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Coagulation effects of biological sludge reject water treatment

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Summary:

This thesis is study of methods for improving the coagulation process of municipal wastewater in Norway, carried out at the Knarrdalstrand wastewater treatment plant in Porsgrunn. In the study two main issue were considered as the aim of the thesis: I) replacing iron with calcium compounds as coagulant to provide a calcium-phosphate rich sludge for fertilizer purposes II) investigating effects of biological reject water treatment on coagulation efficiency when treated reject water is mixed with raw wastewater.

I) Conventionally wastewater treatment at the Knarrdalstrand plant uses ferric chloride as the coagulant. However, the phosphate precipitates as iron phosphate which is so strongly bound that the phosphate is not accessible nutrient for plant uptake. Hence calcium hydroxide was tested as an alternative coagulant to provide a phosphate rich sludge which is easier to recover phosphorus as fertilizer. Proper dosage and fast mixing time for both coagulants were determined through several repeated jar tests and the effects of the two coagulants were evaluated on coagulation of the treatment plant wastewater. Three and 15 seconds for fast stirring time and dosages of 2 mL/L and 800 mg/L coagulant were applied as the initial condition for ferric chloride and calcium hydroxide, respectively. The study shows that calcium hydroxide exhibited less sludge volume with higher solids content and faster settling velocity. The average sludge volume index (SVI) value of calcium hydroxide coagulated sludge was 46 ±5 mL/g which was around six times less than the average SVI of ferric chloride coagulation on the same wastewater. The results also show that the removal of organic matter (i.e. COD) and phosphorus were similar for the two coagulants. The reduction of COD and phosphorus were 89 ±9 % and 95 ±1 %, respectively, for calcium hydroxide while these values for ferric chloride were 76 ±15 % and 93 ±3 %, respectively. A positive effect on biogas methane potential (BMP) of calcium hydroxide compared with ferric chloride coagulant was measured and explained by enhanced hydrolysis.

II) The reject water contains high amounts of organic and inorganic compounds that causes process disturbance on the main coagulation process when it is returned to the main inlet. Two pilot scale biofilm reactors (MBBR) were employed to treat reject water biologically to test if such treatment can reduce the process disturbance and enhance coagulations efficiency. Treated and untreated reject water was mixed with raw wastewater the in ratio calculated for typical full scale plant and coagulation performance was investigated in several repeated Jar-tests with both ferric chloride and calcium hydroxide as coagulants. The results revealed that, when wastewater COD concentration was in the range of 140 to 350 mg/L, treating reject water gave better COD removal using both coagulants, confirming the advantage of biological reject water treatment. E.g. coagulation reduced the wastewater COD to 39 ±11 mg/L when the reject water was biologically treated while coagulation of untreated reject water decreased the COD to 58 ±5 mg/L. In both cases the same amount of ferric chloride coagulant dosage was applied as in the full scale plant. Biological reject water treatment did not show any statistically significant effect on turbidity and phosphorus removal through coagulation. Moreover, The SVI of the coagulated sludge was approximately the same for the treated and untreated reject water cases.

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Preface

This report was made on the topic "Coagulation effects of biological sludge reject water treatment" as a Master Thesis of M.Sc. program in the University of South-Eastern Norway, Faculty of Technology.

Theoretical analysis and practical aspects of research design, experiment setup, results, discussion and recommendations for future investigation are presented in the following report. The thesis mainly focused on comparing efficiency of ferric chloride with calcium based coagulants types to produce efficiently treated wastewater and readily available nutrient rich sludge. This study also investigated the effect of treated reject water on coagulation process in the wastewater treatment plant using both coagulants types at Knarrdalstrand wastewater treatment plant, Norway. The overall aim was to provide nutrient rich sludge which will be readily useable as fertilizer and to establish an efficient treatment solutions to the existing challenges in WWTP.

Porsgrunn, May 2018

Sepideh Niazi

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Nomenclature

AD	Anaerobic digestion
BMP	Biological Methane Potential
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
EDL	Electrical Double Layer
GS	Granular Sludge
HA	Humic Acid
LCFA	Long-Chain Fatty Acids
MBBR	Moving Bed Biofilm Reactor
MSW	Municipal Solid Wastes
MW-A	Microwave-Alkalininty pretreatment
NTU	Nephelometric Turbidity Unit
PAC	Polyaluminium Chloride
PE	Population Equivalent
SVI	Sludge Volume Index
TR	Treated Reject water
TSS	Total Suspended Solid
UR	Untreated Reject water
VSS	Volatile Suspended Solid
WAS	Waste Activated Sludge
WW	Wastewater
WWTP	Wastewater Treatment Plant

1 Introduction

The production of wastewater is an unavoidable process in human life. Wastewater generally consists of many organic and inorganic particles. Because of the many different sources which wastewater comes from, it normally contains high suspended solids, dissolved organics, organic matters including biological oxygen demand (BOD) and chemical oxygen demand (COD), colors and odors [1]. Wastewater is discharged into groundwater or surface water such as rivers and lakes. Organic and inorganic matters can cause rapid depletion of dissolved oxygen in the water and result in unfavorable condition for biological life. Therefore discharging untreated or inadequately treated wastewater leads to water pollution and can cause problems for human, aquatic life and the environment. Due to above reason, wastewater treatment before discharging is crucial issue [1]. Since particles in wastewater are very small and have a surface charge, they need to be treated to enhance coagulation and settling properties for further treatment. Hence, removal of these colloidal particles from the wastewater becomes a serious challenge [2]. Many different techniques such as adsorption, chemical precipitation, coagulation, flocculation, floatation, electrolytic, membrane processes and biological degradation processes are available for wastewater treatment with different technical and economical advantages and disadvantages [1, 3].

Coagulation processes is one of the most commonly used to separate solids and liquids and remove suspended and dissolved solids, colloids and organic matter present in wastewater [4]. It is found to be a cost effective, energy saving and easily controlled treatment alternative [5]. This process applies to wastewater or water, by adding compounds as coagulants, to remove organic and inorganic compounds. Coagulation can be defined as adding positively charged ions such as metal salt to neutralize negative charge particles in wastewater. Coagulants destabilize the colloidal materials and cause the small particles to accumulate into larger particle (flocs) which improve settle ability [1].

The settled particles is sludge with a high water content and it must be stabilized and dried to be used later as a fertilizer or raw material for other purpose [6]. In the conventional treatment process the settled sludge after the coagulation process is directed to the thickener and heated, then used in biogas production in anaerobic digestion (AD) reactors. The effluent from AD is dewatered in a centrifuge and the solid sludge is mainly use as a fertilizer in agriculture, parks, road embankments, etc. [7]. Characteristics of the effluent sludge vary with the type of treatment and biological process. Sewage sludge is a rich source of nitrogen, phosphorus and organic matters which can be of particular benefit to plants and grasslands and usually used to produce fertilizers or used directly in agriculture industry. Therefor it is important to provide sludge in low volume with high solid content [8].

In Norway, there are 2500 municipal wastewater treatment plants (WWTP) in populous areas and about 350,000 small treatment plants in sparsely populated areas. Most wastewater treatment plants were built in 1970 to 1985 [7]. According to Statistics Norway, in more open coastal waters, mechanical treatment is more common, since the aquatic environment there is less sensitive to this type of discharge. High-grade treatment plants are much more efficient to remove pollutants from the wastewater than mechanical treatment plants. The high-grade chemical and/or biological treatment are mostly in the east of the country and the Trøndelag region and more mechanical treatment in the rest of the country. In 2016, almost two third of Norway’s population was connected to high-grade treatment plants, biological and/or chemical treatment [9]. Based on Statistics Norway websites, there are also some natural purification plants in the inner eastern parts of the country which dispersed direct discharges along the coast, from western Norway up to Finnmark in the north. Even though 90-95 % of the bacteria concentration is removed in advanced treatment plants, the remaining is still considerable [9].

Knarrdalstrand wastewater treatment plant is a mechanical-biological-chemical treatment plant in Porsgrunn which was built in 1990. Municipality sewage from Porsgrunn and Skien comes down to this treatment plant. The average current inlet is 52000 population equivalent (PE) and the capacity of the plant is 82000 PE. Figure 1-1 shows the wastewater treatment process in Knarrdalstrand WWTP. The wastewater is treated by a combination of mechanical and chemical processes during primary treatment and there is also biological part to produce biogas in anaerobic digestion reactors (AD). The hydraulic retention time in primary treatment stage is one day. Ferric chloride is used in the coagulation process. Depending on the concentration of the inlet wastewater the dosage ranges from 100 to 250 mL ferric chloride /m^3 of wastewater. The system used for estimation of the optimum coagulant dosage is which estimate the proper dosage based on pH of wastewater. Chemicals are added to main stream after preliminary treatment before flocculation chamber.

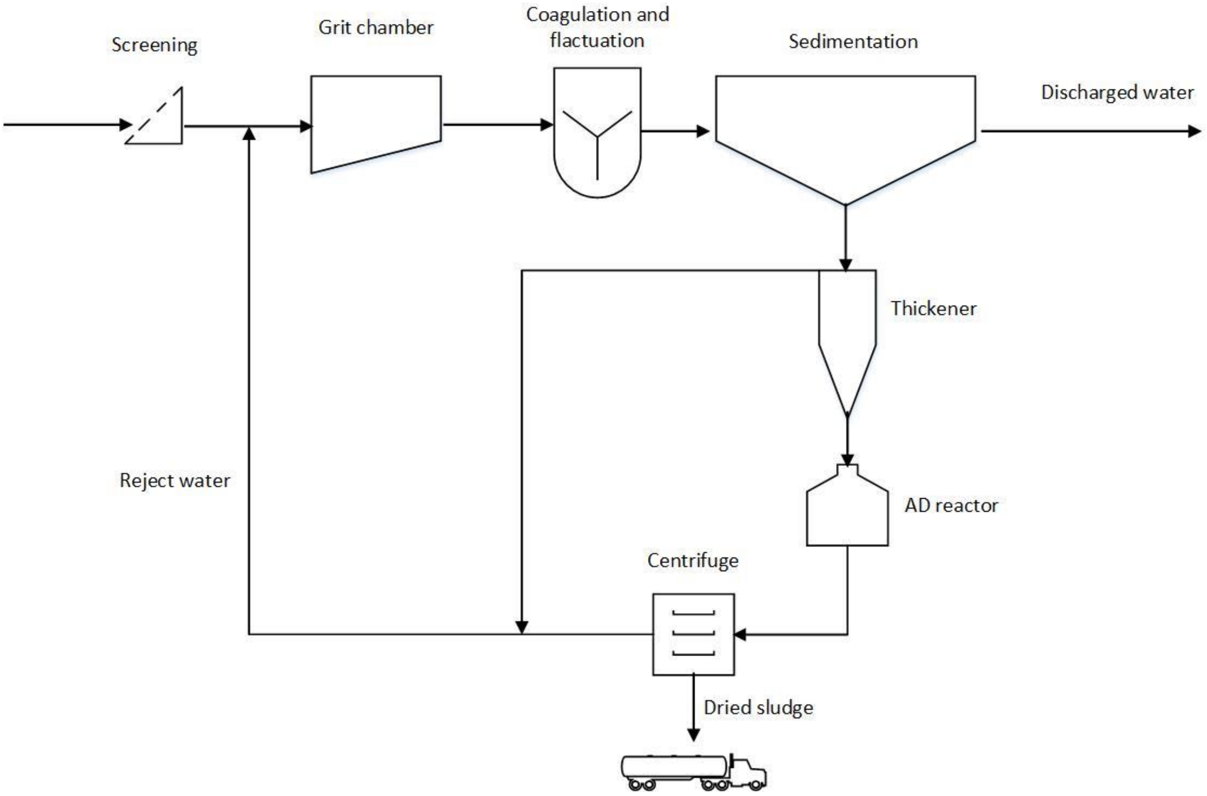

Figure 1-1: A schematic diagram of the wastewater treatment process at Knarrdalstrand WWTP

A semi-solid slurry retained by the coagulation followed by sedimentation is called sewage sludge. Sludge with a high water content flows to the thickener and heated, then used in biogas production in AD reactors. The effluent from the AD is dewatered in a centrifuge. The over flow water from the thickener and the centrifuge reject water returns back to the main system and mixes with inlet wastewater. The dried sludge after the centrifuge is transported out of the treatment plant for further process and disposal.

1.1 Problem description

Sewage sludge is a rich source of nitrogen, phosphorus and organic matters which can be of particular benefit to agricultural plants and grasslands. Hence, dewatered sewage sludge usually used to produce fertilizers or used directly in agriculture industry [8]. Phosphorus is one of the macro-nutrients that is used widely in agriculture practices. In current treatment condition in Knarrdalstrand WWTP, the sludge contains iron since ferric chloride is used as coagulant. The phosphate in the sludge precipitates as iron phosphate strongly bound together that the phosphate is not readily available for plant uptake (i.e. due to phosphate fixation by iron it affected the mobility of nutrient in the soil).

However, phosphorus can be recovered through precipitation as calcium phosphate. Consequently, using calcium based coagulant in wastewater treatment sludge is an opportunity to produce calcium phosphate sludge as readily available phosphorus rich fertilizer [10]. Hence, calcium hydroxide was tested as an alternative coagulant to provide a phosphate rich sludge from which it is possible to recover phosphorus as fertilizer.

On top of that the problem at Knarrdalstrand WWTP is related to the reject water management. The effluent liquid from the thickener and centrifuge contains large amounts of particles and organic matters which is recirculated to the main inlet that has created serious process disturbance in the coagulation process. Currently, Knarrdalstrand WWTP does not have supplement biological process to remove organic matters from reject water. The purpose is to establish an efficient biological treatment for the removal of organic matter in the reject water from the sludge dewatering processes before returning to the original plant inlet.

In the biological treatment process it is hypothesized that four mechanisms (i.e. hypothesis) will be involved [11] as listed below:

1. Dissolved and/or colloidal organics in the reject water will be degraded (oxidized) in the introduced bio-process.

2. Dissolved and/or colloidal organics in the reject water will be converted into biomass through cell synthesis in the introduced bio-process and these cells will be removed by coagulation in the main treatment train.

3. The active biomass synthesized in the bio-process will capture more dissolved organics and colloidal solids from the fresh wastewater, when introduced into the treatment plant inlet; all of which will be removed by coagulation in the main treatment train.

4. The biologically treated reject water will cause less disturbance on the main coagulation process than the untreated reject water does today, implying that the coagulation process can become more efficient.

However, this thesis will focus on mechanisms 3 and 4. In fact the first two mechanisms were purposed for another study which actually conducted in parallel with this study [12]. The thesis emphasized on the biological effects in treating reject water as well as improving the coagulation process in the plant. To investigate this proper experimental was set up and the coagulation efficiency was compared for the untreated reject water (i.e. current condition in the plant) and treated reject water (i.e. proposed biological method).

1.2 Goal of the study

This study has focused on the coagulation process and its performance as the main treatment step in domestic wastewater treatment. Improving the quality of discharged water and final sludge are two main factors, which were evaluated through investigating the effects of a proposed biological reject water treatment and a different coagulant type. Therefore, two main objectives for this study can be listed as:

- To investigate the effects of changing coagulant type from a ferric chloride (PIX 318) to a calcium based coagulant to provide phosphorus (P) rich sludge which can more readily recovered as fertilizer.
- To investigate if biological reject water treatment can have a positive effect on the coagulations processes for wastewater treatment.

The experimental analysis in both objectives are divided in two parts: water analysis and sludge analysis. The reductions of organics (COD), particles (TSS and turbidity) and P by coagulation were used as measurement parameters for water analysis whereas organic particles (VSS), sludge settling efficiency (i.e. sludge volume index, SVI), biological methane potential (BMP) and P content are considered as main parameters to evaluate sludge quality.

2 Literature review

Coagulants are typically chemical compounds that are added in wastewater to destabilize the colloidal particles and form larger particles as flocs. Coagulants play a major role to neutralize the surface charge of colloidal solids and suspended particles are aggregate particles and settle by gravity [13]. Coagulation is mainly induced by natural and synthetic organic polymers, metal salts and prehydrolized metal salts [10]. The most common coagulants are metal salt such as polyaluminum chloride (PAC), aluminum sulfate (alum) and ferric chloride [13].

The main applications of coagulation in modern wastewater treatment are disinfection, phosphorus removal, particulate matters removal, pH control and water stabilization [10]. Various materials and techniques have been developed in recent years to increase the coagulation efficiency. Although different kind of coagulant and many methods have improved the coagulation process, there is still needs research to improve the performance as well as the kind of coagulants [13].

Among others, biological reject water treatment is a novel alternative to enhance coagulation performance which was evaluated in this study.

2.1 Biological treatment

A reject water in a wastewater treatment train contains large amounts of particles and organic matters. Since reject water is recirculated to the main inlet it usually creates process disturbance mainly on the coagulation process. On the other hand, biological treatment is a method to remove dissolved and suspended particles from reject water. Hence, organic matters will be stabilized through the bio-processes [14]. Moreover, Dissolved organics and colloidal solids in the reject water are degraded and converted into biomass through the cell synthesis in the biological treatment. This active biomass capture more dissolved organics and colloidal solids from the wastewater, when return to the main inlet. Therefore, biologically treated reject water will cause less disturbance on the main coagulation process than the untreated reject water and thereby it leads to more efficient coagulation process [11].

In a biological treatment processes the culture control is crucial to reach ideal growth of diverse types microorganisms. Under those circumstances, organic matters decomposition can occur faster by controlling the culture. Beside that it is possible to follow biological performance or control fluctuations by regulating pH, temperature, feed amount, aeration and mixing. For instance, one of the latest version of bioreactors in wastewater treatment plant are moving bed biofilm reactor (MBBR) which has more stable performance [14].

MBBR consists of an aeration system together with huge amount of bio-carriers (usually filled with two thirds of reactor volume) which will move properly through the aeration process inside the reactor. The main idea is to provide broad contact surface of carriers(from 500 to 1200 m^2/m^3) organic or inorganic substances in the wastewater where the biomass grow on carrier’s surface [15].

2.2 Chemical coagulation

Colloidal particles existing in wastewater, have negative surface charge and they are bombarded by small water molecules which are driven by random thermal motions. These random movement (Brownian motion) keeps the particles in suspension. The size of these colloids particles ranges from 0.001 µm and 1 µm while the suspended particles are larger between 0.5 µm and 100 µm [10, 16]. In addition, the presence of organic matters can increase the turbidity, odors, chromaticity (i.e. quality of color) in water [17-19]. Moreover, lots of inorganic and organic compounds in nano-size, are adsorbed easily on the surface of large particles due to their large specific surface area, which cause to improve the stability of the particles [16].

The coagulation process is the vital method to destabilize the colloids and suspended particles that can result in floc formation [10]. The most important factor to stabilize the colloidal is presence of surface charge. Surface charge develops in different ways, such as preplacement and ionization, depending on the chemical composition of the wastewater. When the colloidal particles are charged some positive charged ions attach to the surface. Electrostatic and van der Waals forces are strong enough to overcome thermal agitation. Surrounding this fixed layer (also called stern layer) diffuse layer of ions is forming that prevent from creating compact double layer by thermal agitation. Compact double layer leads to potential drop to zero in the bulk solution. In flocculation the size of particles increase as a result of particle collisions. Figure 2-1 shows the distribution of positive and negative ions around the charged colloid and different layers.

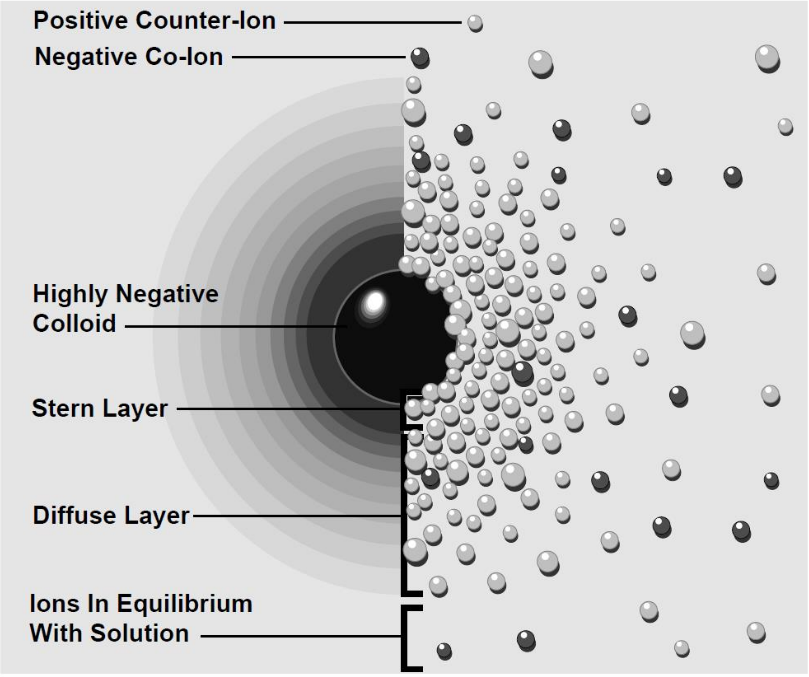

Figure 2-1. Schematic overview of negative particle in suspension (Adapted from zeta-meter.com)

Microflacculation (also known as prekinetic flocculation) occurs by Brownian motion which provide random thermal movement whereas *macroflocculation* (also known as orthokinetic flocculation) is created by mixing the fluid to flocculate the particles. During settling large particles may overtake the small particles and form larger particles. Hence, the purpose of flocculation is to aggregate the particles to produce larger particles, that can be removed by inexpensive particle-separation process such as sedimentation [10].

Coagulants in water treatment always contains ions with positive charges while colloidal contents and suspended particles are of negative charges [16]. In some cases these coagulants are efficient enough in wastewater treatment without flocculants assistant [20, 21]. For the case where the coagulant and particles are opposite charges, generally charge neutralization is mentioned as the major mechanism. Metal salts hydrolyze rapidly in wastewater at isoelectric point to form cationic species and absorbed by colloidal particles which carry negative charges. It leads to surface charge reduction (i.e. reduction of zeta potential) which allows for the formation of van der Waals force to aggregate the colloidal and fine suspended materials to form microflocs [22]. The optimum coagulation occurs if used dosage neutralizes all the particles charges and give zeta potential close to zero (isoelectric point). However, if too much coagulant is used, a charge reversal occur and particles disperse again but in positive charges [23].

In addition to type of coagulant, several operating factors, such as coagulant dosage, pH, stirring speed, stirring time and temperature are essential factors which effect on coagulation process [13].

2.2.1 Coagulant dosage in coagulation process

The load and culture of wastewater always vary. Therefore, a suitable dosage of coagulant is actually depends on the amount of colloidal and suspended particles in the wastewater. Generally the coagulation performance is assumed to be more efficient with increasing the amount of coagulant. However, under a specific conditions the treatment efficiency reaches a peak on certain amount of coagulant and decreases with the further input of dosage [24]. Excess of inorganic coagulant leads to reversal of particle surface charge and re-stabilization which decreases the coagulation efficiency [13, 25]. The treatment cost and the sludge amount will then increase [26].

The relation between coagulant dosage and colloid concentration are shown in Figure 2-2. Four different zones are described in the figure: zone 1: Insufficient coagulant dose applied to suspensions. Zone 2: Destabilization through charge neutralization. Zone 3: Re-stabilization due to coagulant over dosage. Particle surface become positive in this zone. Zone 4: Sweep flocculation due to oversaturation of coagulant. It shows that the particle removal only occur when particle destabilize with proper dosage or sweep flocculation can happen due to oversaturation with very high dosage. Moreover, sweep flocculation occur with high dosage of coagulant due to metal hydroxide precipitation. After absorbing metal ion to particles surface, hydroxide accumulate and entangle with particles. Hence, in addition to destabilized particles, the swept particles with the hydroxide precipitate [27].

In fact, for the low colloids concentration of sample (S_1), high dosage of coagulants is needed to remove particles (zone 4). When particles concentration increase to S2 and S3, the particles remove in zone 2 by charge neutralization. On the other hand, by increasing dosage of coagulant, the particles re-stabilize and then removed due to sweep flocculation with more dosage. Hence, at very high colloid concentration, destabilization and sweep flocculation merges together and particle removal occurs as one form [28]. Thus it is important to determine the exact quantity of coagulant at any time to obtain the maximum efficiency and avoid over dosage on coagulation process.

Yufeng Wang et al. (2013) used Polyaluminum chloride (PAC) as a main coagulant and found that the optimum dosage was around 500 mg/L in COD, ammonia nitrogen (NH3-N) and total suspended solids (TSS) reduction [26]. Gohary et al. (2010) has reported the optimum dose of ferric chloride and alum (aluminum sulfate) around 600 and 700 mg/l while that of ferrous sulfate was 850 mg/L to remove COD [5]. Rana et al. (2017) studied on textile industry wastewater and introduced 4 g/L of ferric chloride as the optimum value for COD removal [1].

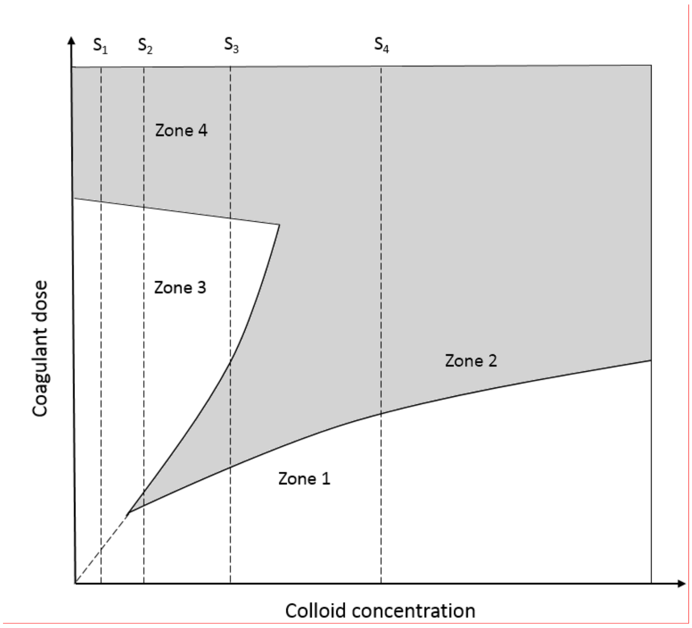

Figure 2-2. Coagulant dosage as a function of colloid concentration [28]

2.2.2 pH in coagulation process

Among others, pH is one of the most well-known parameter which change the coagulation efficiency of wastewater [13, 29]. Maximum coagulation performance can be achieved with optimum level of pH and sufficient amount of effective species. The effective species can destabilize colloidal and suspended particles in wastewater during coagulation [30]. For instance maximum color removal for ferric chloride is achieved at pH 6. The efficiency decreases when the pH is out of optimum range [13]. Rana et al. (2017) has reported that ferric chloride is efficient at pH of 4 and at this pH level maximum reduction of COD is achieved for wastewater from textile industry [1].

2.2.3 Mixing time and velocity in coagulation process

A typical coagulation process consist of two stages of mixing which are rapid and slow stirring. Rapid mixing time is from 60 to 180 seconds with a mixing speed of 75 to 700 rpm and slow mixing time is 5 to 30 min with a mixing speed of 30 to 150 rpm. The purposes of rapid mixing are to provide a good dispersal of coagulant to destabilize the particular matters in the raw water while slow mixing propagate the growth of flocs by limiting the breakdown of aggregates [13, 24].

Coagulation efficiency decreases when the mixing time is too long and mixing velocity is too rapid. Although the collision of flocs is assumed to increase with the higher stirring speed and time, but it cause to disrupt flocs in to irreversible small particles and reduce the coagulation efficiency. On the other hand, slow stirring speed and short stirring time lead to inadequate contact with particles and they fail to join with coagulants and form flocs [13]. Typical mixing times for the chemicals used in wastewater treatment are changed based on the type of chemicals. Recommended initial mixing time for many kind of coagulants is less than 30 seconds [10]. Thus, optimizing the stirring time and speed is important factor in wastewater treatment [13].

2.2.4 Temperature in coagulation process

Temperature is another factor that have effect on the coagulation efficiency. The effect of temperature on coagulation performance varies with materials and culture of wastewater [13]. However, only a limited number of literatures have discussed about its impact.

Zhao et al. (2011) have found that phosphate removal from synthetic wastewater decrease in lower temperature [31]. Gao et al. have reported that higher temperature (5-40 °C) lead to reduce turbidity [32].

2.3 Hydrolyzed metal ions as coagulant

The degree of clarification of treated wastewater depends on type of chemicals used as coagulant. In well-designed and well-operated sedimentation tank, 50 to 70 percent of the solids matters measured as TSS and 25 to 40 percent of organic matters measured as BOD are removed without adding any chemical. These value can be increase to 90 and 80 percent respectively, by adding chemical as coagulant [10].

2.3.1 Iron based as coagulant

Iron based coagulants are the most common metal coagulants used in water treatment because of high effectiveness and low cost. This coagulant is usually produced using ore and hydrochloric acid (e.g. to produce $FeCl3$), which can effect on sustainability [27].

Trivalent metal salts, such as iron can dissociate to produce a negative ion by adding sufficient base. The central metal ions are attached to a group of surrounding molecules (ligund). Ligund compounds of interest in wastewater treatment include: Chloride (Cl^-), hydroxide (OH^-), carbonate (CO_3^{2-}), ammonium (NH_4^+) and water (H_2O) [10].When iron coagulants are added into wastewater, it immediately reacts and form water-coordinated complexes, $Fe(H2O)_6^{3+}$. Thereafter, what follows next is a series ligand substitution, the ligand of interest being OH^- [27]. Iron has the ability to form polynuclear complexes by using OH^- ligand as bridge between metal atoms. Bi-nuclear is the simplest complex and the first step to form the polynuclear complex [27, 28].

All species of iron interacts with the surrounding particles and it is difficult to control the species of metal complexes that are formed. Thus Ferric chloride is usually prepared by reacting the metal with water and various salts. Due to this, species formed during the coagulation process are controlled and, lower dosage required and stronger floc-formation is achieved. Reaction of Iron complexes with species in water include ligand substitution with naturally occurring phosphates and sulfate, which will impact the overall efficiency of coagulation process. Therefore, it is important to use the right dosage of coagulant to add in to water [28]. The reaction of coagulants in the water is very fast which makes initial stirring of coagulant very important [27]. Because of the difficulties to achieve rapid stirring in a large plant, the multiple mixing devices are used. Typical initial mixing time for ferric chloride is reported in the range of 1 to 10 second [10].

2.3.2 Calcium based as coagulant

The Calcium ions are neutral or slightly positive charged and its ability to absorb the negatively charged particles depends on pH value. With increasing pH and in alkaline environment, calcium ions become negatively charged which leads to repulsive electrostatic interaction between particles and calcium ions. Thus the coagulation efficiency drops in high pH [33].

Some studies have indicated that calcium have positive effect on flocculation process specially to remove humid acid. Ryou Sudoh et al. (2015) argued that Ca^{2+} which is derived from calcium carbonate makes humic acid (HA) colloid which are big in size and easier to form flocs because of the compression in the electrical double layer (EDL) between HA colloids [33]. Dong (2012) has indicated that calcium reduce the zeta potential of Humic acid and helps to produce larger and more stronger flocs [34]. HÄGG (2015) has indicated the positive effect of calcium chloride as co-coagulant when pH was above 5 and at low dosage and the UV-VIS results for the samples with $CaCl_2$ gave better results than the sample without $CaCl_2$ [27].

Przepiora et al. (1997) found that calcium sulfate can reduce the turbidity of water after 3h treatment. The turbidity of water was reduced from 400 to 50 by adding 0.55 g/L of calcium sulfate. Moreover, when the concentration of calcium sulfate was increased to 1 g/L, the turbidity reached to 15 NTU [35]. Devesa-Rey et al. (2011) have used calcium lactate as a coagulant–flocculants. They indicated that 6 g/L and 2 g/L of calcium lactate reduced the water turbidity from 300 NTU to 2.5 and 5.5 NTU respectively after 18 h of treatment at pH 5 [36].

2.4 Jar test

Jar test is a robust method to simulate the coagulation process of a full scale plant as well as to test the effect of different parameters such as type of coagulant and dosage on water quality at pilot and/ or Lab. scale. Jar test consist of three levels to simulate different phases of large scale. It starts with rapid mixing as coagulation phase, then slow mixing as flocculation phase and finally no mixing as sedimentation phase.

The time for the each different phases is important for a better coagulation efficiency. In the first level, the required time to form mononuclear and polynuclear is 10^{-10} and 1 second respectively. The time needed to adsorb to particle of complexes and form the double layer is 10^{-10} seconds. Thus there is no benefit to have long rapid mixing time after adding coagulants whereas it may impair coagulation and flocculation process. In flocculation level, small suspended particles steadily become larger immediately after destabilization for seconds. The slow mixing cause collisions between new large particles and provide the steady state situation to break up and form flocs in constant forced convection [27]. Clarification is achieved purely through the help of gravity sedimentation. The required time to settle the created flocs depends on the weight, size and shape of the particles and sample temperature [27, 37]. Large volume of flocs will settle in a given time and provides sludge which contains the most particles, organic and inorganic materials of sample.

2.5 Water and sludge analysis

Waste products of the wastewater treatment process can be a problem or an opportunity as a source for obtaining raw materials [6]. Sludge from coagulation follows to the thickener and heat up (i.e. hygienized) and it is used to biogas production in anaerobic digestion (AD) reactors. The reject water from the AD is dewatered in centrifuge to biosolids (treated sludge) mainly used as a fertilizer in agriculture, parks, road embankments, etc. [7]. Therefore, in addition to the water quality, the characterization of sludge is vital for both aims to estimate the biogas potential as well as suitability as fertilizer.

Turbidity, organic matters content such as chemical oxygen demand (COD), Total suspended solid (TSS) and total phosphorus are some of the most vital environmental concerned parameters on water quality [13]. While VSS, SVI and phosphorus are considered as most important factors to analyze the sludge.

2.5.1 Turbidity

Turbidity is a measure of the light scattering of a liquor which contains suspended and colloidal particles [10]. It is measured by optical properties and indicates water clarity. The technique for analyzing turbidity is called nephelometry. A light beam is directed into the water sample and a detector that is positioned at a 90^{o} angle measures the scattered light. Turbidity measurement is very sensitive to particle size, shape and refractive index, but not amount of particles. Thus there is no direct correlation between the turbidity of the water and amount of suspended matter in the water [27]. When the particles are larger, it cause the beam to be scattered more and turbidity value increase. Turbidity is measured in nephelometric turbidity units (NTU) and it is very useful parameter to control the process and quality of water [27, 28].

2.5.2 Organic matter

The most commonly used method to measure organic matter in wastewater characterization is COD. The COD test is used to measure the oxygen equivalent of the organic material that can be oxidized chemically using dichromate in an acid solution [10].

The electrons from organic matter also may be some inorganic substances react with dichromate. The reaction is performed in hot sulphuric acid solution and catalyzed by silver cations. A few types of organic materials, such as aromatic hydrocarbons and pyridines are resistant to the oxidizing conditions of the test. Only carbonaceous compounds are completely oxidized, so that the COD value does not include ammonia. However, the COD test is relatively easy to perform and the results are obtained in a few hours through the use of commercially available kits [38].

2.5.3 Biomass concentration content

There are several methods to determine the biomass concentration based on different types of measurements, such as mass, volume or linear extent, metabolic rates, light scattering, cell or organelle count. Volatile suspended solid (VSS) is a simple technique to determine biomass concentration as an alternative to the standard method [38].

2.5.4 Sludge volume index (SVI)

The SVI test is used to compare the sludge volume of mixed liquor based on solids. Lower SVI value indicates the more rapid thickening and more efficient clarifier performance. The SVI is expressed in milliliters per gram (mL/g) which shows the volume of 1 gram of sludge after 30 minutes of settling. It is important that sludge volumes are kept at a minimum with a high dry-solids content to reduce disposal costs. The numerical value is computed by the following formula [10]:

$$\text{SVI}\,[\text{mL/g}] = \frac{(\text{settled volume of sludge}\,[\text{mL/L}])(10^{3}[\text{mg/1g}])}{\text{suspended solid}\,[\text{mg/L}]} \qquad \text{Equation 2-1}$$

2.5.5 Phosphorus in wastewater

Even though phosphorous is the beneficial compound in ecosystem, the high amount of phosphorus in water bodies (i.e. lakes, rivers etc.) cause environmental problem such as eutrophication. Dissolved phosphorus elements can be classified in three categories: Orthophosphate (PO_4^{3-}), polyphosphate and organic phosphorus. Among these dissolved phosphorus species, Ortho-P is the main reason for eutrophication [39]. Phosphorus in wastewater can be removed by addition of chemicals or incorporated into biological solids. The most used chemicals which can contribute in phosphorus removal are: ferric iron [Fe(III)], ferrous iron [Fe(II)], aluminum [Al(III)] and calcium [Ca(II)] [10]. On the other hand, phosphorus is a macro nutrients that is widely used in agricultural practices but it is a non-renewable resource. Consequently, recovering phosphorus form residual sludge is an opportunity to produce nutrient-rich sludge fertilizer. Calcium is an element which can recover removed phosphorus as calcium phosphate through precipitation [10]. In this study ferric iron and calcium were used as chemical to remove phosphorous from water and recover it in the residual sludge. However, the chemistry of phosphate removal with iron is quite different with calcium [10].

2.5.5.1 Phosphorus removal with Iron

Iron salt reacts with the soluble orthophosphate to produce precipitate. Organic phosphorous and polyphosphate are removed by more complex reactions. The removal of phosphate with metal salt can occur by formation of hydrous ferric oxides, mixed cation phosphate and ferric phosphate. Phosphate removal is accomplished by removing these compounds with either sedimentation or filtration. The reaction of iron salt for phosphorous removal is described in Equation 2-2:

$$1.6\,Fe^{3+} + HPO_4^{-} + 3.8\,OH^{-} \rightarrow Fe_{1.6}.H_2PO_4(OH)_{3.8}(s) \qquad \text{Equation 2-2}$$

Because of many other competing reactions, it is not possible to calculate the required chemical dosage based on the reaction. Therefore dosages are generally set up based on bench scale test [10].

2.5.5.2 Phosphorus removal with calcium

When calcium hydroxide is added to water it reacts with bicarbonate alkalinity and produce calcium carbonate as precipitate. Excess calcium ions react with phosphate to precipitate hydroxilapatite (i.e. mineral form of calcium apatite) as shown in Equation 2-3.

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

Lime has reaction with alkalinity thus the alkalinity of wastewater has impact on the quantity of required lime. The quantity of required lime for phosphorous removal in wastewater is typically about 1.4 to 1.5 times the total alkalinity as $CaCO_3$ [10].

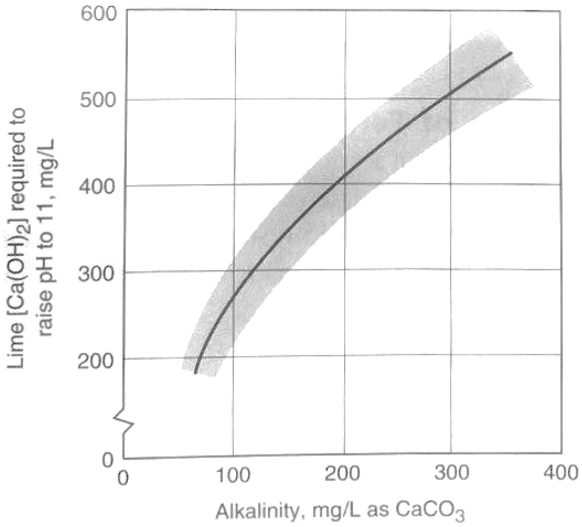

Figure 2-3. Required lime dosage as a function of untreated wastewater alkalinity [10]

2.5.6 Biogas production

Biogas is an important source of energy in heat and electricity generation. As a sustainable clean energy carrier it is one of the most promising renewable energy sources in the world. Biogas is produced by anaerobic digestion of organic materials such as sewage sludge, biodegradable wastes, agricultural slurry and municipal solid wastes (MSW). Several types of microorganisms have the main role to produce biogas.

Biogas is composed of methane (55–75%), carbon dioxide (25–45%), nitrogen (0–5%), hydrogen (0–1%), hydrogen sulfide (0–1%), and oxygen (0–2%). The sewage sludge contains mainly proteins, sugars, detergents, phenols, and lipids. Sewage sludge may also include toxic and hazardous organic and inorganic pollutants sources [40].

The anaerobic digestion occurs in four basic steps: Hydrolysis, acidogenesis, acetogenesis and methanogenesis. During these steps the complex particulate materials is converted to soluble materials, volatile fatty acids (VFAs), CO_2 and hydrogen by acidogenic bacteria. Intermediate products of acidogenesis convert to acetate, CO_2 and hydrogen. Finally methane will be produced by converting the acetate into the methane and CO_2 and/or using hydrogen as electron donor and CO_2 as electron acceptor to produce methane [10].

For instance, during a 30-days digestion period (i.e. hydraulic retention time), approximately, 80–85% of the biogas is produced within the first 15–18 days. Higher digestion were observed within the pH range of 5.5–8.5 and temperature range of 30–60 °C. The optimal C/N ratio for the AD should be between 25 and 35. However, municipal sewage sludge contains low nitrogen, hence nitrogen can be added in an inorganic form (i.e. ammonia) or organic form such as livestock manure, urea, or food wastes [40].

3 Materials and methods

3.1 MBBR reactor

Two MBBR reactors with each has a working volume of 18.8 L were set up at Knarrdalstrand wastewater treatment plant WWTP in Porsgrunn, Norway (Figure 3-1). The filling ratio of bio carriers was 63 % of the volume of the inner section of the reactors. The carriers were BWTX (i.e. dimensions were 14.5*14.5*8.2 mm with a protected surface area of 650 m^2/m^3) which were supplied by Biowater Technology. The reactors were fed with reject water and over flow form the thickener in 1:1 ratio. The feed pipes were from top of the reactors and the effluent outlets were on the outer section of the reactors. The aeration was at the bottom of the inner section of the reactors to provide the required dissolved oxygen (DO) and free movement bio-carriers inside the reactors. The reactors were run for two months at hydraulic retention time of 24 h and 12 h. Average temperature in the reactors was around 14.1 ± 0.2 ºC and DO concentrations at the inner section of the reactor ranged between 2.2 and 7.4 $mg\cdot L^{-1}$.

After two months the reactors were replaced with another two MBBR reactors provided by Biowater Technology company with the working volume of 68 L (Appendix 2).

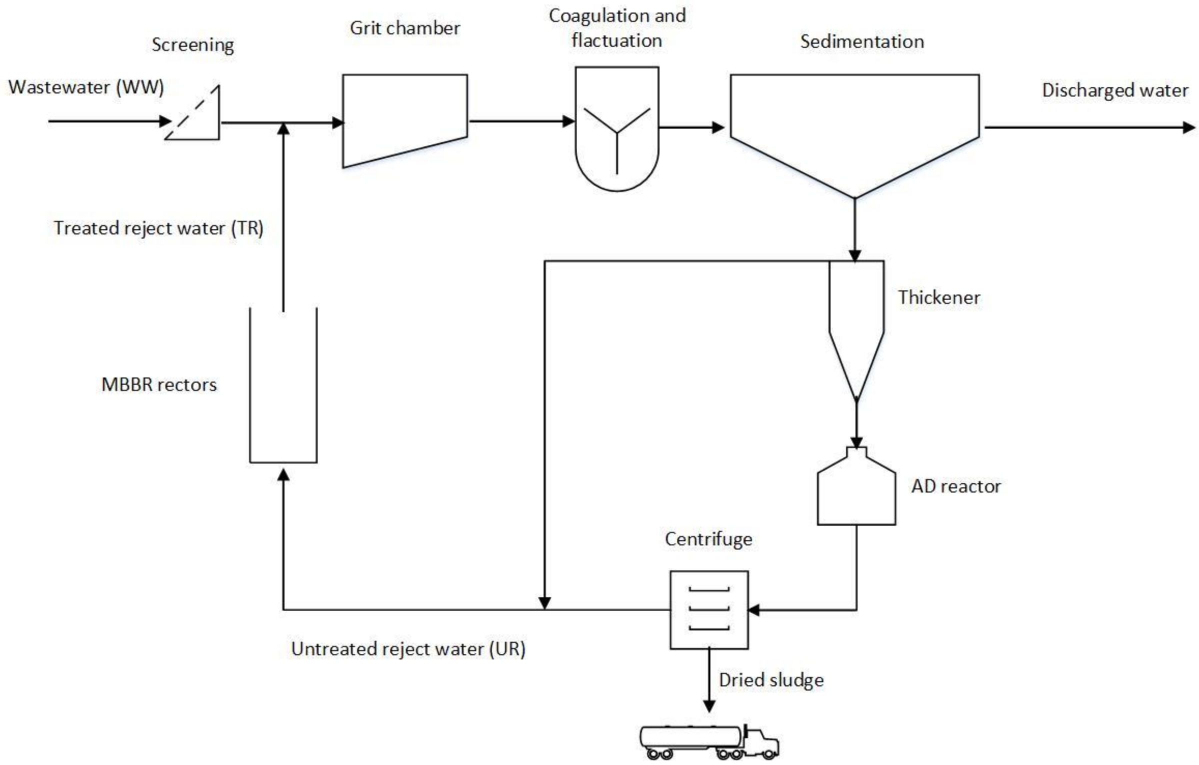

Figure 3-1. Flow diagram of Knarrdalstrand WWTP included biological process in system. Treated (TR) and untreated reject water (UR) are introduced.

3.2 Wastewater in Knarrdalstrand

The wastewater (WW) used in this study was collected from the point after grid at Knarrdalstrand WWTP (Figure 3-1). The quality of raw wastewater varied daily depending on weather condition and precipitation. The experiments were conducted from January to April 2018. A total of The 21 wastewater samples were characterized and analyzed during the experimental period. The experimental parameters used to characterize the wastewater are given in Table 3-1. These parameters were measured based on the standard methods for the examination of water and wastewater [41].

Table 3-1. Characteristics of wastewater

Parameters	Alkalinity (mg $CaCO_3$/L)	COD (mg/L)	Turbidity (NTU)	Phosphorus (mg/L)	pH	TSS (mg/L)
Min	150	42	19	0.73	7.2	25
Max	222	441	126	3.95	8.5	340
Average	186 (±20)	237 (±117)	57 (±30)	3 (±1)	7.8 (±0.3)	139 (±92)

Turbidity was measured using HACH meter model 2100 N. The Gelex Secondary Standards were used for instrument calibration. The COD was measured by spectroquant® Pharo 300 UV/VIS spechtrophotometer (Darmstadt, Germany).

Total suspended solids (TSS) and volatile suspended solids (VSS) were measured according to the standard methods. The filter paper used was Grade G/C glass fiber filter with pore size of 1.2 µm. The phosphorus concentration was determined by HACH colorimeter for certain samples and then changed to spectroquant® Pharo 300 UV/VIS spechtrophotometer. According to the standard procedure phosphorus reacts with acid which results in blue color (Figure 3-2). The difference in color leads to difference in absorption of light and estimate the concentration [39].

Figure 3-2. Different blue color on phosphorus cells showing different concentration of phosphorus

3.2.1 Preparing samples

Since the second objective of this study was to investigate effects of treated and untreated reject water on coagulation when returned to the main treatment train, two different samples were prepared during the experiment: The mixture of wastewater and untreated reject water (UR) that represent the current condition in the plant without biological treatment and the mixture of wastewater and treated reject water (TR) which simulates the proposed method in the pilot scale (Figure 3-1).

According to in and out water mass balance of the treatment plant reported in previous study, proportion of the yearly average flow of main inlet and reject water were 98.9 % to 1.1 % in the full scale plant, respectively (Appendix 3) [15]. Thus the mixture of samples were prepared based on aforementioned ratio to simulate the full scale condition. Untreated reject water and treated reject water samples were collected from the inlet and outlet of the MBBR pilot scale reactor respectively (Figure 3-1). Table 3-2 shows the proportion of samples in the jar test.

Table 3-2. Proportion of sample contents during the jar test

Mixture of jars	Wastewater (WW) (mL)	Untreated reject water (UR) (mL)	Treated reject water (TR) (mL)
WW+UR	989	11	0
WW+TR	989	0	11

3.3 Jar test

The jar test procedure comprising six beakers was set up at room temperature for each test (Kemira- flocculator 2000). Each beakers contained 1 L of mixed wastewater based on aforementioned proportions in Table 3-2.

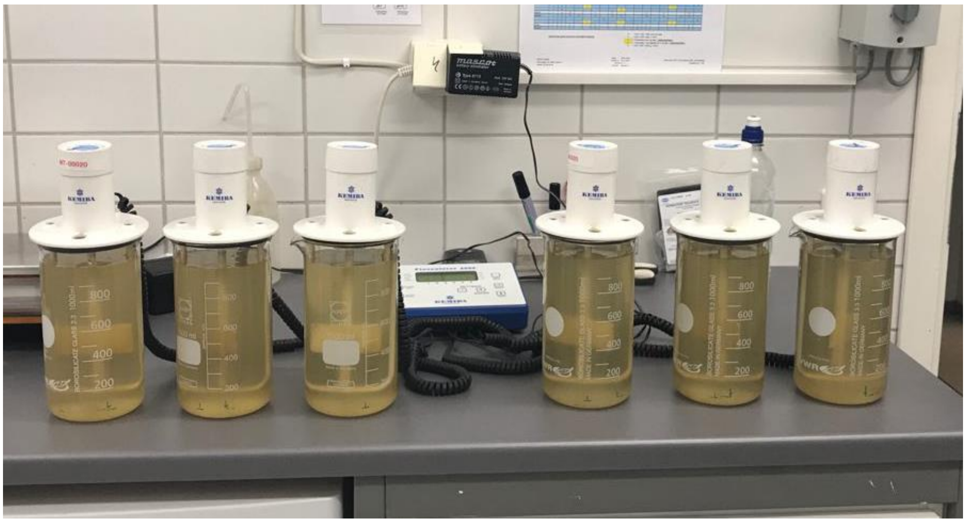

Figure 3-3. Jar test setup which include 6 beakers which are filled with 1 L of wastewater according to the aforementioned proportions

1 L of sample was poured in each jar and it was stirred for a period of 1 min at 200 rpm. After determining the best dosage and fast mixing time (i.e. which is described in section 3.3.2), the selected coagulant dosage was added in each jar at the determined time for rapid mixing. It was followed by a further slow mixing of 20 min at 50 rpm. When the rapid mixing was finished and slow mixing is started the samples pH were measured using Beckman 390 pH-meter. The formed flocs were allowed to settle for 30 min. After settling, the volume of sludge was recorded and clean water sample was taken from 3 cm below the surface. Then 200 mL of sediment which contains mostly sludge was mixed slowly with 800 mL of tap water and the new samples were taken to analyze the sludge. COD, turbidity, phosphorus and TSS of the water and SVI and VSS of sludge were determined based on the standard methods. The raw wastewater and jar test products (i.e. clean water and sediment sludge) were repeatedly analyzed to evaluate the positive or negative effects on discharged water quality and sludge characteristics.

3.3.1 Coagulants

This study attempts to compare calcium based coagulant with ferric chloride as a main coagulant in primary level. In fact calcium chloride was the first option and different dosages (i.e. from 0.3 g to 3 g in one liter of sample) were applied as coagulant to investigate floc development in the samples. However, no sign of floc formation was observed in the coagulation process. Therefore, calcium hydroxide was tested as second option and compared with ferric chloride to evaluate their performance on coagulation.

Ferric chloride is currently used as a coagulant in Knarrdalstrand WWTP. The solution produced by *Kemira* (*Helsingborg*, Sweden) in reddish-brown liquid form as industrial product. Calcium hydroxide was obtained as industrial product, in chalky powder form, from BDH. It was used as slurry form by mixing with distilled water.

3.3.2 Dosage and fast mixing time

Optimization of initial situation can improve the coagulation performance. Optimum dosage and fast mixing time are the two parameters which has been determined in this study for both coagulants. The coagulation performance will improve with the increase of coagulant dosage but when the dosage is too high, the efficiency will drop and lead to extra cost for whole system [26]. Coagulation efficiency decreases when the mixing time is too long [13].

Typical mixing times for the chemicals used in wastewater treatment are changed based on type of chemicals. Metcalf and Eddy Recommend 1-10 seconds fast mixing time for ferric chloride and 10-30 seconds fast mixing time for calcium hydroxide [10]. Therefore Before evaluating the main objects, few jar preliminary tests were done to determine optimum dosage and optimum fast mixing time for both coagulants. The main jar tests were done based on these results as initial adjustments.

To determine the optimum dosage of calcium hydroxide, the alkalinity of wastewater was measured and required lime was estimated (Figure 2-3). Hence, 400 mg/L of lime was estimated as the required dosage of lime in one liter of wastewater to raise pH. Thus the jar tests were conducted with dosages of 300, 400, 500, 600, 700, 800 and 900 mg/L of $Ca(OH)_2$ and effects of dosages on COD and turbidity removal were evaluated.

3.4 Anaerobic digestion

Since the settled sludge after coagulation and thickening is used in anaerobic reactors to produce biogas (Figure 3-1), investigating the biogas potential is one of the important factors to evaluate the sludge quality. Syringe test as a batch anaerobic digesters were used to measure biogas production of sludge from different samples and different coagulants test.

The batch syringes reactors have a volume of 100 mL. The sample of sludge was taken from 200 mL of settled part on the jars. Six type of samples were tested in six syringe anaerobic reactors. The sludge from two different samples which were WW+TR and WW+UR mixture with different coagulants (i.e. ferric chloride and two dosages of calcium hydroxide). The granular sludge (GS) which was used as inoculum for digesting process, originally came from the supplier Opure in the Netherlands, who collects sludge all over Europe, from all sorts of factories and installations. The initial content in the reactors was a mixture of sludge (10 ml) and inoculum (20 ml) (i.e. feed to inoculum ratio was 1:2). Two parallel reactors were considered for each sample and the results presented are based on average value of two parallel syringes. Two blank reactors (i.e. control) were also used with 20 mL of inoculum. Figure 3-4 shows the typical experiment setup.

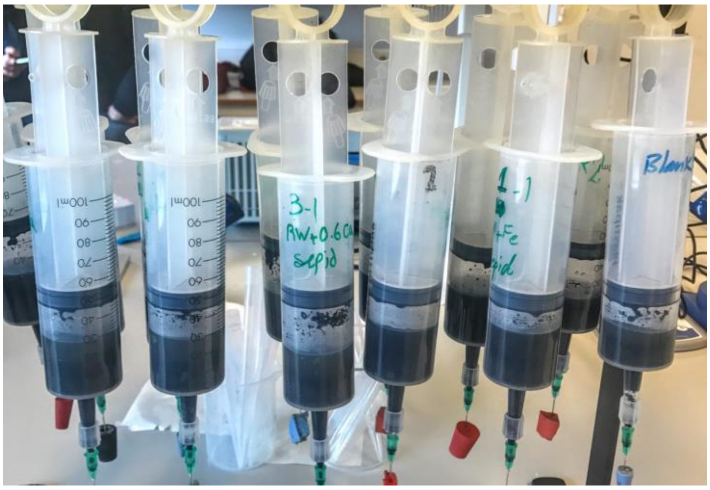

Figure 3-4. Syringes anaerobic reactors set up and Gas production

Rubber stopper were used to keep produced biogas inside the syringes. The temperature was kept around 40 °C and produced gas was measured daily based on expanded volume of syringes. The produced biogas measured during 15 days and it is assumed 65 % of produced biogas is purely CH4 and methane production potential was calculated based on this assumption and VSS and COD of samples.

4 Results

The results of experiments are presented in the following three sub-chapters. First, efficiency of iron coagulant ferric chloride and calcium hydroxide (lime) are compared on coagulation process and sludge quality. Secondly, the effect of treated reject water on coagulation process when mixed with wastewater is evaluated. Third, the results of anaerobic digestion is presented to show the biogas production potential of all alternatives combination in first two sub-chapters. The treated water and settled sludge were analyzed based on several parameters.

Before starting the main experiments, coagulant dosages and optimum stirring times were determined in a preliminary experiment as described in the methods (section 3.3.2) in order to develop best performance for both coagulants and used as an initial conditions in the experiments.

Figure 4-1 shows the effect of different dosages of calcium hydroxide on COD reduction of the samples tested in the preliminary experiment. When $Ca(OH)_2$ dosage increased to 800 mg/L, the reduction of COD increased to the highest value equal to 95 % and declined to 24 mg/L. However, further increase of the $Ca(OH)_2$ dose from 800 to 900 mg/l resulted in decrease COD removal (i.e. by a value of more than 1 %). The lower dosages of $Ca(OH)_2$ can also reduce the COD concentration significantly. Since 0.6 g of coagulant remove 91 % of COD which is more efficiency than 0.5 g and 0.7 g of chemical, both 0.6 g and 0.8 g selected for further study.

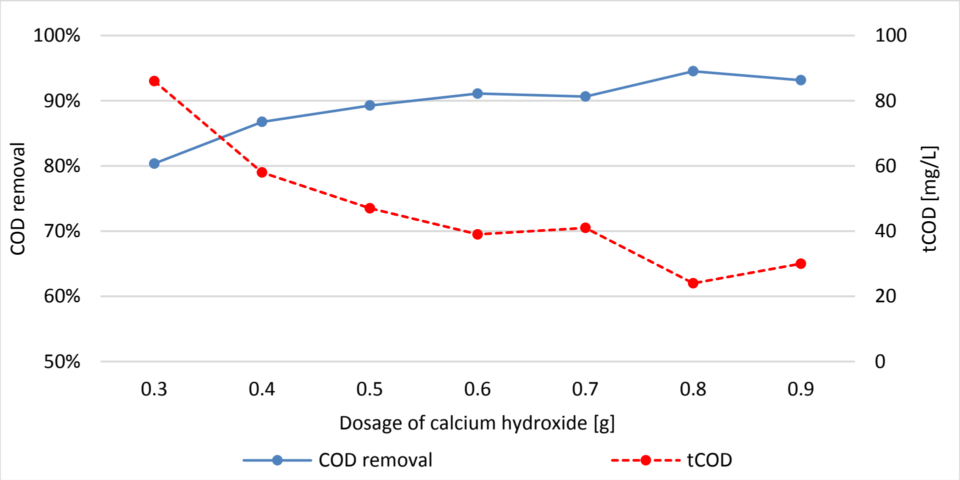

Figure 4-1. Effect of calcium hydroxide dosage on coagulation efficiency.

Figure 4-2 shows that COD and turbidity removal by reducing fast mixing time after adding $Ca(OH)_2$. COD removal increased by reducing mixing time and reached maximum removal, 93 %, on 15 seconds. The turbidity removal rose gradually by reducing mixing time and get maximum removal on 7 seconds and went down again for less time. For $Ca(OH)_2$ 15 seconds fast mixing time showed the good results for turbidity and COD removal and it was implemented for further tests.

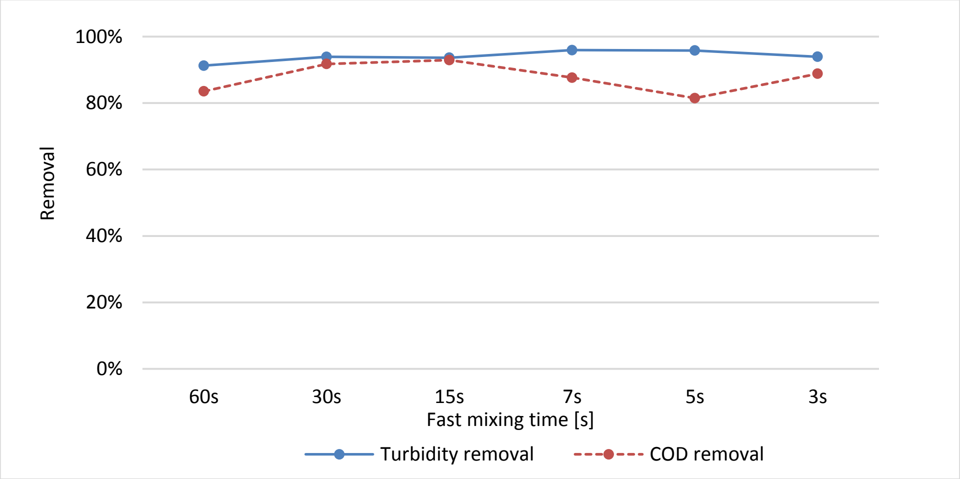

Figure 4-2. Determination the optimum fast mixing time for calcium hydroxide.

Moreover, the optimum dosage of ferric chloride solution was determined 0.2 mL in 1 L of sample from previous study [15].

Figure 4-3 shows the COD and turbidity removal were varied by reducing the fast mixing time, from 60 seconds to 3 seconds, after adding ferric chloride. The COD removal were declined from 87 % to 84 % when the time was decreased from 60 seconds to 7 seconds and increased again to reach the highest removal, approximately 90 %, when the fast mixing time was 3 seconds. Similar result was reported by another study that used ferric chloride as main coagulant [27].

However, the turbidity removal was not very sensitive to mixing time. Although it also showed higher removal in shorter fast mixing time, in general it showed approximately similar removal around 92 %, when the fast stirring time was 30 seconds and/or less. Thus for further tests, 3 seconds was chosen as fast stirring time for ferric chloride.

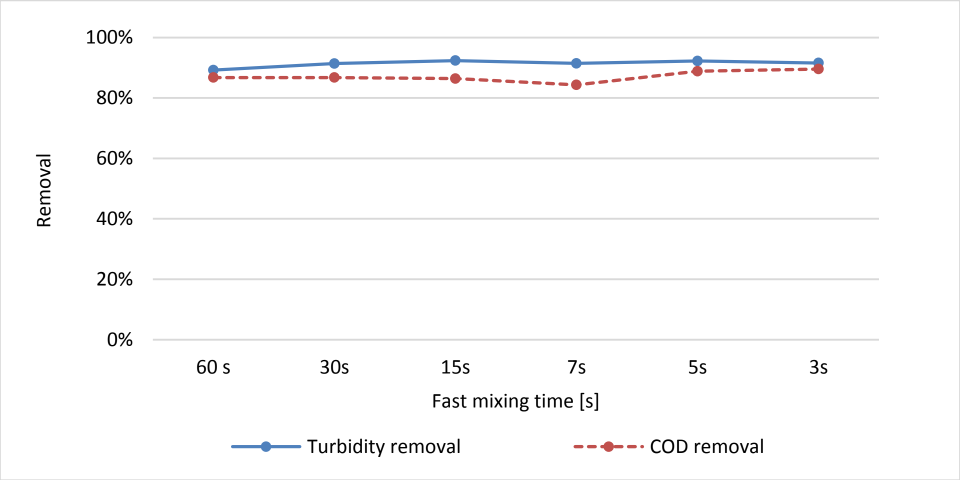

Figure 4-3. Determination the optimum fast mixing time for ferric chloride.

4.1 Ferric chloride and calcium hydroxide performance as coagulant

The samples were prepared by mixing wastewater and untreated reject water according to section 3.2.1. During the study the pH of samples were measured during slow mixing phase. The average pH were 7.5 and 12.5 for samples contained ferric chloride and lime, respectively.

COD removal:

Figure 4-4 presents COD removal of both chemicals during several repeated tests. The results showed that the COD removal is highly dependent on the COD content of the wastewater. The removal efficiency increased when wastewater COD increased. In the highest wastewater COD concentration, which was on the first test, COD removal reached to more than 90 % for both coagulants. However, when COD of wastewater decrease to lowest value at test 6, the removal efficiency drastically dropped to less than 50 %. Ferric chloride and $Ca(OH)_2$ showed approximately similar performance when the COD concentration was in the high range. For middle range of wastewater COD concentration, calcium hydroxide removed 75 %, 83 % and 74% COD during 2nd, 3rd and 5th tests, respectively. On the other hand, these values for ferric chloride dropped to 58 %, 80 % and 64 %, respectively. The lower dosage of calcium hydroxide also showed the efficiency almost similar and even better than ferric chloride during these three tests. In general, when the wastewater COD was higher than 140 mg/L the average COD removal was 83±9 % for higher dosage of calcium hydroxide and 76±15 % for ferric chloride (Table 4-1). In the low range of wastewater COD, which was the last two tests, calcium hydroxide removed 36 % and 77 % of COD while COD removal with ferric chloride increased to 47 % and 81 %. Under such condition lower dosages of calcium hydroxide revealed approximately same removal efficiency as higher dosage.

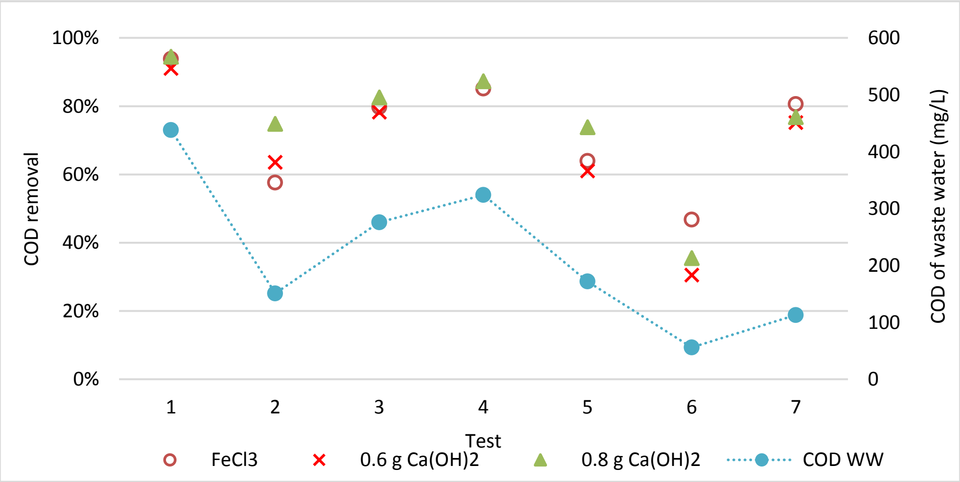

Figure 4-4. Seven experimental tests comparing ferric chloride and two dosage of calcium hydroxide efficiency on COD removal. The COD concentration of wastewater is also shown as reference.

Turbidity and TSS removal:

The turbidity removal with both kinds of coagulants in different value of wastewater COD concentration is shown in Figure 4-5-a Ferric chloride turbidity removal efficiency showed approximately constant value with the average removal of 96 ±2 % in different range of wastewater COD. Generally there was obvious correlation with wastewater COD and turbidity removal. The turbidity removal with calcium hydroxide was nearly close to ferric chloride in high COD concentration of wastewater with average removal of 95 ±1 % for the first four tests. However, when the wastewater COD decreased, at tests 5, 6 and 7, turbidity removal efficiency of calcium hydroxide decreased to an average removal of 81 ±5 % and this was lower than ferric chloride. The lower dosage of calcium hydroxide showed lower turbidity removal than higher dosage in all tests with an exception of 5th test with value of 86 %.

Figure 4-5-b illustrates the efficiency of calcium hydroxide and ferric chloride to remove TSS in different ranges of wastewater COD concentration. The removal efficiency with using ferric chloride range between 81 % and 99 % with the average of 92 ±7 % in different inlet COD ranges, which were more than efficiency of calcium hydroxide in all tests. The calcium hydroxide presents the smaller variation with the average of 84 ±12 % by ignoring the outlier data with the value of 10 % removal efficiency (i.e. last test) (Table 4-1). The performance of lower dosage of calcium hydroxide was 86 ±4 % which normally was lower than the others, except on 5th test that TSS removal was obtained 4 % and 22 % higher than ferric chloride and higher dosage of calcium hydroxide, respectively. Moreover, no significant correlation between TSS removal and wastewater COD was observed.

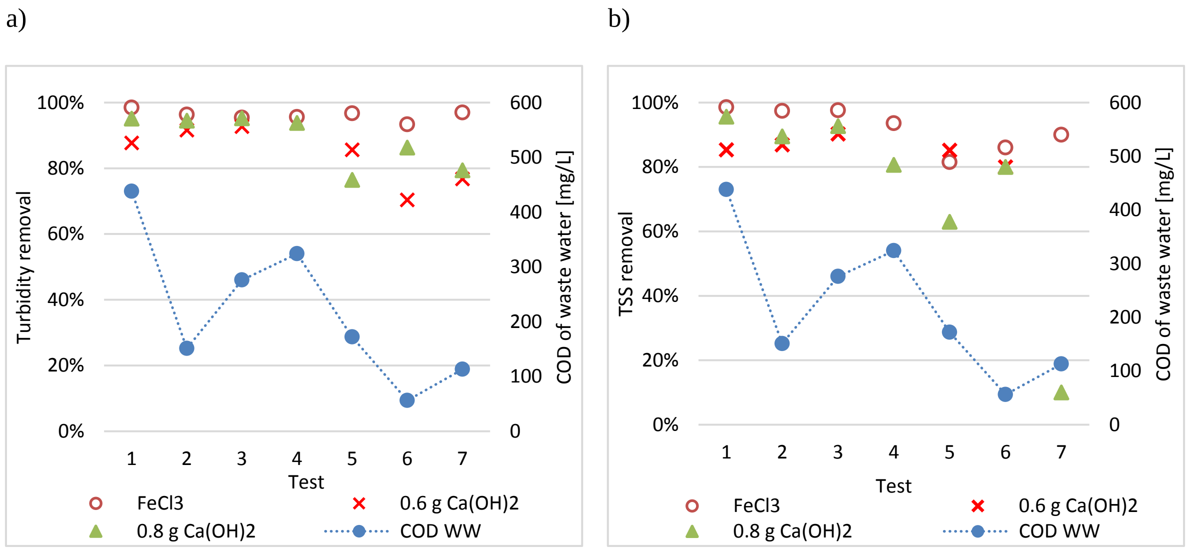

Figure 4-5. Seven tests Comparing ferric chloride and two dosages of calcium hydroxide efficiency on turbidity removal (a). Seven tests Comparing ferric chloride and two dosages of calcium hydroxide efficiency on TSS removal (b). The COD concentration of wastewater is also shown as reference.

Phosphorus removal:

The two coagulants performance to remove phosphorus in different COD of inlet is shown in Figure 4-6. The results showed that when the COD of inlet was in middle and high range (i.e. more than 140 mg/L in the first three tests) both coagulants showed nearly similar removal efficiency. Higher and lower dosage of calcium hydroxide removed approximately constant percentage of phosphorus equal to 95 ±1 % and 93 %, respectively while ferric chloride showed approximately the same removal equal to 93 ±3 % (Table 4-1). Beside this, in lower dosages when wastewater COD concentration decreased in tests 4 and 5, the efficiency of ferric chloride was 59 % and 84 %, respectively. Higher dosage of calcium hydroxide showed slightly less removal efficiency than ferric chloride while the lower dosage removed slightly more phosphorus in the last two tests.

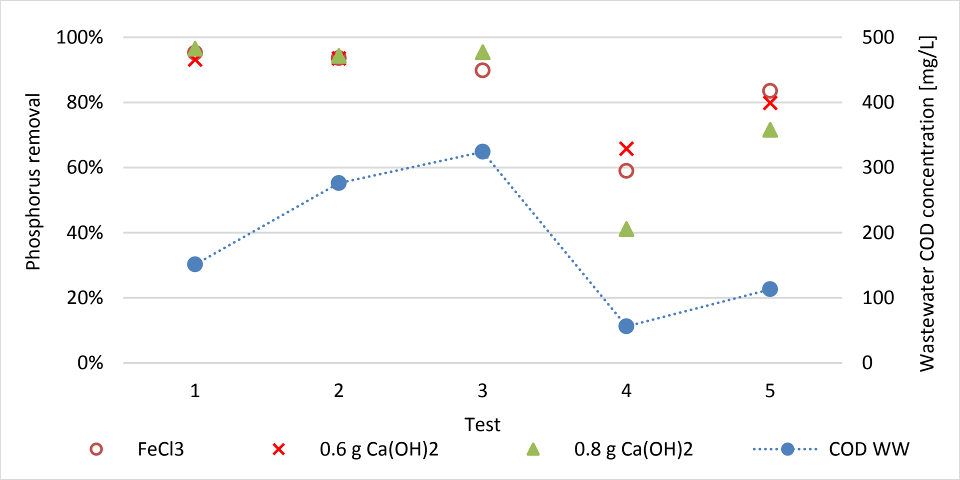

Figure 4-6. Five tests comparing ferric chloride and two dosages of calcium hydroxide on phosphorus removal. The COD concentration of wastewater is also shown as reference.

TSS and VSS of sludge:

Figure 4-7 demonstrates the total suspended solids in diluted sludge when ferric chloride and calcium hydroxide was used as coagulant. The TSS of sludge decreased when wastewater COD concentration dropped and the average TSS was larger in higher wastewater COD. Results in Table 4-1 showed that the amounts of sludge TSS was 620 ±193 when calcium was used as coagulant while this value decreased to 197 ±64 mg/L when ferric chloride was used as coagulant.

The amount of VSS of diluted sludge is presented in Figure 4-8 for both coagulant based on COD concentration of wastewater. Whenever wastewater COD decreased, the VSS of sludge also decreased with both coagulants. The average values in Table 4-1 indicate that amount of VSS was 160 ±63 mg/L for ferric chloride sludge while for lower and higher dosage of calcium hydroxide increased to 114 ±67 and 137 ±58 mg/L, respectively.

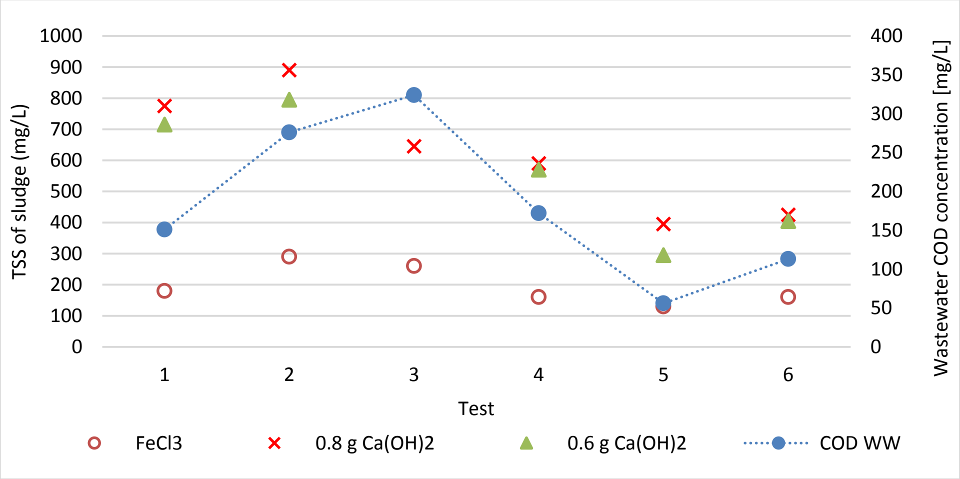

Figure 4-7. Six tests comparing ferric chloride and calcium hydroxide on TSS of diluted sludge according to section 3.3. The COD concentration of wastewater is also shown as reference.

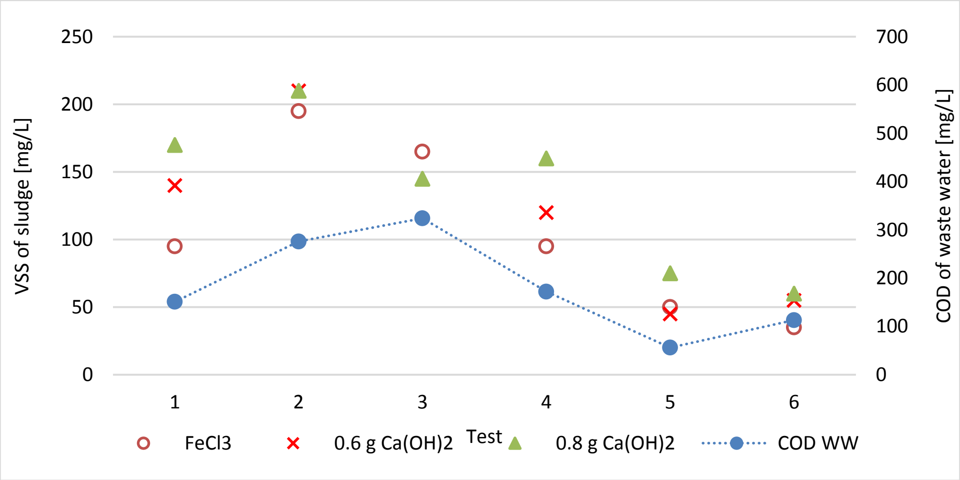

Figure 4-8. Six tests comparing ferric chloride and calcium hydroxide on VSS of diluted sludge according to section 3.3. The COD concentration of wastewater is also shown as reference.

Sludge volume index:

The sludge volume index for both coagulants based on COD concentration of wastewater variation is shown in Figure 4-9. The SVI of ferric chloride has exhibited large variation for different wastewater COD. However, calcium hydroxide produced almost constant amount of SVI which is much lower than ferric chloride. The SVI average was 264 ±68 mL/g for ferric chloride which strongly decreased to 56 ±21 and 46 ±5 mL/g for lower and higher dosage of calcium hydroxide, respectively (Table 4-1). The results showed that SVI value highly dependents on wastewater COD when ferric chloride was used as coagulant. By increasing the wastewater COD concentration, less voluminous sludge produced by ferric chloride and SVI got the minimum value equal to 189 mL/g when the COD of wastewater reach to highest value equal to 324 mg/L at test 3. The maximum SVI for ferric chloride, 362 mL/g, was occurred when wastewater COD was at the lowest level. On the other hand, calcium hydroxide kept approximately similar SVI with very small variation in all situations.

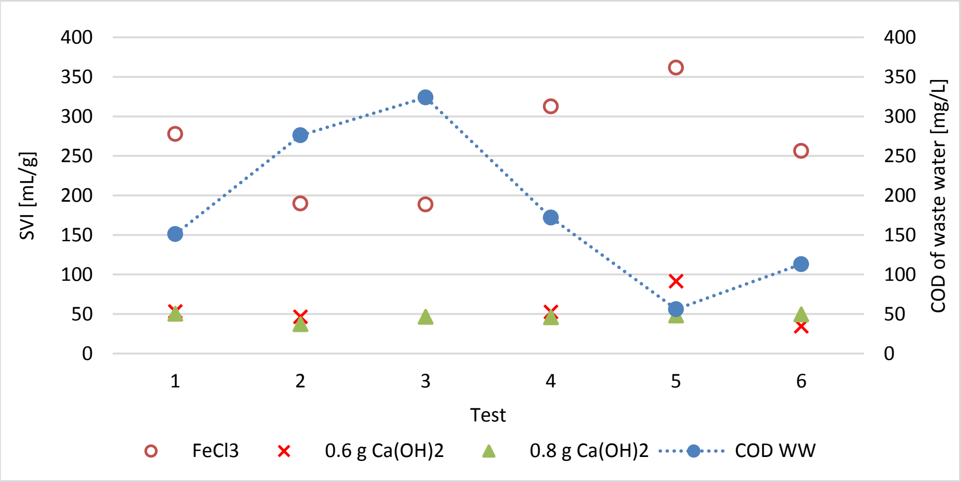

Figure 4-9. Six tests comparing ferric chloride and calcium hydroxide on sludge volume index. The COD concentration of wastewater is also shown as reference.

Table 4-1. Comparison between the efficiency of ferric chloride and two dosages of calcium hydroxide during coagulation process in whole range and high range of COD concentration of wastewater.

	0.2 ml ferric chloride		0.6 g Ca(OH)2		0.8 g Ca(OH)2	
	Whole range	140 mg/L < COD of WW	Whole range	140 mg/L < COD of WW	Whole range	140 mg/L < COD of WW
COD removal	0.73 ±0.17	0.76 ±0.15	0.67 ±0.21	0.73 ±0.14	0.75 ±0.19	0.83 ±0.09
Turbidity removal	0.96 ±0.02	0.96 ±01	0.84 ±0.09	0.89 ±0.03	0.89 ±0.08	0.91 ±0.08
TSS removal	0.92 ±0.07	0.94 ±0.07	0.86 ±0.04	0.87 ±0.02	0.84 ±0.12*	0.84 ±0.13*
Phosphorus removal	0.84 ±0.15	0.93 ±0.03	0.83 ±0.13	0.93 ±0.01	0.8 ±0.24	0.95 ±0.01
SVI (mL/g)	264 ±68	242 ±63	56 ±21	51 ±4	46 ±5	45 ±6
TSS of diluted sludge (mg/L)	197 ±64	223 ±62	556 ±208	693 ±114	620 ±193	725 ±134
VSS of diluted sludge (mg/L)	106 ±63	138 ±51	114 ±67	157 ±47	137 ±58	171 ±28

* The outlier data in test 7 with the value of 10 % TSS removal was ignored

Settling time:

In addition, visual inspections indicated that the floc which were formed with calcium hydroxide settled much faster than floc created with ferric chloride. Figure 4-10 shows the settling phases in jars which contained the same sample (i.e. mixture of wastewater and untreated reject water) but with different coagulants. Both cases run simultaneously and started to settle exactly at the same time. The jar at the left side included 0.2 mL of ferric chloride as coagulant and the right side included 0.8 mg of calcium hydroxide. The pictures was taken during the first 20 minutes of settling phase. It is obvious from pictures that the flocs in the jar which contained calcium hydroxide started to settle earlier and it followed rapid settling while the jar which contained ferric chloride took more time. As it is observable in Figure 4-10, the flocs which created by calcium hydroxide were settled completely while the ferric chloride flocs were suspended in the middle of the jars.

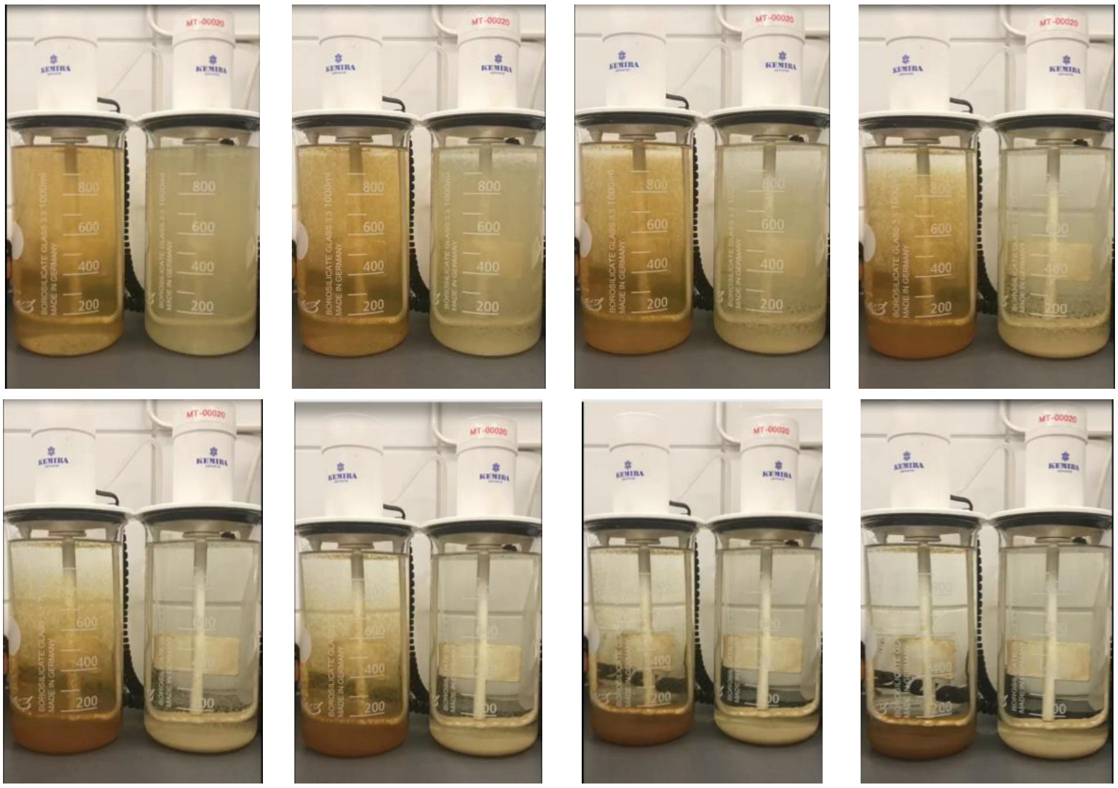

Figure 4-10. Comparing settling velocity of created floc with 0.8 g of calcium hydroxide and 0.2 mL of ferric chloride as coagulant during first 20 minutes of settling phase

4.2 Effect of biological process on coagulation

Two different samples were prepared as mentioned in section 3.2.1 (Table 3-2). Since the main part of studied sample was wastewater (i.e. 98.9% of mixture), the characteristics of wastewater such as COD was considered during the test as the basic parameter to evaluate results.

COD removal

The coagulation efficiency of treated reject water and untreated reject water on COD reduction is shown in Figure 4-11. A total of 17 tests were done from January to March and for each test both samples were analyzed after coagulation which is presented in this figure based on wastewater COD. It shows that when the inlet COD concentration was low i.e. less than 140 mg/L the residual COD after coagulation, was approximately similar for both samples with an average of 28 ±4 mg/L for UR and 25 ±5 mg/L for TR (Table 4-2). Whereas when the inlet

COD increases up to 350 mg/L, the amount of residual COD was increased for both samples but the TR samples exhibited low residual COD. In fact there were few measurements where both TR and UR had approximately similar residual COD. The remained COD reached to an average value of 39 ±10 mg/L for TR and 51 ±14 mg/L for UR. In very high amount of inlet COD for instance higher than 400 mg/L, the remained COD of samples for TR were 29 and 67 mg/L of COD while the UR samples showed lower value equal to 27 and 57 mg/L.

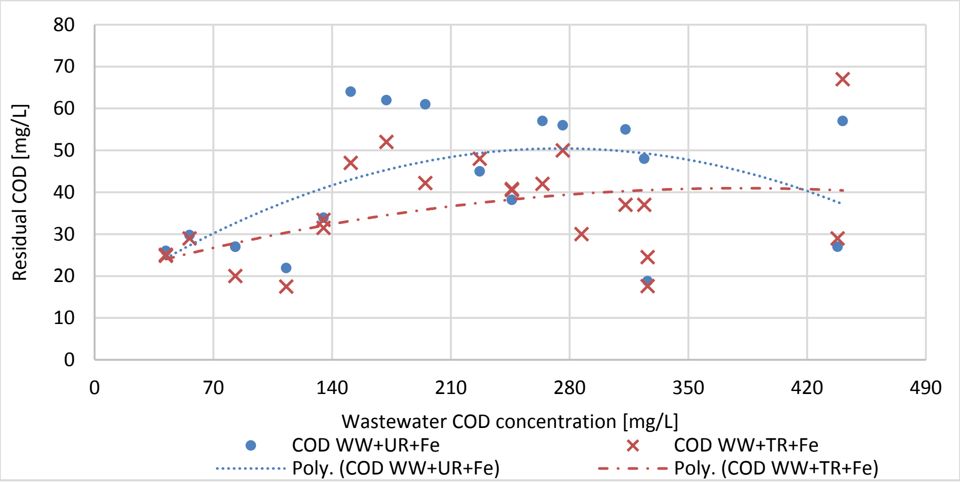

Figure 4-11. Comparing coagulation efficiency on COD removal for two different samples: treated reject water (TR) and untreated reject water (UR) when they mixed with wastewater (WW) in fixed proportion. In both cases a total of 17 tests were compared from January to March. Ferric chloride was used as coagulant.

Table 4-2. Comparing coagulation efficiency of treated reject water (TR) and untreated reject water (UR) on COD removal when they mixed with wastewater (WW) in fixed proportion in different range of wastewater COD. Ferric chloride and calcium hydroxide were used as coagulant.

	Total average of residual COD (mg/L)		Average of residual COD in low range (COD of WW<140) (mg/L)		Average of residual COD in typical range (140<COD of WW<350) (mg/L)	
	UR	TR	UR	TR	UR	TR
ferric chloride	42 ±16	34 ±13	28 ±4	25 ±6	51 ±14	39 ±10
0.8 g lime	40 ±13	46 ±16	31 ±7	28 ±6	44 ±13	53 ±12
0.6 g lime	55 ±19	47 ±16	33 ±8	30 ±9	65 ±11	55 ±12

The same comparison was done using calcium hydroxide as coagulant with two different dosages. Figure 4-12-a and b illustrated the residual COD of samples with higher and lower dosage of calcium hydroxide during 7 tests versus with inlet COD concentration. In low range of wastewater COD, samples of TR and UR after coagulation exhibited approximately similar amount of COD (Figure 4-12-a). However, when the inlet COD increased, the residual COD after coagulation reached to 48 and 41 mg/L for UR and 71 and 55 mg/L for TR.

For lower dosage of $Ca(OH)_2$, the same performance was seen at low concentration of inlet COD and samples UR and TR reached to approximately similar final COD (Figure 4-12-b).

Meanwhile, increasing inlet COD to more than 140 mg/L sample of UR had higher amount of residual COD with an average of 65 ±11 mg/L while TR provided less COD equal to 55 ±12 mg/L.

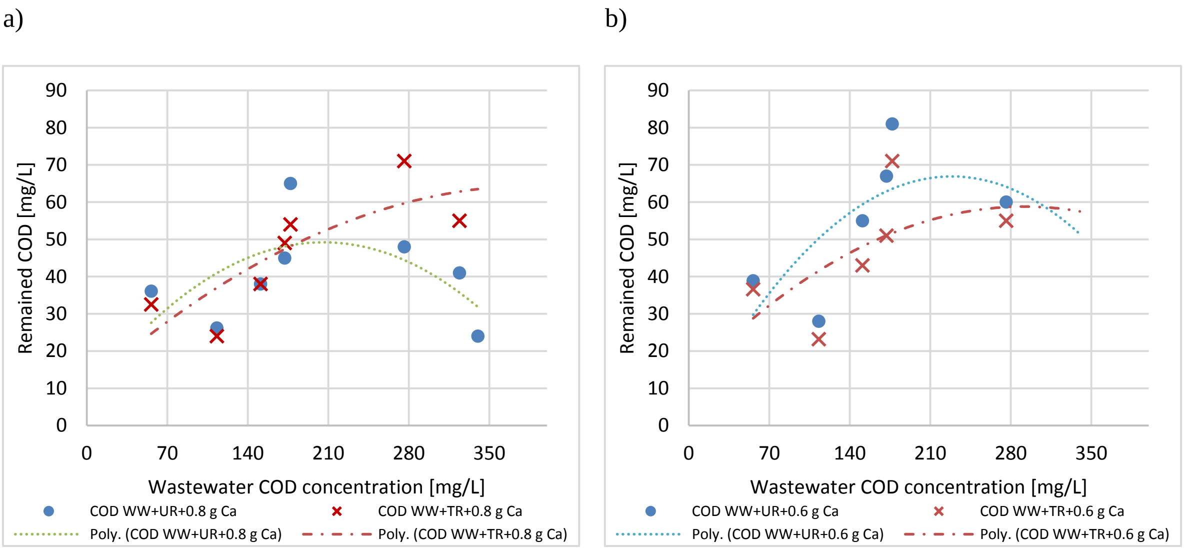

Figure 4-12. Comparing coagulation efficiency on COD removal for two different samples: treated reject water (TR) and untreated reject water (UR) when they mixed with wastewater (WW) in fixed proportion. using 0.8 g calcium hydroxide as coagulant (a). and 0.6 g calcium hydroxide as coagulant (b).

Turbidity removal:

Figure 4-13 reveals the coagulation efficiency with UR and TR wastewater to reduce turbidity of samples using ferric chloride as coagulant based on initial turbidity of inlet. Generally, it was observed that there was no correlation between wastewater turbidity and residual turbidity and in all tests both samples have provided turbidity below 6 NTU. The results showed that the average remained turbidity after coagulation reached to 3 ±1.5 NTU for sample UR and 2.8 ±1.8 NTU for sample TR after ignoring one outlier data for each sample. The outliers have occurred when turbidity of wastewater was 28 NTU and TR and UR samples provided the samples with 12 and 15 NTU respectively.

The performance of TR and UR to remove turbidity from wastewater is compared in Figure 4-14 based on variation of wastewater turbidity. Using higher and even lower dosage of chemical, the samples of TR reduced turbidity of wastewater to less than 8 NTU for whole range of inlet turbidity. Sample UR showed the larger variation for final turbidity after coagulation and in few points it reached to more than 10 NTU. Overall, the mean values of remained turbidity were 5 ±2 and 7 ±1 for sample UR using higher and lower dosage of chemical. For sample TR the mean value increased to 7 ±4 and 9 ±3 NTU, respectively.

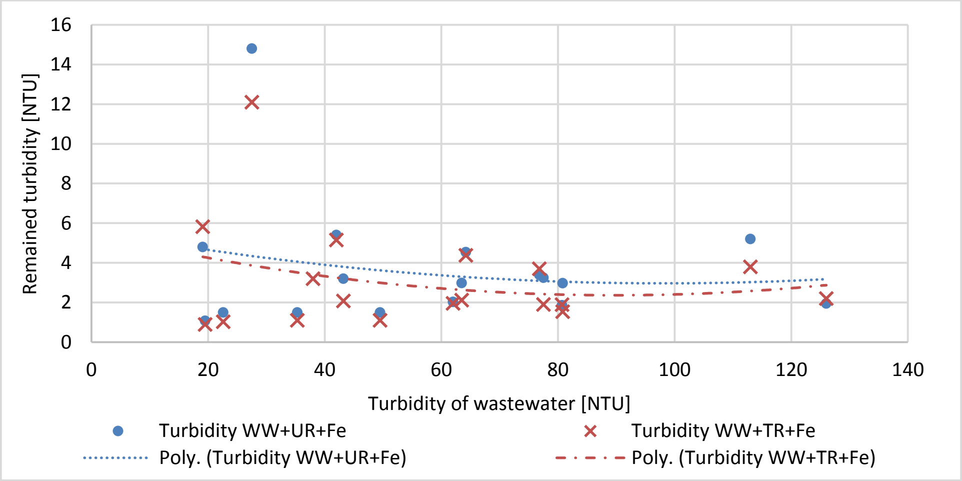

Figure 4-13. Comparing coagulation efficiency on turbidity removal for two different samples: treated reject water (TR) and untreated reject water (UR) when they mixed with wastewater (WW) in fixed proportion. Both cases compared during 17 tests from January to March. Ferric chloride was used as coagulant.

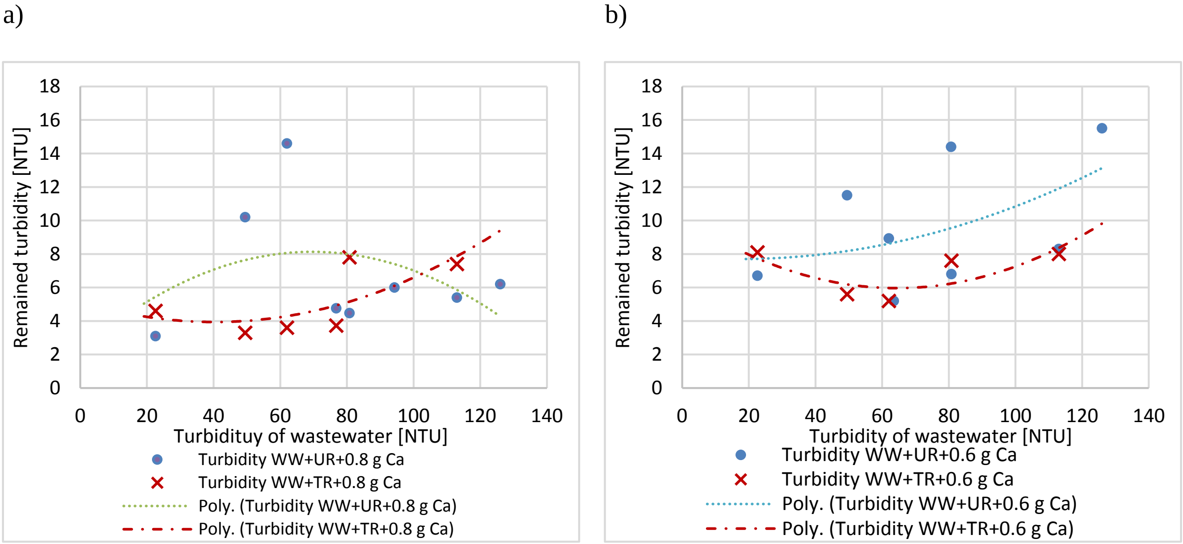

Figure 4-14. Comparing coagulation efficiency on turbidity removal for two different samples: treated reject water (TR) and untreated reject water (UR) when they mixed with wastewater (WW) in fixed proportion. a. With 0.8 g Ca(OH)2 as coagulant (a) and With 0.6 g Ca(OH)2 as coagulant (b).

Phosphorus capturing:

The phosphorus concentration in the settled part is presented in Figure 4-15 for both samples TR and UR based on COD concentration of wastewater using ferric chloride as coagulant. Both samples showed similar trend where the values vary with the inlet COD. With increase in the wastewater COD, the captured phosphorus in the sludge increased. When the COD of wastewater was low, for instance 56 and 113 mg/L, the stored phosphorus in sludge were 1.17 and 1.15 mg/L for TR and 1.1 and 1.3 mg/L for UR, respectively. With a further increase in the inlet COD, the amount of phosphorus which was captured in sludge increased to 3.3 ±0.6 mg/L for TR and 3.2 ±0.5 mg/L for UR.

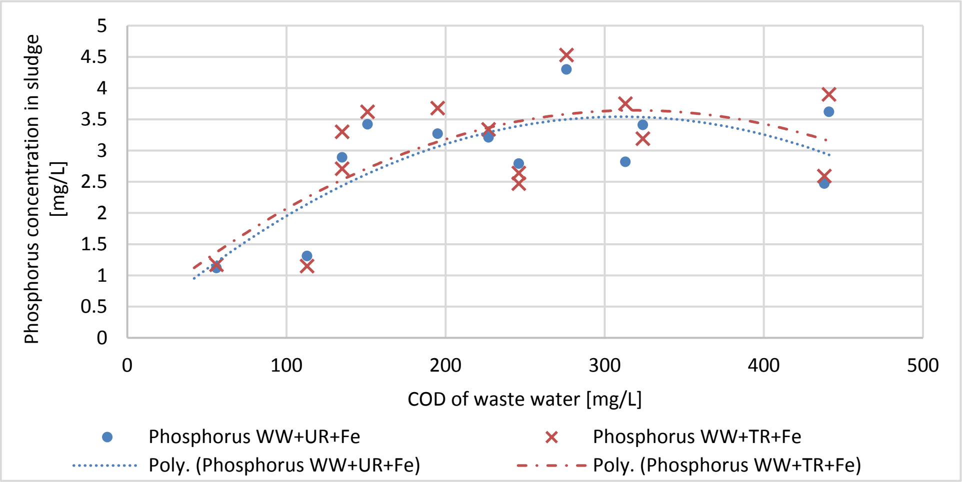

Figure 4-15. Comparing coagulation efficiency on phosphorus capturing for two different samples: treated reject water (TR) and untreated reject water (UR) when they mixed with wastewater (WW) in fixed proportion. Both cases were compared during 12 tests from January to March. Ferric chloride was used as coagulant.

Figure 4-16 demonstrates the amount of phosphorus stored in remained sludge from sample TR and UR after coagulation with two different dosage of calcium hydroxide.

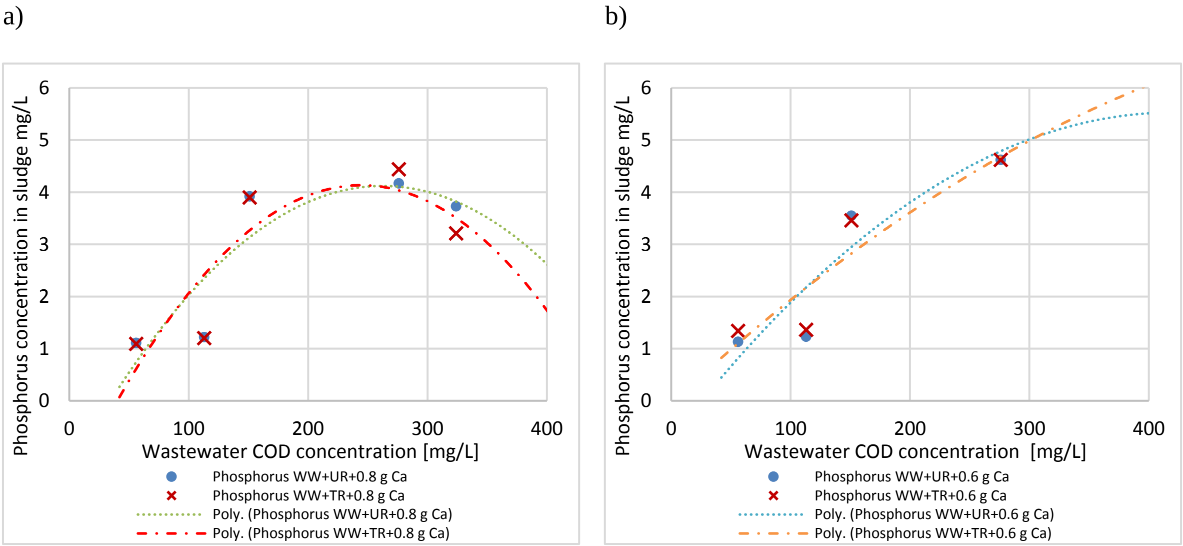

Figure 4-16. Comparing coagulation efficiency on phosphorus capturing for two different samples: treated reject water (TR) and untreated reject water (UR) when they mixed with wastewater (WW) in fixed proportion. With 0.8 g Ca(OH)2 as coagulant (a) and with 0.6 g Ca(OH)2 as coagulant (b).

For both dosages when the wastewater COD concentration was low as 56 and 113 mg/L, the amount of phosphorus in sludge was less than 1.5 mg/L for both samples. However, when COD of the wastewater increases, the phosphorus concentration also increased to more than 3 mg/L for both treatment. The data on the graphs showed the same average of 2.8 ±1.5 mg/L for both TR and UR using higher dosage as well as similar average of 2.7 ±1.6 and 2.6 ±1.7 for TR and UR with lower dosage of lime.

Sludge volume index:

The sludge volume index as one of sludge characteristics of both samples is shown in Figure 4-17 using ferric chloride as coagulant. The results illustrates that SVI value for UR decreased slightly from 425 mL/g to 179 mL/g by increasing inlet COD from 42 to 441 mg/L. Conversely, it was observed that TR has reduced SVI from 365 to 144 mL/g by reducing COD concentration of wastewater. The mean SVI value for sample UR presents 247 ±72 mL/g which is very close to sample TR that provided an average SVI equals to 239 ±62 mL/g.

Figure 4-18 illustrates similar tests with low and high dosage of lime as coagulant. With using 0.8 g of lime the SVI showed approximately constant value for the whole range of inlet COD during all tests. In fact both samples has provided similar SVI with an average of 47 ±5 mL/g for UR and 49 ±5 mL/g for TR.

However, using 0.6 g of lime as coagulant, more variation was observed and SVI value of sample TR and UR decreased when the wastewater COD increased. The SVI for both samples were closely similar during 6 tests with an average of 53 ±18 mL/g for sample UR and 59 ±21 for TR.

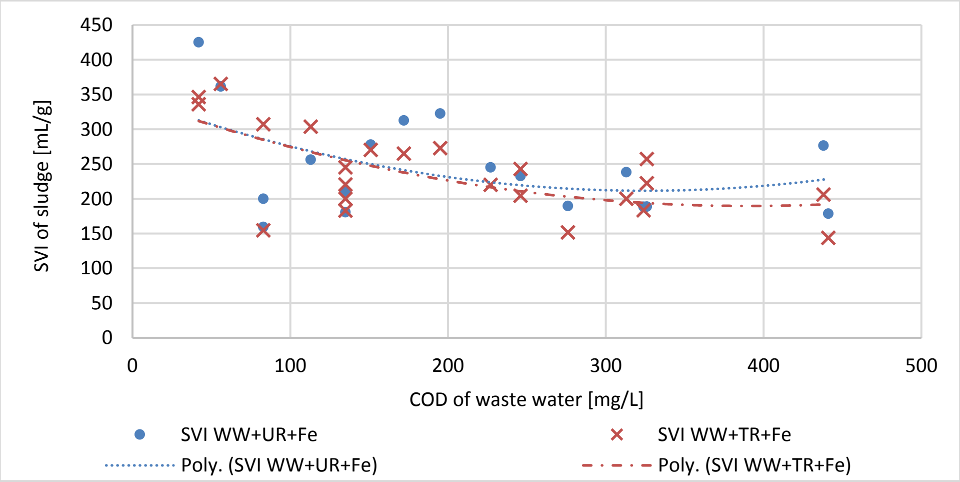

Figure 4-17. Comparing sludge volume index remained from two different samples: treated reject water (TR) and untreated reject water (UR) when they mixed with wastewater (WW) in fixed proportion. With using ferric chloride as coagulant

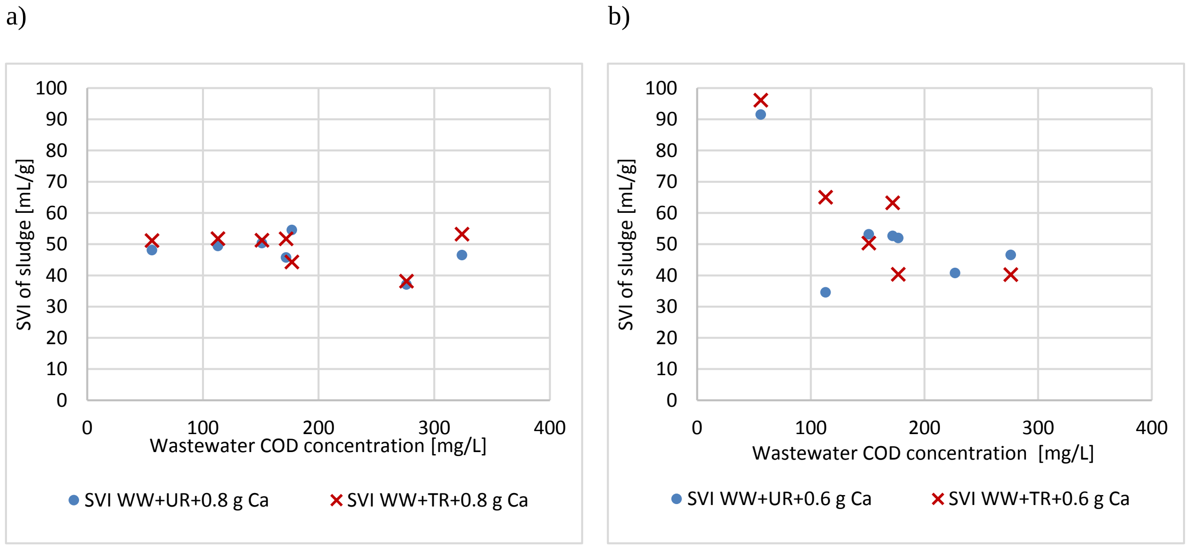

Figure 4-18. Comparing sludge volume index from two different samples: treated reject water (TR) and untreated reject water (UR) when they mixed with wastewater (WW) in fixed proportion. With 0.8 g Ca(OH)2 as coagulant (a) and with 0.6 g Ca(OH)2 as coagulant (b).

TSS removal:

The efficiency of TR and UR on the TSS reduction showed large variation without any correlation with wastewater COD. Generally, the average residual TSS were very similar for both samples. The TSS reduction by using ferric chloride as coagulant showed an average of 15 ±13 mg/L in sample UR and 18 ±17 mg/L in sample TR after coagulation. The average values of remained TSS by using 0.8 g of lime, was 26 ±16 mg/L for sample UR and 18 ±14 mg/L for sample TR. With using lower dosage of lime remained TSS of UR samples was 31 ±18 mg/L and for TR the mean value was 29 ±11 mg/L (Appendix 4).

4.3 Biogas production potential

The results of the syringe test to compare the bio-methane potential (BMP) during 15 days of digestion of the sludge produced with calcium hydroxide and with ferric chloride revealed that the calcium coagulated sludge produced higher amount of biogas. The produced biogas from blank samples (i.e. contain only inoculum) was also high and similar to that produced in the sample which contained TR and ferric chloride. These results are not reliable for quantification of BMP since some cases suggest negative net production and some appeared to produce more than maximum theoretical value. Given this problem and also inconsistent results regarding the other variables of the BMP test, detailed results are not presented here and only given in Appendix 5. Although the amount of produced methane were not in acceptable range, the results clearly show that the coagulated sludge with both dosages of calcium hydroxide produced more biogas than coagulated sludge with ferric chloride. The initial pH of coagulated sludge with calcium hydroxide was 12.5 and coagulated sludge with ferric chloride was 7.5 which were used as substrate in BMP test. The final pH of syringes content, after digesting period, were equal around 7.5 for all samples.

5 Discussion

The results presented in the previous chapter are discussed in following two sub-sections. First, the efficiency of ferric chloride and calcium hydroxide are discussed. Secondly, the comparison between the effect of treated reject water and untreated reject water when they mixed with wastewater are discussed.

5.1 Comparing ferric chloride and calcium hydroxide as coagulant

Evaluation of the coagulation process shows that both coagulants treated the wastewater with closely similar efficiency, except calcium hydroxide provided sludge with higher quality. The visual inspection indicates that flocs which were created with lime settle much faster than ferric chloride. Hence, this fast settling behavior of flocs can lead to smaller sedimentation tank in wastewater treatment plants.

Using ferric chloride in the coagulation process resulted in large sludge volume but with fewer solids content while $Ca(OH)_2$ created less sludge volume with high solids content. The SVI of ferric chloride showed large variation which indicates the negative correlation with wastewater COD as it decreased when COD concentration of wastewater increased. The SVI of calcium hydroxide provided approximately constant value with hardly any variation which was approximately six times smaller than average SVI of ferric chloride (Table 4-1). On the other hand, the total suspended solids in the created sludge with calcium hydroxide were approximately three times higher than sludge which was generated with ferric chloride (Table 4-1). Therefore, calcium hydroxide generated around twice less sludge volume which was observed in visual inspection. Hence, lower sludge volume leads to less water from dewatering process which could save a lot of energy. Studies have reported that SVI value of 100 mL/g TSS or less is an indication of good quality sludge [5].

As far as the literature review for this study no research study was found that used calcium hydroxide as the main coagulant but few studies investigated the effect of calcium ion as co-coagulant to reduce sludge volume. Yao et al. investigated the impacts of Ca^{2+} on coagulation and ultrafiltration performance under different polyaluminum chloride (PAC) as the main coagulant. The research has found that floc size and incompactness were appreciably enhanced at under-dose with increasing Ca^{2+} concentration [42]. Sudoh et al. used polyaluminum chloride (PAC) with calcium carbonate as neutralizer and coagulant aid to remove HA (humic acid). $CaCO_3$ makes HA colloid size bigger and easier to form flocs and it suggested that CaCO3 shortens the settling time. The sludge volume (SV) was reduced about half compared with the PAC method using NaOH as neutralizer [33].

In addition to the superiority of calcium hydroxide in sludge quality, this coagulant had similar efficiency to treat wastewater samples when compared to ferric chloride. Generally, the efficiency of both coagulants was dependent on wastewater COD. By increasing the wastewater COD the removal of COD and phosphorus increased. In lower range of wastewater COD the removal efficiency with both coagulants were very similar while with increase in COD to higher than 140 mg/L calcium hydroxide has slightly higher efficiency (Table 4-1). The data from Knarrdalstrand WWTP in 2017 shows the average inlet COD equals to 214 ±97 mg/L and 80 % of the time the wastewater COD concentration was higher than 140 mg/L (Appendix 6). When calcium hydroxide is added to water it reacts with bicarbonate alkalinity and produces calcium carbonate as the precipitate. Excess calcium ions react with phosphate that can be recovered through precipitation as calcium phosphate. This production can be employed directly as slow-release fertilizer or can be used as a feed to produce other phosphate compounds as fertilizer products such as $Ca(HPO_4^{2-})$. It can also be used together with other nutrients to generate the different kinds of fertilizer [10].

Turbidity and TSS removal was quite stable when ferric chloride was used as the coagulant and there was no obvious correlation with wastewater COD. The removal with calcium hydroxide was not stable as much as ferric chloride and it was slightly less especially in lower wastewater COD concentration (Table 4-1). In fact an optimum dosage of ferric chloride as coagulant has been optimized in the plant for years and showed more stable efficiency while for calcium more variation was observed which may be explained due to lack of wider range of test to optimize the dosage during the experiments. The lower dosage of calcium hydroxide had the very similar performance with the higher dosage and even better performance in some cases especially in the low range of wastewater COD. Since the used dosage for all ranges of inlet COD was constant during the study and was not optimized for each case, the low efficiency of calcium hydroxide in low inlet COD concentration can be explained due to over dosage. Studies have revealed that under high dosage of coagulant particle surface charged positive and colloids re-stabilized which result in negative effects on coagulant performance [41].

Moreover, the sludge which contained calcium as the precipitate produced more biogas than ferric chloride precipitated sludge (4.3). The optimum pH for anaerobic digestion is in the range of 5.5-8 and the precipitate of calcium hydroxide had pH around 12 but it still worked well as feed for biogas production. The reason can be that acids produced quickly lowered the pH to the good range for methane production after mixing sludge with inoculum. The higher yield with calcium compared to ferric coagulated sludge can be explained by more of the particulate COD being solubilized by the high pH. Increasing organic solubility fraction or soluble COD is known to improve waste activated sludge (WAS) biodegradability [43]. Some studies were found and reported positive effects of high pH and alkaline pretreatment of sludge on biogas production. Yu et al. applied microwave and alkaline condition in the pretreatment of swine manure and obtained more biogas production and the manure disintegration degree was maximized at pH of 12 and it also shortened the time to get stable biogas production rate [44]. Hu et al. studied the effect of alkaline pre-treatment on waste activated sludge (WAS) from a WWTP and found that increasing the pH with sodium hydroxide strongly influenced the solubilization of sludge and subsequent anaerobic digestion. The COD and protein solubilization were most effective when sludge was pretreated at high pH value. WAS at higher pH resulted in a better removal of COD, further degradation of VS and larger production of methane [45].

Also, lipids are hydrolyzed to glycerol and long-chain fatty acids (LCFAs), which are inhibitors of anaerobic microorganisms. Using calcium ions provide LCFAs precipitate as calcium salt and it could be an attractive way of preventing the LCFAs from upsetting an anaerobic digestion [46]. Ahn et al. used calcium chloride to evaluate the effect of various calcium concentrations on anaerobic digestion of swine wastewater. They discovered that performance of anaerobic digestion improved with increasing concentration of calcium and reached a maximum at the concentration of 3 g/l [46].

In general, less volume sludge, faster settling and more biogas production potential can be considered as main advantages of calcium hydroxide while higher suspended solids of sludge and higher chemical price are listed as disadvantages. All aforementioned advantages of calcium hydroxide may lead to environmental and economical solution if these lead to better recycling but this study is a only preliminary test that should be continued and expand in further studies.

5.2 Effect of biological treatment on coagulation

As mentioned before, COD removal was highly dependent on COD concentration of the main sample which was raw wastewater. In low range of inlet COD concentration, both treated and untreated reject water showed similar effects on COD removal. By increasing inlet COD in the range of 140 and 350 mg/L, the samples showed the significant difference and treated reject water showed the positive effect to reduce COD of wastewater to lower value (i.e. 39 ±10 mg/L for TR against 51 ±14 mg/L for UR).

The inlet COD is not the only parameters that influence TR and UR performance. Since the idea to evaluate the biological process on coagulation is using two different samples (i.e. mixture of wastewater and untreated reject water and mixture of wastewater and treated reject water) the results can be discussed based on TR and UR characteristics. Characteristics of UR depends on thickener and centrifuge performance which is not related to this study while characteristics of TR was highly dependent on UR and reactor performance. Thus unstable condition of the reactors operation will have direct effects on TR samples. Investigating the characteristics of outlet and inlet of reactors were measured and analyzed in another project [12]. The study showed that in some occasions the MBBR reactors had very high or very low and even negative COD removal due to operational problems (i.e. when the wastewater COD concentration were 135, 227, 246, 326 and 438 mg/L) (Appendix 7). In the range of typical inlet COD, there are few tests which both TR and UR provided the same COD concentration after coagulation. Hence, these points can be explained based on reactor performance. Analysis of data from these two studies reveals that when the reactor removed 3 %, 0 %, -14 %, 80 % and 6 % of soluble/total COD, TR and UR showed similar effects on coagulation. The negative COD removal was occurred due to no oxygen flow through the reactor. The lack of oxygen may cause biomass detachment and increase the COD of the reactor effluent. Therefore, TR had more COD than UR which provides disturbance for coagulation. Very high and very low COD removal was happened due to technical problems such as big particles and clogging of feed pipe. This situation did not provide proper active biomass in TR to improve particle capturing and no improvement in coagulation process was observed. Finally, by ignoring these points, the results in the typical range of inlet COD can strongly confirm the positive effects of TR on COD removal compared to UR and residual COD were 39 ±11 mg/L and 58 ±5 mg/L, respectively. This strongly support the hypothesis of the study (third and fourth mechanisms). The biological process leads to degrading dissolved and colloidal organics which convert to active biomass. The active biomass in treated reject water can capture more dissolved organics and colloidal solids from the wastewater which is removed by coagulation. As a result, the biologically treated reject water will cause less disturbance on the coagulation process than the untreated reject water does [11].

Although ferric chloride confirmed the positive effect of TR on coagulation, calcium hydroxide showed approximately similar residual COD with TR compared to UR. This contradiction can be explained based on the optimum dosage of the chemical. The proper dosage of ferric chloride as coagulant has been optimized in the plant for years and showed more stable efficiency while for calcium more variation was observed and this maybe the selected dosage for this experiment was not really optimum dosage.

Residual sludge from treated and untreated reject water did not show any certain superiority to produce biogas. High amount of produced biogas from blank samples and negative and/or high value of produced methane per feed COD are some parameters that lead to some errors in the results. Thus comparing the biogas production potential of these two samples can be studied in other BMP methods in further studies.

Treated reject water produced higher biogas production than untreated reject water with using the higher dosage of lime (Appendix 5). By using ferric chloride and lower dosage of lime the opposite behavior was observed that UR had more potential to produce biogas. However, superiority of TR and UR on gas production change case by case, in all categories calcium hydroxide showed much more potential to produce biogas than ferric chloride in both samples UR and TR.

TR and UR had the same effects on turbidity removal with ferric chloride but with using calcium hydroxide as coagulant TR removed more turbidity than UR (Figure 4-14). TSS removal, phosphorus capturing and SVI for both TR and UR were approximately equivalent with both coagulants and no significant difference was observed.

5.3 Cost evaluation

The largest operating cost in chemical treatment processes is chemicals. The proper determination of type and dosage of coagulants will not only improve the treatment efficiency on water and sludge quality but also influence the operating cost [5]. Although the chemical cost is not the only expense in operation cost in WWTP, the other costs such as machinery, civil and technology are ignored in this study.

The annual chemical costs to treat 27500 m^3 wastewater /day (i.e. according to mass balance in Appendix 3) are estimated with using ferric chloride and calcium hydroxide as coagulant in Table 5-1. The calculation shows the annual chemical price is 4.4 MNOK if ferric chloride is used as a coagulant. The annual price when calcium hydroxide is used increased to 3 and 4 times more with lower and higher dosage of the chemical, respectively.

Therefore the calcium hydroxide does not seem economical alternative coagulant, however, there are some WWTP that have been using this chemical as main coagulant. This suggests that it is possible to do calcium coagulations with less or cheaper coagulant than estimated here. In addition there are some advantages in using calcium that may have other economic and environmental benefits not included in this simple cost evaluation. Such advantages can include smaller sedimentation tank due to rapid settling and less water from dewatering due to less volume of sludge (section 5.1), which can reduce construction and operation costs. The most important environmental advantage could be improved possibilities for recovering phosphorus from sludge coagulated with calcium rather than iron. There may be no clear economic benefit from this at the moment but increasing focus on P recovery for producing fertilizer can lead to economic advantages in the future. These advantages in addition to more biogas production observed here (section 4.3 and 5.1) can be considered as economic incentives to use calcium hydroxide.

Since aforementioned advantages may not cover the high cost of calcium hydroxide, some other ways to make calcium phosphate can be considered for further study. Biological phosphorus removal (bio-P) is an alternative to coagulation that is gaining popularity mainly due to reduced costs (requires no or little coagulant). If coagulation is replaced by bio-P at a plant like Knarrdalstrand WWTP it would lead to increased phosphate levels in the sludge reject water. Recovering phosphate by calcium precipitation in the reject water therefore seems like an interesting option that could be further investigated. Maximizing the nitrification during reject water bio treatment would remove a lot of alkalinity so that less of the added coagulant would be wasted on alkalinity removal. Much less volume of water and more concentrated phosphate would be treated in such a case, which would lead to much less chemical use and thereby much lower costs than estimated in Table 5-1.

Table 5-1. Comparing annual chemical cost estimation for treatment of 27500 m3/day wastewater (WW) with ferric chloride and calcium hydroxide

Chemical	Unit price	Determined dosage	Cost (MNOK/year)
ferric chloride	1500 NOK/ton*	0.2 mL/L of WW	4.4
Calcium hydroxide	2000 NOK/ ton**	0.6 g/L of WW	12
Calcium hydroxide	2000 NOK/ ton**	0.8 g/L of WW	16

*Data collected from Knarrdalstrand WWTP. 1 ton of ferric chloride =0.6875 m3 of ferric chloride.

**Data collected from Franzefoss minerals company

6 Conclusion and further study

Comparing the effects of ferric chloride and calcium hydroxide on coagulation process in the WWTP during jar tests showed that calcium hydroxide has capabilities to improve sludge quality.

- The created flocs from calcium hydroxide showed faster velocity to settle with smaller SVI compare to ferric chloride. Calcium hydroxide with SVI equals to 46 ±5 mL/g provided 6 times less voluminous sludge that contained more solids than ferric chloride with SVI = 264 ±68 mL/g.
- The biogas production potential of calcium hydroxide sludge with pH around 12.5 was higher than ferric chloride sludge with pH around 7.5. More hydrolysis to soluble COD due to higher pH and the positive effect of calcium salts can be the reason for improved digestion. The final pH after digesting was equivalent for both cases around 7.5.
- The efficiencies of calcium hydroxide on the reduction of COD and phosphorus were slightly higher than ferric chloride when wastewater COD concentration was in typical range and high range (i.e. more than 140 mg/L). But in turbidity and TSS removal ferric chloride showed slightly more stable performance than calcium hydroxide. As an overall conclusion calcium hydroxide and ferric chloride had similar effects on the treated wastewater quality.
- Calcium hydroxide provides sludge with phosphorus that can more easily be recovered for fertilizer production that can lead to environmental and economic improvement in long-term. Much higher chemical costs than for ferric chloride may be the main disadvantage of calcium hydroxide. Higher total solids in sludge can be another drawback for this coagulant.

As the second objective, the effect of biological reject water treatment on the coagulation process was investigated. It appears that it is better for the coagulation when reject water is treated before it is returned to the main inlet and mix with wastewater. It was compared with the effect of untreated reject water in jar tests.

- Biological treatment reject water leads to more COD removal from wastewater especially when wastewater COD concentration is in the typical range of the plant. This is explained by active biomass synthesized in the bio-process capturing dissolved organics when mixed plant inlet water and this biomass was removed by coagulation. Treated reject water reduced the COD of the coagulated sample to 39 ±11 mg/L while untreated reject water ended up with 58 ±5 mg/L (i.e. when ferric chloride was used as the coagulant). This supports (3rd and 4$^{th)}$ mechanisms proposed.
- Efficiencies of treated reject water and untreated reject water on turbidity and TSS removal in the wastewater were equivalent. Moreover, the sludge volume index and captured phosphorus in sludge did not show any significant effects of reject water treatment.
- No the decisive effect of biological treatment on biogas production potential of the coagulated sludge was obtained so more experiments and more accurate method to clarify the effects of biological treatment on biogas production are required.

Since this thesis had the time limitation and was only a preliminary study, the further studies may be needed to obtain more knowledge before the methods investigated can be implemented in full-scale. The proper dosage of ferric chloride as coagulant has been optimized in the plant for years while the required dosage of calcium hydroxide was determined in simple jar test in this study. Optimizing the dosage for the different condition of wastewater and estimating biogas production potential with more accurate methods can be investigated in future studies. Generating calcium phosphate precipitate by different methods, such as biological phosphate removal can be part of further studies to provide phosphate rich sludge for fertilizer production.

Effects of biological treatment of reject water on the main coagulation process is another topic, which can be extended during further research, to obtain design criteria for full-scale implementations. Since the proportion of wastewater and reject water was defined based on annular average, the flow of reject water (i.e. treated or untreated) can be changed to investigate different situations. Comparing the effect of TR and UR with higher or lower proportion can be used for this. The effect of biological treatment on biogas production potential of residual sludge can be studied with advanced BMP method in further studies.

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Appendices

Appendix 1: Master thesis description

Appendix 2: MBBR reactors

Appendix 3: Mass balance

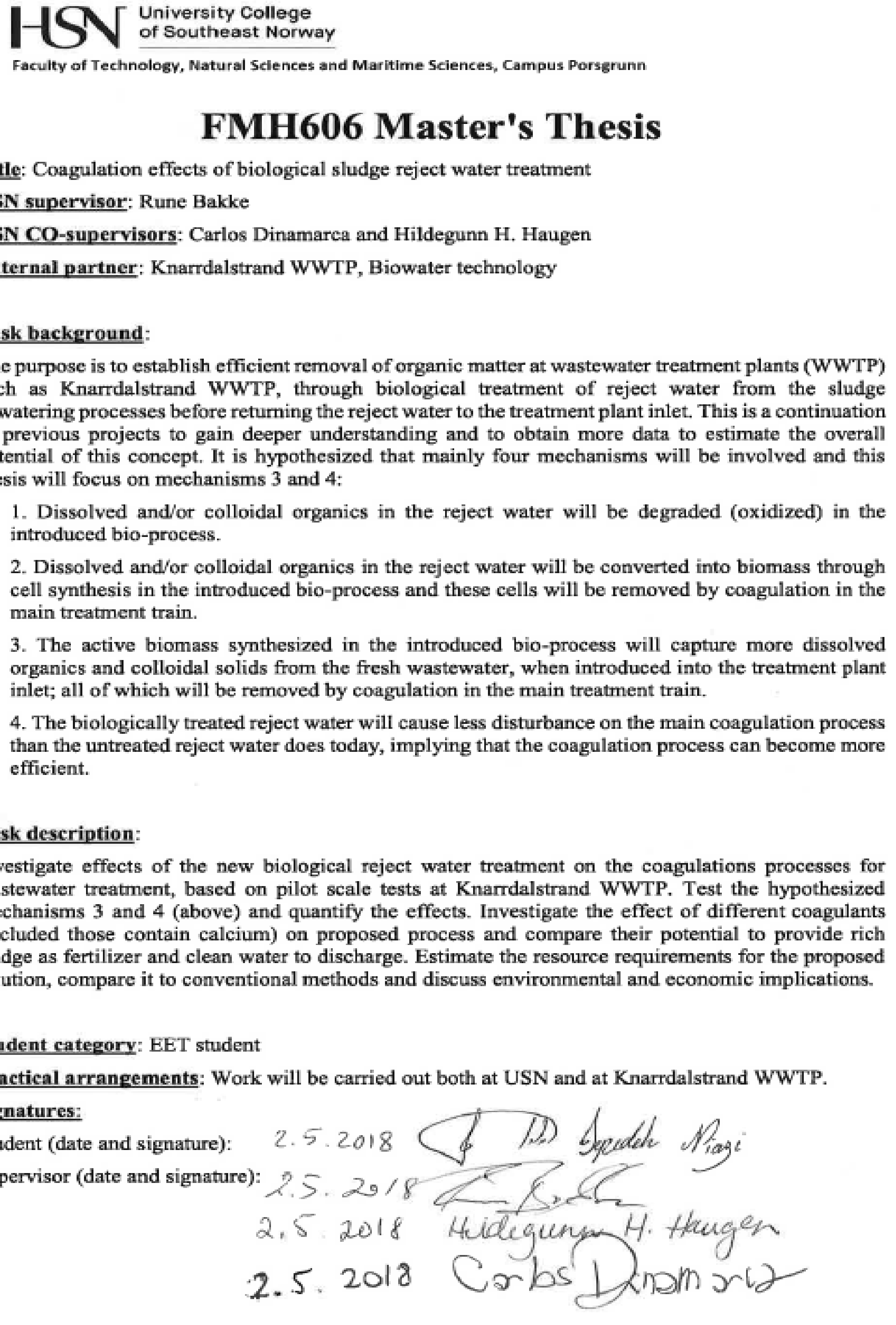
Appendix 4: TSS removal with TR and UR

Appendix 5: Biogas production

Appendix 6: Knarrdalstrand analysis in 2017

Appendix 7: MBBR’s performance

Appendix 1: Master thesis description



HSN University College of Southeast Norway

Faculty of Technology, Natural Sciences and Maritime Sciences, Campus Porsgrunn

FMH606 Master's Thesis

Title: Coagulation effects of biological sludge reject water treatment

USN supervisor: Rune Bakke

USN CO-supervisors: Carlos Dinamarca and Hildegunn H. Haugen

External partner: Knarrdalstrand WWTP, Biowater technology

Task background:

The purpose is to establish efficient removal of organic matter at wastewater treatment plants (WWTP) such as Knarrdalstrand WWTP, through biological treatment of reject water from the sludge dewatering processes before returning the reject water to the treatment plant inlet. This is a continuation of previous projects to gain deeper understanding and to obtain more data to estimate the overall potential of this concept. It is hypothesized that mainly four mechanisms will be involved and this thesis will focus on mechanisms 3 and 4:

1. Dissolved and/or colloidal organics in the reject water will be degraded (oxidized) in the introduced bio-process.
2. Dissolved and/or colloidal organics in the reject water will be converted into biomass through cell synthesis in the introduced bio-process and these cells will be removed by coagulation in the main treatment train.
3. The active biomass synthesized in the introduced bio-process will capture more dissolved organics and colloidal solids from the fresh wastewater, when introduced into the treatment plant inlet; all of which will be removed by coagulation in the main treatment train.
4. The biologically treated reject water will cause less disturbance on the main coagulation process than the untreated reject water does today, implying that the coagulation process can become more efficient.

Task description:

Investigate effects of the new biological reject water treatment on the coagulations processes for wastewater treatment, based on pilot scale tests at Knarrdalstrand WWTP. Test the hypothesized mechanisms 3 and 4 (above) and quantify the effects. Investigate the effect of different coagulants (included those contain calcium) on proposed process and compare their potential to provide rich sludge as fertilizer and clean water to discharge. Estimate the resource requirements for the proposed solution, compare it to conventional methods and discuss environmental and economic implications.

Student category: EET student

Practical arrangements: Work will be carried out both at USN and at Knarrdalstrand WWTP.

Signatures:

Student (date and signature): 2.5.2018 Syedeh Niazi

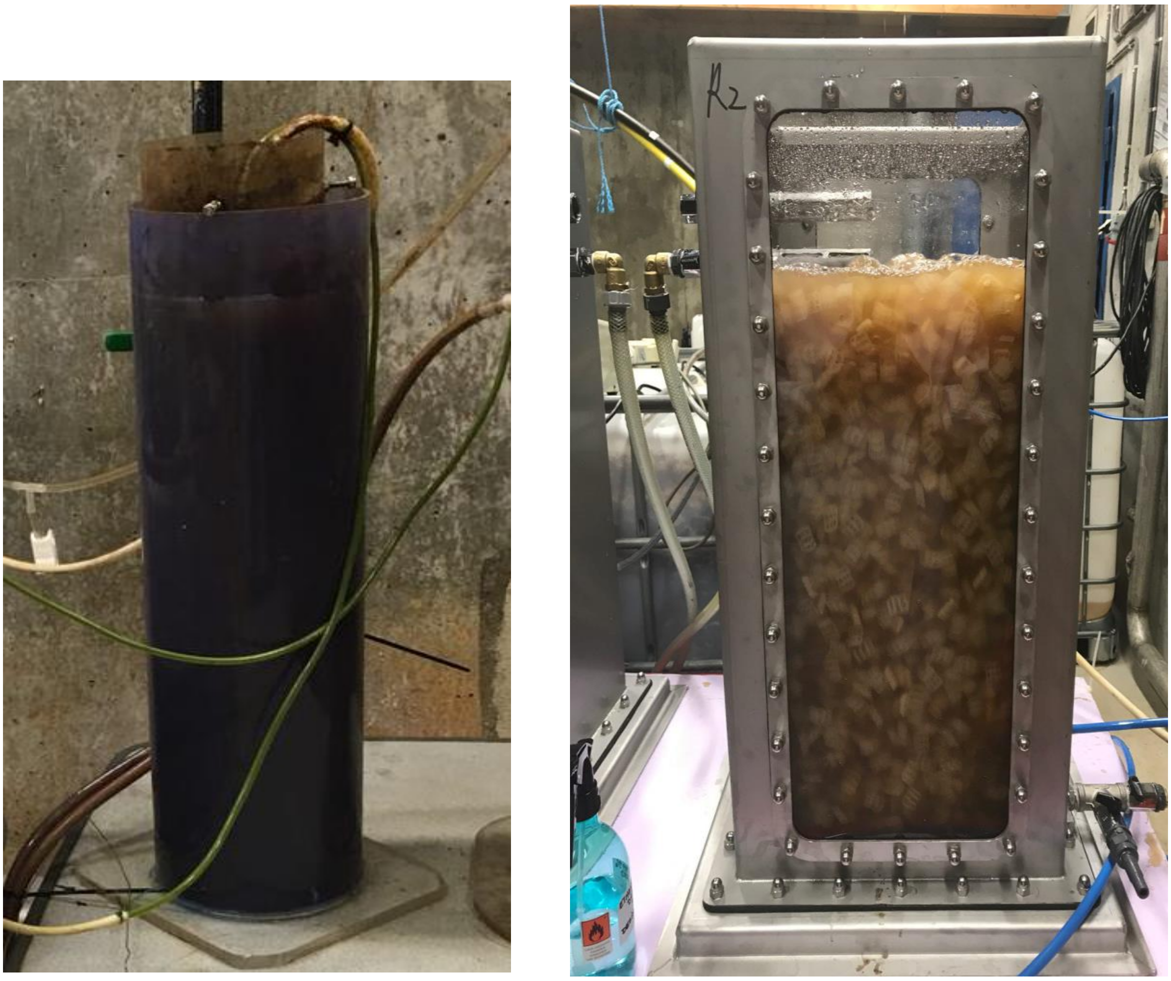
Supervisor (date and signature): 2.5.2018

2.5.2018 Hildegunn H. Haugen

2.5.2018 Carlos Dinamarca

Appendix 2: MBBR reactors

Figure 1-a shows primary MBBR reactors with volume of 18.8 L that was used during first two months. Figure 1-b is Biowater MBBR reactor with volume of 68 L.

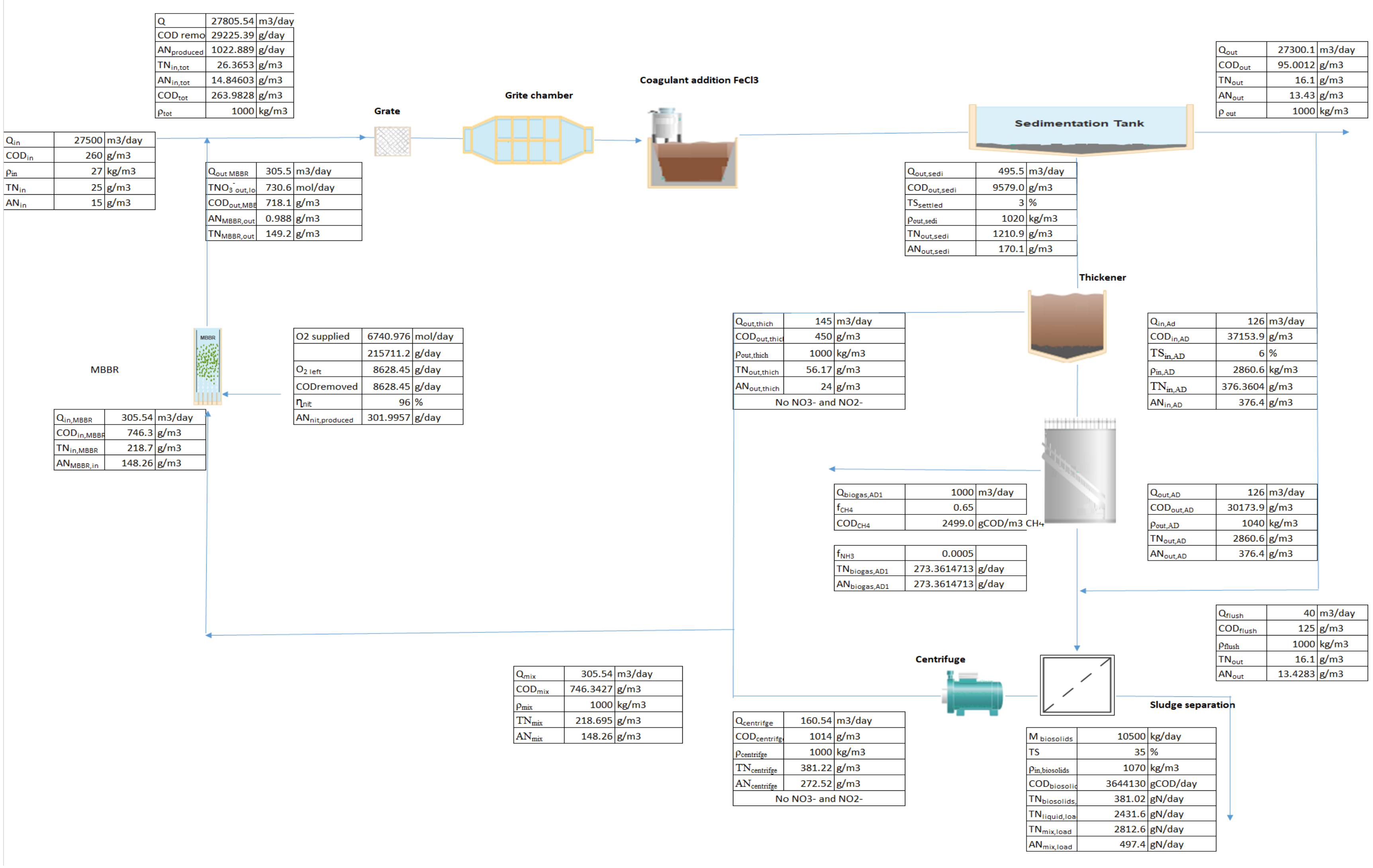


a)

b)

Figure 1. Pilot scale MBBR reactors in biological treatment

Appendix 3: Mass balance



Q	27805.54	m3/day
COD remo	29225.39	g/day
$AN_{produced}$	1022.889	g/day
$TN_{in,tot}$	26.3653	g/m3
$AN_{in,tot}$	14.84603	g/m3
COD_{tot}	263.9828	g/m3
ρ_{tot}	1000	kg/m3

Q_{in}	27500	m3/day
COD_{in}	260	g/m3
ρ_{in}	27	kg/m3
TN_{in}	25	g/m3
AN_{in}	15	g/m3

$Q_{out\ MBBR}$	305.5	m3/day
$TNO_3^-{}_{out,lo}$	730.6	mol/day
$COD_{out,MBB}$	718.1	g/m3
$AN_{MBBR,out}$	0.988	g/m3
$TN_{MBBR,out}$	149.2	g/m3

Q_{out}	27300.1	m3/day
COD_{out}	95.0012	g/m3
TN_{out}	16.1	g/m3
AN_{out}	13.43	g/m3
$\rho_{\ out}$	1000	kg/m3

$Q_{out,sedi}$	495.5	m3/day
$COD_{out,sedi}$	9579.0	g/m3
$TS_{settled}$	3	%
$\rho_{out,sedi}$	1020	kg/m3
$TN_{out,sedi}$	1210.9	g/m3
$AN_{out,sedi}$	170.1	g/m3

O2 supplied	6740.976	mol/day
	215711.2	g/day
$O_{2\ left}$	8628.45	g/day
CODremoved	8628.45	g/day
η_{nit}	96	%
$AN_{nit,produced}$	301.9957	g/day

$Q_{in,MBBR}$	305.54	m3/day
$COD_{in,MBBR}$	746.3	g/m3
$TN_{in,MBBR}$	218.7	g/m3
$AN_{MBBR,in}$	148.26	g/m3

$Q_{out,thich}$	145	m3/day
$COD_{out,thic}$	450	g/m3
$\rho_{out,thich}$	1000	kg/m3
$TN_{out,thich}$	56.17	g/m3
$AN_{out,thich}$	24	g/m3
No NO3- and NO2-		

$Q_{in,Ad}$	126	m3/day
$COD_{in,AD}$	37153.9	g/m3
$TS_{in,AD}$	6	%
$\rho_{in,AD}$	2860.6	kg/m3
$TN_{in,AD}$	376.3604	g/m3
$AN_{in,AD}$	376.4	g/m3

$Q_{biogas,AD1}$	1000	m3/day
f_{CH4}	0.65	
COD_{CH4}	2499.0	gCOD/m3 CH4

$Q_{out,AD}$	126	m3/day
$COD_{out,AD}$	30173.9	g/m3
$\rho_{out,AD}$	1040	kg/m3
$TN_{out,AD}$	2860.6	g/m3
$AN_{out,AD}$	376.4	g/m3

f_{NH3}	0.0005	
$TN_{biogas,AD1}$	273.3614713	g/day
$AN_{biogas,AD1}$	273.3614713	g/day

Q_{flush}	40	m3/day
COD_{flush}	125	g/m3
ρ_{flush}	1000	kg/m3
TN_{out}	16.1	g/m3
AN_{out}	13.4283	g/m3

Q_{mix}	305.54	m3/day
COD_{mix}	746.3427	g/m3
ρ_{mix}	1000	kg/m3
TN_{mix}	218.695	g/m3
AN_{mix}	148.26	g/m3

$Q_{centrifge}$	160.54	m3/day
$COD_{centrifg}$	1014	g/m3
$\rho_{centrifge}$	1000	kg/m3
$TN_{centrifge}$	381.22	g/m3
$AN_{centrifge}$	272.52	g/m3
No NO3- and NO2-		

$M_{\ biosolids}$	10500	kg/day
TS	35	%
$\rho_{in,biosolids}$	1070	kg/m3
$COD_{biosolic}$	3644130	gCOD/day
$TN_{biosolids,}$	381.02	gN/day
$TN_{liquid,loa}$	2431.6	gN/day
$TN_{mix,load}$	2812.6	gN/day
$AN_{mix,load}$	497.4	gN/day

Appendix 4: TSS removal with TR and UR

Residual TSS after coagulation process in the samples contained WW+TR compare to WW+UR with both coagulants:

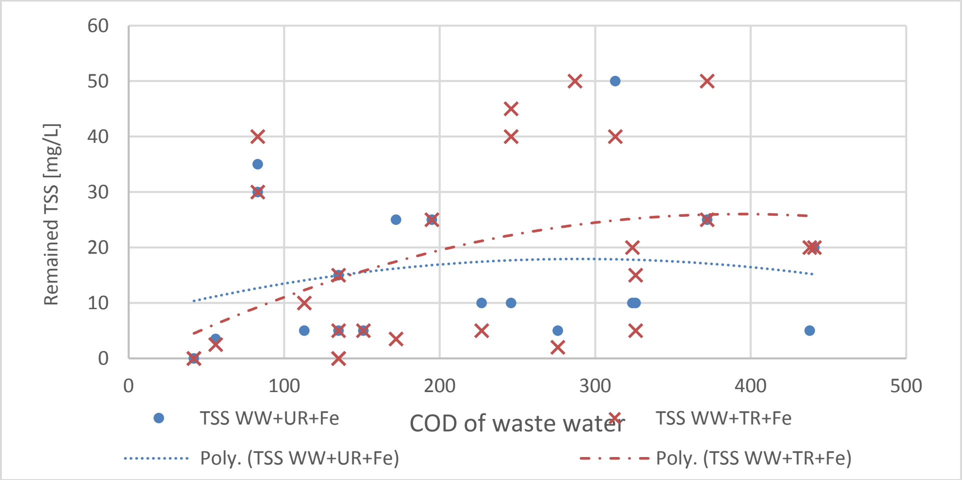


Figure 2. Comparing coagulation efficiency on TSS removal for two different samples: treated reject water (TR) and untreated reject water (UR) when they mixed with wastewater (WW) in fixed proportion With 0.2 mL ferric chloride as coagulant

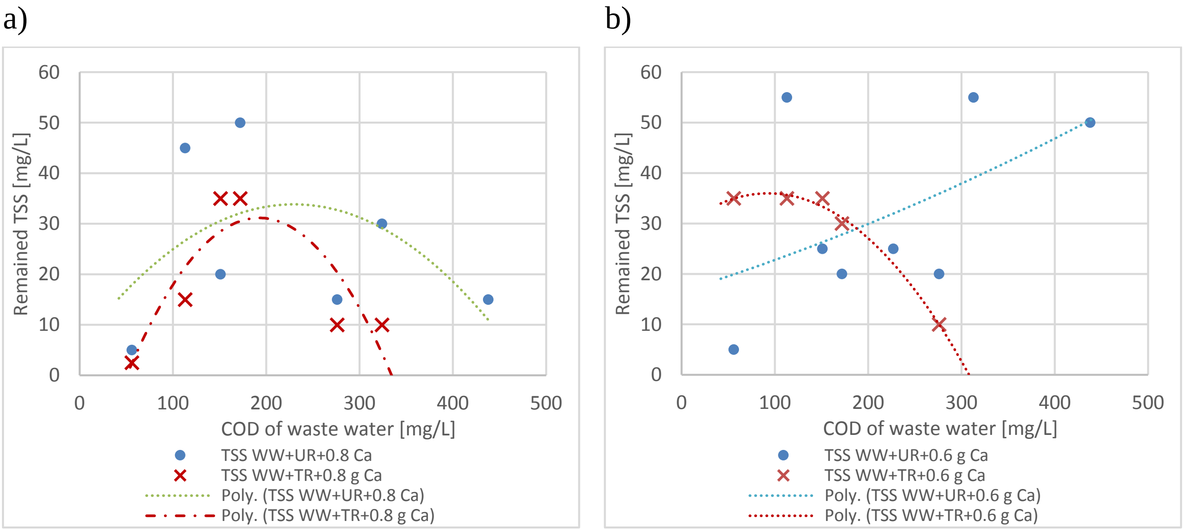


Figure 3. Comparing coagulation efficiency on TSS removal for two different samples: treated reject water (TR) and untreated reject water (UR) when they mixed with wastewater (WW) in fixed proportion. a. With 0.8 g Ca(OH)2 as coagulant. b. With 0.6 g Ca(OH)2 as coagulant

Appendix 5: Biogas production

The results in Table 1 reveals that how much biogas was produced by each sample during 15 days of digesting. Ferric chloride, 0.8 g calcium hydroxide and 0.6 g of calcium hydroxide were used as coagulants. The results showed that calcium hydroxide generally could produce more biogas than ferric chloride. By comparing the sample UR for both coagulants, ferric chloride produced 3 mL of biogas which can present as 0.41 L CH4/g VSS and 0.21 L CH4/g COD. These values for 0.6 g of calcium hydroxide increased to 18 mL of biogas and 1.95 L CH4/g VSS and 0.56 L CH4/g COD. The higher dosage of calcium hydroxide produced more biogas than ferric chloride as well.

By comparing the sample TR and UR for each coagulant, it is discovered that TR produced less biogas when ferric chloride was used as the coagulant. The lower dosage of calcium hydroxide illustrated the same behavior. But when the higher dosage of calcium hydroxide was used as the coagulant, the produced biogas of sample TR was more than UR. The results showed 9 mL biogas, 0.73 L CH4/g VSS and 0.67 L CH4/g COD for sample UR and 13.5 mL biogas, 1.1 L CH4/g VSS and 0.71 L CH4/g COD for sample TR.

Theoretically the maximum methane production is 0.38 L CH4/g COD if all COD was consumed during digestion. Since the produced methane with tested samples are higher than standard amount, some errors can be the reasons for that.

Table 1. Comparing biogas production potential of remained sludge from two different samples after coagulation process: treated reject water (TR) and untreated reject water (UR) when they mixed with wastewater (WW) in fixed proportion. It is assumed 65% of biogas is purely methane.

	Biogas volume [mL]		VSS of sample [mg/L]		L CH4/g VSS		COD of sample [mg/L]		L CH4/g COD	
	UR	TR	UR	TR	UR	TR	UR	TR	UR	TR
ferric chloride	3	-1.5	475	650	0.41	-0.15	922	897	0.21	-0.11
0.6 g of lime	18	8	600	750	1.95	0.69	2080	1444	0.56	0.36
0.8 g of lime	9	13.5	800	800	0.73	1.10	868	1242	0.67	0.71

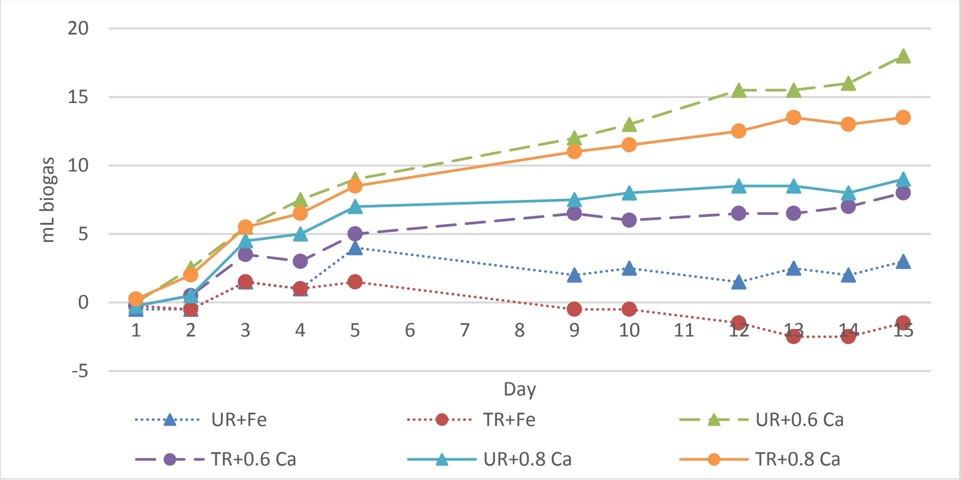


Figure 0-2. Biogas production from precipitates sludge after coagulation during 15 days syringe tests running

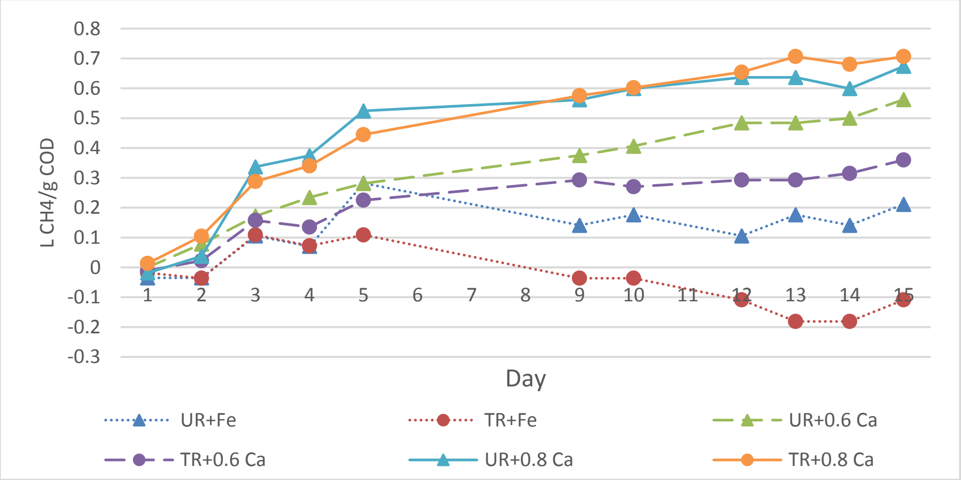


Figure 0-3. Methane production from precipitates sludge after coagulation per COD of sludge during 15 days syringe tests running.

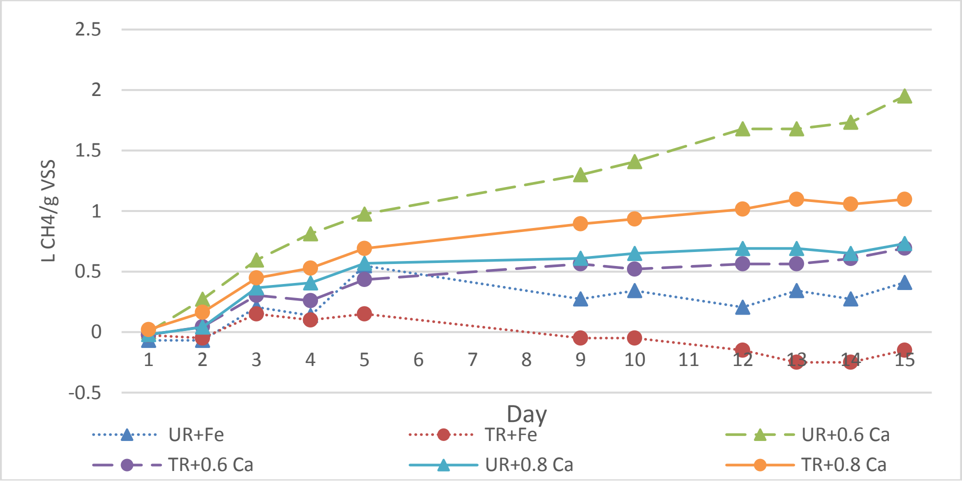


Figure 0-4. Methane production from precipitates sludge after coagulation per VSS of sludge during 15 days syringe tests running.

Appendix 6: Knarrdalstrand analysis in 2017

Table 2. Results of periodic experiments in Knarrdalstrand WWTP in 2017

Date	Q-in(m3/day)	COD-in (mg/L)	COD-out (mg/L)	P-in(mg/L)	P-out (mg/L)
8-Jan	18,800	393	79	3.84	0.18
16-Jan	21,126	289	75	2.70	0.17
22-Feb	33,300	169	71	1.85	0.38
28-Feb	49,165	56	38	0.56	0.05
14-Mar	39,596	113	36	1.17	0.13
10-Apr	17,901	283	78	2.84	0.13
22-Apr	17,160	229	59	3.81	0.16
4-May	22,255	199	66	2.16	0.09
11-May	35,624	142	79	1.15	0.06
11-Jun	36,364	80	47	0.65	0.08
16-Jun	35,136	226	73	1.54	0.24
22-Jun	18,445	349	91	1.52	0.08
10-Jul	18,065	379	56	3.51	0.20
18-Jul	13,591	377	98	3.11	0.11
20-Aug	25,084	173	40	1.98	0.07
28-Aug	15,608	267	63	3.55	0.09
16-Sep	29,004	176	44	1.82	0.10
4-Oct	35,058	103	57	1.14	0.128
12-Oct	26,520	111	44	1.14	0.07
1-Nov	31,630	149	50	1.67	0.07
10-Nov	30,812	156	50	1.72	0.07
16-Nov	27,748	270	52	2.73	0.07
27-Nov	28,800	187	57	2.07	0.06
5-Dec	21,985	258	53	2.74	0.05
Average	**27032**	**214**	**61**	**2.12**	**0.12**

Appendix 7: MBBR’s performance

Based on reactor behavior the operating time can be divided to 3 intervals. From start point to 9th February when some technical problem appeared in reactors. UR carried large particles from thickener and centrifuge that cause very high organic load rate and clogging feeding pipes. Oxygen disconnection and negative COD removal are some other problems during this period. This disturbances made unstable situation for reactors and coagulation tests. After adding a mesh in the way of reactor inlet and controlling the organic load rate and fixing other technical problems, the reactors reached the stable situation from 16th February. The third interval started from 9th March, just after replacing the reactors with two new Biowater reactors.

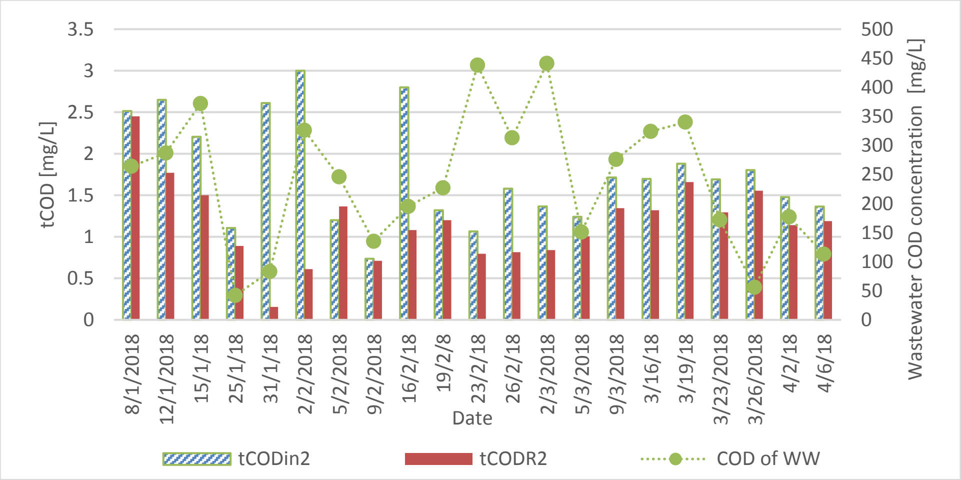


Figure 0-5. tCOD of inlet (UR) and outlet of reactor 2 (TR) .Wastewater COD concentration is also shown

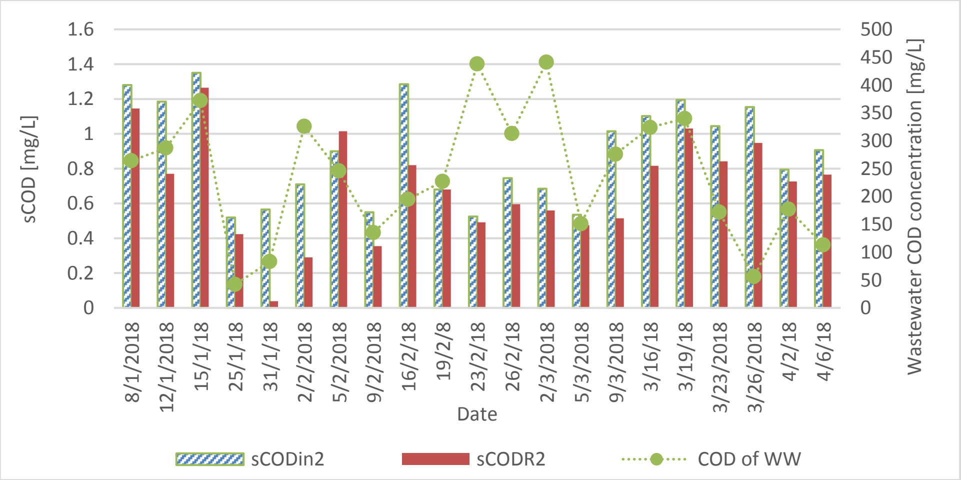


Figure 0-6. sCOD of inlet (UR) and outlet of reactor 2 (TR) . Wastewater COD concentration is also shown

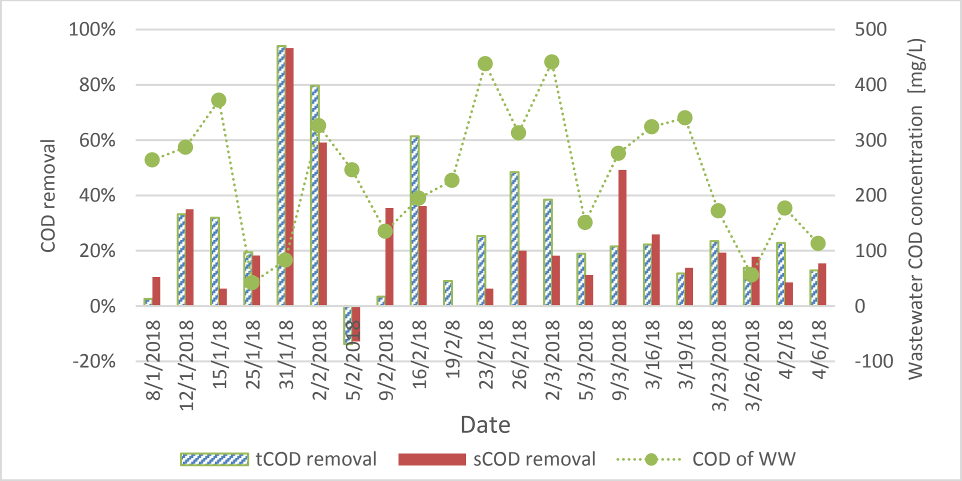


Figure 7. Soluble and total COD removal with reactor 2. Wastewater COD concentration is also shown