

Mirjam Karhu

TREATMENT AND
CHARACTERISATION OF
OILY WASTEWATERS

UNIVERSITY OF OULU GRADUATE SCHOOL;
UNIVERSITY OF OULU,
FACULTY OF TECHNOLOGY;
UNIVERSITY OF OULU,
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MIRJAM KARHU

**TREATMENT AND
CHARACTERISATION OF OILY
WASTEWATERS**

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Supervised by
Professor Juha Tanskanen
Docent Toivo Kuokkanen
Doctor Jaakko Rämö
Doctor Tiina Leiviskä

Reviewed by
Professor Juha Knuutinen
Professor Frank-Dieter Kopinke

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University of Oulu, P.O. Box 8000, FI-90014 University of Oulu, Finland

Abstract

Oily wastewaters are heterogeneous, containing various types of oils, surfactants from detergents, metals etc. Oily wastewaters are produced from a wide range of industries such as metalworking, leum refineries, the petrochemical industry, transportation as well as the textile and food industries. Oily wastewaters, especially those containing stable oil-in-water emulsions, require advanced treatment as conventional treatment methods have their limitations to meet ever-stricter environmental regulations.

Ultrafiltration is a widely accepted and commonly used treatment method for oily wastewaters. The first aim of this thesis was to increase knowledge concerning the performance of an industrial-scaled ultrafiltration-based process treating concentrated real oily wastewaters. The demand for a more effective pre-treatment method for ultrafiltration to enhance performance and decrease fouling of membrane was observed. The second aim of the thesis was to investigate the suitability and efficiency of different methods for treating concentrated model oil-in-water emulsions and real oily wastewaters. The treatment methods studied were electrocoagulation (electrolytic dissolution of anodic metal), conventional coagulation-flocculation followed by either sedimentation or dissolved air flotation, and dissolved air flotation utilising cationic air bubbles. Electrocoagulation was discovered to be a promising treatment method for various types of oil-in-water emulsions. Dissolved air flotation with cationic modified air bubbles was proven to be an efficient method with even higher treatment results with smaller chemical doses when compared to conventional coagulation-flocculation followed by dissolved air flotation.

The biodegradation of various components is an important measure of their impact on the environment in case of spillage. The third aim of the thesis was to explore the biodegradability of different types of oils and surfactants in solution conditions and soils. It was discovered that the biodegradation of light fuel oil continued during a three-month time period, reaching a biodegradation degree of over 60% in mineral-rich soil. For surfactants, their distinct effect on the biodegradation of organic material in soil was observed, and it masked the biodegradation of the surfactants themselves.

Keywords: biodegradation, DAF, dissolved air flotation, EC, electrocoagulation, emulsion, oily wastewater, surfactant, UF, ultrafiltration

Karhu, Mirjam, Öljyisten jätevesien käsittely ja karakterisointi

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Tiivistelmä

Öljyiset jätevedet ovat heterogeenisiä, sisältäen mm. erityyppisiä öljyjä, metalleja ja pesuaineiden pinta-aktiivisia aineita. Öljyisiä jätevesiä muodostuu laajalti eri teollisuuksista, kuten metallintyöstöstä, öljyn jalostuksesta, petrokemian teollisuudesta, ruoka- ja tekstiiliteollisuudesta sekä liikenteestä. Öljyiset jätevedet, varsinkin stabiileja öljyemulsioita sisältävät, vaativat tehokkaan käsittelymenetelmän, jotta ympäristölainsäädännön ja luvituksen ehdot täyttyvät.

Ultrasuodatus on yleisesti käytössä oleva öljyisten jätevesien käsittelymenetelmä. Tämän väitöstyön ensimmäinen tavoite oli lisätä tietoutta teollisen mittakaavan konsentroituneiden öljyisten jätevesien ultrasuodatusprosessien tehokkuudesta. Prosessien strategisista kohdista kerättyjen öljyisten jätevesien karakterisointitulosten perusteella havaittiin, että ennen ultrasuodatusta tarvitaan tehokas esikäsittelyvaihe prosessin tehostamiseksi ja ultrasuodattimen tukkeutumisen vähentämiseksi. Täten toinen väitöstyön tavoite oli selvittää eri menetelmien soveltuvuutta ja tehokkuutta konsentroituneiden malliaineina käytettyjen öljyemulsioiden ja öljyisten jätevesien käsittelyssä. Tutkitut käsittelymenetelmät olivat elektrokoagulaatio (sähkökemiallinen flokkaavien metalli-ionien liuottaminen anodilta), koagulaatio-flokkulaatio ja laskeutus/korkeapaineflotaatio sekä korkeapaineflotaatiomenetelmä, joka hyödyntää kationisia ilmakuplia. Elektrokoagulaation todettiin olevan erittäin tehokas käsittelymenetelmä, jolla saavutettiin korkeat puhdistustulokset erityyppisille öljyemulsioille. Korkeapaineflotaatiolla, joka hyödyntää kationisia ilmakuplia, saavutettiin hyvät puhdistustulokset jopa pienemmillä kemikaalimäärillä verrattuna perinteiseen koagulaatio-flokkulaatioon ja korkeapaineflotaation.

Erilaisten komponenttien biohajoavuus on tärkeä suure arvioitaessa niiden ympäristövaikutuksia. Väitöstyön kolmas tavoite oli selvittää erilaisten öljyjen ja pinta-aktiivisten aineiden biohajoavuutta erilaisissa liuosolosuhteissa ja maa-aineksissa. Tärkeimmät biohajoavuustulokset olivat, että kevyt polttoöljy saavutti kolmen kuukauden mittauksen aikana yli 60 % biohajoavuusasteen mineraalirikkaassa maa-aineksessa. Pinta-aktiivisten aineiden havaittiin lisäävän huomattavasti maan orgaanisen aineksen biohajoamista, ja tämä vaikeutti itse pinta-aktiivisten aineiden biohajoamisen arviointia.

Asiasanat: biohajoaminen, DAF, EC, elektrokoagulaatio, emulsio, korkeapaineflotaatio, pinta-aktiivinen aine, UF, ultrasuodatus, öljyinen jätevesi

*Dedicated to my brother and parents, and above all to my
Heavenly Father*

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as much I do! Thank you to all my friends for brightening my days. I would like to thank God without whom this thesis would never have been completed.

Oulu, June 2015

Mirjam Karhu

List of symbols and abbreviations

Symbols

A_{eff}	effective anode area below the water surface, cm^2
A/S	air/solid ratio
BOD ₇	biological oxygen demand after seven days
C	concentration, mg/L or mg/kg
C_{sat}	chemical concentration in saturator in dissolved air flotation studies, mg/L
COD _{Cr}	chemical oxygen demand, oxidation with potassium chromate
E^0	electrode potential, V
e^-	electron
F	the Faraday's constant, 96500 As/mol
I	current, A
M_{Al}	molecular mass of aluminium, 27 g/mol
$m_{\text{Al}^{3+}}$	amount of dissolved aluminium in electrocoagulation, g
R	resistance, Ω
t	treatment time, s
U	voltage, V
w/w	weight/weight
z	valence of aluminium, +3
ζ	zeta potential, mV

Abbreviations

2MO	2-stroke motor oil
Al	aluminium
APE	alkylphenol ethoxylate
AS	alkyl sulphate
ATU	<i>n</i> -allylthiourea
BOD	biological oxygen demand
CF-DAF	coagulation-flocculation followed by DAF
CF-S	coagulation-flocculation followed by sedimentation
CMC	critical micelle concentration
COD	chemical oxygen demand

Cr	chromium
CTAB	cetyltrimethylammonium bromide
DAF	dissolved air flotation
EC	electrocoagulation
Epi-DMA	epichlorohydrin-dimethylamine copolymer
FCM	flow cytometry
Fe	iron
FSC	forward scatter
GRT	gross register tonnage
GC-FID	gas chromatography with a flame ionisation detector
GC-MS	gas chromatography-mass spectrometry
LAS	linear alkyl benzene sulphonate
MCO	mineral oil-based chain oil
MEF	melamine formaldehyde
MF	microfiltration
MO	motor oil
Mo	molybdenum
MW	molecular weight
NF	nanofiltration
Ni	nickel
OECD 301 F	optimal standard conditions for biodegradation measurement in solution
O/W	oil-in-water
OWW	oily wastewater
PAH	polycyclic aromatic hydrocarbon
PEI	polyethyleneimine
PES-Na	polyethylene sodium sulphonate
PolyDADMAC	polydiallyldimethylammonium chloride
PosiDAF	DAF which utilises cationic air bubbles
QAC	quaternary ammonium-based surfactant
RO	reverse osmosis
RSO	rapeseed oil
SDS	sodium dodecyl sulphate
SFO	sunflower oil
SLFO	summer grade light fuel oil
SS	stainless steel
SSC	side scatter

TC	total carbon
ThOD	theoretical oxygen demand
TMP	trans-membrane pressure
TO	tall-oil based chain oil
TOC	total organic carbon
Triton X-100	4-tert-octylphenol ethoxylate
TSC	total surface charge
UF	ultrafiltration
WFO	winter grade light fuel oil
WWTP	wastewater treatment plant

List of original papers

This thesis is based on the following papers, which are referred to throughout the text by their Roman numerals:

- I Karhu M, Kuokkanen T, Rämö J, Mikola M & Tanskanen J (2013) Performance of a commercial industrial-scale UF-based process for treatment of oily wastewaters. *Journal of Environmental Management* 128: 413–420.
- II Karhu M, Kuokkanen V, Kuokkanen T & Rämö J (2012) Bench scale electrocoagulation studies of bio oil-in-water and synthetic oil-in-water emulsions. *Separation and Purification Technology* 96: 296–305.
- III Karhu M, Leiviskä T & Tanskanen J (2014) Enhanced DAF in breaking up oil-in-water emulsions. *Separation and Purification Technology* 122: 231–241.
- IV Karhu M, Kaakinen J, Kuokkanen T & Rämö J (2009) Biodegradation of light fuel oils in water and soil as determined by the manometric respirometric method. *Water, Air, and Soil Pollution* 197: 3–14.
- V Prokkola H, Karhu M, Kuokkanen T & Lassi U (2015) Biodegradation studies of surfactants, especially in a concrete washing solvent agent, in various environments, Manuscript.

The present author was the corresponding author in Papers I–IV. The co-authors participated in writing the papers by making valuable comments and corrections. The design of the experimental research in Papers I–IV was performed together with the co-authors. The experimental work in Paper II was carried out by the present author together with the second author, and for Paper I together with the fourth author. The experimental work for Papers III and IV was performed solely by the present author. The present author worked as co-author in Paper V and participated in writing the paper by making comments and corrections. The design of studies, and research for Paper V was performed with the corresponding author.

In addition, Karhu *et al.* prepared an abstract for the proceedings and poster “Bench scale electrocoagulation of bio oil-in-water emulsions” at the IWA Regional Conference on Wastewater Purification & Reuse, 28–30.3.2012, in Heraklion, Crete, Greece; and an abstract for the proceedings and poster “Coagulation studies of highly oily wastewaters” at the IWA International Conference on Particle Separation, Advances in Particle Separation - Science, Technology, Practice, 18–20.6.2012, in Berlin, Germany. Part of the results from the abstract and the poster presented in Berlin are discussed in this thesis.

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1 Introduction

Oil and grease are common pollutants in a wide range of industries and domestic sewages. Millions of cubic meters of oil containing wastewaters are produced daily, for example in metalworking, primary metal operations, petroleum refineries, petrochemical, textile, waste collection and transportation (Cheryan 1986) and also by the food industry and restaurants etc. Therefore, oil-contaminated wastewaters may contain not only mineral- and synthetic oils, but also vegetable oils and esters.

Saline produced water, containing different kinds of organic and inorganic components, is the largest waste stream generated by the oil and gas industries (Fakhru'l-Razi *et al.* 2009). Bilge water is also one of the biggest waste streams concerning oily wastewaters produced from naval and commercial vessels. It can be treated on-board or pumped to a tank truck in the port. In Finland, according to the Act on Environmental Protection in Maritime Transport (1672/2009), it is prohibited to discharge oil or oily mixtures not only from ships in Finnish waters or in Finland's exclusive economic zone, but also from Finnish ships outside Finnish waters or Finland's exclusive economic zone. MARPOL 73/78 (International Convention for the Prevention of Pollution from Ships) sets international regulations, for example, for non-tankers of 400 GRT (gross register tonnage) and above, the permitted oil content of the effluent which may be discharged into the sea is 15 parts per million.

Oil spills also produce waters containing oil. Usually the volumes of oil spills in the marine environment are smaller than 7 metric tons, and data concerning them is incomplete due to the inconsistent reporting of smaller incidents worldwide. However, data concerning larger spills of 7 tons and above tend to be more reliable. (ITOPF 2015). According to data gathered by ITOPF (The International Tanker Owners Pollution Federation), medium-sized (7–700 tons) and large (>700 tons) oil tank spills have declined during the last 45 years, so that in 2010–2014 there was on average about 1.8 spills per year.

The composition and concentration of oily wastewaters varies greatly between industries. Data concerning the volumes of oily wastewaters generated globally is very scarce. However, some data can be found, for example, about volumes of wastewaters from oil refineries. A report published in October 2012 by CONCAWE (The oil companies' European association for environment, health and safety in refining and distribution) summarises data gathered up to 2010 concerning effluent water quantity, oil content and treatment processes for refinery installations situated in the EU-27 countries and those in Croatia, Norway and Switzerland. The data

gathered indicated that oil discharged with refined aqueous effluents reduced continuously relative to the refining capacity from 1969 (127 g/t capacity) to 2010 (1.1 g/t capacity or 1.3 g/t feedstock processed). In 2010 the quantity of total oil discharged with refinery effluents from reporting 98 European oil refineries was 798 t/year. The majority of these refineries perform an on-site final treatment including an aerated activated sludge reactor before discharging process effluents. (CONCAWE 2012).

The treatment of various types of oily wastewaters has already been under intense investigation for many decades. As there has been high demand for alternative energy sources to replace fossil fuels, studies have emerged concerning treatment of oily wastewaters, for example from biodiesel production. Also, as raw oil wells are depleting, oil sands are attracting interest although extracting oil from sand requires high volumes of water, therefore producing high volumes of wastewaters.

In Finland, Environmental Protection Act 86/2000 (the new Environmental Protection Act 527/2014 came into force on 1.9.2014) and Environmental Protection Decree 169/2000 (the new Environmental Protection Decree 713/2014 came into force on 1.10.2014) set demands on wastewaters discharged into a sewer network. An environmental permit is required for activities for example for treatment of waste that poses the threat of environmental pollution (Environmental Protection Act). Annex 1 of the Environmental Protection Decree lists substances requiring a permit for discharge into waters including heavy metals and also mineral oils and oil-derived hydrocarbons. However, there are no general limits for oil concentrations in effluents, but the limit is decided case-specifically by the municipal wastewater plant that receives the effluents. Oily wastewaters are usually transported to a wastewater treatment plant unless the treatment is performed in situ by the wastewater producer. However, the space in plants is usually limited, requiring treatment facilities to be compact and therefore effective so that no long treatment trains are needed.

1.1 Scope and objectives

In this thesis, model oil-in-water (O/W) emulsions and real oily wastewaters (OWWs) were characterised and treated. The biodegradation studies were performed for oil products and surfactants, which are the major components of various oily wastewaters. The objectives of the thesis were:

1. To increase knowledge concerning the performance of commercial industrial-scale ultrafiltration (UF)-based treatment process by characterising O/W samples from the most important points of the UF-based process in use at two wastewater treatment plants (WWTPs).
2. To study the efficiency of methods for treating concentrated model O/W emulsions and real O/Ws.
3. To study the biodegradability of components (oils and surfactants) usually present in oily wastewaters, since their biodegradability is an important measure of their impact on environment in case of spillage.

The unit operations studied experimentally in this thesis were electrocoagulation (EC), conventional coagulation-flocculation followed by sedimentation (CF-S) or dissolved air flotation (CF-DAF), and PosiDAF, which utilises modified cationic air bubbles. The CF-S studies were conducted for comparison purposes. Fig. 1 presents the outline of the thesis.

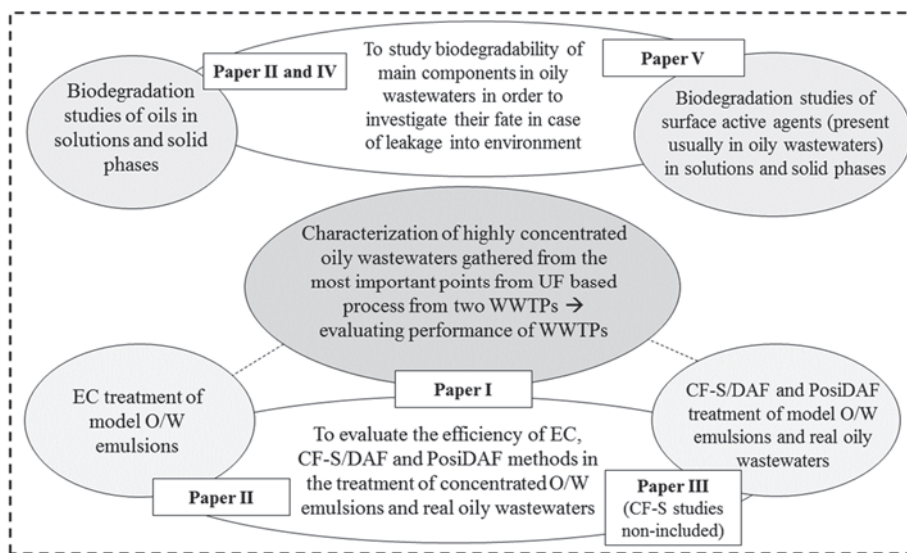


Fig. 1. Outline of the thesis.

2 Literature review

2.1 Treatment of oily wastewaters

Oily wastewaters contain readily removable unstable or stable O/W emulsions that are difficult to break. It is widely known that the effectiveness of conventional treatment methods such as coagulation-flocculation, conventional DAF, and gravitational separation is limited for oily wastewaters containing stable O/W emulsions formed by very small oil droplets. Therefore, there is a great demand for the development of advanced, cost-effective as well as environmentally friendly treatment methods for oily wastewaters to meet ever-stricter environmental regulations. The effectiveness of the treatment method is greatly affected by the varying composition of oily wastewater. Therefore, oily wastewaters are not usually treated by one method alone, but rather a combination of various unit operations is needed to achieve adequate treatment results.

2.1.1 Treatment of oily waters with UF

UF is a widely and commercially used efficient key technology. Ceramic UF membranes in particular are the most widely used for the treatment of industrial oily wastewaters because they have high thermal and chemical stability. Membrane processes have many advantages such as 1) being widely applicable across various industries, 2) no extra chemicals needed, 3) concentrates up to 40–70% oil and solids can be obtained with UF or microfiltration (MF), and 4) the equipment has a small foot print and can be highly automated (Cheryan & Rajagopalan 1998). Fouling of the UF membrane is, however, one of the major drawbacks, slowing down the entire treatment process, and being uneconomical because of the need for washing. The washing step also produces a new waste fraction that requires treatment.

Important parameters for evaluating the performance of UF include water flux through the membrane, contaminant rejection, and fouling time. The water flux through the UF membrane is furthermore affected by the membrane characteristics (porosity and thickness) and the system conditions such as temperature, pressure, contaminant concentration as well as flow velocity through the membrane module. (Tansel *et al.* 2001). In membrane processes, the oil phase often causes concentration polarisation and membrane fouling due to pore blocking, therefore

decreasing the permeate flux. The size of the oil droplets in stabilised emulsions can also be smaller than the pore size of the membrane, increasing the turbidity and oil content of the permeate (Gutiérrez *et al.* 2011).

UF performance is known to have limitations, especially for dissolved hydrocarbons. Therefore, the post-treatment of UF effluents has been studied, as discussed below. Sun *et al.* (2015) discovered that the treatment of phenolic wastewater with polymeric UF resulted in the removal of 50–60% of COD (chemical oxygen demand). However, the removal of total dissolved solids and phenol was below 10%, and the removal efficiency of UF decreased with increasing trans-membrane pressure (TMP). Solids were retained on the surface of the membrane and accumulated. A dense layer was formed due to the higher TMP, thus increasing filtration resistance. By combining UF, especially with reverse osmosis (RO) instead of nanofiltration (NF), a higher phenol removal from phenolic wastewater was achieved with less energy consumption compared with other membrane processes studied elsewhere. (Sun *et al.* 2015). The high level of performance of the hybrid UF-RO process for oil-containing wastewaters has also been proved by Tomaszewska *et al.* (2005) and Norouzbahari *et al.* (2009).

The need for pre-treatment prior to UF has been widely identified as decreasing UF membrane fouling, but also decreasing the organic load prior to UF. In this thesis, the performance of a commercial UF-treatment process for treating highly concentrated oily wastewaters was evaluated and possible improvements were investigated (Paper I). Masoudnia *et al.* (2014) treated industrial oily wastewaters with the hybrid process MF-UF. They discovered that the permeate from MF-UF had better quality in terms of the measured parameters compared with water treated by single MF and UF methods. Ebrahimi *et al.* (2010) also studied MF for the pre-treatment of UF. High oil removal levels (up to 93%) were gained for produced water and model solutions with hybrid MF-UF, and when the effluent from UF was finally treated by NF, the total oil removal was as high as 99.5%.

Although the combination of UF with other membrane processes has been studied, the most studied pre-treatment method for increasing the performance of UF has been coagulation-flocculation, as it has also been shown to decrease the extent of irreversible fouling of the UF membranes (Tansel *et al.* 1995). Tansel *et al.* (2001) found out that, at low oil concentration (150 mg/L), use of coagulant lowered the initial flux, but at higher oil concentration (3000 mg/L), it increased the initial flux. It was suggested that it could be beneficial to leave flocs formed in the pre-treated water prior to UF, because the fouling time and removal efficiency of petroleum hydrocarbons were higher without pre-filtration of flocs before UF.

Pre-filtration improved only the initial flux through the UF membrane. (Tansel *et al.* 2001). If coagulation is performed before UF, and flocs are not removed prior to UF, the flux improvement of UF is only achieved when the flocs are sufficiently resistant to create a cake of large aggregates, allowing water to flow between the structures. The flux through UF will not be improved unless the flocs are sufficiently resistant to the shear stress caused by pumping that breaks the flocs. On the other hand, if the flocs are too small, they will create a dense cake, decreasing the flux. (Barbot *et al.* 2008). Flocs with ferric chloride have been discovered to be non-resistant, thus no improvement of UF flux was gained in the studies performed by Barbot *et al.* (2008). Flocs with polyelectrolytes, especially with PolyDADMAC (polydiallyldimethylammonium chloride), were larger and more resistant to shear stress (Barbot *et al.* 2008). Pre-treatment, for example with coagulation-flocculation, before a ceramic UF membrane is observed to be essential when treating water from oil sands process that is a complex mixture of suspended solids, salts, inorganic and organic compounds as well as metals (Alpatova *et al.* 2014, Loganathan *et al.* 2015). In this thesis, EC (Paper II) and DAF (Paper III) studies were performed on concentrated O/W emulsions and OWWs to investigate their effectiveness as pre-treatment alternatives to UF, although the combination of pre-treatment and UF was not studied experimentally in this thesis.

2.1.2 Fouling of UF membrane

Flux decline in membrane processes can be caused by several factors, such as reversible concentration polarisation, adsorption, gel layer formation, pore blocking, membrane characteristics, salts, pH, temperature, shear stress and pressure (Benito *et al.* 2001). Currently, a hot topic in studies concerning UF is the modification of the UF membrane to decrease fouling or increase understanding of the phenomenon of fouling and concentration polarisation for various types of membranes and the effects of operating conditions.

Hesampour *et al.* (2008a) investigated the optimal conditions for UF in treating emulsified oil in water. They discovered that with a low salt concentration, pH was the most important factor, although with increasing salt concentration temperature became the most important factor. With increasing temperature, the viscosity and the density of emulsion decreased, therefore, permeate flux was increased. The best conditions predicted to obtain the highest flux were an alkaline pH (as much as 11), high pressure (3.5 bar), high temperature (40 °C), and salts as well as an oil

concentration at the lowest level (Hesampour *et al.* 2008b). Similar optimal operating conditions (pH 10, 50 °C, TMP 3 bar and cross flow velocity of 1 m/s) for a steady permeate flux for UF when treating oily wastewaters were also suggested by Salahi *et al.* (2010), although they did not study the effect of salts. The effect of pH on flux through a ceramic UF membrane was also discovered by Lobo *et al.* (2006) when treating O/W emulsions. When the pH was below the isoelectric point (pH 4) of the ceramic membrane, the surface of the membrane was positively charged, enhancing the adsorption of anionic surfactant from the O/W emulsions by electrostatic interactions. Therefore, the initially hydrophilic membrane was modified into a more hydrophobic surface and the flux as well as the removal of COD was reduced. When the pH was over a value of 4, the surface of the membrane was negatively charged and prevented surfactant adsorption and the hydrophobicity of the membrane. The best flux was gained with the highest studied TMP of 3.5 bar. It was observed that higher COD values in the permeate were due to the surfactant molecules passing through the membrane, as their molecular size was smaller than the pore size of the ceramic UF membranes. (Lobo *et al.* 2006).

The effect of UF membrane properties such as its hydrophobic/hydrophilic nature and charge characteristics has been under intensive investigation especially when the waters studied contained surfactants, as oily wastewaters generally do. It was discovered by Byhlin & Jönsson (2003) that for a non-ionic surfactant when the concentration was below the critical micelle concentration (CMC), the reduction of surfactant monomers was about zero for both hydrophobic and hydrophilic membranes. When the concentration was above the CMC, the reduction in surfactant micelle concentration was lower for the hydrophobic membrane, although for both membranes adsorption and concentration polarisation occurred. Rezvanpour *et al.* (2009) concluded that permeate flux for a hydrophilic UF membrane was greater than for a hydrophobic one when treating O/W emulsions, but the drop in flux was greater in the initial stage of filtration for the hydrophilic membrane. It was suggested that the type of fouling was different, being a more cake-layer formation for a hydrophilic membrane and pore-blocking for a hydrophobic membrane.

Membrane fouling could be decreased by modifying UF membranes. The modification methods can be categorised into physical techniques, such as ion beam irradiation, plasma irradiation, and vapour phase deposition, and chemical techniques such as grafting, coating and acid-base treatment of which grafting in particular has an important role in improving membrane performance. Grafting can

be performed by ‘grafting-to’ by coupling polymers to surfaces or by ‘grafting-from’ where monomers are polymerised using an initiation at the surface. (Padaki *et al.* 2015)

2.1.3 Theory of EC

EC is a method based on the anodic dissolution of metal ions due to the applied current. The electrode materials most studied and used are aluminium (Al) and iron (Fe). Fig. 2 presents the main phenomena occurring in EC cell (studied in Paper II) with Al anodes and a stainless steel (SS) cathode. Similar reactions occur when Fe^{2+} ions are electrically dissolved from the SS anode (with Al bars as cathodes, studied in Paper II) but are further oxidised to Fe^{3+} .

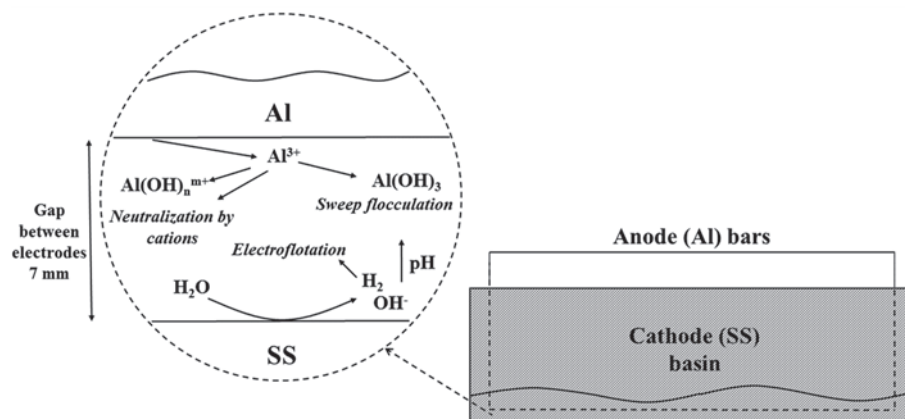
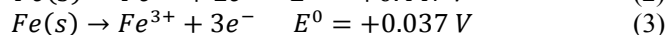
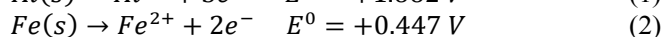
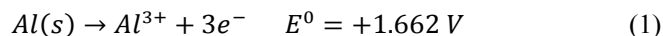


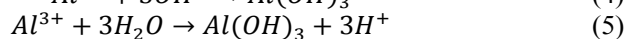
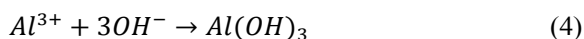
Fig. 2. Simplified phenomena occurring in the EC cell (Paper II) used with Al anodes.

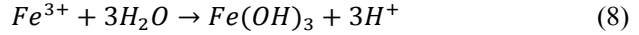
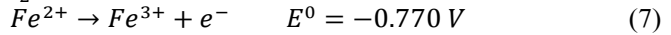
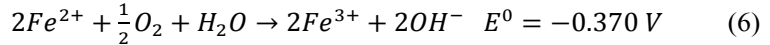
The chemical reactions in EC cell with the Al or Fe anode are presented in Eqs. (1)–(10) with electrode potentials, E^0 , (Chen 2004):

at the anode:

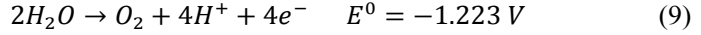


in solution, depending on pH:

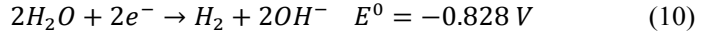




As well as oxygen evolution at the anode can happen from the reaction:



The main reaction at the cathode is generally as follows:

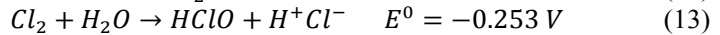
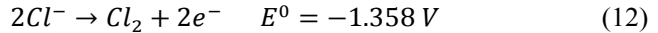


Metal cations from anodic dissolution undergo further spontaneous reactions to form corresponding hydroxides and/or polyhydroxides (Mollah *et al.* 2004). Faraday's law can be used to calculate the theoretical amount of dissolved metal ions, for example the amount of Al^{3+} produced in the EC process, Eq. (11).

$$m_{Al^{3+}} = \frac{ItM_{Al}}{zF} \quad (11)$$

where $m_{Al^{3+}}$ is the amount of dissolved Al^{3+} [g], I is the current [A], t is the treatment time [s], M_{Al} is the molecular mass of Al (27 g/mol), z is the valence of the aluminium cation (+3) and F is the Faraday's constant (96500 As/mol). However, the experimentally observed amount of dissolved metal is usually higher than the theoretical, and this phenomenon is called "superfaradaic efficiencies" (Linares-Hernández *et al.* 2009).

When the water to be treated with EC contains chlorides, the oxidation of chloride ions can lead to the formation of active chlorine species on the electrode surface and in the bulk solution through Eqs. (12)–(14) enhancing the performance of EC (Yıldız *et al.* 2008, Gao *et al.* 2010). Speciation of formed chlorine is pH-dependent so that with increasing pH dominance of hypochlorous acid (HClO) increases but at adequate high pH values hypochlorite (ClO^-) becomes prevailing.



2.1.4 Novel findings on EC

EC has been under intensive investigation for many decades. EC technology has been improved, becoming more economical, and is one of the most promising alternatives for various types of wastewaters, including oily waters. It has been studied for many types of O/W emulsions and also for real oily wastewaters, but

not for highly concentrated ones. The most recent studies on EC treatment of oily waters are presented in this section.

The improvement of dynamic membrane performance with EC for the treatment of model O/W emulsions was investigated by Yang *et al.* (2015). A dynamic membrane was prepared by pre-coating an MF ceramic membrane with kaolin clay. According to the results, the efficiency of the EC-dynamic membrane process for oil removal was better than that of the EC-uncoated ceramic membrane, but in both cases EC as pre-treatment clearly increased efficiencies for both membrane types. The dynamic membrane fouled less than the non-treated ceramic membrane after EC. EC effectively reduced the reversible resistance, and coating the ceramic membrane decreased the irreversible resistance. An iron anode performed better in the hybrid system because with aluminium the oil-gel layer covering the membrane surface was more compacted. The membrane flux increased with increasing current density (optimal 300 A/m²) and with decreasing initial pH (optimal of 3.2). (Yang *et al.* 2015).

EC (Fe anodes and graphite cathodes) has also been studied as pre-treatment for the membrane process when treating produced water (Zhao *et al.* 2014). The experimental setup was a pilot-scale EC-RO process. It was observed that, under refined conditions, EC pre-treatment improved RO performance in terms of both permeate flux and product water quality. Operational parameters, especially pH and current density, had the most significant effects on pollutant recovery, while reaction time was the least significant. The optimal process conditions were pH 7, current density 56 A/m², and electrolysis time of 30 min. (Zhao *et al.* 2014). In the light of the results from Yang *et al.* (2015) and Zhao *et al.* (2014), EC could be a promising pre-treatment for UF also, especially when considering membrane fouling and UF performance.

Electrochemical methods have been combined with oxidation methods to treat very complex petroleum refinery wastewaters containing inorganic substances (Bhagawan *et al.* 2014). An EC cell including Al electrodes performed best when the applied voltage was 20 V, corresponding to a current density of 166 A/m² with a treatment time of 20 min. When the current density of EC was increased to over 170 A/m², the performance of EC decreased, probably because of the reduction in production of flocs due to the faster generation of gas bubbles from the cathode, decreasing the probability of collision between the metal coagulant and pollutant. Addition of hydrogen peroxide (optimal dosage 200 mg/L for removal of phenolic compounds) enhanced the performance of EC, as it did when the process was followed by ultrasonication. However, Maha Lakshmi & Sivashanmugam (2013)

observed that when ultrasonication was combined with EC, the amount of sludge produced was doubled but COD reduction of oil tanning effluent was slightly less for the EC-ultrasonication process. Ultrasonication, however, could be used to treat the passivation of EC anodes. A maximum of 90% COD removal was achieved using iron electrodes, an NaCl concentration of 1g/L, current density of 200 A/m² and treatment time of 15 min.

Sangal *et al.* (2013) studied EC (Al electrodes) for the treatment of wastewater containing cutting oils (initial oil concentration 9600 mg/L). Turbidity was removed to a greater degree than oil concentration. The best conditions for 100% turbidity removal were an initial pH of 6.5, current density of 139 A/m² (treatment time 2 h), and temperature of 20 or 60 °C.

EC could also be used for treating oil-contaminated natural waters. Moussavi *et al.* (2011) performed batch and continuous EC treatment for petroleum-contaminated groundwater. They studied for example Al, Fe and SS electrode materials, and the addition of aeration in the EC process. The best treatment conditions were when using SS as the anode and Fe as the cathode, a neutral pH and current density of 180 A/m². An aeration system equipped with a fine bubble diffuser enhanced EC efficiency by about 22%. Enhancement of the EC process was probably due to the transfer of oxygen into the solution through aeration, which accelerated the oxidation of Fe²⁺ ions from the anode into Fe³⁺ ions. This resulted in the formation of larger Fe(OH)₃ flocs and thereby increased the adsorption of contaminants. (Moussavi *et al.* 2011)

The conditions have a significant influence on the performance of EC. The factors affecting performance include 1) the electrode material, 2) applied current density, 3) initial pH, 4) quality of solution to be treated, 5) temperature, 6) conductivity, 7) presence of chlorides, 8) electrode gap, 9) passivation of the anode and 10) water flow rate (Kuokkanen *et al.* 2013), and also the electrode configuration. Electrode passivation is one of the drawbacks of EC, especially when using Al electrodes due to the formation of alumina (Al₂O₃) from Al oxidation with oxygen (Trompette & Vergnes 2009). When Trompette & Vergnes (2009) studied the influence of some supporting electrolytes on EC with Al electrodes, they discovered that sulphate anions in solution hinder the efficiency of coagulants formed in EC, probably through enhanced screening of the positive charge of the polymeric hydroxoaluminium cations and/or through their adsorption onto the Al(OH)₃. It was stated that if sulphates are present, chlorides must be added so that the ratio of Cl⁻/SO₄²⁻ is approximately 0.1 in order to break the passive film

on the Al electrode and to decrease electricity consumption (Trompette & Vergnes 2009).

2.1.5 DAF

DAF is a widely used treatment method for oily waters. As gravity settling is not usually a feasible treatment method for stable oil emulsions, DAF has been used to enhance the buoyancy difference of emulsified oil droplets by the attachment of small air bubbles (Zouboulis & Avranas 2000). The operating principle in DAF is the production of air bubbles by dissolving air under pressure and releasing water supersaturated with air into the vessel at lower air pressure. When DAF is used as a treatment unit in a water plant, the typical saturator pressure is 5 bar and the recycle ratio is typically 10%. Microbubbles are produced in sizes of 10 to 100 μm . Bubble size is an important property in DAF. It affects collision performance, the attachment of particles to bubbles, and bubble rise velocity. The majority of bubbles in the contact zones have sizes of 40–80 μm . (Edzwald 2010). The key parameter for obtaining microbubbles, with or without the use of chemical additives, is nozzle geometry (Ponasse *et al.* 1998). Other important factors affecting the efficiency of DAF treatment for oily wastewaters are 1) saturator efficiency, 2) recycle ratio, 3) air to oil ratio, 4) pressure, and 5) the geometry of the DAF tank.

When treating oily waters with DAF, air bubbles attach to contaminant particles or droplets and raise them to the surface. Due to the collection and adhesion factors when dealing with flotation separation of very small oil droplets (2–30 μm), fine bubbles, quiescent hydrodynamic conditions in the separation zone and emulsion breakers before flotation are required (Gopalratnam *et al.* 1988). Therefore, studies concerning DAF are typically focused on coupling coagulation and DAF (Al-Shamrani *et al.* 2002, Bensadok *et al.* 2007, Tansel & Pascual 2011, Santo *et al.* 2012, Van Le *et al.* 2012).

Edzwald (2010) suggested that research is needed especially on the ability of DAF to serve as a pre-treatment process with coagulation to remove dissolved organic carbon ahead of MF and UF processes, and to reduce fouling of UF and NF membrane processes. Only a few studies could be found on DAF and MF hybrid processes, but, to my knowledge, the combination of DAF and UF processes for oily wastewater treatment has been studied even less than the combination of DAF and MF. Minhalma & Pinho (2001) combined flocculation-flotation and UF with promising treatment results for cork processing wastewaters containing polyphenols, for example. By pre-treating wastewaters prior to UF with

flocculation with chitosan followed by DAF, the permeate fluxes were increased significantly due to polyphenol removal (62%) already in pre-treatment as well as enhancing the UF performance. However, the selectivity of UF was found to decrease with pre-treatment. Minhalma & Pinho (2001) concluded that the efficiency of the hybrid process was higher than that of UF alone. Çakmakce *et al.* (2008) studied the desalination of produced water by membrane processes. They proposed that when considering permeate flux and water quality before the RO membrane, the best pre-treatment process would be primary sedimentation, followed by an oil/water separator, DAF, a 1 µm cartridge filter and 0.2 µm MF. Braghetta *et al.* (1997) investigated the pre-treatment of surface water with DAF prior to MF. The pre-treatment with DAF resulted in reduced pore blockage and lower cake compressibility compared to MF alone, thus improving filtration run duration and total water flux through the membrane.

2.1.6 Modifying the charge of bubbles in flotation

DAF of performance is greatly affected by the charge of contaminants as both air bubbles and particles carry negative zeta potentials without coagulation. When particles and air bubbles approach each other, a repulsive force originates from the overlapping of the electrical double layers surrounding the particles and bubbles. A repulsive force occurs when no coagulant is added or when the coagulant dose is insufficient. (Edzwald 2010). By modifying the charge of the air bubbles to cationic, the attachment of oil droplets and microbubbles to each other could be enhanced. The separate coagulation-flocculation stage could also be avoided by adding chemicals directly to the DAF saturator (Henderson *et al.* 2008). The modification of the bubble charge has been studied widely, and some of the studies are presented in Table 1. As surfactants and electrolytes can be used to modify the charge of bubbles, anionic surfactants can be used to decrease the size of the bubbles, as proven by Féris *et al.* (2001) and Cho *et al.* (2005).

Table 1. Studies concerning the modification of bubble charge (ζ as zeta potential).

Chemicals studied	Most important findings	Reference
CaCl ₂ , NaCl, and Al ₂ (SO ₄) ₃	Chemicals were added directly to O/W emulsions. Flotation efficiency was largest when oil droplets and bubbles were oppositely charged.	Okada <i>et al.</i> (1988)
Weak/strong electrolyte-type surfactants ¹	Especially for weak electrolyte-type surfactants the ζ of the air bubbles was dependent on pH.	Laskowski <i>et al.</i> (1989)
DAH, SDS (with/without AlCl ₃) and POE ² (with/without electrolytes)	Analysis of latex particle trajectories (with charged particles and bubbles) showed that surface charges became significant when the particle diameter was smaller than 3 μ m. The flotation efficiency of latex particles was strongly affected by the surface charges of particles and bubbles.	Okada <i>et al.</i> (1990a,b)
AlCl ₃ , NaCl and MgCl ₂	Bubbles were cationic with MgCl ₂ in the pH range of 9–11 depending on concentration of MgCl ₂ . The effect of AlCl ₃ was more significant, producing cationic bubbles in a wider pH range when the concentration of AlCl ₃ was increased.	Li & Somasundaran (1991, 1992)
Polymers e.g. PolyDADMAC	Cationic PolyDADMAC coated air bubbles and reversed the bubble charge to cationic. Treatment of drinking water was studied with promising results.	Malley (1995)
AlCl ₃ , NaCl and CaCl ₂	The effect of AlCl ₃ on bubble charge was confirmed. The addition of Ca ²⁺ also produced cationic bubbles, but to a lesser extent than Al ³⁺ .	Yang <i>et al.</i> (2001)
Alkyltrimethylammonium bromide (C _n TAB), SDS	The increasing concentration of SDS decreased the size of nanobubbles. The bubble size increased with increasing chain length of C _n TAB. The ζ of the nanobubbles was cationic and increased with increasing concentration of C _n TAB, but was unchanged at concentrations greater than CMC.	Cho <i>et al.</i> (2005)
Electrolytes, alcohols, HCl and NaOH	Microbubbles were negatively charged in a wide pH range, but cationic under highly acidic conditions without chemicals. Addition of alcohols changed the ζ of the bubbles by affecting the gas-water interface.	Takahashi (2005)
Frothers e.g. aliphatic alcohols and polyglycol SDS	At typical flotation dosages (< 20 mg/L) frothers did not have a significant effect on bubble charge. Flotation with negatively charged colloidal gas aphrons for separation of cationic copper oxide from anionic silicon dioxide succeeded with similar results to conventional flotation.	Elmahdy <i>et al.</i> (2008) Waters <i>et al.</i> (2008)
Non-ionic, cationic and anionic surfactants, aluminium sulphate and polymers	The removal of anionic algae was highest when cationic chemical was used for bubble charge modification in DAF. PolyDADMAC proved to be the most efficient polymer in algae removal.	Henderson <i>et al.</i> (2008, 2009, 2010)

Chemicals studied	Most important findings	Reference
Polyacrylamides	By using cationic polyacrylamide, cationic microbubbles were produced in a pH range of 2 to 8.	Oliveira & Rubio (2011)
Synthesised polymer	The usage of cationic synthesised polymers resulted in comparable removal efficiencies obtained when using PolyDADMAC as a bubble modifier and conventional coagulation-flocculation followed by DAF.	Yap <i>et al.</i> (2014)

¹ Dodecylaminehydrochloride (DAH), lauric acid, sodium oleate, sodium dodecyl sulphate (SDS), sodium dodecane sulphonate, ² Polyoxyethylene 23-lauryl ether (POE).

There are many studies concerning bubble charge modification as seen in Table 1, although only a few utilise them in applications (Okada *et al.* 1988, Okada *et al.* 1990b, Malley 1995, Waters *et al.* 2008, Henderson *et al.* 2008, Henderson *et al.* 2009, Henderson *et al.* 2010, Yap *et al.* 2014). Therefore, in this thesis, the treatment of concentrated O/W emulsions and OWWs with DAF utilising cationic air bubbles was studied (Paper III). Malley (1995) was the first to study the addition of a chemical into the DAF saturator with and without a separate coagulation-flocculation stage for treatment of drinking water. Polymers like PolyDADMAC types resulted in cationic bubbles. DAF utilising cationic bubbles resulted in comparable treatment results with conventional coagulation-flocculation followed by DAF when low turbidity and low colour synthetic waters were treated. DAF with cationic bubbles was not effective for highly coloured and highly turbid waters.

Henderson *et al.* (2008, 2009, 2010) have studied the modification of bubble charges with non-ionic, anionic and cationic surfactants, and also with aluminium sulphate coagulant and polymers such as chitosan, PEI (polyethyleneimine) and PolyDADMAC. They have performed DAF studies for algae-containing waters with cationic bubbles and for comparison purposes also with conventional coagulation-flocculation followed by DAF. They referred to the process where a positively charged chemical was added into the saturator for bubble modification as PosiDAF. The best removal results, about 95%, were gained with PolyDADMAC. The removal efficiencies were similar for PosiDAF and the conventional method, although the onset of removal by the conventional method was achieved at slightly higher doses compared to PosiDAF.

Yap *et al.* (2014) performed studies for modifying the microbubble surface with hydrophobically associated polymers for the treatment of algae/cyanobacteria-laden water. They concluded that the ideal polymer for PosiDAF would consist of increased proportions of hydrophobic functionalisation of long hydrophobic pendant groups.

2.2 Biodegradation

2.2.1 Hydrocarbons

The aerobic biodegradability of an organic chemical is a critical factor, when assessing environmental fate and impact (Miles & Doucette 2001). The biodegradability of various types of hydrocarbons has been studied widely in solution and solid phase conditions. Especially, the biodegradation of PAH (polycyclic aromatic hydrocarbons) has been studied intensively because they are commonly found in oil spillage areas; they have low aqueous solubility and high sorption capacity to soil (Bogan & Sullivan 2003, Eriksson *et al.* 2003, Jacques *et al.* 2008, Zhu & Aitken 2010). Unlike PAH, monoaromatic hydrocarbons such as BTEX (benzene, toluene, ethyl benzene and xylene) are relatively water-soluble but also toxic, posing a serious risk to soil and to groundwater. BTEX are the major aromatic components in various petroleum products. (El-Naas *et al.* 2014). It must be remembered that oil spillages contain a complex mixture of hydrocarbons.

Microorganisms have huge potential to degrade organic compounds under favourable conditions, but there are no single species of microorganisms that can degrade all hydrocarbons; instead a mixture of microorganism populations is required. (Korda *et al.* 1997). Aerobic biodegradation of hydrocarbons is affected by a series of factors, such as the type and concentration of hydrocarbons/oil, pH, available nutrients, amount of oxygen and water, temperature, soil properties, microorganisms, other contaminants present etc. The optimal standard conditions for aerobic biodegradation measurements in solution are described by OECD 301 F standard (OECD 1992) for the manometric respirometric method (used in this thesis), however there are no standard conditions for solid phase biodegradation measurements. In this thesis, the biodegradability of various oil products containing many types of hydrocarbons is studied in optimal OECD 301 F standard solution conditions, in groundwater, and also in borealic forest soils (Paper II and IV) to evaluate their impact in case of spillage.

The petroleum biodegradation in soil or in an aquatic environment after spillage has differences due to the movement and distribution of oil, and also due to the particulate matter present in soil which affects the physico-chemical nature of oil and its susceptibility to microbial degradation. When a high concentration of hydrocarbons is present in water, an oily layer is formed, inhibiting biodegradation by nutrient or oxygen limitations. (Leahy & Colwell 1990). It is assumed that bioremediation of hydrophobic organic contaminants in a soil environment is

limited by their restricted aqueous solubility and strong sorption to soil (Lanzon & Brown 2013) but also due to the patchy distribution of bacterial populations in the soil (Korda *et al.* 1997). Limited solubility and strong sorption to soil might not be always the case, as Huesamann *et al.* (2004) observed for PAHs. The biodegradation of PAH was slow in the final phase of biodegradation, due to the low desorption rates. However, in the initial stage, PAHs were rapidly desorbed from the soil into the aqueous phase. This observation suggests that for example PAHs pose even a greater risk to the environment than previously assumed.

Surfactants can be used to enhance the bioavailability of hydrophobic organic pollutants through 1) emulsification of a non-aqueous phase pollutant, 2) enhancement of the apparent solubility of the pollutant by the presence of micelles, and 3) facilitated transport of the pollutant (Volkering *et al.* 1998). Usage of surfactants can also have negative effects such as depletion of minerals and oxygen, toxic surfactant intermediates and preferential degradation of surfactants (Hutzinger 1992, Tiehm 1994). Chen *et al.* (2000) observed for a non-ionic surfactant that it was sorbed onto the surfaces of both bacteria cells and anthracene particles, possibly inhibiting the uptake of anthracene.

2.2.2 Surfactants

The most studied of the commonly used commercial surfactants as anionic linear alkyl benzene sulphonates (LAS), non-ionic alkylphenol ethoxylates (APE) and cationic quaternary ammonium-based surfactants (QAC). However, the biodegradability studies of surfactants have mostly focused on anionic and non-ionic surfactants. Surfactants have been detected at various concentrations in surface waters, sediments etc., due to their widespread use and high consumption. When surfactants enter the environment they undergo many processes such as sorption and degradation; of these especially sorption into soil, for example, has a strong effect on the bioavailability and biodegradation of surfactants. Anionic surfactants tend to adsorb more weakly onto soil than non-ionic surfactants, but cationic surfactants sorb strongly onto suspended particulates. (Ying 2006). In this thesis, the biodegradability of non-ionic and cationic surfactant was studied in optimal OECD 301 F standard conditions and in topsoils (Paper V).

LASs are generally regarded as biodegradable surfactants, however their biodegradation is affected, for example, by the concentration of dissolved oxygen, complexing with cationic surfactants, the formation of insoluble calcium and magnesium salts, and the presence of other organic compounds. APEs undergo

almost complete primary biodegradation in aerobic conditions, while cationic surfactants are known to be more toxic. (Scott & Jones 2000). Biodegradability is affected by the structure of the surfactants. García *et al.* (2001) discovered that when the chain length of cationic monoalkyl QAC surfactants increased, the biodegradation rate was reduced. This was also confirmed by Qin *et al.* (2005), but they also discovered the same effect for amphoteric surfactants. Biodegradability was inhibited and the degradation rate of surfactants decreased when steric hindrance increased (Qin *et al.* 2005).

3 Materials and methods

3.1 Oily waters

3.1.1 Oily wastewaters

OWWs taken from two Finnish wastewater treatment plants (WWTP1 and WWTP2) were extensively characterised in Paper I. The WWTPs treated various types of OWWs with a UF-based process (Fig. 3), including commonly used treatment units. The UF-based process was almost similar in both plants. The OWWs entering WWTP1 and WWTP2 were routed through a drum filter and then homogenised by mixing different types of OWWs, targeting neutral pH values. The oily wastewaters were conducted through a belt filter before the UF unit. The tubular ceramic UF membrane had a pore size of 50 nm and the water flow was about 700 L/hour. The operational pressure in the lower part of the UF unit was usually about 3.6 bar, and the pressure in the upper part was about 2.2 bar. Cation exchangers containing weakly acidic resins with chelating iminodiacetate groups functioned as the ion exchangers for metal removal. The sand filters contained quartz sand of three different granule sizes. In WWTP1 the pH was adjusted to about the value of 5 before the sand filter (after the point for the post-UF sample). The WWTP2 process included one extra sand filter and ion exchanger. Effluents from both plants were piped finally to municipal sewer treatment plants.

The OWW samples were taken separately from sampling points before UF, after UF, as well as after the first sand filter and ion exchanger. One of the sample series contained samples from three points (sample series numbers are used in the figures in Section 4.1). The parameters determined for the samples in Paper I were the following: biological oxygen demand after seven days (BOD_7), COD_{Cr} , total organic carbon (TOC), total surface charge (TSC), inorganic and organic matter, as well as zeta potential and pH value. The TSC and zeta potential measurements were performed with replicate measurements. The replicates of COD and TOC measurements on selected OWW samples were performed with different sample dilution factors. The OWW samples had to be diluted for BOD_7 measurements, and replicates were performed on selected samples with different dilution factors. The performance of the UF-based processes was evaluated through the extensive characterisation of the samples from the most strategic points of the treatment train.

The real O/Ws taken from WWTP1 were also treated with CF-S and PosiDAF in Paper III.

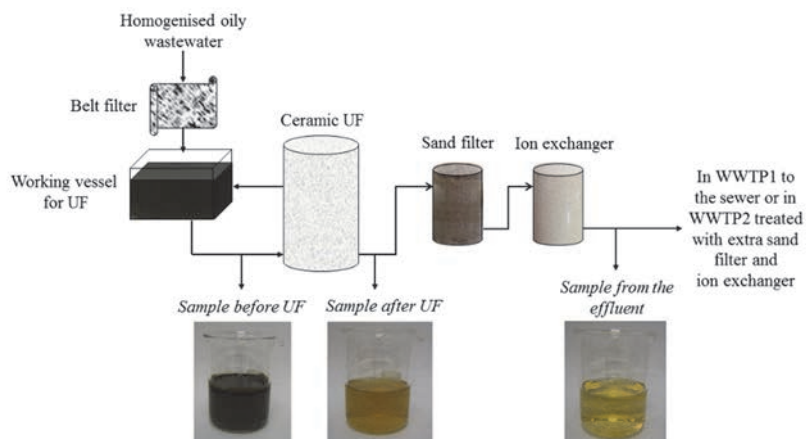


Fig. 3. Unit operations of UF-based treatment train as well as sampling points. Modified from Paper I.

3.1.2 Model O/W emulsions

Model O/W emulsions were prepared by using bio oils (rapeseed oil (RO), sunflower oil, tall oil-based chain oil) (Paper II) or fully synthetic motor oil and mineral oil-based chain oil (Papers II and III). Sunflower oil (SFO), tall oil-based chain oil (TO), synthetic motor oil (MO) and mineral oil-based chain (MCO) were all commercial products.

The oil concentration in the O/W emulsions was 2% (w/w). An anionic surfactant sodium dodecyl sulphate (SDS, $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$) was added for emulsification and for homogenisation of the O/W emulsions, at a concentration of 0.3–1.5 g/L (1.04–5.20 mM). The CMC of SDS is 8.1 mM at 298 K (Aguar *et al.* 2011). Thus, the SDS concentration in O/W emulsions was below the CMC, and micelles were not formed. SDS is one of the most extensively used surfactants from AS (alkyl sulphate) type surfactants, for example in cosmetics. Sodium chloride (NaCl) of 2.2 g/L was added to the O/W emulsions to increase conductivity to the value of about 4.0–4.5 mS/cm. The pH values of the model O/W emulsions were not adjusted and varied between 6.6–9.2. The details concerning the preparation principles of O/W emulsions can be found in Papers II and III. The O/W emulsions

were treated with CF-S, with EC (Paper II), with CF-DAF (Paper III) and with PosiDAF (Paper III).

The stability of the model O/W emulsions prepared for the DAF studies was studied and calculated as a percentage (Paper III) in a similar way to that in Maiti *et al.* (2011), although they used the volume of the emulsions rather than the weight. In the present study, all of the sample batches were combined after mixing and allowed to rest for 24 hours, after which the whole sample was weighed (total weight, m_{tot}) and free oil was removed from the surface. The sample was then weighed again (relative weight, m_{rel}). The stability was calculated as the relation of m_{rel} to m_{tot} and multiplied by 100%.

3.2 Experimental

3.2.1 CF-S studies

Studies of conventional coagulation-flocculation followed by sedimentation (CF-S) were performed for O/W (MO, MCO) emulsions and for OWWs from WWTP1 before UF. The coagulants studied for treatment of O/W emulsions and for OWW samples were ferric chloride (Kemira Oyj, Fe_{tot} content of $13.8 \pm 0.4\%$), polyaluminium chloride (Kemira Oyj, Al^{3+} content of $9.3 \pm 0.3\%$ and alkalinity of $43 \pm 2\%$) and chitosan as 0.5% (w/w) solution prepared from medium molecular weight (MW) chitosan (Fluka Biochemika). The measured charge density of the chitosan solution was 5.2 meq/g. The CF-S studies were also performed with CTAB and PolyDADMAC for O/W emulsions to investigate the separation efficiency of flocs by sedimentation compared to DAF (results presented in Section 4.2.4).

CF-S studies were performed as Jar tests with a sample volume of 300 mL and with flash mixing of 400 rpm for 60 seconds, slow mixing of 40 rpm for between 15 min and 30 min, followed by sedimentation for 30 minutes. COD and TSC were analysed from the samples taken from the clarified part. The replicates for COD measurements were performed on selected samples. The TSC measurements were performed with replicates on all the samples.

3.2.2 EC studies

Bench scale EC studies (Paper II) of O/W emulsions (SFO, RSO, MO, MCO and TO) were carried out with a horizontal flow electrode configuration in batch mode

with water circulation as presented in Fig. 4. The EC cell consisted of austenitic steel with a molybdenum (alloy 316) basin (65 cm × 27 cm × 5 cm) and six rectangular Al bars (58 cm × 8 cm × 1 cm) oriented vertically above the stainless steel (SS) basin. The SS contained mainly iron, but also small amounts of chromium (Cr), nickel (Ni), molybdenum (Mo), manganese and silicon. Treatment of O/W emulsions was performed by using either Al or SS as anode material.

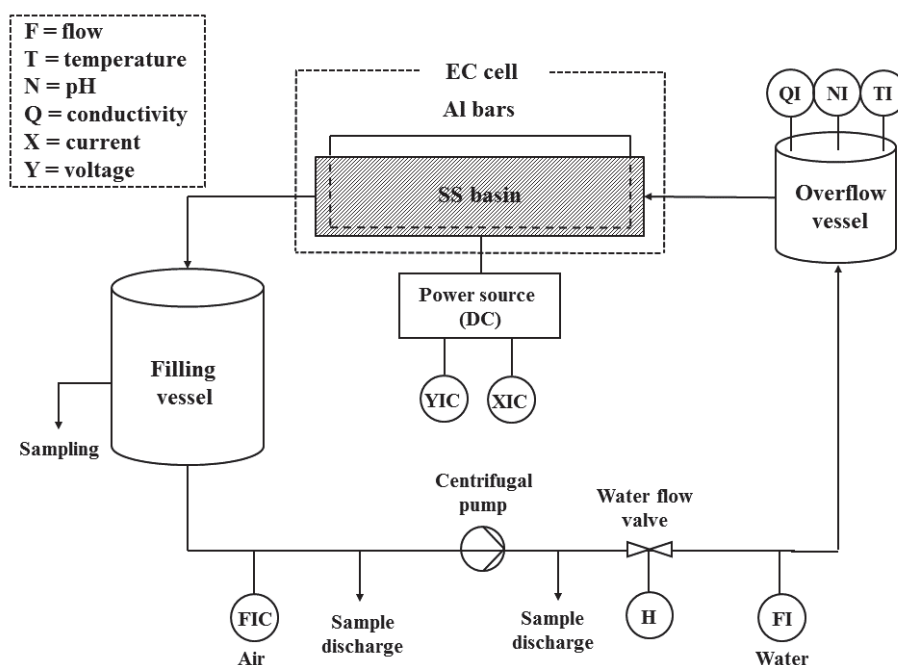


Fig. 4. The apparatus used in EC test runs.

The height of the water column was adjusted with a SS flow barrier installed at the end of the basin. The A_{eff} (effective anode area below the water surface, cm^2) for the SS basin as anode was $1960 \text{ cm}^2/2100 \text{ cm}^2$ when the height of water column was 17 mm/25 mm, respectively. The height of the water column was 25 mm in the studies performed with Al anodes corresponding to an A_{eff} for the Al anodes of 1190 cm^2 . The volume of the electrolytic cell was 1.8 L/2.9 L when the height of the water column was 17 mm/25 mm, respectively.

DC power was supplied to the EC cell using a GW Instek GPR-1810H, 18 V/10 A. The water flow in the system was achieved with an Iwaki MD15R-230GS water

pump. The electrical current was measured with an Amrel 3200 Multimeter, while the water temperature was measured with a TES-1300 Type K Thermometer. The pH of the solutions was measured with WTW inoLab pH 720 and the water flow electromagnetically with a combination of a Toshiba LF470 detector and Toshiba LF420 converter. The conductivity of the samples was measured with either a YSI 600 OMS sonde with YSI 650 MDS or a WTW Multiline P4 Universal meter.

Treatment of O/W emulsions was performed using either the Al or SS as anode material. The parameters analysed for the samples were BOD₇, COD, TOC, TSC and turbidity. The replicate measurements of BOD₇, COD and TOC were performed on selected samples. The samples for BOD₇ and TOC measurements had to be diluted. The replicate measurements of TSC and turbidity were performed on all the samples.

3.2.3 DAF studies

The saturator and the flotation column of the batch DAF studies (Paper III) are presented in Fig. 5.

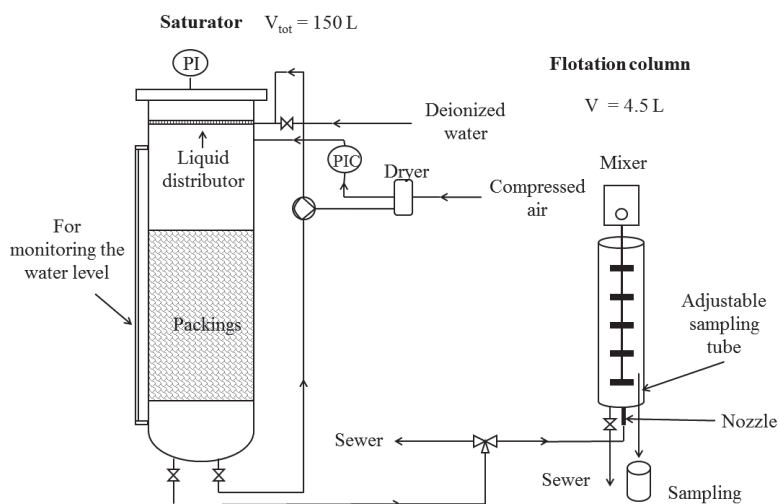


Fig. 5. The apparatus used in DAF studies. Modified from Paper III (published by permission of Elsevier).

The nozzle used in the flotation column was constructed according to the optimal nozzle design discovered by Zhang *et al.* (2009). The nozzle measurements for the constriction region and cylindrical shroud were a diameter of 1 and 5 mm, and

length of 14 and 50 mm, respectively. A bubble size of 42 μm was achieved with the optimal nozzle measurements with a saturator pressure of 5 bar. (Zhang *et al.* 2009).

The packing material and type was plastic random packing, pall ring size of 25 mm with a voidage of 91% (Mulder Tower Equipment (MTE) B.V.). Using a packed saturator may give an efficiency of about 90% compared to an unpacked saturator with 60 to 70% saturator efficiency (Edzwald 1995). Before the DAF experiments, deionised water was added to the saturator until 10% of the packings were under water.

The cationic chemicals were studied by adding them directly to the DAF saturator (PosiDAF) before pressurising the vessel or performing CF-DAF (conventional coagulation-flocculation followed by DAF). All the DAF studies are presented in Table 2. The chemical concentration in the saturator in the PosiDAF studies is presented as C_{sat} .

Table 2. The DAF studies performed. Modified from Paper III.

Sample	Chemical concentration in PosiDAF (stock solution, in saturator (C_{sat}), in column) or in CF-DAF (stock solution, in column)	Study	Absolute pressure [bar]
O/W emulsion	CTAB (¹ , 40 mg/L, 0–8 mg/L)	PosiDAF	5
O/W emulsion	CTAB (¹ , 380 mg/L, 0–80 mg/L)	PosiDAF	5
O/W emulsion	CTAB (¹ , 960 mg/L, 0–210 mg/L)	PosiDAF	5
O/W emulsion	CTAB (2500 mg/L, 0–300 mg/L)	CF-DAF	5
O/W emulsion	PolyDADMAC (62000 mg/L, 1650 mg/L, 0–400 mg/L)	PosiDAF	5
O/W emulsion	PolyDADMAC (160000 mg/L, 2870 mg/L, 0–630 mg/L)	PosiDAF	5
O/W emulsion	PolyDADMAC (10000 mg/L, 0–385 mg/L)	CF-DAF	5
O/W emulsion	Epi-DMA (50000 mg/L, 1470 mg/L, 0–360 mg/L)	PosiDAF	5
O/W emulsion	Epi-DMA (89000 mg/L, 2730 mg/L, 0–650 mg/L)	PosiDAF	5
O/W emulsion	Epi-DMA (12500 mg/L, 0–575 mg/L)	CF-DAF	5
O/W emulsion	MEF (¹ , 1110 mg/L, 0–250 mg/L)	PosiDAF	5
O/W emulsion	MEF (¹ , 0–245 mg/L)	CF-DAF	5
OWW pre-UF	PolyDADMAC (160000 mg/L, 2800 mg/L, 0–690 mg/L)	PosiDAF	5
OWW post-UF	PolyDADMAC (160000 mg/L, 2860 mg/L, 0–700 mg/L)	PosiDAF	5

¹ Chemical added directly into the saturator (PosiDAF) or column (CF-DAF) without dilution.

All the chemicals were studied at lower and higher C_{sat} . The chemicals investigated were the following: the cationic surfactant cetyltrimethylammonium bromide (CTAB, $\text{C}_{19}\text{H}_{42}\text{BrN}$, 99% purity) and the commercial coagulants PolyDADMAC

(40% concentration, Kemira Oyj), epichlorohydrin-dimethylamine copolymer (Epi-DMA, 50% concentration, Kemira Oyj) and an aqueous polymer based on melamine formaldehyde (MEF, 8.1–8.7% concentration) manufactured by Kemira Oyj. The polymers are grouped according to MW as follows: low MW $< 10^5$, medium MW 10^5 – 10^6 , and high MW 10^6 (Bolto & Gregory 2007). PolyDADMAC and Epi-DMA had an MW of 150000 g/mol (a medium MW polymer) and 75000–100000 g/mol (a low MW polymer) as well as charge densities of 6.7 meq/g and 7.9 meq/g, respectively. Jar tests (as presented in Section 3.2.1) with CTAB and PolyDADMAC were performed to evaluate the effect of DAF compared to sedimentation (not presented in Paper III). The MW of MEF was a couple of thousands of g/mol and the charge density changed according to the pH.

The charge density of the cationic chemicals was studied according to the pH (values of 2–12) (not included in Paper III). Charge density was the lowest for MEF at all studied pH values and also the pH had the most significant effect on the charge density of the MEF. At a pH value of 3, the charge density of MEF was almost the same as for CTAB, at 2.5 meq/g. The results from the MEF studies were not included in Paper III. The charge density for CTAB and PolyDADMAC stayed the same at all studied pH values but for Epi-DMA it decreased slightly towards a pH value of 7 and after that point decreased more drastically.

The deionised water with/without chemicals was circulated with a Tapflo or Flojet diaphragm pump for four hours after pressurising the saturator. The sprinkling of water over the packing material occurred through a liquid distributor. After circulation of the water with/without chemicals for four hours the pump was stopped and DAF studies were performed. When CTAB was added into the saturator, the dispersion of the water-CTAB solution was allowed to stand for two hours before performing any experiments, because of the formation of a significant amount of foam. The diluting effect of the dispersion water and diluted chemical addition on the COD removal and on the TSC values were taken into account in the performance evaluation of PosiDAF and CF-DAF. All of the COD removals and the number of hydrophobic particles with flow cytometry (FCM, method is presented in Section 3.3.4) were calculated by comparing the final values to those of the original O/W emulsion or OWW samples.

The interaction between air bubbles and polymer was studied by performing PosiDAF with PolyDADMAC (C_{sat} of 1670 mg/L) for pure deionised water and for comparison CF-DAF for the PolyDADMAC-water solution (the concentration of PolyDADMAC was 470 mg/L or 1680 mg/L). The pressure used for the production of air-saturated dispersion water was 5 bar and the time for feeding the

dispersion water was 25 and 35 seconds. Samples were taken as a function of time from the bottom (height of 5 cm), from the middle (height of 17 cm) of the flotation column and from directly below the foam at the surface after the feed of dispersion water had been stopped. The TSC was then analysed for all the samples, because the TSC value correlated with the PolyDADMAC concentration.

The replicate COD and FCM measurements for samples from DAF studies were performed on selected samples. The samples had to be diluted for FCM measurements, and the dilution factor varied between 10–10000. The replicates of TSC measurements were performed on all the samples.

3.2.4 Biodegradation

All the biodegradation studies in this thesis were performed with the manometric respirometric BOD OxiTop method. European Council Regulation No 440/2008 lists methods in Annex Part C for determining the ecotoxicity of substances and the manometric respirometric test is one of the accepted test methods.

BOD OxiTop measurements in solution

The instrumentation used for the BOD OxiTop measurements in solutions was OxiTop® Control 6 (WTW, Weilheim, Germany). The BOD OxiTop method is based on accurate measurement of the pressure difference due to the consumption of oxygen from the gas phase, while at the same time the CO₂ formed is absorbed into NaOH pellets in closed bottles at constant temperature (20.0 °C ± 0.2 °C). The BOD value [mg/L] is automatically calculated by the instrument using the ideal gas law modified for closed space conditions (Paper IV). The biodegradation degree is calculated by the relation of the BOD [g/g] value to the theoretical oxygen demand (ThOD) [g/g]. The ThOD value is calculated through the carbon and hydrogen content of the sample.

The biodegradation measurements in solution were performed in optimal solution conditions (Papers I, II, IV and V) and in groundwater (Paper IV) with replicate measurements. The biodegradation measurements in the optimal conditions were performed with a mineral medium prepared according to OECD 301 F standard (OECD 1992) (Papers II, IV, and V) or with SFS-EN 1899-1 standard (SFS-EN 1998) (Papers I and IV). The nutrients in the four stock solutions were the same for both standards, however the amount of NH₄Cl added in SFS-EN 1899-1 standard (1.7 g/L) is triple that in OECD 301 F standard (0.5 g/L). In Paper

IV the mineral solution was prepared by adding stock solutions of SFS-EN 1899-1 or OECD 301 F standards in the same volumes (10 mL, 1 mL, 1 mL and 1 mL) to test the effect of ammonium on biodegradation. In Paper I the corresponding volumes of stock solutions of SFS-EN 1899-1 were 1 mL of each.

Filtered wastewater from the municipal wastewater treatment plant in Oulu, Finland was used as an inoculum (a microbe source) in standard conditions, but topsoil was also tested as an inoculum in Paper V. The nitrification inhibitor 5 g/L *n*-allylthiourea (ATU) was added if used in optimal standard conditions as 20 drops per 1 L of solution. The effect of bromide ion on the biodegradation of glucose in the case of CTAB was studied with the addition of glucose in dilution water in OECD 301 F standard conditions, and compared with NaBr. The groundwater used in the biodegradation studies in Paper IV was from Paavola, Finland.

BOD OxiTop measurements in solid matrices

The instrumentation used for biodegradability measurements in solid matrices was OxiTop® Control B6M (WTW, Weilheim, Germany). The studies were performed in closed bottles at a constant temperature ($20.0\text{ °C} \pm 0.2\text{ °C}$). The CO₂ gas formed during biodegradation was absorbed into 1 M NaOH solution. The system for solid matrix measurements is automated but only calculates the difference in partial oxygen pressure $\Delta p(\text{O}_2)$ [hPa]. The BOD value and biodegradation degree had to be calculated through the equations presented in Paper IV. The biodegradation of oils and surfactants was studied in various solid matrices (Papers IV and V) with replicate BOD measurements. The properties of the soils are described in more detail in Papers IV and V. The amount of soil added into the BOD OxiTop® MG bottle was between 40–100 g (Papers IV and V).

Biodegradation studies

Biodegradation studies (Table 3) were performed for various new types of oil products (Papers II and IV) and also for surfactants (Paper V). The BOD₇ values of OWWs (Paper I) and O/W emulsion samples according to EC treatment time (Paper II) were also studied with various dilution factors (not presented in Table 3). The light fuel oils studied in Paper IV were light fuel oils of summer (SLFO 1 and SLFO 2) and winter (WFO 1 and WFO 2) grades. The biodegradation results for a 2-stroke motor oil (2MO) in standard conditions are also presented (not previously published). The studied surfactants were: cationic CTAB with a molecular mass of

364.45 g/mol and charge density of 2.8 meq/g and non-ionic Triton X-100 (4-tert-octylphenol ethoxylate) with a CMC of about 0.24 mM (Hait & Moulik 2001) (Paper V).

Table 3. Biodegradation studies presented in the summary.

Sample	Sample amount ([mg/L] in solution and [mg/kg] in soil)	Conditions for biodegradation study	Incubation time [d]	Original paper
Bio oils (RSO & SFO)				Paper II
RSO & SFO	900–1100	Standard solution	28	
Light fuel oils				Paper IV
SLFOs & WFOs	180–300	Standard solution	28	
SLFOs & WFOs	180–300	Groundwater	28	
SLFOs & WFOs	1000	Mineral-poor sand	30	
SLFOs & WFOs	1000	Mineral-rich soil	30, 189	
Synthetic and mineral oils				
MCO & MO	270–470	Standard solution	28	Paper II
2MO	250, 420	Standard solution	28	
Surfactants and NaBr				Paper V
CTAB	120	Standard solution	28	
CTAB & NaBr	120, 20	Standard solution with glucose	28	
CTAB & Triton X-100	100, 110	Standard solution inoculated with topsoil	28	
CTAB & Triton X-100	110, 200	Topsoil	55, 60	

3.3 Analytical methods

3.3.1 COD

COD values were measured (Papers I–III) using the Hach Lange photometric cuvette test in different measuring ranges. Oxidisable substances in the sample reacted with potassium dichromate in sulphuric acid solution in the presence of silver sulphate as a catalyst. The cuvettes were heated at 148 °C for 2 h using a Hach Lange HT 200S thermostat system. Cr³⁺ ions were formed and the green colouration of the Cr³⁺ ions was determined with Hach-Lange DR 2800 spectrophotometer at a wavelength of 605 nm.

3.3.2 TOC, TSC, turbidity and pH

TOC values were (Papers I and II) measured using a Sievers 900 Portable TOC Analyzer (GE Analytical Instruments, USA). The method is based on measurement of the amount of CO₂ formed from the oxidation of organic compounds in the sample and the detection of inorganic carbon. The samples were first acidified with phosphoric acid to pH 2. The oxidation of the organics was promoted with the addition of ammonium persulphate. The sample stream was then divided into two separate streams to measure inorganic carbon and total carbon. The total carbon stream was exposed to UV light and through production of hydroxyl radicals the carbon from organic compounds was converted to carbon dioxide. The total and inorganic carbon streams were moved to their respective carbon dioxide transfer module where a gas-permeable membrane allowed the transfer of carbon dioxide across the membrane. The carbonic acid produced from the reaction of carbon dioxide and water dissociated into bicarbonate ions. The calculations of total and inorganic carbon were based on conductivity measurements. (GE Water and Process Technologies Analytical Instruments 2009).

TSC (total surface charge) was measured (Papers I–III) with a Mütek PCD 03 pH (Mütek Analytic GmbH, Germany). The TSC measurement was based on the streaming current which was formed between adsorbed molecules (on the plastic surface of the piston and cell walls) and free counter-ions due to the movement of the piston. PolyDADMAC (BTG Instruments GmbH) and PES-Na (polyethylene sodium sulphate, BTG Instruments GmbH) were used as titrants when neutralising the streaming current. Turbidity was determined (Paper II) with a Hach Ratio XR Turbidity meter. WTW inoLab pH 720 was used to measure pH values (Papers I-III).

3.3.3 Elemental analysis

The carbon and hydrogen content of the oil (SFO, RSO, MO, MCO, 2MO and light fuel oils) and topsoil samples were measured with a Perkin-Elmer 2000 Elemental Analyzer Series II or with a Thermo Fisher Flash 2000 Analyzer (Papers I, II, IV and V) in the Trace Element Laboratory (University of Oulu). The elemental analyses of oil samples were performed without sample pre-treatment. Soil samples were dried before the elemental analyses.

3.3.4 Flow cytometry

FCM was used to determine the number of hydrophobic particles per mL in the O/W samples (Paper III). The instrumentation used was a CyFlow ML (Partec GmbH), which measured forward scatter (FSC) and side scatter (SSC) signals as well as fluorescence signals at specific wavelengths. The samples, apart from the samples from the PolyDADMAC DAF studies, were filtered immediately after the DAF studies with a 200-mesh wire sieve, and were only mixed just before the FCM studies with an IKA Labortechnik Eurostar basic blade mixer for 3.5 min at a mixing speed of 500 rpm. The mixing and filtering of samples from the PolyDADMAC DAF studies were performed just before the FCM studies. Samples were then diluted (dilution factor varied between 10 and 10000) with deionised water and stained by adding 20 μ L of Nile red solution (10 μ g/mL ethanol) (Molecular Probes Invitrogen) to 1 ml of diluted sample with a staining time of about 3 minutes. The data was processed using Partec Flomax software. Red fluorescence (FL3) and FSC were used to differentiate and enumerate the hydrophobic particles. The FCM measurements were carried out by present author with Reetaleena Rissanen at CEMIS-Oulu (Finland).

3.3.5 Inorganic matter

The inorganic matter of OWWs (Paper I) was determined at Suomen Ympäristöpalvelu Oy, a FINAS accredited test laboratory (T231) in Oulu, Finland with a Thermo Electron IRIS Intrepid II XDL inductively coupled plasma optical emission spectrometer (Franklin, USA).

The inorganic matter (Cr, Fe, Ni and Mo) of the sludge produced from the EC studies (Paper II) was analysed with a graphite furnace atomic absorbance spectrometer (AAAnalyst 600 Perkin Elmer) by Elisa Wirkkala at the University of Oulu. The sludge samples were dissolved before analysis in concentrated nitric acid (Merck KGaA, Suprapur).

3.3.6 Organic compounds

The organic compounds of the OWW samples (Paper I) were analysed by gas chromatography (GC) using a Hewlett Packard 6890 Series GC system equipped with a flame ionisation detector (GC-FID) or with a mass selective detector (Hewlett Packard 5973 Mass Selective Detector) (gas chromatography-mass

spectrometry, GC-MS), an autosampler (Hewlett Packard 6890 Series Injector) and a fused silica Supelco Equity-1 capillary column (15 m × 0.25 mm) with a nominal film thickness of 0.25 mm or with a J&W Scientific DB-624 column by Agilent Technologies (30 m × 0.32 mm) with a nominal film thickness of 1.8 mm. The Spectrum library was used for identification of the compounds in the GC-MS spectra.

When using the GC-FID method, the GC oven program was started at 50 °C, held for 1 min and then increased to 300 °C at 10 °C/min and then held at 300 °C for 5 min. When using GC-MS method, the GC oven program was started at 40 °C, held for 1 min and then increased to 270 °C at 15 °C/min and then held at 270 °C for 5 min. The most turbid OWWs were filtered before the GC-FID/MS analyses. (Paper I). The measurements and identifications of organic compounds were performed by Päivi Joensuu from the Mass Spectrometry Laboratory (University of Oulu).

3.3.7 Zeta potentials and droplet sizes

The zeta potentials of the OWWs (Paper I) were determined with a Coulter Delsa 440SX (Beckman Coulter, Miami, FL, USA). The Coulter Delsa 440 SX is based on a multi-angle measurement technique where measurements are performed simultaneously at four scattering angles. Light scattering was used to measure the velocity of particles using electrophoresis and the zeta potential was calculated from electrophoretic mobility. The zeta potential measurements were performed with replicates.

The droplet sizes of model O/W emulsions (Papers II and III) were determined using a LS 13320 Laser Diffraction Particle Size Analyser (Beckman Coulter, USA), which measured particle size distribution by measuring the pattern of light scattered. A laser beam was passed through a sample cell where particles scattered the light in characteristic patterns according to their size. Fourier optics collected the diffracted light and focused it onto three sets of detectors. (Beckman Coulter 2011). The droplet size measurements were performed with replicates.

4 Results and discussion

4.1 Evaluating the performance of a commercial UF-based treatment process for treatment of OWWs (Paper I)

The number of scientific publications concerning real commercial treatment processes for concentrated oily waters is limited. Thus, research began by focusing on determining the status of oily wastewater treatment in Finland. Research was performed by characterising the OWW samples from key points in two commercial UF-based treatment processes. This UF-based process was selected, because it included unit operations that were commonly used in treating oily wastewaters. Thus, the process under investigation served as a reference process. For WWTP1, the research was performed in 2008 and 2011 to clarify any change in the OWWs to be treated or in process performance.

4.1.1 Reductions of parameters achieved with the UF-based process for treatment of OWWs

The OWWs were highly concentrated, containing a high organic load according to the COD (Fig. 6) and TOC results (Fig. 5 in Paper I). They were also turbid and coloured with a thin oil layer on the surface (as seen in Fig. 3). Treated samples were yellow in colour and clear, as shown in Fig. 3.

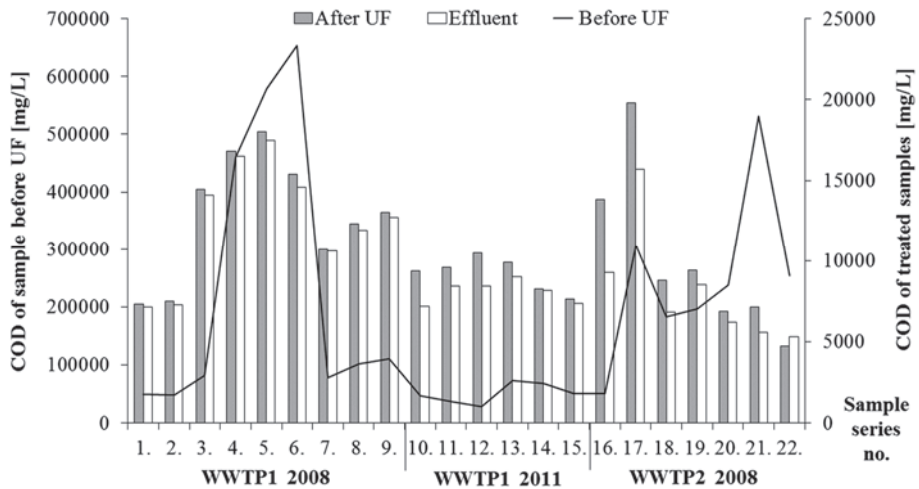


Fig. 6. COD values for OWW samples. Modified from Paper I.

The characterisation results for OWWs from 2008 are discussed below. The COD and TOC values for untreated OWWs for WWTP1 were very high, between 50000–650000 mg/L and 6000–98000 mg/L, respectively. For WWTP2, the corresponding values were 50000–530000 mg/L and 11000–67000 mg/L. The values between the WWTPs were surprisingly similar, although they were treating different types of oily wastewaters. The COD and TOC values for treated samples were substantially reduced for both the plants, being between 1700–18000 mg/L.

The TSC values for the pre-UF samples (Fig. 7) from the WWTPs were strongly negative, proving that the samples contained highly stable O/W emulsions. Zeta potentials could not be analysed from the pre-UF samples due to high turbidity. However, the TSC (Fig. 7) and zeta potential values (Fig. 7 in Paper I) for the treated samples were always less negative than $-550 \mu\text{eq/L}$ and -35 mV , respectively, indicating that the treated samples contained a smaller amount of charged droplets. Thus, UF efficiently removed charged compounds. The lower negative zeta potentials for effluents from WWTP1 were due to pH adjustment to more acidic pH values after UF. The heterogeneous OWWs contained a variety of particles and droplets with different zeta potentials. The presented zeta potentials are, therefore, average values.

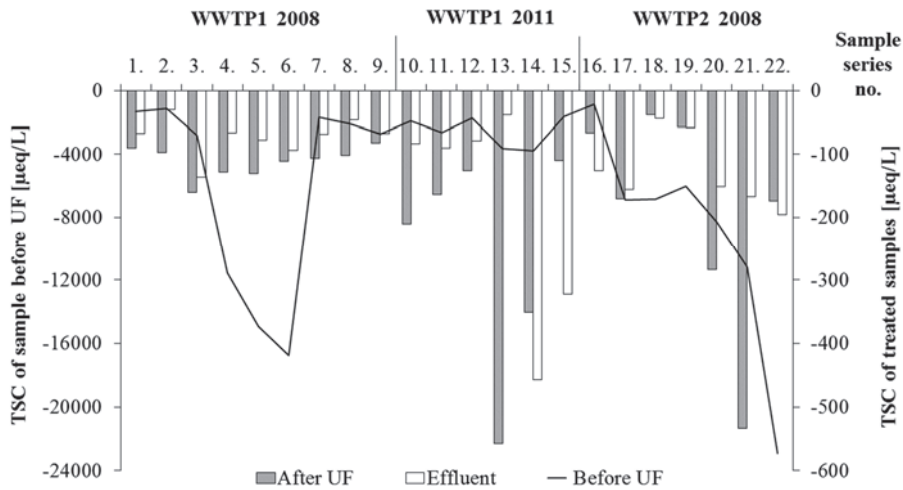


Fig. 7. TSC values for OWWs samples (Paper I). Modified from Paper I.

The BOD₇ values for untreated samples of WWTPs in 2008 varied between 14000–44000 mg/L and for treated samples between 2200–5500 mg/L (Fig. 8 in Paper I). Fig. 8 presents the BOD₇/COD ratio (biodegradability index). The biodegradability index for the pre-UF samples was less than 0.32, indicating that they were poorly biodegradable (Jamil *et al.* 2011). The biodegradability index was significantly enhanced with UF treatment, varying between 0.35–0.65, indicating improved biodegradability.

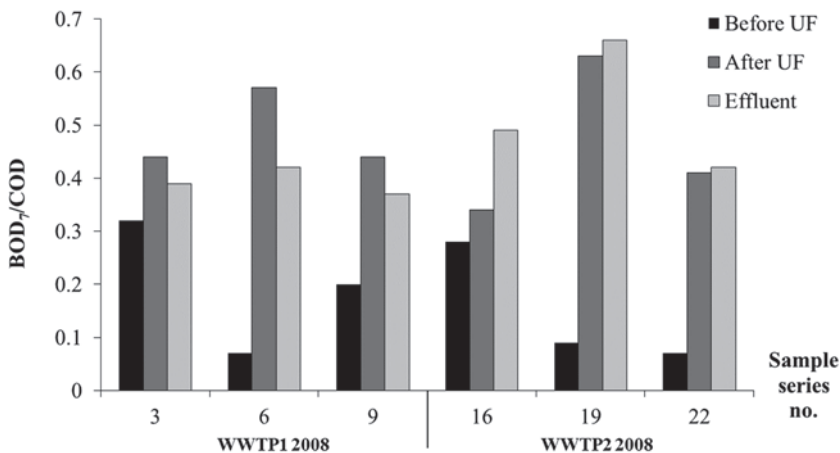


Fig. 8. BOD₇/COD ratios for OWWs.

Both the COD (see Fig. 6) and TSC (see Fig. 7) values of the pre-UF samples for WWTP1 in 2011 had decreased from the corresponding values determined in 2008. However, they were still very high, for example COD values were 47000–73000 mg/L in 2011 (see Fig. 6). Overall, the BOD, COD, TOC and TSC results varied significantly on a daily basis in 2008, as they also did in 2011.

4.1.2 Inorganic and organic matter of OWWs

The pre-UF samples for the WWTPs contained a large amount of inorganic components, especially the amount of boron, calcium, magnesium, iron, phosphorus, potassium, sodium and sulphur were as much as hundreds of milligrams per litre. However, there was no clear difference between WWTPs as far as the inorganic matter of samples was concerned. The inorganic species had already been mostly removed by UF, probably due to the attachment of inorganic species to the oil emulsions. Only a minor decrease in the amount of inorganic matter was due to the sand filter and ion exchanger, probably as a result of the low initial concentrations entering the sand filter and ion exchanger. The amount of inorganic matter of the effluents was small. However, the worst reductions with the UF-based process were typically gained, for example for calcium, potassium, magnesium, sodium, nickel, boron, phosphorus and sulphur (from pH adjustment via sulphuric acid), probably due to the low MW, thus passing through the UF membrane. The same observation was made by Tomaszewska *et al.* (2005), who treated bilge water with a pilot-scale tubular UF. A low retention of inorganic substances (Ca, K, Na, Mg, Mn, SO_4^{2-} and P_2O_5) was achieved. They achieved 80% removal for zinc and aluminium, whereas the iron compounds were completely removed. In the present study, occasionally the concentrations of arsenic, molybdenum and vanadium, for example, were not significantly reduced with the UF-based treatment, although average concentrations in the effluents were quite low, below 1.65 mg/L. The most interesting inorganic species was boron, which was present in high concentrations in the wastewaters at both plants.

The GC chromatograms were inconclusive, containing different types of organic compounds such as benzenes, carboxylic acids and long-chained hydrocarbons. A typical gas chromatogram with the most typical organic compounds (phenol, 2-phenoxyethanol, and triethanolamine borate) in the WWTP1 samples in 2008 can be found in Paper I (Fig. 3 in Paper I). These compounds were also typically present in samples from WWTP2. The WWTP1 samples in 2011 often contained tripropylene glycol because it was not removed

effectively. Overall, it appeared that phenol, 2-phenoxyethanol, triethanolamine borate and tripropylene glycol exhibited only slight reductions with the UF-based process, and from these the amount of triethanolamine borate was reduced the least. The above-mentioned boron compound could explain the high boron content of the wastewaters and its enrichment during the UF-based process. It has been observed that membrane processes are not always able to reduce boron content. The boron removal efficiency of UF could be increased by complexation of borate with water soluble polymers. (Wolska & Bryjak 2013). The efficiency of EC for the removal of boron from produced water has been proven with Al electrodes and at a pH value of 7 (Ezechi *et al.* 2014).

UF is not effective for the removal of organic compounds (especially dissolved ones, such as tripropylene glycol) with molecular sizes smaller than its membrane pore size. The poor UF performance for removal of phenolic compounds has also been observed by Harman *et al.* (2010) and Sun *et al.* (2015). Harman *et al.* (2010) studied the performance of ceramic tight-ultrafiltration membranes (pore size 4 nm) coated with iron oxide layers for removing phenol. Phenol removal at a pH value of 7 was poor (3–7%) for coated and uncoated membranes. However, when the pH was increased to 10.5 and 11.5, phenol removal for the uncoated membrane increased to 63–77%. The higher rejections of phenol at alkaline pH were argued to be due to electrostatic repulsion between the phenolate anion and the negatively charged membrane surface. At neutral pH, phenol is in neutral form, and the ceramic membrane surface is neutral or slightly positive.

4.1.3 Correlation of process parameters

The correlations between different parameters of OWW samples were determined for control purposes of a wastewater treatment process. The best linear correlations were obtained for COD and TOC as well as for COD and TSC (Fig. 9). The TOC and BOD₇ values were linearly correlated only at low concentrations. Fast and easy TSC measurement could be used to control various process parameters. Although oily wastewaters were mixed and homogenised for neutral pH values, it was observed that the quality of influents occasionally fluctuated drastically. This fluctuation probably weakens the reliability of the UF unit. The homogenisation of influent should be performed, for example, based on COD/TSC rather than on the pH value.

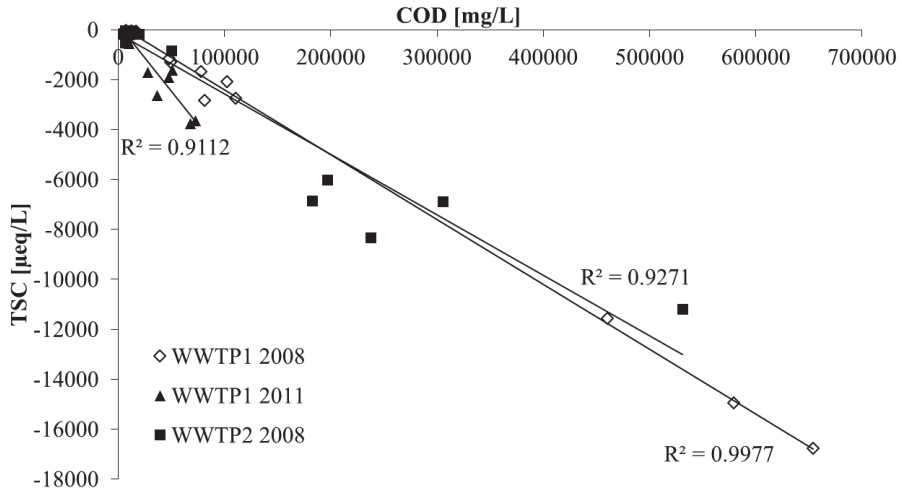


Fig. 9. Correlation for COD and TSC (published by permission of Elsevier).

4.1.4 Performance of UF-based treatment process and process development needs

When evaluating the results, the reductions for the entire UF-based processes were the highest when the initial concentrations were the highest. The reductions in organic load were slightly higher for WWTP1 than for WWTP2, although values for effluents, especially COD values, were slightly higher for WWTP1. The COD reduction of the entire treatment process varied for WWTP1 between 86–98% and for WWTP2 between 82–99%.

When the research was repeated for WWTP1 three years later in 2011, the organic load entering UF was lower than that studied previously. Therefore, the measured reductions in organic load were also lower (70–88%), although the quality of the effluents was enhanced. Overall, the performance of the UF-based process according to the results was very high and there was no significant difference between the performances of the WWTPs.

The most significant reductions of parameters, including the amount of inorganic matter, were gained with UF itself, and only a minor decrease in these parameters with post-treatment. However, residuals were occasionally considerable, probably due to dissolved components and the very small-sized oil droplets passing through the UF membrane, also seen in the studies of organic compounds. The

samples after UF foamed, thus it is possible that treated samples contained surfactants. The passing of surfactants through UF has also been observed by Lobo *et al.* (2006) and Byhlin & Jönsson (2003).

Although the UF-based processes studied efficiently treated heterogeneous OWWs, some important process development needs were issued during the studies. High occasional residuals can cause problems in post-treatment in the municipal wastewater treatment plant, seen as higher chemical consumption or as inhibition in the active sludge process due for example to toxic intermediates. However, in the present study the inhibitive effect of OWW according to the decreasing dilution factor on the BOD₇ value was discovered only for OWWs taken before UF, as the BOD₇ value decreased from about 150000 mg/L (dilution factor 10000) to 40000 mg/L (dilution factor 10). The most significant effect of dilution on BOD₇ values was with a dilution factor between 1000 and 10000. Roppola *et al.* (2006) discovered that inhibition with lower dilution was significant for paper mill samples (taken after coagulation). Inhibition was not observed for pulp mill samples (taken after biological treatment). Roppola *et al.* (2006) suggested that pulp mill samples naturally contained a sufficient amount of nutrients for the biodegradation process. This hypothesis could be partly true also for oily waters, but the concentration of toxic components is also diluted with increasing volumes of the mineral medium.

The fouling and blocking of the UF membrane was noticed to be a huge problem. Fouling could be decreased for example by decreasing the flux. Critical flux is defined as that below which the decline of flux over time does not occur but above which flux decline and fouling are observed (Falahati & Tremblay 2011). When operating at high driving pressures, oil droplets can pass through membranes, and the solute concentration near the membrane surface might cause increased pore clogging and/or membrane polarisation resulting in reduced flux (Lin & Lan 1998). Sometimes chemical backflushing of the membrane even had to be performed daily in the WWTPs studied, and this also generates new waste solutions and higher operating costs. It should be remembered that if the membrane has already become fouled, back-flushing might not be so effective (Srijaroonrat *et al.* 1999). The efficiency of the UF-based treatment train could be enhanced by treating various oily wastewater fractions separately. The decrease in fouling and the amount of passing components such as hydrocarbons could also be achieved by breaking up the oil emulsions and increasing the droplet sizes with coagulation agents or salts prior to UF. Thus, with more efficient pre-treatment for UF than sedimentation and

coarse filtering, the organic load could be decreased and the operation time of the UF membrane could be lengthened.

4.2 Treatment of oily waters with CF-S/DAF, EC and PosiDAF

After discovering the current situation concerning treatment of oily wastewaters with the UF-based treatment process, some of the potential treatment methods such as EC and DAF were selected to be studied for MO and MCO O/W emulsions, although some studies were also performed for OWWs. Treatment with CF-S was performed for comparison purposes (not included in the Papers).

4.2.1 Properties of O/W emulsions

The model O/W emulsions were prepared to minimise variation in sample quality. However, it was observed that the quality of prepared O/W emulsions varied, sometimes significantly (Table 4), especially for O/W emulsions in the EC test runs probably due to the smaller amount of SDS added into the O/W emulsions and the mixing speed. The number of hydrophobic particles measured by FCM varied significantly between $2.5\text{--}39.6 \times 10^6$ per mL, measured only for the O/W emulsions (MO, MCO) used in the DAF studies, although the stability of the O/W emulsions was very high, between 94% and 97% (determination of O/W emulsion stability was presented in Section 3.1.2). The quality variation of the O/W emulsions, might also have been due to the differences in sample preparation (more or less free oil in the surface layer) and the heterogeneous samples taken for analysis. The emulsification of oil is a complex phenomenon and the success of emulsification depends greatly on the sample preparation conditions and also on the oil type.

Table 4. COD, TSC and pH values for 2% O/W emulsions. Some of the data taken from Papers II and III.

Study and O/W emulsion type	COD [mg/L]	TSC [$\mu\text{eq/L}$]	pH
CF-S			
MO, MCO	4600–12000	-2200–(-3700)	7.5 ¹
EC			
SFO	2400–22100	-940–(-1100)	6.0–7.3
RSO	3400	-1900	6.9
MO, MCO	3800–9600	-930–(-1090)	8.7–9.2
TO	20900, 26800	-4900	6.6
DAF			
MO, MCO	1700–8000	-2800–(-4100)	8.2 ¹

¹ pH measured for a few O/W emulsions.

Laser diffraction measurements performed on the model O/W emulsions (MO, MCO) for the EC studies showed that the average droplet size was between 5.1–9.8 μm (Paper II). In the DAF studies the average droplet size was as low as 0.8 μm . However, when the droplet size was presented as a volume distribution, two peaks could be identified for every batch with average droplet size for the peaks of 1.5 μm and 14.3 μm (Paper III). The small droplet sizes proved that the emulsification of oils had succeeded, even though the initial parameter values varied greatly. Droplet sizes for prepared O/W emulsions were in the same range as for stabilised O/W emulsions (often with indigenous anionic surfactant) in oily wastewaters (3–20 μm) (Moosai & Dawe 2003). It must, however, be remembered that the droplet size of O/W emulsions could have been affected by the pumping of the sample during the laser diffraction measurements.

When the O/W emulsions (MO, MCO) were prepared without anionic SDS and NaCl, the TSC values of the O/W emulsions were low, between -50 and -75 $\mu\text{eq/L}$, but logically they became more anionic as the concentration of oil increased. When the O/W emulsions (MO, MCO) were prepared with NaCl, the TSC values almost tripled, to between -110 and -200 $\mu\text{eq/L}$. (Paper III). Thus, the addition of anionic SDS clearly increased the negative TSC values of O/W emulsions (as presented in Table 4).

The O/W emulsions differed from real OWWs before UF in the fact that the O/W emulsions had a smaller COD value, up to 10 times lower, although the TSC values were usually similar or slightly lower, so relatively the charge density was higher for O/W emulsions. The model O/W emulsions were chemically emulsified and stable, and it seemed that the OWWs were mechanically more emulsified. The

OWWs also probably contained neutral compounds, which did not affect the TSC values.

4.2.2 Treatment of O/W emulsions and OWWs by CF-S

Figs. 10 and 11 present the COD reductions and the development of the TSC value for O/W emulsions (MO, MCO) treated with CF-S (conventional coagulation-flocculation followed by sedimentation). Neutralisation of the TSC value for the O/W emulsion was achieved only with 800 mg/L of polyaluminium chloride, corresponding to about 100% removal of COD. The performance of ferric chloride was similar to that of polyaluminium chloride. The highest COD removal with chitosan was 50% with a dose of 500 mg/L. The charge density of the chitosan solution was not adequate to neutralise the TSC values of O/W emulsions at any point. Some of the flocs formed with chitosan rose to the surface and some sedimented to the bottom. Separation of flocs formed with ferric chloride and polyaluminium chloride was better, since all the flocs rose to the surface.

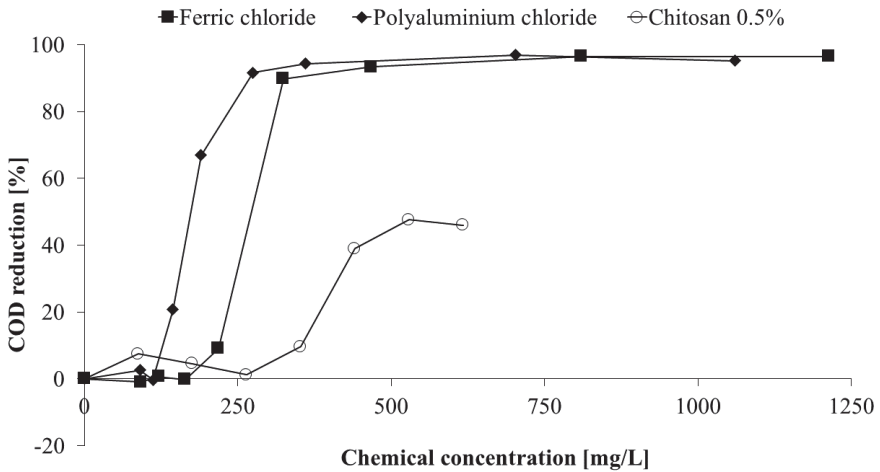


Fig. 10. COD reductions for CF-S studies of O/W emulsions.

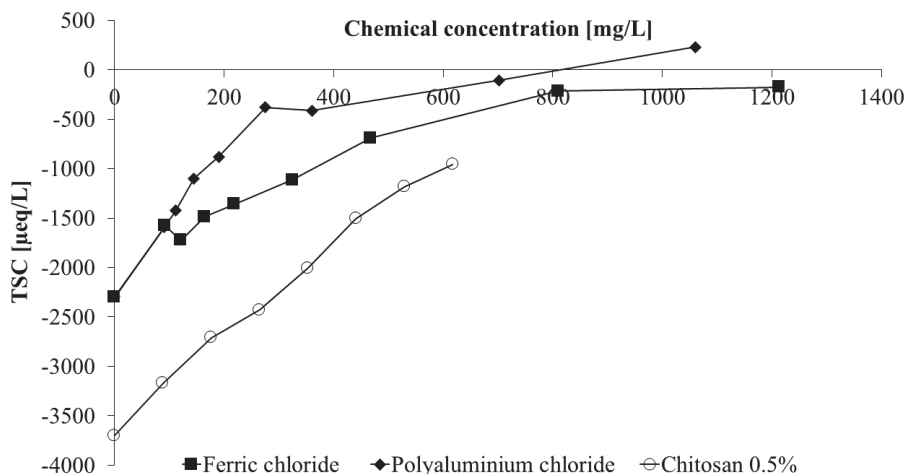


Fig. 11. Development of TSC value for CF-S studies of O/W emulsions.

Figs. 12 and 13 present the COD reductions and the development of the TSC value for OWWs (samples before UF from WWTP1) treated with CF-S, respectively. COD removal of 100% was achieved with 400 mg/L of ferric chloride, while polyaluminium chloride performed the worst, with a maximum of 60% COD removal with a dose of 350 mg/L without neutralising the TSC value. The neutralisation of the TSC values for OWWs was achieved only with chitosan as coagulant with a dose of 450 mg/L, corresponding to 80% COD removal. Separation of the flocs formed with chitosan was better when the OWWs were treated, as all the flocs rose to the surface. Rattanapan *et al.* (2011) studied the coagulation performance of polyaluminium chloride and ferric chloride for real concentrated biodiesel wastewater (initial COD 60–150 g/L) and achieved different treatment results than in this present study, probably due to the different type of wastewater treated. The highest 70% COD removal at pH of 7 was gained with polyaluminium chloride with a dose of 2 g/L. Ferric chloride was less efficient with the highest COD removal 50% with a dose of 1.5 g/L. The performance of polyaluminium chloride was more affected by the pH than the performance of ferric chloride. To conclude, the coagulants must be selected on a case-specific basis.

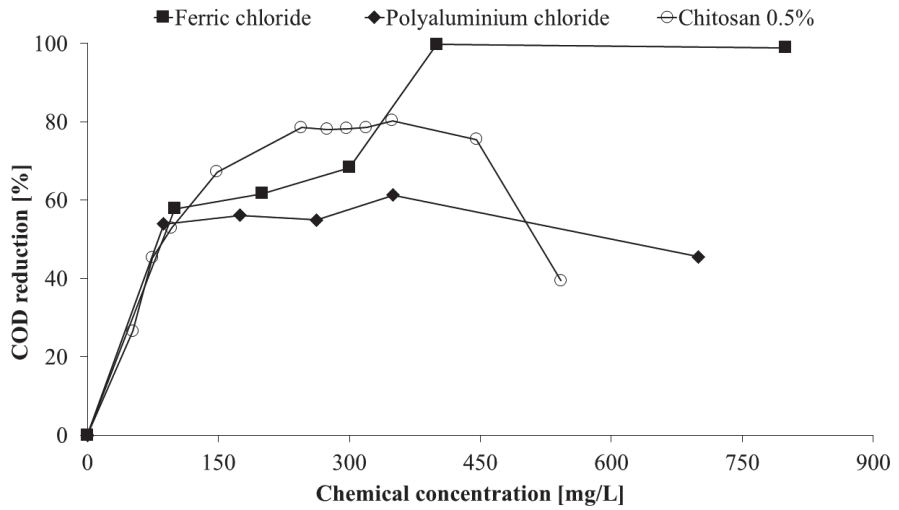


Fig. 12. COD reductions for CF-S studies for OWWs before UF.

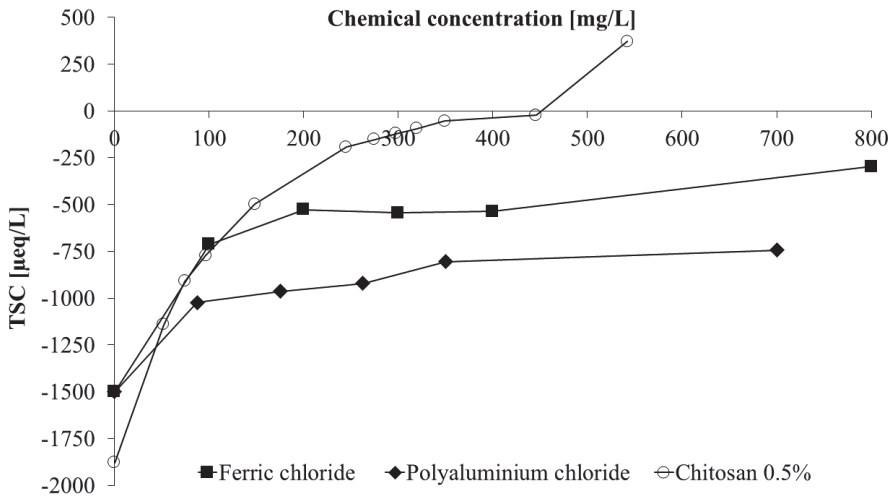


Fig. 13. Development of TSC value for CF-S for OWWs.

The flocs formed with ferric chloride were very large compared to the flocs formed with polyaluminium chloride, which were very fine and fragile. The structure of the flocs was similar with commercial coagulants for OWWs or O/W emulsions. However, the structure of chitosan flocs differed when the OWW or O/W emulsion

was treated. The composition of flocs was large for OWWs, as with ferric chloride, but for O/W emulsions the amounts of flocs was very high and they were fibrous.

The performance of commercial coagulants and chitosan varied greatly when treating either model O/W emulsions or OWWs. The composition of OWWs is very complex, affecting the performance of coagulants and chitosan. In the present study, organic chitosan proved to be suitable for treatment of these types of OWWs. Chitosan possesses several properties, such as non-toxicity, biodegradability and outstanding chelation behaviour, which make chitosan an effective coagulant/flocculant for the removal of contaminants in the dissolved state (Renault *et al.* 2009). Ahmad *et al.* (2005, 2006) studied chitosan as a solid adsorbent and coagulant for treatment of palm oil mill effluent and compared the efficiency of chitosan to other adsorbents and coagulants. Similar removal results for suspended solids and residual oil were achieved with a lower dose of chitosan coagulant and adsorbent compared to commercial coagulants (aluminium sulphate and polyaluminium chloride), and activated carbon and bentonite adsorbent. However, more research is required for studying the application of chitosan coagulant in the treatment of concentrated OWWs.

4.2.3 Treatment of O/W emulsions by EC (Paper II)

The main purpose was to study the effectiveness of a novel bench scale EC apparatus (see Fig. 4) for the treatment of various O/W emulsions when using an Al or SS anode. When sludge produced during EC was studied using an atomic absorbance spectrometer, it was discovered that chromium, nickel and molybdenum were also dissolved from the SS basin when it was used as an anode. The amount of metals in the studied sludge from three EC test runs varied (SS as anode): the iron content (7000–33000 mg/kg) was about three times larger than the chromium content (2100–12000 mg/kg), whereas the nickel content was between 1100–4800 mg/kg, and that of molybdenum was between 200–3000 mg/kg. The stainless steel composition was 67.8, 17.6, 9.9 and 2.5 w/w respectively. The electrode potentials for metals found were also in the order Cr > Fe > Ni > Mo. Thus, also other dissolved metals from SS basin were probably involved in the removal of contaminants, although in significantly less amounts than iron. The toxic heavy metals from the SS anode present in the sludge set demands for its treatment.

The novel bench scale apparatus used in the present study differs from other studied apparatus with continuous recycling of the sample during test runs and with

an electrode configuration consisting of multiple vertical electrodes and one electrode also used as a basin. Fouad *et al.* (2009) used a similar cell configuration with a horizontal cathode. They compared two different electrode configurations for treatment of model O/W emulsions: i) a horizontal Al cathode basin and horizontal Al anode cylinders, and ii) a traditional vertical parallel plate cell, a cell with two vertical parallel Al electrodes. Saur *et al.* (1996) also studied a horizontal Al anode and steel cathode for treatment of O/W emulsions.

Efficiency of EC treatment

The reductions in the parameters and current densities for selected EC test runs (Paper II) for various O/W emulsions are presented in Table 5. The volume of 2% O/W emulsions treated with EC varied between 22.5 and 31.0 L (Table 1 in Paper II). The volume of the once-treated O/W emulsion gathered for continued EC treatment was about 14.0 L (Table 1 in Paper II). The test runs were performed without specific optimisation of the operational parameters. The temperature was the normal room temperature, 18–22 °C, increasing during the test runs by a maximum of 2 °C. The initial conductivity was between 3.8–4.4 mS/cm, and varied during the test runs \pm 0.5 mS/cm. The current densities were calculated with the average current values used in the EC test runs, although the current varied.

Table 5. The reductions of COD, TOC, TSC turbidity and BOD₇ for EC test runs for various O/W emulsions with replicate test runs. Data taken from Paper II.

O/W emulsion	Anode material	Current density [A/m ²]	Treatment time [min]	COD reduction [%]	TOC reduction [%]	TSC reduction [%]	Turbidity reduction [%]	BOD ₇ reduction [%]
RSO 2%	SS	40	80	80	55	70	75	
SFO 2%	SS	35, 40, 40	60	55, 95, 65	50, 60, 50	75, 70, 55	80, 90, 75	
SFO 2%	Al	70	60	80, 70	-	60	98, 95	95
MO+MCO 2%	SS	40	60	90	75, 70	98, 80	95, 100	
MO+MCO _{cont} ¹	SS	40	60	80	-	65	90	
MO+MCO 2%	Al	70	60, 80	90, 85	50, 20	70, 55	85, 98	85
MO+MCO _{cont} ¹	Al	70	60	25	65	40	80	
TO 2%	Al	70	150, 175	95	75, -	85, 90	100, -	89

¹ Effluent from previous test run was treated with continued EC treatment.

EC treatment proved to be highly effective for concentrated O/W emulsions with repeatable high reductions of parameters. As seen in Table 5, EC removed turbidity

the best varying between 75–100%. The reductions in COD and TSC were in the range of 25–95% and 40–98%, respectively. The TOC values decreased the least of all the parameters measured, 20–75%.

When comparing only the EC treatment efficiency for various types of O/W emulsions, the highest reductions in parameters were measured for the TO and MO and MCO O/W emulsions, although reductions were also high for SFO as well as for RSO emulsions. The current density was unequal when different anode materials were used due to the different A_{eff} of the electrodes, although the average applied current was similar in magnitude (~8 A). Although the A_{eff} was significantly lower for the Al anode, the reductions achieved with both anode materials were similar. The most studied anode materials for oily waters are Al and Fe. An Fe anode has been found to be slightly more effective than Al when treating oil-containing waters (Ún *et al.* 2006, Cañizares *et al.* 2007, Maha Lakshmi & Sivashanmugam 2013). Settling of the flocs formed with an Fe anode has also been found to be faster than with Al anode (Zodi *et al.* 2009, Maha Lakshmi & Sivashanmugam 2013). However, the selection of anode material depends on the wastewater to be treated.

When the once-treated MO and MCO emulsion were treated again, the parameters were further reduced (COD reduction 25 and 80%, TOC reduction 65%, TSC reduction 65 and 40%, turbidity reduction 90 and 80%) even though the initial values of COD (~950 mg/L), TOC (~550 mg/L), TSC (-890 and -390 $\mu\text{eq/L}$) and turbidity (100 and 30 NTU) were already quite low.

As with the other parameters, the BOD_7 value also decreased with EC treatment. The BOD_7 removal was 95% for SFO, 85% for MO and MCO emulsion, and 89% for TO emulsion (samples at the beginning and the end were analysed). The decrease in the BOD_7 value occurred very rapidly in the first ten minutes and stabilised after that.

The development of COD, TSC, and turbidity as a function of treatment time are presented in Paper II. A clear correlation was observed, especially between the COD values and TSC values, as reported in Paper I for real OWWs. Thus, the TSC, as an easily performable measurement, can be considered a good process adjustment parameter, even on-line. At the beginning, the COD, TOC and turbidity values in particular sometimes increased, although TSC values typically decreased smoothly. Visible flocs were formed in the very first minutes of the test run. Thus, it is probable that COD and turbidity increased because the amount of dissolved metal (+ metal hydroxides) was not adequate for clear separation and TSC became less negative as a result of charge neutralisation. After the first minutes there was a

decrease in all the parameters asymptotically with increasing time. Although the treatment time in EC studies was between 60 to 175 minutes, analyses of the samples taken during test runs revealed that it is most likely that the optimal treatment times (COD reduction over 70%) would have been much shorter than the applied treatment time, at even less than 20 min.

Overall, the efficiency of EC with this type of electrode configuration was high with a short treatment time. Excellent treatment results of concentrated model O/W emulsions (bio O/W emulsions and synthetic-mineral O/W emulsions) were gained with a small NaCl addition (0.22%, 2200 mg/L) and a low current density of 40 A/m² for SS and 70 A/m² for the Al anode. The results achieved with EC in this thesis are similar to the results gained by Fouad *et al.* (2009) with Al electrodes, although the initial oil concentration was only 500 mg/L. Almost complete oil removal was achieved with 85 mg/L of NaCl, a current density of 80 A/m² and at a temperature of 20 °C (Fouad *et al.* 2009). Saur *et al.* (1996) discovered that EC might not be so effective for all hydrocarbons, since non-polar aliphatic hydrocarbons were removed significantly with EC but polar aliphatic and aromatic hydrocarbons were removed to a lesser extent. They observed that the oil removal decreased with an increasing NaCl concentration and temperature. In the EC studies conducted by Tir & Moulai-Mostefa (2008), Maha Lakshmi & Sivashanmugam (2013) and Bhagawan *et al.* (2014), optimal current densities were generally higher than in the EC studies in this thesis, between 17 and 250 A/m², with treatment times of 15 to 22 min.

Behaviour of essential process parameters during EC treatment

The process parameters which changed significantly during EC treatment were the current and pH value. The change in current (Fig. 14) was very peculiar, and has not been reported anywhere else apart from Paper II. During EC treatment when using an SS anode (Fig. 14a), the current usually increased during the test run, and as a result the voltage had to be decreased by 0.5 V to prevent short-cuts. When the Al anode was used (Fig. 14b), the current usually decreased and so the voltage had to be increased to maintain higher current values. For both anode materials the changing of the current stabilised towards the end of the test runs. The starting value of the voltage (U) (between 4.5 V and 7.5 V) was selected case-specifically and the corresponding current value was between 5.7 A and 8.8 A. The behaviour of current during the EC run was explained in Paper II as being possibly due to the geometry of the EC cell. When SS was used as the anode material, the sludge

formed did not disrupt the dissolving of the SS anode because flocs floated up, probably decreasing the resistance (R) and increasing the current according to Ohm's law ($U = I \times R$). However, when the Al anode was used, a significant amount of floated sludge was built up between the Al anodes, thus clearly disrupting electrolysis and probably increasing the resistance as well as decreasing the current. This disturbance can be seen in Fig. 14b. The disturbance from the sludge could be solved by adding a mixing unit to the EC cell, or by decreasing the number of Al bars, and by thickening the width of one Al bar.

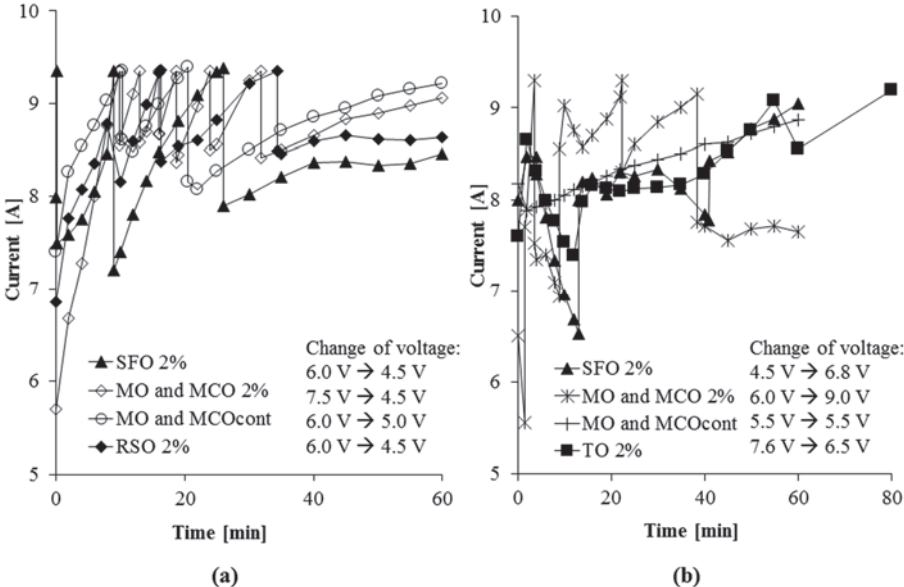


Fig. 14. Development of current during test runs for A) SS anode and B) Al anode. Only example curves presented. Figures also include beginning and end values of voltage.

During the test runs, the pH increased in every test run (Fig. 15), as expected, with the greatest increase in pH occurring during the first 30 minutes until a fairly constant value was achieved. The final pH reached with the SS anode varied between 10.3 and 10.9, being slightly lower for bio oils. The final pH values with the Al anode were lower than with the SS anode, at about 9.4 for the SFO O/W emulsions (for TO emulsions about 9.9), and about 9.1 for the MO and MCO O/W emulsions with the Al anode. For the bio O/W emulsions, the initial pH values were less than those for the MO and MCO O/W emulsions, but the increase in the pH

values for the bio oil O/W emulsions was greater than that for the MO and MCO O/W emulsions with both anode materials. The initial and final pH values for the continued test run for the MO and MCO emulsions were lower than the corresponding values for the once-treated O/W emulsions, due to the more diluted concentrations. The greater pH increase in the SS and Fe anodes than in the Al anode was also observed by Arslan-Anaton *et al.* (2009) and Zongo *et al.* (2009). The overall pH increase was due to the formation of OH⁻ ions (Eq. (10)) and, as can be seen in Fig. 15, the increase was more substantial for emulsions with an acidic and neutral initial pH, as also confirmed by Arslan-Anaton *et al.* (2009).

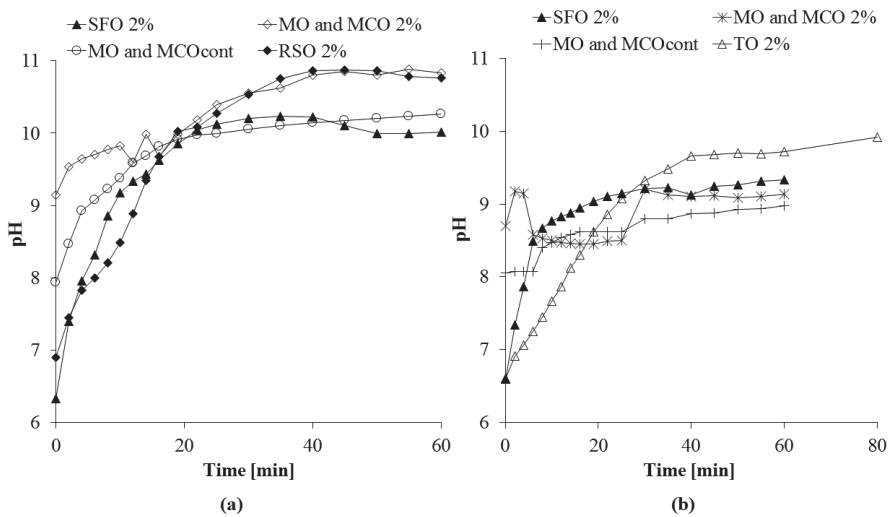


Fig. 15. Development of pH during test runs for A) SS anode and B) Al anode. Only example curves are presented. Modified from Paper II.

4.2.4 Treatment of O/W emulsions by CF-DAF (Paper III)

The CF-DAF (conventional coagulation-flocculation followed by DAF) studies were performed with the instrumentation presented in Fig. 5. The processes behind CF-DAF are presented in Fig. 16. To simplify the figure, the exact surface structure of the oil droplet is not presented. The surfaces of oil droplets are occupied by anionic SDS surfactant molecules, so that the hydrophobic part is towards the oil and the hydrophilic head is towards the water phase. According to the results from this thesis, it is supposed that when the cationic surfactant in CF-DAF was added

to the O/W emulsion, it did not become attached to the oil droplets during mixing and when dispersion water was introduced, but stayed in solution. When cationic polymers were added, an attachment was formed between the oil droplets and polymer chains during flash mixing (flocs) and the size of the flocs increased during slow mixing. In the flotation stage, bubbles attached to the flocs and raised them to the surface. CF-DAF was finalised with a clarification stage of 10 minutes.

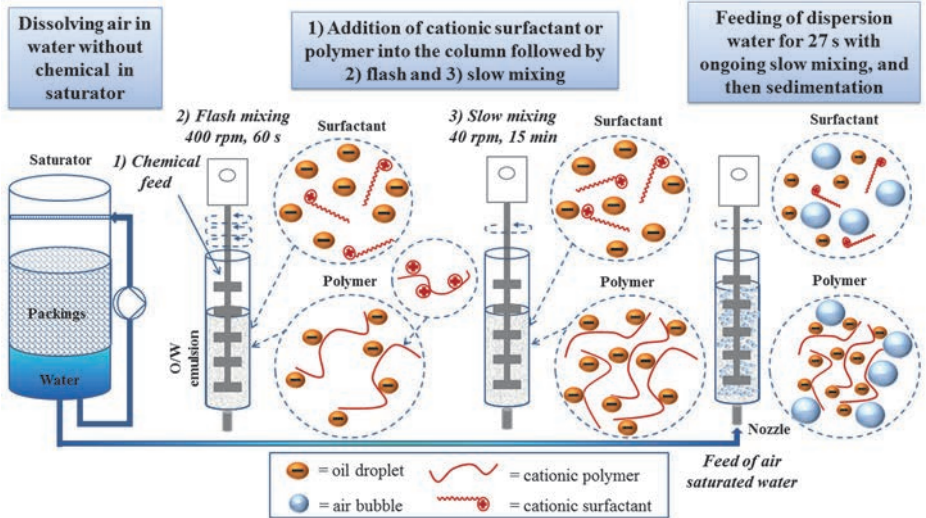


Fig. 16. Steps in CF-DAF using either a cationic surfactant or polymer for O/W emulsion treatment.

Figs. 17 and 18 present the COD reductions and development of TSC values for the CF-DAF studies. The total COD reduction was calculated by comparing the COD value of each treated sample to the original O/W emulsion. The COD removal was calculated by subtracting the effect of the addition of diluted chemical and dispersion water from the total measured COD removal. Fig. 18 also presents the dilution curves, which were calculated by subtracting the diluting effect from the TSC value of the original O/W emulsions.

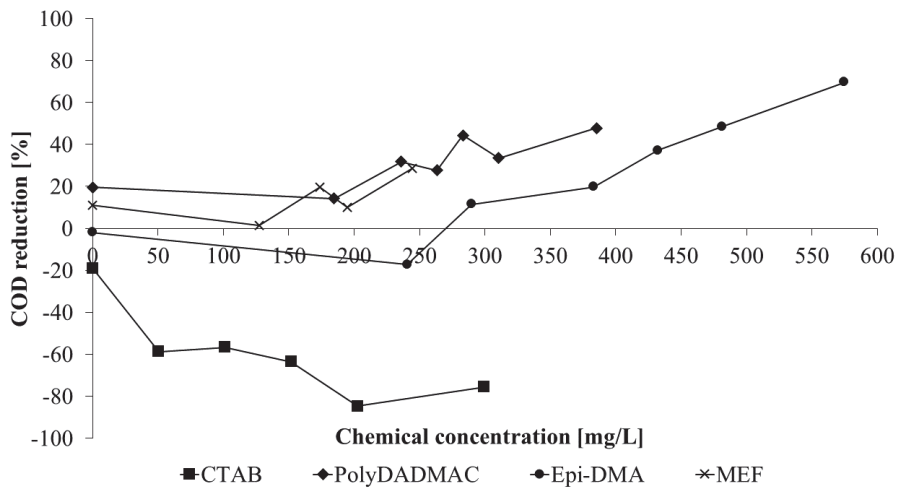


Fig. 17. COD reductions for CF-DAF according to chemical dosage. Data taken from Paper III.

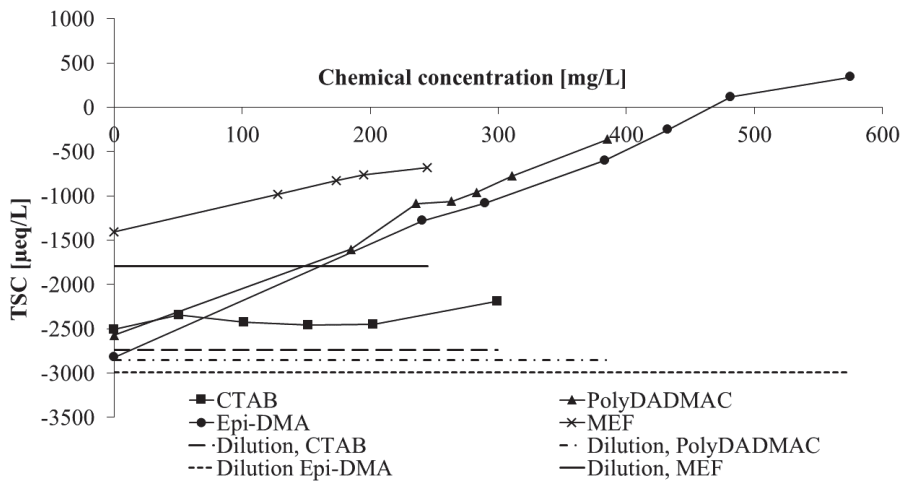


Fig. 18. Development of TSC for CF-DAF according to chemical dosage. Data taken from Paper III.

The CF-DAF studies performed with cationic polymers produced significantly better removal results than those with the CTAB surfactant. The neutralisation of the TSC value was gained with a dose of 465 mg/L of Epi-DMA achieving a COD

removal of about 43%. The highest COD removal for PolyDADMAC was 48% with a dose of 385 mg/L, which was also the highest dose studied for PolyDADMAC. The dose of Epi-DMA needed for a COD removal of 50% was about 485 mg/L. The highest dose studied for MEF was low compared to PolyDADMAC and Epi-DMA. TSC neutralisation was not achieved for MEF and the highest COD removal was 29% with a dose of 245 mg/L. When the results from FCM for PolyDADMAC and Epi-DMA were compared to the COD removals, there was no clear dependency between the results. Although the COD decreased according to the dose, the decrease in the number of hydrophobic particles was observed only with the highest doses of both PolyDADMAC (385 mg/L), 68%, and Epi-DMA (575 mg/L), 77%. PolyDADMAC was a more efficient coagulant for O/W emulsions than Epi-DMA, as far as the removal of COD and hydrophobic particles with a lower chemical dose are concerned. The O/W emulsions treated in the present study contained a high amount of anionic SDS surfactant (1500 mg/L). The performance of both coagulation-flocculation and DAF has been observed to decrease with an increasing concentration of emulsification agent (Hanafy & Nabih 2007).

The worst CF-DAF results were gained for CTAB, which showed continuously negative COD reductions. The TSC value did not significantly change although the amount of cationic CTAB was increased. Thus, according to the negative COD removals, CTAB remained in the solution and increased the COD values, and with a low charge density did not significantly affect the TSC value of the solution. This was also supported by the fact that the number of hydrophobic particles did not decrease during the CF-DAF study with CTAB. The performance of CTAB was similar in the Jar tests where separation of flocs was performed by sedimentation.

When evaluating the CF-DAF results, it must be remembered that the amount of bubbles has an optimal air/solid (A/S) ratio, and that was not studied here. According to the studies conducted by Santo *et al.* (2012), the efficiency of DAF in the removal of total petroleum hydrocarbons increased significantly with an increasing A/S ratio of up to 0.6 kg air/kg of total petroleum hydrocarbons. The optimal floc size for DAF is 25–50 μm since with a higher floc size, the aggregate rise velocity with bubbles decreases (Edzwald 2010). It could have been that the quantity of bubbles was not adequate to raise the flocs to the surface in the CF-DAF studies, which was probably seen in the analyses of COD and hydrophobic particles as a high variation in results. DAF, however, clearly increased the separation of flocs when a comparison was performed between DAF and sedimentation (Jar test) for PolyDADMAC. Difficulties in having reproducible

data for CF-DAF was also observed by Tansel & Pascual (2011) when treating water containing a high concentration (1500 mg/L) of petroleum hydrocarbons.

4.2.5 Treatment of O/W emulsions and OWWs by PosiDAF (Paper III)

Treatment of O/W emulsions by PosiDAF

PosiDAF studies were performed with the instrumentation presented in Fig. 5. The suggested processes behind the production of the cationic air bubbles in DAF when using a cationic surfactant or polymer and the formation of attachment between the cationic air bubbles and anionic oil droplets are described in Fig. 19. As in Fig. 16, the surface structure of oil droplets is simplified. The PosiDAF process is finalised with a 10-minute clarification step. It is assumed that the formation of cationic bubbles occurred in the nozzle. The hydrophobic part of the surfactant was positioned towards the air bubble at the air-liquid interface, leaving the positively charged regions on the outer edge of the bubble. In contrast, the polymers were associated more loosely due to their higher hydrophilic nature, penetrating further into the solution (higher sweeping efficiency). (Henderson *et al.* 2009).

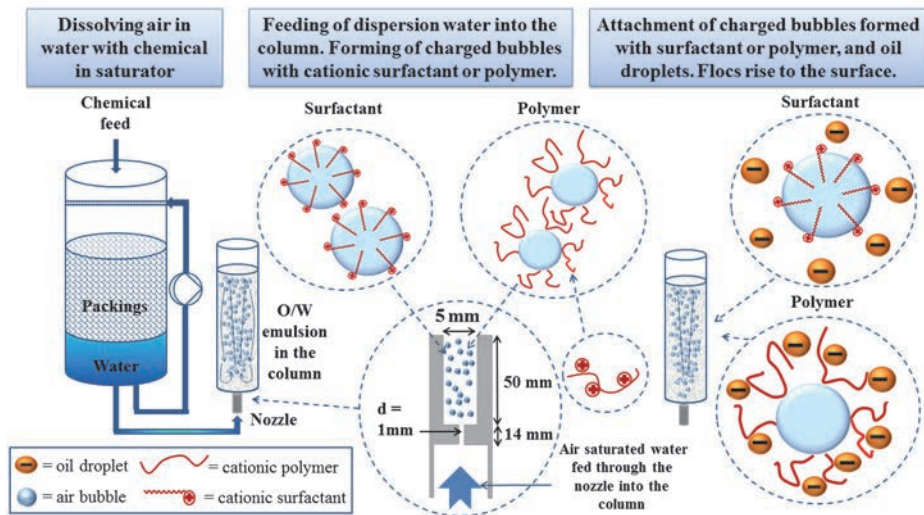


Fig. 19. The steps in PosiDAF for e.g. O/W emulsion treatment (with formation of cationic bubbles when a cationic surfactant or polymer was added directly into the saturator).

Figs. 20 and 21 present the COD reductions for the PosiDAF studies performed with a lower and higher chemical dose in the saturator, respectively. The dilution percentages were subtracted from the total COD removals.

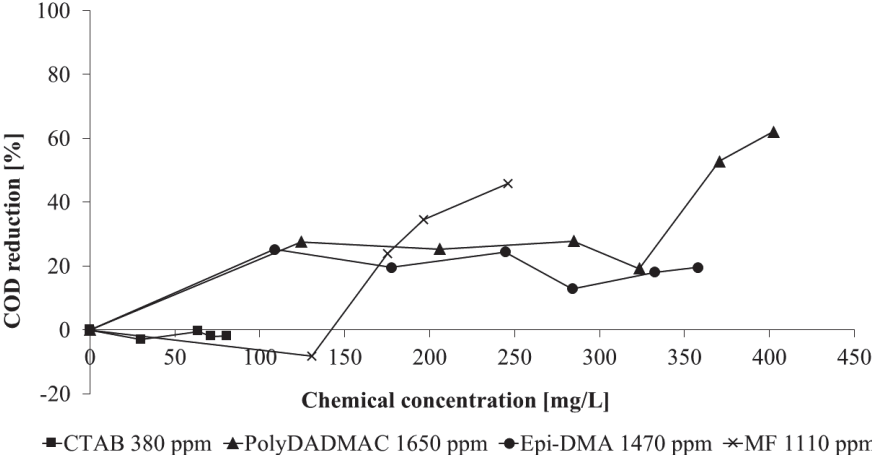


Fig. 20. COD reductions with low concentration of chemicals in PosiDAF for treatment of O/W emulsions. Chemical concentrations in saturator are given in the legend. Some of the data taken from Paper III.

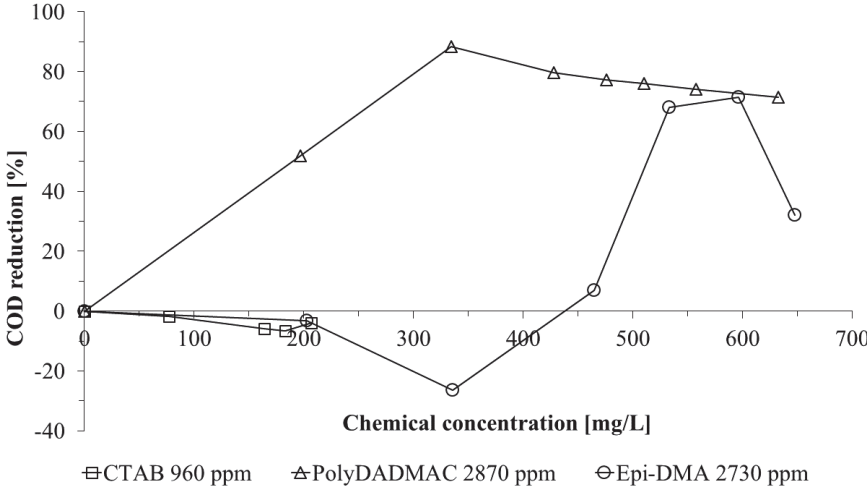


Fig. 21. COD reductions with high concentration of chemicals in PosiDAF for treatment of O/W emulsions. Data taken from Paper III.

Development of the TSC according to the concentration of chemical (Fig. 22) is presented as such, without taking the effect of dilution into account.

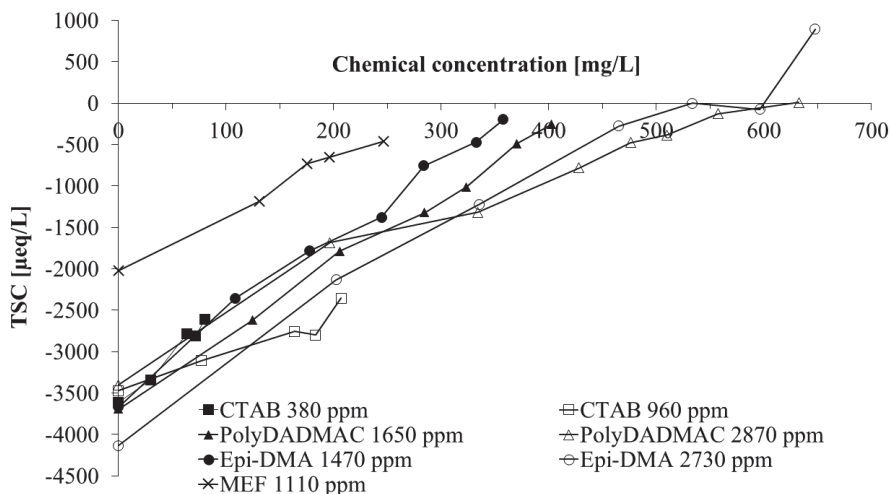


Fig. 22. Development of TSC value for PosiDAF studies performed on O/W emulsions according to chemical concentration of in column. Modified from Paper III.

The COD reductions for the PosiDAF studies performed with CTAB were always negative. PosiDAF with CTAB proved to be inefficient in treating 2% O/W emulsions, as was also proved for CF-DAF with CTAB. It was observed that the COD reductions became radically more negative with CF-S in comparison with PosiDAF; this may be due to some interaction between CTAB and the air bubbles in PosiDAF. The CMC value of CTAB is 1.00 mM (Mohamed *et al.* 2013). The concentration of CTAB in the saturator in the PosiDAF studies was 0.11–2.63 mM and in column 0.00–0.58 mM, thus the CTAB concentration in column was always below the CMC.

PosiDAF performed far better with cationic polymers than with a cationic surfactant. In these PosiDAF studies, the neutralisation of TSC was gained with a dose of 530 mg/L of Epi-DMA (C_{sat} of 2730 mg/L) and with 630 mg/L of PolyDADMAC (C_{sat} of 2870 mg/L) with corresponding COD removals of 70% and reductions in the number of hydrophobic particles of 78%. However, even at the lower dose of 335 mg/L of PolyDADMAC (C_{sat} of 2870 mg/L), the highest COD removal was as much as 88% with a non-neutralised TSC value, and with the reduction in hydrophobic particles of 80%.

The PosiDAF with low C_{sat} with Epi-DMA and PolyDADMAC also removed COD to a lesser extent, without neutralising the TSC value. The COD removal was below 30% each time with low C_{sat} (Epi-DMA); however the removal of hydrophobic particles clearly increased with increasing dosage, with a maximum of 75%. In the case of low C_{sat} (PolyDADMAC), the COD removal reached 62% only with the highest dose of about 400 mg/L, with a reduction in the number of hydrophobic particles of about 75%. Thus, the best COD removals were gained with PosiDAF using PolyDADMAC and with smaller doses in column when a higher C_{sat} was used. As PosiDAF is a novel method, it has been performed only for O/W emulsions (Paper III), for drinking water (Malley 1995), for algae-laden waters (Henderson *et al.* 2008, 2009, 2010), and for algae/cyanobacteria-laden waters (Yap *et al.* 2014). According to Henderson *et al.* (2008, 2009), CTAB proved to be a potential cationic surfactant for the removal of algae with PosiDAF, as the removal efficiency was 63–65% with a dose of 100 times less for PosiDAF compared to that in CF-DAF. However, the best algae removal efficiency was gained with low MW PolyDADMAC (100–200 kDa, charge density 6.2 meq/g) with an increasing recycle ratio (Henderson *et al.* 2010).

The difference in removal efficiency between PolyDADMAC and Epi-DMA can be explained by the difference in the interaction with air bubbles. When comparing the polymers PolyDADMAC and Epi-DMA, PolyDADMAC has a larger MW but a lower charge density than Epi-DMA. Epi-DMA is also a more hydrophilic polymer. Due to its hydrophilic nature, it is supposed that Epi-DMA is even more loosely associated to air bubbles and its sweeping range in the solution is due to the lower MW, in which is shorter than that of PolyDADMAC.

The MEF that was tested only with the lower amount in the saturator proved to be a good candidate for PosiDAF studies although again the TSC was not totally neutralised. A COD removal of 45% was achieved with 245 mg/L. The separation of flocs in PosiDAF with MEF was already visibly much more efficient than in CF-DAF with MEF.

The number of hydrophobic particles and COD values was clearly interdependent (although they differed from each other in some points); however, this was not observed in the CF-S studies. This might be due to the higher standard deviations in FCM measurements for samples from CF-DAF compared to samples from PosiDAF. The standard deviations were higher probably because the samples might have contained residual flocs formed during storage which could not be removed by coarse filtration, or due to poor clarification in CF-S. In the future, the

pre-treatment of oily water samples for FCM should be further developed and optimised.

Treatment of OWW samples with PosiDAF

PosiDAF with PolyDADMAC (C_{sat} of 2800 mg/L) was also performed on OWW samples (see Table 2) with promising removal results (Paper III). The highest COD (initial value of 32000 mg/L) removal for the pre-UF sample was 67% (dose of 330 mg/L) with a reduction in hydrophobic particles of 82%. PosiDAF treatment did not remove COD (initial value of 6600 mg/L) from the post-UF sample, although removal of hydrophobic particles was as high as 72% with the lowest chemical dose. The COD reductions for the pre-UF sample were higher than for the post-UF sample, due to the fact that the pre-UF sample contained more removable contaminants, causing a higher COD. When the development of TSC was studied, the neutralisation of the pre- and post-UF samples had already occurred at dosages of 195 mg/L and 50 mg/L, respectively. Thus, the neutralisation of TSC was more efficient for the post-UF sample because it did not contain as many anionic contaminants to be removed by the cationic coagulant, so the coagulant added into the sample solution stayed in solution and increased the TSC value. For the pre-UF sample, a dose of 200 mg/L of PolyDADMAC was thought to be close to the optimum corresponding to a reduction of COD of 65%. The highest COD reduction was achieved with the same PolyDADMAC concentration (330 mg/L) for both the OWW (COD reduction of 79%) and O/W emulsion (COD reduction of 88%) in PosiDAF. According to the results of the PosiDAF studies, it can be concluded that the model O/W emulsions studied were much more challenging to treat than the emulsions in the OWW samples, probably due to the fact that the chemically emulsified O/W emulsions were more stable than the mainly mechanically emulsified OWWs. The maximum COD reduction for OWW was lower than for the O/W emulsion, although significantly more COD was removed relatively from OWW. It must be remembered that OWWs also contain other substances increasing COD value that cannot be removed with coagulants.

Interaction between air bubbles and polymer

The interaction between the air bubbles and the polymer was verified by studying the spreading of PolyDADMAC in column in PosiDAF (cationic bubbles) and in CF-DAF (Paper III). Verification was performed by measuring the TSC values of

samples taken from the flotation column from different depths according to the time after the dispersion water was stopped for PosiDAF and CF-DAF (with 470 mg/L and 1680 mg/L of PolyDADMAC). Based on these results, it was concluded that: 1) the air bubbles do not raise pure PolyDADMAC as such without contaminants to the surface in CF-DAF, and 2) the interaction between air bubbles and PolyDADMAC was evident in PosiDAF. Details can be found in Paper III.

PosiDAF vs. CF-DAF

Table 6 summarises the removal results of COD and hydrophobic particles for the DAF studies performed with polymers on O/W emulsions (MO, MCO).

Table 6. Removal of COD and hydrophobic particles for DAF studies with the optimal chemical dose performed on O/W emulsions.

Study	Chemical	Dose in column [mg/L]	COD reduction [%]	Removal of hydrophobic particles [%]
CF-DAF	PolyDADMAC	385	48	68
PosiDAF 1650 mg/L	PolyDADMAC	400	62	74
PosiDAF 2870 mg/L	PolyDADMAC	335	88	80
CF-DAF	Epi-DMA	480	50	77 (with 575 mg/L)
PosiDAF 1470 mg/L	Epi-DMA	330	20	75
PosiDAF 2730 mg/L	Epi-DMA	530	70	78
CF-DAF	MEF	245	29	-
PosiDAF 1110 mg/L	MEF	245	45	-

The following conclusions can be drawn from the DAF studies: 1) PosiDAF with PolyDADMAC and MEF performed significantly better compared to CF-DAF, 2) PosiDAF with Epi-DMA performed with similar or worse results than CF-DAF, and 3) PosiDAF with PolyDADMAC resulted in higher COD removals with lower chemical doses compared to CF-DAF.

4.3 Comparison of treatment methods studied

4.3.1 Discussion concerning costs of treatment methods

The treatment costs for EC result mainly from electricity and the replacement of the anode material, but also from chemical costs from adjusting the conductivity (NaCl) and pH values. The tendency is for electricity prices to grow, and in the first

quarter of 2014, the electricity price including all taxes and levies for the industrial consumer (500–2000 MWh) was 0.153 €/kWh (Eurostat). The price of aluminium was 1552 €/t (1798 USD/t) according to LME, the price of stainless steel (hot rolled plate (316)) was 3927 €/t (4551 USD/t) and the price of carbon steel (hot rolled plate) 605 €/t (700 USD/t) at the end of 2014, according to MEPS. According to an extensive review by Kuokkanen *et al.* (2013) on EC treatment for various waters in optimal process conditions, electricity consumptions was between 0.4–4.0 kWh/m³. The electricity consumption (optimal treatment time about 20 min) for the EC studies in the present study was very low, between 0.5–0.8 kWh/m³ of treated O/W emulsions. The EC costs resulting from electricity and anode dissolution in the present study were about 0.55 €/m³ for the Al anode and 2.65 €/m³ for the SS anode for the treatment of O/W emulsions (MO, MCO) when calculated for a 60-min treatment. Stainless steel as an anode material is expensive, and costs could be decreased even to as little as 0.56 €/m³ by using carbon steel as the anode material. The amount of dissolved Fe²⁺ ions in the EC test runs was about three times higher than the amount of dissolved Al³⁺ (Paper II). Thus, the treatment costs would be the same, although aluminium as anode material is more expensive than carbon steel.

Al anodes proved to be a preferable alternative to SS when comparing treatment costs. When comparing only the electrode potentials of Al and Fe, Al would be a much cheaper material (it consumes less electricity) than Fe (Eq. (2)) due to its higher electrode potential (Eq. (1)). However, the usage of an Fe anode would be more environmentally friendly compared to Al, although if EC were part of the UF-based process, the dissolved metal would mainly be removed by an ion exchanger. The electrode configuration in the EC apparatus used proved to be practical and efficient. The anode bar over the cathode basin ensured that hydrogen bubbles from the cathode were well spread over the anode bars, ensuring that the separation of flocs was efficient. This observation was also confirmed by Fouad *et al.* (2009). However, as previously mentioned, a mixing unit should be added to the EC cell or at least the number of anode bars should be fewer, so that sludge would move away from the bars.

The costs of conventional coagulation-flocculation followed by sedimentation come mainly from chemical usage. It proved efficient for O/W emulsions with polyaluminium chloride and ferric chloride, however the neutralisation of the TSC value was gained only with polyaluminium chloride at a dose of 800 mg/L (see Fig. 11). The total consumption of polyaluminium chloride product was 2.3 kg/m³. A complete neutralisation of OWWs was not achieved with commercial coagulants,

but only with 350–450 mg/L of chitosan (see Fig. 13). Therefore, total chitosan consumption for the treatment of OWWs (COD removal of about 80%) was 0.5 kg/m³. COD removal of 100% was gained with ferric chloride (400 mg/L) (see Fig. 12), and the consumption of the product was 1.0 kg/m³. Chitosan would be an interesting non-toxic chemical for future studies; however its current price restricts its wider usage. The volumes of sludge produced from conventional coagulation-flocculation followed by sedimentation are known to be high compared to EC, due to its higher water content.

In CF-DAF and PosiDAF the costs are formed mainly from chemicals usage, pumping and preparation of pressurised air. PosiDAF proved to be an efficient alternative to CF-DAF, with significantly higher removal results and smaller chemical doses. Also, the separation of flocs in PosiDAF, even without separate mixing and longer settling stages, was faster and more efficient than in CF-DAF. When the prices of PolyDADMAC, Epi-DMA and MEF are compared to the prices of ferric chloride and polyaluminium chloride, they are almost ten times greater. Cationic polyelectrolytes are also known to be more toxic than non-ionic and anionic polyelectrolytes, especially to aquatic organisms (Bolto & Gregory 2007). Moreover, the chemical consumption in PosiDAF may be as much as half of that used in CF-S. The costs for preparing dispersion water and pressurised air in DAF were not calculated in this thesis.

4.3.2 EC and PosiDAF as pre-treatment alternatives for UF

It was discovered that in the UF-based process there was a significant need to decrease the organic load before the UF stage, thereby decreasing the fouling of the UF membrane but also enhancing the rejection of contaminants with UF. The methods studied such as EC with a feasible electrode configuration and PosiDAF proved to be highly efficient in removing, for example, COD and decreasing the charge density even without specific optimisation of the operational parameters. The time needed for pre-treatment with either PosiDAF or EC would be about the same, i.e. 10–15 min. In this time period, the resulting COD removal would be adequate to decrease the organic load conducted to the UF membrane, thus lengthening regeneration intervals, although this was not studied in this thesis. When EC and PosiDAF are compared as pre-treatment alternatives for UF, the selection of the more feasible alternative is difficult. The PolyDADMAC used as cationic coagulant in PosiDAF could be almost beneficial as far as further treatment in a municipal wastewater treatment plant is concerned. However, some less

expensive cationic compounds as biodegradable biopolymers such as commercial tannin-based coagulants (produced by e.g. Grove Advanced Chemicals and Tanac S.A.) could also be studied in PosiDAF, since for example chitosan was proven to be an effective coagulant for real oily wastewaters. When considering PosiDAF as a pre-treatment for UF, some of the process effluent could be recycled and saturated with air, thus reducing the amount of pure water used.

As mentioned, various types of OWWs are usually mixed mainly to achieve a stabilised pH and homogenised wastewaters are conducted to UF. EC or PosiDAF might not be so sensitive to oily wastewater quality variations as UF, thus it would be possible to avoid a separate homogenisation stage. However, EC would raise the pH of OWW with an Al or SS anode to a value of 9–10 with 20 min treatment, therefore increasing the volume of acid used after UF for the ion exchangers. In PosiDAF this is not a problem. Both EC and PosiDAF also produce sludge, which must be post-treated. Also, scalability should be studied for PosiDAF. For EC scalability is good, as was discovered recently by Kuokkanen *et al.* (2014). The passivation of the anode, as a result of metal oxides, may be a problem in continuous EC mode but there is also the possibility of corrosion of the saturator in PosiDAF due to direct chemical addition. However, both processes can be highly automated.

PosiDAF, in particular, needs more studies on its performance on removing some difficult compounds such as phenolic compounds that are not well removed with CF-DAF, as was observed by Younker & Walsh (2014) when they treated produced water with DAF after coagulation with ferric chloride. Real OWWs typically contain phenol, which was not efficiently removed by the UF-based processes (Paper I). The efficiency of EC in phenolic compounds removal was proven by Bhagawan *et al.* (2014), as 85% removal of phenolic compounds was achieved with a 20-min treatment.

4.4 Biodegradation of oils and surfactants (Papers II, IV and V)

4.4.1 Oils in solution conditions

The average biodegradation curves for light fuel oils (Paper IV), mineral-based and synthetic oil products (Paper II) in optimal OECD 301 F standard conditions are presented in Fig. 23. The average biodegradation degrees for these oils varied between 15 and 26% with reproducible results. The least biodegradable in 28 days was 2MO and the most biodegradable was MCO. According to the OECD (2006),

a chemical is readily biodegradable in manometric respirometric test (TG 301 F) if 60% ThOD removal is obtained in 28 days, and it has to be reached in a 10-day window. The 10-day window begins when the degree of biodegradation has reached 10% of ThOD. The chemical concentration in standard conditions should be in the range of 2 to 100 mg/L. (OECD 2006). Light fuel oils, mineral-based and synthetic oil products were moderately biodegradable in optimal OECD 301 standard conditions with concentrations of 180–470 mg/L. A short 1-day lag phase can be seen at the beginning of the curves (microbes adapt to a new carbon source), and a plateau (steady state) had not been reached within 28 days.

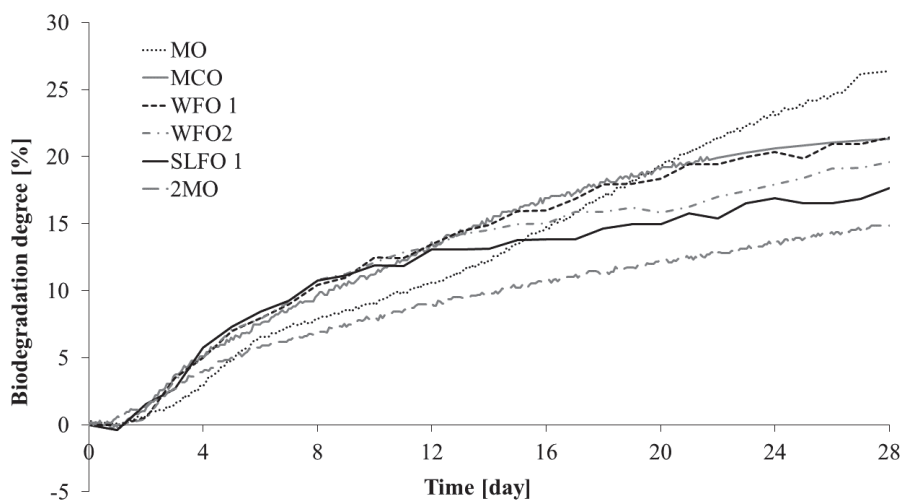


Fig. 23. Curves of the biodegradation degrees over time for light fuel oils, mineral-based and synthetic oil products in standard OECD 301 F conditions. The MCO biodegradation degree was projected from 22 days to 28 days. Some of the data are taken from Papers II and III.

In the studies concerning the effect of ammonium on the biodegradation of light fuel oils in optimal standard solution conditions, a clear increase was observed after 28 days. The biodegradation degrees were even doubled, being 43% on average. When using fertilisation, excessive use can, however, inhibit the assimilation of hydrocarbons; in particular the amount of nitrogen can be inhibitory (Châineau *et al.* 2005).

The biodegradation of light fuel oils in mineral-poor groundwater was poor (Paper IV). Therefore, light fuel oils may cause a major environmental problem if

they are spilled into soil because they finally infiltrate into the groundwater. Kuokkanen *et al.* (2004) studied the biodegradation of bio and mineral oils (forestry hydraulic oils) in groundwater taken from the same location as in Paper IV. The mineral oils and some of the bio oils biodegraded slowly in 28 days with biodegradation degrees of 5 to 10%. However, two of the bio oils achieved a degree as high as 20%. The calculation of ThOD by Kuokkanen *et al.* (2004) was performed with only the carbon content of oils. By taking the hydrogen content of oils into consideration too, the biodegradation degrees would have been lower.

Fig. 24 presents the curves of the biodegradation degrees over time for bio oil products in OECD 301 F standard conditions. The lag phase was even shorter for bio oils than for the other studied oils, and no plateau was reached here either. The RSO and SFO achieved a removal of 44% and 51% of ThOD in 28 days, respectively, with reproducible results. Thus, the biodegradability of bio oils compared to light fuel oils, mineral-based and synthetic oil products was significantly higher. The concentration of bio oils studied in BOD OxiTop studies was even 10 times greater than the concentration according to the OECD standard, and it would be likely that the biodegradation degrees of bio oils would be much higher with a lower oil concentration.

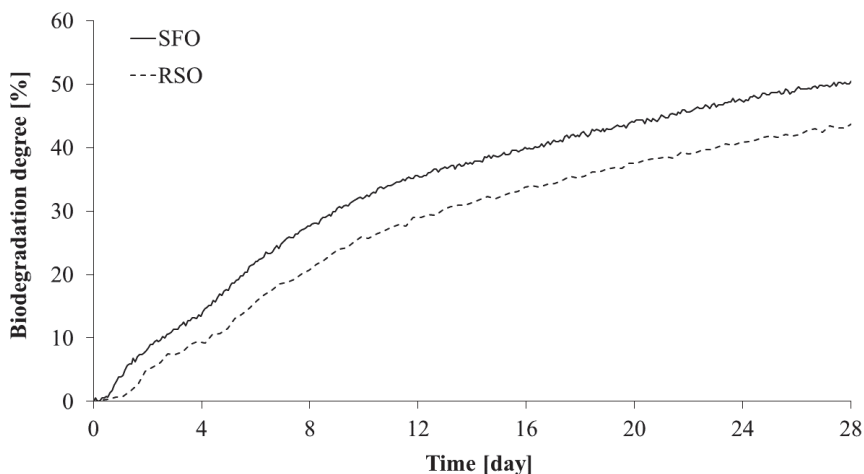


Fig. 24. Curves of the biodegradation degrees over time for bio oil products in standard OECD 301 F conditions. Some of the data are taken from Paper II.

4.4.2 Oils in forest soils

The biodegradation of light fuel oils was studied in mineral-poor and mineral-rich forest soil. The properties of the soils can be found in Paper IV. The biodegradability of light fuel oils in mineral-poor and dry soil was weak, between 0.6–1.1%. Kaakinen *et al.* (2007) observed that when a mineral solution was added to the mineral-poor soil, the biodegradation degrees of rapeseed oil-based oils were significantly increased. The biodegradation of these oils was further enhanced by adjusting the pH of the soil to a value of 8. Biodegradation degrees of light fuel oils in mineral-rich and moist soil were as expected higher, at between 11–12% for summer grade fuel oils and about 8.0% for winter grade fuel oils (Fig. 25) in 30 days. The lag phase in the soil was very long, up to 10 days, but after the microbes had adapted to light fuel oils as a new carbon source, oils continued to degrade steadily for the whole 30-day measuring period without reaching a plateau. Hawle-Ambrosch *et al.* (2007) gained higher biodegradation results for light fuel oil in both sandy and loamy soil in 28 days, at about 30% and 18%, respectively.

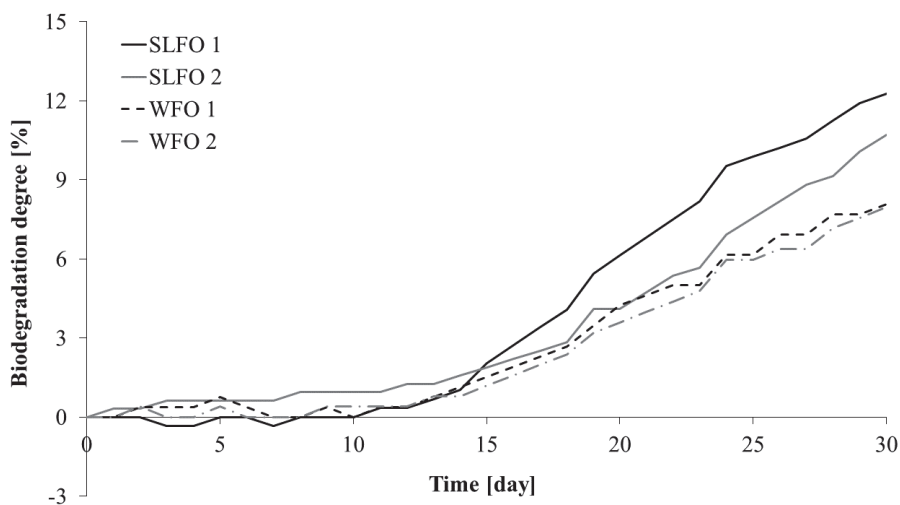


Fig. 25. Curves of the biodegradation degrees over time for light fuel oils in mineral-rich soil. Modified from Paper IV.

A 189-day biodegradation measurement was performed for summer grade light fuel oil (SLFO 1) in mineral-rich soil without the addition of moisture and nutrients. The final biodegradation degree was as high as 63% without reaching a plateau. This is an important result, as light fuel oils are considered toxic. For crude oil in

an agricultural soil, the biodegradation degree in 150 days was lower, 47%, but increased with fertilisation to 62% according to Chaîneau *et al.* (2005). In Paper IV, the biodegradation degree for the 189-day measurement was calculated by taking only the carbon content of the oil into consideration, and in this way a biodegradation degree of over 90% was gained. However, when calculating biodegradation degrees, as shown in Fig. 26, both the carbon and hydrogen content have to be taken into account when evaluating the biodegradation of the oil.

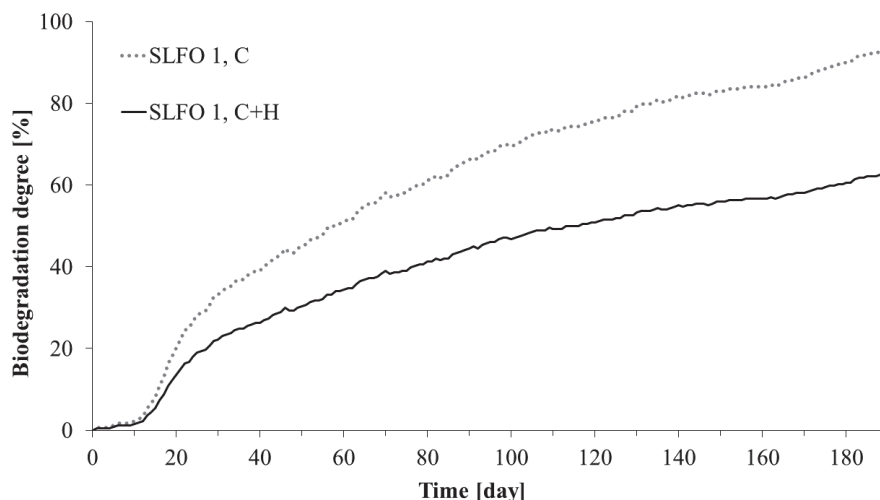


Fig. 26. Curves of the biodegradation degrees (ThOD calculated from C and/or H content of the oil) over time for SLFO 1 in mineral-rich soil for 189 days. Some of the data are taken from Paper IV.

4.4.3 Surfactants in solution conditions

Table 7 presents the biodegradation degrees for cationic CTAB and non-ionic Triton X-100 surfactants in various solution conditions (Paper V). According to the results, CTAB did not biodegrade in optimal OECD 301 F standard conditions. Prokkola *et al.* (2012) studied the biodegradation of Triton X-100 in OECD 301 F conditions, and it biodegraded only 6.0% in 10 days. During this measuring time a plateau was reached. CTAB is a bromide salt and when the possible inhibition of bromide ion was examined, the results indicated that CTAB clearly inhibited the biodegradation of glucose, since biodegradation of glucose-mineral water solution was on average 82%. The NaBr did not inhibit the biodegradation of glucose, as

the results were 64 and 81% after 28 days. These results are confirmed by Zeng *et al.* (2007), who performed biodegradation studies on CTAB, Triton X-100 and SDS. CTAB was recalcitrant to degrade and it also inhibited microorganisms from utilising a readily degradable carbon source. Triton X-100 was also poorly biodegradable, but was not toxic to microorganisms, whereas SDS could be co-degraded as a carbon source with glucose as it did not have any toxicity.

Table 7. Biodegradation degrees for CTAB and Triton X-100 in various solution conditions. Modified from Paper V.

Study	Sample	C [mg/L]	Solution condition	Time [d]	Biodegradation degree [%]
Standard conditions	CTAB	120	OECD 301 F	28	0
Standard conditions ¹	Triton X-100	100, 200	OECD 301 F	10	6 ¹
Inhibition	CTAB	120	Glucose (0.1g/L) + OECD 301 F	28	0 ²
Inhibition	NaBr	20	Glucose (0.1g/L) + OECD 301 F	28	64, 81 ²
Inhibition	Only glucose	100	Glucose (0.1g/L) + OECD 301 F	28	82 ²
Inoculated with soil	CTAB	100	OECD 301 F	28	5 ²
Inoculum addition	CTAB	100	OECD 301 F	28	2 ²
Inoculated with soil	Triton X-100	110	OECD 301 F	28	-3, 4 ²
Inoculum addition	Triton X-100	110	OECD 301 F	28	0, 23 ²

¹ Prokkola *et al.* (2012), ² Biodegradation degree of blank not decreased.

When considering the inoculation results for determining which of the bacteria from organic material-rich soil or wastewater performs best in a water environment, CTAB provided repeatable low biodegradability results, on average 5%, when the OECD 301 F mineral solution was inoculated with topsoil. When this value was compared to the results with CTAB in OECD 301 F conditions with an inoculum from municipal wastewater treatment plant, the results dropped slightly, to 2%. The difference is not significant if the accuracy of the biodegradation measurements is considered. The type of inoculation did not affect the biodegradation of Triton X-100.

4.4.4 Surfactants in topsoils

Table 8 presents the biodegradation degrees for cationic CTAB and non-ionic Triton X-100 in two topsoils rich with organic materials (Paper V). The results are

not unequivocal, although multiple replicate measurements were performed. When the biodegradation degrees were calculated by taking the carbon content of both the soil and surfactant in ThOD into account, all the biodegradation degrees for measurements were practically zero, between -2% and 4%. Topsoil contained a large amount of organic carbon, and it was quite heterogeneous system as was observed in the carbon content measurement, where it varied between 29%–44% for topsoil 1. The mean value of the carbon content of topsoil 2 was 24%. The moisture content was 55% for topsoil 1 and 48% for topsoil 2. For comparison, the mineral-rich soil used in Paper IV had a lower moisture content of 28%, although the carbon content was not measured.

Table 8. Biodegradation degrees for cationic CTAB and non-ionic Triton X-100 in two topsoils. Modified from Paper V.

Sample	C [mg/kg]	Moisture content [%]	Soil	Time [d]	Calculated biodegradation degrees for replicates [%]
CTAB	110	64	Topsoil 1	60	-250, 230, 190
Triton X-100	110	64	Topsoil 1	60	-50, -100, 220
Triton X-100	200	60	Topsoil 1	60	-370, 50
CTAB	110	54	Topsoil 2	55	-280, 10
Triton X-100	110	54	Topsoil 2	55	-515, -15

The calculated biodegradation degrees for CTAB and Triton X-100 fluctuated between -515 and 230%. The fluctuation for a concrete washing agent containing a non-ionic surfactant (discussed more in detail in Paper V) was even worse between -7500 and 1100%. These types of variation in biodegradation degrees for surfactants in biodegradation studies in soil have not been reported earlier, except in Paper V. The shapes of the curves for CTAB and Triton X-100 resembled the shapes of the topsoil blanks, probably being dependent on which bacteria dominate, which can be from the sample or from the soil itself. In BOD OxiTop measurements positive pressure values (negative biodegradation degrees) are due to anaerobic biodegradation producing methane. Anaerobic biodegradation was not studied in Paper V.

The topsoil is a heterogeneous matrix, containing various sizes of pores. A significant amount of the organic material in the soil is located within the pore space. The pore size distribution of a soil affects the ability of decomposer organisms to reach potential substrates. If the pore size is very small,

decomposition of organic material can occur only by diffusion of extracellular enzymes away from organisms to a substrate and products of enzyme reactions diffusing back to organisms. (Baldock & Skjemstad 2000). It is supposed that the addition of a surface-active agent lowers the surface tension of the aqueous phase of the soil (Prokkola *et al.* 2014). Thus, soil is wetted better with surfactants than with only pure water. This provides the opportunity for the microorganisms to biodegrade the organic matter that is otherwise hidden from water and microorganisms. The most disturbing effect on the biodegradation degree in the topsoil is the high organic carbon content of the soil and this is seen as very high calculated biodegradation degrees. This was first distinguished in Prokkola *et al.* (2014) for tall oil soaps in topsoil. The enhanced biodegradation of the organic materials of the soils was obvious for all of the surfactants whether the surfactant was readily biodegradable (non-ionic surfactant in concrete washing agent), weakly biodegradable (Triton X-100), or even inhibitive (CTAB). It should be noted that biodegradation is not a chemical reaction but a biological phenomenon, thus biodegradation is strongly dependent on the surrounding environment where the sample is studied.

4.5 Evaluation of repeatability of the analysis methods

In this section, the repeatability of the most frequently used analysis methods in this thesis is discussed. One of the most important analysis methods used in this thesis was COD measurement using the Hach Lange photometric cuvette test. Some compounds may cause interference in COD analysis, and chloride is the most common cause of interference. Hach Lange cuvette reagents contain mercuric sulphate to eliminate interference up to 2000 mg/L chloride. The reagents also contain silver as a catalyst, because straight-chain aliphatic compounds are not effectively oxidised without a catalyst, although the catalytic activity of silver is diminished when halides are present. The dichromate COD procedure will oxidise most organic compounds with 90–100% efficiency, although some compounds such as benzene, toluene and ethylamines are only partially oxidised. Organic compounds such as pyridine, pyridine derivatives and methylamines resist oxidation. (Boyles 1997). Therefore, it is possible that not all the organic compounds e.g. in OWWs were oxidised with the dichromate COD procedure. The sample amount taken for the COD analysis was as small as 0.2 mL, and although usually one or more replicates were performed, repeatability varied greatly for heterogeneous OWWs and O/W emulsions.

The TOC measurements were performed on OWWs and O/W emulsions. Erratic TOC readings may be due to the high pH (e.g. pH > 8.0) of the sample stream, and the large amount of inorganic carbon (greater than 10 times the TOC value) (GE Water and Process Technologies Analytical Instruments 2009). The low repeatability of TOC for OWWs and O/W emulsions was not for the above-mentioned reasons, because the samples had to be highly diluted due to the measuring range of 0.03 µg/L and 50 mg/L for the Sievers 900 Portable TOC Analyzer (GE Water and Process Technologies Analytical Instruments 2009). The dilution with a high dilution factor of oily samples containing surfactants resulted in even more heterogeneous samples, and is thus the probable cause of the low repeatability of TOC measurements.

When comparing the repeatability of COD, TOC and TSC measurement, it was discovered that TSC measurement was the most reliable analysis method in this thesis. The dilution factors for OWWs and O/W emulsions were lower for TSC measurement than for COD and TOC measurements, and also the sample amount (5 mL) analysed was the highest in TSC measurement.

The BOD measurements using the BOD OxiTop method were successful with repeatable results for OWWs and O/W emulsions in optimal solution conditions, and for oil products in optimal solution conditions, in groundwater as well as in solid phases. Inhibition for OWW samples in solution conditions before UF was observed as discussed in Section 4.1.4, when BOD measurements were performed with different dilution factors. Thus, in the future, it is important to study the BOD value of oily wastewaters with various dilution factors.

The BOD measurements of surfactants, especially in the solid phase, produced results with very low repeatability compared to oily waters and oil products, although multiple replicate measurements were performed. According to the biodegradation results gained for surfactants, generally speaking it is almost impossible to distinguish the biodegradation of surfactants from the biodegradation of the organic material of soil, especially in organic-rich soil. This observation must be taken into account when studying the biodegradation of surfactants or surfactant-containing wastewaters in soil with high organic carbon content.

5 Conclusions

The objective of this thesis was i) to increase knowledge on the performance of commercial UF-based treatment processes by characterising real oily wastewater (OWWs) samples from two WWTPs in Finland, ii) to study the effectiveness of EC and PosiDAF (DAF which utilises cationic air bubbles) in particular for the treatment of concentrated O/W emulsions and OWWs, and iii) to study the biodegradability of individual components usually present in OWWs such as various oils and surfactants. The main findings in this thesis are:

1. The OWWs to be treated in the two WWTPs possessed a very high organic load causing fouling of the UF membrane and short regeneration intervals. However, the overall performance of UF-based processes was high, and there was no significant difference between the performances of the two WWTPs under investigation. Residual concentrations were occasionally very high due to the presence of organic compounds not totally removed by the UF-based process. The main reductions in parameters were achieved by the UF unit and only minor reductions were gained with the subsequent sand filter and ion exchangers. Furthermore, the clear correlation observed for COD and TSC could be utilised for process control purposes.
2. The bench scale EC process studied, using Al or SS as the dissolving anode material was found to be a cost-effective and efficient method for treating stable and concentrated O/W emulsions, even without the specific optimisation of the most important process parameters. The electrode configuration was proven to be feasible and practical.
3. The treatment of concentrated O/W emulsions and OWWs was effective with PosiDAF. It was found to be a competitive alternative for CF-DAF, with even higher removal results with smaller chemical doses. The separation of flocs in PosiDAF, even without separate mixing and longer settling stages, was faster than in CF-DAF.
4. The biodegradation studies performed on light fuel oils, mineral-based and synthetic oil products proved them to be slowly biodegradable in optimal OECD 301 F conditions. As the amount of ammonium was tripled, the biodegradation degrees of light fuel oils were even doubled. When a biodegradation study of light fuel oil in mineral-rich soil without soil conditioning was performed for a lengthened time, over 6 months, the final biodegradation degree was surprisingly over 60%.

5. The cationic CTAB and non-ionic Triton X-100 surfactants studied were poorly biodegradable in optimal OECD 301 F standard conditions. The biodegradation studies of surfactants in organic-rich soils produced highly varying biodegradation degrees. It was assumed that various types of surfactants cause the enhanced biodegradation of the organic material in the soil, thus masking the biodegradation of the surfactants.
6. Flow cytometry proved to be a highly promising analysis method for waters containing oils.

6 Recommendations for future research

This thesis acted as an introduction to the treatment of oily waters with PosiDAF, but also gave rise to the need for further research. In the future, the influence of many process parameters, such as the amount, charge and size of air bubbles when using chemicals in the saturator, nozzle structure, chemicals, pH etc. should be studied in more depth and optimised for PosiDAF. Cost estimates for PosiDAF must also be calculated before it can be considered a real alternative for the treatment of oily waters. EC and PosiDAF both produce sludge, which needs to be managed. The amount and compactibility of the sludge produced in PosiDAF should be investigated in the future and compared to other methods such as EC and conventional coagulation-flocculation followed by DAF.

This thesis also provides the basis for further studies concerning EC and PosiDAF as pre-treatment alternatives for UF. The next step would be to combine pre-treatment and UF, and optimise the entire treatment process. EC has already been the focus of many studies, especially for model O/W emulsions. However, more knowledge is required concerning the performance of EC in the treatment of real oily wastewaters, especially for complex and concentrated wastewaters. The formation potential of dangerous adsorbable organic halides through the anodic oxidation of halides in EC when treating oily wastewaters should be recognised and studied in the future.

Analysis of heterogeneous oily waters is highly problematic, thus new analytical methods such as flow cytometry should be further researched. Flow cytometry is a simple and fast method, although sample preparation, especially for oily waters, must be optimised to produce reproducible analysis results.

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