4-18-2019 10:40 AM

Effect Of Coagulant Recycling on Chemically Enhanced Primary Treatment Performance

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A thesis submitted in partial fulfillment of the requirements for the Doctor of Philosophy degree in Chemical and Biochemical Engineering

Recommended Citation

Chakraborty, Tulip, "Effect Of Coagulant Recycling on Chemically Enhanced Primary Treatment Performance" (2019). *Electronic Thesis and Dissertation Repository*. 6108.
https://ir.lib.uwo.ca/etd/6108

Abstract

Chemically enhanced primary treatment (CEPT) process is a promising method for carbon redirection and improving the performance and efficiency of wastewater treatment processes. CEPT is primarily employed to precipitate colloidal and suspended matter from wastewater; however, this requires a significant amount of coagulant and produces large volumes of sludge. Coagulant recovery (CR) from the precipitated sludge has the potential to reduce sludge quantities, associated costs for disposal of sludge, cost of dosing fresh coagulant by regenerating and purifying the coagulant before reuse. This research was conducted to understand the feasibility and implications of CR in municipal wastewater.

In order to evaluate the use of CR in municipal wastewater, recovery of aluminum and iron, which are the two most widely used coagulants, from primary sludge originated from coagulated raw wastewater and their reuse potential as secondary coagulant was investigated. The recovered coagulant which was obtained through acidification of the primary sludge, reused for treating primary wastewater and overall coagulation efficiency was determined as a function of the recovery cycles (two in number). While with fresh aluminum sulphate, the removal efficiencies of total suspended solids (TSS), chemical oxygen demand (COD), total phosphorous (TP), and total nitrogen (TN) were 85%, 65%, 80% and 33%, respectively, a drop in removal efficiency of TSS and COD was observed with recovered aluminum (85% to 60% and 65% to 50%, respectively). With fresh ferric chloride, 90% TSS, 77% TP, 62% COD, and 18% TN were removed from primary effluent, while with the recovered coagulant a decline in the TSS, COD and TN removal efficiencies and increase in their concentrations in effluent by approximately 10% occurred. Recoveries of both aluminum and iron declined with each cycle. Phosphorous was the most affected parameter with recycled coagulant, however, this could be precipitated as struvite at the end of the second cycle. Equilibrium modeling of various aluminum and iron species was conducted to determine the recovery potential of aluminum and iron at low pH. The chemical equilibrium models predicted the formation of complexes like jurbanite, gibbsite for aluminum and jarosite, strengite for iron, which reduced the recovery. The effects of recycling of coagulant on various water quality parameters in the effluent were also determined. A preliminary operational cost analysis conducted on the recovery process demonstrated that the increased cost of acidification can be offset by the reduction in costs of fresh coagulant, dewatering and sludge disposal.

Distribution of micropollutants (MPs) with fresh and recovered iron and aluminum in recovered coagulant and effluent was investigated. Based on their relative abundance in wastewater and range of octanol-water coefficients, 18 MPs from different groups such as antibiotics, food additives, surfactants were selected. The MPs were spiked into the influent from a primary stream collected from a local wastewater plant. The distribution of MPs in wastewater and the removal during coagulation were compound specific. MPs with log K_{ow} <2.5 were predominantly present in the effluent after coagulation, while MPs with log K_{ow} >2.5 were sorbed on the coagulated sludge. The distribution ratio (K_d) of all the MPs with log K_{ow} >2.5 was calculated and the extent of buildup on sludge due to repeated recycling was determined. Only <10% of the initial loading of MPs with log K_{ow} >2.5 was being recycled with the recovered coagulant. This study thus alleviates the concern of building up of the MPs during recycle of the coagulants.

Additionally, to assess the impact of CR on anaerobic digestion (AD), CEPT sludge, sludge obtained from use of recovered coagulants (recovered sludge), and the residual solids (spent sludge) after CR were subjected to AD at mesophilic conditions for 15 days. Approximately 52% destruction of volatile solids was observed for CEPT and recovered sludges, while for the spent sludge it was 47%. Both CEPT and the recovered sludge had similar methane formation potential reaching a maximum of 205 mL CH_4/gCOD and the spent sludge could produce only 50 mL CH_4/gCOD due to unavailability of organics. A chemical equilibrium model predicted the formation of vivianite and pyrite as iron-phosphorous (Fe-P) and iron-sulfur (Fe-S) compounds, respectively in the CEPT and recovered sludges formed during AD. This observation was key in determining that there was no difference in the Fe-P and Fe-S compounds formed in the CEPT and recovered sludges. The findings of this work demonstrated the potential of CR for wastewater and water treatment facilities for energy and cost saving.

Keywords

Coagulant recovery; phosphorous; sludge; micropollutants; octanol-water coefficients; aluminum; iron; anaerobic digestion; CEPT.

Co-Authorship Statement

This PhD thesis contains material that is published, ‘under review’ or in preparation for submission in peer reviewed journals as listed below.

Chapter 3: Carbon and phosphorous removal from primary municipal wastewater sludge using recovered aluminum.

Tulip Chakraborty, Michelle Gabriel, Ali Safarzadeh Amiri, Domenico Santoro, John Walton, Scott Smith, George Nakhla, Madhumita B. Ray (2017).

Environmental Science and Technology. DOI**:** 10.1021/acs.est.7b03405

The primary author of this chapter was Tulip Chakraborty under the supervision of Dr. Ray and Dr. Nakhla. The experimental plan was developed by Chakraborty with guidance from Dr. Ray and Dr. Nakhla while the execution of experiments, data collection and analysis, and drafting the manuscript was conducted by Chakraborty and Dr. Gabriel. Dr. Smith developed the equilibrium model, Dr. Amiri, Dr. Santoro, and Dr. Walton provided guidance for the work which was conducted at Trojan Technologies. Feedback on the manuscript was received from the co-authors.

Chapter 4: Reusability of recovered iron coagulant from primary municipal sludge and its impact on chemically enhanced primary treatment

Tulip Chakraborty, Dharavi Balusani, Scott Smith, Domenico Santoro, John Walton, George Nakhla, Madhumita B. Ray (2019).

Separation and Purification Technology. Under peer review.

The primary author of this chapter was Tulip Chakraborty under the supervision of Dr. Ray and Dr. Nakhla. The experimental plan was developed by Chakraborty with guidance from Dr. Ray and Dr. Nakhla while the execution of experiments, data collection and analysis, and drafting the manuscript was conducted by Chakraborty. Balusani helped in the lab to perform some of the experiments, Dr. Smith developed the equilibrium modelling, Dr. Santoro, and

Dr. Walton provided guidance for the work. Feedback on the manuscript was received from the co-authors.

Chapter 5: Micropollutants in chemically enhanced primary treatment using recovered coagulants

Tulip Chakraborty, Dharavi Balusani, Lyne Sabourin, Justin Renaud, Mark Sumarah, George Nakhla, Madhumita B. Ray.

In preparation for submission to Environmental Science and Technology.

The primary author of this chapter was Tulip Chakraborty under the supervision of Dr. Ray and Dr. Nakhla. The experimental plan was developed by Chakraborty with guidance from Dr. Ray and Dr. Nakhla while the execution of experiments, data collection and analysis, and drafting the manuscript was conducted by Chakraborty and Balusani. Lyne, Dr. Renaud and Dr. Sumarah helped in running the samples using LC-MS at Agricultural Canada. Feedback on the manuscript was received from the co-authors.

Chapter 6: Anaerobic digestion of recovered chemically enhanced primary sludge and its effect on iron phosphorous speciation

Tulip Chakraborty, Weiben Chen, Basem Haroum, Scott Smith, George Nakhla, Madhumita B. Ray.

In preparation for submission to Water Research.

The primary author of this chapter was Tulip Chakraborty under the supervision of Dr. Ray and Dr. Nakhla. The experimental plan was developed by Chakraborty with guidance from Dr. Ray and Dr. Nakhla while the execution of experiments, data collection and analysis, and drafting the manuscript was conducted by Chakraborty. Dr. Haroum helped with the gas measurements, while Dr. Chen and Dr. Smith developed the equilibrium model using MATLAB and PHREEQC. Feedback on the manuscript was received from the co-authors.

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Acknowledgements

I would like to express my sincere gratitude to my supervisors Dr. Madhumita B. Ray and Dr. George Nakhla. I want to thank both of them for being such tremendous mentors, pushing me to face every challenge with courage, teaching me to think critically while standing on my feet and that fundamentals are the key. Their passion and commitment was extremely contagious and I am deeply indebted to them for their guidance, encouragement and presenting me with opportunities to grow in this profession. I especially want to thank Dr. Ray for believing in my abilities and giving me the opportunity to pursue my post-graduate studies in Canada.

I would like to thank my colleagues that I had the pleasure to work with or alongside, at Western – Dr. Isil Gong, Keller George, Sreejon Das, Dr. Hojat Seyedy, Ziming Zhao, Siddharth Gupta, Dharavi Balusani, Dr. Adnan Khan, Dr. Basem Haroun, Dr. Min Gu Kim, Dr. Xiaoguang Liu, Masuduz Zaman, Mohammad Chowdhury, Andisheh Yezandapah, Dr. Kyriakos Manoli, Dr. Daria Popugaeva and Malini Ghosh. I would like to thank Eliav Eini and Dr. Domenico Santoro, for their help and insightful comments. I am especially thankful and grateful to my friends, Dr. Christopher Degroot, Dr. Michelle Gabriel and Dr. Dang Ho, who have always been there for me and have been a tremendous source of advice, friendship, and contributed immensely to my personal and professional growth. I am also grateful to the university staff, Paul Sheller, Stephen Mallinson, Katherine Manweiler, Whitney Barett, Ashley Jokhu and Cole Handsaeme for their assistance.

I like to thank my co-authors for their support especially Dr. Smith, Dr. Chen, Dr. Walton, Dr. Sumarah, Lyne Sabourin and Dr. Renaud for helping me write the manuscripts. I wish to acknowledge Western Engineering, NSERC-TWNER and MITACS for the financial support.

This journey would not have been so enjoyable without the support of my friends, near or far. I am grateful for all the memories and the time spent with Suchismita Bose, Dr. Madhurima Roy, Emir Malovic and Suvendu Indra. They have been with me through the best and the worst of times. I want to thank my family, in particular my aunt, Bela Chakraborty, my uncles, Gobinda Narayan Chakraborty, Ananda Chakraborty, my grandmother Monica Mukherjee and my relatives especially Dr. Sue Mukherjee, for all her love and care.

I am thankful to my fiancée, Dr. Souvarish Sarkar who suffered through my PhD. Thank you for being my biggest support, listening to me cry, vent, complain and for showering me with encouragement and love.

Finally, I would like to thank my parents Suchandra Chakraborty and Indrani Chakraborty for supporting me in all my pursuits, believing in me and loving me; my sister Rumiya Chakraborty, who by far is my biggest supporter, deals with the worst of my moods and has my back always.

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List of abbreviations and symbols

AD	anaerobic digestion
ASM	activated sludge model
A_{solid}	stoichiometry matrix for solid species
$A_{solution}$	stoichiometry matrix for solution species
BNR	biological nutrient removal
BOD	biochemical oxygen demand (mg/L)
BOD5	5-day biochemical oxygen demand (mg/L)
C	species concentrations
cBOD	carbonaceous biochemical oxygen demand (mg/L)
CEPT	chemically-enhanced primary treatment
COD	chemical oxygen demand (mg/L)
CR	coagulant recovery
DBP	disinfection by product
DD	donnan dailysis
DO	dissolved oxygen (mg/L)
DOC	dissolved organic carbon (mg/L)
EBPR	enhanced biological phosphorous removal
ED	electrodialysis
EDTA	ethylene diamine tetra acetate

EPS	extracellular polymerase substance
FFCOD	filter flocculated chemical oxygen demand (mg/L)
K_a	acid dissociation constant
K_d	distribution ratio
K_{ow}	octanol water coefficient
K_{solid}	logK values for solid species
$K_{solution}$	logK values for solution species
K_{sp}	solubility product
LAS	linear alkyl benzene sulfonate
λ	lag time (hr)
μ	ionic species
MBR	membrane bioreactor
MP	micropollutant
NOM	natural organic matter
NTA	nitrilotriacetate
ON	organic nitrogen
OP	organic phosphorous
OUR	oxygen uptake rate (mg/L)
P	maximum specific cumulative biogas production (mL)
PAC	polyaluminum chloride

PC	primary clarification
pCOD	particulate chemical oxygen demand (mg/L)
PCP	personal care product
PI	primary influent
PPB	parts per billion
RAS	return activated sludge
Rm	maximum biogas production (ml/hr)
rbCOD	readily biodegradable COD (mg/L)
rbsCOD	readily biodegradable soluble COD (mg/L)
R_{mass}	mass balance residuals
RSI	saturation index criteria
RWW	raw wastewater
sCOD	soluble chemical oxygen demand (mg/L)
SI	saturation index
sP	soluble phosphorous (mg/L)
SRT	solids retention time (d)
S_T	total sulphate
T	total of each component species
TA	tetracycline classes of antibiotics
TCEP	tris 2 chloroethyl phosphate

TCOD	total chemical oxygen demand (mg/L)
THM	trihalomethane
TCPP	tris 2 chloroisopropyl phosphate
TDS	total dissolved solids (mg/L)
TKN	total kjeldahl nitrogen (mg/L)
TN	total nitrogen (mg/L)
TOC	total organic carbon (mg/L)
TP	total phosphorous (mg/L)
TS	total solids (mg/L)
TSS	total suspended solids (mg/L)
UASB	upflow anaerobic sludge blanket
VFA	volatile fatty acids (mg/L)
VSS	volatile suspended solids (mg/L)
WLC	whole life cycle cost
WPCP	wastewater pollution control plant
WWTP	wastewater treatment plant
X_{cp}	solid phase concentrations
$X_{solution}$	component concentrations

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Chapter 1

1 Introduction

1.1 Rationale

Production of municipal wastewater worldwide has exceeded over 330 billion m^3 per annum [Florke et al. 2013; Sancho et al. 2015; Sato et al. 2013]. Driven by the shift in municipal treatment goals from merely environmental protection towards resource recovery, municipalities are implementing energy and cost saving measures for sustainable operation and protection of surface waters. Chemically enhanced primary treatment (CEPT) is gaining prominence due to its effectiveness in diverting organic matter from biological treatment and increasing biogas production, while reducing aeration energy and excess biological sludge production. This research was motivated by the concerns regarding increased sludge production rates, stringent effluent guidelines and lack of cost effective solutions in municipal wastewater treatment plants.

Coagulants such as alum, iron among others are added to the CEPT process, which generate significant volume of sludge, contributing up to 5% - 20% and 15% - 40% of the total sludge generated with ferric chloride and alum, respectively [Babatunde and Zhao. 2007; Parsons and Daniels. 1999; Vaezi and Batebi. 2001]. Chemical-based treatment processes such as coagulation-flocculation although inexpensive, account for up to 5% of the total water treatment and supply costs [Niquette et al. 2004]. The annual requirement of aluminum salts in Canada alone crossed 276,000 tons [Cheminfo services. 2008] in 2006. This translates to generation of substantial volume of waste sludge that needs to be treated and disposed appropriately. Biosolids disposal in a municipal plant accounts for up to 40% of the total operating costs [Xu et al. 2009]. This coupled with transportation and other handling costs pose logistical and financial challenges [Keeley et al. 2014]. Hence, reusing coagulant in municipal wastewater is an attractive option, as it not only offsets the disposal cost but also reduces chemical cost.

To retrofit an existing municipal wastewater plant with a technology like coagulant recovery, research needs to be done to test its effectiveness by application of the recovered coagulant on fresh municipal wastewater and monitoring the different water quality parameters like total suspended solids, phosphorous, chemical oxygen demand among others. Other than this, during the recovery process, presence of heavy metals, micropollutants, carbon, phosphorous, inorganics like Na, K, Mg may also be recovered and recycled with the coagulant. Presence of these impurities will only hamper the water quality further by increasing the organic loadings, and causing deflocculation of sludge. It is thus extremely beneficial to characterize the recovered coagulant and understand its effect downstream before large scale application to wastewater. Additionally, cost plays a pivotal role for a process or a technology to be accepted. Understanding all the above mentioned issues is the motivation of this PhD research.

1.2 Objectives

The overall research objective of this PhD research is to determine the effects of recycled coagulants on the water quality parameters (suspended solids, chemical oxygen demand, phosphorous among others), distribution of micropollutants and finally validate a basic chemical equlibrium model to understand Fe-P and Fe-S speciation using real primary influent of municipal wastewater treatment plant.

The specific objectives are:

a) To assess the impact of recycled aluminum on the treatment efficiency of the various water quality parameters by CEPT and optimize the acidification pH for the maximum recovery of alum coagulant. In addition, the impact of repeated recycling of recovered coagulants on treatment of primary influent (PI) is determined.

b) To determine the effect of recycled ferric coagulant on water quality parameters and optimize coagulant recovery.

c) To determine the distribution of several micropollutants (MPs) with diverse properties in CEPT sludge and primary effluent due to the use of recycled alum and ferric chloride.

d) To establish a comprehensive understanding of the iron-phosphorous (Fe-P) and iron-sulphur (Fe-S) chemistry before and after anaerobic digestion and to predict Fe-P and Fe-S speciation (using fresh and recycled iron) by developing a chemical equlibrium model.

e) To determine the cost feasibility of the coagulant recycle process.

1.3 Thesis organization

Chapter 1 presents an overview of the thesis and the rationale behind assessing coagulant recovery as a promising technology for municipal wastewater treatment. It provides the specific research objectives.

Chapter 2 provides a comprehensive literature review on coagulant recovery, extraction techniques from different water/wastewater sludges, application of coagulant recovery to municipal/drinking water, effect of recycled pollutants on water due to recovery. Additionally, the review also investigates the chemistry of Fe-P and Fe-S, providing an in-depth understanding of the various kinetic, thermodynamic, and process models to address speciation of various Fe complexes.

Chapter 3 is a research article entitled “Carbon and phosphorous removal from primary municipal wastewater sludge using recovered aluminum”. The objective of this work was to understand the recovery of aluminum at different pH values from primary sludge and its effect on recycling in municipal wastewater. An optimum pH value of 1.5 was chosen and 73% recovery of aluminum was achieved using acidification. A chemical equilibrium model was constructed which showed the presence of complexes like gibbsite and jurbanite, which inhibited the complete recovery. The main drive for this work was to compare and understand the feasibility of using recovered coagulant with fresh coagulants in municipal wastewater.

Chapter 4 is a research article entitled “Reusability of recovered iron coagulant from primary municipal sludge and its impact on chemically enhanced primary treatment”, that discusses the use of recycled iron in municipal wastewater. At an optimum pH of 1.5, as selected previously, only 31% of the iron could be recovered. This low recovery was possibly due to the presence of complexes like strengite and jarosite as determined by a chemical equilibrium model. An operational cost analysis was conducted to determine the feasibility of the process.

Chapter 5 is a research article entitled “Micropollutants in chemically enhanced primary treatment using recovered coagulants”. In this study, the distribution of MPs in effluent, recovered coagulant during coagulant recovery was investigated. The distribution ratio (K_d) was calculated for compounds with octanol-water coefficient >2.5, as they primarily partition on solids. The possible attachment positions due to chelation with the tetracycline group of compounds of aluminum and iron were determined.

Chapter 6 is a research article entitled “Anaerobic digestion of recovered chemically enhanced primary sludge and its effect on iron phosphorous speciation”. In this study, the impact of AD on CEPT sludge, recovered sludge and spent sludge was investigated and the major Fe-P, Fe-S compounds were determined.

Finally, Chapter 7 summarizes the major findings of this research study along with future recommendations.

1.4 Thesis format

This thesis has been prepared in the integrated-article format according to the specifications provided by the School of Graduate and Postdoctoral Studies located at the University of Western Ontario. Chapter 3 of this thesis has been published in Environmental Science and Technology. Chapter 4 is under review in Separation and Purification Technology. Chapter 5 has been prepared for submission to Environmental Science and Technology. Chapter 6 has been prepared for submission to Water Research journal.

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Chapter 2

2 Literature review

2.1 Background

Chemically enhanced primary treatment (CEPT) is effective in diverting organic matter from biological treatment, while reducing aeration energy and sludge production. Use of chemicals in the form of alum, ferric chloride, polyaluminum chloride (PAC) and others is fairly common in municipal wastewater plants as they are effective, well understood and can be controlled easily. These chemicals are relatively inexpensive and often account for up to 5% of the total water treatment and supply costs [Niquette et al. 2004]. However, the annual requirement of coagulant in UK alone was 325,000 tonnes in 2008, while 278,000 tonnes of coagulant was used in Canada in 2006 [Cheminfo services. 2008]. This chemical consumption generates substantial volumes of sludge resulting in increased handling, disposal and other logistical costs. While the costs of conventional chemicals are not expected to increase dramatically in the next few years, rising environmental concerns, water quality standards, global commodity prices and transportation costs require the need for recycling the coagulants. These challenges are common to many chemical processes where the focus needs to be on implementation of sustainable and green processes. Coagulant recovery (CR) has the potential to improve sustainability of conventional coagulation-flocculation process. Different methods such as acidification, basification, ion exchange, and membrane processes have been tested to recover metal coagulants from sludge [Xu et al. 2009a]. The most efficient and cost-effective method has been shown to be acidification, which involves neutralizing the flocs of hydroxide and phosphate precipitants to release the coagulant salt back into solution [Huang et al. 2010]. Although recycling of coagulant has an overall environmental benefit, the impacts on treated water quality needs to be assessed. Thus, this review seeks to provide an in-depth understanding of the coagulant recovery process by analyzing the benefits and limitations, the fate of background inorganics, organics and metal present in water due to reuse of coagulant, and the complex chemistry associated with coagulant recycling, effect on anaerobic digestion (in municipal wastewater) and finally a cost analysis of the process.

2.1.1 Chemically enhanced primary treatment (CEPT)

The earliest application of CEPT has been reported in England around the 1870's, where it was used extensively before the advent of secondary biological processes [Parker et al. 2001]. The objective of using a chemical coagulant like alum/ferric chloride is to precipitate the colloids and the suspended particles in the wastewater. CEPT has seen wide scale applications with over 70% of the treatment plants dosing these metal salts as a part of their treatment process on a regular basis [Betancourt and Rose. 2004]. Figure 2.1 represents a typical municipal plant employing CEPT.

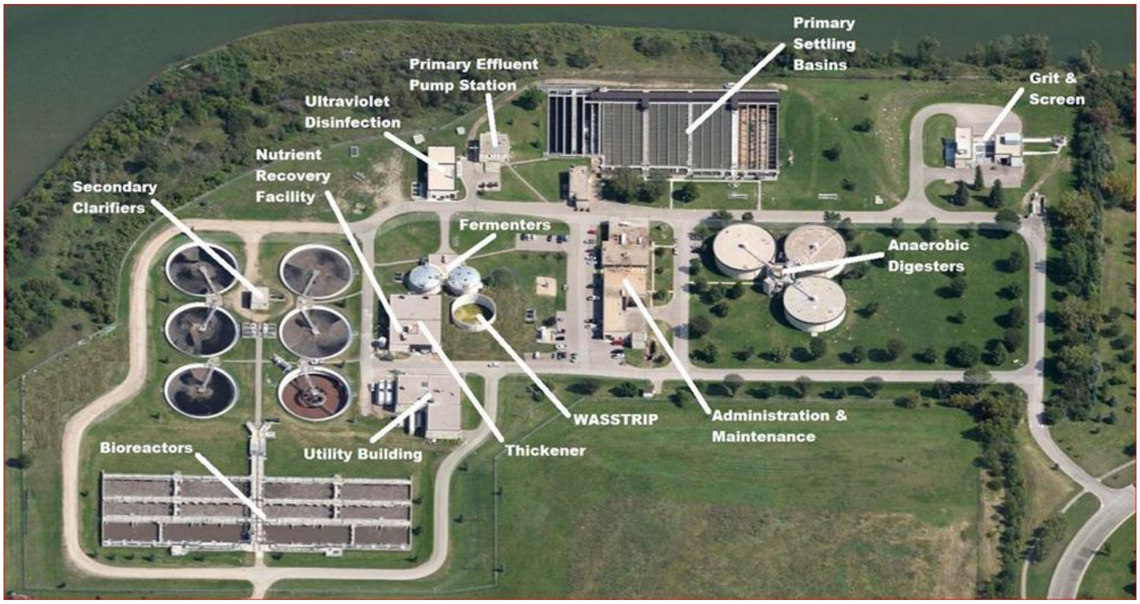

Figure 2.1: A typical municipal wastewater plant diagram

https://www.saskatoon.ca/sites/default/files/images/wastewater_treatment_plant_labelled_areas_for_web_page_-_2014.jpg

Although, the use of coagulants helps in removing bulk of the suspended and colloidal materials in wastewater, the process requires a substantial amount of coagulant and produces considerable amount of sludge. This is a significant limitation as it corresponds to an annual cost of more than 28 million pounds in UK alone [Henderson et al. 2009], which is increasing based on the stringent guidelines for wastewater as imposed by the ministries. On the other hand, sludge treatment in wastewater treatment plants is a costly affair. The capital costs for the sludge treatment facilities are about one third of the costs of the total wastewater treatment plant, and the operating costs for sludge treatment, disposal and reuse are around 40% of the total operational costs of municipal WWTPs [Nowak. 2005]. Therefore reduction in sludge volumes, reduced cost of dosing fresh coagulant, dose optimization and lowering the cost of disposal, are attractive benefits of coagulant recovery.

Dose optimization can be deemed to be a partial solution to reduce coagulant use. Improved understanding of the coagulation-flocculation process has led to dose optimization. Availability of online monitoring and feedback control of coagulant dosing using orthophosphate measurements [Dasoqi et al. 2011], UV measurements [Wang and Hseieh. 2001] have improved the understanding of the process but retrofitting them in a large scale municipal wastewater plant remains a challenge due to high cost. The use of flocculants or coagulant aids and pH optimization has helped achieve better coagulation efficiency with alum doses ranging from 50 mg/L in the 1970's [Westerhoff and Cornwell. 1978] to below 10 mg/L currently [Jarvis et al. 2005]. While coagulant aids reduce the dosage of iron and aluminium coagulants, they are quite expensive. Dose optimization of coagulants only offers a partial remedy to reducing the consumption of coagulants given the fact that during periods of shock loadings and other wet weather events, higher doses would be required to maintain treatment standards. Hence, the concept of coagulant recovery needs to be explored to realize the full potential of the process.

2.1.2 Separation techniques for coagulant recovery

Recovering coagulants from primary municipal sludge minimizes the disposal cost and the cost of dosing fresh coagulant. As mentioned earlier, recovery of coagulant can occur by acidification, basification, ion exchange and membrane processes (Figure 2.2).

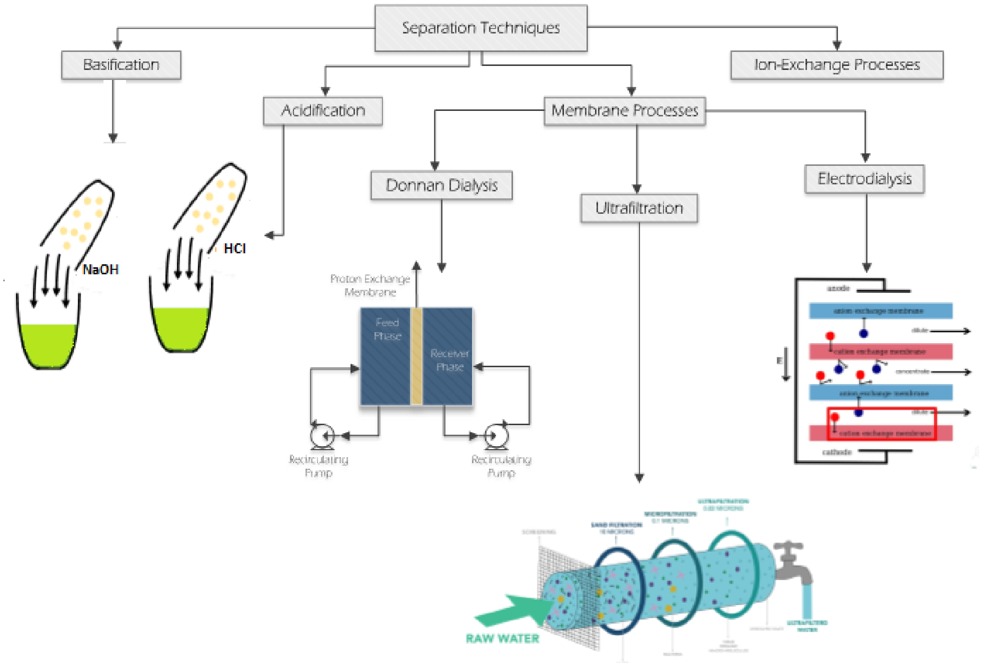

Figure 2.2: Different separation techniques for coagulant recovery

Acidification: Acidification involves neutralizing the flocs of iron/aluminum hydroxides and phosphate precipitates to release the coagulant salt back into solution. The most common acid used for solubilizing the coagulant is sulphuric acid owing to its low cost [Keeley et al 2014]. While acidification with sulfuric acid is probably the most common method to recover coagulant, the optimum operational pH is not reported. Generally, greater amount of coagulant can be solubilized at lower pH values (less than 1), but that requires higher amount of acid increasing the process cost. Studies [Keeley et al. 2016; Saunders and Roeder. 1991; Masschelein et al. 1985] have reported that a good compromise between coagulant recovery and contaminant (humates, fulvates and others) solubilization occurs between pH 2-4. Solubilisation with acid in stoichiometric ratio between the coagulant metal hydroxides and the added sulfuric acid was used. As can be seen in equation 1, about 1.5 moles of acid are required to solubilize 1 mole of trivalent metal (M) [Keeley et al. 2014].

$$M(OH)_3\,(s) + 1.5H_2SO_4\,(aq) \rightarrow 0.5M_2(SO_4)^3\,(aq) + 3H_2O \qquad (1)$$

However, [Babatunde et al. 2009] suggested that the molar ratio of acid: coagulant to be 2:1. The additional acid is used to overcome the buffering capacity of the sludge.

Acidification has also been shown to reduce sludge volumes by dissolving large amounts of suspended solids [Keeley et al. 2016]. While the acid is able to solubilise the coagulant metal from the sludge, many other sludge contaminants like metals, natural organic matter (NOM) are also dissolved at low pH. When using the recovered coagulants directly after acidification in drinking water treatment, these NOM's may introduce potential disinfection by-product precursors. This has led to the development and evaluation of separation technologies such as ion exchange, membrane processes to remove these contaminants, which are discussed in greater detail in the following sections.

Basification: Basification has shown recovery of aluminate salts at a pH of 11.4 [Saunders and Roeder. 1991], however the cost of sodium hydroxide is almost twice that of sulphuric acid [Masschelein et al. 1985], which makes the process unfavorable. While other alternate bases like calcium hydroxide could also be used, they only offer a 50% recovery of aluminum at a pH of 11.4 due to the lower solubility of calcium hydroxides over the aluminates [Masschelein et al. 1985]. It has been reported that basification reduces the carryover of heavy metals, which are generally acid soluble [Isaac and Vahidi. 1961], however, coagulant quality is degraded due to increased solubilisation of organic compounds [Xu and Huang. 2008].

Membrane based processes: The three primary membrane based processes are donnan dialysis (DD), ultrafiltration (UF) and electrodialysis (ED).

Donnan dialysis (DD): The Donnan dialysis process constitutes an ion-selective membrane where the ion flux is driven by electrochemical gradients, instead of pressure differentials as in conventional membrane processes. DD has been used in purifying recovered coagulant [Xu and Huang. 2008; Masschelein et al. 1985], however, when considering diffusion times and specific membrane areas, the cost effectiveness of DD is questionable [King et al. 1975], thus prohibiting practical applications.

Ultrafiltration (UF): UF operates by excluding the larger contaminant particles while selectively permeating the smaller coagulant metal and acid ions. Lower molecular weight NOM molecules will permeate with the coagulant making it unsuitable. UF being a pressure driven process, membrane fouling is likely to be significant and is a significant limitation. In UF, costs are linked to permeate volume than ion concentration when compared to processes like electrodialysis (ED) and DD [Issac and Wahidi. 1961].

Electrodialysis (ED): ED provides an alternative means of extracting coagulants from acidified sludge. Generally, the NOM contaminants have a lower charge to mass ratio than the metal cations, and are expected to be retained, while the metal cations would be extracted by electromotive force [Xu and Huang. 2008]. NOM fouling is expected to be less when compared to UF as it is a diffusive process and not a pressure-driven process.

Ion-exchange processes: Ion-exchange resins, adsorbents and liquid ion exchange processes can recover and purify coagulant. However, the drawbacks of these processes are slow diffusion kinetics for extraction and entrainment of organic solvents during stripping. To regenerate the resin used in an ion exchange process, one needs to add excess sodium hydroxide to strip the bound coagulant. It requires approximately 6 moles of sodium hydroxide to recover 1 mole of aluminum. This is a major limitation since it approaches parity with commercial coagulant prices [Xu and Huang. 2008] and would undermine potential benefits brought about by the recovery process.

2.1.3 Comparative analysis of the current technologies

A comparative analysis conducted on the various recovery processes as mentioned above is presented in Table 2.1.

Table 2.1: Comparative analysis of the various recovery processes

Recovery approach	**% recovery of coagulant**	**Total metal conc.(mg/L)**	**DOC conc. (mg/L)**	**Strengths**	**Weaknesses**	**References**
Acidification	90	2,500	50	Simple, low cost, relatively well understood	Nonselective, heavy metal and organic compounds contamination	Saunders and Roeder. 1991; Xu et al. 2005;King et al. 1975; Keeley et al. 2016
Basification	80	950	-	Simple, rejects heavy metals	Higher cost, specific to alum, low recovery concentrations	Masschelein et al. 1985; Issac and Vahidi. 1961
Ultrafiltration	80	560	75	Relatively selective, well understood technology	Considerable organic compound permeation and fouling	Lindsey and Tongkasame. 1975
Liquid ion exchange	90	30,000	—	Allows high concentrations to be achieved in the stripping stage, quite selective	Risk of toxic solvent carryover, and process complexity	Cornell and Schwertmann. 2003
Cation exchange resins	95	5,000	—	Capable of high yields and purity	Regeneration is inefficient and costly. Problems with scale-up	Petruzzelli et al. 2000

Anion exchange resins	90	—	60	Potential to reduce organic contaminant levels in other processes	Inadequate performance to stand alone, adds complexity when used as a polishing stage	Anderson and Kolarik. 1994
Donnan membranes	80	4,700	17	Robust performance in terms of purity and concentration	Slow kinetics require large membrane areas or contact time, harming process economics	Prakash and Sengupta. 2003; Prakash et al. 2004
Electrodialysis	—	—	—	May be able to accelerate the slow kinetics of other ion exchange membrane processes	Poorly understood in this role and likely to face problems with fouling, scaling and high energy	Keeley et al. 2014

Adapted in part from Keeley et al., Coagulant Recovery from Water Treatment Residuals: A Review of Applicable Technologies. Critical Reviews in Environmental Science and Technology, 44:2675–2719, 2014, DOI: 10.1080/10643389.2013.829766

Table 1 highlights the strengths, weaknesses, coagulant yields and concentrations associated with the different recovery processes. The recovery technologies investigated and highlighted in Table 1, have a wide range of selectivity. While acidification is a low cost option, but susceptible to metal carryover, basification rejects heavy metals but is a more expensive option. Ion exchange has shown the highest recovered coagulant purification but has high cost of implementation. Ultrafiltration is a well understood process, however is susceptible to organic compound permeation and fouling. Although, pressure-filtration recovery shows potential reduction in operating costs when compared to traditional practices, it lacks proper selectivity. Donnan membrane process has shown variable purity in case of different DOC loadings of sludge. Electrodialysis, although can accelerate the slow kinetics when compared to other membrane processes, is not very well understood and chances of fouling and scaling are high. The purity of a single separation stage for coagulant recovery is affected by the variability of raw water quality. This has been reduced by multistage separations; however this is not economically competitive. Furthermore, the low cost of ferric and alum does not necessitate further purification stages especially for wastewater treatment where such purity is not required for the coagulants.

2.2 Coagulant recycling in water treatment

2.2.1 Coagulant recycling in drinking water treatment

Use of recovered coagulant in potable water is challenged by numerous regulatory and economic issues. A number of studies have focussed on coagulant recovery and their reuse in drinking water treatment [Keeley et al. 2014; Keeley et al. 2016; Keeley et al 2012; Yang et al. 2014]. Using these purified coagulants in drinking water is simpler when compared to wastewater matrices as the concentrations of colloids, organics are considerably lower than wastewater, chances of extensive complex formations by organics and metal coagulants are limited. Keeley et al. (2014) looked into comparing purification efficiencies of the recovered coagulant using various techniques like ultrafiltration, and Donnan membranes, where Donnan membrane achieved the highest selectivity of the ferric coagulant and rejection of DOC. Studies conducted by Keeley et al. (2016, 2012) focussed on proving the economic viability of using pressure filtration membranes and Donnan membranes, respectively for purification of the coagulant. However, this resulted in incomplete rejection of the sludge contaminants using pressure filtration membranes and the purified coagulant did not match up to the standards of use in potable water. Moreover, Donnan dialysis proved to be extremely cost ineffective when compared to traditional coagulant dosing practices. They further reported that acid recovery needs to be incorporated in any recovery process as it reduces the process cost by half owing to sludge volume reduction. These studies although aimed at recovering or achieving high purity of the recovered coagulant, were not cost effective. None of these methods documented above combine feasibility and cost effectiveness at the same time. Moreover, dosing recycled coagulants into the drinking water process without purification resulted in higher levels of disinfection by- products (DBP) formation due to higher dissolved organic carbon (DOC) at the final chlorination step. Therefore, it is not advisable to use the recovered coagulant in treating potable water directly without subjecting the coagulant to further purification.

2.2.2 Coagulant recycling in municipal wastewater

Use of recovered coagulant remains a practical target in municipal wastewater due to its less stringent guidelines (based on the quality of the coagulant) when compared to drinking water. Published research on coagulant recovery from biosolids (generated from primary wastewater treatment) is limited [Xu et al. 2009; Ishikawa et al. 2007; Jimenez et al. 2007] mostly due to the complex nature of wastewater as compared to drinking water and other effluents. While, studies like Xu et al [2009] and Ishikawa et al [2007] focussed on aluminum recovery from wastewater (without purification) and clarifier sludge, respectively, they did not elucidate the effect of organics on subsequent cycles due to coagulant recovery. Jiménez et al. (2007) investigated the secondary sludge stabilization with sulphuric acid and the effects on various mixing aspects for coagulant recovery, while focussing on inactivation of microorganisms.

Coagulant recovery in municipal wastewater has a lot of potential by offering greater economic rewards in the dewatering and disposal stages by reducing sludge volumes. It also aids in reducing the demand for fresh coagulant. Purification of the recovered coagulant have shown improved performance, but these might add to already marginal cost benefit of the recovery process. Therefore, acidification to recover the coagulant and reusing it on fresh batches of municipal wastewater and monitoring its effect might be a cheap and effective option.

2.2.3 Coagulant recycling in synthetic wastewater

Nair and Ahammed (2014) used recovered aluminum extracted from dried and powdered sludge to treat synthetic effluent in an upflow anaerobic sludge blanket bioreactor

(UASB) at a dose of 25 mg Al/L. Upto 89% phosphate, 71% COD, 80% turbidity, 77% suspended solids and 99.5% total coliform reduction removal has been reported. Yang et al. (2014) reported removal of upto 100% phosphate from synthetic wastewater using acid recovered coagulant (iron) derived from drinking water residuals. The aforementioned study reported the adsorption of phosphate on the sludge instead of precipitation as means of phosphate removal. Vaezi and Batebi (2001) used the recovered iron from wastewater sludge on textile wastewater, achieving 70% removal of solids. Babatunde et al. (2009) demonstrated the use of recovered aluminum from dewatered sludge to remove phosphate from synthetic solutions. The study achieved 83% removal of phosphate at a pH 4 with the recovered aluminum.

Addition of the coagulated sludge without any further processing was evaluated on various types of waste streams. Chu (2001) demonstrated the use of recycled alum sludge as a coagulant to remove dyes from textile dying wastewater. While the recycled sludge reduced the hydrophobic dye, addition of fresh coagulant to supplement the recycled coagulant was necessary to remove hydrophilic dye, which was detrimental for the recycled water quality. While majority of the studies focus on aluminum recovery, very few focus on iron recovery due to its complex chemistry with phosphorous.

2.2.4 Pilot scale studies on coagulant recycling

During 1970 – 1980, due to the less enforced guidelines on metal concentrations, disinfection by products (DBP), wastewater plants used recovered coagulants to meet effluent guidelines [Bishop et al. 1987; King et al. 1975]. A total of 21 pilot and full scale trials have been reported in Japan [White. 1984], United States, and United Kingdom [Webster. 1966; Saunders and Roeder. 1991]. Particularly in Japan, acidification was employed to extract the coagulant and its effect on sludge volume was investigated. Although using recovered coagulant proved to be a cost effective solution, the main aim was to improved sludge dewaterability using acidification [Tomono. 1977] by reducing sludge volumes due to acidification. Currently there seems to be no pilot scale plant using CR, the last one reported was in 2006 [Prakash and Senguta.2008].

Despite the success in implementing full scale and pilot processes, CR remains a challenge due to the following reasons:

a) Variability in the water quality and the absence of processes to control it. Although, if the coagulant is dosed at a fixed ratio with the influent phosphorous, the process can be controlled to an extent.

b) Production and accumulation of acid soluble impurities such as heavy metals and natural organic matter (NOM), which are further recycled increasing in concentration with every cycle.

Acidification thus remains a possible dewatering aid for sludges as after recovering the metal coagulants, the leftover solids could potentially be easier to dewater, but the use of the acidified/solubilized liquor without purification remains a challenge.

2.3 Recovery efficiency of coagulants

Municipalities commonly dose alum or iron to reduce the amount of suspended and colloidal materials in water. However, the amount of sludge generated is substantial, which needs to be treated appropriately before disposal. Table 2.2 shows the recovery percentages of alum and iron from different water sludges (drinking and wastewater).

Table 2.2: Recovery percentages of iron and aluminum coagulants

Coagulant	Matrix	Optimum pH	% recovery	% recovery in multiple cycles	Reference
Alum	Municipal wastewater sludge	2.5	84.2	84.2; 82; 82; 78	Xu et al. 2009a
Iron	Municipal wastewater sludge	1.5	82	82; 80; 75; 70	Xu et al. 2009b
Alum	Municipal wastewater sludge	2	35	-	Ayoub et al. 2017
Alum	Municipal wastewater sludge	2	65-72	-	Chen et al. 2012

Alum	Municipal wastewater sludge	2	70	-	Jimenez et al. 2007

Table 2.2 reflects only the studies which focussed on use of recovered coagulants without purification in wastewater/water applications. In majority of the cases sulphuric acid was commonly used to recover alum/iron due to its cost effectiveness. Dissolving these coagulants using acid, accounts for 25% of the total operating costs in a CR process [Keeley et al. 2012]. Although acidification is the most widely used method for CR, there seems to be a lack of agreement over the optimum operational pH. Use of low pH values (e.g. 0.5, 1) helps in solubilizing majority of the metal coagulant from the sludge; however the acid requirement increases the cost for the process.

2.3.1 Fe-P and Fe-S chemistry

In comparison to alum, iron salts are more cost effective and aid in better phosphorous removal [Zhou et al. 2008]. While there have been numerous studies on the recovery of alum from sludge, studies on iron recovery has been very limited (refer to Table 2.2). The aluminum-phosphate chemistry is well studied when compared to iron-phosphate [Omoike and Van Loon. 1991; Kumar et al. 2011; Babatunde et al. 2009]. The chemistry of iron and phosphorous pairing is quite complex, and the interactions between these two elements varies from regular adsorption to strong covalent bonds [Smith et al. 2008]. Moreover, in aqueous phase phosphate speciation as well as the binding and release of phosphorous bearing ions into the aqueous phase depend on the solution pH, redox conditions, presence and morphology of organic substances and particle morphology. Phosphorous can be divided into several groups based on its speciation.

- Particulate phosphorous: This particular species maybe adsorbed onto wastewater particles or solid mass.

- Orthophosphates: Can be present as H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-} depending on the pH. H_2PO_4 and HPO_4^{2-} are primarily present in wastewater (pH 7).

- Polyphosphates: Forms an integral part of detergents and can have between 2-7 P molecules

- Organic phosphorous: All living organisms have phosphorous as an essential nutrient in their cells. These could be either particulate or soluble. Examples of organic phosphorous containing compounds are nucleic acids, phosphoric lipids and others.

During chemical precipitation (by iron or alum), particulate phosphorous and orthophosphates can be effectively removed by precipitation reactions, while polyphosphates and organic phosphorous may get adsorbed to a lesser extent [Maurer and Boller. 1999]. Addition of these coagulants help phosphorous get adsorbed onto freshly formed metal-hydro complexes and are then co-precipitated with colloidal matter [Fytianos et al. 1998]. Figure 2.3 represents some of the major iron oxides and their orthophosphate adsorption capacities.

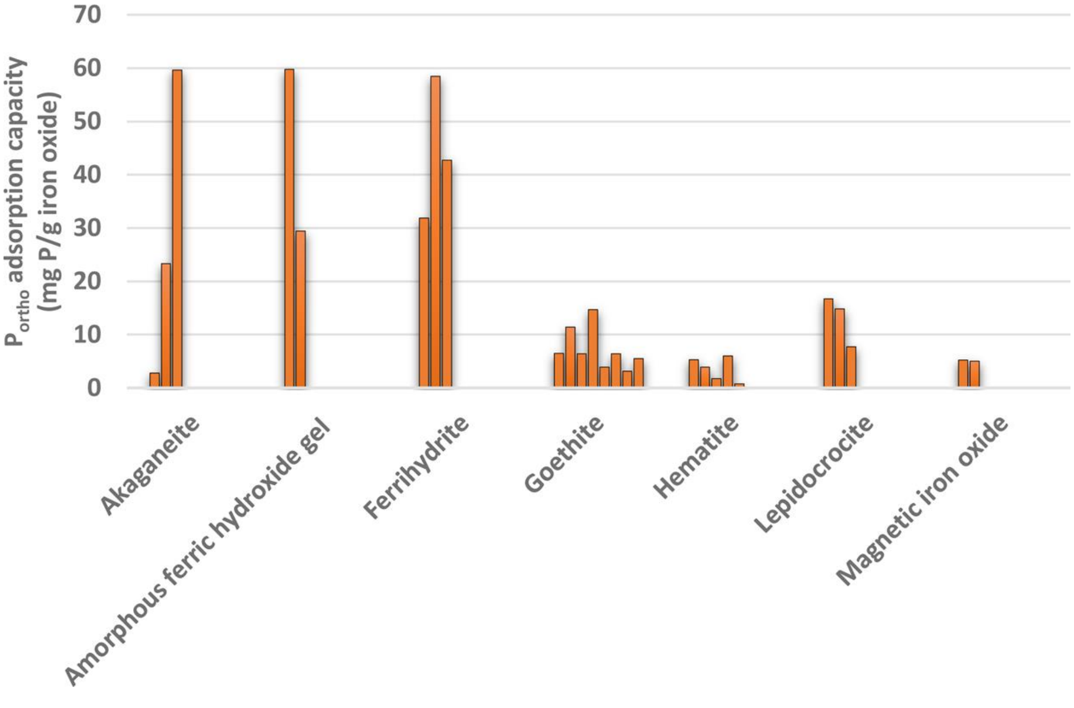

Figure 2.3: Orthophosphate adsorption capacities of various iron oxides

Adapted from Wilfert et al. P. Wilfert, P.S. Kumar, L. Korving, G.J. Witkamp, M.C. van Loosdrecht. The relevance of phosphorous and iron chemistry to the recovery of phosphorous from wastewater: a review. Environ. Sci. & Technol. 2015, 49(16), 9400-14.

The Fe-Ps found in a wastewater plant are typically iron phosphate minerals or adsorption complexes formed by adsorption of orthophosphate on iron oxides [Smith et al. 2008]. The iron oxides (like hematite, goethite, ferrihydrite and others, refer to Figure 2.3) have different crystalline structures which determine specific surface area, solubility, exposed surface sites and reducibility. These properties dictate the adsorption of the orthophosphates on the surfaces of these iron oxides [Wilfert et al. 2015]. Adsorption is not the only mechanism by which the orthophosphates interact with the iron oxides, surface precipitation could be possibly a second one. Surface precipitation could lead to formation of a solid phase phosphate which is not desorbed easily as it is no longer in equilibrium with the solution [Li. 2000].

Iron phosphate minerals are formed by the association of orthophosphate with dissolved iron as opposed to adsorption complexes where orthophosphate is removed from the solution by binding to iron oxides [Sparks. 2003]. The most common iron phosphate minerals are vivianite and strengite among others and their stability may vary with respect to pH and redox conditions of the solution [Nriagu and Dell. 1974].

Solid phase Fe (III) is the form of iron mainly associated with phosphorous (via shared oxygen bonds), while Fe (II) in reducing conditions will associate with sulphide instead of oxygen and release the phosphorous while precipitating FeSx species. Figure 2.4 demonstrates the major Fe-S forms in wastewater. Fe(II) can effectively remove sulfide by precipitating it as FeS (Eq. 1), while Fe(III) can remove sulfide by oxidizing it chemically to elemental sulfur, in turn being reduced to Fe(II), which can produce FeS (Eq. (1), (2)).

$$Fe^{2+}+HS^{-}\rightarrow FeS+H^{+} \qquad (1)$$

$$2Fe^{3+}+HS^{-}\rightarrow 2Fe^{2+}+S^{0}+H^{+} \qquad (2)$$

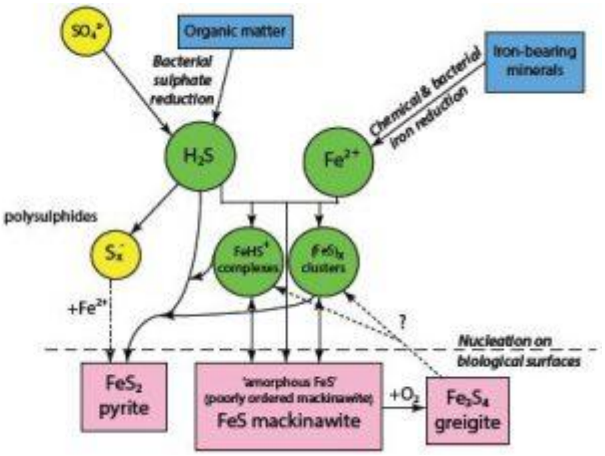

Figure 2.4: Major Fe-S forms in wastewater

Adapted from http://elementsmagazine.org/2017/04/01/mineralogy-of-sulfides/

In municipal wastewater treatment plants, iron is used to control sulfide concentrations in the sewers [Hvitved-Jacobsen. 2002]. However, it is not clear between Fe(II) and Fe(III), which is the most effective in controlling dissolves sulfide concentrations. While Tomar and Abdullah (1994) in their study mentioned the ferric salt solution to be more effective than a ferrous salt solution, on the other hand Jameel (1989) reported ferrous salts to be very effective (almost twice) than ferric salts in controlling the dissolved sulfide concentration. Field studies conducted, revealed that excess iron needs to be added to control dissolved sulfide or else complete control over the process cannot be obtained [Sulfide in Wastewater Collection and Treatment Systems, 1989; Padival et al. 1995].

The most likely inorganic iron precipitate is $Fe(OH)_3$ (Pourbaix, 1963). Decrease in ORP results in sulfate reduction, and buildup of dissolved metal sulfides. Pyrite has been reported to be the most stable inorganic FeS compound in wastewater with ORP around -200mV [Nielsen et al. 2005]. Formation of pyrite is considered to be a slow process under anaerobic conditions, amorphous ferrous sulfide (FeS) is said to be the precursor to pyrite.

For iron to form iron sulfide, the distribution of iron as free-ions, iron bound to organic or inorganic compounds and complex bound iron remains important. Several complexing agents such as nitrilotriacetate (NTA), ethylenediaminetetraacetate (EDTA) and linear alkylbenzene sulfonate (LAS), which are present in minute quantities in municipal wastewater can influence the available iron fraction for sulfide formation [Iliuta and Larachi, 2003]. This could possibly inhibit formation of FeS species.

2.3.2 Mathematical modelling of Fe-P and Fe-S interactions

Mathematical models are effective tools to understand the iron-phosphorous chemistry. Fytianos et al. (1998) and Szabo et al. (2008) developed precipitation models based on experimental data of phosphorous removal by ferric ions and the role of ferric phosphate in phosphorous removals, respectively. These models although effective in calculating the role of solution factors in ferric phosphate precipitation, are extremely complicated given the diverse input options (pH, redox, temperature among others) and time consuming [Maurer and Boller. 1999]. A slightly better chemical precipitation model developed by Luedecke et al. (1989) added an additional mechanism for phosphate adsorption on precipitates. However, this model assumed adsorption and precipitation to be separate phases, which in reality happens almost simultaneously and cannot be separated [Maurer and Boller. 1999].

Thermodynamic modelling using PHREEQC, which is a geochemical computer program and has been used in soil chemistry [Kirpichtchikova et al. 2006; Barna. 2008], can be applied for phosphorous speciation analysis in wastewater. This program can help develop a theoretical guide on reactions affecting chemical precipitations and parameters affecting phosphorous removal. Use of this kind of modelling in wastewater is fairly new with limited literature available [Zhang et al. 2010; Yekta et al. 2014]. Zhang et al. (2010) studied the effect of ferric phosphate precipitation and predicted the parameters responsible for optimum recovery from anaerobic digestion supernatant. They were able to detect 9 ferric iron salts species (i.e. Fe^{3+}, $Fe(OH)_2^+$, $Fe(OH)_3$, $FeOH^{2+}$, $Fe(OH)_4^-$, $FeH_2PO_4^{2+}$, $FeHPO_4^+$, $Fe_2(OH)_2^{4+}$, $Fe_3(OH)_4^{5+}$) and 6 phosphate species (i.e. $FeH_2PO_4^{2+}$, $FeHPO_4^+$, $H_2PO_4^-$, HPO_4^{2-}, $KHPO_4^-$, PO_4^{3-}). The study also showed that pH played an important role in ferric phosphate precipitation by altering the saturation index (SI). The SI followed a polynomial function of pH and the pH of the solution influenced the ionic activities of ferric salts and phosphorous. Yeketa et al. (2014) studied the influence of Fe on the bioavailability of metals in a biogas reactor. In a biogas reactor, Fe is often added to precipitate the sulfide as it is responsible for odor formation, toxicity to the microorganisms and corrodes pipe lines in downstream processes. The study investigated the role of Fe on chemical speciation of the trace metals (Cu, Co, Ni, Zn, Cd, Pb) present in a biogas reactor by using the program, Visual Minteq 3.0. The thermodynamic modelling followed a two-step approach, first the solubility and chemical speciation of Fe was modelled with respect to the other trace metals and in the second step the solubility and chemical speciation of the trace metals were simulated. The results from this modelling exercise showed that Fe:S molar ratio played an important role in trace metal speciation. Although these results elucidate the effect of Fe on phosphorous and other metals, complex formations with recycled iron coagulant were not studied.

Another way to investigate the phosphorous modelling in wastewater is to consider a full scale plant wide modelling approach. Plant wide modelling helps in understanding potential operational strategies which could be implemented in a practical scale. Plant wide models for carbon and nitrogen exist [Batstone et al. 2015] but there seems to be a limitation when incorporating phosphorous in such models. While activated sludge model no. 2d (ASM2d) considers the role of phosphorous accumulating organism (PAO) in the water line [Henze et al. 2000], such distinction seems to be absent in anaerobic digestion model 1 (ADM1). Kazadi et al. (2016) validated a model by incorporating multiple mineral precipitations and their effect on the plant wide scenario. Their model (biological sludge model 2) was effectively able to predict trends in pH, solids, ammonia, phosphate and other variables while showing that mineral precipitation did not affect anaerobic digestion. These models can give a fair estimate of the carbon and nitrogen scenario but remain inadequate in describing the complex phosphorous transformations. This has been addressed by Solon et al. (2017) and Flores-Alsina et al. (2016) in their work where they have developed an analysis of interactions between Fe, phosphorous and sulphur. Their research indicated that operational conditions in a wastewater plant play a key role on the fate of phosphorous compounds which could aid in improving or upgrading the wastewater treatment systems.

2.4 Effect of coagulant recycling on CEPT

While almost all studies have reported that acidification helps dissolve impurities along with the coagulant, but their results are inconclusive. Studies by Xu et al (2009a, 2009b) demonstrated the use of recovered alum/iron coagulants in municipal/synthetic water. Use of the recovered coagulant (alum) led to 36% decrease in sludge volume, 96%, 46%, and 53% removal of turbidity, UV_{254} measurements and COD, respectively. Xu et al. 2009a also states that “some substances” increased in quantity during coagulant recycling, however they should not be affecting the quality of the treated effluent. Their other study on recovered iron (Xu et al. 2009b) shows higher turbidity removal by the recovered coagulant, when compared with the fresh coagulant, 97% phosphorous removal and 10% sCOD removal. Both these studies categorically state that there is no difference in the performance efficiencies of the fresh and recovered coagulant, while the increased dissolved impurities should not compromise effluent quality.

Chen et al. (2012) recovered alum, polyaluminum chloride (PAC) separately from wastewater sludge with sulphuric acid at pH 2. PAC had higher recovery efficiency than alum due to the interparticle bridging. This resulted in higher amount of aluminum ions getting adsorbed on sludge which were eventually released during acidification. They reported that arsenic had the highest probability (90% - 100%) of being in the dissolved liquor during acidification along with heavy metals like copper, nickel among others. They also observed that clay-based sediments have higher chances of adsorbing aluminum during recovery due to their surface area, when compared to sand-based sediments in the sludge. 60% COD and 70% TSS removals with the recovered coagulant was reported. No additional information on organic loadings or effect of the recovered coagulant on water streams has been provided.

Jimenez et al. (2007) recovered alum from secondary wastewater sludge using sulphuric acid at pH 2. The recovered coagulant was supplemented with fresh coagulant (30%) and helped reduce sludge volume by 45%. The study also aimed to reuse the effluent generated by the recovered coagulant on agricultural land.

Majority of studies focussed on the removal of organics in the form of COD/sCOD loadings while inorganics (such as Mg, Cl, K, Na) have not been addressed Xu et al. (2009a, b) showed slight reduction (<10%) in sCOD removals by acidified recovered coagulants, while Chakraborty et al. (2017) showed a significant reduction in sCOD removals (around 25%). This is due to the fact that during acidification of the sludge, NOM are susceptible to dissolution in the acidified liquor and recycled with each run. This results in increased DOC concentrations ranging from 326 mg/L – 1800 mg/L [Saunders. 1989]. The increased DOC concentrations due to recovered coagulant in drinking water treatment has the potential to form trihalomethane (THM) during chlorination which is a suspected carcinogen and is regulated by USEPA [Prakash et al. 2004].

Donnan membrane dialysis has achieved in excluding NOMs along with other anions in the permeate without fouling during aluminum recovery. As the negatively charged anions don’t stick to the membrane surface and the Donnan membrane process is not pressure driven, fouling remains minimum. Although this is a significant step forward in purification of coagulant for application in water treatment, high cost and operator trainings would inhibit the adaptation this process in industries.

2.5 Micropollutants in recovered coagulants

Micropollutants (MPs) are organics whose widespread presence in aquatic systems is a major global concern all across the globe. Although they are present in natural water at almost undetectable (low to subparts per billion (ppb) concentrations, their existence in aquatic systems has been connected to estrogenicity, mutagenicity, and genotoxicity [Baronti et al. 2000]. No compound-specific regulations exist for the removal of MPs in wastewater plants, however some regulations compounds such as pesticides, lindane, nonylphenol, and synthetic hormones exist [Eggen et al. 2014]. There are studies [Vieno et al. 2006; Choi et al. 2008; Huerta-Fontela et al. 2011; Suarez et al. 2009; Asakura and Matsuto. 2009] on removal of MP’s by coagulation or CEPT treatment, but the fate of MPs using recycled coagulants is unknown. Vieno et al. (2006) investigated the role of dissolved organic matter (humates), during coagulation. In the presence of dissolved humates, diclofenac, ibuprofen, and bezafibrate could be removed by $FeSO_4$. In case of diclofenac, 77% removal was achieved, while 50% of ibuprofen and 36% of bezafibrate were removed. Thus, a high amount of dissolved organic matter enhanced the removal of these pharmaceuticals. However, contradictory results were reported by Choi et al. (2008) where removal of seven tetracycline classes of antibiotic (TAs) from synthetic and river water using coagulation was reported. TAs were also assumed to be removed through the charge neutralization by aluminum and polyaluminum chloride (PAC). TAs were removed by being enmeshed into or adsorbed onto the aluminum hydroxide precipitates. They reported that the presence of dissolved organic matter resulted in possible inhibition of MP removal due to preferential removal of the organic matter by the coagulant.

Huerta-Fontela et al. (2011) in their study used alum coagulants, flocculant (diallyldimethyl ammonium chloride homopolymer; poly DADMAC), followed by clarification. Out of the 55 pharmaceutical compounds, only five of them (chlordiazepoxide, zolpidem, bromazepam, clopidogrel, and doxazosin) were completely removed, while warfarin, betaxolol, and hydrochlorothiazide had removals >50%. Negligible removals were obtained for pharmaceuticals such as irbesartan, losartan, or carbamazepine epoxide.

Suarez et al. (2009) investigated the performance of coagulation-flocculation on hospital effluent, both in batch and continuous mode. Galaxolide, tonalide, and synthetic musk (ADBI) had the highest removal efficiencies (>90%) as they are lipophilic compounds, with negative charge, which is beneficial during coagulation. Asakura and Matsuto (2009) studied the effect of coagulation on landfill leachate. Out of the various compounds selected in this study, only nonylphenol showed a removal of >90%, while diethylhexylphthalate (DEHP) removal was about 70%. Poor removals (<50%) were observed for compounds such as diethylphthalate (DEP), dibutylphthalate (DBP), butylbenzylphthalate (BBP), 4 t octylphenol (4tOP), and 4 n octylphenol (4nOP). Table 2.3 highlights some of the studies on MP removal by coagulation in different streams.

Table 2.3: Removal of MP’s by coagulation from different effluents

Coagulant	**Dosage with pH**	**Compound**	**Source**	**Removal %**	**References**
$FeCl_3$/aluminium sulphate	25,50. pH 7	Ibuprofen	Hospital wastewater	12	Suarez et al. 2009
		Diclofenac		21.6	
		Naproxen		31.8	
		Carbamazepine		6.3	
		Sulfamethoxazole		60.	
		Tonalide		83.4	
		Galaxolide		79.2	
$FeCl_3$	100- 200. pH (4,7,9)	Bisphenol A	Landfill leachate	20	Asakuro and Matsuto. 2009
		DEHP		70	
		Noneylphenol		90	
	Not mentioned	Sulfamethoxazole	Drinking water treatment	33	Matamuros and Salvado. 2013
		Acetaminophen		60	
		Cholesterol		45	
		Diazenon		34	
		Metachlor		28	
Aluminum sulfate	200	Aldrin	Surface water	46	Thui et al. 2008
	100	Bentazon		15	
	78	Estradiol	Drinking water	2	Westerhoff et al. 2005
		Estrone		5	

		Progesterone		6	
		Fluoxetine		15	
		Hydrocodone		24	
		Chlordane		25	
		Benzanthracene		26	
		Chrysene		33	
		Erythromycin		33	
		DDT		38	
		Heptachlor		36	
		Aldrin		49	
		Benzofluoranthine		70	
Ferric sulphate	78.5. pH 4.5	Dichlofenac	Lake water with dissolved humic acid	77	Vieno et al. 2006
		Ibuprofen		50	
		Bezafibrate		36	
		Carbamazepine		<10	
		Sulfamethoxazole		<10	
		Celestolide	Secondary effluent from WWTP	50	Matamuros and Salvado. 2013
		Triclosan		24	
		Octylphenol		50	
		Tonalide		24	
		Galaxolide		16	
		Ibuprofen		4	

		Carbamazepine		2	

Adapted from Das et al. S. Das, NM. Ray, J. Wan, A. Khan, T. Chakraborty, MB. Ray .Micropollutants in Wastewater: Fate and Removal Processes. In Physico-Chemical Wastewater Treatment and Resource Recovery. 2017. InTech publishing.

Carballa et al. (2005) reported that during CEPT, lipophilic compounds such as musks were adsorbed in the lipid fractions of the sludge, while acidic compounds such as diclofenac were adsorbed due to electrostatic interactions. Compounds having high sorption (galaxolide, tonalide and diclofenac) were significantly removed (70%) during coagulation flocculation, while compounds with lower K_d (distribution ratio or the distribution of compounds in solids to water) values, such as diazepam, carbamazepine, ibuprofen, and naproxen, were less reduced (25%). Hydrophobicity of the compounds or the distribution of compounds in the octanol-water phases (log K_{ow}) played a major role in determining the removal efficiency in CEPT. The highest removal of 20% – 50% was observed for the compounds with log $K_{ow} \geq 4$ at pH 7–8.

Based on the above discussion, one can assume that the fate of MPs during coagulant recycling will not only depend on their K_{ow} but also other factors such as $K_{d,}$ temperature, pH. This could be key during CR, as MPs which are protonated/deprotonated are subjected to a multitude of pH changes, while the composition of the sludge plays an important role in deciding their K_d value [Ternes et al., 2004]. Future work is required to ascertain the effects and fate of these MPs especially the ones with $K_{ow} > 4$ (as they tend to primarily partition on solids) during CR as their potential disability might jeopardize the acceptance of the process.

2.6 Effect of coagulant recycling on inorganics and heavy metals

One of the major concerns in CR is the dissolution of inorganics in the form of Na, K, Ca, Mg and Cl^-. Cations are considered an integral part of the floc structure in an activated sludge system as it links biopolymer components together. The amount or the ratio of monovalent to divalent cations in wastewater has been shown to impact the properties of formed flocs [Higgins and Novak. 1997]. High concentrations of multivalent cations (Ca, Mg) form strong flocs [Larsen et al. 2008]. The porosity of the flocs has been shown to decrease with increasing Ca concentration [Cousin and Ganczarczyk. 1999]. On the other hand, presence of Na, K has been reported to lower floc strength and often deflocculate sludge particles [Biggs et al. 2001]. During CR, these inorganic ions may cause disruption by entering the liquid stream and deflocculating the waste activated sludge (WAS). This remains a concern and hence their presence in the recovered coagulant needs to be analyzed.

Heavy metals like lead, cadmium, arsenic among others have the potential to contaminate soil. These metals need to be quantified and analyzed before disposal of the biodolids to land. Effect of anaerobic digestion on CEPT sludge

Anaerobic digestion (AD) in wastewater treatment to reduce sludge volumes, pathogens and stabilization of solids is common practice. CEPT sludge when compared to ordinary primary sludge has been reported to have different composition due to its ability to incorporate organics, metals (Fe, Al, Ca, Mg among others) and polymers [Sanin et al. 2011]. This compositional difference between CEPT and primary sludge has been attributed to differences in biomethane production during AD [Ju et al. 2016]. AD of CEPT sludge has been eliciting interest as CEPT is not only a well understood process but also easy to retrofit into an existing municipal wastewater plant. Recent studies by Ju et al. 2016; Kurade et al. 2016; Murugesan et al. 2014; Obulisamy et al. 2016 and Koojiman et al. 2017 have reported the use of CEPT sludge as a substrate for AD.

Ju et al. (2016) reported that the biogas production rate and methane content of CEPT sludges were strongly related to microbial communities rather than any operational parameters (such as organic loading rate, retention time). Kurade et al (2014) and Murugesan et al. (2014, 2016) in their research stated that use of microbial culture like *A. ferroxidans* significantly improved the dewaterability of the CEPT and anaerobically digested sludge. The extracellular polymerase substance (EPS) produced by this culture helps in conditioning the sludge which in turn improved dewaterability. Obulisamy et al (2016) improved methane production by co-digesting CEPT sludge with food waste in mesophilic conditions, while Koojiman et al (2017) investigated the use of flocculent aids for CEPT sludge and their subsequent effect on AD, dewatering. All these studies provide enough background on the biodegradability, methane potential of CEPT sludge as well as anaerobically digested CEPT sludge. However, no information is available on digested sludge using recovered coagulants. Moreover, the spent solids which remain after CR needs to be subjected to AD for understanding their biomethane potential. As majority of these spent solids have been stripped of organics, they should potentially have low biomethane potential. There is no literature available on the fate of these two different kinds of sludges in AD and their effect on dewaterability of solids. This is particularly important, since if the plant decides to use CR, it needs to evaluate the quantity of biosolids reduced through AD, methane production from the recovered sludge, dewaterability of solids and how all these compare with respect to conventional primary or CEPT sludge.

2.7 Cost analysis of the CR process

For any chemical process to be adapted successfully, cost plays a pivotal role. Keeley et al (2012) built a model based on the whole life cost (WLC) of the various CR strategies (unacidified coagulant, acidified coagulant, UF) and validated the data obtained with a water asset company’s in-house tool. They considered a wastewater plant treating 150 MLD producing 33,000 wet tonnes of dewatered ferric sludge at 25% solids per annum. OPEX chemical costs were based on Fe:P removal, project chemical costs included component capital costs plus additional costs for piping, electrical connections, groundworks, engineering and legal/administration costs while the cost of transportation was obtained through quotations from commercial haulers. Their calculations indicate that reuse of coagulants (acidified) can help in reducing the 20-year WLC by approximately 50%, when compared to using fresh iron coagulant and disposal of the biosolids to land. Use of technologies like UF to purify the coagulant before application increased the WLC; however the cost was comparable with conventional CEPT.

2.8 Knowledge gaps in literature

Published research on coagulant (alum and ferric chloride) recovery from primary wastewater treatment biosolids is limited [Xu et al. 2009a,b; Yang et al. 2014; Jiemenez et al. 2007; Ayoub et al. 2017] mostly due to the complex nature of wastewater. Although, the aforementioned studies showed that acidification of sludge effectively released the coagulant, these studies did not investigate the effect of dissolved background organics and nutrients on the performance of the recovered coagulants. In order to understand and maximize the coagulant recovery process, one needs to delve deeper into the chemistry of these coagulants. Even though ferric is extensively used as a coagulant in municipal wastewater treatment, there remains a lack of understanding of the iron-phosphorous chemistry in wastewater. Moreover, to the best of our knowledge, the effect of these recovered coagulants on the MP's in wastewater or AD of the sludges has never been analyzed.

2.9 Synopsis of literature

The global water scenario has been exposed to rising environmental concerns, water quality standards, commodity prices and transportation costs. These challenges are common to many chemical processes; however, the focus needs to be on implementation of sustainable and green processes. CR can improve sustainability of conventional coagulation-flocculation process by alleviating sludge volumes, disposal costs and cost of dosing fresh coagulants. Several separation techniques exist to recover coagulants from sludge, but acidification is the cheapest method available. However, acidification of the sludge leads to dissolution of organics like phosphorous, nitrogen, carbon among others, inorganics like Na, K and heavy metals. Aluminum is the most common coagulant which has been extracted from municipal/drinking water sludge. Several Fe-P complexes like strengite, jarosite among others inhibit iron recovery and a better understanding of these complex formations can be achieved through modelling. AD of CEPT sludge has shown good methane formation potential, while its effect on sludge obtained from recovered coagulant has not been tested.

2.10 References

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Chapter 3

3 Carbon and phosphorous removal from primary municipal wastewater sludge using recovered aluminum

3.1 Introduction

The worldwide production of municipal wastewater exceeds 330 billion m^3 per annum [Florke et al. 2013; Hernandez-Sancho et al. 2015; Sato et al. 2013]. As municipal wastewater treatment plants focus on resource recovery and energy efficiency, chemically enhanced primary treatment (CEPT) is re-gaining importance due to its enhanced removal of organics, thus simultaneously increasing biogas production while reducing aeration energy. The added coagulant in the CEPT process generates significant amounts of chemical sludge contributing up to 5% - 20% of the total solids with ferric coagulant and 15% - 40% with alum [Babatunde and Zhao. 2007; Parsons and Daniels. 1999; Faezi and Batebi. 2001]. Thus, treating these solids or sludge to recover coagulants not only offsets the cost of disposal by decreasing chemical sludge volume but also the cost of dosing fresh coagulant in wastewater [Xu et al. 2005, 2009; Nair and Ahammed. 2014]. Different separation techniques such as acidification, basification, ion exchange and membrane processes have been tested to separate various coagulants from sludge [Xu et al. 2009]. While membrane processes (pressure filtration membranes) have been tested in purification of the recovered coagulant [Keeley et al. 2014, 2016], their inability to adequately remove dissolved contaminants, coupled with membrane fouling is a significant limitation. Precipitation due to basification has shown recovery of aluminate salts at a pH of 11.4 [Saunders. 1991], however, the cost of sodium hydroxide, twice that of sulphuric acid coupled with recovery at high concentrations (950 mg/L Al) makes it a challenging process [Keeley et al. 2014]. While other alternate base such as calcium hydroxide (cheaper than sodium hydroxide) was used, only 50% recovery of aluminum at a pH of 11.4 was possible due to the lower solubility of calcium salts compared to aluminate salts [Keeley et al. 2014]. Ion-exchange processes require organic solvents for regeneration and their marginal cost benefit for low value coagulants make them unfavorable [Maschelein et al. 1985]. The most efficient and cost-effective method to recover coagulant from the chemical sludge has been found to be acidification, which involves neutralizing the flocs of hydroxide precipitant to release the coagulant salt into solution [Chen et al. 2000; Huang et al. 2010; Ishikawa et al. 2007]. The reused coagulant was able to remove turbidity, chemical oxygen demand (COD), total suspended solids (TSS), and total nitrogen (TN) from wastewater [Ahmad et al. 2016; Diamadopolous et al. 2007; Nair and Ahammed. 2016; Xu et al. 2009]. Unfortunately, acidification is not selective and at low pH other contaminants such as organic matter, metals, nitrogen, and phosphorous can also be dissolved [Xu et al. 2009; Keeley et al. 2016].

Previous studies have focused on coagulant recovery and their reuse in drinking water treatment [Prakash et al. 2004; Prakash and Sengupta. 2003]. However, dosing recycled coagulants into the drinking water process resulted in higher levels of disinfection by-products (DBP) formation due to higher dissolved organic carbon (DOC) at the final chlorination step. Hence, in the case of drinking water applications it is not advisable to use the recovered coagulant directly without subjecting the coagulant to further purification.

Addition of the coagulated sludge without any further processing was evaluated on various types of waste streams. Chu (2001) demonstrated the use of recycled alum sludge as a coagulant to remove dyes from textile dying wastewater. While the recycled sludge reduced the hydrophobic dye, addition of fresh coagulant to supplement the recycled coagulant was necessary to remove hydrophilic dye, which was detrimental for the recycled water quality.

Published research on aluminum recovery from biosolids (generated from primary wastewater treatment) is limited [Xu et al. 2009; Ishikawa et al. 2007; Jimenez et al. 2007] mostly due to the complex nature of wastewater as compared to drinking water and other effluents. While Xu et al. (2009) and Ishikawa et al. (2007) focused on aluminum recovery from wastewater and clarifier sludge, they did not elucidate the effect of organics on subsequent cycles due to coagulant recovery. Jiménez et al. (2007) investigated the secondary sludge stabilization with sulphuric acid and the effects on various mixing aspects while focusing on inactivation of microorganisms. These studies mainly focused on the recovery of coagulants and did not investigate the effect of the recycled coagulant on other water quality parameters such as dissolved organics and nutrients. Therefore, the main objective of this study was to assess the impact of recycled aluminum on the removal efficiency of the various water quality parameters like total phosphorous (TP), soluble phosphorous (sP), COD, soluble chemical oxygen demand (sCOD), TSS and TN and to address the organic loading. The optimum acidification pH for the maximum recovery of alum coagulant was established, and the impact of recycled aluminum on the fractionation of additional organic loading in terms of TSS, TP, sP, COD, sCOD and TN was characterized.

3.2 Materials and methods

3.2.1 Aluminum sulphate dose optimization

The different water quality parameters such as TP, sP, TN, TSS, COD and sCOD of the PI collected from the Pottersburg water pollution control plant (WPCP) located in London, Ontario, Canada were measured. A 10% aluminium sulphate [Al2 (SO4)3.18H2O] stock solution in deionized water was used to treat 1L of PI with a phosphorous: aluminum molar ratio of 1:2. Using a jar test apparatus (Phipps & Bird PB-900), the solution was mixed at a fast rate (100 rpm) for 1 minute followed by a slow rate (30 rpm) for 20 minutes. The flocs were allowed to settle for 30 minutes and the effluent was analyzed for TSS, TN, TP and COD.

3.2.2 Aluminum recovery and reuse

The coagulated water from the jar test was centrifuged at 3500 rpm for 5 min and the sludge was collected. The alum was recovered by acidifying the sludge to a pH of 0.5, 1.5 or 2.5 with concentrated H_2SO_4 (36N) or HCl (12N). The acidified sludge was mixed using a magnetic stirrer at 170 rpm for 60 min, and then centrifuged at 3700 rpm for 10 minutes. The supernatant was removed and was analyzed for aluminum concentration using ICP-MS (ICP-OES Vista Pro Axial, Varian, Australia). The recovered aluminum from the supernatant of the centrifuged sludge was then reused to dose a fresh sample of PI and the procedures described above were repeated. There was no significant effect on the pH of PI by the addition of recovered coagulant due to the large difference in volume of the recovered coagulant and PI, decreasing it slightly from 7.1 to 6.9.

3.2.3 Analytical Methods

Solution pH was measured with a digital pH-meter (HACH, HQ11d). COD (method 8000), sCOD (solution filtered through 0.45 µm) (method 8000), TP (method 10209), sP (method 10209), TN (method 10242) were measured using HACH methods. TSS was measured according to standard APHA methods (method 2540d). ICP-MS (ICP OES Vista Pro Axial, Varian, Australia) was used to measure aluminum concentration.

3.2.4 Characterization of sludge

The sludge obtained from the centrifugation of PI dosed with alum was characterized for sludge volume index (SVI). To quantify the amount of residual aluminum (after acidification) in the sludge (denoted henceforth as waste sludge), it was digested with nitric acid for 2 hours and analyzed by ICP-MS.

3.3 Results and discussions

3.3.1 Characteristics of the influent wastewater

PI was collected from the Pottersburg WPCP. The sampling was conducted on heavy rainy as well as bright sunny days; as a result, water quality varied considerably and the average values of TSS, TP, sP, COD, sCOD, TN and pH were 240 ± 87 mg/L, 6 ± 2 mg/L, 2.9 ± 0.64 mg/L, 480 ± 37 mg/L, 230 ± 21 mg/L and 7.4 ± 0.5, respectively (Table S1 in Appendix A).

The phosphorous in the PI was measured and the aluminum-to-phosphorous molar ratio was set to 2:1 for dosing of aluminium sulphate in PI. For data analysis, the TP concentrations in the water were divided into 3 groups: 3.3 – 4.9 mg/L, 5.2 – 6.5 mg/L and 6.9 – 8.2 mg/L. The effects of coagulant dosing on the different water quality parameters i.e. TSS, COD, TN and TP were studied for each phosphorous concentration and are presented in Table 3.1. The percentage removal of suspended solids in the PI marginally increased (2% - 3%) in the different TP levels (Table 3.1). The particulate phosphorous (PP) was removed by enmeshment in the solids. COD removal at three different phosphorous concentrations showed no significant difference. Since on an average the soluble COD accounted for 50% of the total COD, removal efficiencies of ~ 65% for total COD are noticeably high when compared to an average of 85% TSS removal. This is possibly due to the removal of sCOD by adsorption on freshly formed aluminum hydroxide [Chen et al. 2012].

Table 3.1 Removal of TSS, COD, sP, PP due to alum coagulation at different initial total phosphorous concentrations.

TP (mg/L)	TSS removal (%)	COD removal (%)	sP removal (%)	PP removal (%)	TN removal (%)
3.3 – 4.9	84 ± 6.4	64 ± 7.2	82 ± 0.6	63 ± 7.1	15 ± 5.8
5.2 – 6.5	86 ± 1.1	64 ± 7.3	82 ± 0.4	68 ± 2.2	25 ± 5.6
6.9 – 8.2	86 ± 1.7	65 ± 2.7	94 ± 0.1	80 ± 0.2	20 ± 2.7

Table 3.1 shows increasing removal of phosphorous with higher initial concentrations. Conducting ANOVA analysis (with a 95% confidence level) on particulate and soluble phosphorous, the differences in soluble phosphorous removal efficiencies at different initial TP concentrations were deemed as insignificant and the removal of the particulate fraction as significant. A slight variation in the removal of TN was observed probably due to the varying particulate nitrogen concentrations in the wastewater.

After coagulation, the effluent was analyzed for different water quality parameters (aluminum, TP, sP, TN, COD, sCOD and TSS), and was centrifuged to separate the sludge from the effluent. The sludge was then treated with acid for repeated recovery of aluminum.

3.3.2 Aluminum recovery at different pH

In this research, concentrated HCl and H_2SO_4 were used separately to acidify the sludge to pH 0.5, 1.5 and 2.5. The recovery of aluminum from the acidified sludge at three different pH values is shown in Figure 3.1. The recovery of aluminum shown in Figure 3.1 represents the aluminum present in acidified sludge (obtained from coagulation of PI, and as determined by ICP) and not inclusive of the aluminum present in the effluent and the spent sludge. The total mass balance on aluminum includes its concentration in the effluent (1.4 ± 0.1%) and the spent sludge (21 ± 3.1%).

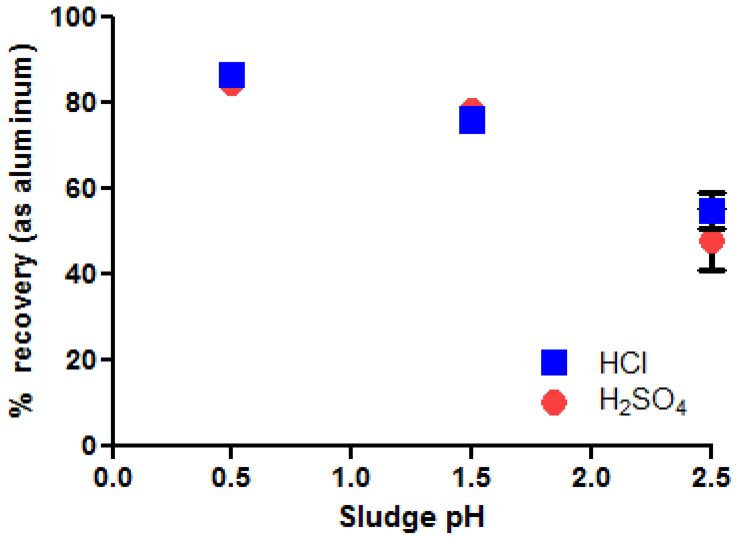

Figure 3.1: Recovery of aluminum from acidified sludge at different pH

It is well-established that at low pH, solubility of metals in water increases [Li et al. 2005]. It is also worth mentioning that addition of concentrated acid helped in the reduction of sludge volume considerably. Acidification with both HCl and H_2SO_4 achieved very similar recoveries as both acid anions, i.e. sulphate and chloride, complex weakly with aluminum. At a pH of 0.5, about 84 ± 2.2% of the aluminum from the sludge was released using H_2SO_4, while HCl was able to release about 86 ± 1.3% of the aluminum. At a pH of 1.5, aluminum recovery using H_2SO_4 and HCl was 77 ± 3.1% and 76 ±3 %, respectively, while at pH 2.5, recovery was only 48 ± 13% and 55 ± 7%, respectively. As stated earlier, the addition of acid would not only help in releasing the bound aluminum but also various other metals present in the sludge. The concentrations of released metals from the sludge by acidification with either of the acids (HCl or H_2SO_4) were measured using ICP-MS (Figure S3 in Appendix A).

Xu et al. (2009) reported that while recovering aluminum from the sludge, there is a high possibility of recovering other metals likes iron, magnesium, manganese, copper, which is confirmed in this work. The average concentrations of copper, manganese and iron in the recovered coagulant were 1.2 mg/L, 1.8 mg/L, and 78 mg/L, respectively. The concentrations of heavy metals like arsenic, lead and cadmium was 0.1 mg/L, 0.7 mg/L, and 0.05 mg/L, respectively. Although there was a minor accumulation of the heavy metals, there was no significant increase (<10%) in the concentrations of As, Pb, and Cd with each subsequent cycle as determined by ICP-MS (Table S2). The LD_{50} values of arsenic, lead and cadmium are 1- 4 mg of arsenic/kg of body weight [Spellman. 2013], 630 mg of lead/kg of body weight, and 225 – 890 mg of cadmium/kg of bodyweight [USAF. 1990], respectively. Therefore, the concentration of these metals released from the sludge due to recycled aluminum coagulant was below the threshold and recycling them would not have any significant impact.

A preliminary cost estimate based on the price of H_2SO_4 or HCl at \$0.28/kg indicates that if about 131 L/m^3 sludge is acidified from pH 1.5 to 0.5, the incremental aluminum recovered (1.3 g/m^3) at pH 0.5 would be at a cost of \$37/m^3 of wastewater. Although the cost of dosing fresh alum to the wastewater is low (\$460/kg), the main expense is typically incurred on the dewatering of the sludge; acidification reduces the sludge volume significantly. Therefore, the most cost effective pH for aluminum recovery is taken to be 1.5 and further experiments were conducted at this pH. A t-test was conducted on percentage recovery of aluminum by both acids at pH 1.5 and 0.5, and no statistical difference was observed. Hence, either of the two acids could be selected for the recovery of the alum coagulant, and H_2SO_4 was chosen for all remaining experiments described in this research.

3.3.3 Modelling aluminum mineral precipitation at low pH

It is known from the acid mine drainage literature that solid phase aluminum and iron species may exist at low pH, such as the formation of jarosite ($KFe^{3+}_3(OH)_6(SO_4)_{2(s)}$) in oxic conditions or melanterite ($FeSO_{4(s)}$) in reducing conditions [Brake et al. 2001]. Thus, at the low pH, and potentially high sulphate conditions (from sulphuric acid) tested here, it is necessary to check if equilibrium modelling would predict any precipitation of species during extraction. This was conducted to determine why a complete recovery of aluminum even at low pH could not be accomplished. Possible sulphate species with aluminum are jurbanite [$(Al(SO_4)(OH)\cdot 5H_2O_{(s)})$], alunogen [$(Al_2(SO_4)_3\cdot 17H_2O_{(s)})$], alunite [$(KAl_3(SO_4)_2(OH)_{6(s)})$], and basaluminite [$(Al_4(SO_4)(OH)10\cdot 5H_2O_{(s)})$], and are considered in this work.

An equilibrium model was generated assuming that total aluminum, total sulphate or chloride and pH were adequate to determine the speciation of aluminum. The equilibrium constants were taken from the National Institute of Standards database (2001) or from Nordstrom et al. (1982) for the sulphate minerals that are not in the NIST database. A summary of the selected equilibrium constants is included in Table S3 (Appendix A). Initial sulphate or chloride concentrations in the original sludge samples were very low, so total sulphate or chloride for the model was determined from the amount of acid added. Equilibrium constants were corrected for ionic strength using the Davies equation.

The equilibrium position of the simultaneous reactions was determined by solving for the mass balance and mass action expressions simultaneously using Newton Raphson optimization to minimize the mass balance and saturation index residuals (R_{mass} and RSI) as a function of vectors of component species concentrations ($X_{solution}$ and X_{solid} for soluble and solid species, respectively). Component species are the minimum number of species that can generate the total number of possible species. The method followed the general equations of Carryou et al. (2002). Expressed in matrix notation these equations are:

$$log\, C = K_{solution} + A_{solution} \times log(X_{solution}) \quad (1)$$

$$R_{mass} = A^T_{solution} \times 10^{\log C} + A_{solid} \times X_{solid} - T \quad (2)$$

$$SI = 10^{(A^T_{solid} \times \log(X_{solution}) + K_{solid})} \quad (3)$$

$$RSI = 1 - SI \quad (4)$$

Where the solid and solution stoichiometric matrices are indicated by A_{solid} (stoichiometric matrix for solid) and $A_{solution}$ (stoichiometric matrix for solution), the vector of species concentrations is given by *C* (concentration of species), the total masses of each component (total aluminum and total sulphate for example) are in the matrix *T*. The values in the *K* vector are specified by the tableau (Table S3). Step one of the iterative protocol involved solving for the equilibrium speciation assuming no precipitation. If no solids were supersaturated based on their ion activity products (i.e., *SI* less than one) then the solver stopped, but if solid phases were predicted, then the most supersaturated phase (highest *SI* value) was allowed to precipitate. Once the algorithm converged for a single solid, the saturation index (*SI*) tested for other solids and if other solids were still predicted, the algorithm continued. In this iterative fashion, the final stable phase assemblage of minerals was determined.

To explore the possibility of sulphate mineral precipitation several different scenarios of total aluminum and pH were explored (note: in the modelling pH determines both the hydroxide concentration and the sulphate concentration). The results of this exercise (shown in Figure 3.2) predict the simultaneous precipitation of jurbanite and amorphous aluminum hydroxide ($Al(OH)_{3(s)}$). None of the other possible sulphate mineral phases was predicted to precipitate based on their reported K_{sp} (solubility product) values, the range of pH, and total aluminum tested in this work. Aluminum sulphate mineral phases could form based on the thermodynamic predictions at the acidic pH used here, i.e. 0.5, 1.5 and 2.5 to recycle aluminum coagulants.

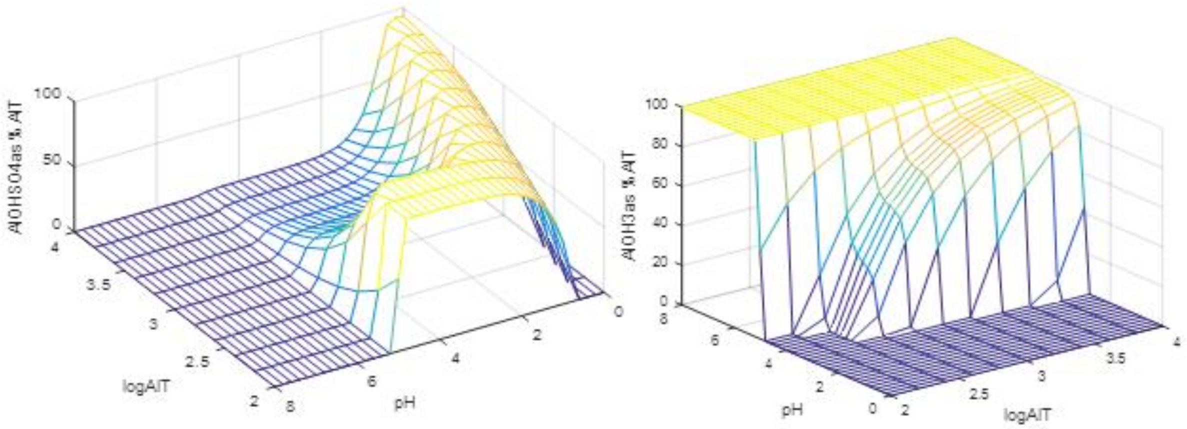

Figure 3.2: Equilibrium model predicted jurbanite precipitation (left) and simultaneous amorphous gibbsite (right) precipitation for variable total aluminum and pH conditions. The total sulphate used for modelling was predicted in the model based on the pH. Aluminum concentrations in mg Al/L; thus, simulations were from 100 to 10,000 mg Al/L.

For the exact test conditions of total sulphate or chloride, pH and total aluminum, the model was run to determine if the % recovered aluminum matched the thermodynamic predictions of aluminum solubility, i.e., did precipitation of sulphate (or chloride) minerals limit the ability to recover aluminum by acidification with sulphuric or hydrochloric acid. The results of these calculations are shown in Figure 3.3. The K_{sp} value for $AlCl_{3(s)}$ was set to 10^{-3} to determine the value of K_{sp} at which aluminum chloride would start to precipitate as solid aluminum chloride. The NIST database did not have any solid aluminum chloride species.

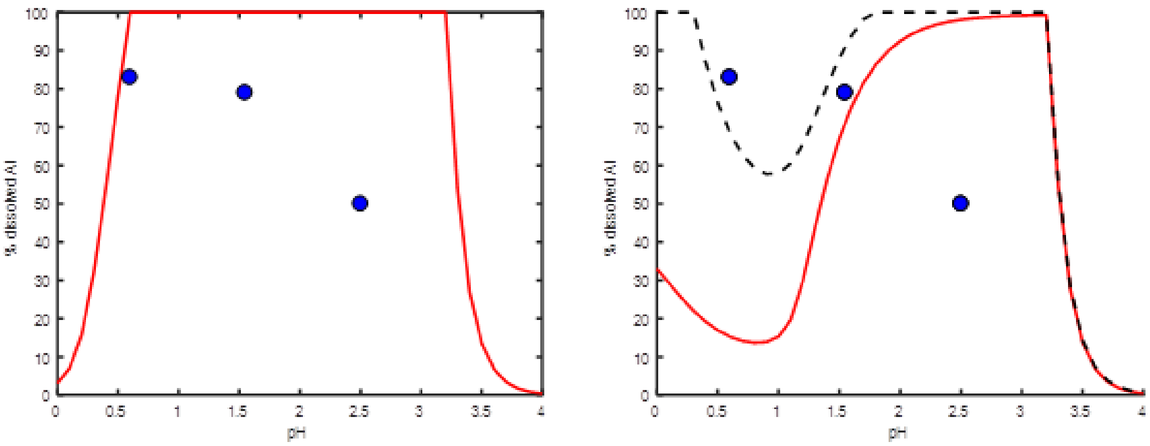

Figure 3.3: Predicted % of aluminum in solution for hydrochloric (a) and sulfuric acid (b). The data points correspond to measured values in this work. The red lines correspond to default model predictions (see text for discussion). The black dashed line corresponds to a modified K_{sp} value (see Table S3) for jurbanite to represent a possible scenario of less complete precipitation.

This modelling exercise shows that precipitation of aluminum sulphate is possible at the conditions of the extractions performed here, but no modelling scenario matches the exact trends of the data. For example, approximate 80% recovery, solubility at low pH is not predicted except by coincidence if there is a precipitation minimum between pH 0.5 and 1.5 for the sulfuric acid extraction. The 60% recovery at pH 2.5 is not predicted by precipitation of aluminum sulphate or aluminum chloride. It was hypothesized that the incomplete recovery at these conditions is more likely related to kinetic rather than thermodynamic constraints. Figure S3 (Appendix A) demonstrates that even after 24 hours the measured soluble aluminium remained constant, so such reactions must occur at timescales longer than exist in wastewater treatment plants. Ridley et al (1997) showed that even after 1000 hours, aluminum sulphate system is not at equilibrium with respect to gibbsite. Thus, if accurate predictions are required, the thermodynamic constants used in this modelling need to be experimentally revised to represent equilibrium at wastewater timescales.

3.3.4 Aluminum mass balance

The aluminum mass balance in different effluent streams at various pH values is presented in Figure 3.4.

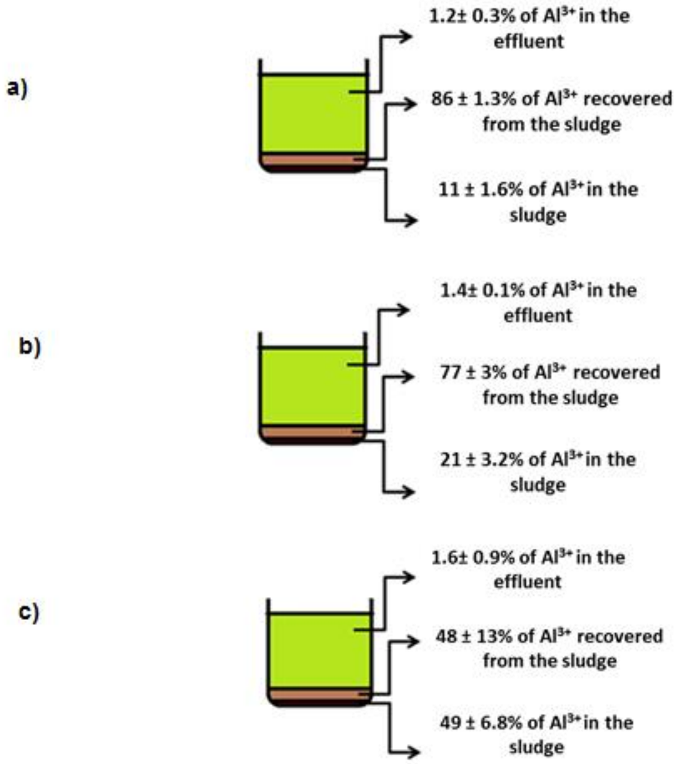

Figure 3.4: Mass balance of Al^{3+} in various streams during recovery from coagulated sludge at pH a) 0.5 b) 1.5 c) 2.5

The recovery of the dosed aluminum at pH 0.5, 1.5 and 2.5 was 86 ± 1.3, 77 ± 3% and 48 ±13% using H_2SO_4. The effluent, which was discarded after centrifugation had 1.2 ± 0.3% (at pH 0.5), 1.4 ± 0.1% (at pH 1.5) and 1.6 ± 0.9% (at pH 2.5), respectively of the total Al^{3+} added. At a pH 0.5, 1.5 and 2.5, complete dissolution of Al^{3+} did not occur with 11%, 21% and 49 % remaining in the solids after acidification (Figure 3.4).

3.3.5 Recycle and reuse of the recovered coagulant

The final step in evaluating the effectiveness of recovering aluminum was to test the performance of recovered coagulant on fresh batches of PI. In this case, the recovered coagulant was dosed volumetrically (2.5 ml/L) corresponding to a dosage of 37 mg/L in 1st recycle and 18.1 mg/L in the 2nd recycle; the decrease in dosage is due to the declining aluminum recovery. The pH of the PI after addition of the coagulant was adjusted to pH 7 using sodium hydroxide. Figure 3.5 shows the effect of the recovered coagulant on the various water quality parameters.

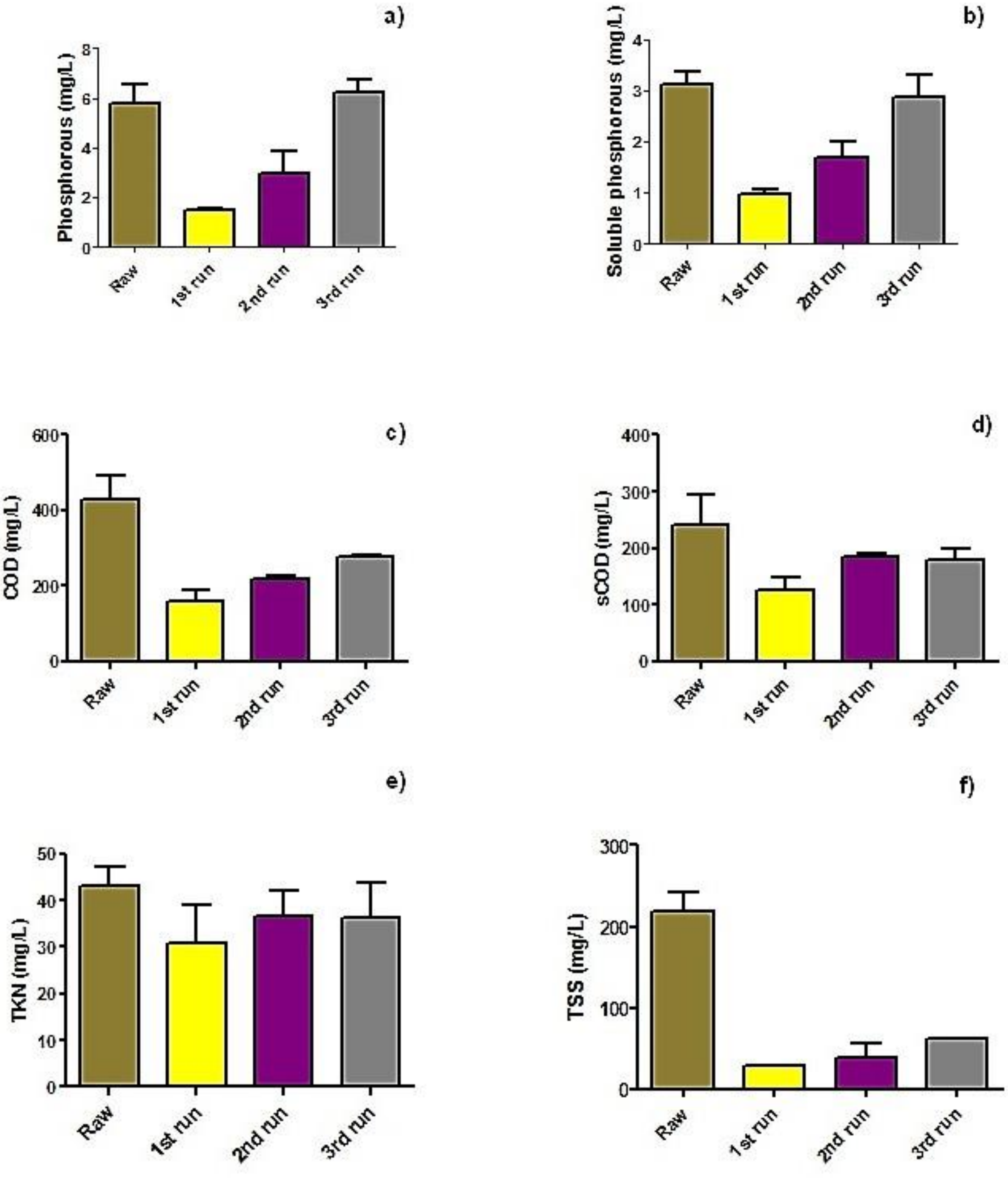

Figure 3.5: Effects of addition of the recovered coagulant on the water quality parameters namely a) total phosphorous, b) soluble total phosphorous, c) chemical oxygen demand, d) soluble chemical oxygen demand, e) total nitrogen, and f) total suspended solids.

The “None” bar refers to the influent PI after clarification (without aluminum sulphate addition). The coagulant was repeatedly recovered for 2 cycles and the water quality parameters were monitored in each cycle. The TP and sP concentrations decreased by 80% in the first cycle with fresh coagulant (Figure 3.5a and 3.5b) but increased in both successive cycles and reached almost the same value as that of the control by the 2nd recycle. This is due to the fact that while recovering aluminum by acid addition, some phosphorous was also released and recycled increasing the overall initial TP concentrations (1 mg/L and 3 mg/L in the first and second recycle, respectively). Figure 3.5c and 3.5d show the effect of the recovered coagulant on the COD and sCOD concentrations. While a removal of 65% COD and sCOD occurred with fresh alum, the removal decreased slightly (by 15%) for both COD and sCOD with recycled alum due to the presence of background sCOD in recycled aluminum, which could be in the form of naturally organic matter (NOM) like humates [Prakash et al. 2004]. The mechanism behind decrease in sCOD during coagulation is attributed to the adsorption of dissolved organics on aluminum hydroxide particles as mentioned earlier [Chen et al. 2000]. The nitrogen concentration remained almost constant in the different recycles. TN decreased by about 33% in the first run followed by an increase of about 5 mg in the first cycle to 6 mg in the second cycle (refer to Figure 3.5e). The TSS concentrations decreased by 85% with fresh alum and removal decreased by 5% - 7% in the following cycles with recycled aluminum (refer to Figure 3.5f). This indicates good coagulation capacity of the recycled aluminum. The recovery of aluminum reduced to 69 ± 4.9% in the first cycle and 42 ± 6.3% in the second cycle. Notwithstanding the impact of the solubilized pollutant loads on downstream processes, which is beyond the scope of this study, significant reduction (about 80%) of the initial volume of sludge by the addition of concentrated sulphuric acid was noticed and its decrease was consistent in each cycle.

The recovered coagulant from each cycle was analyzed to determine the additional organic load occurring in each cycle (Table S4 in Appendix A). The TP and sP concentrations increased with every cycle. This was expected as recycling of orthophosphate would occur with each cycle. The increase in TN and COD concentration was significantly less pronounced than the increase in phosphorous concentration, and their corresponding increases are 18 mg/L and 115 mg/L, respectively.

It was thus crucial to delve deeper and determine the extent of phosphorous, nitrogen and COD addition that occurred with the addition of recycled aluminum in each cycle. The amount of phosphorous, TN and COD added in each cycle (due to only addition of the recovered coagulant) and how it affects the aluminum and phosphorous molar ratio are shown in Figure 4.6. With each cycle, the reduction in aluminum to phosphorous ratio is quite significant. Starting at an initial molar ratio of aluminum:phosphorous of 2:1, it reduced to 0.41 ± 0.17:1 in the first cycle and then to 0.12 ± 0.03:1 in the second cycle (Figure 3.6). Figure 3.6 also presents the amount of TN and COD added in each cycle from the recovered coagulant.

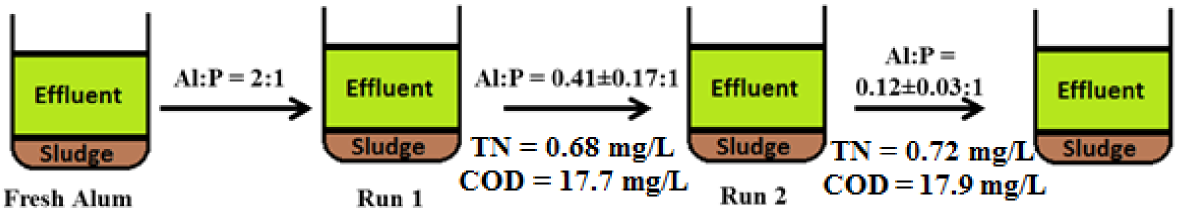

Figure 3.6: The aluminum phosphorous balance coupled with TN and COD due to the use of the recycled coagulant

While the additional nitrogen load is not significant, the amount of COD is comparatively higher. Thus, although the most detrimental effect of recycled aluminum was the increasing phosphorous concentration due to recycling of Al-bound phosphate, there were noticeable changes in total nitrogen, TSS concentrations in the effluent with the recycled aluminum.

A comparison between theoretical [Metcalf and Eddy. 2003] and experimental values for soluble phosphorous removals with changing aluminum ratios is presented (Table S5 in Appendix A). The theoretical values obtained are well in accordance with the experimental observations (Table S5 in Appendix A).

The phosphorous-laden solution at the very end of the second cycle, cannot be discharged to wastewater or water bodies since excess phosphorous is one of the major causes of eutrophication [Kim et al. 2012; Ziong and Peng. 2008] and was precipitated out as struvite. Struvite is a crystalline compound with magnesium, ammonium and phosphate in equi-molar concentrations ($MgNH_4PO_4$. $6H_2O$). It is formed according to the following chemical reaction [Bouroupoulos and Koutsoukos. 2000].

$$Mg_2^{+} + NH_4^{+} + H_2PO_4^{-} + 6H_2O \longrightarrow MgNH_4PO_4.6H_2O + 2H^{+} \qquad (5)$$

Struvite formation was achieved by the external addition of magnesium chloride and ammonium hydroxide to the already existing phosphate in the solution in a 1:1:1 molar ratio. The white crystalline compound thus formed acts as a slow - release fertilizer and the solution now free of the phosphate and organics can be disposed of safely. This is a commonly used method in wastewater processing for precipitating phosphorous as struvite [Pastor et al., 2010; Uysal et al., 2010; Doyle and Parsons. 2002].

Formation of struvite at the end of each cycle inefficient as at a pH between 9.5 -10.5, aluminum would partially precipitate out along with the phosphorous. Hence, struvite formation to separate the phosphorous from the aluminum was deemed feasible only at the end of the second cycle. The aluminum:phosphorous ratio in the recovered coagulant after struvite formation was 1:0.58. This is extremely beneficial, as for full scale application, the recycle of the recovered coagulant with the more favorable molar aluminum:phosphorous ratio is not likely to affect the wastewater pH. Furthermore, this will not only reduce the phosphorous load but will also enhance its recovery.

ASSOCIATED CONTENT

Supporting Information (Appendix A): Concentration of metals in the recovered coagulant solution obtained by acidifying with either HCl or H_2SO_4 (Figure S1), SEM images of the acidified sludge by a) hydrochloric acid b) sulphuric acid (Figure S2), Kinetic study on the concentration of aluminum with a) HCl and b) H_2SO_4 (Figure S3), Variations in water quality parameters (Table S1), Simultaneous equilibria for the aluminum sulphate system written in standard tableau notation (Table S2), Heavy metal concentrations in the recovered coagulant using sulphuric acid at a pH of 1.5 (based on one sample per cycle) (Table S3), Characteristics of the recovered coagulant (Table S4), Expected vs. observed removal efficiencies of influent soluble phosphorous at different Al:P molar ratios (Table S5).

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Chapter 4

4 Reusability of recovered iron coagulant from primary municipal sludge and its impact on chemically enhanced primary treatment

4.1 Introduction

In municipal wastewater treatment, chemically enhanced primary treatment (CEPT) is re-gaining prominence due to its effectiveness in diverting organic matter towards energy recovery treatment processes such as anaerobic digestion. Chemical-based treatment processes like coagulation-flocculation are considered to be a cost effective option, often accounting for only up to 5% of the total water treatment and supply costs [Niquette et al. 2004], Application of coagulant (alum, $FeCl_3$ among others), which aid in removal of suspended solids and colloids from the water, is often considered a common practice in municipalities, although increased sludge handling can be a limitation. The annual requirement of coagulant (aluminum salts) in the year 2006 for Canada alone was over 276,000 tons [Cheminfo Services Inc. 2008] generating substantial volume of waste sludge that needs to be disposed appropriately. This translates to increased handling, disposal and transport costs along with logistical and financial challenges [Keeley et al. 2014a]. Recovering coagulants from waste sludge helps in reducing the fresh coagulant demand and the cost of sludge disposal.

Acidification is the most common method to release the metal coagulant from the sludge due to its cost effectiveness and ease of use [Chen et al. 2000; Huang et al. 2010; Ishikawa et al. 2007]. However, acidification is a non-selective process, which results in the release of organic matter and other metals. The recovered coagulant when used to treat potable water could increase the formation of disinfection-by products due to the presence of organic compounds [Keeley et al. 2014a].Expensive purification methods like ion-exchange and membrane processes can be used for organics removal from the recovered coagulant [Keeley et al. 2014b].

Recovered coagulants have found their use in wastewater treatment [Xu *et al.*, 2005; Xu *et al.*, 2009; Jimenez et al., 2007; Yang et al., 2014; Chakraborty et al., 2017] which is more tolerant of the presence of impurities than in drinking water treatment. Xu *et al* (2005, 2009) investigated the recovery of aluminum and ferric coagulants from drinking water and municipal sludge, respectively. Jimenez et al. (2007) focused on microbial inactivation during sulphuric acid stabilization of recovered wastewater sludge. Yang et al. (2014) used the drinking water sludge residues to treat synthetic and surface water from a lake. Our previous study [Chakraborty et al. 2017] investigated how aluminum can be effectively recovered from the primary sludge by acidification. The study showed that not only can aluminum be extracted at low pH (86%) but also can be efficiently used as a secondary coagulant in the recovery process. The above-mentioned studies showed that acidification of sludge effectively released the coagulant; however, they did not investigate the effect of dissolved background organics on the performance of the recovered coagulants.

While there have been studies [Prakash and Sengupta., 2003; Prakash et al. 2004] focusing on purifying the recovered alum before use in treating potable water and wastewater, research on recovery of ferric coagulant from wastewater sludge has been limited [Xu et al. 2009; Vaezi and Batebi. 2001; Yang et al. 2014]. In addition to its use as a coagulant in wastewater treatment, ferric chloride can be used in phosphorous removal and can prevent emission of hydrogen sulfide during anaerobic digestion [Charles et al. 2006; Higgins and Murthy. 2006; Ge et al. 2013]. Wastewater plants dose ferric compounds in their pipelines to prevent corrosion and manage odors [Gutierrez *et al.*, 2010]. Despite its frequent use in municipal wastewater treatment, there still remains a lack of understanding of the iron-phosphorous chemistry in wastewater. Since our previous work on aluminum recovery [Chakraborty et al. 2017] has already proved the effectiveness of the recovered aluminum as a secondary coagulant, the focus of this work was to understand if iron could be recovered in a similar fashion, as iron is used more often than alum in wastewater plants. Thus, the objective of this work is to determine the effect of recycled ferric coagulant on different water quality parameters such as TSS, TP, sP, COD, sCOD, filtered flocculated (ffCOD), total kjeldahl nitrogen (TKN), ammonia (NH_3-N), nitrites (NO_2-N), nitrates (NO_3-N) and total nitrogen (TN). Additionally, equilibrium modelling was conducted to determine possible Fe-complexes formation during iron recovery, which to date has not been studied in wastewater metrics. A preliminary operational cost analysis determining economic feasibility of the process is also presented.

4.2 Materials and methods

Various water quality parameters such as TP, sP, TN, NO_3-N, NO_2-N, NH_3-N, TKN, TSS, COD, ffCOD, and sCOD of the PI collected from the Adelaide WPCP (London, Ontario, Canada) were measured. A 1g/L ferric chloride [$FeCl_3$] stock solution made in distilled water was used to treat the collected PI. A jar test apparatus (Phipps & Bird PB-900) was used to mix the solution at a fast rate (100 rpm) for 1 minute followed by a slow rate (30 rpm) for 20 minutes. The flocs formed were then allowed to settle for 30 minutes and the effluent was analyzed for all the water quality parameters mentioned above.

4.2.1 Recovery and reuse of ferric coagulant

The coagulated PI with sludge was centrifuged at 3500 RPM for 5 minutes and the sludge was collected after centrifugation. Collected sludge was then acidified to various pH (0.5, 1.5 and 2.5) using 36 N H_2SO_4 and 12 N HCl separately. The acidified sludge was mixed using a magnetic stirrer at 270 RPM for 60 minutes and then centrifuged at 3700 RPM for 10 minutes. The supernatant containing the dissolved coagulant was analyzed for iron concentration using ICP-MS (ICP-OES Vista Pro Axial, Varian, Australia). The recovered iron coagulant obtained from the supernatant of the centrifuged sludge was dosed into fresh batches of PI. The water quality parameters such as TP, sP, TN, NO_3-N, NO_2-N, NH_3-N, TKN, TSS, COD, ffCOD, and sCOD of the effluent were measured. The entire procedure was repeated for two cycles and the recovered iron concentration along with the water quality parameters was monitored in each cycle. Addition of the recovered coagulant did not affect the pH of PI (which ranged from 6.8 – 7.2) due to small volume of added coagulant relative to the volume of primary effluent (volumetric ratio of 1:333). To determine the recovered iron concentration (after acidification and centrifugation) in the coagulated sludge, it was digested using concentrated nitric acid for 2 hours at 105^oC and the supernatant was analyzed for iron using ICP-MS.

4.2.2 Analytical methods

The solution pH was measured with a digital pH-meter (HACH, HQ11d). COD, sCOD (solution filtered through 0.45 µm) were measured using HACH method 8000. About 1 ml 10% $ZnSO_4$ was added to 100 ml of wastewater sample to precipitate the residual colloids in order to determine the filtered flocculated COD (ffCOD) and adjusted to a pH of 10.5 using 6 M NaOH. The supernatant from the solution was then filtered using a 0.45 µm filter**.** Flocculation by $ZnSO_4$ followed by precipitation and filtration using a 0.45 µm filter helps in removal of the colloidal material which would normally pass through a 0.45 µm filter, was measured using HACH method 8000; TP, sP (filtered through 0.45 µm) was measured by method 10209; TN (method 10242), NH_3-N (method 10031), NO_2-N (method 8507), NO_3-N (method 8039) were measured using HACH methods. TSS was measured according to standard APHA methods (method 2540d) [APHA, 1992]. Turbidity was measured by HACH 2100N turbidimeter. ICP-MS (ICP OES Vista Pro Axial, Varian, Australia) was used to measure total iron concentrations in water.

4.3 Results

4.3.1 Variations in influent water quality

Primary influent (PI) collected from the Adelaide WPCP (London, Ontario, Canada) was used for all experiments. The variations in the water quality parameters are presented in Table 4.1.

Table 4.1: Variations in the influent water quality parameters at the Adelaide Water Pollution Control Plant

Influent parameters	**Concentrations**
Total suspended solids (mg/L)	**162±18 (5)***
Volatile suspended solids (mg/L)	**149±15 (5)**
Total chemical oxygen demand (mg/L)	**403±50 (5)**
Soluble chemical oxygen demand (mg/L)	**142±18 (5)**

Particulate chemical oxygen demand (mg/L)	**261±32 (5)**
Filtered flocculated chemical oxygen demand (mg/L)	**112±27 (5)**
Total phosphorous (mg/L)	**9.3±3.7 (5)**
Soluble phosphorous (mg/L)	**6±3.4 (5)**
Nitrites (mg/L)	**0.38±0.32 (5)**
Nitrates (mg/L)	**0.93±0.49 (5)**
Ammonia (mg/L)	**26±2.1 (5)**
Total kjeldahl nitrogen (mg/L)	**34±2.5 (5)**
Total nitrogen (mg/L)	**36±2.6 (5)**
Alkalinity (mg/L $CaCO_3$)	**269±16 (5)**
pH	**7.3±0.4 (5)**
Iron (mg/L)	**0.32 ±0.05 (3)**

[*] Numbers in parentheses indicate number of samples

The variations in water quality parameters are due to the natural diurnal and seasonal variations in the influent to the wastewater treatment plant.

4.3.2 Dose optimization of ferric chloride

The PI was treated with various dosages of Fe^{3+}, 3.5 mg/L, 7 mg/L, 14 mg/L and 28 mg/L, respectively. The corresponding $FeCl_3$ concentrations varied in the range of 10 – 80 mg/L as shown in Figure 4.1, which shows the results of the dose optimization study. The test protocol (1 minute at 100 RPM, 20 minutes at 30 RPM followed by half an hour of settling) was followed and the effluent was analyzed for TSS and turbidity.

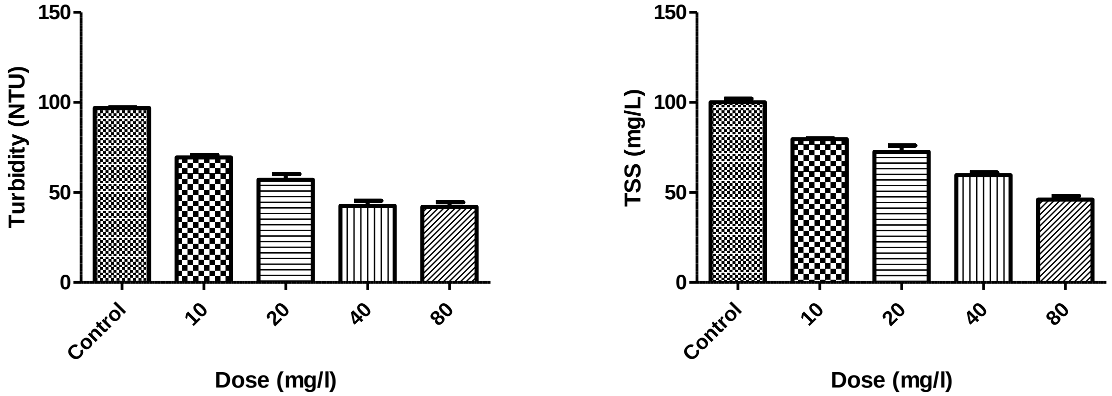

Figure 4.1: Dose optimization of ferric chloride in PI with respect to turbidity and total suspended solids

The percentage removals of TSS using different doses of were 21%, 28%, 41% and 54%, respectively, with comparable removal efficiencies for turbidity at 27%, 41%, 56% and 57%, respectively. It is evident from Figure 4.1 that the removals of TSS and turbidity reached a maximum at a dosage of 40 mg/L. Doubling the dosage to 80 mg/L did not improve removal. Additionally, TP removal also did not increase with increasing dosage from 40 mg/L to 80 mg/L of $FeCl_3$ (TP concentration in the treated effluent was 1.1±0.5 mg/L and 0.9±0.2 mg/L, respectively). Thus, to avoid additional cost of chemicals, 40 mg/L was chosen as the optimum dose and further experiments were conducted using this dose.

4.3.3 Acidification and recovery of ferric coagulant at various pH

The coagulated PI was centrifuged to separate the sludge. The effect of sludge treatment with two different acids, sulphuric and hydrochloric, at different pH based on triplicate samples from the first cycle is shown in Figure 4.2.

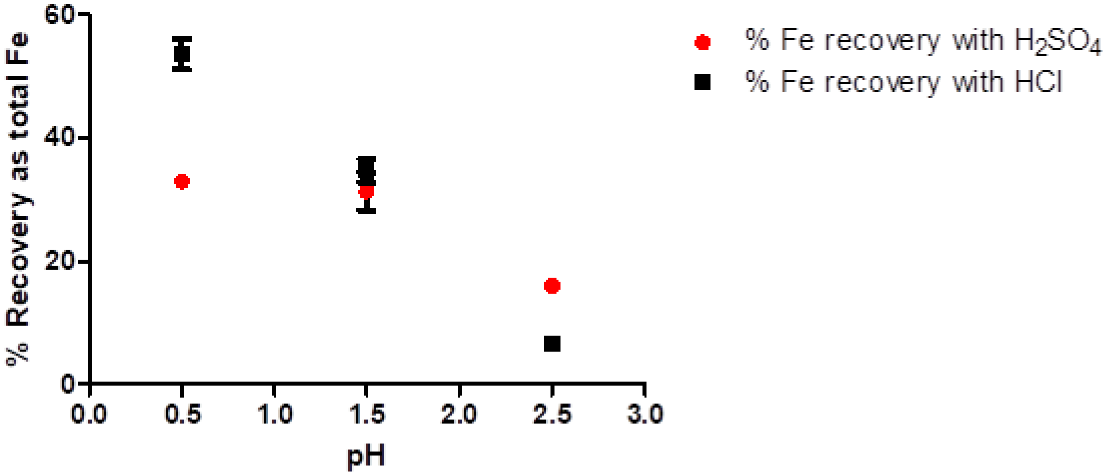

Figure 4.2: Recovery of iron coagulant from acidified sludge using H_2SO_4

Total iron recoveries efficiency using concentrated sulphuric acid at pH 0.5, 1.5 and 2.5 were 33±1%, 31±3% and 16±1%, respectively, while with concentrated hydrochloric acid, the recoveries were 54±3.5%, 35±2.7% and 6.5±0.8% at pH 0.5, 1.5 and 2,5, respectively. Compared to our earlier work with alum coagulant [Chakraborty et al. 2017] where the recovery of aluminum at pH 0.5, 1.5 and 2.5 was roughly 86%, 77% and 48%, respectively; the recovery of iron is very low. This is probably due to the fact that ferrous and ferric ions at different pH are extremely susceptible to forming iron oxides including oxyhydroxides, hydroxides and multiple insoluble oxides [Cornell and Schwertmann. 2003]. The iron oxides depending on surface structure, shape and integrity readily adsorb orthophosphate [Smith et al. 2008; Frossard et al. 1997; Huang and Shenker. 2004] and exist mainly as either ferric phosphate minerals or adsorption complexes in wastewater. In addition, surface precipitation could be another possible method by which the iron oxides interact with the orthophosphate [Sparks, 2003; Davis et al. 1987]. The mechanisms of formation of these complexes and minerals or their breakage from the iron molecule are still not clear [Wilfert et al. 2015].

Although a higher recovery (54%) was obtained using hydrochloric acid at pH 0.5, the amount of acid required to reach that low pH was almost 4 times higher than that required for pH 1.5. Taking into consideration of the marginal cost benefit associated with coagulant recovery, pH 1.5 was deemed to be the optimum pH for iron coagulant recovery. A t-test conducted on the recovery performances of both sulphuric and hydrochloric acids at pH 1.5 was found to be comparable; hence either of the acids could be used for the recovery of coagulant; although H_2SO_4 was chosen for further experiments due to its cost and safer handling than HCl.

A preliminary cost estimate based on the price of H_2SO_4 at 0.12$/Kg [source: www.alibaba.com. last accessed on 07/25/2017], the incremental increase of 2% ferric recovery (33% at a pH of 0.5 vs. 31% at a pH of 1.5) at a pH of 0.5 would be incurred at an additional acid cost of $\$6/m^3$ of wet sludge. Although $FeCl_3$ is relatively inexpensive ($540/ton), the main cost is incurred during sludge handling (30% – 50%) [Mikkelson and Keiding. 2002]. However, it is not only the cost: additional factors such as the effects of acidification on effluent water quality need to be evaluated for safe reuse of the recovered coagulant. Although acidification reduces the sludge volume considerably, it is not a selective process, often releasing other metals, carbon, phosphorous and organic nitrogen in the process [Xu et al., 2009]. This was observed during recycling of the alum coagulant in our earlier study [Chakraborty *et al.,* 2017]. To better understand the process, distribution of iron during the recovery and recycle process was determined and the results are presented in Table 4.2.

Table 4.2: Concentration of iron in the different streams during iron recovery

Cycle number	**Concentration of iron in treated effluent (mg/L)**	**Concentration of iron in recovered coagulant (mg/L)**	**Concentration of iron in sludge (mg/L)**
1	**0.7 ± 0.4**	**14 ± 2.4**	**12 ± 1.8**
2	**0.8 ± 0.4**	**5 ± 1.6**	**8 ± 0.6**
3	**0.8 ± 0.1**	**2 ± 0.7**	**7 ± 0.7**

In the first batch, the total iron dosed to fresh PI at a pH of 1.5 (40 mg/L $FeCl_3$ to 4 liters of PI) was 54.4 mg. The recovered coagulant showed a gradual decline in iron concentration with each cycle, starting from 14 mg in the first to 5 mg in the second and finally 2 mg in the third cycle. This is a sharp contrast to the alum coagulant used in our earlier study, which showed much greater recoveries. The many chemical reactions occurring between the iron species and phosphate among others in wastewater are complicated, requiring a higher iron demand than that needed by the precipitation reactions alone [Fytianos *et al.*, 1998]. This is the possible reason behind the decreasing iron recovery with each cycle.

An iron to phosphorous molar ratio was determined for each cycle and is presented in Figure 4.3.

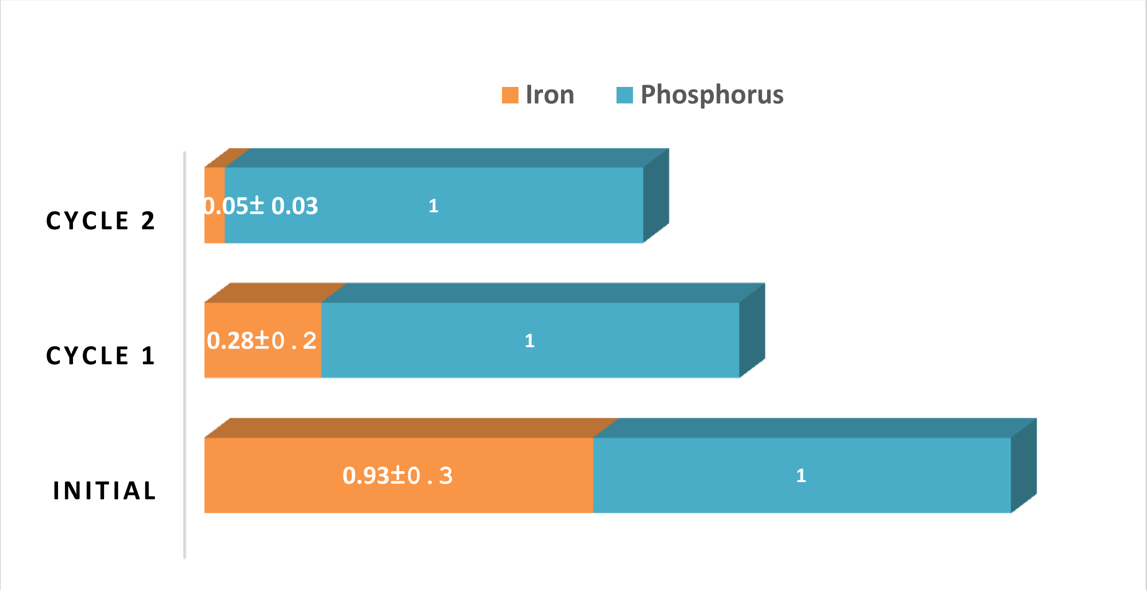

Figure 4.3: Change in the iron-phosphorous molar ratio with recycled iron

The reduction in the amount of iron and increase in phosphorous in the influent due to coagulant recycling is quite significant with each cycle. Starting at nearly equi-molar ratios of iron and phosphorous, the iron concentration consistently decreased in each cycle. In cycles 1 and 2, iron: phosphorous molar ratios were 0.28±0.2:1 and 0.05±0.03:1 respectively. In order to further understand the declining iron recovery, equilibrium-based modelling approach relating iron, chloride and sulphur species was adopted. All stability constants were taken from the National Institute of Standards and Technology (NIST) database (NIST, 2001) except the K_{sp} values of jarosite ($KFe_3(SO_4)_2(OH)_6$), which were taken from Baron and Palmer (1996). All available relevant reactions in the NIST database were included in the modelling (*i.e.*, all reactions involving ferric iron, protons, hydroxide, phosphate and sulphate). Ionic strength effects were modelled by using concentration equilibrium constants determined by interpolation of all available measured values reported in NIST. If, for a given ionic strength, multiple log K values were reported in the NIST database, then the average value was used for interpolation. For reactions with a single reported K value, that value was used directly without correction. Neglecting the influent sulfate concentration compared to the added concentration with the recovered coagulant, ionic strength (μ) and total sulphate (S_T) were determined from the pH according to the following equations:

$$S_T = \frac{[\mathrm{H}^+]^2 + Ka[\mathrm{H}^+]}{2Ka + [\mathrm{H}^+]} \tag{1}$$

$$\mu = \frac{1}{2}([\mathrm{HSO}_4^-] + [\mathrm{H}^+] + 4[\mathrm{SO}_4^{2-}]) \tag{2}$$

Where K_a is the acid dissociation constant for bisulphate and the concentration of each sulphate species was determined from the following equations:

$$[\mathrm{HSO}_4^-] = \frac{[\mathrm{H}^+]S_T}{Ka + [\mathrm{H}^+]} \tag{3}$$

$$[\mathrm{SO}_4^{2-}] = \frac{KaS_T}{Ka + [\mathrm{H}^+]} \tag{4}$$

The total sulphate equation was derived assuming electroneutrality and that only protons, bisulphate and sulphate were significant species at acidic pH. Since the ionic strength and total sulphate depend on the concentrations of bisulphate and sulphate, final values for S_T and μ were determined by iteration until successive results differed by less than 10^{-6} %.

All the simultaneous reactions considered in this modelling exercise are shown in Table S1. Using the same method as Chakraborty et al. (2017), the equilibrium position of the simultaneous reactions was determined by solving the mass balance and mass action expressions simultaneously using Newton Raphson optimization to minimize the mass balance and saturation index residuals following the method presented by Carryou *et al*. (2002).

Jarosite ($KFe_3(SO_4)_2(OH)_6$) is a common mineral in acidic, sulphate-rich environments [Baron and Palmer, 1996]. Many minerals of this form exist with sodium and protons potentially occupying the potassium position. In order to model this solid phase only the potassium form was considered here and the total potassium in solution was estimated as 16.5 mg/L (middle of the reported range of 13-20 mg/L [Arienzo *et al.* 2009]. Strengite ($FePO_4$) is another possible Fe species that may form at acidic pH. There is a wide range of pKsp values (7.12 to 14.8) reported for jarosite in Baron and Palmer (1996); similarly, for strengite two pKsp values are given in NIST 21.76 and 26.4. To test for possible solid phases modelling was performed for a range of total iron and pH with phosphate fixed at an arbitrary value of 100 mg P/L of sludge, potassium fixed at 16.5 mg/L as indicated above, and total sulphur determined as a function of pH using the method described above. A step by step description of the modelling procedure has been provided in Appendix B. The results of this modelling are shown in Figure 4.4.

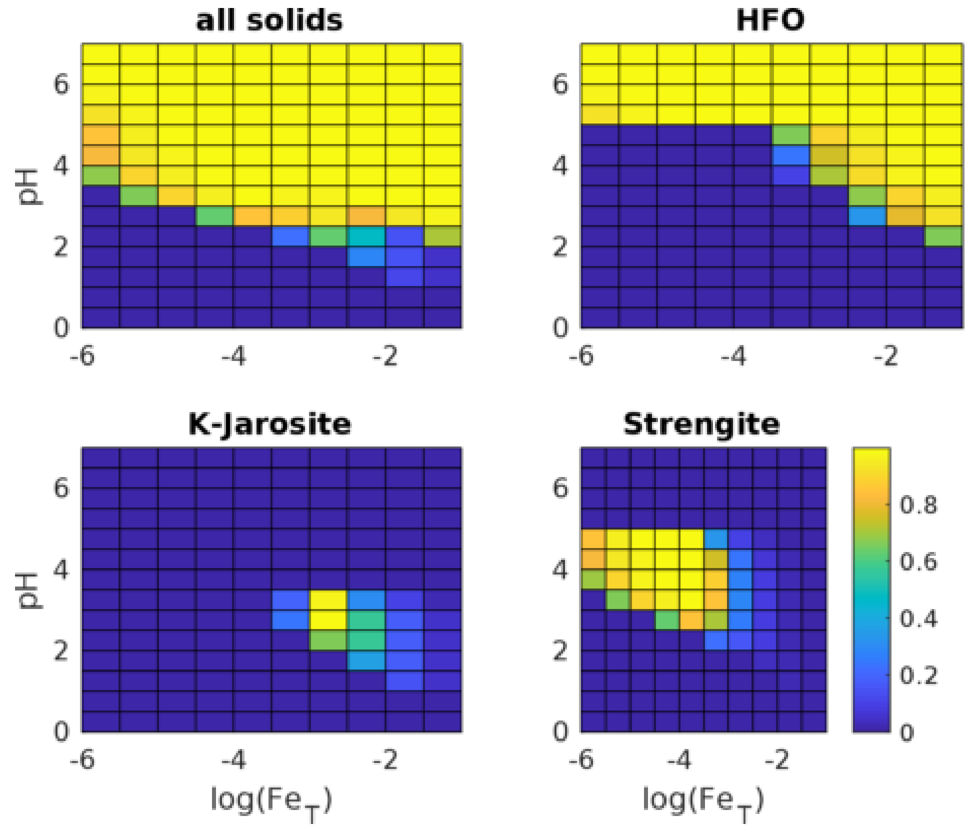

Figure 4.4: Simulations of solid phase speciation for Fe, S, H, K system as a function of total iron (mol/L) and pH. The top left panel shows the sum of all solid species and each other panel shows precipitation of the phase indicated in the title. Models were determined using intermediate K_{sp} values (see text).

As Figure 4.4 demonstrates, there is potential for jarosite and strengite to form at acidic pH. At a pH of 4 and above the preferred solid phase is hydrous ferric oxide (HFO). This is reasonable given that jarosite is known to form in acidic, high sulphate environments such as in acid mine drainage. Strengite has been suggested as a possible form of solid phosphate at low pH in wastewater treatment, but its practicality for chemical P removal is limited by the need for low pH [Smith et al., 2008].

The modelling was done with the species listed in Table S1 (Appendix B) and a fixed pe of 10 was considered with the results shown in Table S2 (Appendix B). To assess the specific conditions of the experiments performed in this research, simulations were performed at 3 pH values (0.5, 1.5 and 2.5) and with total iron (54.4 mg Fe/L), and the results are shown in Figure 4.5. Three scenarios were tested: (1) using the lowest pK_{sp} values, (2) using the highest pK_{sp} values, and (3) using intermediate values. For strengite the intermediate value used was just the average of the two reported values in the NIST database, for jarosite the best value (pK_{sp}=11.0) selected by Baron and Palmer (1996) was used.

Modelling of hydrochloric acid iron recovery was performed in the same way as for sulphuric acid, except in this instance it was not necessary to determine total sulphate concentrations and ionic strength could be estimated directly from the pH. The results of this modelling are shown in Figure 4.5. It can be seen that the model results are very similar to Figure 4.5a for sulphuric acid except the recovery is predicted to increase at lower pH for HCl. The reason for the differences in the two models is mostly due to the activity corrections. The HCl system has a lower ionic strength because chloride is monovalent compared to divalent sulphate.

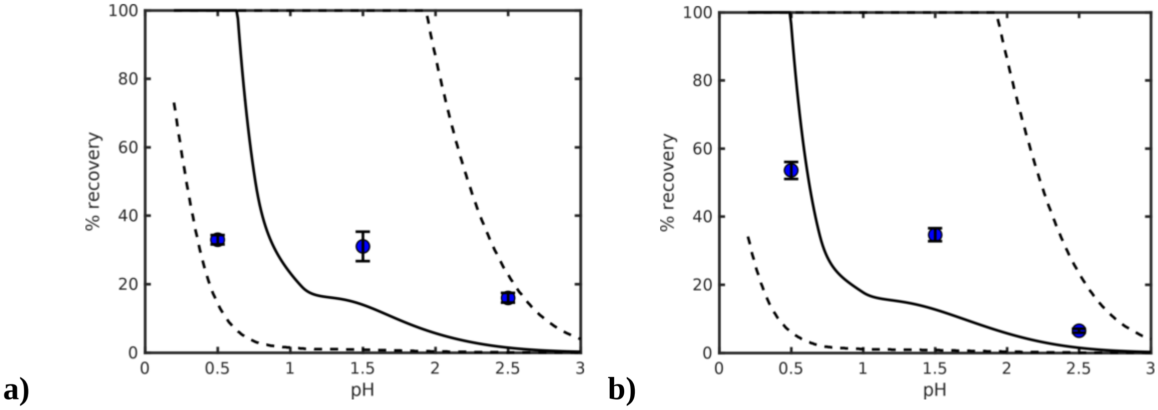

Figure 4.5: Percent coagulant (Fe) recovery versus pH for (a) sulphuric acid and (b) hydrochloric acid additions. Experimental Fe recovery data are shown with error bars (blue circles). The solid line corresponds to the average strengite pKsp value and the recommended pKsp value for jarosite (Baron and Palmer, 1996).

As shown in Table S2 (Appendix B), although the model generally predicted better recovery at low pH consistent with the experimental data, at pH of 0.5 the model predicts 100% iron recovery as compared with 54±3.5% for HCl and 33±1% for H_2SO_4 (Figure 4.2). Simulations demonstrate that the low recoveries of iron are likely related to solid iron precipitation at acidic pH exacerbated by the high sulphate concentrations contributed by the acid (Figure 4.5) and could not be recovered. However, it should be noted that because of the wide range of K_{sp} values reported in the literature, there is large uncertainty in the modelling. In addition, the potential for solids of mixed cations (H^+ and Na^+ substitution for some K^+ in jarosite) is possible, but they are difficult to model. The model predicted better recovery at lower pH (Table S2), which was also seen in the experiments. Other solid phases, such as the mixed cation jarosite could predominate at low pH. Inaccuracy may occur also due to improper measurement of pH at very low pH range; it is very difficult to measure such acidic pH because the surface of the glass pH electrode starts to become saturated with protons.

4.3.4 Characteristics of the recovered coagulant

The recovered coagulant was analyzed for TSS, VSS, TP, sP, COD, sCOD, NO_2-N, NO_3-N, NH_3-N, TKN and TN and the results are presented in Table 4.3.

Table 4.3: Characteristics of the recovered coagulant

Characteristics	**Cycle 1**	**Cycle 2**	**Cycle 3**
TSS (mg/L)	849±60 (3)*	850±82 (3)	853±280 (3)
VSS (mg/L)	773±42 (3)	775±35 (3)	770±99 (3)
TP (mg/L)	227±90 (3)	251±103 (3)	263±98 (3)
sP (mg/L)	158±90 (3)	208±87 (3)	229±92 (3)
COD (mg/L)	4850±495 (3)	5200±282 (3)	5700±140 (3)
sCOD (mg/L)	2900±141(3)	3400±162 (3)	4700±186 (3)
NO_2-N (mg/L)	0.04±0.1 (3)	0.04±0.1 (3)	0.05±0.1 (3)
NH_3-N (mg/L)	56±16 (3)	56±16 (3)	75±7 (3)
TKN (mg/L)	160±91(3)	162±96 (3)	171±120 (3)
TN (mg/L)	232±150 (3)	248±172 (3)	298±128 (3)

* Numbers in parentheses indicate number of samples

The TSS and VSS values remained almost constant with each cycle, showing little to no change. The additional load of TP and sP in the first and second cycles (considering a dose of 3 ml/L of PI) was 0.68 mg/L and 0.75 mg/L, respectively for TP, while for sP it was 0.47 mg/L and 0.62 mg/L, respectively. In case of COD there was an addition to the PI of 15 mg TCOD/L and 16 mg TCOD/L in the first and second cycles, and 6 mg sCOD/L and 10 mg sCOD/L, respectively. There was no significant increase in nitrate or nitrite, as their concentrations in PI were generally low. For NH_3-N and TKN, a slight increase of 0.23 mg/L and 0.5 mg/L, respectively occurred in the second cycle while TN concentrations increased 0.70 mg/L in the first cycle and 0.75 mg/L in the second cycle. These results demonstrate that addition of the coagulant recovered by acidification contributes to increases in almost all parameters due to dissolution from sludge.

4.3.5 Reuse of the recovered coagulant and its effect on performance

The recovered coagulant was further dosed volumetrically (3 ml/L) into fresh batches of PI and the various water quality parameters were analyzed. Due to the declining concentration of iron with each cycle, 3 ml/L corresponded to a concentration of 3 mg/L of iron in the first cycle and 0.73 mg/L of iron in the second cycle. Figure 4.6 shows the effect of the recovered coagulant on the treated effluent.

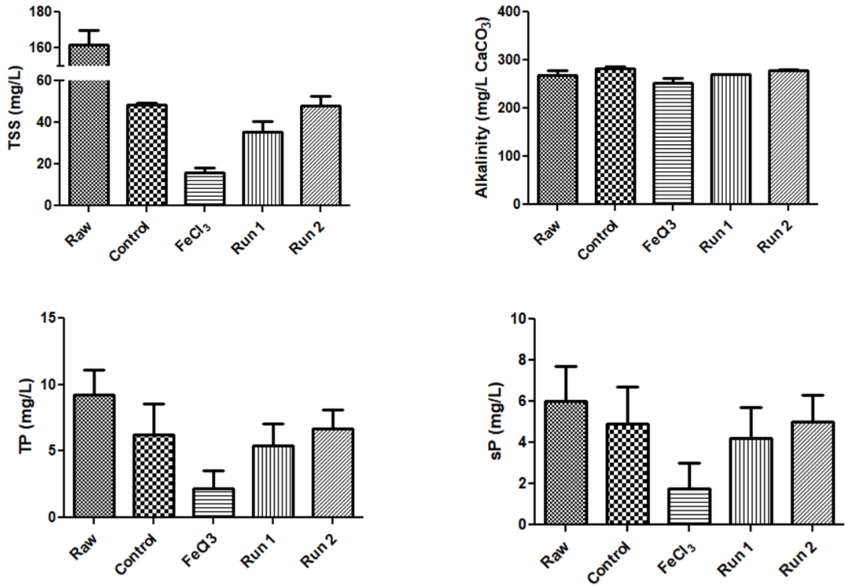

Figure 4.6: Effect of the recovered coagulant when added to fresh batches of PI on TSS, Alkalinity, TP and sP

“Raw” refers to the unclarified PI without any treatment while “Control” refers to the PI sample without addition of ferric chloride but undergoing similar procedures as that of the treated (with ferric chloride) samples. All comparisons are made with reference to the raw sample. Figure 4.6a shows the changes in the TSS concentrations using the recovered coagulant. While with fresh ferric chloride, the TSS concentration decreased by 90%, with the recovered coagulant the percentage removal dropped to 78% and 70% in the first and second cycles, respectively. This is expected, as iron dosage decreased during the first and second cycles of reuse, diminishing the capacity of coagulation. Fresh ferric chloride reduced the alkalinity by 6%, while a slight increase in alkalinity was observed with the recovered coagulant achieving 0.5% and 3.5% increase in the first and second cycles, respectively (Figure 4.6b). In accordance with minimal alkalinity changes, no significant change in pH was observed. For TP (Figure 4.6c), fresh ferric chloride caused 77% removal of TP, while using the recovered coagulant, the removal efficiency decreased to 42% and 28% in the first and second cycles, respectively. For sP (Figure 4.6d), removal with fresh ferric chloride was 70%, while with recycled coagulant it dropped to 29% and 16% in the consecutive cycles, respectively. Theoretical sP removals [Metcalf and Eddy, 2003] with the varying iron:sP ratios in each cycle are 70% - 80%, 30% - 40% and 10% - 20%, respectively. This is in accordance with the experimentally observed values. The increase in both total and soluble phosphorous was due to the acidification of the sludge which solubilized orthophosphate along with the iron coagulant. Moreover, the presence of sulfide in the sludge can reduce different iron compounds [Poulton *et al.,* 2004], causing the release of iron bound phosphorous from the sediments as observed by Smolders *et al.,* 2006; Roden and Edmonds. 1997.

Figure 4.7 shows the effect of recovered coagulant on the various COD fractions in the primary effluent.

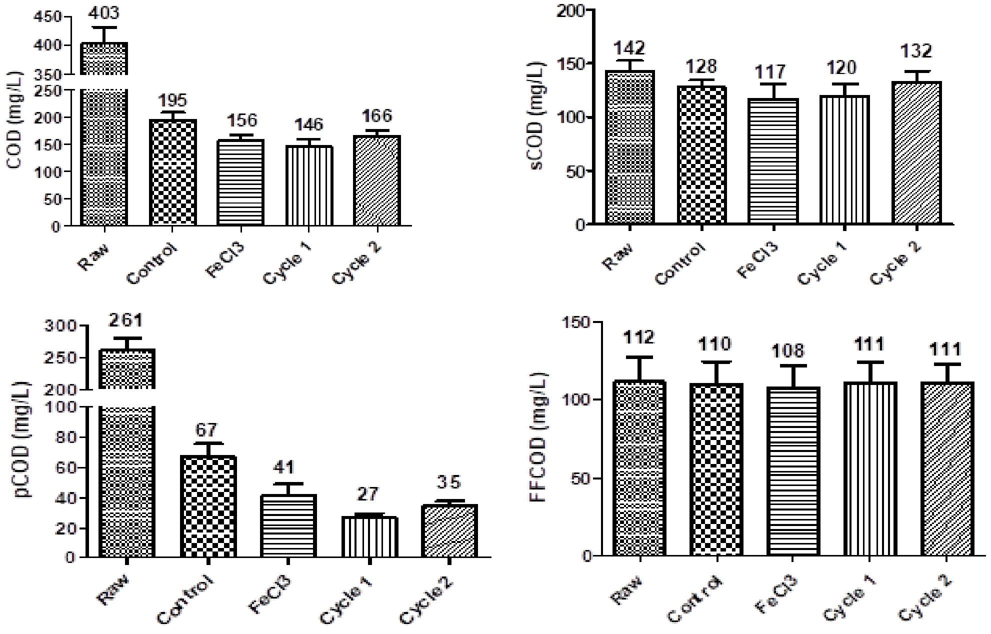

Figure 4.7: Effect of the recovered coagulant when added to fresh batches of PI on COD, sCOD, pCOD, and ffCOD

Addition of fresh ferric chloride resulted in an average removal of 62% of COD, 63% in the first cycle using the recycled coagulant (this is within standard experimental error) and 57% in the second cycle (Figure 4.7). In the case of sCOD (Figure 4.7), the percentage removal was 18% with fresh ferric chloride, 16% in the first cycle, and 7% in the second cycle with recovered coagulant. The removal of sCOD with recycled coagulant is comprised of two opposing factors i.e. increased sCOD concentration due to dissolution of organics and coagulation of the fraction of sCOD. The increase in soluble COD concentration with each cycle is due to the dissolution of humic and fulvic acids contributing up to 40% – 80% of the total weight % of the solids [Tchobanoglous *et al.*, 2013]. For pCOD (Figure 4.7), a decrease of 15 mg/L and increase of 8 mg/L was observed in the first and second cycles, respectively when compared to the treatment with fresh ferric chloride. Readily biodegradable COD, ffCOD, plays an important role in biological phosphorous and nitrogen removal. This particular COD fraction is susceptible to fermentation to form volatile fatty acids which are then taken up by the phosphorous accumulating bacteria. Nominal differences were observed for ffCOD fraction (Figure 4.7) which is expected, as primary treatment of wastewater should not achieve appreciable removals of this fraction.

The effect of addition of the recovered coagulant was studied with respect to the NO_2-N, NO_3-N, NH_3-N, TKN and TN and the results are presented in Figure 4.8.

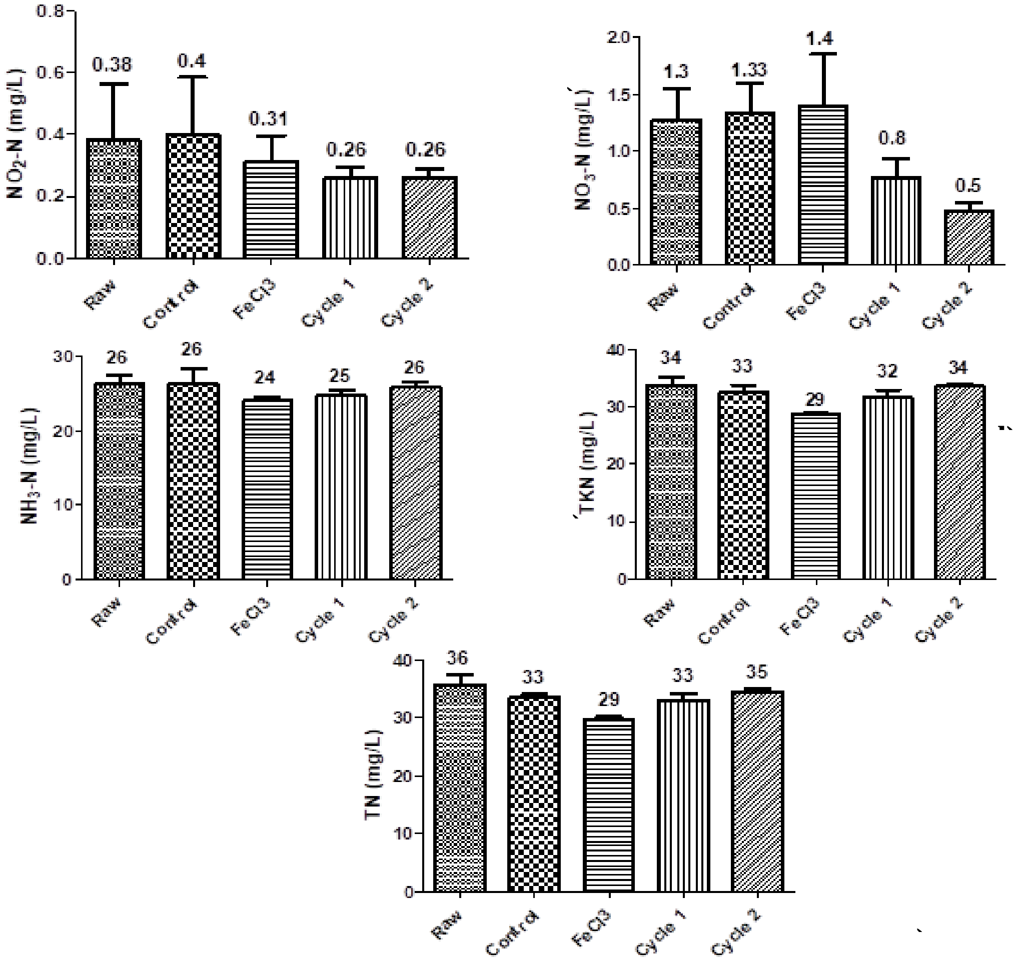

Figure 4.8: Effect of recovered coagulant when added to fresh batches of PI on nitrites, nitrates, ammonia, total kjeldahl nitrogen and total nitrogen

The concentrations of nitrite and nitrate in primary wastewater are generally low. Hence a slight variation in their values due to either experimental error or the changing water quality, would cause significant difference in the values, as can be seen in Figure 4.8 and 4.8. Ammonia concentrations in the treated effluent did not vary significantly with the recycled coagulant. As expected, there are no known mechanisms for removal of the nitrates, nitrites and ammonia in primary treatment and hence negligible effects were observed. TKN, which is a combination of organic nitrogen and ammonia, decreased by 15% with fresh ferric chloride and the removals dropped to 6% and 1% in the first and second cycles, respectively with recycled coagulant (Figure 4.). About 18% overall TN was removed with fresh ferric chloride, with the removal decreasing to 9% and 4% in the consecutive cycles with the recovered coagulant (Figure 4.8e).

The increased phosphorous at the end of the second cycle was precipitated as struvite, which can act as a slow release fertilizer for plants [Nelson. 2001]. Struvite formation was achieved by the addition of magnesium chloride and ammonium hydroxide to the already existing phosphate in the solution in a 1:1:1 molar ratio. The heavy metal concentrations in the precipitated struvite were analyzed using ICP-MS (Table 4.4).

Table 4.4: Concentration of heavy metals in struvite for land application

Arsenic (mg/kg dry sludge)	**Zinc (mg/kg dry sludge)**	**Copper (mg/kg dry sludge)**	**Cadmium (mg/kg dry sludge)**	**Nickel (mg/kg dry sludge)**
0.01±0.2 (2)*	0.01±0.004 (2)	0.003±0.003 (2)	0.002±0.001 (2)	0.01±0.1 (2)

*- Number in parenthesis indicates number of samples

EPA guidelines for sludge disposal to land specify the ceiling concentrations of arsenic, cadmium, copper, nickel and zinc as 75 mg/kg, 85 mg/kg, 4300 mg/kg, 420 mg/kg, and 7300 mg/kg of dry sludge, respectively. The experimental values obtained from ICP-MS (Table 4.4) are much lower than the specified guidelines and thus the disposed struvite can be safely used for land applications.

4.3.6 Operating cost analysis

A cursory operational cost analysis comparing bench scale coagulant recycling and no recycling (CEPT process) was conducted to assess the economic benefits of recycling the coagulant based on the most important parameters such as sludge disposal, sludge dewatering, chemical for TP removal and acid consumption. The schematic for the CEPT process and the proposed coagulant recycling process is presented in Figure 4.9.

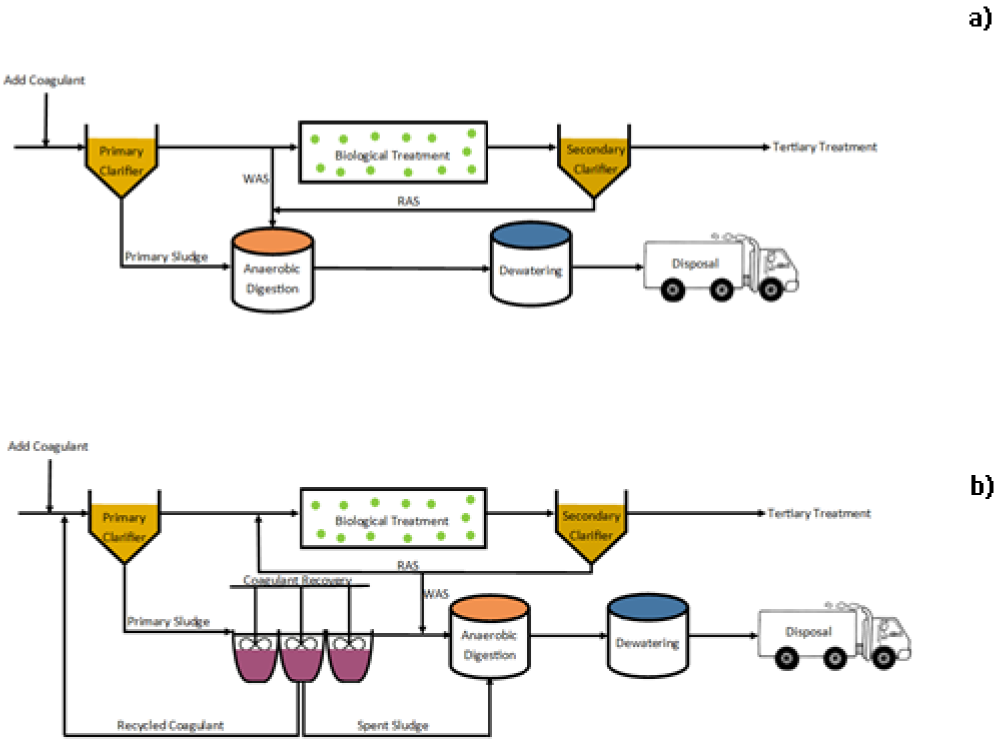

Figure 4.9: Schematic diagrams for a) CEPT process and b) Coagulant recycling process

Figure 4.9 shows the CEPT process and the proposed coagulant recycling process. The coagulant is recovered from the primary sludge before passing the sludge to anaerobic digestion, otherwise the benefits of the process are compromised. In the case of CEPT, the primary sludge is sent directly to anaerobic digestion followed by dewatering and disposal. Accordingly, assuming that the aerobic and anaerobic biodegradability of the primary sludge VSS before and after acidification for coagulant recovery is the same, the major differences in terms of solids handing between the process schematics shown in Figures 4.9a and 4.9b correspond to the differences in inorganic (inert) suspended solids (ISS).

The chemical cost was based on an optimized dose of 40 mg/L of $FeCl_3$. While in the case of no recovery, the calculated cost for a 1MGD plant was straight-forward, in the case of coagulant recovery, the cost is approximately one-third (3 cycles in total) of the coagulant cost plus the additional cost of meeting the effluent phosphorous guidelines, taking into consideration the phosphorous synthesized by the biomass and an effluent TP limit of 0.8 mg/L. A yield coefficient of 0.3 g biomass produced/g COD utilized was assumed for this [Tchobanoglous et al. 2013]. In the case of acidification of sludge, 5 mL concentrated H_2SO_4 was used for one L of sludge, and the acid cost was then calculated based on per m^3 of sludge. Acidification reduces sludge volume [Xu et al. 2009] resulting in additional savings in the dewatering and disposal stages. The calculations for the solids (for dewatering and disposal) were based on the ISS in the WAS and the primary sludge. Based on this, the cost of disposal and dewatering using a polymer dose of 5 kg/ton dry solids were calculated for a 1 MGD plant at $100/ton and $2250/ton of dry solids, respectively. The values obtained from all the parameters are presented in Table 4.5**.**

Table 4.5: Cost analysis of recovery vs. no recovery of coagulant

Parameters		**Recycling**	**No recycling**	**Units**
Chemical cost: $540/ton* **Optimized dose: 40mg/L**	**Primary chemical cost**	**27.3**	**81.8**	**$**
	P in biomass[a]	**1.0**	**1.0**	**mg/L**
	P in effluent	**4.8**	**2.2**	**mg/L**
	Discharge limit	**0.8**	**0.8**	**mg/L**
	P to be removed chemically[b]	**3**	**0.4**	**mg/L**
	$FeCl_3$ required[c]	**16**	**2.1**	**mg/L**
	Cost of additional chemical[d]	**32**	**4.3**	**$/d**
	Total chemical cost	**59.3**	**86.1**	**$/d**

Acid cost: $115/ton* 5mL acid/liter sludge	**Sludge produced/liter PI**	**5**		**mL**
	Sludge produced/MGD	**19**		**m3/d**
	Acid required for a pH of 1.5	**95**		**L/d**
	Acid cost	**19.2**	**0**	**$**
Dewatering: $2250/ton* Polymer dose: 5kg/ton dry solids	**Total ISS in WAS[e]**	**26.1**	**12**	**mg/L**
	Total ISS in primary sludge[f]	**23.3**	**34**	**mg/L**
	Dry solids	**0.12**	**0.17**	**ton/d**
	Cost of polymer dosing	**1.3**	**1.9**	**$/d**
Disposal: $100/ton dry solids**	**Cost of disposal**	**11.6**	**17.3**	**$/d**
Cost	**Total cost on a daily basis**	**91.5**	**105.3**	**$/d**
	Total cost on a yearly basis	**33395.9**	**38448**	**$/year**
	Savings	**5052.1**		**$/year**

*-retrieved from alibaba.com, last accessed 02/27/18. **- unpublished report. # - calculations a through f shown in SI (Appendix B).

In terms of the chemical cost, coagulant recycling (without taking into consideration the excess chemical requirement for meeting discharge specifications) accounts for one third the cost as compared to no recycling ($27/MGD vs. $82/MGD). Furthermore, even with the excess chemical requirement to meet effluent TP regulations, coagulant recycling reduces overall iron costs by $27/day) compared to no recycling. The dewatering and disposal costs in case of coagulant recycling are considerably lower than no recycling. Detailed calculations for the amount of solids and the associated costs are presented in SI and summarized in Table footnotes. In terms of disposal costs, coagulant recycling reduces the cost by roughly $6/day compared to no recycling ($17.3/day vs. $12/day). This is expected as acidification reduces sludge volume and sludge masses as mentioned earlier. Acid consumption which is an additional cost in case of coagulant recycling comes to \$19/m^3 sludge generated., Thus, recovery of coagulant helps in alleviating dewatering, disposal and chemical costs with estimated annual savings of up-to $5052.

4.4 Conclusions

Acidification of ferric chloride coagulated sludge was attempted to recover the coagulant used to treat PI of a wastewater treatment plant. . The recovered coagulant was tested on fresh batches of PI, and the effect of recovered coagulant on the treated water quality was determined. Recycling the coagulant marginally increased the concentration of COD, TN, and TSS in treated effluent, proving the effectiveness of the recovered coagulant. Although phosphorous was the most affected parameter due to recycling, the increased concentration was amenable to precipitation as struvite at the end of second cycle of recycling. Trace concentrations of heavy metals in the struvite indicate possible safe application of it in agricultural lands. A decline in iron concentration in the recovered coagulant was observed with each cycle, and chemical equilibrium modelling attributed this decline in iron recovery to the formation of complexes like jarosite. A preliminary operational cost analysis of the recovery process revealed savings mostly attributable to dewatering, disposal, and chemicals. The analysis also indicates an annual savings in operating costs of a 1 MGD plant of $5,052.

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Chapter 5

5 Micropollutants in chemically enhanced primary treatment using recovered coagulants

5.1 Introduction

Micropollutants (MPs) such as pharmaceuticals, personal care products (PCP) and food additives are ubiquitous in wastewater effluents. In addition to their bio-accumulative properties, many MPs cause adverse ecological effects when discharged to the natural environment [Hollender et al. 2009]. Approximately, 143,000 compounds were registered in the European market in 2012 [UNEP, 2012], and majority of these compounds such as diclofenac, sulfamethoxazole, ibuprofen, etc. are detected in various effluents. Many of these compounds are neither removed nor bio-transformed and may form new chemical species when reacting with background humic substances in presence of sunlight [Das et al. 2017].

Wastewater treatment plants (WWTPs) are a major point source for the MPs and possibly the best location to eliminate them before they enter the aquatic systems. However, traditional WWTPs are designed to reduce carbon, nitrogen, phosphorous loadings only and are generally not equipped with advanced technologies such as adsorption, ozonation and membrane filtration to reduce the concentration of MPs in effluent. Cost of implementing the advanced technologies and their low efficiency in eliminating many refractory MPs such as fire retardants [Tris 2-chloroethyl phosphate (TCEP), Tris 2-chloroisopropyl phosphate (TCPP), insecticide (diazinon) etc., are main deterrence for widespread application in WWTPs [Luo et al., 2014; Jiang et al., 2013].

The physiochemical properties of MPs such as K_{ow} (octanol-water coefficient) play key roles in their partitioning to sludge or the water phase (effluent). Sorption of an organic compound on sludge is highly dependent on its hydrophobicity. Rogers (1996) provided a range of log K_{ow} values indicating sorption potential of organic compounds as: low sorption potential for log K_{ow} <2.5, intermediate potential for log K_{ow} >2.5<4, and high sorption potential for log K_{ow} >4. For example, compounds with high log K_{ow} such as clarithromycin (2.76), monensin (5.4), diclofenac (4.98), diphenyhydramine (3.27) and amitryptiline (4.92) should primarily accumulate on solids or sludge particles based on the assumptions made by Rogers (1996).

WWTPs often use coagulants like alum and $FeCl_3$ to remove suspended and colloidal particulates in water. Although coagulation is a relatively inexpensive process, the main problem lies in the volume of generated sludge. This problem can be somewhat mitigated by recovering the coagulant from the sludge through acidification, basification or other methods [Chakraborty et al. 2017]. This would not only help in reducing disposal costs but also the cost of dosing fresh coagulant.

There have been several studies examining the removal of MPs by the coagulation-flocculation processes [Huerta-Fontela et al. 2011; Suarez et al, 2009; Asakuro and Matsuto. 2009]. Removals of various MPs ranging from 15% to 75% using alum, iron salts, have been reported [Nam et al. 2014; Westerhoff et al. 2005]. These studies focused on the removal of MPs from simulated drinking water/river water using common coagulants, mainly alum and ferric chloride followed by further treatment using UV/activated carbon. None of these studies used primarily coagulation to eliminate MPs but combined advance treatment methods such as UV, ozone or activated carbon as the final step for effluent polishing, adding to the cost. In an earlier study by the authors [Chakraborty et al. 2017], the potential of recycling recovered coagulants by acidification of coagulated sludge was demonstrated. However, with recycling of the recovered coagulants, it is possible that some of the MPs can re-enter the wastewater streams and accumulate resulting in deteriorating water quality of effluents for reuse purposes. This is particularly important as wastewater treatment plants are currently increasingly focused on resource recovery. Thus, this study aims at determining the partition of various MPs in different fractions such as wastewater, recovered coagulant and sludge, due to recycled coagulants. The MPs were selected based on their relative abundance in wastewater and the spread of octanol-water coefficients. This study also tries to understand the fate of the MPs with log K_{ow} >2.5 and determine their K_d (distribution ratio) after being subjected to sludge acidification. For MPs in the tetracycline group, possibility of iron and aluminum chelation was investigated. The effects of recycled coagulants on the removal performance of various water quality parameters like total suspended solids (TSS), chemical oxygen demand (COD), and total phosphorous (TP) among others were also determined.

5.2 Materials and methods

Various water quality parameters such as TSS, TP, COD and sCOD of the primary influent (PI) collected from the Adelaide WPCP (London, Ontario, Canada) were measured and are presented in Table 5.1. Stock solutions of 10% ferric chloride [$FeCl_3.6H_2O$] and 10% aluminum sulfate [$Al_2(SO_4)_3$. 18 H_2O] were made in Milli-Q water. Stock solutions for all 18 MPs (refer to Table 5.2) were made with Milli-Q water at a concentration of 200 mg/L. Based on the TSS removal, an earlier optimized dosage of 40 mg/L and 60 mg/L of ferric chloride and alum, respectively were used to treat the PI. All 18 MPs were dosed into the PI at a concentration of 3.5 mg/L. Jar test (Phipps & Bird PB-900) was conducted using the influent with TSS concentration of 211±10 mg/L**,** using a Phipps & Bird PB-900 apparatus at 100 rpm for 1 minute followed by 30 rpm for 20 minutes and settling for 30 minutes. The effluent was analyzed for the water quality parameters mentioned above. The coagulants (aluminum and iron) were recovered separately from the settled sludge through acidification following the optimized acidification process [Chakraborty et al. 2017],where the sludge was acidified with concentrated sulphuric acid (36N), mixed at 270 rpm for 1 hour and centrifuged at 3700 rpm for 10 minutes to extract the coagulant. Using the recovered coagulant and fresh batches of PI with spiked MPs at a concentration of 3.5 mg/L, the process (coagulation + recovery) was repeated twice. Therefore, recovered coagulant was used in two cycles of coagulation of fresh PI. The concentration of the MPs in the effluent and the recovered coagulant from the two cycles were quantified by high resolution LC-MS.

5.2.1 Analytical Methods

Solution pH was measured using a digital pH-meter (HACH, HQ11d). Wastewater samples were filtered through 0.45 µm filters and COD and sCOD were measured using HACH method 8000, and the TP and sP were measured using HACH method 10209. TN was measured using HACH method 10242. TSS was measured according to standard APHA method 2540d.

The pH of the effluent after coagulation and acidified coagulant was adjusted to 4.00 ± 0.05 using ammonium hydroxide before analysis in LC-MS. The samples were then centrifuged and transferred to 2 mL amber glass HPLC vials. The concentration of MPs in these two types of samples was analyzed using a Q-Exactive™ Quadrupole Orbitrap mass spectrometer (Thermo Scientific, MA, USA) coupled with an Agilent 1290 ultra-high-performance liquid chromatography (UHPLC) system. Compounds were resolved in a Zorbax Eclipse Plus RRHD C18 (2.1× 50 mm, 1.8 µm; Agilent Technologies, CA, USA) column, maintained at 35 °C. The mobile phase was comprised of water with 0.1% formic acid (A), and acetonitrile with 0.1% formic acid (B) (Optima grade, Fisher Scientific, NJ, USA). The gradient consisted of 0% B for 0.5 min before increasing to 100% over 3 min, held at 100% for 2.5 min and reduced to 0% over 0.5 min. The following conditions were used for positive HESI: capillary voltage, 3.9 kV; capillary temperature, 400 °C; sheath gas, 17.00 units; auxiliary gas, 8.00 units; probe heater temperature, 450 °C; S-Lens RF level, 45.00. The data-dependent acquisition method involved a full MS scan at 17,500 resolution over a scan range of 100–1500 m/z; automatic gain control (AGC) target and maximum injection time (max IT) was 3×10^6 and 64 ms, respectively. The three highest intensity ions from the full scan (excluding isotopes) were sequentially selected using a 1.2 m/z isolation window and analyzed at a resolution of 17,500; AGC target, 1×10^6; max IT, 64 ms; normalized collision energy (NCE) 40; threshold intensity 1.6×10^5; and dynamic exclusion of 10 s.

Analytes monitored in the recycled coagulant were analyzed as above with some modifications. For the LC gradient, mobile phase B was held at 0% for 0.5 min, before increasing to 100% over 3 min. Mobile phase B was held at 100% for 1.5 min, before returning to 0% B over 0.5 min. Injections of 5 µL were used with a flow rate of 0.3 mL/min.

The effect of iron and/or aluminum on the ionization was examined by preparing matrix matched calibration curves in blank $FeCl_3$ and alum solutions and diluted to 1:10. Analyte intensity observed in these matrices matched calibration sets were compared to equivalent standard concentrations prepared using MilliQ water as the diluent.

5.3 Results and discussions

5.3.1 Variation in water quality parameters

Primary influent (PI) was collected from Adelaide WPCP (London, Ontario, Canada) and various water quality parameters like TSS, COD, sCOD, TP, sP, and pH were measured and presented in Table 5.1.

Table 5.1: Variations in water quality parameters

Influent Parameters	**Concentrations (mg/L)**
Total Suspended Solids	211±10(3)*
Chemical Oxygen Demand	302±8(3)
Soluble chemical oxygen demand	100±2.1(3)
Total Phosphorous	14±2.0(3)
Soluble phosphorous	11.1±0.2(3)
Total Nitrogen	32±1.3(3)
pH	7.4±0.3(3)

*- Numbers in parenthesis indicates number of samples

The slight variations in the values for the water quality parameters are attributed to the diurnal and seasonal variations in the influent coming to the wastewater treatment plant.

5.3.2 MPs used in this study: structures and presence in wastewater

A wide range of MPs was selected for this study based on their variations in log K_{ow} values and their relative abundance in wastewater. The compounds used in the study are listed in Table 5.2.

Table 5.2: The MPs used in this study

Compound	**Average Concentration in WWTP Effluent (ng/L) [A]**	**Log K_{ow}***	**pKa***	**Solubility (mg/mL)***
Diphenhydramine (DPH)	11.7	3.27	8.87	0.0752
Amitriptyline (AMI)	2092	4.92	9.76	0.0045
Fluoxetine (FLU)	2.1	1.22	9.8	0.0017
Monensin (MON)	400	5.43	6.6	$3.0x10^{-6}$
Chlorhexidine (CHL)	10.45	0.08	10.8	0.80
Antipyrine (AntiP)	681	1.18	0.37	0.373
Diclofenac (DIC)	647	4.98	4.0	0.00447
BDDA	3800	0.59	-	500
Ciprofloxacin (CIP)	96.3	1.28	14.09	1.35
Erythromycin (ERY)	42	2.37	12.44	2

Streptomycin (STP)	-	-7.53	11.2	12.8
Clarithromycin (CLA)	276	3.16	8.99	0.00033
Ofloxacin (OFL)	171	-0.39	6.05	1.44
Chlortetracycline (CHL)	210	-3.60	7.97	0.288
Doxycycline (DOX)	100	-0.02	7.46	0.63
Sulfamethoxazole (SFX)	238	0.79	6.16	0.459
Sulfathiazole (SFZ)	16	0.05	7.2	0.373
Caffeine (CAF)	191	-0.07	10.4	11.0

* All values taken from www.drugbank.ca; www.pubchem.ca;

Among the 18 compounds, amitryptiline (anti-depressant) and BDDA (cationic surfactant) had the highest concentrations in wastewater effluent while chlorhexidine (disinfectant) and diphenyhydramine hydrochloride (anti-histamine) had the lowest concentrations in the effluent (Table 2). Compounds such as diphenyhydramine, amitriptyline, monensin, clarithromycin and diclofenac are expected to partition primarily on to solids due to high log K_{ow} (>2.5) while all the other compounds are expected to be in the effluent after coagulation. The background concentration of the target MPs in the primary influent of Adelaide wastewater plant was below the detection limit except for caffeine (0.031 mg/L), diphenyhydramine (0.075 mg/L), erythromycin (0.027 mg/L), clarithromycin (0.045 mg/L) and ofloxacin (1.5 mg/L). Therefore, all the compounds were spiked into the primary influent (PI) collected from Adelaide WPCP, at the beginning of each coagulation cycle to determine their distribution in recovered coagulant and effluent with both fresh and the recycled coagulant.

5.3.3 Effect on water quality parameters due to coagulant recycling

For each coagulation experiment, the recovered coagulant was dosed into fresh batches of PI while the selected 18 MPs were spiked into the PI. The effects of the recycled coagulant on water quality parameters like chemical oxygen demand (COD), phosphorous and total suspended solids (TSS) are shown in Figure 5.1.

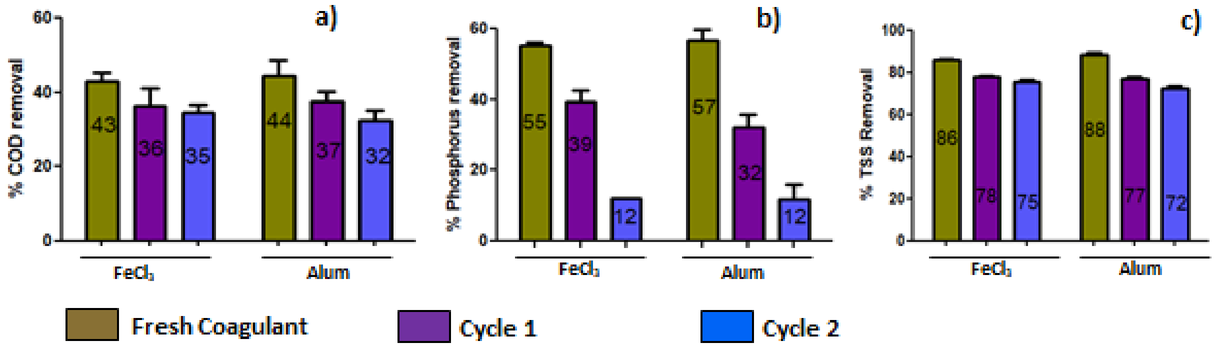

Figure 5.1: Effect on a) COD removal, b) phosphorous removal and c) TSS removal due to recycling of coagulant

It can be seen with the recycled coagulants, the removal of TSS, COD and phosphorous, all declined, and the performance of alum and $FeCl_3$ was quite similar. All experiments were conducted with the PI characteristics as presented in Table 5.1. Removal of COD ranged between 43% - 44% with fresh coagulant (alum and $FeCl_3$), and dropped to < 10% when using recovered coagulant. As expected, phosphorous removal was the most affected parameter since acidification not only recovers the coagulant, but also inorganic phosphorous along with organics and heavy metals [Chakraborty et al. 2017]. An average phosphorous removal of 56% was achieved with fresh coagulants and the removal dropped to 12% in cycle 2. TSS was the least affected parameter with removal declined from 86% for fresh coagulant to 75% for recovered iron, and 88% for fresh to 72% for recovered alum. Compared to our earlier work [Chakraborty et al., 2017] where approximately 65% reduction in COD was observed, the removal was lower in this case. This could be attributed to the additional organic loading in the form of methanol (which was used to dissolve the spiked MPs) which would affect the sCOD concentration in the effluent. Little to no effect (<10%) in particulate COD (pCOD) removal for alum and iron was observed in all three cycles. In real world samples, the results are expected to be more similar to the published work [Chakraborty et al., 2017], i.e. COD removal with fresh alum/iron can reach up to 65% while with the recovered coagulant, removal drops to around 56% with little to no effect on the TSS removals (<10%). There was no significant change in pH due to addition of the recovered coagulant as the volumetric ratio of recovered coagulant: PI was 1:333.

In a traditional wastewater treatment plant, coagulation using iron or alum is typically carried out for removal of the colloids. In that process, some of the dissolved organics can also be removed due to adsorption on the flocs and sludge. Acidification of sludge for recycling the coagulant has the potential to solubilize some of the MPs in the sludge. Thus, it was important to evaluate the percentage removal of the selected MPs using fresh and recovered iron and aluminum, respectively. Figure 5.2 shows the distribution of the selected MPs in the treated primary effluent with fresh and recovered aluminum and iron.

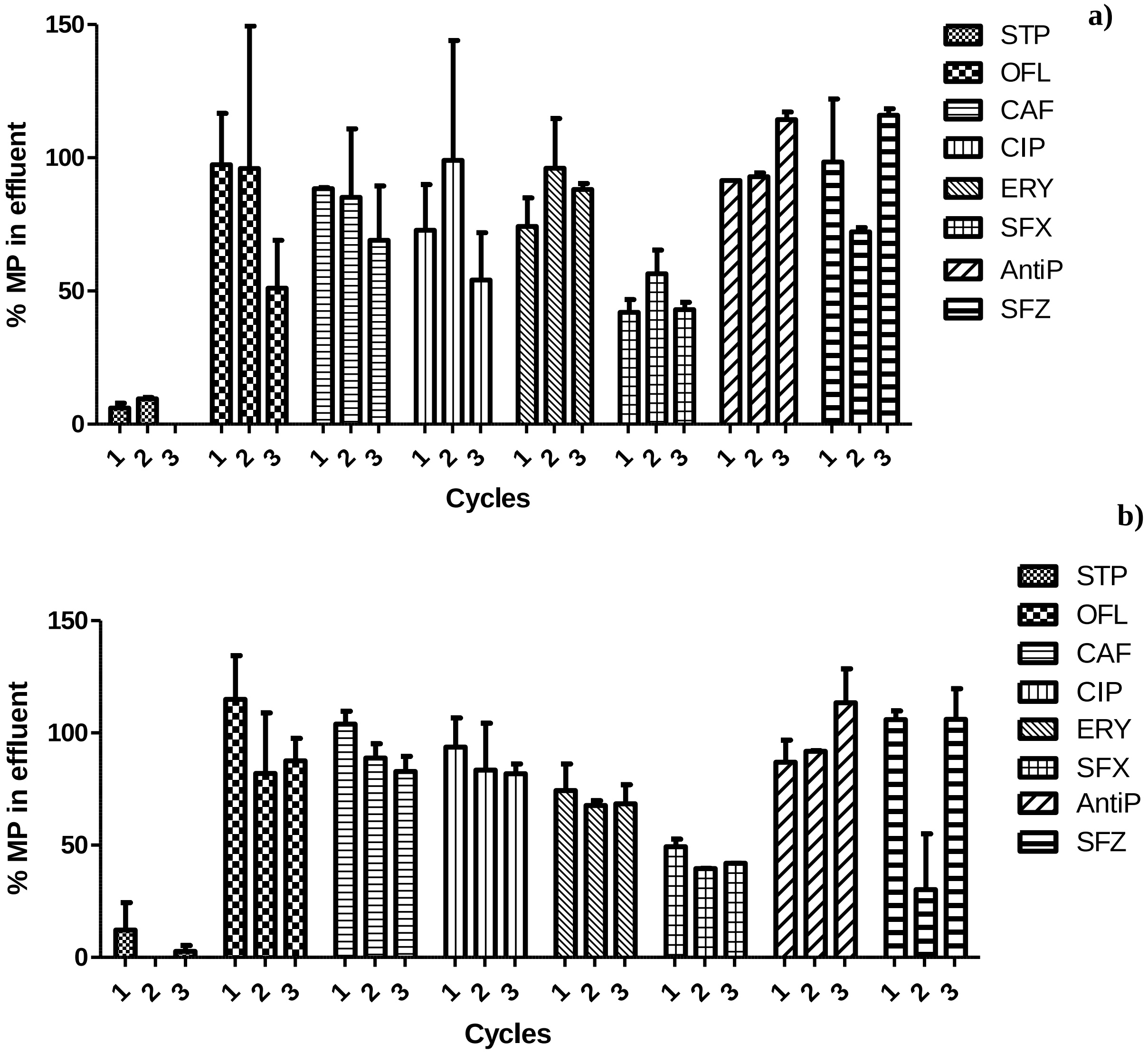

Figure 5.2: Concentration of MPs in effluent in each cycle with a) alum and b) ferric chloride

Cycle 1 refers to the distribution of MPs with fresh coagulant (alum or ferric chloride), while cycles 2 and 3 refer to the distribution of MPs with recovered coagulants. As mentioned previously, the tendency for MPs to accumulate on sludge solids can be determined by their K_{ow} values. According to Rogers (1996), compounds with log Kow <2.5 show low sorption, >2.5 log K_{ow} <4 have medium sorption while log K_{ow} >4 have high sorption potential. However, only the octanol-water coefficient values may not be adequate to estimate the sorption potential of the organics. This is particularly relevant in case of tetracycline and fluoroquinolone group of compounds [Michael et al., 2013]. For example, chlortetracycline (log K_{ow} = -3.6) and doxycycline (log K_{ow} = -0.02) which fall under the tetracycline group of compounds, should predominantly be present in the effluent, based on their log K_{ow}. However, studies [Kim et al. 2005; Drewes. 2008] have indicated the strong biosorption potential of these compounds as they form stable complexes with metals like Ca, Mg among others and remain undetected or detected at very low (ng/L) concentrations in secondary effluent.

Ciprofloxacin with a log K_{ow} <2.5 showed only 6% and 27% removal from the primary influent, using fresh ferric chloride and alum, respectively. In cycles 2 and 3, removal of ciprofloxacin ranged between 17% - 45% for recovered iron and aluminum coagulants. Watkinson et al. (2007) and Golet et al. (2003) in their studies have showed removal of ciprofloxacin ranging from 0% - 22% in primary treatment, which agrees with this work. Erythromycin, which falls under the macrolide group (with 14-, 15-, or 16- lactone groups) exhibits moderate log K_{ow} with very low water solubility and is marginally removed from the PI. At coagulation pH around 6-7, erythromycin would remain positively charged (pKa= 12.44) by protonation of the dimethylamino group, and may not be removed by cationic polymers of aluminum and iron. Approximately 26% removal of erythromycin was observed using fresh iron and alum, while in cycles 2 and 3, the removals were 4% - 12% and 34% with recovered alum and ferric chloride coagulant, respectively. This shows log K_{ow} may not be a good measure of adsorption potential of organics onto inorganic sludge produced by inorganic coagulants such as alum and iron complexes. Other factors such as pKa might play an important role by affecting the dissociation states of these MPs, their solubility and their orientation in the solute itself. If the pH value exceeds the pKa value, the charges on the MPs can be reversed and would follow a different pattern of distribution in wastewater [Bolong et al. 2009]. For example while majority of the MPs have a single pKa value, compounds like chlortetracycline (3.30, 7.40, 9.30) and doxyxyline (3.50, 7.70, 9.70) have three pKa values [Minh et al. 2010]. With a diverse range of pKa, predicting the distribution of these compounds becomes very challenging.

For antibiotics such as sulfamethoxazole, sulfathiozole and ofloxacin with very high solubility and low log K_{ow} values, negative to very little removal by coagulation was observed. This could be attributed to their high solubility and presence of unanalyzed conjugates [Gobel et al.2007].

Fluoxetine, chlorhexidine with very log K_{ow} values and moderate water solubility are expected to remain in the effluent, however, they could not be detected in the effluent for any of the cycles possibly due to unquantified experimental or analytical errors. Consistent with the low log K_{ow} value, removal of antipyrine was less than <15%. This is consistent with literature [Lin et al., 2016] where 16% removal of antipyrine via coagulation-flocculation and sedimentation was reported. Caffeine, which is consumed worldwide daily, has been found present in copious amounts in different wastewater plants [Behara et al., 2011]. With extremely low log K_{ow} value and high water solubility, little to negative removal of caffeine occurred for both fresh and recycled coagulants. Behara et al. (2011) reported negligible removal of caffeine in primary treatment. Overall, results in this section indicate that the removal of the MPs from primary influent by both recovered alum and ferric chloride coagulants is dictated by their water solubility, log K_{ow} and pK_a values, and that the removal was not affected by the recycled coagulants.

The possibility of building up of MPs due to acid solubilization in recycled coagulant can be detrimental for recycling the coagulants. The concentrations of the detected MPs in recycled coagulants are summarized in Table 5.3.

Table 5.3: Concentration of the MPs in recovered aluminum and iron coagulant

Application/Type	Compound	Minimum detection limit (µg/mL)	Conc. of MPs in recovered aluminum (mg/L)	Conc. of MPs in recovered iron (mg/L)
Food Additive	caffeine	0.0010	0.03-0.35	0.03-0.18
Disinfectant	chlorhexidine	0.005	1.8-13	2.06-10.4
Antihistamine	diphenhydramine	0.005	0.14-0.65	0.1-0.4
Antidepressant	amitriptyline	0.005	<DL	<DL
Antidepressant	fluxentine	0.005	<DL	<DL

Analgesic	antipyrine	0.005	<DL	<DL
Analgesic	diclofenac	0.005	<DL	<DL
Antibiotic	streptomycin	0.0010	<DL	<DL
Antibiotic	ofloxacin	0.005	0.33-0.61	0.18-0.40
Antibiotic	ciprofloxacin	0.005	<DL	<DL
Antibiotic	sulfathiazole	0.005	<DL	<DL
Antibiotic	sulfamethoxazole	0.005	0.02-0.12	0.02-0.03
Antibiotic	erythromycin	0.005	0.01-0.02	<DL
Antibiotic	clarithromycin	0.005	0.04-0.09	0.04-0.05

<DL denotes below detection limit.

It is evident from Table 4.3, most of the MPs were not present in the recovered coagulant except for caffeine, chlorhexidine (disinfectant), and antibiotics such as ofloxacin, sulfamethoxazole, and erythromycin. However, dosing the PI with recovered coagulant did not result in detectable concentration of these compounds either in treated PI effluent or sludge as the dosage of acidified coagulant was only 3 mL/L (corresponds to dosages of 37 mg of recovered aluminum/liter PI and 14.3 mg of recovered iron/liter PI). This was the case even for chlorhexidine with the highest concentration (1.8-13 mg/L) in the recovered aluminum, it could not be detected in the primary effluent after dosing with the recovered coagulant. Thus, the potential of building up of MPs due to acidified recovered aluminum and iron coagulants in the treated effluent is not significant. Most of the selected MPs in this work are bases except for antipyrine, which will remain protonated at acidification pH of 1.5; having very low solubility. However, caffeine, chlorhexidine, ofloxacin, sulfamethoxazole have much higher solubility, this could be the reason why they were detected in the acidified coagulant. Only exception is erythromycin, which was detected in recycled coagulant although it showed lower removal from PI due to coagulation and low solubility.

As mentioned previously, compounds with log K_{ow}>2.5 are expected to partition primarily on the solids. For MPs like CLA, DPH, DIC and AMI, it is important to know their distribution with acidification of the primary sludge. The distribution of these compounds in the sludge is presented in Figure 5.3 at different cycles.

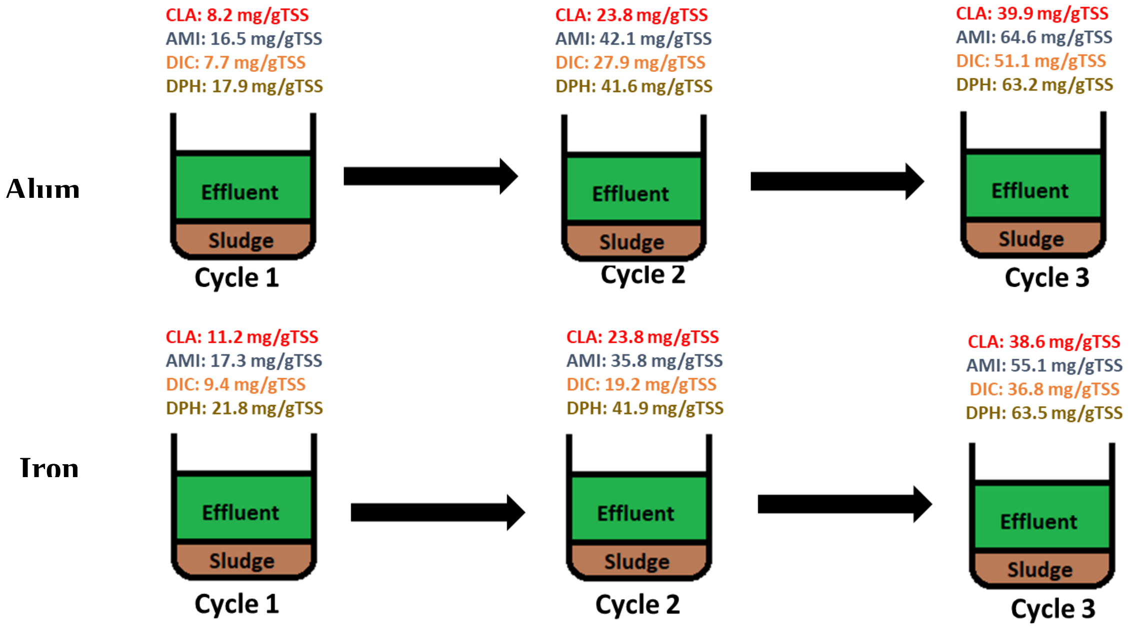

Figure 5.3: Distribution of MPs (log K_{ow}>2.5) in sludge

For all the MPs, a steady build-up in the sludge using fresh and recovered aluminum and iron coagulants was noticed, due to the spiking of the MP before each cycle. CLA removals of 56% and 42% by fresh alum and iron with lower removals with the recovered coagulants were observed. This is within the range as reported in literature [Sponberg and Witter. 2008; Estrada-Arrianga et al. 2016] in a typical municipal WWTP employing coagulation for primary treatment. DPH, which falls under the category of antihistamine, has seen seasonal variations in its concentrations at the WWTP [Du et al., 2014]. Studies on the fate of AMI in primary treatment have been limited. Both AMI and DIC in the increased in the sludge with each cycle for both fresh and recovered coagulants and could not be detected in the recovered coagulants (Table 5.3). Average removals with aluminum and iron ranged between 5% - 15% which is in agreement with Vieno and Sillanpaa (2014). Slight variations in measurements could be attributed to experimental error and over ionization of compounds using LC-MS. As MPs in the sludge have no disposal guidelines, an EPA report found the concentrations of these MPs to be: CLA: 1.57 – 40.2 mg/g dry solids; AMI: 275 mg/g dry solids; DIC: 209 mg/g dry solids and DPH: 15 – 7000 mg/g dry solids. Our values obtained experimentally are well below the above mentioned range.

5.3.4 Sorption of selected MPs on coagulated primary sludge

The distribution coefficients of MPs between liquid and solid phases of sludge were estimated by assuming equilibrium between the two phases. The distribution ratio (K_d) was calculated as described by Ternes et al. (2004).

$$K_d = \frac{Cs\ /TSS}{C_W} \quad (1)$$

Where C_s is the concentration of the MP in the solid phase (mg/L), C_w is the concentration in the liquid phase (mg/L), and TSS is the total suspended solids in kg/L. The experimentally determined K_d for various MPs are compared with the existing values in literature and are presented in Table 5.4. It needs to be noted that the K_d values presented here are approximate estimates, as the chemical characteristics of coagulated sludge using alum and ferric chloride are different from that of suspended solids with considerable organic fraction. Additional variabilities can occur due to non-equilibrium, possible inhomogeneity of the primary sludge, and not taking into consideration the conjugates or the by-products.

Table 5.4: Experimental versus literature K_d values for compounds with log K_{ow}>2.5

Compounds	**Experimental K_d (L/Kg TSS) from cycles 1;2;3**	**K_d (L/Kg TSS) from literature**
Clarithromycin	3.8; 3.3; 3.3 (alum complexes*) 3.7; 3.6; 3.4 (iron complexes)	2.4 (Lautz et al., 2017)
Diphenyhydramine	1.9; $1.7^{\#}$ (alum complexes) 1.7; $2.1^{\#}$ (iron complexes)	2.7 (Ternes et al., 2004)

Amitryptiline	2.9; 2.4$^{\#}$ (alum complexes) 2.9; 2.9; 2.9 (iron complexes)	2.9 (Das et al., 2017)
Diclofenac	3.1; 2.6; 1.9 (alum complexes) 2.1; 2.6; 3.6 (iron complexes)	2.5 (Das et al., 2017)

*- complexes refer to fresh aluminum/iron and recovered coagulants; $^{\#}$- K_d could not be calculated due to negative removals

The K_d values determined in this work are quite comparable with the literature values, even though the nature of CEPT sludge can be very different from the primary sludge due to the presence of inorganic polymers of alum and ferric chloride. The primary mechanisms responsible for sorption onto primary or secondary sludges are electrostatic interactions between the negatively charged surfaces of the micro-organisms with the positively charged groups of the MPs and hydrophobic interactions between the aromatic and aliphatic groups with the lipid fraction of the sludge coupled with cell membrane of the micro-organisms. For MPs which are protonated/deprotonated, pH and composition of the sludge plays an important role in deciding the K_d value [Ternes et al., 2004]. This is particularly important for our study as the MPs go through a wide range in pH during recycling and recovering the coagulant. Majority of the K_d values for the MPs except CLA seems to be within the range as reported in literature while the slight variations in each cycle could be attributed to the change in pH the MPs encounter during coagulant recovery. Based on the obtained values, sorption doesn't seem to be the only mechanism for removal of MPs, biodegradation might also be responsible. However, this is questionable given the amount of time these solids are present in the primary clarifiers and difficult to prove owing to the complex wastewater matrix. The performance of both coagulants was comparable although ferric chloride seems to have slightly better performance in removing the MPs. Study by Estrada-Arianga et al. (2016) on multiple WWTPs revealed that ferric chloride performed better in removing certain MPs like androstenedione, oxytetracycline, hydrochlorothiazide, triclocarban, limcomycin, rantidine among others which seems to be in sync with our findings.

5.3.5 Chelation of MPs with iron, aluminum and probable mechanism of attachment

It is well established that tetracycline group of compounds like chlortetracycline, doxycycline among others, have high affinity to form chelates with metals like iron, magnesium, calcium and aluminum [Potgeiter et al., 2007]. In case of tetracycline group of compounds, high polarity coupled with aqueous solubility (both pH dependent) play an important role in dictating sorption on to solids and environmental mobility [Gu and Karthikeyan. 2005]. Presence of tricarbonylamide, phenolic diketone and dimethylamine groups make pH a deciding factor for solubility and lipophilicity. Tetracyclines generally have three pKa values (3.3, 7.7, 9.7) which are responsible for this group of compounds to exist as cationic, zwitterionic and anionic species in acidic, neutral and alkaline conditions. This ionization behavior has been known to enhance tetracycline sorption to soil particulates. These analytes were not detected in the wastewater samples however, in the calibration curve used, these compounds were detected as the protonated $[M+H]^+$ ion. To investigate the potential that the compounds were present in the wastewater samples and were being ionized with a different adduct or undergoing ionization suppression, different concentrations of these compounds were added to distilled water followed by the addition of either alum or ferric chloride coagulants. The measured concentrations of these compounds in MilliQ water with and without fresh coagulants are presented in Table 5.5.

Table 5.5: Chelation of compounds in MilliQ water

Samples	**Doxycycline (mg/L)**	**Chlortetracycline (mg/L)**
MilliQ + MP	3 ± 0.1	3.5 ± 0.3
MilliQ + $FeCl_3$ + MP	1.3 ± 0.2	2.1 ± 0.1
MilliQ + Alum + MP	1.45 ± 0.01	1.95 ± 0.01

As evident from the results presented above, the concentration of the MPs in water was reduced by the addition of fresh iron or alum. No evidence of iron or aluminum adducts of these analytes was found, however the reduction in water concentration could be attributed to possible chelation with the coagulants into non ionizable forms or ionization suppression. Other possibilities include reactions between the metals and the analytes, as has previously been shown for iron and tetracycline. Figure 5.4 attempts to provide possible attachment positions of iron and aluminum to the tetracycline group of compounds, primarily chlortetracycline and doxycycline.

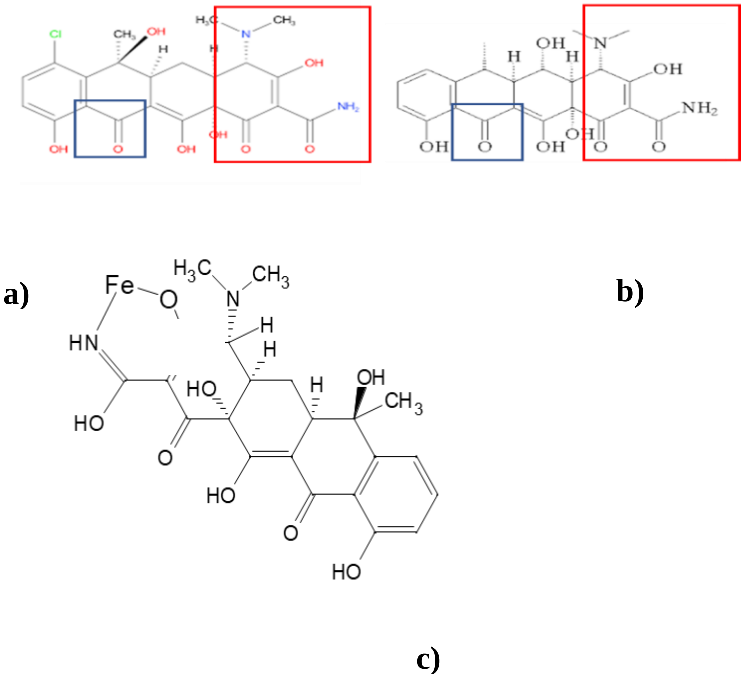

Figure 5.4: Possible attachment positions of iron and aluminum to a) chlortetracycline, b) doxycycline, c) tetracycline

Tetracycline group of compounds forms complexes with cationic metals especially Al^{3+} and Fe^{2+}/Fe^{3+} with formation constants (log K) 0f 12.5 and 13.4 respectively [Gu and Karthikeyan. 2005]. These values have been reported to very similar to other chelating agents, for example log K for Fe complexation with nitrilotriacetic acid and citric acid has been reported to be 15.9 and 11.4, respectively [Martell. 1975], while Al-EDTA complexation has a log K value of 19.07 [Sparks. 1999]. Aluminum and iron hydroxides are considered potential basins for organic/inorganic contaminants due to their high surface area and reactivity [Huang et al. 1977; Goldberg and Johnston. 2001]. Initial formation of Al/Fe:tetracycline complexes at a 1:1 molar ratio, later transitioning to a 2:1

ratio at equilibrium has been proposed by Gu and Karthikeyan (2005). They reported the formation of a binuclear complex due to reactions occurring between charged and uncharged neighboring sites.

Studies [Myers et al. 1983; Gu and Karthikeyan. 2005] have indicated that tetracycline complexation with aluminum and iron hydroxides to be occurring at the tricarbonylamide (C-1:C-2:C-3 in ring A) and carbonyl (C-11 in ring C) functional groups (indicated by boxes in Figure 4), while Santos et al. (2000) reports the involvement of the oxygen (O11, O12) along with the tricarbonylamide group to be responsible for surface chelation al Al/Fe. We predict the possibility of a tridendate complex with the phenolic and the amine group (Figure 5.4c). These groups are known to bind cations like iron and aluminum in general.

Moreover, due to the complexity of the wastewater matrix, similar reactions by other metal cations like calcium, magnesium among others, remain a strong possibility, making it difficult to predict the exact attachment positions of all these cationic metals.

5.4 Conclusions

Aluminum and iron coagulants were successfully recovered after coagulation of municipal primary influent and the effects of these recycled coagulants on various water quality parameters were determined. Recovered iron and aluminum coagulants behaved similarly in terms of COD, TSS and phosphorous removal when compared to fresh coagulants. The removal of phosphorous was the most affected parameter due to the recycling of coagulants, while TSS and COD removals were less affected. The removal of MPs during coagulation was compound specific with varying degrees of removal by aluminum and iron. The MPs (with log K_{ow}<2.5) remained in the effluent as expected. Marginal buildup of the MPs in sludge (with log K_{ow}>2.5) was observed with each cycle, however negligible quantities of these MPs were found in the recovered coagulants. Majority of the MPs excepting chlorhexidine (<10%), were not recycled due to coagulant recovery. MPs like sulfamethoxazole, ofloxacin, and sulfathiazole showed very poor or negative removals due to either dissolution from bile and faeces in wastewater or due to presence of unanalyzed conjugate compounds. Chlortetracycline and doxycyline indicated chelation capability with Al^{3+} and Fe^{3+} and others and their tentative positions of attachment were identified. This study demonstrated that there is no threat of accumulation of MPs in the recycled coagulants for chemically enhanced primary treatment.

5.5 References

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Chapter 6

6 Anaerobic digestion of recovered chemically enhanced primary sludge and its effect on iron phosphorous speciation

6.1 Introduction

At present, municipal wastewater treatment plants are exploring and implementing technologies that can reduce operations and maintenance costs through resource recovery including water reuse, nutrient recovery and enhanced energy recovery. Chemically enhanced primary treatment (CEPT) an effective carbon diversion technology, is often combined with anaerobic digestion (AD) to increase energy generation and reduce aeration energy in municipal wastewater treatment plants [Haydar and Aziz. 2009]. CEPT is an advanced primary treatment process where inorganic coagulants like alum, ferric chloride among others are used to settle the colloids/suspended solids in wastewater. The use of CEPT in treating municipal wastewater has been gaining prominence due to its effectiveness in removing solids, ease of implementation and low energy requirements [Murugesan et al. 2014]. However, one of the major disadvantages of this process is the production of excess sludge which needs to be treated appropriately before disposal. Around 40% of the treatment cost in a wastewater plant is due to sludge (biosolids) handling and disposal [Xu et al. 2009]. Partial cost recovery can be accomplished by recovering coagulant and energy using AD.

Recovering coagulant from sludge not only minimizes the cost of disposal by reducing sludge volumes, but also the cost of dosing fresh coagulant [Keeley et al. 2012, 2014, 2016]. Acidification, basification, ion exchange and membrane processes are primarily employed to extract the coagulant from the sludge with acidification being the cheapest and the most cost effective method [Chakraborty et al. 2017]. However, dissolution of organics during coagulant recovery in the form of phosphorous, carbon, nitrogen along with heavy metals might be a limitation. This can be addressed by using membrane and ion exchange processes which will reduce the marginal cost benefits of the coagulant recovery process. Studies [Xu et al. 2005, 2009; Chakraborty et al. 2017; Jimenez et al. 2007; Yang et al. 2014] have shown the feasibility of re-using recovered coagulants in synthetic wastewater, municipal wastewater, drinking water and its reuse potential. Chakraborty et al. [2017] demonstrated that the concentrations of heavy metals in primary effluent treated with recovered aluminum were below the discharge limits for most metals. Using acidified coagulant for CEPT might affect the bio-gas formation potential of CEPT sludge, however none of the earlier studies investigated the effect of reused acidified coagulant on AD of the recovered sludge or its impact on methane production. Moreover the impact of heavy metals on AD has already been established [Metacalf and Eddy. 2003], however the effect on AD due to addition of the recovered coagulant needs to be investigated.

The use of anaerobic digestion (AD) in wastewater treatment to reduce sludge volumes, pathogens and stabilization of solids is a common practice. CEPT sludge when compared to ordinary primary sludge has been reported to have different compositions due to its ability to incorporate more organics, metals (Fe, Al, Ca, Mg among others) and polymers [Sanin and Clarke. 2011]. This compositional difference between CEPT and primary sludge has been linked to differences in methane production during AD [Ju et al. 2016]. AD of CEPT sludge has been eliciting interest as CEPT is not only a well understood process but also easy to retrofit into an existing municipal wastewater plant. Recent studies by Ju et al. 2016; Murugesan et al. 2014; Kurade et al. 2016 and Obulisamy et al. 2016 have reported the use of CEPT sludge as a substrate for AD, microbial community analysis and the effect on dewaterability of the CEPT sludge after AD. However, none of these studies focused into the speciation of solids especially the Fe-P compounds or the feasibility of using sludge obtained by recovering and recycling coagulants. While the Al-P chemistry has been well studied, knowledge on the Fe-P chemisty has been limited. This is particularly important as the Fe-Ps in AD generally tend to precipitate as vivianite [Roussel et al. 2016], however, their might be formation of new Fe-P species in the sludge obtained from using recovered coagulant which needs to be investigated. Thus, this study aims to understand the fate of Fe-P speciation in CEPT sludge, recovered sludge from recycled iron coagulant before and after AD, and the methane production potential of these sludge.

6.2 Materials and methods

6.2.1 Sludge collection

Various water quality parameters such as TP, sP, TN, TSS, COD, and sCOD of the PI collected from the Adelaide water pollution control plant (WPCP) (London, Ontario, Canada) were measured. A 1g/L ferric chloride [$FeCl_3$] stock solution made in distilled water was used to treat the collected PI. A jar test apparatus (Phipps & Bird PB-900) was used to mix the solution at a fast rate (100 rpm) for 1 minute followed by a slow rate (30 rpm) for 20 minutes. The flocs formed were then allowed to settle for 30 minutes and thereafter collected, while the effluent was analyzed for all the water quality parameters mentioned above.

6.2.2 Recovery and reuse of ferric coagulant

The coagulated PI with sludge was centrifuged at 3500 RPM for 5 minutes and the sludge was collected after centrifugation. Collected sludge was then acidified to pH 1.5 using 36 N H_2SO_4. The acidified sludge was mixed using a magnetic stirrer at 270 RPM for 60 minutes and then centrifuged at 3700 RPM for 10 minutes. The recovered iron coagulant was obtained from the supernatant of the centrifuged sludge and dosed to fresh batches of PI. The entire procedure was repeated for two cycles and the recovered iron concentration along with the water quality parameters were monitored in each cycle. Addition of the recovered coagulant did not affect the pH of PI as the volume of coagulant: volume of PI was 1:333.

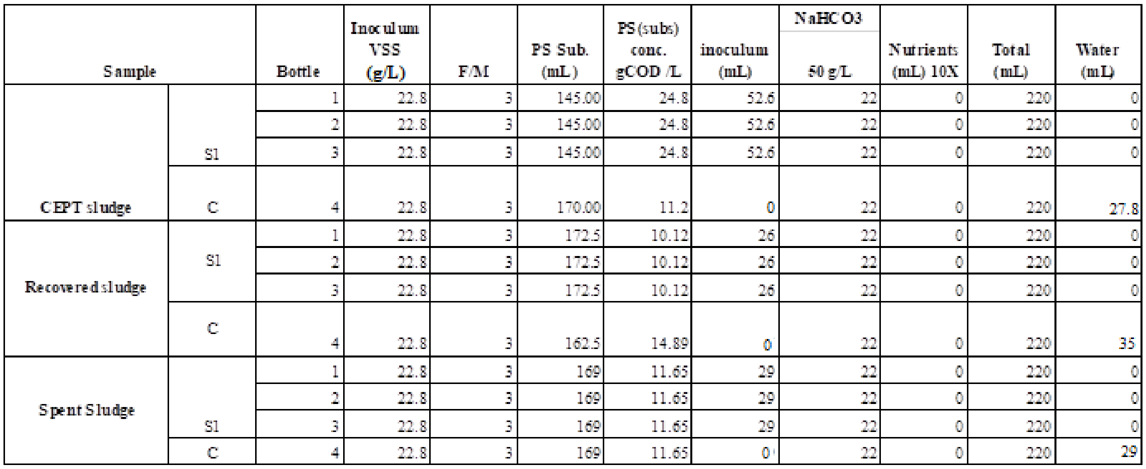
6.2.3 Experimental setup

Triplicates of chemically enhanced primary sludge obtained from addition of fresh $FeCl_3$ to PI, recovered sludge obtained from use of recovered coagulant and spent sludge (from cycle 1) from the coagulant recovery process was mixed with anaerobic digested sludge (ADS; inoculum obtained from Stratford, Ontario) at an F/M ratio of 3:1 based on the following equation:

$$F/M = \frac{COD\ of\ substrate \left(\frac{g}{L}\right) x\ volume\ of\ substrate\ (mL)}{VSS\ of\ inoculam \left(\frac{g}{L}\right) x\ volume\ of\ inoculam\ (mL)} \qquad (1)$$

Table 6.1 provided the experimental setup in a tabulated form. Each of the three categories of sludge had its own control where water was substituted instead of the inoculum. A pure inoculum devoid of any water/sludge was also used in the experimental setup. All experiments were carried out in 250 mL glass Wheaton bottles, in an orbital shaker (Thermo fisher Scientific, Max Q 4000) at 37°C for 15 days. Sludge samples were adjusted to a pH of around 7.2. Methane content was determined daily by a GC (Model 310, SRI Instruments, Torrance, CA) with a thermal conductivity detector (TCD) and a molecular sieve column (Molesieve 5A, mesh 80/100, 6 ft 2mm, Restek). Argon was used as the carrier gas at a flow rate of 30 mL/min.

Table 6.1: Experimental setup



Sample		Bottle	Inoculum VSS (g/L)	F/M	PS Sub. (mL)	PS (subs) conc. gCOD /L	inoculum (mL)	NaHCO3 50 g/L	Nutrients (mL) 10X	Total (mL)	Water (mL)
CEPT sludge	S1	1	22.8	3	145.00	24.8	52.6	22	0	220	0
		2	22.8	3	145.00	24.8	52.6	22	0	220	0
		3	22.8	3	145.00	24.8	52.6	22	0	220	0
	C	4	22.8	3	170.00	11.2	0	22	0	220	27.8
Recovered sludge	S1	1	22.8	3	172.5	10.12	26	22	0	220	0
		2	22.8	3	172.5	10.12	26	22	0	220	0
		3	22.8	3	172.5	10.12	26	22	0	220	0
	C	4	22.8	3	162.5	14.89	0	22	0	220	35
Spent Sludge	S1	1	22.8	3	169	11.65	29	22	0	220	0
		2	22.8	3	169	11.65	29	22	0	220	0
		3	22.8	3	169	11.65	29	22	0	220	0
	C	4	22.8	3	169	11.65	0	22	0	220	29

*- where PS stands for primary sludge used as substrate in this study

6.2.4 Analytical methods

The pH was measured with a digital pH-meter (HACH, HQ11d). COD, sCOD (solution filtered through 0.45 µm) were measured using HACH method 8000. TP, sP (filtered through 0.45 µm) was measured using method 10209; TN (method 10242) was measured by HACH methods. TSS and VSS were measured according to standard APHA methods (method 2540d). Gas measurements were taken using a GC-TCD (Model 310, SRI Instruments, Torrance, CA). A volume of 0.5 ml of biogas was used to measure the CH_4

content by injecting into the GC. Using Eq. (1), CH_4 production was calculated from headspace measurements of gas composition and the total volume of biogas produced.

$$V_{CH4,i} = V_{CH4,i-1} + V_{G,i} X_{CH4,i} + V_{h,i} (X_{CH4,i} - X_{CH4,i-1}) \qquad (1)$$

where $V_{CH4,i}$ and $V_{CH4,i-1}$ are cumulative CH_4 gas volume at current (i) and previous (i-1) time intervals. $V_{G,i}$ is the total biogas volume accumulated between the previous and current time intervals and $V_{h,i}$ is the total volume of the headspace of the reactor bottle in the current interval. $X_{CH4,i}$ and $X_{CH4,i-1}$ are the fractions of CH_4 gas in the headspace of the reactor bottle in the current and previous intervals.

6.3 Results

6.3.1 Variations in influent wastewater and coagulant dosing

The PI was collected from Adelaide water pollution control plant (WPCP) and experiments were conducted during October –November, 2018. The different water quality parameters are presented in Table 6.2.

Table 6.2: Variations in the water quality parameters

Parameters	**Values (mg/L)**
Total suspended solids (TSS)	245 ± 28 (5)*
Volatile suspended solids (VSS)	223 ± 25 (5)
Chemical oxygen demand (COD)	421 ± 39 (5)
Soluble chemical oxygen demand (sCOD)	152 ± 25(5)
Total nitrogen (TN)	38 ± 12 (5)
Ammonia (NH_3-N)	27 ±1.5(5)
Total phosphorous (TP)	9 ± 0.8 (5)
Soluble phosphorous (sP)	6.2 ± 1.1(5)

***-** Numbers in parentheses indicate number of samples

The slight variations in water quality could be attributed to the diurnal differences in the water entering the plant which contributed to the fluctuations in the dataset. The PI collected was then subjected to coagulation by fresh $FeCl_3$. An optimized dose of 40 mg/L of $FeCl_3$ was used based on TSS and TP removals.

6.3.2 Characteristics and effect of AD on the different kinds of sludges

As mentioned previously, three different kinds of sludge were used in this study. The first one generated from CEPT treatment, known as CEPT sludge, the second one from addition of the recovered coagulant to fresh PI, known as recovered sludge and finally, the residual solids during coagulant recovery process, known as spent or waste sludge. Triplicates of each of these sludge types along with their individual controls (1 from each category) were mixed with ADS at an F/M ratio of 3:1 and methane production was monitored daily. It is worth mentioning here, that the control samples had sludge with water instead of inoculum added to it, Table 6.3 represents the effect of AD on the sludge.

Table 6.3: Effect of AD on the sludges

Sample	**% COD removal**	**%TSS removal**	**%VSS removal**	**%TS removal**	**%VS removal**
CEPT control	22±5.2	27±2.4	17±3.8	37±3	25±2.8
CEPT sludge	54±2	40±1.2	25±2.1	50±2	52±1.4
Recovered control	11±3.4	22±3	15±1.4	21±3	28±3
Recovered sludge	54±3	42±4.7	25±2.3	49±2.1	51±2.2
Spent control	14±2.8	33±1.3	19±3.8	38±56	26±4
Spent sludge	24±3.1	41±3	22±2.2	43±1.5	47±2.1

*- average values of triplicate samples have been used for calculations

During AD, conversion of organic matter to methane and carbon dioxide occurs through hydrolysis, acidogenesis, acetogenesis and methanogenesis [Jang et al. 2017]. In case of COD removal, both the CEPT and recovered sludge showed similar removal (54%) after AD, while the spent sludge had only 24% removal of COD. The spent sludge which is the residual solids after the acidification phase of coagulant recovery is expected to have been stripped of majority of the easily digestible organics, correspondingly showing lower removals during anaerobic digestion. It should be noted that COD of the effluent increases marginally after the addition of acidified coagulants to the primary influent. Around 40% - 42% of TSS and 22% - 25% of VSS removals were achieved for all the sludge samples. Similar trends in TS (50% and 49%) and VS (52% and 51%) removals were observed for the CEPT and the recovered sludge, respectively. One of the primary parameters that dictates the performance of AD, is the reduction of VS in the digestion process [Elsayed et al. 2016, Hao et al. 2017]. Studies under mesophilic conditions during AD by Jang et al. (2017) and Park and Novak (2013) achieved 44% - 55% VS removals of CEPT sludge employing $FeCl_3$. Our result of 51% VS reduction is consistent with the reported VS removal. Jang et al (2017) compared primary sludge with CEPT sludge and concluded that addition of $FeCl_3$ played a pivotal role in removal of VS in AD. Additionally, reduction in VS during AD of CEPT sludge is attributed to the dissimilatory reduction of Fe^{3+} [Zhang et al. 2014]. Other than theVS, pH and volatile fatty acids (VFA) play important roles in having stable methane production [Jun et al. 2009] during AD. In this study, low concentrations of total VFAs (84 mg/L – 114 mg/L) of all the three sludge were observed during AD. pH for all experimental sets were maintained in the range of 7.2-7.4.

As mentioned previously, all three sludge were subjected to AD at mesophilic conditions (37^o C) for 15 days and methane production was determined daily. Figure 6.1 shows the cumulative methane production/gCOD of substrate added.

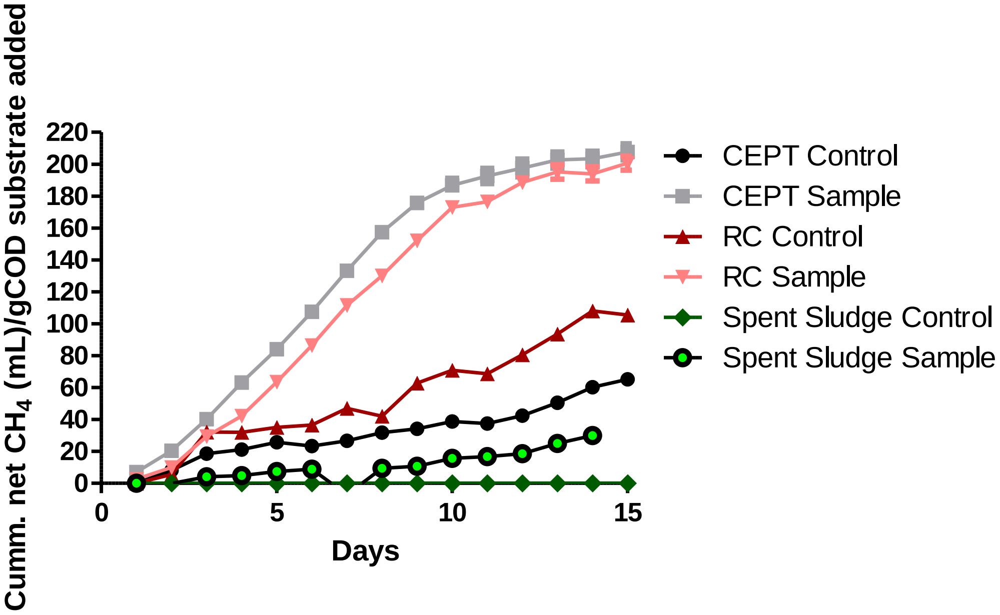


Figure 6.1: Daily methane production of the sludges

The data for cumulative methane productions on daily basis of all the sludge has been presented in Appendix D. As shown in Figure 6.1, cumulative methane production of the CEPT sludge and the recovered sludge was almost the same reaching a maximum of 205 mL of methane/g COD added. While the spent sludge reached a maximum of 50 mL of methane/g COD added. This is expected, as the spent sludge is almost devoid of organics that essentially is converted to methane in AD. Earlier, CEPT sludge had shown higher methane formation in mesophilic conditions by roughly around 47 mL from primary or non-CEPT sludge [Jang et al. 2017]. Additionally, the highest methane yield as reported by the study [Jang et al. 2017] is very similar (approx. 10% difference) to what we observed in our study.

Presence of heavy metals such as nickel, chromium, copper and others such as potassium, calcium, is known to cause toxicity to the microbial biomass and hinder methane production in AD [Metcalf and Eddy. 2003]. All three sludge were tested for metal concentrations and the results are presented in Table 6.4.

Table 6.4: Metal concentrations of the different sludges before and after AD

Anions and Nutrients (Water)	Detection limit		CEPT C	CEPT C	CEPT S	CEPT S	RC C	RC C	RC S	RC S	SS S	SS S
Chloride (Cl)	1	mg/L	116	112	211	230	147	99	145	143	68	65
Sulfate (SO4)	0	mg/L	122	0	229	0	118	0	164	0	707	0
Aluminum (Al)-Total	0	mg/L	4	3	29	32	8	6	14	15	12	12
Barium (Ba)-Total	0	mg/L	1	1	6	7	1	1	3	3	3	3
Calcium (Ca)-Total	0	mg/L	172	158	617	734	224	173	319	338	174	198
Chromium (Cr)-Total	0	mg/L	0	0	2	2	0	0	1	1	1	1
Copper (Cu)-Total	0	mg/L	1	1	10	11	3	2	5	5	5	5
Iron (Fe)-Total	0	mg/L	303	257	202	241	173	156	747	774	720	855
Magnesium (Mg)-Total	0	mg/L	23	21	71	79	32	24	41	41	21	23
Manganese (Mn)-Total	0	mg/L	1	1	13	16	1	1	6	6	6	6
Potassium (K)-Total	0	mg/L	22	22	46	51	34	25	35	36	12	12
Silicon (Si)-Total	0	mg/L	7	8	51	59	9	11	25	28	28	32
Sodium (Na)-Total	0	mg/L	1413	1422	1472	1498	1305	1400	1409	1400	1710	1665
Strontium (Sr)-Total	0	mg/L	1	1	24	27	1	1	10	11	11	12
Sulfur (S)-Total	1	mg/L	41	18	122	62	47	23	68	23	246	31
Titanium (Ti)-Total	0	mg/L	0	0	2	3	0	0	1	1	1	1
Zinc (Zn)-Total	0	mg/L	2	2	21	24	4	3	10	11	9	10

Sample headers in red represent samples after AD, while ‘C’ stands for control and ‘S’ for sample. The inhibitory concentrations of the metals as adopted from Metcalf and Eddy (2003) are: sodium > 5500 mg/L, potassium > 4500 mg/L, calcium > 4500 mg/L, magnesium > 1500 mg/L, copper > 70 mg/L, nickel > 30 mg/L, chromium > 30 mg/L. All the metals are well below the inhibitory levels and reduction in methane formation due to metal toxicity should be minimal.

6.3.3 Gompertz parameters

Gompertz model assumes that the biogas production is proportional to the microbial activity and the modified Gompertz Eq. (1) is used to predict the methane production. Originally this model was used to describe bacterial growth in batch mode [Lay et al. 1997; Nielfa et al. 2015].

$$H = P.\exp[\frac{-\exp(Rm.e)}{P(\lambda - \mathrm{t})} + 1] \qquad (1)$$

In order to determine the maximum specific biogas production rate, Rm (ml/hr) maximum specific cumulative biogas production of P (ml), and lag time λ (h) has been used to predict the following Gompertz parameters with an R^2 value of 0.99.

Table 6.5: Gompertz parameters for the sludges

Gompertz parameters	**CEPT sludge**	**Recovered sludge**	**Spent sludge**
R_m (mL/h)	41.4	28	0.1
P (mL)	873.4	664.2	5.2
λ (h)	44	63	220

The Gompertz model was used in the current study and it showed an excellent fit (R^2 value of 0.99) and has been presented in Appendix D. As expected, the spent sludge had the highest lag time, which is evident from the methane production rate. The CEPT sludge had the lowest lag phase (44 hours) and the highest biogas cumulative production (873.4 mL), while the recovered sludge was not far behind with a lag phase of 63 hours and biogas cumulative production of 664.2 mL.

6.3.4: Fe-P and Fe-S speciation in AD

The precipitation of Fe and P solid species at equilibrium before and after the anaerobic digestion of all the three different wastewater sludge was predicted based on the measured total elemental or species concentrations (Table 6.4). The pH for AD has been assumed to be steady at pH 7.2. The pe is not explicitly measured but estimated from the typical range of oxidation-reduction potential (ORP) documented for the anaerobic conditions in wastewater treatments (i.e., from -600 to -300 mv). The pe estimation is based on a silver-silver chloride reference electrode and following conversion Eq (2):

$$pe = [(\frac{ORP}{1000} + 0.208)/0.059] \qquad (2)$$

This corresponds to a pe range from -6.64 to -1.56. The sensitivity of the modeling results to the pe variation within this range is evaluated with a pe increment of 0.33. The complexation reactions of the wastewater DOC with the principal cations and anions are not considered because of the lack of stability constants and binding capacity for defining these reactions. The total sulfur ($[S_T]$) instead of $[SO_4^{2-}]$ has been treated as an input, for considering the possible conversion from SO_4^{2-} to sulfide under anaerobic conditions. The total Ba, Cr, Cu, Mn, and Ti are not considered as inputs because their concentrations are at trace levels as compared to other cations.

A geochemical model, PHREEQC, was employed for the prediction purpose, and the Minteq database was selected as it includes a wide variety of speciation and precipitation reactions with the involvement of the elements or species identified in Table 6.4. The Minteq database was assumed to be accurate and adequate to describe the complexity of the wastewater system. Two values for the K_{sp} of vivianite were tested (10^{-36} and 10^{-32}). This specific range of K_{sp} values has been reported in the literature [Nanzyo et al. 2010].

An essential step for modeling the precipitants at equilibrium is to define precipitant species. Although many different precipitants are available in the database, we selectively defined the species most relevant to the wastewater and our interests in the Fe-P/Fe-S solid phases. Specifically, only the ferric hydroxide ($Fe(OH)_3(a)$), denoted as ferrihydrite in the Minteq database, was considered for the precipitation due to the alkaline condition (pH = 7.2). Other iron oxide solids, such as hematite, were not included due to their requirement of aerobic conditions and slow kinetics. Siderite, vivianite, strengite, struvite, SrHPO4(s), FeS, pyrite, mackinawite, and greigite are included for the high [CO_3^{2-}], [P], [S], [NH_4^+] [Mg], and [Sr].

To facilitate the modeling with various chemistry conditions (i.e., the loop function to test different pe values), the presentation of the modeling results (i.e., plotting), and further data analysis, were implemented via PHREEQC input and output files through MATLAB using the COM interface (i.e., IPHREEQC). An in-house MATLAB script was created accordingly to calculate the speciation and precipitation for all the wastewater cases described above.

Figure 6.2 demonstrates the various Fe-P and Fe-S compounds formed before and after AD.

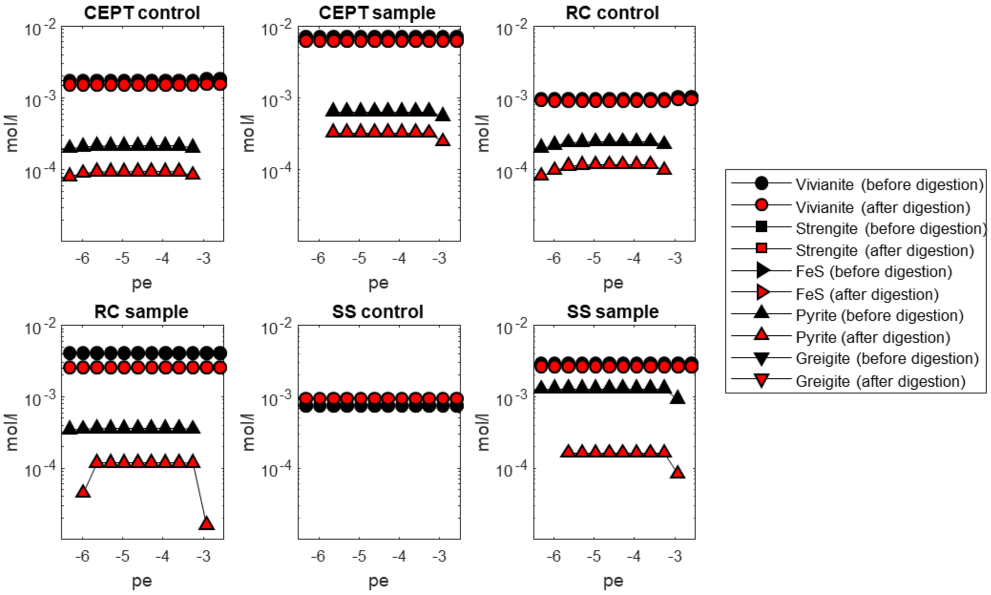


Figure 6.2 The various Fe-P and Fe-S compounds before and after AD

The modeling is based on thermodynamic equilibrium, which cannot sufficiently capture the complexity of a bio-reactor. Additionally, this kind of modeling does not take into account the effects of kinetics, potential local reactions, co-precipitations, and also the impact of microbes on the speciation of various metals. For example, pyrite was the only Fe-S form predicted by PHREEQC, although greigite and FeS were included in the calculations.

From literature [Zhang et al. 2009; Roussel et al. 2016], it can be predicted that once the ferric phosphate is dissolved in the low redox environment of AD, a high concentration of phosphate surrounds the iron thus creating limitation for sulfide to bind with iron. This results in the formation of compounds such as vivianite and reduction in formation of pyrite or Fe-S compounds. Additionally sulfide has a slight tendency to precipitate with zinc, nickel and others; however pyrite is only formed when the sulfide concentration in the reactor has reached 1g/kg dry solids.

Our results show no significant difference in vivianite formation before and after digestion for all the three sludge except for the spent control sludge, while a decrease in the concentration of pyrite was noticed due to competition from vivianite formation (Figure 6.2). This observation is in agreement with the study conducted by Roussel et al. 2016 where they predicted vivianite as the dominating Fe-P species and pyrite as the Fe-S species when using PHREEQC to model iron dosed sludge.

Further to this, the percentage of solid Fe and percentage of solid phosphorous as vivianite (the dominant Fe and P phase) was plotted in Figures 6.3 and 6.4.

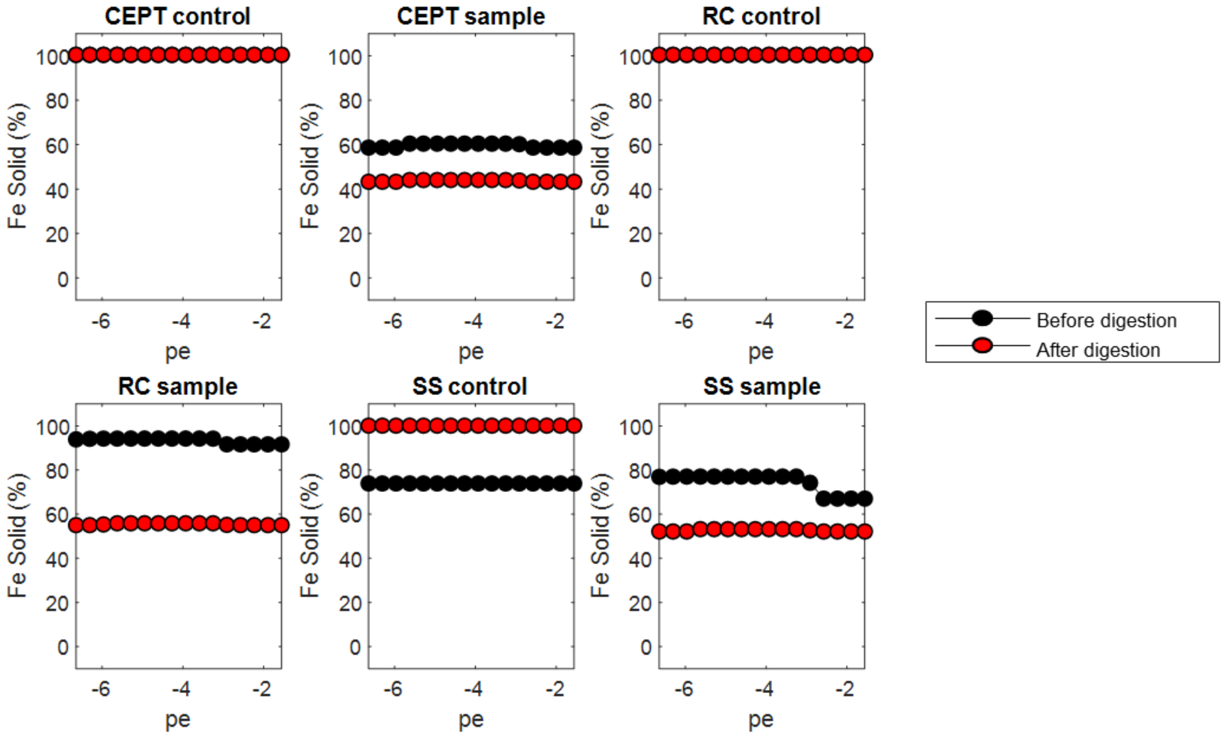


Figure 6.3 Changes in solid iron concentration before and after AD

Quantitative determination of solid iron species in the liquid phase is difficult due to almost undetectable concentrations of individual species [Fermoso et al. 2009]. Studies by Rikard (2006) and Davison et al. (1999) demonstrated that the iron concentration in the liquid phase of a digester, and its speciation, primarily depended on the available sulfur to iron ratio in the digester. They noted an increase in solubility of iron due to secondary iron precipitation along with sulfide precipitation.

Based on our results, increased total iron solubility in the digested CEPT and recovered sludge was noted. This has been discussed in the following sections. Thus, iron speciation in the solids phase influences the reactions in the liquid phase and, ultimately, on the final concentration of iron.

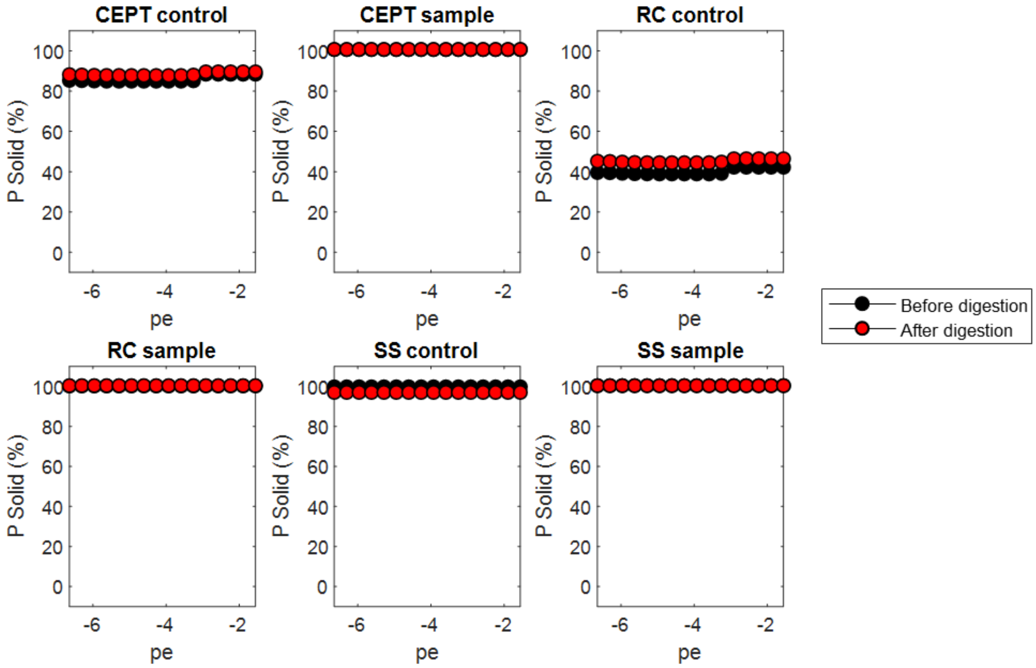


Figure 6.4 Changes in solid phosphorous concentration before and after AD

Other than the recovered sludge control, 80% - 100% of the phosphorous remained in the solid phase before and after digestion. Even though iron solubility is increased after AD, which would mean recovering the iron after AD could be a potential option, significant solubility of phosphorous has also been observed. This means that if coagulant recovery was attempted after AD, significant amount of phosphorous would also be recovered.

The solubility product, K_{sp} of vivianite plays an important role in dictating its formation in AD. We tested two K_{sp} values; 10^{-36} and 10^{-32} and the results are presented in Figure 6.5.

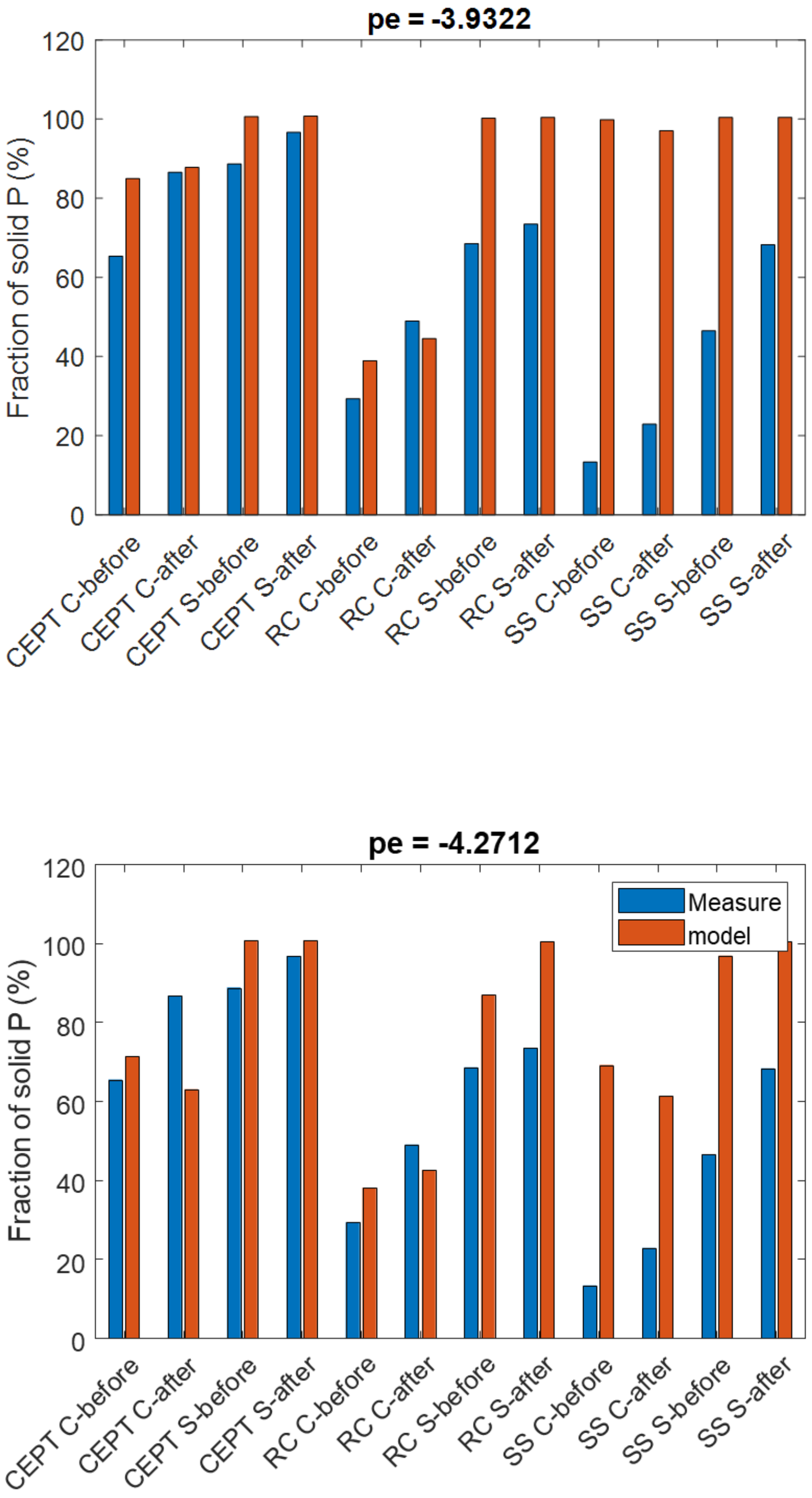


Figure 6.5: Experimental versus predicted solid phosphorous concentration before and after AD with K_{sp} values a) 10^{-32} and b) 10^{-36}

Others have demonstrated that the solubility product of vivianite plays an important role on its formation on AD. Study by Rothe et al. (2016) demonstrated that vivianite is stable in the pH range of 6-9 and detected its formation in presence ferrous and orthophosphate ion. Our experimental values corresponded well with the values obtained from the model, especially with K_{sp} value of 10^{-36}, except for spent sludge samples. This could be attributed to the matrix of the sludge or species not included in the modelling or the system not actually being at equilibrium as noted above.

The results in Figure 6.5 were calculated to minimize the differences between measured and predicted solids for all the experiments as a function of pe. The pe (redox potential) is difficult to determine experimentally so two values, that best matched the experimental observations, were assumed. It could be that the different samples in fact had different pe values and a sample-specific model might be more appropriate rather than a global treatment. Figure 6.6 shows the error measurements in the model as a function of pe.

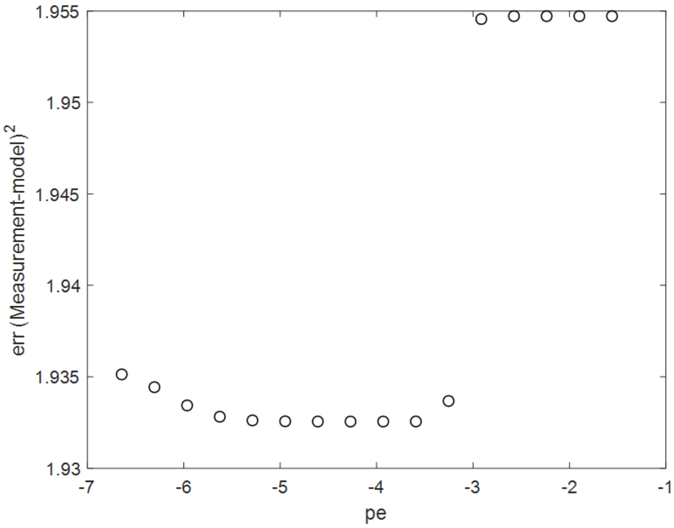


Figure 6.6: Error measurement model

As evident from Figure 6.6, the error is minimized at low pe values.

Future modeling needs to consider calcite and dolomite which were hard to estimate as total inorganic carbon was not available for model input. Hydroxyapatite should also be considered in future modelling – but without calcite competition all the phosphate would be predicted to bind to hydroxyapatite which is not realistic. Also, mixed oxidation state iron minerals need to be considered such as green rust. If more iron were precipitating as non-phosphorous removing species then the model might agree better for the “SS” samples; as it stands now, the model predicts almost all phosphorous is removed as vivianite in those samples. Also, further refinement in the pe inputs will help in future modeling efforts. The assumption that all samples have the same pe range is probably not realistic but without data to constrain the model, this was the best approach to use so far.

6.4 Conclusions

All three sludge, namely CEPT, recovered and spent sludge underwent AD and their biomethane formation potential was determined. Similar methane production was observed for the CEPT sludge and the recovered sludge. The spent sludge, which is the solid residue after acidification of CEPT sludge had almost no methane formation. Inhibitory metals such as chromium, nickel, zinc, calcium among others, were well below the limit, and therefore is not a concern for reusing acidified coagulant. Gompertz model showed the shortest lag phase for the CEPT sludge followed by the recovered sludge. A chemical equilibrium model predicted the formation of vivianite as the dominating Fe-P species and pyrite as Fe-S compounds in both the CEPT sludge and the recovered sludge. Overall this study showed that sludge obtained from coagulant recovery can yield almost similar quantity of methane and that no new Fe-S/Fe-P compounds are formed due to recycling of coagulants.

6.5 References

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Chapter 7

7 Conclusions and recommendations

7.1 Conclusions

The detailed summary of the major findings of the various projects have been included within chapters 3-6. The principal findings of this study are as follows:

1) Of the four available methods for coagulant recovery, including acidification, basification, membrane and ion exchange processes, acidification was chosen as the preferred method of recovery due to its cost effectiveness. Aluminum and iron were both successfully extracted from municipal primary sludge using either sulphuric or hydrochloric acid. Although an optimum pH of 1.5 was used for the recovery process, only 76% and 31% of aluminum and iron could be extracted efficiently. A chemical equilibrium model predicted the formation of aluminum complexes such as jurbanite, gibbsite and iron complexes such as strengite and jarosite, which hindered complete recovery. The recovered coagulants were recycled in fresh municipal wastewater for two cycles and the water quality parameters were monitored. Compared to fresh coagulants, there was an approximate reduction of 10% in the removal efficiencies of TSS, COD, TN with the recovered coagulants. Phosphorous was the most affected parameter and was precipitated as struvite, a slow release fertilizer at the end of the second cycle. An operational cost analysis showed savings of roughly $5000 annually with coagulant recovery for a treatment plant of 1 MGD capacity.

2) The distribution of MPs in fresh and recovered coagulants was compound specific. MPs with log K_{ow} <2.5 for example caffeine, erythromycin among others were predominantly present in the effluent after coagulation, while MPs with log K_{ow} >2.5 such as clarithromycin, diclofenac, amitryptiline were sorbed on the coagulated sludge. The distribution ratio (K_d) of all the MPs with log K_{ow} >2.5 was calculated and the extent of buildup on sludge due to repeated recycling was determined. The tetracycline group of compounds showed possible chelation with iron and aluminum. Only <10% of the initial loading of MPs with log K_{ow} >2.5 was being recycled with the recovered coagulant, thus

reducing the concern of building up of concentration of the MPs during recycle of the coagulants.

3) AD at mesophilic conditions for 15 days of CEPT sludge, recovered sludge and spent sludge was conducted to understand the impact of coagulant recovery on downstream processes. Both CEPT and the recovered sludge showed similar biomethane formation potential, with the spent sludge showing the least. A chemical equilibrium model predicted vivianite and pyrite as the dominating Fe-P and Fe-S compound phases, respectively before and after AD. This helped in determining no difference in Fe-P and Fe-S speciation for the recovered, spent and CEPT sludges. The experimental values for iron and phosphorous corroborated well with the model derived values (using $K_{sp} = 10^{-32}$ or 10^{-36}) except for the spent sludge control.

7.2 Limitations

One of the major limitations of the coagulant recovery process is the dissolution of heavy metals, inorganics, phosphorous along with the coagulants. This when added to fresh batches of wastewater, might end up causing heavy metal toxicity, deflocculation of sludge lines and eutrophication in water bodies. Thus the recovered coagulant needs to be characterized in terms of its organic/inorganic loadings before application.

Presence of MPs especially the tetracycline group of compounds, which chelate with metal ions can become difficult to detect in a complex matrix like wastewater. Additionally, presence of MPs along with other organic/inorganic matter in wastewater may render a strong matrix affect making it almost impossible to detect all the compounds.

7.3 Recommendations

The successful integration and application of coagulant recovery in wastewater treatment plants would require further investigation and validation. The following recommendations for future work are made:

1) A proper CAPEX/OPEX of either a lab scale/ pilot scale plant or a full scale plant employing coagulant recovery needs to be done to understand the logistical and financial challenges.

2) Study the impact of coagulant recovery on tertiary treatment of wastewater. The presence of NOM during recycling might have the potential to act as a precursor for DBP formation.

3) It is recommended to study the impact of acidification on the degradation of cellulose, protein and carbohydrate fractions of the sludge

4) The impact of coagulant recovery on high strength municipal wastewater needs to be determined.

5) Effect of microplastics during recycling of coagulants.

Appendices

Appendix A:

Graphical abstract of CR of alum

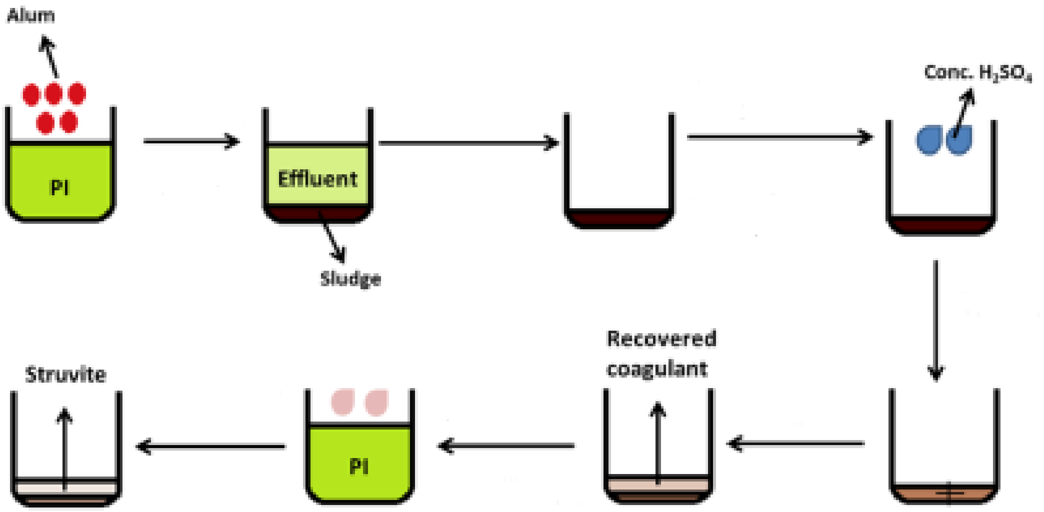


Table S1: Variations in water quality parameters

Parameter	Maximum	Minimum	Mean
TSS (mg/L)	340	140	240
TP (mg/L)	8.7	3.4	6.0
sP (mg/L)	3.5	2.3	2.9
COD (mg/L)	740	210	480
sCOD (mg/L)	290	180	230
TN (mg/L)	57	25	41
pH	8	6.9	7.4

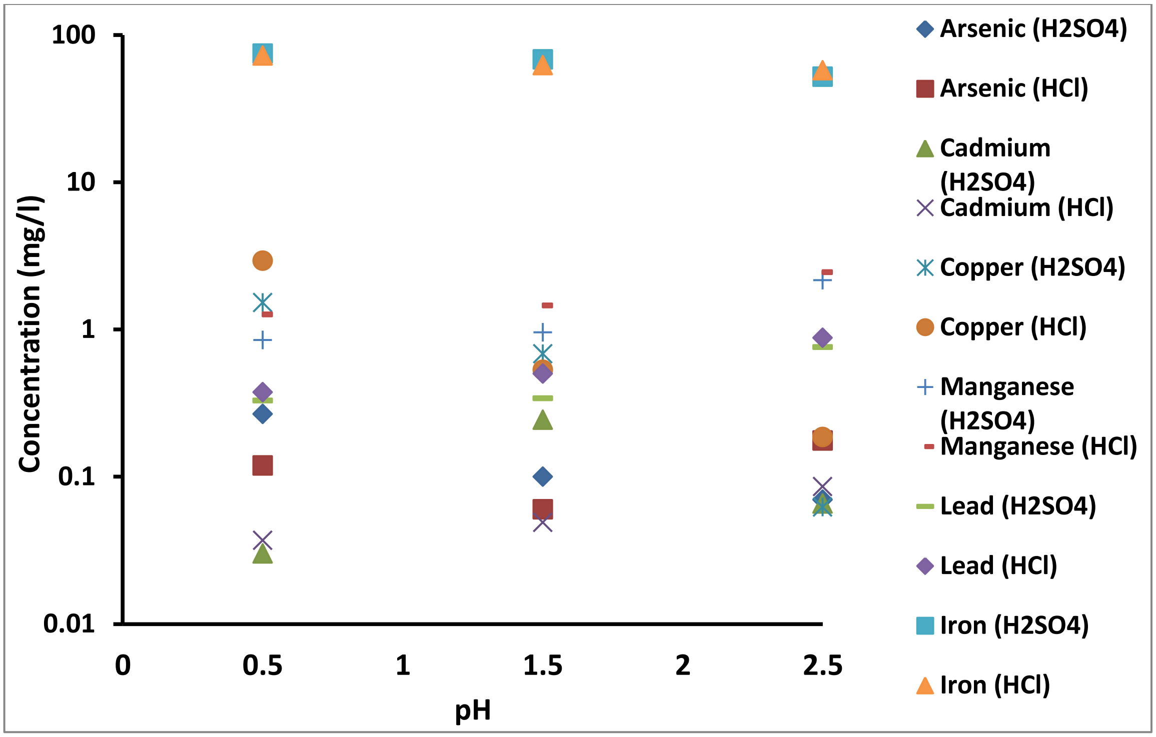


Figure S1: Concentration of metals in the recovered coagulant solution obtained by acidifying with either HCl or H_2SO_4

Table S2: Heavy metal concentrations in the recovered coagulant using sulphuric acid at a pH of 1.5 (based on one sample per cycle)

	Arsenic (mg/L)	**Lead (mg/L)**	**Cadmium (mg/L)**
Fresh Alum	0.09	0.68	0.05
1st Cycle	0.096	0.71	0.052
2nd Cycle	0.11	0.75	0.06

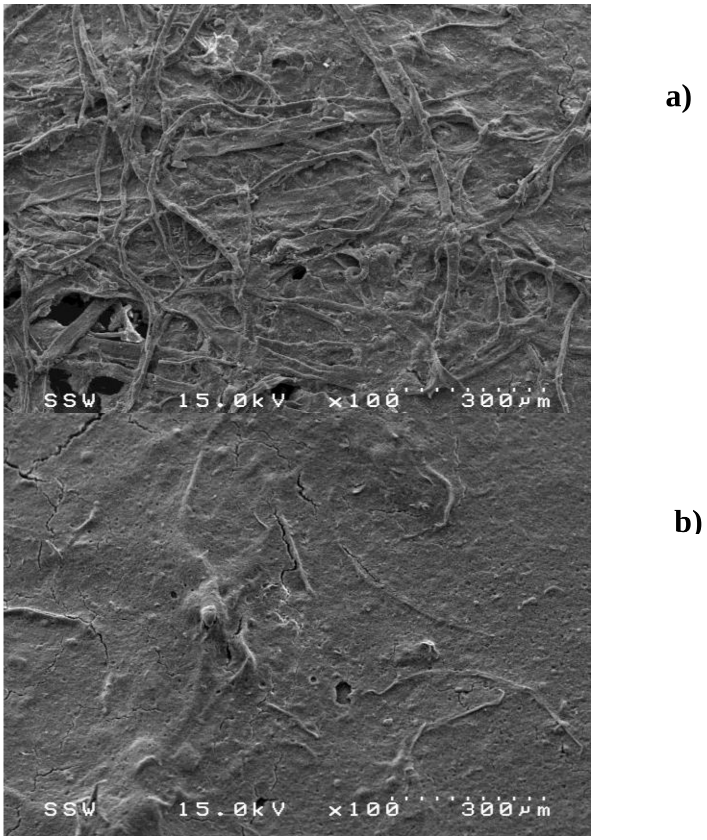


Figure S2: SEM images of the acidified sludge by a) hydrochloric acid b) sulphuric acid

Table S3: Simultaneous equilibria for the aluminum sulphate system written in standard tableau notation. Soluble species and $Al(OH)_{3(s)}$ values from NIST (2001) and aluminum sulphate precipitates from Nordstrom (1982) for alunite 1 mM potassium was assumed in determining the logK value.

H+	**Al^{3+}**	**SO_4^{2-}**	**logK**	**Species name**
1	0	0	0	H^+
0	1	0	0	Al^{3+}
0	0	1	0	SO_4^{2-}
-1	0	0	-14	OH^-
-1	1	0	-5.0	$AlOH^{2+}$

-2	1	0	-10.3	$Al(OH)_2^+$
-4	1	0	-22.7	$Al(OH)_4^-$
1	0	1	1.90	$HSO4^-$
0	1	1	1.48	$AlSO_4^+$
-3	1	0	-8.30	$Al(OH)_{3(s)}$
-1	1	1	3.80	jurbanite
-10	4	1	-257.7	basaluminite
0	2	3	-7	alunogen
-6	3	2	-172.4[a]	alunite

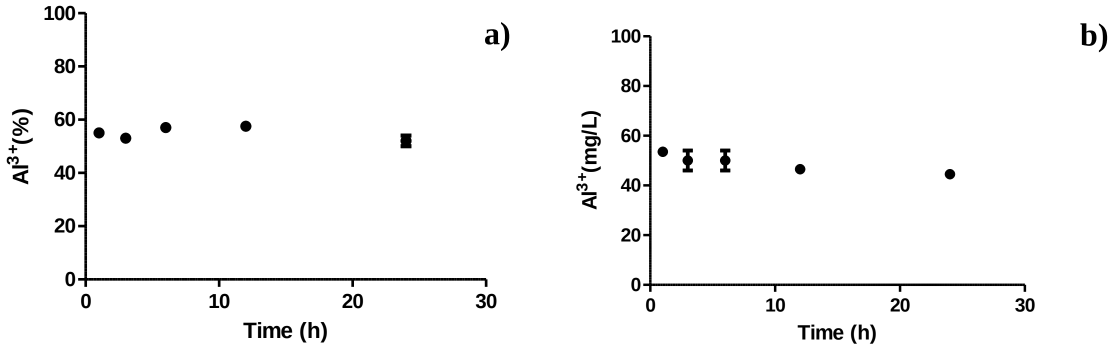


Figure S3: Kinetic study on the concentration of aluminum with a) HCl and b) H_2SO_4

Table S4: Characteristics of the recovered coagulant

Parameters	1st Recycle (mg/L)	2nd Recycle (mg/L)
Phosphorous	**726 ± 48**	**908 ± 16**
Soluble phosphorous	**658 ± 47**	**766 ± 14**
Total nitrogen	**270 ± 11**	**288 ± 17**
Chemical oxygen demand	**7075 ± 35**	**7190 ± 14**

Table S5: Expected vs. observed removal efficiencies of influent soluble phosphorous at different Al:P molar ratios.

Aluminum coagulant	Aluminum : phosphorous molar ratios	Expected removal efficiency of soluble phosphorous*	Observed removal efficiency of soluble phosphorous
Alum	**2:1**	**85% - 90 %**	**77% - 85 %**
1st Recycle	**0.41 : 1**	**22% – 29%**	**28% - 34%**
2nd Recycle	**0.12 : 1**	**10% – 15%**	**14% - 18%**

* - Based on Eddy Metcalf, Inc. Wastewater Engineering, Treatment and Reuse (fourth edition). Tata McGraw–Hill Publishing Co., New Delhi (2003)

Appendix B

Graphical abstract of CR of iron

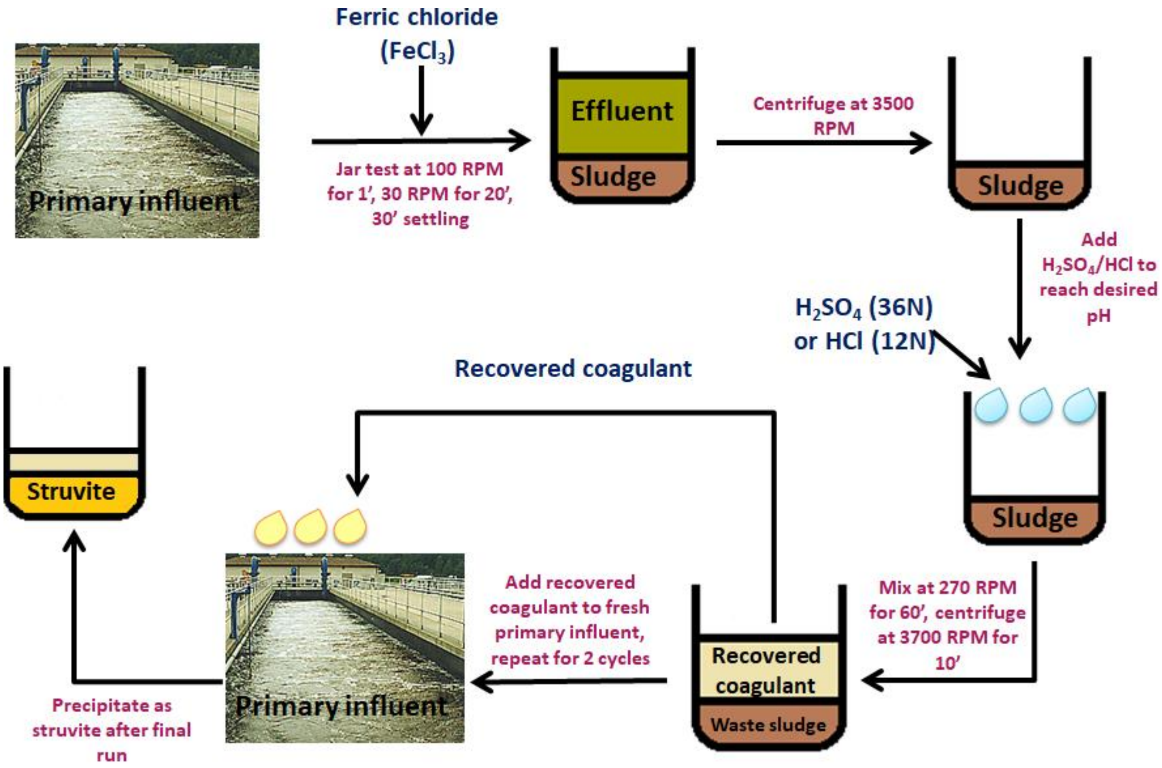


Table S1: Reactions including for geochemical modelling of ferric recovery using sulphuric acid. Each species is formed from the component species indicated at the top of the table. Solid species are indicated after the horizontal line at the bottom of the table.

H^+	Fe^{3+}	PO_4^{3-}	SO_4^{2-}	K^+	species
1	0	0	0	0	H^+
0	1	0	0	0	Fe^{3+}
0	0	1	0	0	PO_4^{3-}
0	0	0	1	0	SO_4^{2-}
0	0	0	0	1	K^+

-1	0	0	0	0	OH^-
-1	1	0	0	0	$FeOH^{2+}$
-2	1	0	0	0	$Fe(OH)_2^+$
-3	1	0	0	0	$FeOH_3$
-4	1	0	0	0	$FeOH_4^-$
-2	2	0	0	0	$Fe_2OH_2^{4+}$
-4	4	0	0	0	$Fe_3OH_4^{5+}$
1	0	0	1	0	HSO_4^-
1	0	1	0	0	HPO_4^{2-}
2	0	1	0	0	$H_2PO_4^-$
3	0	1	0	0	H_3PO_4
0	1	0	1	0	$FeSO_4^-$
1	1	1	0	0	$FeHPO_4^+$
2	1	1	0	0	$FeH_2PO_4^{2+}$
4	1	2	0	0	$Fe(H_2PO_4)_2^+$
6	1	3	0	0	$Fe(H_2PO_4)_3$
3	1	1	0	0	$FeH_3PO_4^{3+}$
0	0	0	1	1	KSO_4^-
-3	1	0	0	0	hydrous ferric oxide ($Fe(OH)_3$)
0	1	1	0	0	Strengite ($FePO_4$)

-5	3	0	2	0	H-Jarosite ($HFe_3(SO_4)_2(OH)_6$)
-6	3	0	2	1	Jarosite ($KFe_3(SO_4)_2(OH)_6$)

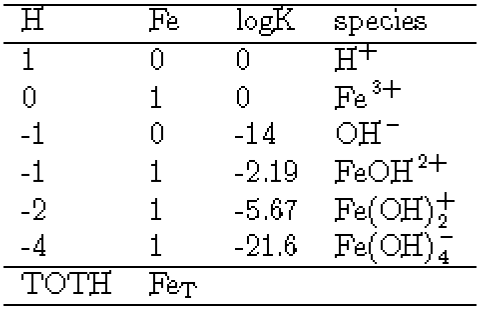
Table S2: Experimental vs. modelled recoveries of iron

Acid	pH	% recovery obtained experimentally	% recovery from modelling with pe = 10
HCl	**0.5**	54±3.5	100
	1.5	34±2.7	37.2
	2.5	6.5±0.8	4.6
H_2SO_4	**0.5**	33±1	100
	1.5	31±3	29
	2.5	16±1	2.4

Modelling protocol:

In environmental modelling, solving for the equilibrium position of a set of simultaneous reactions subject to the constraints of mass balance and mass action is a common problem. There exist many available computer programs for example include MINEQL and PHREEQC. In case of iron, it is desirable for a given system to determine the equilibrium concentration of all species. Using the iron (III) system as an example, a list of species of interest could include H^+, OH^- , Fe $^{3+,}$FeOH^{2+}, Fe(OH)$^{+2}$, and Fe(OH)$_{\{4\}}$. There are other possible species but to keep the discussion simple these are the only ones included here. Also, for dilute solutions water can be assumed as fixed component. The list includes six species so it is necessary to define six relationships in order to solve this system. The situation can be simplified if it is realized that each of these species are not independent. We can select components from the list of species and use those components to solve the equilibrium problem. For example, if we know H^+ (pH) and Fe $^{3+}$ we can determine the concentration of all other species from their logK values (mass action). In matrix notation we think of pH and Fe $^{3+}$ as spanning the basis set.

Now we need two equations and two unknowns. First relation is mass balance of iron and the second is proton balance (related to electroneutrality). A table (Table 1) can be written that defines the equilibrium problem. The entries in the columns are the stoichiometric coefficients required for formation of each species. For example, there is 1 H^+ and 0 Fe $^{3+}$ in H^+.



H	Fe	logK	species
1	0	0	H^+
0	1	0	Fe^{3+}
-1	0	-14	OH^-
-1	1	-2.19	$FeOH^{2+}$
-2	1	-5.67	$Fe(OH)_2^+$
-4	1	-21.6	$Fe(OH)_4^-$
TOTH	Fe_T		

Table 1: Tableau for Fe–H system

Fe(OH)$_{\{4\}}$ is formed with one iron and removing 4 protons from water. Given the tableau, all that remains is to determine the values for [H+] and [Fe 3+] for specified TOTH and Fe_T.

If you multiply across rows it is possible to determine species concentration and if you sum down columns, the total values (mass balance) are recovered. This is best understood by writing out some entries:

$$[H^+] = [H^+]^1 \times [Fe^{3+}]^0 \times 10^0 \tag{1}$$
$$[Fe^{3+}] = [H^+]^0 \times [Fe^{3+}]^1 \times 10^0 \tag{2}$$
$$[OH^-] = [H^+]^{-1} \times [Fe^{3+}]^0 \times 10^{-14} \tag{3}$$
$$[FeOH^{2+}] = [H^+]^{-1} \times [Fe^{3+}]^1 \times 10^{-2.19} \tag{4}$$
$$\ldots. \tag{5}$$

It is necessary to always write the formation reactions for each species from the components. For example to understand equation (3) consider that Kw corresponds to the following reaction:

$$H_2O \rightleftharpoons H^+ + OH^- \quad K_w = [H^+][OH^-] \tag{6}$$

If equation (6) is rearranged to solve for [OH$^-$] then equation (3) is obtained. As another example, to understand equation (4) consider that K_{H1} for the first hydrolysis of iron (III) corresponds to the following reaction:

$$\mathrm{Fe}^{3+} + \mathrm{H_2O} \rightleftharpoons \mathrm{FeOH}^{2+} + \mathrm{H}^+ \quad K_{H1} = \frac{[\mathrm{FeOH}^{2+}][\mathrm{H}^+]}{[\mathrm{Fe}^{3+}]} \qquad (7)$$

if equation (7) is rearranged to solve for [FeOH^{2+}] then equation (4) is obtained. To explain how the summations down the columns is the mass balance. Consider total iron:

$$\mathrm{Fe_T} = 0[\mathrm{H}^+] + 1[\mathrm{Fe}^{3+}] + 0[\mathrm{OH}^-] + 1[\mathrm{FeOH}^{2+}] + 1[\mathrm{Fe(OH)}_2^+] + 1[\mathrm{Fe(OH)}_4^-] \qquad (8)$$

Notice that the coefficients are the entries down the iron column in the tableau.

The problem can easily be expressed in matrix notation. We'll define the 1 X 2 vector of unknown component concentrations as X so we can write X = log [H$^+$] log [Fe^{3+}]. There is a 6 X 1 vector of species concentrations as well:

$$\mathbf{C} = \begin{pmatrix} [\mathrm{H}^+] \\ [\mathrm{Fe}^{3+}] \\ [\mathrm{OH}-] \\ [\mathrm{FeOH}^{2+}] \\ [\mathrm{Fe(OH)}_2^+] \\ [\mathrm{Fe(OH)}_4-] \end{pmatrix} \qquad (9)$$

Total concentrations are in a 2 X 1 vector T = log (TOTH $\mathrm{Fe_T}$). The logK values are summarized in the 6 X 1 vector.

-

$$\mathbf{K} = \begin{pmatrix} 0 \\ 0 \\ \log K_w \\ \log K_{H1} \\ \log K_{H2} \\ \log K_{H4} \end{pmatrix} \qquad (10)$$

Finally, we need a 6 X 2 matrix of stoichiometric coefficients.

$$\mathbf{A} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \\ -1 & 0 \\ -1 & 1 \\ -2 & 1 \\ -4 & 1 \end{pmatrix} \tag{11}$$

Now the minimization problem is to determine X that minimizes the residuals in the mass balance. This calculation is performed as follows:

$$\text{minimize } \mathbf{R} \text{ as a function of } \mathbf{X} \text{ where} \quad \mathbf{R} = \mathbf{A}' \times (10^{\mathbf{C}}) - \mathbf{T} \tag{12}$$

$$\text{and} \quad \mathbf{C} = 10^{(\mathbf{K}+\mathbf{A}\times\mathbf{X}')} \tag{13}$$

Minimization can be performed using all element of R using Newton-Raphson method for example or by using other nonlinear optimization methods on some summation of R such as sum of squares or sum of absolute values of residuals [Carrayrou et al. 2002]. In this case R would be a 2 X 1 vector of mass balance residuals.

For supersaturated systems the criteria must be changed to allow for precipitation of mineral phases. The solid phases must be taken account in the mass balance expression and the new Ksp value must be satisfied. Usually speciation codes change the set of components by taking the precipitated species as a new component. Here we use the approach of Carrayrou et al. (2002), and simply add a new unknown and a new relationship for each solid phase that is precipitated.

For the Fe(III) system the solid phase we'll consider amorphous ferric hydroxide $Fe(OH)_3$ (s). We need to write the reaction as a precipitation reaction:

$$Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_{3\,(s)} + 3H^{+} \tag{14}$$

This relationship can be added to the existing tableau.

H	Fe	logK	species
1	0	0	H^{+}
0	1	0	Fe^{3+}
-1	0	-14	OH^{-}
-1	1	-2.19	$FeOH^{2+}$
-2	1	-5.67	$Fe(OH)_2^{+}$
-4	1	-21.6	$Fe(OH)_4^{-}$
-3	1	-6	$Fe(OH)_{3\,(s)}$
TOTH	Fe_T		

Table 2: Tableau for Fe–H system including one possible solid phase.

Table 2 defines the chemical equilibrium problem. The speciation versus pH was calculated for this system using the Matlab program developed here.

Cost calculations:

1) **Overall basis:**
    - a. **Biomass yield of mg VSS/mg COD**
    - b. **Non-biodegradable COD of the primary effluent was ignored in the calculation of biomass**
    - c. **The volatile fraction of the influent suspended solids is 91%**
    - d. **A molar ratio of $FeCl_3$: TP of 1:1 was used for secondary chemical removal**
    - e. **TP was removed chemically as $FePO_4$ i.e. 1 mg phosphorous removed, produces 4.87 mg TSS**
    - f. **The inorganic fraction of biomass was based on a VSS:TSS ratio of 0.85**
    - g. **All calculations are based on 1 liter of raw wastewater**
    - h. **COD of primary effluent was 156 mg/L**
    - i. **In case of coagulant recycling, average for cycles 1 and 2 for TSS and TP were used for calculations**

Calculations for ISS in WAS and primary sludge:

CEPT:

Primary sludge:

ISS = 0.09(162 mg ISS/L-16 mg ISS/L) = 13 mg ISS/L (refer to Table 1 for PI characteristics)

$FePO_4$ as ISS formed: 4.87 mg $FePO_4$/mg phosphorous*(6mg ISS/L-1.7mg ISS/L) = 20.9 mg ISS/L

Total ISS in primary sludge = 20.9 mg ISS/L +13 mg ISS/L = 33.9 mg ISS/L

WAS:

ISS = TSS – VSS = 162 mg/L-149 mg/L = 13 mg/L (refer to Table 1 for PI characteristics)

P in biomass = 0.3 mg VSS/mg COD*156 mg/L*2.8/113 = 1 mgP/L; P in effluent = 2.2 mg/L

(refer to Figures 6 and 7 for effluent characteristics)

P to be removed chemically= 2.2 mg/L-1 mg/L-0.8mg/L = 0.4 mgP/L

$FeCl_3$ required = 0.4 mg P//L*162/31 =2.1 mg $FeCl_3$/L

Associated cost for a 1 MGD plant = 3785m^3/d*2.1mg $FeCl_3$/L*10^{-6} *540 $/ton= $4.3/d

Total chemical cost = 81.8 $/d+4.3$/d = $86.1/d (40 mg/L @ $540/ton chemicals for 1 MGD = $81.8/d)

$FePO_4$ as ISS formed: 4.87 mg $FePO_4$/mg phosphorous *0.4 mgP/L = 1.95mg ISS/L

ISS in primary effluent = (1-0.9) *16 mg ISS/L= 1.6 mg ISS/L

ISS in WAS = 8.3 mg ISS/L (TSS = VSS/0.85; ISS = VSS (1/0.85-1))

Total ISS in WAS = 1.6 mg ISS/L +1.95 mg ISS/L +8.3 mg ISS/L = 11.85 mg ISS/L

Total solids for dewatering: 3785 m^3/d *(33.9 mg ISS/L +11.85 mg ISS/L) *10^{-6} = 0.17 tons/day

Coagulant recycling:

Primary sludge:

ISS = (162 mg/L- 33.4 mg/L) 0.09= 11.6 mg ISS/L (refer to Table 1 and Figure 6 for characteristics)

$FePO_4$ as ISS formed: 4.87 mg $FePO_4$/mg phosphorous *(6 mg ISS/L-2.4 mg ISS/L) = 11.7 mg ISS/L

Total ISS in primary sludge = 11.6 mg ISS/L+11.7 mg ISS/L = 23.3 mg ISS/L

WAS:

P to be removed chemically= 4.8 mg/L-1mg/L-0.8 mg/L = 2.9 mgP/L

$FeCl_3$ required = 2.9 mg P/L*162/31 =15.7 mg $FeCl_3$/L

Associated cost for a 1 MGD plant = 3785 m^3/d *10^{-6}*15.7 mg $FeCl_3$/L*540$/ton = $32/d

Total chemical cost = 27.3$/d+32$/d = $59.3/d (1/3rd the cost of no recycling + additional cost)

$FePO_4$ as ISS formed: 4.87 mg $FePO_4$/mg phosphorous *2.9 mgP/L = 14.4 mg ISS/L

ISS in PI = (1-0.9)*33.4 mg/L= 3.4 mg ISS/L (refer to Figure 6 for characteristics)

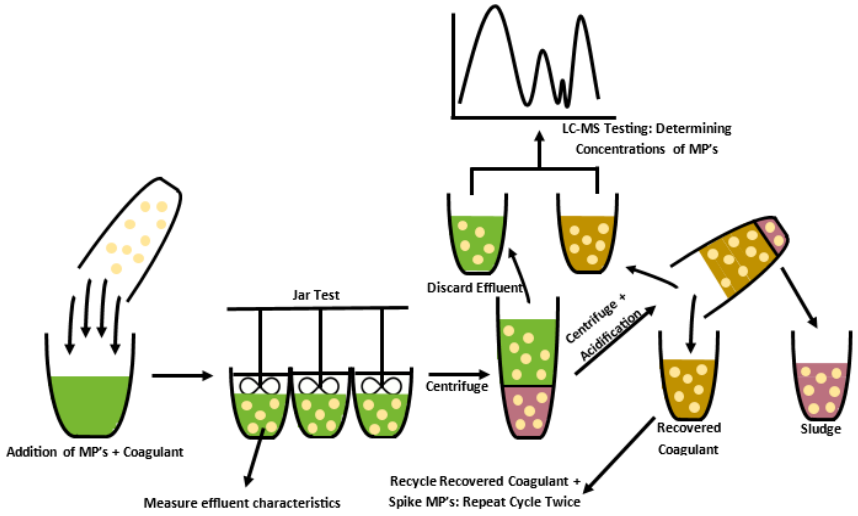
ISS in WAS = 8.3 mg ISS/L (TSS = VSS/0.85; ISS = VSS (1/0.85-1))

Total ISS in WAS = 14.4 mg ISS/L+3.4 mg ISS/L+8.3 mg ISS/L = 26.1 mg ISS/L

Total solids for dewatering: 3785m^3/d*(26.1 mg ISS/L+inert fraction (0.2) *23.3 mg ISS/L)*10^{-6} = 0.12 tons/day (inert fraction from Metcalf and Eddy)

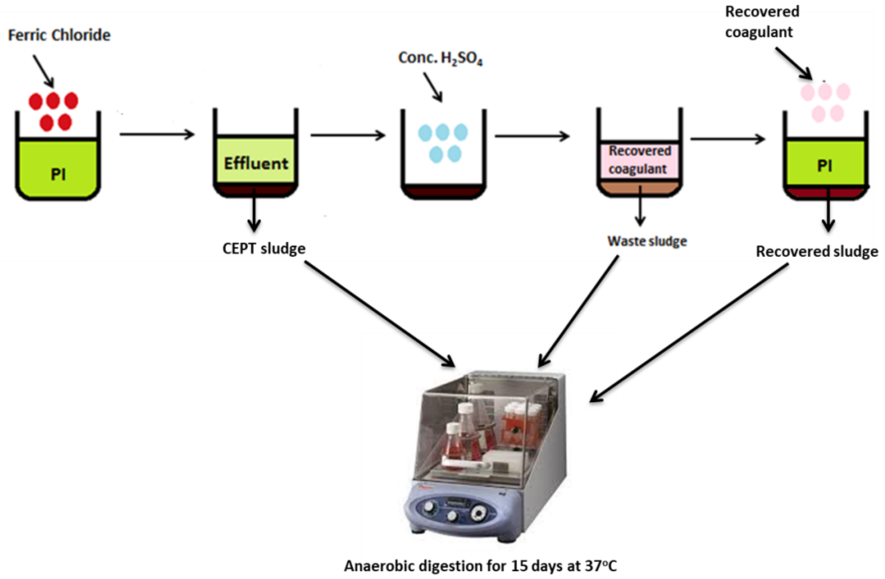
Appendix C:

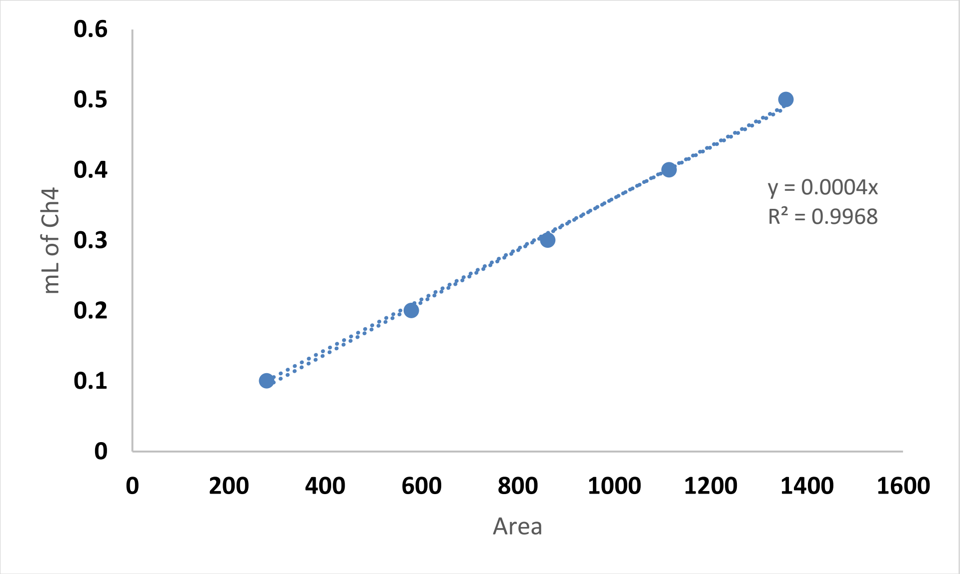
Graphical abstract of Chapter 5:



Appendix D:

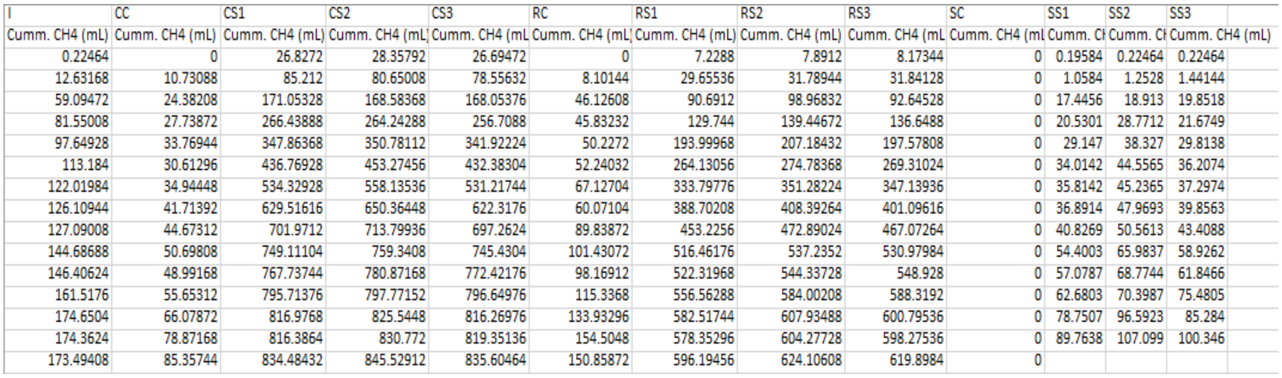
Graphical abstract of Chapter 6:





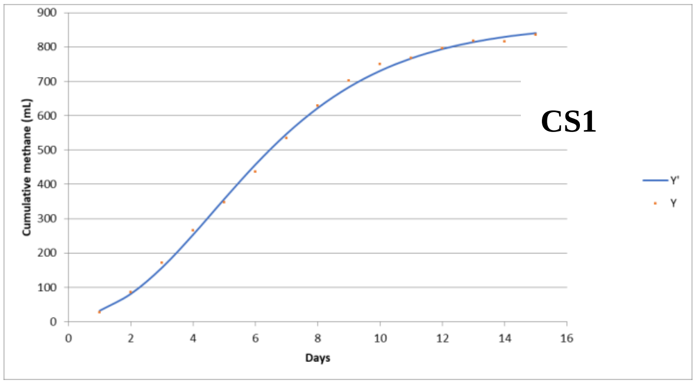
Calibration curve for methane production

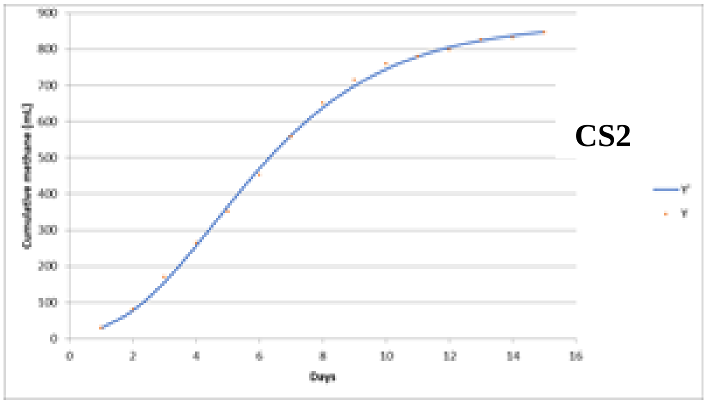
Cumulative methane production from inoculam and all sludge samples

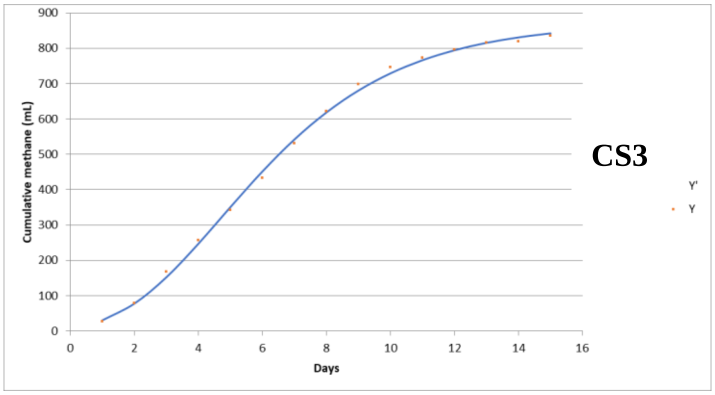


I	CC	CS1	CS2	CS3	RC	RS1	RS2	RS3	SC	SS1	SS2	SS3
Cumm. CH4 (mL)	Cumm. CH4 (mL)	Cumm. CH4 (mL)	Cumm. CH4 (mL	Cumm. CH4 (mL	Cumm. CH4 (mL	Cumm. CH4 (mL)	Cumm. CH4 (mL)	Cumm. CH4 (mL	Cumm. CH4 (ml	Cumm. C	Cumm. C	Cumm. CH4 (mL)
0.22464	0	26.8272	28.35792	26.69472	0	7.2288	7.8912	8.17344	0	0.19584	0.22464	0.22464
12.63168	10.73088	85.212	80.65008	78.55632	8.10144	29.65536	31.78944	31.84128	0	1.0584	1.2528	1.44144
59.09472	24.38208	171.05328	168.58368	168.05376	46.12608	90.6912	98.96832	92.64528	0	17.4456	18.913	19.8518
81.55008	27.73872	266.43888	264.24288	256.7088	45.83232	129.744	139.44672	136.6488	0	20.5301	28.7712	21.6749
97.64928	33.76944	347.86368	350.78112	341.92224	50.2272	193.99968	207.18432	197.57808	0	29.147	38.327	29.8138
113.184	30.61296	436.76928	453.27456	432.38304	52.24032	264.13056	274.78368	269.31024	0	34.0142	44.5565	36.2074
122.01984	34.94448	534.32928	558.13536	531.21744	67.12704	333.79776	351.28224	347.13936	0	35.8142	45.2365	37.2974
126.10944	41.71392	629.51616	650.36448	622.3176	60.07104	388.70208	408.39264	401.09616	0	36.8914	47.9693	39.8563
127.09008	44.67312	701.9712	713.79936	697.2624	89.83872	453.2256	472.89024	467.07264	0	40.8269	50.5613	43.4088
144.68688	50.69808	749.11104	759.3408	745.4304	101.43072	516.46176	537.2352	530.97984	0	54.4003	65.9837	58.9262
146.40624	48.99168	767.73744	780.87168	772.42176	98.16912	522.31968	544.33728	548.928	0	57.0787	68.7744	61.8466
161.5176	55.65312	795.71376	797.77152	796.64976	115.3368	556.56288	584.00208	588.3192	0	62.6803	70.3987	75.4805
174.6504	66.07872	816.9768	825.5448	816.26976	133.93296	582.51744	607.93488	600.79536	0	78.7507	96.5923	85.284
174.3624	78.87168	816.3864	830.772	819.35136	154.5048	578.35296	604.27728	598.27536	0	89.7638	107.099	100.346
173.49408	85.35744	834.48432	845.52912	835.60464	150.85872	596.19456	624.10608	619.8984	0			

Gompertz fits



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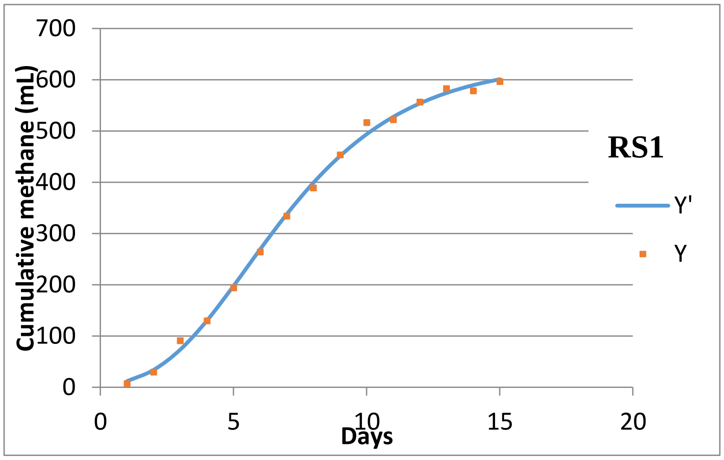
Cumulative methane (mL)
900
800
700
600
500
400
300
200
100
0
0
2
4
6
8
10
12
14
16
Days
Y'
Y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Cumulative methane (mL)
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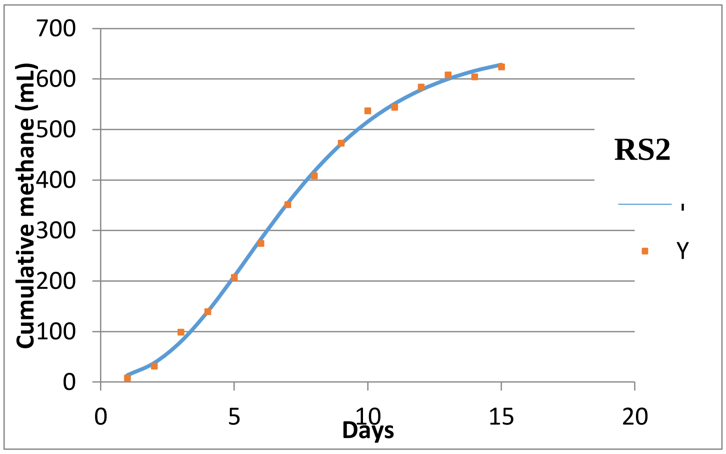
600
500
400
300
200
100
0
0
5
10
15
20
Days
Y'
Y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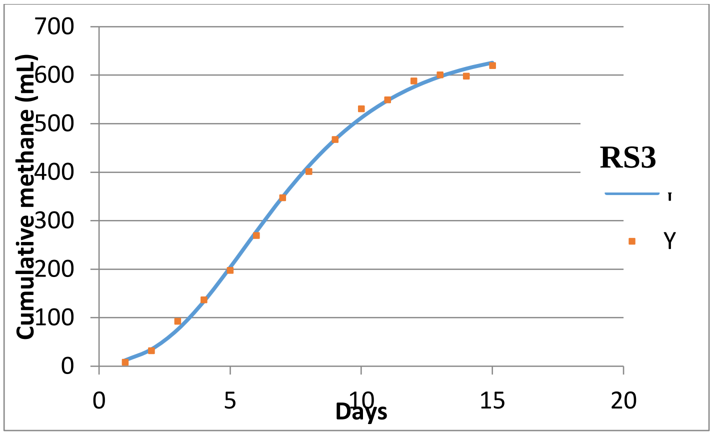
Cumulative methane (mL)
700
600
500
400
300
200
100
0
0
5
10
15
20
Days
Y


RS3
Cumulative methane (mL)
Days
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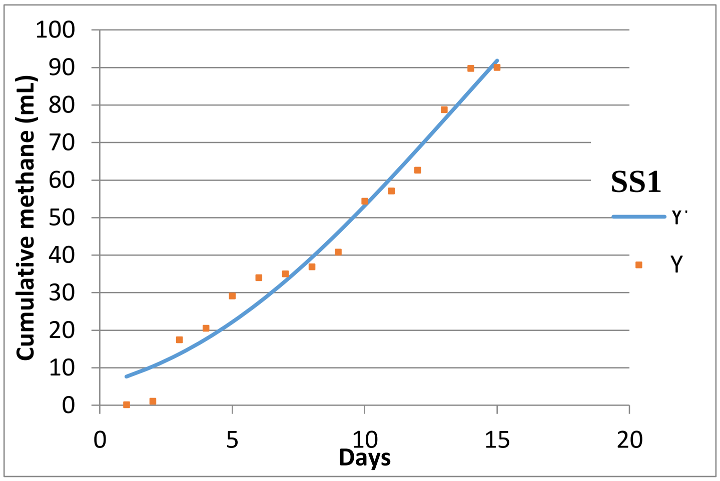
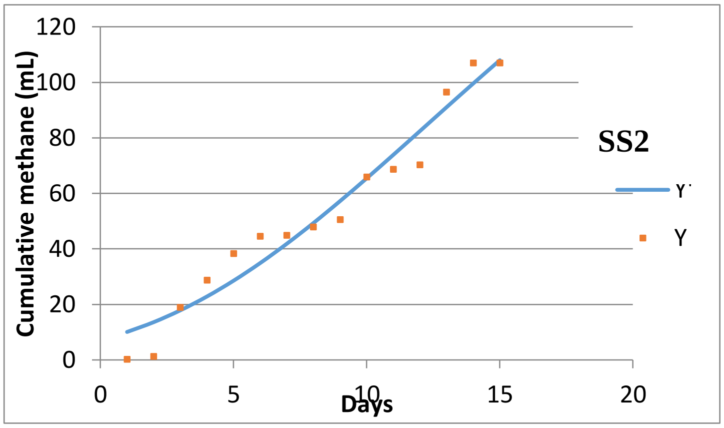
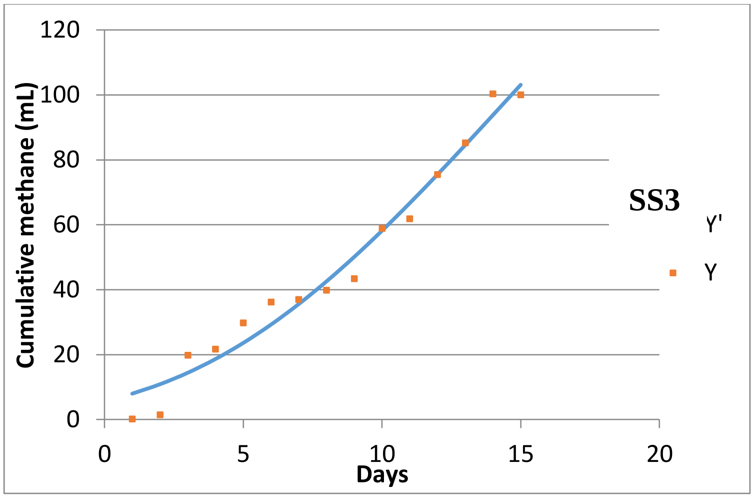
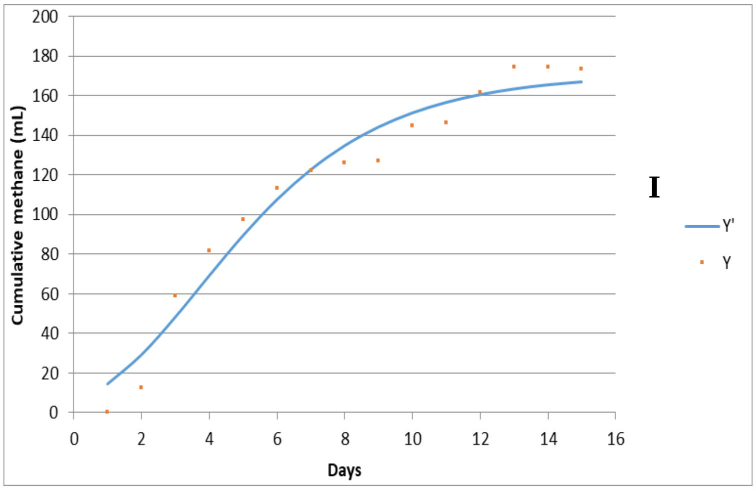
100
200
300
400
500
600
700
0
5
10
15
20
Y


SS1
Cumulative methane (mL)
Days
0
10
20
30
40
50
60
70
80
90
100
0
5
10
15
20
Y'
Y


SS2
Cumulative methane (mL)
Days
0
20
40
60
80
100
120
0
5
10
15
20
Y'
Y


SS3
Cumulative methane (mL)
Days
0
20
40
60
80
100
120
0
5
10
15
20
Y'
Y


I
Cumulative methane (mL)
Days
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20
40
60
80
100
120
140
160
180
200
0
2
4
6
8
10
12
14
16
Y'
Y

Curriculum Vitae

Name:	Tulip Chakraborty
Post-secondary Education and Degrees:	Heritage Institute of Technology Kolkata, West Bengal, India 2009-2013 B.Tech.
	The University of Western Ontario London, Ontario, Canada 2013-2015 M.E.Sc
	The University of Western Ontario London, Ontario, Canada 2015-2019 Ph.D.
Honours and Awards:	Western Graduate Research Scholarship 2013-2019
	MITACS PhD Accelerate Scholarship with Trojan Technologies March 2016 – August 2016
	2nd prize at Sarnia Lambton research meeting, London, Ontario (July 2015)
	1st prize at 3MT competition at Trojan Technologies, London, Ontario (July 2016)
Related Work Experience	Teaching Assistant The University of Western Ontario 2014-2019
	Graduate Intern City of Toronto February 2018 – June 2018
	Graduate Intern Trojan Technologies March 2016 – August 2016

Publications:

Chakraborty, T., Gabriel, M., Amiri, A.S., Santoro, D., Walton, J., Smith, S., Ray, M.B. and Nakhla, G., 2017. Carbon and Phosphorous Removal from Primary Municipal Wastewater Using Recovered Aluminum. *Environmental Science & Technology*, *51*(21), pp.12302-12309.

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Chakraborty, T., Balusani, D., Renaud, J., Sabourin, L., Sumarah, M., Ray, M.B. and Nakhla, G., 2018. Distribution of micropollutants in municipal wastewater by recovered iron and aluminum coagulants, and its effect on water quality. In preparation for submission to *Environmental Science and Technology*.

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Chakraborty T, Ray M, Bassi A. Use of bio-coagulants in treating various industrial effluents. Ontario Quebec biotechnology meeting. February 20th, 2014. Toronto, Ontario, Canada. (Presenting author: Tulip Chakraborty)

Chakraborty T, Smith S, Santoro D, Walton J, Ray M, Nakhla, G. Recovery and recycle of aluminum from municipal wastewater biosolids. 52nd Central Canadian Symposium on Water Quality Research, CAWQ, Feb. 23, 2017.Toronto, Ontario, Canada. (Presenting author: Tulip Chakraborty)

Chakraborty T, Balusani D, Ray M, Nakhla, G. Distribution of micropollutants in wastewater by recovered iron and aluminum coagulants. Canadian chemical engineering (CsChE) conference 22nd - 25th October, 2017. Edmonton, Alberta, Canada. (Presenting author: Tulip Chakraborty)

Chakraborty T, Smith S, Santoro D, Walton J, Ray M, Nakhla, G. Recovery and recuse of aluminum in municipal wastewater. American Institute of Chemical Engineers (AIChE) conference, October 29th – November 3rd, 2017. Minneapolis, Minnesota, USA. (Presenting author: Tulip Chakraborty)

Chakraborty T, Smith S, Santoro D, Walton J, Ray M, Nakhla, G. Chemically enhanced primary treatment using recovered iron. Presented at the ecoSTP 2018, 4th IWA Specialized International Conference, June 26th - 28th, 2018. London, Ontario, Canada. (Presenting author: Tulip Chakraborty)

Chakraborty T, Balusani D, Ray M, Nakhla, G. Impact of coagulant recycle on the distribution of micropollutants in municipal wastewater. Presented at WEAO 47th annual technical symposium and OPCEA exhibition. April 16, 2018. London, Ontario, Canada. (Presenting author: Tulip Chakraborty)

Chakraborty T, Smith S, Santoro D, Walton J, Ray M, Nakhla, G. Chemically enhanced primary treatment using recovered iron. Presented at the WEFTEC 2018, New Orleans, Louisiana USA. (Presenting author: Tulip Chakraborty)

Chakraborty T, Eini E, Gupta S, Ray MB, Nakhla, G. Towards an integrated approach of understanding and implementing a calibrated plant wide simulation model at Highland Creek Wastewater Treatment Plant (HCTP) – a study in progress. Presented at WEAO 48th annual technical symposium and OPCEA exhibition. April 15, 2019. Toronto, Ontario, Canada. (Presenting author: Tulip Chakraborty)