UNIVERSITY OF JVÄSKYLÄ

Department of Chemistry

Determination of surfactants in industrial waters of paper- and board mills

Master's Thesis
University of Jyväskylä
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ABSTRACT

For this thesis, a study of determination methods of surfactants in industrial waters of paper- and board mills was performed. The thesis is divided into two parts. Firstly, the literature part considers different surfactants in general and their determination techniques, including chromatographic, spectrometric and titration techniques. The main focus is on the surfactant determination in environmental- and wastewater samples with liquid chromatographic methods. Also the foam forming process, a new paper making technique, and the basic water circulation systems in paper and board mills are covered briefly. This thesis provides a compact collage of the present-day situation of surfactant determination and removal methods, and foaming tendency of paper industry waters and foam managing.

Secondly, the experimental part of this thesis is composed of three themed parts. The first part deals with the determination of SDS using two different determination methods; solvent extraction spectrophotometry and high-performance reversed-phase liquid chromatography (HPLC-RP), combined with electrical conductivity detection (ECD). The effects of salts (NaCl, $CaCl_2$, $FeSO_4$) and retention aids (c-Pam and microparticle) on the SDS content of kraft white water were examined with RP-ECD and SES-method and the results were compared to see if there are any significant differences.

Results from HPLC-RP analysis method and solvent extraction method differed significantly. According to SES analysis, kraft white water particles, salts or retention aids have quite a small effect on the measured SDS content of the samples. The HPLC-RP showed that for kraft white water, $CaCl_2$ and $FeSO_4$ affect the measured SDS content significantly, but NaCl did not have an effect on SDS concentration. Solid phase extraction needed to be used as a pre-treatment method for salt samples since the salts interfered with the HPLC-RP method. The HPLC-UV (ultraviolet detection) tests of Miranol Ultra (an amphoteric surfactant) were also carried out, including calibration curves, and the effect of salts was successfully determined.

The second part of the experimental work focused on the development of laboratory scale measurement system for the analysis of foaming tendency of SDS containing

wastewaters during aeration. A quick and simple examination test of the foaming behaviour of different water samples with different surfactants and additives was achieved. According to the results, wastewaters containing <100 ppm of SDS do not generate foam with air flow rate of 0.6 L/min.

Flocculation tests were the third part of the experimental work in this study. The aim of the flocculation tests was the examination of precipitation of SDS from pure- and white water samples using trivalent cations Al^{3+} and Fe^{3+} as coagulants, and study the effects of coagulant dosage and pH on the precipitation efficiency of SDS. Experiments performed with deionized water showed that both coagulants, ferric sulfate (PIX-105, Kemira) and polyaluminum chloride (PAX-14, Kemira), can precipitate SDS. Polyaluminum chloride was more effective: 400 µl dosage of PAX-14 yielded ~ 90 % removal efficiency of SDS and 1000 µl dosage of PIX-150 yielded ~ 60 % removal efficiency of SDS. Precipitation efficiency was also found to be pH dependent. The optimal pH value for 1000 µl dose of PIX-105 was about 3 and the optimal pH range for 400 µl dose of PAX-14 was from 4.4 to 5.

TIIVISTELMÄ

Tässä Pro gradu tutkielmassa perehdyttiin surfaktanttien määrittämiseen paperi- ja kartonkitehtaiden teollisuusvesistä erilaisilla määritysmenetelmillä. Työ koostuu kirjallisesta ja kokeellisesta osasta. Kirjallisuusosuudessa keskityttiin erilaisiin surfaktantteihin ja niiden määritystekniikoihin, mukaan lukien kromatografiset, spektrofotometriset sekä titrimetriset tekniikat. Päähuomio on kohdennettu surfaktanttipitoisten vesinäytteiden analysointiin nestekromatografisilla menetelmillä. Lisäksi kirjallisuusosuudessa on käsitelty lyhyesti uusi paperinvalmistus-tekniikka, vaahtorainaus sekä kuvattu tavalliset paperi- ja kartonkitehtaiden vesikiertosysteemit. Määritysmenetelmien lisäksi kirjallisuusosiossa on esitelty surfaktanttien eliminointimenetelmät jätevesistä sekä koottu katsaus paperiteollisuusvesien vaahtoutuvuustaipumuksista ja vaahdon käsittelymenetelmistä.

Pro gradu tutkielman kokeellinen osuus koostuu kolmesta aihealueesta. Ensimmäinen osa käsittelee SDS:n määritystä kahdella eri analyysimenetelmällä. Menetelmät ovat nesteuutto-spektrofotometria ja korkean-erotuskyvyn käänteisfaasinestekromatografia (HPLC-RP) yhdistettynä sähkönjohtokyky detektoriin (ECD). Osiossa selvitettiin molempia menetelmiä käyttäen, kuinka suolat (NaCl, $CaCl_2$, $FeSO_4$) ja retentioaineet (c-Pam ja mikropartikkeli) vaikuttavat kraft-viiraveden SDS pitoisuuteen ja eri menetelmillä saatuja tuloksia verrattiin keskenään.

Tutkimuksessa havaittiin, että HPLC-RP menetelmällä ja nesteuutto menetelmällä saadut tulokset erosivat merkitsevästi toisistaan. Nesteuutto menetelmän mukaan kraft-viiraveden sisältämät hiukkaset, suolat ja retentioaineet vaikuttivat hyvin vähäisesti näytteistä mitattuihin SDS pitoisuuksiin. HPLC-RP taas osoitti, että kraft-viiravesi, $CaCl_2$ ja $FeSO_4$ vaikuttavat merkittävästi ko. menetelmällä määritettyyn SDS-pitoisuuteen. NaCl:lla ei ollut HPLC-RP mittausten mukaan merkittävää vaikutusta näytteiden SDS pitoisuuteen. Suolanäytteet käsiteltiin kiinteä-nesteuutolla ennen HPLC-RP analyysiä, sillä suolat häiritsivät mittausta. HPLC-UV menetelmällä onnistuttiin määrittämään myös amfoteerisen surfaktantin (Miranol Ultra) pitoisuus kraft-viiravesinäytteistä.

Kokeellisen työn toisessa osassa kehitettiin nopeutettu laboratoriomittakaavan mittaussysteemi surfaktanttipitoisten vesinäytteiden vaahtoutuvuuden analysointiin ilmastuksen avulla. Tehtyjen mittausten mukaan alle 100 ppm SDS surfaktanttia sisältävät jätevedet eivät vaahtoa ilmastusmäärällä 0,6 L/min.

Saostustestit olivat kokeellisen työn kolmas osio. Saostuskokeiden tarkoituksena oli tutkia SDS-surfaktantin saostamista puhtaista vesi- sekä viiravesi-näytteistä trivalentisten kationien (Al^{3+} and Fe^{3+}) avulla sekä tutkia saostuskemikaalien määrän ja näytteiden pH:n vaikutusta SDS:n saostustehokkuuteen. Ionivaihdetulla vedellä tehdyt kokeet osoittivat, että molemmat saostuskemikaalit, rautasulfaatti (PIX-105) sekä polyalumiinikloridi (PAX-14), saostavat SDS-surfaktanttia. PAX-14 oli tehokkain, saostaen noin 90 % mitatusta SDS pitoisuudesta jo 400 µl:n annoksella. PIX-105 saosti noin 60 % SDS pitoisuudesta 1000 µl:n annoksella. Saostustehokkuuden todettiin olevan pH riippuvainen. Optimaalinen pH PIX-105 (1000 µl) saostuskemikaalille oli noin 3 ja optimaalinen pH-alue PAX-14 (400 µl) saostuskemikaalille oli 4,4 – 5.

PREFACE

This study was performed May 2015th – February 2016th in co-operation with the University of Jyväskylä and VTT Jyväskylä as a part of a Foam Forming Program (FFP). The literature references are searched using ResearchGate and ScienceDirect scientific databases and VTT library.

I would like to acknowledge my VTT advisors, MSc. Pia Vento and Ph.Lic. Timo Lappalainen, and University supervisor Academy Professor Kari Rissanen for all the support, advice, assistance and inspiration during this project. I would also like to thank laboratory engineer Jukka-Pekka Isoaho for the help, support and ideas with the liquid chromatography instrument. Also, great thanks to the technical research team at VTT Jyväskylä for pleasant working atmosphere and help in practical work. Last but not least I would like to thank all my friends and family for the priceless support and encouragement.

Foam Forming Program FFP is a jointly funded ERDF project. The project started on 1.1.2015 and will end on 31.7.2017. The main target of the program is to accelerate the technology transfer from pilot to industrial scale.

MSc. Pia Qvintus is the responsible director at VTT and Tech.Lic. Harri Kiiskinen the project manager. Steering group members in the project are: Albany International, Billerud-Korsnäs, Domtar, International Paper, Irving Paper, Kemira, Kimberly-Clark, Kuraray, Lenzing, Metsä Board, Moorim Paper, PixAct, Regional Council of Central Finland, Sappi, Smurfit Kappa, Sofidel, Stora Enso, Sulzer Pumps, UPM, Valmet, Wet End Technologies and VTT.

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ABBREVIATIONS

SDS – Sodium dodecyl sulfate

LC – Liquid chromatography

HPLC – High-Performance liquid chromatograph

RPLC – Reversed-phase liquid chromatography

RP-ECD – Reversed-phase chromatography combined with Electrical conductivity detector

ODS(C18/C8) – Octadodecylsilica columns

SES – Solvent extraction spectrophotometry

SPE – Solid-phase extraction

MB-method – Methylene blue method

CMC – Critical micelle concentration

GHP/GH - Hydrophilic polypropylene

ABS – Branched alkylbenzene sulfonate

LAS – Linear alkylbenzene sulfonate

AES – Alkyl ethoxysulfates

AS – Linear alkyl sulfate

AEO – Alcohol polyethoxylate

APEO – Alkylphenol ethoxylate

NPEO – Nonylphenol polyethoxylate

QAC – Quaternary ammonium compound (also called alkylbenzyldimethylammonium compound)

DTDMAC – Dehydrogenated tallow dimethyl ammonium chloride

POE – Polyoxyethylene-unit

WWTP – Wastewater treatment plant

COD – Chemical oxygen demand

BOD – Biological oxygen demand

TOC – Total organic carbon

CTMP - Chemithermomechanical pulp

PAX – Polyaluminum chloride

PIX – Ferric sulfate

LITERATURE PART

1 INTRODUCTION

The literature part of this thesis considers different surfactants in general, their role in foaming and also their effect on the environment. Due to their wide use in different industry fields a wide variety of determination methods have been developed during the resent years and the main techniques, including chromatographic, spectrometric and titration methods, are discussed here focusing on the surfactant determination in environmental- and wastewaters.

Foam forming process, a new paper making technique under intense research and development, uses surfactants in foam generation of water-fibre suspension. Hence, a surfactant concentration of white waters and wastewaters are higher than in ordinary wet web forming of paper and board. In common pulp and paper industry, surfactants are mainly used for washing of the wood, pulp and instruments and out of control foaming can be a serious problem in the process.

Here the basic water circulation systems in paper and board mills are covered briefly. Also, the foaming problems in modern pulp-, paper- and wastewater treatment plants and how the foam and surfactants are eliminated and removed from the water systems are discussed. This thesis provides a compact collage of the present-day situation of surfactant determination and removal methods and foaming tendency of paper industry waters and foam managing.

The experimental part of this thesis is composed of three themed parts where anionic surfactant, sodium dodecyl sulfate (SDS), plays the leading role. The first part deals with the determination of SDS by high-performance reversed-phase liquid chromatography (HPLC-RP), combined with electrical conductivity detection (ECD). The second part focuses on the development of accelerated aeration test. The third part deals with the removal of SDS by using a flocculation method.

2 GENERAL ABOUT SURFACTANTS

This chapter is a general overview of different surfactant classes; anionic, non-ionic, cationic and amphoteric, including the behaviour of surface active agents in the liquid environment and their effect on foam generation. Also environmental aspects are discussed, and an anionic surfactant, Sodium dodecyl sulfate (SDS) is introduced more closely.

2.1 Surfactants

Surfactants are surface active agents with amphiphilic character. They consist of hydrophobic and hydrophilic moieties where hydrophobic tail can include unbranched hydro- or fluorocarbon, an aromatic ring or some other nonpolar organic groups. The hydrophilic tail is a polar and water-soluble group, like sulfonate phosphonate, carboxylate or ammonium. Surfactants are able to can decrease the surface tension and change liquids interfacial properties due to their amphiphilic character and an ability to arrange themselves to micelles and bilayers. Thus, surfactants are used in a many different industry fields to lower the surface tension of a liquid and form foam. [1,2,3]

The decrease of the surface tension in a polar solvent, such as water, results when the surfactant dissolves in a solvent and the hydrophobic part of the surfactant comes to a contact with the polar surroundings and starts to disturb the solvent structure. The free energy of the system increases and to decrease the free energy the hydrophobic parts are expelled to the liquid surface so that the interfering parts are oriented away from the polar liquid. Thus, the surface of the liquid becomes nonpolar, like the air molecules or another nonpolar liquid, and the surface tension decreases since the two phases resemble more each other. [4] Also, the surfactant and water molecules do not attract one another as strongly as two water molecules reducing the surface tension. [5]

An equilibrium prevails between adsorbed and free surfactant molecules in the solution, which can be expressed by the Gibbs equation:

$$\Gamma_2 = -\frac{1}{xRT}\frac{d\gamma}{2.303\ d\ \log c} \quad (1)$$

where Γ_2 is the surface excess concentration, R is the gas constant (8.314 $Jmol^{-1}\ K^{-1}$), T is the temperature in Kelvins, c is the concentration in mol m^{-3} and x holds a value 1 for dilute ionic surfactant solution. [5]

Solvent properties and used conditions dictate the chemical behaviour of the surfactant. In a polar environment, the nonpolar carbon chain acts as a hydrophobic part, and the ionic moiety is the lipophilic group. In a non-polar solvent, like in hexane, the situation is reverse. Temperature and presence of an inorganic or organic additives also affect the surface activity of the liquid, so the amphiphilic character of the surfactant needs to be compatible in the particular system. [6]

Surfactants are commonly classified into four main groups according to the structure of their hydrophilic groups that determine surfactants chemical properties. Groups include negatively charged anionic surfactants (phospholipids, sulfates), positively charged cationic surfactants (quaternary ammonium salts), uncharged non-ionic surfactants (fatty acids) and amphoteric surfactants (zwitterionic betaines). [1, 2, 3]

Surfactants can absorb onto surfaces with electrostatic forces or hydrophobic/hydrophilic interactions. Natural surfaces are usually negatively charged and can be made hydrophobic by using positively charged cationic surfactants. Anionic surfactants can do the same with positive charges surfaces. Non-ionic surfactants absorb with the hydrophilic or the hydrophobic part. Amphoteric surfactants possess both positive and negative charge, depending on the pH of the environment, and can absorb with either one. Amphoterics possess cationic character at low pH and anionic character at high pH. Absorption of amphoteric and non-ionic surfactants does not change the surface charge significantly, whereas cationic and anionic surfactants reduce the charge and can even shift it opposite. [6]

Even though the hydrophilic part of the surfactant determines surfactants chemical properties, the hydrophobic group also affects surfactants nature. The longer the carbon

chain of the molecule, the more non-polar and less water soluble it is. More non-polar molecules also pack tighter and more readily on the surfaces and form micelles easily. Branching, unsaturation and an aromatic moiety on the carbon chain make the molecule more water-soluble and the packing on the surfaces looser. Branched and aromatic molecules are also more biodegradable than straight-chained ones. Surfactant properties can also be modified with functional groups. For example, polyoxyethylene unit makes the molecule more hydrophilic, and polyoxypropylene unit turns the molecule more hydrophobic. [6]

In addition to the surfactant ability to adsorb interphases, they tend to form micelles. The critical micelle concentration (CMC) is surfactant concentration dependent and is simply determined as the concentration of surface active agents above which micelles start to form. Below CMC, changes in the surfactant concentration have an effect on the surface tension but after the critical point, the tension remains rather constant. [7] The driving force for micelle formation is systems desire to achieve the minimum free energy state and decrease the entropy of the system, which is caused by the discrimination between the hydrophobic groups of the surfactants and water molecules. [5]

Micelles are spherical structures, containing 60-100 surfactant molecules, with a hydrophobic core and hydrophilic shell called a Stern layer. The Stern layer is surrounded by a Gouy-Chapman electrical double layer composed of neutralizing counter ions of the Stern layer. Micelle formation in a nonpolar solvent is reverse generating micelles with hydrophilic core and hydrophobic shell. Micelle structure is shown in Figure 1. [5]

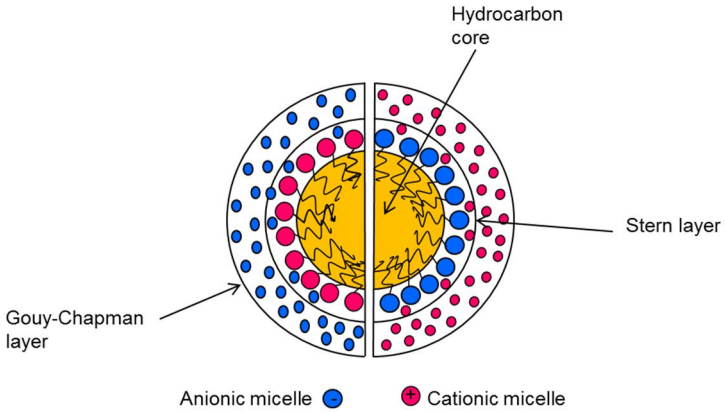


Figure 1. The structure of a micelle. Orange colour describes the hydrophobic carbon core. Blue colour describes negative charge (anions) and pink colour describes positive charge (cations). Stern layer and Gouy-Chapman layer also marked in the figure. [5]

Both the organic- and the hydrophilic group of the surfactant affect the critical micelle concentration. Alkyl and aryl groups decrease and branched groups increase CMC. The growing length of the carbon chain increases the micellar size but decreases the CMC. The presence of electrolytes in the solution has the same effect increasing micellar size but decreasing CMC values. Temperature does not have a significant effect on CMC of ionic surfactants but on non-ionic surfactant its affects more greatly. Non-ionic surfactants have a characteristic temperature where they turn turbid. This turbidity point is called the could point and when the temperature rises above this micellar size of the surfactants start to increase, and the CMC decreases. [5]

Krafft temperature (Krafft point), is the temperature at which ionic surfactants can form micelles. Under this point, the surfactant molecules are in crystalline form. As the temperature rises the solubility of the surfactant increases as well. Surfactants with low Krafft points can be used in hot and cold environments more efficiently surfactants with other higher Krafft points. Krafft temperatures of different surfactants vary according to their chemical structure. The Krafft point is lower with molecules with longer carbon chain. The hydrophilic part and counter-ions also affect the Krafft temperature. The presence of salts usually increases the Krafft point, but counter-ions do not follow any general trend. Low Kraff temperature surfactants can include branched chains, double ponds and a polar part, like an oxyethylene group, between the hydrophilic head and the hydrophobic tail. [8, 9]

Surfactants are used in many different fields such as detergents, fibres, food, polymers, pharmaceuticals and pulp-paper industries.[1] Surfactant consumption in different fields of application in Western Europe is shown in Figure 2. In 2010, the production of anionic and non-ionic surfactants in Europe were 1200 ktons of anionic and 1400 ktons of non-ionic surfactants according to the European Committee of Organic Surfactants and their Intermediates (CESIO). The total surfactant production was 2900 ktons, meaning that anionic and non-ionic surfactants cover 90% of the total surfactant production in Europe. [10]

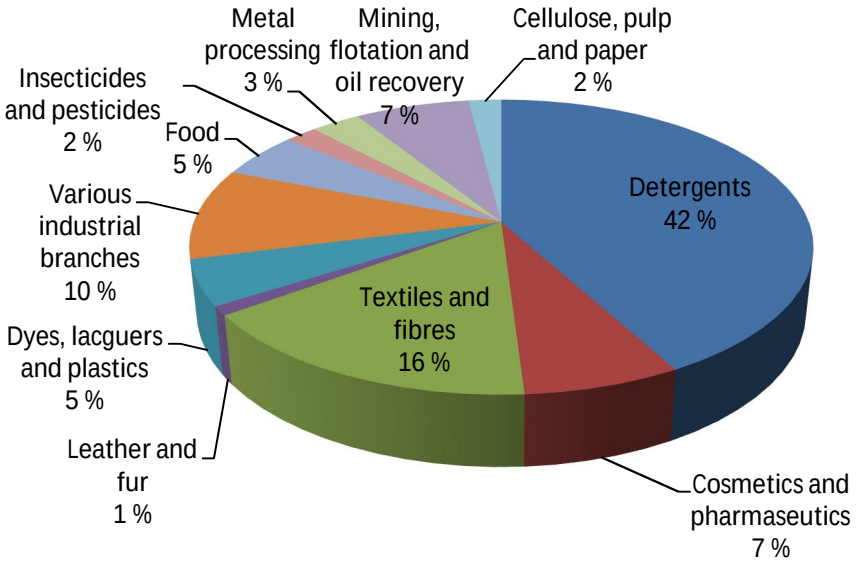


Figure 2. Surfactant consumption in different fields of application in Western Europe.[8]

2.1.1 Anionic surfactants

Anionic surfactants cover approximately half of the surfactant production and use in worldwide. Anionic surfactant products are good foamers, thus commonly used in detergent production. Anionic surfactants can be found, for example, in household and laundry formulas, hand dishwashing liquids and shampoos. Detergent builders, such as calcium and magnesium, are usually complexed with anionic surfactants since they tend to be sensitive to hard water. Another application of anionic surfactants is particulate soil removal, in which they have found to be more effective than other surfactants.

Many detergent powders include anionic surfactants due to their easiness of spray-drying.[11]

Anionic surfactants can be roughly classified as branched alkylbenzene sulfonate (ABS), linear alkylbenzene sulfonate (LAS), alkyl ethoxysulfates (AES) and linear alkyl sulfate (AS).[1,2,3] ABS and LAS are comprised of an alkyl chain and a phenyl group with a sulfonate substituent. The length of the alkyl chain can vary between 8 to 14 carbons, and the phenyl group attachment position depends on an isomer. The benzene ring is always para-substituted. ABS carbon chain is branched which makes it poorly biodegradable. Thus, ABS is not used in industrial countries. LAS is, on the other hand, well biodegradable, low cost and one of the most used surfactants throughout the world.[11] Linear alkyl sulfate (AS), or alcohol sulfates, consists of 12 to 16 carbons long chain with a sulfate group attached at the terminal end. AES resembles AS but also includes ethylene oxide (EO) units which improve water solubility and foaming behaviour.[10,11] Structures, molecular formulas and molecular weights (MW) of different anionic surfactants are presented in Table 1a.

2.1.2 Non-ionic surfactants

Non-ionic surfactants are usually hydroxylated ethylene oxide and propylene adducts of hydrophobic organic compounds [1] and can be combined with all other surfactant types. They can be modified to dissolve in both polar and nonpolar solvents, and resist solutions with a high ion concentration including polyvalent metallic cations. Disadvantages are that non-ionic surfactant products are usually in a liquid or paste form, not an easy-handled solid, and contain a mixture of surfactant molecules with different chain lengths. They are also poor foamers, have no electrical effects and ethylene oxide derivatives can precipitate out from water when heated.[6, 4]

Alcohol polyethoxylates (AEOs) are the most produced surface active agents among non-ionic surfactants. They are formed from linear, 12 to 18 carbons long alkyl chain attached to an ethylene oxide via an ether bond. Alkylphenol ethoxylates (APEOs) hold second place in production volumes. APEOs are para-substituent benzene rings where

one substituent is an alkyl chain, and the other is ethylene oxide. It is suspected that APEOs forms estrogen-like intermediates (e.g. NPEOs, nonylphenol polyethoxylates) during biodegradation. Thus, its use and production have faced some restriction. Both, AEOs and APEOs, can be found in detergents, emulsifiers, wetting and dispersing agents, industrial cleaners, textile, pulp and paper processing.[1,10] Structures, molecular formulas and molecular weights (MW) of different non-ionic surfactants in Table 1b.

2.1.3 Cationic surfactants

Cationic surfactants are quaternary ammonium compounds (QACs), also called alkylbenzyldimethylammonium compounds, consisting of positively charged nitrogen atom with organic substituents where at least one is a hydrophobic hydrocarbon chain. Other substituents can be alkyl groups like methyl or benzyl groups.[1,10] The positive charge makes the cationic surfactants absorbable on a large variety of surfaces. Therefore, they are commonly used for modification of surface properties. Cationic surfactants can be used together with non-ionic and amphoteric surfactants but lose their activity when combined with anionic surfactants. Cationic surfactants are also more expensive than anionic and non-ionic surfactants.[6, 4]

QACs are mostly used in fabric industry as softeners, in metal industry as corrosion inhibitors, in pigments as dispersants and laundry detergents as antiseptics. For example, cleaning industry favours alkyltrimethylammonium chlorides and since the 1960's dehydrogenated tallow dimethyl ammonium chloride (DTDMAC) has been a common fabric softener in home laundry formulations. In 1990's ester-type quaternary surfactants prepared from ethanolamines and tallow fatty acids entered the European market and have replaced DTDMACs due of their tendency to hydrolyse and biodegrade more easily. Bio-industry uses benzalkylmethylammonium chlorides (benzalkonium salts) as biocides.[1,10,6] Structures, molecular formulas and molecular weights (MW) of different cationic surfactants are shown in Table 1c.

2.1.4 Amphoteric surfactants

Amphoteric, or zwitterionic, surfactants have both anionic and cationic moieties in the same molecule and can be used together with all other surfactant types. Zwitterionics are usually more user-friendly than other surfactants being less skin and eye irritating hence being used in shampoos and cosmetics. Because of their two-sided charges, zwitterionics adsorb both negatively and positively charged surfaces and do not cover the surface with a hydrophobic layer. Disadvantage is that they do not dissolve in organic solvents and are expensive to manufacture.[6, 4]

Zwitterionics can be pH-sensitive or pH-insensitive. pH-sensitive molecules are ampholytic that change molecular charge depending on the pH of the solution. At high pH, the molecule can be anionic, at low pH cationic and close to the isoelectric point zwitterionic. Examples of pH-sensitive molecules are β-N-alkylaminopropionic acids used in bactericides and corrosion inhibitors, N-alkyl-β-iminidipropionic acids used in fabric softeners and imidazoline carboxylates used in cosmetic and toilet preparations. pH-insensitive molecules are not affected by the pH and are zwitterionic in all solutions. Sulfobetaines used in soap-detergent formulations are an example of the pH-insensitive zwitterionic.[6] Structures, molecular formulas and molecular weights (MW) of different amphoteric surfactants are shown in Table 1d.

Table 1a. Structures, molecular formulas and molecular weight (MW) of different anionic surfactants

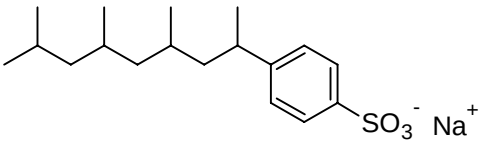
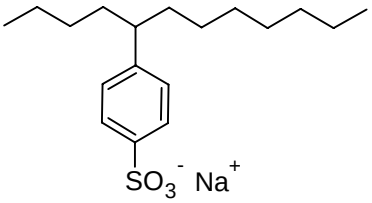
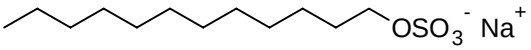
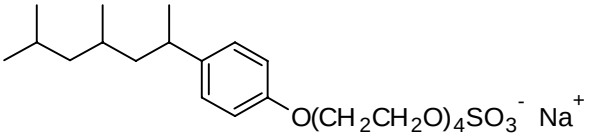
Surfactant name and structure	Molecular formula	MW
Anionics:		
Sodium tetrapropylenebenzenesulfonate (ABS)	$C_{18}H_{29}SO_3Na$	348.48
		
Sodium 5-dodecylbenzenesulfonate (LAS)	$C_{18}H_{29}SO_3Na$	348.48
		
Sodium *n*-dodecylsulfate (SDS)	$C_{12}H_{26}O_4SNa$	289.39
		
Sodium nonylphenoltetraethoxy sulfate	$C_{23}H_{39}O_8SNa$	498.60
		

Table 1b. Structures, molecular formulas and molecular weight (MW) of different non-ionic surfactants

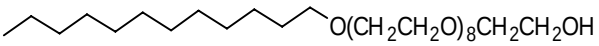
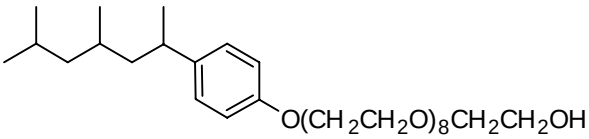
Surfactant name and structure	Molecular formula	MW
Nonionics:		
Dodecanol 9-mole ethoxylate	$C_{30}H_{63}O_9$	567.81
		
Nonylphenol 9-mole ethoxylate	$C_{33}H_{61}O_9$	601.83
		

Table 1c. Structures, molecular formulas and molecular weight (MW) of different cationic surfactants

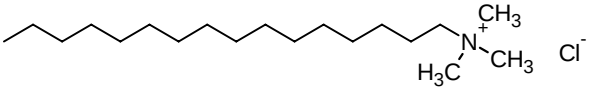
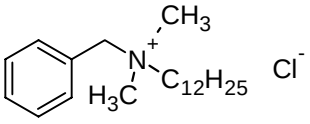
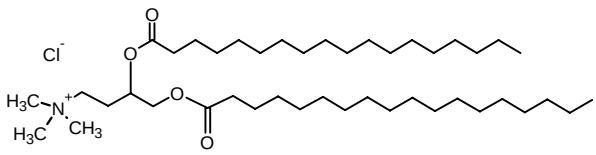
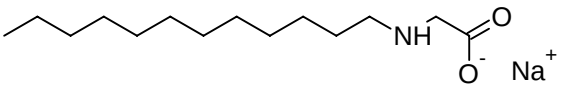
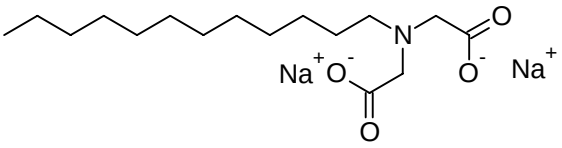
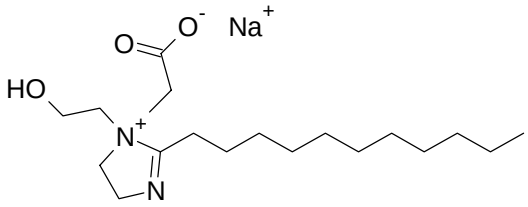
Surfactant name and structure	Molecular formula	MW
Cationics:		
N-Hexadecyltrimethylammonium chloride	$C_{19}H_{42}ClN$	319.99
		
Benzyldodecyldimethylammonium chloride	$C_{21}H_{38}ClN$	339.98
		
Ditallow ester of 2,3-dihydroxypropanetrimethylammonium chloride	$C_{43}H_{86}ClNO_4$	716.60
		

Table 1d. Structures, molecular formulas and molecular weight (MW) of different amphoteric surfactants

Surfactant name and structure	Molecular formula	MW
Amphoterics:		
N-dodecylaminoacetic acid, sodium salt 	$C_{14}H_{28}NNaO_2$	265.37
N-dodecyliminoacetic acid, disodium salt 	$C_{16}H_{29}NNa_2O_4$	345.38
Miranol Ultra L 32 E (Sodium lauroamphoacetate) 	$C_{18}H_{34}N_2NaO_3$	349.47

2.2 Surfactants and foam

Foam is a non-equilibrated mixture of gas bubbles and a surfactant-containing liquid. Gas bubbles are dispersed and usually concentrated in a quite small amount of liquid. The appearance of a surfactant in a formation of foam is essential since cohesive forces and gravity prevent pure liquids from foaming. The foam collapses instantly, or they do not foam at all. With surfactant, the interfacial tension is lower, and the formation of gas bubbles is faster than their breakdown which enables foam generation. [12]

Amphiphilic nature of surfactants allows them to adsorb at interfaces. Hydrophilic groups are settled away from the water, and hydrophilic heads are gravitated in the liquid solution so that they form a thin lamella at the gas/liquid interface. The heterogeneous system of a gas trapped it the liquid is stabilised by the surfactant layer. [4]

Formability and foam stability are commonly mixed terms but should be used as isolated concepts. Formability describes how easily foam generates, and stabilises, and foam stability denotes the time foam holds together before it starts collapsing. Foam stability can be determined by observing changes in bubble size distribution (BSD) or foam half-time (the time elapsed until the half of the foam is collapsed). [7]

There are several methods for foam generation where gas is introduced to the liquid surfactant solution. Industry favours mechanical mixing where mechanical energy is used to create gas-bubbles in the liquid phase. Mixing is carried out with high shear forces which break large bubbles into smaller ones and solution gets homogenised. In addition, to mechanical mixing, another common foam generation method is to blow air or gas directly into the liquid phase. [7, 12]

Foams can be defined by their liquid fraction. The liquid fraction is the ratio between the liquid volume and the total volume of the foam. In wet foams, the liquid fraction is approximately 37 %, bubbles have a lot of liquid between them, and they are spherical in shape. A bubbly liquid is a term for foam where the liquid fraction is considerable high and bubbles move freely without touching each other. In dry foams, the liquid fraction is small, bubbles are polyhedral and immobile. [7, 12]

As mentioned earlier, the presence of a surfactant alone is not enough for foam generation but also, a sufficient amount of energy is required. In the foam generation process work is done against surface tension which tries to keep the surface area as small as possible. This work W (J) is also called surface energy which measures the free surface energy per unit area and can be calculated by an equation

$$\mathbf{W = \gamma \Delta A} \qquad (2)$$

where γ (J/m^2) is the surface tension of the solution and ΔA (m^2) is the new surface area. For estimating the required work for foam generation the change in the surface area ΔA needs to be determined. This can only be done if precise knowledge of the bubbles size distribution is on the record. [7, 12]

Foams have a high interfacial area and a high surface free energy between gas and liquid phases which makes them thermodynamically unstable. Thus, foams have a tendency to collapse to minimise the surface free energy and form separate regions of water and air. The surface tension and the free surface energy on a bubble can be reduced by surface active agents to generate more stable foams. Also viscosity and elasticity of the surface affect the foam stability. Viscose liquid is stouter and furthers foam generation.[6]

Foam evolution involves tree basic mechanisms. When a gas bubble reaches the liquid surface, it starts to expand by the consequence of the pressure change outside the bubble. The pressure inside the bubble is higher in smaller bubbles, and the gas starts to diffuse from a smaller to larger bubbles. The wall of the bubble gets thinner, and the liquid drains downwards due to the gravity and finally leads to rupture.[7,13]

The gravity makes the liquid between the foam bubbles return to the liquid phase. The water drains along the liquid lamellae, Plateau borders and nodes which are the junction points of two, three and four bubbles. When the foam gets drier, the liquid flows only in the Plateau borders and nodes. The drainage rate depends highly on the properties of the used surfactant and viscosity of the liquid.[6] In the foam a lot of bubbles join together and form a shape so that their surface areas are minimal. The pressure difference *P* between the inside and outside of a spherical bubble can be calculated by an equation

$$\boldsymbol{P = \frac{2\gamma}{r}} \quad (3)$$

where γ is the surface tension of the liquid surrounding the bubble and r is the bubble radius. The pressure difference ΔP between spherical bubbles of a different size is

$$\boldsymbol{\Delta P = 2\gamma\left(\frac{1}{r_{small}} - \frac{1}{r_{large}}\right)} \quad (4)$$

Smaller bubbles have a larger pressure inside them. Hence, the gas diffuses from smaller bubbles to larger ones making then expand until they reach a critical dimension. Small bubbles vanish and foam forms a coarse structure before expanded bubbles start to rupture.[6]

The viscosity of the liquid affects the foam stability by slowing down the water drainage. This is also called the Gibbs-Marangoni effect which makes bubbles resist rupture. It is possible to calculate the Gibbs elasticity E_G for a foam using the equation

$$\mathbf{E_G = 2A\frac{d\gamma}{dA}} \quad (5)$$

where γ is the surface tension of the liquid, and A is lamellae surface area. According to the equation 4, the more viscose liquid and smaller bubbles the more stable foam. The Gibbs elasticity applies best below CMC.[6]

2.2.1 The effect of surfactant type on foamability

Foamability of a solution is greatly affected by the concentration, type and structure of the used surfactants. Increase in surfactant concentration results in an increase in initial foam number (foam volume in millilitres) and foam half-time (the time elapsed until the half of the foam is collapsed), which describes foam stability since formed surfactant layer on the liquid interface is more solid and stable with higher surfactant concentrations. However, there is a critical value of surfactant concentration, after which the increase in concentration does not effect on the foamability of the solution anymore. Anionic surfactants are usually the best foamers and non-ionic surfactants tend to be quite

poor but on the other hand, nonionics have a much better resistance to salts than anionics. Sometimes recombined systems turn out to be the best option especially when the solution matrix and used conditions are demanding. [14]

When it comes to surfactant structure, the straight-chained molecules give a better foaming behaviour than the branched ones. Branched-chain surfactants can lower the surface tension fast, and the generated foam volume can be large indeed, but the foam stability is poor resulting fast collapse since the molecular interactions between branched chains are weak. Straight-chained molecules arrange themselves closer one another giving a much stable foam, although a little less in volume than the branched-chained.[15, 14]

The carbon chain length, at the same molecular structure, increases the foamability as the carbon number increases. Traube's rule describes the relationship between the length of the carbon chain and surface activity by stating that the surface activity of the molecule triples for every additional CH_2-group in the molecule chain length. In other words, at the same molecule structure, to produce the same decrease of the surface tension the needed volume of surfactant decreases for every extra CH_2-group in the molecule. [5]

The intermolecular interactions between short carbon chains (less than ten carbons) are weak resulting poor adsorption on interfaces and unstable surfactant layer. With extreme long carbon chains, the molecular interactions become too strong, and the solubility decreases along with film elastics. The ideal carbon number depends on the surface tension of the solution and the intermolecular interactions between the surfactant molecules. [15, 14]

The solution temperature and salt concentration also effect on the foamability. The increase in temperature makes the solution more viscose and the foam generation easier. Thus, the foam volume increases but the foam stability decreases since the small bubbles merge into larger ones faster as the gas molecules move and the water drains more quickly at a higher temperature. Also, the surfactant might get more soluble in the liquid phase as the temperature rises and its adsorbance on the interfaces decreases resulting weaker surfactant layer. High salinity has a negative effect on the foamability. Low salt

concentrations do not have a significant effect but salinity over 10 g/L makes foaming extremely difficult. [14]

2.3 Surfactant biodegradation, toxicity and effect on environment

As mentioned earlier, surfactants are used in wide range of industry fields, including detergents, cleaning products, cosmetics and pharmaceuticals, and production is constantly increasing. Hence, surfactants toxicity and effect on the environment is under constant observation. It has been found, that surfactants are harmful to the environment in high doses. They end up to the environmental water systems with wastewaters of waste-water treatment plants or direct disposal. They have a decreasing effect on water quality due to their tendency to the froth that can be a significant problem in a wastewater treatment plants and a nature rivers and lakes.[8]

Surfactants can also lyse biological cell surfaces because of their amphiphilic character. They are not lethal for higher organisms but are highly toxic to fresh- and marine water organisms, such as algae, fishes and crustaceans. Anionic surfactants are able to damage fish gills and non-ionics affect the nervous system causing narcotic behaviour. Surfactants possess an affinity against proteins thus being able to interfere enzyme activity.[16]

In consequence, regulations of the biodegradation of surfactants and limitations of the concentrations in the water systems have been enacted. Regulatory authors of health and environment have set limits for anionic surfactant concentration in drinking water (0.5 mg/l) and other purposes (1.0 mg/l).[17] It has been reported that LAS concentration in domestic wastewater alternate between 3 - 21 mg/l.[18] European directive 73/405/CE controls impose of surfactants on environment by instructing that a global biodegradability for detergents should be higher than 90% and for ionic surface active agents higher than 80%. [9] Anionic and non-ionic surfactants have the primary focus in regulations due to their large consumption and rather a low biodegradability.[8]

Biodegradation of surfactants is a result of enzymatic brake down done by microbes of soil and aquatic environment and is the most effective in the presence of oxygen (aero-

bic degradation). Ultimate degradation of organic molecules leads to the formation of water, CO_2, CH_4, SO_4^{2-} and NO_3^-. Anaerobic degradation of surfactants is mostly studied with anionics, and it is noted that biodegradation in oxygen is lacking environments, like in sewage sludge, is very poor with sulfonated anionic surfactants but better with sulfated anionics, soaps and fatty acids.[27,8]

Linear alkyl chains in the hydrophobic site of the surfactant make the molecule more biodegradable than those with branched alkyl chains. This knowledge has been applied when new and more biodegradable surfactants have been synthesised. Among anionic surfactants, LAS, AS and AES are noted "well biodegradable" whereas ABS are noted "poorly biodegradable".[9,8]For example, Jurado *et al.* have studied primary biodegradation of LAS with aerobic screening biodegradation test and observed a clear decrease in surfactant concentration when the initial concentrations were 5- 50 mg/l. Higher concentrations did not show biodegradation. [28] The degradation of isomeric alkylbenzene and alkylphenol derivatives changes according to the position of the phenyl group.[6] Non-ionic alkylphenol ethoxylates (APEO) and fatty alcohol ethoxylates (AEO) are considered readily biodegradable in aerobic conditions. [27]

Positively charged cationics bind easily on the negative surfaces of sewage sludge particles, thus being easily transferred from wastewater into sewage sludge. It has been noted that quaternary ammonium compounds are aerobically biodegradable, so anaerobic condition in the sludge does not promote biodegradation of QACs. The same problem concerns also other surfactants. [27] In addition, in cationic QACs, the degradation slows down as the amount of alkyl chains attached to the nitrogen increases. Imidazolium compounds biodegrade easily, and pyridinium compounds degrade slowly.[6]

An example of an alkyl sulfate biodegradation by microbes is shown in Figure 3. First the sulfate-group is cleavaged by sulfatase enzymes yielding an alcohol. Alcohol is then oxidised to carbon acid (via aldehyde) and the final step is β-oxidation that produces acetyl-CoA molecules and electron carries NADH and FADH2. β-Oxidation is a catabolic process in energy metabolism of a cell that produces energy from fatty acids.[8]

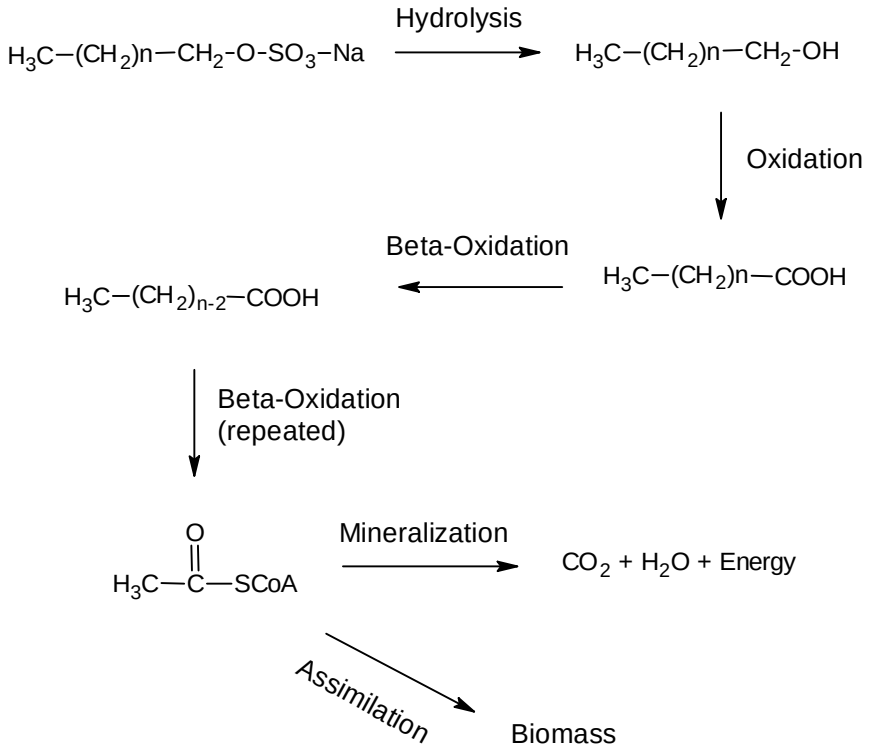


Figure 3.Example of alkyl sulfate biodegradation by microbes.[8]

Surfactants toxicity to marine organisms highly depends on how readily the surfactants adsorb on the biological surfaces and are they able to penetrate the cell membranes. Long hydrophobic carbon chain makes the surfactants more readily binding and more toxic. Branching decreases the toxicity. Molecules with phenyl group are less toxic if the phenyl is in the terminal position. Toxicity of polyoxyethylene (POE) non-ionic increases as the number of oxyethylene units decrease.[6] Alkyl- and ethoxylated alkyl sulfates become more soluble when the number of ethylene oxide units increases. At the same time the surfactants turns to less toxic and less irritating.[9]

Toxicity of anionic surfactants to the aquatic organisms is generally higher than 0.1 mg/l. Toxicity increases as the length of the carbon chain increases. For LAS with carbon number $C_{10\text{-}13,}$ the LC_{50} value is 3-10 mg/l. Sulfosuccinates have a rather mild toxicity w the LC_{50} value 33-39 mg/l. Alkyl sulfates and alkyl ether sulfates have the LC_{50} value between 3-20 mg/l. Alkane sulfonates have the LC_{50} value ranging from 1 to over 100 mg/l depending highly on the carbon chain length. Toxicity on cationics, nonionics

and zwitterionics are quite similar with anionic excluding cationic di-tallow dimethylammonium chlorides (DTDMACs) that are very poorly biodegradable and have the LC50 value 1-6 mg/l. DTDMACs have been replaced with more biodegradable QACs. Table 2 shows aquatic toxicity of different surfactants.[8]

Sometimes hazardous metabolites can be formed when a molecule degradates. When considering surfactants, the toxic intermediates are mainly a problem with alkylphenol ethoxylates (APEOs). Formed metabolites are nonylphenol and ethoxyl compounds that tend to be more toxic than the complete molecule. The opposite happens with anionic LASs whose intermediates are low toxic sulfophenolic fatty acids.[8]

Bioaccumulation of substances in the environment is connected to their lipophilicity. Surfactants are highly water-soluble in general, and dissolution into lipid membranes is unlikely. Laboratory studies concerning surfactant, bioaccumulation and bioconcentration have been performed, and results have showed that bioaccumulation of surfactants in organisms and accumulation in soil and sludge do not possess any significant risk. There is also some evidence that some invertebrate species of aquatic species can metabolize hydrophobic groups of surfactants.[8,19]

Table 2. Aquatic toxicity of surfactants [8]

Surfactant	Fish toxicity, LC_{50} (mg/l)	Daphnia toxicity, EC50 (mg/l)	Toxicity for other species (mg/l)
LAS ($C_{10\text{-}13}$; $C_{11.6}$) MW 348	Zebra fish, 7.8	8.9-14	Algae (cell multiplication inhibition), 10-300
Alcohol sulfate (C12-C18-FA-, C12/15FA-oxoalcohol sulfate)	3-20	5-70	Algae (growth), 60
Alcohol ether sulfate (C12/14FA + 2EO sulfate, C12/15 oxo-alcohol + 3EO sulfate)	1.4-20	1-50	Algae (growth), 65
Alkyl ethoxylate (Ci2/i5-(3-10)EO)	Zebra fish, 1.2-2.3	0.41-4.17	Luminescent bacteria, 1.5
Nonylphenol ethoxylate (9EO)	Fathead minnow, 4.5	12.9	Luminescent bacteria, 60
DTDMAC	1-6	0.1-1-0	Algae, 0.71
Esterquat	Trout, 3.0	78.3	Algae, 1.4
Cocamidopropyl betaine	Zebra fish, 6.7	3.7	Algae, 0.96

2.4 Sodium dodecyl sulfate (SDS)

One known alkyne sulfate (AS) is sodium dodecyl sulfate (SDS), also known as sodium lauryl sulfate (SLS). It is an anionic surface active agent with a hydrophobic tail of 12 carbon atoms and hydrophilic sulfate head. Like all anionic surfactants, SDS has an amphiphilic nature and is used as a detergent to remove oil and form foam. It can be found in cleaning and hygiene products like various soaps, shampoos, toothpaste, shaving foams and engine degreasers.

In biological applications, SDS is used in DNA extraction for its cell lysing effect and in SDS-PAGE (Sodium dodecyl sulfate – polyacrylamide gel electrophoresis). SDS-PAGE is a technique where proteins are treated with the anionic detergent to unfold them and to generate a negative charge. Negatively charged linearized proteins are then transferred into a polyacrylamide gel and separated according to their size and mass to change ratio in the applied electrical field. [20]

SDS is synthesized from lauryl alcohol and sulphuric acid. The sulfation reaction produces hydrogen lauryl sulfate which is deprotonated to sodium dodecyl sulfate by adding sodium carbonate. Lauryl alcohol is derived from coconut or palm kernel oil. Hydrolyzation of the oil produces fatty acids which are then reduced to alcohols. Thus, commercial SDS is not completely pure but a mixture of dodecyl sulfate and other alkyl sulfates. Purity is usually varying from 90 % to 95 %.[6] Materials and proposed reaction mechanism of preparation of SDS in Table 4.

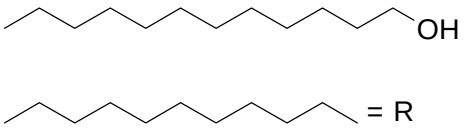
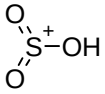
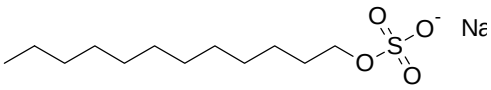
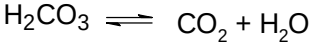
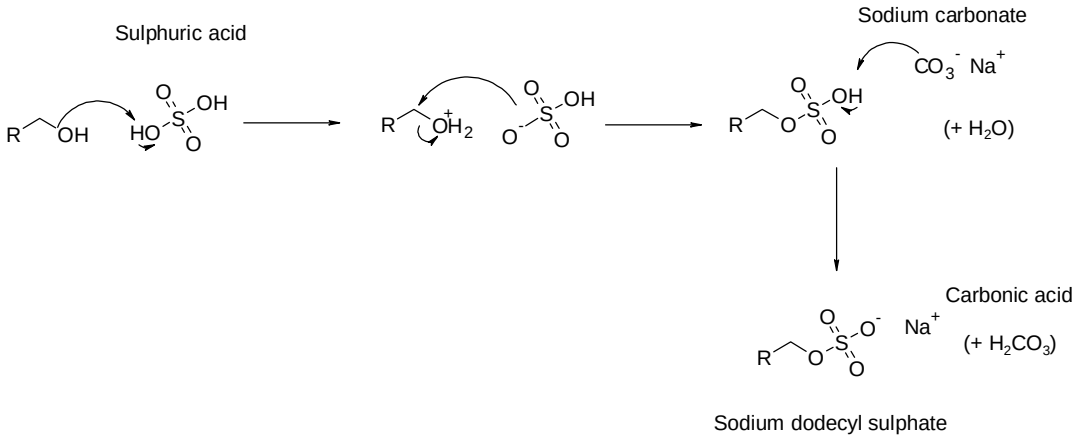
Like mentioned, SDS lyses lipid membranes and denatures proteins, and therefore can irritate the skin, eye and mucous membranes if exposure is prolonged and constant [21,22] Also continual and slowly healing mouth ulcers appearing in a mouth can be caused by an SDS-containing toothpaste.[23] The amount of SDS in healthcare products is infinitesimal, and so exposure is low but can cause problems to hypersensitive persons. SDS is highly soluble in water (130 g/l at 20°C) and biodegradable (Chapter 2.4.2). LC_{50} value of SDS for fished is 10-100 mg/l and it has not been found to be carcinogenic, genotoxic or reproductive toxicant. Critical micelle concentration of SDS is (2.38 g/l) and Krafft temperature approximately 18°C.[24]

According to The HERA (Human and Environmental Risk Assessment) project (1999) alkyl sulfates are not an environmental risk. The usage of SDS in pharmaceutical preparations and food additives has been approved by FDA (Food and drug administration, USA).[25,26] Key figures of sodium dodecyl sulfate (SDS) are listed in Table 3.

Table 3. Key figures of sodium dodecyl sulfate (SDS) (1) SDS in water (no other additives or salts) at 25°C and at atmospheric pressure. [At 55°C CMC of SDS is 9.9 mmol/l] (2) Below Kraft temperature ionic surfactant remains in crystalline form. It is also the minimum temperature at which surfactant form micelles. (3) Predicted no effect concentration. (4) For example, if SDS concentration is 0.2 g/l then COD is 380 mg/l. (5) Animals are exposed for 4 hours. The animals are clinically observed for up to 14 days. The concentrations of the chemical that kill 50% of the test animals during the observation period is the LC50 value. (6) Readily biodegradable

Sodium dodecyl sulfate (SDS)	
Structure	
Molecular formula	$C_{12}H_{26}O_4SNa$
Molecular weight	289.38 g/mol
CMC (Critical Micelle Concentration)	(1) 8.2 mmol/l (2.38 g/l)
Maximum of Gibbs elasticity at SDS dosage	0.6 – 0.7 g/l
(2) Krafft temperature	TK ~18°C
Solubility in water	130 g/l (at 20°C)
(3) PNEC value for sewage treatment plant	1.08 g/l
(4) COD (Chemical oxygen demand) equivalent for SDS.	1.9 mg/ mg SDS
(5) LC_{50} (Lethal Concentration) for fish	10-100 mg/l (= ppm/l)
Biodegradation (28 days test)	(6) 95 %

Table 4. Preparation of sodium dodecyl sulfate: materials and proposed reaction mechanism

Preparation of sodium dodecyl sulfate		
	Lauryl alcohol	Sulphuric acid
The starting materials:		
	Sodium dodecyl sulfate	Carbonic acid
The end products:		H_2CO_3  $H_2CO_3 \rightleftharpoons CO_2 + H_2O$
Reaction mechanism:		
		

2.4.1 Hydrolysis of SDS

Rapid hydrolysis of long chain sodium primary alkyl sulfates has been observed in elevated temperatures (80°C). The formal reaction equation is shown in equation 6.

$$\mathbf{RCH_2OSO_3^-Na^+ + H_2O \rightarrow RCH_2OH + HSO_4^-Na^+} \qquad (6)$$

Bethell *et al.* studied the rate of sodium dodecyl sulfate (SDS) hydrolysis in water. Acidimetric titration was used to determine the SDS concentration in solutions of different initial SDS concentrations, buffers and sulfuric acid. Hydrolysis of SDS was found to be autocatalytic having two reaction pathways, uncatalysed and acid catalysed. In uncatalytic pathway, initially neutral SDS solution produces slowly hydrogen sulfate anions decreasing the pH of the solution which finally leads to an overtaking by the acid catalysed pathway. [29,30]

The reaction mechanism for uncatalysed hydrolysis was proposed to involve an attack by the water of the α-carbon via S_N2 mechanism. Mechanisms are presented in Figure 4. Another observations of the study were that hydrolysis could be accelerated at a higher temperature and also the higher concentration of SDS (10 %) hydrolysed faster than lower concentration (1 %) in initially neutral solutions. Reaction rate constants varied with both catalysed and uncatalysed reactions when the initial surfactant concentration was changed which was probably due to the complex nature of the surfactant solutions.[29,30]

Uncatalysed reactions seemed to be more influenced by the water concentration, especially at low SDS concentration just above the CMC (micelles start to form) showing a decrease in reaction rates as the water concentration decreased. This was suggested to be a result of surfactant aggregation and changes in the microenvironment that becomes more hydrophobic as the surfactant concentration increases. In acid catalysed reactions the concentration of water does not affect the reaction rates.[29,30]

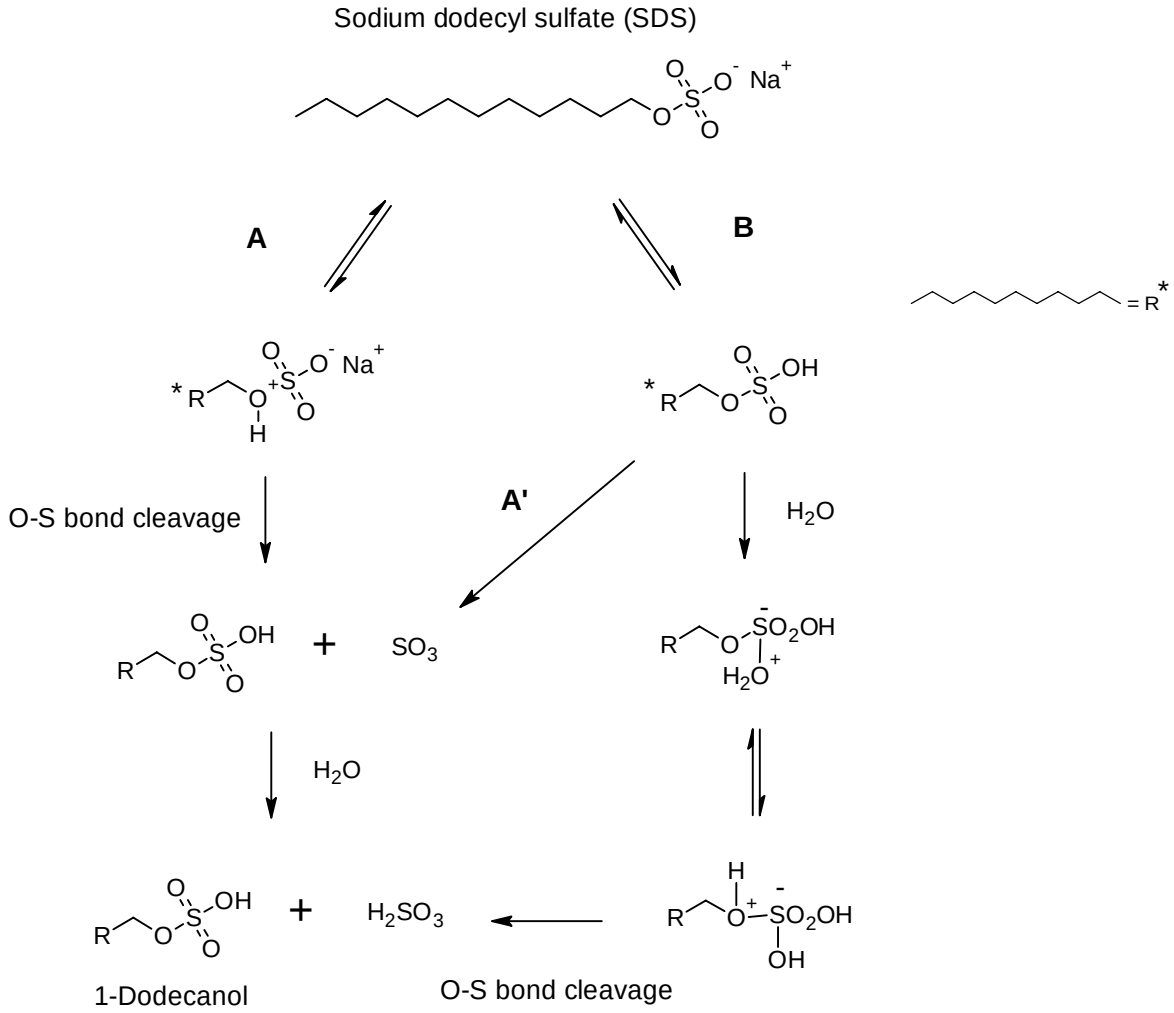


Figure 4. Reaction mechanism of acid catalysed the hydrolysis of SDS. Acid catalysed hydrolysis is initiated by a proton, which can A) attack on oxygen atom attached to the alkyl group resulting a formation of a zwitterion, or B) attack on the negative oxygen atom of the sulfate head of the molecule yielding and alkyl hydrogen sulfate. Both routes involve a cleavage of S-O bond and formation of 1-dodecanol and sulphuric acid. [29]

2.4.2 Biodegradation of SDS

Sodium dodecyl sulfate (SDS) is a commonly used detergent in house hold and hygiene care products, and large amounts of SDS ends up to wastewater treatment plants (WWTPS). Thus, SDS biodegradation in the WWTPs and also in the environment has aroused interest. SDS biodegradation has been studied all the way from the 1960s and several different bacterial strains have been found that can degrade SDS and utilize it as a carbon source. Strains like *Pseudomonas sp, Bacillus cereus, Acinetobacter calco-aceticus, Pantoea agglomerans, Klebsiella oxytoca, Pseudomonas betelli* and *Acineto-bacter johnsoni* have been reported to degrade SDS.[53]

Thomas and White[54] investigated SDS degradation by *Pseudomonas* sp. C12B using ^{14}C radiolabelled SDS molecules and observed that 70 % of labelled SDS turned into $^{14}CO_2$. They also detect radiolabelled 1-dodecanol and 1-dodecanoic acid and proposed a pathway for SDS degradation where primary alkyl sulfatase initiates the biodegrada-tion by cutting of the sulfate head of SDS. Alcohol dehydrogenase oxidises the formed 1-dodecanol to 1-dodecanonic acid which is then metabolized by β-oxidation pathway or is used to synthesize phospholipids. Proposed SDS biodegradation is pictured in Fig-ure 5.[53]

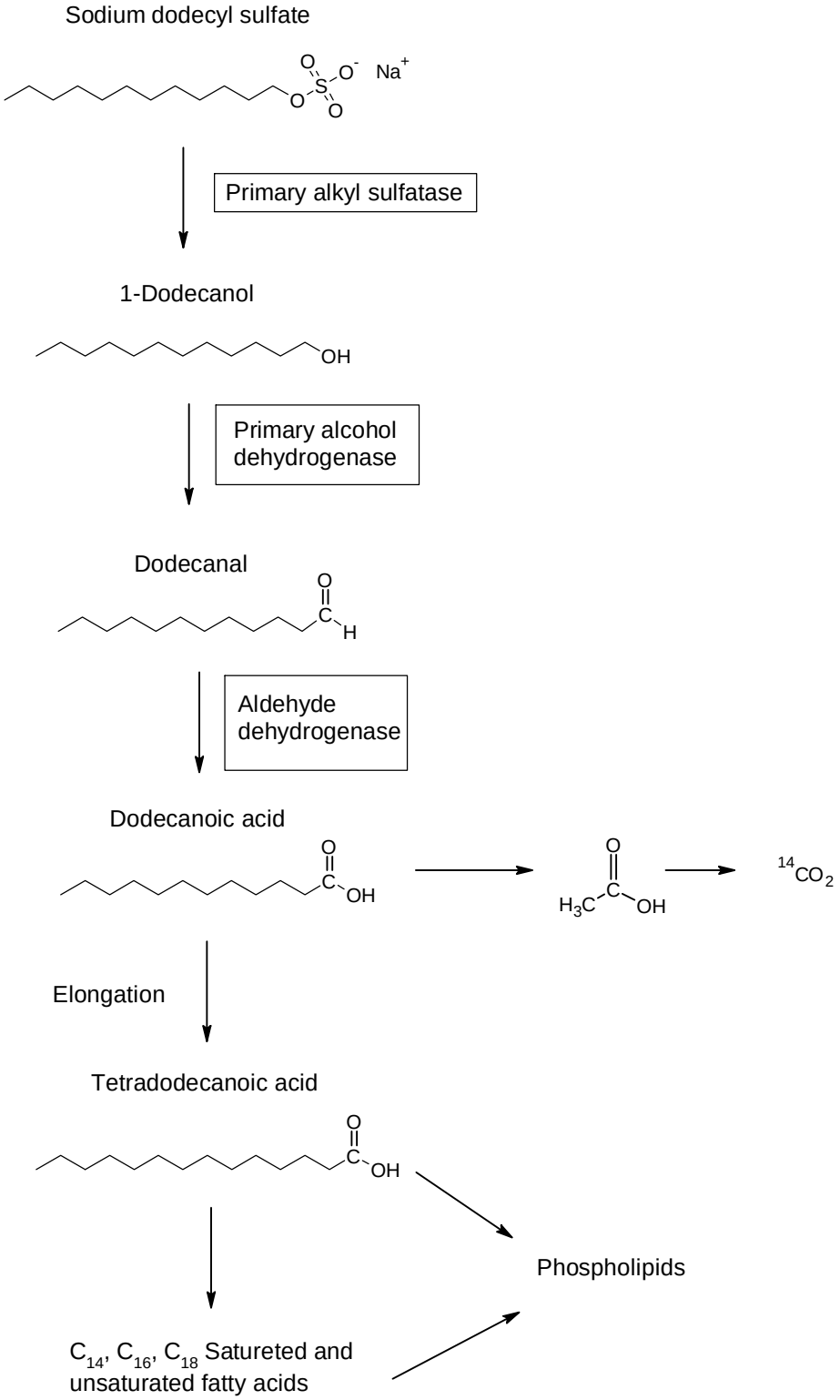


Figure 5. A proposed SDS degradation pathway.[53]

3 DETERMINATION METHODS OF SURFACTANTS

The legal enactments considering surfactants are a consequence of the increased consumption and disposal of surfactants in the environment. This has awoken a need for the development of analytical methods for the surfactant determination. First came colorimetric and titration procedures which were followed by more exact methods, such as high-performance liquid chromatography (HPLC), gas chromatography (GC) and mass spectrometry (MS). Also, the measurement of total organic carbon (TOC) and chemical oxygen demand (COD) are used for directive analyses of water quality and surfactant concentration in water samples.[8] TOC and COD are discussed in Chapter 6.1

This chapter covers sample preparation and determination of different surfactant samples. Determination methods discussed are chromatographic liquid-, thin layer-, supercritical fluid-, and gas chromatography methods. Spectrophotometric methods are UV/VIS spectrophotometry, mass spectrometry, infrared (IR) spectroscopy and nuclear magnetic resonance (NMR). Also, titration methods are covered shortly. The main focus is on liquid chromatography methods.

3.1 Sample preparation

Sample preparation is one of the most important and, in many cases, the most challenging step of the analysis. For liquid chromatography analysis, the sample must be in dissolved form and preparation can involve crushing, homogenization, digestion, dissolution, stabilization and filtration.[31] Chemical treatment of the samples might be necessary in some cases to ensure the preservation of the sample, modificate the sample in a proper form for the analysis or to remove interfering constituents. Sample stabilization and preservation can be made by membrane filtration through 0.45 µm filter, storing samples in a fridge, removing oxygen from the samples or by adding chemicals, such as formaldehyde, chloroform or sodium azide. Formaldehyde is used to stabilize sulphite and sample acidification. [10]

Neutralization of the samples if often very important since many column materials cannot tolerate strong acids or bases and the large pH difference between the sample and the mobile phase can lead to a major baseline variations. Neutralization can be done by adding acid or base or by using ion-exchange resin. An example of the sample modification is the conversion of cyanide to cyanate using sodium hypochlorite. Thus, cyanide can be detected indirectly by electrical conductivity. However, when adding extra chemicals into an ion chromatograph samples, the purity of the chemicals and their effect on the analysis must be considered carefully. Chemical must always be extra pure grade.[31]

In the case of surfactants, biodegradation of the analytes might be considerable. Samples should be processed, for example by filtration, right after sampling and analysed within 48 h. Surfactant concentration in environmental samples are usually very low (ppb levels) and out of the detection range of most analysation methods. Thus, extraction, isolation and preconcentration of the sample are needed before the proper analysis. [10]

3.1.1 Extraction of solid samples

When the sample matrix is solid methods like Soxhlet extraction, and solid-liquid extraction (SLE) are the most usable techniques for extraction of the surfactants and other analytes.[32,33,34] Even though these methods are cheap and easy to perform, they consume large amounts of organic solvents (150-500 ml) and the execution time is long (4-18 hours). Soxtec is a method similar to Soxhlet but uses boiling and rinsing of the sample to enhance the extraction. The execution time for Soxtec is 45 min and solvent consumption 50-100 ml.[35] Another cheap and easy method for sample preparation is ultrasounds followed by centrifugation and filtration. The execution time is short but solvent requirement large.[36] New extraction methods, like Microwave-assisted extraction (MAE), pressurized fluid extraction (PFE) and supercritical fluid extraction (SFE), have been used for extraction of surfactants form solid samples.[10]

3.1.2 Purification and preconcentration of aqueous samples

Liquid-liquid extraction (LLE), or solvent extraction, can be done for both non-ionic and ionic surfactants and is used for determination of the total concentration of the target analyte in the sample. Analyte surfactants are separated from the liquid sample matrix, and in some cases from each other, according to their solubilities in polar and non-polar phases, which usually are water and some organic solvent. Extraction of ionics can be done by using chloroform or toluene as an organic phase and extraction of non-ionics can be done with dichloromethane or ethyl acetate.

The disadvantage of the method is that it requires quite a high volume of sample (100-500 ml) and toxic organic solvents. Also, amphiphilic surfactants tend to adsorb on the interfacial layers between the phases thus causing emulsification, which can be avoided by using ion-pairing. For example cationic methylene blue reagent binds with anionic surfactants and the formed complex dissolves in organic solvents, such as toluene.[10] More about solvent extraction is discussed in Chapter 3.2.1.

In solid-phase extraction (SPE) the liquid sample (mobile phase) is eluted through a column containing a solid material that can retain the target analyte but water and other impurities, such as salts, flow through without difficulty. After this, target compounds can be collected form the solid phase by eluting with an appropriate solvent. This way the analyte is isolated from the sample matrix and purified form unwanted impurities. Advantage of SPE over LLE is that in sample and organic solvent requirements are considerably less (7-100 ml of sample and 5-20 ml of solvent).[10]

Solid-phase extraction of anionic surfactants, like LAS, can be done by using octadodecylsilica (C18), graphitized black carbon (GBC) or polystyrene-divenylbenzene (SDB) as a solid material and, for example, methanol or acetonitrile as a collecting solvent. Also anionic-exchange (SAX) resins can be used in the solid phase material to improve purification. Retention of the polar component can be enhanced by adding salts or lowering the pH of the sample.[37] Nonionics, like AEOs and APEOs, can be extracted with the C18 or GBC materials and same solvents than anionics. Sometimes cationic-exchange (SCX) and SAX resins can be used in the solid material for removing interfering ionic surfactants.[38,39] Consequently, C18 and GBC columns are able to separate

simultaneously both anionic and non-ionic surfactants making then rather used technique.[40]

Solid-phase extraction of cationic surfactants is not that popular since QACs cannot be used with silica based phases, like C18, due to their tendency to bind strongly with the silanol groups. Colum materials, such as neutral polymeric sorbents or alumina resin with attached sodium dodecyl sulfate (SDS) hemimicelles, have been provided for the separation of cationics.[10] Olkowska *et al.*[42] reported the successful application of SPE extraction with column filled with a polymeric sorbent (Starta-X) in the purification of cationic surfactants in environmental water samples. However, the general view is that LLE is better method extraction of cationic surfactants than SPE.[32, 41]

New SPE related techniques that are used for isolation and purification of different surfactants are matrix solid-phase dispersion (MSPD)[43], dispersive liquid-liquid microextraction (DLLME) [Hultgren], solid-phase microextraction (SPME) and stir-bar sorptive extraction (SBSE).[44,45]

3.1.3 Membrane Filtration

Membrane filtration is another method to isolate and purify the target analyte from the sample matrix. In chromatography analysis, the sample filtration and dilution protects the sensitive column material and thin capillary tubings from overloading and plugging effects. Sample matrix should also be cleared form disturbing contaminants. Filtration is usually done by disposable syringe filters with pore size 0.45 μm. Membranes with a smaller pore size (0.22 μm) are used for biological samples to prevent the bacterial activity from alternating the sample matrix. [31]

Filtration is a technique where different components of a solution are separated by forcing the solution through a membrane. A membrane is a thin film of semi-porous material that separates substances of a solution into a precipitate and a filtrate. Filtration is mostly used to clear the sample from impurities, such as bacteria, micro-organisms, organic substances or other particles. The membrane material can be anything from paper to glass fibres or organic polymers to inorganic silver depending on the purpose of

the use. Different materials possess different chemical, thermal and mechanical properties and the character of the sample defines what kind of material is suitable for the filtration.[46,47]

The membrane processes used in the sample purification are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Microfiltration covers membranes with pore sizes from 0.03 – 10 µm, molecular weight cut-off (MWCO) more than 1000000 Da (Daltons) and operating pressure of 100 – 400 kPa. MF can be used to remove sand, fibres, silt, clay, algae and some bacteria but it is not suitable for viruses and organic matter. In such cases it can be combined with nanofiltration or reverse osmosis as a pretreatment process.[46]

Ultrafiltration membranes are applied when removal of microbiological species, some viruses or organic matter is necessary. The pore size of UF is 0.002 – 0.1 µm, MWCO is 10000 – 100000 Da and operating pressure 200 – 700 kPa. Nanofiltration is used for the nanoscale sample to remove all bacteria, viruses and organic matter. NF is also able to remove 90 % of salts form the sample. The pore size of NF is approximately 0.001 µm, MWCO between 1000 – 100000 Da and operating pressures from 600 – 1000 kPa. Reverse osmosis is able to remove particles larger than 200 Da including an inorganic material. Salt removal can be as high as 99 %. RO uses semipermeable membranes and high pressure to pump the sample through the membrane.[46,48]

Filtration of samples for chromatography analysis is most easily carried out by syringe filters (or wheel filters). It is not necessary to filter the whole sample and with syringe filters, small volumes of sample can be filtrated directly into the HPLC sample tube (vial). Syringe filter is a round shaped plastic cartridge with membrane inside. Membrane material depends on the sample.

Chemical compatibility of the sample and the membrane is one of the first things that need to be considered when selecting filter material for the analysis. Incorrect membrane-sample selection can result in degradation of the membrane and its elution into the sample with all impurities and cause faulty results and even damage to the column.

Even if the membrane would not be damaged, it can interact with the sample some other way and alter the final results. For example, proteins and peptides have a high affinity to bind membrane surfaces, so the filter material needs to be low binding, like PVDF, RC or GHP.[49] If the purpose is to remove proteins, then ultrafiltration with high binging membranes is a right choice.[31]

Aqueous samples require hydrophilic membranes. Membranes affinity for water eases the membrane wetting, and the sample flows steadily through the filter. Materials like GHP, PES, Nylon and PVDF are hydrophilic membranes. Hydrophobic membranes, such as PTFE, repel water and are suitable for filtration of organic solvents and gases. Sometimes solutions are not that easily fractionated into the water and organic phases and the sample is a mixture of both. Universal filters, like hydrophilic polypropylene (GHP), are chemically resistant for vide range of solvents and usually a good choice for difficult samples.[50] Descriptions and applications of different filter membranes materials are listed in Appendix 1.

The porosity of the membrane is the second thing to consider when selecting the appropriate filter. There is an accurate method for determination of the right pore size based on the size of the column packing material. The polymers of the stationary phase are arranged side by side and the eluent flows through the open spaces between them. If the mobile phase carries particles bigger than these spaces the column blocks. Hence, the filter needs to remove all the impurities larger than the spaces. In general, when using larger than 3 µm packing material the suitable pore size for the membrane is 0.45 µm. For columns with 3 µm packing or smaller, a 0.2 µm membranes are recommended.[50]

Filter size is directly proportional to the filtration volume. Larger surface area increases the filtration capacity of the membrane. 4 mm membrane is able to filter up to 5 ml of sample and 13-17 mm filters manage up to 10 ml of sample. 25 mm or 30 mm filters are for samples volumes larger than 10 ml.[49] For highly contaminated samples prefiltration is recommended since low pore size membranes get clogged rather easily. Glass fibres, with pore size 0.5 – 5 µm, are commonly used materials for prefilters. In syringe filters, the prefilter is placed on top of the proper filter thus protecting it from the premature clogging and extending its life.[50,51]

In addition to syringe filters another filtering assemblies are plate-, funnel-, and pressure filtration systems. The plate filters are a sandwich-kind a structure with the prefilter, filter membrane, filter screen between two holder plates. The plate filters come with multiple variations and sizes. Funnel filters and connected with vacuum pumps which suck the liquid sample through the membrane while pressure filtering uses compressed nitrogen or air to push the sample through the filter.[52]

3.2 Chromatographic methods

This chapter covers four different chromatographic methods that can be used for surfactant separation and determination. Methods are liquid chromatography (LC), gas chromatography (GC), thin-layer chromatography and supercritical fluid chromatography. Major focus is on liquid chromatography (LC) and its different applications including normal-, and reversed-phase chromatography (NPLC and RPLC), ion chromatography (IC) and size-exclusion chromatography (SEC).

3.2.1 Liquid chromatography (LC)

Liquid chromatography (LC) is a useful technique for both qualitative analysis and quantitative determination of the wide range of surfactants, especially for anionic and non-ionic. LC can separate different surfactants from mixtures according to their homological differences, such as length of alkyl chain and degree of polymerization. Surfactants are a diverse group of molecules with a various structures and functionalities and most of them dissolve easily in common LC mobile phases but are not volatile enough to be analysed with gas chromatography (GC) or mass spectrometry (MS). Analysing surfactants by LC the mobile phase should contain organic solvents to prevent micelle formation. Micelles and air bubbles disturb LC analysis and can damage the instrument.[55]

LC is commonly used in quality control laboratories of detergent and pharmaceutical industries. Also environmental analysis uses LC but not for the routine control of effluents, unless the composition of a sample is already known. Concentration determination of a surfactant from well-known formulations is relatively quick and easy. For unknown mixtures LC analysis can be challenging due to a rather limited range of separation of any single LC-instrument. The velocity and easiness are naturally depending on the character of the sample and the surfactant. Surfactants are often separated from the sample matrix by extraction. Depending on the sample, the extraction method can be liquid-liquid extraction or solid-phase extraction (SPE) of and an aqueous solution or solvent extraction of the dried solid (chapter 3.1). Since the LC system is capable only to separate the analytes, different spectrophotometric (or other convenient) detection methods can be combined with the LC. The structure of surfactants defines the detection method.[55]

3.2.1.1 High-performance liquid chromatography (HPLC)

High-performance liquid chromatography (HPLC) is upgraded LC technique. At the present, it is the top-rated method for the surfactant analysis due to its effective separation ability of analytes with both high and low molecular weight, unnecessity for derivatization in most cases and capability to separate both ionic and non-ionic surfactant species.[10]

The chromatographic system is an ensemble composed of different instrumentation units and chemical components. The instrumentation includes the pump, injector, column, suppressor (in the case of ion chromatography), detector and data station. Chemical components consist of the mobile phase, stationary phase and regenerating eluent of the suppressor. The efficient separation is achieved by using high-pressure pumps which pressurizes the mobile phase running inside the system (50-350 bars). Singe-piston pumps are used for isocratic elution and dual-piston pumps for gradient elution. Pulse dampers assure the pulse-free flow of the mobile phase. Constant flow is obligatory for the accurate sample detection. [56,57]

The column is the heart of the chromatographic system and is the place where the separation of the analytes is accomplished. In most cases the column is kept at room temperature but some samples, like long-chain fatty acids, demand an elevated temperature for their higher melting temperatures. The stationary phase is usually porous silica, or some other polymer, based material and the eluents are selected depending on the properties of the column and the analyte. Column tubing is usually inert components like Tefzec, epoxy resins or PEEK (polyether ether ketone). [31]

The separation of analytes is based on their mass-transfer between the stationary and the mobile phase. The distribution equilibria between the analyte and the column material determine the resolution efficiency and can be manipulated with stationary phase material and solvent choices. The retention strength depends on two factors that are a competition of adsorption between the target analyte and other components in the solvent, and analytes solubility in it the eluent. Both factors are affected by the mobile phase composition. The elution of the analyte can be described with the retention factor (*k*) shown in equation (7):

$$\boldsymbol{k} = \frac{\boldsymbol{t_R} - \boldsymbol{t_M}}{\boldsymbol{t_M}} \qquad (7)$$

where, t_R is the retention time of a component and t_M is the dead time (time needed to eluent go through the column). The ideal *k*-value is from 1 to 5. The selectivity factor α is used when two analytes and their separation relative to each other is compared. Equation (8) describes how the selectivity factor of two different analytes A and B can be determined:

$$\boldsymbol{\alpha} = \frac{(\boldsymbol{t_R})_B - \boldsymbol{t_M}}{(\boldsymbol{t_R})_A - \boldsymbol{t_M}} \qquad (8)$$

where, $(t_R)_B$ is the retention time of more strongly retained component B and $(t_R)_A$ is the retention time of weaker retention component A. If the α-value is 1, the two analytes cannot be separated with the given system.[58,59]

Column efficiency is highly dependent on the column length and particle size. Column length affects the retention times. The longer the column the longer is the retention time and the better it the resolution. On the other hand, longer columns consume more eluent due to longer retention times and higher pressures. With shorter columns the retention time is also shorter and eluent consumption less. Particle size defines the peak sharpness thus affectin on the resolution. Small particles give better peak efficiencies, but the backpressure is higher than with larger particles. Commonly used particle sizes are 3 µm and 5 µm.[60]

The column efficiency can be determined by using the plate model. The plate model assumes that the column of the chromatographic system is composed of multiple theoretical plates. The analyte then equilibrates between these stationary plates and the eluent. The number of theoretical plates (N) can be calculated:

$$\boldsymbol{N = \frac{L}{H}} \tag{9}$$

where, L is the column length and H is the plate height. A new column has a large number of theoretical plates and high column efficiency thus producing thin and sharp peaks in the chromatogram. As the column gets older and more used, it loses efficiency, and the peaks start to broaden. The ageing can be monitored by determining the plate number shown in equation 10:

$$\boldsymbol{N = 5.54 \times \left(\frac{t_R}{W_{\frac{1}{2}}}\right)^2 = 16 \times \left(\frac{t_R}{W}\right)^2} \; ^* \tag{10}$$

where, t_R is the retention time, $W_{1/2}$ is the peak width at half of the peak height and W is the peak width at the baseline.[58]

* Measuring the peak width at the baseline is not always easy due to baseline variations and a large number of peaks. In that case, it is possible to use the peak width measured at half of the peak height.[58]

The column resolution (R) is a quantitative measure used to describe columns separation ability of two different analytes in a sample. Equation 11 describes the resolution calculation for two components, A and B:

$$\boldsymbol{R} = \frac{\boldsymbol{2[(t_R)_B - (t_R)_A]}}{\boldsymbol{W_A + W_B}} \qquad (11)$$

where, $(t_R)_B$ is the retention time of more strongly retained component B, $(t_R)_A$ is the retention time of weaker retention component A, W_B is the peak width of the B at the baseline and W_A is the peak width of the A at the baseline. R-value less than 1 means overlapping of the components and R-value grater or equal to 1 tells that separation on efficient.[58]

Different HPLC applications are classified based on the interactions between analytes and stationary phases. Methods like reversed-phase liquid chromatography (RPLC), normal phase liquid chromatography (NPLC) and ion chromatography (IC) are commonly used for surfactant separations. Size-exclusion chromatography is more seldom used, usually in mixed modes with other chromatographic methods.

3.2.1.2 Reversed- and normal-phase liquid chromatography (RPLC & NPLC)

In reversed-phase liquid chromatography (RPLC) the separation of analytes is based on hydrophobic interactions between the sample and the stationary phase. The technique involves non-polar stationary phase and polar mobile phase. Analytes are retained according to their polarity. Hydrophobic molecules eluate more slowly than the hydrophilic ones. Usually, the mobile phase is a mixture of water and polar organic solvent, like acetonitrile or methanol. Organic modifier ensures that the analytes interact properly with the stationary phase and also cleans the column from organics after the analysis. In normal-phase liquid chromatography (NPLC) the stationary phase is polar (silica) and the mobile phase is nonpolar (hexane, THF). Figure 6 represents a polarity chart of materials and solvents used in stationary phases, mobile phases and analytes.[61]

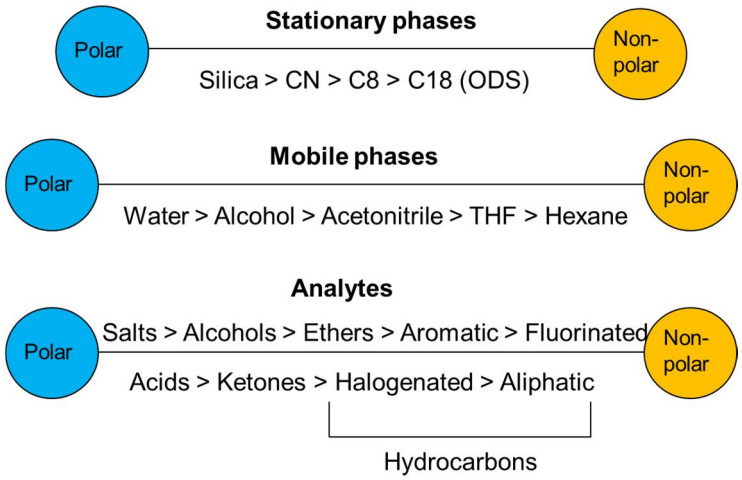


Figure 6. Polarity chart of stationary phases, mobile phases and analytes.[61]

HPLC columns for separation of anionic, non-ionic and cationic surfactants are usually reverse-phase (RP) octadecylsilyl (ODS) columns, like C18 and C8, where the increasing hydrophobicity of the analytes is the separating force. Mixtures of different solvents (deionized water, acetonitrile and methanol) are used as a mobile phase and additives, like ammonium acetate (AMAC) or trimethylamine, can be added to the mixture to enhance the separation. Modifiers, like acetic acid (AA) and formic acid (FA), are also used.[10,55, 62]

For example, anionic linear alkylbenzene sulfonates (LAS) have been determined in polluted soil samples using Soxtec apparatus for sample preparation and RPLC-fluorescence (FL) for surfactant detection with detection limit 5 µg/kg. The used column was reversed-phase ODS and the mobile phase was acetonitrile and a premixed water/acetonitrile (75/25, v/v) solution containing sodium perchlorate (10 g/l). Gradient programme was applied and the fluorescence detector operated at excitation-emission wavelengths of 225–305 nm.[35]

Anionic sodium laureth sulfates (SLES) have been determined in a commercial liquid detergent sample using RPLC combined with evaporative light scattering detection (ELSD). The sample preparation included only dissolving in methanol and filtration with 0.45 µm PTFE filter. The used column was a C8 bonded silica gel, and the mobile

phase was an acetonitrile–water gradient containing AA or TFA (trifuoloroacetic acid). The detection limit was 80 µg/mL.[63]

Cationic quaternary ammonium compounds have been determined in seawater by liquid chromatography–mass spectrometry (LC–MS). SPE cartridges were used for sample extraction. The column was reverse-phase C18 and the mobile phase was a solution of acetonitrile acidified with 1% (v/v) acetic acid and aqueous 50mM ammonium acetate acidified to pH 3.6 with acetic acid. Eluation method was isocratic and the detection limit was parts-per-trillion (ng/l) level.[64]

Ethoxylated non-ionic surfactants have been determined in samples of raw and treated wastewater of sewage treatment plants. Sample pretreatment included isolation by solvent sublation and Soxhlet extraction, purification with open-column alumina chromatography and derivatization with phenyl isocyanate. Analyzation was done with RP-HPLC and UV detection. Used column was C18 and the mobile phase was a gradient of methanol / water (8:2 v/v) to 100% methanol. The alcohol ethoxylates were detected with UV absorption at 235 nm. The detection limit was 3.0 pg/L. Found concentrations of target surfactants in wastewaters were between 1.0 and 5.5 mg/L (influent wastewater), and between 13.0 and 12 pg/L (effluent wastewater).[65]

Normal phase amino-silica and cyanopropyl columns with strong non-polar solvents, like hexane, chloroform and isopropanol, can be used to separate NPEOs (nonylphenol polyethoxylates) and QACs (quaternary ammonium compounds).[66] Development of columns and stationary phases has led to new phases that are specialized in the separation of ethoxylated surfactants. For example, NPEO and NP components can be separated by mixed-mode HPLC system where the column is filled with a polymeric phase that possess characters of both size-exclusion and reversed-phase chromatography mechanisms.[67,68] This same system has also been used to separate OP and OPEOs (octylfenol ethoxylates).[10,69]

New polar-embedded columns

Even though, the C18 silica based columns are the most popular packing material for the reversed-phased stationary phases they have limitations, like basic compounds tend to cause peak tailing and in highly aqueous condition the stationary phase gets de-wetted*. Development in synthesis and bonding technology of stationary faces have yielded alternative polar –embedded stationary phase materials with both hydrophobic (alkyl chains) and hydrophilic (amide) properties.[70]

Columns are filled with silica material with very high purity, high surface coverage and almost complete end-capping*. These improvements have been able to diminish the base tailing but the de-wetting is still a problem. New stationary phases have been tested for separation of anionic, cationic and non-ionic surfactants simultaneously. The separation mechanism is multi-mode combining reversed-phase, anion-exchange and dipole-dipole interactions. Polar-embedded phases are hydrolytically stable *and can be combined with both 100 % aqueous and 100 % organic phases.[70]

* Definitions for the dewetting, end-capping and hydrolytic stability of HPLC columns are in Appendix 2.

Both of the mentioned drawbacks of C18 columns have been able to overcome with these new stationary phases. The stationary phase tolerates highly aqueous environments and the peak shape of basic analytes is improved. The most distinct difference between the conventional C18 phases and the polar-embedded phases is the extreme hydrolytic stability of the polar-embedded phase. The polar-embedded phases also possess different selectivities since they are mostly hydrophobic but have also some polar hydrophilic groups attached next to the silica base. Thus, the simultaneous separation of both non-ionic and ionic surfactants is possible. Attached groups are usually amide, urea, ether and carbamate functionalities.[70]

Surfactant determination in complex matrices consisting of a mixture of different surfactants and inorganics is demanding and time-consuming. Thus, an analytical method capable of simultaneous determination of both non-ionic and ionic surfactants is very desirable. Even though many HPLC columns and detectors are available for analysis of surfactant the simultaneous analysis is usually not an option. Mass spectrometry and evaporative light scattering detectors can detect all surfactant types, but columns com-

monly used for separation of surfactants (C18 and CN) require a different chromatographic conditions for different structures. In addition, cationic surfactants tend to cause peak-tailing on RP-columns since they bind readily with the silanol groups of the stationary phases.[62]

Liu *et al*. have reported new methods for the simultaneous analysis of non-ionic, anionic and cationic surfactants have been tested. For example, the new mixed-mode polar-embedded stationary phase (the Acclaim Surfactant column) have been successfully used for the simultaneous analysis of anionic, non-ionic, and cationic surfactants with a volatile mobile phase system containing a gradient of ammonium acetate buffer and acetonitrile. Evaporative light-scattering detection (ELSD) was used for detection. The sample matrix was a mixture of different commercial surfactants.[62]

3.2.1.3 Ion chromatography

Ion chromatography is a technique of liquid chromatography that is used to separate ions. Ion chromatography includes three classical separation methods which are Ion-Exchange Chromatography (HPIC, High-Performance Ion Chromatography), Ion-Exclusion Chromatography (HPICE, High-Performance Ion Chromatography Exclusion) and Ion-Pair Chromatography (MPIC, Mobile Phase Ion Chromatography). Reversed-phase liquid chromatography (RPLC) is also used as an alternative method of ion chromatography and in some cases the combination of multiple methods are applied.[31]

In the analysis of surfactants and sulphur containing compounds, the ion-pair chromatography is the mostly used technique. MPIC uses adsorption as a separation mechanism where the stationary phase can be made of a neutral, low polarity porous divinylbenzene resin or even lower polarity chemically bonded octadecyl silica phases. Mobile phase contains an ion-pairing reagent that posses an amphiphilic character. Negatively charged reagents (e.g. alkyl sulphonic acids) are used for cationic analytes and positively charged reagents (e.g. tetrabutyl ammonium chloride) for anionic reagents.[31,72,73]

The ion-paring reagent interacts with the nonpolar stationary phase via the hydrophobic tail of the molecule and creates an adsorbate film on top of the surface of the stationary phase. The charged head of the ion-pairing reagent sticks out into the eluent and attracts the analyte with the opposite charge thus achieving the separation of the analytes. [31,72,73] Figure 7 presents the operation mechanism of the ion-pair chromatography.

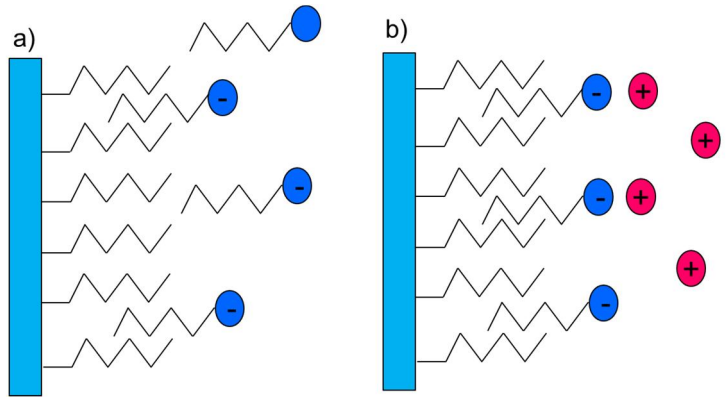


Figure 7. a) Mobile phase contains amphiphilic ion-pairing reagent (blue). The ion-paring reagent interacts with the nonpolar stationary phase (light blue) via the hydrophobic tail. b) The charged head of the ion-pairing reagent sticks out into the eluent and attracts the analyte (pink) with the opposite charge thus achieving the separation of the analytes.[72]

There are several disadvantages in the ion-pairing technique. The concentration of the ion-pair reagent in the column material is dependent on the volume of the organic solvent and temperature. Thus, gradient elution is challenging. Also, the column equilibration for the analysis takes approximately two times longer with the ion-pairing reagent than with other methods. Some of the ion-pairing reagents can be UV-active and interfere the UV-detection. And, if the column is once used for ion-pairing it cannot be used any other LC method any more since the ion-pairing reagents pair so strongly with the stationary phase that they are practically impossible to wash out. Therefore, ion-paring technique is usually replaced with another alternatives, such as new amine embedded-, or mixed-mode columns.[72]

Nair & Saari-Nordhaus[74] applied ion-pair reversed-phase chromatography with suppressed conductivity detection for analysis of anionic and cationic surfactants. A neutral polydivinylbenzene column (Alltech Surfactant/R) was used for separation of both

anionics and cationics with different mobile phases. The mobile phase for anionics consisted of lithium hydroxide, acetonitrile, methanol and water and, for cationics, the mobile phase was acetonitrile, water and nonafluoropentanoic acid. Thus, the same column could be used for detection of both anionic and cationic surfactants, and only the change of mobile phase was required.[74]

Levine *et al.**[75] tested ion pair reverse-phase chromatography connected with supressed conductivity for detection of anionic surfactants. Portet *et al.**[76] reported a simultaneous analysis of mixtures of a non-ionic polyethylene oxide (PEO) and an anionic sodium dodecyl sulfate (SDS) surfactants in salty water using ion-pair reversed-phase liquid chromatography for separation and differential refractometry for detection of the analytes. Wei *et al.** [74] used ion-pair chromatography connected with suppressed conductivity detection for simultaneous determination of seven anionic alkyl sulfates in environ-mental water samples.

* Better description of the applied procedures used in the experiments of Levine and Wei can be found under the conductivity detection chapter (page 46) and for Portet under the refractive index detector chapter (page 48)

3.2.1.4 Size-exclusion chromatography

Size exclusion chromatography (SEC) is an HPLC separation method which separates analytes based on their size. SEC column is a porous material, and when the different sized analytes flow in the column, the low molecular weight molecules penetrate deeper into the pores than the molecules of high molecular weight. Thus, the stationary phase retains smaller molecules longer whereas large molecules eluate faster. Gradient elution cannot be applied in SEC system which makes it a bit more simple technique when compared with other HPLC methods but, on the other hand, also less usable.[59]

In surfactant analysis, SEC is usually used in mixed modes with other chromatographic methods. As mentioned earlier, mixed-mode HPLC with MS detection have been applied for analysis of nonylphenol (NP) and nonylphenol ethoxylates (NPEOs) in wastewater and sediment. The combination of the mixed-mode column with elec-

trospray-MS detection enabled simultaneous and full range detection of NP and NPEOs in a single run.[68] This same mixed-mode HPLC method has also been used to separate octyl- and nonylphenol, and their ethoxylates (1-5) in water and sediment samples.[69]

3.2.2 Detectors for liquid chromatography

The detection method of surfactants depends on the structure and chemical properties of the analyte. Detector selection is not always straightforward due to the wide diversity of surfactant structures and challenging sample matrices. Liquid chromatography separation technique is commonly combined with ultraviolet (UV), fluorescence (FL), refractive index (RI), evaporative light scattering detection (ELSD), mass spectrometry (MS) and suppressed conductivity detectors that can be applied for identification and quantification of surfactants.[62]

UV absorbance is the most preferred method for surfactant detection due to it easiness and cheapness for compounds that have UV-active chromophores. UV-inactive compounds can be detected with ELSD, MS, RI or suppressed conductivity detectors without derivatization treatment. Mass spectrometry is a very effective detection method for all kinds of surfactants, but is rather expensive and is usually used for trace analysis and identification of unknown samples.[62]

ELSD is a universal and inexpensive method for all surfactants structures, but its reproducibility, sensitivity and selectivity are poor, so it is suitable only for routine analysis and high concentration samples. However, it can be combined with gradient techniques and is more sensitive than RI, so its usage has increased attention. The refractive index (RI) is an easy and cheap method for universal detection but cannot be combined with gradient methods and is also very insensitive. Suppressed conductivity can be used for ionic surfactants and is often applied for quantitative and routine analysis since it provides better sensitivity and selectivity than ELSD and RI and is cheaper than MS.[62]

3.2.2.1 (Suppressed) Conductivity detection

Conductivity detector is the most often used detector in ion chromatography applications. It measures alternations in the resistance (or impedance) in an electronic circuit. Conductivity cell contains two electrodes made of marine-grade 316 stainless steel closed into a polyether ether ketone (PEEK) cell body. Conductivity is highly temperature dependent, especially with high conductivities, so the temperature compensation is necessary to secure the reproducibility and stability of the baseline. [56,77]

The operation model of the conductivity detector is a Wheatstone Bridge, where the two electrodes inside the conductivity cells electric circuit are one arm of the bridge. The impedance between the electrodes is changed by conductive ions in the eluent flow and this "out of balance signal" is sent to an electronic circuit that modifies the signal so that it is directly proportional to the ion concentration of the sample. The signal goes through an amplifier, and the digitized output is sent to a data processing computer. The voltage between the electrodes is alternating current (AC) voltage, usually about 10 kHz. Direct current (DC) would lead to a polarization and gas generation at the electrode surfaces. This would interfere the impedance between the electrodes. [59,77]

Any conducting compound in the mobile phase produces a response in the conductivity detector. In addition to analytes there are buffer salts and organic modifiers and other organic solvents that cause alternation in the conductivity cell. Thus, mobile phase should be non-conducting that the detection of the analytes would be possible. The ion suppressor function is to reduce the conductivity of the mobile phase and increase the conductivity of the analyte. Micromembrane suppressor is to most common suppressor type now days.[31]

Simplistically, the suppressor removes all desired ions from the mobile phase and replaces them with hydronium or hydroxide ions. Anion suppressor removes cations and replaces them with hydronium ions, and cation suppressor removes anions replacing them with hydroxide ions. Thus, the eluent ions are converted into non-ionized species, such as water and weak acids or bases, and their conductivity is reduced. The sample anions go through the same treatment, but the effect is opposite as their conductivity increases when they combine with the extremely conductive hydronium or hydroxide

ions. The result is a low conductivity background and an analyte with a conductance clearly distinguishable from the background. [31,56,59]

Suppressed conductivity is often applied for quantitative, and routine analysis since it provides better sensitivity and selectivity than RI and ELSD and is much cheaper than MS.[62] Determination of anionic surfactants using mobile-phase ion chromatography combined with suppressed conductivity detection was tried first time by Weiss in 1986[78]. In his study Weiss used isocratic elution and was not able to separate different components, and quantitative analysis could not be done. The development of column packing materials, like crosslinked, macroporous copolymer of polystyrene and divinylbenzene, and ion suppressors have improved the separation efficiency and allowed the use of gradient elution.[75]

Levine *et al*.[75] tested ion pair reverse-phase chromatography connected with suppressed conductivity detection to study biodegradation of anionic surfactants during wastewater recycling through hydroponic plant growth systems and fixed-film bioreactors.[75] The column used in the experiments was a polymeric reversed-phase column (The IonPac® NS1-10 μm) packed with a neutral, macroporous, high-surface-area, ethylvinylbenzene polymer crosslinked with 55% divinylbenzene. The suppressor was an anion self-regenerating suppressor (Dionex ASRS Ultra 4 mm).[60] The Mobile phase comprised a gradient of acetonitrile and 5 mM ammonium hydroxide. [75]

Sample matrix consisted high concentrations of inorganic ions and some amounts of non-ionic surfactants. Even though no pretreatment was done, interference did not occur and, impurities did not affect the measurement process. The method was able to quantitatively determine sulfonated and sulfated anionic surfactants. Tested surfactants were Igepon TC-42, ammonium lauryl sulfate, sodium laureth sulfate and sodium alkyl (C_{10} – C_{16}) ether sulfate giving linear ranges 2~500, 1~500, 2.5~550 and 3.0~630 μg/ ml, respectively.[75]

Liu *et al*.[79] reported a new method of HPLC analysis where new reversed phase column and conductivity detection was used for determination of anionic surfactants New method offers an enhanced selectivity and efficiency along with improved hydrolytic stability and is also compatible with ion chromatography mobile phases and can sepa-

rate a wide range of anionic surfactants.[79] These qualities are a result of a silica-based reverse phase column (Acclaim® PolarAdvantage II, PA2) with a patented bonding chemistry that possesses hydrolytic stability from pH 1.5–10 and can separate a broad variety of polar and nonpolar compounds. The used suppressor was the anion-ICE micro-membrane suppressor (AMMS® III 4 mm suppressor).[60]

Mobile phase contained acetonitrile and borate buffer solution, and both isocratic and gradient methods were tested. The isocratic method was used when the sample matrix was well-known, and the gradient was applied when unknown samples and complex matrixes were analysed. The linear responses for sodium dodecyl sulfate (SDS) were 0.1 to 1000 ppm under both isocratic and gradient conditions.[79]

Wei *et al.*[73] used ion-pair chromatography connected with suppressed conductivity detection for simultaneous determination of seven anionic alkyl sulfates in environmental water samples. Sodium decylsulfate (C10), sodium undecylsulfate (C11), sodium dodecylsulfate (C12), sodium tridecylsulfate (C13), sodium tetradecylsulfate (C14), sodium cetylsulfate (C16), and sodium octadecylsulfate (C18) were separated by a neutral polymer column (IonPacNS1) made of ethyl vinyl benzene cross-linked polystyrene-divinylbenzene substrate (EVB-DVB). The mobile phase was gradient elution of asetonitrile and water containing ammonium hydroxide as an ion pairing reagent and sodium carbonate as an inorganic additive to improve the separation. Suppression was done with anion chemical suppressor, and the detection limits were 10 mg/l for the seven sodium alkyl sulfates.[73]

3.2.2.2 Refractive index (RI)

Refractive index (RI) detector (or differential refractometer (DRI)) can detect non-ionic, chromophore lacking surfactants that are not UV active or do not fluoresce. RI is easy to use, but is not compatible with gradient methods and is insensitive. The differential refractive index is the mostly used optical system.[79]

The differential refractometer detects the difference of the refractive index between the sample and reference cell. A light bulb (tungsten filament lamp) sends a beam of light

that travels through the optical mask and lenses through the sample and reference cell and collides with a mirror that reflects the beam back, and finally it reaches a photocell. Beam location and angular deflection in the photocell is determined and electronically modified into a signal that is proportional to the sample concentration. RI is a common method for detection of carbohydrates that have no chromophores and are not ionic. The tolerance of gradient elution would make RI very popular method due to its catholic nature.[59]

Desbène *et al*. used reversed-phase HPLC combined with differential refractometry for separation and detection of complex non-ionic polyethylene oxide-type (PEO) surfactant mixtures. In the experiment, RP-C8 column was applied, and the mobile phase was a mixture of acetonitrile and water. Detection limit for the POE was 0.25 µg/l.[80]

Portet *et al*.[76] reported a simultaneous analysis of mixtures of a non-ionic polyethylene oxide (PEO) and an anionic sodium dodecyl sulfate (SDS) surfactants in salty water using ion-pair reversed-phase liquid chromatography for separation and differential refractometry for detection of the analytes. Column was RP C8 column (octyl Ultrasphere Beckman) and mobile phase was a gradient of acetonitrile and water containing tetraethylammonium as an ion-pairing reagent and NaCl as an inorganic additive.[76]

3.2.2.3 Evaporative light scattering detection (ELSD)

Evaporative light scattering detection (ELSD) is a universal method for both ionic and non-ionic surfactant detection. It is more sensitive than RI and considerably cheaper than MS. Additionally, ELSD can be used with gradient techniques and the same chromatographic conditions of ELSD can be adapted almost directly to LC-ESI-MS applications. [62] Disadvantages are that the method requires high concentration samples and possess poor reproducibility and sensitivity along with nonlinear response when compared more accurate techniques like MS or conductivity detection.[81]

ELSD detector nebulizes the incoming solvent from a liquid chromatography system with an inert stream of gas (nitrogen) resulting fine aerosol droplets that contain the sample and a mobile phase. The size of the droplets can be altered by changing the gas

flow rate. Aerosol flows into a drift tube which is kept at a high temperature, and the mobile phase evaporates from the droplets. Small droplets require lower temperatures for evaporation than larger ones.[59,82,83]

The dried solute particles reach the ETL detector and are exposed to a beam of light. The light scatters when it hits the molecule surface, and scattered light is then focused onto a photomultiplier. The detector measures the intensity of the scattered light that is dependent on the particle size. The photomultiplier converts the detected signal to a voltage that is processed into a chromatogram peak. The intensity of the scattered light is a rough estimation of the compounds mass. The light scattering is easily affected by many factors, such as impurities and solvent residues. There is also different kind of light scattering directions (Rayleigh, Mie, refraction-reflection) depending on the particle size. Thus, the response of the method is not linear, and reproducibility and sensitivity are quite a low.[59,82,83]

However, the ELSD is a universal method for surfactant analysis and in many cases the best option for determination non-ionic, UV-inactive and poorly ionisable compounds.
For example, ELSD have been used for simultaneous analysis of four (anionic, amphoteric, nonionic, and cationic) surfactants in shampoo and hair conditioner. The analysis was performed using a reversed-phase HPLC and evaporative light scattering detection. The ELSD temperature was adjusted at 95◦C and a nitrogen flowrate was 2.54 l/min. The RP column was C18 (YMC-J'sphere ODS-H80) and the mobile phase was a gradient of acetonitrile, tetrahydrofuran and water. The detection limits for surfactants were 2.5–30 µg/ml, except for anionic sodium laureth sulfates (SLES) the detection limit was (150 µg/ml).[63]

Anionic sodium laureth sulfates (SLES) have been determined in a commercial liquid detergent sample using RPLC combined with evaporative light scattering detection (ELSD)[84] and a simultaneous analysis of non-ionic, anionic and cationic surfactants in a mixture of different commercial surfactants have been done by using mixed-mode HPLC system and ELSD detection.[62]

3.2.3 Thin-Layer Chromatography

Thin-layer chromatography (TLC) can be applied for the qualitative determination of surfactants. The chromatographic retention mechanisms of TLC are adsorption, partition and ionic exchange which are basically the same than in high-performance liquid chromatography (HPLC). Even though the TLC is not that accurate and sophisticated technique for surfactant determination than HPLC, it has its advantages. TLC is cheap, quick and easy to perform providing semiquantitative results.[85]

TLC can be applied as a pre-preparation technique prior the proper instrumental determination. Separated spots can be carefully removed from TLC-plate and extracted with an appropriate solvent. Separation of surfactants from complex matrices can be achieved based on their behaviour on TLC-plates. For example, alumina plates with ethyl acetate/pyridine mobile phase do not carry anionics but non-ionics and cationics eluate far up. Also, reversed-phase TLC-plates can be used for separation of anionic, non-ionic and cationics.[11] Reversed-phase TLC have also been used for successful determination of HLB-values for non-ionic surfactants.[86-89]

3.2.4 Supercritical fluid chromatography

Supercritical fluid chromatography (SFC) is commonly used for determination of chiral and low molecular weight compounds. SFC can be compared with normal-phase high performance liquid chromatography (NP-HPLC) except in SFC the mobile phase is low-viscosity fluid, like carbon dioxide (CO_2), meaning that the eluent system needs to be under very high pressure. Advantages of SFC are that samples do not need to be volatile like they need to be in GC analysis, and it has a better resolution and greater speed than HPLC. Disadvantages involve extreme sensitivity for temperature and pressure changes and high-pressure instrumentation makes the technique expensive.[11,90,95]

In surfactant analysis, the determination of non-ionic surfactants is more common than ionic surfactants, since ionics dissolve poorly in carbon dioxide. Nonionic alcohol ethoxylates (AEOs) can be analysed with a silicone-coated capillary column and CO_2 mobile phase combined with the flame ionization detection.[11] Oligomers of alcohol ethox-

ylates (AEOs) and propoxylates (APOs) samples have been separated with tandemly stacked octadodecylsilica (ODS) stationary phase and a polar-embedded alkyl phase.[91-93] The effect of different ionic additives on retention of anionic LAS (sodium 4-dodecylbenzene sulfonate and sodium 4-octylbenene sulfonate) has been reported.[94]

3.2.5 Gas chromatography (GC)

Gas chromatography is a very effective separation method for volatile organic substances. Although GC is able for more complete separation of surfactant homologues and isomers than HLPC, it is not that commonly used for analysis of surfactants. This is due to the fact that many surface active agents are not volatile. However, when investigating the biodegradability and toxicity of anionic LAS and their metabolites the ability to separate the different homologues is rather important.[10,96]

Derivatization needs to be done for all anionic and non-ionic analytes before they can be analysed by GC to ensure good separation, sensitivity and volatilization. Substances, like trifluoroethanol, diazomethane, N,O-bis(trimethylsilyl)trifluoro acetamide (BSTFA), acetic anhydride and hydrogen bromide can be used for derivatization. Capillary columns used for separation of anionic and non-ionic surfactants have been nonpolar 5%-phenyl-95%-dimethylpolysiloxane columns, like HP-5, ES-54 and DB-5, and high purity helium has been used as a carrier gas with a flow rate 0.58 – 3.4 ml/min.[10,96] Some degradation products of non-ionic surfactants with low molecular mass, such as NPs and NPEOs, have been run through GC without derivatization.[97]

There are not many papers published about the determination of cationic or amphoteric surfactants by GC applications. Like anionic and non-ionic surfactants, they are not volatile, and derivatization or decomposition is needed before GC analysis. QACs can be firs hydrogenated to alkyldimethylamines and then derivatized to the cyanamide or trichloroethyl carbamate for analysis with GC. Methanolysis and methylation of ester quats with methanol in the presence of an acid catalyst (like HCl) produces volatile fatty acid methyl esters (FAMEs). Amphoteric surfactants with a carboxylic acid moiety, like

W-alkylaminopropylglycines, can also be converted into methyl esters and analysed with GC.[11]

Surfactant detection after separation in GC system can be done by common flame-ionization detector (FID) or more accurate single quadrupole (MS), tandem mass spectrometers (MS-MS) or time-of-flight ((TOF)MS) with electron impact (EI), electrospray ionization (ESI) or chemical ionization (CI) techniques.[10] For example, FID have been used for detection of anionic surfactants[98] and multidimensional GC-GC-(TOF)MS combination have been used for the simultaneous determination of nonionic, anionic and several cationic surfactants in industrial cleaners.[99]

3.3 Spectrophotometric methods

This chapter covers four different spectrophotometric methods that can be used for surfactant determination. Methods are UV/VIS spectrophotometry, handling UV-detection and solvent extraction spectrophotometry, mass spectrometry (MS), infrared spectroscopy (IR) and nuclear magnetic resonance (NMR). The main focus is on UV/VIS spectrophotometry.

3.3.1 UV/VIS spectrophotometry

Spectrophotometric techniques, which give approximate total concentrations for ionic and non-ionic surfactants, are suitable detection methods for routine monitoring. Even though, they are not that accurate methods than chromatographic HPLC and GC and suffer easily interference of impurities, in some cases they are very useful for detection of different surfactants from environmental waters and other sample matrices.[55]

Ultraviolet (UV) absorbance detection can be used for surfactants with UV active chromophores. In the case of chromophore lacking analytes, the spectrophotometric analysis involves the formation of coloured ion-pair complex of the analyte and its counter ion. The complex is then extracted with organic solvents, and the absorbance is measured

with appropriate ultraviolet or visible light wavelength. This kind of colorimetric method is called solvent extraction spectrophotometry. Even though the method is quick and simple to perform, it has limitations, interference of impurities occurs easily and a lot of toxic organic waste (e.g. chloroform) is generated as a by-product.[10]

3.3.1.1 UV absorbance

UV absorbance is the most preferred method for surfactant detection, especially coupled with HPLC or SFC separation techniques, due to its simplicity, easiness and cheapness. Anionic alkylbenzenesulfonates (LAS) have an aromatic ring in their structure and can be detected directly with UV absorbance at λ_{ex} = 225 nm and fluorescence at λ_{ex} = 225 nm, λ_{em} = 295 nm.[100,101] Direct analysis of LAS in complex matrices is not that useful since the same wavelength is absorbed by many other aromatic compounds.[11]

Non-ionic alkylphenol ethoxylates (APEOs) and nonylphenol ethoxylates (NPEOs) are aromatic and can be detected directly by ultraviolet (UV) at λ_{ex} = 277 nm[102] and fluorescence (FL) at λ_{ex} = 230 nm and λ_{em} = 302 nm.[103] Aryl groups in some cationic and amphoteric surfactants make them strongly UV active. Cationics that contain imidazoline-ring have an absorbance at 235 nm, but this is strongly pH dependent since imidazoline ring opens in a basic environment.[11] Cationic benzalkonium chlorides (BACs), have been separated with HPLC and detected with UV at λ_{ex} = 254 nm.[104]

Aliphatic structures, such as non-ionic alcohol polyethoxylates (AEOs) and anionic alkyl ethoxysulfates (AES), do not absorb UV-light and cannot be detected directly by UV or FL. The analyte structure can be altered by derivatization treatment with e.g. phenyl isocyanate, naphthyl isocyanate or naphthyl chloride (NC). [65,105] These molecules have an easily reactive chloride (Cl^-) or isocyanate (–N=C=O) group and a UV-active aromatic ring in their structure. Reaction between the analyte and derivatization reagent leads to derivative that can be detected by UV or FL detectors.[106]

3.3.1.2 Solvent extraction spectrophotometry

Solvent extraction spectrometry involves complex formation between the ionic analyte and its counter ion. The complex is then extracted with organic solvents, and the absorbance of the organic phase is measured with appropriate UV/VIS wavelength. In the case of anionic surfactants, the counter part is cationic compound. Methylene blue method (MB-method) has been the most used technique for determining anionic sulfonates and sulfates in different water samples.[11] Molecular structure and formula of methylene blue in Table 6.

MB-method is a simple and rather sensitive, but it require a large amount of sample (100 ml) and contain multiple steps, including extraction into chloroform 3-4 times (total 35-50 ml of chloroform). Thus, the procedure is laborious, time-consuming (90 min) and also consumes large volumes of toxic chloroform.[28] In addition, methylene blue, and other cationic dyes, tend to lose their positive character in a basic environment and at a very low pH the anionic anatyles start to protonate, the pH control of the solutions is rather important. This means that different kind of buffer solutions (e.g. Na_2HPO_4) is also used in the analysis.[11]

Sample matrix can easily interfere the results of MB-method by alternating the volume of the colouring agent that transfers into the organic phase. In anionic analysis, a positive interference can be caused by organic sulfonates, sulfates, carboxylates, phenols, inorganic tiocyanates, cyanates, nitrates and chlorides which transfer more or less colour into the organic phase. Cationic surfactants and other cationic substances also readily bind to anionic parts and compete with the colouring agents in the ion pair formation causing negative interference.[75]

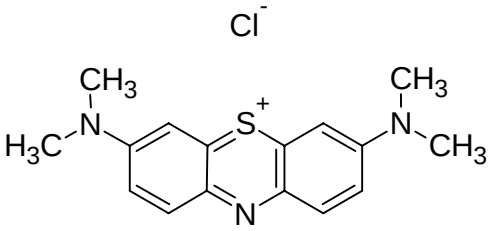
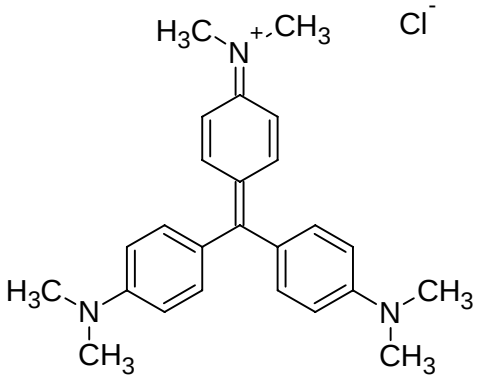
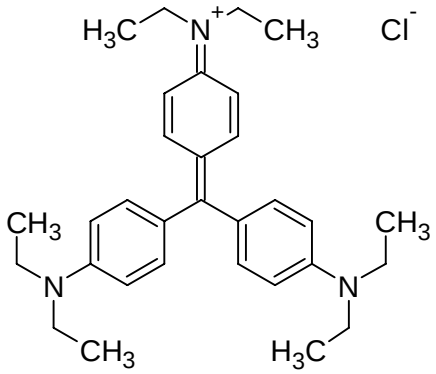
The original MB-method has been subsequently improved by many authors. For example, Koga *et al*. studied the equilibrium between anionic surfactant (sodium dodecyl sulfate SDS) and MB and SDS-MB complex transfer into the organic phase. They concluded that the complex formed (1:1) molar ratio and could be assigned as ion association complex. They also stated that both SDS and MB do not transfer into organic phase by themselves but only as a complex. Consequently, they reduced the required sample (50 ml) and chloroform volume (5 ml).[107]

Jurado *et al*. applied the MB-procedure for monitoring LAS degradation process. They further simplified Kogas procedure by increasing the volume of solvent (4 ml of chloroform) with respect to the sample volume (5 ml). They stated that this way it is possible to enhance the mass-transfer of the surfactant-MB-complex towards the organic phase and perform the extraction only in a single step.[28]

Alternative cationic dyes for anionic analysis are ethyl violet (triphenylmethane) and crystal violet. Molecular structures and formulas of ethyl and crystal violet in Table 6. Motomizu *et al*.[108] optimized the ethyl violet procedure and concluded that advantages of the ethyl violet method were the high extraction tendency of the surfactant-dye complex into the organic phase, such as toluene and benzene, making the method more sensitive, selective and less susceptible to interference of the matrix. The used organic solvents were also less toxic than chloroform, and the overall procedure was more simple and shorter. Sample volume was 100 ml and solvent volume 5 ml. The absorbance maximum for the anionic surfactants (sodium bis(2-ethylhexyl) sulfosmcinate (Na^+DESS^-), sodium dodecylbenzenesulfonate (Na^+DBS^-) and sodium dodecylsulfate ($NafD^-OSO3^-$) used was λ_{ex} = 615 nm.[108] Yamamoto *et al*.[109] studied the effect of interfering salts (Cl^-) on the ethyl violet method and modified the procedure to be more suitable for sea water analysis.[109]

Santosh *et al*.[110] optimized a detection procedure for anionic surfactants by using crystal violet (methyl violet) as a cationic dye. Like ethyl violet, it has a high solubility in water, forms readily complex with anionic counterpart and has a high extractability in an organic solvent in a complex form. In this study, benzene was found to be the most effective solvent and used sample (SDS) volume was 10 ml and solvent volume 5 ml (volume ratio 1:1/2). The absorbance was measured at λ_{ex} = 565 nm.[110] Other cationic dyes used for anionic surfactant detection are for example rhodamine [111] and acridine orange.[18]

Table 5. Cationic dyes commonly used for detection of anionic surfactants. Methylene blue, crystal violet and ethyl violet

Dye name and structure	Molecular formula	MW
Methylene blue 	$C_{16}H_8ClN_3S$	319.86
Crystal violet 	$C_{25}H_{30}ClN_3$	407.99
Ethyl violet 	$C_{31}H_{42}ClN_3$	492.14

Nonionic polyethers, at least, four units in length, have a tendency to form complexes with large positive ions, like K^+ and Ba^{2+}. Cobalt thiocyanate method is commonly used for detection of ethoxylated non-ionic surfactants, and it is based on the complex formation between the polyether linkages and cobalt ion (Co^{2+}). The tetrathiocyanatocobaltate(II)complex can be detected by UV at λ_{ex} = 318 nm or at visible light region at λ_{ex} = 620 nm (orange). There are many this kind of methods based on the complex formation for determination of non-ionic surfactants. Examples are barium iodobismuthate methods, potassium picrate methods and iodine methods. Nonionics have a cationic character at low pH areas and can be detected with same procedures than cationic surfactants.[11]

Detection of cationic surfactants follows the same general idea than detection of anionics. Coloured complex is formed between the cationic sample and its anionic dye counterpart. The complex is soluble in organic solvent and can be extracted and finally detected with a spectrophotometer. Ion exchange is commonly used as a prepreparation technique for concentration and purification of the sample. Many different anionic dyes have been used for cation detection, and some are more specific for certain surfactants than others. pH optimization is always necessary when developing a procedure for a specific surfactant to achieve proper colour formation and good absorbance.[11]

Disulfine blue method can be applied for cationic surfactant detection. The sample is first rinsed through an anion exchange column. Sample complex is extracted into chloroform and absorbance is detected at λ_{ex} = 628 nm. Other anionic dyes used for cationic surfactant detection are for example picric acid, tetraiodobismuthate and orange II.[11]

3.3.2 Mass spectrometry (MS)

Mass spectrometry comprises an ion source, a mass analyser and a detector. The ion source ionizes the sample molecule into charged fragments, the mass analyser separates the fragments based on their mass-to-charge ratio, and the detector detects the relative abundance of the incoming ions. The mass spectrometer can provide information about the component structure, like the location of saturation or side chain and degree of

branching, and it also gives molecular weight distribution of the molecule oligomers and isomer distribution. [112]

The development of soft ionization techniques with a liquid introduction, like atmospheric pressure ionization (APCI) and electrospray ionization (ESI), have enabled the connection of HPLC separation technique with mass spectrometer (MS) detection and are found to be suitable ionization methods for surfactants. HPLC-MS combination is very effective identification technique since MS provides high sensitivity, selectivity and is able to characterise multiple surfactant classes simultaneously. However, these techniques require quite large concentration of target analyte in the sample, and quantitative analysis is not possible.[11,113]

Jewett and al.[113] compared these two soft ionization techniques (ESI vs. APCI) in the analysis of anionic alkyl ethoxylates (AES). Liquid chromatograph was used for sample delivery and triple quadrupole as a mass analyser. ESI is the most commonly used for anionic surfactant analysis since it provides good spectras for already ionized analytes. APCI is a bulk method is not that easily interfered by matrix effects.[113]

There are several different mass analyzers, including single quadrupole [36], triple quadrupole[41,113] ion trap techniques[40] and time-of-fligt (ToF)[114] which have been used for surfactant identification and quantification. Isobaric interferences which usually lead to problems with sensitivity and resolution can occur with single quadrupole. Triple quadrupole and ion trap are more stable systems than single quadrupole and are the most used techniques in trace analyses. Disadvantage of these techniques is that there is a limitation on number of predetermined ions that are possible to observe during one experiment.[10]

Time-of-flight (ToF)[114] is not that often used MS analyser in environmental analyses in LC-MS systems. However, the advantage of ToF is its capacity to measure mass accurately and to scan a wide mass range with high spectral sensitivity. Thus, a lot of different analytes and their decomposition products can be identified and quantified in variable matrices. Hybrid detectors, like quadrupole time-of-flight (Q-ToF)[115] have been used to determine surfactants but they are expensive, and they cannot compete HPLC coupled with tandem mass spectrometry (MS-MS)[69] in sensitivity.[10]

In the analysis of anionic and non-ionic surfactants, the ESI ionization technique operating in the negative mode for anionics and positive mode for nonionic usually provides the best sensitivity and selectivity.[11] MS detection of non-ionic is mainly focused on ethoxylated compounds (NPEOs, AEOs).[67,68] Simultaneous determination of various anionic and non-ionic surfactants in environmental samples have been done by LC-MS using both APCI and ESI ionization techniques.[36,40] Cationic QACs can be detected with LC-tandem/MS using ESI ionization operating in the positive mode [32,41]

HPLC-MS is the most used separation-detection technique in the surfactant analysis, but MS can also be combined with techniques like supercritical fluid chromatography (SFC)[91] (chapter 3.2.3) or gas chromatography (GC) (chapter 3.2.4).[99]

3.3.3 IR spectroscopy

Qualitative analysis and identification of surfactants by infrared spectroscopy (IR) is comprehensively dealt by Hummel (1996)[116] and one of the earliest studies published in this field is done by Nettles (1969)[117]. Identification of pure molecules or even mixtures of compounds by IR is based on the knowledge that molecules exposed to infrared light absorb the different wavelengths of radiation according to their structure.[118] Viana *et al*. have studied the vibrational features of an anionic SDS, cationic surfactants (hexadecyl-trimethylammonium bromide (CTAB) and dodecyl trimethylammonium bromide (DTAB)), and a zwitterionic surfactant (N-hexadecyl-N-N-dimethyl-3-ammonio- 1-propane-sulfonate (HPS) by using FTIR-ATR spectroscopy.[119]

In the classic Fourier transform infrared spectroscopy (FTIR) sample (liquid or crushed solid) is placed between infrared transparent salt (KBr) plates. In the new ATR (attenuated total reflectance) application, the sample is placed on top of the ZeSe/diamond crystal.[120] Both methods, especially ATR, requires only small amount of sample. Modern data processing also enables the spectra subtraction of known molecules making the mixture analyzation even easier.[11]

Quantitative determination of surfactants has been successfully studied by Carolei *et al*.[121] They performed a simultaneous analysis of anionic, non-ionic and amphoteric

surfactants in shampoo by ATR-FTIR technique using multivariate analysis in the optimization of the procedure. Samples were analysed directly from the shampoo without dilution or other sample treatment. Absorbance data of the target compounds and calibration standards was collected in the middle infrared region of the spectrum (800-1600 and 1900-3000 cm^{-1}). Broad band of water did not interfere the analysis and the survey states that the presence of small amounts of additives, such as colourants and perfumes, are not a problem but large volumes will cause interfering bands.[121] Similar ATR-FTIR methods have been applied for anionic and non-ionic surfactant determination in hand dishwashing liquids[122] and determination of sodium alpha-olefin sulfonate (AOS) in liquid detergent formulations.[123]

3.3.4 Nuclear magnetic resonance (NMR)

Nuclear magnetic resonance (NMR) is mainly used for characterization of pure compounds. NMR can be said to be more exact technique than IR but sample treatment (samples need to be liquid form) is necessary for NMR. Micelles also cause interference and peak broadening. [11] The application of ^{13}C NMR spectroscopy in surfactant identification has been published.[124,125] Söderman *et al.*[126] used NMR to determine surfactant characteristics such as micellar size and structure, ion-binding and solubilisation.[126] In surfactant analysis NMR often used to confirm the results which have been accomplished by other detection techniques (like HPLC-ELSD).[84]

3.4 Titration methods

This chapter considers titration of surfactants and surfactant specific electrodes. Other analytical techniques, such as polarography, gravimetric methods, flow injection analysis, X-Ray fluorescence, Atomic Absorption Spectroscopy (AAS), fluorometry and chemiluminescence are not described here and can be found in the literature.[11] Determination of total organic carbon (TOC), biochemical oxygen demand (BOD) and chemical oxygen demand (COD) are discussed in chapter 6 (Surfactant removal methods). There

is a lot of information available about surfactant determination by titrimetric methods. For example, many laboratory equipment manufacturers[127,128] provide comprehensive manuals of modern and mechanized titration techniques of surfactants.

Volumetric titration of surfactants is a very useful method, especially in quality control. Most commonly used methods are two-phase titration of anionics with cationic surfactants (and reverse) and one-phase potentiometric titration. Titrimetric techniques are simple, rather quick and easy to perform, and they do not require expensive laboratory equipment. However, they cannot distinguish different surfactants form each other.[11]

In an analysis of anionic surfactants, acid-base titration can be applied since many anionics are classified as salts of moderately strong acids and direct titration with base is possible. The two phase titration (involves water and an organic phase) with a cationic surfactant is based on ion pair formation, and colour change of the organic phase as the titrant displaces a cationic dye. The two-phase titration, and many its modifications can be used for determination of anionic alkyl aryl sulfonates, alkyl sulfates, sulfated APE and AE, and sulfosuccinates in concentrates and detergent formulations. Cationic titrants commonly used are the disinfectant benzethonium chloride (Hyamine® 1622) and l,3,-didecyl-2-methylimidazolium chloride (TEGO®trant A100).[11]

Another widely used method is one phase potentiometric titrametration. The technique uses detectors which measure changes of electric charges of analysts in water samples as the target surfactant ion forms a hydrophobic ion pair with a titrant and leaves the water phase. The potentiometric method cannot distinguish different surfactants and its reproducibility, and signal stability are not fully reliable.[10] Detection of anionic alkylbenzenesulfonates, a-olefin sulfonates, alcohol sulfates and alcohol ether sulfates can be done with potentiometric titration using hexadecylpyridinium chloride, hexadecyltrimethylammonium chloride, trioctylmethylammonium chloride or l,3-didecyl-2-methylimidazolium chloride as the cationic titrant.[11]

As already noted in spectrophotometric determination of non-ionic surfactants, polyethers, at least, four units in length, have a tendency to form complexes with large positive ions, like K^+ and Ba^{2+}. Used titrants are usually anions, like tetraphenylborate , but also,

substituted tetraphenylborates, ferrocyanide, tetraiodobismuthate, and heteropoly acids are used. [11]

For example, when using tetraphenylborate as a titrant, non-ionic analysts, like poly-alkylene glycol adducts, an excess of a divalent salt is added into the solution. Potentiometric titration of the formed complex is done with sodium tetraphenylborate solution, using electrode (metal indicator or PVC-membrane detector) for the detection.[129] Another methods for non-ionic determination are, for example, two-Phase titration with potassium tetrakis(4-chlorophenyl)borate. Hydroxyl groups containing nonionics can be determined like anionics using potentiometric titration, and basic amine oxides can be titrated directly with HCl.[11]

Cationic amines are usually titrated directly with perchloric acid by unspecific acid-phase titration. Two phase titration methods include tetraphenylborate or anionic surfactants.[130] Photometric titration with picrate ion is also possible. Tetraphenylborate can also be used in the one phase potentiometric titration using metal electrode as a detector. Amphoterics behave like cationics at low pH, and some become anionic at basic pH range so many methods used with cationics and anionics can be applied with zwitterionic surfactants. Potentiometric titration with different electrodes is also possible. For example, zwitterionics with carboxylate groups and some imidazolium compounds can be titrated at acidic pH with tetraphenylborate using a membrane electrode or a coated-wire electrode.[11]

3.4.1 Surfactant specific electrodes

Li *et al*. have published a comprehensive article about surfactant ion-selective electrodes.[131] Electrodes (or sensors) used in potentiometric titration analysis of anionic and cationic surfactants are a silver/silver chloride electrodes inside a glass tubes filled with a solution an anionic surfactant and chloride salt. The bottom of the tube is sealed with a PVC (polyvinylchloride) – membrane that contains a high volume of plasticizer and a surfactant ion pair, such as hexadecyltrimethylammonium dodecyl lsulfate. Different

forms of electrodes are e.g. the coated wire electrode, the solid state electrode and the flow-through electrode.[11]

PVC membranes for ionic surfactants contain PVS resin, plasticizer, ion pair and other additives. The selectivity of the electrode towards a specific surfactant can be enhanced by incorporating additives into the membrane. Specificity towards anionics can be enhanced by adding long chained cation counter ion (tetrabutylammonium dodecylsulfate) into the membrane and specificity towards cations can be achieved by adding short chained anion counter ion (hexadecyltrimethylammonium 1-pentanesulfonate). Non-ionic surfactants with polyethoxylate chains can be detected with electrodes made of PVC-membrane containing the tetraphenylborate salt of a barium/ethoxylated nonylphenol complex.[11]

For example, anionic sodium dodecyl sulfate (SDS) have been determined in toothpaste using the PVC-membrane sensor. The sensor contains cetyltrimethylammonium-tetraphenylborate (CTA-TPB) ion-pair complex as electroactive material in PVC matrix and dioctyl phthalate as a solvent mediator.[132] SDS have also been successfully detected with PVC-membrane using neutral ion pair complex of dodecyltrimethylammonium-dodecyl sulfate (DTA^+DS^-) as ionophore and Hyamine standard solution as titrant.[133]

4 WATER CIRCULATION SYSTEMS IN PAPER AND BOARD MILLS

Water is very important component in paper and pulp making. In Nordic countries, the access to the clean raw water is easy due to the rather clean nature waters provided by rivers and lakes. Nowadays an increasing demand for high-quality paper with excellent brightness and cleanness properties and also, at the same time, a growing attention for environmental aspects and more green paper production processes, makes the water quality, purity, purification and reuse very important factors.

Environmental raw water needs to be treated before use. Humus and clay are removed, microbes disposed and factors like hardness, pH and alkalinity are regulated by both mechanical and chemical techniques. All water treatment processes in the paper mill are described in Figure 8. In this chapter, the main focus is on white water circulation (short circulation) and wastewater treatment processes.

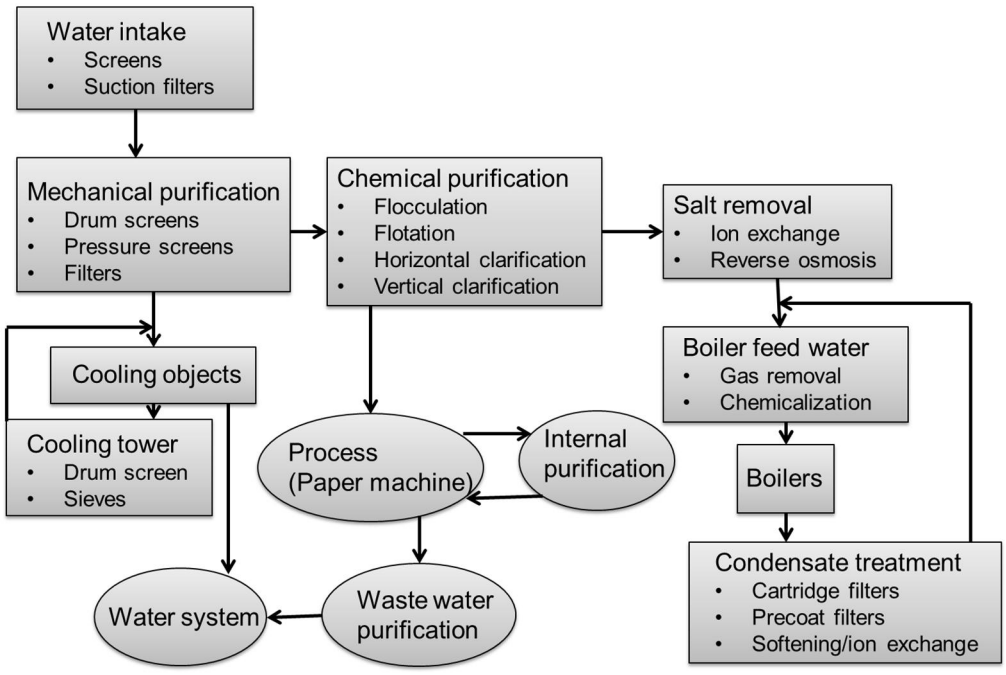


Figure 8. Water treatment in a paper mill.[135]

4.1 White water system

Water circulation systems, including fractionation, purification and reuse, improve the economy and reduce the environmental impact of the paper making process. Dewatering of pulps forms water fractions containing solids and chemicals depending on the used application. The discharged water from the wire section of the paper machine generates the largest water fraction that carries very short fibres and small fines and filler substances, dissolved and colloidal substances (DCS) and non-retained chemicals. Rest of the process water fractions are formed at broke precipitators and press section.[134]

A counter-current principle is applied in operation of water circulation system. Hot water system preheats the new and treated water. For example, the wire and press section showers of the paper machine utilises the pure and heated fresh water. Short circulation comprises the part of the paper making process where the water streamed through the wire is recycled and used for stock dilution and fed back to the head box.[134]

Traditionally, the wire flume collects the white water streaming from the wire section and returns it to the wire pit. In the wire pit the section of the white water that has fallen down is pumped through the fan pump to the centrifugal cleaning plant and after that is used for dilution of the stock and pumped back to the head box. Thus, fibres and fillers are recycled in the short circulation. Short circulation and white water recycling in paper making process is illustrated in Figure 9.[134]

Overflowing water fraction of the wire pit, which can be considered being the cleanest portion, is transferred via the circulation water tank (or white water tank) to the purification processes and long circulation. Water runs from the circulation water tank through the disc filter where solids are separated from the water. Collected filtrates are divided into superclear, clear and cloudy filtrate. Disc filter removes the solids but not small solutes or microbes.[134]

Filtered water can be further treated with membrane filtration techniques (micro-, ultra-, and nanofiltration), flotation process and biological-, and chemical treatments depending on the final use. Treated white water can be recycled back to the broke system or to the wire and press section showers. Part of the purified white water is stored in the

white water towers which can be used in pulpering or serve as a buffer in exceptional situations, like web break.[134] The simplified presentation of the paper machine circulation water system in Figure 10.

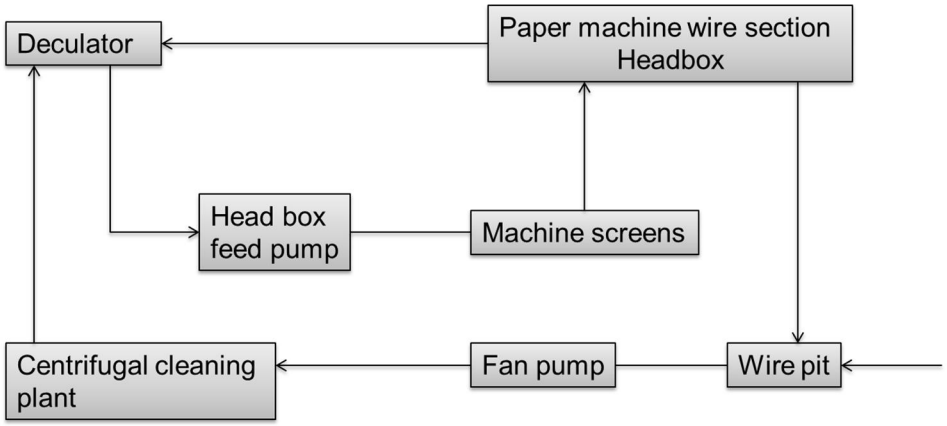


Figure 9. Short circulation and white water recycling in paper making process.[135]

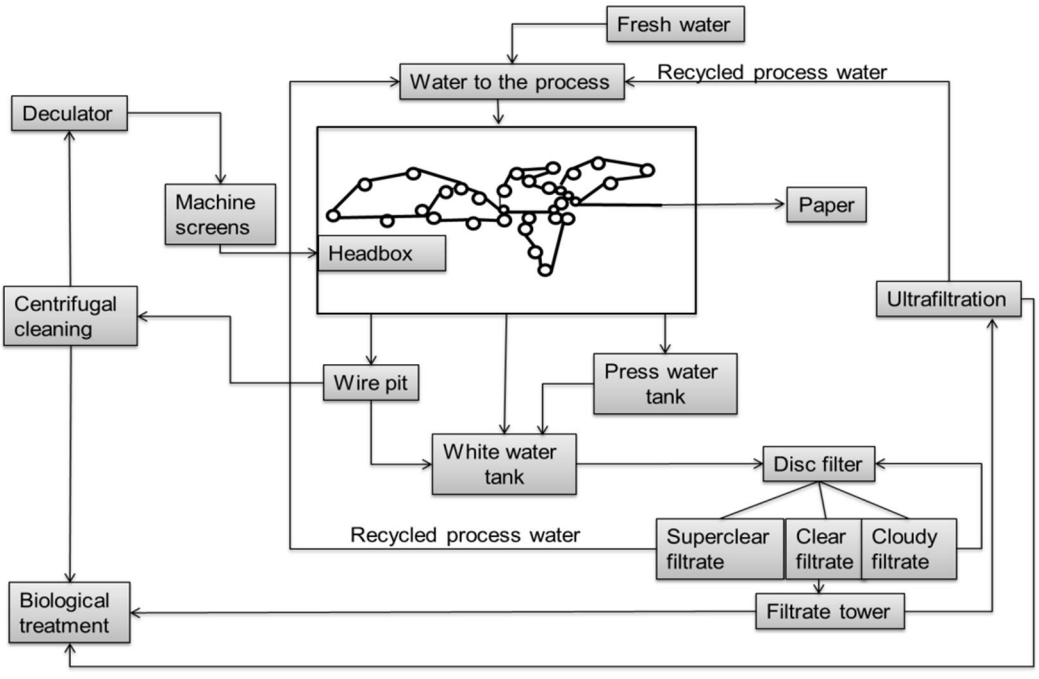


Figure 10. Simplified presentation of paper machine circulation water system.[136]

Modern mills consume fresh water approximately 2-20 L/kg of paper. Technical and special paper types can consume 100L/kg or more. Water consumption has been significantly decreased form the 1970's.[134] Table 6 shows modern paper mill water consumption in two thousand century in comparison to the 1970's mill consumption. The usage of fresh water in the paper making can be done with the closure of the circulation system. Increase in water pressure and well-considered equipment form, construction and placement can diminish the need for fresh water in systems like water showers and seals. Fresh water can be totally or partly replaced with circulation water by investing in internal water treatment processes, such as membrane techniques.[134]

Table 6. Modern paper mill water consumption in comparison to the 1970's mill consumption[134]

Paper grade	2000 century (L/kg)	The 1970s (L/kg)
Newsprint	5-15	85
Wood-free fine paper	5-10	180
Supercalendered (SC) paper	10-15	120
Lightweight coated (LWC) paper	10-20	-
Tissue	5-15	290
Liner and fluting	2-10	40-85
Multiply board	8-15	130

4.2 Wastewater system

The external effluent treatment is a self-contained plant in a paper mill and does not affect the paper making process. Even though, alternations in paper making process have an effect on wastewater composition and can cause variations and problems, especially in biological wastewater treatment. Wastewater and sludge that is released back to the environment need to fulfil the environmental permits and different wastewater treatment processes (mechanical, chemical, and biological), are used to reach these benchmarks.[137]

Wastewater treatment comprises pre-, primary, secondary and the tertiary treatment stages. Pre-treatment stage removes largest solids using mechanical screening or grift separation methods. Also, neutralization, cooling and pH adjustment can be included in

pre-treatment. In primary treatment stage mechanical settling, using clarification or flotation, is applied to clarify the wastewater form smaller solids, fibres, bark pieces and sand. Chemical precipitation can be used to boost the settling.[137]

Secondary treatment involves biological methods to remove organic substances. Micro-organisms are used to consume organic material and nutrients, like nitrogen and phosphorus, and decrease biological oxygen demand (BOD). Tertiary treatment is applied only if the three former treatments have not succeeded to reach the environmental permit limits. For example flotation, mechanical filtering, oxidation techniques, membranes, disinfection or anaerobic micro-organisms can be used to remove remaining organics, solids and viruses. Tertiary treatment is expensive and rarely used.[137]

Mechanical methods include clarification, flotation (foaming) and filtration. Also screening (separation of the most coarse solids form wastewater) and grit removal of sands and minerals are used. Mechanical treatment of the wastewater is the first step of the purification process where the largest solid are separated from the water. In clarification (settling/sedimentation) the effluent flow is slow, and particles sink into the tank bottom forming sludge. Sludge is collected with the rotating doctor and pumped to a condensation basin. Flotation method is commonly used after biological treatment to clarify wastewater from light and poorly settling solids. In flotation air is pumped into the tank at the bottom of the container and formed air bubbles grasp fine solids on their way to the surface. Sludge gathered on the surface and is collected to a sludge channel. In filtration, various types of filter can be used including screen, wire cloth, sand and membrane filters and is usually applied in internal white water treatment and tertiary treatment of wastewater. Filter material gets blocked easily that makes the technique rather expensive.[137]

Chemical precipitation of the wastewater involves precipitation chemicals (coagulants like aluminium salts, iron salts and lime) which precipitate/flocculate with organic material and phosphorous forming flocs. Mechanical methods (e.g. flotation) are used to separate flocs from the wastewater. Chemical treatment of the wastewater can also be done by oxidation, disinfection, neutralization, ion exchange and adsorption. In oxidation, the organic material is oxidised to water and carbon dioxide using ozone, hydrogen

peroxide, catalysts (TiO_2) or UV-radiation to form free radicals. Oxidation technique is very sensitive to pH, temperature, oxygen concentration and amount of impurities. [137]

In biological treatment the organic material is removed from the wastewater using microbes that consume organics for nutrition turning them into the water, carbon dioxide (or methane) and biomass (Figure 11). Thus, the chemical oxygen demand (COD) and biological oxygen demand (BOD) – loads are reduced. Biological treatment is most often used as secondary treatment process so that the effluent do not contain a large amount of solids anymore. Living microbes, that run the process, make it also demanding since they require a right ratio of nutrients (carbon, phosphorus), correct pH, temperature and oxygen (aerobic) or total absence of oxygen (anaerobic). Thus, the process is sensitive to variations.[137]

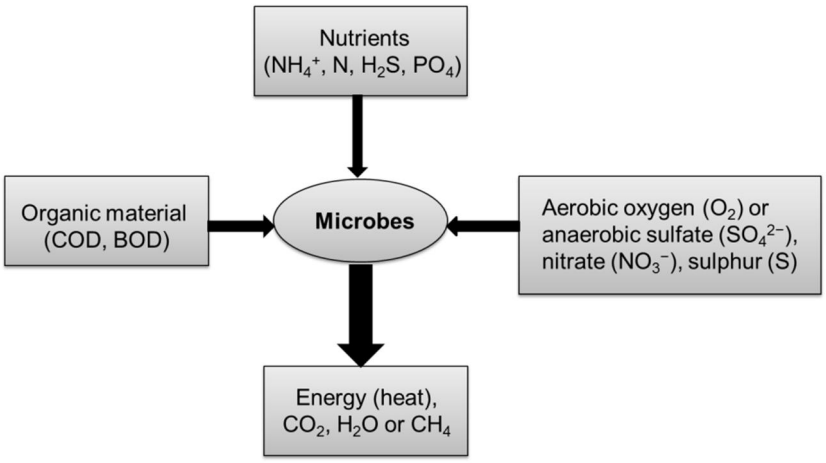


Figure 11. In biological treatment the organic material is removed from the wastewater using microbes that consume organics for nutrition turning them into water, carbon dioxide (or methane) and biomass.[135]

4.2.1 Aerobic wastewater treatment and activated sludge

In aerobic wastewater treatment, microbes use oxygen as the final electron acceptor of their energy metabolism processes. Oxidation of carbon substances releases energy and forms carbon dioxide, water and biomass (equation 12). Aerobic wastewater treatment processes are activated sludge process, aerated pond, different carrier based methods and membrane bio reactor (MBR). These methods can reduce COD about 80 % and

BOD about 96-99 %. When one kilogram of BOD is reduced, 0.4-0.7 kg of bacterial mass is formed, and 0.5-0.9 kg of oxygen is consumed.[137]

$$\textbf{Organic material} + \mathbf{O_2} + \textbf{nutrients} \rightarrow \mathbf{CO_2} + \mathbf{H_2O} + \textbf{biomass} \quad (12)$$

Activated sludge process is the most common biological method for wastewater treatment in forest-, and paper industry. The process uses activated sludge, formed of microbes and biomass, and can be divided into two units, aeration basing and clarification. At first, solid particles are removed in a pre-clarifier. Then the effluent goes through an equalization basin that neutralizes (Ca_2CO_3 or H_2SO_3) and adds nutrients (phosphoric acid H_3PO_4 and urea $(NH_2)_2CO$) into the water. Aeration basin mixes activated sludge with the effluent water, and sludge microbes start to oxidise carbon compounds. Secondary clarification basin separates the purified water and sludge. Part of the sludge is returned to the aeration basin, and rest is pumped to the sludge handling process. Clarified water flows to water bodies or goes through the tertiary treatment process.[137]Activated sludge process presented in Figure 12.

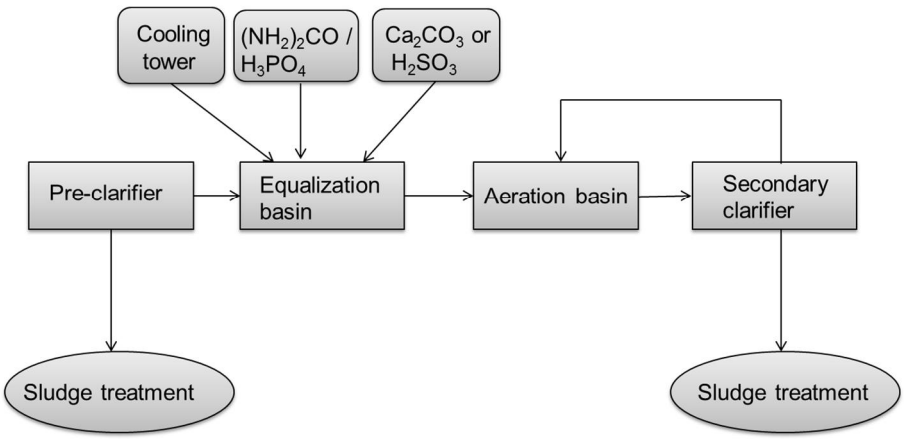


Figure 12. Activated sludge process.[135]

4.2.2 Anaerobic wastewater treatment

Anaerobic wastewater treatment happens in the absence of oxygen. Anaerobic microbes degrade organic compounds using sulfate (SO_4^{2-}), nitrate (NO_3^-), sulphur, or fumarate as the final electron acceptors in the respiratory chain. Final products are methane (biogas), carbon dioxide and biomass (equation 13). 90 % of COD can be turned into biomass in anaerobic treatment producing < 0.1 kg of biomass per one kilogram of COD. Anaerobic wastewater treatment processes are for example a continuously stirred tank reactor (CST), fluidized bed reactor (FBR) and internal circulation reactor (IC).

$$\textbf{Organic material + nutrients} \rightarrow \textbf{CO}_2 \textbf{ + CH}_4 \textbf{ + biomass} \quad (13)$$

The temperature of the anaerobic system can be adjusted ether for mesophilic (35°C) or thermophilic (60°C) microbes. pH needs to be neutral (pH 6.5-8) and right rate of nutrients available. The advantage of the anaerobic process is the formation of biogas that can be used in energy production, and weakness is its sensitivity to process changes (pH, temperature, nutrients) and other microbes. Also, it is not that effective as aerobic degradation process and is often used as a pre-treatment before anaerobic treatment.[137]

4.2.3 Sludge treatment and disposal

The amount and quality of generated sludge differ between wastewater treatment plants. However, all sludge always contains a large amount of water and low solid content which makes the sludge treatment energy consuming process and requires quite a lot of different process steps. Rigorous dewatering of the sludge and high dry matter content makes the following treatment steps more simple.[137]

The first step of sludge handling is thickening followed by pre-treatment methods, conditioning (with pressure or heat) and stabilization. Stabilization prevents microbial decomposition thus reducing odor problems. Stabilization can be done with chemical (lime), biological (anaerobic), aerobic (composting) or physical (thermal drying) meth-

ods. Pre-treatment is usually done before water separation to enhance the sludge quality and increase the dry matter content.[137]

Sludge drying can be achieved with mechanical and thermal methods. Mechanical water separation methods include, for example, centrifuge, belt filter press, screw press and disc press. Thermal methods are different contact- or convection driers. After thickening, in most cases, comes a drain tape press that separates the water and then the dry content is burned in a bark boiler with bark (from wood treatment) for energy production or disposed to the landfill. Also, biological treatment of sludge with anaerobic microbes for biogas production is possible. Other end use resorts can be soil cultivation or fertilization.[137] The complete wastewater treatment process from effluent pre-treatment to sludge dewatering is presented in Figure 13.

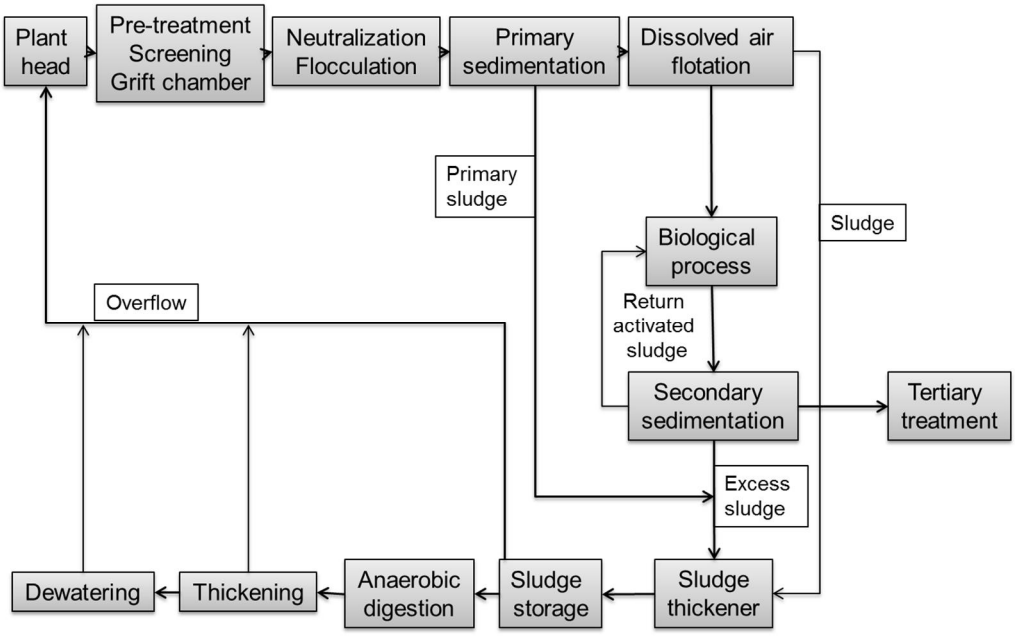


Figure 13. The complete wastewater treatment process from effluent pre-treatment to sludge dewatering.[135]

4.3 Foam forming

Foam is used in a diverse industry fields due to its useful rheological and mechanical properties. In addition to viscoelastic behaviour of liquid foams they are also able to flow and deform like a liquid. Air bubbles are utilised in wastewater treatment and mineral flotation processes. For example, paper industry uses flotation processes for ink removal from the newspaper. Foam is also a good carrier material for different agents. Textile industry exploits foams in a fabric finishing processes where dyes and chemicals are mixed with foam and applied to a textile. Dye colours migrate smoothly with foams and drying is faster and less energy consuming than with a liquid based carriers. Other applications can be found in cosmetics, oil recovery, multilayer laminates and composites.[7]

Paper industry uses wet web forming in a paper making process. Fibres and other components of paper are mixed with a large amount of water and transferred from the head box to the web of the paper machine forming section. In the water forming method, a dilute suspension of water and fibres is essential since fibres tend to pile up, tangle, curl and flocculate which leads to non-uniformity of the paper sheet and loss of quality and mechanical properties. However, the water forming method is very usable when short and stiff cellulosic fibres are used even though the water consumption is high and a lot of energy is needed for the drying section.[7]

The technique, where foam acts as a carrier for fibres was developed and used first time in 1970's. The technique was named the Radfoam process after its inventor Ben Radvan. The method is based on an idea that the fibres readily bind to foam bubbles. 0.75 % - 1 % of fibres (w/w) are suspended in a foam containing 60 % - 70 % of air and applied on the wire of the paper machine through the head box. Foam generation is done with a surfactant which is added to the water-fibre suspension and air is injected into the solution until the desired volume is achieved. The bubbles forming the foam suspension are usually 20 μm – 100 μm in diameter and foam is pseudoplastic. Foams high viscosity at low shear forces and low viscosity at high shear forces guarantee that the fibres are attached to the bubbles and do not move across each other until the suction boxes remove the water and the foam collapses, and fine fibre dispersion is achieved.[138]

Replacing water with foam could decrease the water and energy consumption, thus making the process more cost-effective. The more diverse range of raw materials could be used, including long fibres, and there would be no need for retention chemicals. Foam forming can produce papers sheets of a higher uniformity and bulk comparing to wet web forming, yet the strength properties are better with water-laid sheets. Again it is possible to regain the strength loss with wet pressing. Another way to improve strength properties is to add micro-fibrillated cellulose (MFC) to the foam-fiber suspension.[138,139]

4.3.1 Surfactants in foam forming

In spite of successful research work in the 1970's the foam forming method did not pique any interest until several decades later. The need for more cost-effective and diverse techniques for paper and board making has awaken the foam research. Development of new paper products made of new raw materials, including nanoparticles, nanocellulose and long fibres, need a sophisticated manufacture technique and foam method could provide that. Yet, many technical and production challenges need to be settled before the technique can be fully implemented.[138,139]

Surfactants are one keen interest of the foam research. The surfactant used in the first experiments done in the 1970's was not revealed in the articles. Research now focuses on the influence of surfactants in foaming properties of fibre suspensions and chemical interactions between surface active agents, fibres and other papermaking materials.[138,139]

According to the latest research published in 2014 [Mira, Lappalainen] the foaming properties of a mixture of commonly used CTMP pulp and a surfactant was dependent on the surfactant concentration. One of the surfactants investigated was SDS (sodium dodecyl sulfate) and the experiments showed that both the foamability and the liquid drainage rate altered according to the SDS concentration. Critical micelle formation of SDS was not affected by the fibres or other filler chemicals, but the foam generation and the liquid drainage rate was slower and lesser than in pure water-SDS solutions. Also, the foam generation of SDS-CTMP suspension stops when the concentration reaches 0.5 x

CMC. One possible explanation for these findings is that fibres and additives in the SDS-pulp suspension are physically interfering the adsorption of SDS molecules on the surfaces of gas bubbles and slowing down the liquid drainage rate.[138]

Also other surfactants, such as MixSAES (a mixture of alkyl and ethoxylated alkyl sulfates) and C8/C10Gluc (a mixture of short chain alkyl glucosides), were tested in the experiments. Results showed that the foamability cannot be entirely explained by surfactants properties like ionic character, critical micelle concentration or structure of the hydrophilic head. The foamability is more likely an effort of rightly proportioned mixture of surface active agents with the suitable molecular structures. In spite of these conclusions, anionic surfactants seemed to be most effective agents in foam generation.[138]

The effect of surfactants on the mechanical properties and quality of the paper was also investigated. It was observed that paper samples made of foam-pulp were bulkier and had a better formation than normally formed paper made of water-pulp. Different foaming agents had differing effects on the bulk, and the formation was particularly affected by ionic surfactants. Tensile strength (the in-plane mechanical properties) was almost the same between foam and water formed samples, but out-of-plane properties (Scott bond delamination energy) were considerably lower. Delamination properties are important factors for the grade and functionality of the board. Dryness achieved by wet pressing was better with foam formed samples than water formed samples and influence of different surfactants was notable. Retention of filler chemicals was better with non-ionic surfactants than anionic surfactants.[139]

5 FOAMING PROBLEMS AND ELIMINATION OF FOAM

This chapter covers the foaming problems of a modern pulp and paper industry process waters and effluent waters of wastewater treatment plants (WWTPs). Also, the foam elimination methods, including defoamers and different physical techniques, are covered briefly.

5.1 Foaming in the pulp and paper industry

The consumption of defoamers in pulp and paper industry is one of the largest in the world. 160,000 tonnes of defoamers were consumed in 1990. Paper making, all away from dispersion of wood to the proper paper, requires dozens of different chemicals in pulping, bleaching, process control and paper modification.[140]

In chemical pulping, the largest volumes of defoamers are used after cooking in the washing step of unbleached pulp. Careful washing of the pulp ensures efficient bleaching and reduces extra chemical consumption. Antifoamers are added to prevent the foaming that can hinder the washing process. In mechanical pulping pulps are not washed. Screening and cleaning is done, but the foaming problems are not that severe than with chemical pulping. In the paper mill different additives are added in the pulp slurry depending on the final paper type. Many of these additives tend to foam or stabilize it. All the wet stages of paper making process are prone to foaming that is not desired since it affects the quality of the final product.[140]

The pulp contains surface active agents in the lignin and wood resin fractions and, in the washing step, where water and the air is mixed with the pulp the foaming is inevitable. In the paper mill, chemical additives (e.g. retention aids, wet strength resins, dyes) increase the surfactant load. Many of these are not actual surfactants but can stabilize foam when formed. Foam can generate a floating raft on top of a stock surface or from small foam bubbles inside the liquid bulk and adhere to the solids of the stock. Floating foam is more easy to observe and handle than the internal foam.[140]

There are several problems that are encountered with the excessive foaming. Foam tends to clog pumps and tanks reducing output and capacity of washers, refiners, mixing tanks and bleaching towers. Foam binds solids, fibres and fillers reducing the material volume of the pulp. Foam also cause a mess and can be a safety hazard. Dried foam on the tank or vessel walls can contaminate the pulp. In the paper mill, the foam softens the pulp and reduces the efficiency of beater and refiner. In the paper machine foam causes channeling and reduces drainage. Paper sheet gets marked or even thinned as the foam bubbles break in the fibre web thus affecting greatly on the paper quality. The foam is also harmful to paper coating since bubble spots make it heterogeneous.[140]

5.2 Foaming problems at WWTP

Foaming in activated sludge treatment of wastewater is a familiar problem in many wastewater treatment plants (WWTP). Foam can occur in the aeration tank, secondary clarifier and also in an anaerobic digester. Foam accumulates on the tank surfaces and binds solids and other material from the effluent, thus reducing its quality and degradation of organics. Large volumes of foam can overflow the tank and clog gas systems and cause problems to operation and environment.[141]

Unwanted foaming can be caused by hydrophobic sludge particles, slowly degrading surface active agents or a large amount of easily foaming exopolymers or hydrophobic filamentous organisms in combination with a gas supply (aeration) of the tanks. Generated foam is brown, sticky, very stable and hard to destroy. Especially hydrophobic filamentous bacteria (e.g. *Candidatus Microthix parvicella*, *Mycolata*) are associated with the foam stabilizing in WWTP. Due to their hydrophobic character, they readily bind on hydrophobic surfaces, such as grace, oil and fat (lipids, long-chain fatty acids) and consume them as a food supply. Thus, they are also useful to the process.[141,142]

Suppression of the foam or its control can be achieved by various methods having very different efficiencies. Strategies like, sludge load increase, floating sludge removal, sludge age reduction (to wash out foaming bacteria), separate stabilization of surplus sludge, mechanical destruction of foam (mixers), thermal or mechanical pre-treatment

of surplus sludge (cell disintegration), the addition of selectors or defoaming (antifoaming) agents or chlorination. Some methods have limitations, for example, sludge age reduction (to wash out foaming bacteria) usually results in failure in nitrification that requires 10 days or more to succeed. In that time, foaming bacteria is able to grow the stable population. Chlorination kills filamentous bacteria but also protozoa and nitrifying bacteria and interferes the activated sludge process.[141,142]

One proposed foaming control strategy is the prevention of seeding of filamentous bacteria through recycle stream returns. Elimination can be achieved by capturing a high volume of solids in activated sludge treatment process. Chemical precipitation of foaming agents (including filamentous bacteria) using polyaluminum chloride (PAX) can reduce 75 % of the sludge foaming potential. Foaming bacteria get trapped inside the formed flocs of PAX and solids and are removed with the excess sludge. Also, mechanical removal of foam (foam and scum harvesters) has found to be effective. Outlets for foam can be applications like trial bell mouth scum withdrawal or tipping scum pipe.[141] Foam has a poor rheological character but mixing the foam with, for example, secondary effluent, its viscosity can be reduced significantly.[143]

Investigation of enzymatic, mechanical and thermal cell disintegration as pre-treatment of surplus sludge has revealed that the foam in anaerobic digester can be destroyed efficiently with thermal (121°C) treatment. Heat is used to destruct cell membranes of micro-organisms and also exo-polymers that readily cause foaming.[142]

5.3 Foam elimination methods

Unwanted foam can be eliminated by chemically with antifoamers or by physical methods which include thermal temperature control or various mechanical methods, such as sonic defoaming, liquid sprays or foam breakers (centrifugal basket and rotating disk). In cases when antifoamers can be a contamination risk or can prevent refoaming, the mechanical methods are applied. Mechanical methods are also used with heat-sensitive materials that cannot tolerate thermal treatments.

5.3.1 Defoamers

Defoamers, or antifoaming agents, are used to reduce undesirable foaming. In some cases, the replacement of the surfactant with a poorer foamer can help to diminish the foam volume. If the replacement is not effective enough or the foaming is caused by another component that are not surfactants, the antifoaming agents can be added into the solution. Antifoaming agents work by transferring the surface active agents from the interfacial surfaces back into the liquid phase. For example soil particles and hydrophobic silica can adsorb and transfer surfactants between phases. Hydrophobic particles also tend to form lenses at the Plateau borders of the foam thus destabilizing the foam structure by enhancing dewetting.[6]

Another way to reduce foam is to remove the surfactant film on top to the liquid surface by displacing it with poorly foaming molecules. These molecules need to be rapidly diffusive, non-cohesive and not totally soluble in the solution. Substances, like tertiary acetylenic glycols, reduce the surface tension and the elasticity of the solution so that the bubbles break instantly back to the solution. Foaming can also be prevented by reducing surface viscosity. For example, tributyl phosphate intercalates into the surfactant layer and interferes the cohesive forces between the surfactant molecules. Thus, the surface viscosity lowers, and foam drainage accelerates leading to collapse.[6]

5.3.2 Physical methods

Thermal treatment of the foam comprises temperature changes. At high-temperature foam tend to collapse due to decreased viscosity of the surface, solvent evaporation and chemical degradation of the foaming agent. A low-temperature surface elasticity decreases or freezes unstabilizing the foam structure. Heat collapse of the foam can be done using hot wire placed over the foam solution, wrapping a heat tape around a foam container, passing hot steam or water on top of the foam or by reducing the temperature.[144] Heat treatment can be applied, for example, in wastewater treatment plant (WWTP) to eliminate undesired foaming of the sludge digester.[142]

Liquid spraying uses strong liquid and sprayers to collapse foam. Impact, compression and shear forces destruct the foam structure and cause the collapse. Foam can be sprayed, for example, with pure water which in addition to mentioned physical effects also dilutes the foam solution and instabilizes the foam. The addition of antifoamers into the spray solution further enhances the collapse process. Liquid spraying is applied in many WWTPs for foam control.[144]

Mechanical foam beakers expose foam under rapid pressure change or shear, compression or impact force. Whirling paddle, or rotating rod, is a foam breaker used mainly for dry foams. Rotating rod breaks the foam with impact and shear forces. The centrifugal basket can be used for large amounts of wet and stable foams. Centrifugal foam breaker is made of a metal bowl of mesh screen that spins inside an overturned bottle and breaks the foam with pressure change and shear forces. In orifice foam breaker the foam is drawn through an orifice using a vacuum that generates a pressure change breaking the foam.[144] Different mechanical foam breakers pictured in Figure 14.

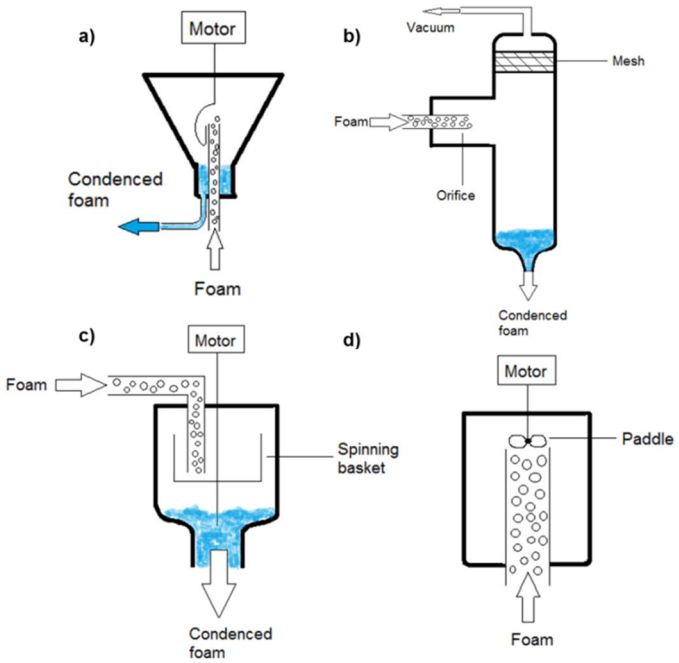


Figure 14. Mechanical foam breakers. a) bent rotating stirring rod, b) orifice, c) centrifugal basket, d) whirling paddle.[144]

Sound (< 20 kHz) and ultrasound (> 20 kHz) can be used for foam elimination. Sonic defoaming crates acoustic pressure, the resonance of the bubble and cavitation of the liquid film causing foam collapse. Sound wave reflection can be done from the surface or inside of the foam. Sound frequency, pressure and viscosity of the liquid have an effect on the efficiency of the foam destruction.[145] Ultrasounds enhance the foam collapse but affects the liquid drainage rate only at the top of the foam layer.[146] Foam elimination by sound created by a loudspeaker revealed that sound caused detaching of small droplets form the surface of the foam layer and inside the foam a strong cavitation.[147]

6 SURFACTANT REMOVAL METHODS

Removal of surfactants from environmental water and wastewater can be done with different kind of removal methods that can be divided into degradation and separation methods (Figure 15). Degradation methods include biodegradation by microbes, photo-catalytic degradation and electrochemical oxidation. Separation can be achieved with adsorption or chemical precipitation/flocculation, where surfactant in the influent is transferred into a sludge, or with membrane technologies and foam fractionation, where influent is divided into two separate sections with different surfactant concentrations. The removal efficiency of the methods can be confirmed by determining the surfactant concentration of the water sample (Chapter 3.) or by measuring the amount of organic material in the water sample using TOC, COD and BOD tests.

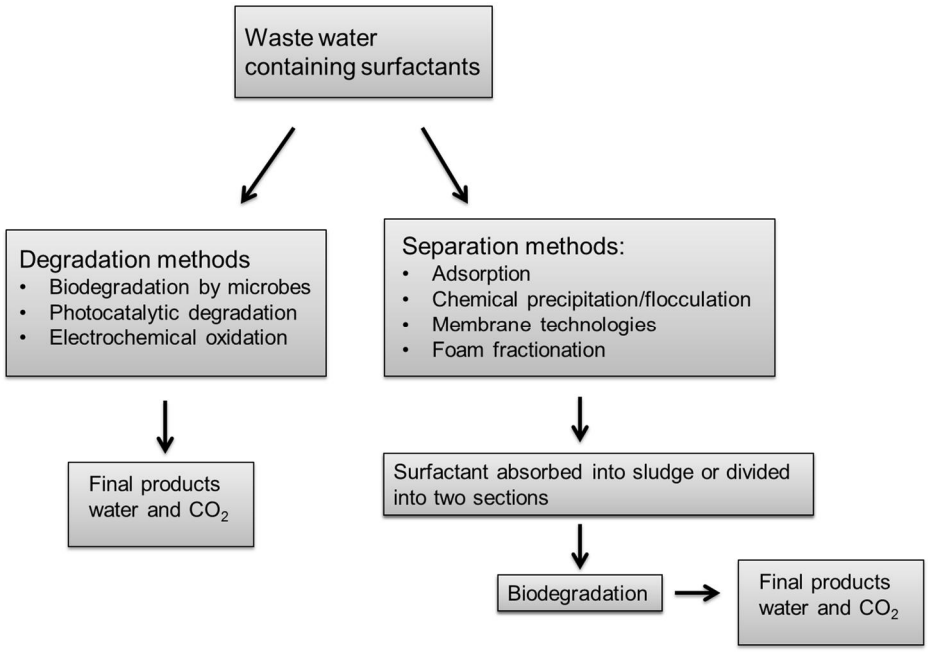


Figure 15. Surfactant removal methods.

6.1 TOC, COD and BOD tests

Removal of organic material and surfactants and quality of the water is often confirmed with simple analytical methods. Total organic carbon (TOC) is the amount of carbon in an organic molecule and can be used as a water quality indicator. In water analysis, TOC is an alternative option for the classical water quality measurement methods, biological oxygen demand (BOD) and chemical oxygen demand (COD). TOC measurement is done with TOC analysers that determine the total carbon (TC) content of the sample. The measurement involves two stages. First the total carbon content of the sample is measured and second the dissolved inorganic carbon (DIC) content is measured. TOC can be calculated form the results by subtracting the value of inorganic carbon form the total carbon content. Determination of TOC done by the analyser is quick and accurate.

TOC can also be determined without TOC analyser. Equation 14 shows definition of total carbon (TC)

$$\boldsymbol{TC = DOC + PC + DIC} \qquad (14)$$

where DOC is dissolved organic carbon, PC is particulate carbon and DIC is dissolved inorganic carbon (CO, CO_2, H_2CO_3). The procedure involves three steps. First the PC is removed by filtration (0.45 µm membrane). DICs can be converted into carbon dioxide with pH adjustment (pH 2) and then inert gas (nitrogen) is used to displace the CO_2 from the solution. The remaining carbon content is determined by first combusting the sample (> 680°C) and detecting the formed CO_2 with infrared detector.[148,149]

The biological oxygen demand (BOD) describes the consumption of oxygen by microbiological metabolism in water environment as they degrade organic material in a defined time period and at a certain temperature. BOD values are commonly presented oxygen consumption (mg) / litre of the sample, the incubation time is 5 days and temperature 20°C (symbol BOD_5). Chemicals (sanitizers, biocides) present in environmental/wastewater may reduce or inhibit microbiological activity and affect greatly on the BOD values. BOD_5 value measured from untreated wastewater in Europe is around 600

mg/L. Natural rivers should have BOD5 value below 1 mg/L, higher values indicate pollution.[148,149]

The chemical oxygen demand (COD) describes the amount of organic material in a water sample. In the COD test all organics are oxidised into carbon dioxide (CO2) using strong a strong oxidizing agent (potassium dichromate $K_2Cr_2O_7$) under acidic conditions. In practice, an excess of oxidizing agent is added into the sample, and the remaining agent is then determined by titration or spectrophotometer. A large amount of oxidizable inorganic compounds can disturb the results. BOD_5, COD, and TOC values are related and the BOD_5/COD ratio is often used to describe the biodegradability level of organic material in environmental- or wastewater. However, the correlation between BOD_5, COD, and TOC values depends on the location. Thus, the relationship should be established before drawing conclusions from the results.[148,149]

In general, the BOD_5/COD ratio ranges between 0-1. BOD_5/COD ratio less than 0.1 indicates high volumes of poorly biodegradable organic material and is classified as a toxic zone, which is harmful to living organisms. The biodegradable zone is between 0.1-1.0 and can be divided into low, moderate and highly biodegradable areas. BOD_5/COD ratio > 0.4 indicates the presence of thoroughly biodegradable organics. If the BOD_5/COD ratio of wastewater is below 0.1 it needs to be treated with suitable removal method of organic material (discussed below) to achieve BOD_5/COD level suitable for the microbial activity. After this, wastewater can be released into the environment. Wastewater quality standards vary between countries and different factories. Example limits of forest industry WWTPs discharges in Finland are COD 2-9 tons/day, phosphorus < 20 kg/day and nitrogen < 150 kg/day depending greatly on the factory.[148,149]

6.2 Separation methods

Separation of surfactants from wastewaters can be done with adsorption or chemical precipitation/flocculation, where surfactant in the influent is transferred into a sludge, or with membrane technologies and foam fractionation, where influent is divided into two separate sections with different surfactant concentrations.

6.2.1 Chemical precipitation/flocculation

The chemical precipitation/flocculation process has been found to be a very efficient method for removal of organic pollutants and, in addition, is simple to perform, selective and cost-effective.[3] In chemical flocculation the organic matter is sedimented out of solution and the solid precipitate is separated from the liquid phase. Precipitation is initiated by a coagulant agent which, suspends small particles in solution and gathers them into large flocculates.[150]

Coagulants are generally polymers with long carbon chain and high molecular weight. Polymers can be synthetic or from natural origin and are characterised by their charge (anionic, cationic or nonionic). Due to the electrical quality of the coagulants they can neutralize particles or form bridges between dissolved materials in the solution. Table 7 lists the most commonly used coagulation agents.[150]

Precipitation of anionic surfactants is best performed by trivalent cations Al_3^+ and Fe_3^+ due to the electrical attraction between the anionic head of the surfactant and positive coagulant. In addition to precipitation mechanism, and adsorptive micellar flocculation (AMF) is another removal method of surfactants. In AMF cation coagulant binds to a surfactant micelle causing repulsion suppression between micelles which leads to flocculation and removal of surfactant micelles as aggregates.[151]

Talens-Alensson *et al.*[151] studied $Fe_3(SO_4)_3$ and $Al_2(SO_4)_3$ in AMF of SDS. Aluminium sulfate ($Al_2(SO_4)_3 \cdot 14H_2O$) was found to be more efficient in the precipitation process but is also more expensive compared to iron compounds (ferric sulfate $Fe_2(III)(SO_4)_3$, ferric chloride $FeCl_3$ and ferrous sulfate $Fe(II)SO_4$). There has also been some anxiety

for the use of Al_3^+ in water treatment processes since aluminium is suspected to be an exposing factor for Alzheimer's disease.[151]

The amount of coagulant and solution pH need to be adjusted to get the best results. Aboulhassan *et al.* [3] treated wastewater samples containing an anionic surfactant (ammonium nonylphenol ether sulfate) with ferric chloride. 900 mg/l of $FeCl_3$ at pH range 7-9 was needed to get 88 % COD removal and 99 % surfactant removal. BOD5/COD ratio of the wastewater increased from 0.17 to 0.41.[3]

Adak *et al*. used alumina (Al_2O_3) for precipitation of anionic sodium dodecyl sulfate (SDS) in laundry wastewater. Initial SDS concentration was 8068 mg/l and 94 % removal efficiency was achieved with coagulant dose 120 g/l at pH 5.5. SDS removal by Al_3^+ with respect to time was found to follow the pseudo-second order reaction model.[18]

Vanjara & Dixit precipitated cationic quaternary ammonium compound (cetyl pyridinium chloride CPC) using anionic iodide (I^-) forming a low solubility iodine salt. CPI was transferred back to chloride salt using $CuCl_2$ with 85 % of recovery.[152] Nonionic surfactants, in general, adsorb readily onto the soil particles by hydrophobic interactions forming surface micelles or surfactant bilayers on the soil surface. Thus, soil particles become hydrophobic and coagulate form the solution.[153]

Table 7. Coagulation agents most commonly used[150]

Coagulation chemical	Description	Characteristics
Aluminium sulfate - $Al_2(SO_4)_3 \cdot 14H_2O$ (Alum)	Coagulation of anionic surfactants. Used also water softening and phosphate removal chemical. Reaction with alkaline compounds, like carbonate, bicarbonate and hydroxide, forms low solubility aluminium salts.	Water soluble, white crystal as solid. Forms acidic conditions when dissolved. Can be applied both solid and liquid (50 % solution).
Ferrous sulfate - $Fe(II)SO_4$ and Ferric sulfate - $Fe_2(III)(SO_4)_3$	Coagulation of anionic surfactants. The combination with lime forms insoluble calcium sulfate and ferric hydroxide and can be used for water softening.	Acidic solutions
Ferric chloride - $FeCl_3$	Coagulation of anionic surfactants. Forms insoluble iron salts.	Can be applied both solid (hydrate or anhydrous) or liquid (35-45 % solution) form. Highly corrosive chemical.
Polymers	Coagulation of anionic, cationic and nonionic surfactants. Synthetic, high molecular weight compounds. Act as a neutralizer, emulsion-breaker, or bridge-maker depending on the electrochemical characteristics.	Can be applied both solid (dry powder) or liquid form.
Calcium oxide - CaO (Lime)	Forms calcium carbonate in solution containing organic material and coagulates particulate matter and water hardness (calsium and magnesium). Used in combination with other coagulant agents.	Usually applied as dry form (quickline CaO or hydrated lime $Ca(OH)_2$).

6.2.2 Adsorption

Adsorption is a removal method of organic compounds that does not involve any chemical reactions but the separation is achieved by physical interactions between an adsorbent material and a target analyte. Adsorbents are usually materials with high porosity and large surface area. Removal happens when the surfactant containing wastewater flows through the adsorbent pores and adheres on the surface. Interactions between the adsorbent and surfactant can be hydrophobic (by hydrocarbon tail of surfactants) or electrostatic (by ion head of surfactant). Thus, the pH of the water needs to be con-

trolled. For example, alumina surface gets positively charged at pH below the zero point charge (Z_{PC}) and adsorbs anionic molecules. With uncharged surfaces (at pH Z_{PC}) hydrophobic interactions are in the main role.[154, 155]

After the surfactants are removed from the wastewater further actions can involve adsorbent regeneration, disposal to landfill or destruction in combustion (sludge disposal in chapter 4.2). Absorbent materials, such as activated carbon, activated alumina, silica gel, rubber granule, wood charcoal, granite sand, chitosan and sawdust have been tested for surfactant removal, activated carbon and alumina being the most used materials. Activated carbon has a superior adsorbent characteristics compared to other materials and is also toxic resistant. Regeneration can be done with steam, thermal or physical/chemical treatment methods.[156]

Anionic surfactants can be removed with neutral or positively charged alumina. Alumina can also be used in chemical precipitation. Removal is achieved through electrostatic interaction between positive surface and negative head groups of surfactants. Also hydrophobic interactions occur in higher surfactant concentrations, as they form bilayer structures. 94 % removal of surfactants is possible by alumina in the presence of high dissolved solids (TDS), which enhance the absorption process. Regeneration of alumina is achieved with NaOH solution.[18]

However, activated carbon and alumina are not that cost-effective. Rubber granule[157] and granite sand[154]have been tested as additional absorbent materials with removal efficiencies 96.5 % and 70 %, respectively. There is also growing interest towards biosorbent materials and more green removal methods. Soni *et al.*[156] studied the removal of sodium dodecyl sulfate (SDS) by the seeds of *Ponganmia pinnata* and achieved 80-96 % removal at pH around 3. Modified sawdust has been tested in the removal of anionic dyes[158] and purification of brewery industry wastewater.[159] Keränen *et al.*[160] prepared anion exchangers made of sawdust of different tree species with quite promising results and Paria *et al.* [161] studied anionic and non-ionic surfactant absorption of the cellulosic surface.

6.2.3 Membrane technologies

Membrane filtration of wastewater divides the incoming effluent into retentate and permeate. Separation is achieved with semi-permeable membranes that are able to retain solids and high molecular weight compounds but is permeated by the solvent and low molecular weight particles. Filtration process can be dead-end or cross-flow (Figure 16). In the dead-end process, the incoming fluid comes from the vertical direction to the membrane and in cross-flow the fluid direction is tangential. Dead-end membranes are easily fouled so conventional pre-filters (cartridge, bag filters) are used to remove the largest particles. In the cross-flow system, the shear rates of the fluid prevent the fouling of the membrane.[111,162]

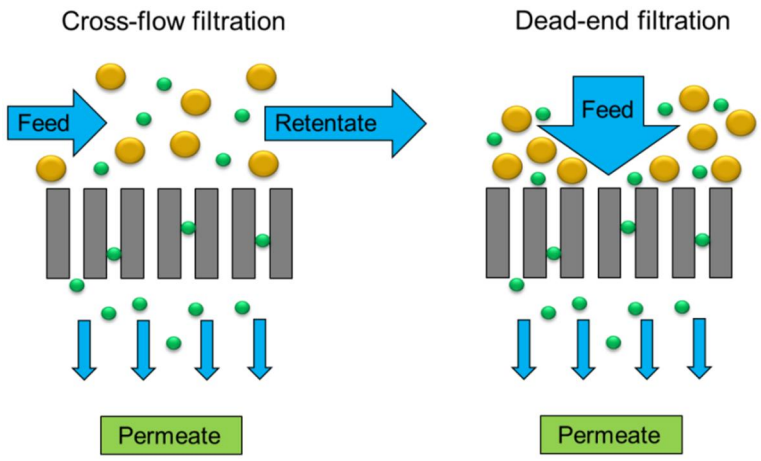


Figure 16. Configurations of cross-flow filtration (left) and dead-end filtration (right).[166]

The permeability of the membrane is dependent on of the membrane characteristics (pore size), process conditions (pressure, temperature) and wastewater composition. Filter membranes can be divided into four different categories based on their filtration capacity. Categories are microfiltration, ultrafiltration (UF), nanofiltration and reverse osmosis (Table 8). Low molecular weight molecules, like anionic sodium dodecyl sulfate SDS (MW 288 g/mol, 0.3 kDa) can be filtrated only with nanofilters or reverse osmosis. However, surfactants tend to form micelles as the concentration rises above CMC. Micelles, formed of 10 to 100 molecules, can have a molecular weight 50 times greater than a single molecule (MW of SDS micelle 14.4 kDa). Thus, the ultrafiltration process is also possible. [111,162]

Table 8. Filter membrane categories, membrane pore sizes, MWCOs and transmembrane pressures. MWCO is the molecular weight cut off (in Daltons) and is defined as the minimum MW of a spherical molecule that is retained to 90% by the membrane[134]

Category	Membrane pore size	MWCO	Transmembrane pressure
Microfiltration (MF)	> 0.1 µm	> 5000 kDa	< 2 bar
Ultrafiltration (UF)	2 - 100 nm	5 – 5000 kDa	1 - 10 bar
Nanofiltration (NF)	1 - 2 nm	0.1 - 5 kDa	3 - 20 bar
Reverse osmosis (RO)	< 1 nm	< 100 Da	10 - 80 bar

There have been done several studies about ultrafiltration of surfactants. For example, Kowalska *et al*. studied separation of anionic SDS by UF-membranes made of polyethersulphone (PES) and polysulphone (PS).[111] They also tested vide range of different UF-membranes (regenerated cellulose and PES) in a treatment of detergent containing wastewater.[163] Fernandez *et al.*[164] investigated ceramic membranes in ultrafiltration of anionic (SDS) and non-ionic (Tergitol NP-9) surfactants.

Micellar-enhanced ultrafiltration (MEUF) uses a UF-membranes and surfactants in the removal of heavy metals (cadmium, zinc), toxic organics (phenol) and low molecular weight impurities (dyes).[162] General representation is shown in Figure 17. Aoudia *et al*.[165] used anionic and non-ionic surfactants and MEUF in the removal of multivalent metal ion (Cr_3^+).

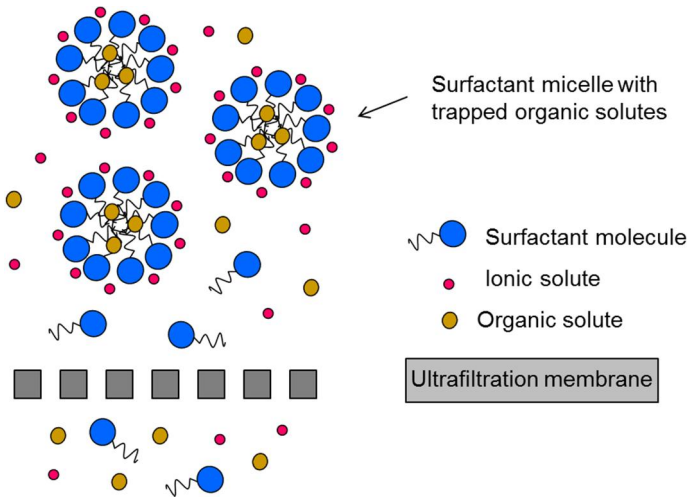


Figure 17. General representation of micellar-enhanced ultrafiltration.[162]

6.2.4 Foam fractionation

Foam fractionation is a specific separation and collection method of surfactants and utilizes the surfactants easy foaming behaviour. Foaming is caused by blowing gas into the surfactant containing water. Formed bubbles rise on top of the container and foam starts to dry do to drainage of liquid back to the water phase. Concentrated foam overflows the container, collapses and the foamate is collected. Thus, the recovery of surfactant is possible in some extend.[167,168] Figure 18 shows the principles of foam fractionation.

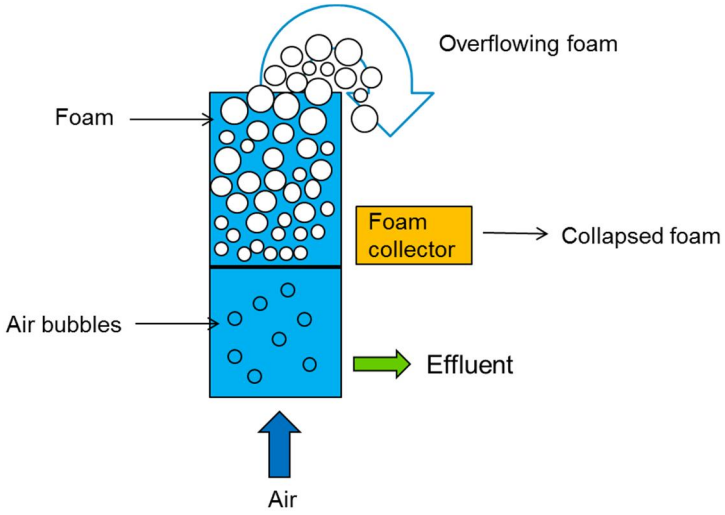


Figure 18. The principle of foam fractionation. Air is blown into the surfactant containing water. Formed bubbles rise on top of the container with surfactants attached to the gas-liquid interface of the bubbles and generate foam. Overflowing foam is collected and collapsed foam is analysed. [167]

Boonyasuwat *et al.*[168] studied the recovery of a cationic (cetylpyridinium chloride, CPC) and an anionic surfactant (sodium dodecyl sulfate, SDS) from water by multistage foam fractionation (figure 20) in a bubble-cap trayed column and concluded that raising the air flow the surfactant recovery increases while enrichment ratio decreases. Higher foam, on the other hand, decreases the recovery but gives a better enrichment ratio. In the multistage separation, the foam high do not carry that much relevance. When increasing the surfactant concentration the enrichment drops and recovery increases. Also, the cationic CPC gave better recovery rates than anionic SDS. Comparison between a

single-staged and multi-staged foam fractionation revealed that multi-stage fractionation increases enrichment of the surfactants.

6.3 Degradation methods

Degradation methods include biodegradation by microbes, photocatalytic degradation and electrochemical oxidation. Biodegradation by microbes is a commonly applied method for surfactant removal in WWTPs. Photocatalytic degradation uses ultraviolet (UV) or sunlight with a suitable photocatalyst to destruct surfactants and other organic molecules in wastewater, and electrochemical degradation uses electric current and electrodes posited in a surfactant containing solution to oxidise them into carbon dioxide.

6.3.1 Biodegradation

Surfactant biodegradation, toxicity and effect on the environment have been discussed in chapter 2.3. In this chapter, the focus is on general aspects of surfactant biodegradation tests and how surfactants can be considered as one removal method of wastewater treatment plant (WWTP).

Organic molecules are enzymatically broke down into CO_2 and water by microbes, and this process is called biodegradation. Degree and efficiency of the degradation is strongly dependent on the used test method and analytical measurement technique (BOD, COD, TOC). Monitoring surfactant biodegradation in the environment is an important issue. However, biodegradation can also be considered as one removal method of surfactants from wastewater. In the process surfactant molecules are transformed into biomass and the formed sludge is then disposed by the WWTP.[8]

Biodegradation tests give good estimations of biodegradation behaviour of the target analytes in a certain environment. The test conditions must be standardized and factors, like material concentrations, nutrients and toxic effects, must be taken into account. Also, microbes are living organisms and do not always behave as they are expected.

Full degradation of surfactants always requires a culture of mixed microbes. One strain of bacteria cannot fully decompose all molecules.[8]

Standardized OECD and International Organization for Standardization (ISO) methods for surfactant biodegradability surveillance are listed in Table 9. ISO 7827 and OECD 301 A involve methods for determination of complete biodegradation in water environment by incubating samples for 28 days and measuring DOC (dissolved organic carbon). Zahn-Wellens Test (OECD 302 B) is a similar method as ISO 7827 and OECD 301 A, but due to larger biomass volumes, it resembles more real life WWTP. Another simulations of WWTP technique are The ISO 11 733 and OECD 303, which uses continuous flow and activated sludge.[8]

The activated sludge process used in WWTPs is transforms organic material into CO2 and water in aerobic conditions generating new biomass. Intermittent Cycle Extended Aeration System (ICEAS) is a modified activated sludge process where influent wastewater goes through the cycles of react, settling and decant non-stop. Oxidation, nitrification, denitrification, phosphorus removal, settlement and sludge stabilization is included in a single reactor. Mortazavi el al. [170] studied ICEAS in the removal of anionic sodium dodecyl sulfate (SDS) from wastewater and managed to achieve 98 % removal of SDS. Some foaming problems were observed with high concentrations (> 100 mg/l).

The recent development of WWTPs, including design and construction as well as the proper wastewater treatment, have enabled vary high surfactant degradation efficiency (90-99 %) with a wide variety of surfactants. These figures are achieved in aerobic conditions. Like mentioned, surfactants possess and amphiphilic character and readily bind on the surface of particles of the wastewater. Also, other wastewater treatment methods, such as chemical precipitation followed by sedimentation, can result that aerobic degradation is prevented.[8]

Anaerobic biodegradation uses alternative electron acceptors in the place of oxygen when transforming organic compounds into nitrogen gas (N_2), hydrogen sulfide (H_2S), ammonia (NH_3) and methane (CH_4). Degradation reactions in anaerobic environment differ from the aerobic degradation reactions and are not yet well studied. General observations are that most surfactants are poorly biodegradable in anaerobic conditions.

Exceptions are sulfated anionics, fatty acids and soaps that seem to degrade well despite the lack of oxygen.[8]

For example, Wyrwas *et al.* [171] studied continuous flow biodegradation process in the removal of non-ionic octylphenol ethoxylates (Triton X-100, Triton X-15) and octylphenol. 90 % of Triton X-100 degraded within 36 h in both aerobic and anaerobic conditions. Triton X-15 degraded over 90 % in aerobic conditions but only 35 % in an anaerobic environment. Same happened with octylphenol which was consumed totally by microbes in aerobic condition within 32 h but in anaerobic condition only 20 %.

Table 9. OECD and ISO standards for biodegradation tests. [8]

Test method	OECD Guideline	ISO Standard
DOC Die-Away Test	301 A	7 827
CO_2 Evolution Test	301 B	9 439
Modified MITI Test (I)	301 C	-
Closed Bottle Test	301 D	10707
Modified OECD Screening Test	301 E	7 827
Manometric Respirometry Test	301 F	9 408
Modified SCAS Test	302 A	9 887
Zahn-Wellens/EMPA Test	302 B	9 888
Modified MITI Test (II)	302 C	-
Aerobic Sewage Treatment: Coupled Units Test	303	11733
Inherent Biodegradability in Soil	304	-
Biodegradability in Seawater	306	-
Test Guidance for Poorly Water-soluble Substances	-	10634
Anaerobic Degradation Test	-	11734
Two-phase Closed Bottle Test	-	10708
Biodegradation Test at Low Concentrations	-	14 592
CO2 Test in Sealed Vessels	-	14 593

6.3.2 Photocatalytic degradation

Photocatalytic degradation uses ultraviolet (UV) or sunlight with a suitable photocatalyst, like titanium oxide (TiO_2), to destruct surfactants and other organic molecules in wastewater. Oxidation is an effective method to speed up surfactant biodegradation, which in normal circumstances can be rather slow.[172] Photocatalytic reaction can be carried out in a quartz reactor/tube. The reaction mixture of the photocatalyst and sur-

factants containing wastewater is then irritated with UV-light (e.g. xenon or mercury lamp). The suspension is continuously stirred and kept under atmospheric air. Photoexcitation of TiO_2 valence electrons creates electron-hole pairs, which generate free radicals from the water of dissolved oxygen (·OH, ·OOH) (Figure 19). Free radicals start to oxidise organic compounds, and the degradation can be monitored by measuring the generated carbon dioxide (CO_2).[173]

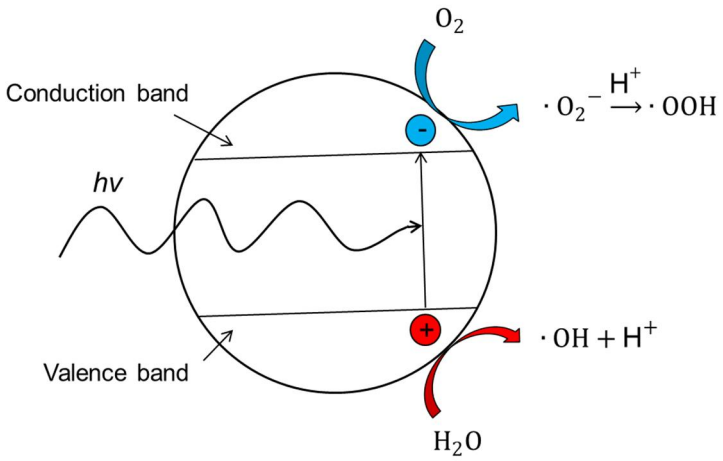


Figure 19. Generation of radicals on the TiO_2 particle.[173]

Ohtaki *et al.*[173] used oxidative mineralization and TiO_2 photocatalyst in degradation of various surfactants and observed deviating stepwise degradation in alkyltrimethylammonium surfactants. They also stated that halide anions have a strong inhibition effect on oxidation process. Also, water hardening ions interfere the degradation by radicals.[172] Terechova *et al.* combined coagulation/flocculation method with UV-photolysis in the removal of anionic LAS. They used mineral ash, $ZnCl_2$, and P-650 as coagulants, achieving approximately 70 % removal efficiency. Remaining surfactant was degraded by UV-oxidation, and they also stated that degradation was most efficient in alkaline environment.[174]

6.3.3 Electrochemical degradation

Electrochemical degradation uses electric current and electrodes posited in a surfactant containing solution to oxidise them into carbon dioxide. The positive electrode (anode) oxidises compounds in solution by removing electrons. Electrons flow to the negative electrode (cathode) that reduces compounds by donating electrons. Organic compounds can be oxidised indirectly using chorine and hypochlorite generated by the anode at high chloride concentration. Another indirect oxidation uses hydrogen peroxide. Direct anodic oxidation generates physically adsorbed "active oxygen" (adsorbed hydroxyl radicals •OH) or chemisorbed "active oxygen" (oxygen in the oxide lattice, MO_{x+1}).[175]

Anode materials can include, for example, dimensionally stable anodes (DSA), such as RuO_2 or ZrO_2 coated Ti, thin film oxide anodes (PbO_2, SnO_2), noble metals (platinum) and carbon-based anodes. New synthetic boron-doped diamond (BDD) thin film electrodes have received attention due to their particularly high efficiency to degrade organics. Lissens *et al.* [176] studied electrochemical oxidation anionic (sodium dodecylbenzenesulfonate) and cationic (hexadecyltrimethyl ammonium chloride) at a BDD (boron-doped diamond) electrode. Degradation was monitored by measuring TOC of the solution. They reached 82 % removal of surfactants and stated that alkaline pH enhanced the oxidation process.

Louhichi *et al.*[177] used the electrochemical oxidation on BDD-electrode of wastes waters containing surfactant sodium dodecylbenzenesulfonate (SDBS) and concluded that NaCl seemed to be most efficient electrolyte in surfactant oxidation monitored by measuring COD of the solution. Ciorba *et al.*[178] investigated an electro-coagulation process of anionic, cationic and non-ionic surfactants with an aluminium electrode and got a 40 to 60% COD removal.

SUMMARY

The character of surfactants; their effect on foaming, toxicity and biodegradation, is highly dependent on the surfactants structure (alkyl chain length and branching). Sodium dodecyl sulfate (SDS), an anionic surface active agent, is a common detergent in hygiene care and cleaning products due to its easy hydrolysis and rather environmental friendly nature, when compared to other surfactants. Its vide use has made it a popular research target and, is also used in experimental part of this thesis.

A wide variety of different surfactant determination methods are available and, again the surfactant structure determines the best technique for the analysation. Careful sample preparation can ease significantly the final separation and detection, even though the prepreparation methods usually consume more time than the actual instrumental analysis. Chromatographic methods are used for sample separation from impurities or other surfactants. Liquid chromatography, and its modifications, being the most used methods for both qualitative and quantitative analysation of environmental and wastewater samples.

Detector choice depends on the nature of the target compound, the sample matrix and the need for qualitative or quantitative determination. Mass spectrometry (MS) can provide exact results with high accuracy and ability to distinguish different homologues of surfactants, but is expensive and thus not suitable for routine analysis. Other detection methods, such as conductivity detection and evaporative light scattering, are not as accurate as MS, but still provide good separation efficiencies and can also be used for routine control.

Foaming can be a problem in a paper- and board mills and a wastewater treatment plants (WWTPs). Foam managing is mainly handled using antifoamers of physical removal methods. The presence of surfactants in environmental- and wastewaters increases the carbon load of the water. Surfactants need to be removed from the wastewater before the release back to the environment. A wide range of different methods using chemical-, physical- and biological techniques have been developed and provide an efficient removal rates for lager variety of surfactant classes.

EXPERIMENTAL PART

7 OBJECTIVES

The experimental part of this thesis is composed of three themed parts where anionic surfactant, sodium dodecyl sulfate (SDS), plays the leading role. The first part deals with the determination of SDS by high-performance reversed-phase liquid chromatography (HPLC-RP), combined with electrical conductivity detection (ECD)(Chapters 8.2, 10.2 and 11.1). The second part focuses on the development of accelerated aeration test (Chapters 8.3, 10.3 and 11.2). The third part deals with the removal of SDS by using a flocculation method (Chapter 8.4, 10.4 and 11.3).

Solvent extraction spectrophotometry[108,109,110] (here abbreviated SES) using cationic dye (e.g. ethyl violet) as a colouring agent, is one of the most used determination methods of anionic surfactants (Chapter 8.1 and 10.1). It is a simple, rather sensitive and cheap method for analysing the total amount of SDS in a sample. However, it also consumes large volumes of toxic organic solvents and sample matrix can easily interfere the results by alternating the volume of the colouring agent that transfers into the organic phase. Thus, another common but more sophisticated anionic surfactant detection method, high-performance reversed-phase liquid chromatography (HPLC-RP), was tested in SDS determination.[73,75,79]

SDS is known to hydrolyse rather easily over the time, and the process can be accelerated by heating and pH change.[29,30] Thus, the long-term storage of SDS solutions is doubtful. One week time monitoring test was performed to get information about the shelf life of SDS solution. SDS concentration was determined with both SES- and RP-ECD-methods. The accelerated hydrolysis of SDS would be an alternative removal method of SDS from wastewaters. SDS hydrolysis experiments by heating and pH change was performed to define optimal hydrolysis conditions.

The effects of additives (salts and retention aids) to SDS content of white water were examined with RP-ECD and SES-method and the results were compared to see if there are any significant differences. It was assumed that the SES does not distinguish intact

SDS from hydrolysed parts (free sulfate head), and positive interference may occur. White waters also contain large amounts of fibres and additives (salts and retention aids) that might disturb the results. RP-ECD was assumed to be able to distinguish hydrolysed parts of SDS from the intact molecule and determine the free SDS content of the samples. It is rather important to know the amount of free SDS (SDS in monomeric form) in the sample since only the free SDS can affect the surface tension and foam generation of a liquid.

In addition, during the SDS analysis by RP-ECD some problems occurred in sample purification and syringe filtration. Hence, tests with different filter membrane materials (GHP, nylon) and solid-phase extraction (SPE) method, were performed, and procedures and results are also included in this work.

SDS was not the only surfactant used as a foaming agent in foam forming. Miranol Ultra is an amphoteric surfactant and cannot be determined with solvent extraction spectrophotometry method. However, due to its imidazole based structure it can be detected with UV-detector (205 nm). Thus, RP-UV tests were carried out, including calibration curves and effect of salts and retention aids.

The second part of the experimental work focused on the development of laboratory scale measurement system for the analysis of foaming tendency of SDS containing wastewater during aeration. The aim was to imitate real aeration tanks of wastewater treatment systems in paper-, and board factories and observe how SDS addition affects the foaming behaviour of the samples in the WWTP aeration tanks.

Two criteria in the selection of air flow rate for the aeration tests was applied. Firstly, the air flow values at wastewater treatment plants (WWTP) were considered and secondly, the target was to develop an accelerated test (test period max 2-3 hours). Since the air flow rate in the real aeration tank is 0.5-1.5 m^3/h per 1m^3, it was calculated that the air flow rate should be at least 0.25 l/min in the laboratory vessel (water volume 10 l). According to preliminary laboratory tests, air flow rate 0.6 l/min, which corresponds to air flow rate 3.6 m^3/h at WWTP, was high enough to generate foam when the SDS concentration of white water sample was 50 ppm. Thus, 0.6 l/min was chosen for the

further experiments. When analysing water samples having low SDS concentration (< 50 ppm) air flow rate 1 l/min could be more useful.

The aeration procedure was generated based on the preliminary tests. Aeration time 1.5 h per sample and foam dying time 15 min were found to be suitable for the foaming behaviour observations. The purpose of dying foam observations was to study how the other agents of the sample (fibres, additives) affect the foam stability and behaviour.

Flocculation tests were the third part of the experimental work. The aim of the flocculation tests was the examination of precipitation of SDS from pure- and white water samples using trivalent cations Al^{3+} and Fe^{3+} as coagulants. The objectives were to study the effects of coagulant dosage and pH on the precipitation efficiency of SDS. The determination of SDS was done by using SES-method. Precipitation/flocculation is a common wastewater treatment method, and the purpose of these experiments was to define optimal conditions for SDS removal from wastewaters.[3,18,151]

8 DEVICES

8.1 Hitachi Double Beam U-2900 spectrophotometer

Double beam spectrophotometer divides the light source energy into two using a half mirror. One part goes through reference, and the other one goes through the sample. Optics is a common concave diffraction grating monochromator (Seya-Namioka monochromator) which has both beams condensing and dispersing functions. Thus, fewer mirrors are used meaning that optical path is shorter, optics are bright and free from aberration and resolution is higher.[179] Hitachi Double Beam U-2900 spectrophotometer in Figure 20 and double beam optics are presented in Figure 21.

Figure 20. Hitachi Double Beam U-2900 spectrophotometer

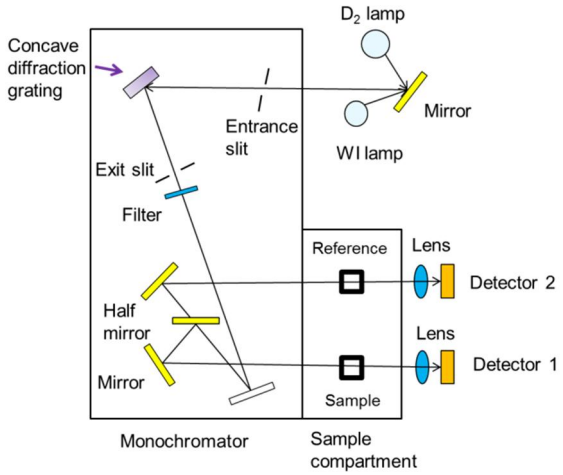


Figure 21. Double beam optics [179]

8.2 Liquid chromatography instrumentation

A Dionex DX-600 system (Dionex, Sunnyvale, CA, USA) equipped with an GS50 Gradient Pump, AS50 Autosampler with a 25 µL injection loop, LC25 Chromatography Oven, PDA-100 Photodiode Array Detector, IC25 Conductivity detector, and CRS™500 Chemically Regenerated Suppressor, was used in the HPLC-RP experiments. Separation was achieved on a reversed-phase Acclaim® PolarAdvantage II (PA2) column (dp = 5 µm, 4.6 × 150 mm) using a gradient of acetonitrile and borate buffer (6.2 g/L boric acid in milliQ-water, pH 8.3 adjusted with 50% NaOH).[79] HPLC instrumentation in Table 10.

The following gradient program was employed throughout the experiment: starting at 33% acetonitrile followed by a linear increase to 67% over the next 15 min and then return to 33% within 5 min. Flow-rate of the mobile phase was kept at 1 ml /min. Samples were filtrated through 0.45 µM GHP syringe filters before injection. The suppressor was operated in the chemically regenerated mode using 40 mM sulfuric acid as a regenerant. Used reagents and solvents are listed in Table 16.

Table 10. HPLC instrumentation and materials

Instrument	Details
HPLC column	Acclaim® PolarAdvantage II (PA2), dp = 5 µm, 4.6 x 150 mm
Instrumentation	DX-600 Ion Chromatograph (Dionex) equipped with a GS50 Gradient Pump, AS50 Autosampler with a 25 µL injection loop, LC25 Chromatography Oven, PDA-100 Photodiode Array Detector, IC25 Conductivity detector, and CRS™500 Chemically Regenerated Suppressor.
Software	Chromeleon® Chromatography Management Software (Dionex)

Theory of the instrumentation

HPLC is an ensemble composed of different instrumentation units and chemical components. The instrumentation includes the pump, injector, column, suppressor, detector and data station (Figure 22). Chemical components consist of the mobile phase, stationary phase and regenerating eluent of the suppressor. The mobile phase, or eluent, flows steadily through the system maintained by the high-pressure pumps. Singe-piston pumps are used for isocratic elution and dual-piston pumps for gradient elution. Pulse dampers assure the pulse-free flow of the mobile phase. Constant flow is obligatory for the accurate sample detection.

Autosampler introduces the analyte into the system. Injection volume is normally between 5 – 100 µL. After sample loop, the analyte flows through the guard column into the analytical reversed-phase column where the separation of analytes occurs. Separated analytes flow to the suppressor that reduces the conductivity of the eluent and increases the conductivity of the sample. The detector detects the change in the eluent conductivity as the analyte flows in and sends the data to the data collection computer which converts it into a chromatogram. The surface area of the sample peaks in the chromatogram is directly proportional to the sample concentration.[56,57]

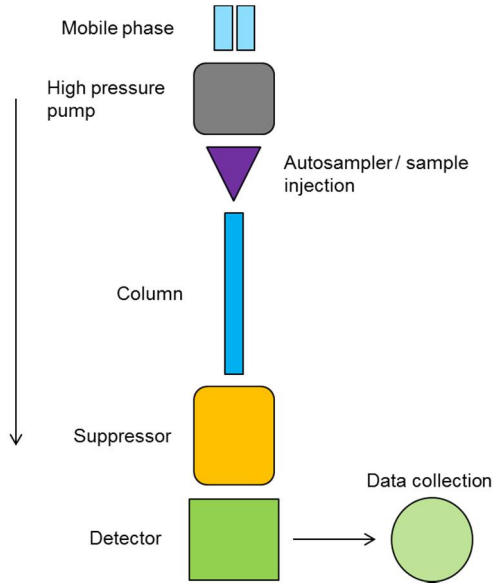


Figure 22. Schematic view of an HPLC instrumentation

The Column (Thermo Scientific™ Acclaim™ PolarAdvantage II, PA2)

Reversed-phased silica-based amide polar-embedded column (Figure 23). Enhanced hydrolytic stability (pH 1.5 – 10), 4.6X150mm and 5µm particle size. Selectivity complementary to conventional C18 columns such as the Acclaim 120 C18 and it can be combined with 0 - 100 % aqueous and 0 - 100 % organic eluents. PA2-column can separate both polar and non-polar samples.

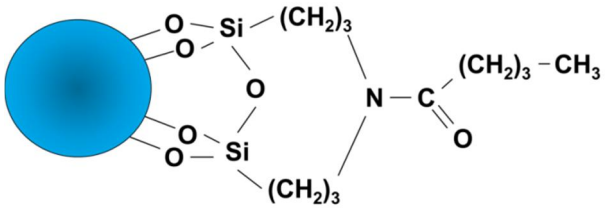


Figure 23. Thermo Scientific™ Acclaim™ PolarAdvantage II (PA2) Reversed-Phase Analytical HPLC Column[60]

Anion suppressor (Dionex CRS 500)

After the column, the separated analytes flow to the suppressor. The anion suppressor removes mobile phase cations (Na^+) replaces them with hydronium ions (H^+). Thus, the eluent anions are converted into non-ionized species (H_3BO_3, H_2O) and their conductivity is reduced. The sample anions (Na^+) go through the same treatment, but the effect is opposite as their conductivity increases when they combine with the extremely conductive hydronium ions. For example, sodium dodecyl sulfate (SDS) is a salt of a moderately strong acid and when the Na+-ions are removed and replaced with H^+-ions SDS turns into easily dissociative acid form and can be detected with a conductivity detector. The results are a low conductivity background and an analyte with a conductance clearly distinguishable from the background. The anion suppressor (Dionex CRS 500) is presented in Figure 24.[56]

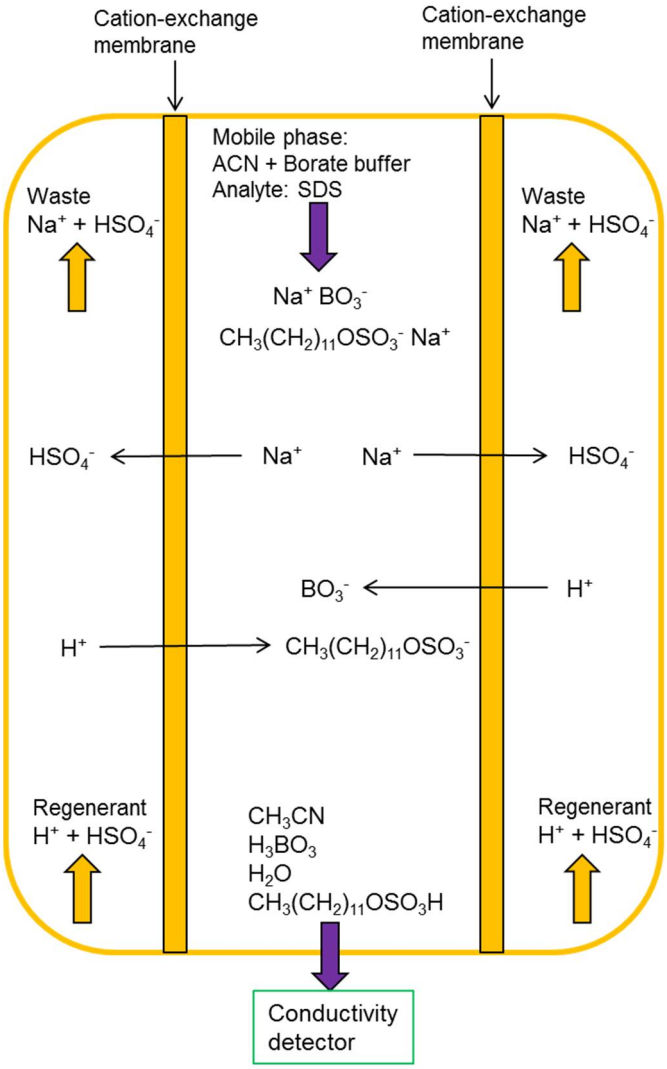


Figure 24. Anion suppressor (Dionex CRS 500 – Chemically regenerated suppressor)[56]

The Electrical Conductivity Detector

Conductivity cell contains two electrodes made of marine-grade 316 stainless steel closed into a polyether ether ketone (PEEK) cell body. The volume of the passing mobile phase inside the cell is about 1.0 µL, the cell constant is 160 cm^{-1}, and the calibration is done electronically. A temperature sensor is placed after the two electrodes to measure the eluent temperature. Conductivity is highly temperature dependent, especially with high conductivities, so the temperature compensation is necessary to secure the reproducibility and stability of the baseline. Effect of the temperature on the analysis can also be decreased by suppressing the mobile phase conductance and installing the

conductivity cell inside a detection stabilizer. DS3 detection stabilizer controls temperature keeping it constant at 25 degrees, ensuring that the baseline stays stable, and peak heights do not alternate. [77] Conductivity cell presented in Figure 25.

The operation model of the conductivity detector is a Wheatstone Bridge, where the two electrodes inside the conductivity cells electric circuit are one arm of the bridge. The impedance between the electrodes is changed by conductive ions in the eluent flow and this "out of balance signal" is sent to an electronic circuit that modifies the signal so that it is directly proportional to the ion concentration of the sample. The signal goes through an amplifier, and the digitized output is sent to a data processing computer. The voltage between the electrodes is alternating current (AC) voltage, usually about 10 kHz. Direct current (DC) would lead to a polarization and gas generation at the electrode surfaces. This would interfere the impedance between the electrodes. The tubing of the first electrode is always grounded.[77]

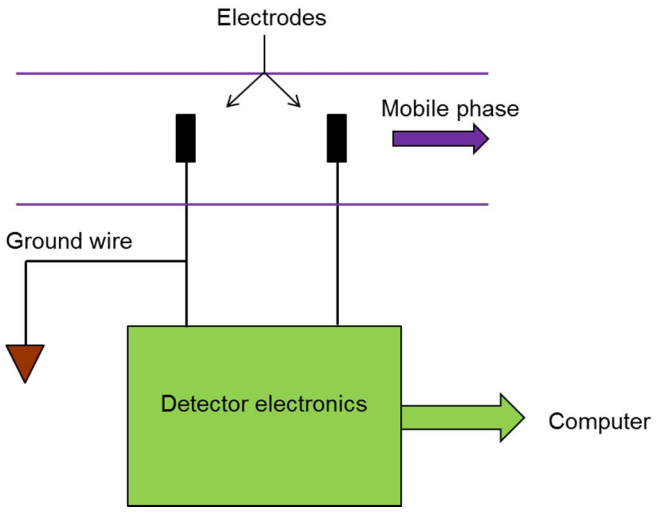


Figure 25. Conductivity cell

8.2.1 Syringe filters

SDS samples with additives needed to be filtrated through syringe filters to protect the IC equipment and the column from clogging. The SDS samples were filtered with 0.45 µm GHP filter. The particle size of the column was 5 µm, so the 0.45 µm filter was suitable for the filtration. GHP (hydrophilic polypropylene) was chosen to be the filter material since its chemical versatility with high tolerance against acids, bases and organic solvents and low binding (Appendix 1). It was not fully clear how the sample would react with the membrane, so the universal GHP filter seemed to be the most reasonable alternative. Also nylon syringe filters and vacuum filtration with GH (hydrophilic polypropylene) membrane filter were tested. Nylon is also common filter material and can be used with both aqueous and organic samples. The main disadvantage is its low tolerance against acids and high affinity for proteins. Filters used in this study are listed in Table 11.

Table 11. Filter materials and types tested in the experiments

Membrane	Material	Filter type	Figure
GHP Acrodisc (PALL, 13mm, 0.45 µm)	Hydrophilic polypropylene	Syringe filter	
GH Polypro (PALL, 47 mm, 0.45 µm)	Hydrophilic polypropylene	Membrane filter	
Nylon (Titan3, 17 mm, 0.45 µm)	Hydrophilic nylon	Syringe filter	

8.2.2 Solid phase extraction (SPE)

SPE cartridges containing hydrophobic bonded silica sorbent (Varian, Bond Elut – C18 LO, 500 mg, 3 ml) were used for purification of SDS from white water impurities (salts, fibres, additives). Purified samples were collected in centrifuge tubes. The vacuum used for elution was approximately 20 bar. SPE-equipments are listed in Table 12 and shown in Figure 26.

Table 12. SPE-equipment

Equipment	Details
SPE column	Varian, Bond Elut – C18 LO (500 mg, 3 ml)
Instrumentation	SPE vacuum chamber (including a rack and centrifuge tubes)
Vacuum apparatus	~ 20 bar

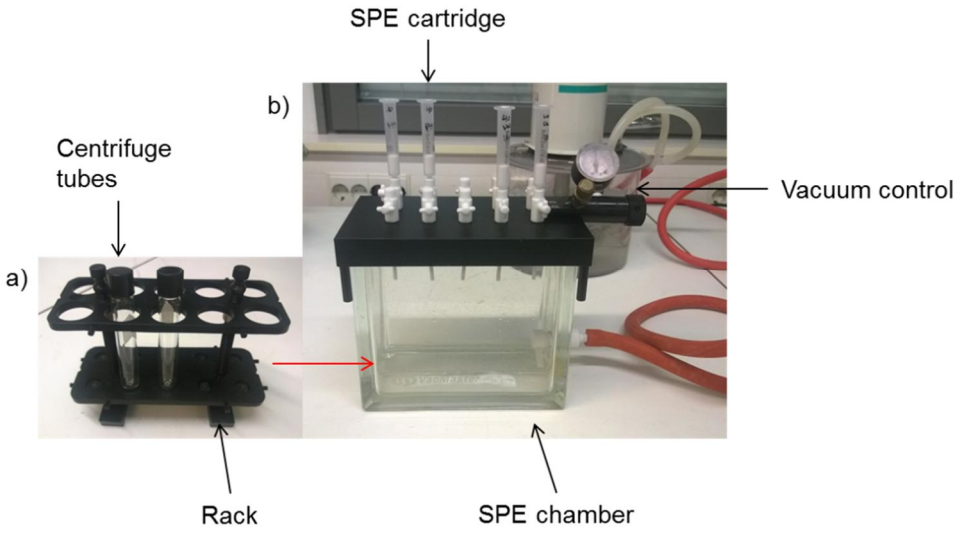


Figure 26. SPE equipment. a) A rack for centrifuge tubes goes inside the b) SPE chamber. SPE cartridges are on top of the chamber and vacuum(~ 20 bars) is used to elute the sample and solvents through the column

8.3 Accelerated aeration test

A laboratory scale aeration device for the analysis of foaming tendency of surfactant containing wastewater. The system consists of the transparent vessel (total volume approximately 28 L) calibrated with 5 L scale. An aeration plate is placed at the bottom of the vessel. Flow rate of air is controlled using a rotameter. Dissolved oxygen level is measured using Hach HQ30d LDO101 Portable Meter, and foaming dynamics is recorded with a camera (Microsoft LifeCam 1080p Sensor) using Foam Grabber image acquisition program. The generated foam volume was calculated using ImageJ image processing programme. Instrumentation listed in Table 13 and Figure 27 shows a presentation of aeration device.

Table 13. Instrumentation of accelerated aeration test

Instrument	Details
Aeration devise	Plexiglass tube (V = 28 L, r = 15.5 cm, h = 37 cm), aeration plate at the bottom, evacuation outlet aside
Microsoft LifeCam 1080p Sensor	Camera for foam imaging
Rotameter	Air flow measurement
Hach HQ30d LDO101 Portable Meter	Oxygen concentration measurement
Mettler Toledo Portable pH and conductivity meters	pH and conductivity measurement
Software	FoamGrabber image acquisition program ImageJ image processing

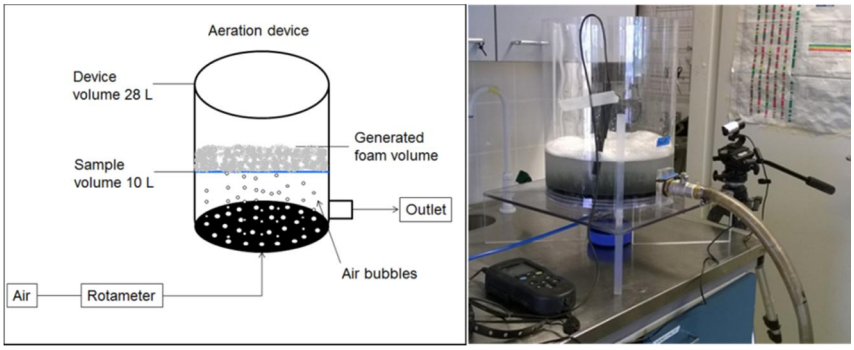


Figure 27. Schematic presentation of aeration device on left and picture of the experimental arrangements on right

8.4 Kemira Flocculator 2000 device

Precipitation/flocculation tests were performed using Kemira Flocculator 2000 device shown in Figure 28.

Figure 28. Kemira Flocculator 2000 device

9 REAGENTS AND SOLVENTS

Solvent extraction spectrophotometry

All reagents and solvents used in SDS solvent extraction analysis are listed in Table 14.

Table 14. Reagents and solvents used in SDS solvent extraction analysis

Reagent/solvent	Manufacturer
Ethylviolet	Sigma-Aldrich
Sodium acetate (CH_3CO_2Na)	VWR chemicals
Acetic acid, 100%	Merck
Toluene	Merck
Deionized water	Milli-Q water purification system (Millipore)

Flocculation experiments

All reagents and solvents used in flocculation tests are listed in Table 15.

Table 15. Reagents and solvents used in flocculation tests

Reagent/solvent	Manufacturer
Sodium dodecyl sulfate (SDS)	Merck (≥95 %)
Ferric sulfate (PIX-105)	Kemira
Polyaluminum chloride (PAX-14)	Kemira
NaOH	VWR chemicals
Deionized water	Milli-Q water purification system (Millipore)

Aeration experiments

The only reagent used in aeration experiments was sodium dodecyl sulfate, SDS (Sigma Aldrich, purity ≥ 90 %).

HPLC-RP analysis

All reagents and solvents used in HPLC-RP experiments, including SDS hydrolysis, SDS and additives, filter membrane tests, SPE-experiments and Miranol Ultra tests, are listed in Table 16.

Table 16. Reagents and solvents

Reagent/solvent	Manufacturer	Purity grade
Sodium dodecyl sulfate (SDS)	Merck	≥95 %
1-dodecanol	Sigma Aldrich	98 %
Miranol Ultra L 32 E	Rhodia	-
HPLC grade acetonitrile	J.T.Baker	HPLC grade
Methanol	J.T.Baker	HPLC grade
Deionized water	Milli-Q water purification system (Millipore)	
Sulfuric acid	Sigma Aldrich	HPLC grade
Boric acid	EM Science	-
Sodium Hydroxide (NaOH 50 %)	J.T.Baker	HPLC grade
Salts (NaCl, $CaCl_2$, $FeSO_4$)	VWR chemicals	-
[(1)]C-pam (PC435)	Kemira	-
[(2)]Microparticle (SP7200DR)	Ashland	-

[(1)] Cationic polyacrylamide
[(2)] Anionic microparticle with high surface area. Consists of colloidal silica, bentonite or certain organic molecules

10 SAMPLES

Water samples analysed in different experiments listed in Table 17.

Table 17. Samples used in different experiments. White water samples were collected from VTT pilot paper machine or prepared by hand from kraft or CTMP pulp by filtrating through the former fabric. Wastewater samples were form WWTP of a Paper Mill (Finland).

Experiment	Samples
HPLC-RP analysis	SDS + tap water
	SDS + white water (kraft/CTMP)
	Miranol Ultra + tap water
	Miranol Ultra + white water (kraft/CTMP)
	(+ salts and retention aids)
Aeration experiments	SDS + tap water
	SDS + white water (Pilot)
	SDS + wastewater
Flocculation	SDS + deionised water
	SDS + white water (Pilot)

11 EXPERIMENTAL PROCEDURES

11.1 Solvent extraction spectrophotometry (SES)

Solvent extraction spectrophotometry[108,109,110] can be used for detection of anionic surfactants, such as SDS, from water samples. The samples were filtrated through 0.45 µm Whatman RC55 before the SDS-analysis. Filtered samples were diluted with deionized water (500x dilution, sample volume 100 µl, total volume 50 ml) in a separating flask. Acetate buffer* (5 ml, 0.5 M, pH 5), ethyl violet (2 ml, 0.001 M) and toluene (5 ml) were added in the flasks respectively. The flasks were shaken for 2 min. Layers of water and toluene were let to separate at least for 10 minutes (recommended time 30 min)(Figure 29). The water layer was disposed, and toluene (~5 ml) was collected in a centrifuge tube. SDS concentration was measured by Hitachi U-2900 spectrophotometer at wavelength 615 nm.

*Acetate buffer: acetic acid (0.5 M, ~350 ml) and sodium acetate solution (0.5 M, ~800 ml) mixed so that the pH 5 was achieved.

Figure 29. SDS-analysis and toluene extraction: layers of water and toluene are let to separate for 30 minutes

11.2 HPLC-RP and conductivity detection (ECD)

11.2.1 SDS hydrolysis

All 400 ppm SDS samples were prepared by weighting SDS powder and diluting with milliQ-water (0.42 g SDS / L).

Hydrolysis by heating

50 ml of 400 ppm SDS solution was measured into 100 ml bottles and sealed with pressure balancing caps. The bottles were heated in an ovens at temperatures 60°C and 90°C for 4, 8 and 24 hours (3 samples/temperature). After heating samples were kept at room temperature and analysed within 24 h. Samples were diluted (10x) with milliQ-water for the HPLC-RP analysis.

Hydrolysis by pH change

50 ml of 400 ppm SDS solution was measured into 100 ml bottles, and pH (initial pH ~7) was adjusted with sulphuric acid. pH adjustments were pH 6, pH 5, pH 4, pH 3 and pH 2 (5 samples). Samples were kept at room temperature and analysed 24 h after preparation. Samples were diluted (10x) with milliQ-water for the HPLC-RP analysis.

Hydrolysis by combination of heat and pH

50 ml of 400 ppm SDS solution was measured into 100 ml bottles, and pH (initial pH ~7) was adjusted with sulphuric acid. pH adjustments were pH 4 and pH 3. The bottles were sealed with pressure balancing caps and heated in an oven at temperature 60°C for 4, 8 and 24 hours (3 samples/pH). After heating samples were kept at room temperature and analysed within 24 h. Samples were diluted (10x) with milliQ-water for the HPLC-RP analysis.

Time monitoring

SDS sample (400 ppm, 100 ml) was monitored for one week (7 days) using two different determination methods: Solvent extraction spectrophotometry and RP-ECD. Measurement days were day zero (fresh sample), one day old, two days old, five days old, and seven days old sample. Before measurements samples were diluted (10x) with milliQ-water for the HPLC-RP analysis and (500x) for the spectrophotometric analysis.

11.2.2 SDS and additives

Salt additives (10 x dilutions)

All SDS samples (40 ppm) were prepared from SDS stock solution (1000ppm, 1.05 g/L). Kraft and CTMP white waters were diluted (5x) with milliQ-water. Salt (NaCl, $CaCl_2$ and $FeSO_4$) additions were 0, 500 and 5000 ppm (salt stocks 10000 ppm). Samples were prepared in measuring bottles (50 ml). The final volume was achieved by diluting with milliQ-water. Sample preparation examples are shown in Table 18.

Table 18. SDS (40ppm) sample with NaCl salt additions (500 and 5000 ppm) and kraft white water. The final volume was achieved by diluting with milliQ-water.

Sample	SDS dosage (stock 1000 ppm)	Salt dosage (stock 10000 ppm)	Kraft dosage	Final volume
SDS (40 ppm) + NaCl (500 ppm)	2 ml	2.5 ml	5 ml	50 ml
SDS (40 ppm) + NaCl (5000 ppm)	2 ml	25 ml	5 ml	50 ml

Salt additives (500 x dilutions)

All SDS samples (0.8 ppm) were prepared from SDS stock solution (1000ppm, 1.05 g/L). Kraft and CTMP white waters (WW) were diluted (500x) with milliQ-water. Salt (NaCl, $CaCl_2$ and $FeSO_4$) additions were 0, 10, 100 and 1000 ppm (salt stocks 10000 ppm). Samples were prepared in measuring bottles (50 ml). The final volume was achieved by diluting with milliQ-water. Sample preparation examples are shown in Table 19.

Table 19. SDS (0.8 ppm) sample with NaCl salt additions (10, 100 and 1000 ppm) and kraft white water. The final volume was achieved by diluting with milliQ-water.

Sample	SDS dosage (stock 1000 ppm)	Salt dosage (stock 10000 ppm)	Kraft dosage	Final volume
SDS (0.8 ppm) + NaCl (10 ppm)	40 µl	50 µl	100 µl	50 ml
SDS (0.8 ppm) + NaCl (100 ppm)	40 µl	500 µl	100 µl	50 ml
SDS (0.8 ppm) + NaCl (1000 ppm)	40 µl	5000 µl	100 µl	50 ml

Retention aid additives (500xdilutions)

All SDS samples (0.8 ppm) were prepared from SDS stock solution (1000ppm, 1.05 g/L). Kraft white waters (WW) were diluted (500x) with milliQ-water. Retention aid (c-Pam and microparticle) additions were 200, 400 and 800 g/t (aid stocks 500 ppm). Also, two component system with both retention aids were analysed. Additions were 200, 400 and 800 g/t per retention aid. Retention aid dosages were based on the knowledge that paper product of 80 g/m^2 grammage can contain from 200 to 800 g/t of retention aid. Samples were prepared in measuring bottles (50 ml). The final volume was achieved by diluting with milliQ-water. Sample preparation examples are shown in Table 20.

Table 20. Sample preparation examples. SDS (0.8 ppm) sample with c-Pam additions (200, 400 and 800 g/ts) and kraft white water. The final volume was achieved by diluting with milliQ-water.

Sample	SDS dosage (stock 1000 ppm)	Aid dosage (stock 500 ppm)	Kraft dosage	Final volume
SDS (0.8 ppm) + c-Pam (200 g/t)	40 µl	800 µl	100 µl	50 ml
SDS (0.8 ppm) + c-Pam (400 g/t)	40 µl	1600 µl	100 µl	50 ml
SDS (0.8 ppm) + c-Pam (800 g/t)	40 µl	3200 µl	100 µl	50 ml
SDS (0.8 ppm) + 2-components(200 g/t + 200 g/t)	40 µl	800 µl + 800 µl	100 µl	50 ml

11.2.3 Filter membrane tests

GHP and nylon syringe filters

SDS samples (40 ppm) were prepared by diluting SDS stock solution (1000 ppm) with milliQ-water and filtrated through GHP (13mm, 0.45 µm) or nylon (17 mm, 0.45 µm) syringe filters.

Vacuum filtration using GH membrane

SDS samples (0.8 ppm) were prepared by diluting SDS stock solution (1000 ppm) with milliQ-water. Retention aid (c-Pam) wad added (dosages 200 g/t and 800 g/t) into the SDS samples and filtrated through GH-membrane (47 mm, 0.45 µm) using vacuum filtration. Prepared samples are listed in Table 21.

Table 21. SDS samples for vacuum filtration tests.

Pure SDS reference (no additives)	c-Pam additions (500 ppm)
0.8 ppm SDS	0.8 ppm SDS + 200 g/t c-Pam
	0.8 ppm SDS + 800 g/t c-Pam

Crude NaCl samples

Effect of NaCl on the SDS determination by RP-ECD method was also examined. Different dilutions of SDS (10-100 ppm) with and without NaCl addition (500 ppm) were analysed. Samples were analysed crude, meaning without syringe filtration. Prepared samples are presented in Table 22.

Table 22. SDS samples (10-100 ppm) of crude sample NaCl tests. Addition of NaCl 500 ppm.

Crude SDSsamples	Crude SDS samples with NaCl addition
10 ppm	10 ppm + 500 ppm NaCl
20 ppm	20 ppm + 500 ppm NaCl
40 ppm	40 ppm + 500 ppm NaCl
60 ppm	60 ppm + 500 ppm NaCl
100 ppm	100 ppm + 500 ppm NaCl

11.2.4 Solid-phase extraction (SPE)

SDS samples (40 ppm) for the SPE purification tests were prepared from SDS stock solution (1000ppm, 1.05 g/L). Salt (NaCl, $CaCl_2$ and $FeSO_4$) additions were 0, 500 and 5000 ppm (salt stocks 10000 ppm). Kraft white water was diluted (5x) with milliQ-water. Samples were prepared in measuring bottles (50 ml). The final volume was achieved by diluting with milliQ-water. Sample preparation examples are shown in Table 24.

Table 23. SDS (40ppm) sample with NaCl salt additions (500 and 5000 ppm) and kraft white water. The final volume was achieved by diluting with milliQ-water.

Sample	SDS dosage (stock 1000 ppm)	Salt dosage (stock 10000 ppm)	Kraft dosage	Final volume
SDS (40 ppm) + NaCl (500 ppm)	2 ml	2.5 ml	5 ml	50 ml
SDS (40 ppm) + NaCl (5000 ppm)	2 ml	25 ml	5 ml	50 ml

SPE – procedure

SPE cartridges contained nonpolar C18 stationary phase that retains effectively hydrophobic organic compounds but polar molecules, such as salts, are passed through unretained. The solid phase extraction procedure includes four main steps. First the SPE cartridge was preconditioned (or activated) by wetting with methanol (3 ml) and then washed with milliQ-water (3 ml). An approximately 20 bar pressure was used in the vacuum chamber to eluate the solvents through the SPE column. Elution was performed slowly, and it was carefully controlled that the stationary phase remained wet.

In the second step, the SDS samples (10 ml) were slowly passed through the SPE cartridges and then washed with milliQ-water (3ml) (step three). Loaded sample solution and washing water can be collected by placing a rack with centrifuge tubes inside the vacuum chamber. After washing the taps of the SPE cartridges were let open left open and the stationary phase was dried under air suction for 30 min. In the final step, a rack with centrifuge tubes was placed inside the vacuum chamber for sample collection. The samples were eluted slowly form the SPE cartridge with pure acetonitrile (3 ml) into the centrifuge tubes. All the SPE-procedure steps are presented in Figure 30.

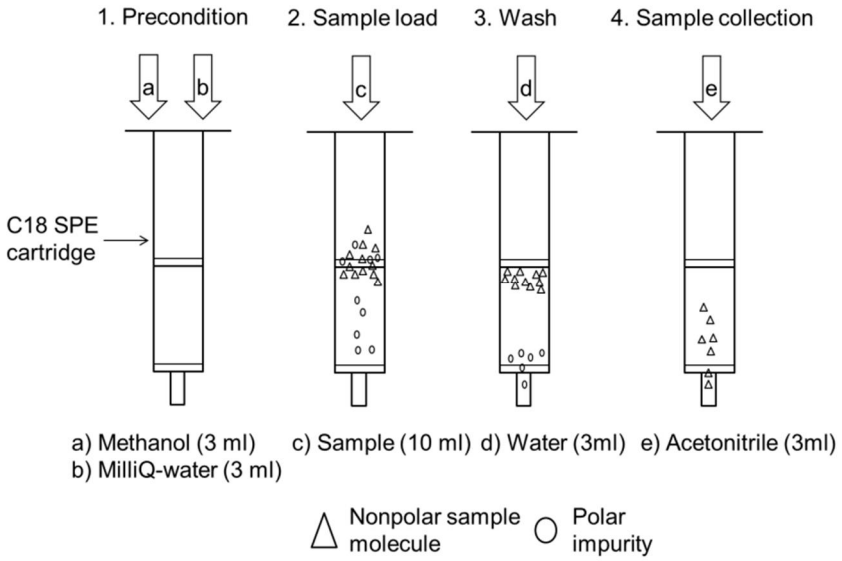


Figure 30. SPE-procedure steps

11.2.5 Another surfactant: Miranol Ultra

Miranol Ultra samples (1, 2.4 and 4 g/L) were prepared from 10 % stock solution and diluted with white water (kraft, CTMP) made from the pulp by filtrating through the former fabric. The salt (NaCl and CaCl2) addition was 100 ppm (salt stocks 10000 ppm). Samples were prepared in measuring bottles (50 ml). The determination was done with HPLC-RP combined with UV-detector at wavelength 205 nm. Sample preparation examples are shown in Table 25.

Table 24. Miranol Ultra (1, 2.4 and 4 g/L) samples with NaCl addition (100 ppm) diluted with kraft white water. The final volume was 50 ml.

Sample	Miranol Ultra dosage (10 %)	Salt stock dosage (10000 ppm)	Kraft dosage	Final volume
Miranol Ultra (1 g/L) + NaCl (100 ppm)	0.5 ml	0.5 ml	49 ml	50 ml
Miranol Ultra (2.4 g/L) + NaCl (100 ppm)	1.2 ml	0.5 ml	48.3 ml	50 ml
Miranol Ultra (4 g/L) + NaCl (100 ppm)	2.0 ml	0.5 ml	47.5 ml	50 ml

11.3 Accelerated aeration experiments

All 400 ppm SDS samples for aeration tests were prepared by measuring 10 % SDS stock solution (90 %, Sigma) in the water sample (10 L).The water sample (10 L) was poured into the aeration devise and oxygen concentration, temperature, conductivity and pH were measured. Oxygen concentration and temperature were monitored through the experiment. 10 % SDS solution was pipetted to the sample and stirred carefully. Aeration was switched on and adjusted by a rotameter. Aeration time was 90 min and after the aeration, the foam dying was recorded for 15 min. Table 25 shows procedure details of performed aeration experiments and in Table 26 is the shooting sequence of the aeration tests.

Table 25. SDS concentrations of 10 L water samples (tap water/white water/wastewater) and 10 % SDS stock dosages. Two set of experiments were performed: Aeration experiments 1 were done with tap water and white water samples using air flow rate 8.0

L/min and SDS dosages of 50-400 ppm. Aeration experiments 2 were done with tap-, white-, and wastewater samples using air flow rate 0.6 L/min and SDS dosages of 10-100 ppm. Air flow rate 1.0 L/min with 10 ppm SDS dosage was also tested.

Aeration experiments 1			
SDS sample	10 % SDS dosage	Water sample	Air flow
50 ppm	5 ml	10 L	8.0 L/min
100 ppm	10 ml		
200 ppm	20 ml		
400 ppm	40 ml		
Aeration experiments 2			
10 ppm	1 ml	10 L	0.6 L/min
20 ppm	2 ml		
40 ppm	4 ml		
60 ppm	6 ml		
100 ppm	10 ml		
10 ppm	1 ml	10 L	1.0 L/min

Table 26. The shooting sequence of the aeration tests. The imaging program recorded 90 min foam generation and 15 min foam dying.

	Interval	Duration	
Period 1	60 s	15 min	Generation
Period 2	300 s	75 min	
Period 3	30 s	15 min	Dying

11.4 Flocculation experiments

Six flocculation experiments were performed using Kemira Flocculator 2000 device. All 400 ppm SDS samples were prepared by weighting SDS powder and diluting with milliQ-water (0.42 g SDS / L).Tree of these tests were done with ferric sulfate coagulant

and two with polyaluminum chloride coagulant. Five tests included pure deionised water, and one test was done with white water.

SDS solution (600 ml, 400 ppm) was added to every jar and solution pH was adjusted with 2 M NaOH. The coagulant was added at the first stage of the jar test program during rapid mixing (10 sec). Coagulant precipitated SDS during the second stage involving slow mixing (10 min, 40 rpm). Formed flocs were let to settle down during the third stage (no mixing, 10 min). The jar test programme in Table 27. 50 ml sample was collected by pipette and pH was measured. The sample was filtrated (0.45 µm Whatman RC55) and SDS concentration was determined by solvent extraction spectrophotometry (Chapter 11.2)

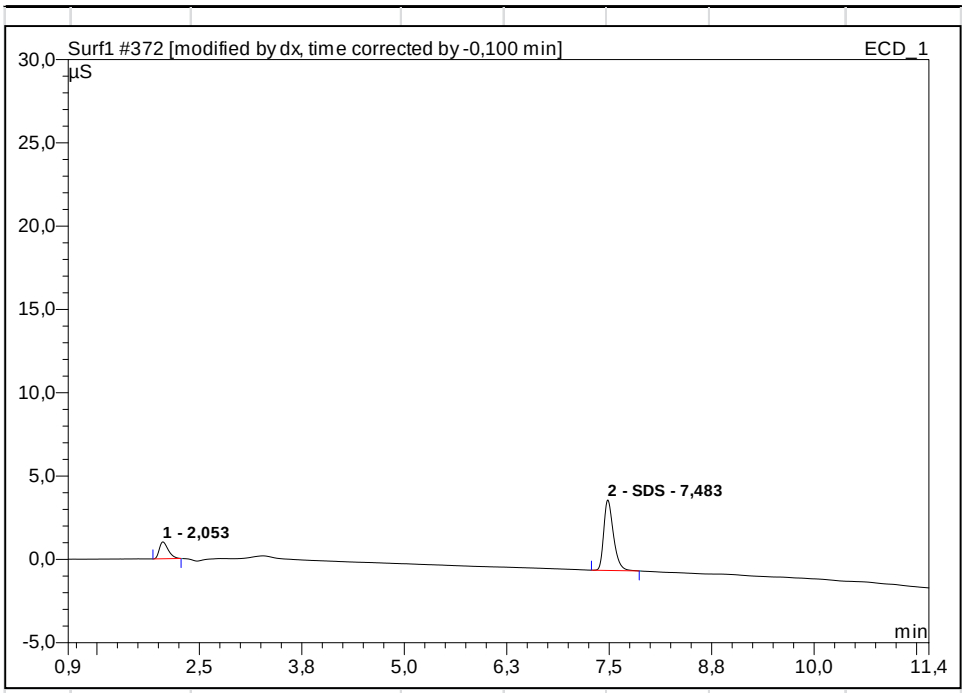
Table 27. The jar test programme

	First stage	Second stage	Third stage
Mixing speed	350 rpm	40 rpm	0 rpm
Time	10 s	10 min	10 min

12 RESULTS AND DISCUSSION

12.1 HPLC-RP analysis

The determination of sodium dodecyl sulfate (SDS) with reversed-phase chromatography and conductivity detection succeeded. Figure 31 shows the electrical conductivity detector (ECD) spectrum of sodium dodecyl sulfate. ECD calibration curve (correlation coefficient 0.9997) for SDS concentration range 2 – 200 ppm is attached in Appendix 3. Calibration curve for concentrations under 1 ppm (0.2 – 1.0 ppm) was also prepared (correlation coefficient 0.9998). The results from the RP-DC were multiplied by the dilution factor (x10 or x500) before data processing so that results from different tests were comparable.



No.	Ret.Time	Peak Name	Height	Area	Rel.Area	Amount	Type
	min		µS	µS*min	%		
1	2,05	n.a.	1,011	0,127	18,03	n.a.	BMB*
2	7,48	SDS	4,229	0,580	81,97	39,775	BMB*
Total:			5,240	0,707	100,00	39,775	

Figure 31. ECD spectrum of sodium dodecyl sulfate (SDS). SDS concentration 40 ppm (39.775 ppm), retention time 7.5 minutes. Inorganic impurities eluate first (retention time 2.0 min).

12.1.1 Hydrolysis by heat and pH

SDS samples were kept at temperatures 60°C and 90°C for 0, 4, 8, 24 h before analysation with RP-ECD. No increase in SDS concentration was detected during the experiment, so heating at 60°C or 90°C do not have a major effect on SDS hydrolysis. The variation in SDS concentrations between different time points (0, 4, 8, 24 h) is between 390 – 410 ppm and can be explained by the internal variation. A probable explanation is that the SDS concentration increases during the test due to water evaporation through leaking caps which concentrates the sample.

The same heating test was done with pH adjusted (pH 3 and pH 4) SDS samples at the temperature of 60°C. Even though there were rather significant variations between the time points of pH 4 adjusted samples, there was no significant drop in the measured SDS concentration, i.e. no sign of SDS hydrolysis. The difference between the two time points is caused by some other factors, such as water evaporation or baseline disturbances. Figure 32 shows that pH adjustment at 3 clearly decreases the SDS concentration (SDS concentration at the time point 0 h was ~ 300 ppm, approximately 30 % SDS removal efficiency). The heating at 60°C did not accelerate the hydrolysis. Calculation of SDS removal efficiency is shown in equation 19 in Appendix 8.

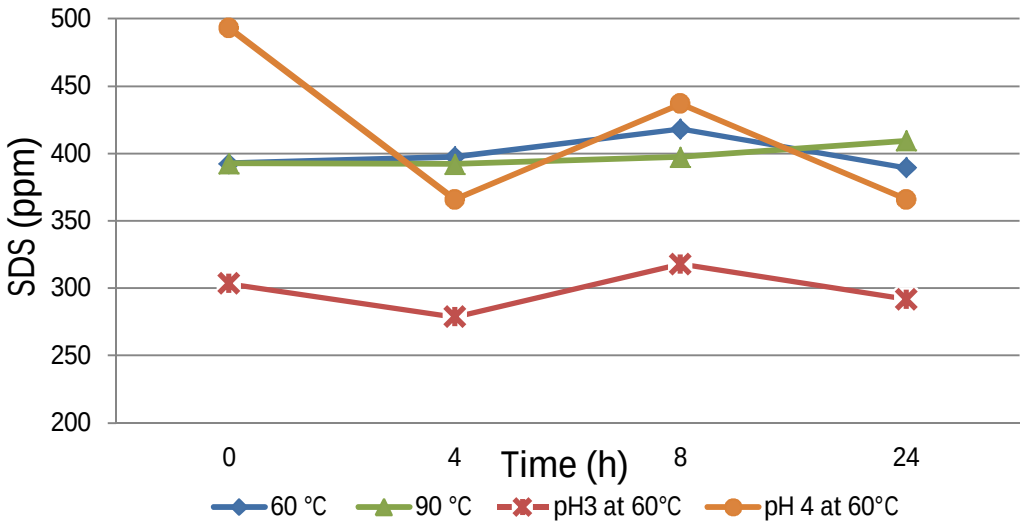


Figure 32. The SDS hydrolysis by heat and the combination of heat and pH. SDS concentration (ppm) of the sample on the y-axis and heating times on the x-axis. SDS samples with no pH adjustment heated at 60°C are marked with a blue line and at 90°C with

a green line. At pH 3 and pH 4 adjusted samples heated at 60°C are marked a read line and an orange line, respectively.

Figure 33 presents the results from the SDS pH change tests and shows that there is no sign of SDS hydrolysis at pH between 4 – 7. At pH ~3.8 SDS concentration dropped slightly and as the pH decreases the SDS hydrolysis accelerates. At pH 2 approximately 50 % of the SDS was hydrolysed within 24 hours. The combination of heat (60°C) and pH (pH 3 and pH 4) did not considerably boost the pH effect on SDS hydrolysis.

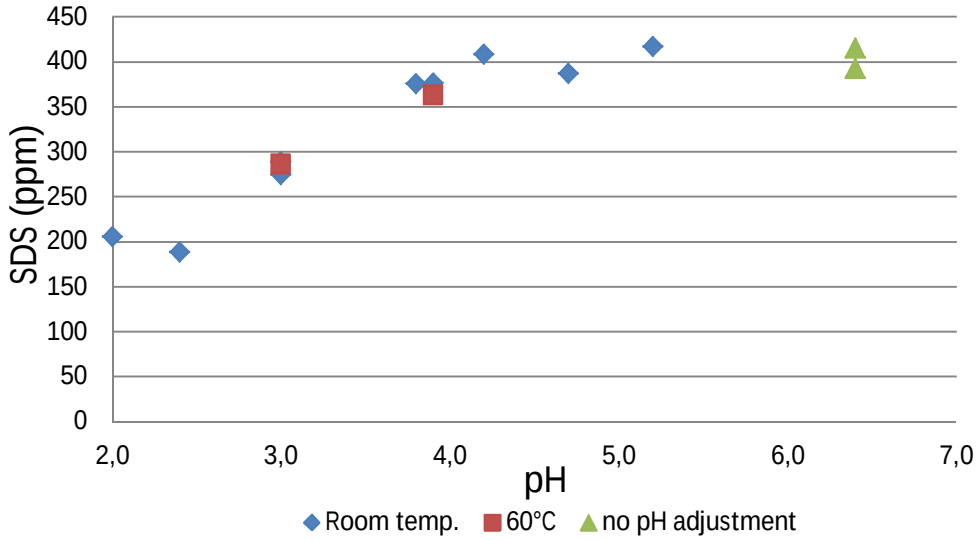


Figure 33. SDS hydrolysis by the pH change. SDS concentration (ppm) of the sample on the y-axis and pH-values on the x-axis. Blue dots indicate the hydrolysis effect on a certain pH at room temperature. Red dots indicate the combination effect of heat (60°C) and pH (pH 3 and pH 4) on the SDS hydrolysis. Green dots indicate the starting point, meaning the pH-value of an untreated SDS solution.

According to the studies of Bethell *et al.*[28] SDS hydrolyses through two reaction pathways where one is uncatalysed and the other of catalysed. In the presence of water initially neutral SDS solution produces dodecanol and hydrogen sulfate anions, solution pH decreases and SDS hydrolysis accelerates as the acid catalysed pathway takes over. They stated that hydrolysis can be accelerated at a higher temperature (100°C) and as the pH of the solution drops under pH 2.7 the hydrolysis accelerates considerably. In

their test 10 % SDS sample hydrolysed totally within 10 hours and 1 % (10000 ppm) sample hydrolysed within 28 hours when heated at 100°C.

In our test, the effect of pH of SDS concentration was clear when the pH dropped under three but there was no sign of accelerated hydrolysis or change in pH when the pH adjusted samples were heated at 60°C. The SDS concentration (400 ppm) of initially neutral solution was not affected by the heating at 60°C or 90°C for 24 hours. SDS concentrations and heating temperatures of our tests were lower than in Bethells tests since one aim was to investigate SDS hydrolysis by heat as a one removal method of SDS from waste- or process waters and the SDS concentration in these waters are rarely higher than 400 ppm. Also, the heating temperature should not be too high since heating consumes energy. Probably these factors (low concentration and lower temperatures) resulted that pure SDS samples did not show accelerated hydrolysis rates at elevated temperatures. Further tests with white water samples could show how the presence of fibres and impurities affect the SDS hydrolysis.

12.1.2 Time monitoring

SES method showed that the mean of the SDS concentration of the time monitoring samples was approximately 360 ppm and did not change considerably during one week storage time (±2s.d. and relative standard deviation (RSD) 0.6 %). Average of SDS concentration measured with RP-ECD was 390 ppm, and the concentration did not change significantly during one week (±11s.d. and RSD 2.7 %). The two methods were compared by applying F-, and t-tests. The F-value (24.6) exceeded the critical F value ($F_{0.05(7,7)}$ =5.0), so the accuracy of the two methods is not the same (95 % level of significance). T-test value (7.8) for unequal variances also exceeded the critical t value (t_5=2.3) so the means of the methods differ significantly (95 % level of significance), and this kind of error is not random. Figure 43 (Appendix 6) and Table 29 (Appendix 7) shows the results and calculations of the SDS time monitoring test.

According to time monitoring tests, 400 ppm SDS solution can be stored for one week at room temperature. Relative standard deviation (RSD) of the results were under 5 % in

both methods so they can be considered reliable even though there is a significant difference in the results between the two methods. SES gives systematically lower concentrations for SDS than RP-ECD method. This inconsistency might be due to the extraction procedure of SES where all sample is not fully extracted into the organic phase. The solvent extraction procedure includes only one extraction step so further tests for investigating the missing SDS should be carried out.

12.1.3 SDS and additives

The retention aid dosages in the samples imitated the real additive content of the paper machine process water, and were based on the knowledge that paper product of 80 g/m^2 grammage can contain from 200 to 800 g/t of retention aid. The presence of salts (NaCl, $CaCl_2$ and $FeSO_4$) in the white water can also be high. Yamamoto *et al.*[109] reported that a high salt concentrations (0.5 M) of the environmental sample matrices can interfere the solvent extraction method as the cationic ions compete with the cationic colouring agent in the bonding with the anionic surfactant and cause a positive error. Santosh *et al.*[110] reported that their solvent extraction procedure (crystal violet as a cationic dye, benzene as an organic solvent and SDS concentration range 0.75-10 ppm) can tolerate chloride and sulfate ions up to 1000 ppm of salt. They also stated that heavy metals, such as Fe and Zn, show a significant effect on the solvent extraction procedure at concentrations over 50 ppm.

The concentration of SDS in the foam forming white waters varies between 0 – 400 ppm. White water samples are diluted (x500) for the solvent extraction procedure so that the final concentration is 0 – 0.8 ppm of SDS. Based on the study of Santosh *et al.*[110] it was decided to investigate the salt effect on the measured SDS content of white water samples by adding known amounts (10 – 1000 ppm) of different salts (NaCl, $CaCl_2$ and $FeSO_4$) into the diluted (x500) samples (SDS concentration was 0.8 ppm).

However, such a high dilution factor was assumed to be problematic with RP-ECD due to the background noise of the conductivity detector and the small alternations in the suppressor eluent flow or the mobile phase composition. These factors could produce

significant errors and make the results unreliable. Thus, the dilution factor (x10) was chosen for the RP-ECD test so that the SDS concentration was 40 ppm and salt dosages were 500 – 50000 ppm. Final results were multiplied so that the comparison with SES result could be done. Unfortunately, only half of these samples were analysed before the column was clogged. All the samples were filtrated before the HPLC-RP analysis, but the salts (especially Ca^{2+} and Fe^{2+}) probably precipitated into the column.

Test were continued with a new column (also a guard column was now attached) and since the column clogged in the previous tests it was decided to repeat the tests with even higher dilutions. Dilution factor (500x) was chosen due to the knowledge that the same dilution was applied in solid extraction spectrophotometry method so that the SDS concentration of the samples were 0.8 ppm and salt dosages 10 and 100 ppm (1000 ppm was deliberately left out). However, like mentioned earlier, such a small SDS concentrations (under 1 ppm) might be problematic. Despite high dilution factors, syringe filtration and salt sample purification with solid-phase extraction the cartridges of the guard column was clogged after measurements of 200 samples, but the main column survived unclogged.

12.1.3.1 Salt additives and Solid-phase extraction

HPLC-RP analysis of SDS samples with salt additives and kraft white water (10 x dilution) gave the following results. Firstly, SDS removal efficiency of kraft white water alone, without any salt addition, was 40 %. Secondly, the combination of NaCl salt and white water gave similar removal efficiencies, 32 % and 44 % for 500 ppm and 5000 ppm NaCl addition, respectively. This indicates that NaCl does not have an effect on the determination of SDS content. However, NaCl sample (5000 ppm) without white water gave removal efficiency 46 % for SDS, which tells totally another story, indicating that NaCl can have an effect on SDS determination. These results were conflicting since it is known that NaCl does not precipitate SDS. There was no sign of visible precipitate in the water samples.

Both $CaCl_2$ and $FeSO_4$ coagulated SDS, which was expected, forming a visible precipitate in the sample bottles. SDS removal efficiency of $CaCl_2$ (5000 ppm) alone was 67 %. The combination of $CaCl_2$ and white water resulted in 68 % removal efficiency despite the coagulant dose. SDS removal efficiency of pure $FeSO_4$ (5000 ppm) was 56 % and combination with white water boosted the effect. $FeSO_4$ (500 ppm) gave 78 % SDS removal efficiency and $FeSO_4$ (5000 ppm) gave 64 % SDS removal efficiency. The removal efficiencies of pure salts are listed in Table 30 and 31 (Appendix 8) and RP-ECD results are shown in Figure 44 (Appendix 9).

HPLC-RP analysis of SDS samples with salt additives and kraft white water (x500 dilution) gave the following results. Firstly, SDS removal efficiency of kraft white water alone, without any salt addition, was 32 %. The result is in line with (x10) dilution experiments. Secondly, the combination of NaCl salt and white water gave 89 % SDS removal efficiencies for both 10 ppm and 100 ppm NaCl additions, indicating strong precipitation tendency for NaCl. Also, the pure NaCl sample (100 ppm) without white water gave removal efficiency 89 % for SDS.

Both $CaCl_2$ and $FeSO_4$ additions formed a visible precipitate in the sample bottles. SDS removal efficiency of $CaCl_2$ (100 ppm) alone was 51 %. The combination of $CaCl_2$ and white water had SDS removal efficiencies of 80 % and 86 % for 10 ppm and 100 ppm $CaCl_2$ dosages, respectively. It seems that removal efficiency increases in the present of white water and as the coagulant dosage increases, which do not correlate with the results of (x10) dilution experiments. SDS removal efficiency of pure $FeSO_4$ (100 ppm) was 98 %. 10 ppm of $FeSO_4$ gave 94 % SDS removal efficiency and 100 ppm of FeSO4 gave 100 % SDS removal efficiency. The higher dosage of $FeSO_4$ precipitated SDS a slightly more efficiently. RP-ECD results are shown in Figure 45 (Appendix 10) and removal efficiencies of pure salts are listed in Table 30 and 31 (Appendix 8).

HPLC-RP analysis of SDS samples with salt additives and CTMP white water (x500dilution) gave the following results. Firstly, CTMP white water alone did not show any effect on the measured SDS content of the sample (SDS removal efficiency 0 %). Secondly, the combination of NaCl salt and white water gave 84 % and 87 % SDS removal efficiencies for 10 ppm and 100 ppm NaCl additions, respectively. This, again, indicates strong precipitation tendency for NaCl. Also, the pure NaCl sample (100 ppm)

without white water gave removal efficiency 89 % for SDS. NaCl results were consistent with the previous test made with kraft white water.

Both $CaCl_2$ and $FeSO_4$ additions formed a visible precipitate in the sample bottles. SDS removal efficiency of $CaCl_2$ (100 ppm) alone was 51 %. The combination of $CaCl_2$ and white water resulted in 79 % and 83 % SDS removal efficiencies for 10 ppm and 100 ppm $CaCl_2$ dosages, respectively. It seems that higher coagulant dose does not significantly improve the removal efficiency. SDS removal efficiency of pure $FeSO_4$ (100 ppm) was 98 %. The combination of white water and 10 ppm of $FeSO_4$ gave 99 % SDS removal efficiency and 100 ppm of $FeSO_4$ gave 98 % SDS removal efficiency. The removal efficiency of all $FeSO_4$ dosages is high, telling that Fe^{2+} is a very strong coagulant for SDS. RP-ECD results are shown in Figure 46 (Appendix 11) and the removal efficiencies of pure salts are listed in Table 30 and Table 31 (Appendix 8).

Effect of NaCl on the SDS determination by RP-ECD method was examined by measuring crude NaCl samples. Different dilutions of SDS (10-100 ppm) with and without NaCl addition (500 ppm) were analysed. Samples were analysed without syringe filtration. The presence of NaCl decreased the SDS concentration in all samples approximately 50%. Results are presented in Figure 51 (Appendix 16). ECD spectrum of sodium dodecyl sulfate (40 ppm SDS) with 500 ppm NaCl addition is shown in Appendix 4. The impurity peak (2.0 min) is huge, and approximately 50 % of the SDS concentration is missing.

SES analysis of SDS samples with salt additives and kraft white water (x500 dilution) gave the following results. Firstly, SDS removal efficiency of kraft white water, NaCl or $CaCl_2$ was approximately 5 %, which can be included in the internal error of the method, so they did not have any effect on the measured SDS content of the sample. Secondly, only $FeSO_4$ coagulated SDS, and the highest dose (1000 ppm) was not measurable since the coagulant formed a gel when added to the sample. Removal efficiency was 24 % and 22 % for 10 ppm and 100 ppm $FeSO_4$ dosages, respectively. SES results shown in Figure 34 and removal efficiencies are listed in Table 30 (Appendix 8).

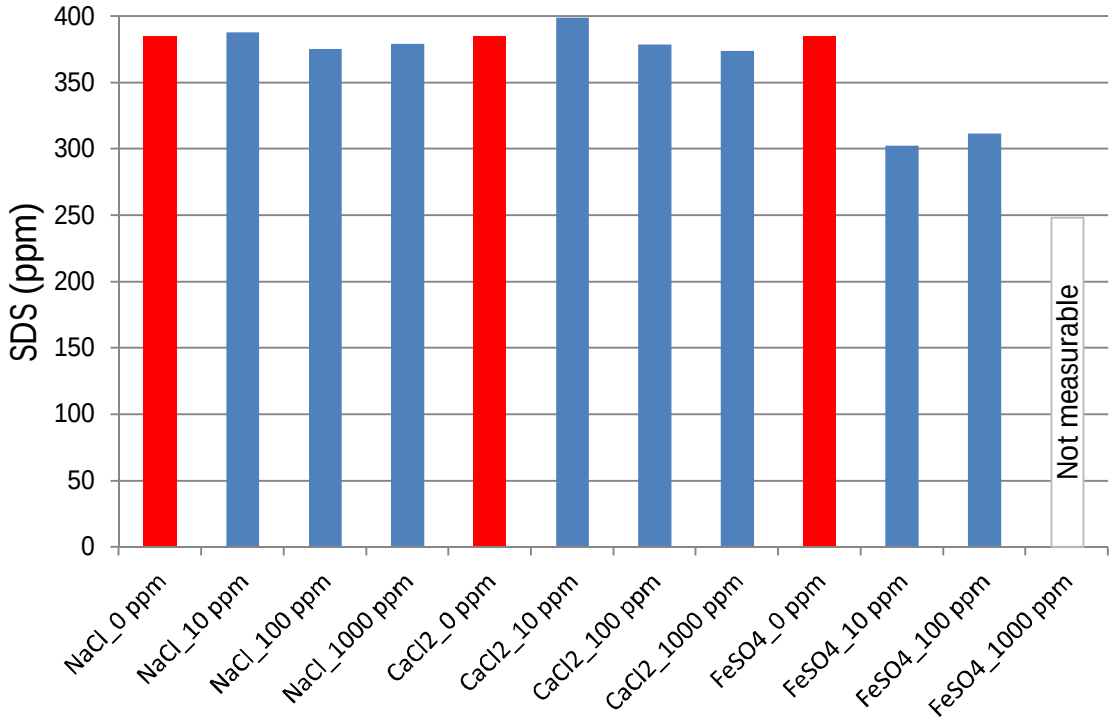


Figure 34. SES results of salt additions in kraft white water (500x dilution). SDS concentration (ppm) on the y-axis and samples on the x-axis. Sample without salt addition (SDS and white water) is marked with the red column, and different salt samples are blue. Added salts 10 ppm, 100 ppm and 1000 ppm of NaCl/CaCl2/FeSO4. Not measurable = sample could not be measured due to gel formation during the extraction procedure.

SES analysis of SDS samples with salt additives and CTMP white water (x500 dilution) gave the following results. Firstly, the removal efficiency of CTMP white water, NaCl or $CaCl_2$ was approximately 5 %, which can be included in the internal error of the method, so they did not have any effect on the measured SDS content of the sample. Secondly, only $FeSO_4$ coagulated SDS, and the highest dose (1000 ppm) was not measurable since the coagulant formed a gel when during the extraction process. Removal efficiency was 14 % and 17 % for 10 ppm and 100 ppm $FeSO_4$ dosages, respectively. SES results are shown in Figure 47 (Appendix 12) and removal efficiencies are listed in Table 30 (Appendix 8).

It is very desirable if samples under investigation can be instrumentally analysed without any pre-treatment methods. Usually the final determination procedure, such as liq-

uid chromatography, is rather easy and quick to perform, but the sample preparation (like SPE) before the analysis demands lots of time and materials. Levine *et al.*[75] tested ion pair reverse-phase chromatography connected with suppressed conductivity detection to study biodegradation of anionic surfactants (concentrations were between 2 – 500 ppm) during wastewater recycling. Sample matrix consisted high concentrations of inorganic ions and some amounts of non-ionic surfactants. Even though no pre-treatment was done, interference did not occur, and impurities did not affect the measurement process.

Wei *et al.*[73] used ion-pair chromatography connected with suppressed conductivity detection for simultaneous determination of seven anionic alkyl sulfates in environmental water samples without any pre-treatment of the samples. Results of Levines and Weis studies encouraged to test the SDS determination from white water samples without pre-treatment since it would considerably fasten the procedure. However, in these experiments, the presence of salts disturbed the determination of SDS. The presence of NaCl decreased the measured SDS concentration in all samples systematically approximately 50%. Thus, the sample pre-treatment with SPE-extraction was examined more closely.

Almost all salts could be removed by SPE. According to SPE results, NaCl additions of 500 ppm and 5000 ppm gave SDS removal efficiencies 0 % and 3 %, respectively. Thus, the presence of NaCl does not affect the measured SDS content of the sample. This result confirmed that salts indeed significantly disturb the HPLC-RP analysis and salt impurities need to be removed before the analysis. SDS removal efficiencies of 500 ppm and 5000 ppm of $CaCl_2$ were 90 % and 97 %, respectively and 500 ppm of FeSO4 gave 91 % removal efficiency of SDS. $CaCl_2$ and $FeSO_4$ strongly coagulate SDS.

SDS removal efficiency of kraft white water alone was 50 % and in combination with 500 ppm of NaCl the SDS removal efficiency was 36 %. Therefore, the particles in white water alone can coagulate SDS. CTMP white water alone gave SDS removal efficiency of 23 %. Results are shown in Appendix 17. ECD spectrum of sodium dodecyl sulfate (40 ppm SDS) with 500 ppm NaCl addition after solid phase extraction (SPE) pre-treatment is shown in Appendix 5. The impurity peak (2.0 min) is negligible, and SDS concentration was 37 ppm.

The recovery of SDS was calculated based on the results of pure SDS samples that were analysed without SPE-extraction procedure. The washing waters were collected and analysed to see if any SDS went through the column in elution and washing steps. SDS recovery was approximately 86 %. The analyte recovery can be improved by perfecting the procedure and with more careful performing (slower eluation).

12.1.3.2 Retention aid additives and filter membrane tests

HPLC-RP analysis of SDS samples with retention aid additives and kraft white water (x500dilution) gave the following results. Firstly, the SDS removal efficiency of kraft white water alone, without any retention aid addition, was 24 %. The result is similar to the salt experiments. Secondly, the combination of c-Pam and white water gave 50 %, 59 % and 63 % SDS removal efficiencies for 200, 400 and 800 g/t additions, respectively. Thirdly, c-Pam (400 g/t) sample without white water addition gave removal efficiency 64 % for SDS. The SDS removal efficiency of c-Pam increases as the concentration of the aid increases. According to the results C-pam retention aid can bind approximately 50 – 60 % of SDS in the water sample.

Microparticle (400 g/t) alone did not remove SDS (0 % removal efficiency). The combination of the microparticle and white water resulted in 95 %, 99 % and 33 % SDS removal efficency for 200, 400 and 800 g/t additions, respectively. The results are inconsistent. There were problems with the filtration due to the high amounts or retention aid, and the filter was clogged easily. Baseline variations may also have caused the error in the results.

SDS removal efficiency of pure two component systems of c-Pam and microparticle (400 + 400 g/t) was 92 %. The combination of two component system and white water resulted in 70 %, 85 % and 83 % SDS removal efficiencies for 200, 400 and 800 g/t additions, respectively. The higher dose of retention aids seems to remove SDS more efficiently. According to the results approximately 80 % of SDS can be removed with the two component system. Filtration was difficult also with these samples and could

have effected on the results. RP-ECD results are shown in Figure 35. The removal efficiencies of pure retention aids (without white water) are listed in Table 32 and Table 33 (Appendix 13).

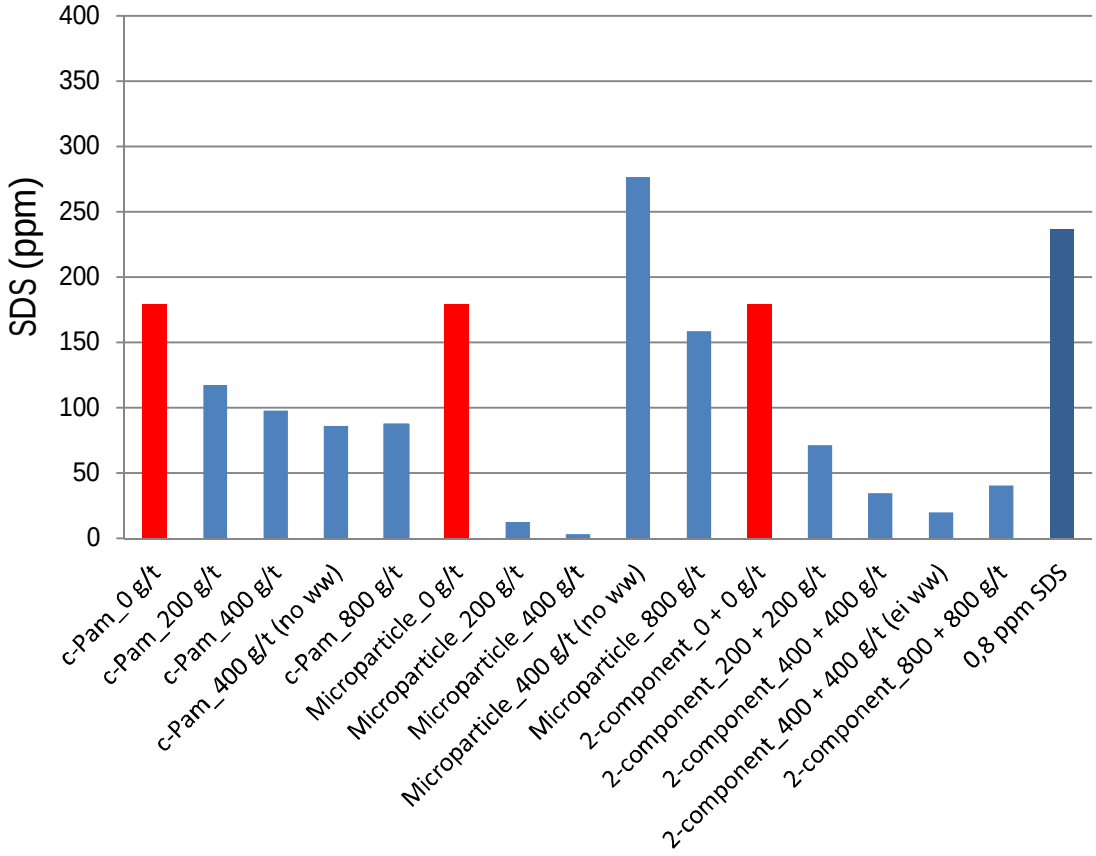


Figure 35. RP-ECD results of retention aid additions in kraft white water (500x dilution). SDS concentration (ppm) on the y-axis and samples on the x-axis. Pure SDS reference is marked with the dark blue column, a sample without aid addition (SDS and white water) is marked with the red column, and different retention aid samples are blue. Added retention aids 200 g/t, 400 g/t and 800 g/t of c-Pam/microparticle/2-component system. No ww = SDS sample with pure retention aid addition (no white water).

SES analysis of SDS samples with retention aid additives and kraft white water (x500 dilution) gave the following results. Firstly, kraft white water alone did not affect the measured SDS content of the sample (1 % removal efficiency) like it was in the SES analysis of salts. Secondly, the combination of c-Pam and white water gave 4 %, 7 %

and 10 % SDS removal efficiencies for 200, 400 and 800 g/t additions, respectively. Only the c-Pam dose of 800 g/t can clearly precipitate SDS, but the two lower dosages do not considerably affect the measured SDS content. Thirdly, SDS removal efficiency of 200 g/t of microparticle was 11 %. Microparticle dosages of 400 g/t and 800 g/t could not be analysed since the sample formed a gel during the extraction process. The same outcome happened with the two component system, and the dosages of 400 g/t and 800 g/t could not be measured. SDS removal efficiency of 200 g/t dosage of two component system was 12 %. SES results are shown in Figure 48 (Appendix 14) and removal efficiencies are listed in Table 32 (Appendix 13).

The retention aids blocked the syringe filters easily so larger GH membranes (47 mm, 0.45 µm) with vacuum filtration was tested and compared with GHP syringe filtration. GH membrane retained 8 % of pure SDS (initial concentration 0.8 ppm) and GHP filter 79 %. The result of GHP filter is inconsistent and probably caused by the baseline alternations. GH filtrated SDS with 400 g/t and 800 g/t c-Pam additions gave 17 % and 46 % SDS removal efficiencies, respectively. GHP filtrated SDS with 400 g/t and 800 g/t c-Pam additions gave 54 % and 66 % SDS removal efficiencies, respectively. Vacuum filtration eased the sample filtration process considerably and gave better SDS recovery. Results are shown in Figure 49 (Appendix 15).

Vacuum filtration was also tested with higher retention aid dosages. C-Pam (2500 g/t) and microparticle (2500 g/t) could be filtrated easily, 5000 g/t filtrated slowly and 12500 g/t could not be filtrated. Thus, up to 2500 g/t of retention aid (meaning that sample can contain up to 10 ppm of SDS) can be filtrated with vacuum filtration without any problems.

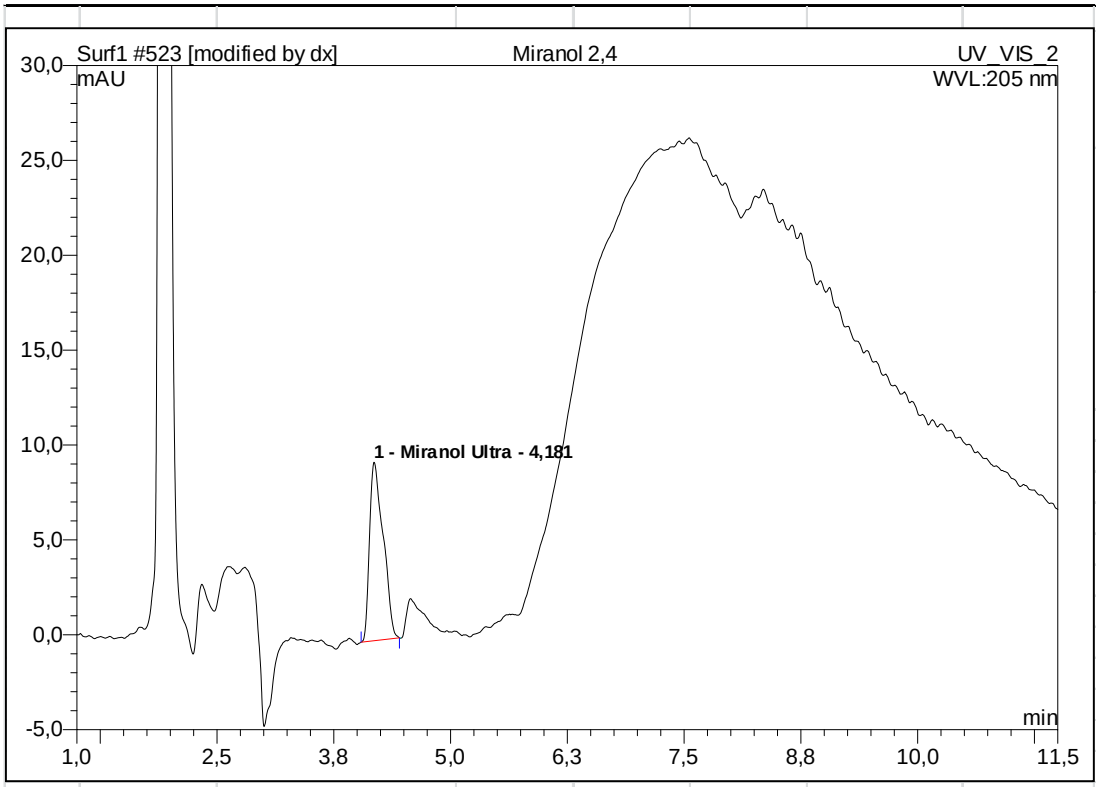
Pre-filtration of the samples could enable the use of higher SDS and retention aid concentrations so that the largest particles could be removed from the sample before the final filtration with the 0.45 µm filter. Glass fibre membrane or inorganic silver filters are common materials for pre-filtration. Pickering [52] recommended a silver filter for the filtration of organic solutes, but Leenheer[180] advised in his book that organic solutes with sulphur content can interact with silver membrane filters. The chemical compatibility of silver and glass fibres with other solvents is almost the same. The exception is that

silver cannot be used with nitric or sulfuric acid. Silver is also more expensive material than glass fibres.

Since it was not fully clear how SDS would interact with syringe filter materials a couple of syringe filters test were performed with GHP and nylon syringe filters. The GHP filter retained approximately 3 % of SDS and the nylon filter 18 % ppm of SDS. The effect of GHP filtration is not that significant, but the effect of nylon can be considered problematic. Especially with really small SDS concentrations (under 1 ppm) the syringe filtration can cause a significant error in the results. The results of syringe filtration effect of GHP and nylon membranes on the measured SDS content are presented in Figure 50 (Appendix 15).

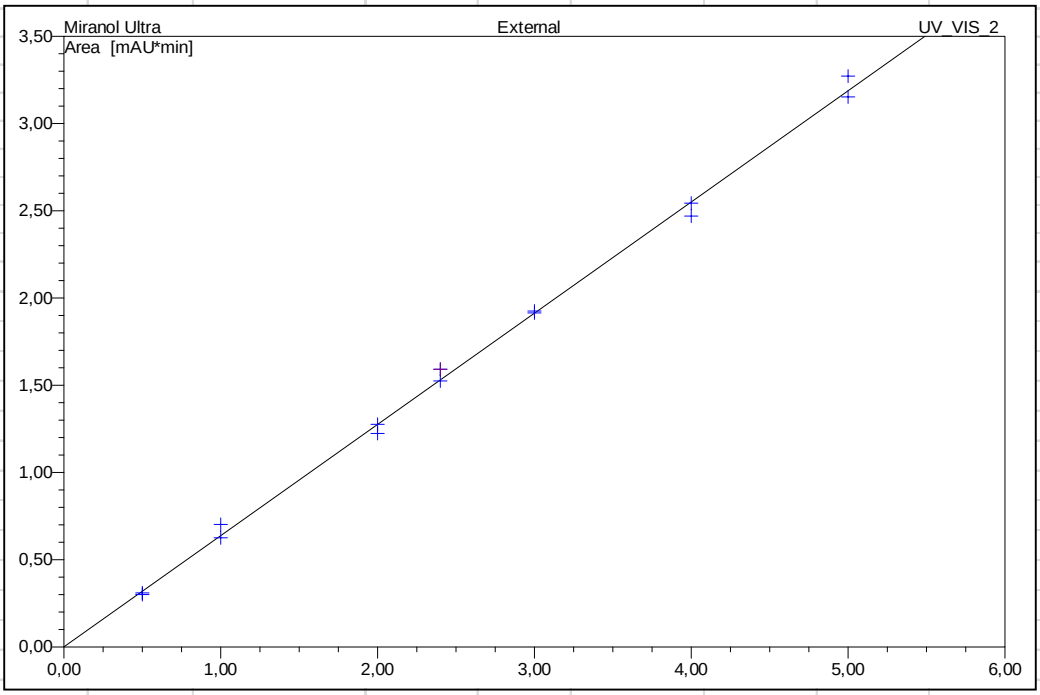
12.1.4 Miranol Ultra

The determination of Miranol Ultra (MU) with reversed-phase chromatography and UV-detection (205 nm) succeeded. The retention time of MU was 4.2 minutes. UV-active impurities could be seen at retention time 2.0 minutes. UV spectrum at wavelength 205 nm of pure MU sample and calibration curve (correlation coefficient 0.9989) for MU concentration range 0.5 – 5.0 g/L are presented in Figures 36 and 37.



No.	Ret.Time	Peak Name	Height	Area	Rel.Area	Amount	Type
	min		mAU	mAU*min	%		
1	4,18	Miranol Ultra	9,404	1,591	100,00	2,496	BMB*
Total:			9,404	1,591	100,00	2,496	

Figure 36. UV spectrum (205 nm) of Miranol Ultra (MU). MU concentration 2.4 g/L and retention time 4.2 minutes. Some UV active impurities can be seen at retention time 2.0 min. The rise in the baseline UV absorbance is caused by the increasing portion of acetonitrile in the eluent composition.



No.	Ret.Time	Peak Name	Cal.Type	Points	Corr.Coeff.	Offset	Slope	Curve
	min				%			
1	4,18	Miranol Ultra	0LOff	14	99,8944	0,0007	0,6374	0,0000
Average:					99,8944	0,0007	0,6374	0,0000

Figure 37. UV detection (205 nm) of Miranol Ultra (MU). Calibration curve 0.5 – 5.0 g/L of MU. Correlation coefficient 0.9989.

The effect of impurities on the MU analysis was investigated with kraft white water and 100 ppm NaCl and $CaCl_2$ additions. MU concentrations were 1 g/L, 2.4 g/L and 4.0 g/L. MU removal efficiency of kraft white water was 12 %, 3 % and 0 % from the samples 1 g/L, 2.4 g/L and 4.0 g/L of MU, respectively. MU removal efficiency of pure NaCl was 17 %, 0 % and 0 % from the samples 1 g/L, 2.4 g/L and 4.0 g/L of MU, respectively. Combination of kraft and NaCl gave 17 %, 6 % and 0 % MU removal efficiencies for samples 1 g/L, 2.4 g/L and 4.0 g/L, respectively. MU removal efficiency of kraft combined with $CaCl_2$ was 35 %, 24 % and 11 % from 1 g/L, 2.4 g/L and 4.0 g/L the samples, respectively. Results are shown in Table 34 and Figure 52 (Appendix 18).

12.2 Accelerated aeration experiments

Aeration experiments with very high air flow rate (8.0 L/min) and SDS concentrations (50 – 400 ppm) were performed to see how the samples behave with extreme conditions. The temperature of the samples was approximately 20°C and the oxygen concentration was between 8.0 – 9.0 mg/L. Samples containing 50 ppm and 100 ppm generated 9 L and 14 L of foam, respectively. The foam layer started to collapse rather fast during the aeration test. Tap water samples containing 200 ppm and 400 ppm SDS overflowed the tank (over 18 L foam generation) and the airflow needed to be adjusted to 2 L/min during the experiment to keep the foam in the vessel. Results are presented in Figure 53 (Appendix 19).

Due to the results of tap water samples the air flow rate for white water tests was adjusted to 2 L/min. The temperature of the white water samples was approximately 20°C, the oxygen concentration was between 8.0 – 9.0 mg/L, pH 7 – 8 and conductivity 151 µS. Samples containing 50 ppm and 100 ppm of SDS generated 12 L and 18 L of foam, respectively. The foam started to collapse slowly during the aeration. The white water samples containing 200 ppm and 400 ppm of SDS overflowed (over 18 L foam generation). Results are presented in Figure 54 (Appendix 20).

According to the results, the highest SDS concentration of tap water that can be used with air flow rate 8 L/min is 100 ppm and with air flow rate 2 L/min is 400 ppm. The highest SDS concentration in white water sample that can be used with air flow rate 2 L/min is 100 ppm. In general, the foam generated slower in white water samples than in pure tap water sample. However, the foam layer on the surface of white water sample was more stable than that on the surface of tap water sample. White water sample contains fibres, fines and impurities that can stabilise the foam. In wastewaters, there are even more compounds present so it was assumed that foam generation might be rather slow, but the generated foam can be extremely stable.

These results and the knowledge that the air flow rate in the real aeration tank is 0.5-1.5 m^3/h per 1m^3 were used to optimise the procedure for the second aeration experiments with tap-, white-, and wastewater samples. It was calculated that the air flow rate should be at least 0.25 l/min in the laboratory vessel (water volume 10 l). Since the target was

to develop an accelerated test (test period max 2-3 hours) 100 ppm of SDS was chosen to be the maximum dose and air flow rate 0.6 L/min (well below 2.0 L/min) was used.

Tap water samples of 10 and 20 ppm (0.6 L/min) and 10 ppm (1.0 L/min) SDS generated very delicate foam (foam volume under 0.5 L), that died immediately after stopping the aeration. With 40 ppm SDS sample the foam increased slowly up to 3.4 L within 90 min of aeration and after 15 min without aeration, there was 1.5 L left of the foam. With 60 ppm SDS sample the foam increased up to 4.3 L during the first 30 min and stayed stable rest of the aeration time. After the aeration was stopped the foam died to 2.2 L during 15 min. With 100 ppm SDS sample, the foam increased steadily up to 5.5 L within the 90 min of aeration and died to 2.9 L after 15 min the aeration was stopped. The temperature of the samples was approximately 20°C and the oxygen concentration was between 8.0 – 11.0 mg/L. The oxygen concentration is temperature dependent and varies slightly during the aeration as does the temperature. SDS concentration did not show a significant correlation to the oxygen concentration. Results are presented in Figure 38.

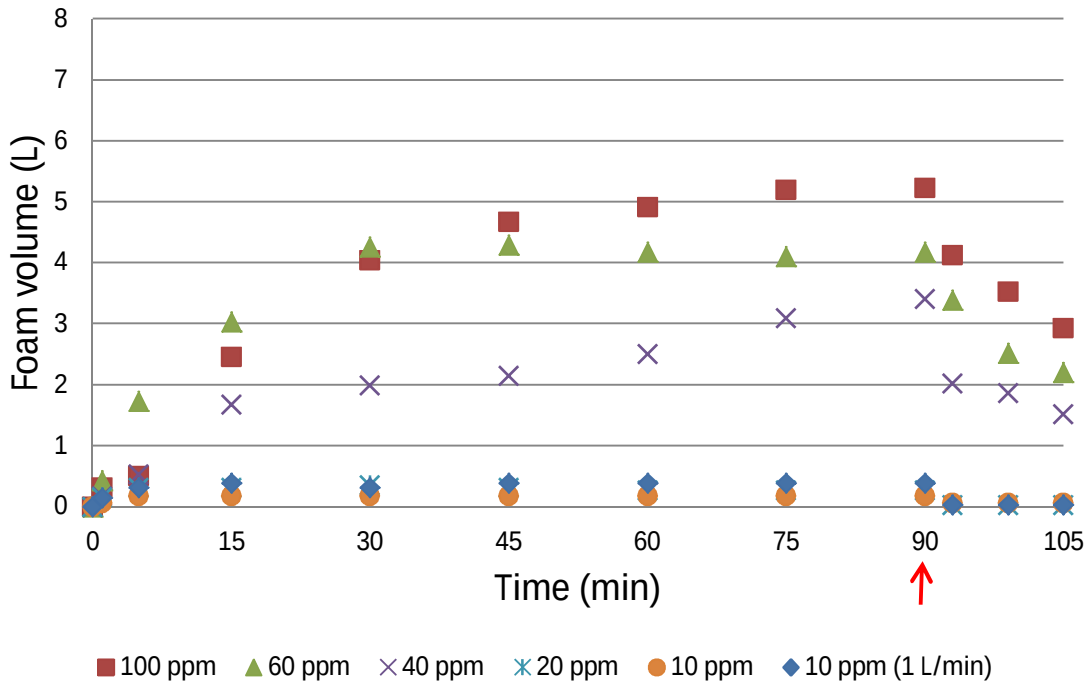


Figure 38. Tap water samples. 10 ppm SDS with air flow rate 1.0 L/min (blue), 10 ppm SDS (orange), 20 ppm SDS (blue star), 40 ppm SDS (violet), 60 ppm SDS (green) and

100 ppm SDS (red) with air flow rate 0.6 L/min. Foam volume (L) on the y-axis and aeration time on the x-axis. The aeration was stopped after 90 min (read arrow) and 15 min of foam dying was recorded.

White water samples of 10, 20 and 40 ppm SDS with air flow rate 0.6 L/min generated very delicate foam (foam volume under 0.5 L), that died immediately after stopping the aeration. With 60 ppm SDS sample the foam increased slowly up to 5.0 L within 75 min and after 15 min without aeration, there was 2.0 L left of the foam. With 100 ppm SDS sample the foam increased up to 6.8 L during the first 45 min. Then the foam volume started to decrease (the top layer dried) and was 5.9 L at 90 min of aeration. After the aeration was stopped the foam died to 3.4 L during 15 min. The temperature of the samples was approximately 20°C, the oxygen concentration was between 8.0 – 9.0 mg/L, pH was 7 – 8 and conductivity 215 µS. Results are shown in Figure 55 (Appendix 21).

Wastewater samples containing 10, 20 and 40 ppm SDS with air flow rate 0.6 L/min did not generate foam. 60 ppm SDS sample generated very delicate foam (foam volume 0.2 L), that died almost immediately after stopping the aeration. Sample of 100 ppm SDS also formed very delicate foam (0.25 L) that died in 3 min after stopping the aeration. The temperature of the samples was approximately 20°C, initial oxygen concentration was between 2.0 – 4.0 mg/L and after aeration 7.0 – 9.0 mg/L , pH was 6.5 – 7.5 and conductivity 1.2 mS. The oxygen concentration increased clearly during the aeration. Microbial activity consumes oxygen during the sample storage, so it is evident that the oxygen concentration increases when the air is fed into the effluent. Results of waste water samples containing 10 to 100 ppm of SDS with air flow rate 0.6 L/min are presented in Figure 39. Pictures of foam generation in tap-, white-, and wastewater samples of 20, 40, 60 and 100 ppm SDS dosages after 60 minutes of aeration are shown in Figure 40.

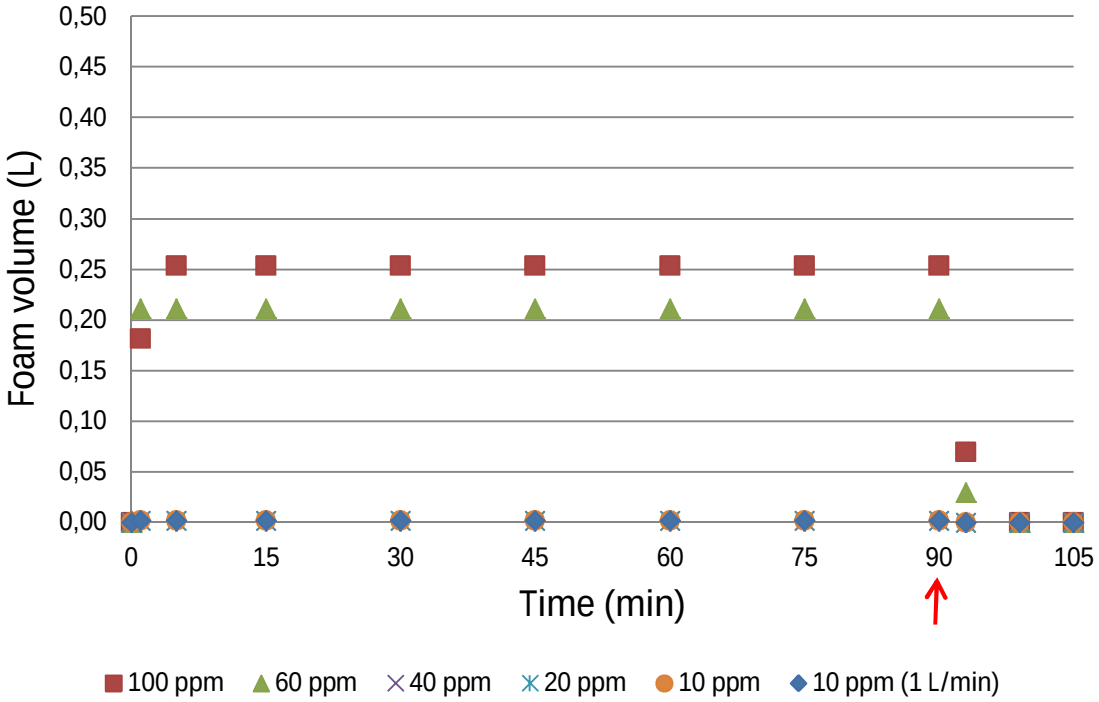


Figure 39. Wastewater samples. 10 ppm SDS with air flow rate 1.0 L/min (blue), 10 ppm SDS (orange), 20 ppm SDS (blue star), 40 ppm SDS (violet), 60 ppm SDS (green) and 100 ppm SDS (red) with air flow rate 0.6 L/min. Foam volume (L) on the y-axis and aeration time on the x-axis. The aeration was stopped after 90 min (read arrow) and 15 min of foam dying was recorded.

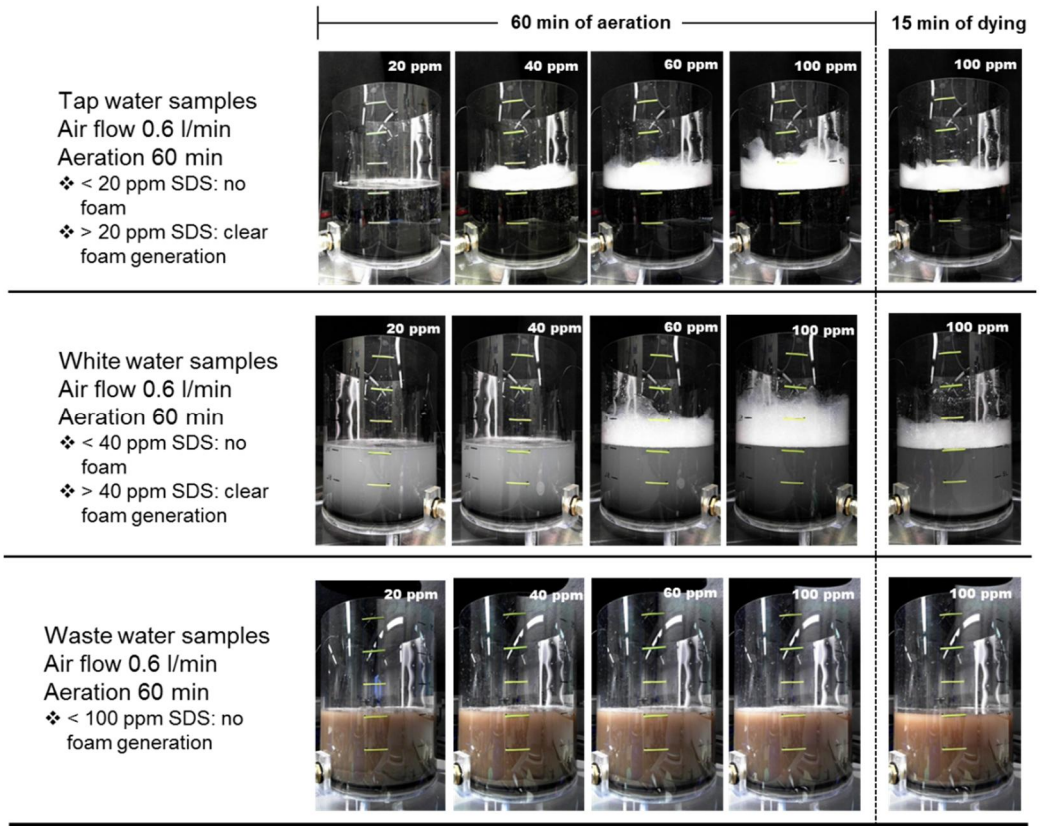


Figure 40. Foam generation in tap-, white-, and wastewater samples of 20, 40, 60 and 100 ppm SDS dosages after 60 minutes of aeration. On the right side, there is 100 ppm SDS sample after 15 minutes from stopping the aeration (foam dying).

12.3 Flocculation experiments

Two different doses of PIX-105 coagulant (500 µl and 1000 µl) were tested, and the addition of NaOH was planned so that pH varied from acidic to neutral or basic. Results of 500 µl dose of PIX-105 showed that the optimal pH range was between 3 and 6 giving ~33 % SDS removal efficiency. At pH over 6 removal efficiency collapsed quickly under 5 %. For bigger (1000 µl) coagulant dose results showed better SDS removal efficiency. The optimal pH was around 3 and SDS removal efficiency was 59 %. SDS removal efficiency started to collapse when pH changed towards basic but collapse was steady and did not reach 5 % until pH was close to 10. Results of PIX-105 experiments

are shown in Tables 35 and 36 and illustrated in Figure 56 and 57 (Appendixes 22 and 23).

Two different doses of PAX-14 coagulant (200 µl and 400 µl) were also tested and the addition of NaOH was planned so that pH varied from acidic to neutral or basic. Results of 200 µl dose of PAX-14 showed that the optimal pH range was between 4 to 5 giving ~65 % SDS removal efficiency. In basic conditions, PAX-14 showed 27 % SDS removal efficiency. For bigger (400 µl) coagulant dose results showed better SDS removal efficiency. The optimal pH range was narrow, from 4.4 to 5 and SDS removal efficiency was ~95 %. SDS removal efficiency started to collapse when pH changed towards basic but collapse was steady and at pH 8 SDS removal efficiency was still 38 %. Figure 41 shows the SDS removal results of PAX-14 (400 µl) experiments. Results of PAX-14 experiments are also listed in Tables 37 and 38 (Appendixes 24 and 25) and the SDS removal results of PAX-14 (200 µl) experiments are illustrated in Figure 58 (Appendix 24).

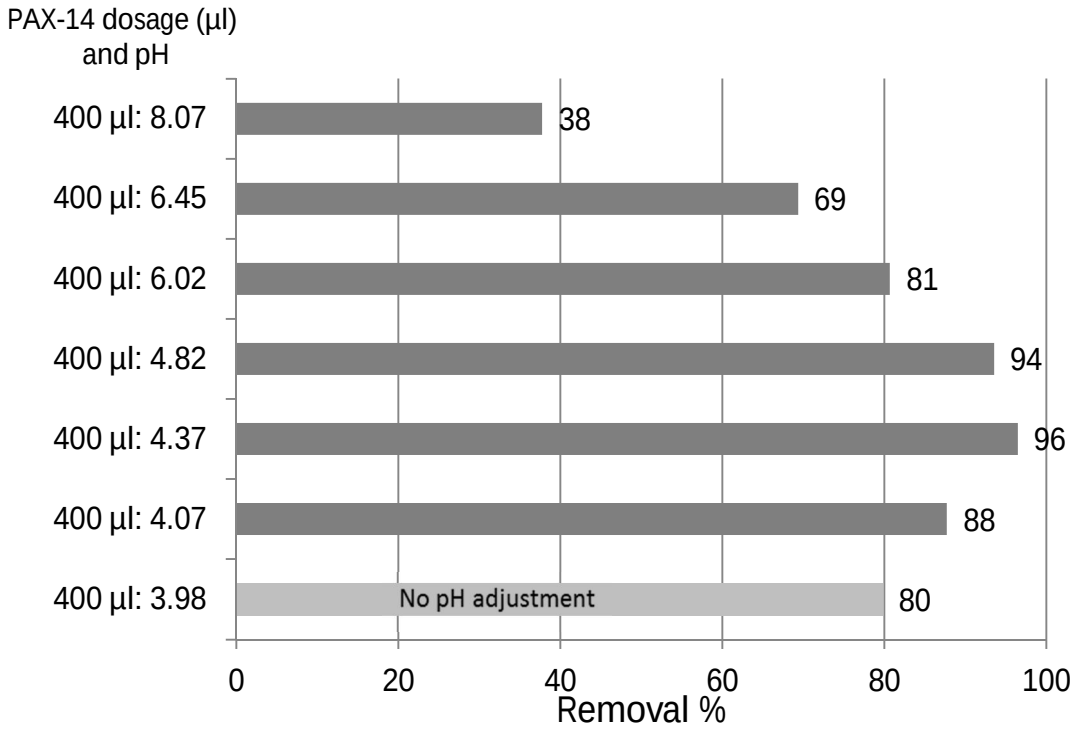


Figure 41. SDS removal results of PAX-14 (400 µl) experiments. The sample was 400 ppm SDS in deionized water. Coagulant dose and sample pH on the y-axis and SDS removal (%) on the x-axis

Experiments with a white water using both coagulants PIX-105 and PAX-14 were also made. The aim was to compare the best results of these two coagulants and observe how sample impurities affect the precipitation efficiency and pH of the sample. With 400 µl dose of PAX-14 pH range from 4 to 6 gave ~80 % SDS removal efficiency which is the same efficiency than with the deionized water samples at the same pH areas. With the smaller 200 µl dose of PAX-14 pH over 6 gave 36 % SDS removal efficiency for the white water sample and 27 % SDS removal efficiency for the deionized water sample.

Results of 1000 µl dose of PIX-105 at pH 2.5 gave 47 % SDS removal efficiency for the white water and 48 % for the deionized water sample. At pH 3 the same dose gave 48 % SDS removal efficiency for the white water and 59 % for the deionized water. The smaller 500 µl dose of PIX-105 at pH range from 6 to 7 showed 15 % SDS removal efficiency for the white water sample and 2 % SDS removal efficiency for the deionized water.

Figure 42 shows the comparison of SDS precipitation efficiency of PAX-14 between the deionized water and the white water samples at the same pH ranges. Results of the white water experiments are also listed in Table 39 and Table 40 (Appendixes 25 and 26). Comparison of results of SDS precipitation efficiency of PIX-105 between the deionized water and the white water samples at the same pH ranges are illustrated in Figure 59 (Appendix 26).

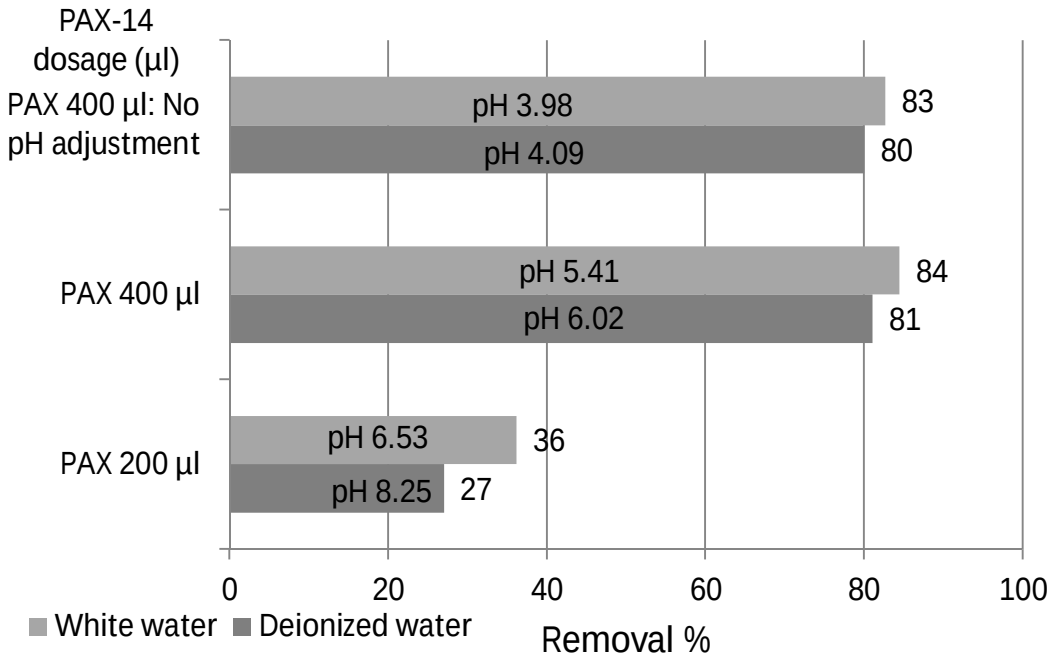


Figure 42. Comparison of SDS precipitation efficiency between the deionized water and the white water samples at the same pH ranges. The samples were 400 ppm SDS in white water and 400 ppm SDS in deionized water. Coagulant: polyaluminium chloride PAX-14. Coagulant dose on the y-axis and SDS removal (%) on the x-axis. pH is written down on the bars.

Comparing added NaOH doses and pH values between the white water and the deionized water samples the following results were observed. Firstly, 400 µl dose of PAX-14 and no pH adjustment gave the same pH values (pH 4) for both the white and the deionized water. Secondly, 1080 µl dose of NaOH changed pH of the white water samples to 5.4 and the deionized waters to 4.7. 200 µl dose of PAX-14 and 600 µl addition of NaOH gave pH 6.5 for the white water and pH 4.7 for the deionized water. Thirdly, 1000 µl dose of PIX-105 and no pH adjustment also gave the same pH values (pH 2.6) for both the white and the deionized water. Fourthly, 2880 µl dose of NaOH gave similar results for both of the samples, pH 3.2 for the white water and pH 3.0 for the deionized water. Fifthly, 500 µl dose of PIX-105 and 2040 µl addition of NaOH gave pH 6.9 for the white water samples and 6.1 for the deionized waters. Comparison results of added NaOH doses and pH values between the white water and the deionized water samples are shown in Table 41 and illustrated in Figures 60 and 61 (Appendix 27-29).

Experiments made with deionized water showed that both coagulants, ferric sulfate and polyaluminum chloride, precipitate SDS. Polyaluminum chloride was more effective: 400 µl dosage of PAX-14 yielded ~ 90 % removal efficiency of SDS and 1000 µl dosage of PIX-150 yielded ~ 60 % removal efficiency of SDS (Table 28). Larger doses of coagulant improved removal efficiency.

Removal efficiency was found to be pH dependent. The optimal pH range for 500 µl dose of PIX-105 was between 3 and 6. The optimal pH for 1000 µl dose of PIX-105 was 3. The optimal pH range for 200 µl dose of PAX-14 was from 4 to 5 and for 400 µl dose of PAX-14 it was from 4.4 to 5. In conclusion, the optimal pH range is wider with smaller coagulant doses thus pH does not affect significantly on precipitation efficiency. With higher coagulant doses the optimal pH range is narrow and pH affects considerably on removal efficiency.

Results are consistent with the literature in outline. Aluminium was more efficient in the precipitation process than iron compound, and larger coagulant dosages gave better removal efficiencies as Talens-Alensson *et al.*[151]stated in their study. Overall, pH also played an important role in precipitation efficiency like was expected. Aboulhassan *et al.*[3] reported that the optimal pH range for $FeCl_3$ coagulant was from 7 to 9. According to findings of this study, the optimal pH value for ferric sulfate was about 3. In a neutral or basic solutions, iron coagulant worked poorly. Results are truly divergent. On the other hand Aboulhassan *et al.* [3] made their experiments with a microelectronic factory wastewaters in which case the sample has been totally different than a deionized water. However, this study revealed convergent results with Adak *et al.*[18] who defined pH 5.5 to be the optimal pH value for Al_2O_3 and in this study the optimal pH range for polyaluminum chloride was found to be from 4.4 to 5 also.

Table 28. Best SDS precipitation results of coagulants. The addition of NaOH (µl) and sample pH after the addition of NaOH are also shown. Samples contained 400 ppm SDS (600 ml) in deionized water (600 ml).

Sample code	2 M NaOH (µl)	PIX-105 (µl)	PAX-14 (µl)	pH	SDS removal (%)
1. PIX-105	2040	500		6.10	34
2. PIX-105	2880	1000		3.00	59
1. PAX-14	600		200	4.65	68
2. PAX-14	1080		400	4.37	96

Comparison experiments between pure and impure samples revealed that there was no significant difference in precipitation efficiency between the deionized and the white water samples when pH was not adjusted. With PAX-14 precipitation, efficiency remains similar when pH was at the optimal range. In more basic conditions precipitation was weaker with the white water samples. With PIX-105, the deionized water sample precipitated better at the optimal pH range. In more basic conditions, out of the optimal pH range, precipitation was extremely poor with the deionized water sample while the white water sample precipitated better.

It was also found that the same addition of NaOH gave different pH values for deionized water and white water samples. White water samples became more basic than deionized water samples. This can be explained by the fact that the deionized water is slightly acidic (pH 6.5) from the start. This is due to dissolved CO_2 that is always present in the water. The lack of ions in deionized water makes it more sensitive to the effect of CO_2. In a tap water, ions tend to buffer CO_2 and keep pH neutral.[17] It can be assumed that smaller NaOH dose is sufficient for pH adjustment of impure samples.

CONCLUSIONS

The main issues addressed in the experimental part of this study were, firstly, the determination of SDS by using high-performance reversed-phase liquid chromatography (HPLC-RP) combined with electrical conductivity detection (ECD). Secondly, the accelerated aeration test of SDS and, thirdly, the flocculation tests of SDS. The main focus was on the determination of SDS by HPLC-RP combined with electrical conductivity detector (ECD).

SDS hydrolysis

SDS concentration of the SDS hydrolysis samples was determined with solvent extraction spectrophotometry (SES), and reversed-phased high-performance liquid chromatography (HPLC-RP) combined with electrical conductivity detection (ECD).

One week time monitoring test was performed to get information about the shelf life of SDS solution. According to the results, 400 ppm SDS solution can be preserved for one week at room temperature without any significant changes in the SDS concentration of the sample. RSD of the results were under 5 % in both methods so they can be considered reliable even though there is a significant difference in the results between the two methods. SES gives systematically lower concentrations for SDS than RP-ECD method. This is probably due to an incomplete transfer of SDS from a water phase to an organic solvent during extraction step of the solvent extraction procedure.

SDS hydrolysis experiments by heating and pH change was performed to define optimal hydrolysis conditions. The effect of pH on SDS concentration was clear when the pH dropped under 3 but there was no sign of accelerated hydrolysis or change in pH when the pH adjusted samples were heated at 60°C for 24 hours. The SDS concentration (originally 400 ppm) of initially neutral solution was not affected by the heating at 60°C or 90°C for 24 hours. According to this study, SDS removal by heating requires a higher temperature than 90°C and longer heating time than 24 hours to hydrolyse. Therefore, one can assume that SDS hydrolysis by heat not a cost-effective method.

Salts

The effects of additives (salts and retention aids) on the measured SDS content of white water samples were examined with RP-ECD and SES-method and the results were compared to see if there are any significant differences. Conclusions made, based on the salt additive tests performed with RP-ECD, tell that kraft white water removes SDS while the effect of CTMP is not that significant. It can be assumed that the positively charged fine compounds present in Kraft white water sample probably bind anionic SDS.

NaCl showed unexpected tendency to remove SDS from the sample (30 – 90 %) which raised suspicions that the RP-ECD-method cannot tolerate high salt concentrations. Furthermore, it seems that very low concentration of SDS increases the error. Salt might affect the elution of SDS molecule in the column or disturb the detection process on conductivity detector. SDS removal efficiency of $CaCl_2$ was between 50 – 86 % and was higher with the higher coagulant dose. $FeSO_4$ was the most effective coagulant with the SDS removal efficiencies between 50 – 100 %.

Results from HPLC-RP analysis method and solvent extraction method differed significantly. According to SES analysis, white waters (both kraft and CTMP) do not bind SDS. Also, NaCl and $CaCl_2$ gave really negligible SDS removal efficiencies (3 – 7 %). Only $FeSO_4$ showed precipitation tendency for SDS even with low coagulant dosages (14 – 24 %) and it seemed that in kraft white water the SDS removal efficiency was higher. The 1000 ppm dosages of $FeSO_4$ were not measurable since the coagulant formed a gel when added to the sample.

Solvent extraction spectrophotometry involves anionic sample that binds with a cationic colouring agent and the formed complex is extracted in an organic solvent, and the transferred colour is detected with a spectrophotometer. Even though other cationic compounds in the sample matrix can disturb the analysis, the affinity of the cationic dye against anionic SDS molecule is very strong and might be able to displace other compounds already attached to SDS. Thus, even if the SDS would have been coagulated with, for example, fine compounds of white water or Ca^{2+}-ions, it is possible that during the extraction procedure the cationic dye steals the SDS molecule for itself, and the

method measures the total amount of SDS in the sample. Hence, the solvent extraction spectrophotometric method is not sensitive to interactions between SDS and additives.

By contrast, RP-ECD method measures the free SDS concentration of the sample and is a potential analysis method for investigation of interactions between the analyte and different additives. It is rather important to know the amount of free SDS (SDS in monomeric form) in the sample since only the free SDS can affect the surface tension and foam generation of a liquid. The only sample treatment step is filtration, that removes particles larger than 0.45 µm, and does not affect the analyte content of the sample any other way. Thus, if the analyte forms a solid precipitate with the cationic impurity, part of the analyte could be removed during the filtration. If the neutral complex of the anionic molecule and cation impurity survives from the filtration, they most likely stay attached for the whole time from the autosampler to the detector. Anion exchange suppressor might be able to remove small cations (such as Ca^{2+}) but if the displacing with H^{+}-ions fails the conductivity detector is not able to detect neutral compounds.

SPE

Salts interfered the HPLC-RP analysis so solid-phase extraction (SPE) was tested as a sample pre-treatment method to remove interfering impurities. Almost all salts could be removed by SPE. The presence of NaCl did not affect the measured SDS content of the sample, but $CaCl_2$ and $FeSO_4$ strongly coagulated SDS. This result confirmed that salts indeed interfere significantly the HPLC-RP analysis and salt impurities need to be removed before the analysis. SDS recovery was approximately 86 %, so the procedure needs some modification.

Retention aids

RP-ECD tests showed that retention aids can bind significant amounts of SDS from the sample matrix, and a higher dose leads to a higher removal efficiency. C-Pam has a cationic nature, so the affinity for anionic SDS is easy to understand. Microparticles have an anionic character so interactions with SDS should not be that strong. However, microparticles tend to block the filters (0.45 µm GHP) effectively, so it is possible that instead of binding with microparticles, SDS just got stuck into the filter. Pre-filtration

prior the syringe filtration would have been desirable with water samples containing retention aids.

According to SES analysis, the retention aids can remove SDS in some extend. Large amounts of aids cannot be analysed by this technique since they form emulsions and gels when combined with a colouring agent and organic solvent during the extraction process. The results from RP-ECD method and SES analysis are rather difficult to compare due to the difference in analytical procedures. However, according to this study, it seems that there are interactions between retention aids and SDS.

Filter membrane tests

The retention aids tend to block the syringe filters easily so larger GH membranes (47 mm, 0.45 µm) and vacuum filtration was tested and compared with GHP syringe filtration. There is a dilemma with the retention aids (and also with salts). When reducing the amount of the retention aid also, the concentration of SDS needed to be reduced. On the other hand, determination of SDS concentrations below 1 ppm SDS is questionable with RP-ECD method. However, vacuum filtration eased a lot of the filtration process of retention aid samples and could enable the usage a bit higher SDS concentrations (max. 10 ppm of SDS and 2500 g/t of retention aid). Also, a pre-filtration of the samples with a glass or silver pre-filters could enable the use of higher SDS and retention aid concentrations so that the largest particles could be removed from the sample before the final filtration with the 0.45 µm filter.

Since it was not fully clear how SDS would interact with syringe filter materials a couple of syringe filters test were performed with GHP and nylon syringe filters, and the results showed that the effect of GHP filtration is not that significant, but the effect of nylon can be considered a problem.

Miranol Ultra (amphoteric surfactant)

Miranol Ultra is an amphoteric surfactant and cannot be determined with solvent extraction spectrophotometry method. However, due to its imidazole based structure it can be detected with UV-detector (205 nm). RP-UV tests of Miranol Ultra (MU) were carried out, including calibration curves and effect of salts and retention aids, and the determi-

nation succeeded. The lowest concentration of MU (1 g/L) seemed to be most susceptible to impurities. Miranol Ultra concentrations of 2.4 and 4.0 g/L were not affected by the presence of kraft white water or NaCl. $CaCl_2$, on the other hand, affected significantly on all MU concentrations. SPE purification of the samples would be the most secure method to remove the impurities and also protect the column. Acetonitrile in the eluent can also be a slight problem since it adsorbs UV at wavelength 190 – 200 nm and can mask the MU peak. Further tests are needed to investigate the UV determination of Miranol Ultra.

Accelerated aeration experiments

The second part of the experimental work focused on the development of laboratory scale measurement system for the analysis of foaming tendency of SDS containing wastewaters during aeration. Two criteria in the selection of air flow rate for the aeration tests was applied. Firstly, the air flow values at wastewater treatment plants (WWTP) were considered and secondly, the target was to develop an accelerated test (test period max 2-3 hours). Since the air flow rate in the real aeration tank is 0.5-1.5 m^3/h per 1m^3, it was calculated that the air flow rate should be at least 0.25 l/min in the laboratory vessel (water volume 10 l). According to preliminary laboratory tests, air flow rate 0.6 l/min, which corresponds to air flow rate 3.6 m^3/h at WWTP, was high enough to generate foam when the SDS concentration of white water sample was 50 ppm. Thus, 0.6 l/min was chosen for the further experiments.

The foam generation in all water samples was negligible with SDS concentrations under 20 ppm and only tap water generated foam with 40 ppm SDS dosage. The maximum foam volume in tap water samples was 5 L (100 ppm SDS) and in white water samples 6.8 L (100 ppm) so there was no concern about overflowing. The maximum foam volume in wastewater samples was 0.25 L (100 ppm).

In conclusion, pure waters generate easily foam even with low SDS concentrations (under 100 ppm) and air flow rate (0.6 L/min), but the foam collapses rather quickly. SDS concentration needs to be over 50 ppm to generate foam in white water samples with air flow rate of 0.6 L/min. Wastewaters containing <100 ppm of SDS do not generate foam with air flow rate of 0.6 L/min. The aim to develop an accelerated laboratory scale

measurement test for observation the foaming behaviour of surfactant containing wastewaters was achieved. Also other surfactants can be tested in the accelerated aeration device, and it can be used for a quick and simple examination of the foaming behaviour of different water samples with different surfactants and additives.

Flocculation experiments

Flocculation tests were the third part of the experimental work in this study. The aim of the flocculation tests were the examination of precipitation of SDS from pure- and white water samples using trivalent cations Al^{3+} and Fe^{3+} as coagulants and study the effects of coagulant dosage and pH on the precipitation efficiency of SDS. Experiments made with deionized water showed that both coagulants, ferric sulfate and polyaluminum chloride, can precipitate SDS. Polyaluminum chloride was more effective: 400 µl dosage of PAX-14 yielded ~ 90 % removal efficiency of SDS and 1000 µl dosage of PIX-150 yielded ~ 60 % removal efficiency of SDS. Larger doses of coagulant brought about better flocculation efficiency.

Precipitation efficiency was found to be pH dependent. The optimal pH range for 500 µl dose of PIX-105 was from 3 to 6 and for 1000 µl dose of PIX-105 the optimal pH was about 3. The optimal pH range for 200 µl dose of PAX-14 was from 4 to 5 and for 400 µl dose of PAX-14 from 4.4 to 5. In conclusion, the optimal pH range is wider with smaller coagulant doses thus pH does not affect significantly on precipitation efficiency. With higher coagulant doses the optimal pH range is narrow and pH affects considerably on precipitation efficiency.

REFERENCES

1. J.J. Morelli & G. Szajer. Analysis of Surfactants: Part I. *Journal of Surfactants and Detergents*, **2000**, Vol. *3*, No. 4.
2. J.W. Steed & J-L. Atwood. Supramolecular chemistry. 2nd edition, Chichester, Wiley, 2009.
3. M.A. Aboulhassan, S. Souabi, A. Yaacoubi and M. Baudu. Removal of surfactant from industrial wastewaters by coagulation flocculation process. Int. J. Environ. Sci. Tech. 2006, 3(4), 327-332.
4. J, Eastoe. Surfactant chemistry. Bristol. UK, 2003, Chap 1, p 4.
5. D. Attwood & A.T. Florence. Physical Pharmacy. 2nd edition, London, UK, Pharmaceutical Press, 2012.
6. M. J. Rosen. Surfactants and interfacial phenomena. 3rd edition, New Jersey, Wiley & Sons, 2004.
7. T. Lappalainen & J. Lehmonen. Determinations of bubble size distribution of foam-fibre mixture using circular hough transform, *Nordic Pulp and Paper Research Journal*, **2012**, Vol *27*, no 5.
8. K. Holmberg. Handbook of applied surface and colloid chemistry. Chichester, Wiley, 2002.
9. A. Lavergne, Y. Zhu, A. Pizzino, V. Molinier, J-M. Aubry. Synthesis and foaming properties of new anionic surfactants based on a renewable building block: Sodium dodecyl isosorbide sulfates, *Journal of Colloid and Interface Science*, **2011**, *360*, 645–653.
10. J.M. Traverso-Soto, E. González-Mazo and P. A. Lara-Martín. Analysis of Surfactants in Environmental Samples by Chromatographic Techniques. In book: Chromatography - The Most Versatile Method of Chemical Analysis edited by L. Calderon, 2012.
11. T.M. Schmitt. Analysis of surfactants. 2nd edition. New York. Marcel Dekker, Inc. 2001.
12. D. Weaire & S. Hutzler. The Physics of foams. Oxford University Press, Oxford, U.K. 1999.

13. H.C. Cheng and R. Lemlich. Theory and experiment for interbubble gas diffusion in foam. *Ind. Eng. Chem. Fundam.* **1985**, *24*(1), 44-49.
14. W. Wu & J. Pan. Study on the foamability and its influencing factors of foaming agents in foam-combined flooding in Power and Energy Engineering Conference (APPEEC). **2010**.
15. D. Beneventi, B. Carre and A. Gandini. Role of surfactant structure on foaming properties. *Colloids and Surfaces A: Physiochemical and Engineering Aspects*, **2001**, *189*, 65-73.
16. T. Cserháti, E. Forgács, G. Oros. Biological activity and environmental impact of anionic surfactants. *Environment International*, **2002**, *28*, 337– 348.
17. The Relationship between pH and Deionized Water. http://puretecwater.com/resources/relationship-between-ph-and-deionized-water.pdf, Puretec Indusrial water (12.6.2015)
18. A. Adak, M. Bandyopadhyay and A. Pal. Removal of anionic surfactant from wastewater by alumina: a case study. *Colloids and Surfaces A: Physicochem. Eng. Aspects.* **2005**, 254, 165–171.
19. P. McWilliams. Bioaccumulation Potential of Surfactants: A Review. *European Oilfield Speciality Chemicals Association*. Bergen, Norway, 2000. Chap 5-6.
20. C. Hunte, G. von Jagow and H. Schägger. Membrane protein purification and crystallization. A practical guide. 2nd edition, Amsterdam, Boston, Academic Press, 2003.
21. T.J. Hall-Manning, G.H. Holland, G. Rennie, P. Revell, J. Hines, M.D. Barratt and D.A. Basketter. Skin Irritation Potential of Mixed Surfactant Systems. *Food and Chemical Toxicology*, **1998**, *36*, 233-238.
22. S. Ghosh & D. Blankschtein. The role of sodium dodecyl sulfate (SDS) micelles in inducing kin barrier perturbation the presence of glycerol. *J. Cosmet. Sci.* **2007**, *58*, 109-133.
23. Y.J. Shim, J-H. Choi, H-J. Ahn, J-S. Kwon. Effect of sodium lauryl sulfate on recurrent aphthous stomatitis: a randomized controlled clinical trial. *Oral Diseases*, **2012**, *18*, 655–660.
24. NICNAS. Existing chemicals information sheet. Sodium lauryl sulfate. 2003.

25. HERA. Alcohol Sulfates. Human Health Risk Assessment. 2002. http://www.heraproject.com
26. FDA. Food additives permitted for direct addition to food for human consumption. Sodium lauryl sulfate. http://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfcfr/cfrsearch.cfm?fr=172.822 (3.1.2016)
27. M.J. Scott and M.J. Jones. Review: The biodegradation of surfactants in the environment. *Biochemica et Biophysiva Acta.* **2000**, *1508*, 235-251.
28. E. Jurado, M. Fernaández-Serrano, J. Nunez-Olea, G. Luzon, M. Lechuga. Simplified spectrophotometric method using methylene blue for determining anionic surfactants. Applications to the study of primary biodegradation in aerobic screening tests. *Chemosphere,* **2006**, *65*, 278–285.
29. D. Bethell, R. Fessey, E. Namwindwa and D.W. Roberts. The hydrolysis of C12 primary alkyl sulfates in concentrated aqueous solutions. Part 1. General features, kinetic form and mode of catalysis in sodium dodecyl sulfate hydrolysis. *J. Chem. Soc., Pe kin Trans.* 2001, *2*, 1489–1495.
30. D. Bethell, R. Fessey, E. Namwindwa and D.W. Roberts. The hydrolysis of C12 primary alkyl sulfates in concentrated aqueous solutions. Part 2. Influence of alkyl structure on hydrolytic reactivity in concentrated aqueous mixtures of sodium primary alkyl sulfates: 1-benzoyl-3-phenyl-1,2,4-triazole as a probe of water activity *J. Chem. Soc., Pe kin Trans*. **2001**, *2*, 1496–1520.
31. J.Weiss. Handbook of ion chromatography. 3rd edition. Wiley-VCH. Weinheim. 2004.
32. E. Martinez-Carballo, A. Sitka, C. Gonzalez-Barreiro, N. Kreuzinger, M. Furhacker, S. Scharf and O. Gans. Determination of selected quaternary ammonium compounds by liquid chromatography with mass spectrometry. Part I. Application to surface, waste and indirect discharge water samples in Austria. *Environmental Pollution*. **2007**, *145*, 489-496.
33. V.M. Leon, E. Gonzalez-Mazo, A. Gomez-Parra. Handling of marine and estuarine samples for the determination of linear alkylbenzene sulfonates and sulfophenylcarboxylic acids. *Journal of Chromatography* A. **2000**, *889*, 211–219.

34. A. Selberg, J. Budashova and T. Tenno. Column study of the leaching and degradation
of anionic surfactants in oil-polluted soil. *Proc. Estonian Acad. Sci. Chem*. **2007**, *56*, 2, 87–97.
35. C.Sablayrolles, M. Montrejaud-Vignoles, J. Silvestre and M. Treilhou. Trace Determination of Linear Alkylbenzene Sulfonates: Application in Artificially Polluted Soil—Carrots System. *International Journal of Analytical Chemistry* . **2009**.
36. M. Petrovic, and D. Barcelo. Determination of Anionic and Nonionic Surfactants, Their Degradation Products, and Endocrine-Disrupting Compounds in Sewage Sludge by Liquid Chromatography/Mass Spectrometry. *Analytical Chemistry*, **2000**, Vol. *72*, No. 19.
37. P. Eichhorn, O. López, D. Barceló. Application of liquid chromatographyelectrospray- tandem mass spectrometry for the identification and characterization of linear alkylbenzene sulfonates and sulfophenyl carboxylates in sludge-amended soils. *J. Chromatogr. A*. **2005**, *1067*, 171-179.
38. N.J. Fendinger, W.M. Begley, D.C. McAvoy and W.S. Eckhoff. Measurement of alkyl ethoxylate surfactants in natural waters. *Environ. Sci. Technol*. **1995**, *29*, 856-863.
39. J.C. Dunphy, D.G. Pessler and S.W. Morrall. Derivatization LC/MS for the Simultaneous Determination of Fatty Alcohol and Alcohol Ethoxylate Surfactants in Water and Wastewater Samples. *Environ. Sci. Technol*. **2001**, *35*, 1223-1230.
40. A. Lara-Martin, A.Gomez-Parra, E. Gonzalez-Mazo. Development of a method for the simultaneous analysis of anionic and non-ionic surfactants and their carboxylated metabolites in environmental samples by mixed-mode liquid chromatography–mass spectrometry. *Journal of Chromatography A*, **2006**, *1137*, 188–197.
41. E. Martinez-Carballo, A. Sitka, C. Gonzalez-Barreiro, N. Kreuzinger, M. Furhacker, S. Scharf and O. Gans. Determination of selected quaternary ammonium compounds by liquid chromatography with mass spectrometry. Part II.

Application to sediment and sludge samples in Austria. *Environmental Pollution.* **2007**, *146*, 543-547.

42. E. Olkowska, Z. Polkowska and J. Namiesnik.. A solid phase extraction–ion chromatography with conductivity detection procedure for determining cationic surfactants in surface water samples. *Talanta*, **2013**, *116*, 210–216.
43. J. Tolls, M. Haller and D. T. H. M. Sijm. Extraction and Isolation of Linear Alkylbenzenesulfonate and Its Sulfophenylcarboxylic Acid Metabolites from Fish Samples. *Anal. Chem.* **1999**, *71*, 5242-5247.
44. R. Alzaga, A. Penab, L. Ortiz, J.M. Bayona. D etermination of linear alkylbenzensulfonates in aqueous matrices by ion-pair solid-phase microextraction–in-port derivatization–gas chromatography–mass spectrometry. *Journal of Chromatography A*, **2003**, *999*, 51–60.
45. A. Halasz and J. Hawari. SPME in Environmental Analysis: Biotransformation Pathways. *Journal of Chromatographic Science*, **2006**, Vol. *44*.
46. Membrane filtration. Minnesota Rual Water Accociation (17.1.2016) http://www.mrwa.com/WaterWorksMnl/Chapter%2019%20Membrane%20Filtration.pdf,
47. Filtration. Lenntech, Water Treatment Solutions. (17.1.2016) http://www.lenntech.com/chemistry/filtration.htm
48. Reverse osmosis. Puretec, Industrial Water. (17.1.2016) http://puretecwater.com/what-is-reverse-osmosis.html#understanding-reverse-osmosis
49. Filter Selection for HPLC and UHPLC. Syringe-filters.com. (17.1.2016) http://www.syringe-filters.com/filter-selection-hplc-uhplc.php
50. Syringe filter selection guide. PALL Corporation. (17.1.2016) http://www.pall.com/main/laboratory/syringe-filter-selection-guide-part-2-of-51077.page
51. Choosing the Appropriate Membrane. Sterlitech Corporation. (17.1.2016) http://www.sterlitech.com/choosing-the-appropriate-membrane/
52. R.J. Pickering. Water Quality: Field filtering of water samples for chemical analysis. Quality of water branch technical memorandum. 1978, No 78.06.

53. C. Venkatesh & K. Ashok. Bacterial utilization of sodium dodecyl sulfate. *International Journal of Applied Biology and Pharmaceutical Technology*, **2010**, Vol *1*, Iss 3, 1126-1131.
54. O. R. T. Thomas & G. F. White. Metabolic pathway for the biodegradation of sodium dodecyl sulfate by Pseudomonas sp. C12B. *Biotechnology and Applied Biochemistry*, **1989**, *11*, 318- 327.
55. T.M. Schmitt. Surfactants. Liquid Chromatography. BASF Corporation, Wyandotte, MI, USA. 2000.
56. Thermo Scientific. Dionex Eluent Suppressors for Ion Chromatography: Product data sheet. 2015. (2.11.2015) http://www.dionex.com/en-us/webdocs/114797-PS__Eluent-Suppressors%20for%20IC-PS70690.pdf
57. Levin, S. 1997. Analysis of Ions Using High Performance Liquid Chromatography: Ion-Chromatography (22.1.2016) http://www.forumsci.co.il/HPLC/ion_chrm.html
58. P. Bedson & E. Prichard. Valid Analytical Measurement: High Performance Liquid Chromatography. The Royal Society of Chemistry. Cambridge. 2003.
59. E. Katz. Handbook of HPLC. Marcel Dekker, Inc. New York. 1998.
60. Thermo Scientific. Dionex Acclaim. Bonded silica-based colums for HPLC. 2007. http://www.dionex.com/en-us/webdocs/11650-Catalog_Acclaim_14Jul2007_LPN1668_03.pdf
61. Waters. HPLC Separation Modes. (22.1.2016) http://www.waters.com/waters/en_FI/HPLC-Separation-Modes/nav.htm?cid=10049076&locale=en_FI
62. X. Liu, C.A. Pohl and J. Weiss. New polar-embedded stationary phase for surfactant analysis. *Journal of Chromatography A*, **2006**, *1118*, 29–34.
63. S. Hyun Im, Y. Han Jeongb and J. Jeong Ryoo. Simultaneous analysis of anionic, amphoteric, nonionic and cationic surfactant mixtures in shampoo and hair conditioner by RP-HPLC/ELSD and LC/MS. *Analytica chimica acta*, **2008**, *619*, 129–136.
64. P. Bassarab, D. Williams, J.R. Dean, E. Ludkin and J.J. Perry. Determination of quaternary ammonium compounds in seawater samples by solid-phase extraction and liquid chromatography–mass spectrometry. *Journal of Chromatography A*, **2011**, *1218*, 673–677.
65. A.T. Kiewiet, J.M.D. van der Steen and J.R. Parsons. Trace Analysis of Ethoxylated Nonionic Surfactants in Samples of Influent and Effluent of Sewage

Treatment Plants by High-Performance Liquid Chromatography. *Anal. Chem*. **1995**, *67*, 4409-4415.

66. J. Norberg, E. Thordarson, L. Mathiasson and J.a. Jönsson. Microporous membrane liquid-liquid extraction coupled on-line with normal-phase liquid chromatography for the determination of cationic surfactants in river and wastewater. *J. Chromatogr. A*, **2000**, *869*: 523-529.
67. P.L. Ferguson, C.R. Iden and B.J. Brownawell. Analysis of Alkylphenol Ethoxylate Metabolites in the Aquatic Environment Using Liquid Chromatography-Electrospray Mass Spectrometry. *Anal. Chem.* **2000**, *72*: 4322-4330.
68. P.L. Ferguson, C.R. Iden and B.J. Brownawell. Analysis of nonylphenol and nonylphenol ethoxylates in environmental samples by mixed-mode high-performance liquid chromatography–electrospray mass spectrometry. *Journal of Chromatography A*, **2001**, *938*, 79–91
69. 73 J.E. Loyo-Rosales, I. Schmitz-Afonso, C.P. Rice and A. Torrents. Analysis of Octyl- and Nonylphenol and Their Ethoxylates in Water and Sediments by Liquid Chromatography/Tandem Mass Spectrometry. *Anal. Chem*. **2003**, *75*: 4811-4817.
70. X. Liu. Development of a polar-embedded stationary phase with unique properties. *Journal of Chromatography A*, **2006**, *1119*, 120–127.
71. J.W. Dolan. HPLC Solutions #36: End-capping (23.11.15) http://www.sepscience.com/Techniques/LC/Articles/321-/HPLC-Solutions-36-Endcapping
72. J.W. Dolan. Ion Pairing — Blessing or Curse? *LCGC Europe*. **2008**, Volume *21*, Issue 5. http://www.chromatographyonline.com/ion-pairing-blessing-or-curse
73. Z. Wei, W. Bo, Y. Chun-li and Z. Tong. Determination of Seven Sodium Alkyl Sulphates in Environmental Water by Ion-pair Chromatography with Suppressed Conductivity Detection. *LCGC Europe*. **2014**, Volume *27*, Issue 2. http://www.chromatographyonline.com/determination-seven-sodium-alkyl-sulphates-environmental-water-ion-pair-chromatography-suppressed-co
74. L.M. Nair and R. Saari-Nordhaus. Recent developmetns in surfactant analysis by ion chromatography. *Journal of Chromatography A*, **1998**, *804*, 233–239.

75. L.H. Levine, J.E. Judkins and J.L. Garland. Determination of anionic surfactants during wastewater recycling process by ion pair chromatography with suppressed conductivity detection. *Journal of Chromatography A*. **2000**, *874*, 207–215.
76. F.I. Portet, C. Treiner and P.L. Desbene. Simultaneous quantitative trace analysis of anionic and nonionic surfactant mixtures by reversed-phase liquid chromatography. *Journal of Chromatography A*, **2000**, *878*, 99–113.
77. K. Scott. Ion Chromatography - The Electrical Conductivity Detector. Chromatography online. (23.1.2016) http://www.chromatography-online.org/ion-chromatography/Detectors-for-Ion-Exchange-Chromatography/The-Electrical-Conductivity-Detector.php
78. J. Weiss. Retention of aliphatic anionic surfactants in ion chromatography. *Journal of Chromatography A.* **1986**, Volume *353*, Pages 303-307.
79. X. Liu, M. Tracy and C. Pohl. Analysis of anionic surfactatns using RPLC and surpressed conductivity detection. Thermo Scientific, Dionex Corporation, Pittcon **2008** Presentation.
80. P.L. Desbene, F.I. Portet and G.J. Goussot. Quantitative trace analysis of surfactant mixtures by reversed-phase high-performance liquid chromatography with refractometric detection. *Journal of Chromatography A*, **1996**, *730*, 209-218.
81. X. Liu, M. Tracy and C. Pohl. The Strategy of Surfactant Analysis by HPLC. Thermo Scientific, Dionex Corporation. 2010.
82. Waters. Evaporative light scattering detector. Operator's guide. Waters Corporation 2006-2009. https://www.waters.com/webassets/cms/support/docs/71500121802rb.pdf
83. T.H. Mourey and L.E. Oppenheimer. Principles of Operation of an Evaporative Light-Scattering detector for Liquid Chromatograpy. *Anal. Chem*. **1984**, *56*, 2427-2434.
84. S. Hyun Im and J. Jeong Ryoo. Characterization of sodium laureth sulfate by reversed-phase liquid chromatography with evaporative light scattering detection and 1H nuclear magnetic resonance spectroscopy. *Journal of Chromatography A*. **2009**, *1216*, 2339–2344.

85. J. Esquena & C. Solans. Influence of the HLB parameter of nonionic surfactants on normal and reversed-phase thin layer chromatography. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. **2001**, *189*, 85–92.
86. G. Trapani, C. Altomare, M. Franco, A. Latrofa and G. Liso. Determination of hydrophile-lipophile balance of some polyethoxylated non-ionic surfactants by reversed-phase thin layer chromatography. *International Journal of Pharmaceutics*. **1995**, *116*, 95-99.
87. W.C. Griffin. Classification of surface-active agents by HLB. *Journal of the Society of Cosmetic Chemists.* Atlas Power Company, Wilmington, Del. **1949**.
88. W.C. Griffin. Calculation of HLB values of non-ionic surfactants. *Journal of the Society of Cosmetic Chemists*. Atlas Power Company, Wilmington, Del. **1954**.
89. J.T. Davies. A quantitative kinetic theory of emulsion type I. Physical chemistry of the emulsifying agent. Gas/Liquid and Liquid/Liquid Interfaces. Proceedings of 2nd International Congress Surface Activity, Butterworths, London **1957**.
90. K. Takahash, R. Takahashi, Y. Horikawa, S. Matsuyama, S. Kinugasa and K. Ehara. Optimization of experimental parameters for separation of non-ionic surfactants by supercritical fluid chromatography. *J. of Supercritical Fluids.* **2013**, 82, 256– 262.
91. B. J. Hoffman, L.T. Taylor, S. Rumbelow, L. Goff and J.D. Pinkston. Determination of alcohol polyether average molar oligomer value and distribution via supercritical fluid chromatography coupled with UV and MS detection. *Journal of Chromatography A*, **2004**, *1043*, 285–290.
92. B. J. Hoffman, L.T. Taylor, S. Rumbelow, L. Goff and J.D. Pinkston. Separation of derivatized alcohol ethoxylates and propoxylates by low temperature packed column supercritical fluid chromatography using ultraviolet absorbance detection. *Journal of Chromatography A*, **2004**, *1034*, 207-212.
93. B. J. Hoffman, L.T. Taylor, S. Rumbelow, L. Goff and J.D. Pinkston. Increasing UV detection sensitivity in the supercritical fluid chroma-tographic analysis of alcohol polyethers. *Journal of Chromatography A*, **2004**, *1052*, 161-166.
94. J. Zheng, L.T. Taylor, J.D. Pinkston and M.L. Mangels. Effect of ionic additives on the elution of sodium aryl sulfonates in super-critical fluid chromatography. *Journal of Chromatography A*. **2005**, *1082*, 220–229.

95. J.D. Pinkston, D.T. Stanton, D. Wen. Elution and preliminary structure-retention modeling of polar and ionic substances in supercritical fluid chromatography using volatile ammonium salts as mobile phase. *J Sep Sci.* **2004**, *27*(1-2), 115-23.

96. E. Olkowska, Z. Polkowska and J. Namiesnik. Analytical procedures for the determination of surfactants in environmental samples. *Talanta*. **2012**, 88, 1– 13.

97. P.M. Nagarnaik, M.A. Mills and B. Boulanger. Concentrations and mass loadings of hormones, alkylphenols, and alkylphenol ethoxylates in healthcare facility wastewaters. *Chemosphere*. **2010**, *78*, 1056-1062.

98. J. McEvoy & W. Giger. Determination of Linear Alkylbenzenesulfonates in Sewage Sludge by High-Resolution Gas Chromatography/Mass Spectrometry. *Environ. Sci. Technol.* **1986**, *20*, 376-383.

99. V. Wulf, N. Wienand, M. Wirtz, H-W. Kling, S. Gäb and O.J. Schmitz. Analysis of special surfactants by comprehensive two-dimensional gas chromatography coupled to time-of-flight spectrometry. *Journal of Chromatography A*, **2010**, *1217*, 749–754.

100. M. Villar, M. Callejon, J.C. Jimenez, E. Alonso and A. Guiraum. Optimization and validation of a new method for analysis of linear alkylbenzene sulfonates in sewage sludge by liquid chromatography after microwave-assisted extraction. *Analytica Chimica Acta*. **2007**, *599*, 92–97.

101. A. Nakae, K. Tsujl and M. Yamanaka. Determination of trace amounts of alkylbenzenesulfonates by high-performance liquid chromatography with fluorimetric detection. *Analytical Chemistry*. **1980**, Vol. *52*, No. 14.

102. M. Ahel & W. Giger. Determination of alkylphenols and alkylphenol mono- and diethoxylates in environmental samples by high-performance liquid chromatography. *Analytical Chemistry*. **1985**, Vol.*57*, No. 8.

103. V. Croce, L. Patrolecco, S. Polesello and S. Valsecchi. Extraction of Nonylphenol and Nonylphenol ethoxulates from river sediments. comparison of different extraction techniques. *Chromatographia.* **2003,** *58*, 145-149.

104. J.K. Autry, E.G. Vaught and E.D. Conte. Preconcentration of bezalkonium chloride using sodium dodecyl sulfate attached to a strong anion exchange resin. *Microchem. J.* **2005**, *80*, 25-29.

105. M. Zanette, A. Marcomini, E. Marchiori and R. Samperi. High-performance liquid chromatographic-fluorescence determination of aliphatic alcohol polyethoxylates and polyethyleneglycols in aqueous samples. *Journal of Chromatography A*, **1996**, 756, 159-174.

106. S. Raktomanga, A. Baillet, F. Pellerin and D. Baylocq-Ferrier. Identification of by-products in phenylisocyanate pre-column derivatization by thermospray liquid chromatography-mass spectrometry. *Chromatographia*. **1991**, Volume *32*, Issue 3-4, p 125-129.

107. M. Koga, Y. Yamamichi, Y. Nomoto, M. Irie, T. Tanimura and T. Yoshinaga. Rapid determination of anionic surfactants bu improved spectrophotometric method using methylene blue. *Analytical Sciences.* **1999**, Vol *15*, 563-568.

108. S. Motomizu, S. Fujiwara, A. Fujiwara and K. Toel. Solvent Extraction-Spectrophotometric Determination of Anionic Surfactants with Ethyl Violet. *Analytical Chemistry.* **1982**, Vol *54*, No 3.

109. K.Yamamoto & S. Motomizu. Solvent Extraction = Spectrophotometric Determination of Anionic Surfactants in Sea Water Ethyl Violet. *Analyst*. **1987**, Vol *112*, 1405-1408.

110. K. Santosh, V. Chanda, K.P. Piyush and B. Ashish. Reliable Technique for the Determination of Sodium Dodecyl Sulphate by Crystal Violet in Relation to the Effluents of Durg-Bhilai Region. *Journal of the Chinese Chemical Society*. **2009**, Volume *56*, Issue 6, pages 1250–1256.

111. I. Kowalska, M. Kabsch-Korbutowicz, K. Majewska-Nowak and T. Winnicki. Separation of anionic surfactants on ultrafiltration membranes: Rhodamine G6. *Desalination.* **2004**, *162*, 33-40.

112. M, Lee. Mass spectrometry-Handbook. John Wiley & Sons, Hoboken, New Jersey. 2012.

113. B.N. Jewett, L. Ramaley and J.C.T. Kwak. Atmospheric Pressure Ionization Mass spectrometry techniques for the analysis of alkyl ethoxysulfate mixtures. *J Am Soc Mass Spectrom.* **1999**, *10*, 529–536.

114. Lara-Martín P.A, González-Mazo E, Brownawell B.J Multi-residue method for the analysis of synthetic surfactants and their degradation metabolites in

aquatic systems by liquid chromatography-time-of-flight-mass spectrometry. *J. Chromatogr. A*. **2011**, *1218*, 4799-4807.

115. S. González, M. Petrovic, M. Radetic, P. Jovancic, V. Ilic and D. Barceló. Characterization and quantitative analysis of surfactants in textile wastewater by liquid chromatography/quadrupole-time-of-flight mass spectrometry. *Rapid Commun. Mass Spectrom.* **2008**, *22*, 1445-1454.
116. D.O. Hummel. Analysis of Surfactants: Atlas of FTIR Spectra with Interpretations, Hanser/Gardner Publications, Inc. Cincinnati, 1996.
117. J.E. Nettles. IR spectroscopy for identifying surfactants. Text. Chem. Color. 1969, 430-441.
118. B. Stuart. Infrared spectroscopy : fundamentals and applications. Wiley, Hoboken, England. 2004.
119. R.B. Viana, A.B. F. da Silva and A.S. Pimentel. Infrared Spectroscopy of Anionic, Cationic, and Zwitterionic Surfactants. *Advances in Physical Chemistry*. **2012**, Article ID 903272.
120. B. Stuart. Infrared spectroscopy: fundamentals and applications. Wiley, Hoboken, England. 2004.
121. L. Carolei & I.G.R. Gutz. Simultaneous determination of three surfactants and water in shampoo and liquid soap by ATR-FTIR. *Talanta*. **2005**, *66*, 118–124.
122. K. Kargosha, S.H. Ahmadi, M. Mansourian and J. Azad. Simultaneous determination of one nonionic and two anionic surfactants using Fourier transform infrared spectrometry and multivariate analysis. *Talanta.* **2008**, *75*, 589–593.
123. J.F. Ventura-Gayete, B.F. Reis, S. Garrigues, A. Morales-Rubio and M. de la Guardia. Multicommutation ATR-FTIR: determination of sodium alpha-olefin sulfonate in detergent formulations. *Microchemical Journal.* **2004**, *78*, 47– 54.
124. G. Carminati, L. Cavalli and F. Buosi. 13C NMR for identification of surfactants in mixture. *J.Am. Oil Chem. Soc.* **1988**, *65*, 669-677.
125. T.Ahlnäs, G. Karlström and B. Lindman. Dynamics and Order of Nonionic Surfactants in Neat Liquid and Micellar Solution from multified 13C NMR relacation and 13C chemical shifts. *J. Phys. Chem.* **1987**, *91*, 4030-4036.

126. O. Söderman, P. Stilbs and W.S. Price. NMR Studies of surfactants. *Concepts in Magnetic Resonance Part A*. **2004**. Vol. *23*A(2), 121–135.

127. Mettler Toledo. Good. Titration practive in Surfactant titration. (23.1.2016) http://us.mt.com/dam/labdiv/campaigns/gp/gtp/gtp_surfactant.pdf

128. Mettler Toledo. Titration sensors, Titration of large variety of surfactants. (23.1.2016) http://us.mt.com/dam/mt_ext_files/Editorial/Generic/1/Titration_Sensors_Surfactant_brochure_Editorial-Generic_1196082025277_files/51724619_surfactantbrosche1196082025277.pdf

129. R.D. Gallegos. Titrations of non-ionic surfactants with sodium tetraphenylborate using the orion surfactant electrode. *Analyst*. **1993**,*118*, 1137-1141.

130. L. Cui, M. Puerto, J.L. López-Salinas, S.L. Biswal and G.J. Hirasaki. Improved Methylene Blue Two-Phase Titration Method for Determining Cationic Surfactant Concentration in High-Salinity Brine. *Anal. Chem.* **2014**, *86* (22), 11055–11061.

131. G. Li, H. Ma and J. Hao. Surfactant ion-selective electrodes: A promising approach to the study of the aggregation of ionic surfactants in solution. *Soft Matter*. **2012**, *8*, 896–909.

132. S. Devi and M.C. Chattopadhyaya. Determination of Sodium Dodecyl Sulfate in Toothpastes by a PVC Matrix Membrane Sensor. *J Surfact Deterg.* **2013**, *16*, 391–396.

133. J.Wang, Z. Du, W. Wang and W. Xue. Titrimetric determination of anionic surfactant content in anionic/nonionic surfactant mixture solution by anionic surfactant selective electrode. *Turk J Chem.* **2012**, 36, 545 – 555.

134. H. Paulapuro. Papermaking Part 1, Stock preparation and wet end. Fapet Oy, Helsinki, Finland. 2000.

135. KnowPap. Learining environment of Papermaking and Automation. (24.1.2016) http://www.knowpap.com/english/

136. Directive IED. Internal treatment of white water by use of membrane filtration and recycling of treated process water. (24.1.2016) http://ied.ineris.fr/sites/default/interactive/brefpap/bref_pap/english/bref_gb_fabrication_technique.htm

137. O. Dahl. Environmental Management and Control. Book 19. Papermaking Science and Technology. 2nd edition. Finnish Paper Engineers' Association/Paperi ja Puu Oy, Finland. 2008.

138. I. Mira, M. Andersson, L. Boge, I. Blute, G. Carlsson, K. Salminen, T. Lappalainen, and K. Kinnunen. Foam forming revisited Part I. Foaming behaviour of fibre-surfactant systems. *Nordic Pulp & Paper Research Journal*. **2014**, Vol *29*, no (4).

139. T. Lappalainen, K. Salminen, K. Kinnunen, M. Järvinen, I. Mira and M. Andersson. Foam forming revisited. Part II. Effect of surfactant on the properties of foam-formed paper products. *Nordic Pulp & Paper Research Journal*. **2014**, Vol 29, no (4).

140. P.R. Garret. Defoamin: Theory and industrial applications. Chapter 3: Defoaming in the pulp and paper industry written by S. Lee Allen, L.A. Allen and T.H. Flaherty. Marcel Dekker, Inc. New York. 1993.

141. P. Griffiths and H. Stratton. Foaming organisms in sewage treatment – friend or foe: Victim of bad publicity. 35th Annual Qld Water Industry Operations Workshop. Community Sports Centre, CQ University – Rockhampton. 2010.

142. M. Barjenbruch and O. Kopplow. Enzymatic, mechanical and thermal pretreatment of surplus sludge. *Advances in Environmental Research*. **2003**, *7*, 715–720.

143. D. Mamais, M. Marneri and C. Noutsopoulos. Causes and control practices of filamentous foaming in wastewater treatment plants. *Water Practice & Technology*. **2012**, Vol *7*, No 3.

144. M. Goldberg and E. Rubin. Mechanical foam breaking. *Ind Eng Chem Proc Design Dev*. **1967**, 6, 195–200.

145. G. Rodrígueza, E. Riera, J. Gallego-Juárez, V.M. Acosta, A. Pinto A, I. Martínez and A. Blanco. Experimental study of defoaming by air-borne power ultrasonic technology. *Physics Procedia*. **2010**, *3*, 135–139.

146. A.C. Dedhia, P.V. Ambulgekar and A.B. Pandit. Static foam destruction: role of ultrasound. *Ultrasonics Sonochemistry*. **2004**, *11*, 67–75.

147. S.V. Komarov, M. Kuwabara and M. Sano. Suppression of slag foaming by a sound wave. Ultrasonics Sonochemistry. **2000**, *7*, 193–199.

148. G. Samudro & S. Mangkoedihardjo. Review on BOD, COD and BOD/COD ratio: A triangle zone for tixic, biodegradable and stable levels. *International Journal of Academic Research.* **2010**, Vol.*2,* No. 4.

149. E. Chamarro, A. Marco and S. Esplugas. Use of fenton reagent to improve organic chemical biodegradability. **2001**, Vol. *35*, No. 4, p. 1047-1051.

150. United States Environmental Protection Agency (EPA). Wastewater technology fact sheet - chemical precipitation. Washington, D.C. EPA 832-F-00-018. 2000.

151. F.I. Talens-Alensson, S.T. Hall, N.P. Hankins and B.J. Azzopardi. Flocculation of SDS micelles with Fe3+. *Colloids and Surfaces A: Physicochem. Eng. Aspects*. **2002**, 204, 85–91.

152. A.K. Vanjara & S.G. Dixit. Recovery of cationic surfactant by using precipitation method. *Separations Technology.* **1996**, *6*, 91-93.

153. T. Chatterjee, S. Chatterjee, D.S. Lee, M.W. Lee and S.H. Woo. Coagulation of soil suspensions containing nonionic or anionic surfactants using chitosan, polyacrylamide, and polyaluminium chloride. *Chemosphere.* **2009**, *75*, 1307–1314.

154. M.N. Khan & U. Zareen. Sand sorption process for the removal of sodium dodecyl sulfate (anionic surfactant) from water. *Journal of Hazardous Materials.* **2006**, *B133*, 269–275.

155. R. Marsalek. The Adsorption of SDS on Ferro-Precipitates. *World Academy of Science, Engineering and Technology.* **2011**, Vol. *5*, 10-28.

156. A. Soni, N. Rai and S.K. Sar. Removal of SDS from wastewater of (bilaspurregion) by using natural biosorbent. International Journal of Advanced Engineering Research and Studies. **2012**, Vol. II/ Issue I. 76-79.

157. P. Purakayastha, A. Pal and M. Bandyopadhyay. Adsorbent selection for anionic surfactant removal from water. *Indian Journal of chemical Technology.* **2005**, Vol *12*, p.281-284.

158. R. Ansari and B. Seyghali. Application of wood sawdust modified with cation-icsurfactants for efficient removal of acidic dyes from aqueous solutions: kinetic and thermodynamic studies. *Eur. Chem. Bull.* **2013**, *2(7),* 499-506.

159. I. Obiora-Okafo and O.D. Onukwuli. Utilization of sawdust (Gossweilerodendron balsamiferum) as an adsorbent for the removal of total dissolved solid particles from wastewater. *International journal of multidisciplinary sciences and engineering.* **2013**, Vol *4(4).*

160. A. Keränen, T. Leiviskä, B-Y. Gao, O. Hormi and J. Tanskanen. Preparation of novel anion exchangers from pine sawdust and bark, spruce bark, birch bark and peat for the removal of nitrate. *Chemical Engineering Science.* **2013**, *98,* 59–68.

161. S. Paria, C. Manohar and K.C. Khilar. Adsorption of anionic and nonionic surfactants on a cellulosic surface. *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* **2005**, Volume *252,* Issues 2–3, Pages 221–229.

162. S.W. Puasa, M.S. Ruzitah and A.S.A.K. Sharifah. An overview of Micellar – Enhanced Ultrafiltration in Wastewater Treatment Process. International Conference on Environment and Industrial Innovation IPCBEE. 2011. vol.12, © (2011) IACSIT Press, Singapore.

163. I. Kowalska, M. Kabsch-Korbutowicz, K. Majewska-Nowak and M. Pietraszek. Removal of detergents from industrial wastewater in ultrafiltration process. Environment Protection Engineering. **2005**, Vol. *31*, No. 3–4.

164. E. Fernández, J.M. Benito, C. Pazos, J. Coca. Ceramic membrane ultrafiltration of anionic and nonionic surfactant solutions. *Journal of Membrane Science.* **2005**, *246,* 1–6.

165. M. Aoudia, N. Allal, A. Djennet and L. Toumi. Dynamic micellar enhanced ultrafiltration: use of anionic (SDS)–non-ionic (NPE) system to remove Cr3+ at low surfactant concentration. Journal of Membrane Science. **2003**, *217,* 181–192.

166. CDD-liquid filtration. Dead-end and cross-flow-filtration. Huss Group. (24.1.2016) http://www.hussgroup.com/cdc-liquid/en/infocenter/Dead-End.php

167. A. Šonc & V. Grilc V. Batch foam fractionation of surfactants from aqueous solutions. Acta Chim. Slov. **2004**, *51*, 687−698.

168. S. Boonyasuwat, S. Chavadej, P. Malakul and J.F. Scamehorn. Anionic and cationic surfactant recovery from water using a multistage foam fractionator. *Chemical Engineering Journal.* **2003**, *93*, 241–252.

169. B. Meena, A.A. Gaikwad and A.N. Bhaskarwar. Foam fractionation of surfactant using a semi-batch foam-bed reactor. Department of Chemical Engineering Indian Institute of Technology, Delhi. 2008.

170. S.B. Mortazavi, A. Khavanin, G. Moussavi and A. Azhdarpoor. Removal of sodium dodecyl sulfate in an intermittent cycle extended aeration system. Pakistan Journal of Biological Sciences. 2008, 11(2), 290-293.

171. B. Wyrwas, Z. Dymaczewsk,, A. Zgola-Grzeskowiak, A. Szymanski, M. Franska, I. Kruszelnicka, D. Ginter-Kramarczy, P. Cyplik, L. Lawniczak and L. Chrzanowski. Biodegradation of Triton X-100 and its primary metabolites by a bacterial community isolated from activated sludge. *Journal of Environmental Management*. **2013**, *128*, 292-299.

172. N.N. Rao & S.Dube. Photocatalytic degradation of mixed surfactants and some commercial soap /detergent products using suspended Ti02 catalysts. *Journal of Molecular Catalysis A: Chemical.* **1996**, *104*, L197-L199.

173. M. Ohtaki, H. Sato, H. Fujii and K. Eguchi . Intramolecularly selective decomposition of surfactant molecules on photocatalytic oxidative degradation over TiO2 photocatalyst. *Journal of Molecular Catalysis A: Chemical.* **2000**, *155*, 121–129.

174. E.L. Terechova, G. Zhang, J. Chen, N.A. Sosnina and F. Yang. Combined chemical coagulation–flocculation/ultraviolet photolysis treatment for anionic surfactants in laundry wastewater. Journal of Environmental Chemical Engineering. 2014, 2, 2111–2119.

175. G. Chen. Electrochemical technologies in wastewater treatment. *Separation and Purification Technology.* **2004**, *38*, 11–41.

176. G. Lissens , J. Pieters, M. Verhaege, L. Pinoy and W. Verstraete. Electrochemical degradation of surfactants by intermediates of water discharge at carbon-based elec-trodes. *Electrochimica Acta.* **2003**, *48*, 1655-1663.

177. B. Louhichi, M.F. Ahmadia, N. Bensalah, A. Gadri and M.A. Rodrigo. Electrochemical degradation of an anionic surfactant on boron-doped diamond anodes. *Journal of Hazardous Materials*. **2008**, 158, 430–437.

178. G.A. Ciorba, C. Radovan, I. Vlaicu and L. Pitulice. Correlation between organic component and electrode material. consequences on removal of surfactants from wastewater. *Electrochimica Acta*. **2000**, **46**, 297–303.

179. Hitachi. Double Beam Spectrophotometer U-2900/2910. (3.2.2016) http://www.hitachi-hightech.com/global/product_detail/?pn=ana-u2900

180. J.A. Leenheer. Concentration, partitioning and isolation techniques in a book Water analysis of Organic Species edited by R.A. Minear & L.H. Keith. Academic press, Inc. 1984.

APPENDIXES

Descriptions and applications of different filter membranes materials[49,50,51]

Membrane	Material	Description	Applications
GHP / GH / PP	Hydrophilic polypropylene	General purpose membrane for both aqueous and organic solvents. Low protein affinity and high tolerance of acids and bases	General filter, biological samples, aggressive organic solvent-based solutions
Nylon	Hydrophilic nylon	Mechanically resistant and low ion extractable. Thermally stable up to 50°C and can be used with aqueous and organic sample-bases. Do not tolerate acids and binds readily with proteins	General filter, nucleic acid detection
PTFE	Hydrophobic polytetrafluoro-ethylene	Chemically very resistant and can be used with all solvents, acids and bases. Low extractable and thermally stable. Hydrophobic so prewetting is necessary	Aggressive organic solvents and highly basic sample bases
GMF	Glass microfibre	Prefilter with larger pore size than other membranes (0.5-3.0 µm). Used for difficult-to-filter samples. Chemically resistant.	Prefilter for samples with a high particle concentration. Extends life of the final membrane. Wastewater analysis, cell / dna filtration.
PVDF	Hydrophilic polyvinylidene fluoride	Low protein affinity and vide chemical compatibility. Can be used with biomolecules, alcohols and weak acids but do not tolerate strong acids and bases.	Biological filtration
PES	Hydrophilic polyethersulfone	Extreme penetration power and low protein affinity. Thermal stability up to 100°C. Can be used with strong bases, alcohols and protein but do not tolerate acids.	Biological, pharmaceutical and sterilizing filtration
CA	Cellulose acetate	Mechanically resistant, extremely low protein affinity membrane used for aqueous solutions. Cannot be used with organic solvents due to poor chemical tolerance.	Biological aqueous based samples
RC	Regenerated cellulose	Low protein affinity and good chemical resistance. Cannot be used with strong acids, chloroform or THF.	Biological filtration
Silver	Hydrophilic 99.97 % pure silver (inorganic)	Extreme chemical and thermal resistance. Bacteriostatic and conductive. Tolerates aggressive solvents but cannot be used with nitric or sulfuric acid.	Industrial hygiene applications. Analysis of silica, lead sulfide, boron carbide, and chrystotile asbestos. Recommended collection media and subsequent x-ray diffraction substrate for quantifying unknown substances.

Definitions for dewetting, end-capping and hydrolytic stability of HPLC columns

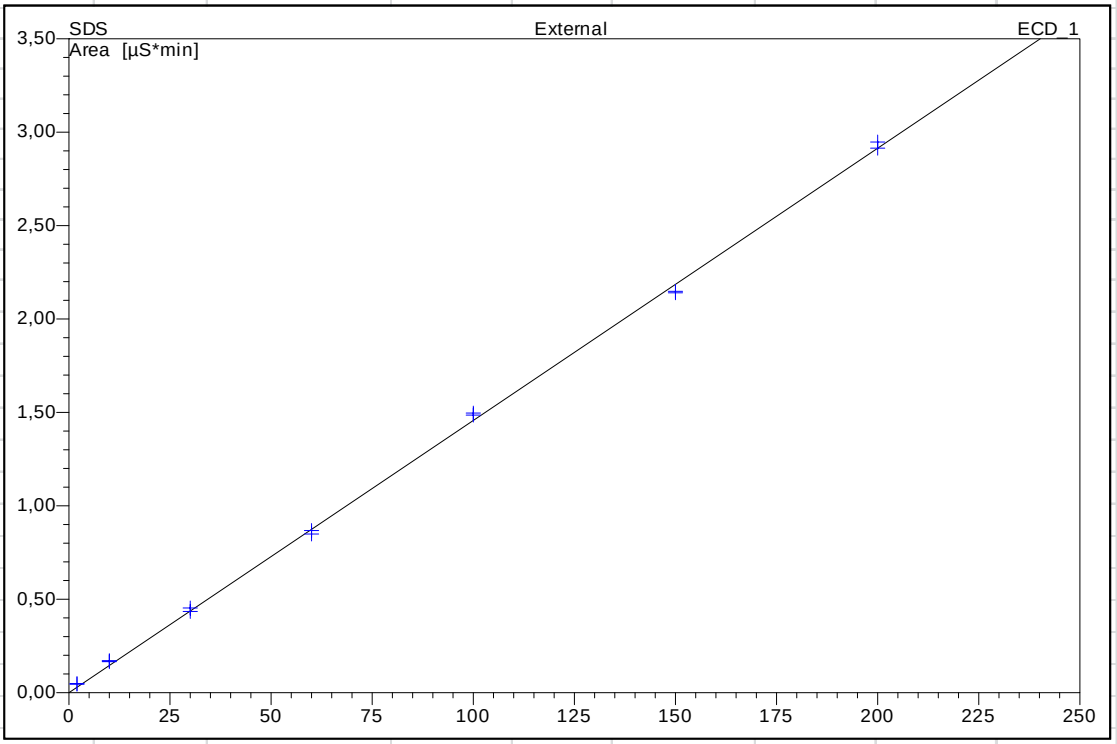
Dewetting is a phenomenon where dissolved gas of the hydrophilic mobile phase expels into the pores of the hydrophobic stationary phase. Dewetting hinders the separation efficiency of the column and is usually initiated when the flow of the mobile phase through the column is stopped. By adding hydrophilic parts into the stationary phase surface, the dewetting can be prevented since the mildly hydrophilic surface now stays in contact with the aqueous mobile phase.[60]

End-capping is deactivation of the free silanol groups of the stationary phase by the small end-capping reagent, such as Cl(CH3)2SiCH3. When silica surface is functionalized some of the silanol groups do not react mostly due to the hindering effect of the bulky adjacent molecule. Polar silanol groups interfere analyte retention by interaction with polar molecules. End-capping makes the stationary phase more hydrophobic and ensures better resolution and separation of analytes. In polar-embedded phase, the end-capping molecules are polar in purpose to create a stationary phase with both hydrophilic and hydrophobic properties. Phases like this are usually 100 % compatible with both aqueous and organic mobile phases and resistant against de-wetting.[71]

Hydrolytic stability is the column ability to resist hydrolytic effect, or cleavage of the attached groups of the stationary phase, caused by low or high pH. The column tolerance against rough environment can be done by protective bonding of the stationary phase. Protecting groups extend column life and reduce column replacements and instrument downtime.[60]

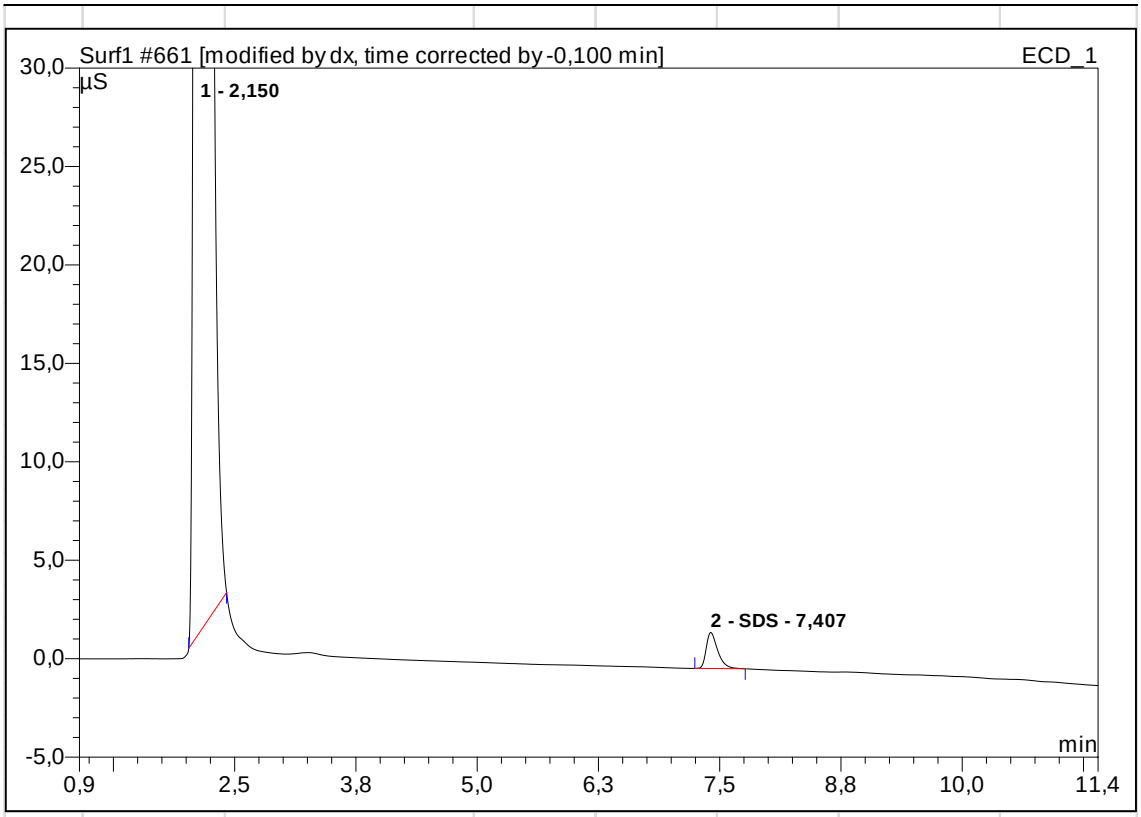
ECD Spectrums

Calibration curve of sodium dodecyl sulfate (SDS) concentrations 2 – 200 ppm. Correlation coefficient 0.9997.



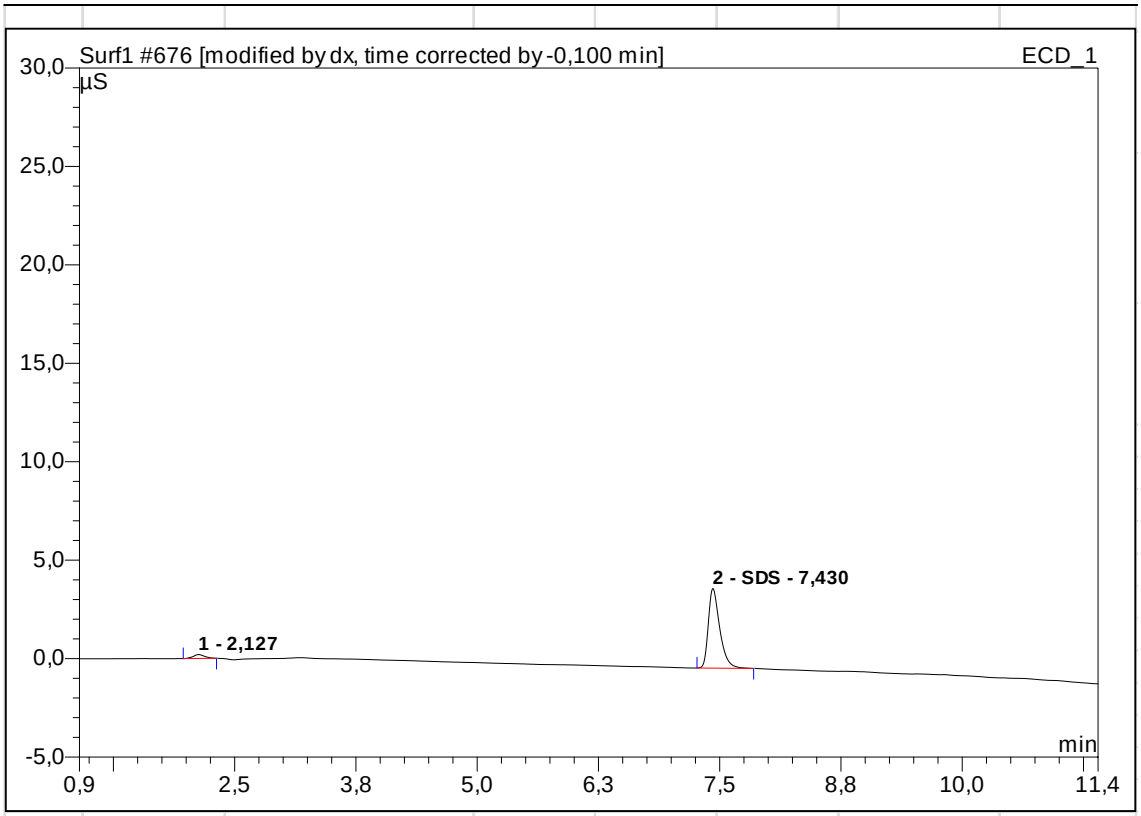
No.	Ret.Time min	Peak Name	Cal.Type	Points	Corr.Coeff. %	Offset	Slope	Curve
1	2,05	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2	7,48	SDS	Lin	14	**99,9698**	0,0000	0,0146	0,0000
Average:					99,9698	0,0000	0,0146	0,0000

ECD spectrum of sodium dodecyl sulfate (40 ppm SDS) with 500 ppm NaCl addition. The impurity peak (2.0 min) is huge, and approximately half of the SDS concentration is missing.



No.	Ret.Time	Peak Name	Height	Area	Rel.Area	Amount	Type
	min		µS	µS*min	%		
1	2,15	n.a.	450,479	51,196	99,51	n.a.	BMB*
2	7,41	SDS	1,832	0,251	0,49	17,231	BMB*
Total:			452,310	51,447	100,00	17,231	

ECD spectrum of sodium dodecyl sulfate (40 ppm SDS) with 500 ppm NaCl addition after solid phase extraction (SPE) pre-treatment. The impurity peak (2.0 min) is negligible, and SDS concentration is back in normal range.



No.	Ret.Time	Peak Name	Height	Area	Rel.Area	Amount	Type
	min		µS	µS*min	%		
1	2,13	n.a.	0,197	0,027	4,69	n.a.	BMB*
2	7,43	SDS	4,042	0,552	95,31	37,891	BMB*
Total:			4,239	0,579	100,00	37,891	

Results of SDS hydrolysis experiments

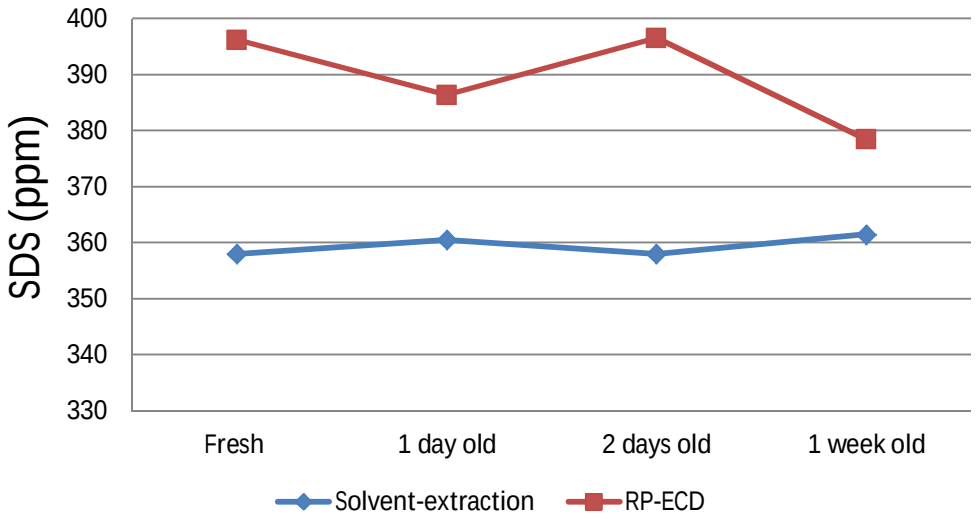


Figure 43. SDS time monitoring. SDS concentration (ppm) of the sample on the y-axis and time scale on the x-axis. A blue line indicates the results obtained by solvent extraction spectrophotometry (SES) method and a red line indicates the results obtained by RP-ECD method.

Table 29. Results of SDS time monitoring experiment. Calculations include mean, standard deviation (±s.d.) and relative standard deviation (RSD) for both methods (Equations 15 and 16). Method comparison was applied with F-Test for two-sample variances (Equation 17) and t-Test for two-sample assuming unequal variances (Equation 18). Calculated using Exel

Sample	SES	RP-ECD	F-test [17]	F Critical $F_{0.05(3,3)}$	t-test [18]	t Critical
Fresh	356.5	394.7	24.6	5.0	7.8	2.3
	359.5	397.8				
1 day old	358.5	383.2				
	362.5	389.7				
2 days old	358.0	386.7				
	358.0	406.5				
1 week old	361.0	371.1				
	362.0	385.7				
Mean ($\bar{x}$)	359.5	389.4				
St.dev (*s*) [15]	2.1	10.6				
RSD [16]	0.6	2.7				

$$s = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(x_i - \bar{x})^2} \quad (15)$$

$$RSD = 100 \times \frac{s}{\bar{x}} \quad (16)$$

$$F = 100 \times \frac{s_1^2}{s_2^2} \quad (17)$$

$$t = \frac{(\bar{x} - \bar{y}) - (\mu_x - \mu_y)}{\sqrt{\frac{s_x^2}{n_x} + \frac{s_y^2}{n_y}}} \quad (18)$$

Results of SDS with additives experiments

Salt additives

Table 30. Results of RP-ECD (10x and x500 dilutions) and SES method (x500 dilution) The percentage SDS removal efficiencies (equation 19) of different salts (NaCl, $CaCl_2$ and $FeSO_4$). A = 10 ppm for dilutions (x500) and 500 ppm for dilution (x10), B = 100 ppm for dilutions (x500) and 5000 ppm for dilution (x10) and C = 1000 ppm

Sample (SDS + salt)	RP-ECD (x10) Kraft SDS Removal (%)	RP-ECD (x500) Kraft SDS Removal (%)	RP-ECD (x500) CTMP SDS Removal (%)	SES (x500) Kraft SDS Removal (%)	SES (x500) CTMP SDS Removal (%)
No salt	40	32	0	4	3
NaCl A	32	89	84	3	3
NaCl B	44	89	87	6	4
NaCl C	-	-	-	5	6
$CaCl_2$ A	68	80	79	0	3
$CaCl_2$ B	68	86	83	5	6
$CaCl_2$ C	-	-	-	6	7
$FeSO_4$ A	78	94	99	24	14
$FeSO_4$ B	64	100	98	22	17
$FeSO_4$ C	-	-	-	Not measurable	Not measurable

$$\frac{\boldsymbol{c(\text{SDS reference}) - c(\text{SDS sample})}}{\boldsymbol{c(\text{SDS reference})}} \times \mathbf{100} \qquad (19)$$

Table 31. Results of RP-ECD (10x and x500 dilutions) SDS removal efficiencies (%) of pure salts (NaCl, $CaCl_2$ and $FeSO_4$) without white water. B = 100 ppm for dilution (x500) and 5000 ppm for dilution (x10)

Sample (SDS + salt)	RP-ECD (x10) Kraft SDS Removal (%)	RP-ECD (x500) Kraft SDS Removal (%)	RP-ECD (x500) CTMP SDS Removal (%)
NaCl B (no ww)	46	89	89
$CaCl_2$ B (no ww)	67	51	51
$FeSO_4$ B (no ww)	56	98	98

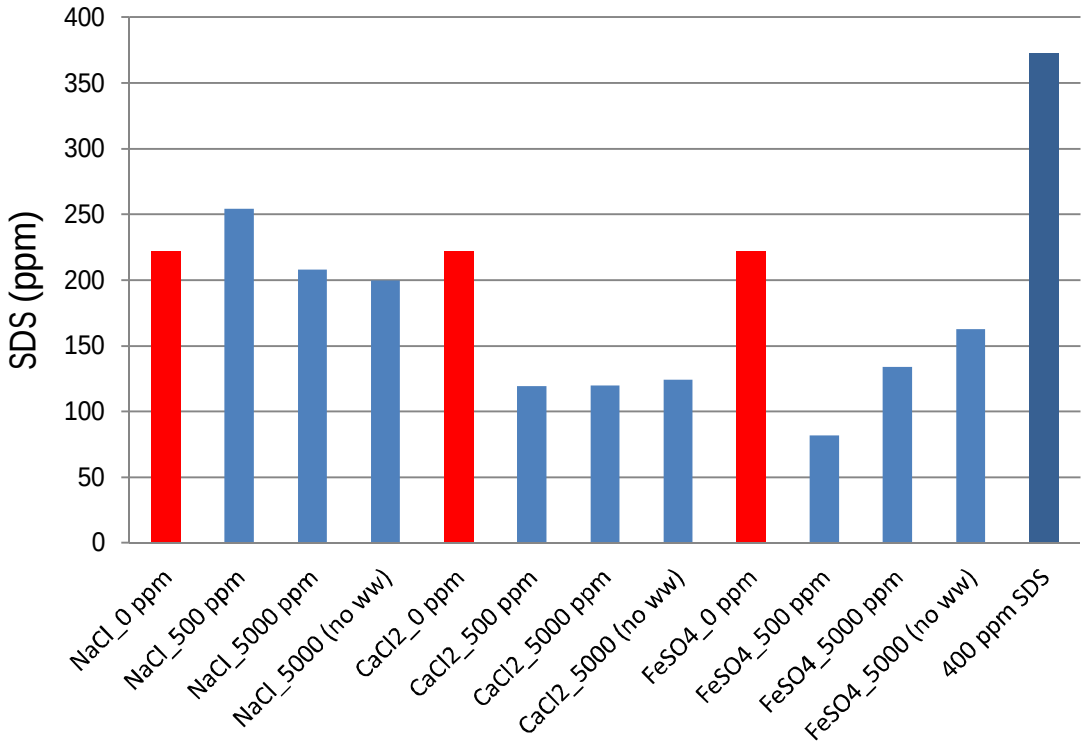


Figure 44. RP-ECD results of salt additions in kraft white water (10x dilution). SDS concentration on the y-axis and samples on the x-axis. Pure SDS reference is marked with the dark blue column, a sample without salt addition (SDS and white water) is marked with the red column, and different salt samples are blue. Added salts 500 ppm and 5000 ppm of NaCl/$CaCl_2$/$FeSO_4$. No ww = SDS sample with pure salt addition (no white water).

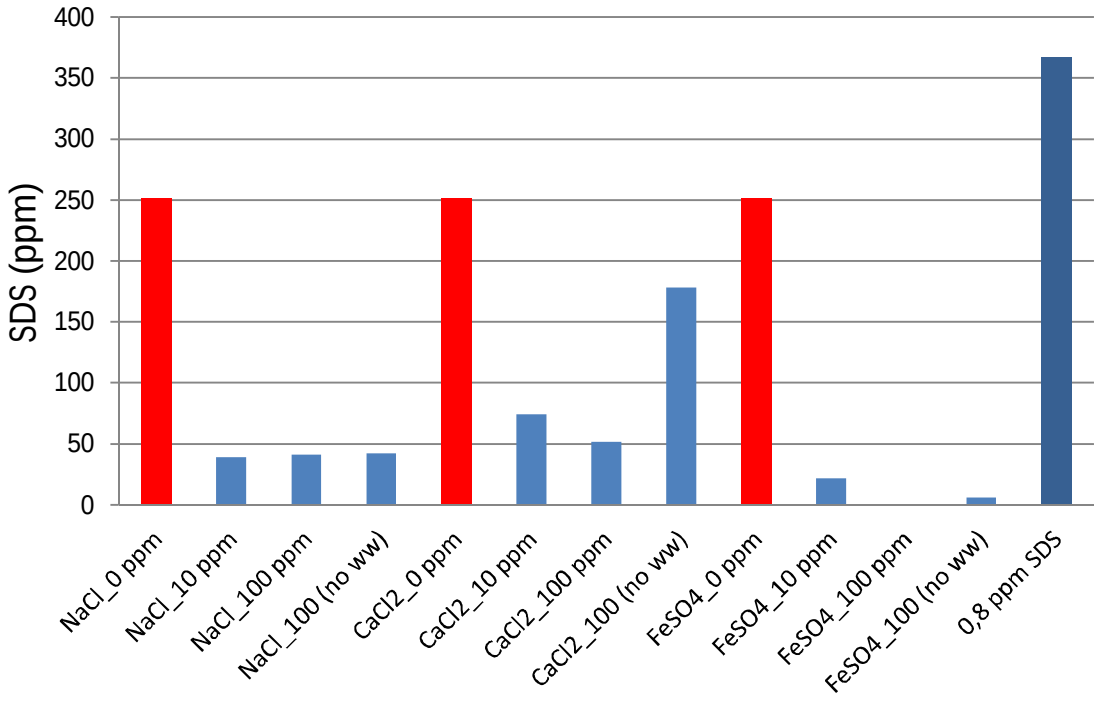


Figure 45. RP-ECD results of salt additions in kraft white water (500x dilution). SDS concentration on the y-axis and samples on the x-axis. Pure SDS reference is marked with the dark blue column, a sample without salt addition (SDS and white water) is marked with the red column, and different salt samples are blue. Added salts 10 ppm and 100 ppm of NaCl/$CaCl_2$/$FeSO_4$. No ww = SDS sample with pure salt addition (no white water).

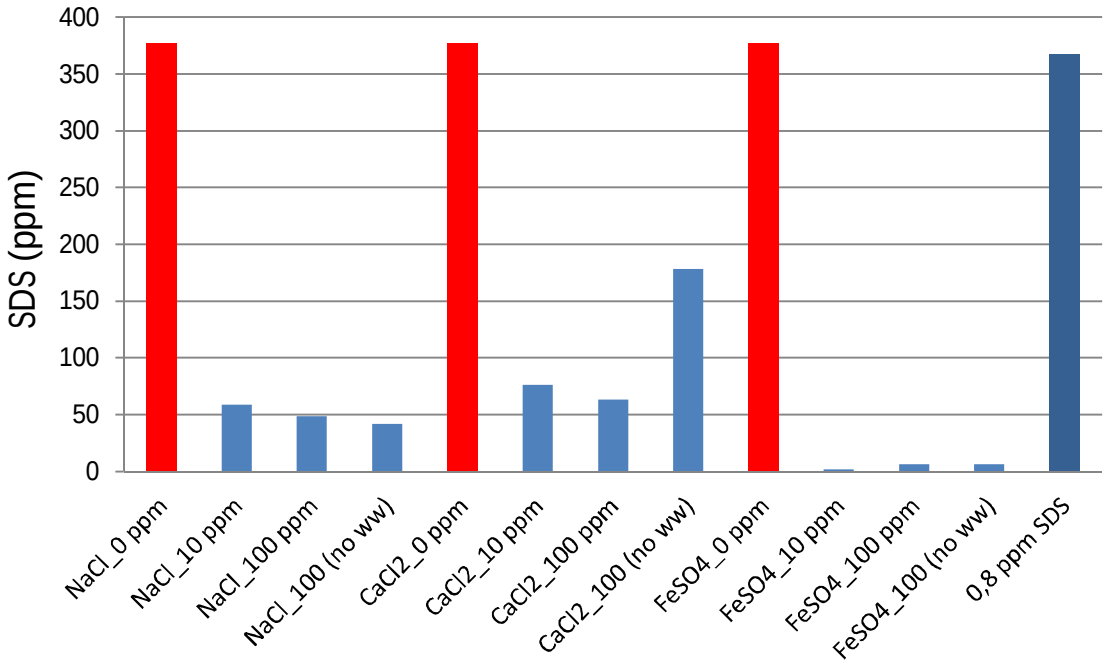


Figure 46. RP-ECD results of salt additions in CTMP white water (500x dilution). SDS concentration on the y-axis and samples on the x-axis. Pure SDS reference is marked with the dark blue column, a sample without salt addition (SDS and white water) is marked with the red column, and different salt samples are blue. Added salts 10 ppm and 100 ppm of NaCl/$CaCl_2$/$FeSO_4$. No ww = SDS sample with pure salt addition (no white water).

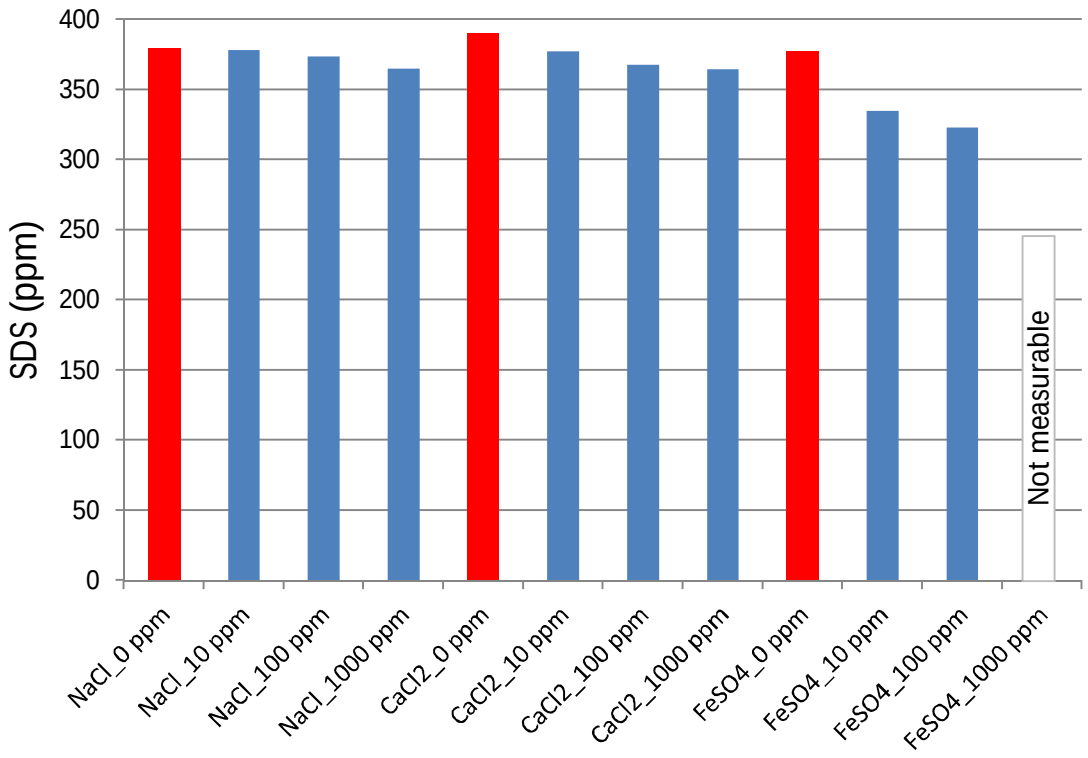


Figure 47.SES results of salt additions in CTMP white water (500x dilution). SDS concentration (ppm) on the y-axis and samples on the x-axis. Samples without salt addition (SDS and white water) are marked with the red column and different salt samples are blue. Added salts 10 ppm, 100 ppm and 1000 ppm of NaCl/CaCl2/FeSO4. Not measurable = sample could not be measured due to gel formation during the extraction procedure

Retention aid additives

Table 32. Results of RP-ECD (x500 dilutions) and SES method (x500 dilution) SDS removal efficiencies (%) of different retention aids (c-Pam and microparticle). Two componen system (c-Pam + microparticle) A = 200 g/t + 200 g/t, B = 400 g/t + 400 g/t and C = 800 g/t + 800 g/t

Sample (SDS + retention aid)	RP-ECD (x500) Kraft ww SDS Removal (%)	SES (x500) Kraft ww SDS Removal (%)
No aid (SDS + ww)	24	1
c-Pam 200 g/t	50	4
c-Pam 400 g/t	59	7
c-Pam 800 g/t	63	10
Microparticle 200 g/t	95	11
Microparticle 400 g/t	99	Not measurable
Microparticle 800 g/t	33	Not measurable
2-component A	70	12
2-component B	85	Not measurable
2-component C	83	Not measurable

Table 33. Results of RP-ECD (x500 dilutions) SDS removal efficiencies (%) of pure retention aids (c-Pam and microparticle) without white water. Two componen system (c-Pam + microparticle) B = 400 g/t + 400 g/t

Sample (SDS + retention aid)	RP-ECD (x500) Kraft SDS Removal (%)
c-Pam 400 g/t	64
Microparticle 400 g/t	0
2-component B	92

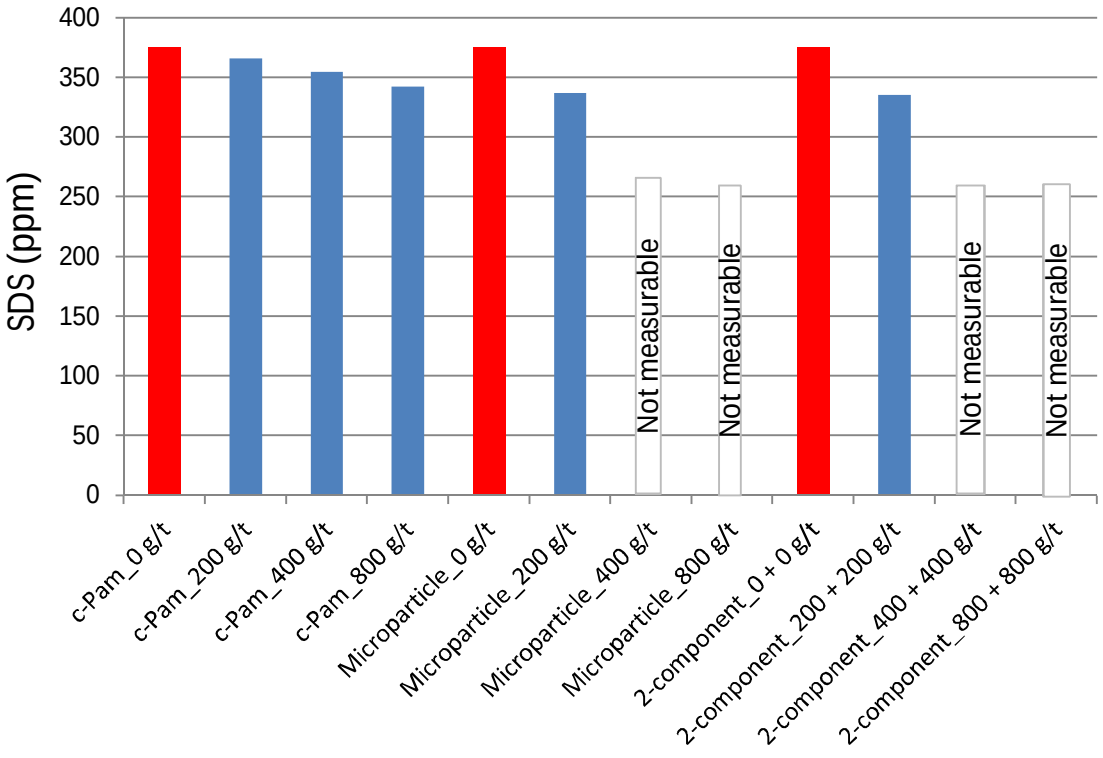


Figure 48. SES results of retention aid additions in kraft white water (500x dilution). SDS concentration (ppm) on the y-axis and samples on the x-axis. Sample without salt addition (SDS and white water) is marked with the red column, and different salt samples are blue. Added retention aids 200 g/t, 400 g/t and 800 g/t of c-Pam/Microparticle/2-component system. Not measurable = sample could not be measured due to gel formation during the extraction procedure

Filter membrane tests

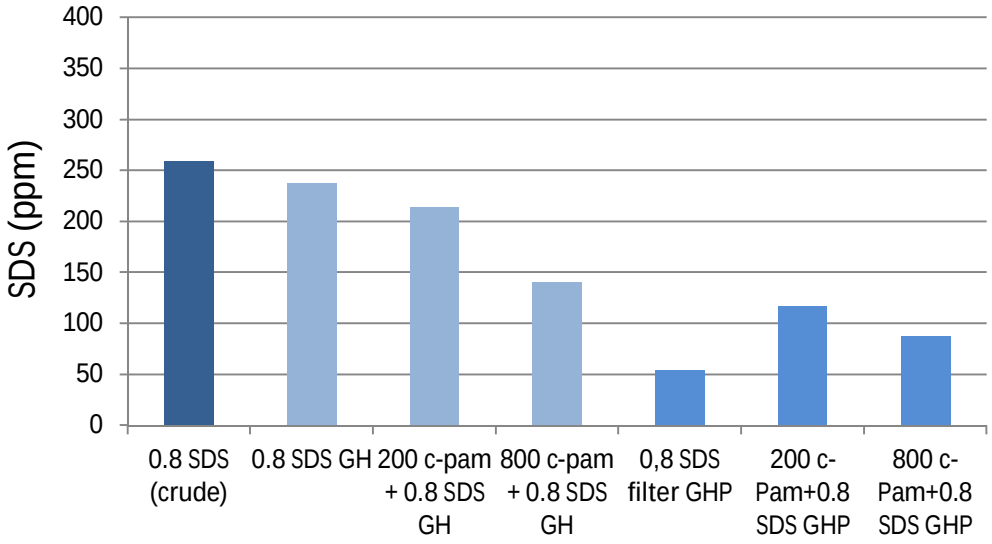


Figure 49. Vacuum filtration using GH membrane (47 mm, 0.45 µm) compared with GHP syringe filtrated samples. SDS concentration on the y-axis and samples on the x-axis. Initial SDS concentration in the samples 0.8 ppm. Pure SDS sample (0.8 SDS crude) marked with the dark blue column; GH filtrated samples marked with light blue and GHP filtrated samples marked with blue column. Results from RP-ECD multiplied with dilution factor (x500). Crude = sample not filtrated

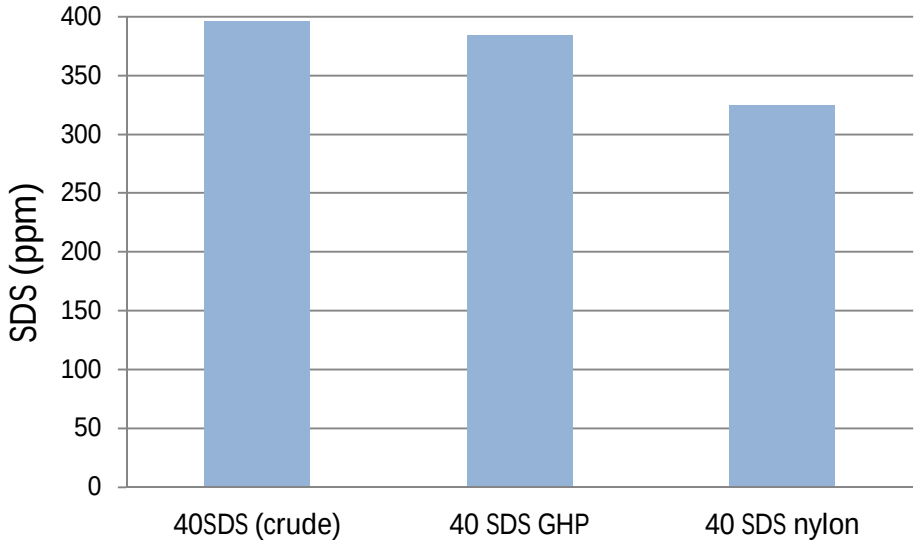


Figure 50. Syringe filtration effect of GHP and nylon membranes of the measured SDS content (40 ppm). SDS concentration on the y-axis and samples on the x-axis. Results from IC-CD multiplied with dilution factor (x10). Crude = sample not filtrated

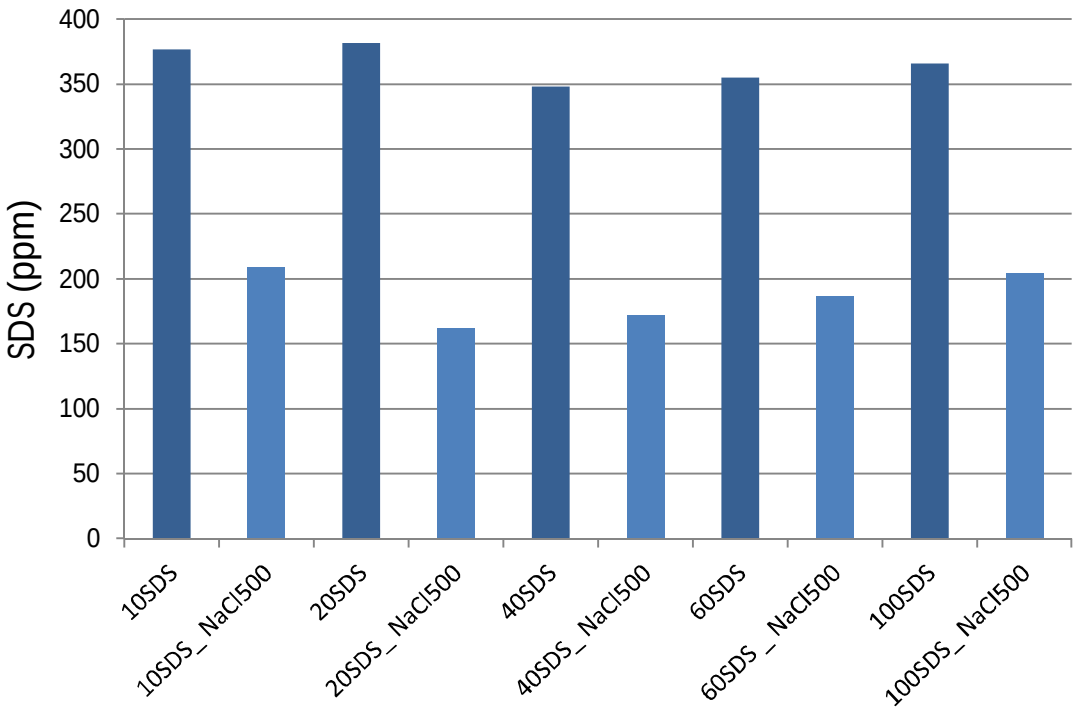
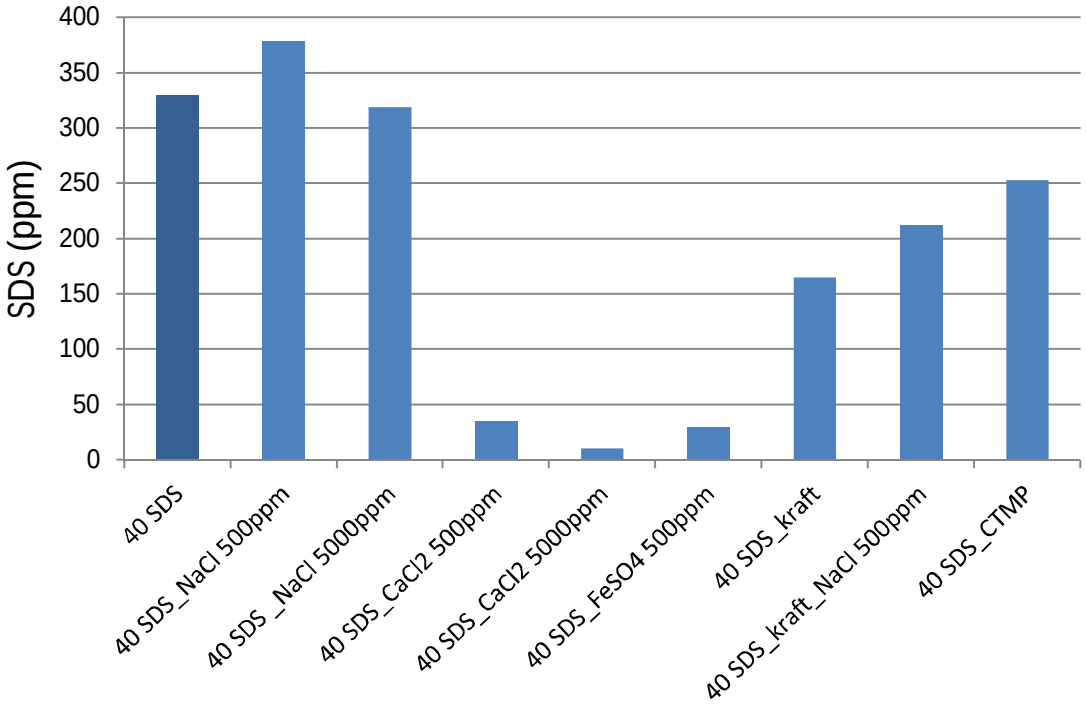


Figure 51. Crude NaCl samples. Different dilutions of SDS (10-100 ppm) with and without NaCl addition (500 ppm). SDS concentration on the y-axis and samples on the x-axis. Samples were analysed crude (without filtration). Pure SDS samples marked with dark blue columns and salt samples marked with blue columns. Results from RP-ECD multiplied with sample-specific dilution factors.

Solid-phase extraction (SPE)



Solid-phase extraction. SDS concentration (ppm) on the y-axis and SDS samples (40 ppm) with different salt additions (500/5000 ppm of NaCl/$CaCl_2$/$FeSO_4$) on the x-axis. Pure 40 ppm SDS sample marked with the dark blue column and additive samples marked with blue columns.

Miranol Ultra

Table 34. Miranol Ultra (MU) determination with RP-UV. Removal efficiencies (%) of kraft white water and 100 ppm of NaCl / $CaCl_2$ salts. Miranol Ultra concentrations 1, 2.4 and 4 g/L.

MU sample + additive	Removal (%)
1 g/L MU+kraft	12
2,4 g/L MU+kraft	3
4,0 g/L MU+kraft	0
1,0 g/L MU+NaCl	17
2,4 g/L MU+NaCl	0
4,0 g/L MU+NaCl	0
1 g/L MU+kraft+NaCl	17
2,4 g/L MU+kraft+NaCl	6
4,0 g/L MU+kraft+NaCl	0
1 g/L MU+kraft+$CaCl_2$	35
2,4 g/L MU+kraft+$CaCl_2$	24
4,0 g/L MU+kraft+$CaCl_2$	11

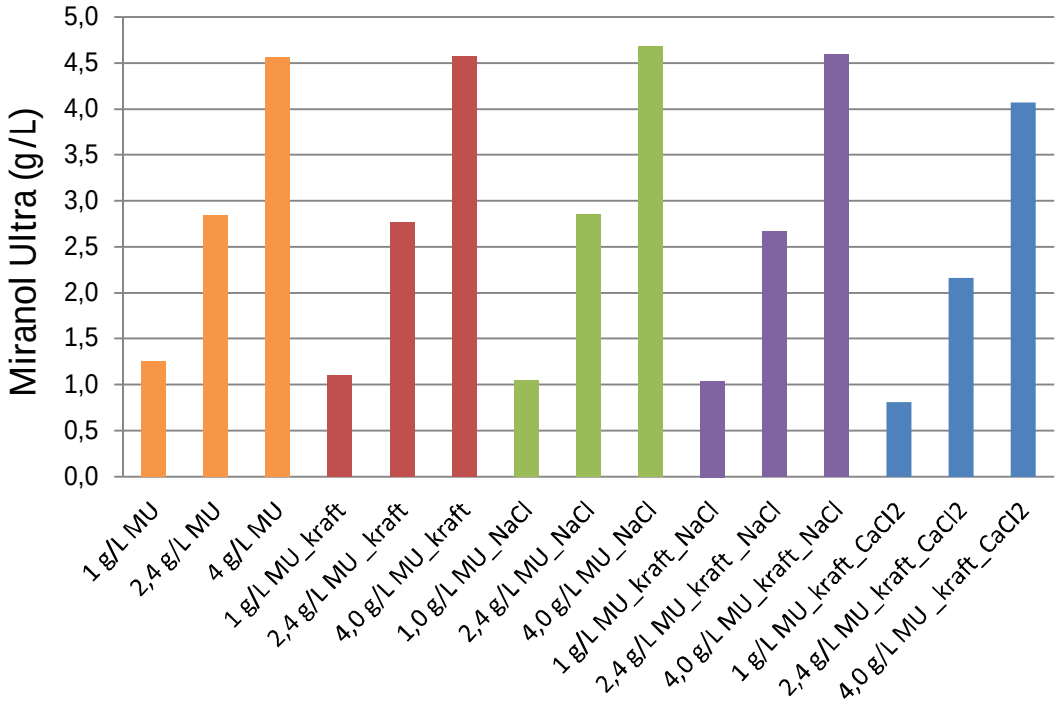


Figure 52. Miranol Ultra samples with kraft white water and salt additives determined with RP-UV. Miranol Ultra concentration (g/L) on the y-axis and samples on the x-axis. Pure Miranol Ultra (1.0, 2.4 and 4.0 g/L) samples (orange), kraft white water samples (red), 100 ppm NaCl samples (green), kraft and 100 ppm NaCl combination (violet) and kraft and 100 ppm $CaCl_2$ combination (blue).

Results of accelerated aeration experiments

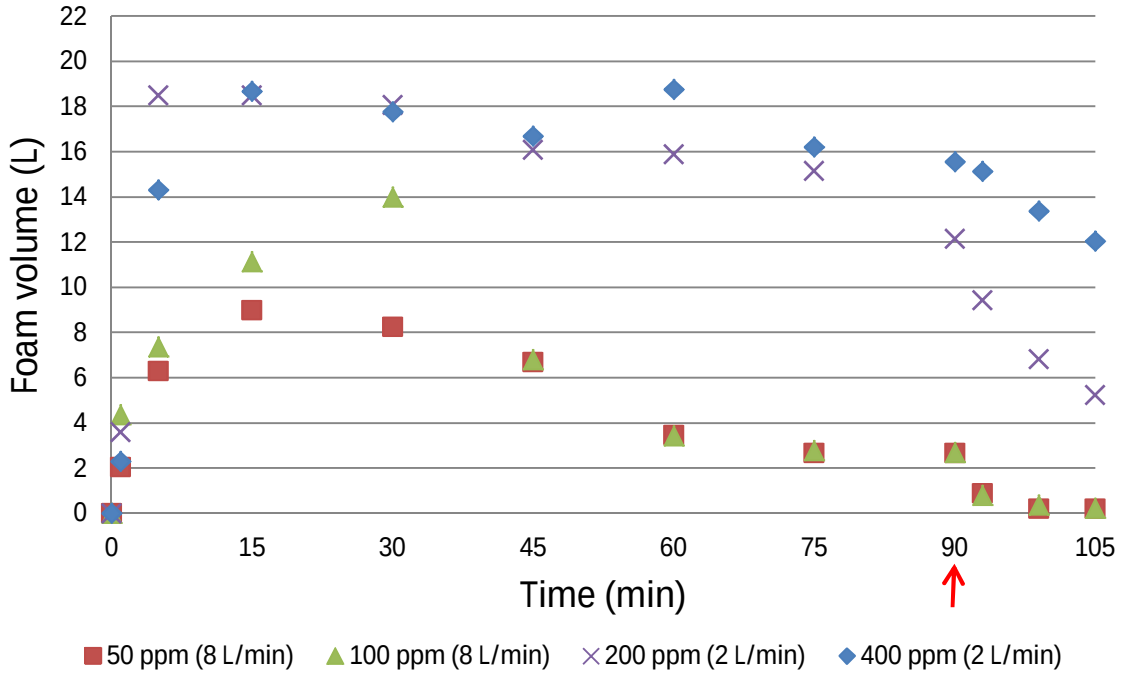


Figure 53. Tap water samples. 50 ppm SDS with air flow rate 8 L/min (red), 100 ppm SDS with air flow 8 L/min (green), 200 ppm SDS with air flow rate 2 L/min (violet) and 400 ppm SDS with air flow rate 2 L/min (blue). Foam volume (L) on the y-axis and aeration time on the x-axis. The aeration was stopped after 90 min (read arrow) and 15 min of foam dying was recorded.

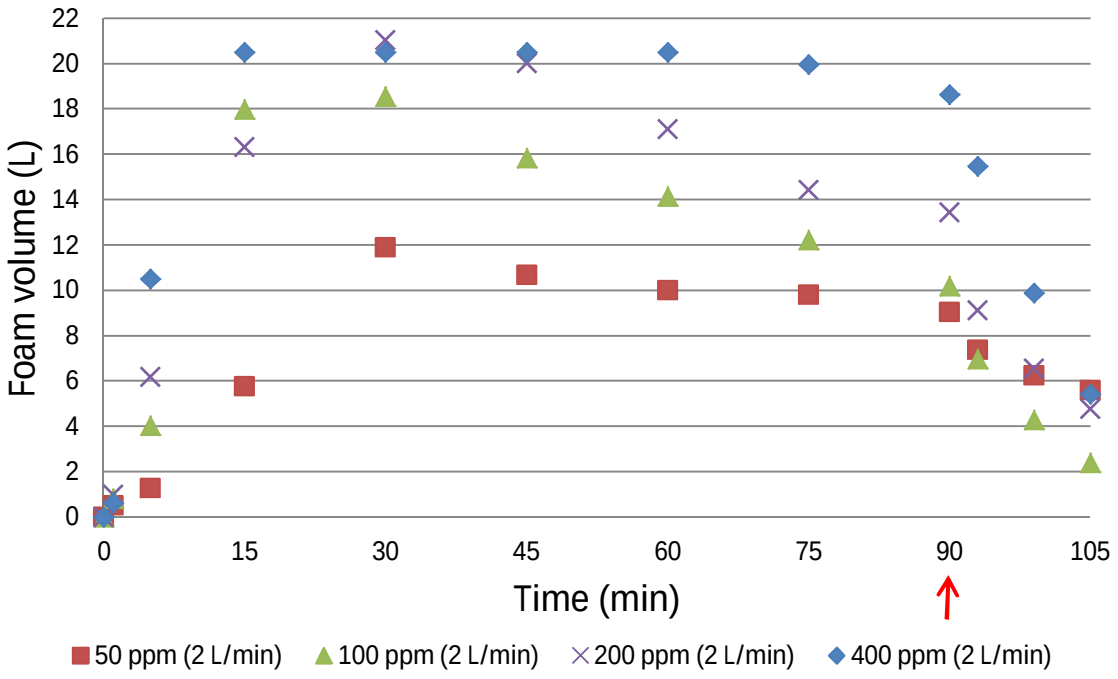


Figure 54. White water samples. 50 ppm SDS (red), 100 ppm SDS (green), 200 ppm SDS (violet) and 400 ppm SDS (blue) with air flow rate 2 L/min. Foam volume (L) on the y-axis and aeration time on the x-axis. The aeration was stopped after 90 min (read arrow) and 15 min of foam dying was recorded.

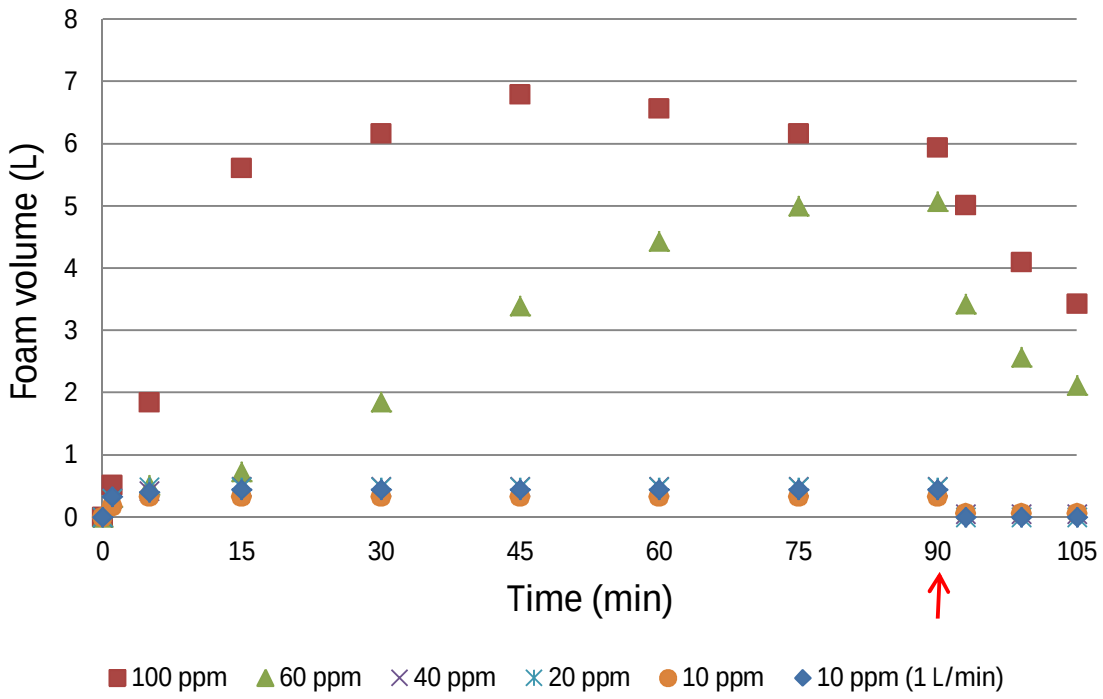


Figure 55. White water samples. 10 ppm SDS with air flow rate 1.0 L/min (blue), 10 ppm SDS (orange), 20 ppm SDS (blue star), 40 ppm SDS (violet), 60 ppm SDS (green) and 100 ppm SDS (red) with air flow rate 0.6 L/min. Foam volume (L) on the y-axis and aeration time on the x-axis. The aeration was stopped after 90 min (read arrow) and 15 min of foam dying was recorded.

Results of flocculation experiments

Table 35. PIX-105 (500 µl) experiments (600 ml, 400 ppm SDS). The table shows NaOH and PIX-105 dosages in each sample, pH of the solution, sample absorbance, calculated SDS concentration, SDS concentration in the sample and SDS removal efficiency in percentage.

Sample	2 M NaOH (µl)	PIX-105 (µl)	pH	Absorb. (615 nm)	SDS (ppm) in diluted (500x) sample	Conc. (ppm) in sample	SDS removal (%)
A	1440	500	3.14	1.986	0.486	243	33
B	1920	500	4.39	2.017	0.495	247	32
C	2040	500	6.10	1.963	0.427	240	34
D	2160	500	6.33	2.223	0.549	274	24
E	2220	500	6.53	2.766	0.693	347	4
F	2280	500	6.74	2.827	0.709	355	2
0	-	500	2.65	2.125	0.523	261	28

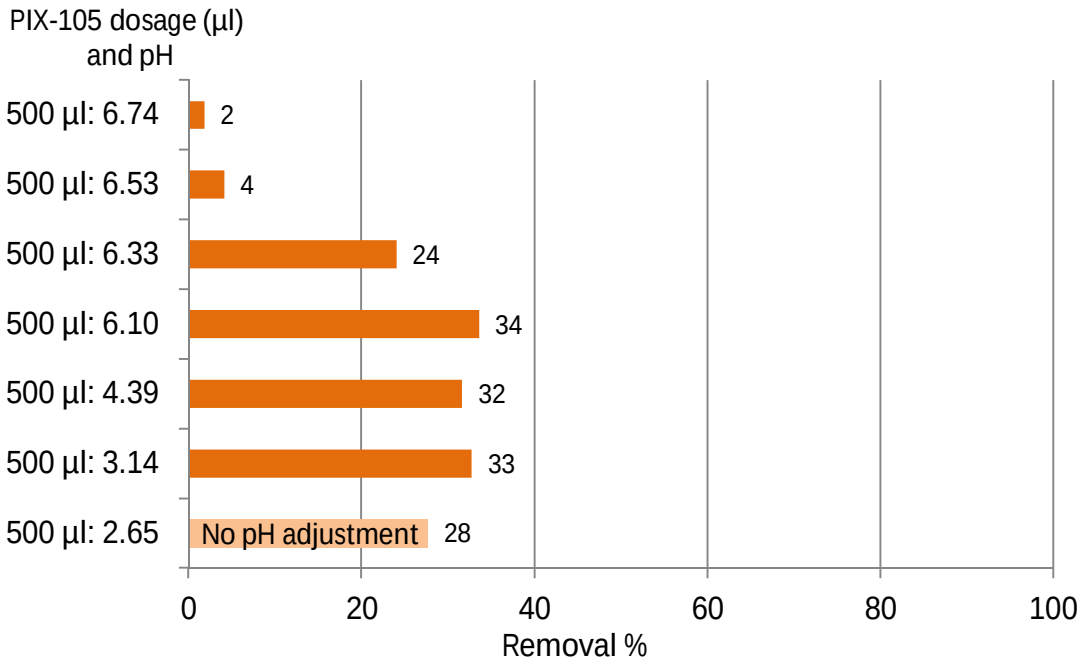


Figure 56. SDS removal results of PIX-105 (500 µl) experiments. The sample was 400 ppm SDS in deionized water. Coagulant dose and sample pH on the y-axis and SDS removal (%) on the x-axis. Fig 51

Table 36. PIX-105 (1000 µl) experiments (600 ml, 400 ppm SDS). The table shows NaOH and PIX-105 dosages in each sample, pH of the solution, sample absorbance, calculated SDS concentration, SDS concentration in the sample and SDS removal efficiency in percentage.

Sample	2 M NaOH (µl)	PIX-105 (µl)	pH	Absorb. (615 nm)	SDS (ppm) in diluted (500x) sample	Conc. (ppm) in sample	SDS removal (%)
A	2880	1000	3.0	1.314	0.308	154	59
B	4020	1000	5.5	1.667	0.402	201	47
C	4200	1000	6.18	2.016	0.494	247	34
D	4560	1000	7.02	2.463	0.613	306	18
E	4740	1000	9.61	2.850	0.715	358	5
F	4860	1000	3.0	2.916	0.733	366	2
0	-	1000	2.59	1.633	0.392	196	48
Ref.	-	-	6.47	2.986	0.752	376	0

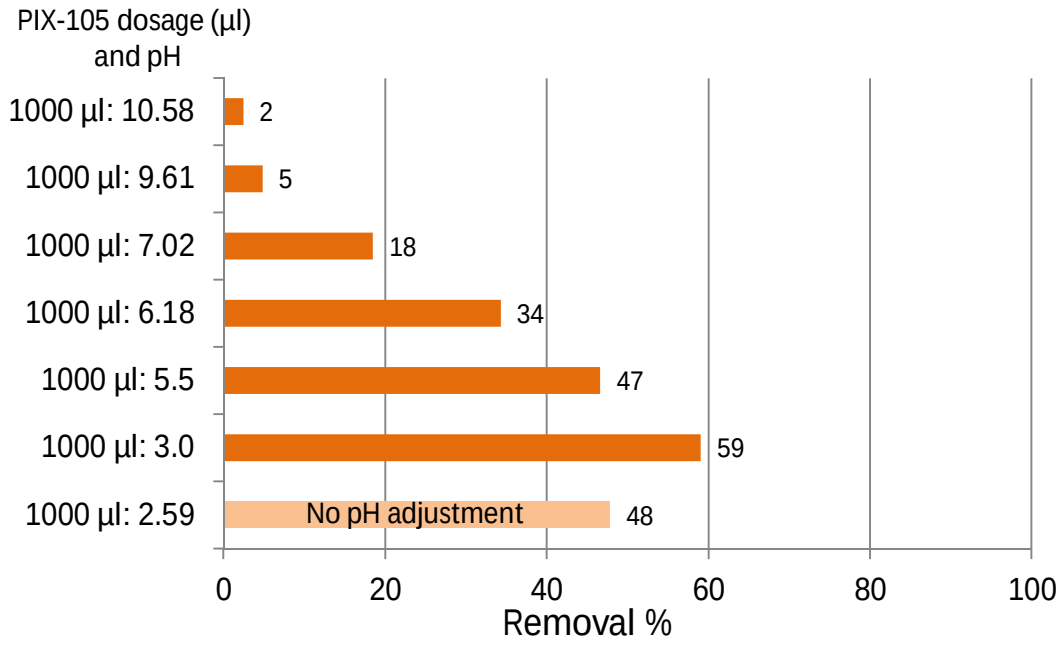


Figure 57. SDS removal results of PIX-105 (1000 µl) experiments. The sample was 400 ppm SDS in deionized water. Coagulant dose and sample pH on the y-axis and SDS removal (%) on the x-axis

Table 37. PAX-14 (200 µl) experiments (600 ml, 400 ppm SDS). The table shows NaOH and PAX-14 dosages in each sample, pH of the solution, sample absorbance, calculated SDS concentration, SDS concentration in the sample and SDS removal efficiency in percentage.

Sample	2 M NaOH (µl)	PAX-14 (µl)	pH	Absorb. (615 nm)	Conc. (ppm) in diluted (500x) sample	Conc. (ppm) in sample	SDS removal (%)
A	240	200	4.16	1.283	0.300	150	63
B	480	200	4.51	1.228	0.285	142	65
C	600	200	4.65	1.150	0.264	132	68
D	660	200	5.61	1.605	0.385	192	51
E	720	200	5.75	1.305	0.305	153	62
F	840	200	8.25	2.262	0.559	280	27
0	-	200	4.05	1.232	0.286	143	65

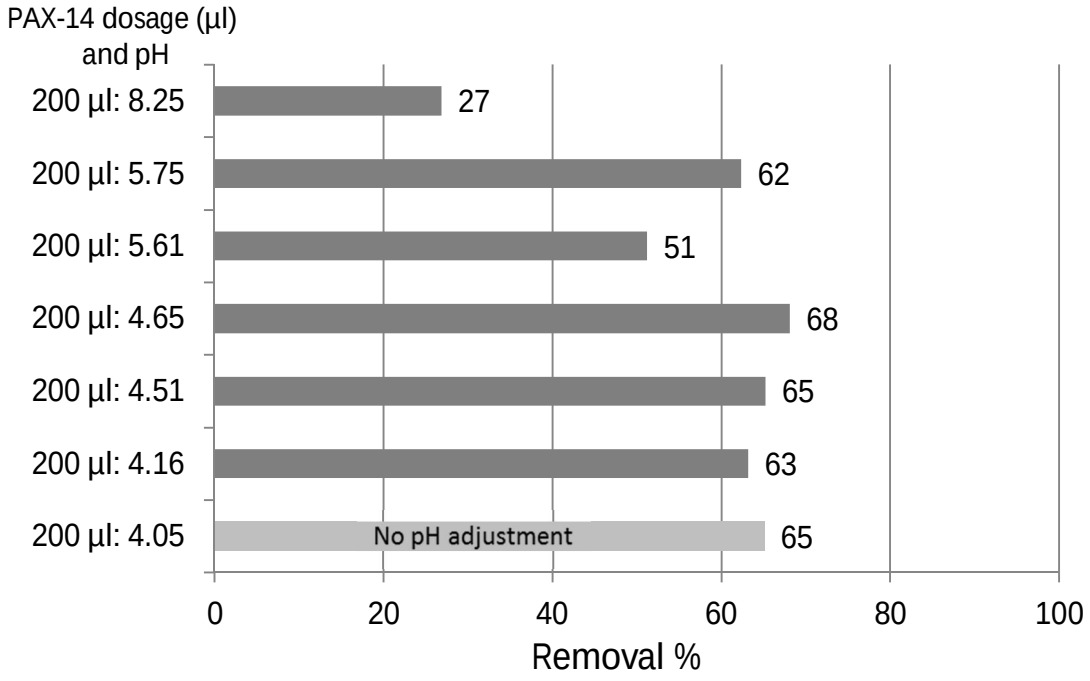


Figure 58. SDS removal results of PAX-14 (200 µl) experiments. The sample was 400 ppm SDS in deionized water. Coagulant dose and sample pH on the y-axis and SDS removal (%) on the x-axis

Table 38. PAX-14 (400 µl) experiments (600 ml, 400 ppm SDS). The table shows NaOH and PAX-14 dosages in each sample, pH of the solution, sample absorbance, calculated SDS concentration, SDS concentration in the sample and SDS removal efficiency in percentage.

Sample	2 M NaOH (µl)	PAX-14 (µl)	pH	Absorb. (615 nm)	Conc. (ppm) in diluted (500x) sample	Conc. (ppm) in sample	SDS removal (%)
A	480	400	4.07	0.490	0.089	45	88
B	1080	400	4.37	0.251	0.026	13	96
C	1260	400	4.82	0.331	0.047	23	94
D	1380	400	6.02	0.683	0.140	70	81
E	1440	400	6.45	0.993	0.223	111	69
F	1680	400	8.07	1.858	0.452	226	38
0	-	400	3.98	0.708	0.147	73	80
Ref.	-	-	6.47	2.893	0.727	363	0

Table 39. White water experiments (600 ml, 400 ppm SDS). The table shows NaOH and coagulant dosages in each sample, pH of the solution, sample absorbance, calculated SDS concentration, SDS concentration in the sample and SDS removal efficiency in percentage.

Sample	2 M NaOH (µl)	Coagulant (µl)	pH	Absorb. (615 nm)	Conc. (ppm) in diluted (500x) sample	Conc. (ppm) in sample	SDS removal (%)
A	2040	PIX 500	6.90	2.364	0.586	293	15
B	2880	PIX 1000	3.20	1.497	0.356	178	48
C	-	PIX 1000	2.65	1.520	0.363	181	47
D	600	PAX 200	6.53	1.810	0.439	220	36
E	1080	PAX 400	5.41	0.558	0.107	54	84
F	-	PAX 400	4.09	0.605	0.120	60	83
Ref.	-	-	7.00	2.747	0.688	344	0

Table 40. Comparison of SDS precipitation efficiency between deionized water and white water samples at the same pH ranges. The samples were 400 ppm SDS in *white water and 400 ppm SDS in deionized water. Coagulants used were ferric sulphate PIX-105 and polyaluminium chloride PAX-14.

Sample	pH	SDS removal %
PIX 500 µl*	6.9	15
PIX 500 µl	6.1	34
PIX 1000 µl*	3.2	48
PIX 1000 µl	3.0	60
PIX 1000 µl*	2.7	47
PIX 1000 µl	2.6	48
PAX 200 µl*	6.5	36
PAX 200 µl	8.3	27
PAX 400 µl*	5.4	84
PAX 400 µl	4.4	96
PAX 400 µl*	4.1	83
PAX 400 µl	4.0	80

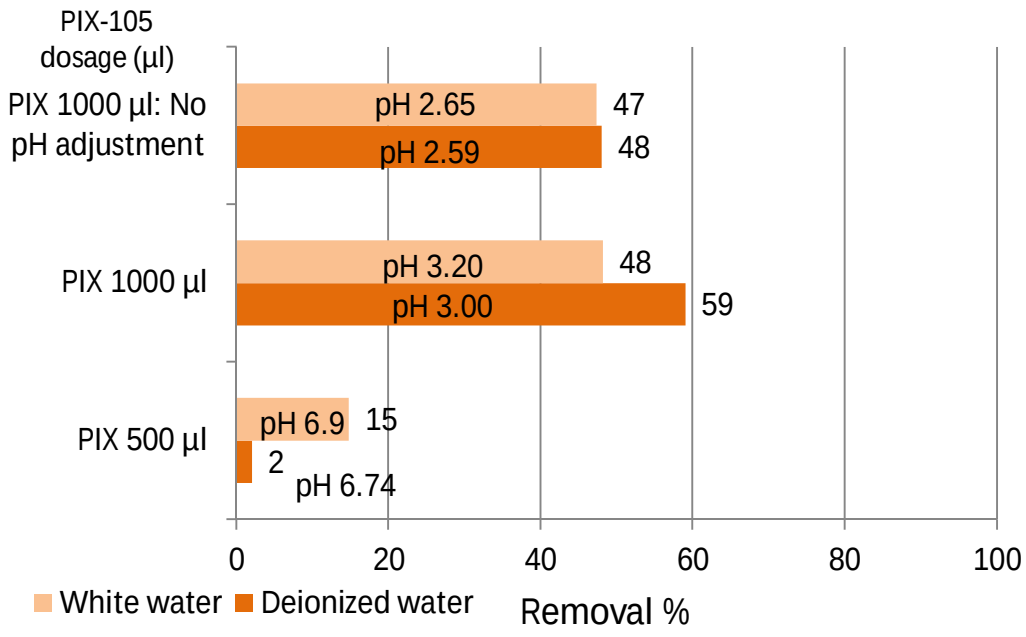


Figure 59. Comparison of SDS precipitation efficiency between the deionized water and the white water samples at the same pH ranges. The samples were 400 ppm SDS in white water and 400 ppm SDS in deionized water. Coagulant: ferric sulphate PIX-105. Coagulant dose on the y-axis and SDS removal (%) on the x-axis. pH is written down on the bars.

Table 41. Comparison of results of added NaOH doses and pH values between the white water and the deionized water samples. The samples were 400 ppm SDS in *white water and 400 ppm SDS in deionized water. Coagulants used were ferric sulphate PIX-105 and polyaluminium chloride PAX-14

Sample	pH	NaOH dose (µl)	SDS removal %
PIX 500 µl*	6.9	2040	15
PIX 500 µl	6.7	2040	2
PIX 1000 µl*	3.2	2880	48
PIX 1000 µl	3.0	2880	59
PIX 1000 µl*	2.7	-	47
PIX 1000 µl	2.6	-	48
PAX 200 µl*	6.5	600	36
PAX 200 µl	5.6	600	62
PAX 400 µl*	5.4	1080	84
PAX 400 µl	6.0	1080	81
PAX 400 µl*	4.1	-	83
PAX 400 µl	4.0	-	80

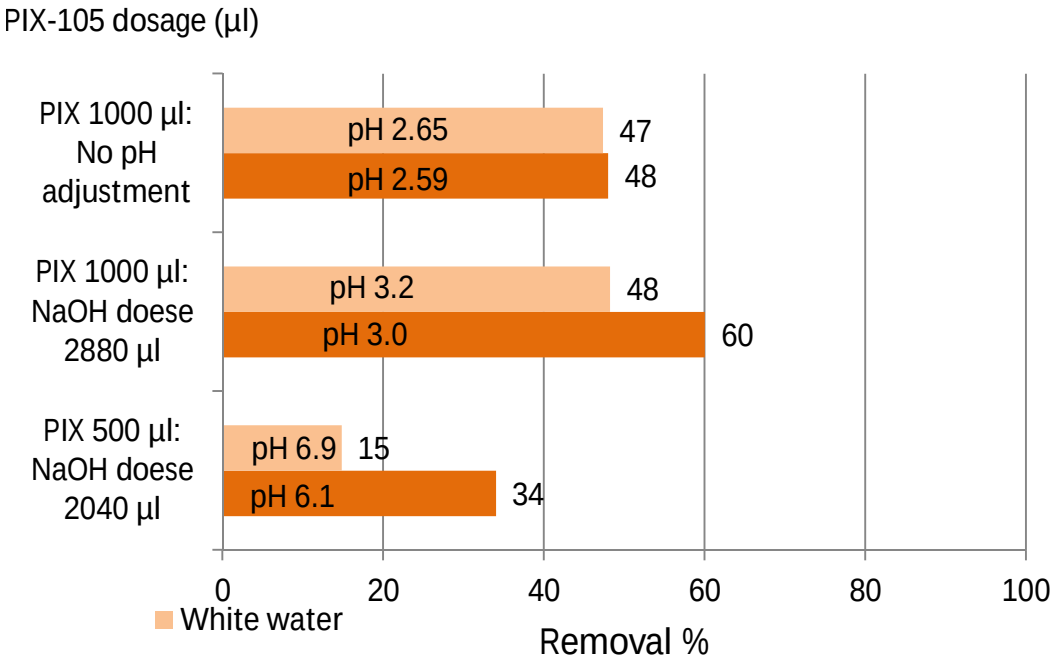


Figure 60. Comparison of results of added NaOH doses and pH values between the white water and the deionized water samples. The samples were 400 ppm SDS in white water and 400 ppm SDS in deionized water. Coagulant: ferric sulphate PIX-105. Coagulant and NaOH dosage on the y-axis and SDS removal (%) on the x-axis. pH is written down on the bars.

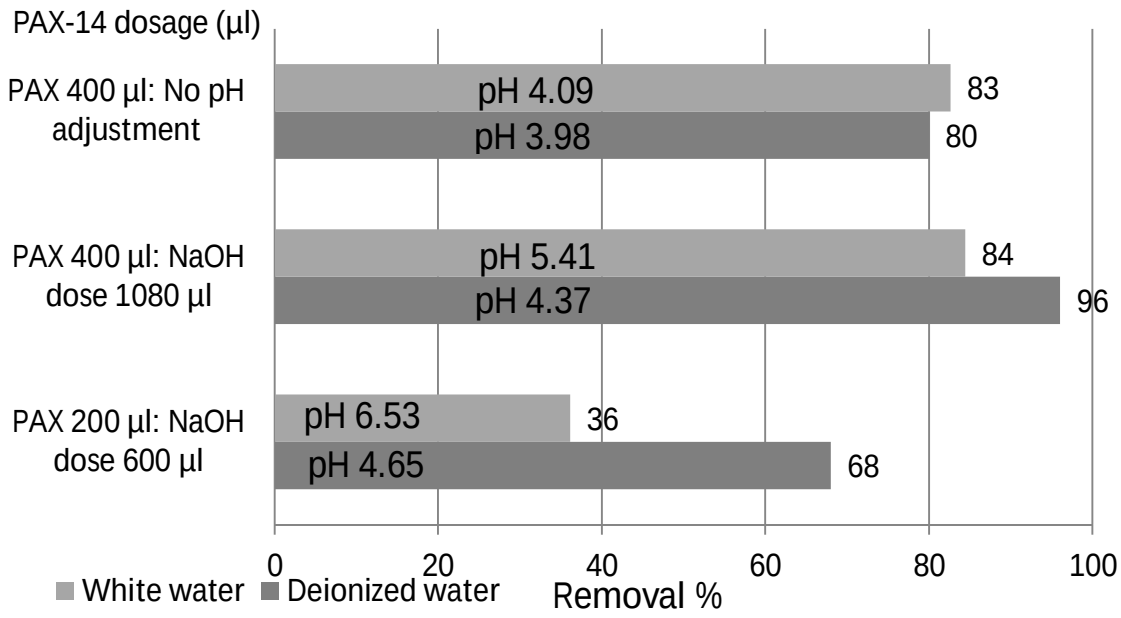


Figure 61. Comparison of results of added NaOH doses and pH values between the white water and the deionized water samples. The samples were 400 ppm SDS in white water and 400 ppm SDS in deionized water. Coagulant: polyaluminium chloride PAX-14. Coagulant and NaOH dosage on y-axis and SDS removal (%) on x-axis. pH is written down on the bars.