

Evaluation of Optimal Chemical Aids and Process Parameters in Oil Refinery Wastewater Flocculation and Flotation

Thesis for M.Sc. in Chemical and Process Engineering

by

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Abstract

Wastewater treatment of oil refinery effluents is a prerequisite for refinery operations in a continuously stricter environmental regulatory framework. One effective method of treating typical refinery wastewaters with oil-in-water emulsion is chemical destabilisation by metal salts, followed by separation of oil by flotation. The aim of this work was to improve the performance of the Naantali Oil Refinery Wastewater Treatment Plant with respect to oil, chemical oxygen demand, suspended solids, phosphorus, and turbidity removal. This was done experimentally, by assessment of chemicals, pH, and dissolved air flotation (DAF) process parameters. The performance of aluminium sulphate, polyaluminium chloride, ferric sulphate and ferric chloride and six different polyacrylamide flocculants were evaluated by jar testing. Ferric sulphate and low charge density cationic and anionic polyacrylamides were then evaluated in industrial scale experiments. The novel chemicals and DAF parameters recommended were found on average to reduce all the flotation overflow impurities by more than 50% compared to the conventional process. The optimal operating parameters in the industrial scale were found to be 1-2 mg/l of flocculant, an average dose of 35 mg/l ferric sulphate and pH 7-8. Various process disturbances can require up to 180 mg/l of ferric sulphate, which increases purification in a dose-dependent manner. The DAF system airflow was raised from 20 Nm³/h to 30 Nm³/h, which reduced suspended solids by 34% compared to the reference. For future research it is recommended to assess the performance of combinations of Al and Fe-based coagulants for disturbances caused by high levels of hydrogen sulphide.

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List of abbreviations

LDL	Lower detection limit
COD	Chemical oxygen demand
BOD	Biological oxygen demand
TSS	Total suspended solids
SS	Suspended solids
WWTP	Wastewater treatment plant
DAF	Dissolved air flotation
IAF	Induced air flotation
Nm ³ /h	Normal cubic meters (of air) per hour at NTP
HMW	High molecular weight
Initial pH	pH measured before adding metal coagulants
ICB	Intermediate bulk container (1 m ³)
Me ⁺	Metal ion, usually Fe ²⁺ , Fe ³⁺ or Al ³⁺

1 Introduction

1.1 Background

Untreated wastewaters are an environmental hazard. Wherever humans live and function, they produce different kinds of wastewaters. In spite of recent advances in technology, fossil fuels still account for the majority of energy used in the transportation of humans and goods, also in the foreseeable future. Refinement of crude oil to different fuels is an integral part of enabling these transport processes. As a side product, oil refineries produce wastewater containing oil and chemicals. Therefore, wastewater treatment is essential to reduce the load on nature, not to mention the continually stricter legal requirements on refinery effluents.

This thesis concerns the improvement of the performance of the Naantali Oil Refinery Wastewater Treatment Plant, operated by Neste Oyj Corporation. The work was focused on the chemical treatment process, consisting of two parts; flocculation and flotation. The work describes the underlying principles, the experimental activities carried out at the bench scale, and the implementation of the gained knowledge to the full-scale plant including test runs.

1.2 Objectives

This research aims to improve and optimise the chemical treatment of refinery wastewater at the Naantali Oil Refinery Wastewater Treatment Plant (WWTP). Chemical treatment has not been optimised in over a decade, moreover, the wastewaters have changed during this time, and therefore it is reasonable to investigate the performance and possible improvements. If feasible, these improvements will then be applied at the industrial scale. There are several hypotheses about the performance of the WWTP:

First, oxidation of ferrous sulphate used for coagulation is incomplete, and the process would thus benefit from changing it to a coagulant based on trivalent metal ions.

Second, strict pH adjustment which is practised at the industrial scale is unnecessary. The pH of the process is presently adjusted to 9-9.5 using sodium hydroxide. This procedure is probably redundant because of more efficient coagulants available (instead of ferrous sulphate). A pH closer to neutral is probably sufficient.

Third, the dissolved air flotation unit performance can be improved by finding optimal parameters such as recycle flow, saturator pressure, and airflow.

Finally, the polyelectrolyte flocculant type and dosage are sub-optimal.

By confirming these hypotheses, the efficiency and performance of the plant could possibly be increased. Moreover, a decrease or complete elimination of the use of sodium hydroxide would improve the safety of operators. The increase in efficiency could also lead to the reduction of operation costs.

1.3 Research methods

The approach to the research objectives was primarily experimental. Wastewaters vary significantly depending on the wastewater plant, and underlying mechanisms are not yet fully understood. Gathering experimental data was thus considered essential for eventual future modelling. The hypotheses are based on the literature review and the on-site working experience of the author. The acquired experimental data were then used to optimise the plant and produce a new set of parameters to run the plant. The main idea presented in this work was to start experiments on a small scale, and then gradually scale up the results to the full-scale process. This is done not only to reduce risks but also to gradually build a solid understanding of the behaviour of the chemicals used.

In this work, two experimental methods were used. First, preliminary combinations and dosages of chemicals were determined by bench-scale jar tests. Secondly, the acquired chemical combinations were tested in the full-scale process. In addition, the influence of the physical parameters in the full-scale process was examined.

The experimental data were collected by taking samples from the process water. In the case of jar tests, the process water was treated in batches of six jars, simultaneously. In the full-scale experiments, the samples were taken from the inlet and outlet of the chemical treatment process, i.e. upstream flocculation, and downstream the dissolved air flotation unit.

All samples were analysed by several analytical methods to quantify the contaminants. The main contaminants analysed were chemical oxygen demand (COD), suspended solids (SS), oil, turbidity, phosphate content, and pH.

1.4 Overview

This thesis consists of a literature review, bringing up to light the general phenomena and theoretical understanding of the chemistry and physics involved in the process. A chapter describing the Naantali Oil Refinery Wastewater Treatment Plant, to give the context in which the experiments were conducted, follows the literature review. The rest of the thesis is experimental, beginning with descriptions of the methods used, followed by Results and Discussion. Finally, the implications and results of the experimental part are summarised in the Conclusions chapter. Because the experiments were done iteratively, each experimental section is organised in a way that laboratory-scale experiments are discussed first, followed by the full-scale experiments.

2 Literature review

2.1 Introduction

Untreated wastewaters are an environmental hazard. The type of wastewater varies considerably depending on the source, e.g. oil refinery wastewaters contain oil and chemicals, municipal sewerage is high on phosphorus and nitrogen, and process waters from mining operations contain dissolved metals. Most wastewaters also contain significant amounts of suspended solids. Standard measures of contamination include “biological oxygen demand” (BOD₅ or BOD₇), “chemical oxygen demand” (COD), phosphate or phosphorus, ammonium, turbidity, suspended solids (SS), and oil and grease. Oil can be present in three forms:

- Free oil
- Colloidal oil
- Dissolved oil

The type of oil determines which methods for separation are the best ones in a particular case. Usually, all three forms of oil are present in refinery wastewaters. Regardless of the origin of the wastewater, it must be treated before being discharged back into nature. The most common chemical methods are coagulation and flocculation with metal salts, polymers, or both, followed by sedimentation. An alternative to sedimentation is flotation. Coagulation and flocculation processes aim to destabilise colloidal systems and increase the particle size, while sedimentation and flotation are separation processes. The increase in the particle size is done to facilitate the separation. It can be easily seen that large particles are considerably easier to separate than the small ones, and this was also confirmed in the current work. In this chapter, the four process steps are discussed in detail.

2.2 Colloids

Understanding colloidal systems and particles is paramount to understanding the chemical treatment of wastewaters. Colloids are defined as “...substances consisting of a homogeneous medium and of particles dispersed therein”, colloidal particles are viewed as “smaller than coarse, filterable particles but larger than atoms and small molecules”.¹ The range of colloidal particles is in the micro- (10⁻⁶) to nanometre (10⁻⁹) scale in microheterogeneous systems.² In other words, colloidal particles are tiny

particles or drops dispersed in a medium such as water, and cannot be seen with the naked eye. In wastewater treatment, particles (oil/solids) in water that do not rise to the surface or settle to the bottom are usually regarded as colloids. Milk is a typical example of a colloid, specifically of a colloidal emulsion, where liquid particles are dispersed uniformly and do not separate by gravity. As can be seen in the case of milk, colloidal particles can affect the scattering of light (Tyndall effect). Because of this scattering, colloidal substances of oils and fats usually have a greyish, bluish or white colour.² The scattering of light can be quantified and measured with a nephelometer (turbidimeter).

Emulsions are stable because the particles carry an electric surface charge, thus repelling each other.³ In the case of oil in water, the charge is usually negative.^{2,4} There are several reasons for this. Cations are usually more hydrated than anions, therefore residing in the bulk phase of water, which leads to more polar anions to adsorb on particles. Surface active molecules usually also have a negative charge, e.g. carboxylic acids and their salts. When they dissociate, the molecules concentrate on the oil-water interface, contributing to the negative charge.⁵ Moreover, solid particles tend to gather on the oil-water interface, hindering the coalescence of oil droplets. Due to the tiny size of the particles, the specific surface area is large. Consequently, the surface behaviour of colloidal particles dictates much of their properties.⁴

Colloids can be either hydrophilic or hydrophobic. Oil molecules are non-polar and hydrophobic, which means they do not have an affinity for water. When mixed with water, the oil and water phases would normally separate by coalescence. Coalescence is the process when two or more small oil droplets collide and combine into a larger droplet and rise to the surface. However, if polar molecules with hydrophilic and hydrophobic parts or surfactants are present, they gather at the oil-water interface hindering the coalescence of the hydrophobic droplets. Figure 1 illustrates different types of particles found in wastewater, and how surfactants concentrate on the interface of particles and the bulk phase.

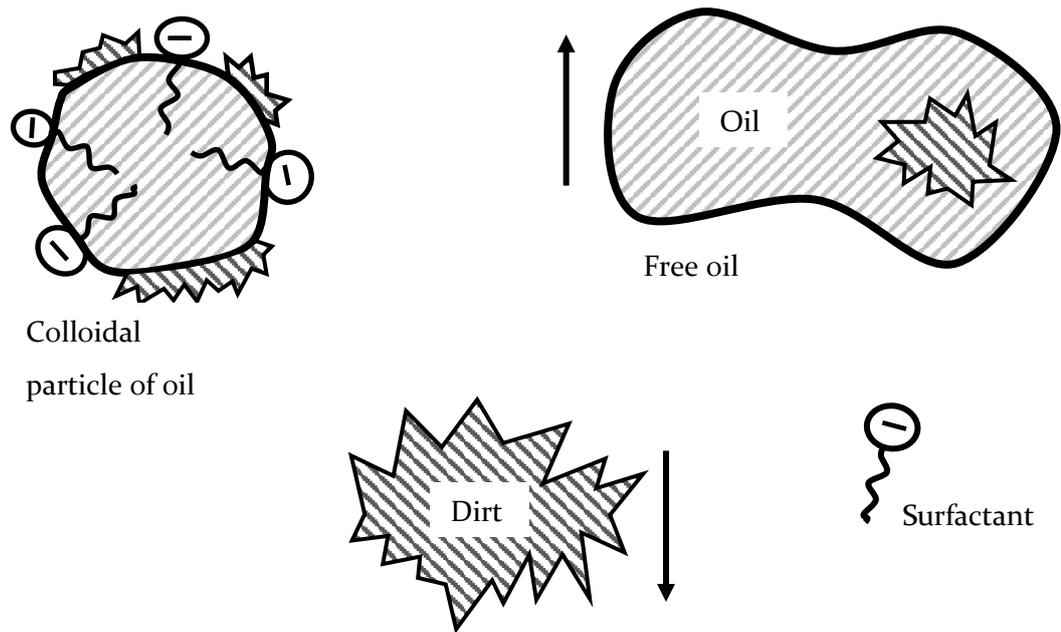


Figure 1: Different types of particles in refinery wastewaters. Colloidal particles are stable, free oil will rise to the surface, and solid particles settle at the bottom. Surfactants gather at the oil-water interface.

Charged colloidal particles lead to phenomena described by the theory of the electrical double layer. Because particles are charged, ions of the opposite charge will migrate towards the particle surface, forming a diffuse layer around the particle.^{2,5} This layer is illustrated in Figure 2.

Closest to the negatively charged particle is a layer of positively charged counter-ions, for example, Na^+ or H_3O^+ in water, which is known as the Stern layer. These ions are strongly attracted by the negative particle surface and do not move with the bulk fluid. However, the attractive electrostatic force decreases with distance. When the distance is large enough, the counter-ions will begin moving with the bulk fluid instead of staying adjacent to the charged particle surface.

Because the surface potential cannot be measured, the zeta-potential is measured instead. It is defined as the potential at a certain distance from the particle (beginning of shear plane). The shear plane is the distance from the surface where ions are not attached to the particle anymore but, instead, move with the bulk fluid. A large zeta-potential corresponds to a large surface charge and vice versa. In other words, zeta potential is a good approximation for the particle charge. An illustration of the theory of the electrical double layer and zeta-potential can be seen in Figure 2.

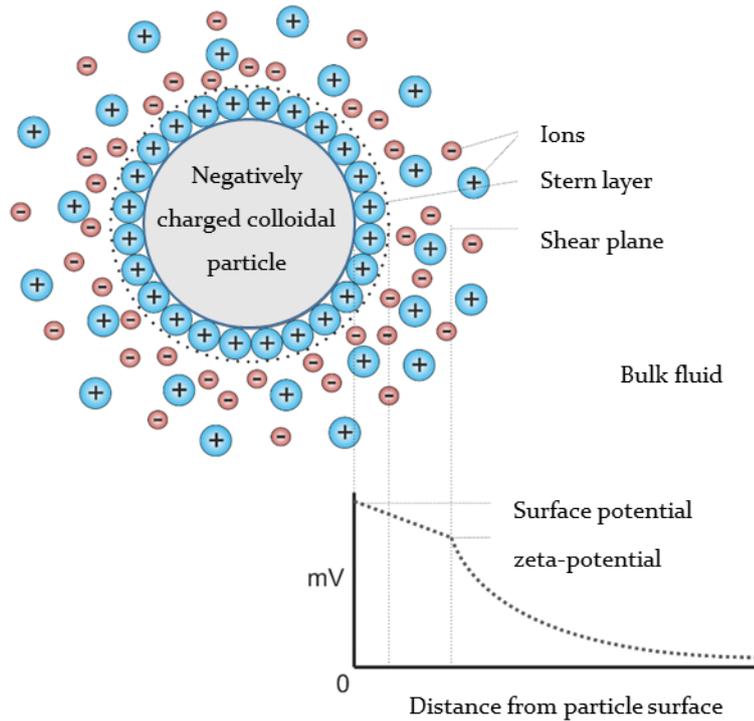


Figure 2: The electrical double layer and zeta-potential

2.3 Coagulation

Coagulation refers to the destabilisation of colloids, and the subsequent agglomeration of particles to form micro flocs.⁴ Agglomeration refers to the process of particles binding to each other. For agglomeration to be possible, the particles first need to collide and secondly, the energy of the collision needs to surpass the repulsive forces caused by similar particle charges. If both conditions are met, small aggregates known as micro flocs will be formed. First, attracting and repelling forces of the collisions will be considered, followed by measures to improve aggregation.

Particles are naturally attracted by one another, mainly caused by Van der Waals forces.^{2,5} However, if the repulsion between the particles surpasses the attractive forces, agglomeration will not take place. It has been proven that higher zeta-potential values, analogous to a higher surface charge, correspond to higher repulsion between the particles.⁵ In other words, the surface charge is the primary stabilising factor in colloidal suspensions. In the case of wastewater treatment, this electrostatic stability needs to be destabilised to separate the particles from the water.^{4,6} This can be done by addition of chemicals with opposing charges to the particles. In the majority of cases of wastewater

treatment, these agents are positively charged. The destabilisation of wastewater colloids is usually done by addition of inorganic metal salts of iron or aluminium. These are often called primary coagulants. Sometimes natural or synthetic organic polymers can be used. However, these are often significantly more expensive compared to the conventional metal salts, even if producing less sludge. Some inorganic polymers of aluminium also exist, namely polyaluminium chloride. All these additives are collectively called coagulants. Commonly used coagulants are listed in Table 1.

Table 1: Commonly used coagulants for wastewater treatment

Inorganic coagulants

Aluminium Sulphate (alum)	$Al_2(SO_4)_3$
Aluminium Chloride	$AlCl_3$
Polyaluminium Chloride	$[Al_n(OH)_mCl_{(3n-m)}]_x$
Ferrous Sulphate	$FeSO_4$
Ferric Sulphate	$Fe_2(SO_4)_3$
Ferric Chloride	$FeCl_3$

Organic coagulants

PolyDADMAC	$(C_8H_{16}NCl)_n$
Polyamines	Epichlorohydrin + dimethylamine, polymerised
Melamine Resin	Melamine + formaldehyde, polymerised

When metal salts dissociate, the metal ions will acquire a cationic charge (positive zeta-potential). This positive charge will serve to neutralise the anionic surface charge on the colloidal particles.⁴ Metal ions carry bivalent (Mg^{2+} , Fe^{2+} , Ca^{2+}), or more efficiently, trivalent charges (Fe^{3+} , Al^{3+}). Neutralising the surface charge leads to a compression of the electrical double layer and overall reduction of repulsive forces, which results in a higher chance of two colliding colloid particles attaching to one another, thus resulting in agglomeration. According to the Schulze-Hardy rule, the most effective coagulants are oppositely charged ions, with increasing coagulation (precipitation) power with increasing valence.² Typical coagulant dosages naturally depend on the properties of water, usually varying from a few to hundreds of milligrams per litre, but can go as high as thousands of milligrams per litre.⁴ According to The NALCO Water Handbook, the

coagulant dosage is directly dependent on the surface area, which means the size and concentration of particles.⁴

In most wastewater treatment conditions, metal ions are not in solution in the form Fe^{3+} or Al^{3+} , but partially or fully hydrolysed, e.g. $\text{Me}(\text{OH})^{2+}$ or $\text{Me}(\text{OH})_3$. Fully hydrolysed metal salts are not soluble but precipitate as hydroxides. Most coagulation reactions are hypothesised to involve metal hydroxides and not un-hydrolysed metal ions. However the mechanisms are not yet fully understood.⁷ Insoluble metal hydroxides also take part in coagulation, by a phenomenon called sweep flocculation. Hydroxide precipitates are amorphous and voluminous, which can be detrimental when considering the sludge volume. The solubility of different metal hydroxide species varies depending on the pH of water, which means that the pH considerably affects the effectiveness of the above-mentioned coagulants.³ Pre-hydrolysed organic and inorganic polymers can presumably carry even higher positive charges, making them adsorb more tightly onto particles. These usually produce less sludge and are required in smaller amounts, being more expensive.

Summarising, for coagulation to be possible two processes need to happen. The particles must be destabilised, and they must be transported within collision range of each other. Destabilisation can be achieved by the addition of metal salts, and the collision frequency is facilitated by stirring.

2.4 Flocculation

Flocculation refers to the process of agglomeration, where particles form large, visible agglomerates, known as macro flocs. Flocculation can be viewed as a physical transport process, while coagulation is more like a chemical reaction. Flocculation is done to increase the floc size to facilitate separation. Flocculation is accomplished through slow agitation and the addition of polymers, known as flocculants.

For the destabilised colloids formed in the coagulation step to grow in size, they have to be brought in contact with each other. Molecular transport phenomena are physical processes. According to Ghernaout et al. three main driving forces for particle collision exist:³

- Brownian diffusion
- Fluid motion

- Differential sedimentation

Brownian diffusion, or movement, is the result of thermal energy in the fluid. It only affects tiny particles, including colloids. These particles are constantly bombarded by surrounding molecules in motion. Because the particles are small, the kinetic energy of molecules colliding with them will result in what appears to be movement in random directions. This movement can lead to two particles spontaneously colliding, causing agglomeration. Brownian motion affects the coagulation process but is negligible once the particles grow in size.⁸

The most significant reason for particle collisions in wastewater treatment is fluid motion. Fluid motion, or shear forces, is the result of mixing or flow. Stirring and turbulence lead to different velocity gradients in the liquid, varying depending on the position and time. This causes particles to move with differing velocities and directions, leading to collisions.³

Finally, differential sedimentation exists, a gravity induced phenomenon. Differential sedimentation describes the tendency of particles of different sizes to collide when settling (or rising). Large particles settle faster and collide and agglomerate with or enmesh smaller particles on the way down.³

The theory of sedimentation is worth consideration at this point. So far only a need to increase the particle size, for easier separation, has been mentioned. The reason that larger particles separate faster compared to small particles can be described by the law of Stokes'. The law makes some assumptions such as laminar flow and involvement of hard spherical particles. Stokes' law states that settling velocity is proportional to the diameter squared.

$$V = \frac{G(\rho_1 - \rho_2)D^2}{18\eta} \quad (1)$$

where

V = settling velocity, cm/s

G = gravitational acceleration, cm/s²

ρ_1 = particle density, g/cm³

ρ_2 = liquid density, g/cm³

D = particle diameter, cm

η = liquid viscosity, s/cm²

Because the Stokes' law describes an ideal, simplified situation, it is not directly applicable. However, it demonstrates the influence of the particle diameter and density difference on the settling speed. Table 2, modified from The NALCO Water Handbook Table 6.1, illustrates different settling times of typical particles calculated using Stokes' law.⁴

Table 2: Typical settling times for particles of different sizes

Typical Suspended Solid	Diameter (mm)	Settling time to fall 1 m
Coarse sand	1	10 s
Fine sand	0.1	125 s
Slit	0.01	108 min
Bacteria	0.001	180 h
Colloids	0.0001	755 d

Particles of bacterial and colloid sizes are evidently too small to sediment within a reasonable time. Process equipment needs to be designed in such ways that the particle speeds are accounted for. Stokes' law is not applicable under turbulent conditions, where settling velocities are significantly slower.

Metal coagulants efficiently destabilise colloids and increase agglomeration, growing the particle size, but the addition of a flocculating agent can rapidly increase the floc size further. Polyelectrolyte flocculants are either cationic, anionic or non-ionic polymers of high molecular weight. Flocculants work by interparticle binding. The polymer chains form a net together with smaller agglomerates of colloidal particles and metal hydroxides. When this net moves around in the fluid it will enmesh and trap smaller particles, continually growing in size.⁴ Polymer flocs are visible, can be up to several centimetres in size, and stronger than flocs formed by metal salt type coagulants used on their own. Flocculants work mainly by interparticle binding, not by charge neutralisation. The choice of polymer can only be determined by experiments, because of the complexity of wastewater chemistry and process design.⁴

Flocculation is usually followed by a separation step of either sedimentation, filtration or flotation. Of these three phenomena, flotation will be discussed in the next section. Sometimes coagulation/flocculation is also preceded by separation. In the case of oily

water, coagulation/flocculation is usually preceded by gravity separation of oil. While gravity separation of oil follows Stokes' law just like sedimentation, because oil has a lower density than water, the goblets will rise to the surface instead. In this way, non-colloidal particles, such as free oil, can be significantly reduced before the coagulation step.

2.5 Flotation

2.5.1 Dissolved air flotation

Dissolved Air Flotation (DAF) is a highly effective method to remove emulsified oil and suspended solids from water. Removal rates exceeding 99% of oil and suspended solids have been achieved.⁹⁻¹¹ Flotation works by attaching tiny air bubbles (20-120 μm) to suspended solids or oily particles. The bubbles are produced by pressurising a part of the effluent stream to 3-5 times the atmospheric pressure in the presence of air and then recycling it back to the influent. Subsequently, as the pressure is reduced back to atmospheric in the flotation unit, microbubbles nucleate on the particles. The attached bubbles grow and reduce the specific gravity of the bubble-particle agglomerates and force them to the surface. Macroflocs and metal hydroxides formed in the flocculation step will also trap bubbles and rapidly rise to the surface, "sweep flocculating" smaller particles.^{4,6} The floating particles, oil, and froth are then skimmed off and removed from the process. Flotation being an effective process by itself is significantly enhanced by pre-treating water with coagulants and flocculants. Flotation in combination with chemical pre-treatment can remove most of the free and emulsified oil.¹² Chemical treatment units (flocculation/flotation) in refineries usually have gravity separation of free oil (API-separators) upstream to reduce the load. Such gravity separation is a natural choice when dealing with oily wastewater, because oil and oily particles usually have a lower density than water. However, when dealing with heavier hydrocarbons with a density close to water, e.g. heavy crude oil, flotation is the only efficient method of removal.¹³

While different kinds of flotation processes exist, e.g. Induced Air Flotation (IAF) and electroflotation, this work is limited to the most common Dissolved Air Flotation (DAF). A DAF clarification unit consists of six main components:

- Flotation vessel
- Recycle pump

- Air saturation tank
- Source of high-pressure air
- Pressure regulation system
- Chemical addition system or separate flocculator tank

A recycle pump is needed if the system operates on a recycle basis, which means taking a part of the effluent for pressurising. Other alternatives are *full flow* or *partial flow* pressurisation, pressurising the influent instead. Most DAF units are of the recycle type, proved to be the most efficient already in 1954.¹⁴

2.5.2 Theory of flotation

2.5.2.1 Rise rate

The flotation process aims to adsorb and absorb air bubbles on the particles and oil globules, to reduce the relative density with respect to water. In other words, it is a form of gravity separation by increasing the buoyancy of particles. Flotation follows Stokes's law similarly to sedimentation but reversing the force field. Flotation basins can be divided into two zones: the contact zone and the separation zone. In the contact zone, the supersaturated influent forms bubbles and the flow regime is turbulent. Here the Stokes's law cannot be applied. In the separation zone, further away from the inlet, laminar flow can be assumed. The bubble-particle agglomerates surface is undisturbed, and the Stokes's law is valid.

Air bubbles rise rate can be calculated using Stokes's law for bubbles under 130 μm .¹⁵ Larger bubbles rise significantly faster in pure water because they take an elliptical shape. Then again, because surfactants are always present when treating oily wastewater, the bubble shape will stay spherical for longer. Therefore, according to Moosai and Dawe (2003), Stokes's law holds reasonably well for bubbles up to 200 μm .¹³ For bubble-floc aggregates more exact models exist, being more complicated. These models take into consideration the number of attached bubbles in relation to floc size.¹⁶ According to Edzwald (2010) flocs slightly denser than water with a diameter of 50 μm with one attached bubble ($d = 100 \mu\text{m}$) will rise with an approximate velocity of 20 m/h.¹⁷ When air bubbles are attached to oil droplets or particles, the density difference to the bulk liquid increases and the diameter of the agglomerate increases. Flotation is thus more efficient than sedimentation since sedimentation does not alter the density difference or the particle diameter in the Stokes's equation.

When designing and operating flotation units, the rise rate of flocs is not used. Instead, a parameter called hydraulic loading rate (HLR) is applied. Hydraulic loading rate, also named as rise rate or surface loading rate, is defined as the volume of flow per hour applied to the surface area available for separation. The NALCO Water Handbook states that normal ranges vary between 3.7 to 4.9 m³/ (h · m²).⁴ According to Bennett and Shammas (2010) for industrial DAF units for oil-removal, the HLR varies from 2.2 to 9 m³/ (h · m²).¹⁰ The HLR can be calculated if the total flow (influent + recycled) and the surface area are known: ⁴

$$HLR = \frac{F_i + F_r}{A} \quad (2)$$

where

HLR = hydraulic loading rate (m³/ [h · m²])
 F_i = influent flow (m³/h)
 F_r = recycle flow (m³/h)
 A = flotation area (m²)

2.5.2.2 Size and number of bubbles

The size and quantity of gas bubbles are important parameters. Too large bubbles will not combine with small oil droplets. The size and number of bubbles are influenced by the saturation system pressure. The amount and size of bubbles are a function of the pressure in the saturation vessel because the pressure determines the amount of dissolved air in the liquid.¹² The dissolution of gas to liquid follows Henry's law:

$$C = \frac{p}{k} \quad (3)$$

Where p is the partial pressure of the gas over the liquid, C is the concentration of dissolved gas, and k is the Henry's law constant. Henry's law describes the equilibrium amount of dissolved gas. Complete saturation is seldom achieved however, because of limited retention time in the saturation vessel.¹⁷ When the pressure is reduced almost all of the dissolved air is flashed out of the solution. In other words, the amount of air is a direct function of the saturation pressure. Moreover, the Henry's law constant k is temperature dependent. The solubility of gases in water usually decreases with temperature (Figure 3).

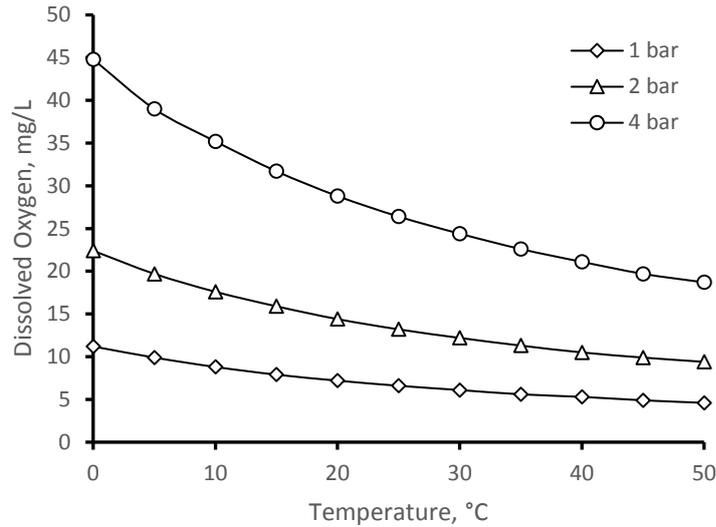


Figure 3: Calculated solubility of oxygen in salty water at different pressures.¹⁸

The retention time of the recycle stream in the saturation vessel is limited. Therefore the equilibrium concentration predicted by Henry's law is not reached. A larger surface area of the air-liquid interface in the saturator increases the mass-transfer, leading to a higher degree of saturation. According to Edzeward,¹⁷ packed saturators reach 80-95% of the equilibrium, while unpacked ones reach around 50-70%. It has been stated by Edzeward that DAF with small bubbles is more efficient than DAF with large bubbles, and the easiest way to improve the efficiency is to increase the saturator pressure, which decreases the bubble size and increases the number of bubbles. However, DAF units usually operate at a constant saturation pressure, which means that the only way for operators to adjust the amount of air is by changing the recycle flow. Increasing the recycling rate increases the amount of air in the system. At the same time, too much of air leads to large bubbles causing turbulence and disturbing separation.

The performance of DAF units also depends on the air-to-solids and oil ratio (A/S - ratio).⁴ A sufficient amount of air bubbles needs to be released in relation to the suspended solids and oil to increase the contact probability. When designing DAF units the A/S ratio is often used, but when operating the unit the recycle rate is more convenient because influent TSS and oil are usually not monitored continuously.

2.5.2.3 Bubble-particle agglomeration

In flotation, the inter-particle forces are dominated by electrostatic, van der Waals, hydrophobic and hydrodynamic effects.¹⁷ A lot of research suggests that air bubbles

carry a negative zeta-potential unless adjusted by addition of chemicals or lowering the pH below two.^{9,17,19} It is suggested that OH⁻ ions gather at the air/water interface.^{19,20} This negative charge leads to electrostatic repulsion between similarly charged colloidal particles, such as colloidal oil droplets and bubbles. Charge neutralising coagulants are thus used, usually in a coagulation/flocculation unit preceding the flotation unit. For optimal operating conditions, a minor charge on the particles or its absence is achieved by the addition of charge neutralising species, such as metal salts. Han et al.²¹ concluded that a slight coagulant overdose is better when dosed in relation to the measured zeta-potential. It is considerably more difficult to change the type of charge on the bubbles. A slightly negative charge of air bubbles is the reason for the extensive use of cationic polymers in DAF units in refineries.^{4,19} Oliveira & Rubio¹⁹ examined the effect of anionic, cationic and non-polar polyacrylamide flocculants effect on bubble zeta-potential. They noted that the anionic and non-polar polymers make the bubble surface more negative. When a cationic polymer was used, charge reversal was observed. Above pH 8 also the cationic-polymer coated bubbles turned negative. However, because they used rather high doses of polymers at 10 mg/L probably a charge reversal on bubbles should not be expected at more conventional doses. Despite a negative bubble charge, a well-designed flotation unit can, without the use of chemical aids, remove up to 73% of oil contaminants.¹²

There are several reasons for an efficient operation of the DAF units without chemical aids. As bubbles nucleate from the supersaturated solution, they will be primarily formed on low-energy sites on solid particles, or if such sites are not available homogeneously in the continuous phase (water). Nucleation directly on particles implies that the electrostatic charge barrier is “bypassed”. Another major reason is the fact that air bubbles are hydrophobic, such as oil, and therefore seek hydrophobic particle surfaces, even when slightly charged.¹⁷ Ducker et al.²² have shown that the hydrophobic forces are the primary reason for air bubble attachment on hydrophobic particles.

An opposing force hindering the bubble-particle collision and subsequent attachment is the hydrodynamic effect. This effect refers to the fluid motion caused by the movement of a particle, e.g. the rise of a bubble, which then affects all nearby particles. When a bubble approaches a particle, water between them must make way for a collision to occur. This thinning of the water layer is countered by viscous forces and

the surface tension of water. Water between the particles flows to the sides, excreting a drag force on the particles themselves.¹⁷

In the contact zone, bubble-particle aggregates are formed through various mechanisms illustrated in Figure 4. These aggregates will then slowly rise to the surface for skimming in the separation zone.

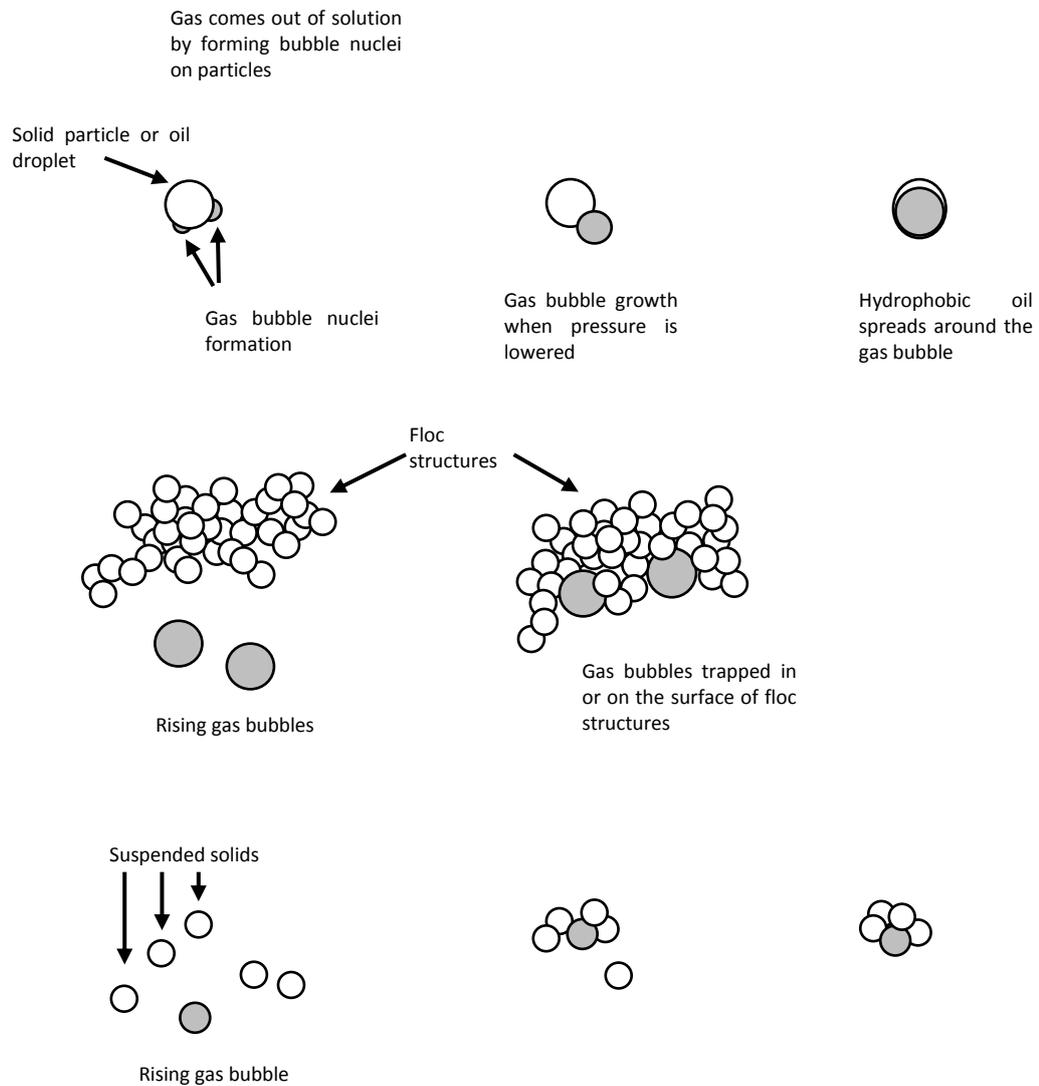


Figure 4: Particle bubble agglomeration. Modified from Bennett and Shammas.¹²

2.6 Industrial coagulation, flocculation and flotation

Oil refineries are widely equipped with decanting type gravity separators (API-separators, named after the *American Petroleum Institute*) for free oil, and many of them also utilise flotation or both. A suitable solution for refinery wastewaters containing oil is API-separation of free oil, followed by flotation for removal of colloidal oil and finally a biological treatment for dissolved oil. Flotation is mostly combined with the use of chemicals, with mixing either in an upstream coagulation/flocculation tank or directly in the flotation unit influent. Typical refinery effluents (= chemical treatment influents) after API-separators can be seen in Table 3.⁴ Without API-separators, the contaminants can be more than ten times higher.

Table 3: Expected concentrations after API-separation

Contaminant	Concentration, mg/l
Oil	20 – 100
COD	260 – 700
SS	50 – 350
BOD ₅	250 – 350

A significant number of studies has been done on the effectiveness of flocculation and flotation. However, because wastewater properties vary much from plant to plant, it is difficult to obtain reliable correlations. Bennett and Shamma¹² analysed the performance of various flotation systems, especially oil refineries, and concluded that:

*"Because of numerous variables associated with the data/testing, especially the type and amount of chemical additives, it is essentially futile to try to construct correlations"*¹²

However, certain trends, such as those discussed in this section, seem to be valid. Overall, the performance of the flotation systems varies greatly. Bennett and Shamma¹⁰ extensively summarised over forty studies describing the expected DAF performance (Table 4).¹⁰

Table 4: Expected DAF performance ¹⁰

Contaminant	Expected removal (%)
Oil	85 – 95
COD	65 – 85
SS	70 – 75

Bennett and Shammass have reported that removal percentages can be misleading, because the effectiveness of DAF units depends on the influent oil concentration.¹⁰ Higher influent concentrations lead to improved removal percentages. The authors state that a removal of more than 90% can be expected for influent concentrations of 150 mg/L or more, and 75% removal for influent oil concentrations of ca. 25 mg/L.

Below some of the published results regarding wastewater treatment with flotation units and different kinds of coagulants are described. The recurring theme is that the optimal pH and coagulant dosages vary to a large extent, from case to case.

Al-Shamrani et al.⁹ investigated the oil removal in a bench-scale DAF reactor. They compared the influence of ferric and aluminium sulphates, pH, mixing time and intensity and measured the zeta-potential. The best oil removal was found to be in the neutral pH range, with a 10% recycle rate. The highest removal (99.94%) was achieved with ferric sulphate (120 mg/L) at pH 7. Overdosing the coagulant after charge reversal of the zeta-potential impaired the performance. Ferric sulphate had a broader area of influence on the pH scale and performed better than aluminium sulphate.

Megid et al.²³ compared coagulants in a pilot-scale DAF unit for oil removal. The highest removal was 72.7% for alum, 74% for ferric chloride and 67.3% for ferrous sulphate at pH values of 10, 8 and 10 respectively. DAF without coagulants resulted in oil removal of 60.9%. The worst results were observed, as expected, for divalent ferrous sulphate.

Weltz et al.²⁴ investigating the flotation kinetics under turbulent conditions compared aluminium sulphate and lime. The results were in agreement with the Schulze-Hardy rule. The trivalent aluminium ion was more effective than the divalent calcium ion. The best performance was achieved with 50 mg/L of aluminium sulphate and 0.5 mg/L of

anionic flocculant at pH of 5.5. It was concluded that the rate of oil removal increases at higher levels of air in the flotation unit.

Tansel and Pascual²⁵ treated brackish pond water contaminated with emulsified fuel oils with and without coagulants in a pilot scale DAF unit. Addition of coagulants increased the removal by 5-15%. In an early study carried out by Rohlich¹⁴, an increase by 15-23% was achieved in the presence of coagulants. However, in that work the feed had already passed an API-separator where all the non-emulsified oil was removed. Because of variations in wastewaters depending on a particular refinery, it was recommended by Rohlich to find for each specific case the optimal treatment conditions.

Rhee et al.²⁶ stated that pH of 8.5 afforded the best oil removal (almost 100%) with 100 mg/L of aluminium sulphate or 50 mg/L of ferric sulphate, using a DAF system. A dose of 10 mg/L at pH 8.5 removed 85% of the oil, with the initial oil concentration of 200 mg/L. The authors concluded that pH has a larger influence on oil removal than the dose of coagulant. Interestingly enough, ferric sulphate was twice as effective as aluminium sulphate.

Tzoupanos and Zouboulis²⁷ compared different novel pre-polymerised aluminium compounds, as well as polyaluminium chloride (PAC) and aluminium sulphate for wastewater treatment (not oily water). In almost all cases, the pre-polymerised molecules performed better than aluminium sulphate concerning turbidity reduction.

Aghaali et al.²⁸ investigated COD removal in refinery wastewaters. The authors examined the optimal coagulant dose (in the range 15-25 mg/L) and saturator pressure (range 3-5 bar) for a DAF system, using polyaluminium chloride, and concluded that 15 mg/l PAC gave the best results. It was stated that the pressure should be as high as possible (5 bar) independent of the chemical dosage.

Sawain et al.²⁹ treated biodiesel wastewaters with jar test apparatus, using ferric chloride as a coagulant. The pH range of 5-7 was found to be optimal, for all doses of coagulant, resulting in 97% removals of SS, COD, and grease and oil.

As can be seen from the literature overview, the results vary significantly depending on the wastewater properties.

3 Naantali Oil-Refinery WWTP

3.1 Introduction

The Naantali Oil Refinery was built in 1957 and after that it has been updated and reconfigured several times. Today it processes daily around 50 000 barrels of crude oil to LPG, gasoline, diesel, kerosene, solvents, bitumen and other products. The wastewater plant was built gradually over the years; each part is operating based on different scientific principles. The first part was the API-separator completed in 1957, with the capacity expansion later on. The chemical treatment and the biological activated sludge processes were started in 1973, and are still in operation today. It can thus be concluded that the facility is rather old.

The refinery wastewaters are somewhat typical for oil refineries.³⁰ There are several sources of water coming to the WWTP: process water, tank-drawdowns, stormwater, sewerage, and ship ballast water from the harbour. Process water includes desalter effluent, sour water, and occasionally spent caustic. Historical water properties for the past year can be seen in Table 5 beneath, compiled by the author. The rest of this chapter will clarify how the three stages API, chemical, and biological processes operate, from up- to downstream.

Table 5: Historical WWTP feed properties after API-separation

Test	Units	Count	Min	Max	Average	St. deviations
Oil and Grease	mg/L	130	4,9	299	37.2	34.3
COD	mg/L	180	32	2100	427.4	233.6
Phosphate	mg/L	64	0.035	2.7	0.59	0.69
Suspended Solids	mg/L	119	5.3	233	46.9	32.9
pH		65	6.8	10.5	7.7	0.8

3.2 API oil-water separators

The first process step of the WWTP is separation of heavy suspended solids and oil droplets, achieved using an API oil-water separator. The purpose of the API-separator is to remove free oil, as it is not capable of removing emulsified or dissolved oil. At the inlet of the separator, the wastewater is screened for coarse contaminants. The screen is a large grate, with manual cleaning. The grating is followed by a grit chamber, used

for trapping sand and heavier suspended solids. The solids settle, with the difference in specific gravity as the driving force (Stokes's law), to the bottom of the grit trap. After the grit chamber, the oily wastewater slowly flows through the separator basin, because of in- and outlet elevation differences. In the separator, the oil rises to the surface, while suspended solids settle to the bottom. The oil is skimmed off the surface by skimming plates, pushing the oil towards the skimming scoop at the outlet end of the basin. The water in the middle layer continues downstream after surpassing under-flow baffles at the outlet. The recovered oil is pumped to tanks, and later re-fed as feedstock to the refinery. There are a total of four parallel separators, each one with a grit chamber, with the overall separator volume of 1936 m³. Because there are no bottom scrapers, regular and sequential emptying and cleaning of the basins is required to remove amassed solids from the bottom of the separators. After the API-separators the effluent water can go three ways: pumped to chemical treatment, pumped to a (small) equalisation tank, or in case of capacity problems, downstream water can be led to a safety basin.

The performance of the API-separators affects the processes downstream. If the flow rate increases significantly, e.g. during sustained rainfall, the residence time of the water in the separator decreases. Shorter residence time means that the time for oil droplets to surface is decreased, thus causing more oil to continue downstream. Another problem is related to emulsifying agents (surfactants), as occasionally surfactants used in the refinery operations can cause emulsion stabilising conditions in the wastewater. Since API-separators only work to separate free oil, the effectiveness is reduced, leading to increased oil loading for the chemical treatment unit.

3.3 Chemical treatment

The chemical treatment system consists of two reactors, the “Flocculation tank” and the Dissolved Air Flotation (DAF) unit. The flocculation tank, or “Flocculator”, is the first reactor downstream after the API-separators. It functions like a continuously stirred tank reactor. By the addition of chemicals and air, coagulation of colloids is achieved. Ferrous sulphate (FeSO₄), caustic soda (NaOH), and air are continuously added to the wastewater. Submerged aerators accomplish mixing of the fluid with impellers. Compressed air is also injected from the bottom of the tank. The purpose of the aeration is to oxidise the divalent ferrous ions to trivalent ions, leading to improved coagulation of colloids, as discussed in Section 2.3. The destabilised colloidal particles will begin to collide and agglomerate, forming microflocs. The average residence time

varies between 30 min and two hours, depending on the flow rate. The varying residence time raises a question on its influence on the formation and breakdown of flocs. The outlet, leading to the DAF unit, is a waterfall in the far corner of the rectangular basin. Into this effluent waterfall, a stream of anionic polyelectrolyte is added, mixing with the water in the turbulent conditions of the falls. The polymer is added after the main part of the reactor to prevent the breakdown of larger polymer flocs because of excessive agitation. Thereafter, the effluent flows through a large pipe for approximately ten meters into the centre of the dissolved air flotation (DAF) unit.



Figure 5: Naantali refinery WWTP DAF unit in December (photo of author).

The dissolved air flotation unit (Figure 5) uses tiny air bubbles to raise the floc to the surface for skimming. The main components of the DAF unit in the refinery are the flotation tank (300 m³), the saturation pressure vessel (4 m³), the circulation pumps, and a source of pressurised air (8 bar refinery pressurised air network). Water saturated with air at high pressure is mixed with the effluent water from the flocculator, just before the flotation basin. Then the wastewater flows to the middle and bottom of the circular flotation basin, where it is released. Because the pressure is lowered back to

atmospheric, tiny air bubbles nucleate on particles in the now supersaturated water, causing oil and solids to rise to the surface. The flotation basin has a cylindrical structure in the middle of the tank, which together with four inlets, forces water to rise upwards in a helical pattern. The bubble nucleation and attachment takes place in the contact zone, while the separation occurs in the separation zone. These zones and the flow of the water are illustrated in Figure 6. On the surface level, three fixed radially placed scoops, together with three continually moving skimmer paddles, skim off the surfaced floc and foam. The DAF unit operates on a recirculation basis with a 25-80% recirculation ratio. The saturation tank operates at a pressure of 3.8 bar, with a safety valve set at 3.9 bar. The circulated water is pumped to the saturation tank with one or two pumps (recycle flow 65 and 75 m³/h, both pumps 130 m³/h). Pressurised air is fed into a recycle water line upstream the saturation tank, where air and water are mixed with an inline static mixer. The hydraulic retention time in the DAF unit is between one to three hours, depending on the flow rate. The DAF properties are summarised in Table 6.

Table 6: DAF unit parameters

Parameter	Variable		Units
	Range	Average	
Influent	70—400	120	m ³ /h
Hydraulic loading rate (including recycle)	1.4—5.6	2.1	m ³ /(m ² h)
Recycle flow	60—130	70	m ³ /h
Recycle rate	15—100	50	% of raw influent feed rate
Retention time	0.75—4	3	h
Airflow	5—30	15	Nm ³ /h
Pressure	3.5—3.9	3.8	bar
Pressurisation tank retention time	2—4 min	3.4	min

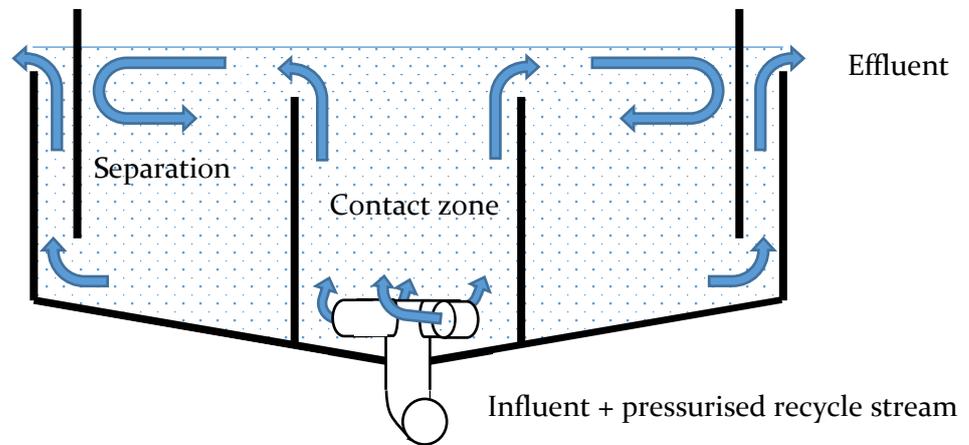


Figure 6: Simplified flow of water in Naantali refinery DAF unit.

3.4 Biological treatment

After the chemical treatment, the water flows by gravity to the biological treatment unit, composed of an activated sludge (AS) process. The activated sludge process is a wastewater treatment method utilising bacteria and protozoa. The microbes will digest the impurities and use some of the compressed air injected into the wastewater for cell respiration. Subsequently, the bacteria are removed from water by sedimentation, yielding purified water. The process consists of three main parts; first the aeration tank, followed by the sedimentation or clarification tank, and finally, the sludge recycle and removal system.

The aeration tank (730 m³) is a bioreactor with compressed air introduced as small bubbles from the bottom. When contaminated water enters the aeration tank, the bacteria in the basin will begin digesting organic molecules and nutrients, ammonia, and phosphorus in the water, and utilising oxygen for cell respiration. This mix of bacterial sludge and wastewater is called “mixed liquor”. The feeding causes the bacteria to grow, and after a specified residence time in the reactor, depending on the water flow rate, the mixed liquor continues to the clarifier.

In the clarifier tank, the bacterial floc slowly settles to the bottom of the basin. On the far end of the tank cleaned water flows to the next process step. Bottom scrapers collect the bacterial sludge that settles at the bottom of the basin and recycles the sludge back

to the aeration tank. A bleed-off on the recycle stream removes excess sludge at unspecified intervals. The amount of bacterial sludge should be kept constant. If the excess sludge is not removed the biomass will accumulate, decreasing the effectiveness significantly. Similarly, if too much sludge is removed the effectiveness also declines. Possible reasons are either a lack of nutrients in the case of a large quantity of bacteria, causing their death, or an abundance of nutrients surpassing the bacterial digestion capacity, in the case of excessive removal of sludge.

After the AS process automatic water sampling takes place, and the samples are analysed daily. This is also the sampling site for regulatory purposes. For process follow-up, the samples are taken twice per week from each process step. Field operators can also perform quick field analyses several times per day for phosphorus and nitrogen. As the last process step, for further biological treatment, the water flows to a large lagoon (approx. 35 000 m³) for prolonged aeration and sedimentation. The lagoon drains off into the sea. The final water purity is sufficient enough to sustain fish living in the lagoon.

The AS process and the DAF unit generate sludge, which is processed mechanically by centrifugation to concentrate the sludge by removing water and oil. Cationic polymers are added to facilitate the separation. Water separated by the centrifugation is recycled back to the chemical treatment, while the oil is pumped to the API-separators. The remaining sludge is mixed with burnt lime (CaO) to dry and solidify it further, before being removed from the premises.

4 Methods

4.1 Chemicals aids

Six types of primary coagulants were tested. Some types included different product names and were therefore tested more than others. Coagulants studied included: ferrous sulphate, ferric sulphate, ferric chloride, aluminium sulphate (alum), and polyaluminium chloride. All coagulants were supplied in the liquid state, except ferrous sulphate currently used in the WWTP. Ferrous sulphate was dissolved in water on site. The chemicals were obtained from Kemira Oyj.

Table 7: List of coagulants used

Coagulant	Product name	Metal-ion conc.
Polyaluminum Chloride (42% basicity)	PAX-XL100	9.30 ± 0.3%
Polyaluminum Chloride (26% basicity)	PAX-14	7.20 ± 0.3%
Aluminium Sulphate	ALS-50	4.00 ± 0.3%
Ferric Sulphate	PIX-II5	11.90 ± 0.3%
Ferric Chloride	PIX-III	13.4 ± 0.6%
Ferrous sulphate (dissolved)	Ferrous sulphate 175	~1.75 %

In the literature coagulant dosages are commonly compared in two different ways, either in mg/L of the active substance or mg/L of the chemical, which might cause confusion when comparing results of different studies.³¹ In this work, the coagulants were compared based on the concentration of active substance, in milligrams per litre (mg/L) of metal ions, because the chemical specifications were supplied by the manufacturer in this form.

Different types of organic polyelectrolyte flocculants were tested in combination with the primary inorganic coagulants and compared based on the weight to volume ratio (mg/L) of dry powder to water. The primary differences between the polyelectrolytes were the charge density and the molecular weight. The majority of tested polymers were polyacrylamides intended for flocculation processes. During preliminary jar-testing, it was found that cationic and non-ionic polymers seemed to flocculate considerably better. Such preliminary testing was done by visual observation of floc

formation by several persons. According to the supplier of chemicals, their cationic polymers usually work better when treating oily waste.

Table 8: List of polyelectrolyte flocculants tested

Name	Charge Density	Charge
SUPERFLOC C-491 /HMW	Very Low	Cationic
SUPERFLOC C-492 /HMW	Low	Cationic
SUPERFLOC C-493 /HMW	Medium-low	Cationic
SUPERFLOC C-494 /HMW	Medium-high	Cationic
SUPERFLOC C-496 /HMW	High	Cationic
SUPERFLOC C-498 /HMW	Very High	Cationic
AI00-HWM	Low	Anionic

A series of twelve different cationic and one anionic polyacrylamide-based polyelectrolytes were tested (Table 8). There were six levels of charge density ranging from very low to very high. For each charge density, normal and high molecular weight (HMW) were tested.

4.2 Bench-scale jar tests

4.2.1 Choice of the method

Bench-scale jar tests in is a standard method to investigate wastewater flocculation and sedimentation properties. Jar tests aiming to determine the best conditions for coagulation and flocculation include selection of the type of coagulants and flocculants, dosage, and the most efficient pH level at which to operate. The name “jar tests” refers to the procedure of using several 1-2 litre jars to conduct the experiments in. According to the Nalco Water Handbook ⁴, “observational results in a jar test remain the best method for coagulant selection”. Bratby ³¹ also claims jar testing to be an ideal tool for coagulation optimisation, with many studies in the past 85 years supporting the validity and applicability of the method. Further supporting the choice of method, Edzwald ³² stated that:

“The chemistry of coagulation for sedimentation and DAF plants is similar, therefore coagulant dosages and pH conditions are identical to forming flocs“.

4.2.2 Jar test experimental design

The jar test experiments were designed and executed in the following order:

1. Determination of best coagulant and pH.
2. Determination of the best polymer in combination with the coagulant from step one.
3. Dosages optimisation

In addition to the three primary goals above, the influence of mixing time was investigated, and one experiment regarding H₂S removal was conducted.

The performance of five different coagulants (Table 7) was examined in step one. In the first step, a coagulant dosage equal to the one used in the full-scale process (10 mg/l calculated as metal) was used. Removal of COD, oil, phosphorus, and turbidity was investigated as a function of pH. The pH pre-coagulant addition was varied in steps of one, from pH 5 to 10. One sample was taken for each coagulant and pH combination. The results were then plotted as the removal rate, remaining contaminant or both, parameters vs pH. The best coagulant was then chosen for the next step, based on several criteria.

In step two, the coagulant chosen in step one was combined with different polyelectrolyte flocculants. The pH, pre-coagulant addition, was varied from 7 to 9. The type of coagulant was the independent variable while the measured contaminants were the dependent variables. The coagulant dose was kept constant, at 10 mg/L of Fe³⁺.

In the third step, the optimal chemical dosages were determined. The wastewater was treated with coagulant dosages (mg/l calculated as metal), in several different experiments for different feed water samples. Some experiments were done with the coagulant only, others with both coagulant and flocculants. In these experiments, only turbidity was analysed.

4.2.3 Jar test experimental procedure

Six one litre transparent cylindrical glass jars were used, and the experiments were run side-by-side. The jar testing apparatus (Flocculator 2000) was supplied by Kemira Oyj. Each jar could be separately adjusted for rapid agitation time (400 rpm), slow agitation time (40 rpm), and settling time (no mixing). A program of 30-sec rapid mixing followed by 4 min 30 sec min slow mixing and then 5 min settling was used. The

agitator was of the paddle type, and the axis was kept in place by a frame also working as a baffle (Figure 7).

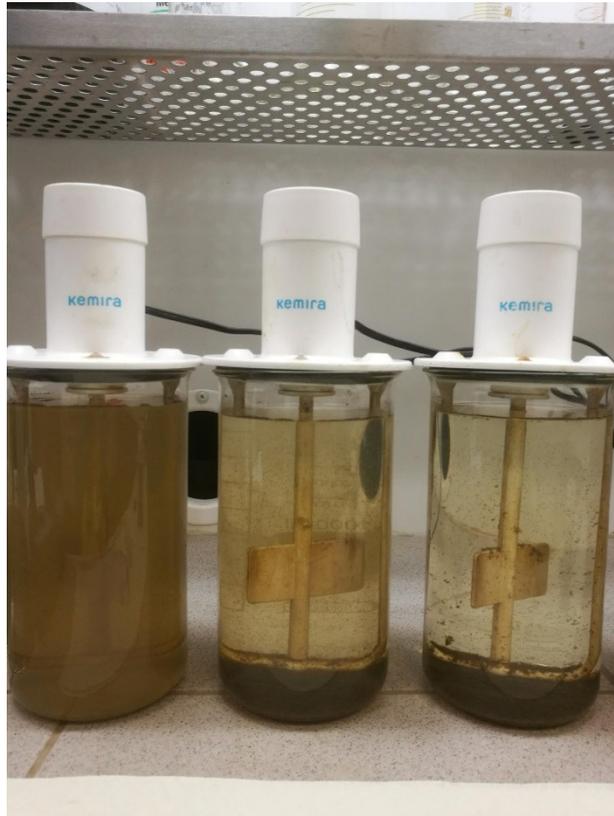


Figure 7: Jar test in progress. Coagulant doses from the left: 5, 10, 20 mg/L Fe from ferric sulphate.

Water samples were taken from a side stream of the flocculation tank inlet pipeline, after the API oil-water decanting treatment. Ten-litre plastic buckets were used. Before transferring the sample to the one-litre jars, the initial pH was adjusted with NaOH and H₂SO₄, the temperature was measured, and water was thoroughly mixed. Thereafter the six jars were filled with one litre each. All experiments were carried out at approximately room temperature (25°C).

Before starting an experiment, the jars were mixed for 5 seconds using the rapid setting (400 rpm). At t=0 s the experiment and rapid mixing were commenced, and the coagulant was added. If a flocculant was used in addition to the coagulant, it was added at t=20 s. At t=30 s mixing was slowed down to the slow setting (40 rpm). At t=4 min 30 sec mixing was discontinued. Experiments were concluded at t=9 min 30 sec, and the samples were taken from the jars for analysis from the middle part of the jar, halfway to the bottom from the surface. Floc formation was observed during the whole

experiment. The final pH was measured, and samples for analysis Floc strength was also visually observed by mixing the fluid rapidly for a couple of seconds after sampling.

Coagulants were added directly from the concentrated stock solution using a micropipette. Flocculation polymer solutions had to be prepared on site. The polymer solutions were prepared from dry powder and tap water (as in the full-scale process). The dry polymer powder was weighed and slowly dosed into the water vortex created in the magnet stirred beaker. Stirring was sustained for 30 min, thereafter the homogeneity of the solution was inspected. After discontinuing the mixing, the solution was let to settle for 30 minutes or more. The polymer solutions were added to the jars with microliter pipettes. The solutions were stored at room temperature, covered with aluminium foil to prevent evaporation, for a maximal time of a week. New polymer solutions were made weekly, all on the same day.

4.3 Full-scale experiments

4.3.1 Materials used

Full-scale experiments were conducted because jar tests cannot completely simulate the real process, especially the real degree of ferrous sulphate oxidation in full-scale processes. In the full-scale experiment, 100% of the refinery wastewater stream was treated for several months. The properties of the feed water varied to a high degree during the experiment, e.g. the oil index (section 4.4.4) varied from 15 mg/l to > 100 mg/l. Ferric sulphate was used as a coagulant with either anionic or cationic polyacrylamides. In order to feed the coagulation chemical to the flocculation-reactor during the experiment, a pump station was built. The reason for this was twofold. First, the existing pumps used for the dilute ferrous solution were too large for the novel highly concentrated coagulant, and with unknown corrosion durability. Second, the existing infrastructure and chemicals were used for control experiments. The coagulation chemicals were fed to the process with two piston pumps and pipes, from one cubic meter intermediate bulk containers (IBC). The coagulant pump station is pictured in Figure 8 and Figure 9.



Figure 8: Picture of the full-scale experimental equipment feed pumps and piping



Figure 9: Picture of the full-scale experimental equipment and ferric sulphate solution "feed tank".

The new polymer solutions were prepared with an identical polymer solution preparation system (Figure 10), as used in the process normally consisting of a mixing eductor, a polymer granule silo, a mixing tank and a storage tank. The solution was fed to the process with the fixed pumps on site. Before changing from one polymer to another one all vessels and pipes were thoroughly washed.

The feed rates of coagulants and flocculants were adjusted by manually changing the pump settings. The chemical feed flow rate adjustments were also regularly controlled by recording time to fill a one (or ten) litre bottle/bucket. The pH was adjusted with caustic soda using the existing pH-regulation system and was measured with an on-line industrial pH meter with automatic washing. The pH meter was calibrated every week. The influent wastewater flow rate was adjusted by choking the feed, at the main feed valve.



Figure 10: Polymer solution preparation system. The storage silo is on top of the vortex mixer with an eductor below it. The solution is pumped to the storage vessel seen to the top right.

4.3.2 Parameters

Different system parameters were investigated. To understand how varying the parameters affected the process, the interdependence of variables was determined first. In Table 9 process variables, the possibilities of their adjustment, and which other process variables are presumably affecting a particular variable are presented.

Table 9: Chemical treatment variables

Variable	Adjustability	Interdependence
Temperature	not possible to affect	Independent
Influent composition	not possible to affect	Independent
Flow rate	Maximal flow can be set; minimum cannot be set	Independent
Coagulant	Type and dosage	Concentration dependent on flow
Flocculant	Type and dosage	Concentration dependent on flow

pH	Limited adjustability, fluctuates	Dependent on coagulant type and dosage, influent composition, temperature
Flocculator mixing and aeration	aerator on or off (1 or 0) No other mixing available	Independent
Saturator pressure	3.5 - 4.0 bar	Dependent on recycle flow, air flow rate, excess air removal rate
Recycle flow	Adjustable in discrete steps	Absolute flow dependent on saturator pressure, air flow rate, excess air removal. Recycle flow percentage also dependent on flow rate.
Air flow rate	Adjustable	Dependent on saturator pressure, excess air removal rate, recycle flow rate
Excess air removal	Adjustable	Dependent on recycle flow, air flow rate, saturator pressure

CSTR and two CSTR in series residence times and step responses were calculated to determine an appropriate interval for sample collection. Calculations were made with the assumption of the flocculator and flotator being ideal continuously stirred tank reactors (two CSTR in series). A safety margin of 2 h was added to the results to account for the non-ideal conditions when taking samples.

Because of a small size of equalisation tank, and absence of large buffer capacity the flow is difficult to control. However, the feed can be choked at a particular maximum flow rate for a limited time.

4.3.3 Experimental design

4.3.3.1 Determination of adjustable parameters

First, the adjustable parameters and their interdependence were examined, based on the operators and the author's experience with the process. The full-scale experiments were designed so that other variables than the independent variable were kept as constant as possible.

4.3.3.2 Suspended solids as a function of pressure:

The efficiency of the DAF unit was investigated by adjusting the dispersion tank pressure between 3.5 to 4.0 bars, in two discrete levels, high and low. The dispersion tank pressure was the independent variable, while the amount of suspended solids in the DAF effluent was the dependent variable, and all other parameters were kept constant as much as possible. The pressure was alternated between low and high values, changing every 24 h. The samples were taken every 20-24 h after changing the pressure from the DAF overflow. The hypothesis was that there is a statistically significant difference in flotator efficiency as a function of pressure. The process was run with standard parameters and chemical aids, approx. 10 mg/l Fe as ferrous sulphate, 4 mg/L of anionic polyacrylamide, and pH 9.0 - 9.5.

4.3.3.3 Suspended solids as a function of airflow

The pressure was adjusted to 3.9 bars, and the air volume flow was varied as an independent variable. The pressure was adjusted with the excess air removal valve, and keeping the recycle flow constant. A set of experiments were done using only one recycle pump, with a recycle-flow of 65 m³/h. Airflow was varied in steps of 5, 10, 20, 30, 40 Nm³/h. The flotator surface was observed visually to determine bubble quantity and flotation behaviour. Experiments, where the quantity of SS was analysed, were done with 20 and 30 Nm³/h of air.

4.3.3.4 Turbidity, SS, Oil, COD, phosphorus content as a function of pH

An experiment determining the effects of pH as an independent variable was carried out. The pH in the flocculator was adjusted between 7—9.5 and the ferric sulphate and anionic polyelectrolyte AI00-HMW doses were kept constant at approximately 10 mg/l Fe and 4 mg/L polymer respectively.

4.3.3.5 Turbidity, SS, Oil, COD, phosphorus content as a function of anionic polymer dose

The coagulant was changed to ferric sulphate, and run at an equivalent dose of iron in comparison to the current process with ferrous sulphate, in the range of 7-10 mg/L. The polymer used was the same as in the current process (A100-HMW), and the dose (independent variable) was varied in the range 0.35 - 4.6 mg/L.

4.3.3.6 Turbidity, SS, Oil, COD, phosphorus as a function of cationic polymer dose

Ferric sulphate was used as a coagulant, and run at an equivalent dose of iron in comparison to the current process with ferrous sulphate, in the range of 7-10 mg/L. The polymer was changed to cationic (C491-HMW), and the dose (independent variable) was varied in the range 0 - 4.6 mg/L.

4.3.3.7 Coagulant dosage

When ferric sulphate was used instead of the conventional ferrous sulphate, it was dosed in an equal molar ratio of Fe^{3+} to Fe^{2+} . Not too much weight was put on investigating the optimal coagulant dosage because it changes daily depending on the wastewater properties. As commonly known, increasing the coagulant dosage yields better purification results up to a certain point. Therefore based on the known facts, confirmed by the jar test results, adjusting the coagulant dose based on the flotator overflow turbidity was done instead, for all experiments after 1.3.2018. The method is used industrially. In the case of rising turbidity, the iron dose was increased, and the opposite was done when turbidity went down. The setpoint turbidity was chosen based on an educated guess due to the limited available turbidity data, and the turbidity of 8 NTU was chosen to be the point where the coagulant dose was increased. When more process data are available, these levels should be revised, to better represent the correlation of turbidity to other impurities.

4.4 Analytical methods

4.4.1 Introduction to analytical methods

Samples were analysed for several different types of impurities. Some analysis was done by the Naantali Refinery quality control laboratory; others were conducted in the field laboratory where the jar tests were done. All applied analytical methods are standard ones in the wastewater industry. This section lists the analytical methods used in this work.

4.4.2 COD

Chemical Oxygen Demand (COD) was determined according to the ISO 15705:2002 standard by the Naantali Refinery QC-laboratory. A sealed tube method (ST-COD) was used, and the absorbance at 440 nm was measured with a HACH LANGE DR3900 spectrophotometer. The reagent tubes/cuvettes used were HACH LCI 500. The samples were oxidised with sulphuric acid and potassium dichromate in the presence of silver sulphate and mercury(II)sulphate for two hours at 150°C. Absorbance was automatically calculated to chemical oxygen demand (mg O₂/l) by the spectrophotometer.

4.4.3 Phosphate

Phosphorus ($PO_4^{-3} - P$), as mg/L of elemental phosphorus, was determined by using HACH Lange LCK 349 cuvettes and a HACH LANGE DR3900 spectrophotometer (standard ISO 6878).

4.4.4 Oil, gas chromatography

Hydrocarbons were quantitatively determined (hydrocarbon oil index, mg/l) by solvent extraction and gas chromatography (ISO 9377-2:2000) by the Naantali refinery QC-laboratory. Extraction was done using n-pentane. Extracts were filtered using Florisil-filtration, particle size 150-250 µm (60-100 mesh). A Perkin Elmer Clarus 680 gas chromatograph was used, the column was fused silica (5 m, 0.1 mm, 0.1 µm) with 5% phenyl methylpolysiloxane while as the pre-column Retention GAP 4m, id 0.5 mm methyl deactivated was applied. Hydrogen served as a carrier gas, and detection was done by a flame ionisation detector (FID). Results were calculated by the peak integration. The lower detection limit for the method is 0.1 mg/l. Calibration was done according to the ISO standard.

4.4.5 Suspended solids

Suspended solids (SS) were determined gravimetrically by vacuum filtering a fixed volume, drying the filter and then measuring the weight gain. The procedure was done by the Naantali Refinery QC-laboratory.

4.4.6 Turbidity

Turbidity was measured using a HACH LANGE 2100Q portable turbidimeter. The meter measures transmitted and scattered (90°) light. The measurement mode used was signal averaging of 12 measurements. Results were given in nephelometric turbidity units (NTU) and were automatically calculated. Turbidity measurements were done within one minute of taking the sample. The meter was calibrated once, and the calibration was verified several times during the experiments with standards.

4.4.7 Measurement of pH

In the jar tests, the pH was measured using semi-automatic pH-meter. The pH of the full-scale experiments was measured with an on-line pH meter (AI-3404) and confirmed with the pH meter in the laboratory. Both meters were calibrated once per week.

4.4.8 Hydrogen sulphide

Hydrogen sulphide was determined by potentiometric titration in water solution with AgNO₃. 20 ml of ammonium-NaOH buffer solution was added to the 100 ml sample before titration. Autotitrator Mettler Toledo T90 and combination electrode Metrohm Ag Titrode 6.0430.100 was used.

4.5 Calculations

4.5.1 Efficiency calculations

The relative removal of a substance (contaminant) was calculated as follows:

$$\text{removal \%} = \frac{C_{in} - C_{out}}{C_{in}} \cdot 100\% \quad (4)$$

where C_{in} is concentration of substance in untreated water and C_{out} is the concentration of substance in treated water.

4.5.2 Residence time and step change calculations

The residence time is given by equation (5)

$$\tau = \frac{V}{Q} = \frac{[m^3]}{[m^3/h]} = [h] \quad (5)$$

where τ [h] is the residence time (or time constant), V [m³] is the reactor volume, and Q [m³/h] the flow rate. To determine the step response for the flocculator and the flotator, e.g. the time required for the reactors to reach a sufficient steady state after a parameter change for sampling purposes, the following equation (6) was used:

$$c_{out}(t) = c_o + \left(1 - e^{-\frac{t}{\tau}}\right) \Delta c_{in} \quad (6)$$

where $c_{in}(t)$ is the overflow concentration, c_o the initial concentration, t [h] the time from the step change creating the imbalance, and Δc_{in} the magnitude of the step change. Equation (6) assumes perfect backmixing. Most samples were collected from the flotator, but the coagulants were added to the flocculator. Therefore, to calculate the step response for two CSTRs in series, equation (7) was used:

$$c_{out}(t) = c_o + \Delta c_{in} \left[1 - \frac{\tau_1}{\tau_1 - \tau_2} e^{-t/\tau_1} + \frac{\tau_2}{\tau_1 - \tau_2} e^{-t/\tau_2} \right] \quad (7)$$

where τ_1 and τ_2 are the time constants for the flocculator and flotator, respectively.

4.5.3 Cost calculations

The cost of chemicals were calculated with fixed prices retrieved from the procurement department or indicative prices received from the chemical supplier. The annual costs of chemicals were calculated using the following formula:

$$\text{annual cost in } \text{€} = \frac{c \cdot \dot{V} \cdot P}{x \cdot 10^6} \quad (8)$$

where c [mg/L] is the desired average concentration of the active component of the chemical in the wastewater, x is the fraction (wt/wt) of the active component in the chemical, \dot{V} [m³/year] is the annual flow of wastewater, and P the price of a chemical in €/ton.

4.5.4 Statistical methods

In all the experiments where t-tests were used to analyse results, except for the regression line p-values, a more robust t-test with two tails and unequal variance (Welch's t-test) was used. In the regression line fitting, the Excel Analysis ToolPak's regression analysis was used (Student's t-test).

5 Results

5.1 Jar test results

5.1.1 Coagulant selection

A coagulant for the full-scale experiment was selected by jar testing, which is a standard method for determining the optimal coagulation and flocculation conditions in wastewater treatment. The pH dependence of the contaminant reduction was investigated for five coagulants. The coagulants were dosed and compared by equal weights of metal, in mg/L. The initial pH refers to the level of pH at which the samples were adjusted, before the addition of coagulants. The post-treatment pH was usually between 0.5 to 1 pH levels lower. The post-treatment pH corresponds to the full-scale process.

5.1.1.1 Turbidity as a function of pH (unfiltered)

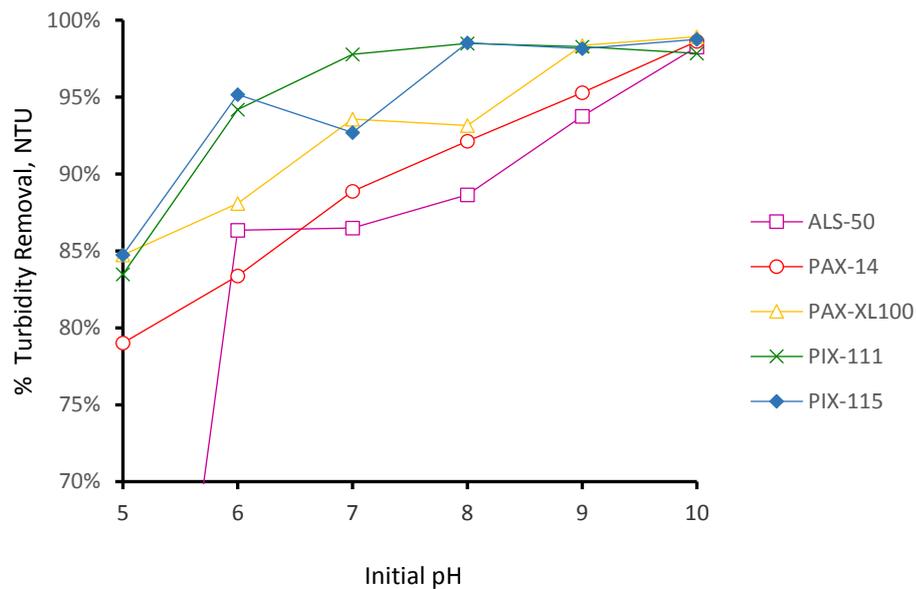


Figure II: Turbidity removal as a function of initial pH for unfiltered jar test supernatant.

Changes in turbidity were investigated at different initial pH levels. The pH was adjusted before adding the coagulant and starting the mixing program. As shown in

Figure II, all coagulants except PIX-III (ferric chloride) have their highest observed removal of turbidity at an initial pH of 10. PIX-III has a maximum removal of 98.5% at initial pH 8. Turbidity removal is > 98% for both ferric coagulants when the initial pH is 8 or higher.

5.1.1.2 Turbidity as a function of pH (filtered)

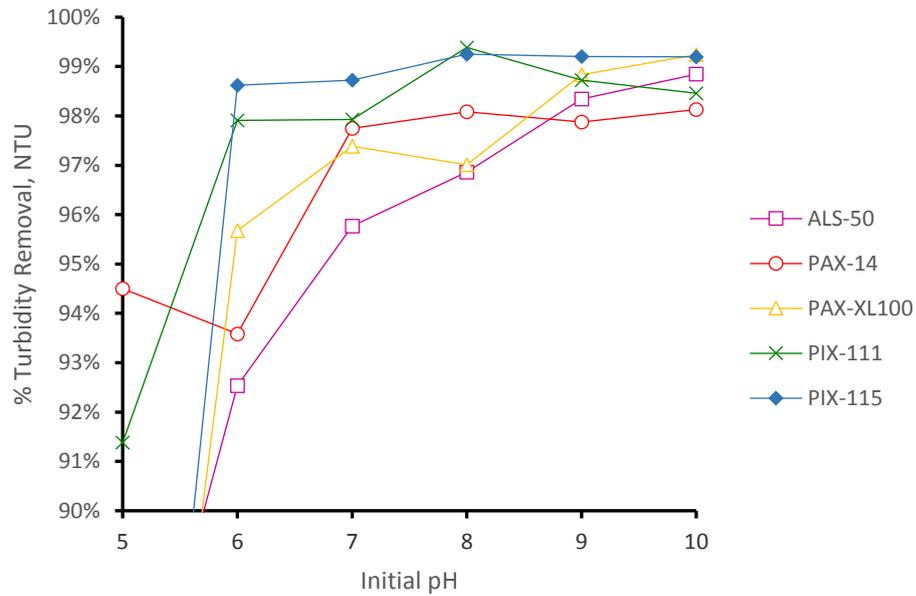


Figure 12: Turbidity removal as a function of initial pH for filtered jar test supernatant.

A part of the supernatant was filtered to remove non-settled floc and micro floc. As Figure 12 indicates, the highest removal of turbidity was achieved by PIX-III (ferric chloride) at 99.4% and PIX-II5 (ferric sulphate) at 99.3% at an initial pH of 8. The iron-based coagulants made larger flocs, as observed visually and indicated by the results of the filtered turbidity experiments (Figure 12). A larger part of the iron-floc remained in the filter, while some of the smaller aluminium-floc went through, as shown when comparing Figure 11 and Figure 12.

5.1.1.3 Oil removal as a function of pH

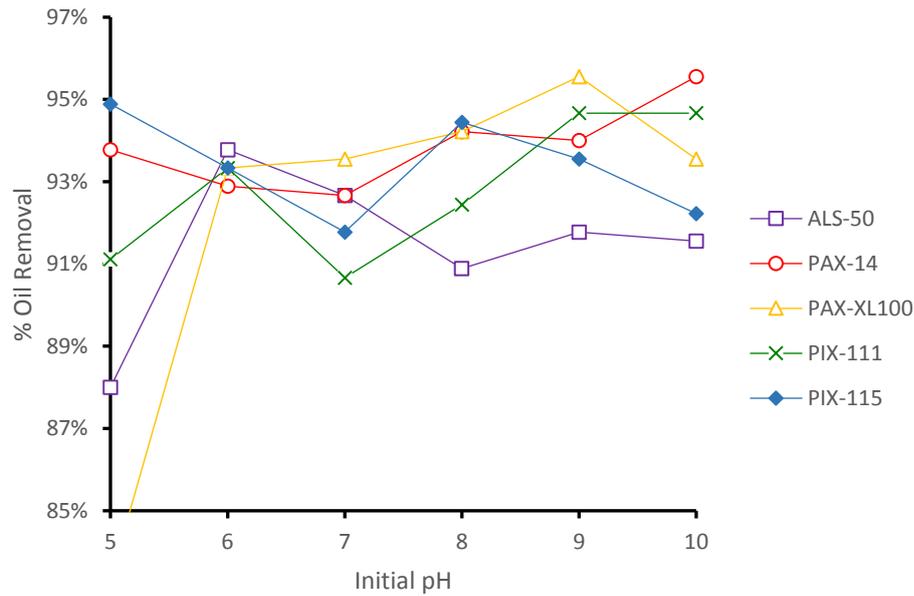


Figure 13: Oil removal as a function of initial pH

The effect of initial pH and type of coagulant on oil removal is presented in Figure 13. Depending on the initial pH, different coagulants performed better. The highest degree of oil removal was achieved by the two polyaluminium chlorides: PAX-XL100 at the initial pH 9 and PAX-14 at the initial pH 10, both resulting in an oil removal of 95.6% in relation to the zero sample. At pH 8 PIX-115 (ferric sulphate) displayed the best performance, removing 94.5% of the oil. Post-treatment pH was 0.5-1 pH units lower than the initial pH, therefore applying it to the full-scale process, the results suggest that the best coagulant at pH 5-6 is aluminium sulphate, for pH 6-7 PAX-XL100, pH 7-8 ferric sulphate or either PAC, and above pH 8 either PAC or ferric chloride. Overall, the oil removal performance of the coagulants as a function of pH is somewhat irregular.

5.1.1.4 Phosphorus removal as a function of pH

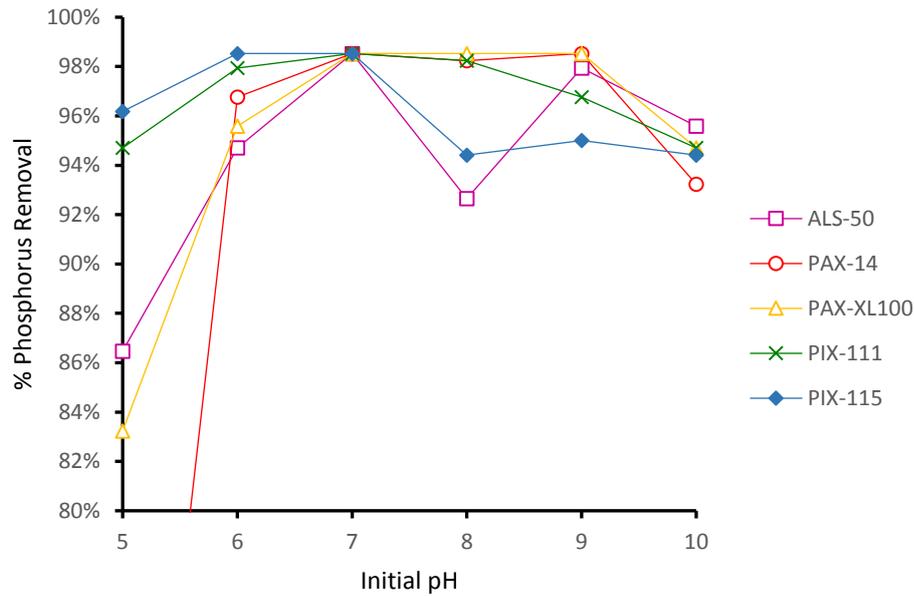


Figure 14: Phosphorus removal as a function of initial pH

The highest possible degree of phosphorus removal was 98.5%, with the results being limited by the relationships of the lower detection limit of the analytical method used to the initial phosphate concentration (LDL = 0.005 mg/l, zero sample phosphate concentration = 0.34 mg/l). In reality, the percentage of phosphate removal might have been anything between 98.5% and 100%. All coagulants had a phosphate removal of $\geq 98.5\%$ when samples with an initial pH of 7 were treated (Figure 14). The post-treatment pH varied between 6-6.7 for all samples with an initial pH = 7. PIX-115 (ferric sulphate) also achieved a removal rate of $\geq 98.5\%$ at an initial pH of 6. The pre-hydrolysed polyaluminium chloride coagulant PAX-XL100 removed $\geq 98.5\%$ in all samples with initial pH of 7-9. PAX-14 also removed $\geq 98.5\%$ at initial pH 9. The final pH for the treated samples was usually slightly lower than the initial pH, with a maximum of 1.0 pH units lower than the initial pH. The results also suggest that ferric coagulants remove phosphate better below neutral pH, while PAC-coagulants perform better in more alkaline environments. Aluminium sulphate and ferric sulphate have interesting trend-breaking dips in the curve at initial pH 8 (post-treatment pH 7-8). When applying the findings to industrial scale, the best phosphate removal was found at around pH 6-6.5. These results are well in line with the research of³³, who found the optimum for both aluminium- and iron-based coagulants to be at pH 5-7.

5.1.1.5 COD removal as a function of pH

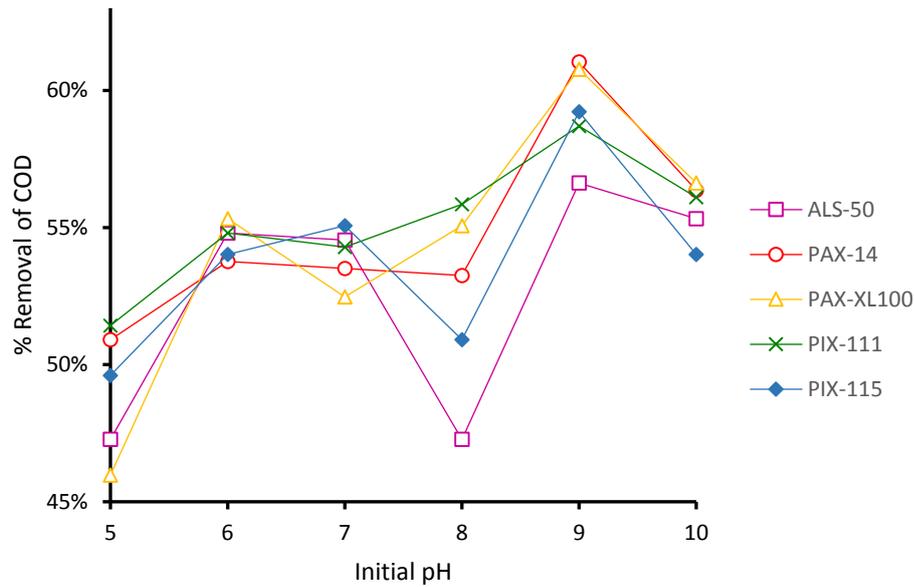


Figure 15: Removal of Chemical Oxygen Demand (COD) as a function of initial pH

The jar tests examining COD removal as a function of pH suggested that COD removal is more effective in more alkaline conditions. Figure 15 illustrates how the initial pH influenced the reduction of COD. All coagulants had their maximum removal of COD at an initial pH 9. The highest degree of COD removal (61.0%) was in the sample treated with PAX-14, followed by PAX-XL100 (60.8%), both polyaluminium chlorides. The removal% trends upwards with increasing pH. The maxima for all coagulants were observed at initial pH 9, or post-treatment pH 8-9. For ferric sulphate and aluminium sulphate the COD removal trend-braking behaviour was again observed at the initial pH 8. All coagulants performed similarly below neutral pH, while PAC performed better under alkaline conditions. Aluminium sulphate performed worst compared to other coagulants at initial pH >7.

5.1.1.6 Removal of hydrogen sulphide

An experiment for H₂S removal with trivalent iron (PIX-115) and aluminium (PAX-XL100) based salts was conducted. The coagulant dose was 20 mg/L of the metal ion (a molar ratio of 0.6:1 of Fe³⁺ to H₂S and 1.2:1 of Al³⁺ to H₂S). The data (Figure 16) suggest that trivalent iron removed 95% and aluminium 29% of H₂S, respectively. The experiments were carried out simultaneously but the analysis was started with the zero sample.

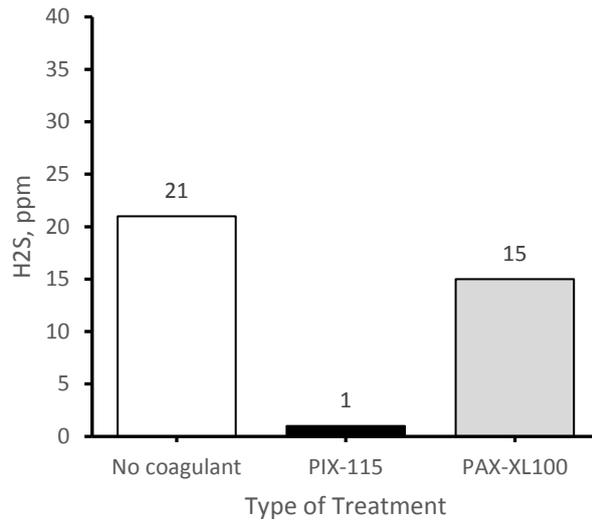


Figure 16: H₂S removal. A comparison of trivalent iron and aluminium for the removal of H₂S from the WWTP feed.

5.1.2 Polymer selection

5.1.2.1 Turbidity as a function of pH

The turbidity as a function of the initial pH was compared for six cationic polymers (Figure 17). All polymers had a minimum of remaining turbidity in the samples with an initial pH 8.4, which was the sample with non-adjusted pH. The initial pH was measured before the addition of 10 mg/L of Fe from ferric sulphate. The polyelectrolyte

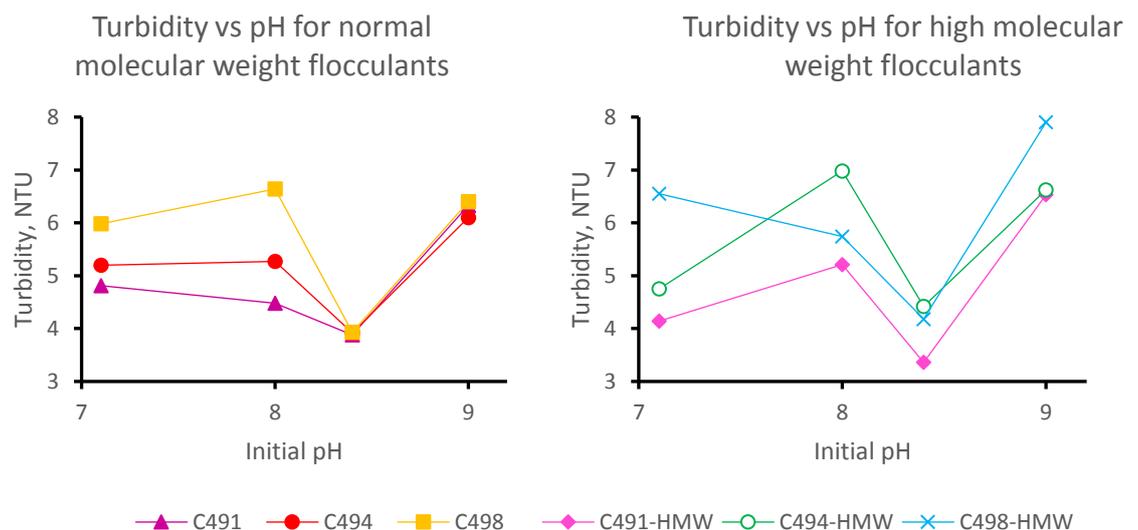


Figure 17: Comparison of polymers with different charge densities and molecular weights. Turbidity as a function of initial pH. Polymers with standard molecular weight on the left side, and high molecular weight on the right.

C491-HMW resulted in the lowest turbidity of 3.4 NTU at the initial pH 8.4. The overall

difference between the polymers is small in comparison with the non-treated water with a turbidity of 123 NTU. The more neutral polyelectrolytes performed better than polymers with a higher cationic charge density.

5.1.2.2 Turbidity as a function of polymer dosage and type

The influence of the polymer dosage on the turbidity was examined (Figure 18). The experiments were done with a feed water sample different from the ones in Figure 17. The results suggest that a lower polymer dose is better for the removal of turbidity. Polyelectrolyte C494 had the lowest remaining turbidity at 5.5 NTU for 1.25 mg/L, but also the highest at 24.6 NTU and 5 mg/L. Polymer C491 showed the lowest variance. Overall, more neutrally charged polymers performed better than strongly charged ones, and the results were more stable. Results in the literature vary greatly depending on the wastewater properties and the specific combination with metal coagulants.

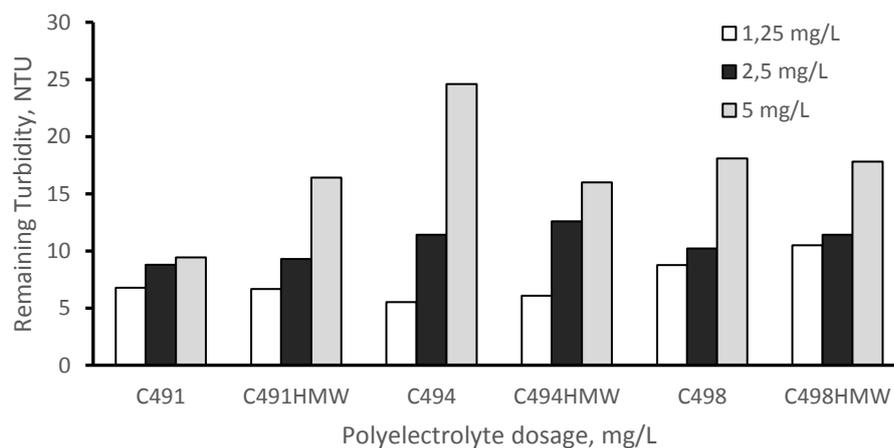


Figure 18: Turbidity vs polyelectrolyte dose for different polyelectrolytes. A dose of 10 mg/L Fe^{3+} of ferric sulphate was used at pH 8. Initial turbidity was 101 NTU.

5.1.3 Optimal dosages during process disturbances

When process disturbances and anomalies appeared, the feed was analysed, and the following jar tests were conducted. This was done to learn if the chemicals screened can be used in more demanding situations, thus increasing the practical usefulness of this work.

During process disturbance A, the flotator (AD-3403) effluent was a slightly white-coloured, unspecified emulsion. The DAF effluent was also grey with turbidity of 203 NTU, caused by the emulsion flowing through the unit. A sample was taken and treated

with ferric sulphate. A rapid reduction in turbidity was observed between 0 and 20 mg/L Fe³⁺, and a minimum (possible colloid charge reversal) of 7.7 NTU was observed at 40 mg/L Fe³⁺ (Figure 19). This is four times the standard dose of 10 mg/L Fe.

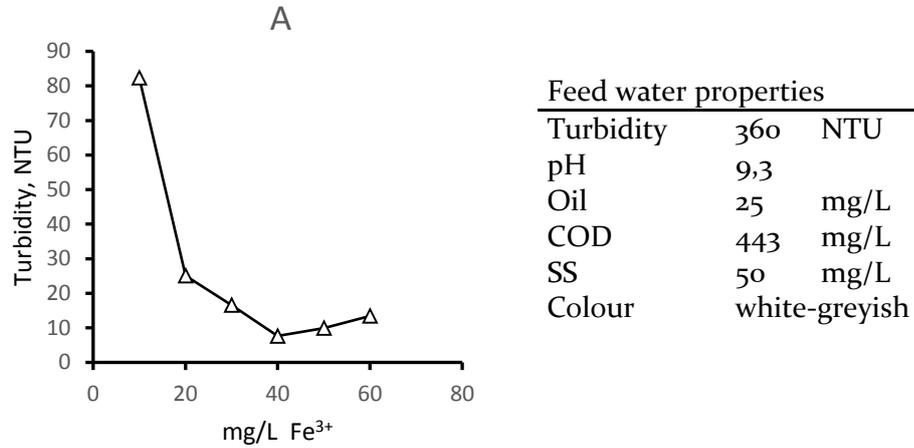


Figure 19: Disturbance A. Turbidity as a function of ferric sulphate dosage.

Process disturbance B occurred because of very high amounts of hydrogen sulphide (>200 ppm, normal <20 ppm) and a moderately high concentration of oil (59 mg/L) in the feed, combined with a high feed pH of 9.3 (normal pH 7-8). Chapter 3.3 (Table 5) contains more detailed data of the typical feedwater properties. The full-scale process operating on ferrous sulphate performed poorly.

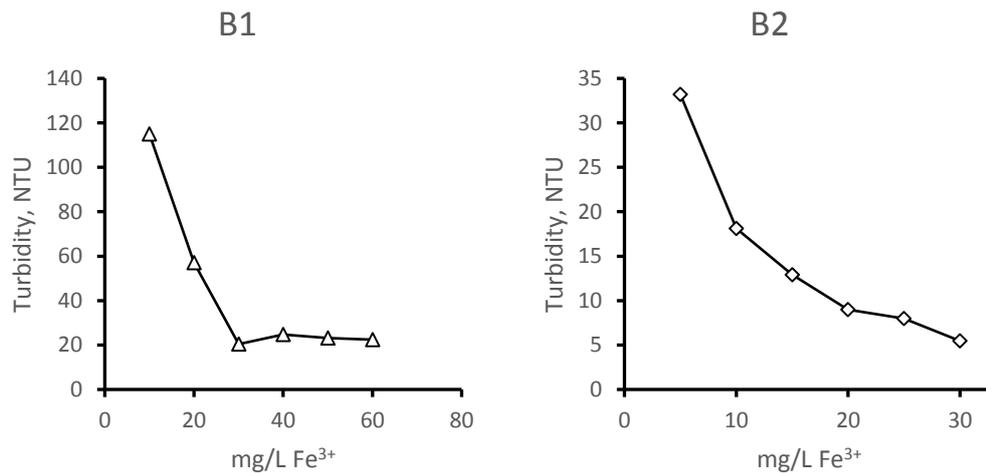


Figure 20: Disturbance B. Turbidity as a function of ferric sulphate dose without (B1) and with (B2) polyelectrolyte. The polymer used was C491-HMW at 2.5 mg/L.

A sample was taken for jar tests. Half of the feed water sample was treated with ferric sulphate only (Figure 20 B1) and the other half with ferric sulphate combined with a

constant dose of polyelectrolyte C491HMW (Figure 20 B2). For ferric sulphate only, the highest removal of turbidity was observed at 30 mg/L Fe. For ferric sulphate and polyelectrolyte, the turbidity decreased with the iron dosage, however no maximum of removal was found within the studied concentration range. The combined application of polymer and ferric sulphate lowered the turbidity to less than a quarter of the level achieved by ferric sulphate alone.

Disturbance C (Figure 21) is a more common situation, with high levels of hydrogen sulphide (60 ppm) in the feed. The feed turbidity was only 120 NTU, which is in the normal range of 100-200 NTU. A water sample was taken and treated with various doses of ferric sulphate and polyelectrolyte C491-HMW at 2.5 mg/L. When treated with a low dose (5 mg/L Fe) of ferric sulphate, the turbidity increased to 133 NTU, and thereafter decreased. Interestingly, the lowest measured turbidity of all experiments in this thesis (1.44 NTU) was observed at the iron dose of 25 mg/L.

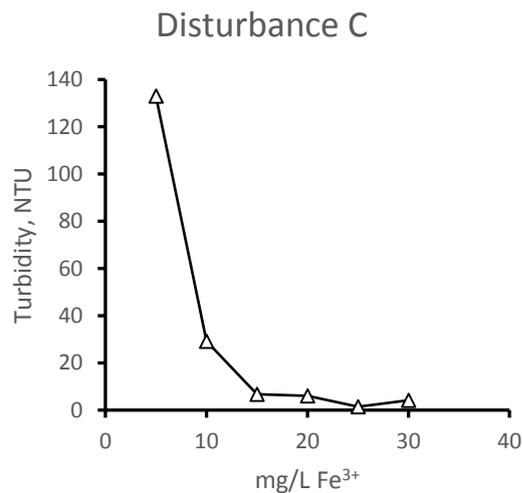


Figure 21: Disturbance C. Turbidity as a function of ferric sulphate dosage, with 2.5 mg/l of polyelectrolyte C491-HMW.

5.1.4 Turbidity as a function of mixing time

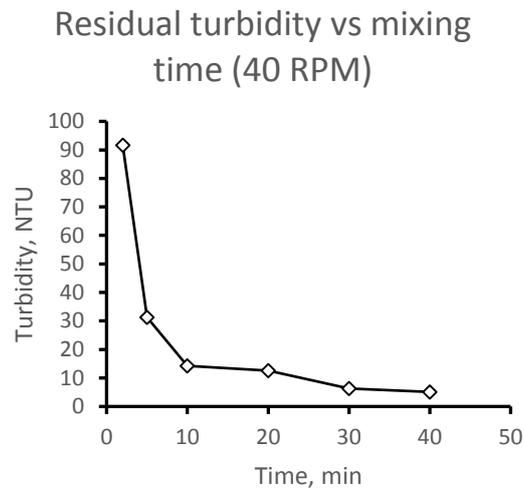


Figure 22: Residual turbidity as a function of mixing time using the slow setting (40 rpm) and 5 minutes of settling. Ferric sulphate was used with a 5 mg/L dosing (calculated as Fe).

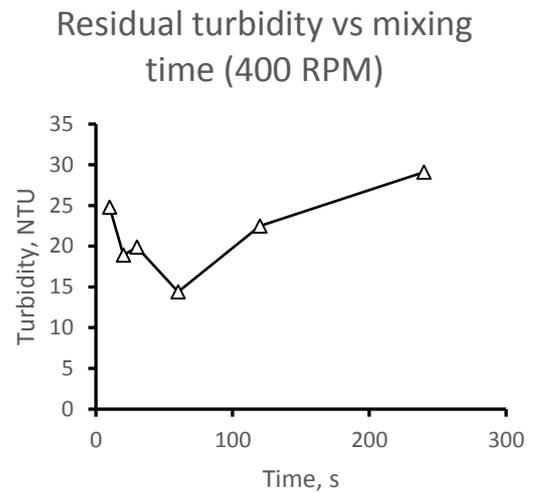


Figure 23: Residual turbidity as a function of fast mixing time (400 rpm), followed by 2 min slow mixing (40 rpm) and 5 minutes of settling. Ferric sulphate with a 5 mg/L dosing (calculated as Fe).

The influence of the stirring speed and mixing time on the turbidity was investigated by jar testing. Figure 22 shows that the turbidity correlates inversely with the mixing time when the stirring speed was 40 rpm. More efficient mixing at 400 rpm (Figure 23) decreased the turbidity faster, reaching a minimum of 14.4 NTU after one minute, followed thereafter by increasing turbidity. Slow mixing (40 rpm) allowed to reach similar turbidity (14.2 NTU) after 10 minutes. The rpm-levels were chosen based on the two discrete levels for rapid and slow mixing available in the jar test equipment.

5.2 Full-scale experimental results

5.2.1 Determining sampling intervals

A step change response and residence time calculations were undertaken to determine appropriate sampling intervals. The time to reach the steady state was calculated. The change in the reactor coagulant concentration when changing the dose from 10 to 20 mg/L, for a flow of 100 and 200 m³/h, can be seen in Figure 24 and Figure 25. The calculations are based on the ideal cases (assuming complete backmixing, a CSTR), a safety margin of 2 h should be added to yield more reliable results.

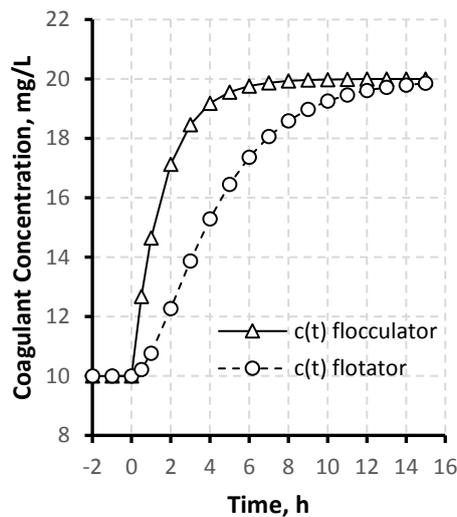


Figure 24: The step response $c(t)$ for the flocculator and flotator at 100 m³/h flow, when increasing the coagulant dose from 10 to 20 mg/L.

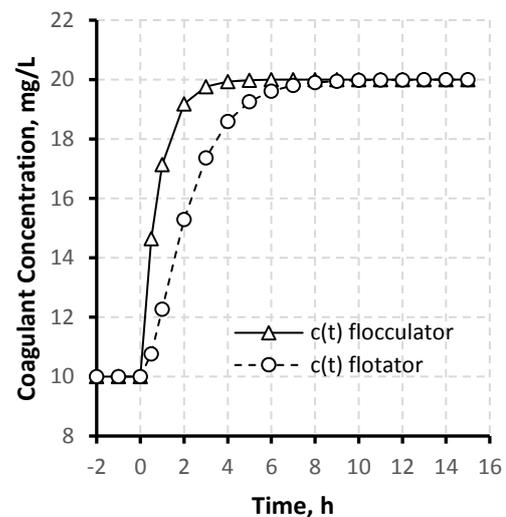


Figure 25: The step response $c(t)$ for the flocculator and flotator at 200 m³/h flow, when increasing the coagulant dose from 10 to 20 mg/L.

5.2.2 Saturator pressure

The saturator tank pressure as an independent variable was varied, in two levels: low (3.5 bar) and high (4.0 bar) (Figure 26). The amount of total suspended solids (TSS) was the dependent variable. Because no pressure-dependent differences could be seen in the results, a two-sample t-test assuming unequal variances was conducted to test the null hypothesis; that pressure does not influence the TSS concentrations. The results were not significant ($p = 0.76 > \alpha = 0.05$). Thus, the results suggest that the saturator pressure did not influence the flotator performance regarding TSS in a significant way.

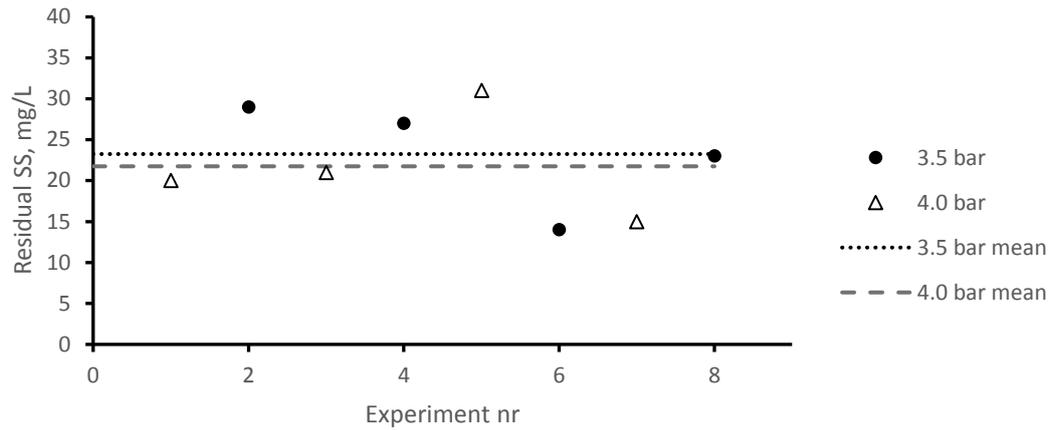


Figure 26: Total suspended solids response for two levels of saturator pressure (3.5 and 4 bar).

Because this experimental result conflicted with previous findings in the literature, where higher pressure improves the performance, the reason was investigated.^{17,28} It was found that the air flow meter FC-3407 was not malfunctioning, as was the consensus on site, but the FC-3407-CON flow controller was stuck, or the pressurised air pipe was clogged at the mixing point with the recycled water. Nevertheless, the problem was fixed by opening the controller fully and then adjusting it to the desired level. Another finding was that either the saturator pressure meter K_PG3410 showed the wrong pressure or the safety valve SV-3406 did not open at 3.9 bars.

5.2.3 Air volume to saturator

After the saturator pressure experiments, the effect of the air volume flow was investigated. Visually the flotator performance increased up to an air flow of 20 Nm³/h, thereafter looking the same until 40 Nm³/h of air. Slightly before 40 Nm³/h the saturator vessel stopped working properly, because air started replacing water in the saturator vessel, and instead of forming micro-bubbles, 1-10 cm sized bubbles rose to the flotator surface. Because no apparent differences in the performance of 20 and 30 Nm³/h could be observed visually, these two levels were compared by analysis of TSS from the overflow.

A two-sample t-test with assumed unequal variances (Welch's t-test) was thus conducted to compare total suspended solids in the flotator effluent for 20 and 30 Nm³/h of air. There was a significant difference in the SS concentration (mg/L) for 20 Nm³/h (M=19.8, SD=6.1, N=10) and 30 Nm³/h (M=13.1, SD=4.4, N=10); $t(16)=2.83$, two tail $p = 0.012$. The results suggest 30 Nm³/h air flow caused an average reduction of 6.7

mg/L TSS which equals 34% less suspended solids in the flotator overflow, compared to the 20 Nm³/h air flow. These results can be compared with the air flow from the previous years. In most of 2017, the process was run on 3-5 Nm³/h air. In 2016, the air flow averaged slightly below 20 Nm³/h, with occasional drops below 10 Nm³/h.

5.2.4 Influence of pH

Residual turbidity, oil, SS, COD, and the phosphate content were measured as a function of the flotator feed pH (Figure 27). No correlation of turbidity with pH could be observed. The linear regression shows no correlation ($R^2 = 0.03$) and is not statistically significant ($\alpha = 0.05$). Removing the outlier at pH 8 does not change the result in any meaningful way.

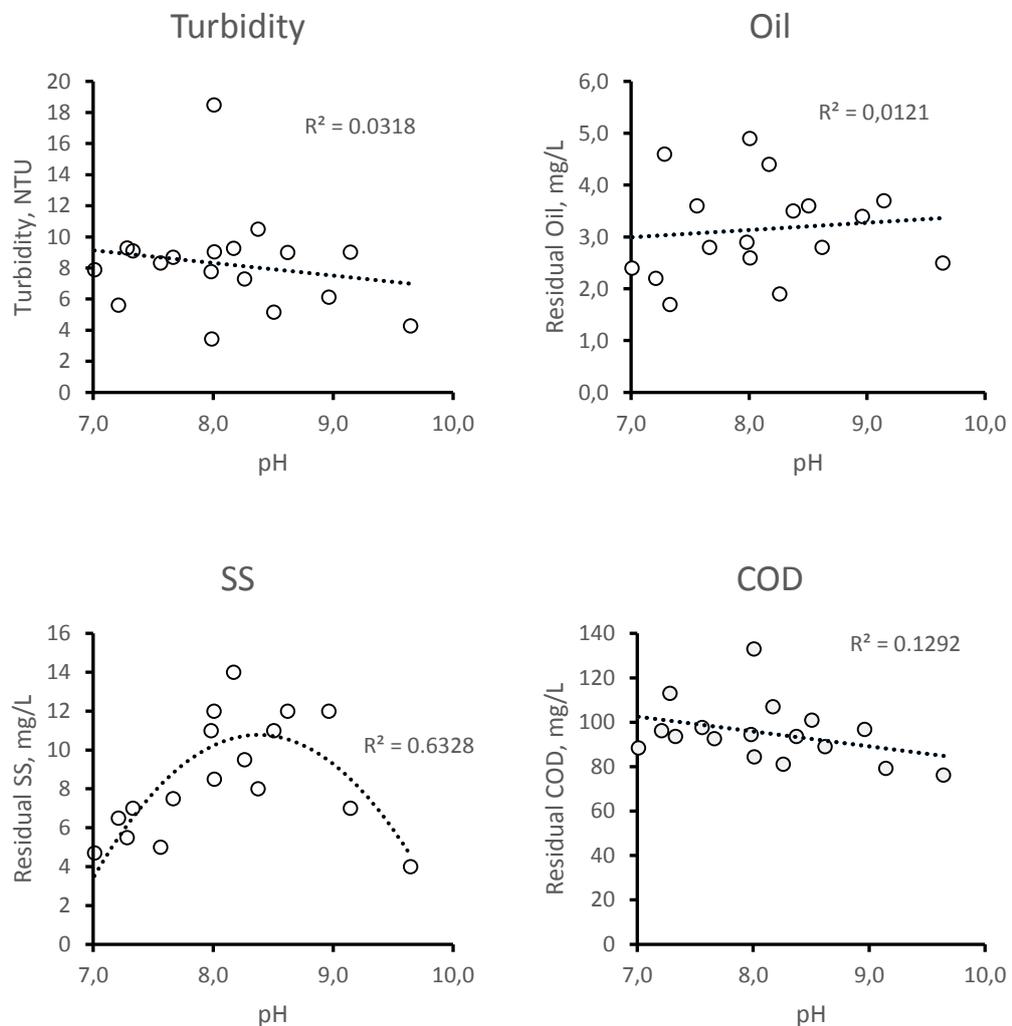


Figure 27: Contaminants as a function of pH. Chemical doses were ferric sulphate 8-10 mg/L Fe and 4 mg/L anionic polymer.

No clear dependence on the oil content and pH was found for the flotator effluent. As shown in Figure 27, the linear regression line fits the data poorly ($R^2 = 0.012$) and is not significant ($\alpha=0.05$). Thus, the data suggest that the variance of the amount of residual oil in the flotator effluent is caused by something else than the pH level.

A statistically significant ($p<0.05$) downward like curve relationship was found for suspended solids to pH ($R^2 = 0.63$). Multiple linear regression of the residual SS in the flotator effluent resulted in a 2nd-degree polynomial (Figure 27). The data suggests, that there is a maximum of SS in the flotator effluent at pH 8-8.5 while decreasing or increasing the pH outside this interval will lower the residual SS in the effluent.

The removal of COD (Figure 27) seems to increase with an increase of pH ($R^2 = 0.13$), but additional data are needed to verify this hypothesis. This result, in combination with the results from the jar tests, suggests that there is indeed a positive correlation between pH and COD removal. However, the results were not statistically significant ($\alpha = 0.05 < p = 0.16$).

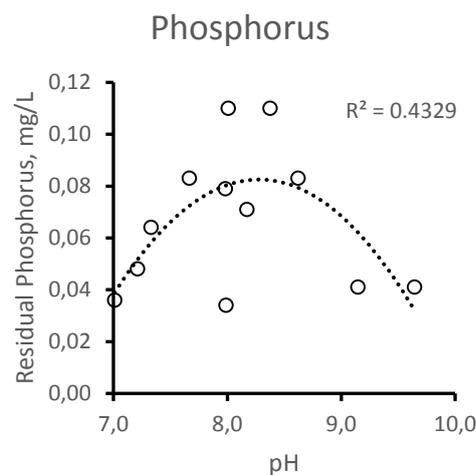


Figure 28: Removal of phosphate as a function of pH.

In the area of interest, removal of phosphate did not show statistical significance. Figure 28 illustrates the relationship of residual phosphate with pH. Similarly to the jar tests, the phosphate removal seems to be better closer to pH 7, as expected from the jar-tests and literature³³. The results also show a low residual phosphorus content at pH > 9. However, because of the large variance in the sample, no conclusion can be drawn with any statistical certainty. One apparent reason for this high variance is that sanitary

water is pumped to the feed intermittently (pump GA-3410). The best fitting equation was a polynomial of second order ($R^2 = 0.43$).

5.2.5 Anionic polymer dosage (A100-HMW)

Residual contaminants in the DAF overflow were examined as a function of anionic polymer dosage (A100-HMW) in the pH range of 7.2-7.6 and using ferric sulphate for 15 days. The results are illustrated in Figure 29. The turbidity increased with the polymer dose but had a minimum in the vicinity of 1 mg/L. The residual turbidity showed a high positive correlation to the polymer dose and was statistically significant ($R^2 = 0.69$, $p < 0.05$). With respect to the oil content, there was no correlation with pH. Suspended solids showed a minor correlation and borderline significance ($R^2 = 0.23$, $p = 0.08$). Remaining COD also increased with the polymer concentration ($R^2 = 0.29$, $p = 0.06$), also bordering on significance when $\alpha = 0.05$. The overall trend suggests that increasing the polymer concentration above 1 mg/L leads to less satisfactory results.

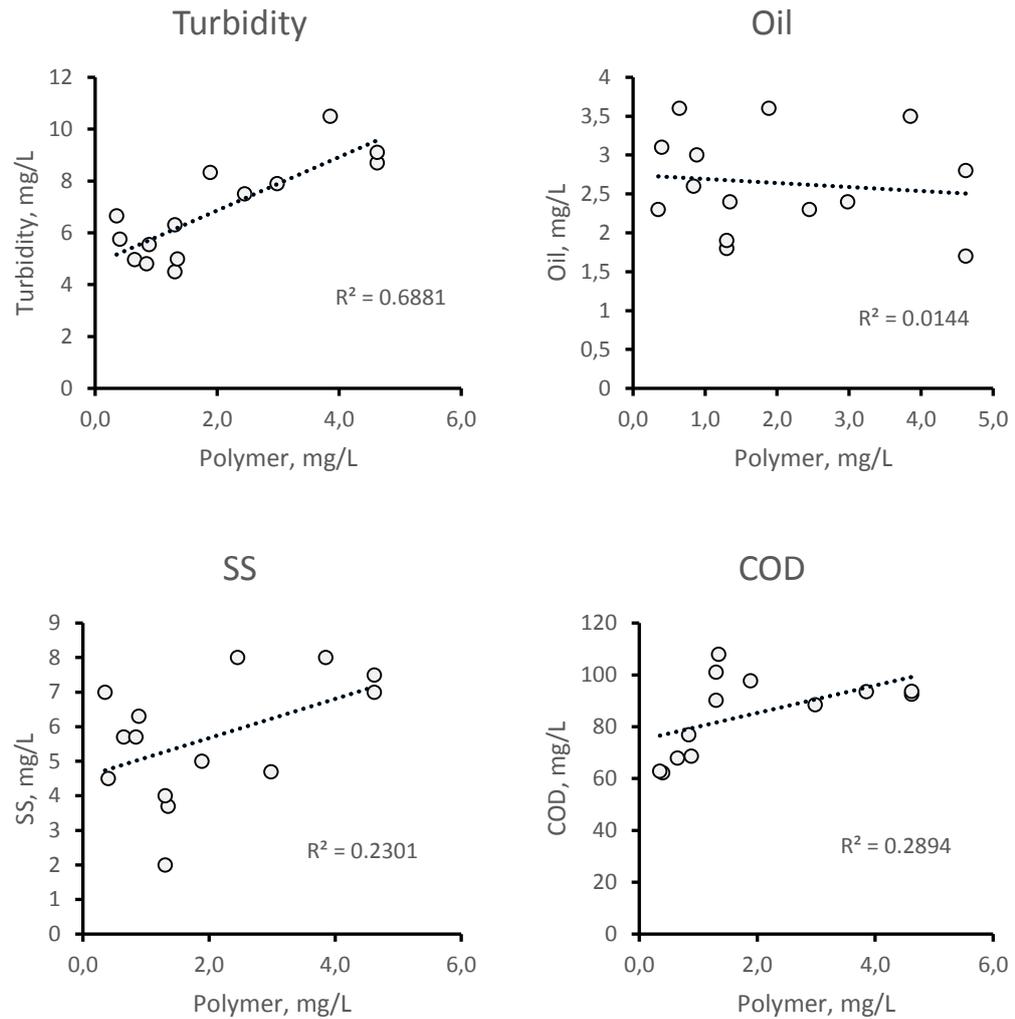


Figure 29: Contaminants as a function of anionic polymer dosage. Coagulant 7-10 mg/L ferric sulphate and pH 7.2-7.6

5.2.6 Cationic polymer dosage (C491-HMW)

Residual contaminants in the DAF overflow were examined as a function of cationic polymer dosage (C491-HMW) in the pH range of 7.1-7.6 and using ferric sulphate for 8 days (Figure 30). It should be noted that the sample count was lower in this experiment than in the experiments with the anionic polymers, therefore the feed water properties had a larger significance on the results, and the variance was smaller. Samples were taken twice per day, instead of once, as in the case with the anionic polymer (Section 4.3.3.5).

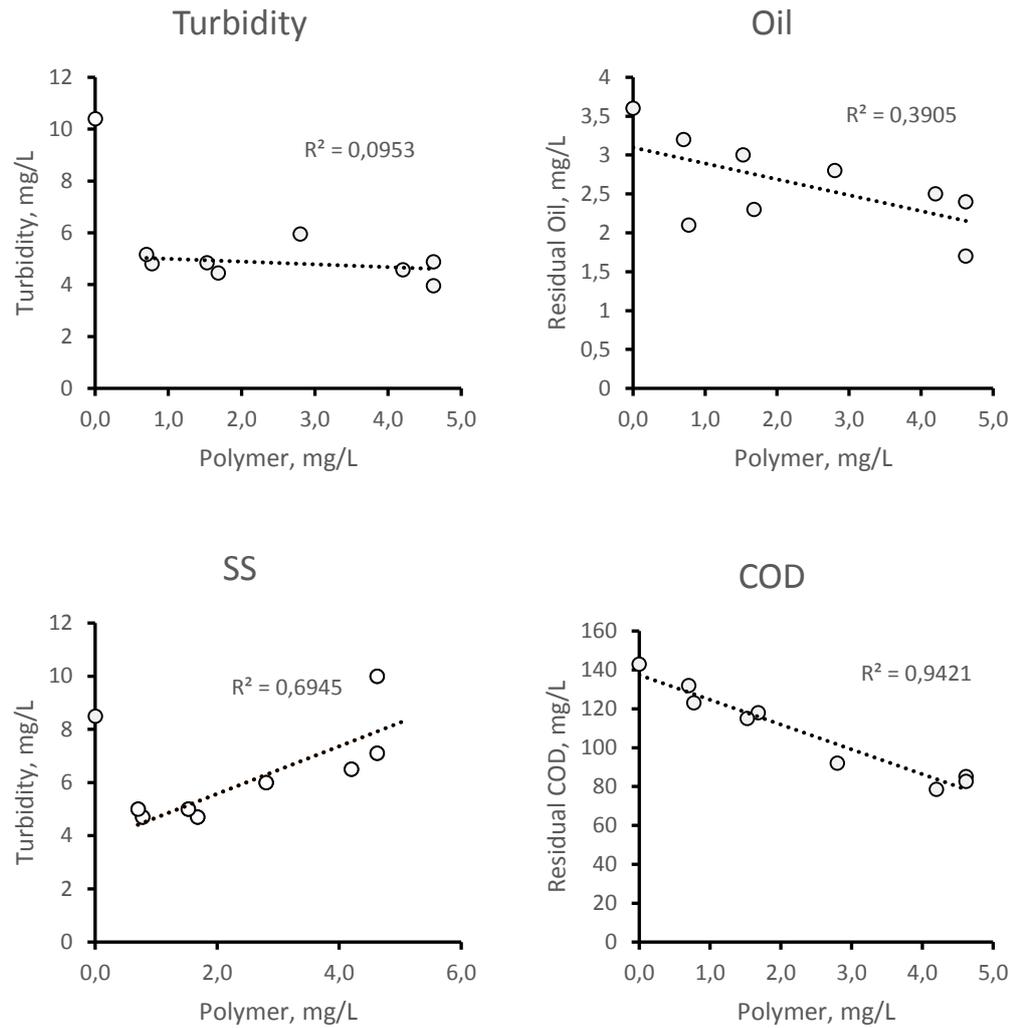


Figure 30: Contaminants as a function of cationic polymer dosage. Coagulant 7-10 mg/L ferric sulphate and pH 7.1-7.6

No correlation with the cationic polymer dose was observed for the turbidity. Oil and SS showed clear correlations, $R^2 = 0.39$ and $R^2 = 0.69$ respectively. The SS result was statistically significant ($p < 0.05$). The removal of COD showed a very high statistically significant ($R^2 = 0.94$, $p < 0.05$) correlation, which raises several questions regarding validity of the results. An observation was that the turbidity showed no correlation with the polymer dose, despite the large changes in oil, SS, and COD.

5.3 Performance of ferric sulphate versus ferrous sulphate

5.3.1 Turbidity

The purpose of Figure 31 is to demonstrate how ferric and ferrous sulphates behave in comparison to each other and the flow rate. The results suggest that the variance is much higher when using ferrous sulphate, and that ferrous is more sensitive to fluctuations in the flow rate. Each time ferrous sulphate was changed to ferric sulphate, the turbidity decreased, and vice versa. The ferrous sulphate curve (circles) represents the behaviour of the current industrial-scale chemical treatment, while the triangles represent different experiments with ferric sulphate, with the dose averaging an equivalent amount of iron (10 mg/L Fe) and various doses of polymers (mostly lower than with ferrous sulphate). These samples were taken once per day, between 7-9 am. The average costs for running the process with ferric sulphate (triangles) is 30% lower, being more efficient than the conventional process. Cost calculations are presented in section 5.5.

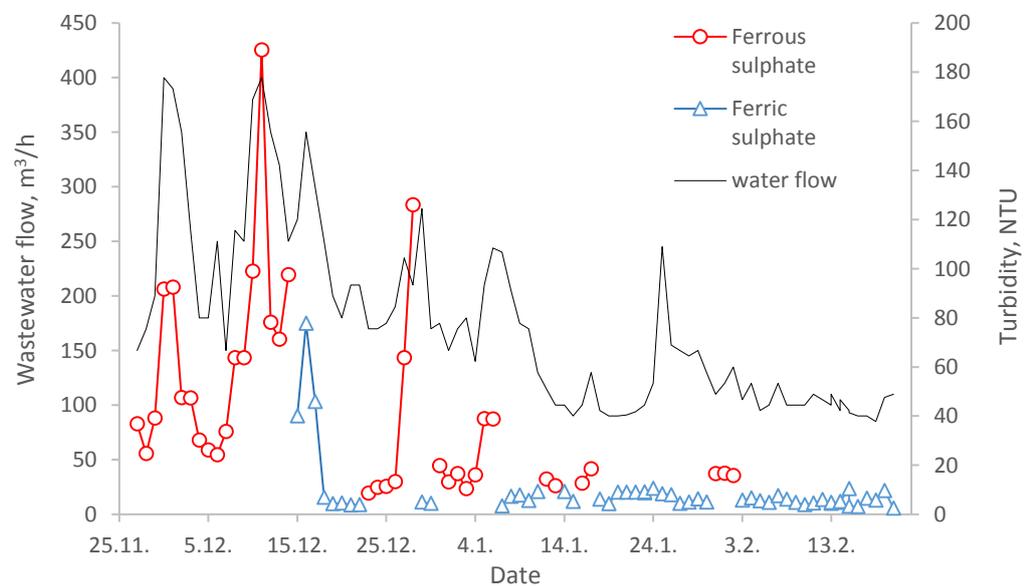


Figure 31: Time dependence of wastewater flow rate (left axis) and flotator overflow turbidity (right axis), for ferric (triangles) and ferrous (circles) sulphate.

5.3.2 Oil

As can be seen in Figure 32, the overflow oil content was lower when ferric sulphate was used. Noteworthy is the lower volatility with this additive, similarly to the turbidity. Again, changing from ferrous sulphate to ferric sulphate yielded, in most cases, better results. The difference is not as pronounced for oil as for turbidity. Overall, for the illustrated set of data, the residual oil was 53% lower when using ferric sulphate compared to ferrous sulphate (average values 5.8 mg/l and 2.7 mg/l for ferrous and ferric sulphate respectively).

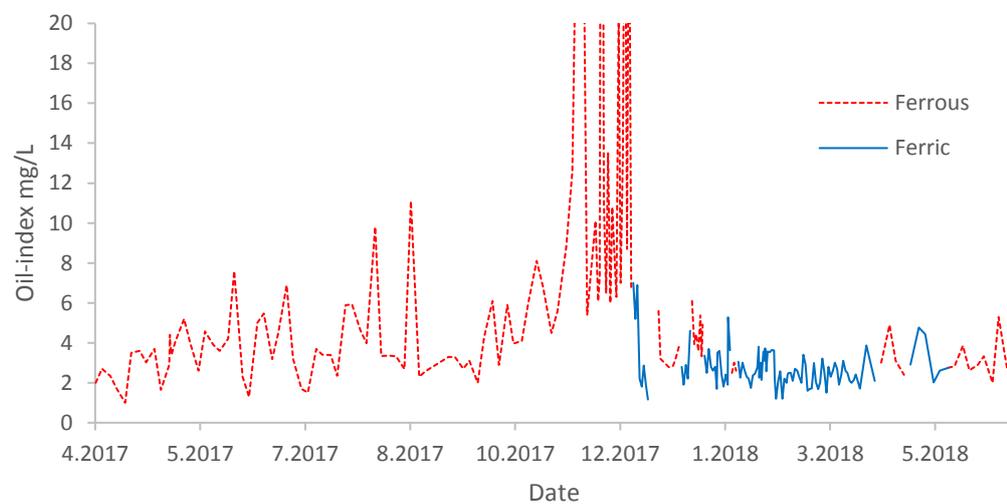


Figure 32: Time dependence of oil content in flotator overflow. The solid line represents the test-runs with ferric sulphate. The process was run in the modified way (ferric dosing based on turbidity measurements) from 1.3.2018 onwards.

5.3.3 COD

Removal of COD is improved when using ferric sulphate, and the variance was lower (Figure 33). For this set of data, the average remaining COD for ferric sulphate is 87 mg/l, while the average for ferrous sulphate is 202 mg/l. Thus, for the duration of the experiments, the observed COD is 57% lower when using ferric sulphate compared to the conventional process.

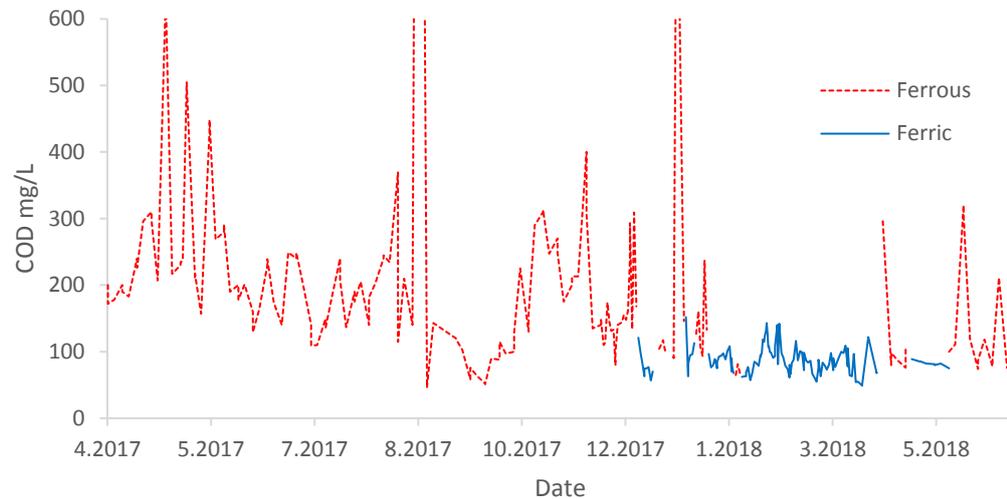


Figure 33: Time dependence of COD content in flotator overflow. The solid line represents the test-runs with ferric sulphate. The process was run in the modified way (ferric dosing based on turbidity measurements) from 1.3.2018 onwards.

5.3.4 Suspended solids

Suspended solids (SS) show an evident reduction in the variance values when using ferric sulphate (Figure 34). The average SS for ferrous- and ferric sulphates are 17.3 mg/l and 6.7 mg/l respectively, which corresponds to a total decrease of 61% with the novel procedure.

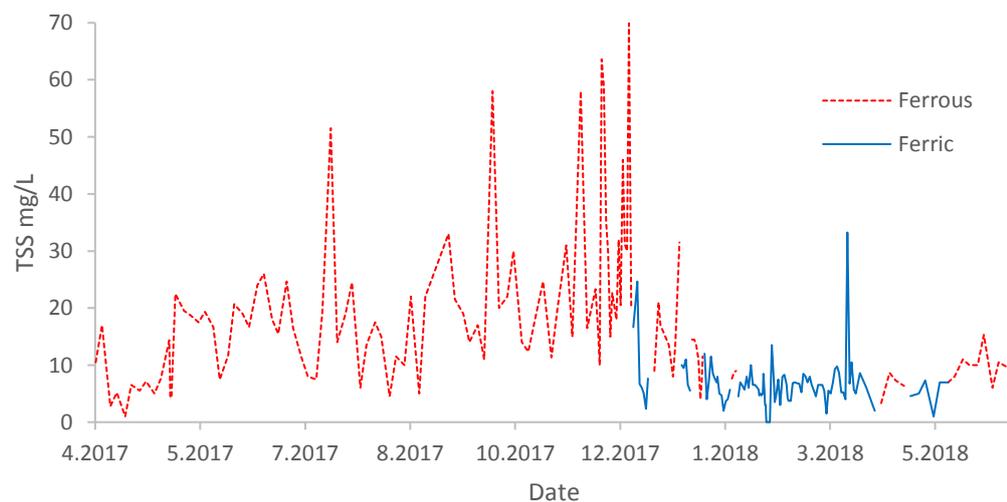


Figure 34: Time dependence of suspended solids content in flotator overflow. The solid line represents the test-runs with ferric sulphate. The process was run in the modified way (ferric dosing based on turbidity measurements) from 1.3.2018 onwards.

5.3.5 Phosphorus

For the accumulated set of data, residual phosphorus is 76% lower when using ferric sulphate (ferric 0.055 mg/l, ferrous 0.233 mg/l). As noted for all other impurities, the variance was lower when ferric sulphate was used (Figure 35).

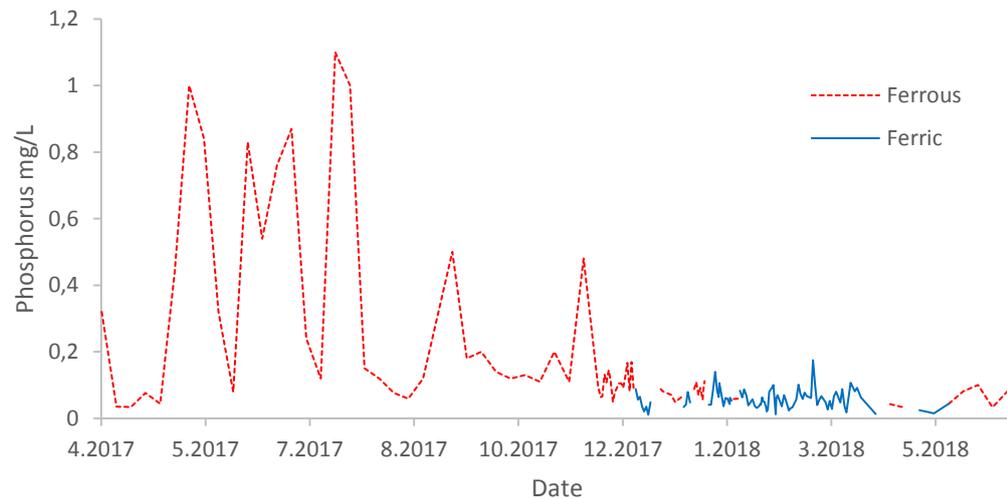


Figure 35: Time dependence of phosphorus content in flotator overflow. The solid line represents the test-runs with ferric sulphate. The process was run in the modified way (ferric dosing based on turbidity measurements) from 1.3.2018 onwards.

5.4 Other observations

5.4.1 Sediment deposits in DAF

Before the thesis work started, the author was working as a field operator in the WWTP and had the privilege to observe the flocculator and DAF unit empty of water. An interesting observation was made; there was almost no settled deposits on the bottom of the flocculator, but large deposits in the DAF unit. When observing the settled floc, the floc in the flocculator was very small, while the floc in the flotation unit was larger and contained polymers.

5.4.2 Effects downstream

When experimenting with the chemical treatment process, some effects on the biological process downstream became visible. Too high phosphorus removal in the flotation step results in a lack of phosphorus for bacterial growth in the activated sludge

process. A lack of phosphorus leads to a need to add phosphate to the biological treatment. Removing phosphate upstream and then adding it in the next process step is counterproductive.

Another observation was that the biological sludge seemed to settle better in the clarifier downstream when cationic polyacrylamide was used in the DAF unit. However, the water properties also changed at the same time, and the polymers were only changed once. However, a single observation is not sufficient for a general conclusion.

5.4.3 Aerator deposits

Previously, deposits have been found on the two flocculator aerators. The aerators suck air from above the flocculator surface, mix it with the wastewater sucked from the bottom, and then ejects the dispersion to the middle of the basin. The one to two centimetre thick and hard deposits block the aerator ejection channels. During the test runs, the aerators were inspected at one-month intervals. No deposits were found, as can be seen in Figure 36. Thus, application of ferric sulphate combined with a lower pH helps to reduce the occurrence of deposits in the system.



Figure 36: Two pictures of the same aerator of the flocculation basin. On the left the aerator when inspected at the beginning of the test run, on the right the aerator after four months of test runs with ferric sulphate.

5.5 Cost estimation

5.5.1 Costs of chemicals

Costs of chemicals for the flocculation and flotation systems were calculated. The present costs (Table 10) were calculated using two different methods. The first method summed up the chemical procurement costs for the past three years, and an annual average was calculated. The second method was to measure the consumption of

chemicals for a month, in case of incomplete purchase data, and to project the costs for a whole year. Both methods gave a similar result, and can thus be considered reliable.

Table 10: Cost of chemicals

Chemical	Average annual purchases, past three years	Annual average, based on past 30 days
Ferrous sulphate	7 245 €	7 817 €
Polyelectrolyte Al00-HMW	17 579 €	15 983 €
Caustic soda	47 702 €	45 662€
Sum	72 526 €	69 462 €

The largest cost item is caustic soda, used for regulating the pH to 9-9.5, covering 60-70% of the total costs for chemicals. In comparison to NaOH, ferrous sulphate is inexpensive, covering approximately 10% of the expenses. Increasing the ferrous sulphate dose would also require an increase in the caustic dosage to compensate for the ferrous acidity and keeping the pH within the required interval.

5.5.2 Alternative cost calculations

An alternative cost structure was calculated, based on the experiment results and the author's recommendations for novel process implementation. The main purifying effect stems from the use of a coagulant, while the polyelectrolyte has a secondary role to increase the separation. Because equally good or better results could be achieved at a lower pH using ferric sulphate, the largest expenditure, caustic soda, could be significantly reduced. Results also suggest that the polyelectrolyte was overdosed, and reducing the dose by half would yield a better result. Two alternatives are put forward, both with the same or better efficiency of contaminant removal than the conventional process using ferrous sulphate (calculated as the equivalent dose of $\text{Fe}^{3+}:\text{Fe}^{2+}$).

Table 11: Alternative costs of chemicals

Chemical	Equivalent dose of iron	Double dose of iron
Ferric sulphate	21 000 €	42 000 €
Polyelectrolyte	7 000 €	7 000 €
NaOH	12 000 €	18 000 €
Sum	40 000 €	66 000 €

This proposal for a new operating cost structure for chemicals is based on the following assumptions:

- The wastewater flow and quality do not deviate considerably from the previous years.
- The new chemicals are ordered as liquid bulk shipments, and not in intermediate bulk containers. One cubic meter intermediate bulk containers are considerably more expensive than bulk shipments.
- The new cationic polyacrylamide C49I-HMW is in a similar price range as A100-HMW.

Possible capital investment expenditure (CAPEX) is not included.

6 Discussion

The purpose of this research is to improve the performance of the Naantali oil refinery wastewater treatment plant, find the optimal process parameters and chemical dosages while simultaneously increasing the cost-effectiveness. Because the chemical treatment is still running according to design from 1979, only with some improvements, it was decided that more effective solutions should be examined, especially regarding the chemicals used. It was also hypothesised that the process parameters could be adjusted for increased performance. Jar tests were conducted to choose the best combination of coagulants and flocculants, which were then tested in the full-scale process.

The findings suggest that the process indeed is in need of optimisation. The DAF unit performance can be improved by adjusting the operating parameters, especially air flow. The results have indicated that ferric sulphate is more efficient than ferrous sulphate in treating oil refinery wastewaters with flocculation and dissolved air flotation, as expected considering the Schulze-Hardy rule.² Ferric sulphate also seems to work in a broader pH range, hence reducing the need of regulating pH, resulting thereby in lower operating expenditure. Another possibility is that instead of diminishing the costs, to double the average iron dose keeping the operating chemical costs the same. Overall, the new way of operating the plant, optimised process parameters, and new chemicals, could on average reduce all examined contaminants remaining after the chemical treatment by more than 50% compared to the conventional process.

6.1 Selection of the coagulant and flocculant

Based on the results from the jar tests (Section 4.2), ferric sulphate and a low charge density cationic polyacrylamide were chosen for the full-scale testing. The pH 7-8 was chosen (equivalent to jar test initial pH 8-9). The reasoning for the choice of ferric sulphate is as follows:

- Best performance concerning turbidity removal
- Good performance in oil removal at post-treatment pH 7-8 (initial pH 8-9)
- A moderate removal of phosphate*
- Good COD removal at post-treatment pH 6-8 (initial 7-9)**
- Less corrosive than ferric chloride and PAC
- Effective hydrogen sulphide removal

- Relatively inexpensive and easily available
- Safe choice, because the chemistry is similar to ferrous sulphate

* A moderate removal of phosphate is preferred because the activated sludge process requires phosphorus for the bacterial growth. If problems with phosphate arise, the removal can be increased by lowering the pH to 6 (initial pH 7), as shown in Figure 14.

** Assuming the dip in the trend of COD-removal for ferric sulphate in the jar test experiments was non-representative, and the trend follows the ferric chloride trend. This was later shown to be the case in the full-scale experiments.

The jar test showed that among different alternatives to ferrous sulphate, ferric sulphate was the most suitable for full-scale experiments, for the reasons mentioned above. Polyaluminium chloride performed slightly better than other coagulants for oil removal. The difference (1.2% for ferric sulphate and 1% for ferrous chloride, at initial pH 8 and 9 respectively) is, however, almost negligible. The PAC performance was the most consistent for oil removal, regardless of pH.

The performance differences are more apparent for the turbidity removal, as iron-based coagulants out-performed Al-based ones by an average of 10% around neutral pH. At higher pH, the difference was not as noticeable. For phosphate removal, iron coagulants performed well at low to neutral pH ranges, while Al-based coagulants performed better in neutral to alkaline conditions. Based on the jar test results there is a clear curvilinear relationship between pH and phosphate removal. The phosphate results suggest that the optimal conditions for phosphate removal are between pH 6 and 7 for all coagulants. Similar results were shown by Szabo et al.³³, who found the optimal pH to be within the interval 5-7 for both aluminium and iron-based coagulants.

The hydrogen sulphide experiment showed that ferric sulphate could remove H₂S as expected. However, the level of the H₂S removal was higher than that predicted by Firer et al.³⁴, and also, interestingly, PAC removed 29% of H₂S in the sample. Aluminium ions should not be able to remove hydrogen sulphide, as aluminium sulphide dissociates in water. Probably a part of the H₂S had evaporated before commencing the titration analysis. When observing H₂S removal with ferrous iron, Nielsen et al.³⁵ found that at pH > 8 all ferrous iron will react by sulphide precipitation if H₂S is in abundance, while at pH < 7 only 40% reacted this way.

When considering that Al-based coagulants do not remove hydrogen sulphide, what is left is to choose between the two ferric compounds, ferric chloride or sulphate. Ferric chloride corrodes metals much more aggressively due to the high chloride content. Thus, the stainless steel type 316L piping on site would not be capable of withstanding the chloride-induced corrosion. Otherwise, the two ferric coagulants performed more or less equally well. Therefore, ferric sulphate was chosen.

Polyelectrolyte C491-HMW was selected, because of an overall trend in the polymer experiments, where more neutral polymers performed better opposed to the higher-charged polyacrylamides (Figure 17 and Figure 18). C491-HMW also showed the lowest turbidity in the pH-dependent experiment (3.4 NTU at initial pH 8.5). However, a noteworthy result of the jar-test was a clear negative relationship between the polymer dose and turbidity in the tested interval. Of the three dosages tested, the lowest dose, corresponding to a polymer dose of 1.25 mg/L, was the best for all polymers. This is notable because the conventional full-scale process operates with an average polymer dose of 4.5 mg/L.

Some possible limitations to the reliability of the results and explanation were identified. Flotation was predicted by sedimentation performance in jar tests. There are evidence that the particle agglomeration and charge neutralisation are the same regardless of the separation method, while gas bubble attachment is less clear. A lab-scale flotation device is probably more reliable, however, was not available. The utilisation of a lab scale flotator, on the other hand, has its problems. There are substantial differences depending on the flotator parameters, and full-scale flotator performance is usually not the same as in the lab scale. Nevertheless, it has been shown that proper sedimentation also predicts good flotation characteristics, in an inexpensive and effective way. Thus, the method was considered to be the most efficient in terms of complexity and costs.

Another possibly important limitation is that many of the experiments were performed on water samples from one day only. A high variance in the incoming water properties can be observed, which might result in an unrepresentative sample. However, the analysed sample was, based on the daily QC-laboratory analyses, typical for the wastewater plant. Therefore, it was considered to be representative. During process disturbances, it is possible that some other coagulants besides ferric sulphate might have worked better.

A variable influencing the reliability of the lab results is, of course, the natural human induced error. This was speculated to be the reason for the deviations displayed in Figure 15. Later when the full-scale experiments were done, this trend-changing error was not present. The stock coagulant dosages have a $\pm 0.3\%$ accuracy of the metal concentration. This margin of error can result in a slightly below 10% maximal error in the 1:1 ratio of the metal dosing, at which the coagulants were compared. These errors, however, do not conflict with the premises for the coagulant selection.

One aspect in the lab-scale experiments would have been using the conventional coagulant ferrous sulphate in the coagulant comparison. However, ferrous sulphate needs the infusion of air to work. If air had been added, this should also have been done in the experiments with other coagulants to have similar conditions. Air infusion was tried. However, it was not possible to replicate the flocculator environment reliably. Adding air bubbles resulted in lifting the precipitates to the surface, not to mention the problems with the air pipe interfering with the agitator. The reduction and oxidation conditions in the flocculator and the jar were also different. Thus, ferrous sulphate was excluded from the jar test experimental design. Instead, the newly selected coagulant was compared to the conventional process performance in the full-scale experiments.

6.2 Full-scale parameters

The hypothesis was that the new combination of coagulant and flocculant selected in the jar-tests would perform better in full-scale than the current process with ferrous sulphate. Based on the jar tests, ferric sulphate was selected as the coagulant and C491-HMW (cationic low-charge density polyacrylamide of high molecular weight) as the flocculant. The purpose of the full-scale experiments was to improve the purification and to find the optimal dosages and pH for the new chemicals in the coagulation and flotation steps. As shown in the results, the new combination of chemicals and pH performs better than the conventional way of running the process. The optimal levels of flotation air flow and dispersion tank pressure were investigated, too.

The full-scale results suggest that the pH does not influence the process as much as the ferric sulphate jar-test would indicate. Turbidity and oil in the flotator overflow showed very low correlations ($R^2 < 0.04$) with pH. The relationship for COD to pH is more unclear. The COD correlation to pH has a quite low R^2 value of 0.13 and is not statistically significant ($p = 0.16$), being consistent with the jar-test results. Both types of

tests show reductions in the COD levels when raising the pH. Thus, this result seems reliable. Contrary to other impurities, suspended solids show a strong and significant curvilinear correlation to pH (Figure 27). A maximum can be observed around pH 8-8.5, which can be explained by the curvilinear pH dependence of the solubility for the different iron hydroxide species (Figure 37).^{31,36} Phosphorus shows a similar curvilinear relationship, with the highest removal at pH 7, which is the lowest pH tested. However, if the jar-test results are valid, the best phosphorus removal is at a slightly lower pH, around pH 6. Szabo et al.³³ found the optimum to be between pH 5-7.

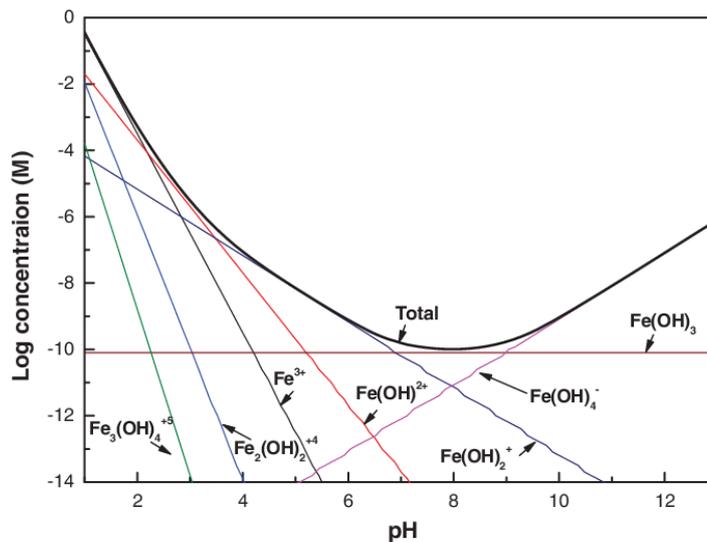


Figure 37: Solubility of various ferric hydroxide species in water. The lowest solubility is observed around pH 8. Figure from "Treatment of radioactive waste seawater by coagulation-flocculation method using ferric hydroxide and polyacrylamide (2015)".³⁶

One important note is that flotation does not remove dissolved oil, only free and emulsified. The flotator overflow usually contains between 1 and 5 ppm of oil, which is a sum of emulsified and dissolved oil. Because the solubility of oil varies depending on the oil type and water properties, it will affect the measured flotator performance, which contributes to the variance and the error.

An interesting finding was better performance results of the cationic polymer than the anionic one. The results showed much higher R^2 - values and statistical significance when using the cationic polymer. However, these results are not as reliable as the ones for the anionic polymer. In particular, the duration of the experiment and the sampling interval for the cationic polymer were shorter. Thus, changes in the flocculator feed had a more prominent effect on the experiment. Concerning the turbidity, the full-scale cationic experiment was contradictory to the laboratory scale experiments, not showing

any correlation between the turbidity and the polymer concentration. The laboratory scale test resulted in a clear negative correlation when increasing the dose over 1.25 mg/l. It is highly probable that changes in the wastewater properties had a skewing impact on the results. Additional polymer dosage experiments should be conducted with the cationic polymer to form a more reliable picture. For the anionic polymer, the results are more robust and reliable, because of the longer time-span and a higher number of samples. The oil content was not affected by the dose, while turbidity, COD and SS were positively correlated with an anionic polymer dose above 1 mg/l. In other words, the results suggest that an increase of the polymer dose above 1 mg/l impairs the removal of impurities.

To summarise the optimal chemical parameters, when using ferric sulphate, the following can be considered valid for the Naantali WWTP wastewaters in the pH range 7-9.5: Oil removal and turbidity are not pH dependent, and COD removal is slightly better at a higher pH. The suspended solids removal is efficient when the pH is lower than 8 or higher than 9, being poor in-between. Phosphorus removal is better at lower pH, possibly having an optimum at pH 6. Anionic polyelectrolyte dosage should be kept around 0.5-2 mg/l, as higher doses will only worsen the purification results. The cationic polyelectrolyte dosage is unclear, but it is possible that a higher dose is justified. The most economical pH is between pH 7 and 8, which is recommended for industrial implementation.

In addition to the pH and chemical variations, the influence of two physical parameters; the airflow and the saturator pressure were examined. The results revealed that increasing airflow to 30 Nm³/h improved the separation of suspended solids by 34%, compared to an air flow of 20 Nm³/h. When considering that the saturator had been running with an actual air flow of 3 Nm³/h for several months with bad removal results, and that the normal flow is between 10-20 Nm³/h, the performance of the system was restored to its usual performance and also improved significantly ($p < 0.05$) by increasing the air flow from 20 to 30 Nm³/h. Running the process in the new way reduced the SS content in the flotation overflow by 34%, even when using conventional chemicals.

The saturator pressure experiments were inconclusive. During the experiment, the system was not working correctly, and there was not enough time to repeat the experiment. However, because of the experiment, the problem causing the malfunction

was resolved (see Section 5.2.2). The pressure is not very adjustable if system stability is desired. Therefore, based on the flotation theory (Section 2.5) and the plant operator experience, the air pressure was kept as high as possible, close to 3.9 bars. It was also noted that the dispersion air system was more stable when the bigger one of the two recycle pumps were used.

The benefits achieved by implementing the changes discussed above are clear. As showed in section 5.3, all contaminants remaining after the chemical treatment could be reduced by more than 50%. Overall, for the whole test-run period, remaining contaminants were reduced by 53% for oil, 57% for COD, 61% for suspended solids, and 76% for phosphorus. Historical turbidity data were not available, but also turbidity shows the benefits of using ferric sulphate (Figure 31). In Figure 38, showing combined data from the results chapter, the remaining contaminants are plotted as a function of time. The solid lines represent the time of the full-scale test runs with ferric sulphate. The average dose of the trivalent iron (ferric) was slightly lower than the average dose of the divalent iron (10.5 mg/L Fe^{2+} vs 9.7 mg/L Fe^{3+}).

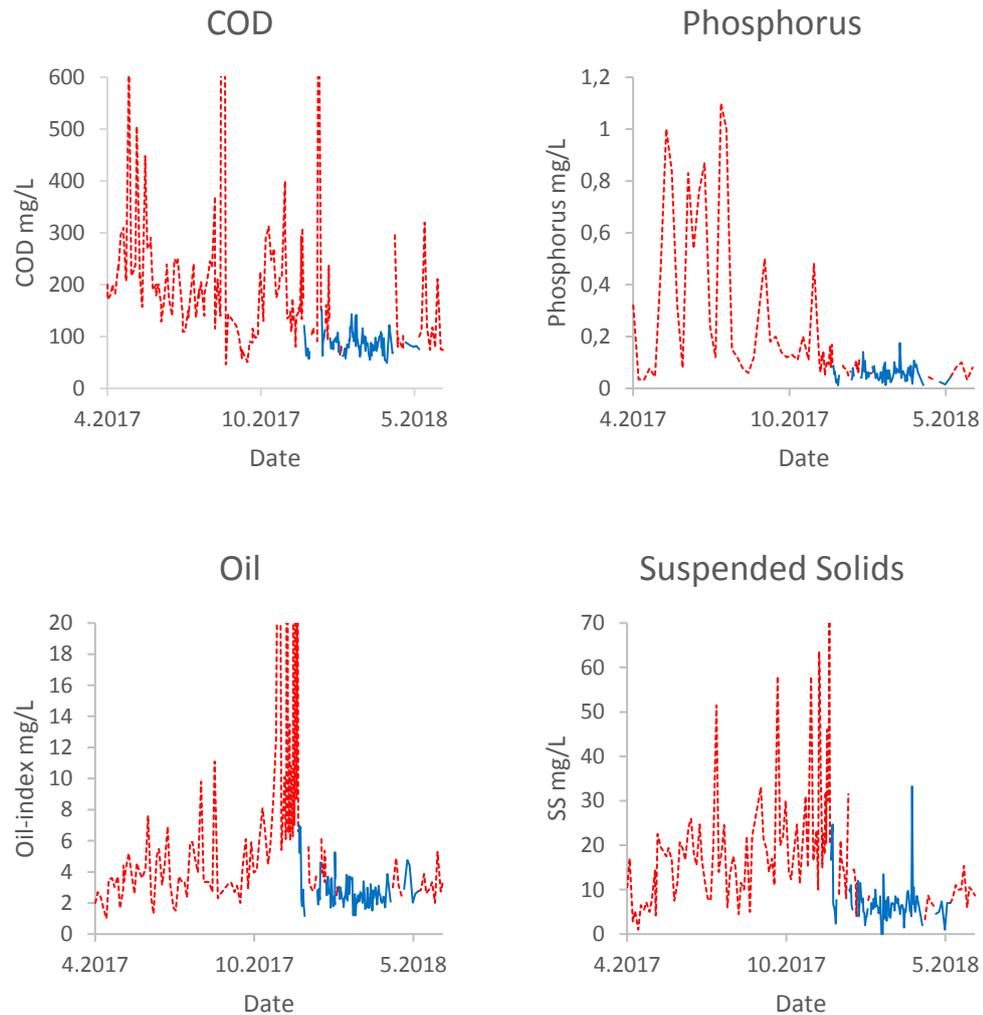


Figure 38: Combined figures from the results chapter. Remaining COD, phosphorus content, oil, and suspended solids are illustrated as a function of time. The solid line represents various test runs with ferric sulphate, while the dashed line represents the conventional way of operation.

As can be observed, the data are presented as "remaining contaminants in mg/L", instead of "percentage removal". This is because of economic reasons, as taking input and output samples would have doubled the necessary samples, not to mention that the wastewater feed quality fluctuations are much larger than for the purified water. The feed sample analyses showed the water was on average typical for the plant.

6.3 A consideration of the findings in light of existing research

Overall, the full-scale results are well in line with the previous research on wastewater treatment. Naturally, the optimal conditions vary depending on the wastewater properties and types of chemicals, and no wastewaters are the same. As written above, there are numerous variables present in wastewater treatment. When looking at the

research of oil refinery WWTP performance, many articles and reports were missing several critical variables, e.g. the recycle rate or the residence time.

One interesting observation was that when comparing coagulants on an mg/L Me^{3+} basis, the most commonly used coagulant, aluminium sulphate, exhibited the weakest performance in the jar tests. In addition, the findings suggest that ferric ions are more efficient coagulants than aluminium-based ones, also on a molar basis, as the ferric ion has a considerably heavier atomic weight.

In contrast to Rhee et al.²⁶ who found that the pH had a more prominent influence on oil removal than coagulant dosage with DAF, the opposite was found in the full-scale experiments in this work. However, higher efficiency of ferric sulphate than of aluminium sulphate is similar to this work. In particular, ferric sulphate was twofold more effective for oil removal compared to aluminium sulphate at pH 8.5.

The benefits of using polyelectrolyte flocculants are undeniable. Every time a flocculant was added during the jar tests, the turbidity was lowered by a factor of up to five. More neutral flocculants performed better than charged ones, supporting the theory that flocculants work mainly by bridging, not by charge neutralisation.⁴ The results about polyelectrolyte charge vary considerably depending on the wastewater properties. The turnaround showed expected evidences of the benefits of using polyelectrolyte flocculants in addition to metal coagulants, in line with Bratby.³¹ When the flotator and flocculator were emptied, there were no deposits of settled matter at the bottom of the flocculator, where only coagulant was used, only minor particles were observed. In stark contrast, in the flotator, where polymers are present, there was a several decimetres thick layer of settled matter, consisting of large flocs.

The stirring speed was found to have a significant effect on the turbidity removal. As illustrated in section 5.1.4, slow stirring (40 rpm) for a longer period of time continuously improved the performance. Rapid stirring (400rpm) initially improved the turbidity removal, but after two minutes of agitation, additional stirring was not beneficial. Continuing the rapid stirring for a long time is therefore counterproductive. Ghernaout et al.³ report similar results, and that the most effective method is short and rapid stirring followed by a period of longer and slower mixing. Al-Shamrani et al.⁹ concluded in their study that 120 s of rapid mixing (200 rpm) followed by 15-20 min slow mixing (20-80 rpm) was the optimal.

6.4 Practical considerations for implementation

If ferric sulphate is to be applied in full scale, some practical considerations must be taken into account. Chemical properties of ferric sulphate place stricter requirements on the process equipment, such as the pumps and piping. For example, during the full-scale test run some connector parts which were not made of acid-proof stainless steel and were in contact with ferric sulphate corroded to failure in approximately two weeks.

The existing ferrous sulphate pumps GA-3412 and GA-3412S have larger outputs than needed. Pump GA-3412S with the max flow 220 l/h according to specifications, exhibited a max flow of 190 l/h with 10% ferrous sulphate solution, while the pump GA-3412 has a theoretical maximum of 980 l/h. The new pumps for ferric sulphate should produce a similar output as the experimental ones, in the range of 0-50 l/h, with an average of around 5-15 l/h. One suggestion is changing the larger pump GA-3412, which is very rarely used, to a smaller one capable of moving the denser and more viscous ferric solution with a suction head of up to 5 meters and a discharge head of minimum 5 m. The pump should also be strong enough to work even if there are air pockets in the suction line.

Ferric sulphate is acidic displaying $\text{pH} < 1$, is recommended to be stored between 0 and 30 °C, and has a freezing point of -20 °C. Because the storage basins FA-3411 (10 m³) and FA-3412 (25 m³) are in contact with the outside air, there should be a way of warming them, without diluting the ferric sulphate (as dilution might cause precipitation), e.g. a steam heating coil. Still, the freezing temperature of ferric sulphate is lower than for the ferrous sulphate solution in use, because it is a more concentrated one. Then again, overheating the solution will increase the corrosivity significantly, therefore, controlling heating is essential. The concrete basins are lined with stainless steel. Acid proof steel, rubber lined steel or fibreglass reinforced polyester should be used. Therefore, if the existing basin steel lining is not sufficient, the walls could be lined with fibreglass on top of the metal layer. Another alternative is to build a new vessel designed for storing ferric sulphate. Cheremisinoff ⁶ recommends stainless steel of type 316 for storage vessels and piping.

The storage time must also be considered, because the solution will begin to precipitate if it stands for too long. The recommended maximum storage time is six months.

According to the product specifications of ferric sulphate (PIX-115), less than 0.2 weight-% of the solution is insoluble particles, which will precipitate with time. This happens also with ferrous sulphate, probably even to a higher degree because of precipitation by oxidation with air. Therefore, no special precautions when changing from ferrous to ferric sulphate are required with respect to sedimentation.

The piping is made of stainless steel. The newer parts indoors are made of stainless steel type SS316L, while the material of the older parts could not be confirmed from the available documentation (probably SS304 or SS316). During winter times, the outside temperature sometimes falls below -20 °C, therefore the pipes outside should be traced with heating cables, at a minimum in the flocculator AD-3403 basin end. Because the total flow of the ferric sulphate in the feed pipes can be quite low, it is at a higher risk of being frozen.

Some changes are suggested to the chemical feed points in the flocculator AD-3403. Caustic soda and the coagulant should be fed to different points, as not to shift the hydrolysis reactions. The coagulant should also be fed further away from the basin overflow to avoid short-circuiting and increase the residence time of ferric sulphate. These changes were done during the thesis work, because the ferrous sulphate feed piping had to be renewed due to severely clogged lines. If the piping has to be renewed when implementing the full-scale use of ferric sulphate, the new as-is feed points should be used. The old and new dosing points are marked in Figure 39.

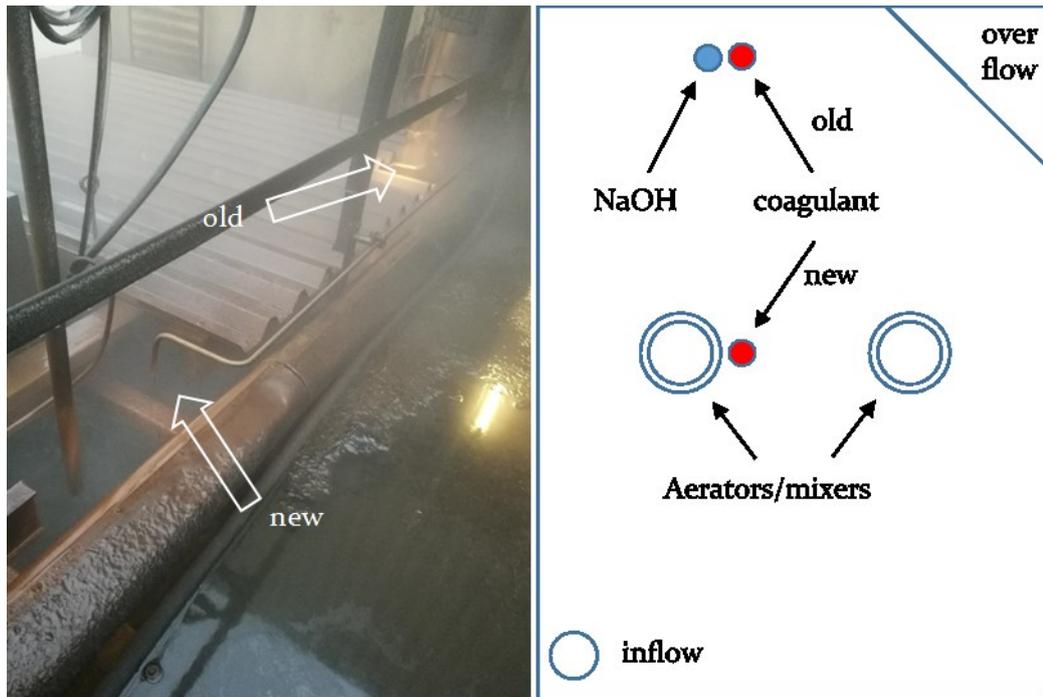


Figure 39: The new coagulant dosing point in the flocculator. The top view of the flocculator on the right.

The polymer feed point at the flocculator basin (AD-3403) overflow falls should be widened, to spread the polymer into different streams, or in other ways increase the mixing. It should also be ensured that the polymer is sufficiently diluted. A concentrated polymer solution tends to clump more and diffuse more slowly than a diluted one. Another alternative is more efficient mixing. However, the agitation should not produce high shear rates, as the polymers and already formed floc might break. This was also confirmed by the jar test experiments.

7 Conclusions

In this thesis different coagulants, flocculants and process parameters were evaluated to improve the performance of the Naantali Refinery Wastewater Treatment Plant. Experiments were first done in lab-scale, whereafter the most promising chemicals and process parameters were used in full-scale test runs.

By applying the suggested changes, significant process improvement can be gained. During the full-scale experiment, all remaining flotation overflow contaminants were reduced on average by more than 50%, compared to the conventional way of operation. Hence, the aim of this work to improve the performance of the chemical treatment was successfully accomplished. All the improvements can be achieved while simultaneously reducing the operating costs.

The main reasons for the improvement are considered to be:

- A stronger fully oxidised trivalent coagulant.
- Overdosing of polyelectrolyte was reduced.
- Dosing based on objective on-demand measurements of purification.
- The flotation recycle-stream level of air-saturation was increased.

The tested coagulants were ferric chloride, ferric sulphate, aluminium sulphate and two polyaluminium chlorides with different basicity. Of all the coagulants tested at the laboratory scale, ferric sulphate was chosen for the full-scale experiments. The test runs revealed that ferric sulphate consistently performed better than the current coagulant ferrous sulphate. When ferric sulphate was used, the remaining impurities also showed reduced fluctuations. This is very important for the downstream biological treatment, which is destabilised by shocks. The optimal ferric sulphate dosage varied depending on the influent composition, however 10 mg/L of Fe^{3+} (or 36 mg/L as $\text{Fe}_2(\text{SO}_4)_3$) in combination with DAF is sufficient for most situations. During disturbances, doses of up to 50 mg/L of Fe^{3+} (or 180 mg/L as $\text{Fe}_2(\text{SO}_4)_3$) can be required for optimal results. A pH of 7-8 was found to be optimal for ferric sulphate, based on several criteria. In addition to the five coagulants, six polyacrylamide flocculants were investigated. The jar test results suggest that neutral, e.g. cationic polymers with low charge densities, displayed the best performance. The optimal dosage of the flocculant was between 1-2 mg/L, regardless of the charge density.

In this thesis, turbidity measurements were introduced to the operators as a daily method to monitor the DAF performance. Because the turbidity analysis is fast, reliable and sensitive to changes in the water properties, the coagulant was dosed based on the novel measurements. In essence, a faster way of recognising problems was introduced, thus lowering the variance of impurities in the product. In addition to the turbidity analysis, more informative, but much slower, laboratory analysis was performed once per day.

The physical parameters of the flocculation and dissolved air flotation were investigated, too. The most relevant result was finding the optimal setting for the air-flow to the DAF saturation tank. By increasing the flow to the upper ends of the operating window, the DAF performance with respect to suspended solids removal was significantly increased.

This research is of limited direct applicability to other refinery WWTP:s because of different water qualities depending on the specific site. However, the author suggests that an option to use ferric sulphate instead of using a more common aluminium sulphate should be explored in other refineries and that overdosing of polymers should be avoided.

Combining ferric- and aluminium-based coagulants in the chemical treatment is worth further investigations. Because aluminium-based coagulants do not remove hydrogen sulphide, combining ferric- and aluminium based salts can be an option to improve overall performance. In a scenario where concentration of H₂S is high, the aluminium ions could possibly still coagulate particles instead of being consumed in reactions with sulphides.

8 Svensk sammanfattning

I denna avhandling för diplomingenjörsexamen evaluerades användning av olika kemikalier och processparametrar för vattenreningsverket vid Nestes oljeraffinaderi i Nådendal. På grund av allt strängare miljölagstiftning, ställs det ständigt hårdare krav för industriell avfallshantering. Inom den kemiska industrin, så som oljeraffinering, uppstår stora mängder förorenat vatten, som måste renas före det kan ledas tillbaka ut i naturen. Målet med detta arbete var att förbättra och effektivera den kemiska behandlingen av avloppsvattnet i raffinaderiets vattenreningsverk.

Avloppsvattnet från oljeraffinaderiet i Nådendal består bl.a. av vatten som separerats från olja, tankfartygens tvättvatten, skrubbevatten, råoljans avsaltningssvatten samt övrigt processvatten. Vattnet är vanligtvis kontaminerat med olja och olika kemikalier, varav många har ytaktiva egenskaper, dvs. de är surfaktanter. Surfaktanterna möjliggör bildning av dispersioner och emulsioner av olja i vatten, vilket försvårar behandlingen av vattnet med enbart fysikaliska metoder. Emulsionerna är stabila, eftersom de stabiliseras av repulsiva elektrostatiska krafter mellan partiklarna, i detta fall främst anjoniska. De laddade kolloidala partiklarna stöter bort varandra, och förhindrar därmed att oljedropparna växer tillräckligt stora för att kunna separeras genom att flyta till ytan. För att bryta emulsionerna och åter möjliggöra en fassetparation, används därför koaguleringsmedel bestående av katjoniska metaljoner, från salter av järn eller aluminium. Då de repellerande elektrostatiska krafterna neutraliseras, börjar de kolloidala partiklarna koagulera. Denna process kan för snabbas genom att förstora aggregaten med hjälp av polyelektrolyter, dvs. laddade polymerer. Denna process kallas flockning. Då partiklarna vuxit tillräckligt kan de lätt separeras, t.ex. genom dekantering eller flotation. Flotation fungerar genom att luftbubblor skapas i vätskan, som lyfter partiklarna till ytan, varefter skummet skalas av och samlas upp. I detta arbete undersöktes en process bestående av upplöst luft-flotation (eng. dissolved air flotation, DAF), där en del av det renade vattnet trycksätts och återcirkuleras varefter trycket sänks och luftbubblor bildas.

I detta arbete evaluerades användning av olika kemikalier för koagulering och flockulering, närmare bestämt polyaluminiumklorid, aluminium(III)sulfat, järntriklorid och järn(III)sulfat för koagulering, samt sex olika katjoniska polyakrylamider med olika molära massor och laddningsdensiteter för flockbildning.

Även det optimala pH-värdet undersöktes. Experimenten genomfördes i labbskala, varefter de mest lovande kemikalierna provkördes under flera månaders tid på raffinaderiets vattenreningsverk. Inverkan av processparametrar så som lufttillförsel och tryck på upplöst luft-flotationsanläggningen funktion undersöktes också. För koagulanttillförsel konstruerades ett tillfälligt doseringssystem, medan det befintliga systemet användes för polymerupplösning och dosering. Prov togs nedströms från flotationsanläggningen, och de analyserades för olja, COD, suspenderade ämnen, fosfor, pH och turbiditet i raffinaderiets laboratorium.

På basis av de erhållna resultaten från experimenten i labbskala valdes koaguleringsmedlet järn(III)sulfat och en svagt katjonisk polyakrylamid med hög molekylvikt för fullskaliga experiment. Dessa kemikalier valdes, eftersom laboratorieexperimenten visade att neutrala flockuleringsmedel fungerade bättre än starkt laddade. Järn(III)sulfat valdes eftersom sänknigen av turbiditeten var störst (98,5%) och olja (94,5%) samt COD (55%) renades väl vid neutralt pH, och kemikalien korrosiva egenskaper var mildare jämfört med polyaluminiumklorid och järntriklorid. En fördel var även moderat rening av fosfor (95%), vilket behövs i den påföljande biologiska processen. En stor fördel med järnbaserade koagulanter är också förmågan att oxidera svavelväte (H_2S), vilket aluminiumbaserade koagulanter inte klarar av. Polyaluminiumklorid fungerade dock bäst för att rena COD (61%).

Järn(III)sulfat har för anläggningen bekant kemi jämfört med det tvåvärda järn(II)sulfatet som används för tillfället. I den befintliga processen oxideras det tvåvärda järnet till trevärt järn med luft i ett högt pH på 9,5. Järn(III)sulfat fungerade under experimenten utmärkt i neutralt pH 7-8, vilket innebär förhållandevis stora kemikaliebesparingar via ett minskat behov av pH justering med natriumhydroxid.

De fullskaliga experimenten visade att en medeldos på 35 mg/l av järn(III)sulfat i kombination med de rekommenderade nya flotationsparametrarna förbättrade reningen avsevärt. Koncentrationen av alla de undersökta föroreningarna i flotationsanläggningens utlopp minskade med mer än 50% jämfört med den befintliga processen, med en motsvarande dos av järn (förhållandet $Fe^{2+}:Fe^{3+}$ -joner). Vid större processproblem uppströms och således smutsigare avloppsvatten kan doser på upp till 180 mg/l av järn(III)sulfat behövas. De optimala doserna på flockuleringsmedlet var 1-2 mg/l då både större och mindre doser försämrade reningen av speciellt suspenderade ämnen. Flotationsanläggningens återcirkulationsvolym användes så som förut under

ett maximalt lufttryck på 3,9 bar, men luftströmmen ökades från mindre än 20 Nm³/h till 30 Nm³/h. Ökningen av luftmängden minskade på koncentrationen av suspenderade ämnen med över 34% jämfört med det tidigare systemet.

Resultaten överensstämde överlag bra med tidigare rön, som visat att högre oxidationstal på metalljoner innebär bättre koagulering. De fullskaliga experimenten visade också att fosfor kan renas bäst vid ca. pH 6, vilket är i linje med tidigare forskningsresultat. Suspenderade ämnen och olja renades bäst vid pH 7,5-8, medan COD renades bättre vid högre pH. Optimala värden är dock mycket varierande beroende på typen av avloppsvatten, och resultaten kan inte generaliseras till att gälla alla vattenreningsverk i oljeraffinaderier. För vidare utveckling vid Nådendals raffinaderi rekommenderas undersökning i hur kombinationer av järn- och aluminiumbaserade koaguleringsmedel fungerar, speciellt vid processtörningar i raffinaderiet.

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10 Appendices

Appendix A: Naantali DAF pictures



Figure 40: DAF unit working correctly. Notice the bubbles in the froth layer on the surface.



Figure 41: DAF unit working correctly. White water caused by pressure reduction lifting the floc to the surface.

Appendix B: Chemical dosing tables

(for operators)

PIX dosing
(L/h)

Flow	5 mg/L Fe	10 mg/L Fe	20 mg/L Fe	30 mg/L Fe	40mg/L Fe
100 m ³ /h	2,7	5,4	10,8	16,3	21,7
200 m ³ /h	5,4	10,8	21,7	32,5	43,4
300 m ³ /h	8,1	16,3	32,5	48,8	65,1
400 m ³ /h	10,8	21,7	43,4	65,1	86,7

Polymer
dosing (L/h)

	1 mg/L	2 mg/L	3 mg/L	4 mg/L	5 mg/L
100 m ³ /h	48	95	143	190	238
200 m ³ /h	95	190	286	381	476
300 m ³ /h	143	286	429	571	714
400 m ³ /h	190	381	571	762	952