that enable faster settling of particulate and colloidal solids and dissolved ions such as phosphate to enhance removal efficiency. Comprehending the dynamic behaviour of CEPT clarifiers is critical to not only develop a reliable whole plant simulation but also fully understand the efficacy of the treatment plant performance. Towards this, a great amount of effort has been contributed to the advancement of primary clarifier models. Modelling and controlling the primary clarifier have vital impacts to characterize the downstream biological and sludge treatment performance accurately, and subsequently, the full plant modelling (WWTP). This research compares and contrasts the performance of three primary clarifier models, including volume-less point separator, three-compartments clarifier and layered flux clarifier concerning the accuracy in describing the CEPT performance. Most importantly, the characterization focused on the models' capability to accurately represent COD fractions, including colloidal COD (C_{COD}), soluble COD (S_{COD}), particulate COD(X_{COD}) and suspended solids (TSS) concentrations of the influent wastewater. For practical applications, our study has shown that among the three clarifier models, the three-compartments model provides a better description of chemicals and polymers addition impacts on primary treatment, and relatively a more straightforward calibration procedure compared to the layered-flux model. The calibrated three-compartment model showed 100% removal of C_{COD}, increased effluent soluble fractions and 87% removal of TSS concentration. Furthermore, the impact of CEPT on the downstream solid train processes was also investigated. An experimental study was conducted on CEPT sludges with different pretreatments (ozonation and low-temperature thermal alkali pretreatments (LTTAP)) in relation to the performance of anaerobic digestion for resource recovery. LTTAP demonstrated an effective COD solubilization degree of 2.30% and 8.71% in ferric-based sludge (CEPT-I sludge) and ferric alum-based sludge (CEPT-II sludge), respectively. Reactive phosphorus increased by 23.05% (CEPT-I LTTAP) and 29% (CEPT-II LTTAP) compare to the control groups. Also, among sludge samples without pretreatment and after ozonation pretreatment, LTTAP presented the highest methane yield (230.11 ±9.97 mL/g VSS added) with an improvement of 46.28% in CEPT-II sludge. During ozonation, the mineralization process occurred along with solubilization, resulted in sCOD concentration decrease in CEPT-I sludge and barely change in CEPT-II sludge. The ozonation improved RP release by 59% in CEPT-II sludge compared to the control sample. Moreover, ozonation pretreatment led to the highest biogas production 233.46±3.53 mL/g VSS added among CEPT-I ozonated sludge and control sludge without pretreatment, with an increase of 41.80% compared to the control. Noteworthy, the sludge produced from CEPT dosed with ferric chloride and PACl showed a slightly lower methane production rate compared to the sludge produced from CEPT dosed with ferric chloride.

Keywords

Modelling, Primary clarifier, Chemically enhanced primary treatment (CEPT), colloidal COD removal, solids COD removal, soluble COD removal, CEPT sludge treatment; pretreatments, ozone, low-temperature thermal alkali treatment, solubilization, anaerobic digestion.

Summary for Lay Audience

Municipal wastewater is a potential resource, and future WWTP designs will primarily target the recovery of energy, nutrients, and potable water from wastewater. Design considerations must be factored not only to produce high-quality effluent but also to minimize operating costs associated with labor, energy (electrical and heating), and byproduct stabilization and disposal/reuse. As a result, advancing/maximizing the use of unit processes or implementing additional treatment processes would be required to achieve those requirements. Primary sedimentation is one of the key processes to remove readily settleable solids and floating material in the liquid stream and to reduce the load to the downstream biological process. Advanced primary treatment such as chemically enhanced primary treatment (CEPT) is a technology that uses suitable chemicals to enhance pollutants removal in the primary stage of the wastewater treatment. To develop the whole plant simulation, and fully understand the effectiveness of the treatment plant, comprehending the dynamic behaviour of CEPT clarifiers is critical. Thus, advancement of primary clarifier models has been the main interest. Nevertheless, very limited study sufficiently evaluated the influences of CEPT on COD and P fractions. Also, almost no studies have fully characterized CEPT effluent and compared and contrasted the effectiveness of 0-D and 1-D models. Furthermore, the CEPT sludge contains a substantial number of all these valuable resources and has high energy value that should be recovered. Anaerobic digestion is a widely used biological process to stabilize activated sludge. This process not only converts organic waste to produce methane (CH_4) energy but also releases organically bound P making it available for recovery. Additionally, numerous amounts of research have been conducted different pre-treatment techniques to overcome the single process limitations (hydrolysis step), However, little research has been focused on the effectiveness enhancement of the anaerobic digestion process on methane and phosphors recovery from CEPT sludge through organic hydrolysis and conversion of non-reactive P (NRP) to reactive P (RP). In our research, we performed combined physical-chemical method and biological method to fully characterize the impacts of chemical addition process on COD on raw wastewater and CEPT effluents, simulation of CEPT process, fractionation of phosphorus in CEPT sludge, ozonation and low temperature thermal alkali pre-treatment techniques to enhance anaerobic digestion performance, and phosphorus recovery analysis.

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List of Abbreviations and Symbol

AD	anaerobic digestion
AHP	acid hydrolysable phosphorus
$Al\ (OH)_3$	aluminum hydroxide
AOPs	advanced oxidation process
BOD	biochemical oxygen demand
BOD_5	5-day biochemical oxygen demand
b_H	decay coefficient
C_{COD}	colloidal cod
C_B	colloidal biodegradable COD
C_U	colloidal unbiodegradable COD
CEPT	chemically enhanced primary treatment
CFD	computational fluid dynamic
EBPR	enhanced biological phosphorus removal
EDCs	endocrine-disrupting chemicals
EPS	extracellular polymeric substances
HAOs	aluminum oxides
HFOs	hydrous ferric
LTTAP	low temperature thermal alkali pretreatment
NRP	non-reactive phosphorus
OP	organic phosphorus
OUR	oxygen uptake rate
PACL	poly aluminum chloride
pAHP	particulate acid hydrolysable phosphorus
PAO	polyphosphate accumulating organisms
PC	primary clarifier
PE	primary clarifier effluent
PFS	poly ferric sulfate
pNRP	particulate non-reactive phosphorus
pOP	particulate organic phosphorus
PO_4-P	orthophosphate-phosphorus
pP	particulate phosphorus
pRP	particulate reactive phosphorus
PSI	polyciliate-iron
PSVD	particle settling velocity distribution
r2	the coefficient of determination
sAHP	soluble acid hydrolysable phosphorus

S_B	soluble readily biodegradable cod (non-VFA) "truly soluble COD"
SC_{COD}	filtered COD
S_{COD}	filtered flocculated COD
sNRP	soluble non-reactive phosphorus
sOP	soluble organic phosphorus
sP	soluble phosphorus
sRP	soluble reactive phosphorus; orthophosphate
SRT	sludge retention time
SWD	side water depth
TAD	thermophilic aerobic digestion
TCOD	total chemical oxygen demand
TDS	total dissolved solids
TKN	total kjeldahl nitrogen
TP	total phosphorus
TPAD	temperature phased AD
tRP/RP	total reactive phosphorus
TS	total solids
TSS	total suspended solids
μ_{max}	maximum specific growth rate of heterotrophs
VDS	volatile dissolved solids
VS	volatile solids
VSS	volatile suspended solids
WAS	waste activated sludge
WERF	water environment federation
WWTP	wastewater treatment plant
X_B	slowly biodegradable COD
X_{COD}	particulate COD
X_E	endogenous decay products
X_{OHO}	ordinary heterotrophic organisms
X_U	particulate unbiodegradable COD
Y_H	biomass yield coefficient

1 Introduction

1.1 Rationale

Primary treatment in wastewater treatment plants has been recognized as a significant research area in advancing wastewater treatment processes sustainability (Tchobanoglous et al.,2014). An improved effort has been made for the optimization and modelling of primary treatment, resulted in a more accurate understanding of the primary effluent characterization and sludge wastage (Banchis et al.,2015). Typically, chemicals are added to the primary clarifier to enhance the removal efficiency and effluent quality. Chemically enhanced primary treatment (CEPT) has been widely used targeting to remove organic carbon, nutrients and contaminants, and concentrate them in the sludge produced, which can increase further the resource recovery (Shewa and Dagnew, 2020). CEPT process involves chemicals adding such as metal salts and/or polymers to accelerate the rate and efficiency of gravitational settling. It has been summarized that CEPT can remove 43.1-95.6% of COD, 70-99.5% of suspended solids, and 40.0-99.3% of phosphate depending on the different wastewater characteristics and type of coagulants and /or flocculants applied (Shewa and Dagnew, 2020). Moreover, CEPT is often operated under excess wet weather conditions to minimize investments on new infrastructure. It has been reported that CEPT improved the hydraulic capacities by up to three times compared to the conventional primary clarifier, which is sufficient enough to handle peak wet weather flows (Banchis et al.,2015). To date, minimal literature exists on the topic of CEPT effluent fractionation and CEPT modelling.

Furthermore, the concept of resource recovery from chemically precipitated sludge has gained great attention. With the improved removal efficiency of CEPT compared to the traditional primary treatment, a large number of organics and nutrients are concentrated in the sludge. The degradability and biogas production from CEPT sludge have been investigated using anaerobic digestion; however, the literature reported contrasting results. Kooijman et al. (2017) stated that the increased organic carbon existence in CEPT sludge could increase in a higher biogas yield in the anaerobic digester or promote autogenous combustion in sludge incineration. On the contrary, Lin et al. (2017) found that poly aluminum chloride (PACL) chemical has an adverse impact on methane generation potential of the sludge, the produced Al-based sludge inhibits the organic hydrolysis due to strong bonding limit the access of bacteria and enzymes. Thus, further studies on the different type of polymers affect the downstream treatment process need to be conducted. More importantly, high phosphate concentration in CEPT sludge could largely benefit the P recovery and recycle process, to produce more fertilizers or other P products. To maximize P recovery and support circular economy, different available pre-treatment technologies (biological, mechanical, thermal and chemical) can be applied to enhance the performance of anaerobic digestion. Specifically, limited data on optimizing P release and non-reactive P (NRP) conversion from CEPT sludge are currently available.

Accordingly, although some studies have been conducted on chemically enhanced primary process modelling with various models and CEPT sludge digestibility, very few have demonstrated detailed CEPT effluent fractionation and the comparison between 0-D and 1-d models to describe CEPT process. Furthermore, almost no studies further investigated how pre-treatment techniques improve CEPT sludge biodegradability and phosphorus release when substantial carbon and nutrients are chemically concentrated into the sludge.

1.2 Objectives

The goal of this research is to (1) characterize CEPT effluent fractions and modelling CEPT process to evaluate the effectiveness of three clarifier models: volume-less point separator, three-compartment and layered-flux, and (2) characterize CEPT sludge and enhance its anaerobic digestibility and phosphorus release with pre-treatment approaches.

First of all, by comparing the performance of three primary clarifier models in regard to accurately describing the long-term full scale CEPT clarifier process in terms of composite and state wastewater parameters. Moreover, the experimental work of wastewater characterization (fractionation) under CEPT using both the physical-chemical method and biological (respirometry) methods were further conducted to substantiate the model performance. Experimental characterization results of raw wastewater (RWW) were fed into the aforementioned three clarifier models as inputs, then compared with the modelled CEPT effluent fractions and experimental CEPT effluent fractions to find which model captures the most realistic results.

Secondly, to overcome the potential inhibition effect of polymer addition and to enhance the performance of solids reduction, biogas production and phosphorus recovery properties of anaerobic digestion, low-temperature thermal alkali pre-treatment and ozonation pre-treatment were selected to implement prior to AD process. The phosphorus characteristic of CEPT sludge was determined at the beginning. The comparative evaluation of different pre-treatments techniques on sludge solubilization and phosphorus release before AD was conducted later. Lastly, the behaviour of anaerobic digestion on pre-treated CEPT sludge and un-treated CEPT sludge in terms of biogas yield and conversion of NRP to RP was evaluated.

1.3 Thesis Format and Organization

Chapter 1 presents an overview of the thesis and rationale behind evaluating CEPT technology as a promising method for efficient solids and nutrients removal. In addition, the importance of characterizing the CEPT process with modelling. It briefly introduces the background of this study and states specific research objectives. Chapter 2 provides a comprehensive literature review of COD and phosphorus fractionation, and the background of the CEPT process, primary clarification process and existing CEPT modelling portfolios, and phosphorus removal technologies and potential pretreatment techniques to enhance AD and phosphorus recovery. Chapter 3 demonstrated a case study of dynamic and Steady-State Modelling of Chemically Enhanced Primary Treatment. Furthermore, phosphorus removal (liquid-stream) and potential release routes (solid-stream) prior to anaerobic digestion from the CEPT process are described in Chapter 4. Finally, Chapter 5 summarizes the main findings of this study and makes several recommendations for future research.

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2 Literature Review

2.1 Introduction

Wastewater is primarily produced from households, institutions, offices and industries, and can be attenuated with rainwater, groundwater and surface water. Direct disposal of untreated wastewater could lead to severe environmental and public health issues such as the production of odors, the depletion of dissolved oxygen and the release of nutrients, pathogenic microorganisms and organic contaminants. Therefore, contaminant source reduction, followed by wastewater treatment, reuse or disposal, is necessary to protect the environment and public health.

Wastewater treatment can remove the constituents by combining various physical, chemical thermal and biological processes. These methods are categorized as physical, chemical and biological unit processes. It has been observed that even these processes are applied in different combinations, the theories involved in each process unit do not change. Physical unit processes include treatment methods predominantly driven by physical forces, for example, screening, settling, mixing, flocculation, sedimentation, flotation, filtration and adsorption. For instance, adsorption is the process of molecules adhesion onto the surfaces of the solid using the forces of attraction to enable the removal. Chemical unit processes involve constituents removal by the addition of chemicals or by other chemical reactions. For example, precipitation, coagulation, gas transfer and disinfection. Chemical precipitates are produced with chemical precipitation and can be removed by settling, filtration, or membrane processes. The most typical example of gas transfer is providing oxygen to water then encourage aerobic reactions. The use of chlorine for wastewater disinfection is another common practice for the chemical unit process. Moreover, biological unit processes involve the removal of constituents by biological activity. The main focus of biological treatment is to remove dissolved and colloidal biodegradable organic substances found in wastewater. These substances are either converted into gases that can escape to the air or biological cell tissue that can be removed by settling or another separation process. Biological wastewater treatment also aims to remove nutrients, including nitrogen and phosphorus. Biological reactions utilize the naturally occurred bacteria; with the proper environmental system, natural bioconversion limitations can be overcome. Overall, to carry out all the wastewater treatment targets, providing an appropriate environment and effective control are the keys.

Plenty of unit processes are combined together to achieve the removal targets and meet the regulations, known as preliminary (physical unit processes), primary (physical unit processes), secondary (chemical and biological unit processes), tertiary (all three unit processes) and advanced treatment. Noteworthy, these terms are arbitrary and insignificant, whereas the required degree of treatment is of the essence. Advanced primary treatment is usually implemented with a chemical addition to enhance suspended solids and organic matter removal. Moreover, advanced treatment can be applied after conventional biological treatment to further remove residual dissolved and suspended materials for water reuse applications.

Municipal wastewater is a potential resource, and future WWTP designs will primarily target the recovery of energy, nutrients, and potable water from wastewater. Design considerations must be factored not only to produce high-quality effluent but also to minimize operating costs associated with labor, energy (electrical and heating), and byproduct stabilization and disposal/reuse. As a result, advancing/maximizing the use of unit processes or implementing additional treatment processes would be required to achieve those requirements.

Clarifiers in wastewater treatment plants are designed to provide four main functions: flocculation, clarification, thickening and storage. Clarifier should facilitate the aggregation of dispersed particles and prevent flocs breakup. Clarified effluent is produced by the separation of liquid and solids fractions. The produced sludge is thickened to reduce the volume. Lastly, clarifiers should be able to store solids under storm weather with peak flowrates. Generally, clarifiers should operate with low sludge blankets, and solids accumulation should only implement during high flow periods. The degree of performance of clarifiers is dependent on the type of unit process. Primary sedimentation is one of the key processes to remove readily settleable solids and floating material in the liquid stream and to reduce the load to the downstream biological process. Performance design objectives for primary clarifiers are typically quantified based on total suspended solids (TSS) and biochemical oxygen demand (BOD) (or chemical oxygen demand (COD)) removal. Efficient primary sedimentation tanks normally can achieve 50 to 70 percent of TSS removal and 25 to 40 percent of the BOD removal (Tchobanoglous et al., 2003). To maximize the performance, the design of primary clarifiers must include considerations of flocculation acceleration and hydraulic short-circuiting prevention. Coagulation and flocculation in primary clarifiers are greatly enhanced in chemically enhanced primary treatment (CEPT), this process uses coagulant and/or flocculant chemicals to remove pollutants such as organic carbon (carbon redirection) and nutrients. The removed constituents from wastewater then concentrate in the sludge produced that can be considered as valuable resources to increase energy and/or nutrient recovery.

Anaerobic digestion emphasizes on energy conservation and recovery and obtains beneficial use of wastewater biosolids; thus, this technique continues to be the widely used process for sludge stabilization (Tchobanoglous et al., 2003). Anaerobic digestion involves the decomposition of organic matter and reduction of inorganic matter without oxygen, CO_2 and CH_4 and a number of byproducts are yielded; the remaining organic matter is in a chemically stable form (Frnazini et al.,1992). The organic carbon transferred to CEPT sludge could enhance the gas production or promote autogenous combustion in sludge incineration. Moreover, the release of organically bound P via hydrolysis under anaerobic conversion, making the P available for recovery (Venkiteshwaran et al.,2018). The removed COD and P fractions from the liquid stream can be recovered from the CEPT sludge through various techniques such as physical, thermal, chemical and biological. Further discussion regarding different techniques is available in section 2.4.2.

2.2 Wastewater Fractionation (fractionation on COD and P)

Due to the fact that the future of a treatment facility is unpredictable, it is necessary to involve process models in the life cycle of a treatment plant. The wastewater treatment plant expects to respond to the increasing level of nutrient removal requirements induced by updated regulations, ageing infrastructures, new processes and changing influent characteristics (Melcer, 2004; Rieger et al.,2012). When applying and developing process models, treatment plants not only can optimize an existing facility but also better coping with the uncertainties about future loads and treatment requirements. To date, few significant trends have been observed in the use of process modelling: whole plant models have been extensively used to investigate interactions between unit processes; integrated models with upstream and downstream water system to further comprehending the mutual effects outside of the plant barrier-line; and basin-scale modelling that gather models from other parts of the water cycle together. Moreover, models are being developed to combine physical-chemical processes and biological processes and other involved equilibrium chemistry to responsible for elemental speciation. Advanced processor power and model development enables the combination of computational fluid dynamics (CFD) and biological models. It should be recognized that modelling gaps in current knowledge and areas can be enhanced and improved as modelling practice become more extensive.

A properly calibrated model can be modified and adjusted over time to correspond with the current situation of the plant, therefore allowing critical decision making (Phillips et al.,2010; Rieger et al.,2012). Good model calibration not only requires the information of model parameters but also adequate knowledge of wastewater characteristics. Wastewater characteristics can be grouped into five categories: carbonaceous constituents, nitrogenous compounds, phosphorus compounds, total and volatile suspended solids and alkalinity. Typically, influent wastewater characteristics vary from one municipal waste to another, from day to day and from site to site. Wastewater fractionation can significantly impact system performance, especially for nutrient removal systems. For example, unbiodegradable particulate COD directly impacts the sludge production and oxygen demand. Thus, the proper characterization of wastewater constituents is crucial in modelling to predict rationale system behaviour.

2.2.1 Fractionation on COD

It has been demonstrated that the characterization of wastewater has a profound impact on the design, operation, and modelling of the biological treatment process. Thus, further analysis based on biodegradability provides a better understanding of wastewater composition (Tran et al., 2015). Typical analytical tests used to determine the total amount of organic matter are biochemical oxygen demand (BOD) and chemical oxygen demand (COD). BOD values represent the amount of oxygen required by microorganisms to break down biodegradable organic materials. The COD value represents the total amount of organic compounds in wastewater. Compared to BOD, COD tests provide complete mass balance among substrates, including biomass, contaminants and dissolved oxygen in terms of electron equivalence. However, the main disadvantage is that the total COD test does not differentiate between biodegradable and inert substances. Thus further COD fractionation is required to represent contaminant removal and biomass growth numerically. Characterization of COD fractions enables a specific decomposition of wastewater but also allows quantification of non-biodegradable contaminants, which reduces the efficiency of biological treatment (Myszograj et al., 2017).

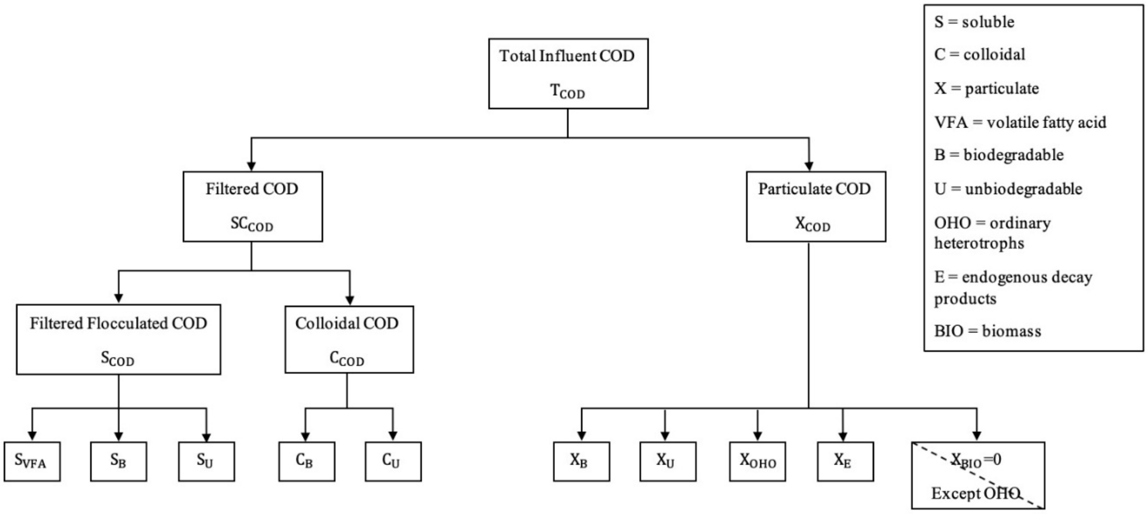

Figure 2-1:Distribution of COD fractions in wastewaters (Adapted from Dynamita SALR)

Figure 2-1 illustrated the various form of COD in wastewater. COD is divided into soluble, colloidal, and particulate categories. Each category can be further fractionated based on biodegradability. Soluble readily biodegradable COD (rbCOD) can be absorbed easily by the biomass, whereas the colloidal and particulate COD has to be dissolved by extracellular enzymes first then to be assimilated. Further, rbCOD consists of volatile fatty acids (S_{VFA}) and complex fermentable soluble COD(S_B). From a modelling standpoint, this fraction has a significant impact on the performance of activated sludge and other biological and nutrients removal processes. Also, accurately quantifying the COD removal in primary clarifier based on a solids percent removal requires to distinguish between non-settable(colloidal) and settable (particulate) matters. The soluble unbiodegradable COD(S_U) leaves the system in the effluent and wastage stream.

Particulate unbiodegradable COD (X_U) contributes to the VSS concentration of the wastewater and end up in the sludge.

2.2.1.1 COD fractions determination based on physical-chemical methods

A substantial amount of work has been demonstrated to develop appropriate experiment protocols for COD characterization, either with physical-chemical methods or with biological methods (Petersen et al., 2003). It has been claimed that the physical-chemical method mostly depends on the filter pore size used. The larger effective pore size of the filter leads to more particulates pass across the filter, which makes the separation between readily biodegradable fraction (rbCOD) and a slowly biodegradable fraction (X_B) less accurate (Gatti,2010). Previously, the pore size of 0.45 μm membrane filters is chosen to be the effective one to collect rbCOD without the presence of colloidal matter. However, the research demonstrated a distinct difference in rbCOD between the sample using 0.45 μm pore size membrane and the pre-precipitated samples (Fall et al.,2011). Currently, the separation over a pore size of 0.1 μm membrane is accepted as an effective size to differentiate the true soluble and particulate organics fractions (Tran et al.,2015).

It is noted that there is no direct or straightforward way to measure the soluble unbiodegradable COD matters (S_U). In 1992, Henze proposed that this fraction can be determined by the measurement of soluble effluent COD subtract the soluble effluent Biochemical Oxygen Demand (BOD) multiplied by a BOD/COD factor ratio (Henze,1992). Moreover, a combination of the physical-chemical and biological method was developed that a long-run COD test with the influent can determine the inert soluble fraction (Lesouef et al., 1992). Nevertheless, high production of S_U might happen during the long-term test may lead to the overestimate of the influent S_U (Sollfrank et al., 1992). Some researches proposed to obtain the total soluble COD by performing flocculation of raw wastewater then pass through a 0.45 μm membrane filter. After that, applying the same method discussed before to quantify the soluble unbiodegradable COD fraction on the treated effluent sample. To conclude, experiments to measure this component can be conducted in a lab-scale continuous or batch reactor, and whether it is necessary to characterize this component is case dependant.

The readily biodegradable COD fraction (rbCOD) can be simply calculated by subtracting the S_U fraction from the influent soluble COD. The accuracy of this approach highly depends on the separation filter pore size used. As mentioned earlier, a 0.1 µm membrane filter has been accepted as the actual cut-off size of the soluble readily biodegradable substrate (Gatti, 2010). On the contrary, it was found that the biological response of filtered wastewater that passes through 0.45 µm membrane filter was lower than the response of unfiltered wastewater, which means that part of rbCOD fraction was retained on the filter (Spanjers and Vanrolleghem, 1995). Until 1993, Mamais and her co-workers developed a rapid physical-chemical method based on flocculation using Zn $(OH)_2$ at pH 10.5 to obtain truly soluble COD (eliminate colloidal matter of 0.1-10 µm). This approach is highly depending on the pH value during flocculation. In one study, it has been introduced that zinc sulphate can be replaced with aluminum sulphate and has the advantage of no pH adjustment and good flocculation (Wentzel et al.,2001).

Particulate Unbiodegradable COD (X_U) can be determined the same way as readily biodegradable COD (rbCOD) (Lesouef et al., 1992). Assuming there is no growth of X_U during a long-term BOD test, then influent X_U concentration is characterized as the residue particulate COD. In practice, this assumption is quite doubtful since the decay of biomass will generate X_U. Thus, the reliability of this approach needs to be further evaluated.

It is critical that the physical-chemical method does not apply to slowly biodegradable COD (X_B). X_B can be calculated from subtracting the S_B fraction from total biodegradable COD;

however, it is challenging to obtain accurate values of BOD at 20 days due to reliability concern (Tran et al., 2015). Moreover, it was found that parts of the soluble substrate and the settleable matters may belong to slowly biodegradable COD, which makes it even harder to characterize X_B through physical-chemical method (Sollfrank and Gujer,1991). Therefore, the particulate biodegradable COD can be determined through mass balance if other components are known (S_B, S_U, X_B, X_U) and if the biomass concentration is assumed to be negligible (Petersen et al., 2003). Evidently, biomass fractions cannot be differentiated through a physical-chemical method.

As discussed above, it can be concluded that the physical-chemical method has the advantages of being a rapid and easier tool for COD characterization, while using this approach alone will not provide sufficient information on the distribution of organic substrate. The two main drawbacks of applying this method solely include: the determination of truly soluble COD fraction largely depends on the decision of membrane filter pore size used; the separation of X_{OHO}, X_E, X_B, X_U components is not achievable because parts of the soluble and settleable fractions may belong to X_B (Petersen et al., 2003).

2.2.1.2 COD fractions determination based on biological methods

Before introducing biological (respirometric) measurement of wastewater characterization, some biochemical background on how respiration is correlated to microbial substrate utilization and growth is explained first. In the definition of biochemistry, respiration is the adenosine triphosphate (ATP) generating metabolic process in which electrons are removed from the electron donor transferred along the electron transport chain to the terminal electron acceptor (van Loosdrecht et al.,2016). The electron donor can be either organic or inorganic compounds, and the ultimate electron acceptor is usually inorganic compounds such as O_2, NO_2^- or NO_3^-, SO_4^- etc. The biomass converts the energy of intramolecular bonds in the substrate to the high energy phosphate bonds of ATP. The energy is then used for biomass growth, maintenance and reproduction. If the oxygen is the electron acceptor, then the conversion is accomplished by heterotrophic bacteria, and the process is called aerobic respiration. The utilization of electron donor for energy production and synthesis by heterotrophic biomass is shown in Figure 2-2:

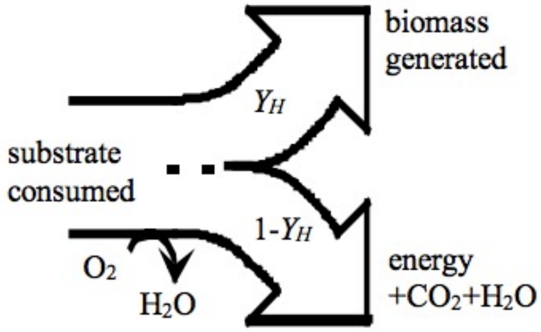

Figure 2-2:Schematic illustration of aerobic respiration by heterotrophic biomass (van Loosdrecht et al.,2016)

Heterotrophic biomass relying on the intake of nutrition from a carbonaceous substrate because it cannot produce its own food. Y_H is the heterotrophic yield coefficient that represents the COD fraction that is converted to cell mass. As shown above, only a portion (1- Y_H) of the consumed organic substrate is oxidized to generate energy, while the other part of the substrate molecules (Y_H) is converted into active bacterial cells (Spanjers and Vanrolleghem, 2017)

The biological(respirometric) wastewater characterization methods have been widely used to measure and interpret biological oxygen consumption rates that can help understand the biomass activity. Also, microorganisms concentration, substrate concentration and kinetic parameters can be obtained from respirometric measurement. Biological oxygen uptake rate (OUR) generated by respirometry allows the determination of slowly and readily biodegradable substrate concentrations in wastewater. Further details on the experiment set up and equation used to determine COD fractions and biokinetic parameters can be found in Chapter 3.

The level of characterization depends on the modelling goals and processes. In this study, both the physical-chemical method and the respirometric method are combined to determine COD fractions.

2.2.2 Fractionation on phosphorus

Phosphorus, usually in the form of phosphates, originates from sources such as human and animal waste, detergents and food residues (Burton et al., 2014). Wastewater treatment plant targets at reducing the level of contaminants, including phosphorus, to protect the environment and ecosystem. The effective removal of phosphorus in wastewater treatment plant depends on the treatment methods applied and the available equipment (Tchobanoglous et al., 2014). On the other hand, P is an essential non-renewable agriculture nutrient and obtained from subsurface mining of phosphate minerals. However, 90% of minable P is produced by only 5 countries in the world. To address the scarcity of P resources, those removed phosphorus from water and wastewater streams should be recovered for beneficial reuse (Venkiteshwaran et al.,2018). In particular, non-reactive P is not readily reactive and has been ignored as a target for removal and recovery. This fraction has to be converted to reactive P prior to recovery and reuse (Venkiteshwaran et al.,2018). Therefore, the determination of major phosphorus fractions is of importance, not only to enhance understanding of sample characteristics but also to validate the removal/recovery process through changes of fractions.

The different forms of P are summarized in Figure 2-3. Phosphorus in wastewater can be divided into reactive (RP) and non-reactive compounds (NRP). Reactive phosphorus (RP) is defined as inorganic phosphorus, orthophosphate, or molybdate reactive P, accounted for 70-90% of total phosphorus, which is readily assimilated by microorganisms. The NRP forms, known as acid hydrolyzable (AHP) or organic (OP) forms, include inorganic polyphosphate. Polyphosphate (AHP) can form naturally by a wide range of bacteria and accumulate as a phosphate reserve in comparatively low amounts (Tchobanoglous et al., 2014). Organic phosphorus can be further divided into biodegradable form and non-biodegradable form. Each of these compounds (orthophosphate, acid hydrolysable phosphorus, and organic phosphorus) can be further fractionated into a particulate and soluble form. Soluble forms of phosphorus (sP) and particulate forms of phosphorus (pP) are separated through a 0.45 μm filter. sRP fraction is the normally dominant form of P in wastewater, accounts for 50-90% of total phosphorus (Venkiteshwaran et al., 2018). PolyP level was observed in a wide range, Dueñas et al. (2003) reported 20-100% of polyp contributing 8-16 mg-TP/L. Particulate organic P is typically deposited and removed in the sludge via physical separation processes, while soluble, biodegradable organic P has to be converted into a solid phase to be removed. Noteworthy, most of the research characterize phosphorus in total phosphate, sRP, and with limited polyp data, the other P fractions are mostly not reported (Venkiteshwaran et al., 2018)

Due to the characteristic of non-reactive compounds (NRP), this fraction is not removed in the biological wastewater treatment and contributes to total phosphorus effluent discharges. Moreover, P-recovery strategies only can be implemented after the conversion of NRP to RP, which requires bonds to break in complex NRP compounds. Unfortunately, minimal data is available on strategies to remove and recover non-reactive phosphorus fraction (Venkiteshwaran et al., 2018).

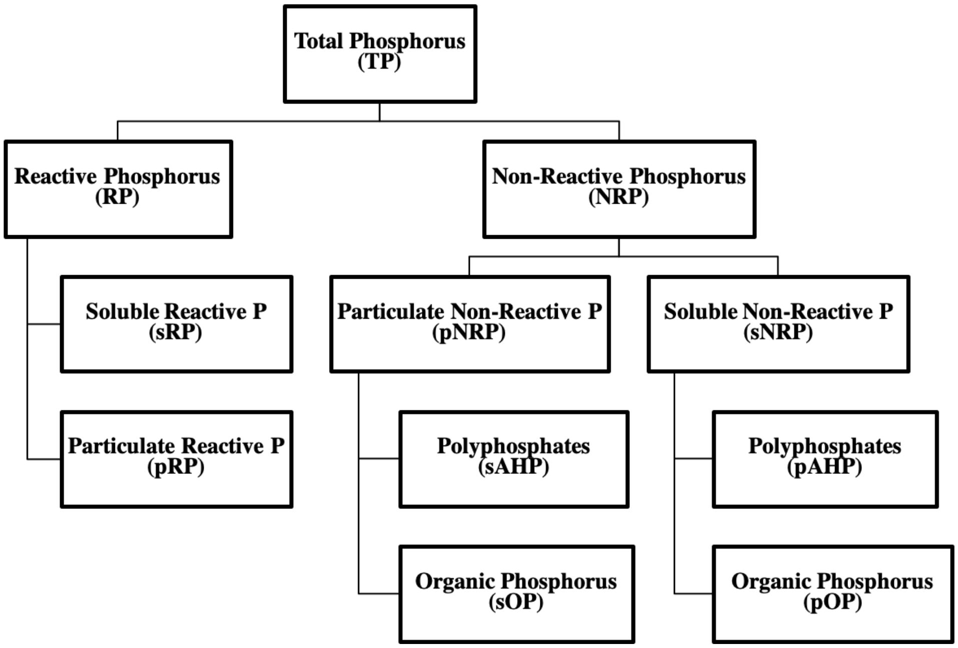

Figure 2-3:Phosphorus fractionation in wastewater (Adapted from Venkiteshwaran et al. (2018))

2.3 Chemically enhanced primary clarifier modelling

2.3.1 CEPT process

Chemically enhanced primary treatment (CEPT) is a technology that uses suitable chemicals to enhance pollutants removal in the primary stage of the wastewater treatment. The commonly used synthetic coagulants are either based on aluminum or ion. Aluminum-based coagulants include aluminum sulphate (alum), aluminum chloride, sodium aluminate, aluminum chloralhydrate, and sodium aluminate. Iron-based coagulants include ferric sulphate, ferrous sulphate, chlorinated copperas, ferric chloride, polyciliate-iron (PSI). Pre-hydrolyzed form of aluminum (poly aluminum chloride (PACl)) and iron (poly ferric sulphate (PFS)) can also be applied due to higher efficiency than traditional additives (Renault et al., 2009). Flocculants serve as coagulant aid that can be categorized into three types depending on their charge: positively charged cationic, negatively charged anionic and uncharged non-ionic (Renault et al., 2009). By adding a relatively low dosage of metal salts, sometimes combined with polymers, coagulation, flocculation, and sedimentation processes are enabled to form larger particles that can settle faster. Coagulation, also defined as particle destabilization, colloidal and fine particles are destabilized either through sweep coagulation, charge neutralization, and/or interparticle bridging. Sweep coagulation occurs when a large amount of metal salts is added to wastewater, causes the metal hydroxide formation that could settle faster. Charge neutralization is considered as the second destabilization process that negatively charged products are neutralized by the positively charged coagulant. Positively charged coagulants such as ferric chloride, aluminum chloride and cationic polymers compress the positively charged diffusive layer around the negatively charged particles, resulting in a more significant Van der Waal's forces between cationic coagulant and negatively charged particles than the repulsive force, thereby larger flocs are formed through the aggregation of particles. Moreover, cationic dosing system is normally installed at the location where the wastewater has a high turbulence degree because rapid mixing could trigger or enhance this process. Interparticle bridging is regarded as the third destabilization process that happens with the addition of polymer coagulant. Between two similar charged particles that repel each other, a 'bridge' is established by a large polymer, then these bridges and coagulated particles are formed as a floc.

Flocculation is defined as the aggregation of coagulated particles to form larger particle groups. The flocculation process normally operated under gentle, slow mixing conditions. This process enhances the collision between the destabilized particles and brings them together. The mechanism involves (i) Brownian motion (perikinetic flocculation), (ii) shear force (orthokinetic flocculation), and (iii) differential settlement (a special case of orthokinetic flocculation) (Atkinson et al., 2005). Brownian motion is mainly important for collisions between particles size less than 1 μm, the thermal energy of the fluid induces the process. Shear forces, due to fluid motion by mixing, mostly affect particles of a size larger than 1 μm. The differential settlement, caused by external forces such as gravity acting on the particles, leading to a more rapid settling, and a further vertical collision occurs between the larger particles and smaller particles. Noteworthy, mixing speed and time should be controlled during coagulation and flocculation to minimize the potential negative effect that rapid mixing could cause rupture of already formed flocs (Gotovac, 1999; Morrissey, 1990)

The main objective of CEPT is to optimize tCOD, TSS, and TP removal. It has been reported that CEPT can remove around 70.0-99.5% of suspended solids, 43.1-95.6% of COD and 40.0-99.3% of phosphate depending on the type of coagulants and/or flocculants added and the characteristics of treated wastewater (Shewa and Dagnew, 2020). Dong et al. (2019) found that the optimal coagulant ferric chloride (15 mg/L) and flocculant poly aluminum chloride (PACl,0.5 mg/L) combined can achieve total COD, soluble COD, TSS and TP removal efficiencies of 76%, 58%, 89% and 84%, respectively. Moreover, CEPT is the main method to remove dyes from wastewater. Nearly 100% removal of dye was achieved by the combination of membrane filtration and CEPT (Riera-Torres et al., 2010). CEPT can also be applied to remove micropollutants; Zhou et al. (2020) demonstrated that aluminum-based CEPT effectively removed 65% of retinoids and 73% of endocrine-disrupting chemicals (EDCs) from the liquid train.

To better comprehend the impact of CEPT on clarifier performance, evaluation of COD and P fractions is essential. CEPT has been studied extensively in both bench- and full-scale implementations, no single study sufficiently covers the effect of chemical addition process on COD and P fractions. In most of the literature, COD compositions are reported as readily biodegradable, inert soluble, slowly biodegradable and inert particulate fractions in raw influent and primary effluent (without any chemicals). Due to enhanced colloidal removal from CEPT, this fraction has been separated out as an individual fraction beside particulate and soluble fractions.

Nevertheless, limited work has fully characterized COD, especially in CEPT effluents. Literature values of COD fractionation in raw wastewater and effluents are further discussed in Chapter 3. Furthermore, the sludge produced after CEPT contains not only concentrated organics but also chemical coagulants. Organic carbon in CEPT sludge can be released and recovered by hydrolysis and acidogenesis, the produced VFA-rich fermentation liquor can then be utilized in the mainstream complementing carbon deficit for denitrification. Effective phosphate removal of CEPT leads to a significant amount of phosphate in CEPT sludge. The phosphorus recovery process provides high-value products such as fertilizer and, more importantly, advances the circular P economy. However, reactive P is the most amenable to recovery for direct reuse; the non-reactive P fraction has been greatly neglected for removal and recovery. Therefore, fractionation of different form of P in CEPT sludge is critical when investigating potential techniques that can convert NRP to RP. Specific studies focused on phosphorus release and conversion of NRP to RP of CEPT sludge are currently lacking. Further details are discussed in Chapter 4.

2.3.2 Primary clarification processes

Figure 2-4 demonstrates the schematic diagram of settling regions. Particles in sedimentation clarifiers settle in four distinct regimes based on the particle concentration and the interaction between particles. As settling begins, a compressed layer of particles begins to form at the bottom. As the compression layer forms, a region containing a successively low concentration of solids than those in the compression region extend upward in the cylinder (Tchobanoglous et al., 2014)

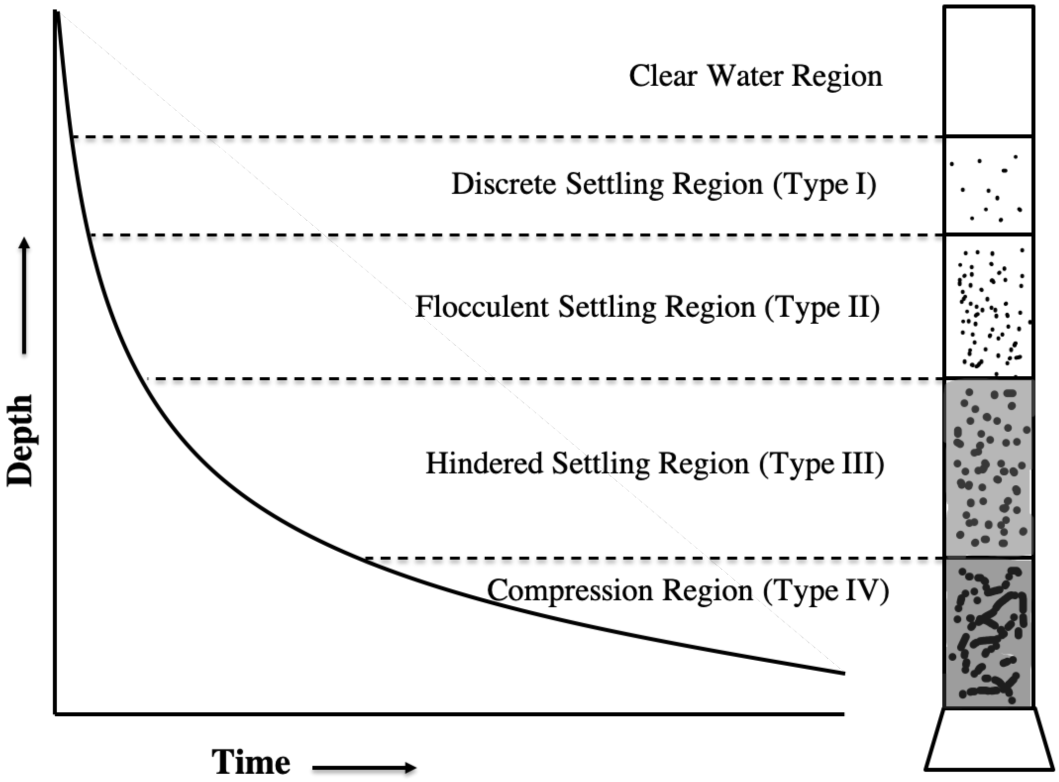

Figure 2-4:Schematic diagram of settling regions (Kharagpur)

2.3.2.1 Models based on Discrete Particles Settling

Discrete particle settling assuming solids settle as independent units with minimal or no interaction with other particles. The settling of discrete particles can be analyzed based on the classic Newton and Stokes laws. Newton's law is demonstrated in Equation (2-1) when the drag force equal to the gravitational force for spherical particles (Tchobanoglous, 2014)

$$V_{sp} = \sqrt{\frac{4}{3}\frac{g}{C_D}\frac{(\rho_P - \rho_l)}{\rho_l} d_p} \qquad (2\text{-}1)$$

Where V_{sp} is the terminal settling velocity of the primary particles (m/s) ; C_D is the drag coefficient (unitless) ; ρ_P is the particle density (kg/m^3) ; ρ_l is the liquid density (kg/m^3); g is the acceleration due to gravity (9.81 m/s^2); d_p is the diameter of the particles (m).

Also, the drag coefficient for spherical particles is different depending on whether the flow around the particles is laminar or turbulent. The drag coefficient is a function of the Reynolds number (N_R) and the particle shape.

$$N_R = \frac{V_{sp} d_p \rho_l}{\mu} = \frac{V_{sp} d_p}{\nu} \qquad (2\text{-}2)$$

Where ν = kinematic viscosity (m^2/s), and μ = dynamic viscosity (N•s/m^2)

In laminar flow (N_R< 1), viscosity is the predominant force governing the settling process, and the drag coefficient equals to 24/N_R. Stoke's law is yielded, and the settling velocity equation becomes:

$$V_{sp} = \frac{g(S_S - 1){d_p}^2}{18\, \nu} \qquad (2\text{-}3)$$

Where S_S = the particle specific gravity

Besides the theoretical equations shown above, some research had tried to quantify the actual settling velocity of discrete flocs and particle aggregates, and then correlate them with particle characteristics (Li and Ganczarczyk, 1987; Gorczyca and Ganczarczyk,2002; Kinnear, 2002). For example, Li and Ganczarczyk (1987) demonstrated the correlation of the activated sludge flocs settling velocity (mm/s) with the cross-sectional diameter (d_p,mm) and longest dimension (L_f, mm):

$$Vsp = 0.35 + 1.77\,dp \qquad (2\text{-}4)$$

$$Vsp = 0.33 + 1.28\,Lf \qquad (2\text{-}5)$$

As per equations shown above, the research (Li and Ganczarczyk,1987) also found that the first power of the floc size is preferred to correlate with the individual floc settling velocity instead of the second power proposed by Stoke's law, which might occur due to different floc densities and irregular shape of the flocs.

2.3.2.2 Models based on Flocculent settling

Particles start interacting with each other, and the flocculation of solids happens due to differential settling. As particle aggregates, settling velocity increases as well. Malcherek (1994) modified the power model, including the average velocity gradient (G) to evaluate the effect of flocculation on the settling velocity.

$$V_s = qX^b\,\frac{1+cG}{1+dG^2} \qquad (2\text{-}6)$$

Where V_s is the settling velocity at concentration X and q, b, c and d are fitted parameters. However, Rasmussen and Larson (1996) developed a similar method but applying the exponential models:

$$V_s = V_O e^{(BX+\Theta G)} + \Gamma \qquad (2\text{-}7)$$

Where V_O is the maximum settling velocity(m/d), $B\ and\ \Theta$ are empirical constants, and Γ is the minimum settling/compression velocity(m/d). Equation 2-7 demonstrates a negative relationship between velocity gradient G and the settling velocity. Higher V_s when G=0, whereas flocculation theory, an optimum G value higher than 0 should exist.

2.3.2.3 Models based on Hindered settling

Hindered settling happens when strong inter-particle forces to disturb the settling process results in suspension. This type of settling is typical in the secondary clarifier for the activated sludge process. The rate of settling is a function of the concentration of solids and their characteristics. Typically, it can be measured in a batch test, column settling test, that the velocity of the sludge interface is directly determined. The most important controlling factor of zone settling velocity is the initial sludge concentration and expressed by the classic Vesilind equation:

$$V_s = V_0 e^{-rhX} \qquad (2\text{-}8)$$

Where V_s is sludge settling velocity (m/d), V_0 is maximum theoretical sludge settling velocity (m/d), rh is the hindered zone settling parameter (m^3/g) and X is sludge concentration (g/m^3).

However, Vesilind equations are only practical for the hindered settling, and the predicted value will not be realistic if the initial sludge concentration goes to zero. Therefore, Takacs et al. (1991) modified the equation into a double exponential velocity equation, that when sludge concentration reaches zero, the settling velocity decreases.

$$V_s = V_0(e^{-rh(X-X_{\min})} - (e^{-rf(X-X_{\min})}) \qquad (2\text{-}9)$$

$$X_{min} = f_{ns}X_0 \qquad (2\text{-}10)$$

$$0 \le V_s \le V_{0,max} \qquad (2\text{-}11)$$

where rf is flocculent zone settling parameter (m^3/g), X_{min} is minimum attainable suspended solids concentration (g/m^3), X_0 is mixed liquor suspended solids entering the settler(g/m^3), f_{ns} is the non-settlable fraction of mixed liquor suspended solids and $V_{0,max}$ is the maximum practical settling velocity (m/d). The first term $V_0 e^{-rh(X-X_{\min})}$ represents the settling velocity of large, well flocculating particles. The second term $V_0 e^{-rf(X-X_{\min})}$ is the velocity correction factor to represent the smaller, slowly settling particles.

2.3.2.4 Models based on Compression settling

Compression settling occurs at very high particle concentration, particles at one level are influenced by particles on lower levels. The weight of particles results in compression. In solids flux analysis, the compression settling zone has been treated as an extension of Vesilind's equation. However, these empirical models cannot describe the relationship with the physical properties of activated sludge flocs and solid-water interaction (De Clercq et al.,2008). De Clercq followed the fundamentals of mass and force balances of water and solids, developed the following equation to account for compression settling velocity (v_c):

$$v_c = v_h\left(1 - \frac{\rho_s}{(\rho_s - \rho_f)gX}\frac{d\sigma}{dX}\frac{dX}{dz}\right) \qquad (2\text{-}11)$$

Where v_h is the hindered settling velocity (m/d); ρ_s and ρ_f are sludge and water density, respectively (kg/m^3); g is the gravity of constant (m/s^2); X is the sludge concentration (g/m^3) ; z is the depth (m); and σ is the effective solids stress (N/m^2). The highlight of this developed model is the consideration of hindered settling and effective solids stress function.

The primary clarification is primarily governed by discrete settling in conjunction with minimum flocculent settling (Griborio et al., 2014). Compression settling (Type IV) occurs in the sludge blanket region of the primary clarifiers. When applying CEPT, flocculent settling (Type II) is enhanced, and chemical precipitates formed in coagulation and other destabilization processes tend to aggregate while settling as a result of interparticle collisions. In other words, particle size, shape and specific gravity will all change. As a result, Stoke's law will not be applicable, and it's impossible to develop a general formula to determine settling velocities of flocculent particles. Therefore, a batch settling column test must be performed.

2.3.3 Model portfolio and engineering practices

Clarifier models can be utilized at different aspects of wastewater engineering, such as design, operation, optimization and troubleshooting (Henze et al., 2008). Various model options with various complexity are available depending on the targets: zero-dimension (0-D) models, one-dimensional (1-D) models, and two-or three-dimensional (2-D/3-D) models. Figure 2-5 demonstrates three different types of models that will be introduced in this section.

2.3.3.1 Zero dimensional models

0-D models are 'volumeless' clarifier model without area or depth. Such as 'simple point clarifier' or 'ideal clarifier with volume' have been widely used to model the separation of particles but not the settling behaviour. Point clarifier model complete separate particulate and soluble state variables. In this model, all particles go to the sludge line, as shown in Equation 2-12:

$$\left(Q_{Influent}\right) * X_{Influent} = Q_{underflow} * X_{underflow} \qquad (2\text{-}12)$$

Where $Q_{Influent}$ is the influent flow (m^3/h); $X_{Influent}$ is the influent mixed liquor suspended concentration(kg/m^3); $Q_{underflow}$ is the sludge flow (m^3/h) and $X_{underflow}$ is the effluent solids concentration (kg/m^3).

Noteworthy, in the secondary clarifier, recycle flow is included, and the mass balance is presented in Equation 2-13:

$$\left(Q_{Influent} + Q_R\right) * X_F = Q_R * X_R \qquad (2\text{-}13)$$

Where $Q_{Influent}$ is the influent flow(m^3/h); Q_R is the return flow(m^3/h); $X_F$is the bioreactor mixed liquor suspended solids concentration (kg/m^3) and X_R is the return solids concentration (kg/m^3). However, an additional term to represent the loss of particles through the effluent is included in most commercial simulators. The effluent solids or removal efficiency can be either a direct model input or a function of the flow rate through the clarifier. Thus, the mass balance equation should be:

$$\left(Q_{Influent}\right) * X_{Influent} = Q_{Sludge} * X_{Sludge} + \ Q_{Effluent} * X_{Effluent} \quad (2\text{-}14)$$

The ideal clarifier with volume models uses a completely mixed reactor (no biological reactions) to simulate simpler hydraulic behaviour and sludge storage capacity of the clarifier. In most cases, only the sludge blanket is modelled but not a separate clear water zone. If adding a clear water zone or several reactors, the hydraulic delay of the eluent can be modelled.

2.3.3.2 One-dimensional models

1-D models consider the volume of the clarifier. Few variations occurred under this category: simple two-compartment models (clarified phase and sludge blanket are included), or a combination of empirically-based models and mass balance using an algebraic equation to evaluate effluent, underflow and sludge blanket concentration (Henze et al., 2008). The most widely applied is the first order 10-layer model by Takács et al. (1991), based on the hyperbolic partial differential equation (PDE). The more recently developed second-order 1-D model (convection-dispersed model) was presented as Plósz model (2007), based on parabolic partial differential equations.

First-order 1-D models are governed by the equation that involves convective ‘bulk’ movement (U)and gravity sedimentation (V_S) on a small section of height, leading to the hyperbolic continuity equation (Plósz et al.,2011):

$$-\frac{\partial X_{TSS}}{\partial t} = U\frac{\partial X_{TSS}}{\partial z} + \frac{\partial (V_S X_{TSS})}{\partial z} \qquad (2\text{-}15)$$

Where X_{TSS} are the solids concentration that depends on the time (t) and the spatial coordinate (z)

With respect to models based on Equation 2-15, Takács model is the most well-known. The novelty of this model is the proposed double-exponential gravity settling function, as demonstrated in Equation 2-9, which is valid for both hindered and compression settling. The hyperbolic PDE is solved numerically by discretizing the settler into 10 horizontal layers, with the assumption that horizontal velocities are uniform, and horizontal gradients in concentration are negligible. The number of layers was determined to 10 to induce a high numerical dispersion, thus further improve the numerical behaviour of the model. Approximating the solution of PDE by difference equation in the finite elements of the discretized time and space domain results in numerical dispersion. In other words, the more massive error is induced to the solution as the coarser the discretization of the space domain. The effectiveness of the model in predicting the narrow flow boundary conditions is limited due to the weakness of control over the introduced numerical dispersion (Plósz et al., 2011). More importantly, another major drawback of this model is that the solids concentration depends on the height of the layer (z) but not the concentration gradient (Plósz et al., 2007). Therefore, incorporating the impact of the spatial concentration by adding a second-order dispersion term could result in more realistic model performance (Plósz et al.,2007). The more recently developed second-order 1-D models, based on 1-D advection-dispersion partial differential equation (Plósz et al.,2007; De Clercq et al.,2008), demonstrated a different way of discretization and dispersion.

The mass transport equation of second-order 1-D models is shown below:

$$-\frac{\partial X_{TSS}}{\partial t} = U\frac{\partial X_{TSS}}{\partial z} + \frac{\partial (V_S X_{TSS})}{\partial z} - D_C\frac{\partial^2 X_{TSS}}{\partial z^2} \qquad (2\text{-}16)$$

Where $D_C$is the dispersion coefficient, which is similar to the coefficient of molecular diffusion in Fick's law of diffusion (Henze et al., 2008). In this model, optimization was proposed by applying a dynamic feed layer, with depth limitation and a feed-flow dependent convection reduction factor. The novelty of this study is the use of a 2-D axisymmetric CFD model of a flat-bottom circular secondary settling tank to produce data in a range of feed flow rates and then calibrate the dispersion coefficient and the reduction factor of the 1-D model. They identified that the reduction factor dependent on the feed flow rate, and the dispersion coefficient is governed as a function of the overflow rate.

On the contrary to the first-order method, the number of discretized layers is not limited and can be increased to perform a mesh independent solution. The optimum number of layers is found between 60 and 100, and it's determined based on the structure of the dispersion term, responsible for compression settling velocity or for solids dispersion (De Claerq et al.,2008; Burger et al.,2012), or a flow-dependent dispersion (Plósz et al.,2007). To obtain a smooth and accurate concentration profile, the numerical fluxes are treated by applying a numerical algorithm that imposes an entropy condition. Godunov scheme (Jeppsson and Diehl, 1996) was applied to formulate minimum settling conditions above and below the feed layer (Plósz et al.,2007). This method has been proved to be accurate, easier to implement and requires less computation (Diehl & Jeppsson, 1998; Burger et al.,2005, 2011; Plósz et al.,2007). Further details of the model description can be found in Plósz et al. (2007)

2.3.3.3 Computational Fluid Dynamic models

Due to the fact that 1-D layered models cannot be applied for evaluating the clarifier construction details, 2-3D computational fluid dynamic (CFD) models are desired. CFD models are designed based on conservation of fluid mass, conservation of momentum in the horizontal and vertical directions, conservation of solids mass, conservation of heat balance, and a turbulence model (Henze et al.,2008). 2-D models incorporate 2D tank hydraulics, involve the factors affecting clarifier performance and capacity, such as boundary, turbulence, flocculation, density and temperature. This type of model can be applied for geometric optimization of symmetrical elements. 3-D models have the advantage of capable of configuring geometric features as small as several inches using very detailed grids, essential for non-symmetric features modelling (Samstag and Wicklein, 2007). The first 2D clarifier CFD model was developed by Larsen (1977), who modelled the flow field in a rectangular clarifier using the combination of a vorticity-stream function formulation and a Prandtl mixing length theory for turbulent modelling. Since then, great efforts have been made to improve the output of the CFD models by mathematical structure optimization in terms of turbulence, buoyant flow modelling, and in some cases, the settling velocity function and the rheology sub-model (Adams and Rodi, 1990; Lyn et al., 1992; Zhou and McCorquodale, 1992b; Deininger et al., 1998; Lakehal et al., 1999; De Clercq, 2003)

In this case, the models are usually applied to verify and optimize the details of clarifier design before the implementation of a full-scale clarifier. The simulation results provide a specific image of the distribution of solids and flow patterns. Whereas, with the increasing complexity of dimension, simulation time increases as well.

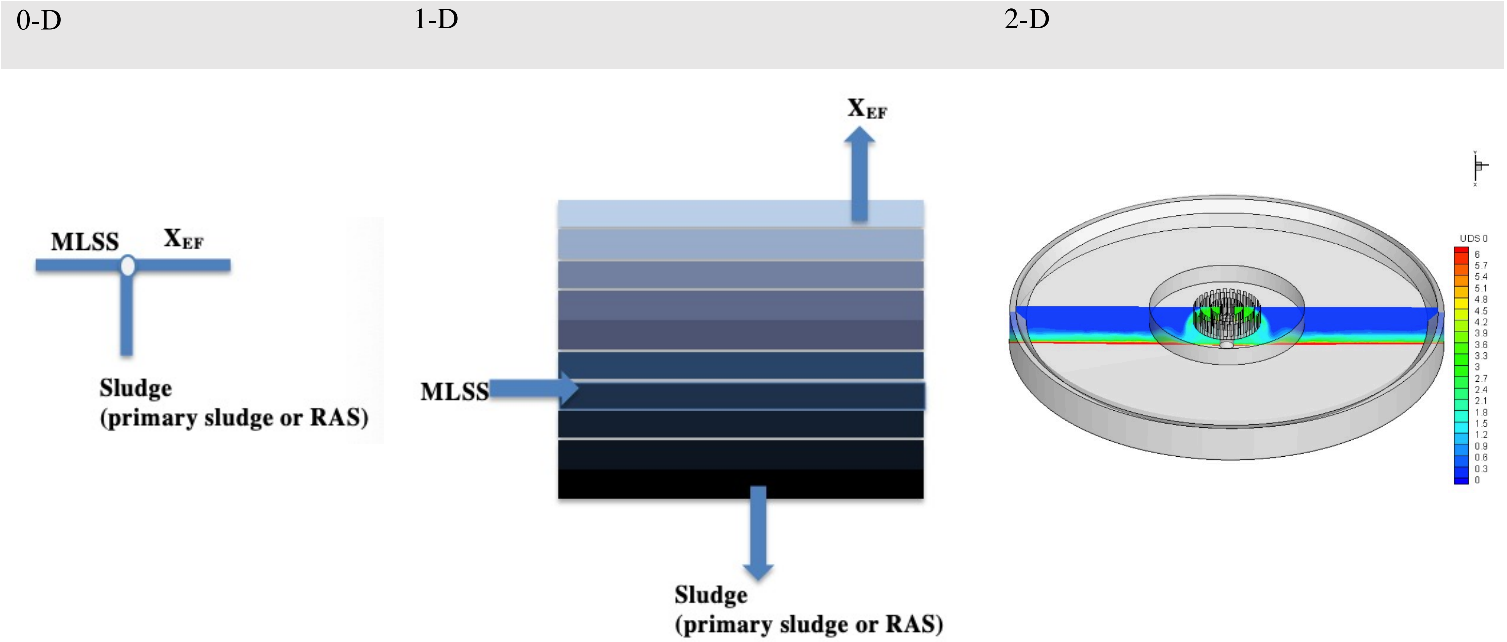

Figure 2-5:Zero, one, two-D representation of the clarifiers (Henze et al., 2008)

Besides the modelling of traditional primary clarifiers, limited literature has been done on chemically enhanced primary treatment (CEPT) modelling and CEPT effluent fractionation. Banchis et al. (2015) proposed an improved primary settler model based on the five-classes particle settling velocity distribution (PSVD), this approach effectively characterized the effect of CEPT on the PSVD, representing a potentially useful tool for the modelling of primary clarifier under CEPT.

Furthermore, the five-classes PSVD was further applied in Ludin's (2014) research, used to evaluate the impacts of different chemical additives (Fe^{2+}, cationic polymer and anionic polymer) on the distribution of settling velocity. The experimental procedure was based on ViCA's (a French acronym for Settling Velocity for Wastewater) protocol. It was found that as more coagulant is added, the slowest class of suspended particles is increased due to precipitation of soluble materials.

Class 2 and 3 are then increased if a cationic polymer is also added to form the particles in heavier flocs. Fast particles settling in Class 3 and 5 were independent of chemical enhancement. Moreover, Tik and Vanrolleghem (2017) used a well-developed CEPT model (WEST modelling software) to find an adequate control strategy of the chemical addition based on effluent quality, chemical savings, and maintenance effort. A constant polymer dose was added, and the turbidity-based CEPT controller was developed in the 1-D model to observe the effect of alum addition on sedimentation. The calibration and validation process demonstrated that the CEPT model was able to forecast effluent TSS concentrations in accordance with influent TSS concentration, alum concentration, and inflow rates. However, there was no discussion on how the process impacted the effluent COD fractions.

In summary, CEPT modelling practices discussed above were all based on a 1-D layered flux model, and particle settling velocity distribution approach can successfully predict TSS effluent concentration. Nevertheless, there is still a lack of study demonstrating the impact of CEPT on other wastewater fractions (e.g. COD) or estimating wastewater fractions using CEPT models.

2.4 Phosphorus release from CEPT sludge

2.4.1 Phosphorus removal from the liquid stream

Phosphorus enter surface water either from domestic and industrial waste discharge (point – source) or from urban and agriculture lands (non-point source) (Burton et al., 2014). In freshwaters, phosphorus affects the growth of algae and biological organisms, and excessive P can cause eutrophication. Eutrophication most commonly arises from the oversupply of nutrients, such as nitrogen and phosphorus, that results in overgrowth of plants and algae in the aquatic system. This process leads to the depletion of oxygen in the water body, which has dramatic consequences for ecosystems and recreational water bodies (USEPA,1997). In order to control the occurrence of algal bloom in surface water, regulating the amount of phosphorus compounds has been a great interest (Stratful et al., 1999; Duenas et al., 2003; De-Bashan and Bashan, 2004 and Burton et al., 2014).

Phosphorus removal from wastewater can be achieved by either the enhanced biological P-removal (EBPR) process or by chemical dosing method to form phosphorus precipitation, followed by efficient sludge disposal (Lin et al., 2017). Both of these processes aim at reducing only soluble ortho-P or those forms that can be converted into ortho-P during the treatment process by transforming it into solid phase followed by subsequent solid and liquid separations (Gu et al., 2011). Particulate phosphorus is amenable via the physical separation process. On the other hand, the chemical P removal process was found more effective in removing sRP (95.89%), sAHP (56.37%) and pOP (56.30%), but was not as efficient for removing pAHP (37.12%), and nearly no removal of sOP (Gu et al., 2011)

2.4.1.1 Biological Phosphorus removal

EBPR is the biological uptake and removal system, which is more effective than the conventional aerobic activated sludge system due to the enhanced growth of polyphosphate accumulating organisms (PAO) (Henze et al., 2008; Seviour et al., 2003). It involves the microbial metabolic cycling through a few microbial-accumulated biopolymers (polyphosphate, PHA and glycogen). This metabolic cycling is operated by two bioreactor conditions, anaerobic and aerobic. Under anaerobic conditions, the PAOs residing in the sludge exhaust the organic matter and carbon matter, some of the stored polyP has been consumed and P released to the bulk solution; therefore, bulk solution VFAs and intracellular polyp and glycogen decrease; soluble phosphate, Mg^{2+}, K^+ and intracellular PHA accumulate (De-Bashan and Bashan, 2004; Henze et al., 2008). Under aerobic conditions, in the presence of oxygen, the PAOs utilize the stored PHA as a carbon and energy source for energy generation and growth of the new cells as well as for recovering the glycogen consumed in the anaerobic stage. Therefore, intracellular poly P and glycogen increase; and soluble phosphate, Mg^{2+}, K^+ and intracellular PHA decrease (Maurer et al., 1999; De-Bashan and Bashan, 2004; Henze et al., 2008).

After the EBPR process, the secondary effluent still contains both particulate/soluble reactive P and non-reactive P fractions (poly P and organic P associated with the biomass), which requires further P removal strategies via tertiary physical/chemical treatment process. Techniques such as granular, micro-, or ultra-filtration; coagulation; flocculation; precipitation; ion exchange; and adsorption are efficient in RP and some pNRP fractions removal but cannot reduce sNRP fraction level. Even NRP account for a small percentage of influent wastewater TP (1-10%), inefficient removal of sNRP still can result in failure in reaching standard effluent regulation (Venkiteshwaran et al., 2018).

2.4.1.2 Chemical Phosphorus removal

On the other hand, chemical precipitation with iron, alum, or lime is the typical full-scale wastewater treatment practice for phosphorus removal in the liquid stream. They can be added at different points in the treatment process. Metal salts can be added in the influent (before primary clarifier), the activated sludge aeration tank, or the tertiary clarifier. The dominant process in aluminum and iron removal is co-precipitation, defined as the simultaneous precipitation of a normally soluble component with a macro-component from the same solution by the mixed crystals, by adsorption, occlusion or mechanical entrapment. With adequate alkalinity, adding aluminum or iron leads to rapid precipitation of hydrous ferric (HFOs) or aluminum oxides (HAOs) (Smith et al., 2008). Mechanisms governing the removal of phosphorus include adsorption onto or co-precipitation with HFO/HAO; precipitation of ferric or aluminum phosphates; and precipitation of mixed cation phosphates (for example, Ca, Mg, Fe, Al phosphates, or hydroxyphosphates) (Smith et al., 2008). With the addition of aluminum and iron, they react with soluble orthophosphate to form phosphate precipitation (the formation of pRP products) (Venkiteshwaran et al., 2018). Moreover, if a specific organic polymer is added along with metal salts, colloidal particle coagulation is enhanced to reduce the effluent TSS load (Tchobanoglous et al., 2014). The reactions involved to describe the precipitation of phosphorus with aluminum and iron are as follows:

Phosphate precipitation with aluminum:

$$Al^{3+} + H_nPO_4^{3-n} = AlPO_4 + nH^+ \qquad (2\text{-}17)$$

Phosphate precipitation with ferric:

$$Fe^{3+} + H_nPO_4^{3-n} = FePO_4 + nH^+ \qquad (2\text{-}18)$$

However, these reactions are deceptively simple and normally do not apply, it has been reported that ferric phosphate occurs near a pH value of 3.5 and does not form above pH 5 (Smith et al.,2008). Moreover, other competing reactions and their associated equilibrium constants, and the effect of alkalinity, pH, trace elements should also be considered. Thus, a more recent study (Sedlak, 1991; WEF, 2011) demonstrates the following overall reaction that better describe phosphorus removal with metal salts addition:

$$rMe^{3+} + HPO_4^{-} + (3r-1)OH^{-} \longrightarrow Me_r \cdot H_2PO_4(OH)_{3r-1}(s) \qquad \text{(2-19)}$$

Where r=1.6 for Fe (III) and 0.8 for Al (III).

Thistleton et al. (2002) analyzed the impacts of iron (III) salts on phosphorus removal using jar tests. A strong link between phosphorus removal and iron: phosphate ratio was observed. 80% total phosphorus removal was achieved at a dose of 1.48:1 molar ratio Fe:P with iron chloride. To achieve similar phosphorus removal using pre-formed iron (III) hydroxide, a significant higher dose was required, and the corresponding molar ratio to achieve the same performance was 4.8:1 (Fe:P). Also, after a molar ratio of 4.0:1.0, minimal improvement with additional dose in phosphorus removal by iron hydroxide addition. Thus, compared to iron chloride, metal hydroxides are less efficient in phosphorus removal. Aluminum hydroxide Al $(OH)_3$ is a strong adsorption agent and precipitate orthophosphate and condensed phosphate rapidly, whereas a low pH of 3.6 is required to precipitate organic phosphorus. It has been demonstrated that orthophosphate removal is not achieved through the precipitated $AlPO_4$ when using traditional alum, but through precipitation of aluminum hydroxide phosphate (De-Bashan and Bashan, 2004). Baker et al. (1998) showed that a column packed with silica sand, limestone, and activated aluminum oxide removed 99% of phosphorus, even after 2 years, indicated that the adsorption capacity of aluminum oxide is high enough to maintain long periods, iron oxide has the similar characteristics as well.

Lime has been applied in both primary sedimentation tanks and the secondary clarification tanks. The main variable that controls the dosage is the degree of removal targeted and the alkalinity of the wastewater, which can be determined by testing. With the addition of lime, both calcium and the hydroxide react with the orthophosphate to form insoluble hydroxyapatite [$Ca_{10}(OH)_2(PO_4)_6$] (De-Bashan and Bashan, 2004). High lime dose system raises the pH, without inducing the re-carbonation usually can negatively affect the downstream process. The removal efficiency in this process ranged from 75% to 85% (Moriyama et al.,2001)

Phosphate precipitation with lime:

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \rightleftharpoons Ca_{10}(PO_4)_6(OH)_2 \qquad (2\text{-}20)$$

It has been reported that 60% of North American survey respondents demonstrated that their facilities apply physicochemical phosphorus removal, and this approach is dominant in Eastern Canada (Oleszkiewicz et al.,2015). Due to high capital costs and operational complexity, biological phosphorus removal systems are generally avoided in Ontario (Oleszkiewicz et al., 2015). In this research, chemical addition strategies have been applied to the primary sedimentation tank, and the following discussion on phosphorus recovery will be principally on chemically enhanced primary sludge. Due to most P is transferred from wastewater to primary sludge, chemically enhanced primary sludge is concentrated with organics and phosphorus, these valuable resources should be recovered instead of wasted. The typical practice with sludge handling is either anaerobic digestion followed by land application (as a source of fertilizer), incineration followed by landfill or just thickening and landfill. Further evaluation of the fate of phosphorus and carbon would be of importance.

2.4.2 Potential routes for NRP conversion from the side stream

Phosphorus (P) is an essential non-renewable agricultural nutrient and an environmental pollutant (Venkiteshwaran et al., 2018). The increasing population and the following high demand for agricultural productivity have led to an increasing desire for fertilizers. However, due to the fact that phosphorus is a scarce non-renewable resource and 90% of minable P are available in only five countries, the market price of fertilizers has increased consequently (Venkiteshwaran et al., 2018). Consequently, the phosphorus in the wastewater treatment process sludges, and return flows may be seen as a valuable asset that should be recovered and reused. In particular, sludge P release with NRP conversion is the most critical step for P recovery.

Anaerobic digestion (AD) is an acknowledged process for sludge stabilization. This process includes the breakdown of organic matter to produce biogas energy and reduce inorganic matter in the absence of oxygen (Henze et al.,2008; Carrere et al.,2010; Rittmann et al.,2011). Specifically, organically bound P is released via hydrolysis, enable the P availability for further recovery process (Venkiteshwaran et al., 2018). To date, the technical and scientific interest has shifted towards the process optimization to maximize yields. To achieve this purpose and overcome the rate-limiting step of hydrolysis, pretreatment technologies have been developed (Cesaro and Belgiorno.,2014).

In this section, potential sludge pretreatment technologies to enhance P release and NRP conversion, including biological, mechanical, thermal, and chemical pretreatment, are introduced. These mechanisms initiate and/or boost hydrolysis or redox reactions and can be implemented for converting NRP to the more readily recoverable RP form.

2.4.2.1 Biological pretreatment methods

Biological pretreatment prior to AD in an additional stage targeting at hydrolysis intensification either by the use of microorganisms with high ability in substrate degradation or the addition of enzymes that support biological reactions within AD. Such as aerobic pre-digestion, dual digestion, enzyme addition techniques (Burgess and Pletschke, 2008; Dursun et al., 2006; Jang et al., 2014; Mshandete et al., 2005; Rubio-Loza and Noyola, 2010). **Anaerobic digestion** process includes two steps: the direct oxidation of biodegradable matter and endogenous respiration where cellular material is oxidized (Roš and G.D, 2002). Under the thermophilic environment, this process has a faster degradation rate resulting in an increased amount of soluble organic products that can benefit the methane yield and self-heating ability, decrease the operational costs (Gomez et al.,2007). It has been reported that thermophilic aerobic digestion (TAD) as a pre-treatment, solubilized 8% of COD, when combined with mesophilic anaerobic digestion (MAD), increased the overall methane production by 10-79%, VS reduction by 11-67%, the concentration of methane and diversity of microbial communities (Miah et al.,2005; Dumas et al.,2010; Jang et al.,2014). **Dual digestion** targets to enhance AD by adding an anaerobic pre-digestion step oriented to hydrolysis. Compare to mesophilic conditions, the thermophilic condition is preferred due to reported high hydrolysis kinetics. Temperature phased AD (TPAD) is the most often used method, either with thermophilic (~55 °C) or hyperthermophilic (60-70 °C) (Carre`re et al. 2010). An amount of research reported that pre-digestion resulted in 13-23% COD solubilization and removed up to 25% VS. The overall dual-digestion improved 11-50% biogas production, 10-53% VS reduction and 97% inactivation of helminth eggs (Nges and Liu, 2009; Rubio-Loza and Noyola,2010; Ge et al.,2010,2011; Yu et al.,2013). Hydrolytic enzyme plays a critical role of converting polymeric substances into more biodegradable compounds (Yang et al.,2010). **Enzyme additions** to AD benefit dewaterability and methane yield (Dursun et al.,2006). Different enzymes and enzyme mixtures could lead to various impacts on sludge hydrolysis. Thus, selecting the proper one is the key step to maximize the influence of pretreatment on AD. Studies regarding enzyme addition as pretreatment presented 15.1-25.0% increase in SCOD/TCOD ratio and up to 58% VSS reduction. The overall performance with AD was 12% biogas improvement and 1-16.3% solids reduction improvement (Davidsson and Jansen, 2006; Dursun et al., 2006; Yang et al.,2010; Rashed et al.,2010).

In summary, these pretreatment methods all have the advantage of no chemical addition, low operating cost, and no restriction to specific AD technologies, whereas the corresponding drawbacks include long reaction time and low increase of biogas yield. During the biological process, the breakdown of complex organic material is expected to release P; however, most of the research presented the results of COD solubilization (before/after pretreatment), and the overall improved CH_4 production and VS removal. Little information is available specifically for phosphorus solubilization or NRP conversion.

2.4.2.2 Mechanical pretreatment methods

Among the mechanical pretreatments, ultrasonic, lysis-centrifuge, liquid shear (collision plate, high-pressure homogenizer), and grinding have to be listed (Carrere et al.,2010; Cesaro and Belgiorno, 2013). **Ultrasonic** treatment disrupts the cell structure and floc matrix mechanically. Two main mechanisms involved are cavitation (preferred at low frequencies) and chemical reaction (the formation of OH•, HO_2•, H• radicals at high frequencies). Low frequencies (20-40kHz) are the most efficient in sludge treatment (Carrère et al.,2010). Sludge floc disintegration and microorganisms lyses is expected to occur from sludge sonication (Chu et al.,2002). Nevertheless, the required energy for lysis is high, and inactivation of microorganisms was found prior to the cell lysis process (Chu et al.,2002). Thus, the solubilization threshold of 1000 to 16,000 kJ kg^{-1} is reported; this specific energy also enhanced biogas production from 24 to 40% in batch systems and from 10 to 45% in continuous or semi-continuous systems (Carrère et al.,2010) when applied as pre-treatment of AD. Furthermore, ultrasound pretreatment technology has been applied in small-scale research for sludge disintegration and disinfection (Khanal et al.,2007; Rittmann et al.,2008). This process includes both physical and chemical effects, and cavitation occurs at low frequencies (20-40 kHz) and chemical oxidation through the formation of free radicals at higher frequencies (Carrere et al.,2007; Khanal et al.,2007). Wang et al. (2010) observed more than 60% P (80% are in the sRP form) release in an EBPR sludge with high-intensity ultrasound 500 kWH/m^3 in 1 hour.

Lysis centrifuge is applied in a dewatering centrifuge directly on the thickened sludge, then resuspended with the liquid stream (Dohányos et al.,1997). This technique increased biogas production from 15 to 26% when implemented as a pretreatment prior to AD (Dohányos et al.,1997, Zabranska et al.,2006). ***Liquid shear*** provides mechanical disruption to cells and flocs based on high liquid flows induced by high pressure system. High pressure homogenization process includes sludge pressure increase up to 900bar, then goes through a homogenization valve under high depressurization (Choi et al.,1997). 30% increase in biogas production and 23% increase in volume reduction were demonstrated when a fraction of digested sludge was treated at 150bar and re-introduced in the digester (Onyeche, 2007). Moreover, as reported by Muller (2000), supernatant P concentration increased by three times after 80MPa high-pressure homogenization. A similar increase was observed in sP fraction after15 mins pretreatment of an EBPR with a deflaker (Kampas et al.,2007). As more NRP is released, more RP will be converted from hydrolysis and recovered for beneficial use. ***Grinding*** technique disintegrate sludge by stirred ball mills. This technique is preferred on digested sludge (60% increase in batch biogas production) and waste activated sludge (24% increase) than activated sludge with a higher SRT (7% increase) (Baier and Schmidheiny,1997; Kopp et al.,1997)

In sum, these techniques advance solids disintegration and destruction in high solids stream to accelerate further anaerobic digestibility (Venkiteshwaran et al., 2018). Intracellular compounds like nitrogen and P are increasingly released due to improved cell destruction. Nevertheless, the power requirement of mechanical pretreatment approaches can be high based on the targeted size reduction (Cesaro and Belgiorno, 2013).

2.4.2.3 Thermal pretreatment methods

Thermal pretreatment has been applied to improve sludge dewaterability properties and anaerobic digestion at a large scale (Bougrier et al.,2007; Carlsson et al.,2012). The heating process is able to modify the structure of the insoluble fractions and make it more readily biodegradable. In other words, thermal treatment leads to the breakdown of the gel structure of the sludge and then releases intracellular bound water (Weemaes and Verstraete, 1998). Accordingly, this technique enables a high degree of solubilization, an enhancement in biogas yield, modification in sludge characteristics (increase in filterability and viscosity reduction) and elimination of pathogen microorganisms (Anderson et al.,2002; Valo et al.,2004; Bougrier et al.,2007). Kuroda et al. (2002) proposed a simple method treating EBPR sludge for polyP releasing and P recovering in a reusable form. This method was based on the findings that polyP could release from sludge by 70°C heating for an hour and then precipitated by adding $CaCl_2$ at room temperature without pH adjustment.

They found that 90% of the organically bound P was released under the thermal process at 70°C for 1h (Kuroda et al.,2002). Almost complete P release was found using 80°C treatment for 20 min, 87% of the released P was polyP, whereas 10min treatment stated the same removal at 90°C with 40% released polyP. Continuing exposure to temperature 70-90°C can hydrolyze and convert polyP to sRP (Kuroda et al.,2002).

Moreover, Liao et al. (2005) evaluated phosphorus release and recovery from EBPR sludge using a rapid microwave process. The main advantages of microwave heating include uniform heating and accurate control of the temperature. Via the realignment of dipoles, energy is generated from the uniform microwave field, and then heat is produced both internally and at the surface of the treated sludge. This energy is dissipated as heat and rely on the microwave frequency, the dielectric loss factor, and the electrical field strength within the material (Liao et al.,2005). The result showed that only 5mins microwave process could release up to 76% phosphate from the sludge into the solution. No chemical addition is required in this process. Also, sludge could also be stabilized by microwave technology when conducting at a temperature above 100°C. Thus, microwave heating is preferred when the heating process can be accurately controlled, and heat produced inside the material is more uniform both internally and on the surface.

Accordingly, there have been studies that demonstrated efficient thermal treatment on polyphosphate conversion, whereas the effect of thermal on the release of other NRP fractions is still lacking.

2.4.2.4 Chemical pretreatment methods

The chemical pretreatment process is based on oxidative reactions. In the field of chemical pretreatments, the most typical applied are ozonation, advanced oxidation and acid/alkali processes (Carlsson et al.,2012; Neumann et al.,2016). The ozonation process results in partial sludge solubilization, and yield increases with ozone dose. Ozone dose has to be well-controlled because a high dose of ozone might lead to a reduction in solubilization due to oxidation of the solubilized components. Organic matter degradation by ozone involves two steps: (i) solubilization due to the disintegration of suspended solid and (ii) mineralization due to oxidation of soluble organic matter (Neumann et al., 2016). Ozone as pre-treatment can achieve partial oxidation and hydrolysis of sludge (Carballa et al., 2007). Weemas et al. (2000) investigated the impacts of an oxidative pre-treatment on the anaerobic digestibility of the sludge. The sludge sample used was the mixture of both primary and secondary sludge. A range of ozone between 0.05 and 0.2 $gO_3/gCOD$ was applied. It was found that the soluble COD concentration increases gradually and reaching 29% solubilization with a dose of 0.2 $gO_3/gCOD$. Moreover, methane production was improved by 80% at an ozone dose of 0.1 $gO_3/gCOD$, whereas the negative effect on dewaterability was diminished after AD to levels close to untreated sludge. Different from the ozone process, the advanced oxidation process (AOPs) depends primarily on oxidation with hydroxyl radicals instead of direction oxidation with the aqueous zone. The advanced oxidation process (AOPs) can help release NRP that is locked in complex organic matrices and enable hydrolytic conversion to RP or produce sRP through complete oxidation (Venkiteshwaran et al., 2018). The process includes the formation of hydroxyl radicals (HO•) that are the most powerful oxidizing agent. It can mineralize organic compounds to simple molecules, for example, P to phosphate or phosphoric acids and carbon to carbon dioxide (Parsons, 2004).

An example of hydroxyl radicals reacts with carbon monoxide to form carbon oxidation is shown below:

$$HO \bullet + CO \rightleftarrows HOCO \rightarrow H \bullet + CO_2 \qquad (2\text{-}21)$$

Liao et al. (2005) showed 84% TP release from EBPR sludge using 30% H_2O_2 and 5 min microwave heating at 170°C. Yin et al. (2008) also reported more than 95% P release from sewage sludge using 1L/min ozonation for 9 mins, then 30% H_2O_2 addition, and lastly, microwave heating of 120°C for 4 min. These studies showed that higher hydrogen peroxide concentration, higher temperatures, and/or longer treatment time resulted in more P release.

Furthermore, acids and alkali pretreatment has been studied as an effective approach to sludge solubilization. Alkalis is more appropriate with the anaerobic digestion process since the bioconversion typically requires pH adjustment by increasing alkalinity (Pavlostathis and Gossett.,1985). Alkaline chemicals that can be added are NaOH > KOH >Mg $(OH)_2$ and $Ca(OH)_2$, in the order of sludge solubilization efficacy(Kim et al., 2003). Acids addition technique can be effective for protein-rich substrate, which might bring ammonia inhibition (Hansen et al.,1998). Strong acid H_2SO_4 and HCI can enhance anaerobic digestibility of sludge and dairy manure (Devlin et al.,2011). Many studies reports P release by observing sRP before and after treatment; however, whether the increase in sRP came from the conversion of NRP or pRP is hard to tell. The pRP fraction, including divalent cation precipitates (for example, calcium or magnesium phosphates) has been observed more easily to be solubilized after acid treatment compared to alkali treatments. Star et al. (2016) studied the leaching of phosphate from ash by alkali/acid for product recovery purposes. 25 mL hydrochloric acid (HCI) or sodium hydroxide (NaOH) with different concentrations up to 1M was added to four ash samples. The results demonstrated that acid leaching released more phosphate than with base. In the range of concentrations 0.5 to 1M, phosphate release with acid increased from 75 to 85%, whereas a 55 to 70% increase was observed with alkaline leaching. Specifically, it was found that 83% release of Ca^{2+} ions after 1M HCI treatment, while only 0.19% release of Ca^{2+} ions after 1M NaOH treatment. Consequently, acid treatment can convert both NRP and pRP to sRP; however, alkali treatment mainly converts NRP to sRP (Venkiteshwaran et al., 2018). Furthermore, according to Mavinic and Koch (2003), 2-4 times increase in P solubilization was found with 10mM HCI or NaOH addition for 30g. In sum, although oxidation, AOP and acid/alkali pretreatment are effective in P solubilization and NRP conversions to RP, these techniques highly depend on chemicals and/or energy, which could lead to high operating cost.

Overall, most of the abovementioned literature were conducted on EBPR, secondary, primary or mixed sludge samples. Below is the research that has been worked on chemical enhanced primary sludge. Sludge produced by coagulation and flocculation in CEPT with ferric or alum was observed to be less degradable than the conventional primary sludge, through quantification of biogas or methane production (Dong et al., 2018). The aluminum and sulphate compounds inhibited the specific methane activity by decreasing 50%-72% of methanogenic bacteria and 48% to 65% of acetogenic bacteria (Cabirol et al.,2003). Lin et al. (2017) applied sludge fermentation process for Fe-sludge to analyze the fermentation potential and related VFAs production. The results showed that 27% organic carbon could be recovered via sludge fermentation, mainly in the form of VFAs. Further, phosphorus recovery efficiency was conducted on conventional primary sludge, Fe sludge, Fe sludge pre-treated by ultrasonication (Fe-S) and alkali addition (Fe-Na). Up to 16.6 mg-P/L was released into the liquid phase from Fe-sludge after fermentation, whereas 6.9 mg-P/L from the primary sludge. Sonication did not have any impacts on P release from Fe-sludge, whereas alkali treatment had negative impacts that reduced the P release by 50% and P dissolution. Less P is released into the supernatant due to decreased iron solubility under higher pH level (6.5 vs.5.3). Released PO_4^{3-} was recovered by P-Fe precipitation with the co-existence of soluble Fe^{2+}/Fe^{3+} through adjusting the pH to 8.0 or higher. It was found that 23.4% of phosphate can be recovered as a fertilizer resource. In 2018, Lin and Li investigated the effects of the initial pH (in a range between 2 to 10) on the performance of Al-sludge fermentation at mesophilic temperature. The effects of abiotic and biotic hydrolysis on sludge disintegration, organics solubilization and hydrolytic enzyme activity were also conducted. The results demonstrated that compared with acidic pH (2.0-6.0) pretreatment, alkaline pH (8.0-10.0) was more favourable and effective, also moderated the inhibition effect of Al coagulant through the enhancement of abiotic and biotic hydrolysis process. The highest VFA yield (275 mg-COD/g-VS) for the initial pH of 10 resulted from enhanced enzymatic activities of protease and α-glucosidase with the high pH values. Nevertheless, little phosphorus <0.1 mg/L was released into the fermenting liquid, indicating that P removal is not required before the VFAs can be used.

Overall, the objective of applying pretreatments to anaerobic digestion is not only to increase sludge amount reduction and to intensify biogas yield but also to enhance nutrients release and recovery. Biological, mechanical, thermal, and chemical pretreatments all have high potential techniques for the purpose of NRP conversion from different sludge samples; however, there is a shortage of such evaluation.

2.5 Research Gap

As discussed above, studies addressing the superior performance of CEPT technology, impacts of CEPT on the effluent fractionation, and downstream phosphorus release and anaerobic digestibility should be addressed. Although CEPT has been studied extensively in both bench- and full-scale implementations, no single study adequately describes the impacts of chemical addition process on COD and P fractions. Furthermore, even though the concept of modelling chemical enhancement in primary settling tank has raised researchers' attention, almost no studies have fully characterized CEPT effluent and compared and contrasted the effectiveness of 0-D and 1-D models. Besides, although different pretreatments have been extensively studied to enhance anaerobic digestion performance, limited research has investigated the impact of pretreatments on the sludge biodegradability, and phosphorus release and NRP conversion when substantial carbon and nutrients are chemically concentrated into the sludge. More importantly, it has been reported that PACL has an inhibitory effect on the organic hydrolysis and methane production, even alkali pretreatment has been proved to effective relieve such effect (Lin and Li,2018), low level of P release from the Al-based chemically enhanced primary sludge will limit the followed P recovery process. Further work on improving P release from chemical sludge should be addressed. Overall, these research gaps will be addressed in this thesis.

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3 Dynamic and Steady-State Modelling of Chemically Enhanced Primary Treatment: A case study

3.1 Introduction

The chemically enhanced primary treatment (CEPT) process is gaining momentum for carbon redirection, thereby lowering the downstream liquid train load and maximizing energy recovery from the primary sludge. CEPT process promotes coagulation and flocculation, which allows faster settling of particulate and colloidal solids and dissolved ions such as phosphate to enhance removal efficiency. To develop the whole plant simulation, and fully understand the effectiveness of the treatment plant, comprehending the dynamic behaviour of CEPT clarifiers is critical. Towards this, numerous efforts have been contributed to the advancement of primary clarifier models.

The current existing model collocation to practical clarifier modelling includes zero-dimension (0-D) models, one-dimensional (1-D) models and two-or three-dimensional (2-D/3-D) models. 0-D clarifier models are ideal phase separators that only represent the liquid-particles separation process but not the settling behaviour. 1-D clarifier models describe the dynamic clarification-thickening system based on the solids flux theory to predict particle flux via discrete horizontal layers (Plósz et al.,2012). The 1-D (layered-flux models) was initially designed to model the settling behaviour under dynamic condition, instead of predicting effluent suspended solids. Among the 1-D models, the 10-layer Takács clarifier model (Takács et al.,1991) has been most commonly used for both primary and secondary clarifiers simulation. A study by Gernaey et al. (2001) using the Takacs clarifier model in the original WEST platform showed that the clarifier effluent soluble component concentration was identical to the influent concentration. Gernaey et al. (2001) suggested the addition of soluble residence time and a flocculation term to the model structure in order to develop a reactive primary clarifier model and improve the model for soluble COD estimation. The flocculation term was required to describe the conversion of soluble unbiodegradable COD to particulate unbiodegradable COD and soluble readily biodegradable COD to slowly biodegradable COD. Moreover, the simulation study of Banchis et al. (2015) developed the five-classes particle settling velocity distribution (PSVD), combined with "multiple Vitesses de Chute en Assainissement (ViCAs)" experiments to predict TSS effluent concentrations accurately and describing the dynamic TSS behaviour at the outlet of a primary clarifier. The study also applied the PSVD model with chemicals addition (coagulation/flocculation) on the primary clarifier, and the results showed a significantly improved TSS removal compared with TSS simulated without CEPT.

The highest degree of 2-D/3-D models has been developed in Computational Fluid Dynamics (CFD). In this case, the models simulate the internal hydrodynamics and processes in the clarifier, also visualize the internal conditions, including the flow pattern and position of the sludge blanket (Plósz et al., 2012). Typically, the solution of the momentum and mass conservation equations constrained by specific initial and boundary conditions and density equation, are the principles of all CFD models (Griborio et al., 2014). 2-D and 3-D modelling of primary clarifier using software 2Dc and ANSYS FLUENT was completed in the Georgia WWTP (Griborio et al., 2014). Analysis of the percent removals, the solids inventory, and density currents were conducted using the 2-D model, and analysis of inlet and outlet configuration was conducted using the 3-D model. The results demonstrated that 2-D models are preferred to evaluate the effects of macro-scale modification on tank performance, and steady-state 3-D models can accurately evaluate the inlet and outlet configurations. (Griborio et al., 2014).

Besides the modelling of traditional primary clarifiers, limited literature has been done on chemically enhanced primary treatment (CEPT) modelling and CEPT effluent characterization. One of the studies by Banchis et al. (2015) mentioned above presented the five-classes PSVD model for CEPT modelling but only concerning TSS removal prediction. Another research published by Tik and Vanrolleghem (2017) used a well-developed CEPT model (WEST modelling software) to find an adequate control strategy of the chemical addition based on effluent quality, chemical savings, and maintenance effort. A constant polymer dose was added, and the turbidity-based CEPT controller was developed in the 1-D model to observe the effect of alum addition on sedimentation. The non-settleable suspended solids fraction (f_{ns}) and settling velocity (V_0) were modelled depending on the alum concentration at the inlet of the primary clarifier (PC) and the local alum concentration in the considered layer. The calibration and validation process demonstrated that the CEPT model was able to forecast effluent TSS concentrations in accordance with influent TSS concentration, alum concentration, and inflow rates. However, no information is available on how the process impacted the effluent COD fractions.

Indeed, an adequate COD fractionation measurement is considered necessary in primary clarifier modelling / CEPT modelling (Banchis et al. 2015; Melcer et al. 2004; Phillips et al. 2009). The reliability of primary effluent characterization and sludge wastage description need to be enhanced as the process occurring in the primary clarifier being modelled. It is well known that improper fractionation of the wastewater composition in model calibration results in significant parameter estimation errors (Rieger et al. 2002). Comprehensive wastewater characterization is considered as the most critical step providing all essential information for dependable modelling, design of activated sludge treatment process, and design of biological nutrient-removal processes (Metcalf, 2013; Orhon & Cokgor, 1997). A considerable amount of studies has been conducted to establish adequate experimental protocols for COD fractionation, either with physical-chemical methods or with biological methods (Petersen et al., 2003). In reality, COD fractions are analyzed with the combination of both methods. The physical-chemical method has the advantages of being a more rapid and uncomplicated tool for COD fractionation while using this approach alone will not provide sufficient information on the distribution of organic substrate. For example, the determination of truly soluble COD fraction largely depends on the decision of membrane filter pore size used. Also, defining the slowly biodegradable COD fraction (X_B) as being colloidal could induce errors because colloidal fraction may also contain unbiodegradable matter. Parts of the soluble and colloidal fraction may belong to X_B. Thus, the separation of ordinary heterotrophic organisms (X_{OHO}), endogenous decay products (X_E), slowly biodegradable COD (X_B), particulate unbiodegradable COD (X_U) components is difficult (Petersen et al., 2003). Due to the restrictions in analyzing biodegradability through long-term BOD measurements, the biological wastewater fractionation methods have been found more applicable and efficient with respect to organic matter determination. Respirometry has been widely accepted as one of the most popular biological characterization methods (Petersen et al., 2003).

Respirometric measurement provides direct and indirect information: direct information such as oxygen consumption rate of the biomass activity and indirect information such as COD fractionation, kinetic parameters and stoichiometric coefficients (van Loosdrecht et al., 2016; Spanjers et al., 1996). Usually, indirect information is obtained as essential inputs for modelling purposes. Although no clear standard measurement procedure has emerged, WERF recommended that a flocculation step should be used to separate soluble, colloidal, and particulate fractions (Melcer et al. 2004). Therefore, the standard of choosing a proper characterization method should be based on whether the developed model matches the purpose of using it. Some of the effects of wastewater fractionation on modelling outputs include: 1) the estimated inert particulate COD effect on sludge production; 2) the estimated total biodegradable COD effect on oxygen demand; 3) the estimated readily biodegradable COD effect on anoxic denitrification rate and anaerobic phosphorus release; 4) the estimated inert soluble COD effect on effluent COD (Philips et al. 2009; Petersen et al. 2002; Henze et al. 2000). However, studies are limited to show the accuracy of clarifier models with regards to their potential in estimating these wastewater fractions.

This study aims to characterize the volumeless point separator, three-compartments clarifier, and layered flux clarifier models with respect to typical primary clarifier performance parameters and fractions. The paper compares and contrasts the performance of the three primary clarifier models in regard to accurately describing a long term full scale CEPT clarifier process in relation to COD fractions, including colloidal COD (C_{COD}), soluble COD (S_{COD}) and suspended solids (TSS) concentrations of wastewater. In addition, an experimental work of wastewater characterization (fractionation) under CEPT using both the physical-chemical method and biological (respirometry) methods were further conducted to substantiate the model performance. Experimental characterization results of raw wastewater (RWW) were fed into the aforementioned three clarifier models as inputs, then compare the modelled CEPT effluent fractions and experimental CEPT effluent fractions to find which model captures the most realistic results.

3.2 Materials And Methods

3.2.1 Clarifier Long Term Performance Data Collection

The data used to develop and calibrate the primary clarifier models were collected from the Vauxhall Pollution Control Plant (PCP) (Figure SD1), and the data used to validate were obtained from Adelaide WWTP, that are two of the five wastewater treatment plants in London (ON, Canada). The primary treatment in Vauxhall WWTP has two sections, Section 1 and Section 2, to treat two-thirds and one-third of the total flow, respectively. According to the 2018 Annual Vauxhall WWTP report, the Section 1 primary clarifier has two 9.14 m x 29.6 m x 3.05 m SWD (side water depth), and Section 2 has two 4.8 m x 22.86 m x 3.05 m SWD primary clarifiers (Fig SD1). During the experimental period, the inflow of each section was controlled to maintain a similar surface overflow rate and detention time. Two types of CEPT was performed, ferric chloride (15 mg/L) addition was applied in Section 1 influent (CEPT-I), while ferric chloride + poly aluminum chloride PACL (0.15 mg/L + 0.5 mg/L, respectively) was added in Section 2 influent (CEPT-II). Same as the Vauxhall WWTP, the primary treatment in Adelaide WWTP also has two sections; the CEPT experiment was conducted on Section 1, which has four primary clarifiers, with the dimension 16.5 m x 4.9 m x 2.4 m SWD each. Two types of CEPT were operated in the same section with a pre-determined chemical addition setup (CEPT-I: 15 mg/L ferric chloride; CEPT-II: 15 mg/L ferric chloride followed by 0.5 mg/L poly aluminum chloride PACL), but the studies were conducted sequentially during different periods in 2019.

The design data, including general plant description, and the physical characteristics, such as configuration, process units, volumes, and capacities, were compiled from the Vauxhall WWTP 2018 annual report provided by the plant. The operational data and measured data were obtained from the previous study conducted by our research team (Dong et al., 2019) on full-scale primary clarifier operation on Vauxhall WWTP (2018 July 20 – 2018 October 1). Moreover, the available dynamic data, including influent flow, primary sludge, TSS and T_{COD} concentration, was used for the CEPT process model setup and calibration. The input parameters used for the volume-less point separator, three-compartment clarifier, and the layered flux clarifier are shown in the supporting document (Table SD1). More importantly, model validation was performed on CEPT-I and CEPT-II based on data collected from Adelaide PCP (2019 March 28 – June 11 and 2019 June 13 – 2019 September 10, respectively), the second plant in the city of London, ON (Canada). The influent characteristics and the CEPT process (type and rate of chemical addition) of both WWTP were similar.

3.2.2 Setup of Primary clarifier

CEPT modelling configuration has consisted of four process streams: influent, metal dose ($FeCl_3$), primary sludge, and effluent. Both types of CEPT was modelled using such a configuration. The simulation was conducted on a SUMO (Dynamita, 2019) simulation platform.

3.2.2.1 Volumeless point separator (0-D model)

The volumeless point separator (0-D) is an ideal separator of liquid and solids. The model implements the separation of particles but not settling behaviour in which the effluent removal efficiency of solids, colloidal, and soluble material is a direct model input. The default percent removals were modified to match the actual CEPT primary clarifier performance to achieve chemical addition scenarios. Both CEPT-I and CEPT-II require a ferric addition process unit. The input parameters of colloidal material removal and soluble material removal were calibrated as well. Soluble material removal of CEPT-I and CEPT-II was found to be 35±10% and 58±7%, respectively, according to Dong et al. (2019). The averaged primary sludge flow was calculated as

45.6±9% and 34.2±7% m^3/d. The default and calibrated values of the input parameters for the volumless point separator model are shown in Table 3-1.

Table 3-1:CEPT-Volumeless point separator model Setup in SUMO

Input Parameter	Unit	Default	Calibrated CEPT-I	Calibrated CEPT-II
Solids percent removal	%	75	75	89
Colloidal material removal	%	50	30	50
Soluble material removal	%	10	35	58
Sludge flow	m^3/d		45.6	34.2

3.2.2.2 Layered flux model (1-D model)

The layered flux clarifier(1-D) represents the hydrodynamic behaviour in one dimension and its interaction with the flocs that are settling. It is based on the 10-layers model proposed by Takacs et al. (1991). Through adjusting the settling parameters based on valid assumptions, both CEPT scenarios can be conducted. Moreover, settling solids in each layer have different flocculent characteristics; thus, an analysis of chemical addition impacts on sludge settling velocity distribution can be conducted as well. Since hindered settling is not considered in the primary clarifier, the coefficient for this parameter was set to 0. Due to the addition of polymers, more solids are settled at higher settling velocities. Therefore, the coefficient of flocculent settling for CEPT-I and CEPT-II was calibrated to 0.003 m^3/g and 0.0057 m^3/g, respectively. Ideally, suspended solids in the compression settling zone are greatly affected by the dosage of coagulants due to the precipitation of soluble components, and this parameter was calibrated from 8000 to 800,000 g/m^3. The fraction of non-settleable solids was adjusted to 24% and 10% for Type I CEPT and Type II CEPT, respectively, to match the assumption of efficient removal of non-settleable solids with coagulation and get an optimal fit on effluent data (Gernaey et al.,2001). The default and calibrated values of the input parameters for the Layered flux model are shown in Table 3-3.

Table 3-2: CEPT – Layered flux model Setup in SUMO

Input Parameter		Unit	Default	Calibrated CEPT-I	Calibrated CEPT-II
Clarifier settings	Surface area	m^2	600	541	219
	Depth	m	5	3.1	3.1
	Depth of influent layer from top	m	2	2	2
	Sludge flow	m^3/d	200	45	34.2
Settling parameter	Boundary settling velocity	m/d	220	220	220
	Maximum Vesilind settling velocity	m/d	220	220	220
	Coefficient for hindered settling	m^3/g	0.0005	0	0
	Coefficient for flocculent settling	m^3/g	0.0015	0.0029	0.00571
	Coefficient for compression	m^3/g	0.0006	0.0006	0.0006
	Boundary compression concentration	g/m^3	8000	800000	800000
	Fraction of non-settleable solids	%	99	24	10
	Non-settleable TSS	g/m^3	50	50	50
	Concentration at top of sludge blanket	g/m^3	3000	3000	3000

3.2.2.3 Three-compartment model (1-D model)

Similar to the layered flux model, the three-compartments primary clarifier model is governed by discrete settling, flocculent settling, and compression settling. However, in this model, the polymer addition is adequately described whereas, in the layered-flux model, the polymer addition is indirectly modelled through adjusting settling parameters. The three-compartment model consists of a feed well, a point separator, a clear water compartment, and a sludge blanket, as shown in the supporting document (Figure SD2). The three compartments are reactive completely-mixed reactors with diffused aeration and input DO. The PACL was added in feed well; after passing through the solids separation unit, the liquid flow goes directly to the clear phase and the underflow to the blanket, which further separates to sludge wasting and clear phase (Figure SD2). The polymer addition was characterized by inputting parameters including concentration, rate of precipitation with polymer and half-saturation of polymers, colloidal substrate and solids percent removal in flocculation. The concept of polymer addition in the three-compartment model enhances solids removal in two aspects: the colloidal substrate flocculation (calculated based on Monod saturation function on the colloidal substrate and the polymer concentration, equation in supporting document, Equation SD1) and the removal efficiency of solids (adjusted based on field or experimental data with and without polymer addition and using a Monod function with the half-saturation of polymers for solid percent improvement parameter).

The volume of Section 1 and Section 2 primary tanks was calculated and used as input. Ferric flow rate and concentration were setup in the metal dosage process unit for both CEPT types. In CEPT-II, polymer concentration was set to 0.5 mg/L, the same as the dosing concentration during the experimental period. As shown in Table 3-2, the model does not have a provision to input the type of polymer; however, the polymer dosage can be modified. Half saturation of polymers for solids percent removal was calibrated to the minimum value of 0 to enhance solids removal. The default and calibrated values of the input parameters for the three-compartment model are shown in Table 3-2.

Table 3-3: CEPT - Three-compartment model Setup in SUMO

	Input Parameter	Unit	Default	Calibrated CEPT-I	Calibrated CEPT-II
Settings	Total volume	m^3		1650	669.3
	Feed well volume	m^3	200	200	200
	Sludge blanket volume	m^3	300	270.5	50
	Sludge flow	m^3/d		45.3	34.2
	Solids percent removal without polymer (with metal)	%	50	76	76
	Solids percent removal with polymer (with both metal dosage and polymer)	%	50	89	89
Clarifier geometry	Surface of clarifier	m^2		541	219
Flocculation parameters	polymer concentration	g/m^3	0	0	0.5
	Half-saturation of polymers for solid percent removal improvement	g/m^3	0.25	0.25	0
	Rate of precipitation with polymer	1/d	5000	5000	5000
	Half-saturation of polymers flocculation	g/m^3	0.5	0.5	0.5
	Half-saturation of a colloidal substrate in flocculation with polymers	g/m^3	0.1	0.1	0.1

3.2.3 Wastewater sample collection and fractionation

Raw wastewater (screened and gritted), CEPT-I effluent, CEPT-II effluent, and return activated sludge (RAS) were collected from Vauxhall PCP (London, Ontario) to determine the wastewater and CEPT effluents fractions. CEPT clarifier was operating under the pre-determined optimum condition: coagulant (15 mg/L ferric chloride) and flocculant (0.5 mg/L poly aluminum chloride (PACl)) in a full-scale primary clarifier operation (Dong et al., 2019). Filtered samples and filtered-flocculated samples were prepared on the same day of sampling.

As shown in Figure 3-1, total chemical oxygen demand (T_{COD}) is classified based on solubility and biodegradability. From a modelling standpoint, it is critical to distinguish between soluble (filtered-flocculated), colloidal and particulate fractions of COD in the biological reactor. The total COD was evaluated in terms of soluble COD (S_{COD}), colloidal COD (C_{COD}), and particulate COD (X_{COD}) (Eq.1).

$$T_{COD} = S_{COD} + C_{COD} + X_{COD} \qquad (Eq.1)$$

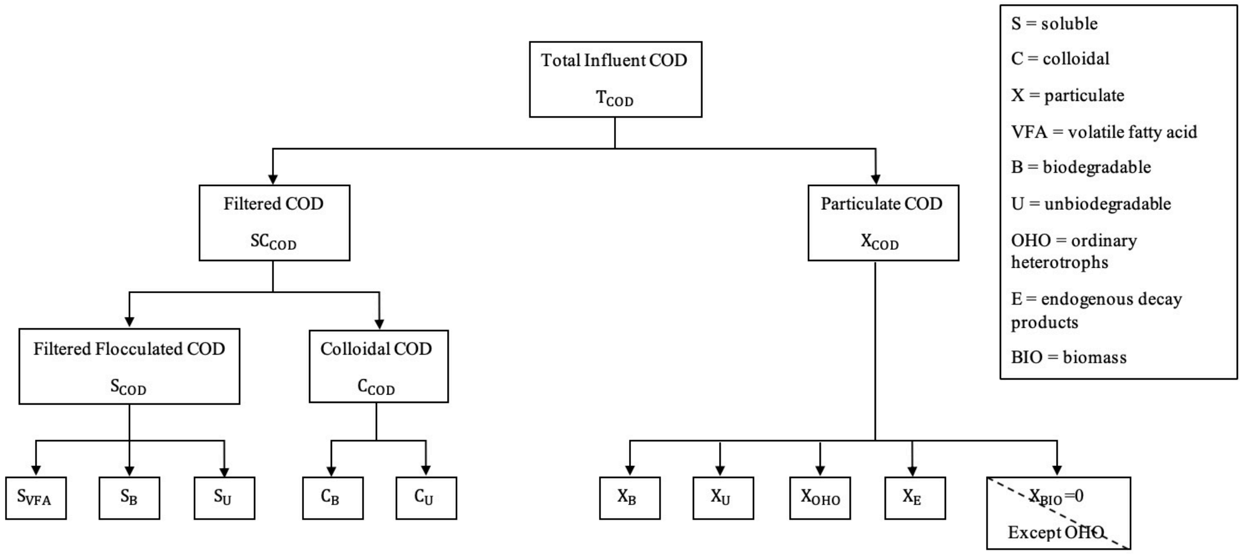


Figure 3-1:Distribution of COD fractions in wastewaters

S_{COD} was further divided into soluble VFA biodegradable (S_{VFA}), soluble non-VFA biodegradable COD (S_B), and soluble unbiodegradable COD (S_U) (Eq.2). The readily biodegradable COD (rbCOD) consisted of short-chain volatile fatty acids and fermentable (non-VFA) biodegradable COD (Eq.3).

$$S_{COD} = S_{VFA} + S_B + S_U \qquad (Eq.2)$$

$$rbCOD = S_{VFA} + S_B \qquad (Eq.3)$$

Similarly, the total particulate COD (X_{COD}) consists of slowly biodegradable COD (X_B), particulate unbiodegradable COD (X_U), heterotrophic biomass fraction (X_{OHO}), and endogenous particulate residue (X_E) (Eq.4).

$$X_{COD} = X_B + X_U + X_{OHO} + X_E \qquad (Eq.4)$$

Lastly, the total colloidal COD can be further divided into two groups: colloidal biodegradable COD (C_B) and colloidal unbiodegradable COD (C_U).

$$C_{COD} = C_B + C_U \qquad (Eq.5)$$

Estimation of COD fraction was made using both physical-chemical and biological (respirometry) methods. 1.5µm filter paper was used to differentiate between filtered COD (SC_{COD}) and particulate COD (X_{COD}). T_{COD} is measured using HACH test kits (HACH, London, Ontario, Canada). Mamais (1993) developed the most accepted approach to determine filtered-flocculated COD (S_{COD}). This approach is based on flocculation using Zn $(OH)_2$ at pH 10.5 to obtain truly soluble COD (eliminate colloidal matter of 0.1-10µm). However, it highly depends on the pH value during flocculation. In one study, it has been introduced that zinc sulphate can be replaced with aluminum sulphate and has the advantage of no pH adjustment and good flocculation (Wentzel et al., 2001). Both methods were applied to examine the accuracy, and the result showed a percentage difference of 1.5 (%), basically no difference in S_{COD} values. Therefore, the second method using zinc sulphate was chosen in this study for the measurement of truly soluble COD. Colloidal COD was calculated as the difference between filtered COD (SC_{COD}) and filtered-flocculated COD (S_{COD}).

Respirometry is the technique used to assess the fractionation of biodegradable organic matter and identify kinetic parameters for modelling purposes. One difficulty of applying the respirometry technique is that the quality or accuracy of kinetic information is profoundly affected by the initial substrate to biomass ratio ($S_0/X_{0:}$ mg COD/mg VSS). A low S_0/X_0 ratio (0.01-0.025 mgCOD/mgVSS) leads to short-term reaction, the biodegradable organic matter is rapidly assimilated, and no significant occurrence of biomass growth due to the lack of synthesis reactions. Conversely, a high S_0/X_0 ratio (>1.5 mgCOD/mgVSS) enables a thorough assessment of organic matter biodegradation, but the concentration of microorganism changes over time leads to a difficult understanding of multicomponent kinetics (Gatti et al.,2010; Chudoba et al.,1992; Kappeler & Gujer,1992). Some studies demonstrated that the optimal ratio could be decided based on a trial and error procedure (Kappeler & Gujer,1992; Xu & Hultman, 1996). In this research, the substrate to biomass ratio (S_0/X_0) of 4 mg COD/mg VSS was chosen (Kappeler & Gujer, 1992). The respirometry was conducted for CEPT-1 and CEPT-II processes independently. For each CEPT process, the test was conducted using four influent wastewater, and CEPT effluent samples: (1) raw sample, (2) filtered sample (1.5μm), (3) a mixture of filtered flocculated sample supernatant, and an activated sludge sample at So/Xo of 4 mg of supernatant COD/ mg of activated sludge VSS, and (4) activated sludge sample. Samples were analyzed every two hours during the first ten hours of experiments to capture the substantial changes of the readily and slowly biodegradable substrate; then, a daily sample was taken. The analysis included total COD and soluble COD analysis.

The biomass yield coefficient (Y_H) was determined from the OUR profile by plotting net oxygen consumption and S_{COD} reduction. S_B was calculated from the equivalent oxygen consumption in the test sample after subtracting the oxygen consumption of the blank. The decay coefficient (b_H) was determined using an activated sludge sample without a substrate. The maximum specific growth rate of heterotrophs (u_{max}) was determined from the OUR data of the filtered-flocculated sample using equation 8. Ordinary heterotrophic organisms (X_{OHO}) was calculated from equation 9; the procedure backtracks the amount of heterotrophic biomass initially present in the wastewater by comparing the initial respiration rate with the respiration rate after significant (hence, well quantifiable) growth of X_{OHO}. Table 3-4 summarizes the equation to determine COD fractions from the respirometry test.

Table 3-2:The equation to determine biokinetic parameters and COD fractions

Parameter		**Equation**	**Eq.**
Biomass yield coefficient	Y_H	$Y_H = 1 - \frac{\Delta O_2}{\Delta ff_{COD}}$	(6)
Decay coefficient	b_H	$\ln OUR = [\ln(1 - \mathrm{fe}) b_H X_{OHO}] - b_H t$	(7)
Maximum specific growth rate	μ_{max}	$\ln \frac{OUR}{OUR_{initial}} = (\mu_{max} - b_H)t$	(8)
Ordinary heterotrophic organisms	X_{OHO}	$X_{OHO} = \frac{OUR_{initial}}{(\frac{1 - Y_H}{Y_H})\mu_{max} + (1 - f_e) b_H}$	(9)
Readily biodegradable COD (non-VFA)	S_B	$S_B = \frac{\Delta O_2}{1 - Y_H}$	(10)
Volatile fatty acids	S_{VFA}	Measured	
Soluble unbiodegradable COD	S_U	$S_U = S_{COD} - S_{VFA} - S_B$	(11)

Colloidal biodegradable COD	C_B	$C_B = BODult\ (filtered\ sample) - BODult\ (filtered - flocculated\ sample)$	(12)
Colloidal unbiodegradable COD	C_U	$C_U = C_{COD} - C_B$	(13)
Slowly biodegradable COD	X_B	$X_B = BODult(raw\ sample) - BODult(filtered\ sample) - X_{OHO}$	(14)
Slowly unbiodegradable COD	X_U	$X_U = X_{COD} - X_B - X_{OHO}$	(15)

3.2.4 Evaluation of model performance

Parameter fitting was done by calculating the mean, standard deviation for actual data and model prediction data, and the coefficient of determination (r^2) between model prediction and actual concentrations. The evaluation of the slope, the intercept, and the R-squared value of the trendline fitted to the data provide factors for judging and establish reliability on model performance (Piñeiro et al., 2008).

3.3 Results And Discussion

3.3.1 Primary clarifier model calibration and validation using long term full-scale clarifier performance data

As mentioned in data collection, the measured data were collected from a previous full-scale study, and the parameters available for calibration include influent, effluent and underflow TSS and TCOD concentration, flow fractions and chemical dosing rate and concentration. Experimental COD concentrations were manually reconciled, including mass balance check and specific ratio check (Supporting material: Tables S1-S6). The reconciled COD concentrations were converted into model influent fractions form (SUMO form) as model input.

Figures 3-2 and 3-3 summarized the calibrated dynamic model performance. Influent TCOD data fluctuates significantly throughout July to August 2018 (416.7 ± 172.1 g COD/m^3, ranging from 230 - 785 g COD/m^3), mainly due to dilution during wet weather periods. Influent data of TSS at that period were relatively stable, ranging from 120 - 293.3 g TSS/m^3 with an average value of 210 ± 47.35 g TSS/m^3. The averaged influent TSS/COD ratio was calculated to be 0.583 and comparable to the typical raw influent TSS/COD ratio of 0.503 stated by Hauduc et al. (2010). The averaged CEPT-I and CEPT-II effluent TSS/COD ratio was estimated to be 0.30 and 0.26, respectively and lower than the typical PE TSS/COD 0.38 (Hauduc et al., 2010), mainly due to higher removal of TSS and COD in CEPT than traditional primary treatment. The modelled effluent TSS/COD ratio of CEPT-I and CEPT-II from volumeless point separator, three-compartment clarifier and layered flux clarifier were: 0.32, 0.30 and 0.23; 0.29, 0.23 and 0.16, respectively. It can be observed that predicted results from the three-compartment clarifier is the closest matching the actual facility performance (Supporting document, Figures SD5-10). Moreover, R-squared values (Figures 3.2 and 3.3), in conjunction with residual plots (supporting document, Figures SD17-22), were evaluated to observe how well the model fits the data. The residual plot of modelled value and actual value of TCOD and TSS from three clarifier models showed a random pattern, which means the line is a good fit for the data (Supporting material: Residual plots SD17-SD22). R-squared values of TCOD model-fit analysis from the calibrated CEPT-I and CEPT-II clarifiers were 0.76, 0.9, 0.76 and 0.85, 0.91, 0.86, respectively (Figure 3.2).

Similarly, for TSS model-fit analysis, an R-squared value of 0.65, 0.70, 0.43 and 0.79, 0.81, 0.62 were observed from the CEPT-I and CEPT-II volumeless point separator, three-compartment clarifier and layered flux clarifier models, respectively (Figure 3.3). Following by R-squared values comparison and visual inspection of the dynamic data (Supporting document, Figures SD5-

10), model performance from the calibrated three-compartment clarifier demonstrated the best fit to the actual performance during the sampling period. 0-D model describes chemically enhanced primary treatment and predict effluent characteristics based on the inputs of solids, colloidal and soluble material removal, which cannot fully describe the fraction changes in the effluent. The layered flux model is more complex and can accurately describe suspended solids removal based on settling theory, which requires more experimental efforts to determine the corresponding settling coefficient to achieve effective calibration. However, the three-compartment model incorporates polymer addition process to solids removal, which substantially enhanced the accuracy of predicted CEPT effluent fractions.

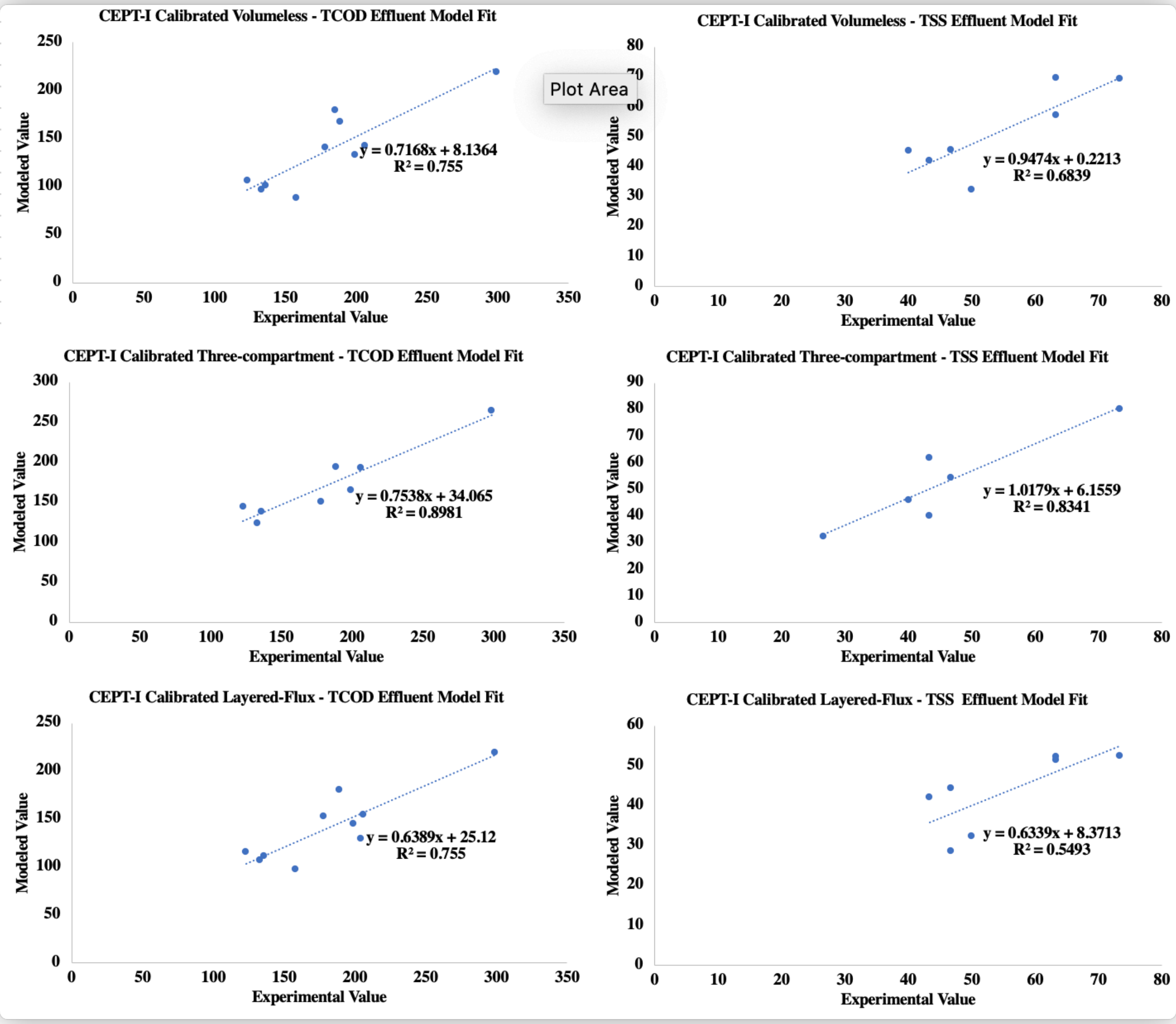
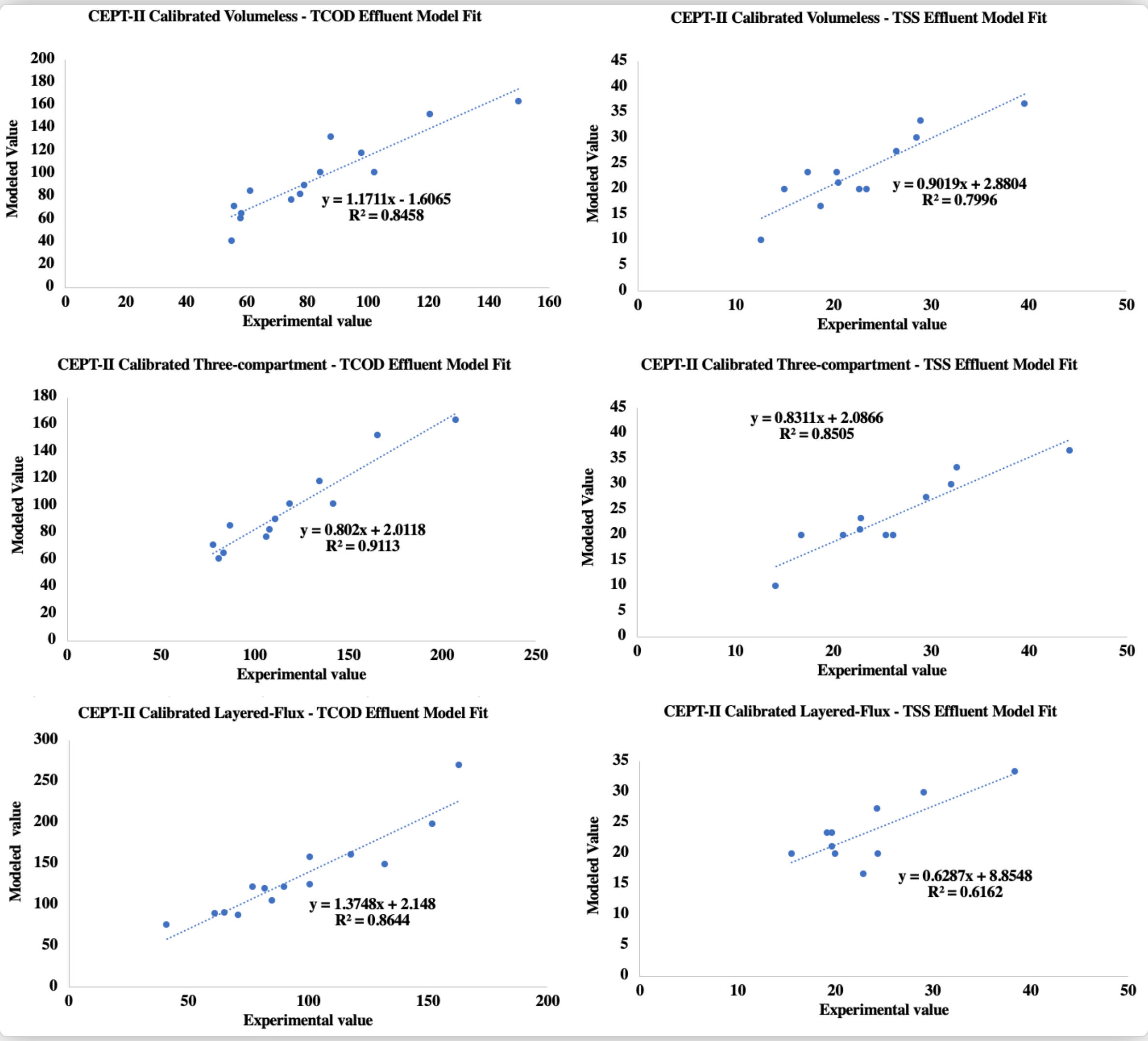


Figure 3-2:CEPT-I Model Fit for Simulated Effluent TCOD and TSS Concentration (Calibrated Dynamic Results)


CEPT-II Calibrated Volumeless - TCOD Effluent Model Fit

CEPT-II Calibrated Volumeless - TSS Effluent Model Fit

CEPT-II Calibrated Three-compartment - TCOD Effluent Model Fit

CEPT-II Calibrated Three-compartment - TSS Effluent Model Fit

CEPT-II Calibrated Layered-Flux - TCOD Effluent Model Fit

CEPT-II Calibrated Layered-Flux - TSS Effluent Model Fit

Figure 3-3:CEPT-II Model Fit for Simulated Effluent TCOD and TSS Concentration (Calibrated Dynamic Results)

Once the model was calibrated using Vauxhall's PCP data, the three-compartment model was further validated using Adelaide PCP data. Raw influent and primary effluents data after the CEPT reactor from March 28 to June 11 and from June 13 to September 10-2019, in Adelaide PCP (London, ON) were selected for CEPT-I and CEPT-II model validation, respectively. Some of the site-specific parameters (e.g., geometry data, ferric chloride dosage) were updated in the model to match the actual CEPT performance in Adelaide PCP. The Adelaide data were obtained from the city of London; hence the model efficacy was compared using typical parameters measured by the plant. In this case, three target parameters, including total suspended solids (TSS), five-day biological oxygen demand (BOD$_5$), and total Kjeldahl nitrogen (TKN), were considered. Figure 3-4 to 3-6 summarized the validated dynamic three-compartment clarifier performance. In the case of CEPT-I clarifier, 261.1 ± 44.1 g TSS/m^3, 205 ± 47.8 g BOD/m^{3,} and 32.1 ± 4.1 g N/m^3 were reported as the influent characteristics. Experimental effluent concentrations for the before-mentioned three parameters were 84 ± 22.8 g TSS/m^3, 104.8 ± 27 g BOD/m^{3,} and 26.3 ± 3.1 g N/m^3, respectively. The average influent value of TSS, BOD$_{5,}$ and TKN for the second case CEPT-II were 254.9 ± 39.3 g TSS/m^3, 257.8 ± 39.8 g BOD/m^{3,} and 41.2 ± 4 g N/m^3, respectively. The average experimental effluent values of TSS, BOD$_{5,}$ and TKN were 84.22 ± 17.36 g BOD/m^3, 106.5 ± 23 g TSS/m^{3,} and 33.05 ± 2.51g N/m^3, respectively.

Dynamic simulation of the calibrated three-compartment model predicted an averaged value of 70.1 ± 22.8 g TSS/m^3, 131.2 ± 28.8 g BOD/m^{3,} and 24.4 ± 3g N/m^3 (CEPT-I); 63.4 ± 21 g TSS/m^3, 149.4 ± 20.4 g BOD/m^{3,} and 34.7 ± 2.1 g N/m^3 (CEPT-II). The residuals did not show any conspicuous patterns (Supporting material: Figure SD23-SD24), and R-squared values were 0.84, 0.78 and 0.82 (CEPT-I); 0.9, 0.75, and 0.84 (CEPT-II) for TSS, BOD and TKN, respectively, showing comparable results to the ones observed during calibration. The TSS, BOD and TKN profile data can be found in the supporting material (Figure SD11-SD16).

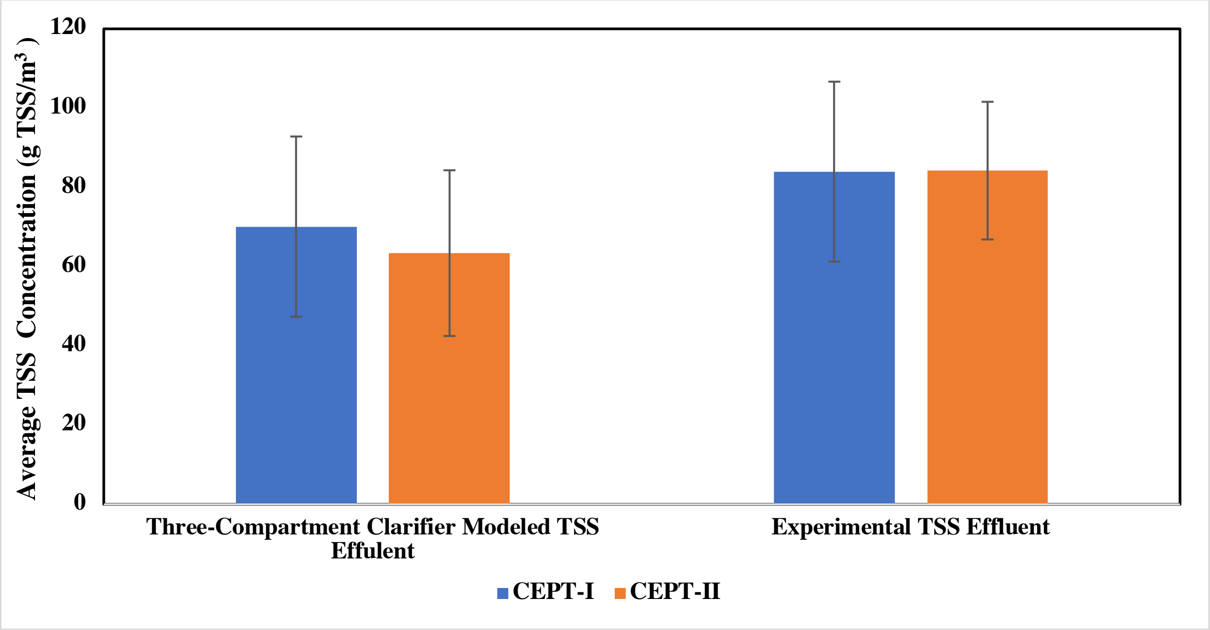


Figure 3-4:Model Fit for Simulated Effluent TSS Concentration (Validated Dynamic Results)

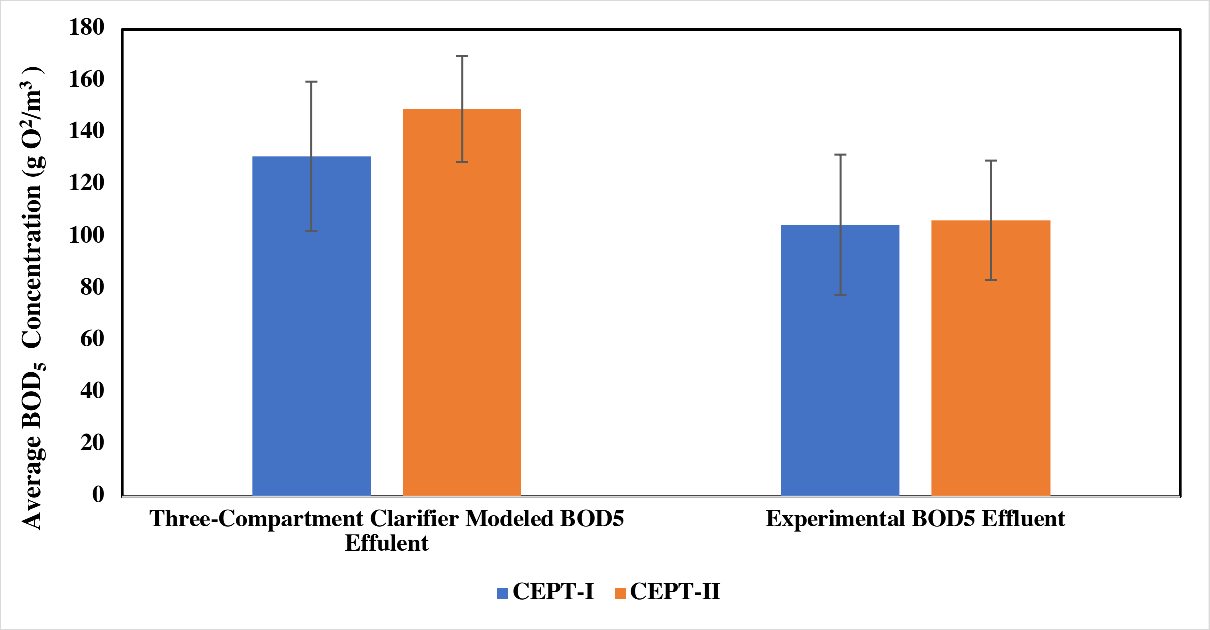


Figure 3-5:Model Fit for Simulated Effluent BOD5 Concentration (Validated Dynamic Results)

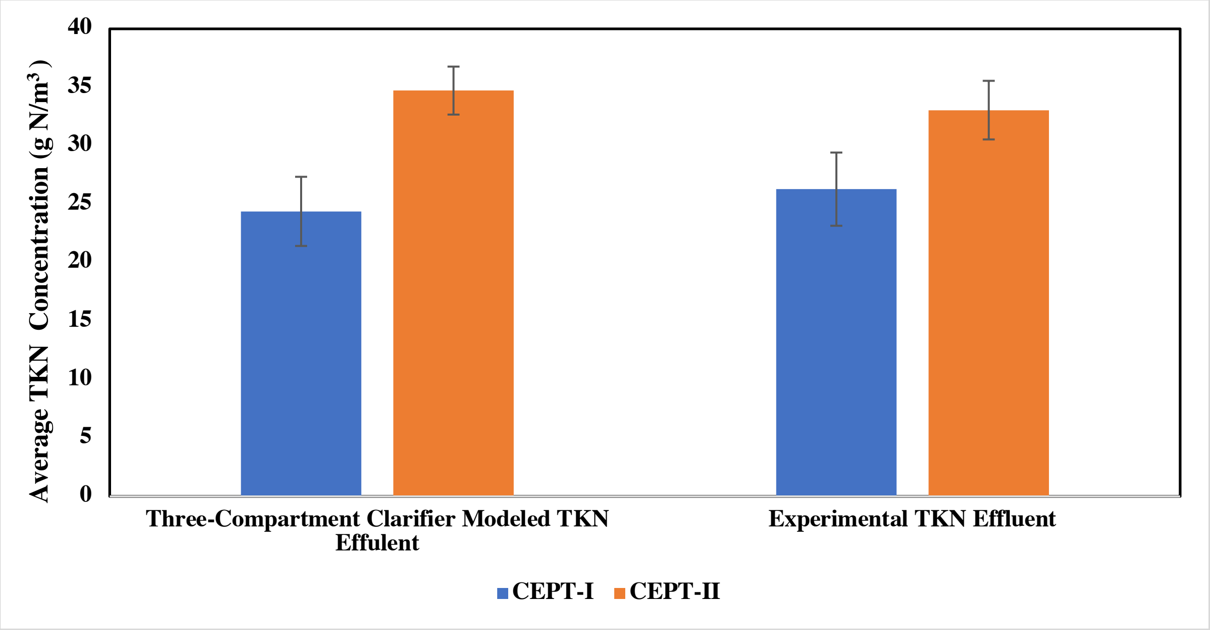


Figure 3-6:Model Fit for Simulated Effluent TKN Concentration (Validated Dynamic Results)

3.3.2 Measured wastewater and primary effluent fractions

Experimental characterization results of raw wastewater and CEPT effluents were compared with literature values, as shown in Tables 3-5 and 3-6. In most of the literature (Table 3-5), the biodegradable fraction includes readily biodegradable COD (S_S), readily hydrolyzable COD (S_H), and slowly biodegradable COD (X_S) (Xu and Hultman, 1996). Due to stringent wastewater effluent criteria, the determination of colloidal COD modelling has become more significant in recent years; thus, the colloids are added as an individual fraction besides soluble matters and particulate matters. Therefore, the biodegradable fraction analyzed in this study is more detailed than before-mentioned, as shown in Table 3-6. Notwithstanding, a number of studies have presented COD fractionation on raw influent and primary effluent (without any chemicals); little work has characterized COD in these specific CEPT effluents: ferric chloride addition only and ferric chloride followed by an optimized polymer (PACL).

Table 3-6 also demonstrates the experimental results for wastewater COD fractions of RWW, CEPT-I, and CEPT-II effluents. Quantifying readily biodegradable COD (rbCOD) concentration in the wastewater is of essential importance for the design and operation of biological nutrients removal system (Wentzel et al., 2001; Henze et al., 2008). The rbCOD portion is hydrolyzed immediately and be absorbed by the microorganisms, while the adsorption of colloidal and particulate COD takes a longer time because they have to be dissolved by extracellular enzymes first (Henze et al.,2008). The unbiodegradable soluble COD (S_U) is discharged with secondary effluent. S_B was determined to be 19.3±6%, 45±3.4%, and 49.4±6.1% of the T_{COD} for RWW, CEPT-I and CEPT-II effluents, respectively. It was found that CEPT-II effluent contains comparatively more soluble biodegradable material than CEPT-I effluents. The S_B (RWW) observed in this study are in the range of 9-42% of TCOD, as summarized in Table 3-6. Orhon et al. (1999) used both alum and iron salts as coagulants together with an anionic polyelectrolyte for chemical pre-treatment, S_B was found to be 35% of TCOD in chemical-settling effluent. Compared to the literature, the S_B fraction observed in CEPT-II effluent was higher. S_{VFA} of RWW was determined using the Hach test kit (HACH, London, Ontario, Canada). Typically, individual VFAs fraction in raw municipal wastewater and primary effluent is in the range of 0 to 8.8% and 0-16%, respectively (Pasztor et al.,2009). However, no VFA was found in RWW, which might be due to the measurement range of the test kit (from 50 to 2500 mg/L). S_U was determined from the soluble COD mass balance equation (Eq.11), accounting for 0.8%, 1.9%, and 2.25% of the T_{COD} in RWW, CEPT-I and CEPT-II effluents, respectively. The S_U value range anywhere from 2-15% and 2.2-9.5% of the T_{COD} for RWW and primary effluent (without any chemicals), respectively.

Compared to soluble and particulate fractions, the colloidal fraction was found relatively smaller in all the RWW (17.6% of TCOD), CEPT-I (1.44% of TCOD), and CEPT-II (2.50 of TCOD) samples (shown in Table 3-6). ASM1 and ASM2d models do not distinguish between colloidal and particulate COD, and the models assume that influent colloidal material will be adsorbed immediately onto the sludge matrix and removed from the liquid phase (Melcer, 2004). Also, the possibilities of whether the colloidal COD is biodegradable or not is not taken into consideration. These issues are potentially problematic when it comes to organics removal modelling in a primary clarifier. Some other models include the distinction, which has the advantages of accurate quantification of solids percent removal and better prediction of sludge production (Petersen et al. 2003). The addition of flocculant chemical dosing improves the formation of aggregates from colloidal materials; therefore, improving the determination of the colloidal COD fractions is critical for CEPT modelling. ~~T~~he C_B fraction was determined through the BOD_{ult} test of filtered sample and filtered-flocculated sample, as shown in Eq.12, as 12.4±0.6%, 0.56% and 2.22±1.39 of T_{COD} in RWW, CEPT-I and CEPT-II effluents, respectively and most were removed after primary treatment. Henze et al. (2008) reported a C_B fraction ranging from 47 - 53%; however, Rickert and Hunter (1972) reported 10% of colloidal COD fraction in raw wastewater. Accordingly, the significant difference reported from different literature was mainly due to the wastewater composition, which varies between different sites. Henze et al. (2008) also reported a larger colloidal fraction (29 - 36% of TCOD) remained after primary clarification (without any chemicals addition). The C_U concentration was calculated by subtracting C_B from colloidal COD (Eq.13). Colloidal materials removal in CEPT-I and CEPT-II effluents was calculated as 91.8% and 85.8%, respectively. The colloidal removal under CEPT was expected to be higher than the removal under PE. The possible source of error could be due to the non-ideal

BOD test environment (temperature) that leads to unreliable BOD measurement for C_B. Particulate COD fractions decreased in both effluents.

The biodegradable particulate and colloidal organic compounds are essential components of the slowly biodegradable fraction in accordance with the maximization of sedimentation and chemical precipitation in primary clarifiers (Drewnowski & Makinia, 2013). The high concentration of unbiodegradable particulates (X_U) has an imperative influence on the quality of effluent, and it can affect the maintenance of sludge age and nitrification. Heterotrophic biomass (X_{OHO}) growth is converted from readily biodegradable COD (rbCOD), and the endogenous residue X_E is produced from the endogenous respiration (activities include decay, lysis, maintenance, and predation) of X_{OHO} (Ramdani et al., 2010). The XB fraction was determined through the BOD_{ult} experiment by taking the difference between the raw sample and filtered sample (Eq.14). 39.9% of the TCOD was found to be slowly particulate material (X_B) in RWW, 28.2% and 24.5% were discovered in CEPT-I and CEPT-II effluents, respectively. More slowly, biodegradable particulate COD was removed in CEPT-II effluent than CEPT-I effluent possibly because of improved hydrolysis rate. The X_U fraction was calculated using particulate COD mass balance (Eq.15). It was discovered that the X_B fraction makes up 10 - 58% of $T_{COD,}$ and the XI fractions make up 7% - 50% of T_{COD} from previous literature summarized in Table 3-6. Lastly, X_{OHO} was calculated (Eq.9) to be comparable for RWW (3.3 % of T_{COD}), CEPT-I (1.6 % of T_{COD}), and CEPT-II effluent (1.5% of T_{COD}). 74.9% of the T_{COD} in raw wastewater was found to be biodegradable, and only 25.1% was observed to be unbiodegradable. The biodegradable fraction increased to 80% in primary clarifier effluent due to inert COD removal by coagulation. Similarly, 86% of biodegradable T_{COD} was discovered in CEPT-II effluent due to enhanced solids removal by flocculation. S_{COD} concentrations in the effluent are higher than influent S_{COD} can be explained by hydrolysis reaction of X_B and C_B to S_B. The removal of X_{COD} under CEPT-II was higher than the removal under CEPT-I (25% and 40% of T_{COD}).

Table 3-3:Literature values for Raw Wastewater COD fractionations

Raw Wastewater Characteristics, % COD fraction

S_S	S_H	S_I	X_S	X_I	X_H	References
%	%	%	%	%	%	
20		5		13		Ekama et al.,1986
9		11	58	10	12	Kappeler and Gujer, 1992
20		2	40	18	20	Henze, 1992
10	17	15	33	17	8	Xu and Hultman, 1996
10	27	3	53	7		Orhon et al., 1999
9-42		3-10	10-48	23-50		Roeleveld et al.,2002
18.3		6.4	49.3	11.3	14.7	Wichern et al., 2003
26-34	4-12	1.6-2.4	28-34	25-29	1.4-2.6	Gupta et al.,2018
13.3-25.3		0.3-1.3	39.9	9.7-28.5	1.3-5.3	This study

Primary Clarifier Effluent Characteristics (without any chemicals), % COD fraction

S_S	S_H	S_I	X_S	X_I	X_H	References
%	%	%	%	%	%	
28		8		4	-60	Ekama et al.,1986
19	28.5	9.5	31.5	7	11.5	Orhon et al., 1999
29		3	43	11	14	Henze, 1992
43-49	14-22	2.2-3.8	15-25	14-22	1.3-2.7	Gupta et al.,2018
46.2-54.1		1.5-2.3	27.3-29	14.2-19.4	1.5-1.6	This study

CEPT-II Effluent Characteristics (% of total COD), % COD fraction

S_S	S_H	S_I	X_S	X_I	X_H	References
%	%	%	%	%	%	
35	49	16				Orhon et al., 1999
49.5-66.4		1.6-2.9	24.3-24.7	10.4-12.3	1.5	This study

*** S_S : Readily biodegradable COD ; S_H : Readily hydrolysable COD ;**
S_I : Soluble inert COD and X_S : Slowly biodegradable COD ; X_I : Particulate inert COD ; X_H : Heterotrophic biomass

Table 3-4:Summary of COD fractionations in the current study

State Variables (COD Fractions)	RWW	CEPT-I EFFLUENT	CEPT-II EFFLUENT
		(% of TCOD)	
S_B (non-VFA)	19.3±6	44.95±3.39	49.40±6.05
S_{VFA}	0±0	5.18±0.59	8.52±2.41
S_U	0.8±0.5	1.90±0.42	2.25±0.64
C_B	12.4±0.6	0.56±0.00	2.22±1.39
C_U	5.2±0.3	0.88±0.01	0.28±0.39
X_B	39.9±0	28.15±0.89	24.49±0.22
X_U	19.1±9.4	16.84±2.60	11.35±0.98
X_{OHO}	3.3±2	1.55±0.06	1.50±0.02

3.3.3 Evaluation of primary clarifier model performances in relation to particulate, soluble and colloidal COD fractions

To further investigate the three primary clarifier effectiveness, the measured influent COD fractions were fed into the model. A summary of modelled CEPT-I and CEPT-II effluent fractions are illustrated in Tables 3-7 and 3-8. All models were able to present reliable results on the removal of particulate COD in most of the cases, whereas the three-compartment clarifier modelling showed the closest value when simply comparing the experimental effluent fractions and predicted effluent fraction. Significant differences were observed with respect to (i) particulate biodegradable COD (the slowly biodegradable fraction, X_B) during CEPT-II modelling, (ii) VFA (S_{VFA}) fraction, (iii) colloidal biodegradable (C_B) and unbiodegradable (C_U) fraction during both CEPT-I and CEPT-II modelling and (iv) unbiodegradable fraction (X_U) in both CEPT-I and CEPT-II modelling. In all cases, the three-compartments clarifier model showed the most realistic value when comparing to the experimental effluent results.

Table 3-5:CEPT-I simulation of three primary clarifiers

	% of TCOD			
State variables	Experimental Effluent	Predicted Effluent		
		Volumeless Point separator	Three-Compartment clarifier	Layered Flux clarifier
S_{VFA}	5.18	0.07	7.01	0.07
S_B	44.95	45.81	50.93	47.03
S_U	1.9	1.87	2.02	1.92
C_B	0.56	20.48	0.00	21.03
C_U	0.88	3.67	0.00	3.77
X_B	28.15	17.53	25.95	16.32
X_U	16.84	9.19	12.40	8.56
X_{OHO}	1.55	1.33	1.61	1.24

Table 3-6:CEPT-II simulation of three primary clarifiers

	% of TCOD			
State variables	Experimental Effluent	Predicted Effluent		
		Volumeless Point separator	Three-Compartment clarifier	Layered Flux clarifier
S_{VFA}	8.52	0.08	7.42	0.08
S_B	49.40	51.79	52.98	51.65
S_U	2.25	2.11	2.10	2.10
C_B	2.22	12.86	0.00	23.09
C_U	0.28	2.31	0.00	4.10
X_B	24.49	19.23	24.29	11.83
X_U	11.35	10.09	11.61	6.20
X_{OHO}	1.50	1.46	1.51	0.90

The layered flux model captured excessive particulate biodegradable COD(X_B) during CEPT-II and to some extent CEPT-I process. For example, in CEPT-II, compared to the actual measured effluent X_B fraction, the model captured an additional 52% of the X_B fraction to the sludge, in comparison to only 21% and 8% by the volumeless point separator and three-compartment models, respectively. The influent wastewater X_B fraction was about 40%, due to chemical addition, solids removal was enhanced, explained by its higher molecular weight and bridging ability; however, this was overestimated by the layered flux model.

With respect to soluble COD, results corresponding to volatile fatty acid fractions, readily biodegradable substrate(non-VFA) and soluble unbiodegradable substrate were compared. All three models showed an actual release of readily biodegradable components in both CEPT reactors, where there was no significant change in the VFA and soluble un-biodegradable fraction. In the three-compartment model, the flocculation process and hydrolysis process are both captured while those details were not clearly captured by the other two models. C_U, C_B, S_U and S_B were converted to X_U and X_B during the flocculation process. X_B was converted to S_B during the hydrolysis process. Both processes are highly correlative but also can be counteracted. Therefore, the observed higher effluent soluble concentrations than influent soluble concentrations represented the net production of soluble COD in the primary clarifier.

Moreover, colloidal removal was 100% achieved in the three-compartment model. The volumeless point separator model has comparative higher removal of colloidal material than the layered-flux clarifier. In volumeless point separator, 15.17 % of effluent TCOD was observed as colloidal fractions, whereas a relative higher colloidal fraction (27.19% of effluent TCOD) occurred in layered flux clarifier model results. As mentioned before, the three-compartment model was able to capture the effect of polymer addition and incorporate it to solids removal. The rate of colloidal substrate flocculation with polymer is determined based on a Monod saturation function on the colloidal substrate and the polymer concentration. Then, the solids removal efficiency is adjusted between solids percent removal without polymer and solids percent removal with a polymer. Thus, more realistic results on colloidal removal from the three-compartment model further prove the effectiveness of this model.

CEPT-II reactor effluent had more soluble and colloidal COD matters compare to CEPT-I effluent; nevertheless, less particulate COD matters left. The performance of three clarifiers between CEPT-I and CEPT-II was observed to be similar as well. It is worth mentioning that the amount of carbon entering a secondary process requires additional fossil energy for carbon oxidation. Thus from an energy consumption, CEPT-II treatment not only remove solids effectively but also benefit the following treatment.

3.4 Conclusions

This study mainly focuses on the effectiveness of three clarifier models; volume-less point separator, three-compartment and layered-flux, on modelling effluent fractions such as colloidal COD, particulate COD and soluble COD and composite parameters such as TSS. CEPT data from Vauxhall WWTP and Adelaide WWTP were applied for calibration and validation of the three clarifier models. The calibrated three-compartment model showed 100% removal of C_{COD}, increased effluent soluble fractions and 87% removal of TSS concentration. The validated three-compartment model also can accurately describe the performance of CEPT in Adelaide WWTP. COD fractions of RWW, CEPT-I and CEPT-II effluents were determined through the combination of physical-chemical and biological methods. The fractions in the primary clarifier are assumed to remain unchanged under all conditions. However, wastewater composition changes in accordance with particles removed. The effect of primary treatment on these fractions is neglected or oversimplified. Experimental CEPT-I and CEPT-II effluent fractions were closely predicted by the three-compartment model. Volumeless point separator is the ideal setup for simple conventional primary clarifier, the removal of influent materials is predefined as direct model input, which cannot well-describe the fraction changes in CEPT clarifier. The Layered-flux model can give a reasonable description of the effluent TSS concentration of the primary clarifier. For practical applications, our study has shown that among the three clarifier models, the three-compartment model provides a better description of chemicals and polymers addition impacts on primary treatment, and relatively simpler calibration procedure compared to the layered-flux model.

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4 Enhancing Biomethane Production And Phosphorus Recovery From CEPT Sludge Through Different Pre-Treatment Methods

4.1 Introduction

Phosphorus is a water pollutant but also an essential non-replaceable agricultural nutrient. Cordell et al. (2011) estimated that in 2035, the worldwide P demand would surpass its supply due to the growing population and declining sources. The P-based eutrophication and the issues of phosphorus depletion necessitates a feasible long-term solution in enhancing its removal from wastewater/water streams and then recovering it for beneficial use (Venkiteshwaran et al., 2018). The application of dosing chemicals to enhance coagulation, flocculation and precipitation in primary treatment has been widely accepted as an effective method of suspended solids, organic, and phosphorus removal. Furthermore, the CEPT sludge contains a substantial number of all these valuable resources and has high energy value that should be recovered. Anaerobic digestion is a widely used biological process to stabilize activated sludge. This process not only converts organic waste to produce methane (CH4) energy but also releases organically bound P making it available for recovery (Carey et al.,2016; Peccia and Westerhoff, 2015; Venkiteshwaran et al.,2018). However, little research has been focused on the effectiveness of the anaerobic digestion process on methane and phosphors recovery from CEPT sludge through organic hydrolysis and conversion of non-reactive P (NRP) to reactive P (RP).

Dentel et al. (1981) concluded that although coagulants (alum or ferric) can improve effluent quality, but lower the anaerobic digestibility of the resulting sludge of coagulated organic material. Cabirol (2002) also found that aluminum and sulphate inhibit the specific methanogenic activity of methanogenic and acetogenic bacteria resulting in a 50%-72% decrease and 48%-65% decrease, respectively. Furthermore, the impacts of coagulants $FeCl_3$ and PACL in CEPT sludge were compared in terms of pollutants removal efficiencies from wastewater and resource recovery from the acidogenic fermentation of sludge (Lin et al., 2017). The results concluded that $FeCl_3$ dosed at 10 to 30 mg Fe/L_{sewage} had little impacts on organic hydrolysis and acidogenesis of the sludge, whereas Al addition had a significant inhibitory effect on sludge hydrolysis. More importantly, over the 48 days of fermentation, Fe-sludge released an increasing amount of orthophosphate-phosphorus PO_4-P (measured based on standard methods (APHA,2005), reaching up to 30 mgP/L in the supernatant, while only 0.1 mg P/L PO_4-P was observed in the supernatant of the fermented Al-sludge. Such adverse impacts of organic and inorganic coagulant on acidogenic fermentation was further evaluated in terms of volatile fatty acids (VFA) conversion (Kim and Chung, 2015), and results demonstrated a 10% decreased conversion ratio of organic substrates to VFA when PAC and $FeCl_3$ dosages exceeded 46mg/L and 120 mg/L, respectively. A greater inhibitory effect by Al on acidogenic fermentation was observed compared to that by Fe. These findings contrast with that of Koojimen et al. (2017), who concluded the use of cationic/anionic coagulant and organic flocculant could actually lower the viscosity, resulting in the increased diffusion rates of metabolic intermediates and, therefore, an increased hydrolysis rate and higher biomethane potential. Therefore, although some literature has been conducted on the impact of CEPT processes on the downstream solid-train, conflict discoveries of whether the coagulant and flocculant enhance or inhibit the performance of sludge fermentation or the methane production still remain questionable.

Even though AD is a favoured stabilization technology, the existence of high molecular weight compounds such as extracellular polymeric substances (EPS) and complex organic material in sludge imposes a limitation on the hydrolysis step of AD, which leads to long retention time and large reactor volume (Neumann et al., 2016). Accordingly, pretreatment technologies could play a role in enhancing the disintegration of these compounds, improve hydrolysis and enhance the performance of solids reduction, biogas production and digested sludge properties. Pretreatment includes single or combined biological, physical, thermal and chemical technologies (Carrere et al., 2010). However, all pretreatment methods have been found to have drawbacks of high capital costs and high energy consumption (Kim et al., 2013). To date, numerous amounts of research have been conducted comparing different disintegration methods to overcome single process limitations, for example, thermo-chemical, physical-chemical and combined biological processes (Kim et al., 2013 and Shehu et al., 2012).

For the thermo-chemical pretreatment, a wide range of temperatures (from 60 to 270 °C) has been assessed. The temperature ranges from 60 to 180°C were the most commonly applied; however, temperatures above 200°C led to the production of refractory organics or inhibitory intermediates (Stuckey et al., 1984). Pretreatment at low temperature had been considered as the practical method in improving methane production from both primary and secondary sludge (Ferrer et al., 2009). In addition, alkali pretreatment involves the usage of chemical agents and is comparatively efficient in sludge solubilization with the following descending order: NaOH > KOH > $Mg\ (OH)_2$ and $Ca\ (OH)_2$. Therefore, the combination of these two methods, called low-temperature thermal-chemical pretreatment, consists of thermal disintegration with the simultaneous addition of alkaline compounds, which can be a reliable alternative to eliminate the need for high temperatures and issues of alkali solubilize sludge. Kim et al. (2013) demonstrated an optimum of 0.16 M NaOH, 90 °C resulted in sludge disintegration of 78%, and an optimum of 0.10 M NaOH, 73.7 °C resulted in an increase methane production of 73.9%. The continuing increase in temperature and NaOH concentration led to decreased hydrolysis activity and methane production due to Na^+ toxicity. Besides solubilization and methane production, Kuroda et al. (2002)

evaluated the release and recovery of EBPR sludge and claimed 90% release of the polyphosphate by heating activated sludge at 70°C for 1 hour. Approximately all of the poly-P released within 20 mins at 80°C and 10 mins at 90°C. Extended heating time at temperatures (70–90°C) can hydrolyze and convert the polyphosphate (NRP) to sRP. Moreover, the released polyp could easily be precipitated by the addition of $CaCl_2$ without pH adjustment at room temperature (Kuroda et al., 2002). Moreover, Stark et al. (2006) showed 0.19% Ca^{2+} ions and 70% P release after treating incinerated sludge ash with 1 M NaOH, low Ca^{2+} ions released, indicating that alkali treatment primarily converts NRP to sRP instead of converting both NRP and pRP to sRP. In conclusion, although alkali pretreatment and low-temperature thermal pretreatment have been investigated individually in terms of either sludge solubilization or phosphorus release, there has been relatively scarce information discussing the efficacy of combined low-temperature thermo-alkali process on chemically enhanced primary sludge regarding methane production and nutrient release and potential recovery.

Ozone oxidation pretreatment was also performed during the experiments in parallel with low-temperature thermo-chemical pretreatment. Ozone, as a strong oxidant, is widely applied for various purposes in wastewater treatment. The oxidant characteristics of ozone can partially hydrolyze organic material and increase the biodegradability of waste activated sludge (Carrere et al., 2010; Neumann et al., 2016; Zhang et al., 2017). During ozonation, extracellular and intracellular materials are released into the supernatant, whereas part of this material is mineralized to CO_2 and H_2O, resulting in sludge reduction (Zhang et al., 2017). To enhance AD performance, ozone dosage is the critical parameter of the process. It is worth pointing out that excess ozone can lead to the production of refractory compounds and organic matter consumption (Kim et al., 2013). Neumann et al. (2000), in their review paper, stated that the optimal dose is around 0.05-

0.5 gO_3/gTS. Furthermore, 37% solids solubilization (change in VSS concentration before and after ozonation) with a dose of 0.05 gO_3/gTS was reported, which resulted in an increased solids reduction (35%-90%) efficiencies and improved methane production during anaerobic digestion (Goel et al., 2003). Weemaes et al. (2000) tested ozone in the range of 0.05-0.2 $gO_3/gCOD$ and found increasing soluble COD concentration with increasing ozone dose, reaching 29% solubilization with a dose of 0.2 $gO_3/gCOD$ particularly. At the same time, 38% of the organic matter was also oxidized; in total, a 67% change in the sludge VSS composition. During sludge ozonation, the locked NRP would release from the complex organic matrices and be available for hydrolysis conversion to RP, leads to an increase of soluble phosphorus concentration due to the transformation of organic P (Chu et al., 2008; Venkiteshwaran et al., 2018). An increase of reactive phosphorus content from 1.9 to 3.6 mg PO4-P/g $MLSS_{in}$ (89.5%) with a 19.4% COD release was observed after sludge ozonation. Although many researchers have shown the superiority of ozone-pretreatment in solids reduction and increased methane production, the applicability of this process has not been fully evaluated in the case of sludge type (PS, CEPT sludge, WAS, a mixture of CEPT sludge and WAS). For example, different level of effects is expected owing to the characteristics of sludge samples. Until now, little is known about the performance of sludge solubilization and P-release via ozonation of CEPT sludge.

Overall, this experimental study was conducted on CEPT sludges with different pretreatments in relation to the performance of anaerobic digestion for resource recovery. As illustrated in Figure 4-1, The objectives of this work include to 1) compare characteristics and digestibility of $FeCl_3$ coagulated sludge (herein referred as CEPT-I sludge) and $FeCl_3$ +PACl coagulated sludge (herein referred as CEPT-II sludge); 2) evaluate the impacts of low-temperature thermal-alkali pretreatment and ozone pretreatment in terms of sludge solubilization and phosphorus release; 3) assess the behaviour of anaerobic digestion on pre-treated CEPT sludges and un-treated CEPT sludges in terms of biogas yield and conversion of NRP to RP.

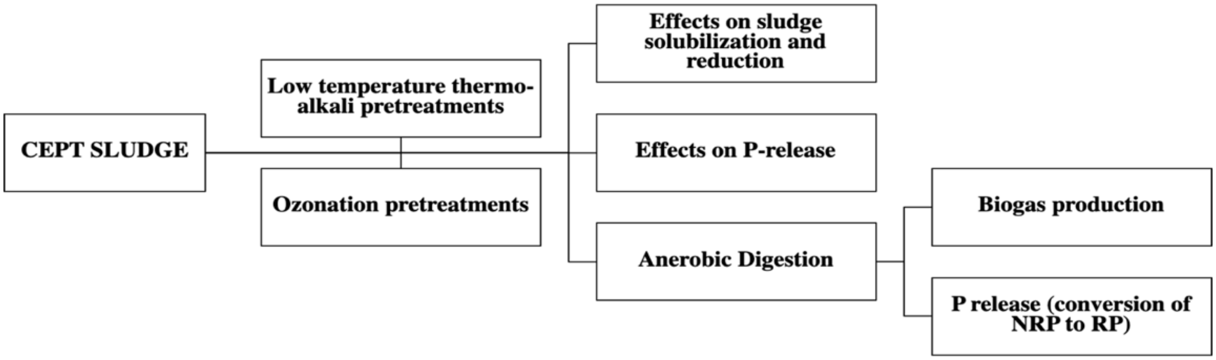


Figure 4-1:Logic diagram of the study's objectives

4.2 Materials and Methods

4.2.1 Sources of primary sludge/substrate and seed

CEPT sludge samples were collected from control and test full-scale primary clarifiers located at the Vauxhall pollution control plant (PCP) (London, ON) 1). The control-primary clarifier was dosed with ferric chloride (15 mg/L), and the test-primary clarifier was (dosed with ferric chloride (15mg/L) and PACl (0.5 mg/L)). The ferric and PACl dosage was based on a recommendation from a previous study on the Vauxhall PCP (Dong et al., 2019). Anaerobic seed sludge sample was collected from an anaerobic digester of the Stratford Water Pollution Control Plant (Stratford, ON). Around 20L of samples were collected in plastic buckets and transferred to the laboratory for further analysis and treatment. Part of the samples was stored at 4°C for TS, VS, TSS, VSS, T_{COD}, S_{COD} analysis, and the other part was preserved by freezing at below -10°C for phosphorus analysis.

4.2.2 Pre-treatment methods

Carlsson et al. (2012) summarized that ozone/oxidative pretreatment had been shown a positive effect on solubilization, formation of refractory compounds, and both positive and no effect had been shown on the particle size reduction and biodegradability enhancement. The latter was reported by Bougrier et al. (2006), with 0.1 and 0.16 O_3/g TS ozone dose on waste activated sludge, no particle size decreased and low enhancement in biodegradability that might occur due to inhibitory conditions or refractory compounds. Furthermore, thermal pretreatment(<100°C) has been shown positive effects on particle size reduction, solubilization and biodegradability enhancement, but no effects on the formation of refractory. Alkali pretreatment has been demonstrated positive impacts on solubilization and formation of refractory, and both positive and no effects have been reported on biodegradability enhancement. No information available on whether alkali can reduce particle size or not (Carlsson et al., 2012)

4.2.2.1 Low-temperature thermal-alkali pre-treatment (LTTAP)

When alkali agents are added, COD solubilization increased through a variety of reactions: saponification of uronic acids and acetyl esters, reactions occurring with free carboxylic groups and neutralization of various acids formed from the degradation of a particular material (Neumann et al., 2016). Moreover, the primary mechanism of low-temperature hydrolysis is thermal solubilization by hydrolytic enzymes released from the sludge. Combined LTTAP can be a reliable alternative to overcome the potential production of refractory compounds due to high temperatures and avoid the use of high temperatures (Climent et al.,2007).

Thermo-chemical treatment of the sludge was performed in a graduated beaker using Isotemp hot plate stirrer (Fisher Scientific, PA, USA). A schematic diagram of the thermo-chemical treatment system is presented in Figure 4-2. Initially, the beaker was filled with 1L well-mixed sludge, and the pH was adjusted to 10 -12 using NaOH. Then, the content of the beaker was heated and simultaneously allowed to mix thoroughly with a stirrer operating at 800 rpm to achieve high-shear mixing. The temperature of the content of the beaker was kept to 70°C for 30 min. The temperature was monitored with a thermometer. Finally, the thermo-chemically treated sludge was cooled to room temperature, and its pH was adjusted to neutral pH using 2 M HCl.

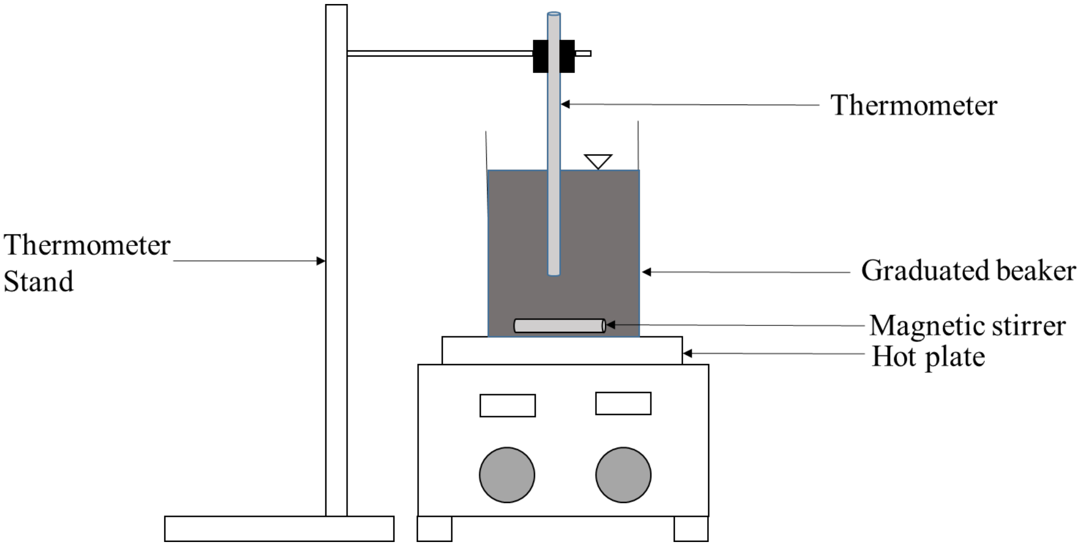
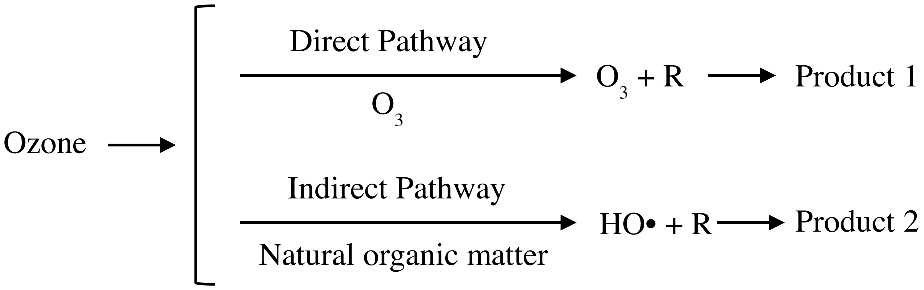


Figure 4-2:Schematic showing the setup of low-temperature thermal-alkali pretreatment treatment

4.2.2.2 Ozone treatment

Ozone is one of the frequently used oxidants in wastewater treatment plants, can effectively oxidize both particulate and soluble organic matter either by direct reaction with O_3 or indirect reactions with HO•. The Direct reaction rate relies more on the structure of the reactants, whereas indirect reactions depend on the high reactivity of hydroxyl radicals (Carballa et al. 2007).



Ozone degrades organic matter in two steps: solubilization resulting from the disintegration of suspended solids and mineralization due to subsequent oxidation of soluble organic matter to carbon dioxide (Ahn et al.,2002). It is supposed that one-oxygen atom of O_3 reacts with the oxidant, indicating that 48g of ozone can decompose 16g of COD (mineralization). Usually, the quantified mineralization is lower than this value. Complete oxidation should be eliminated because the aim of pretreatment is partial oxidation and hydrolysis of the sludge (Carballa et al.,2007)

A well-mixed 1 L sludge was added in an ozone treatment reactor and treated with ozone for 30 minutes. The treatment was made by bubbling ozone through the sludge. The applied ozone dose was maintained at a gas-phase concentration of 1000 ppm and a flow rate of 4.2 L/min. The ozone treatment was carried out at room temperature. An ozone generator (model TG–40, Ozone Solution, IA, USA) was used to generate the ozone from compressed oxygen (ultra-pure) at a pressure of 15 psi. Ozone in the gas phase was measured using an ozone analyzer (model UV–100, Eco Sensors, Newark, CA, USA).

4.2.3 Anaerobic digestion and Biochemical methane potential (BMP) test

The anaerobic digestion experiments were performed in two different setups for liquid and gas phase analysis in an orbital shaker (Thermo scientific Model Max Q 4000) (Figure 4-3.) and Automated Methane Potential Test System (AMPTS II; Bioprocess Control AB, Lund, Sweden) (Figure 4-4), respectively. The liquid and gas phase test was conducted using 28 bioreactors (14 on each system) as per the experimental design shown in Table 4-1. The anaerobic digestion study was conducted to evaluate the impact of pretreatment on anaerobic digestion of two CEPT sludges, including the gas production (using the AMPTS) and the liquid phase parameters such as COD, P and solids fractions (using the orbital shaker, mixing speed). The bioreactors incubated in an AMPTS had a working volume of 400 mL and were mixed using a rotating agitator (150 rpm) to maintain complete mix conditions. The biogas produced in each bioreactor passes through an individual vial containing 3 M NaOH and 0.4% Thymolphthalein pH indicator. Several acid gas fractions, such as CO_2 and H_2S, are retained by chemical interaction with the NaOH, only allowing CH_4 to pass through to the biomethane gas volume measuring device. The methane-potential test was conducted for 30 days. The bioreactors incubated in the orbital shaker had a volume of 200, the shaker speed was set at 150 rpm, and the testing was conducted for 15 days. Both the orbital shaker and the BMP reactors were set at 38.5°C. The experiments were conducted using pre-determined food to microorganism (F/M) ratio of 0.25 (Shewa et al., 2019) calculated as per Equation 4-1. The working volume between the substrate/pre-treated and seed sludge for both experiments was calculated accordingly. Control samples include seed only to determine a baseline for the biogas produced by the seed during the BMP test, and CEPT-I and CEPT-II mixture without pretreatment to compare the efficiency of pretreatment processes in regarding the anaerobic digestibility of the primary sludge (Table 4-1). All experiments were conducted in duplicates. The fraction of methane production exclusively from the substrate was determined by subtracting the methane yield from the seed (control bioreactors) from the methane production of the mixed samples.

$$\frac{F}{M} = \frac{VSS_{substrate} * Volume_{substrate}}{VSS_{seed} * Volume_{seed}} \tag{4-1}$$

Where VSS is the volatile suspended solids (mg/L) of substrate or seed, and Volume (L) is the volume of substrate or seed added.

Table 4-1:Experimental plan for gas-phase analysis in AMPTS II system

Test condition* Seed sludge + substrate	Primary sludge coagulated with $FeCl_3$ addition (CEPT-I Sludge)	Primary sludge coagulated with $FeCl_3$ + PACl addition (CEPT-II Sludge)
AD sludge + DI water (Control)	2 reactors (CEPT-I not added)	2 reactors (CEPT-II not added)
Seed sludge +untreated primary sludge	2 reactors (untreated CEPT-I sludge)	2 reactors (untreated CEPT-II sludge)
Seed sludge + ozone-treated sludge	2 reactors (ozone treated CEPT-I sludge)	2 reactors (ozone treated CEPT-II sludge)
Seed sludge + thermo chemical treated sludge	2 reactors (thermo-chemical treated CEPT-I sludge)	2 reactors (thermo-chemical treated CEPT-II sludge)

*A similar experimental plan was followed for liquid phase analysis

Figure 4-3:Anaerobic digestion batch test setup for liquid phase

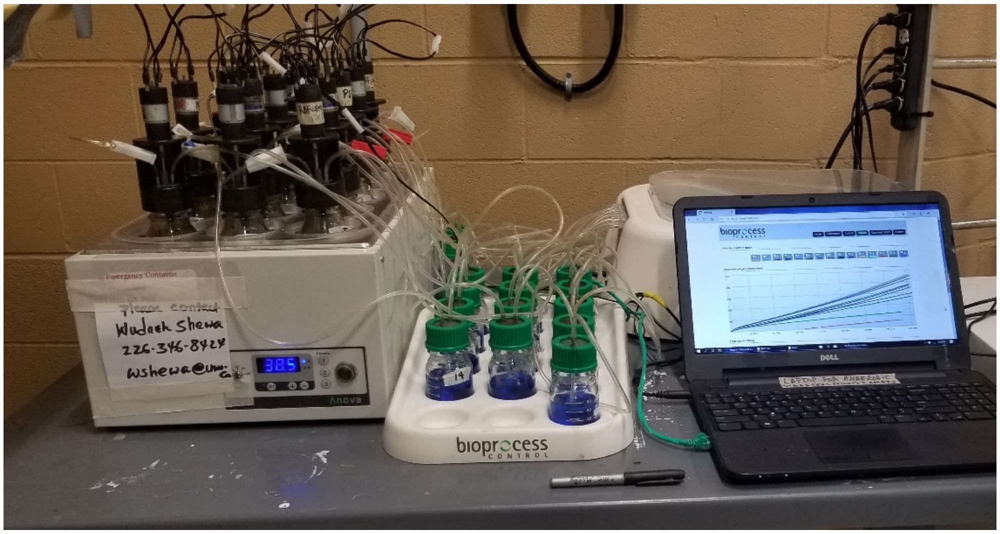


Figure 4-4:Automated Methane Potential Test System (AMPTS) test setup for biomethane production analysis

4.2.4 Analytical methods

Duplicate samples were collected before/after pretreatment and at 0th, 1st, 4th, 8th and 15th days during anaerobic digestion experiment. The samples were analyzed for total solids (TS), volatile solids (VS), total suspended solids (TSS), volatile suspended solids (VSS), total COD (TCOD) and soluble COD (sCOD). The TS, VS, TSS and VSS was measured using the standard method (APHA, AWWA, & WPCF, 2005). The TCOD and sCOD (after filtered through 0.45µm membrane filter) were determined using the HACH method (method #8000) (Hach, Loveland, COD, USA). Moreover, duplicate samples were collected at the 1st and 15th day of anaerobic digestion test for conventional P fractionation analysis, including total phosphorus (TP), reactive phosphorus (RP) and non-reactive phosphorus (NRP) as per the Standard Method (4500-P). The methane produced was auto measured and recorded over time by the Bioprocess Control unit.

The degree of sludge COD solubilization was quantified as COD solubilization represented by the increased portion of soluble COD, calculated as shown in Equation (4-2). Moreover, solids solubilization was illustrated by the increase in the ratio soluble to total volatile solids (VDS/VS).

$$Degree\ of\ COD\ solubilization(\%) = \frac{sCOD_{after} - sCOD_{before}}{TCOD_{before}} * 100 \qquad (4\text{-}2)$$

Where $sCOD_{after}$ and $sCOD_{before}$ are the sCOD concentrations of the sludge before and after different pretreatments, respectively. $TCOD_{before}$ is the TCOD of the sludge before pretreatments

4.3 Results and Discussion

4.3.1 Primary sludge & Seed sludge characteristics

The general characteristics of the two types of CEPT sludges and the seed sludge are summarized in Table 4-2. TS content of CEPT-I and CEPT-II sludge samples were around 40200 mg/L and 14700 mg/L, and total VS were around 30800 mg/L and 11900 mg/L, with a high but comparable VS/TS ratio of 0.77 and 0.81 respectively. The higher VS/TS ratio indicates a high organic content typical from fresh non-stabilized sludge. Besides, the soluble material only occupied a small percent (0.06 (CEPT-I) and 0 (CEPT-II) from this organic content, as shown by the volatile dissolved solids to total volatile solids ratio (VDS/VS). Since CEPT-II sludge did not contain any biodegradable dissolved solids, which means all dissolved solids in this sludge are inert (unbiodegradable). The absence of VDS concentration in CEPT-II sludge also can be explained by the enhanced dissolved solids removal with polymer addition.

In comparison, CEPT-II sludge had about 50% lower organics and solids content than CEPT-I sludge, which was the indication of improved removal performance when adding PACl in the liquid stream. Moreover, a higher VSS/TSS ratio was observed in CEPT-II sludge manifested more particular organic solids existing. The sCOD/TCOD fraction was observed to be 0.05 and

0.03 in CEPT-I and CEPT-II sludge, respectively. Further, compared to CEPT-I sludge, less RP fraction but more NRP was found in CEPT-II sludge, representing that more reactive phosphorus was removed in the liquid stream with PACL addition, which is in accordance with the purpose of chemical phosphorus removal.

Seed sludge sample (anaerobically digested sludge) contains a much lower organic matter but more biodegradable dissolved solids compared to CEPT-sludge samples, which represents the characteristics of anaerobic sludge. Furthermore, the soluble COD in seeding sludge was higher than CEPT-II sludge but lower than CEPT-I sludge.

Table 4-2:Characteristics of raw sludge and seed sludge

Parameters	CEPT-I sludge	CEPT-II sludge	Seed
TS (mg/L)	40200±565.69	14700±282.84	37400±424.26
VS (mg/L)	30800±0.00	11900±141.42	22500±0.00
VS/TS	0.77±0.01	0.81±0.01	0.52±0.00
TSS (mg/L)	35900±424.46	14900±141.42	33500±141.42
VSS (mg/L)	29000±565.69	13000±282.84	18900±424.26
VSS/TSS	0.81±0.01	0.87±0.01	0.56±0.01
TDS*/TS	0.11±0.02	0±0.00	0.11±0.00
VDS*/TDS	0.41±0.04	0±0.00	0.45±0.00
VDS/VS	0.06±0.02	0±0.00	0.09±0.00
TCOD (mg/L)	41400±0.00	19640±57	29625±0.00
sCOD (mg/L)	2160±141	580±28	1075±57
sCOD/TCOD	0.05±0.00	0.03±0.00	0.04±0.00
RP/TP	0.30±0.00	0.17±0.00	0.55±0.00
NRP/TP	0.69±0.00	0.85±0.00	0.44±0.00

*TDS and VDS fraction are not directly measured, both fractions were calculated based on solids fractionation mass balance (Tchobanoglous, 2014): TDS=TS-TSS ; VDS=VS-VSS.

4.3.2 Effect of sludge pre-treatment on sludge solubilization and reduction

Sludge solubilization is one of the parameters to evaluate the efficiency of sludge ozonation performance. Noteworthy, there is various definitions for sludge solubilisation effectiveness, for example, COD solubilization, TSS or VSS elimination and TOC (total organic carbon) solubilization. COD solubilization and TSS elimination are the most used (Chu et al.,2009). It was expected to observe an elevation in soluble fractions as a result of enhanced degradation speed and extent. Figure 4-5 and Figure 4-6 compared the concentration of key parameters before and after pretreatment.

Ozone, as a strong cell-lytic agent, destroys microorganisms in activated sludge and facilitates the oxidation of released intracellular organic materials (Chu et al., 2008). The low-temperature thermo-alkali pretreatment (LTTAP) consists of thermal destruction with simultaneous addition of NaOH, which not only disintegrated the sludge flocs, also greatly promoted the dissolution of the organic clusters and molecules (Nuemann et al., 2016).

The impacts of both pre-treatment methods on TSS and VSS concentration reduction were relatively consistent. LTTAP treated CEPT-I sludge decreased around 84% in VSS concentrations, whereas ozone-treated sludge decreased around 76%. The decreased VSS mainly due to solubilization and converted to VDS. During pretreatments of CEPT-I sludge, an increase of VDS from around 1800 mg/L in raw sludge to 7075 mg/L and 5181.12 mg/L after pretreatments, respectively, resulting in a significant improvement in VDS/TS ratio from 0.04 to 0.38(ozonation) and 0.20 (thermo-chemical) and increase in VDS/VS ratio from 0.06 to 0.5 (ozonation) and 0.53 (thermo-chemical) in CEPT-I sludge. This means that the proportion of soluble organic material increased by nearly 9 times. Furthermore, sCOD solubilization induced by low-temperature thermo-alkali processes increased slightly by 2.30%, while sCOD concentration decreased after ozonation. This can be interpreted by that sCOD concentration changes not merely because of organic solubilization, but also organics degradation to oxidize species such as CO_2. Also, other studies found declining sCOD concentration, which resulted from the mineralization and degradation of the soluble organics as a result of ozone oxidation (Tian et al., 2015; Erden and Filibeli, 2011). 20.05% TCOD concentration loss in CEPT-I sludge further proved the phenomenon of mineralization. This indicated that ozone was consumed during sludge solubilization and sludge mineralization.

In CEPT-II sludge, VSS concentration decreased by 77.88% after ozonation and around 76.54% after LTTAP. Same as treated CEPT-I sludge, the elimination of VSS fraction contributed to the increase of VDS fraction. Solids solubilization induced by ozone and LTTAP increased the VDS concentration to 2525 mg/L and 3650 mg/L with an improvement of the VDS/TS ratio by 33% and 31%, respectively. In terms of total organic solids, VDS fraction occupied 46% (ozonation) and 54% (LTTAP) after pretreatments. At the same time, sCOD solubilization rate after thermo-alkali pretreatment significantly increased to 8.71%.

In comparison, the sCOD release rate after ozonation remained at a low level at 0.10%. The same conclusion can be made, as discussed above, that a 10.79% decrease in T_{COD} concentration indicated the contribution of mineralization. Further, Cosgun and Semerci (2019) reported a 32.3% VSS reduction after 225mg O_3/gTSS of waste activated sludge and indicated that ozone oxidation was effective as a pretreatment for sludge stabilization and reduction. The VSS reductions shown in the current study were much higher than the one reported above, representing high oxidation to CO_2; this could be due to the wastewater type and ozone dosage difference.

In summary, the solids solubilization indicated that ozone oxidation was effective as a pretreatment for sludge stabilization and reduction; however, the sCOD release was not improved. This phenomenon indicated the effects of mineralization. It means that the ozone dosage applied for CEPT-I sludge (0.06 gO_3/gTS) was probably too high so the solubilization was reduced due to mineralization of the released cellular compounds. On the other hand, LTTAP could both disintegrate the sludge and release organic materials from sludge effectively.

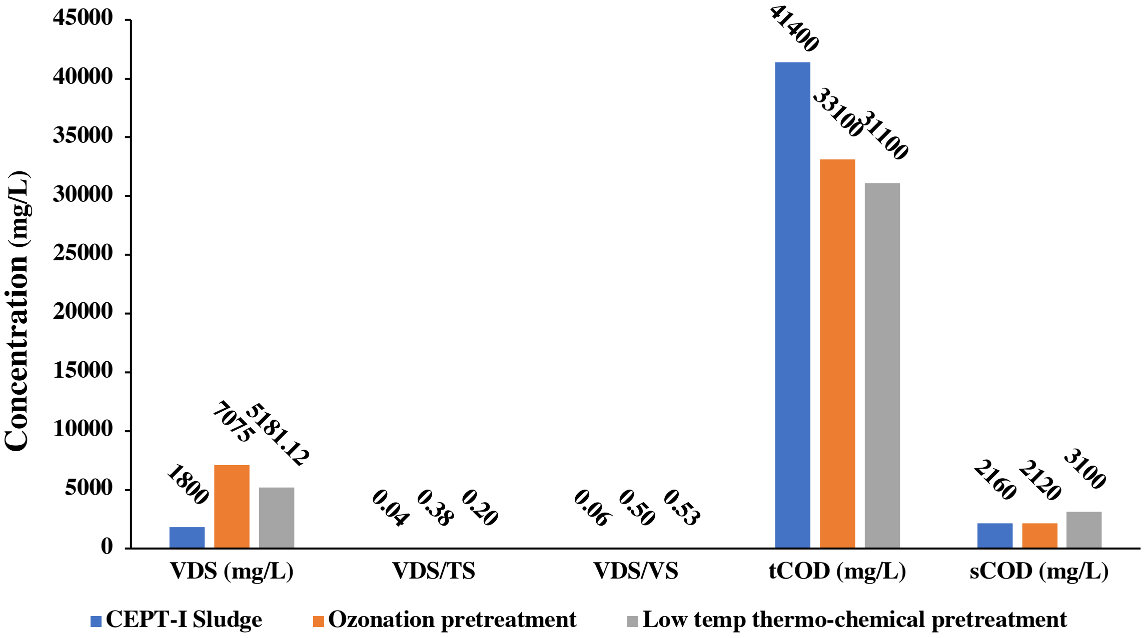


Figure 4-5:Effects of pretreatments on CEPT-I solubilization

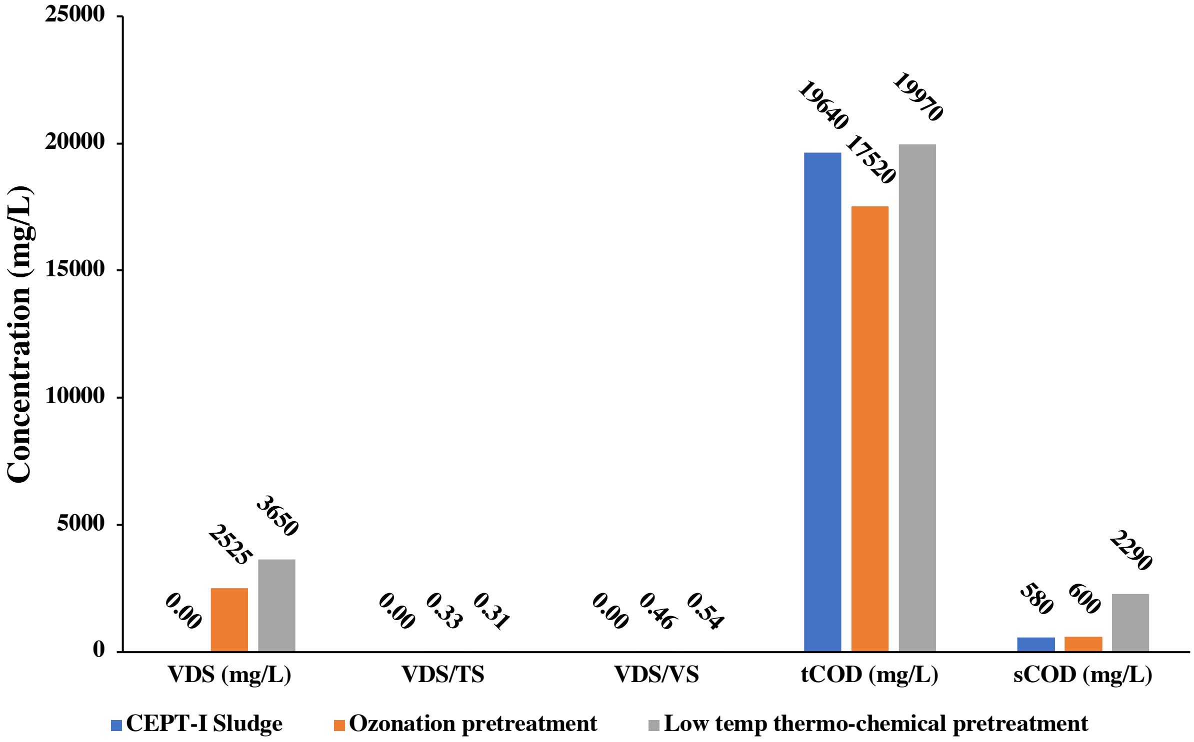


Figure 4-6:Effects of pretreatments on CEPT-II sludge reduction and solubilization

4.3.3 Effects of sludge pre-treatments on P conversion process (Shift of NRP to RP)

During the sludge ozonation pretreatment processes of waste activated sludge, organic and inorganic phosphorus is released into supernatant as orthophosphate(sRP) and acid hydrolysable P(NRP) (Cosgun and Semerci, 2019). Xu et al. (2018) reported that alkali could be used to dissolve Al-P and Fe-P. Since LTTAP created a high alkali environment (pH=10-12), P in sludge was released as OH^- replaces $PO4^{3-}$ due to the lower solubility of ferric hydroxide than ferric phosphate (Chen et al., 2019). CEPT-II sludge with the addition of PACl, Al (OH_3), $AlPO_4$ and organics were formed in the sludge flocs. Al (OH_3) and $AlPO_4$ have the lowest solubility in the pH range of 5.5-7.0, and the solubility of PO_4-P and Al increases at lower of higher pH. Significant release of P and Al was observed at pH 2.0 and at pH 9.0-10.0 (Lin & Li., 2018).

Table 4-3 compares the fraction of RP/TP, and NRP/TP in CEPT-I and CEPT-II sludge also describes the conversion of NRP to RP after pretreatments. Theoretically, the summation of NRP and RP fraction should be 100%, whereas two of the samples (CEPT-II control and CEPT-II thermo-chemical treated) exceeded 100%. The error due to this measure was around 10%. One thing worthy of mentioning is the missing data of CEPT-I sludge (ozonated); the data point was not considered here as the standard deviation of the duplicates was too found too high.

RP fraction of CEPT-I sludge and CEPT- II sludge was 30.17% and17.40%, and a substantial fraction of the TP was non-reactive P. CEPT- I sludge had more reactive P, which is consistent with the findings in terms of dissolved solids discussed above in section 4.3.2. CEPT-II sludge had considerably lower RP/TP but higher NRP/TP ratio, which was owing to the stronger bond of P with Fe+Al-based complex than with the Fe based complex, which led to substantial P removal.

Phosphorus release is highly dependent on the phosphorus fraction. What can be seen in this table (Table 4.3) is the release of organic and inorganic phosphorus elements during ozonation and thermo-chemical processes, which also facilitates sludge dissolution. Total P concentration decreased to 302.47 mg/L and 668.26 mg/L due to the release of phosphorus from sludge solids into the supernatant. RP/TP fraction in ozonated CEPT-II sludge increased from 17.40% (CEPT-II control) to 76.38%, which was a 59% improvement in RP fraction release. Cosgun and Semerci (2019) reported that ozonation treatment is an effective technology for solubilization and release of waste activated sludge, 19.4% COD release and 89.5% increase in reactive phosphorus content (from 1.9 to 3.6 mg PO4-P/g MLSSin) were observed at ozone dose of 225 mg O_3/g MLSS. Compared to the literature, a lower reactive phosphorus content increase after ozonation was mainly due to the difference in sludge sample characteristics and to some extent to the non-optimal ozone dose. Furthermore, the LTTAP process increased reactive phosphorus components by 23.05% (CEPT-I sludge) and 29% (CEPT-II sludge) compared to the control samples.

Ruiz-Espinoza et al. (2012) demonstrated a solubilization degrees of 1.69% at a pre-treatment at 70°C for 30 min, with total soluble phosphorus (sP) increased from 24.33 mg/L to 48.52 mg/L (99% improvement). It makes sense that reactive phosphorus improvement is less than the reported improvement in total soluble phosphorus because sP also includes soluble organic P (sOP) and soluble polyphosphates (sAHP). Organically-bound P and AHP also contribute to P release during thermal treatment (Kuroda et al.,2002). In contrast to earlier findings of sludge solubilization, the ozonation process has the potential of providing greater NRP conversion in CEPT-II sludge than the LTTAP process.

Table 4-3:Pretreatment effects on reactive P and non-reactive P

	RP/TP (%)	NRP/TP (%)
CEPT-I sludge (control)	30.17	69.83
CEPT-I sludge (LTTAP)	53.22	46.78
CEPT-II sludge (Control)	17.40	85.91
CEPT-II sludge (LTTAP)	46.43	63.79
CEPT-II sludge (Ozonation pre-treatment)	76.38	23.62

4.3.4 Effects of sludge pre-treatments on anaerobic sludge digestion

4.3.4.1 sCOD/TCOD improvement

The anaerobic digestibility of pre-treated/non-treated sludge was evaluated by the biochemical methane potential (BMP) test. Biodegradable organic matters, both soluble and particulate, were converted to methane and carbon dioxide while leaving mineralized compounds like NH_4 and $PO4^{3-}$ in the solution (Grady et al., 2011). After 15 days of anaerobic digestion, the soluble fraction (sCOD/TCOD) increase (58.8%) was much lower than the soluble fraction increase in ferric-based sludge (87.4%). This phenomenon further proved the inhibitory effects of PACL on the organic hydrolysis rate during AD (Shewa and Dagnew, 20120).

Compared to the control digester, an improvement in TCOD removal efficiency during anaerobic digestion was observed for the digester processing the pre-treated sludge except CEPT-II ozonated sludge. The TCOD removal for the control and pre-treated sludges in the CEPT-I group was 27.8% (control), 30.3% (LTTAP) and 20.2% (ozonation), whereas, in the CEPT-II group, the removals were 23.5%, 29.4% and 41.7%, respectively. Furthermore, instead of reduction, soluble COD percentage (sCOD/TCOD) was prominently released during AD for all samples. Soluble fraction improved to 87.4% (control), 99.7% (LTTAP) and 63.9% (Ozonation) in CEPT-I sludge group, while 58.8%, 49.4% and 227.7% increase were observed in CEPT-II sludge group, respectively. The lower sCOD/TCOD ratio shown in pre-treated ozonized CEPT-I sludge and thermal-alkali treated CEPT-II sludge was mainly due to the enhanced consumption of soluble compounds by anaerobes during the digestion process for biogas production.

4.3.4.2 Phosphorus released during anaerobic digestion

Anaerobic digestion utilizes anaerobic conversion of organic compounds to produce methane energy, meanwhile release organically bound P through hydrolysis, enabling the P available for recovery (Rittmann et al., 2011; Peccia and Westerhoff., 2015; Venkiteshwaran et al., 2018). Changes of the RP/TP percentage in the sludges during anaerobic reaction demonstrated that the percentage in the pretreatment groups was higher than in the control group on Day 1 (Table 4-4). LTTAP process improved the conversion of NRP by around 10% and 28% from CEPT-I and CEPT-II sludges, respectively. Similarly, the ozone process improved the conversion of NRP by around 16% and 24% from CEPT-I and CEPT-II sludges, respectively. Both pretreatment processes showed enhanced NRP to RP conversion in CEPT-II sludge. The higher conversion was associated with the relatively higher P fraction coagulated, flocculated and settled in the CEPT-II process. However, a lower extent of P release from the pretreatment group was observed compared to the control group on the 15th day. LTTAP treated CEPT-I sludge showed only 1.8% lower RP fraction, and LTTAP treated CEPT-II sludge showed 1.61% more RP fraction than the control samples, respectively.

Table 4-4:NRP conversion on Day 1st and 15th during anaerobic digestion

	DAY 1		DAY 15	
	tRP/TP (%)	**NRP/TP (%)**	**tRP/TP (%)**	**NRP/TP (%)**
CEPT-I sludge (control)	46.82	53.18	73.15	32.24
CEPT-I sludge (LTTAP)	55.77	44.23	71.35	46.04
CEPT-I sludge (Ozone pre-treatment)	62.63	37.37	63.33	41.18
CEPT-II sludge (Control)	37.40	62.60	69.70	40.73
CEPT-II sludge (LTTAP)	65.70	34.30	71.38	41.85
CEPT-II sludge (Ozone pre-treatment)	61.14	38.86	55.95	47.51

By comparing the reactive P release over the whole anaerobic digestion period, each sample showed an increasing conversion of RP/TP from Day 1 to Day 15. The profound change was found in control samples, 26.33% increase in CEPT-I control and 32.37% increase in CEPT-II sludge, respectively. However, changes in LTTAP treated samples (15.58% and 5.68%) were not as high as the control samples, and ozone pre-treated sludge even showed a decreasing trend after 15 days. The numbers also indicated that lower P-released in thermal-alkali treated CEPT-II than CEPT-I sludge after Day 1. This can be presumably explained by the process of pH adjustment from alkali to neutral using 2M HCl (to avoid the potential anaerobes destroy due to high pH in AD) diluted the soluble Al and phosphate content level in the solution. As explained by (Lin and Li., 2018), $AlPO_4$ and Al $(OH)_3$ have the lowest solubility in the pH range of 5.5-7.0. Ozone pre-treated sludge showed barely increased P-release (CEPT-I sludge) and even decreased P release (CEPT-II sludge) after Day 1. During ozonation treatment, the COD profile suggests the leaking of biopolymers. Since ozone can hydrolyze organic polymer to smaller compounds, hence increasing their biodegradability. The assimilable end-products are mainly consisted of carboxylic acids

(Yasui and Miyaji,1992). Accordingly, pH decrease as a result of ozonation due to the formation of acidic compounds(Weemaes et al.,2000). Bougrier et al. (2006) reported a pH value reduced to 5.8 after 0.1-1.16 gO3/gTS ozone treatment of waste activated sludge. Thus, a pH of 5.8 is in the range of 5.5-7.0, a pH range where PO_4-P and Al solubility is the lowest, which reduces the release of P and Al. Noteworthy, reactive phosphorus in ozonized CEPT-II sludge decreased from 76.4% (after ozone treatment on Day 0) to 61.14 % (Day 1), then to 56% (Day 15) during the whole AD process.

4.3.4.3 Cumulative methanogenesis

The removed organic matter was converted into biogas in AD, and the variations of net methane production per VSS added are summarized in Figures 4-7 and 4-8. The comparison of two control samples showed a 7% higher methane yield of ferric-based sludge than ferric + PACL-based sludge, indicated the inhibitory effect by the PACl coagulant on sludge digestion. The methane yield curve for CEPT-I sludge showed an immediate increase with time from Day 1 to Day 3, and then a slow generation was observed after Day 3. After 10 days of digestion, biogas production tended to stagnate. With ozonation and thermos-chemical (70°C with pH of 10-12) pretreatment conditions, the biogas production exceeded the control sample on the 3rd day of reaction. The accumulated biogas production at the end of 15 days was around 164.64 ± 3.81 mL/g VSS added for the control sample, while ozonation and LTTWP process increased the methane generated by 41.80% and 16.33%, respectively. The improved methane yield was due to the improved hydrolysis rate of particulate biodegradable substrates, and also owing to the increased biochemical methane potential of the slowly biodegradable substrate (Wang et al., 2019). The ozonation process in CEPT-I sludge showed the superiority that can promote anaerobic reactions and increase gas production.

As presented in Figure 4-8, the biogas produced in the CEPT-II sludge groups significantly increased in the first two days and stabilized after. The methane yield of three samples was 157.31 ± 6.68 mL/g VSS added (control), 230.11 ± 9.97 mL/g VSS added (LTTAP), and 218 ± 1.05 mL/g VSS added (Ozone) respectively. Both pretreatments showed a close improvement of 46.28% and 38.58% in AD. Interestingly, the result suggested that thermal alkali had a better effect on methane production, which is contrary to the previous finding in CEPT-I sludge.

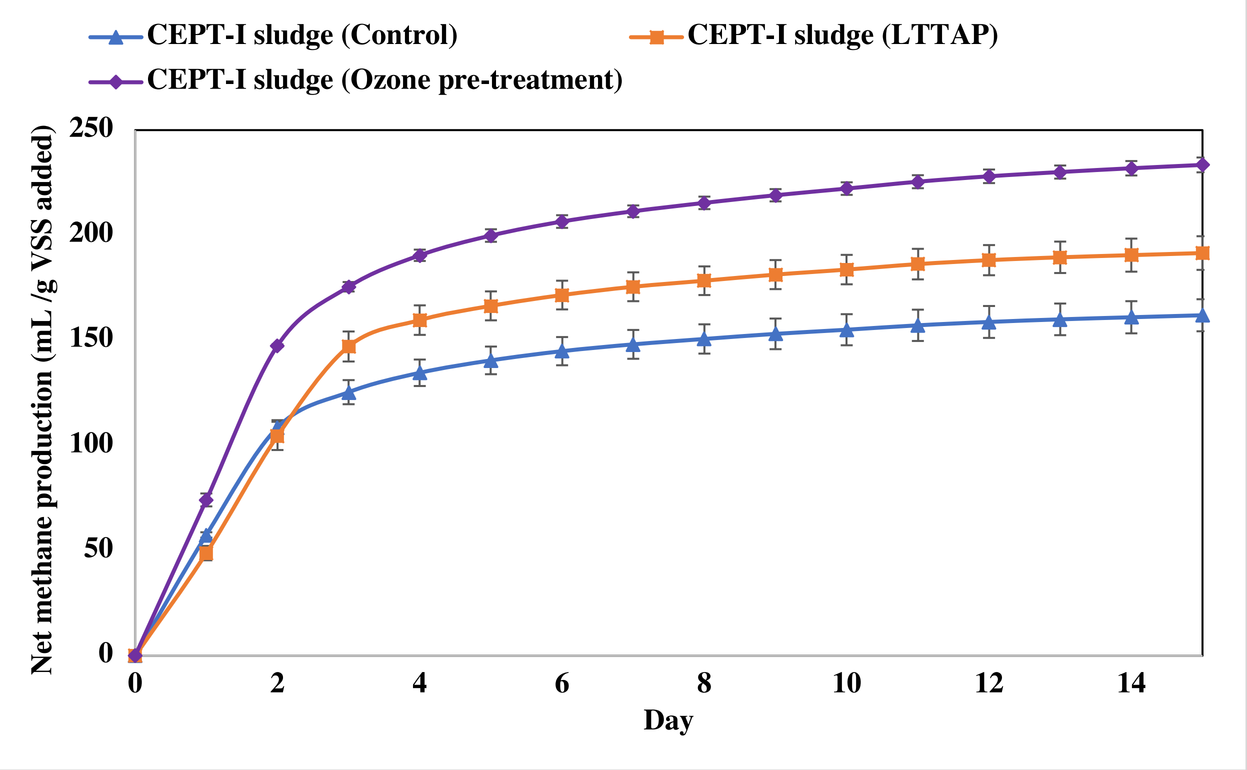


Figure 4-7:Net methane production of CEPT-I sludge (mL/g VSS added)

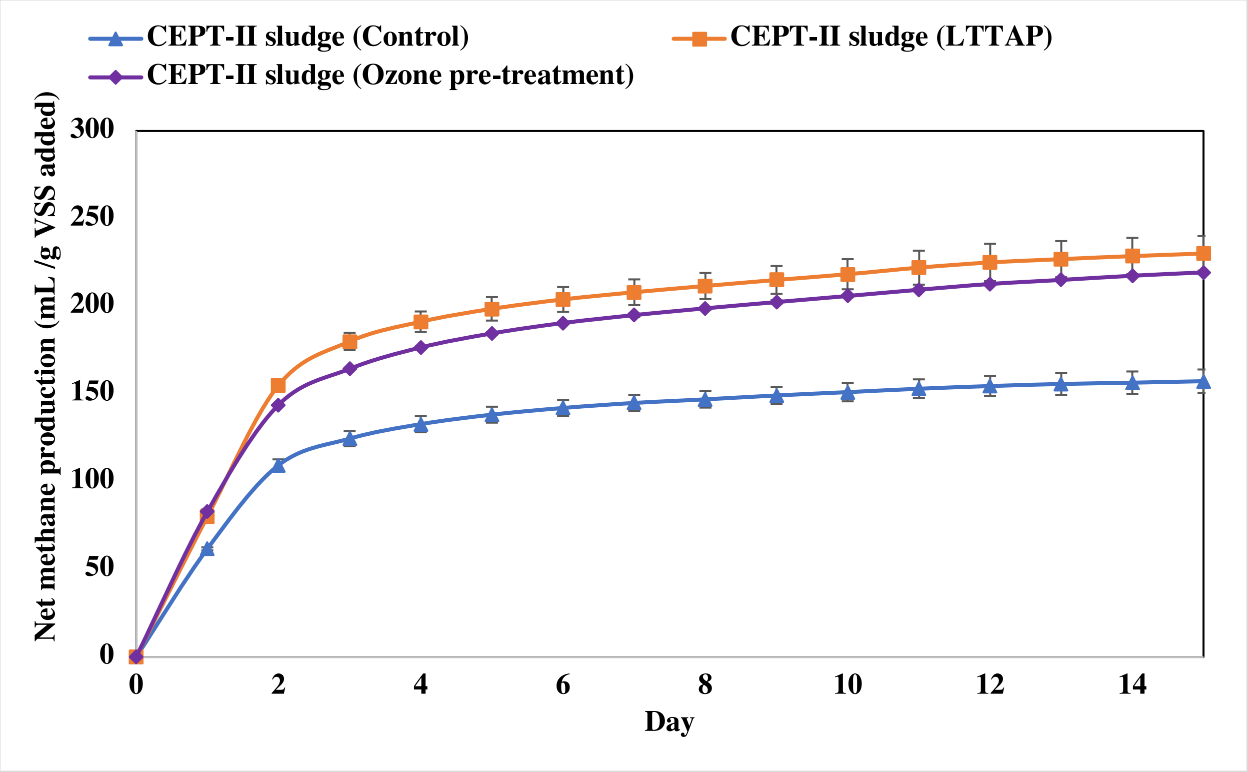


Figure 4-8:Net methane production of CEPT-II sludge (mL/g VSS added)

To further substantiate the result difference is significant, a statistical method called "two factors analysis of variance (ANOVA)" was applied. The assumptions include that: the populations from which the samples were obtained must be normally or approximately normally distributed; the samples must be independent, the variance of the populations must be equal; the groups must have the same sample size. These assumptions were verified using Minitab. The two most important factors in using ANOVA to reject the null hypothesis are: F-value larger than the F critical value and p-value smaller than the chosen alpha level. Three samples (control, ozonation, LTTAP) of CEPT-I sludge were regarded as one set, same applied to CEPT-II sludge. As shown in Table 4-5 below: for both sets, the p-value was less than the specified alpha of 0.05 and the calculated F is much larger than the value of F critical; thus the null hypothesis was rejected. Thus, there is a significant statistical difference in the calculated means of the three samples (Control/LTTAP/Ozone pre-treatment) for both CEPT I and CEPT II sludge.

Table 4-5:Statistical results of Anova: Two factors

	F	F crit	p-value
CEPT-I sludge set	108.04	3.32	0.00
CEPT-II sludge set	125.64	3.32	0.00

The correlation between sludge degree solubilization after different pretreatments and the final biogas production was demonstrated in Figures 4-9 and 4-10. In ferric based sludge, there was no positive relationship between methane yield and solubilization degree. The highest degree solubilization was observed in LTTAP sludge (2.27%). It can be speculated that the decomposition of the substrates was more efficient than the solubilization of sludge cells in pretreatments. Specifically, the substrate might be decomposed by the hydrolysis of anaerobic bacteria rather than by the pretreatments. Such a phenomenon was also reported in other literature (Xu et al., 2014). Furthermore, Li et al. (2012) found that NaOH addition, followed by neutralization with HCl provides a high saline environment but also could lead to significant inhibition of anaerobic digestion efficiency. This could be the reason for comparatively low methane produced by LTTAP than ozone pretreatment. On the other hand, a positive relationship between biogas production and degree solubilization occurred in Fe-Al based sludge. Compared to the control and ozonized sludge, thermo-chemical pretreatments demonstrated the highest methane yield (CEPT-I LTTAP:191.53 mL/VSS added and CEPT-II LTTAP: 230.11mL/VSS added) with the highest degree solubilization (CEPT-I LTTAP: 2.27% and CEPT-II LTTAP: 8.71%).

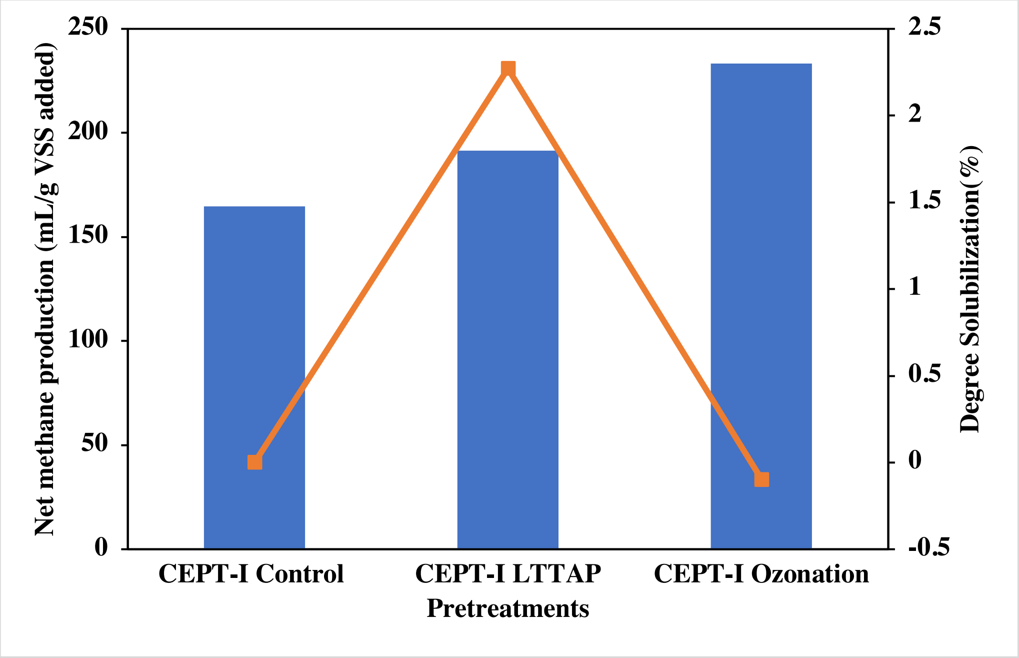


Figure 4-9:Relationship between solubilization by the different pretreatments and the final methane yield of CEPT-I sludge

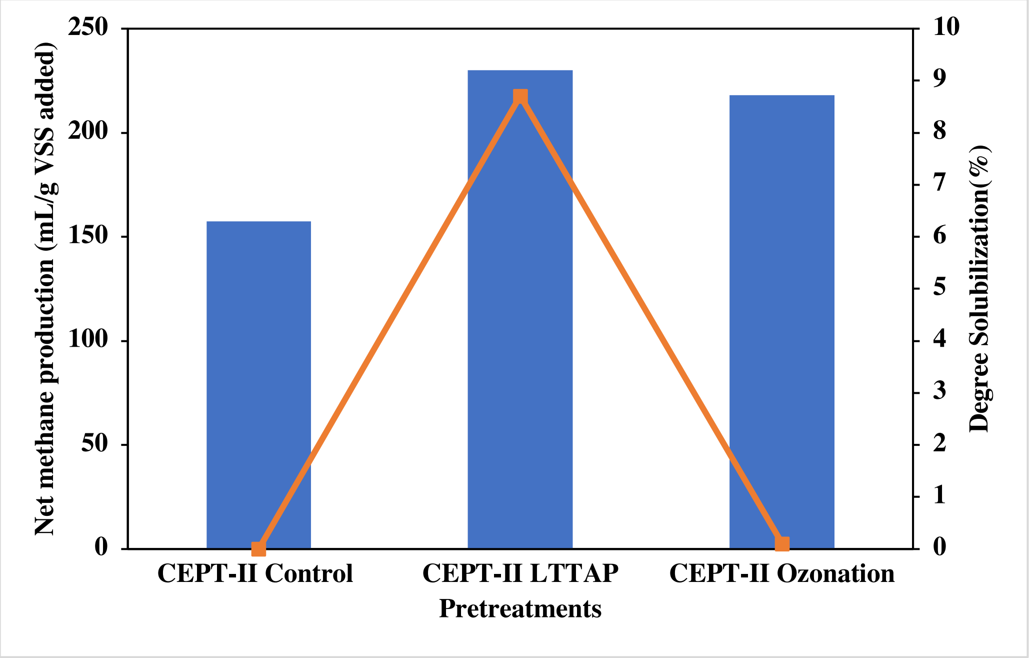


Figure 4-10:Relationship between solubilization by the different pretreatments and the final methane yield of CEPT-II sludge

4.4 Conclusion

This study has evaluated the impacts of two pretreatment methods (ozonation and low-temperature thermal alkali) on the anaerobic digestibility and phosphorus recovery of CEPT sludges. Based on the experimental results and analysis, the following conclusions can be drawn:

- In terms of solids reduction and solubilization of pretreatments, LTTAP demonstrated an increased by 2.30% and 8.71% in CEPT-I and CEPT-II sludge of solids solubilization, accompanied by an 84.46% and 84.42%, 76.85% and 76.54% decrease in TSS and VSS concentration, respectively. Ozonation showed decreased sCOD in CEPT-I sludge due to mineralization and nearly no change in CEPT-II sludge, with a 76.18% and 75.78%, 78.19% and 77.88% reduction in TSS and VSS concentration, respectively.
- In terms of NRP conversion of pretreatments, RP fraction increased after LTTAP pretreatment by 23.05% (CEPT-I LTTAP) and 29% (CEPT-I LTTAP) compare to the control groups. 58.98% higher of RP was released in ozonized sludge compare to CEPT-II control sludge.
- In terms of anaerobic biodegradability, ozonation pretreatment led to the highest biogas production 233.46±3.53 mL/g VSS added in CEPT-I sludge with an increase of 41.80% compared to the control, whereas LTTAP demonstrated the highest methane yield (230.11 ±9.97 mL/g VSS added) with an improvement of 46.28% in CEPT-II sludge compared to the control
- However, during anaerobic digestion, both ozonation and thermo-alkali treated sludge showed lower solids removal compare to the control groups indicated no enhancement on the particulate matter biodegradability during digestion. Nevertheless, higher TCOD removal and improved soluble COD fraction greatly contributed to the methane gas

production. More importantly, LATTP demonstrated 71.35%(CEPT-I) and 71.38%(CEPT-II) of reactive p-release, which was slightly higher than the control sludges, whereas ozonation showed 63.33%(CEPT-I) and 55.95% (CEPT-II) P-release.

- In terms of chemically enhanced primary sludge sample, LTTAP demonstrated around 8% higher solids reduction rate in ferric based sludge, but very similar removal in ferric alum-based sludge compare to the ozonation process. Also, LTTAP showed an effective solubilization degree in both samples. After pretreatments and further anaerobic digestion, 3.38%(control) and 7.38%(ozonation)higher reactive P was released in ferric based sludge than ferric alum-based sludge. The final biogas production indicated not much difference in the control samples. Ozonized ferric sludge had the highest methane yield, whereas LTTAP was more suitable for ferric alum-based sludge.

To sum, low-temperature thermal alkali is preferred to provide efficient sludge disintegration and solubilization in relation to the overall performance of anaerobic digestion for resource recovery. However, further works on the optimal ozone dose and NaOH dose to adjust pH should be studied.

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5 Conclusion And Future Research Direction

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

5.3 Conclusions

The results presented in this study lead to the following conclusions:

- COD fractions of RWW, CEPT-I and CEPT-II effluents were determined through the combination of physical-chemical and biological methods.
- Volumeless point separator is the ideal setup for a simple conventional primary clarifier; the removal of influent materials is predefined as direct model input, which cannot well-describe the fraction changes in the CEPT clarifier. The Layered-flux model can give a reasonable description of the effluent TSS concentration of the primary clarifier. For practical applications, the three-compartment model provides a better description of chemicals and polymers addition impacts on primary treatment accurately modelling primarily clarifier and providing the most accurate estimation of clarifier performance with respect to composite and state variables. Moreover, the calibration procedure was more straightforward compared to the layered-flux model.
- LTTAP demonstrated an increased by 2.30% and 8.71% in CEPT-I and CEPT-II sludge of solids solubilization, combined with an 84.46% and 84.42%, 76.85% and 76.54% decrease in TSS and VSS concentration, respectively. RP fraction increased after LTTAP pretreatment by 23.05%(CEPT-I LTTAP), and 29%(CEPT-I LTTAP) compare to the control groups. LTTAP also presented the highest methane yield (230.11 ±9.97 mL/g VSS added) with an improvement of 46.28% in CEPT-II sludge compared to the control.

- Ozonation showed decreased sCOD in CEPT-I sludge due to mineralization and nearly no change in CEPT-II sludge, with a 76.18% and 75.78%, 78.19% and 77.88% reduction in TSS and VSS concentration, respectively. 58.98% higher of RP was released in ozonized sludge compare to CEPT-II control sludge. Moreover, ozonation pretreatment led to the highest biogas production, 233.46±3.53 mL/g VSS added in CEPT-I sludge with an increase of 41.80% compared to the control.
- In terms of chemically enhanced primary sludge sample, LTTAP demonstrated around 8% higher solids reduction rate in ferric based sludge, but very similar removal in ferric alum-based sludge compare to the ozonation process. Also, LTTAP showed an effective solubilization degree in both samples. After pretreatments and further anaerobic digestion, 3.38%(control) and 7.38%(ozonation)higher reactive P was released in ferric based sludge than ferric alum-based sludge. The final biogas production indicated not much difference in the control samples. Ozonized ferric sludge had the highest methane yield, whereas LTTAP was more suitable for ferric alum-based sludge.

5.4 Recommendations

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

- Eliminate mineralization in ozone pretreatment is necessary and requires further study to determine the optimum dose for both chemical sludge samples. It is recommended to conduct ozonation at different levels;
- Alkali dose to adjust pH should be determined;

- Further detail fractionation on soluble phosphorus and particulate phosphorus should be determined to understand the released P sources fully. Organic P and acid hydrolysable P should also be addressed.

Supporting Material

(For Chapter 3)

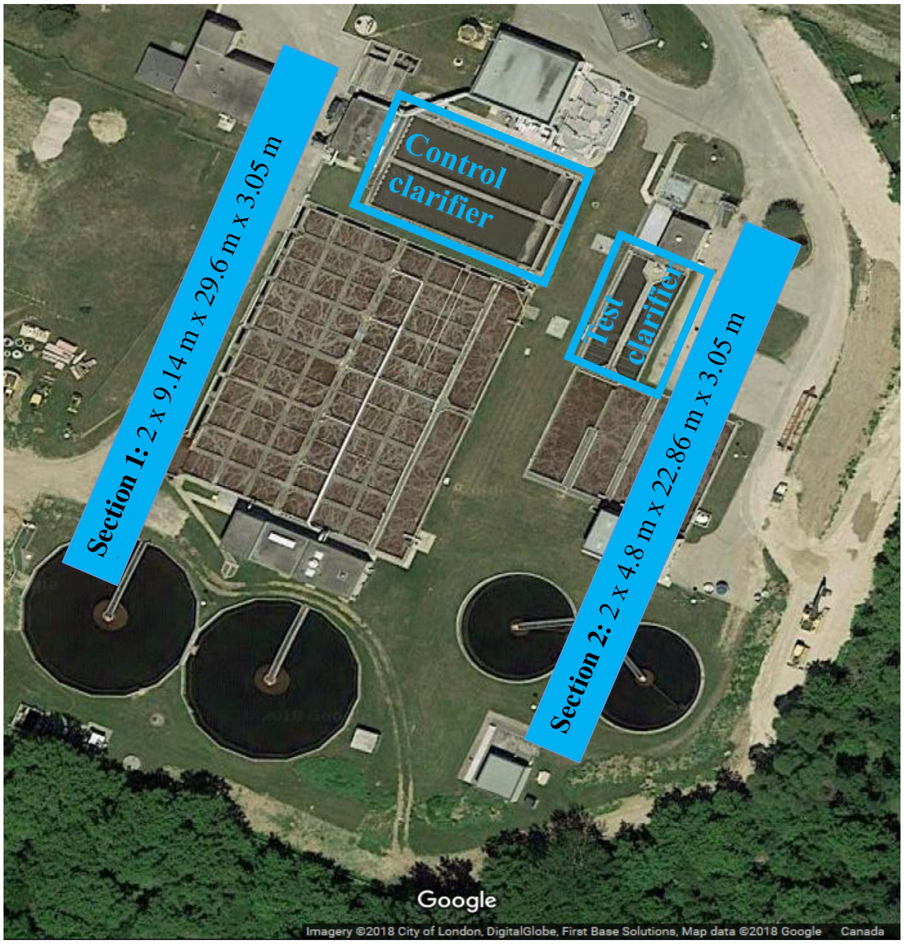


Figure SD1. Layout of Vauxhall WWTP

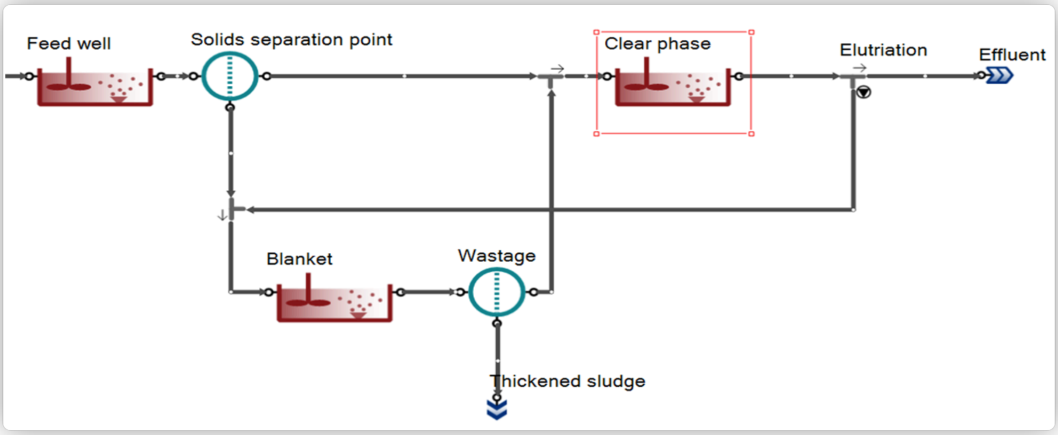


Figure SD2. Three compartment 1-D model (Dynamita,2019)

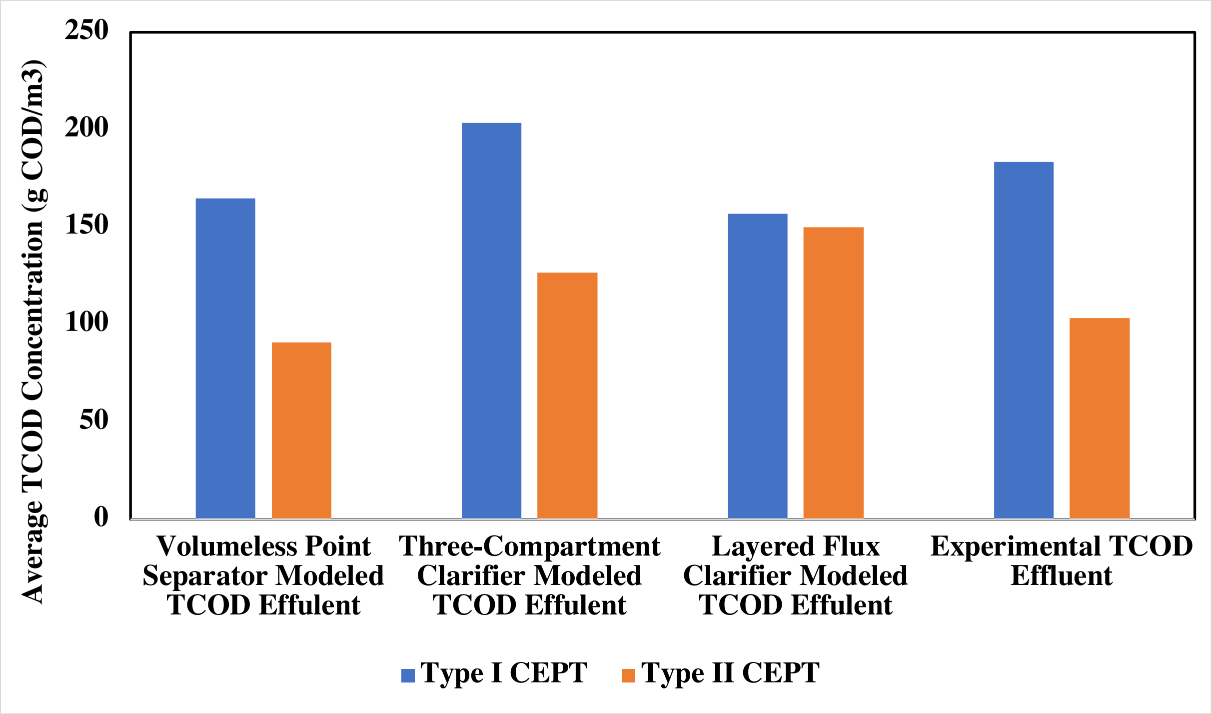


Figure SD3. Model Fit for Simulated Effluent T_{COD} Concentration (Calibrated Dynamic Results)

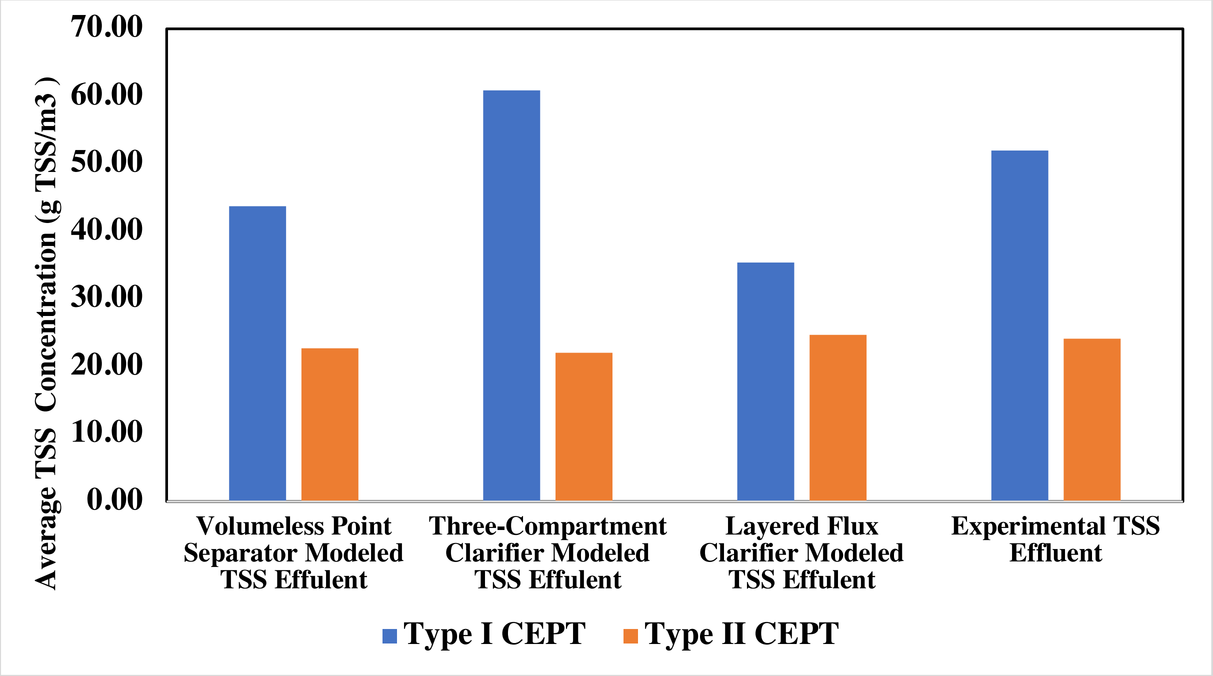


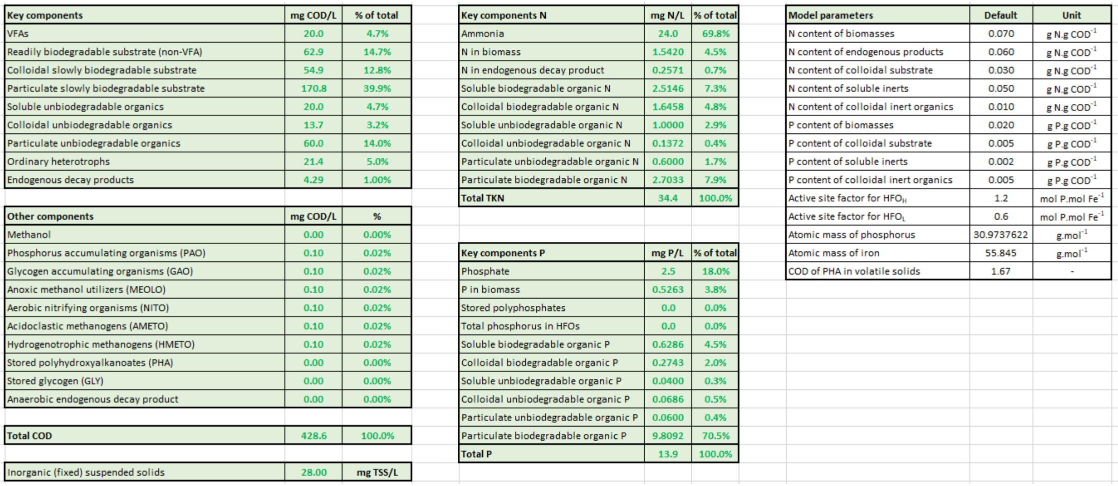
Figure SD4. Model Fit for Simulated Effluent T_{COD} Concentration (Calibrated Dynamic Results)

Table SD1. Input parameters set-up for the three primary clarifier models

Hydraulics	Volumeless point separator		Three-compartment clarifier		Layered flux clarifier	
Process units	Influent, ferric chloride flow, primary clarifier, primary sludge and Effluent					
Underflow specification	Sludge flow		Sludge flow		Sludge flow	
Reactions	Non-reactive		Reactive		Reactive	
Effluent specification	Percent solids and colloidal removal (CEPT)		Percent solids removal		Calculated effluent solids	
Input Parameters Setup	Percent solids and colloidal removal (CEPT)	Solids percent removal	SettingTables	Total volume	Clarifier settings	Surface area
		Colloidal material removal		Feed well volume		Depth
		Soluble material removal		Sludge blanket volume		Depth of influent layer from top
		Sludge flow		Sludge flow		Sludge flow
				Solids percent removal without polymer (with metal)	Settling parameter	Boundary settling velocity
				Solids percent removal with polymer (with both)		Maximum Vesilind settling velocity
			Clarifier geometry	Surface of clarifier		Coefficient for hindered settling
			Flocculation parameters	polymer concentration		Coefficient for flocculent settling
				Half-saturation of polymers for solid percent removal improvement		Coefficient for compression
				Rate of precipitation with polymer		Boundary compression concentration
				Half-saturation of polymers flocculation		Fraction of non-settleable solids
				Half-saturation of colloidal substrate in flocculation with polymers		Non-settleable TSS
						Concentration at top of sludge blanket

CALIBRATION – DATA RECONCILATION

Table SD2. CEPT-I Mass balances of TCOD, TN and TP provided by SUMO influent tool



Key components	mg COD/L	% of total
VFAs	20.0	4.7%
Readily biodegradable substrate (non-VFA)	62.9	14.7%
Colloidal slowly biodegradable substrate	54.9	12.8%
Particulate slowly biodegradable substrate	170.8	39.9%
Soluble unbiodegradable organics	20.0	4.7%
Colloidal unbiodegradable organics	13.7	3.2%
Particulate unbiodegradable organics	60.0	14.0%
Ordinary heterotrophs	21.4	5.0%
Endogenous decay products	4.29	1.00%

Other components	mg COD/L	%
Methanol	0.00	0.00%
Phosphorus accumulating organisms (PAO)	0.10	0.02%
Glycogen accumulating organisms (GAO)	0.10	0.02%
Anoxic methanol utilizers (MEOLO)	0.10	0.02%
Aerobic nitrifying organisms (NITO)	0.10	0.02%
Acidoclastic methanogens (AMETO)	0.10	0.02%
Hydrogenotrophic methanogens (HMETO)	0.10	0.02%
Stored polyhydroxyalkanoates (PHA)	0.00	0.00%
Stored glycogen (GLY)	0.00	0.00%
Anaerobic endogenous decay product	0.00	0.00%

Total COD	428.6	100.0%
Inorganic (fixed) suspended solids	28.00	mg TSS/L

Key components N	mg N/L	% of total
Ammonia	24.0	69.8%
N in biomass	1.5420	4.5%
N in endogenous decay product	0.2571	0.7%
Soluble biodegradable organic N	2.5146	7.3%
Colloidal biodegradable organic N	1.6458	4.8%
Soluble unbiodegradable organic N	1.0000	2.9%
Colloidal unbiodegradable organic N	0.1372	0.4%
Particulate unbiodegradable organic N	0.6000	1.7%
Particulate biodegradable organic N	2.7033	7.9%
Total TKN	34.4	100.0%

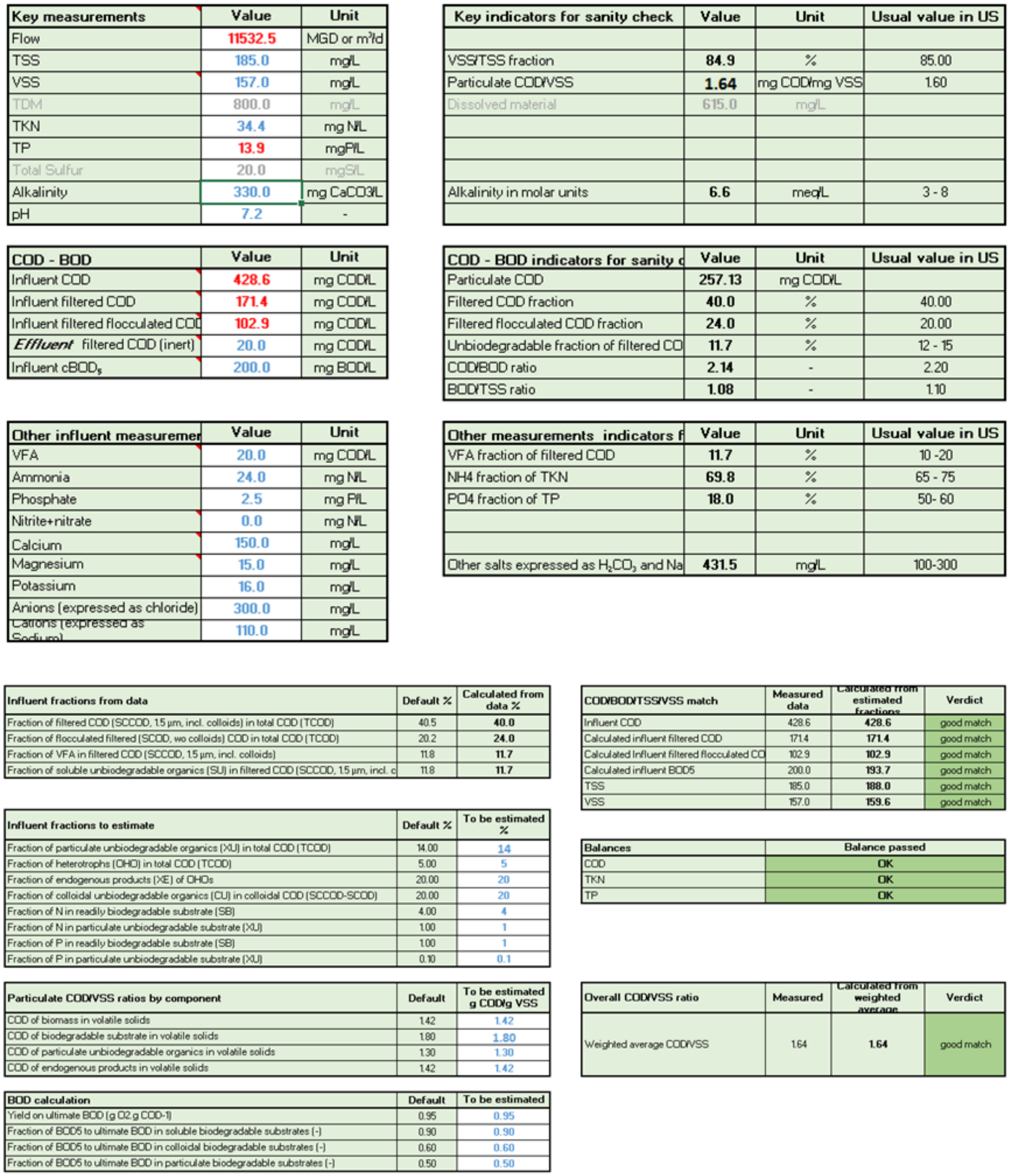
Key components P	mg P/L	% of total
Phosphate	2.5	18.0%
P in biomass	0.5263	3.8%
Stored polyphosphates	0.0	0.0%
Total phosphorus in HFOs	0.0	0.0%
Soluble biodegradable organic P	0.6286	4.5%
Colloidal biodegradable organic P	0.2743	2.0%
Soluble unbiodegradable organic P	0.0400	0.3%
Colloidal unbiodegradable organic P	0.0686	0.5%
Particulate unbiodegradable organic P	0.0600	0.4%
Particulate biodegradable organic P	9.8092	70.5%
Total P	13.9	100.0%

Model parameters	Default	Unit
N content of biomasses	0.070	g N.g COD^{-1}
N content of endogenous products	0.060	g N.g COD^{-1}
N content of colloidal substrate	0.030	g N.g COD^{-1}
N content of soluble inerts	0.050	g N.g COD^{-1}
N content of colloidal inert organics	0.010	g N.g COD^{-1}
P content of biomasses	0.020	g P.g COD^{-1}
P content of colloidal substrate	0.005	g P.g COD^{-1}
P content of soluble inerts	0.002	g P.g COD^{-1}
P content of colloidal inert organics	0.005	g P.g COD^{-1}
Active site factor for HFO_H	1.2	mol P.mol Fe^{-1}
Active site factor for HFO_L	0.6	mol P.mol Fe^{-1}
Atomic mass of phosphorus	30.9737622	g.mol^{-1}
Atomic mass of iron	55.845	g.mol^{-1}
COD of PHA in volatile solids	1.67	-

Table SD3. CEPT-I Comparison of typical wastewater ratios and Vauxhall influent ratios

			Typical wastewater ratios				Vauxhall influent ratios			
	Ratio	Unit	**Mean.**	**Min.**	**Max.**	**STD(%)**	**Mean.**	**Min.**	**Max.**	**STD(%)**
Raw influent	**Total nitrogen/COD**	g N / g COD	0.095	0.05	0.15	17				
	NH3-N / TKN	g N / g N	0.684	0.5	0.9	8				
	Total phosphorus / COD	g P / g COD	0.016	0.007	0.025	22				
	PO4-P / total phosphorus	g P / g P	0.603	0.39	0.8	16				
	COD / BOD5	g COD / g BOD	2.06	1.41	3	11				
	fCOD / COD	g COD / g COD	0.343	0.12	0.75	29				
	TSS / COD	g TSS / g COD	0.503	0.35	0.7	18	0.583	0.246	0.927	0.180
	XCOD / VSS	g COD / g VSS	1.69	1.3	3	12				
	VSS / TSS	g VSS / g TSS	0.74	0.3	0.9	20				
	BOD5 / BODult	g BOD / g BOD	0.74	0.58	0.74	7				
	Alkalinity	Moleq / L	5.173	1.5	9	35				

Table SD4. CEPT-I Data and fractions check provided by SUMO Influent Tool



Key measurements	Value	Unit
Flow	11532.5	MGD or m^3/d
TSS	185.0	mg/L
VSS	157.0	mg/L
TDM	800.0	mg/L
TKN	34.4	mg N/L
TP	13.9	mgP/L
Total Sulfur	20.0	mgS/L
Alkalinity	330.0	mg CaCO3/L
pH	7.2	-

Key indicators for sanity check	Value	Unit	Usual value in US
VSS/TSS fraction	84.9	%	85.00
Particulate COD/VSS	1.64	mg COD/mg VSS	1.60
Dissolved material	615.0	mg/L	
Alkalinity in molar units	6.6	meq/L	3 - 8

COD - BOD	Value	Unit
Influent COD	428.6	mg COD/L
Influent filtered COD	171.4	mg COD/L
Influent filtered flocculated CO	102.9	mg COD/L
Effluent filtered COD (inert)	20.0	mg COD/L
Influent $cBOD_5$	200.0	mg BOD/L

COD - BOD indicators for sanity c	Value	Unit	Usual value in US
Particulate COD	257.13	mg COD/L	
Filtered COD fraction	40.0	%	40.00
Filtered flocculated COD fraction	24.0	%	20.00
Unbiodegradable fraction of filtered CO	11.7	%	12 - 15
COD/BOD ratio	2.14	-	2.20
BOD/TSS ratio	1.08	-	1.10

Other influent measuremer	Value	Unit
VFA	20.0	mg COD/L
Ammonia	24.0	mg N/L
Phosphate	2.5	mg P/L
Nitrite+nitrate	0.0	mg N/L
Calcium	150.0	mg/L
Magnesium	15.0	mg/L
Potassium	16.0	mg/L
Anions (expressed as chloride)	300.0	mg/L
Cations (expressed as Sodium)	110.0	mg/L

Other measurements indicators f	Value	Unit	Usual value in US
VFA fraction of filtered COD	11.7	%	10 -20
NH4 fraction of TKN	69.8	%	65 - 75
PO4 fraction of TP	18.0	%	50- 60
Other salts expressed as H_2CO_3 and Na	431.5	mg/L	100-300

Influent fractions from data	Default %	Calculated from data %
Fraction of filtered COD (SCCOD, 1.5 µm, incl. colloids) in total COD (TCOD)	40.5	40.0
Fraction of flocculated filtered (SCOD, wo colloids) COD in total COD (TCOD)	20.2	24.0
Fraction of VFA in filtered COD (SCCOD, 1.5 µm, incl. colloids)	11.8	11.7
Fraction of soluble unbiodegradable organics (SU) in filtered COD (SCCOD, 1.5 µm, incl. c	11.8	11.7

COD/BOD/TSS/VSS match	Measured data	Calculated from estimated fractions	Verdict
Influent COD	428.6	428.6	good match
Calculated influent filtered COD	171.4	171.4	good match
Calculated Influent filtered flocculated CO	102.9	102.9	good match
Calculated influent BOD5	200.0	193.7	good match
TSS	185.0	188.0	good match
VSS	157.0	159.6	good match

Influent fractions to estimate	Default %	To be estimated %
Fraction of particulate unbiodegradable organics (XU) in total COD (TCOD)	14.00	14
Fraction of heterotrophs (OHO) in total COD (TCOD)	5.00	5
Fraction of endogenous products (XE) of OHOs	20.00	20
Fraction of colloidal unbiodegradable organics (CU) in colloidal COD (SCCOD-SCOD)	20.00	20
Fraction of N in readily biodegradable substrate (SB)	4.00	4
Fraction of N in particulate unbiodegradable substrate (XU)	1.00	1
Fraction of P in readily biodegradable substrate (SB)	1.00	1
Fraction of P in particulate unbiodegradable substrate (XU)	0.10	0.1

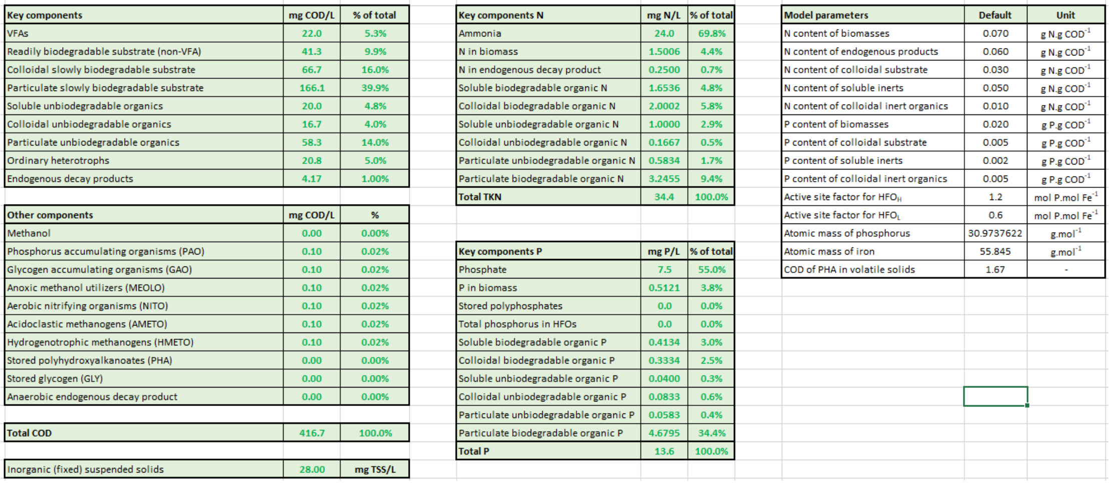
Balances	Balance passed
COD	OK
TKN	OK
TP	OK

Particulate COD/VSS ratios by component	Default	To be estimated g COD/g VSS
COD of biomass in volatile solids	1.42	1.42
COD of biodegradable substrate in volatile solids	1.80	1.80
COD of particulate unbiodegradable organics in volatile solids	1.30	1.30
COD of endogenous products in volatile solids	1.42	1.42

Overall COD/VSS ratio	Measured	Calculated from weighted average	Verdict
Weighted average COD/VSS	1.64	1.64	good match

BOD calculation	Default	To be estimated
Yield on ultimate BOD (g O2.g COD-1)	0.95	0.95
Fraction of BOD5 to ultimate BOD in soluble biodegradable substrates (-)	0.90	0.90
Fraction of BOD5 to ultimate BOD in colloidal biodegradable substrates (-)	0.60	0.60
Fraction of BOD5 to ultimate BOD in particulate biodegradable substrates (-)	0.50	0.50

Table SD5. CEPT-II Mass balances of TCOD, TN and TP provided by SUMO influent tool.



Key components	mg COD/L	% of total
VFAs	22.0	5.3%
Readily biodegradable substrate (non-VFA)	41.3	9.9%
Colloidal slowly biodegradable substrate	66.7	16.0%
Particulate slowly biodegradable substrate	166.1	39.9%
Soluble unbiodegradable organics	20.0	4.8%
Colloidal unbiodegradable organics	16.7	4.0%
Particulate unbiodegradable organics	58.3	14.0%
Ordinary heterotrophs	20.8	5.0%
Endogenous decay products	4.17	1.00%

Other components	mg COD/L	%
Methanol	0.00	0.00%
Phosphorus accumulating organisms (PAO)	0.10	0.02%
Glycogen accumulating organisms (GAO)	0.10	0.02%
Anoxic methanol utilizers (MEOLO)	0.10	0.02%
Aerobic nitrifying organisms (NITO)	0.10	0.02%
Acidoclastic methanogens (AMETO)	0.10	0.02%
Hydrogenotrophic methanogens (HMETO)	0.10	0.02%
Stored polyhydroxyalkanoates (PHA)	0.00	0.00%
Stored glycogen (GLY)	0.00	0.00%
Anaerobic endogenous decay product	0.00	0.00%

Total COD	416.7	100.0%

Inorganic (fixed) suspended solids	28.00	mg TSS/L

Key components N	mg N/L	% of total
Ammonia	24.0	69.8%
N in biomass	1.5006	4.4%
N in endogenous decay product	0.2500	0.7%
Soluble biodegradable organic N	1.6536	4.8%
Colloidal biodegradable organic N	2.0002	5.8%
Soluble unbiodegradable organic N	1.0000	2.9%
Colloidal unbiodegradable organic N	0.1667	0.5%
Particulate unbiodegradable organic N	0.5834	1.7%
Particulate biodegradable organic N	3.2455	9.4%
Total TKN	34.4	100.0%

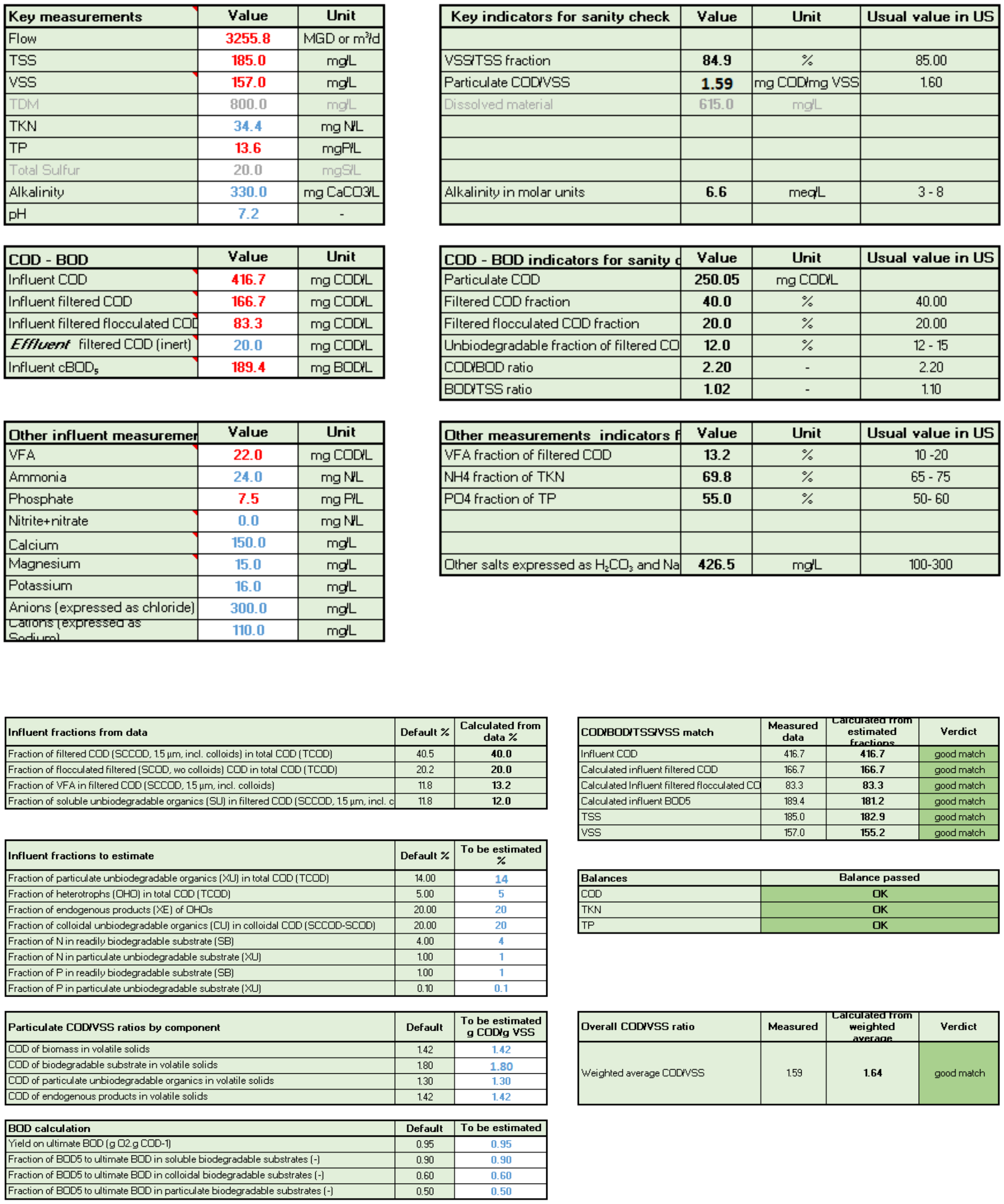
Key components P	mg P/L	% of total
Phosphate	7.5	55.0%
P in biomass	0.5121	3.8%
Stored polyphosphates	0.0	0.0%
Total phosphorus in HFOs	0.0	0.0%
Soluble biodegradable organic P	0.4134	3.0%
Colloidal biodegradable organic P	0.3334	2.5%
Soluble unbiodegradable organic P	0.0400	0.3%
Colloidal unbiodegradable organic P	0.0833	0.6%
Particulate unbiodegradable organic P	0.0583	0.4%
Particulate biodegradable organic P	4.6795	34.4%
Total P	13.6	100.0%

Model parameters	Default	Unit
N content of biomasses	0.070	g N.g COD^{-1}
N content of endogenous products	0.060	g N.g COD^{-1}
N content of colloidal substrate	0.030	g N.g COD^{-1}
N content of soluble inerts	0.050	g N.g COD^{-1}
N content of colloidal inert organics	0.010	g N.g COD^{-1}
P content of biomasses	0.020	g P.g COD^{-1}
P content of colloidal substrate	0.005	g P.g COD^{-1}
P content of soluble inerts	0.002	g P.g COD^{-1}
P content of colloidal inert organics	0.005	g P.g COD^{-1}
Active site factor for HFO$_H$	1.2	mol P.mol Fe^{-1}
Active site factor for HFO$_L$	0.6	mol P.mol Fe^{-1}
Atomic mass of phosphorus	30.9737622	g.mol^{-1}
Atomic mass of iron	55.845	g.mol^{-1}
COD of PHA in volatile solids	1.67	-

Table SD6. CEPT-II Comparison of typical wastewater ratios and Vauxhall influent ratios

			Typical wastewater ratios				**Vauxhall influent ratios**			
	Ratio	Unit	**Mean.**	**Min.**	**Max.**	**STD**	**Mean.**	**Min.**	**Max.**	**STD**
Raw influent	**Total nitrogen/COD**	g N / g COD	0.095	0.05	0.15	17				
	NH3-N / TKN	g N / g N	0.684	0.5	0.9	8				
	Total phosphorus / COD	g P / g COD	0.016	0.007	0.025	22				
	PO4-P / total phosphorus	g P / g P	0.603	0.39	0.8	16				
	COD / BOD5	g COD / g BOD	2.06	1.41	3	11				
	fCOD / COD	g COD / g COD	0.343	0.12	0.75	29				
	TSS / COD	g TSS / g COD	0.503	0.35	0.7	18	0.583	0.246	1.066	0.222
	XCOD / VSS	g COD / g VSS	1.69	1.3	3	12				
	VSS / TSS	g VSS / g TSS	0.74	0.3	0.9	20				
	BOD5 / BODult	g BOD / g BOD	0.74	0.58	0.74	7				
	Alkalinity	Moleq / L	5.173	1.5	9	35				

Table SD7. CEPT-II Data and fractions check provided by SUMO Influent Tool



Key measurements	Value	Unit
Flow	3255.8	MGD or m³/d
TSS	185.0	mg/L
VSS	157.0	mg/L
TDM	800.0	mg/L
TKN	34.4	mg N/L
TP	13.6	mgP/L
Total Sulfur	20.0	mgS/L
Alkalinity	330.0	mg CaCO3/L
pH	7.2	-

Key indicators for sanity check	Value	Unit	Usual value in US
VSS/TSS fraction	84.9	%	85.00
Particulate COD/VSS	1.59	mg COD/mg VSS	1.60
Dissolved material	615.0	mg/L	
Alkalinity in molar units	6.6	meq/L	3 - 8

COD - BOD	Value	Unit
Influent COD	416.7	mg COD/L
Influent filtered COD	166.7	mg COD/L
Influent filtered flocculated COD	83.3	mg COD/L
Effluent filtered COD (inert)	20.0	mg COD/L
Influent cBOD$_5$	189.4	mg BOD/L

COD - BOD indicators for sanity c	Value	Unit	Usual value in US
Particulate COD	250.05	mg COD/L	
Filtered COD fraction	40.0	%	40.00
Filtered flocculated COD fraction	20.0	%	20.00
Unbiodegradable fraction of filtered CO	12.0	%	12 - 15
COD/BOD ratio	2.20	-	2.20
BOD/TSS ratio	1.02	-	1.10

Other influent measuremer	Value	Unit
VFA	22.0	mg COD/L
Ammonia	24.0	mg N/L
Phosphate	7.5	mg P/L
Nitrite+nitrate	0.0	mg N/L
Calcium	150.0	mg/L
Magnesium	15.0	mg/L
Potassium	16.0	mg/L
Anions (expressed as chloride)	300.0	mg/L
Cations (expressed as Sodium)	110.0	mg/L

Other measurements indicators f	Value	Unit	Usual value in US
VFA fraction of filtered COD	13.2	%	10 -20
NH4 fraction of TKN	69.8	%	65 - 75
PO4 fraction of TP	55.0	%	50- 60
Other salts expressed as H_2CO_3 and Na	426.5	mg/L	100-300

Influent fractions from data	Default %	Calculated from data %
Fraction of filtered COD (SCCOD, 1.5 µm, incl. colloids) in total COD (TCOD)	40.5	**40.0**
Fraction of flocculated filtered (SCOD, wo colloids) COD in total COD (TCOD)	20.2	**20.0**
Fraction of VFA in filtered COD (SCCOD, 1.5 µm, incl. colloids)	11.8	**13.2**
Fraction of soluble unbiodegradable organics (SU) in filtered COD (SCCOD, 1.5 µm, incl. c	11.8	**12.0**

COD/BOD/TSS/VSS match	Measured data	Calculated from estimated fractions	Verdict
Influent COD	416.7	**416.7**	good match
Calculated influent filtered COD	166.7	**166.7**	good match
Calculated Influent filtered flocculated CO	83.3	**83.3**	good match
Calculated influent BOD5	189.4	**181.2**	good match
TSS	185.0	**182.9**	good match
VSS	157.0	**155.2**	good match

Influent fractions to estimate	Default %	To be estimated %
Fraction of particulate unbiodegradable organics (XU) in total COD (TCOD)	14.00	14
Fraction of heterotrophs (OHO) in total COD (TCOD)	5.00	5
Fraction of endogenous products (XE) of OHOs	20.00	20
Fraction of colloidal unbiodegradable organics (CU) in colloidal COD (SCCOD-SCOD)	20.00	20
Fraction of N in readily biodegradable substrate (SB)	4.00	4
Fraction of N in particulate unbiodegradable substrate (XU)	1.00	1
Fraction of P in readily biodegradable substrate (SB)	1.00	1
Fraction of P in particulate unbiodegradable substrate (XU)	0.10	0.1

Balances	Balance passed
COD	OK
TKN	OK
TP	OK

Particulate COD/VSS ratios by component	Default	To be estimated g COD/g VSS
COD of biomass in volatile solids	1.42	1.42
COD of biodegradable substrate in volatile solids	1.80	1.80
COD of particulate unbiodegradable organics in volatile solids	1.30	1.30
COD of endogenous products in volatile solids	1.42	1.42

Overall COD/VSS ratio	Measured	Calculated from weighted average	Verdict
Weighted average COD/VSS	1.59	**1.64**	good match

BOD calculation	Default	To be estimated
Yield on ultimate BOD (g O2.g COD-1)	0.95	0.95
Fraction of BOD5 to ultimate BOD in soluble biodegradable substrates (-)	0.90	0.90
Fraction of BOD5 to ultimate BOD in colloidal biodegradable substrates (-)	0.60	0.60
Fraction of BOD5 to ultimate BOD in particulate biodegradable substrates (-)	0.50	0.50

DYNAMIC MODEL FIT GRAPHS (SIMULATED VS. EXPERIMENTAL)

CEPT-I Calibrated Model (Model fit for simulated effluent concentrations)

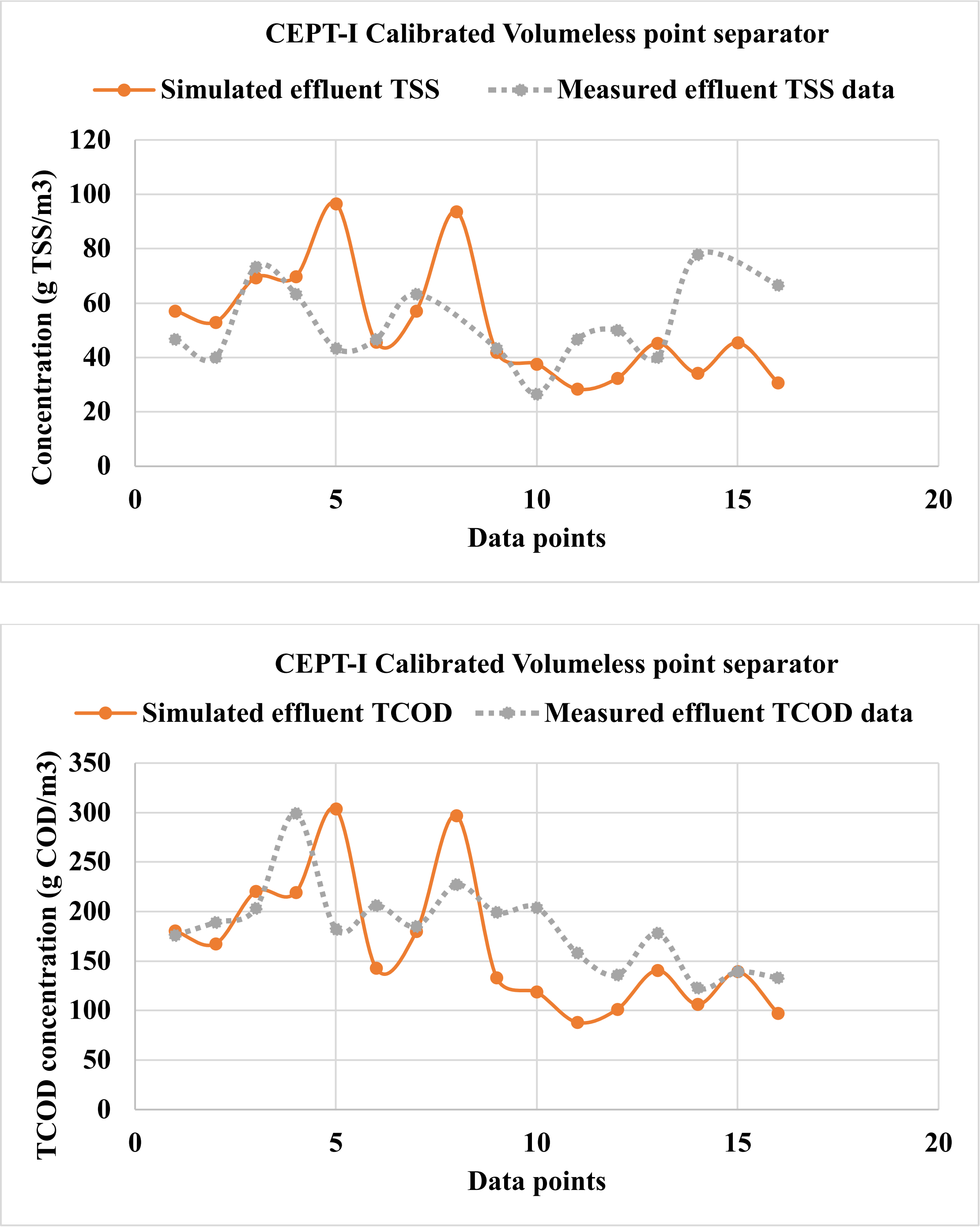


Figure SD5. CEPT Volumeless point separator-simulated and Measured (a) TSS and (b) COD profile in CEPT-I: Calibration

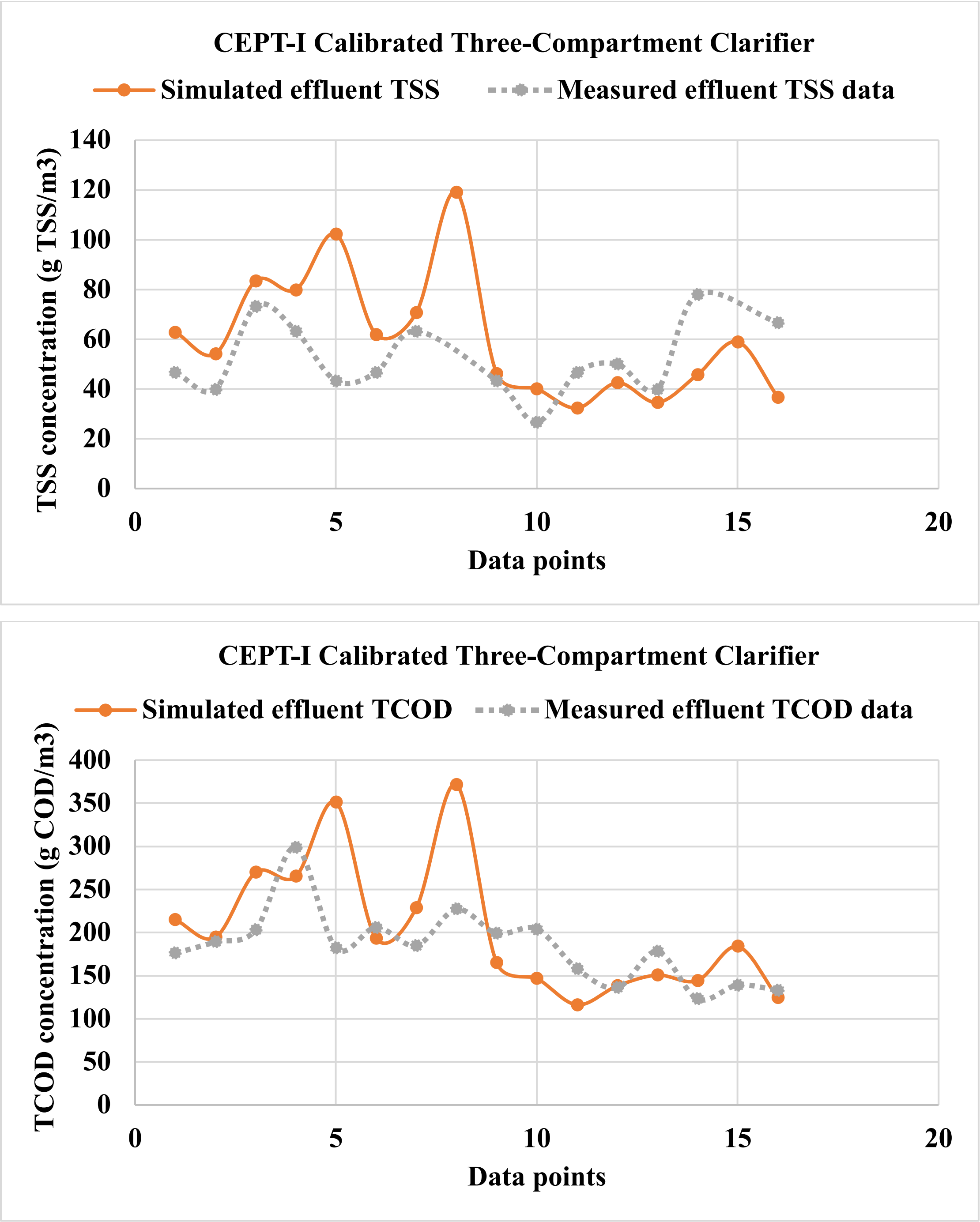


Figure SD6. Three compartments model-simulated and Measured (a) TSS and (b) COD profile in CEPT-I: Calibration

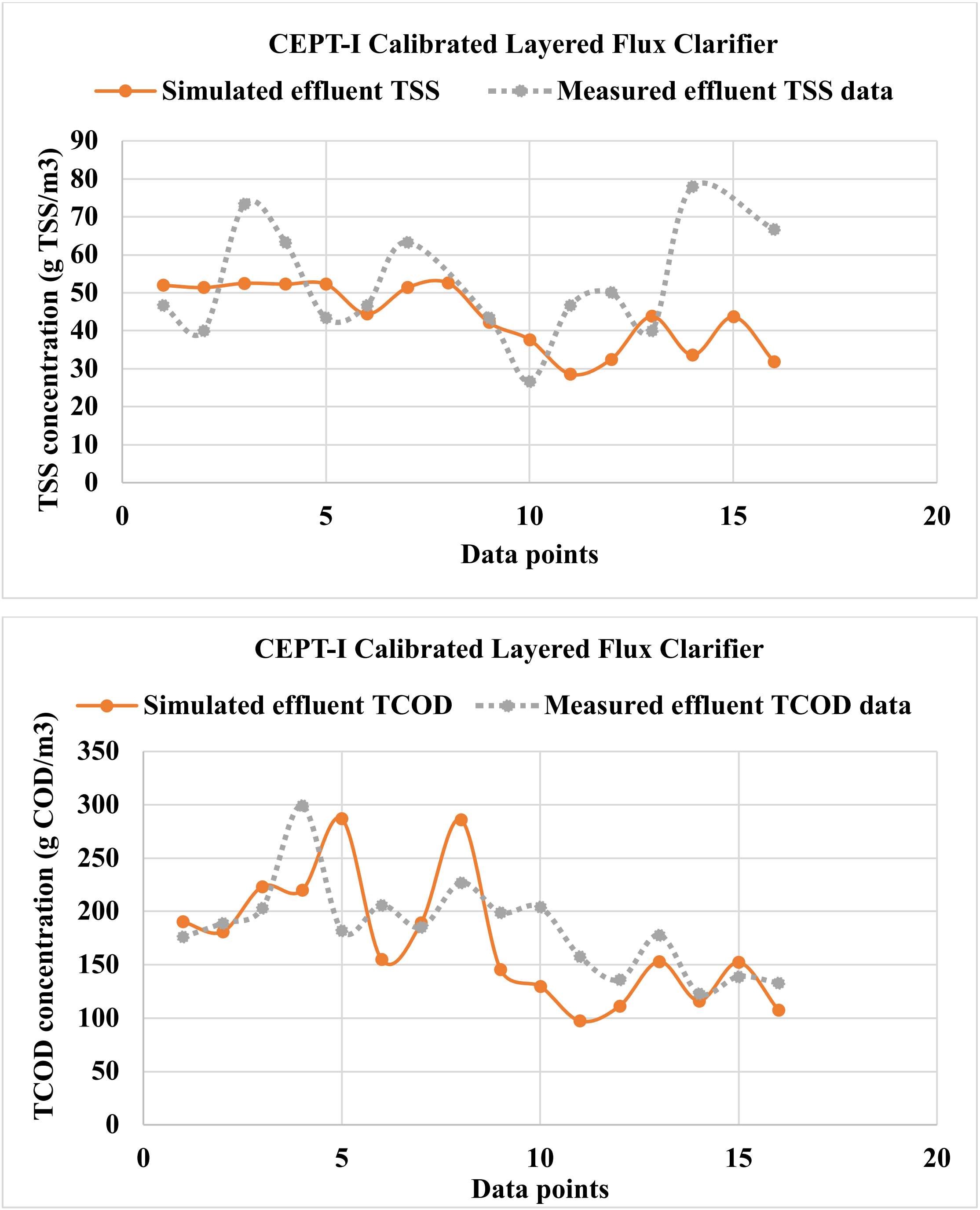


Figure SD7. Layered flux model-simulated and Measured (a) TSS and (b) COD profile in CEPT-I: Calibration

CEPT-II Calibrated Model (Model fit for simulated effluent concentrations)

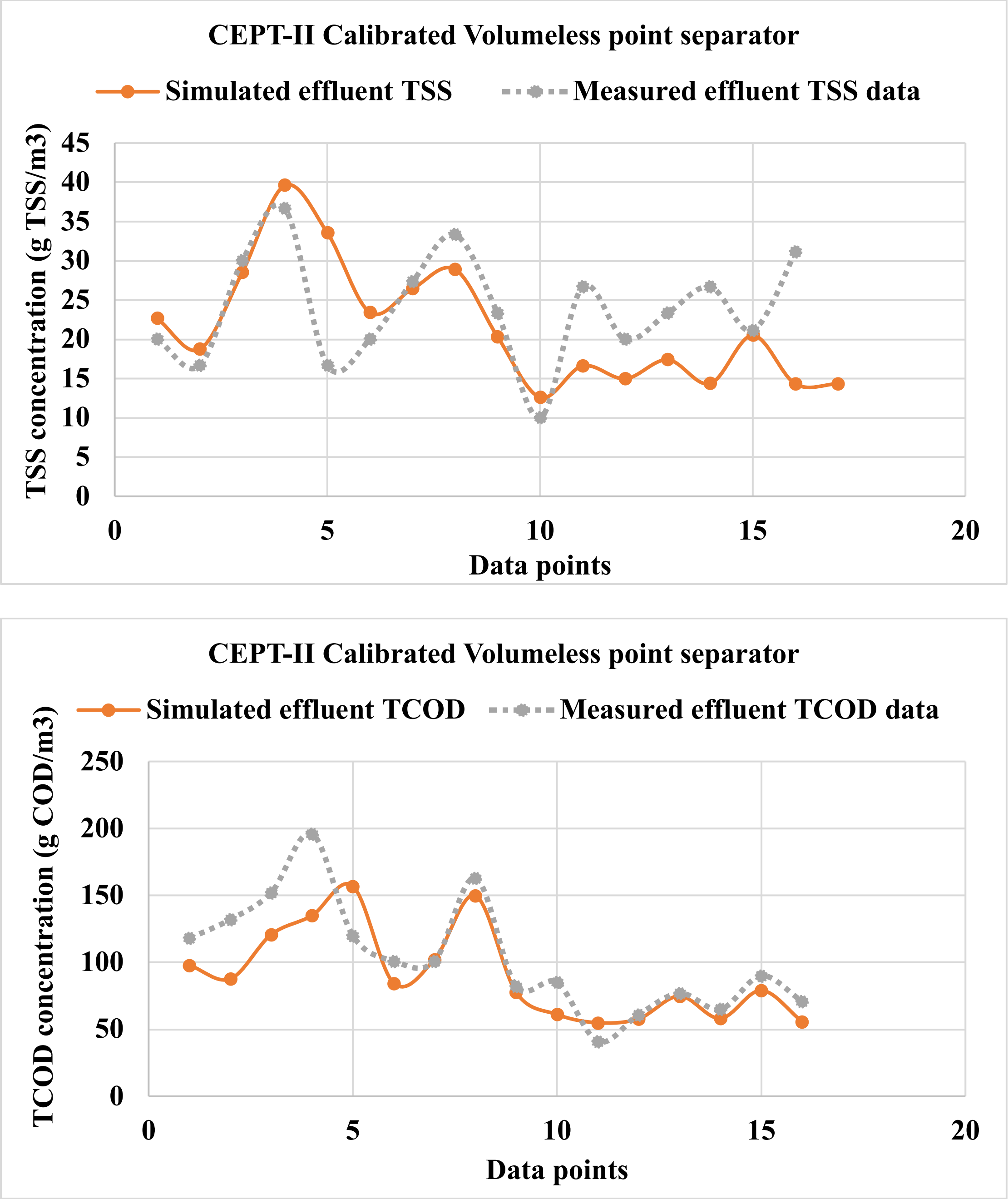
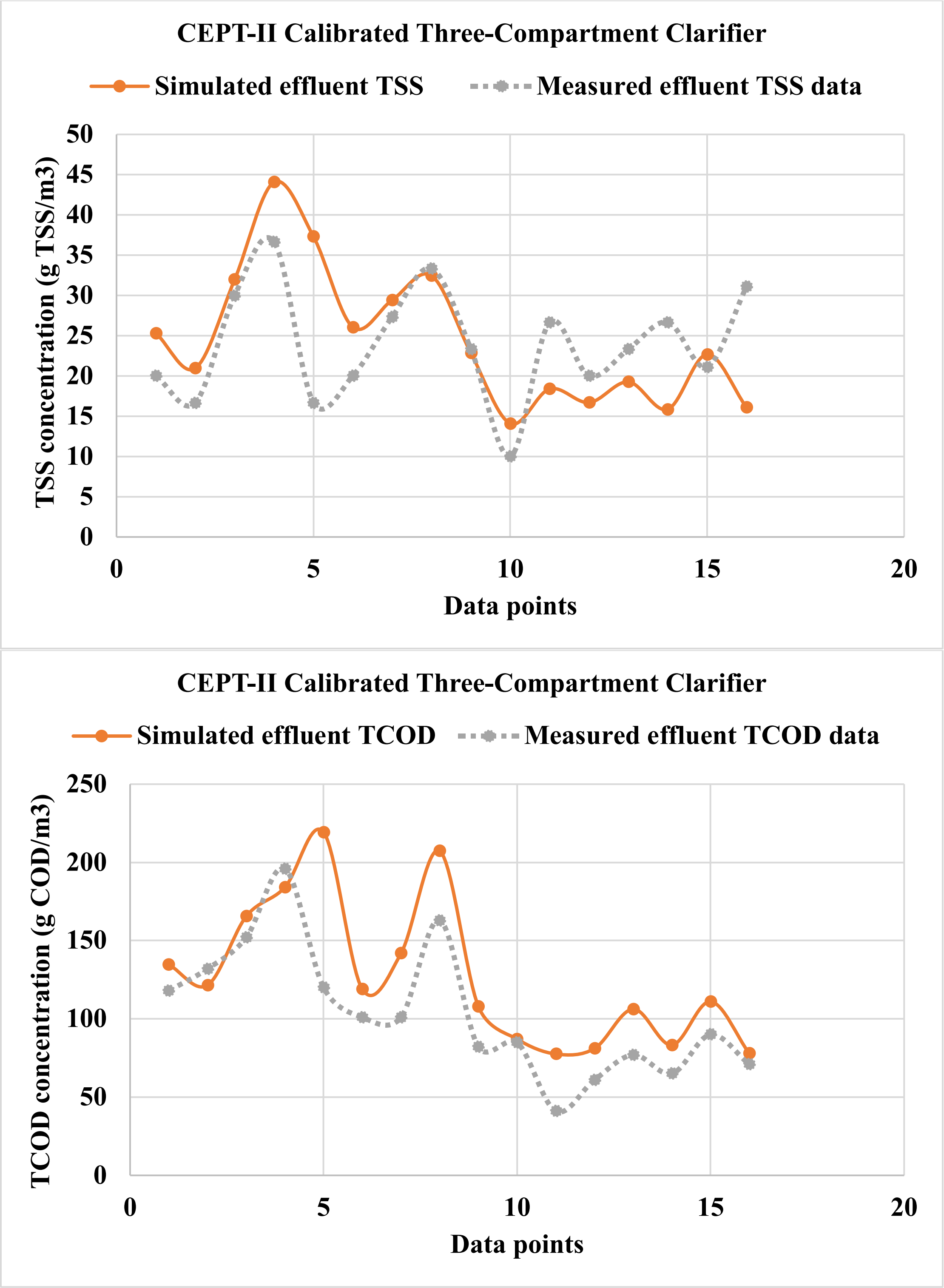


Figure SD8. Volumeless point separator-simulated and Measured (a) TSS and (b) COD profile in CEPT-2: Calibration



CEPT-II Calibrated Three-Compartment Clarifier

CEPT-II Calibrated Three-Compartment Clarifier

Figure SD9. Three compartments-simulated and Measured (a) TSS and (b) COD profile in CEPT-2: Calibration

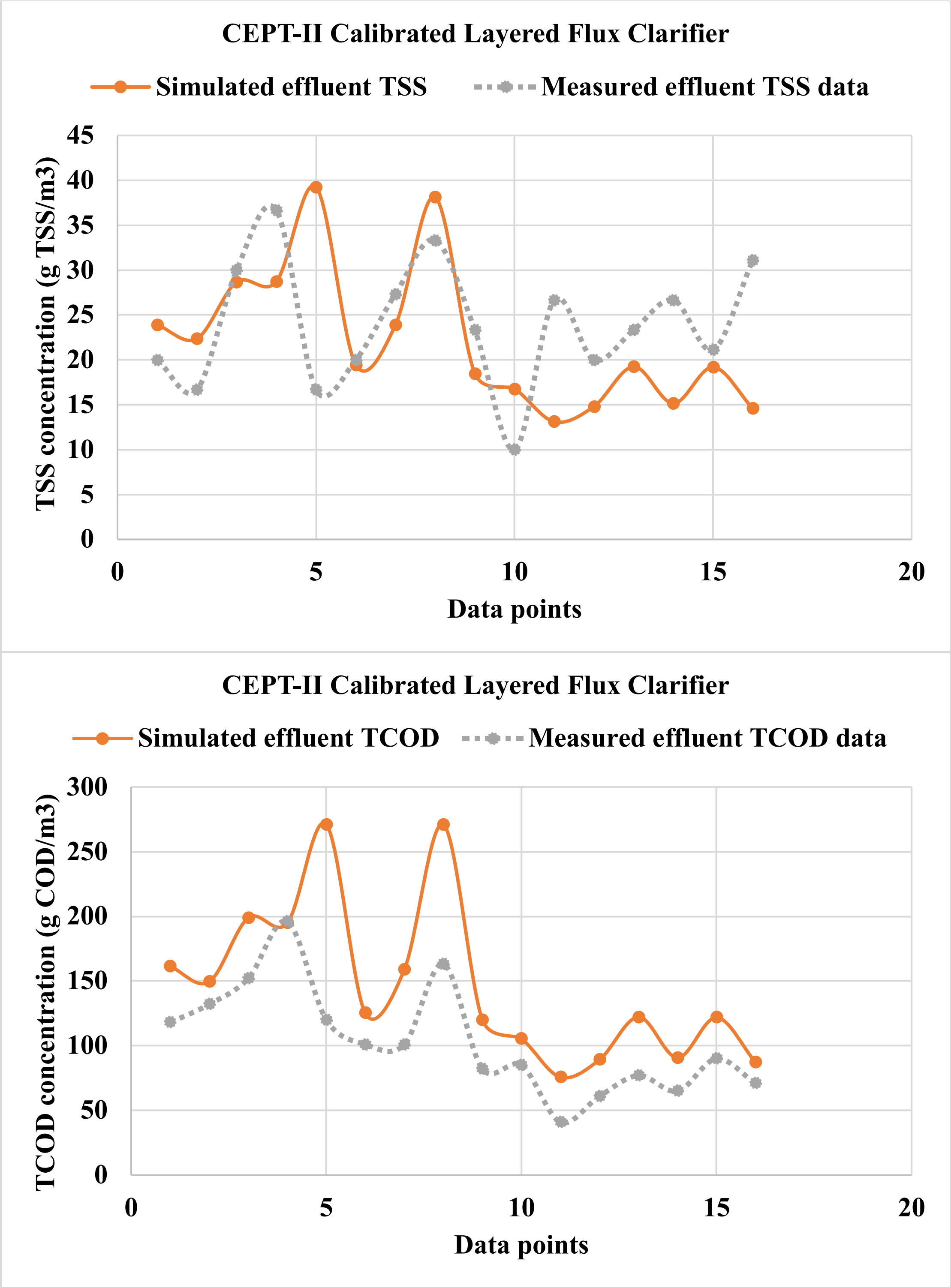


Figure SD10. Layered flux model-simulated and Measured (a) TSS and (b) COD profile in CEPT-2: Calibration

CEPT-I Validated Model (Model fit for simulated effluent concentrations)

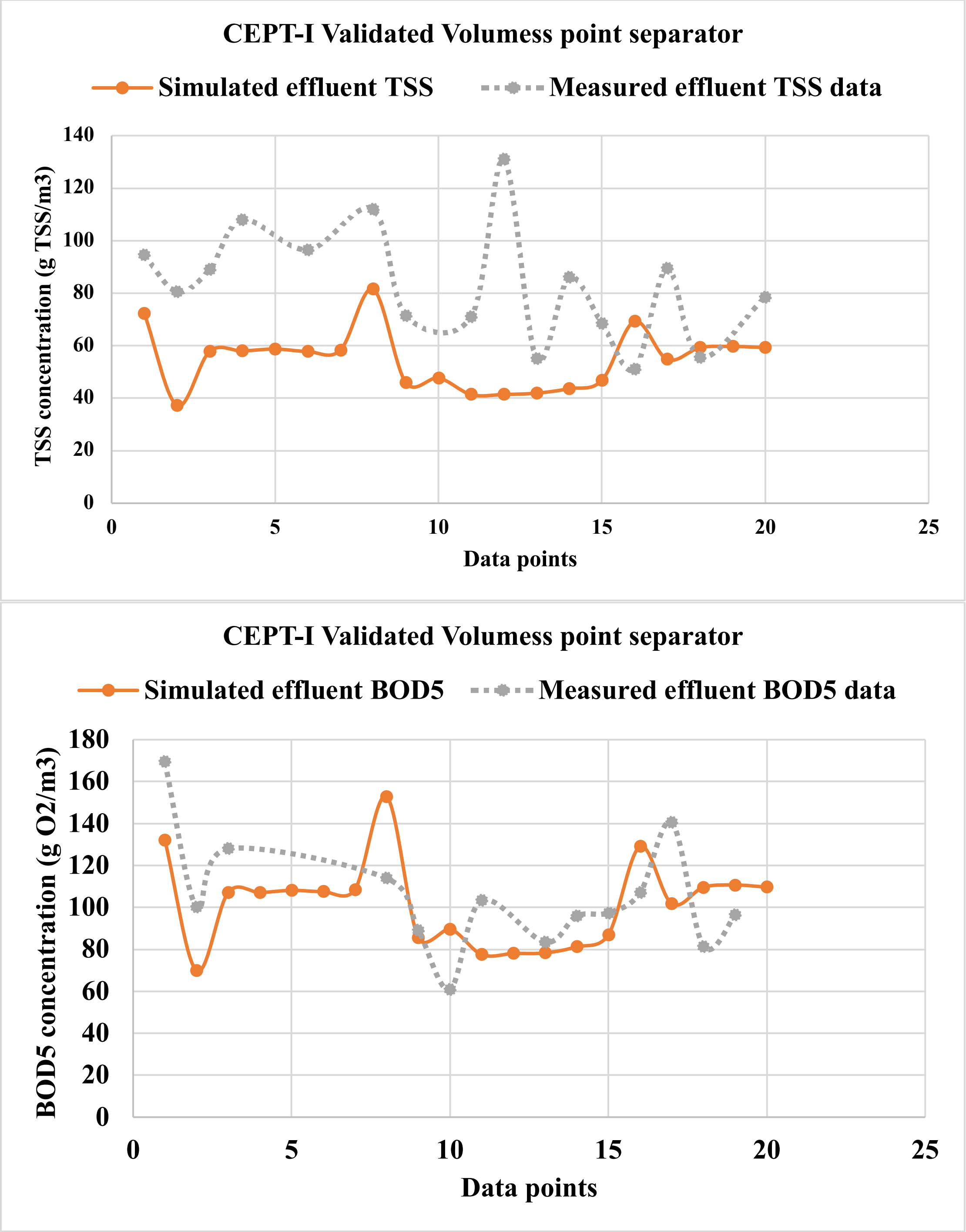


Figure SD11. Volumeless point separator-simulated and Measured (a) TSS and (b) BOD5 profile in CEPT-1: Validation

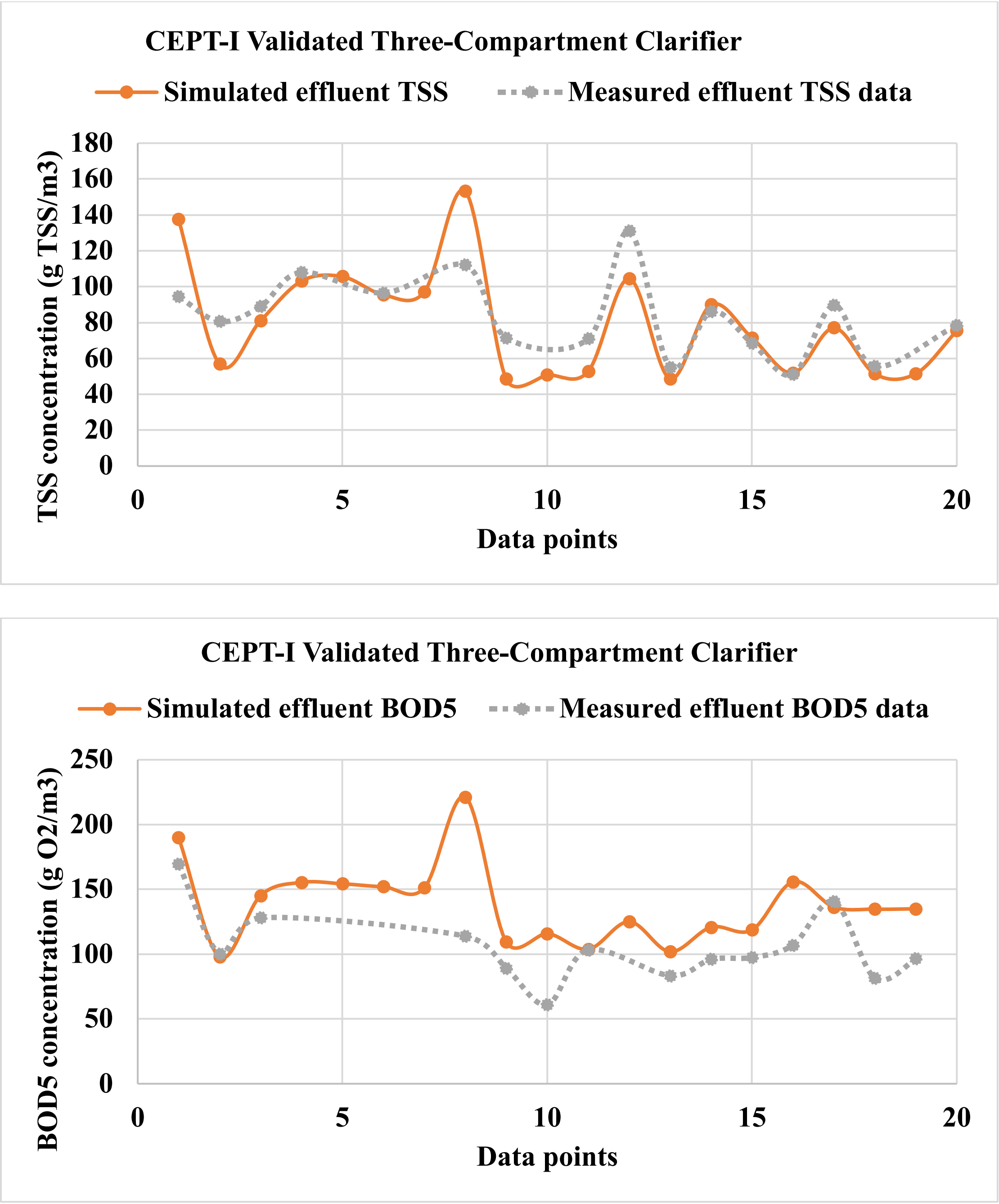


Figure SD12. Three compartments model-simulated and Measured (a) TSS and (b) BOD5 profile in CEPT-1: Validation

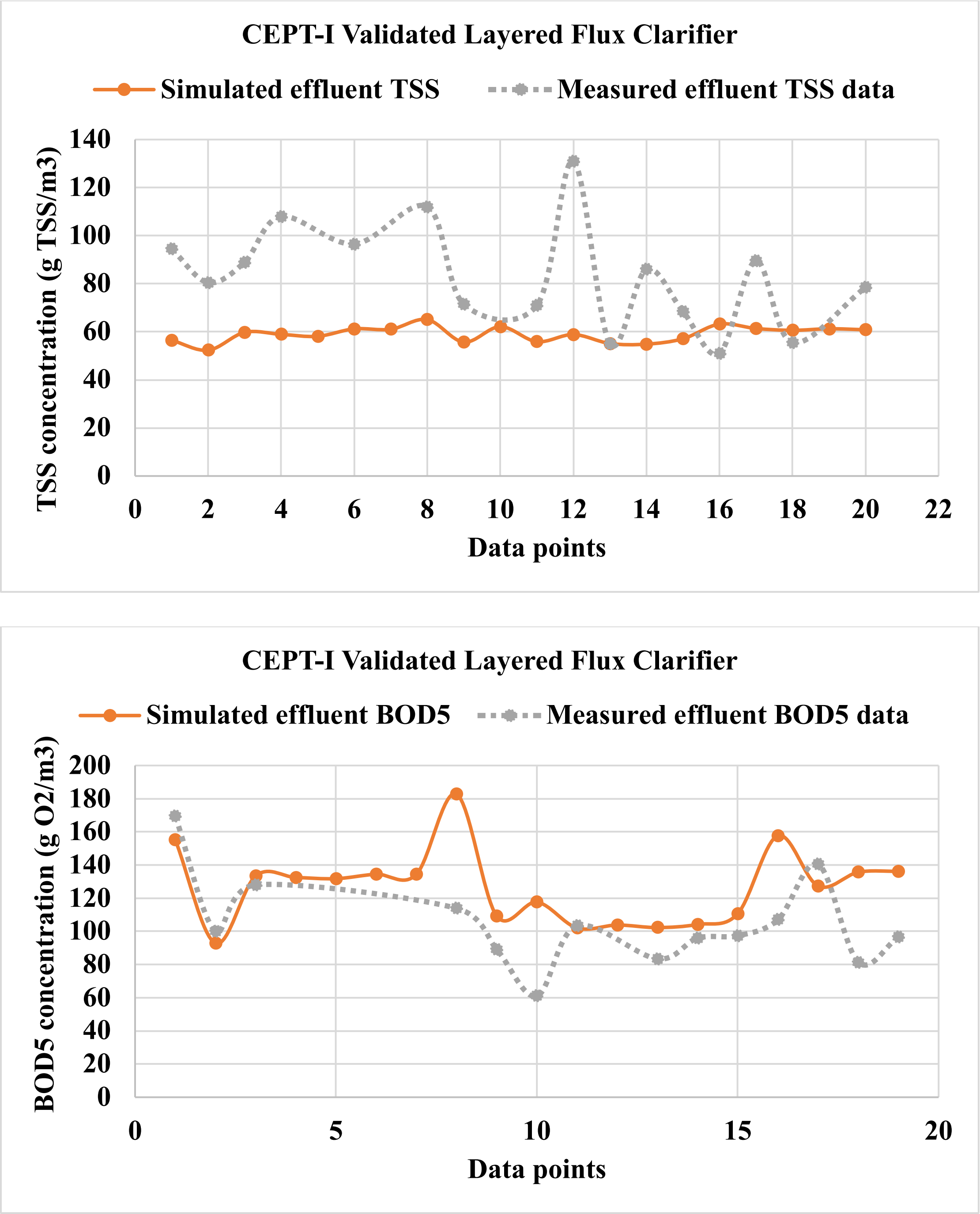


Figure SD13. Layered flux model-simulated and Measured (a) TSS and (b) BOD5 profile in CEPT-1: Validation

CEPT-II Validated Model (Model fit for simulated effluent concentrations)

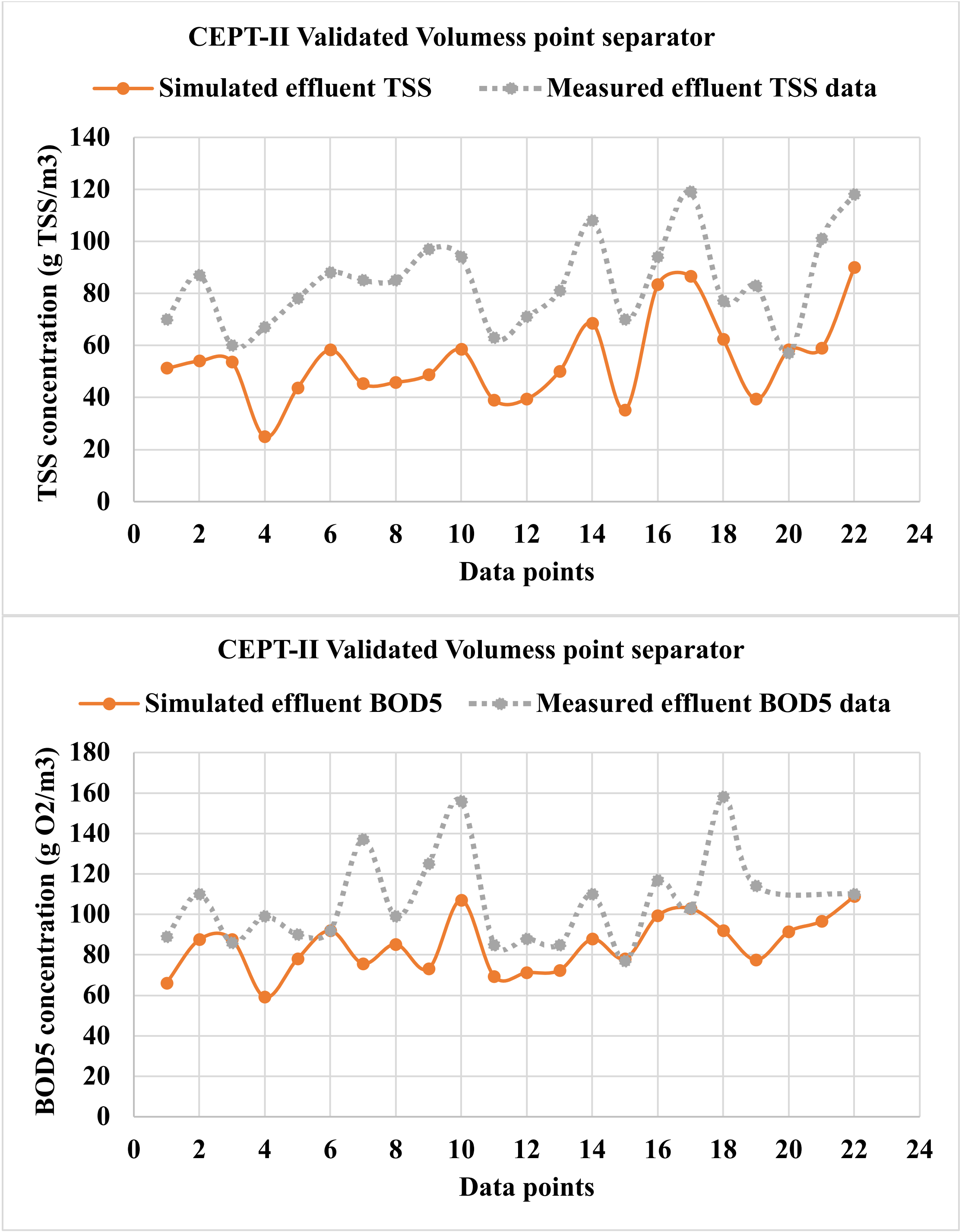


Figure SD14. Volumeless point separator model-simulated and Measured (a) TSS and (b) BOD5 profile in CEPT-2: Validation

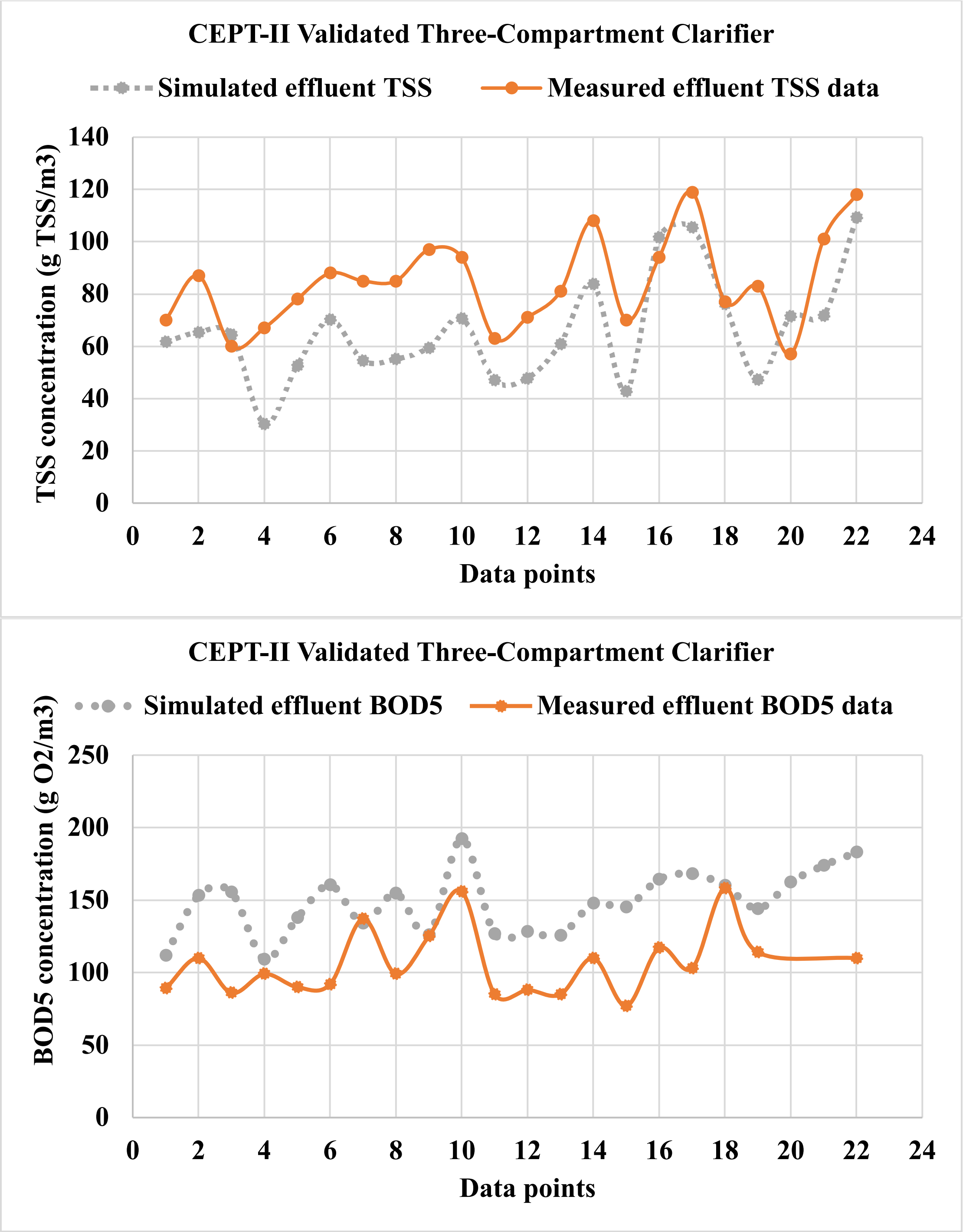


Figure SD15. Three compartments model-simulated and Measured (a) TSS and (b) BOD5 profile in CEPT-2: Validation

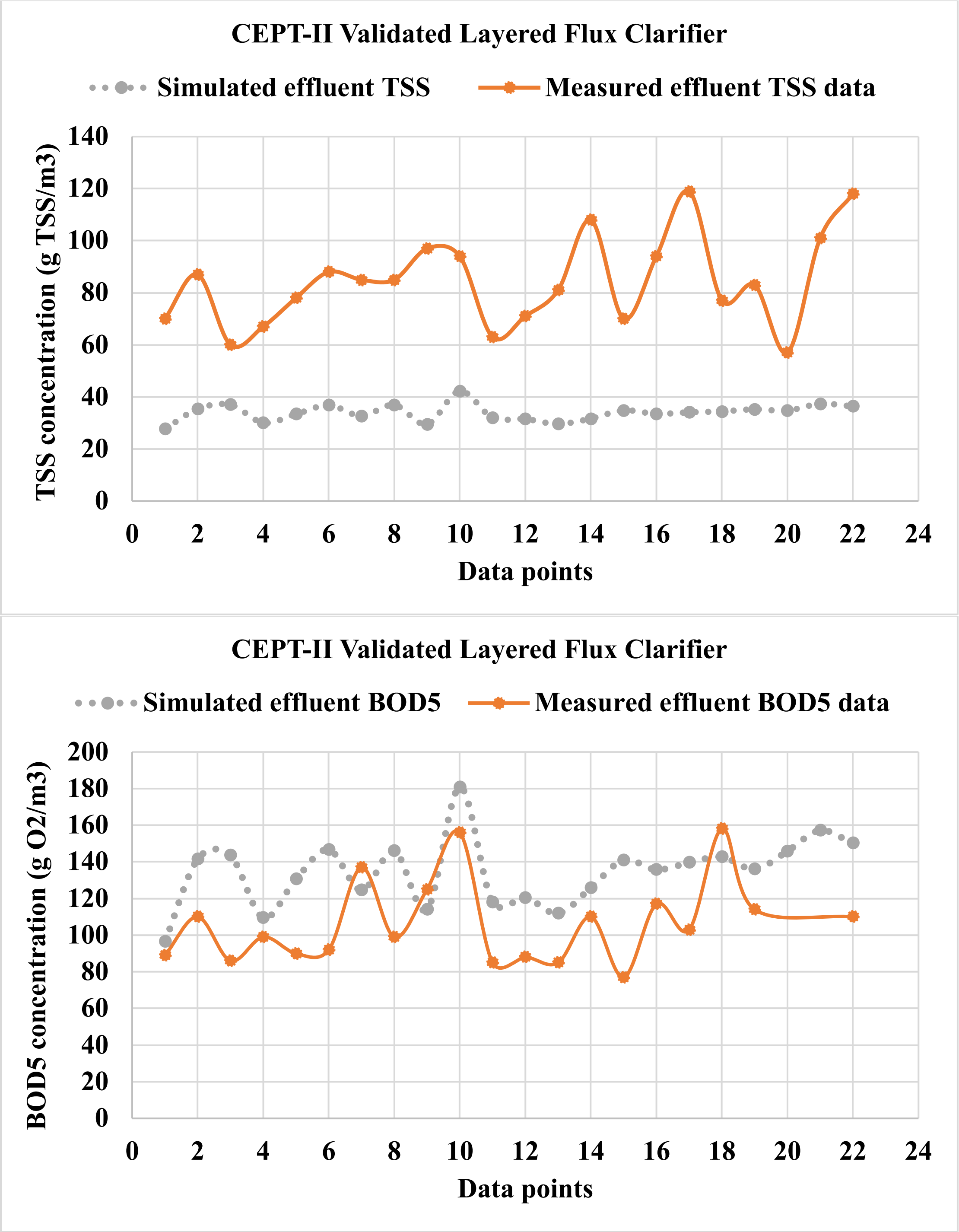


Figure SD16. Layered flux model-simulated and Measured (a) TSS and (b) BOD5 profile in CEPT-2: Validation

RESIDUAL PLOTS

CEPT-I Calibrated Model (Model fit for simulated effluent concentrations)

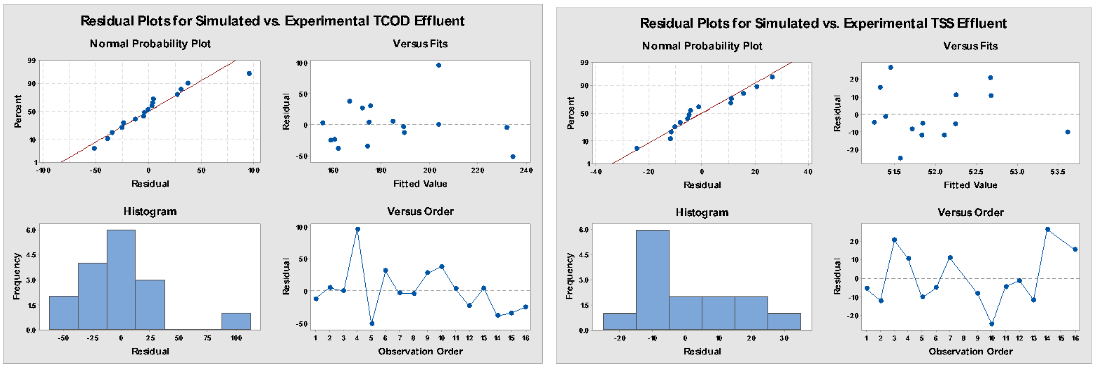


Figure SD17. Residual plots for TCOD & TSS effluent concentration in the calibrated CEPT-I Volumeless point separator clarifier

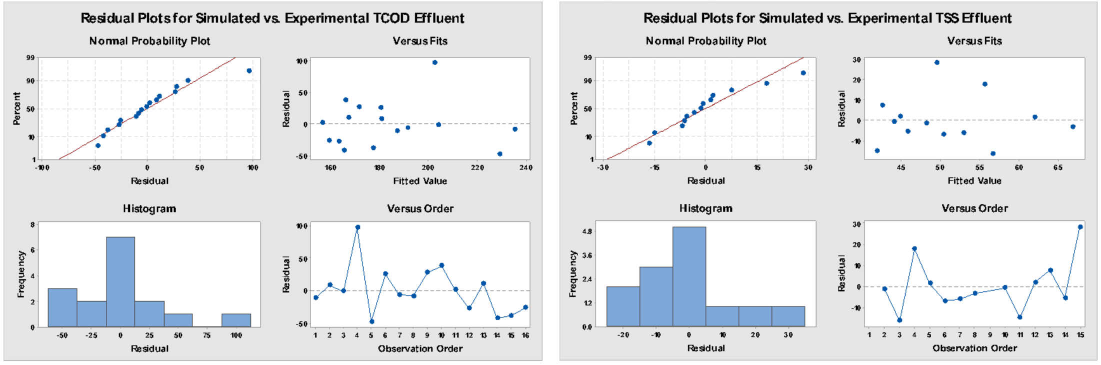


Figure SD18. Residual plots for TSS & TCOD concentration in the calibrated CEPT-I Three-compartment clarifier

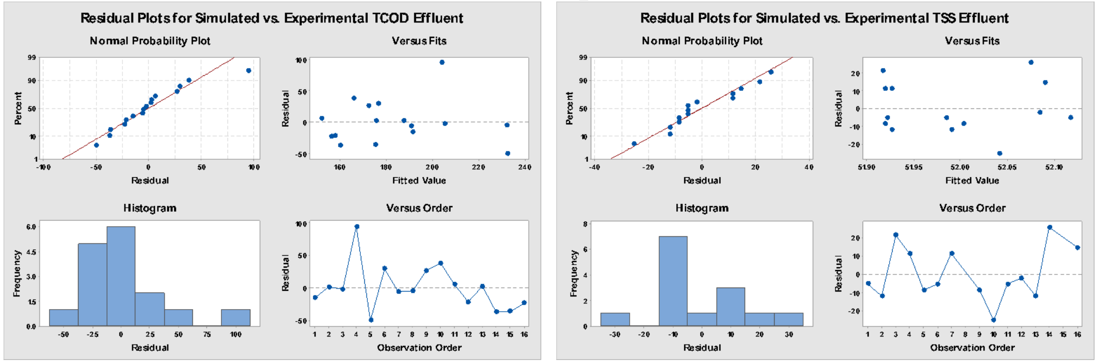


Figure SD19. Residual plots for TCOD & TSS concentration in the calibrated CEPT-I Layered-flux clarifier

CEPT-II Calibrated Model (Model fit for simulated effluent concentrations)

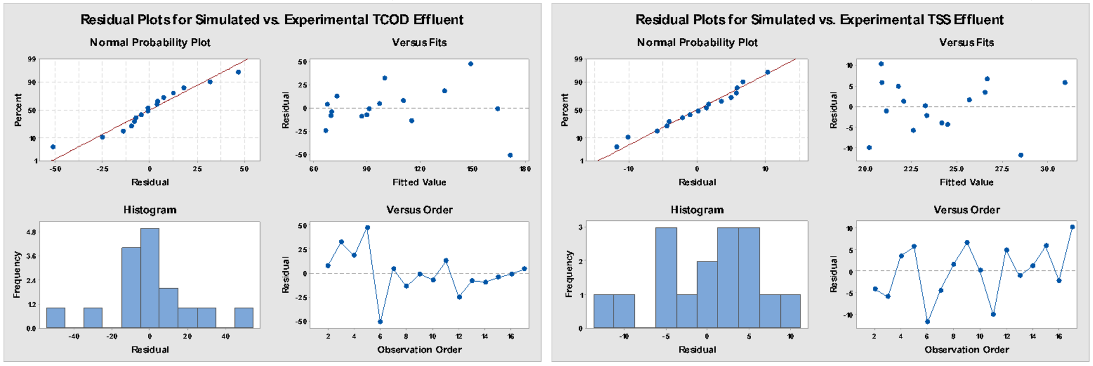


Figure SD20. Residual plots for TCOD & TSS concentration in the calibrated CEPT-II Volumeless point separator clarifier

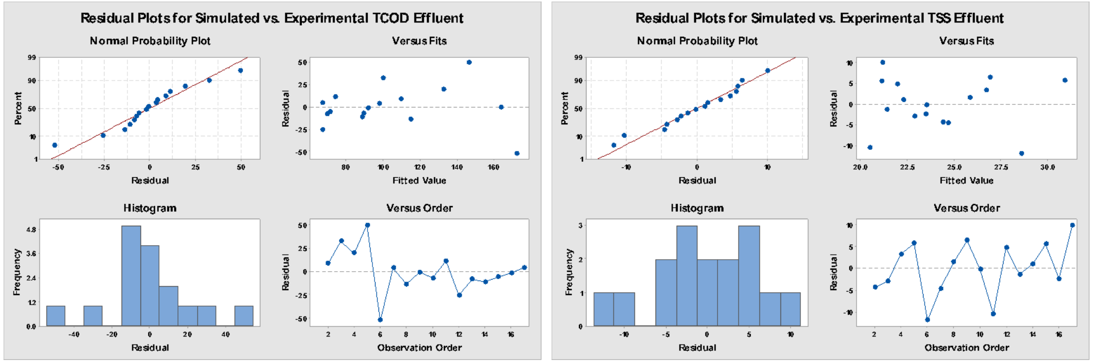


Figure SD21. Residual plots for TCOD & TSS concentration in the calibrated CEPT-II Three-compartment clarifier

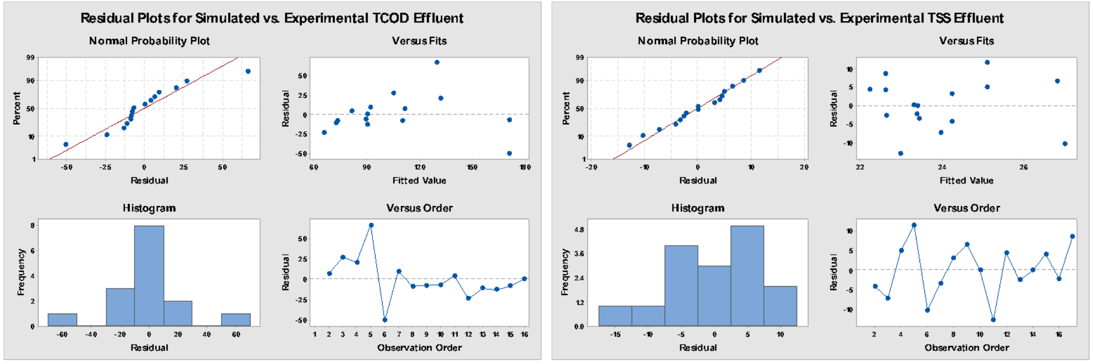
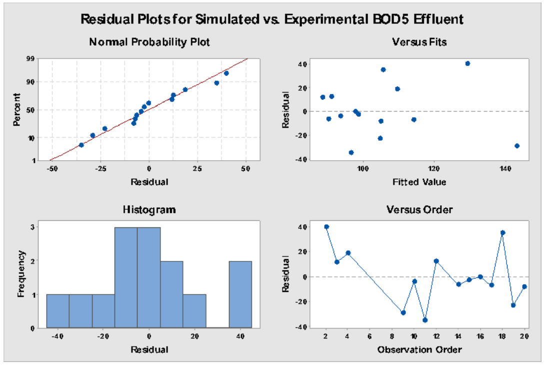
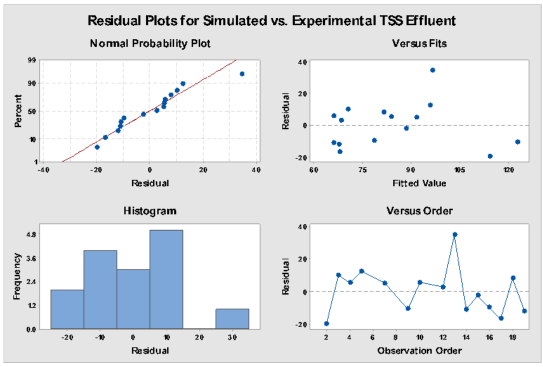


Figure SD22. Residual plots for TCOD & TSS concentration in the calibrated CEPT-II Layered-flux clarifier

CEPT-I Validated Three-Compartment Clarifier (Model fit for simulated effluent concentrations)





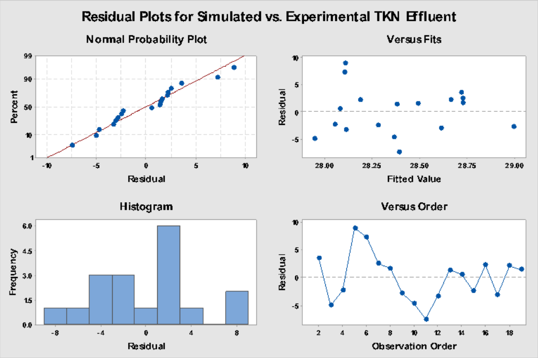
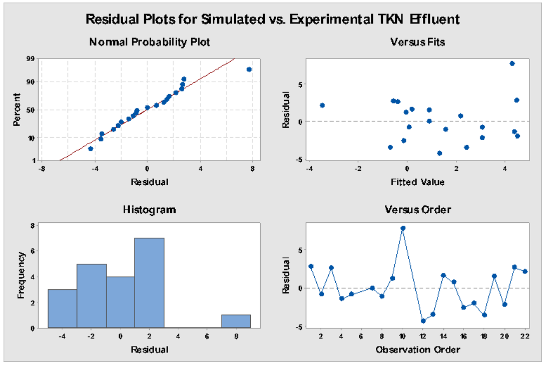


Figure SD23. Residual plots for BOD5, TSS and TKN concentration in the validated CEPT-I Three Compartment Clarifier

CEPT-II Validated Three-Compartment Clarifier (Model fit for simulated effluent concentrations)



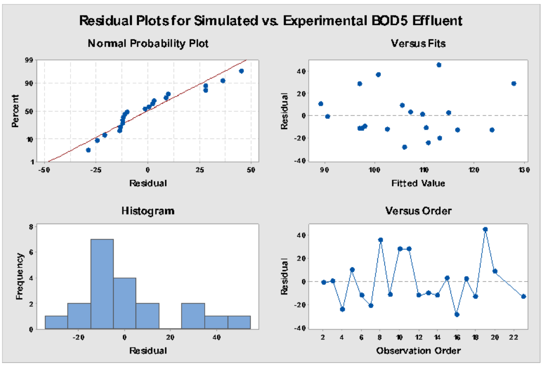
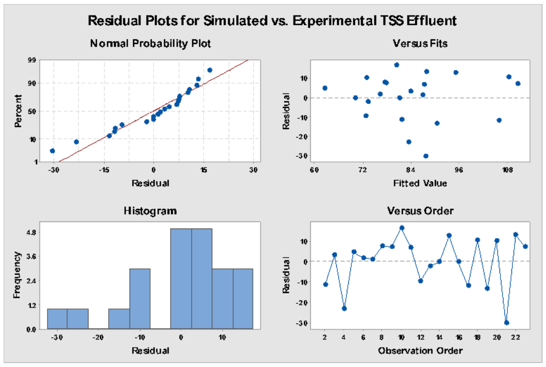


Figure SD24. Residual plots for BOD5, TSS and TKN concentration in the validated CEPT-II Three Compartment Clarifier



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Shewa, W. A., Dong, T., Mu, W., Murray, K., & Dagnew, M. (2020). The impact of chemically enhanced primary treatment on the downstream liquid and solid train processes. *Water Environment Research*, *92*(3), 359-368.

Conference presentations/publication

Mu, W, Shewa, W., Dagnew, M. (2020). MODELING OF CHEMICALLY ENHANCED PRIMARY TREATMENT (CEPT). WEAO 2020 Technical Conference, Toronto, Ontario