

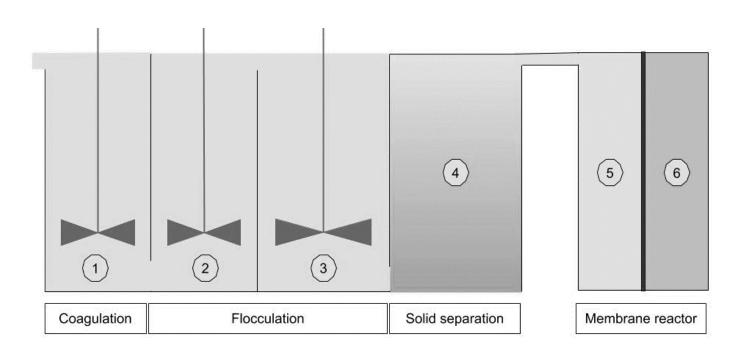
Nitrogen and phosphorus harvesting from liquid waste using hydrophobic gas permeable membranes

NPHARVEST – Suspended solid separation 1d/2018

Simon Reuillard

Anna Mikola

Riku Vahala



Foreword

This report is published in Aalto University's NPHarvest project. NPHarvest project develops a technology to recover nutrients from liquid waste and studies the market potential of the method. This project report includes the study of various methods for solid separation to prepare the water for nutrient recovery. NPHarvest is a part of a larger project called "A breakthrough in the circular economy and clean solutions" by the Finnish government.

The project is supported by a consortium of companies including Nordkalk Ltd, Gasum, HSY, Biolan and Sulzer. The Ministry of Environment has funded NPHarvest with 457499.7 euros in the program "Enhancing nutrient recycling and the condition of Saaristomeri". NPHarvest has also been financially supported by Nordkalk Ltd and Gasum. We would like to thank HSY, Kemira, Nordkalk, Hyxo for their valuable support and suggestions during the experiments.

Acknowledgement

First of all, I would like to express my gratitude to Aalto University, Water and waste water engineering group within the research group of Water and environmental Engineering, to enabling me to complete this thesis. The master opportunity I had in the Water team was a great chance for learning and professional development. I am grateful for having a chance to meet so many wonderful people who led me though this master thesis.

I am using this opportunity to express my deepest gratitude and special thanks to Professor in charge of me, Riku Vahala, who took time out to welcome me in the project at their esteemed organization.

I express my deepest thanks to my tutor, Anna Mikola, "NPHarvest project manager and Postdoctoral researcher, who in spite of being extraordinarily busy with her duties, took time out to hear, guide and keep me on the correct path. I choose this moment to acknowledge her contribution gratefully, giving necessary advices and guidance.

It is my pleasure to write my best regards and deepest sense of gratitude to Mr. Järvinen Ari, Laboratory manager, Mr. Kaljunen Juho, Doctoral student, Mr. Pradhan Surendra, Postdoctoral researcher, Ms. Peltola Aino, Senior laboratory technician and Louhio Antti, Senior laboratory technician for their careful and precious guidance which were extremely valuable for my study both theoretically and practically.

Reuillard Simon

CONTENTS

1	Abs	tract		5
2	Intr	oduc	ction	6
2	2.1	Вас	kground	6
2	2.2	Pro	blem	6
3	Bib	liogr	aphy	8
3	3.1	Intr	oduction	8
	3.1.	1	Water properties	8
3	3.2	Coa	gulation and flocculation	8
3	3.3	Alte	ernative solid separation methods	10
	3.3.	1	Ballasted sedimentation	10
	3.3.	2	Dissolved Air Flotation (DAF)	13
	3.3.	3	Disc Filtration	14
3	3.4	Infl	uence of process conditions on SS removal	15
4	Met	thod	and Experiments	16
4	4.1	Cha	racterization of the reject water	16
4	4.2	Pre	sentations of experiments	17
	4.2.	1	Coagulation-Flocculation	19
	4.2.	2	Ballasted sedimentation	19
	4.2.	3	DAF	19
	4.2.	4	Disc filtration	20
2	4.3	Lab	measurements	21
2	4.4	Che	emical selection and dosage	22
	4.4.	1	Coagulant selection and dosage	22
	4.4.	2	Polymer selection and dosage	23
5	Res	ults.		24
į	5.1	Pre	-treatments results	24
	5.1.	1	Disc filtration	24
	5.1.	2	DAF	25
	5.1.	3	Ballasted sedimentation	26
Ţ	5.2	DAI	F and sedimentation comparison	26
Ţ	5.3	Tur	bidity and SS	29
6	Disc		on	
6	5.1	Wa	ter properties after pre-treatment	31
6	5.2	LKI	innovation	31
6	5.3	Ver	ification of the results with other streams	33
6	5.4	Eco	nomical possibilities	35
7	Con	onclusions3		
R	Rof	eferences 37		

Table of Figures

FIGURE 3.3-1: FORCES ON A DISCRETE PARTICLE	FIGURE 2.2-1: DECISION PATH FOR PRE-TREATMENT SELECTION	7
FIGURE 3.3-2: SCHEMATIC OF THE ACTIFLO BALLASTED FLOCCULATION CLARIFICATION PROCESS, FROM I. KRUGER INC., A VEOLIA WATER SOLUTIONS & TECHNOLOGIES COMPANY	FIGURE 3.3-1: FORCES ON A DISCRETE PARTICLE	10
KRUGER INC., A VEOLIA WATER SOLUTIONS & TECHNOLOGIES COMPANY. 12 FIGURE 3.3-3: CONVENTIONAL DISSOLVED AIR FLOTATION SYSTEM, FROM MOLAER COMPANY 13 FIGURE 3.3-4: PROCESS SELECTION DISGRAM BASED ON AVERAGE RAW WATER QUALITY CONDITIONS, REPRINTED FROM VALADE ET AL. (2009). 14 FIGURE 3.3-5: SCHEMATIC DISC FILTER AND ITS DIFFERENT SECTIONS, FROM SUTHERLAND (2008). 15 FIGURE 4.2-1: SCHEME OF THE ENTIRE PRE-TREATMENT PROCESS AND MEMBRANE REACTOR 18 FIGURE 4.2-2: PICTURE OF FLOTATION UNIT . 19 FIGURE 4.2-3: PICTURE OF FLOTATION UNIT . 20 FIGURE 4.1-1: VARIOUS PAX COMPARISON FOR SS REMOVAL . 22 FIGURE 4.2-2: POLYMER COMPARISON FOR SS REMOVAL . 23 FIGURE 5.1-1: DISC FILTRATION RESULTS REGARDING PH FOR DIFFERENT COAGULANTS . 24 FIGURE 5.1-2: SS REMOVAL REGARDING POLYMER DOSE FOR DAF . 25 FIGURE 5.1-3: POLYMER DOSE OPTIMISATION . 26 FIGURE 5.1-3: POLYMER DOSE OPTIMISATION . 26 FIGURE 5.2-2: FLOTATION AND SEDIMENTATION POLYMER COMPARISON . 27 FIGURE 5.2-3: FLOTATION AND SEDIMENTATION COAGULANT COMPARISON . 27 FIGURE 5.2-3: SAS AND TURBIDITY CORRELATION . 29 FIGURE 5.2-3: SAS AND TURBIDITY CORRELATION . 29 FIGURE 6.2-1: INFLUENCE OF LIKD DOSE ON SS REMOVAL . 32 FIGURE 6.2-3: EVOLUTION OF INORGANIC CONTENT IN SS REGARDING LIKD DOSE . 33 FIGURE 6.2-3: EVOLUTION OF INORGANIC CONTENT IN SS REGARDING LIKD DOSE . 33 FIGURE 6.2-3: COMPARISON OF WATER PROPERTIES AFTER PRE-TREATMENT FOR DIFFERENT WWTP . 34 FIGURE 6.3-1: COMPARISON OF WATER PROPERTIES AFTER PRE-TREATMENT FOR DIFFERENT WWTP . 34 FIGURE 6.3-1: COMPARISON OF WATER PROPERTIES AFTER PRE-TREATMENT FOR DIFFERENT WWTP . 34 FIGURE 6.3-1: COMPARISON OF WATER PROPERTIES AFTER PRE-TREATMENT FOR DIFFERENT WWTP . 34 FIGURE 6.3-1: COMPARISON OF WATER PROPERTIES AFTER PRE-TREATMENT FOR DIFFERENT WWTP . 34 FIGURE 6.3-1: COMPARISON OF WATER PROPERTIES AFTER MESOPHILIC DIGESTER AND DEWATERING IN VIKINIMÄKI WATP 34 FIGURE 6.3-1: EXPERIMENT TIME AND ORDER . 21 TABLE 4.4-1: FAR PROPERTIES AFTER SLUDGE CENTRIFUGATION IN DIFFERENT WWTP . 35 TABLE 4.4-2: PIX 105 PROPERTIES AFTER SLUDGE CEN		
FIGURE 3.3-3: CONVENTIONAL DISSOLVED AIR FLOTATION SYSTEM, FROM MOLAER COMPANY	·	
FIGURE 3.3-4: PROCESS SELECTION DIAGRAM BASED ON AVERAGE RAW WATER QUALITY CONDITIONS, REPRINTED FROM VALADE ET AL. (2009)		
REPRINTED FROM VALADE ET AL. (2009)		
FIGURE 3.3-5: SCHEMATIC DISC FILTER AND ITS DIFFERENT SECTIONS, FROM SUTHERLAND (2008)	·	-
FIGURE 4.2-1: SCHEME OF THE ENTIRE PRE-TREATMENT PROCESS AND MEMBRANE REACTOR		
FIGURE 4.2-3: PICTURE OF DISC FILTRATION UNIT		
FIGURE 4.4-1: VARIOUS PAX COMPARISON FOR SS REMOVAL	FIGURE 4.2-2: PICTURE OF FLOTATION UNIT	19
FIGURE 4.4-2: POLYMER COMPARISON FOR SS REMOVAL	FIGURE 4.2-3: PICTURE OF DISC FILTRATION UNIT	20
FIGURE 5.1-1: DISC FILTRATION RESULTS REGARDING PH FOR DIFFERENT COAGULANTS	FIGURE 4.4-1: VARIOUS PAX COMPARISON FOR SS REMOVAL	22
FIGURE 5.1-2: SS REMOVAL REGARDING POLYMER DOSE FOR DAF	FIGURE 4.4-2: POLYMER COMPARISON FOR SS REMOVAL	23
FIGURE 5.1-3: POLYMER DOSE OPTIMISATION	FIGURE 5.1-1: DISC FILTRATION RESULTS REGARDING PH FOR DIFFERENT COAGULANTS	24
FIGURE 5.2-1: FLOTATION AND SEDIMENTATION POLYMER COMPARISON	FIGURE 5.1-2: SS REMOVAL REGARDING POLYMER DOSE FOR DAF	25
FIGURE 5.2-2: FLOTATION AND SEDIMENTATION COAGULANT COMPARISON		
FIGURE 5.2-3: FLOTATION AND SEDIMENTATION COMPARISON FOR ACTIVE SUBSTANCE IN COAGULANT 28 FIGURE 5.3-1: SS AND TURBIDITY CORRELATION		
FIGURE 5.3-1: SS AND TURBIDITY CORRELATION		
FIGURE 6.1-1: WATER PROPERTIES AFTER PRE-TREATMENT		
FIGURE 6.2-1: INFLUENCE OF LKD DOSE ON SS REMOVAL		
FIGURE 6.2-2: A CLOSER LOOK ON HOW LKD DOSE INFLUENCES SS REMOVAL		
FIGURE 6.2-3: EVOLUTION OF INORGANIC CONTENT IN SS REGARDING LKD DOSE		
FIGURE 6.3-1: COMPARISON OF WATER PROPERTIES AFTER PRE-TREATMENT FOR DIFFERENT WWTP		
Table of tables Table 3.2-1: ADVISED DOSES FOR COAGULANTS		
Table of tables Table 3.2-1: Advised doses for coagulants		
TABLE 3.2-1: ADVISED DOSES FOR COAGULANTS	FIGURE 6.3-2: COAGULANT DOSE COMPARISON FOR DIFFERENT STREAMS REGARDING SS REMOVAL	34
TABLE 3.2-1: ADVISED DOSES FOR COAGULANTS	Table of tables	
TABLE 3.3-1: SOME SETTLING RATES FOR DIFFERENT PARTICLES (ASSUMED SPHERICAL) AND SIZES; FROM (CHEREMISINOFF, 2002)		0
(CHEREMISINOFF, 2002)	TABLE 3.2-1: ADVISED DUSES FUR CUAGULANTS	9 D∩M
TABLE 3.3-2: ACTIFLO RANGE OF APPLICABILITY, MODIFIED FROM VEOLIA WEBPAGE		
TABLE 4.1-1: REJECT WATER PROPERTIES AFTER MESOPHILIC DIGESTER AND DEWATERING IN VIIKINMÄKI WWTP	TARI F 3 3-2. ACTIFI O RANCE OF APPI ICARII ITY MODIFIED FROM VEOLIA WERPACE	12
WWTP	TABLE 5.5-2. ACTILEO KANGE OF AFTER MESOPHILIC DIGESTER AND DEWATERING IN VIIKIN	MÄKI
TABLE 4.2-1: EXPERIMENT TIME AND ORDER		
TABLE 4.3-1: STANDARD MEASUREMENT PROCEDURES		
TABLE 4.4-1: PAX PROPERTIES		
TABLE 4.4-2: PIX 105 PROPERTIES		
TABLE 6.3-1: REJECT WATER PROPERTIES AFTER SLUDGE CENTRIFUGATION IN DIFFERENT WWTP33 TABLE 6.4-1: CHEMICAL DOSES AND NEED FOR PILOTING THE PRE-TREATMENT		
TABLE 6.4-1: CHEMICAL DOSES AND NEED FOR PILOTING THE PRE-TREATMENT35		

1 ABSTRACT

This report reviews attempts to find a way to pre-treat reject water coming out of centrifugation of digested sludge after a mesophilic digester. Indeed, it is a stream rich in nutrients, what makes it interesting for recovering nutrients. Unfortunately, it is also full of suspended solids (SS) that prevent a good recovery process. Therefore, different solid separation for suspended solid removal are studied in laboratory scale batch process, including disc filtration, dissolved air flotation (DAF) and ballasted sedimentation.

With a SS concentration close to 1500 mg/L, this stream is coagulated using iron and aluminium based coagulants and flocculated with synthetic polymers to enhance floc creation. A series of batch tests were performed to find optimal combinations. Best results succeed more than 90 % SS removal, which is enough for downstream nutrient recovery in membrane reactor. Those removal rates were achieved with DAF and ballasted sedimentation but were not possible with disc filtration. DAF works properly despite literature information given against using this solid separation for this type of reject water. This report also assesses the possibility to use Lime Kiln Dust (LKD), a side product of lime production, instead of micro sand for ballasted sedimentation. Results with this product in batch process were satisfying and will be conducted in continuous flow in a bigger pilot.

It is hoped this thesis will help people dealing with this special kind of stream, to have a better understanding on how suspended solid removal works and to help choosing the best solid separation process.

Keywords: Suspended solid removal – Digested sludge – Lime Kiln Dust – Nutrient recovery

2 INTRODUCTION

2.1 Background

Nutrient removal from wastewater is a process known for a couple of decades, developed along with the rapid expanding society post World War II (Ashley et al., 2011). However, the recovery of those nutrients, especially nitrogen, remains complicated and high energy consumer, due to a three step process, ammonification, nitrification and denitrification (Maurer et al., 2002). The large energy and environmental footprint of nutrient removal from wastewater, in turn, aggravates the sustainability of fertiliser production for food security (Xie et al., 2016). This is the reason why the NPHarvest project has for main purpose to find a cost and energy efficient process for nutrient recovery by using a membrane reactor. The process uses a gas permeable membrane where ammonia gas selectively passes through. These membrane processes for nutrient recovery, still under development, are referenced only for a few years. The innovation added by this project is mainly focused on increasing the pH of the reactor to have better recovery ratio using lime. Zhu et al. (Zhu et al., 2005) investigated the effect of the pH of the effluent containing ammonia and showed that higher ammonia removal efficiencies could only be attained at relatively higher feed pH values, that is to say, above 11. As a result, nutrient recovery from wastewater using membrane reactor can become a promising way of producing fertiliser, and at the same time, bring benefits to wastewater treatment plants (Grant et al., 2012; Guest et al., 2009; Verstraete et al., 2009).

In order to have an efficient reaction for nitrogen recovery, the raw water, mixture of various components, needs to be treated to ensure that the concentration of suspended solids is decreased before the membrane reactor. Different solid separation processes were studied: Ballasted sedimentation, Dissolved Air Flotation (DAF), and Disc Filtration. The final goal was to make a comparison between their efficiencies and costs in the case of Viikinmäki wastewater treatment plant (WWTP) in order to decide how to run the continuous flow pilot. Moreover, an innovation is studied using Lime Kiln Dust (LKD), a side product of lime production, instead of microsand for ballasted sedimentation.

2.2 Problem

In conventional WWTP, reject water from centrifugation of the sludge is sent back to the inlet of the plant. Its composition is high in suspended solids (SS) therefore, the membrane used in the reactor for retrieving nutrients is clogged instantly with SS if used as such. A solid separation process, also called pre-treatment (prior to the nutrient recovery reactor), is necessary. The purpose was to remove the SS to reach a concentration inferior to 200mg/L and a removal of SS which exceeded 90%. As the water doesn't settle easily, it needs to be processed with a SS removal pre-treatment. The study will focus on answering these questions:

Q1: Which pre-treatment can be used for this type of reject water?

Then, while trying to find an answer to Question 1, that is the main purpose of the project, other questions will be studied.

- Q2: What are the possibilities for the use of Lime Kiln Dust (LKD) instead of microsand in ballasted sedimentation?
 - Q3: Is it possible to apply the same treatment to similar streams in different WWTP?
 - Q4: What are the costs involved in the pre-treatment?

High number of tests are conducted to find the best pre-treatment to use and its optimal conditions in term of SS removal and costs.

Those questions give the basis for the decision chart presented below. The chart gives the criteria for choosing the pre-treatment that will be used in the final project. First, the SS limit must be reached. From the combinations that fulfil this first requirement, tests were done to ensure that nitrogen remains in the water so that the reactor will recover it. Finally, an economic assessment decides from those combinations which will be the final one.

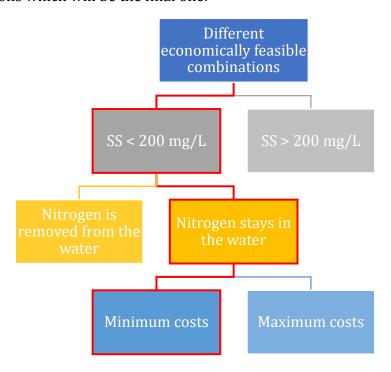


Figure 2.2-1: Decision path for pre-treatment selection

The decision should follow the red path to fulfil every requirement.

The interest is also focused on LKD, that is a side product of lime production. It is a fine powder with a lower size distribution than micro sand. Using this LKD would provide a possible alternative to the micro sand. Indeed, there is no need to recycle LKD, it can be left in the sludge. This way, the process uses less "sand" and the recycling part can be removed, reducing the price of the process at the same time.

A literature review on suspend solids separation and removal from various sources is presented in the next section.

3 BIBLIOGRAPHY

Purpose of this part is to provide a background on the topic and explanations on the motivation of the experimental part. It includes details about water properties, destabilisation of suspended solids and separation processes. Every separation process is presented and detailed providing an understanding of the process in full-scale and their advantages and limits.

3.1 Introduction

Removal of suspended solids consists of separation processes such as filtration, sedimentation, flotation, usually preceded by coagulation and flocculation. They are all commonly used so, a lot of studies have been conducted to have a better understanding of the process. However, they remain empirical techniques that need to be tested in Jar-test with the water studied.

3.1.1 Water properties

Wastewater represent multiphase fluids (mixtures) of various elements. It is referred as water in this thesis. It is not a pure element but a complex combination of organic and non-organic substances, of which some are dissolved and others in suspension. Its detailed composition is not perfectly known. However, municipal WWTP sludge is an important field of research and its composition is usually well known. It contains large amounts of organic matter and N, P, K and other nutrients. It also contains amounts of heavy metals such as Cd, Hg, Pb, Cr, As, Ni, Zn, Cu and B (Tao et al., 2012). Reject water coming out of the centrifugation of the sludge has similar composition with a high concentration of organic matters. The sludge composition varies based on the wastewater treatment process, e.g. sludge retention time and chemicals added and is usually known only at the plant level where some analysis is made.

3.2 Coagulation and flocculation

Conversion of stable wastewater mixture i.e. colloidal solids that stay in suspension into the unstable state is termed destabilisation and the processes of destabilisation are coagulation and flocculation (Tripathy & De, 2006). Used worldwide, those processes are usually used one after another.

The first step of any of those pre-treatment processes mentioned above is to "coagulate", that is to say destabilise, the suspended solids in the water. The destabilisation is induced through charge neutralisation. Coagulation involves the addition of a chemical coagulant (or coagulants) for the purpose of conditioning the suspended, colloidal, and dissolved matter for subsequent processing by flocculation (Howe et al., 2012). Because most of the smaller suspended solids in surface waters carry a negative electrostatic charge, the natural repulsion of these similar charges causes the particles to remain dispersed almost indefinitely (Cheremisinoff, 2002). To allow these small suspended solids to agglomerate, the negative electrostatic charges must be neutralized. Inorganic coagulant such as aluminium and iron salts, added to the water, tend to form pre-flocs. Basic reactions are presented below:

With Aluminium salt, the ion first reaction is the formation of an aluminium precipitate according to the overall reaction below:

$$Al^{3+} + 3HCO_3^- \rightarrow Al(OH)_3 + 3CO_2$$
 (1)

But the actual mechanisms are more complex with the creation of Al components that are halfway between Al^{3+} ion and hydroxide $Al(OH)_3$: $Al(OH)_3^{3-x}$ with 1<x<2.5. These ions can also

hydrate themselves as $Al_n(OH)_p^{(3n-p)+}$ and form Aluminium polymers. Reactions are similar with iron-based salts.

When metal coagulants are added to water, the metal ions (Al and Fe) hydrolyse rapidly, but in a somewhat uncontrolled manner, forming a series of metal hydrolysis species. The efficiency of rapid mixing, the pH, and the coagulant dosage determine which hydrolysis species is effective for treatment (Bratby, 2006). Bratby explains that, in order to produce the correct hydrolysis species, there has been considerable development of pre-hydrolysed inorganic coagulants. The principal advantages of pre-polymerised inorganic coagulants are that they are able to function efficiently over wide ranges of pH and raw water temperatures. They are less sensitive to low water temperatures; lower dosages are required to achieve water treatment goals; less chemical residuals are produced; lower chloride or sulphate residuals are produced.

Those pre-polymerised hydroxide chains leave many $A\ell^{3+}$ sites available for coagulation: $Al_n(OH)_pC\ell_{3n-p}$. These are complex ions, that tend to migrate to the surface of the particles. It allows these particles to be thoroughly mixed into the floc as it forms. Particles, attached to those pre-flocs, are destabilized and are more likely to form bigger structures. Therefore, floc formation can be regarded as hydroxo-aluminous complexes forming bridges between the initial colloids found in raw water (Suez, n.d.).

Same reactions occur with ferric sulphate (PIX). The absence of iron prepolymer on the market should be noted.

To have an efficient coagulation, chemicals are mixed in two steps: Rapid mixing that ensure the repartition of the chemical and slow mixing that provide time for the reaction. Coagulation constitute "pre-flocs" easier to agglomerate during later flocculation.

Coagulant dose is based on TOC concentration, measurement of non-organic matters (NOM). According to Edzwald & Johannes in their book Dissolved Air Flotation pages 6.36 and 6.37 (review of seven different sources), advised doses are presented in the Table 3.2-1. They clearly refer to drinking water treatment applications where NOM is an issue. They are suitable for any separation process. Details about doses are presented in section 4.4.1.

Ref	PAX	PIX
(Edzwald & Johannes, 2012)	0.7-1 mg Al per mg TOC	3-4 mg Fe per mg TOC

Table 3.2-1: Advised doses for coagulants

It is important to note that the coagulant dose is different in the case of aluminium and iron-based coagulants. The reason is that the Aluminium coagulants are pre-polymerised so that they require less chemical than PIX.

An overdosing of metal coagulant can cause the effect of "salting-out". It is the reaction of the dissolved gas e.g. N_2O with the metal salt that transfer the dissolved gas from liquid phase to gas phase, creating a stripping phenomenon and, therefore, bubbles (Kosse et al., 2017). This phenomenon can be used to recover nitrogen from wastewater but is a problem for ballasted sedimentation because it can prevent flocs from settling.

Flocculation is the second step. It is the aggregation of destabilized particles (particles from which the electrical surface charge has been reduced) [...] into larger particles known as flocculant particles or, more commonly, "floc". As the repulsive interaction is reduced, the attractive van der Waals forces cause any particles that came near each other to stick to each other. Particles will collide with each other due to the random movement of particles caused by Brownian motion (micro flocculation) or due to gentle mixing of the water (macro flocculation)(Howe et al., 2012; Tripathy & De, 2006). Moreover, flocculation is made easier by the addition of synthetic polymers. The "pre-flocs"

created during coagulation are aggregated by long polymers to make bigger flocs during another step of slow mixing.

It is explained by Edzwald and Johannes that "The goal of what size to produce depends on the downstream separation process. For sedimentation, the flocs size should be 100s of μm . However, it is more efficient to separate smaller flocs in DAF, around 10s of μm ."

Various polymers are available on the market from which the synthetic polymers are the most commonly used in wastewater treatment. They are divided in three categories depending on their surface charge: Anionic (negative), Cationic (positive), Non-ionic (neutral) (Brostow et al., 2009).

Coagulation and flocculation are the most important steps of the entire SS removal process. They determine the efficiency of the separation process and the retention time of the pre-treatment. They also influence the downstream recovery. Finally, those two steps determine the cost of the complete process. The flocs formed are later removed using one of the three conventional separation processes: sedimentation, flotation or filtration.

3.3 Alternative solid separation methods

Once formed, the flocs are removed using a physical separation process, using gravity or filtration. This part aims to present three of the mainstream separation processes.

3.3.1 Ballasted sedimentation

When wastewater mixture is stopped from movement, the denser phases are separated by gravity by a downward movement (gravimetric separation). This separation is due to the differences in specific mass of the particles in the suspension and flocs, thus achieving a sedimentation or decantation process. The solid particles, which fall off to the bottom of the sedimentation vessel, form a solid – liquid mixture, more or less concentrated, in the form of a sediment called precipitate, slurry or sludge (Zârnoianu et al., 2015).

The sedimentation of particles is based on the gravity force from the differences in density between particles and the fluid. Consider the settling of a discrete particle, see Figure 3.3-1, reprinted from Carlsson (1998). The sedimentation is obtained by the Newton and Stokes law.

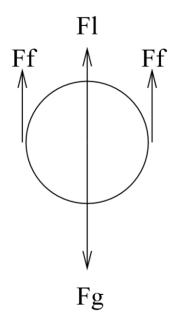


Figure 3.3-1: Forces on a discrete particle

Fg is the gravitational force, Fl is the "lifting" force from the liquid, and Ff is the frictional force between the particle and the liquid.

Newton second law gives:

$$m\frac{dv}{dt} = F_g - F_l - F_f \tag{1}$$

where v is the velocity of the particle, and m is the mass.

The gravity force Fg is given by:

$$F_{q} = mg = \rho_{p}V_{p}g \tag{2}$$

where ρ_p is the density of the particle and V_p is the volume.

The lifting force Fl is given by:

$$F_l = \rho_f V_p g \tag{3}$$

where ρ_f is the density of the fluid.

The frictional drag force Ff depends on the particle velocity, fluid density, projected area, and a drag coefficient. The following empirical expression is used:

$$F_f = \frac{C_D A_p \rho_f v^2}{2} \tag{4}$$

where C_D is the drag coefficient and A_P is the projected area of the particle perpendicular to the velocity.

By inserting those expression to Newton law yields to:

$$m\frac{dv}{dt} = g(\rho_p - \rho_f)V_p - \frac{C_D A_p \rho_f v^2}{2}$$
(5)

As it can be concluded from this equation, the settling velocity depends mainly on the density difference between the granular particles and the fluid and the size of the particle (volume and projected area).

In term of particle size, the bigger the particle is, the faster is the sedimentation. It is presented in Table 3.3-1, considering spherical particles at 10°C.

Table 3.3-1: Some settling rates for different particles (assumed spherical) and sizes; from (Cheremisinoff, 2002)

Particle Diameter (mm)	Particle Type	Time to settle one foot
10.0	Gravel	0.3 sec.
1.0	Coarse sand	3.0 sec.
0.1	Fine sand	38.0 sec
0.01	Silt	33.0 min.
0.001	Bacteria	35.0 hours
0.0001	Clay particles	230 days
0.00001	Colloidal particles	65 years

Considering density, as the density of the fluid is constant, the only way to increase the density difference is by increasing the flocs density.

Ballasted sedimentation is a concept developed by Veolia under the name of Actiflo®. Ballasted flocculation pilot plants (Figure 6-3) are basically small full-scale systems without filters using sand to improve sedimentation. The microsand enhances the formation of robust flocs and acts as ballast, significantly increasing their settling velocity (Veolia, web page Actiflo®). As with the full-scale process, selection of the polymer and inorganic coagulant is the key to proper performance. Because the ballast, when attached to the floc, is principally responsible for sedimentation, the denser floc size is not as critical to performance as it is with other processes. However, smaller flocs work well with ballasted flocculation and therefore allow for smaller floc basins and lower chemical dosages than those required for sedimentation (AWWA, 2011). The removal is therefore more efficient.

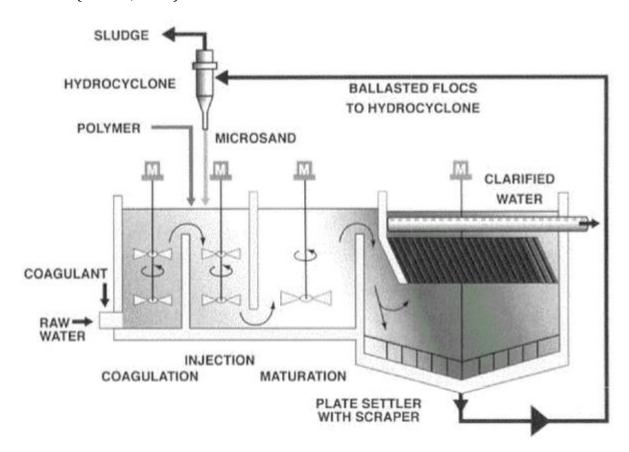


Figure 3.3-2: Schematic of the Actiflo ballasted flocculation clarification process, from I. Kruger Inc., A Veolia Water Solutions & Technologies Company

Actiflo® has been in use for municipal and industrial water and wastewater treatment for more than 25 years. The removal efficiencies are well-known for various water. The water properties found in Viikinmäki are in the range of Actiflo® possibilities as described in Table 3.3-2.

Table 3.3-2: Actiflo range of applicability, modified from Veolia webpage

	Unit	Raw water	Clarified water
Turbidity	NTU	0 - 2000	0.2 - 2.0
SS	mg/l	0 - 3000	0.5 - 5.0

With an average turbidity of 1020 NTU and 980 mg/L SS, this wastewater can clearly be processed with Actiflo®.

Actiflo® uses sand as ballast, controlling the particle distribution of this sand. Indeed, because it is recycled in a hydro cyclone, the minimum particles size is limited. The use of a finer micro sand is not

possible with a recycling process, even though, a lower size distribution would benefit the process. Indeed, it would increase the contact area and therefore, increase the efficiency of the "sand".

3.3.2 Dissolved Air Flotation (DAF)

Air flotation is one of the oldest methods for the removal of solids, oil & grease and fibrous materials from wastewater (Shan-pei et al., 2007)

Therefore, it is a well-known process in WWTP. The process consists of injecting bubbles to the water to bring the flocs to the surface for removal. Before the flotation takes place, the raw water goes to a coagulation and flocculation tank (see section 3.2). Then, the water enters the flotation tank. It is divided into two sections with different process functions (see Figure 3.3-3). First compartment, called contact zone, is the place where the water enters in contact with gas, usually air, bubbles. Collisions occur between the flocs produced previously and bubbles. Bubbles may attach to the flocs, what leads to aggregate bubble-floc that may rise to the surface in the second compartment. In this separation zone, aggregates and bubbles rise to the surface to form a float layer. This part is finally removed and water from the bottom goes to the next steps of the treatment. In the case of WWTP it usually goes to a filtration process.

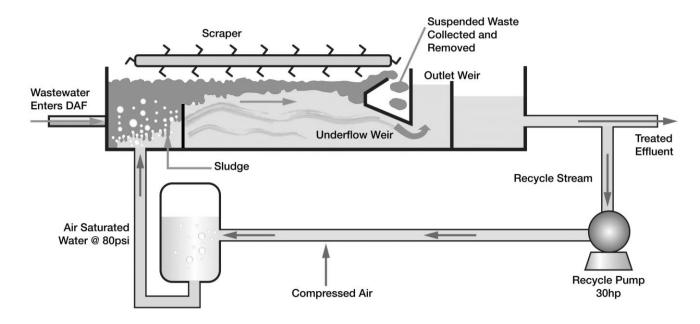


Figure 3.3-3: Conventional Dissolved Air Flotation System, from Molaer company

Attachment of the bubble with the flocs is a complex phenomenon, not detailed here but that can be developed by reading the book *Dissolved Air Flotation for water clarification* by Edzwald & Johannes. Bench-scale tests are usually realized in a DAF jar tester to assess the applicability of DAF. The main purpose of the pilot part is to change the recycle ratio and eventually the rapid mixing.

3.3.2.i Method to assess DAF applicability

DAF is not always applicable. Valade et al. (2009) suggested measuring two parameters to check the DAF applicability: Turbidity and Total Organic Carbon (TOC). Those results will be added to the Figure below and will determine if DAF is relevant.

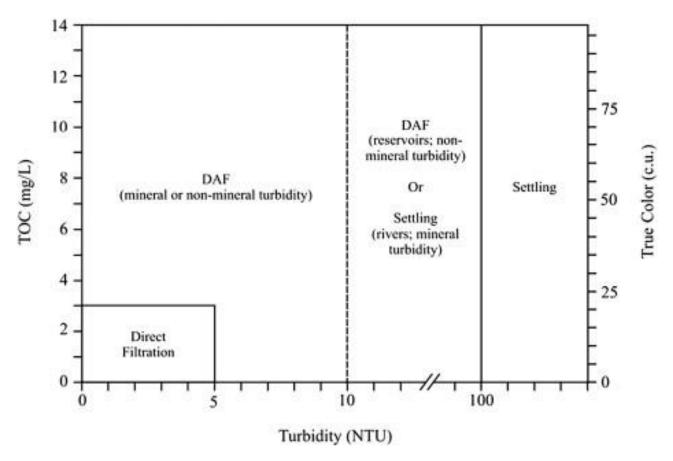


Figure 3.3-4: Process selection diagram based on average raw water quality conditions, reprinted from Valade et al. (2009).

Low TOC and low turbidity would lead to direct filtration. Low turbidity and TOC above 5 mg/L are good conditions for DAF. For turbidity higher than 5, DAF is applicable in any case below 10 NTU; only for non-mineral turbidity between 10 and 100 NTU; and not applicable above.

3.3.3 Disc Filtration

A little theory of filtration is required before explaining the disc filter. Filtration operates entirely on particle size (and, to some extent, shape), such that particles below a certain size will pass through the barrier, while larger particles are retained on or in the barrier for later removal. The separating size is a characteristic of the barrier, the filter medium. The operation of a filter usually needs a pressure differential across the filter medium, and this can be effected by means of fluid pressure upstream of the medium (pressure filters) or suction downstream (vacuum filters) (Sutherland, 2008).

The disc screen is a large frame carrying two circles of wire mesh, sealed together at their circumference, and mounted on a substantial hollow shaft (Sutherland, 2008). In a WWTP, several filter discs are mounted, parallel to one another, on a horizontal shaft. Usually less than half of the disc (typically 35-40%)(Sutherland, 2008) is immerged in the water to clean (contained in the trough). Water passes through the filter and escapes through the core while the cake is formed outside of the disc. On Figure 3.3-5, the disc is divided into different sectors (or cells). This principle is used in water and wastewater treatment but also pulp industry for example, where the disc rotates continuously, and cells are washed one by one. The particularity of the disc filter, that is a continuous process for water, is that the washing of the filter is usually a batch process made without stopping the filtration.

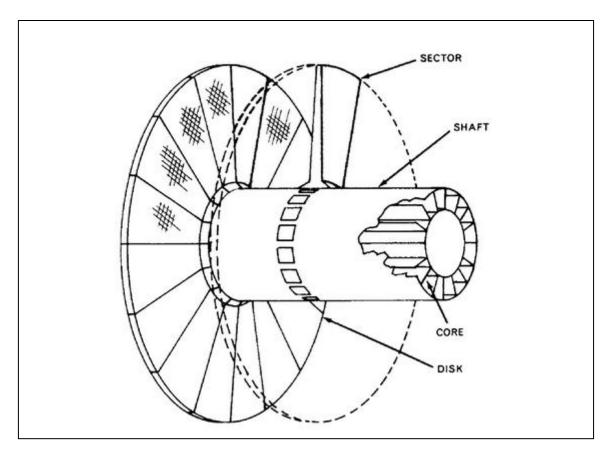


Figure 3.3-5: Schematic disc filter and its different sections, from Sutherland (2008)

A typical cycle is initiated by causing the discs to rotate through the trough of suspension where the internally applied vacuum induces cake formations on both sides of each disc. As the cakes move out of the trough, washing commences and proceeds until the discs rotate to reach the cake discharge point (Tarleton & Wakeman, 2007).

Performance is governed by the mesh elements or filter screen apertures, typical standard openings being from 250 to $25\mu m$. With this form of construction, however, performances materially improve as dirt collects on the screen surfaces, providing increasingly finer filtration. The design provides a large surface area in a compact volume, with a moderately low pressure drop (Parks & Chase, 2016).

3.4 Influence of process conditions on SS removal

Water properties during solid separation and nutrient recovery are of main importance for water treatment because they influence the efficiency of those processes. Most important process conditions are described below with an emphasis on their influence on SS removal.

1. nH

pH is probably the most important parameter of the overall process. It highly influences coagulation and flocculation, steps that affect later separation process. Variation of the pH will lead to variations in nutrient solubility. Consequently, it can change the recovery efficiency later in the reactor, improving or decreasing it.

A particular attention should be given to the tests made with aluminium or ferric coagulant. Experiments must be made in a range of pH where the remaining dissolved coagulant in the downstream effluent is as low as possible. Indeed, iron and aluminium salts have a varying solubility in water depending on the pH. The minimum solubility is around pH 7 so all tests with those metal coagulants must be made around this range of pH.

2. Coagulant type and dose

Three distinct types of coagulants are used nowadays: Aluminium hydroxides (PAXs), Ferric hydroxides (PIXs) and Calcium carbonates. Metal coagulants PIXs and PAXs are widely used whereas calcium carbonates is less and less used. They are described more into details in section 3.2.

Aluminium and ferric hydroxides are well known in coagulation processes to destabilize particles dissolved in water to enhance later flocculation. Jar-tests help choosing the proper coagulant for any stream and give an approximate dose of coagulant needed for a certain water. First calculations based on TOC measurement or KMnO4 –analysis for the organic matter is usually used to approximate the coagulant necessary for a certain stream.

Calcium hydroxide (also called hydrated lime) was used in the old days for water clarification. It presents some challenges but is also interesting in the case of this research.

3. Polymers type and dose

As described in section 4.4.2, they are plenty of different polymers available for water clarification with a wide range of properties. Kemira provides different polymers from the series "Superfloc®", suitable for various separation processes (filtration, flotation and sedimentation). Those "Superfloc®" flocculants are working in a wide range of pH (from Kemira technical data sheet). The best one is chosen by Jar-testing and then its dose is optimised.

4. Temperature

In any chemical process, temperature is very important for the kinetic of reaction. As depicted by Morris & Knocke (1984), effect of temperature on coagulation and flocculation is not a well-known topic. Commonly, increasing temperature increases the kinetic of the reaction but the effect on flocs varies. Fitzpatrick et al. (2004) found out that floc formation is slower at lower temperatures for all coagulants. In mesophilic digesters, temperature is 37 °C.

Those process conditions are identified as the most important ones in solid separation. They must be controlled or at least measured.

4 METHOD AND EXPERIMENTS

From the above review, experiments were conducted in the laboratory. The purpose of all those experiments and the measurements related to them is to find out which conditions are the best ones for solid separation and how to optimize them in batch process before experiments in continuous flow. The expected results and experiments are presented below.

4.1 Characterization of the reject water

Reject water used for the project comes from the dewatering of the digested sludge after a mesophilic digester in the WWTP of Viikinmäki. It is important to notice that the water used for the experiments in the lab is a little different than the water that will be used in the pilot phase. Indeed, the experiments used reject water directly from the centrifugation of the sludge, but, the pilot will be using water that goes through a settler. This settler has a two hours retention time and doesn't change much of the properties of this water. Properties after clarifier, in the case of Viikinmäki, are presented in Table 4.1-1, furnished by the wastewater treatment plant (WWTP). Those properties were tested for the "unclarified" reject water in the laboratory using standard procedures. Results are presented in the last column.

Those measurements don't include heavy metals and micro-pollutants, they will be studied in further details during the pilot phase of the project.

Table 4.1-1: Reject water properties after mesophilic digester and dewatering in Viikinmäki WWTP

		Clarified wate	r	Unclarified water
	Average	Minimum	Maximum	Measurement
SS (mg/l)	980	560	4200	1350
Total-P (mg/l)	13	10	47	19.2
PO ₄ -P (mg/l)	1.4	0.5	2.7	1.2
Total-N (mg/l)	980	820	1250	1026
NH4-N (mg/l)	790	680	900	904
рН	8	7.5	8.1	7.9
Alkalinity (mmol/l)	67	57	77	Not measured
CODCr sol (mg/l)	1380	860	2100	Not measured

Table above shows the wide range of water properties that can be found, even after clarification. Most problematic change is the SS concentration. The average is around a thousand milligrams per litre but the maximum that can be found is four times more. In this case, the pre-treatment cannot handle this water and the reactor could not be running, SS concentration would remain too high for the membrane.

Besides, water properties don't change much before and after clarifier so that, it was concluded that results could be applied directly to the "clarified" water.

Turbidity and TOC measurement were made to verify DAF applicability. With a turbidity of 1020 NTU and TOC concentration of 664 mg/L, this water is completely out of the recommended range. Advices were considering turbidity below 100 NTU and TOC below 14 mg/L. The water is not included in this range. As no study assessed the DAF possibilities on this particular stream, it will be tested. Indeed, in this range of SS, only a few studies in pulp and paper industry or in brewery waste water are known.

4.2 Presentations of experiments

Experiments were performed in batch process. However, Figure 4.2-1 shows the entire process (pre-treatment and reactor in the case of ballasted sedimentation). It's important to notice that any change in water quality during pre-treatment will have an impact on downstream reactor and, therefore, on nutrient recovery.

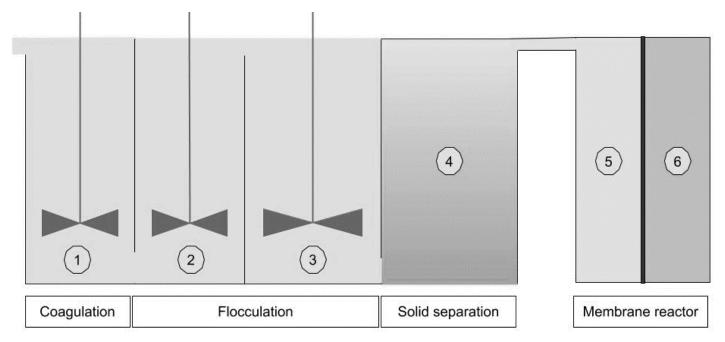


Figure 4.2-1: Scheme of the entire pre-treatment process and membrane reactor

In pilot scale, presented in Figure above, water will be coagulated with rapid mixing (1), then flocculated first with rapid mixing (2) and then slow mixing (3). Then the water enters a solid separation process (DAF, filtration or sedimentation) (4). The "pre-treated water" (after solid separation) enters the left part of the membrane reactor (5) where nutrient passing through the ammonia selective membrane is recovered in the acid (6),

All tests are made in a bench scale batch process, that is to say in Jar-tests. It is necessary to make those tests with a batch process because it would cost a lot more in continuous flow. Purposes are various:

- Find out which polymers are working as different ones are available;
- Which coagulant to use;
- Optimise chemical dosages;
- Find out if the treatment can reach the expected concentration of suspended solids.

A detailed description of the bench and the experiments is presented in Section 4.2.

When it comes to design, Howe et al. (2012) identify four process issues: (1) the type and concentration of coagulants, (2) the mixing intensity and the method used to disperse chemicals into the water for destabilization [coagulation], (3) the mixing intensity and time for flocculation, and (4) the selection of the liquid–solid separation process (e.g., sedimentation or DAF). Those parameters are to be tested in the bench scale testing, described above. One more issue for every solid separation process is to find the right polymer to enhance the flocculation. Then, every case has its own issues to solve: filter size for filtration, type of sand for sedimentation, bubble size for flotation.

The bench for the experiments is the same for the coagulation and flocculation part. It is composed of a graduated plastic tube, opened on top and with two controlled openings near the bottom (Figure 4.2-2). A stirrer with a range from 45 to 1500 rpm mixes the water inside. It is positioned at the bottom so that the mixing is made everywhere.

The pH of the raw water is around 8 (see Table 4.4-1). Consequently, experiments will be handled for pH 8 to start. As seen in section 3.4, it is close enough to pH 7 to have low coagulant residuals in the effluent.

4.2.1 Coagulation-Flocculation

The coagulation was done as follow, once the tube filled with water:

- 1. Addition of coagulant while rapid mixing (t_0 =0 second)
- 2. Rapid mixing (300 rpm) for 15 seconds (t₁)
- 3. Slow mixing (45 rpm) for 45 seconds (t₂)
- 4. Change to rapid mixing and addition of flocculant at t₂.

Then, every experiment has its own separation process and distinct steps depicted in the three sections below.

4.2.2 Ballasted sedimentation

Sedimentation is done directly inside the plastic tube. After step 4, sedimentation is done as follow:

- 5. Addition of microsand or LKD by spreading it on the surface while rapid mixing for 15 seconds (t₃)
- 6. Slow mixing for 1 minute 45 seconds (t₄)
- 7. Stop mixing and sedimentation for 1 minute (t₅)
- 8. Sampling the surface

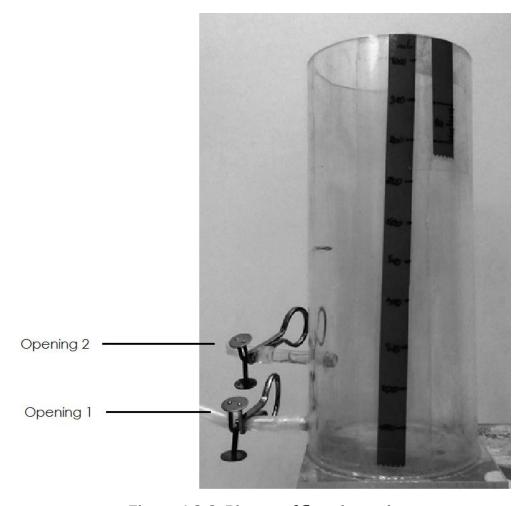


Figure 4.2-2: Picture of flotation unit

4.2.3 DAF

Flotation is also made in the plastic tube, by injecting air at the bottom of the tube (opening 1). Unlike sand, air has to be injected after the injection of flocculant and a certain flocculation time (15).

seconds rapid mixing). (as advised in #REF DAF book). So, it was realised as follow, after flocculant addition:

- 5. Rapid mixing for 15 seconds (t₃)
- 6. Change to slow mixing and air injection at the bottom by opening 1
- 7. Slow mixing for 15 seconds (t₄)
- 8. Stop mixing and flotation for 5 minute (t₅)
- 9. Sampling the bottom with opening 2.

4.2.4 Disc filtration

Unlike the two first pre-treatments, disc filtration is carried out in a PVC pipe, presented Figure 4.2-3. After coagulation and flocculation in a plastic Becher, water is poured at the top of the black pipe and a filter placed in the pipe retains the flocs. Some water goes through and arrives in the second Becher. The remaining water stays inside the pipe for 30 second and is removed afterwards. The sample is the water in Becher 2. Steps after flocculant addition are the following:

- 5. Rapid mixing for 15 seconds (t₃)
- 6. Slow mixing for 1 minute 45 seconds (t₄)
- 7. Stop mixing and pouring of water in the pipe
- 8. Wait for 30 seconds (t₅)
- 9. Removal of the pipe on top of Becher 2 and sampling of water inside this latter.



Figure 4.2-3: Picture of disc filtration unit

All those tests were performed during a period of three months. Table below presents an overview of all the experiments made during those months, in the right order.

Table 4.2-1: Experiment time and order

Experiment description	Time necessary
Water properties measurements	One week
Disc filtration	One month
Ballasted sedimentation	Two weeks
DAF	Two weeks
Optimisation of best results in DAF and ballasted sedimentation	One month

4.3 Lab measurements

A certain number of measurements is necessary to follow and understand reject water behaviour during experiments. Therefore, for every sample, measurements of pH, temperature, and SS are done. For the best results that can potentially be used in the full-scale process, complementary analysis is carried out including total phosphorus, phosphates, total nitrogen, ammonia, organic content of SS, dry solid content of the sludge and organic content of the sludge. These complementary analyses will help to choose the optimal parameters for the pilot scale study.

Nutrient measurements are important for the overall process. Indeed, in DAF for example, the process is like a stripping process. It's important to make sure that nitrogen stays in the water to be retrieved in the membrane reactor.

pH, as discussed in section 3.4, is an important parameter. It has to be around 7 for a proper use of metal coagulant. Moreover, if pH stays below 8 there's no risk of stripping ammonia because it will be NH4+ form as a liquid. Acidity of the coagulant will be enough to be in the proper range of pH to have low metal residuals and no stripping. Besides, it will be increased between the pre-treatment and the nutrient recovery to reach pH 11-12. Consequently, pH during pre-treatment will not be decreased by any chemical addition, except coagulant addition.

Lab measurements such as SS, total phosphorus, phosphate, total nitrogen, ammonia and dry solid content were executed following the standard procedure. For a deeper look, please consult Table 4.3-1, referencing standard procedures.

Table 4.3-1: Standard measurement procedures

Properties measured	Standard procedure		
Total Nitrogen	SFS-EN ISO 11905-1, dated 1998 + Standard Methods (dated 2005)		
Total Nitrogen	4500 B. Ultraviolet Screening Method + Ganimede N device instructions		
Total Phosphorus	Oxidation: SFS-EN ISO 6878, dated 2004; Measuring: SFS-EN ISO 15681-		
Total i Hospiloras	1 (flow injection method), dated 2005		
Phosphate (PO ₄)	Measuring: SFS-EN ISO 15681-1 (flow injection method), dated 2005		
Ammonia (NH ₄)	ISO 11732 (flow injection method), dated 2005		
Suspended Solids (SS)	SFS-EN 872, dated 2005; Whatman GF/A – glass fiber filter		
Total residue and total fixed residue	SFS 3008, dated 1990 (only in Finnish)		
(dry matter + organic matter)			
TOC	SFS-EN 1484, dated 1997; Shimadzu TOC-5000A		
Turbidity	SFS-EN ISO 7027, dated 2000		
COD	SFS 5504, dated 1988 (only in Finnish)		
BOD	SFS-EN 1899-1, dated 1998 + Oxitop-manual		
рН	SFS-EN ISO 10523, dated 2012		

4.4 Chemical selection and dosage

4.4.1 Coagulant selection and dosage

Three categories of coagulant were tested during the experiments: Hydrated lime Ca(OH)₂, iron-based salt (PIX) and aluminium based salts (PAX). PAX includes a wide range of different aluminium-based salts. Relative basicity ranges from 40 to 85% and aluminium contents range from 5 to 12% as Al in the liquid products. The most effective one was found to be PAX XL 100. Other tested PAX are XL 19 and XL 63, but they didn't give as good results as XL 100 (see Figure 4.4-1).

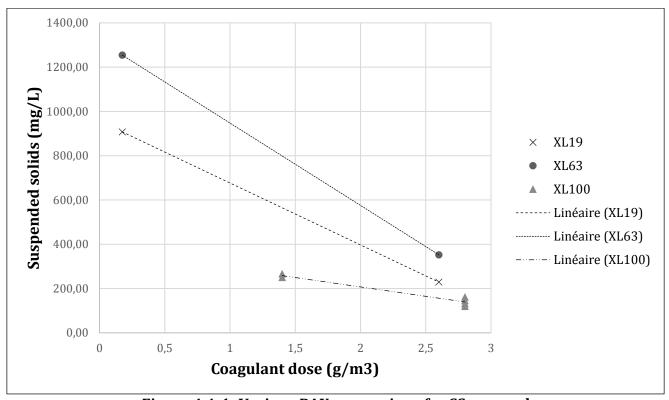


Figure 4.4-1: Various PAX comparison for SS removal

From Figure 4.4-1: Various PAX comparison for SS removal Figure 4.4-1, it is concluded that PAX XL 100 is more efficient than other for SS removal.

	PAX XL 19	PAX XL 63	PAX XL 100
Basicity	85 ± 5 %	65 ± 5 %	43 ± 2 %
Al ₂ O ₃	23.6 % ± 0.6	9.6 ± 0.4 %	17.6 ± 0.6 %
Al ³⁺	12.5 % ± 0.3	5.1 ± 0.2 %	9.3 ± 0.3 %

Table 4.4-1: PAX properties

In the same combination with polymers and microsand, coagulant XL 100 shows better results (Figure 4.4-1). The chemical consumption for the same SS removal efficiency is lower. Its basicity is 43 \pm 2 % and the Aluminium content in ion form is 9.3 \pm 0.3 %.

Only one type of PIX was tested (PIX 105). The properties of this coagulant are presented in the table below.

Table 4.4-2: PIX 105 properties

Chemical	Name	Concentration	Density (kg/L)	рН
Ferric sulphate	PIX 105	11.5 %	1.5	<1

A comparison with PIX is made to select the final coagulant. It is presented in section 5.2. Hydrated lime had an influence on pH mainly, discussed in section 5.1.1.

4.4.2 Polymer selection and dosage

Two sub-categories of polymers from the category Polyacrylamides (PAM) provided and recommended by Kemira were used: cationic (C) and anionic (A) polymers. The properties of such chemicals are complicated, and their formula is commercial secret. Therefore, all of them must be tested with this particular reject water, after a first screen made by Kemira experts. It leads to the following selection: C492, C496, C494 High Molecular Weight (HMW), C496 HMW, C498 HMW, A100 and A120. Jar-tests were realised with those polymers in order to select them. Results were different also depending on the separation process used.

Polymer is, like coagulant, a crucial chemical to choose and dose. Cationic ones were used in a previous study in the lab. They first showed satisfactory results, but dosages were too high and weren't realistic in terms of costs. For this type of water, anionic polymers showed as satisfactory results as cationic for high dosage (25-50 mg/L) but superior results at lower dosages (2 to 5 mg/L), see Figure 4.4-2. To ensure the SS limit of 200 mg/L, low polymer dose is enough, using anionic polymers. Two different anionic were tested of which only one gave interesting results: A120.

Finally, the combination of right coagulant and flocculant leads to an efficient removal. The dose must be optimised too. End results with right polymer and coagulant are presented in the next section.

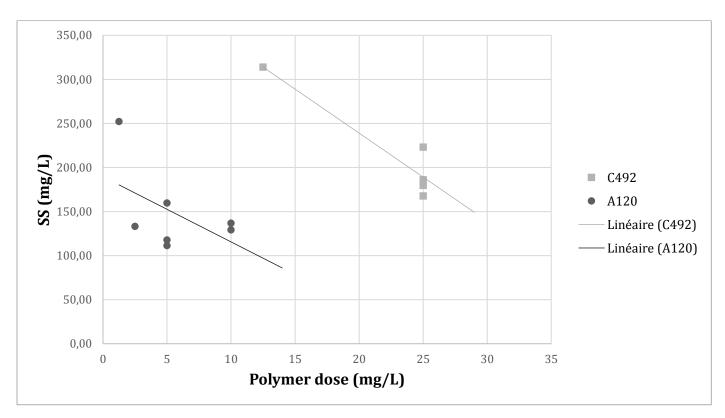


Figure 4.4-2: Polymer comparison for SS removal

Polymer A 120 is more efficient than polymer C492 for SS removal. A lower dose is necessary to achieve high SS removal.

5 RESULTS

Here are presented some of the results obtained in the bench scale tests for different solid separation processes. It is important to notice that the composition of the reject water, the entering effluent, varies depending on the sample because of variations in the WWTP. However, the variations in SS were not considered and the comparison is made between the final SS concentrations without any correcting factor. Moreover, this water was stored in cool place (4 °C) for a maximum time of ten days. But, after some experiments, it was obvious that the water properties still changed in this environment (release of gas during coagulation for example) even after a few days. This is the reason why some experiments had to be done a second time, with fresher water and only those results are presented.

5.1 Pre-treatments results

5.1.1 Disc filtration

This pre-treatment was difficult to handle due to numerous parameters that depend on each other. For example, polymer type changed floc size but also changed floc resistance. In this case, it was difficult to know if the process was not working because flocs were too small or too weak. In general, it was difficult to conclude on the effect of one of the chemical process conditions. Moreover, the filter size is very important in this separation process. However, no correlation was found between the filter size and the SS removal.

In the end, no combination of coagulant, polymer and filter studied reached the wanted removal efficiency, see Figure 5.1-1. The lowest SS concentration after disc filtration were find around 500 mg/L, that is to say between 60 and 70 % removal where the goal is close to 90% (200 mg/L maximum). It was achieved with PIX and polymer C496. Best results are presented below. Disc filtration was abandoned for the pre-treatment possibilities.

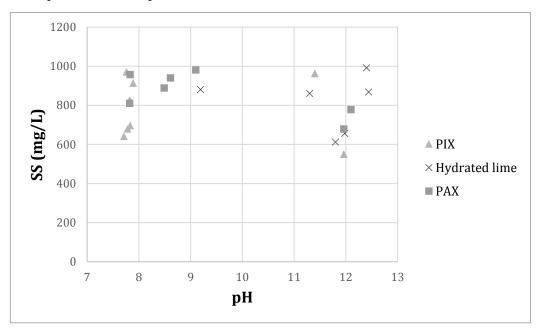


Figure 5.1-1: Disc filtration results regarding pH for different coagulants

Despite the poor results concerning disc filtration, analysis of the SS concentration showed that the disc filtration is working better in two pH zones (see Figure above): Neutral zone (around 7) and basic zone (around 12). Removal at high pH is obviously linked to the hydrated lime action as a coagulant, but not any simple correlation was found. Low pH is found with metal coagulant only, but their efficiencies were low. Therefore, the coagulant doses were increased. But it led to a problem. Indeed, it is impossible to increase polymer or coagulant dose because the filter was clogged too quickly and almost nothing passed through the filter in this case (whatever the filter size from 20 to $100 \mu m$).

Some tests were performed with metal coagulant and hydrated lime (PIX and PAX with pH around 12 on Figure 5.1-1). It worked well but high pH is a condition to avoid with metal coagulant because, as seen previously, it leads to high metal residuals in the effluent.

5.1.2 DAF

Turbidity and TOC tests were performed before handling the experiments, as recommended by "Dissolved Air flotation for water clarification" (Edzwald & Johannes, 2012). Results, as seen in water properties, were out of the range presented in Figure 3.3-4, with a turbidity above 1000 NTU and 664 mg TOC/L. The graph is not applicable. Since there were nevertheless some positive experiences with DAF in high TOC industrial wastewater it was decided to try DAF with this stream because no reference described the applicability of DAF for this type of reject water.

This second separation process showed interesting results for SS removal. The goal of 200 mg/L was reached, and interesting results were observed, presented in the next paragraph.

First, best results were achieved with "big" flocs". Flocs were obviously bigger than $10~\mu m$, which was supposed to be the perfect size for DAF. Some flocs were more than one millimetre long and sometimes formed bigger heap. Those big heaps were very stable, so the separation was clear and easy. It is important to notice that C496 was performing well for disc filtration but not for flotation. C492 was first used but then it was discovered that Anionic polymers were also working and A120 was better for low doses. It is presented Figure 5.1-2.

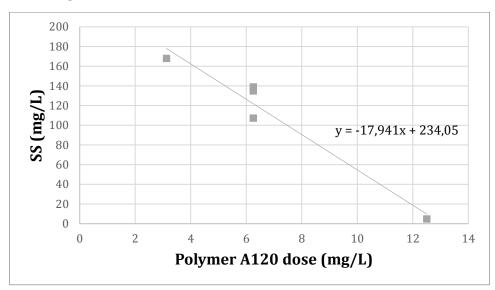


Figure 5.1-2: SS removal regarding polymer dose for DAF

Second, flocs floated easily using PIX, compared to the use of PAX. The required amount of bubbles was lower with PIX. In the experiments using PAX, flocs tend to sink, no matter the polymer, coagulant or dispersed water dose.

Third, any limit can be reached using DAF. Indeed, the limit of SS removal is mainly fixed by the coagulant dose. Yet, the limit of coagulant dose in sedimentation is fixed by the effect of salting-out (discussed in section 3.2). For too high coagulant doses, N_2O and other dissolved gases react with the iron coagulants and creates bubbles that disturb and prevent the flocs from settling. In DAF, this salting out effect is a benefit because it increases the flotation of those flocs. However, it is not recommended to overdose the coagulant because of the costs it generates and the risk of removing nitrogen before the reactor.

5.1.3 Ballasted sedimentation

As expected, ballasted sedimentation with microsand was very efficient. Settling times are very short, ranging from one to five minutes. It quickly appeared to be the best solid separation method, so enough tests were made to optimise coagulant and polymer dose to be able to pilot this pre-treatment.

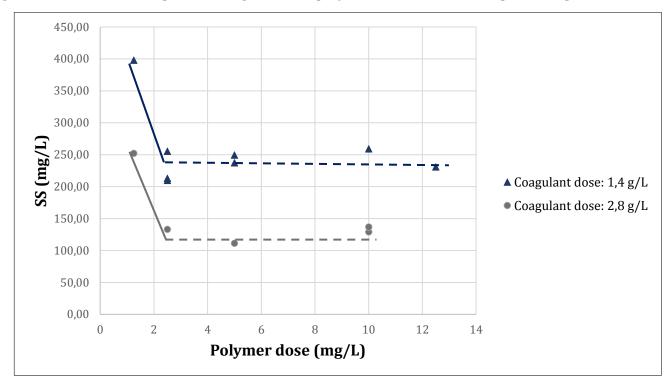


Figure 5.1-3: Polymer dose optimisation

Figure 5.1-3 shows the optimisation of polymer dose depending on coagulant dose. Goal is to minimize polymer dose but to have enough flocculant to remove flocs efficiently. Left part of both curves (continuous) present too low dosages and right parts are saturated in polymer. Optimised doses are located at the intersection of both parts for the two different curves.

Some problems appeared with PIX. It created bubbles when high-dosed. Those bubbles prevented the flocs from settling. This effect, after investigation, is called salting out and is explained in section 3.2.

Interesting finding concerned the use of LKD. Indeed, no studies have been made before with this type of "sand" or powder, but results were very promising. Findings are developed in section 6.2.

5.2 DAF and sedimentation comparison

In light of the previous results, a comparison between Dissolved Air Flotation and Ballasted Sedimentation is made, excluding Disc Filtration from the possibilities for the project. It compares the chemical dosing and removal efficiency in both pre-treatments and finally compares the running costs of those processes.

The first comparison to be made is about the polymer dose. Polymer dose is crucial in term of costs in this process (see section 6.4). With a price up to 2500 €/tn, the dosage must be optimised. Polymer A120 was selected as the best one because low doses could be used compared to any other polymers tested (Super flocculants series C and A100). Then, DAF and sedimentation gave different results on the optimal dose of polymer to use. A comparison is presented Figure 5.2-1. Slightly overdosed coagulant is used for those results to ensure that coagulant is not limiting the reaction.

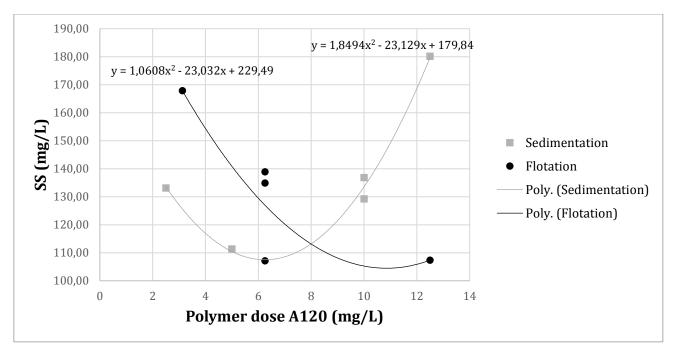


Figure 5.2-1: Flotation and sedimentation polymer comparison

The figure shows that, no matter the pre-treatment, with "low" doses of polymer (3 mg/L), it is possible to achieve a sufficient SS removal (below 200 mg/L). Then, when it comes to details, sedimentation shows better results in low polymer doses but the performance decreases when this dose is increased. It is the exact opposite for flotation where the more polymer is added, the better is the SS removal. In order to reduce costs and use as low polymer as possible (because it can be harmful for the environment), sedimentation gives the best opportunities.

Then the coagulant dose is more difficult to compare. Indeed, it's not only a difference of coagulant used but also different processes (PIX for flotation and PAX for sedimentation). A first comparison is given Figure 5.2-2. Both coagulant doses are compared without any correction. Amounts of PAX varied from 1.2 to 2.8 g/L where PIX was between 4 to 15 g/L. It shows that the process requires less PAX (XL100) than PIX to work at the same removal efficiency (100-150 mg/L SS).

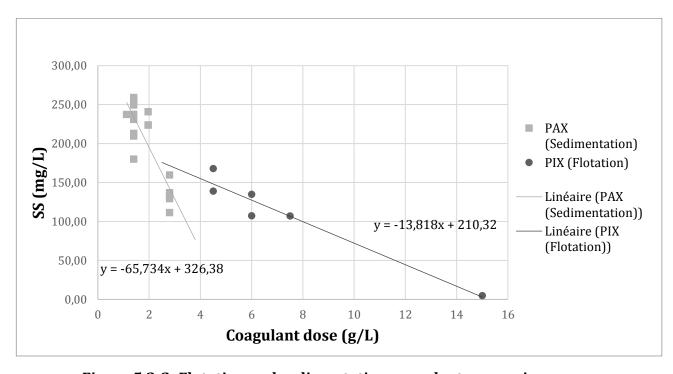


Figure 5.2-2: Flotation and sedimentation coagulant comparison

But those results do not include the difference in concentration of active substances in the coagulants. So, other comparisons are made. Two other comparisons are suggested: Coagulant dose corrected by the concentration and coagulant price.

The second comparison is made with taking into account the concentration of the product. Indeed, concentration of PAX XL 100 is 17.6 % and PIX 105 concentration in active substance is 11.5 %. The new coagulant dose, in term of active substance (subscript "a.s.") is calculated as:

$$m_{PAX_{a.s.}} = m_{PAX} \times C_{PAX}$$
 and $m_{PIX_{a.s.}} = m_{PIX} \times C_{PIX}$

With CPAX and CPIX the active substance concentration in PAX and PIX respectively. A new comparison is presented below:

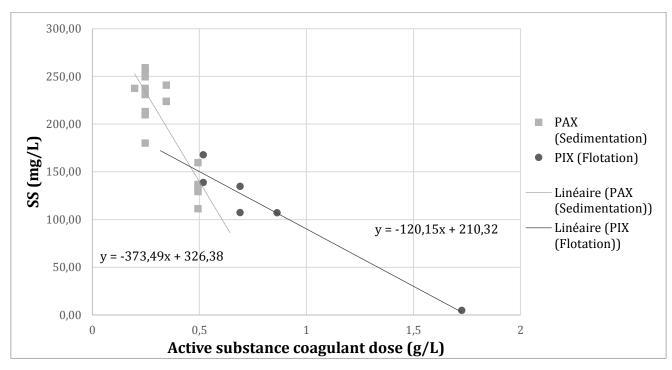


Figure 5.2-3: Flotation and sedimentation comparison: SS remaining regarding active substance in coagulant

With this second comparison, PAX XL 100 stays a better chemical for SS removal but PIX is not far in terms of doses.

A third comparison, with a price correction, was suggested. Prices for PIX 105 and PAX XL 100 are presented Table 5.2-1.

Table 5.2-1: Coagulant prices

Substance	Price per ton
PIX 105	155 €
PAX XL 100	250 €

Difference is big enough to take it into account for comparison. It gives the Figure below.

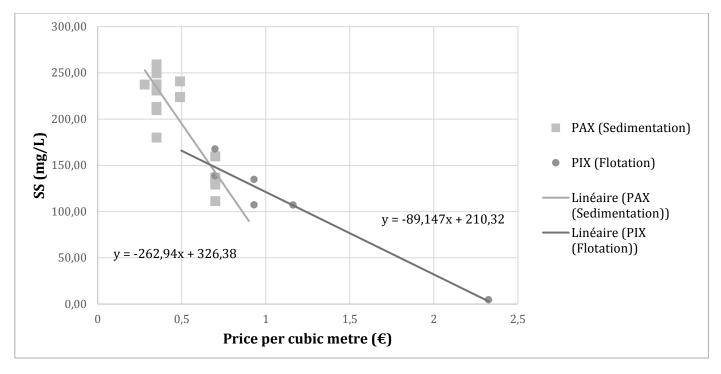


Figure 5.2-4: Flotation and sedimentation comparison: SS remaining regarding coagulant price

Both PAX XL 100 and PIX 105 can be used in the range of SS 100 to 150 mg/L.

In light of the previous conclusions, PAX XL 100 with A120 for ballasted sedimentation was selected as the best process conditions for SS removal.

5.3 Turbidity and SS

Suspended solids is a laborious measurement to make in large number. During the pilot phase, measurement will be needed very often. This is the reason why a correlation had to be found with another parameter, easier to measure, such as turbidity. Turbidity is a simple and quick measurement compared to SS concentration.

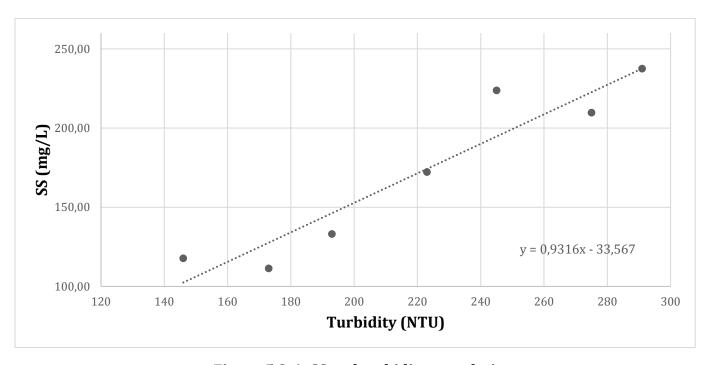


Figure 5.3-1: SS and turbidity correlation

The above curve shows a clear correlation between SS concentration and turbidity. This correlation is necessary to run the pilot in continuous flow.

The correlation is given as:

$$x_{SS} = 0.93 \times T - 33.57 \tag{6}$$

With x_{SS} the correlated SS concentration (mg/L) and T the measured turbidity (NTU).

6 DISCUSSION

6.1 Water properties after pre-treatment

Q1: Which pre-treatment can be used for this type of reject water?

After pre-treatment, water enters the membrane reactor. Its properties are of main importance. Unknown remained on the ammonia removal. Measurement were then made to check the applicability of those separation processes. Average results for a 90% SS removal are presented below.

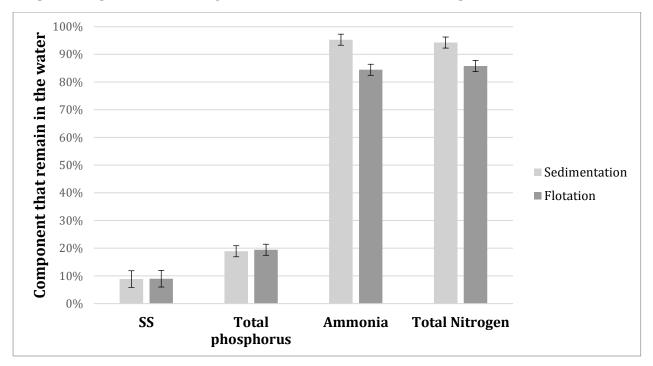


Figure 6.1-1: Water properties after pre-treatment

As expected, the flotation pre-treatment removes more Ammonia and Total Nitrogen than the ballasted sedimentation. This is due to the stripping similarities of the flotation. For the same SS removal efficiency, 10% more nitrogen is removed with DAF. This has to be avoided to have a maximum nitrogen recovery in the reactor. Phosphorus is 80% removed and the value is similar for both separation processes. Note that phosphate concentration is not presented because measurements weren't usable, due to a malfunction during measures.

The removal of more nitrogen in DAF than in sedimentation adds one more advantage to the ballasted sedimentation.

6.2 LKD innovation

Q2: What are the possibilities for the use of Lime Kiln Dust (LKD) instead of microsand in ballasted sedimentation?

The research on LKD dosage led to interesting results. It worked well, and 90% SS removal was achieved for different combinations of chemical with the use of LKD. Experiments showed a possibility on using LKD in low dosage. Indeed, first experiments were conducted with doses from 1 to 15 g/L (5-15 g/L is the recommended dose from Veolia for their sand in Actiflo process). Results are presented below.

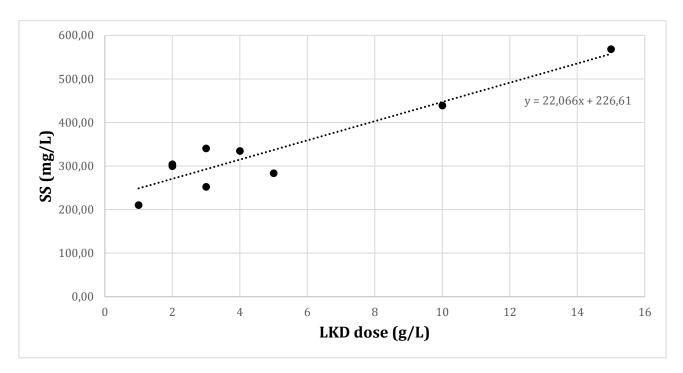


Figure 6.2-1: Influence of LKD dose on SS removal

From this Figure, it is clear that LKD doesn't work as microsand. Indeed, lower concentrations lead to better results. From a visual control first and measurements, at higher doses, LKD stays in suspension and leads to a high SS concentration in the effluent (mineral instead of organic but still problematic for the membrane downstream). Considering those results, a more precise study in the range from 1 to 5 mg/L was made. Figure 6.2-2 presents the results.

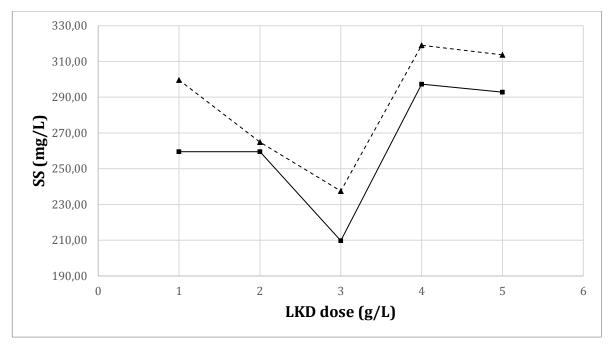


Figure 6.2-2: A closer look on how LKD dose influences SS removal

What seems to be an anomaly was noticed while running those experiments. The SS concentration after ballasted sedimentation drops for an LKD dose of 3 g/L. Performed with other coagulant concentrations, results are similar. This concentration seems optimal for the LKD dosage. The hypothesis is that below this dose, there is not enough LKD to attach to all the flocs, so the settling is not efficient; and above, there is too much LKD and some remains in suspension. This was confirmed

by organic and inorganic measurements in the SS showed in Figure 5.3-1. There is a clear correlation between LKD dose and inorganic content in remaining SS (polymer A120 dose: 2.5 mg/L and coagulant PAX XL 100 dose: 1.4 mg/L).

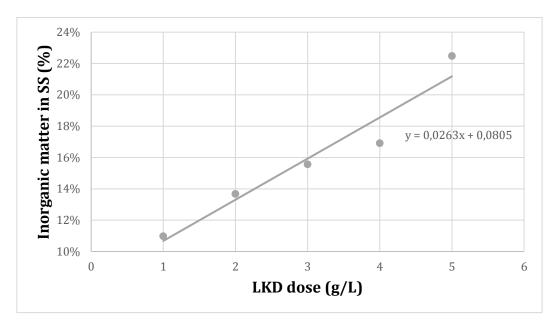


Figure 6.2-3: Evolution of inorganic content in SS remaining in suspension regarding LKD dose

LKD to replace micro sand accumulates benefits:

- Uses very low doses;
- Makes use of a side-product, so it helps recycling it;
- Removes the costly hydro-cyclone used for sand recycling.

It was concluded that LKD can be used to replace microsand in ballasted sedimentation. Eventually, it will be used in the pilot process to test its applicability in continuous flow.

6.3 Verification of the results with other streams

Q3: Is it possible to apply the same treatment to similar streams in different WWTP?

All tests were performed using Viikinmäki reject water because the pilot will run in this WWTP. To ensure that the findings can work in different WWTP, some more experiments were done with water from Suomenoja WWTP.

Water properties are slightly different with lower TOC but higher SS concentration. This lower TOC concentration leads to lower coagulant and polymer doses.

	Unclarified water from Viikinmäki	Reject water from Suomenoja
SS (mg/l)	1350	2850
TOC (mg/l)	664	499
Total-P (mg/l)	19.2	33.9
PO ₄ -P (mg/l)	1.2	No data
Total-N (mg/l)	1026	887
NH4-N (mg/l)	904	760
рН	7.9	8.1

Table 6.3-1: Reject water properties after sludge centrifugation in different WWTP

Nitrogen comparison and SS is depicted in Figure 6.3-1. Despite a higher SS concentration, Suomenoja water has lower Total Nitrogen and Ammonia (NH₄) concentration. This difference is low (around 10%) so that the nitrogen concentration available for recovery is still high enough to process.

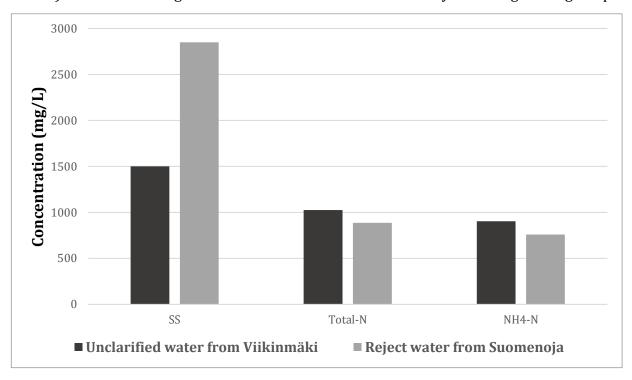


Figure 6.3-1: Comparison of water properties after pre-treatment for different WWTP

Experiments showed similar reactions (visual control) and results (measurements presented Figure 6.3-2). SS results after ballasted sedimentation are presented below.

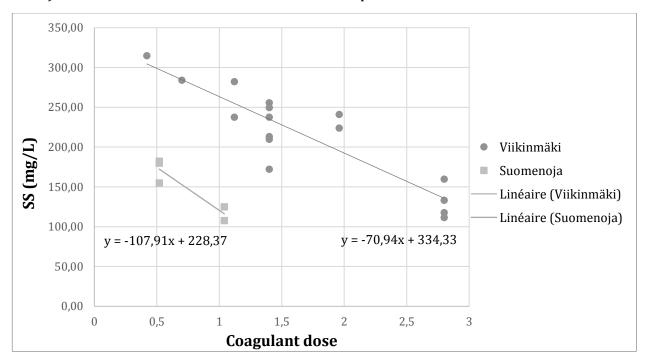


Figure 6.3-2: Coagulant dose comparison for different streams regarding SS removal

Suomenoja reject water is easier to process. Indeed, it starts with a higher SS concentration than Viikinmäki but has better removal efficiencies. The only short coming for using this water is that the nitrogen concentration is slightly lower than in Viikinmäki water, but results are similar and confirm the previous results on Viikinmäki water.

6.4 Economical possibilities

Q4: What are the costs involved in the pre-treatment?

Given that the SS concentration in this particular stream is high, the pre-treatment might have an important cost. It is anyway compulsory to have this step before the reactor. Running costs are presented below with some price and flows estimations. Investment costs are not presented but would need to be considered separately.

Some hypothesis is made to calculate the approximate demand in chemicals:

- (1) The pilot will be running for three weeks;
- (2) The wastewater flows through the pre-treatment at a rate of 100 L/h;
- (3) Doses are constant to reach 150-200 mg/L SS (maximum doses observed to reach this limit).

The required chemicals amounts are calculated in table below:

Table 6.4-1: Chemical doses and need for piloting the pre-treatment

	Flow	Need
Coagulant dose	2.5 g/L	42 kg
Polymer dose	2 mg/L	34 g
LKD dose	3 g/L	50 kg

Based on the demand, a first offer was given by Kemira, suggesting the prices presented in Table 6.6-2. A first running cost is presented per cubic metre.

Table 6.4-2: Cost estimation for pre-treatment selecting ballasted sedimentation

Product	Dose min g/m3	Dose max g/m3	Unit cost (€/tn)	Cost min (€/m3)	Cost max (€/m3)
PAX XL 100	1400	2500	250.00	0.35	0.63
A 120	2	5	2500.00	0.005	0.013
LKD	2000	3000	30.00	0.06	0.09
			Total:	0.415	0.728

The running costs are low for a pre-treatment as the minimum for treating a cubic metre is 0.42€. Moreover, this can be partly compensated by giving value to the sludge produced during the pre-treatment process. Indeed, it contains almost all the phosphorus originally in the wastewater and a high calcium content, contained in LKD. Therefore, it could have a value for agriculture. Some measurements will be done to assess the hygienic quality of the sludge and its composition.

7 CONCLUSIONS

In a conventional WWTP, nutrient recovery by membrane process is still an uncommon process. Membrane processes offer an energy efficient solution for nutrient recovery, the solid separation processes prior to membrane reactors must be efficient. Therefore, specific solid separation methods for this purpose needs to be developed. This research had for main objectives to find the best solid separation method for this particular stream regarding SS removal rate, price and nitrogen stability in water. Disc filtration, DAF and ballasted sedimentation were tested in batch process at a lab scale. Those experiments demonstrated that solid separation by gravity (ballasted sedimentation and DAF) work better than filtration for a high SS concentration stream. Removal rates were above 90% in the best cases, what is very good to be able to process the water in the downstream reactor (SS lower than 150 mg/L). Moreover, nitrogen is not removed in those solid separation methods what allows to use them before a nutrient recovery process.

Another objective was to check the applicability of LKD to replace microsand in ballasted sedimentation. A surprisingly good finding was that using LKD to replace microsand works well. It allows to use less sand and to remove the recycling part of standard ballasted sedimentation clarifiers. This makes easier the process and makes it more flexible. It also contributes to recycle LKD, side product of lime production. Therefore, it is economically feasible to use LKD in a ballasted sedimentation process. It is very interesting because chemicals are not particularly expensive, LKD is a side product so its price is low, and the cyclone used for recycling sand in standard clarifiers can be removed.

The method was tested using Viikinmäki WWTP reject water and the results were confirmed using reject water from another WWTP, with slightly different reject water properties.

8 REFERENCES

- Ashley, K., Cordell, D., & Mavinic, D. (2011). A brief history of phosphorus: From the philosopher's stone to nutrient recovery and reuse. *Chemosphere*, 84(6), 737–746.
- AWWA, A. W. W. A. (2011). Operational Control of Coagulation and Filtration Processes Manual of Water Supply Practices (3rd ed., pp. 137–140).
- Bratby, J. (2006). *Coagulation and Flocculation in Water and Wastewater Treatment*. (I. Publishing., Ed.) (2nd Editio).
- Brostow, W., Hagg Lobland, H. E., Pal, S., & Singh, R. P. (2009). Polymeric Flocculants for Wastewater and Industrial Effluent Treatment. *Journal of Materials Education*, *31*, 157–169. Retrieved from http://www.unt.edu/LAPOM/;
- Carlsson, B. (1998). An introduction to sedimentation theory in wastewater treatment, 1–7.
- Cheremisinoff, N. P. (2002). *Handbook of Water and Wastewater Treatment Technologies A Closer Look at the Mechanical Clarification Process and the Chemistry of Clarification.* (Elsevier, Ed.).
- Edzwald, J. K., & Johannes, H. (2012). Dissolved air flotation. (2011 McGraw Hill Professional, Ed.).
- Fitzpatrick, C., Fradin, E., & Gregory, J. (2004). Temperature effects on flocculation, using different coagulants. *Water Science Technology*, (50(12):171-5.). Retrieved from https://www.ncbi.nlm.nih.gov/pubmed/15686018
- Grant, S. B., Saphores, J.-D., Feldman, D. L., Hamilton, A. J., Fletcher, T. D., Cook, P. L. M., ... Marusic, I. (2012). Taking the "Waste" Out of "Wastewater" for Human Water Security and Ecosystem Sustainability. *Science*, *337*(6095), 681 LP-686. Retrieved from http://science.sciencemag.org/content/337/6095/681.abstract
- Guest, J. S., Skerlos, S. J., Barnard, J. L., Beck, M. B., Daigger, G. T., Hilger, H., ... Love, N. G. (2009). A New Planning and Design Paradigm to Achieve Sustainable Resource Recovery from Wastewater. *Environmental Science & Technology*, 43(16), 6126–6130. https://doi.org/10.1021/es9010515
- Howe, K. J., Hand, D. W., Crittenden, J. C., Trussell, R. R., & Tchobanoglous, G. (2012). *Principles of Water Treatment Role of Coagulation and Flocculation in Water Treatment.*
- Kosse, P., Lübken, M., Schmidt, T. C., & Wichern, M. (2017). Quantification of nitrous oxide in wastewater based on salt-induced stripping. *Science of the Total Environment*, 601–602, 83–88. https://doi.org/10.1016/j.scitotenv.2017.05.053
- Maurer, M., Muncke, J., & Larsen, T. a. (2002). Technologies for nitrogen recovery and reuse. *Iwa*, (3), 491–510.
- Morris, J., & Knocke, W. (1984). Temperature Effects on the Use of Metal-Ion Coagulants for Water Treatment. *American Water Works Association*, (76(3)), 74–79. Retrieved from https://www.jstor.org/stable/41271959?seq=1#page_scan_tab_contents
- Parks, T., & Chase, G. (2016). Filters and Filtration Handbook. (Elsevier, Ed.) (6th ed.).
- Shan-pei, L., Qi-shan, W., Wen-jie, H., Hong-da, H., Xue-hong, F., & Tian-jia, G. (2007). omparison of Dissolved Air Flotation and Sedimentation in Treatment of Typical North China Source Water. *The Chinese Journal of Process Engineering*, 7(2).
- Suez. (n.d.). SUEZ's degremont® water handbook. Retrieved May 21, 2018, from https://www.suezwaterhandbook.com/water-and-generalities/fundamental-physical-chemical-engineering-processes-applicable-to-water-treatment/coagulation-floculation/typical-reagents
- Sutherland, K. (2008). Filters and Filtration Handbook. (Elsevier, Ed.) (5th ed.).

- Tao, J., Wu, S., Sun, L., Tan, X., & Yu, S. (2012). Composition of Waste Sludge from Municipal Wastewater Treatment Plant, 12(Icese 2011), 964–971. https://doi.org/10.1016/j.proenv.2012.01.372
- Tarleton, E. S., & Wakeman, R. J. (2007). Solid/Liquid Separation Equipment Selection and Process Design (Elsevier).
- Tripathy, T., & De, B. R. (2006). Flocculation: A new way to treat the waste water. *Journal of Physical Sciences*, *10*, 93–127.
- Veolia. (n.d.). Water treatment technologies, Actiflo®. Retrieved from http://technomaps.veoliawatertechnologies.com/actiflo/en/
- Verstraete, W., Van de Caveye, P., & Diamantis, V. (2009). Maximum use of resources present in domestic "used water." *Bioresource Technology*, 100(23), 5537–5545. https://doi.org/https://doi.org/10.1016/j.biortech.2009.05.047
- Xie, M., Shon, H. K., Gray, S. R., & Elimelech, M. (2016). Membrane-based processes for wastewater nutrient recovery: Technology, challenges, and future direction. *Water Research*, 89, 210–221. https://doi.org/10.1016/j.watres.2015.11.045
- Zârnoianu, D., Popescu, S., & Brăcăcescu, C. (2015). Computational Mechanics and Virtual Engineering. In THEORETICAL AND EXPERIMENTAL RESEARCH ON THE SEPARATION PROCESS OF IMPURITIES FROM WASTE WATER THROUGH DECANTATION (pp. 183–190). Braşov, Romania.
- Zhu, Z., Hao, Z., Shen, Z., & Chen, J. (2005). Modified modeling of the effect of pH and viscosity on the mass transfer in hydrophobic hollow fiber membrane contactors. J. Membr.Sci. 250 (1–2), 269–276.