LAPPEENRANTA UNIVERSITY OF TECHNOLOGY

SCHOOL OF TECHNOLOGY

LUT Chemtech

Jutta Tiitinen

MEMBRANE DEVELOPMENT FOR OIL CONTAMINATED WATER TREATMENTS

Examiners: Prof. Mika Mänttäri
                     Dr. Tech. Arto Pihlajamäki
Supervisors: Dr. Tech. Arto Pihlajamäki
                     Ph.D. Antti Grönroos
                     Ph.D. Harri Setälä

ALKUSANAT

Tämä diplomityö tehtiin VTT:lle tammikuun 2014 ja kesäkuun 2014 välisenä aikana. Kiitos VTT:lle minulle annetusta mahdollisuudesta tehdä työ mielenkiintoisesta aiheesta.

Laboratoriotyöt tehtiin pääasiassa Lappeenrannan teknillisen yliopiston Membraanitekniikan laboratoriossa. Haluaisin kiittää työni ohjaajaa ja tarkastajaa Arto Pihlajamäkeä avusta laboratoriotöissä sekä kaikkia muita Membraanitekniikan laboratoriossa avuksi olleita henkilöitä. Membraanien pintakäsittely tehtiin VTT:n laboratoriossa Espoossa ja siitä suuret kiitokset Harri Setälälle. Haluaisin osoittaa kiitokseni myös työni tarkastajalle Mika Mänttärille sekä VTT:n puolesta työtäni ohjanneelle Antti Grönroosille. Ilman teidän kaikkien apua työni ei olisi valmistunut.

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TIIVISTELMÄ

Membraanien kehitys öljyisten vesien käsittelyyn

Tämän diplomityön tarkoituksena oli kehittää membraani, joka soveltuu öljyisten vesien käsittelyyn. Öljyiset vedet ovat iso ympäristöongelma ja siksi niiden käsittelyyn olisi löydettävä tehokas menetelmä. Käsittelymenetelmiä on useita, mutta yksi lupaavimmista käsittelymenetelmistä on membraanisuodatus.

Kirjallisessa osassa käytiin läpi membraanitekniikkaa ja polymeeristen membraanien valmistusta faasi-inversiolla sekä membraanien muokkausmenetelmiä. Työssä käytiin läpi myös membraanien tärkeimpiä ominaisuuksia. Öljyisistä vesistä, niiden käsittelymenetelmistä ja käyttökohteista kerrottiin tarkemmin.

Kokeellisessa osassa valmistettiin membraaneja selluloosa-asetaatista sekä muokattiin membraaneja kahdella eri tavalla. Muokkausmenetelmät olivat pinnan muokkaus sekä polymeerien sekoitus. Muokkauksella oli tarkoitus saada membraaneista hydrofiilisempiä sekä saada niille suurempi pinnan varaus, jotka voisivat vähentää membraanien likaantumista. Membraaneita karakterisoitiin määrittämällä niille zeta -potentiaali, kontaktikulma, öljyretentio, puhtaan veden permeabiliteetti, paine-normalisoitu vuo ja likaantuminen. Suodatukseen käytettiin sekä synteettistä öljy-vesi emulsiota, että oikeaa käytettyä öljy-vesi emulsiota. Pinnan muokkauksella saatiin aikaiseksi membraani, jolla oli paremmat ominaisuudet kuin käsittelemättömällä membraanilla. Pinnan muokkauksessa käytetyn aineen määrä vaikuttaa kuitenkin paljon ominaisuuksiin, joten eri määrien kokeileminen olisi tarpeen parhaan membraanin kehittämiseksi öljy-vesi emulsioiden käsittelyyn.

ABSTRACT

Membrane development for oil contaminated water treatments

Master's thesis

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45 pages, 16 figures, 7 tables, 5 appendixes

The aim of this Master's thesis study was to develop a membrane for oil contaminated water treatments. Oily wastewaters are a big problem to environment and therefore it is important to find an efficient method for their treatment. There are several treatment methods, but one of the most promising methods is membrane filtration.

In the theoretical part of this study the membrane technology and polymeric membrane preparation with phase inversion and membrane modification methods was discussed. It was also told about the most important properties of the membranes. Oily waters, their treatment methods and oily wastewater sources were discussed more specifically.

In the experimental part membranes from cellulose acetate were prepared and membranes were modified with two different methods. Modification methods were surface modification and polymer mixing. The modification purpose was to make membranes more hydrophilic and increase surface charge, which can reduce fouling. Membranes were characterized by determining zeta potential, contact angle, oil retention, pure water permeability, pressure-normalized flux and fouling. It were used both synthetic and real spent oil-water emulsion in membrane filtration. Surface modification resulted membranes, which had better properties than unmodified membrane. The amount of substance used in surface modification affected a lot to membrane properties, so it would be necessary to try different amounts of substance to develop the best membrane for oil-water emulsion treatment.

NOMENCLATURE

Symbols	Description	Unit
A	Membrane filtration area	m^2
c_f	The solute concentration in the feed	ppm
c_p	The solute concentration in the permeate	ppm
J	Flux	$kg/(m^2\ h)$
J_p	A steady flux of filtration solute	$kg/(m^2\ h)$
J_{w1}	Pure water flux before filtration tests	$kg/(m^2\ h)$
J_{w2}	Pure water flux after filtration tests and cleaning	$kg/(m^2\ h)$
m	Permeate mass	kg
P	Permeability	$kg/(m^2\ h\ bar)$
p	Filtration pressure	bar
R	Retention	%
t	Filtration time	h
V	Permeate volume	L

Abbreviations

C	Cellulose
CA	Cellulose acetate
CA-*g*-PAN	Cellulose acetate-*graft*-polyacrylonitrile
CAN	Cerium ammonium nitrate
CFR	Cross flow rate
DAF	Dissolved air flotation
DMAc	Dimethyl acetamide
DMF	*N,N*-Dimethylformamide
DR	Flux decay ratio
FO	Forward osmosis
FR	Flow rate

FRR	Flux recovery ratio
HCl	Hydrochloric acid (Salt acid)
HNO_3	Nitric acid
IEP	Isoelectric point
KCl	Potassium chloride
KOH	Potassium hydroxide
LUT	Lappeenranta University of Technology
MAA	Methacrylic acid
MBAAM	Methylene-bis-acrylamide
MD	Membrane distillation
MF	Microfiltration
MMCO	Molar mass cut-off
NaCl	Sodium chloride
NaOH	Sodium hydroxide
NF	Nanofiltration
NMP	N-methyl pyrrolidone
OH	Hydroxyl group
PMAA	Poly(methacrylic acid)
PNIPAAM	Poly(*N*-isopropylacrylamide)
O & G	Oil and grease
PA	Polyamide
PAA	Polyacrylic acid
PAN	Polyacrylonitrile
PC	Polycarbonate
PDEAAM	Poly(*N,N*-diethylacrylamide)
PDMAAM	Poly(*N,N*-dimethylacrylamide)
PE	Polyethylene
PEEK	Polyetheretherketone
PEG	Poly(ethylene glycol)
PEI	Poly(ether imide)
PEO	Poly(ethylene oxide)

PES	Polyethersulfone
PI	Polyimide
PP	Polypropylene
PPO	Poly(propylene oxide)
PS	Polysulfone
PTFE	Polytetrafluoroethylene
PVA	Polyvinyl alcohol
PVC	Poly(vinyl chloride)
PVCL	Poly(N-vinylcaprolactam)
PVDF	Poly(vinylidene fluoride)
PVP	Polyvinylpyrrolidone
RC	Regenerated cellulose
RH	Relative humidity
RO	Reverse osmosis
SDS	Sodium dodecyl sulphate
SPMMA	Spiropyran-containing methacrylate
TFC	Thin film composite
TSPU	Thermo-sensitive polyurethane
UF	Ultrafiltration

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1 Introduction

Oily wastewaters are a big problem to environment and therefore it is important to find an appropriate method to purify oily waters. In recent years it has been used many methods for oily wastewater purification. The traditional methods have many disadvantages like costs and large energy requirement. Because of the disadvantages of traditional methods it has been developed new methods like membrane filtration for oily wastewater purification.

Membrane filtration is a promising method for oily wastewater purification but it has also some disadvantages like fouling. The costs of the membrane filtration are lower than many other methods but if the fouling is high the costs increase because the membrane has to be cleaned.

The aim of this study was to develop polymeric membrane which is suitable for oily wastewater filtrations and which has low fouling potential. With different modification methods the purpose was to make membranes more hydrophilic and raise the membrane surface charge. The main polymer used in membranes was cellulose acetate and it was modified with a couple of ways. The membranes were tested with different methods and filtrations were made with synthetic and real oil-water emulsions.

THEORETICAL PART

2 Membrane technology

A membrane can be considered as a semi-permeable barrier between two phases. Liquid compounds can be separated from each other using different kind of membranes. At the filtration process there has to be some driving force. The most common driving force is pressure difference across the membrane. Other methods are for example concentration difference across the membrane, e.g. gas separation and dialysis, thermally driven processes, e.g. membrane distillation (MD) and electrically

driven processes, e.g. electrodialysis and fuel cells. [Mulder 1996, Lenntech BV 2014b]

2.1   Pressure driven membrane operations

Pressure driven membrane operations can be classified into four groups on the basis of the pore sizes of the membranes. These four groups are micro-, ultra- and nanofiltration and reverse osmosis. The mean pore sizes of microfiltration (MF) membranes vary from 0.05 to 10 µm and ultrafiltration (UF) membranes from 1 to 100 nm. Nanofiltration (NF) membranes mean pore sizes are 1-10 nm. Reverse osmosis (RO) membranes are very dense and they have mean pore sizes only 0.1 to 1 nm. The pore sizes indicate how big molecules or other particles can pass through membrane. MF membranes are used for retaining suspensions and emulsion. UF membranes are suitable for retaining macromolecules, colloids and suspended solids from water. NF membranes are used for multivalent ions, for example inorganic salts and small organic molecules such as sugars. RO membranes can retain all other particles than water. [Mulder 1996, Karakulski *et al.* 1998, Gryta *et al.* 2001, Fakhru'l-Razi *et al.* 2009, The Membranes Research Environment MemRE; Pore Size 2014]

At the pressure driven membrane process the feed solution goes through the membrane under pressure. The membrane permeates some compounds and retains other which means it is semi-permeable. Membrane process can be either dead-end or cross-flow filtration. The dead-end filtration means that all the feed solution is forced through the membrane. At the cross-flow filtration the feed solutions separate to retentate and permeate. The retentate can be recycled back to the feed. The retentate can also be called as concentrate. Usually permeate is the product of interest at the membrane filtration. At some applications the purpose is to concentrate the feed solution and at these cases the concentrate is the desired compound. The cross-flow filtration is more used at industrial applications than dead-end filtration, because of its lower fouling compared to dead-end filtration. Dead-end filtration has less energy loss than cross-flow filtration. [Mulder 1996, Lenntech BV 2014c]

2.2 Pressure driven membrane applications

There are many applications for pressure driven membrane operations. One of the most common applications is water treatment. Desalination of brackish and seawater with NF or RO membranes to produce drinking water is a very important application to areas where drinking water is not easily available. An important application is also the production of ultrapure water in the semiconductor industry. [Mulder 1996, Lenntech BV 2014d]

Membranes are used at different industries. In the food industry MF and UF are used to clarify fruit juices and alcohol beverages. The juices and sugar can be concentrated with RO. Applications in the dairy industry are for example the concentration of milk and cheese making and the recovery of whey proteins. Membranes are also used in pharmaceutical-, textile-, chemical- and paper industries. At the metal engineering the membranes are used for treatment of oil-water emulsions. [Mulder 1996, Cheryan and Rajagopalan 1998]

3 Polymeric membrane preparation

Membranes can be polymeric, ceramic or metallic. At this study polymeric membranes were the only membranes used. There are many preparation methods for polymeric membranes. Methods are sintering, stretching, track-etching, template leaching, phase inversion, coating and electrospinning [Mulder 1996, Shirazi *et al.* 2013]. The method used in this study was phase inversion.

3.1 Phase inversion

Phase inversion methods are very generally used polymeric membrane preparation method. There are few phase inversion methods available. The most common method is immersion precipitation, which was also used in this study. Other methods are dry-casting, double-pass casting, precipitation by solvent evaporation, precipitation from the vapour phase, precipitation by controlled evaporation and thermal precipitation. [Mulder 1996, Young *et al.* 2000, Sossna *et al.* 2007, Dang *et al.* 2008]

At first in immersion precipitation the polymer solution is prepared. The polymer is dissolved in a solvent or solvent mixture. When polymer has dissolved, the solution is left to allow complete release of air bubbles. The membrane is prepared by spreading the solution with casting knife onto a supporting layer. A supporting layer can be for example a glass plate. The casting thickness is selected according to the film thickness desired. The thickness can vary from 50 to 500 μm. The film with the supporting layer is then immersed in a coagulation bath containing nonsolvent (for example water). At the coagulation bath the polymer precipitates because of the exchange of solvent and nonsolvent. After coagulation the membranes are rinsed with water to remove residual solvent. [Mulder 1996, Chen *et al.* 2009b]

3.2 Polymeric membrane materials

Polymeric MF and UF membranes can be prepared only from one polymer or they can be composite membranes. NF and RO membranes are usually composite membranes. Relatively hydrophobic (contact angle >90°) polymer materials are for example polytetrafluoroethylene (PTFE), poly(vinylidene fluoride) (PVDF), poly(vinyl chloride) (PVC), polypropylene (PP), polyethylene (PE), polycarbonate (PC), polysulfone (PS) and polyethersulfone (PES). Relatively hydrophilic (contact angle <90°) materials are among others cellulose esters, e.g. cellulose acetate (CA) and regenerated cellulose (RC), polyacrylonitrile (PAN), polyimide (PI), poly(ether imide) (PEI), polyamide (PA), polyetheretherketone (PEEK) and polyvinyl alcohol (PVA). [Mulder 1996, Karakulski *et al.* 1998, Chakrabarty *et al.* 2008, Chen *et al.* 2009b, Yang *et al.* 2011]

At this study the focus was on CA. It is a versatile material and it has good toughness, high biocompatibility, good desalting, relatively low cost, excellent hydrophilic characteristic and with it the fouling can be minimized. It has also some disadvantages. On the CA membrane doesn't exists reactive functional groups and therefore the CA membranes are often modified by blending with other polymers. This way the membrane can have for example higher flux and selectivity. [Han *et al.*

2013] Other disadvantages for CA are poor mechanical strength and low thermal and chemical resistances [Zavastin *et al.* 2010].

3.3 Membrane modification

Membranes can be modified with different methods to change their properties. The surface modification of membrane is one of those. Surface modification methods can be for example surface graft polymerization, surface coating and surface segregation [Maguire-Boyle and Barron 2011]. The modification methods can reduce fouling by making the membrane more hydrophilic, reduce roughness and change membrane charge, or blends of these [Gorey and Escobar 2011, Maguire-Boyle and Barron 2011]. The modification method used in this study was surface graft polymerization. The developed grafting methods can be divided to three groups: (1) free radical, (2) ionic and (3) condensation and ring opening polymerization [Majumdar *et al.* 2006]. The free radical method was used in this study and that method is generalized because of its practicality [Majumdar *et al.* 2006].

Majumdar *et al.* (2006) and Gorey and Escobar (2011) have studied the free radical method with C and CA membranes, respectively. Cerium ammonium nitrate (CAN, $Ce(NH_4)_2(NO_3)_6$) was used as initiator. The grafting was done in nitrogen atmosphere. The CA or C reacts with CAN and it forms free radicals on the CA or C surface. Gorey and Escobar (2011) have modified the membrane surface with poly(*N*-isopropylacrylamide) (PNIPAAM) and Majumdar *et al.* (2006) with polyacrylic acid (PAA). [Majumdar *et al.* 2006, Gorey and Escobar 2011] The PAA reaction with C is shown in Figure 1.
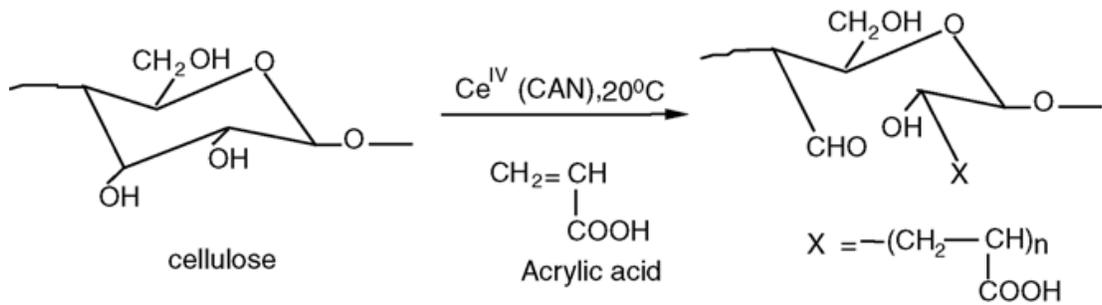
Figure 1.   The polyacrylic acid grafting to cellulose using CAN as initiator. [Majumdar *et al.* 2006]

One membrane modification method is the use of stimuli-responsive polymers. Using these stimuli-responsive polymers temperature-, pH- and ionic strength-, photo- and electric- and magnetic field responsive membranes can be prepared. Surface modification of stimuli-responsive membranes is made for example with grafting method, physical adsorption method or with different polymerization methods, e.g. photo-initiated and plasma-*graft*-filling polymerization using stimuli-responsive functional polymers and polymeric membranes. There are many different kind of functional polymers, for example PNIPAAM which Gorey and Escobar (2011) have used and PAA which Majumdar *et al.* (2006) have used. Others are, for example, poly(*N,N*-dimethylacrylamide) (PDMAAM), methylene-bis-acrylamide (MBAAM), thermo-sensitive polyurethane (TSPU), poly(*N,N*-diethylacrylamide) (PDEAAM), poly(*N*-vinylcaprolactam) (PVCL), poly(methacrylic acid) (PMAA) and spiropyran-containing methacrylate (SPMMA). Different polymeric membranes like PTFE, PVDF, PVA, PE and PP have been used with stimuli-responsive membranes. [Majumdar *et al.* 2006, Wandera *et al.* 2010, Gorey and Escobar 2011]

4   Membrane properties

Membranes have many properties that affect to their filtration ability. Properties indicate different things about membranes and they can be determined with various methods.

4.1 Retention and MMCO

Retention indicates the membranes selectivity. It detects the extent of the feed solution compounds the membrane retains. The apparent retention R for some component in feed solution can be measured as equation (1)

$$R = \left(1 - \frac{c_p}{c_f}\right) \cdot 100\ \%, \tag{1}$$

where R retention, %

  c_p the solute concentration in the permeate, ppm

  c_f the solute concentration in the feed, ppm.

The retention varies between 0 and 100 %. The closer to 100 % the value is, the better the membrane retains the desired compounds. 100 % means complete retention and 0 % means that all compounds pass through the membrane. The units of the concentrations can be for example mol/L or ppm.

Molar mass cut-off (MMCO) indicates the molar mass which is 90 % retained by the membrane. MMCO-values are usually at the unit Da or kDa.

4.2 Flux and permeability

To membranes it can be calculated the flux (J) and permeability (P). The membrane flux is defined as the amount of permeate which pass through the membrane in relation to filtration area and time. It can be measured as equation (2)

$$J = \frac{V\ or\ m}{A \cdot t}, \tag{2}$$

where   V   Permeate volume, L

  m   Permeate mass, kg

  A   Membrane filtration area, m^2

  t   Filtration time, h.

Permeability indicates the amount of permeate which pass through the membrane in relation to filtration area, time and pressure. The unit of the P can be L/(m^2 h bar) or kg/(m^2 h bar). It can be defined by equation (3)

$$P = \frac{\Delta J}{\Delta p},$$ (3)

where ΔJ flux, L/(m^2 h) or kg/(m^2 h)

Δp filtration pressure, bar.

With the equation (3) the permeability can be defined by the graph in which the y-axis is flux and the x-axis is pressure. The permeability is a slope of the curve.

4.3   Fouling

Fouling is a big problem in membrane filtration process. Fouling means, for example, that membrane pores can be blocked or onto the membrane surface can be formed a cake. It causes flux decline. When the pores are blocked, the membrane does not pass through so many compounds and also the flux decline. Fouling causes a higher energy use and cleaning frequency and shorter life span of the membrane [Lenntech BV 2014a]. That means higher costs. There are four membrane fouling types: inorganic fouling, organic fouling, particle/colloid fouling and microbial/biological fouling [Membrane Solutions 2014].

Fouling can be reversible or irreversible. Reversible fouling is follows from the deposition of components on the membrane surface and irreversible fouling from the deposition of macromolecules within the membrane pores. [Tansel *et al.* 1995, Karakulski *et al.* 1998]   There are some ways, how the fouling can be reduced. Membrane properties impacts to the fouling. Using rather hydrophilic than hydrophobic membranes can reduce fouling. The charge of the membrane can also affect to the fouling. When the membrane charge is same as the charge of the compounds in the feed solution, the fouling can reduce. Also the pre-treatment of the feed solution can reduce fouling. Pre-treatment methods are for example heat treatment, pH adjustment, chemical clarification and pre-filtration. Membranes can be

cleaned with different methods and the method depends on the type of membrane, the module configuration, the chemical resistance of the membrane and the type of foulant. The methods are hydraulic (e.g. back-flushing and alternate pressuring), chemical (e.g. acids and detergents), mechanical and electric cleaning. The most used method is chemical cleaning. [Mulder 1996]

The membrane fouling-resistant can be determined with two equations. Equation (4) is a flux recovery ratio (FRR) and equation (5) flux decay ratio (DR).

$$FRR = \left(\frac{J_{w2}}{J_{w1}}\right) \cdot 100 \text{ \%},\tag{4}$$

where J_{w1} pure water flux before filtration tests, L/(m^2 h) or kg/(m^2 h)

J_{w2} pure water flux after filtration tests and cleaning, L/(m^2 h) or kg/(m^2 h).

$$DR = \left(1 - \frac{J_p}{J_{w1}}\right) \cdot 100 \text{ \%},\tag{5}$$

where J_{w1} pure water flux before filtration tests, L/(m^2 h) or kg/(m^2 h)

J_p a steady flux of filtration solute, L/(m^2 h) or kg/(m^2 h).

The higher FRR and lower DR values mean the better antifouling property of the membrane.

4.4 Hydrophilicity and hydrophobicity

Higher hydrophilicity of membrane can reduce fouling in water phase and is therefore an important membrane property. Hydrophilicity can be defined with contact angle measurements for example with sessile drop method. Membrane is hydrophilic if the contact angle is under 90° and hydrophobic if the contact angle is over 90°. The smaller the contact angle the greater the hydrophilicity of membrane. The Figure 2 demonstrates the difference between hydrophobicity and hydrophilicity.
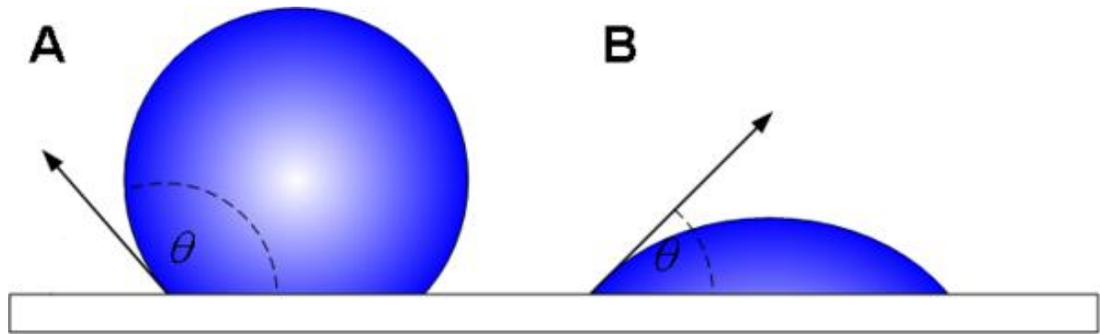
Figure 2.   The contact angle measurement. A demonstrates the hydrophobic membrane and B the hydrophilic membrane. [The Membranes Research Environment MemRE; Sessile Drop Method 2014]

The contact angle measurement is rather simple and there are some equipments to measure it. Figure 3 represents one example of equipment. A water droplet is placed on the membrane surface and an image of that is captured by camera. Then the internal angles for both sides of the droplet are determined. It can be placed several water droplets on the different points of membrane surface and then calculate the mean value of the contact angles. The membrane surface can be heterogeneous, therefore it is good to use the mean value of several water droplets to get reliable result.
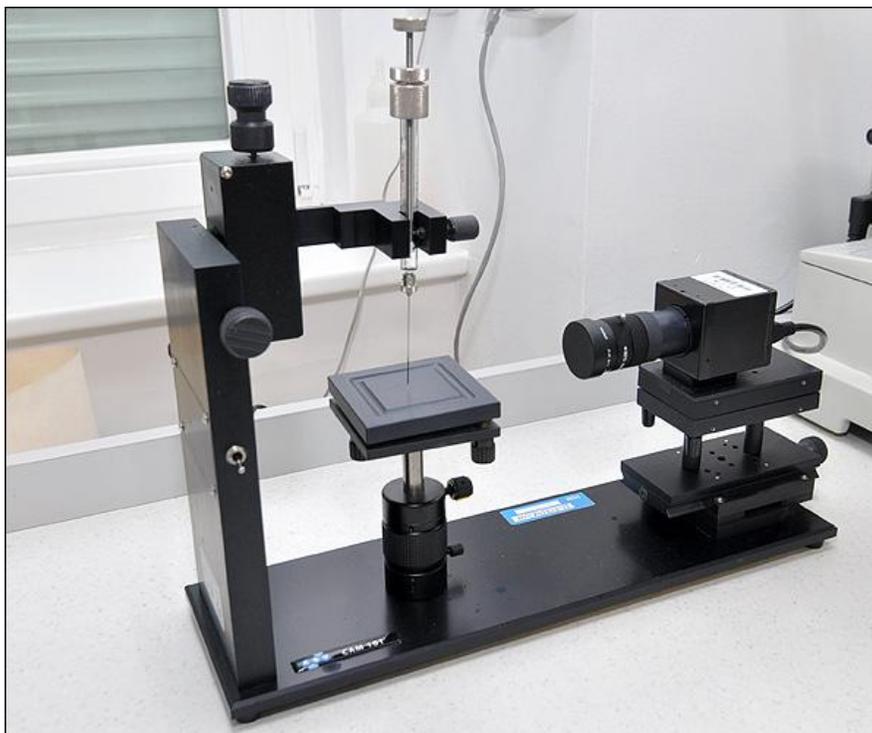
Figure 3.   The contact angle meter of KSV Instruments [Institute of Organic Chemistry and Biochemistry AS CR 2014]

4.5   Surface charge

The surface charge of the membrane has an effect on membrane fouling [Mulder 1996] and is thus an important property of membrane. To avoid fouling it should be use the membrane which has the same charge as the compounds in the feed solution [Mulder 1996]. Oppositely charged compounds attracts each other and that can cause membrane fouling when oppositely charged compounds fasten to membrane pores and surface. The surface charge is determined with an equipment where is used some basic and acid solution for pH adjustment and some electrolyte. Basic solution can be for example NaOH and acid solution HCl and electrolyte KCl [Nguyen *et al.* 2013]. The equipment measures the electrokinetic potentials of membranes at different pHs and then it could be defined the isoelectric point (IEP) of the membranes. IEP means the pH-value where zeta potential is zero which means that the net charge of membrane is zero. When zeta potential is negative also the charge of the membrane is negative and otherwise. The example of zeta potential- and IEP-measurements is shown in Figure 4.
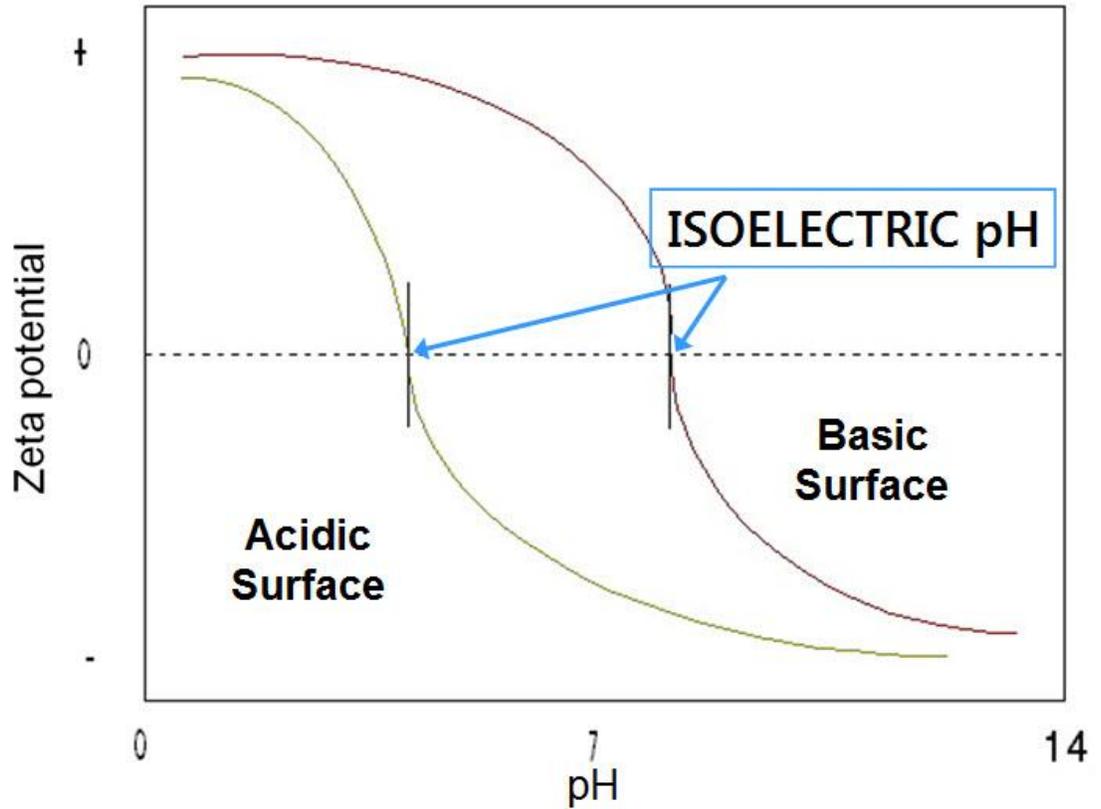
Figure 4.   The zeta-potential at different pHs and the isoelectric points. [HORIBA, Ltd 2014]

5   Oily wastewater

5.1   Impact to environment

Oily wastewaters and oil-water emulsions are two of the major pollutants to water environment [Karakulski *et al.* 1995] and they create a huge ecological problem worldwide [Gryta *et al.* 2001]. There are many sources for pollution of the water environment. They are, for example, sewage disposal, land run off, atmospheric fallout and industrial wastes. Oil refineries are one of the largest oily wastewater producers. The discharged oily wastewater by oil refineries has decreased over the years in European refineries. In 1969 the total aqueous effluent was 3119×10^6 t year^{-1} (80 refineries) and in 2000 it was decreased to 2543×10^6 t year^{-1} (84 refineries). [Wake 2005]

The amount of oily wastewater is huge and therefore it is important to develop suitable methods to purify them. There are also some limits for oil and grease (O & G). United States Environmental Protection Agency (USEPA) has set the limits for O & G for treated produced water discharge offshore. The daily maximum limit for O & G is 42 mg/L and the monthly average limit is 29 mg/L [Fakhru'l-Razi *et al.* 2009]. In the US in 1998 for Metal Products and Machinery (MP&M) the limits were for one day 35 mg/L and the monthly average 17 mg/L [Cheryan and Rajagopalan 1998]. Later the limits have tightened and new maximum daily limit is 15 mg/L and monthly average 12 mg/L [Whalen 2001].

5.2   Oily wastewater sources and compositions

Oily wastewater sources are many industries such as steel, aluminium, food, textile, leather, petrochemical, metal finishing [Cheryan and Rajagopalan 1998] and pharmaceutical [Chen *et al.* 2009a]. Food processing, e.g. fish processing, is at food industry and the wool scouring in textile industry the source of oily waters [Cheryan and Rajagopalan 1998]. At metal finishing industry the oily waters are generated during mechanical operations including grinding, rolling, alkaline degreasing and transportation [Gryta *et al.* 2001]. From harbours is collected bilge water [Karakulski *et al.* 1998]

Oily wastewaters can be grouped into three board categories: free-floating oil, unstable oil/water emulsions and highly stable oil/water emulsions. O & G exists in oily wastewater in several forms which are based on droplet size. Free oil droplet size is greater than 150 µm, dispersed oil 20-150 µm and emulsified oil under 20 µm. [Cheryan and Rajagopalan 1998, Karakulski *et al.* 1998]

Oily wastewaters contain many chemicals and compounds depending on the process where they are produced. Emulsified oily wastewater is a complicated composition because it can contain mineral, vegetable or synthetic oil, fatty acids, emulsifiers (anionic and non-ionic surfactants), corrosion inhibitors (amines), bactericides and other chemicals [Karakulski *et al.* 1995, Gryta *et al.* 2001]. O & G can also contain petroleum hydrocarbons, phenolic compounds and naphthenic acids [Cheryan and

Rajagopalan 1998]. All oil refineries don't have same processes and therefore their wastewaters have different chemical compositions. For example petroleum refinery wastewaters can include O & G, phenols, sulphides, ammonia, suspended solids, cyanides, nitrogen compounds and heavy metals, e.g. chromium, copper and zinc. [Wake 2005]

5.3 Traditional methods for the oily wastewater treatment

There are many methods to treat oily wastewaters. The appropriate treatment method depends on the oil droplet size in wastewater [Hua *et al.* 2007]. The treatment methods can be classified to chemical, biological [Gryta *et al.* 2001, Fakhru'l-Razi *et al.* 2009], mechanical, thermal [Gryta *et al.* 2001] and physical [Fakhru'l-Razi *et al.* 2009] methods. Gravity separation and skimming is a suitable treatment method for removing free oil from wastewater [Cheryan and Rajagopalan 1998]. Other treatment methods for removing free and dispersed/unstable oil are dissolved air flotation (DAF), coagulation and flocculation, de-emulsification methods, electro flotation, electro coagulation [Cheryan and Rajagopalan 1998], chemical emulsion breaking [Cheryan and Rajagopalan 1998, Hua *et al.* 2007], mechanical coalescence, micro- and ultrasonic wave treatment [Hua *et al.* 2007] and thaw and heat treatment [Hua *et al.* 2007, Fakhru'l-Razi *et al.* 2009]. De-emulsification methods are e.g. thermal [Mittal *et al.* 2011], chemical [Karakulski *et al.* 1995, Yang *et al.* 2011], centrifuge and electric field [Yang *et al.* 2011] de-emulsifications.

All these traditional methods have disadvantages. These methods cannot effectively remove micron or submicron sized oil droplets (under 10 µm) [Chen *et al.* 2009a, Mittal *et al.* 2011]. They are useful only for free oil solutions and dispersed/unstable oil/water emulsions [Duong and Chung 2014] and when the concentration of oil is very low [Gryta *et al.* 2001]. Other disadvantages are low efficiency [Gryta *et al.* 2001, Chen *et al.* 2009a], high operation costs [Gryta *et al.* 2001, Chen *et al.* 2009a, Fakhru'l-Razi *et al.* 2009], corrosion and recontamination problems [Chen *et al.* 2009a], the use of toxic chemicals, space for installation and secondary pollution [Fakhru'l-Razi *et al.* 2009] and large requirement of energy [Gryta *et al.* 2001].

5.4 Membrane technology for oily wastewaters

5.4.1 Membrane advantages

Because of the disadvantages of the traditional methods new methods for oil/water separation have to be developed. Recently the membrane technology has been one of the most promising methods to oil/water separation [Maguire-Boyle and Barron 2011]. The advantages of membrane technology compared to the traditional methods are higher efficiency and low energy and operating costs [Gryta *et al.* 2001, Yang *et al.* 2011], high quality of the permeate [Gryta *et al.* 2001], stable effluent quality, small area requirement and no chemical additions needed [Hua *et al.* 2007], usable at many industries, membrane equipment has smaller foot print and the process can be automated [Cheryan and Rajagopalan 1998]. The membrane process is suitable also for large-scale oily wastewaters separation [Maguire-Boyle and Barron 2011].

5.4.2 Ultrafiltration

UF is one the most effective membrane technology methods for oily wastewater treatment because of its suitable pore size [Chen *et al.* 2009b, Fakhru'l-Razi *et al.* 2009]. The pore sizes of the UF membranes are usually 2-50 nm and the size of the oil droplets in emulsion is 0.1-10 μm. Therefore the most of the oil droplets can be efficiently removed with UF and the permeate is nearly free from emulsified oil [Chen *et al.* 2009b]. UF can also be used as a pre-treatment process before NF or RO if needed [Chen *et al.* 2009a].

5.4.3 Membrane materials

As been mentioned earlier, the hydrophilic membranes have better fouling resistance. Hydrophilic membranes have been developed also to oil/water separation. Materials such as C, CA and PVA have excellent fouling resistance. [Chen *et al.* 2009b] With membrane modification higher permeate flux and even better fouling resistance, the flux recovery and the efficiency of membrane washing can be achieved [Chen *et al.* 2009a].

Chen *et al.* (2009a, 2009b) have prepared an asymmetric cellulose acetate-*graft*-polyacrylonitrile (CA-*g*-PAN) and Pluronic F127 modified PES UF membranes to oil/water separation. Pluronic F127 contains hydrophilic poly(ethylene oxide) (PEO) and hydrophobic poly(propylene oxide) (PPO). [Chen *at al.* 2009a, Chen *et al.* 2009b]. The contact angle of CA-*g*-PAN-membrane was almost same as pure CA so the grafted membrane was as hydrophilic as pure CA-membrane. The grafted membrane had much higher pure water flux than CA-membrane. Depending on the amount of acrylonitrile in membrane the pure water flux of CA-*g*-PAN-membrane could be even 100 times bigger than CA-membrane. The FRR value of CA-membrane was 100 % and DR value 0 % (oil concentration in feed solution 900 ppm), which means excellent fouling resistance. Since the pure water flux of CA-membrane is very low, 3.4 L/(m^2 h) (p=0.1 MPa, T=25 ± 1 °C), it is not potential for practical oil/water separation application. The FRR values of CA-*g*-PAN-membranes were over 90 % and DR values about 40 and 70 % depending on the amount of acrylonitrile in membrane and the oil concentration in feed solution. [Chen *et al.* 2009b]

Chen *et al.* (2009a) made five different membranes. The formation of the casting solutions are represented in Table I. The DR- and FRR-values of PES/Pluronic F127 membranes are shown in Table II.

Table I.   The formation of casting solutions. [Chen *et al.* 2009a, modified]

Membranes	Composition of casting solution			
	PES, g	PEG, g	F127, g	DMF, g
1#	3.60	3.00	-	13.40
2#	3.60	3.00	0.18	13.22
3#	3.60	3.00	0.36	13.04
4#	3.60	3.00	0.54	12.86
5#	3.60	3.00	0.72	12.68

Table II. The DR- and FRR-values of PES/Pluronic F127 membranes. FRR-values are calculated after pure water and SDS solution cleaning. [Chen *et al.* 2009a, modified]

Membrane	DR, %	FRR, %	
		Pure water	SDS
1#	65.34	25.20	62.07
2#	56.00	35.83	70.93
3#	50.17	39.42	84.74
4#	48.38	47.45	87.10
5#	34.20	63.33	93.33

The higher was the amount of Pluronic F127 in membrane, the lower the DR value of membrane. Using sodium dodecyl sulphate (SDS) for cleaning, the FRR values of modified membranes were much higher than cleaning with pure water and the higher amount of Pluronic F127 increases the FRR-value. [Chen *et al.* 2009a]

5.4.4 Applications for membranes

5.4.4.1 Produced water in oil and gas industry

Membranes are used widely in different industries for oil/water separation. The largest waste stream produced in oil and gas industry is industrial oily water (produced water) [Fakhru'l-Razi *et al.* 2009, Chakrabarty *et al.* 2010]. Produced water is a mixture of different organic and inorganic materials and its major compounds are dissolved and dispersed oil compounds, dissolved formation minerals, production chemical compounds, production solids and dissolved gases. UF is effective method for produced water treatment. UF advantages are high oil removal efficiency, no necessity for chemical additives, low energy costs and small area requirement. [Fakhru'l-Razi *et al.* 2009] Chakrabarty *et al.* (2010) used two different kinds of membrane in produced water filtration. The other membrane was prepared from the solution which contained 12 wt% PS, 5 wt% polyvinylpyrrolidone (PVP) and 83 wt% N-methyl pyrrolidone (NMP) and the other from the solution which contained 12 wt% PS, 5 wt% PVP and 83 wt% dimethyl acetamide (DMAc). The oil concentration in produced water in feed solution was 366 ppm. For two prepared membranes the fluxes were determined. After about one hour filtration the fluxes

were 128 and 70 L/(m^2 h) (p=103.4 kPa, T≈25 °C). [Chakrabarty *et al.* 2008, Chakrabarty *et al.* 2010]

5.4.4.2 Bilge water

The oily wastewater collected from harbours is bilge water, which is a two-phase dispersive system. The continuous phase is water and the dispersed phase is oil. The bilge water contains fuel, oils, lubricating oils, hydraulic oils, detergents etc. and its characteristics and generation rates depend on ship type and ship operating mode. Karakulski *et al.* (1998) used PVDF (MMCO 100 kDa), PVC (MMCO 70 kDa) and PAN (MMCO 70 kDa) membranes to bilge water purification. The oil retention of all membranes was over 96 %. The fluxes after 50 h bilge water filtration vary from 29 to 42 L/(m^2 h) (p=200 kPa, T=30 °C). [Karakulski *et al.* 1998] Gryta *et al.* (2001) used UF and MD to bilge water purification. The wastewater was first purified with UF. Then permeate of UF process was still purified with MD. The membrane material was PVDF. The oil retention of UF process was 98.64 % and UF/MD process 100 %. Gryta *et al.* used two concentrations of oil in bilge water, 124 ppm and 360 ppm. The fluxes after 50 h bilge water filtrations were 36 kg/(m^2 h) and 22 kg/(m^2 h) (p=200 kPa, T=30 °C), respectively. [Gryta *et al.* 2001]

5.4.4.3 Crude oil

Crude oil is oily wastewater from refineries. Mittal *et al.* (2011) used crude oil with three different oil concentrations, 50, 100 and 200 ppm. The membrane was hydrophilic ceramic-polymeric composite membrane. The higher the oil concentration the lower was the flux and the other way around with retention. [Mittal *et al.* 2011] Chakrabarty *et al.* (2010) purified synthetic oily water (crude oil) with different PS-membranes. The oil concentration in feed solution was 100 ppm. Depending on the membrane properties (the used solvent and additive) and cross flow rates (CFR) the permeate fluxes after 1 h filtration varied from 17.6 to 223.0 L/(m^2 h) (p=103.4 kPa, T≈25 °C). Oil retentions varied from 87 to 97 %. [Chakrabarty *et al.* 2010]

5.4.4.4   Soybean oil

Chen *et al.* (2009a) and Duong and Chung (2014) studied soybean oil and surfactant as oil/water emulsion. Chen *et al.* (2009a) used UF PES-membranes modified with Pluronic F127. The oil concentration in feed solution was 900 ppm. The pure water fluxes were from 115 to 135 L/(m^2 h) (p=0.1 MPa) for pure PES- and modified PES-membranes. The oil/water emulsion fluxes were from 45 to 85 L/(m^2 h) (p=0.1 MPa). The highest flux was with the membrane having the most Pluronic F127 content. The oil retentions for pure PES-membrane and for modified membranes were 100 %. [Chen *et al.* 2009a] Duong and Chung used forward osmosis (FO) polyacrylonitrile - thin film composite (PAN-TFC)-membranes. The pure water flux was 3.43 L/(m^2 h) at 5 bar (T=23 $\pm$ 2 °C). The oil retention was 99.88 % when the total oil and surfactant concentration in feed solution was 200 000 ppm and the ratio of oil and surfactant was of 9 to 1 respectively. [Duong and Chung 2014]

5.4.4.5   Vacuum pump oil

Chen *et al.* (2009b) used high-speed vacuum pump oil and surfactant (SDS) as feed solution. The membrane material was CA-*g*-PAN as mentioned earlier. They prepared few different membranes with different amounts of acrylonitrile. The oil retention was 100 % for all membranes. The oil concentrations in feed solutions were 300, 600, 900, 1200 and 1800 ppm. The fluxes after 1 h filtration were between 80 L/(m^2 h) (1800 ppm) and 160 L/(m^2 h) (300 ppm) (p=0.1 MPa, T=25 °C). [Chen *et al.* 2009b]

5.4.4.6   Gas oil

Fouladitajar *et al.* (2013) and Madaeni *et al.* (2013) filtrated gas oil mixed with surfactant. Fouladitajar *et al.* (2013) used MF as a filtration method while Madaeni et al. (2013) used MF and UF. Fouladitajar *et al.* (2013) used oil concentrations from 1 000 to 20 000 ppm and filtration pressures were between 0.5 and 2.0 bar. Oil retentions vary from 65 to 92 % depending on pressure and oil concentration. [Fouladitajar *et al.* 2013] At the study of Madaeni *et al.* (2013) the operating

pressures were between 1 and 3.5 bars at MF and between 1 and 5.5 bars at UF. With MF the retention was the lowest at 2 bars, about 60 %, and the highest at 1 bar, over 90 %. The flux after 5 h filtration was about 100 kg/(m^2 h) (p=1.5 bars, T=35 °C). With UF the retention was from 90 to 100 %. The flux after 5 h filtration was nearly the same as with MF. [Madaeni *et al.* 2013]

5.4.4.7   Edible oil

Hua *et al.* (2007) prepared feed solution by mixing edible oil, distilled water and surfactant. They used ceramic (α-Al$_2$O$_3$) MF membrane in their filtration studies. When the oil concentration was 500 ppm and filtration pressure vary from 0.05 to 0.30 MPa, the permeate flux vary from 30 to 220 L/(m^2 h) respectively. At the same pressures the retentions were between 92 and 99 % so that higher retention was at lower pressure. Hua *et al.* (2007) tested also how the oil concentration affects to flux and retention. Oil concentrations were from 250 to 2 000 ppm and pressure 0.2 MPa. Fluxes were from 125 L/(m^2 h) to 170 L/(m^2 h). The flux decreased when oil concentration increased. Retentions vary from 96 to 98 %. [Hua *et al.* 2007]

EXPERIMENTAL PART

6 Materials and methods

6.1 Materials

Cellulose acetate (CA, M_n=50 000 g/mol, batch number MKBK7408V) supplied by Sigma-Aldrich Co., USA was used as main polymer in membrane casting solution. Polyacrylic acid (PAA, M_w=1 000 000 g/mol, batch number 541449) was purchased from Polysciences Inc., USA. *N,N*-Dimethylformamide (DMF, anhydrous 99.8 %, batch number STBD5684V), cerium ammonium nitrate (CAN), methacrylic acid (MAA, 99 %) and nitric acid (HNO_3, 65 %) were supplied by Sigma-Aldrich Co., USA. The surfactant sodium dodecyl sulphate (SDS, assay min 95 %, batch number 21898) was purchased from J.T. Baker, USA. The oil for synthetic oil-water emulsion was purchased from Neste Oil, Finland. The real oil-water emulsion was supplied by LUT mechanical workshop. The commercial UP005-membrane (membrane material PES) was purchased from Microdyn-Nadir, Germany. Pure water was prepared with CENTRA-R 60/120 equipment. That is produced by Elga and it generates at least 15 MΩ·cm purity of water.

6.1.1 Synthetic oil-water emulsion

The oil used for synthetic oil-water emulsion was Neste Special 30 Monograde motor oil. The oil-water emulsion was prepared by mixing SDS and oil to pure water by using the mixer. The oil concentration in emulsion was 3 wt% and the ratio of oil/SDS was 9:1. The emulsion was stored at room temperature.

6.1.2 Real oil-water emulsion

Real oil-water emulsion was cutting oil for metal finishing used in LUT mechanical workshop. The cutting oil was TILIA TEU 97 and its supplier was PRO Teollisuustarvike Oy, Finland. The emulsion was pre-filtered with a fine metal wire mesh.

6.2 Membrane preparation

In the study, four different casting solutions which had different amounts of polymers were prepared. The composition of the casting solutions are shown in Table III.

Table III.   The composition of the casting solutions.

Amount of substance, g					
CA	PAA	DMF	Total mass, g	CA concentration, wt%	PAA concentration, wt%
17.0	0	83	100	17.0	0.0
16.9	0.1	83	100	16.9	0.1
16.7	0.3	83	100	16.7	0.3
16.5	0.5	83	100	16.5	0.5

The polymer or polymers were first dissolved in a solvent (DMF). After the polymer was dissolved, the solution was left over night to allow complete removal of air bubbles.

Membranes were prepared from the casting solutions with immersion precipitation method. The thickness of the casting knife was 170 μm and membranes were casted directly on a glass plate. Precipitation occurred in a DMF/water (5/95) coagulant bath at room temperature. Membranes were kept in coagulation bath for 15 minutes and then moved to water bath for removal residual solvent.

Free radical method was used to graft pure CA-membranes with MAA. CAN was used as an initiator in free radical grafting using 25 mM water solution. The membrane was closed to a chamber which was placed in to water bath at 45 °C and bubbled with nitrogen gas for about 5 minutes. Then into the chamber was added 21 mL 0.1 M HNO_3 (water solution), 60 mL H_2O, 1 mL 25 mM CAN and 99 % MAA-solution. Grafting was made with two different concentrations of 99 % MAA-solution, 3.5 vol% and 5.7 vol%. The mixture was allowed to react for 2 h and after that the membrane was rinsed with water. Figure 5 shows the methacrylic acid grafting to cellulose acetate.
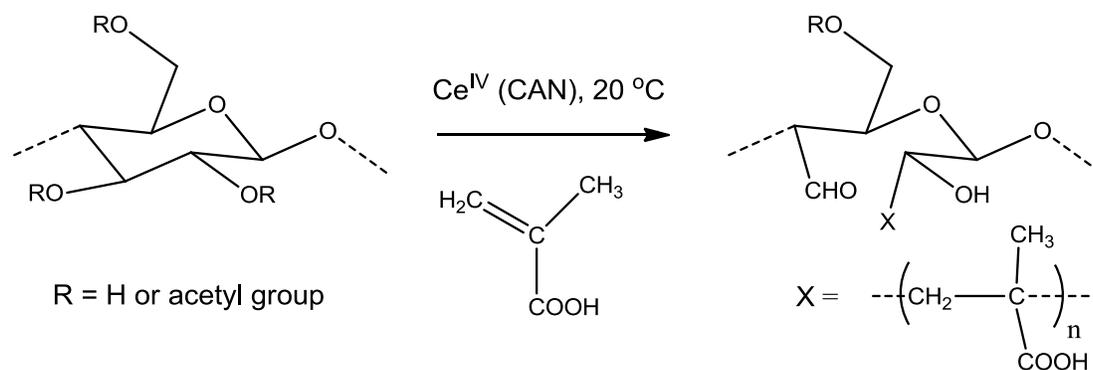
Figure 5.   The methacrylic acid grafting to cellulose acetate using CAN as initiator.

6.3   Characterization of membranes

The zeta potential of the membrane surfaces was measured from the electrokinetic potential which was defined with SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria). The measurements were made at pH 3-7 at room temperature using 1 mM KCl as electrolyte and 0.05 M KOH and 0.05 M HCl for pH adjustment. The samples were wet. The measurement was done in a surface direction in an adjustable gap cell between two same sizes samples. The gap height was controlled to about 100 μm at the beginning of the measurements. First the acidic pH values were adjusted using HCl. After that the membrane samples were rinsed with pure water without detaching them from the analyzer and then the basic pH values was adjusted using KOH.

The contact angles of the membranes were determined with Attension Theta optical tensiometer (Biolin Scientific AB, Sweden) with sessile drop method with deionized water. The samples were dried in a desiccator before measurements. Measurements were made at constant climate room where temperature was 23 ± 1 °C and relative humidity (RH) 50 ± 2 %. Membranes were attached to a glass plate with double-sided tape. The droplet size was 3 μl and dispenser was automatic. The angle of both sides of the droplets was determined for six droplets per membrane and the mean value was calculated.

The retentions of oil were calculated with equation (1) by determining the concentrations   in   the   feed   and   permeate   samples   with   Jasco   V-670

Spectrophotometer at a wavelength of 228 nm. The absorbances at wavelength between 180 and 1 000 nm were determined to permeate and feed sample. 228 nm was clear peak for both permeate and feed samples so that wavelength was used at measurement.

Pure water permeabilities before and after oil-water emulsion filtration were determined with equation (3) from the slope of the J(p)-curve. Fluxes were calculated with equation (2).

Pressure-normalized fluxes to oil-water emulsion filtration were calculated with equation (3). ΔJ was the mean value of the flux during filtration and Δp was the pressure used in filtration.

Membrane fouling was determined with equations (4) and (5). FRR-values were determined at three different pressures and DR-values at one pressure.

6.4 Filtrations

Filtrations were made with the cross-flow filtration system represented in Figure 6.
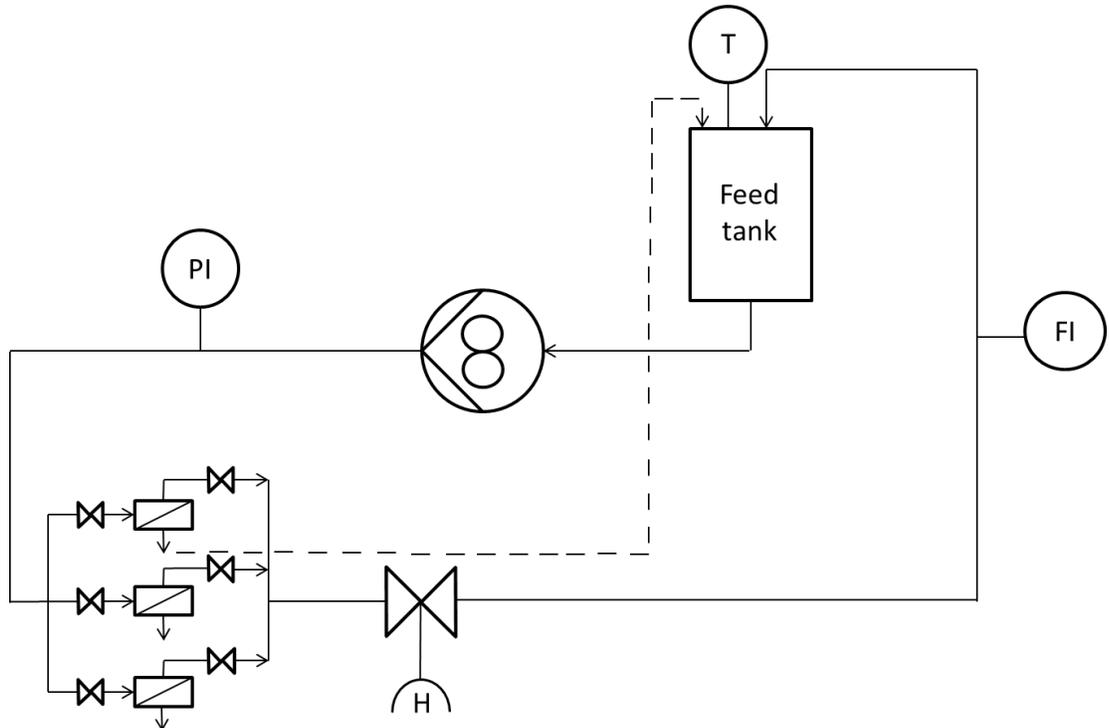
Figure 6.   The cross-flow filtration system.

The system has three membrane cells in parallel, but only one cell was used in synthetic oil-water emulsion filtrations. The membrane filtration area was 0.00104 m^2 and the cross-flow rate (CFR) was so high that rotameter was at the maximum at all measurements. Then CFR was 1.4 m/s and Reynolds number 2900. Filtrations were made at room temperature. Before pure water and oil-water emulsion filtrations the membrane was pressurized for 30 minutes at 4 bars to avoid membrane compaction during filtrations. After that pure water fluxes at 1, 2 and 3 bars were measured. Then the filtration system was rinsed with 0.5 L of oil-water emulsion and then the feed tank was filled with 1 L of oil-water emulsion. Oil-water emulsion was filtered for 4 hours if possible and permeate was collected all the time. The permeate flux was measured at regular intervals during the filtration. After oil-water emulsion filtration the system was rinsed with pure water for 20 minutes and then the pure water flux was measured again like before oil-water emulsion filtration. With 0.3 % and 0.5 %

PAA membranes the synthetic oil-water emulsion filtration time was only few minutes, but pure water flux and cleaning was made same way as with all the other membranes.

The real oil-water emulsion was first filtrated by using one cell. Then it was used three cells which all had different membrane. The filtrations were made same way as synthetic oil-water emulsion filtrations.

6.5   pH and conductivity measurement

The pH and conductivity of the feed solutions and at some cases also of permeate was determined. pH was measured with Ω Metrohm 744 pH Meter and conductivity with Knick Konduktometer 703. Measurements were made at room temperature.

7   Results and discussion

7.1   Permeabilities, fouling and retention

Pure water permeabilities before synthetic oil-water emulsion filtration and after synthetic oil-water emulsion filtration and cleaning are shown in Figures 7 and 8. The result tables of the pure water flux measurements before and after synthetic oil-water emulsion filtration and cleaning can be found in Appendix I.

Figure 7.   Pure water permeabilities before and after synthetic oil-water emulsion filtration (T = 21 ± 1 °C, p = 1-3 bar, FR = 1.4 m/s, Re = 2900).

Figure 8.   Pure water permeabilities before and after synthetic oil-water emulsion filtration (T = 21 ± 1 °C, p = 1-3 bar, FR = 1.4 m/s, Re = 2900).

Synthetic oil-water emulsion pressure-normalized fluxes are shown in Figures 9 and 10. In Appendix II result tables of synthetic oil-water emulsion fluxes can be found.
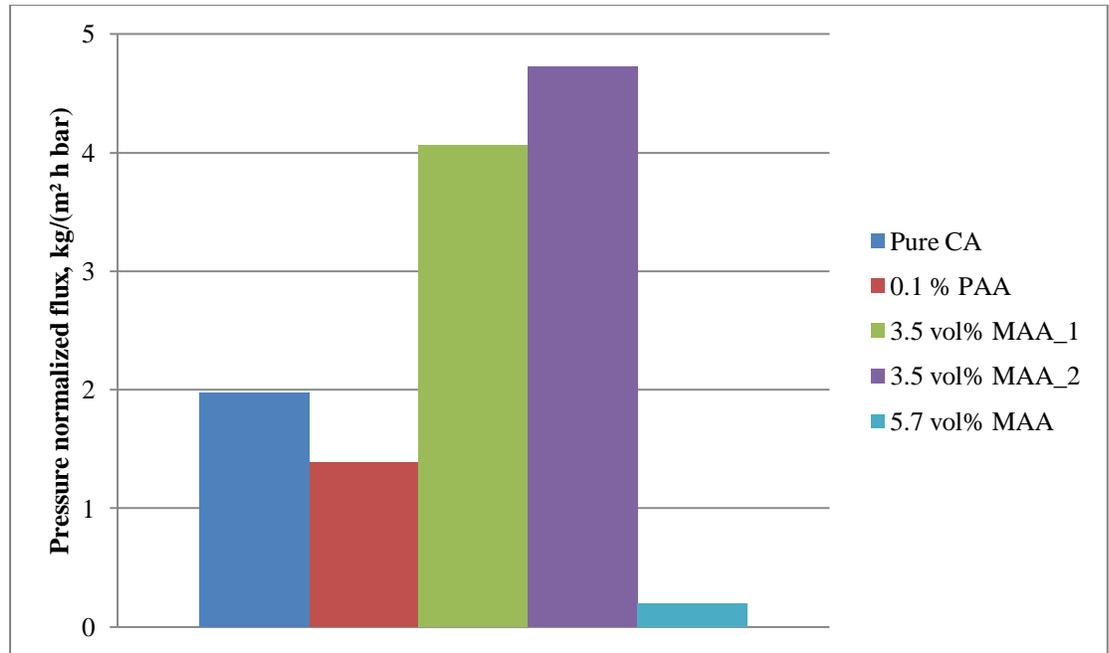
Figure 9. Synthetic oil-water emulsion pressure-normalized fluxes ($T = 23 \pm 2\ °C$, p = 3 bar, oil concentration in the feed 3 wt%, FR = 1.4 m/s, Re = 2900).
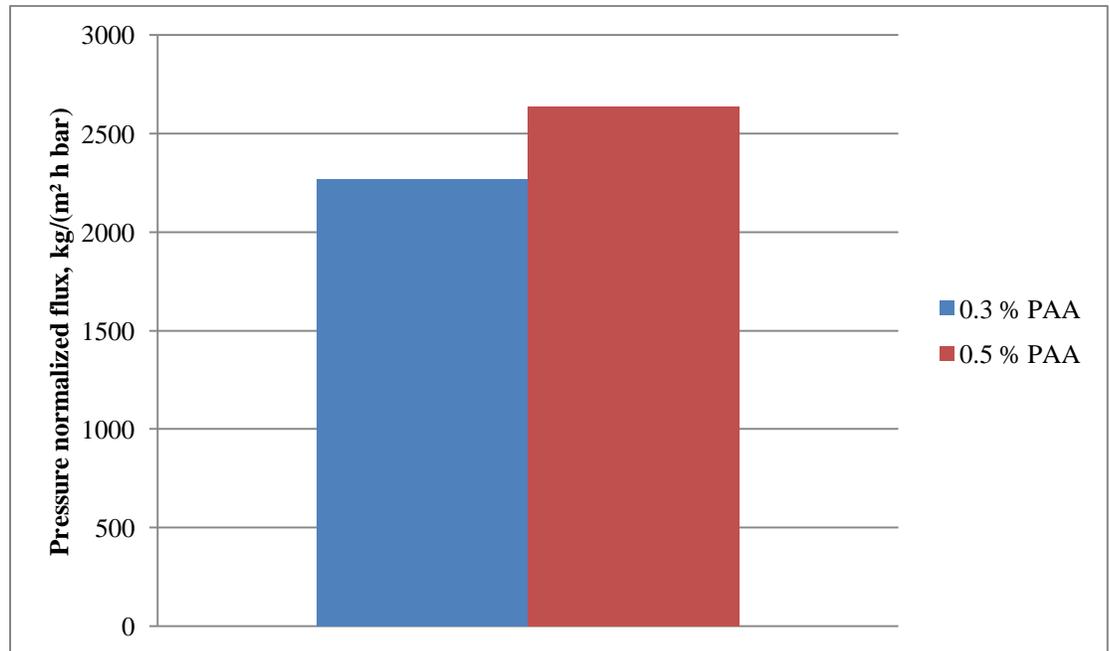
Figure 10. Synthetic oil-water emulsion pressure-normalized fluxes ($T = 20\ °C$, p = 3 bar, oil concentration in the feed 3 wt%, FR = 1.4 m/s, Re = 2900).

Figures 7 and 9 show that pure water permeabilities and synthetic oil-water emulsion pressure-normalized fluxes are low for pure CA, 0.1 % PAA, 3.5 vol% MAA and

5.7 vol% MAA membranes. The biggest flux of those membranes has the surface modified 3.5 vol% MAA membrane. The small amount of PAA (0.1 %) doesn't affect much to permeability. 5.7 vol% MAA membrane has a much smaller permeability than 3.5 vol% MAA and pure CA membrane so 5.7 vol% MAA is clearly too big amount in surface modification. Two 3.5 vol% MAA membranes were measured because it had the best results and was compared that the results was repeatability.

0.3 % PAA and 0.5 % PAA membranes had very big permeabilities and pressure-normalized fluxes as can be seen from Figures 8 and 10. Membrane non-uniformity could be observed already right after casting and coagulation. It may be due to incomplete dissolving of CA and PAA in DMF.

Flux recovery ratio (FRR)- and flux decay ratio (DR)-values and retention of different membranes of synthetic oil-water emulsion filtration are represented in Table IV.

Table IV.   FRR- and DR-values and retentions to different membranes of synthetic oil-water emulsion filtration.

	FRR, %			DR, %	
Membrane	1 bar	2 bar	3 bar	3 bar	Retention, %
Pure CA	70.0	70.8	100	22.6	89.9
0.1 % PAA	41.2	32.3	58.5	57.8	94.9
0.3 % PAA	79.4	79.4	81.9	15.5	-11.3
0.5 % PAA	37.6	43.7	50.0	30.4	-34.4
3.5 vol% MAA_1	100	81.6	92.7	7.71	89.5
3.5 vol% MAA_2	70.8	84.4	100	-1.69	90.0
5.7 vol% MAA	65.0	73.0	74.5	55.4	97.8

From Table IV it can be seen that 3.5 vol% MAA membranes have the biggest FRR- and lowest DR-values which means they have the lowest fouling. The FRR-values for pure CA membrane are high but DR-value is not as good as 3.5 vol% MAA membrane. 5.7 vol% MAA membrane FRR- and DR-values are not very good but it has the best retention. 0.1 % PAA membrane has good retention but fouling parameters are poor. So it is not good membrane for oil-water emulsion filtration.

0.3 % and 0.5 % PAA membranes have no retention. 0.3 % PAA membrane has rather good FRR- and DR-values but oil-water emulsion filtration time was only few minutes which can explain those results.

Pure CA and 3.5 vol% MAA membranes have quite similar retentions but because of lower fouling and higher permeability of 3.5 vol% MAA membranes it is better choice for oil-water emulsion filtration. Chen *et al.* (2009b) had also that kind of results that pure CA membrane had smaller flux than surface modified membrane and FRR- and DR-values and retention were good. The pure water fluxes with PAN grafted membranes were over 200 and 300 L/(m^2 h) (T=25 °C, p=1 bar, pure CA membrane 3.4 L/(m^2 h)) and other values were good so the modified membrane was much better [Chen *et al.* 2009b]. At this study the difference in permeabilities between pure CA membrane and surface modified membrane was not so high but the results are promising that it can be developed the membrane which has high permeabilities, low fouling and high retention.

Pure water permeabilities before real oil-water emulsion filtration and after real oil-water emulsion filtration and cleaning are shown in Figure 11. First was used only one membrane and then for a comparison of a self-made and commercial membrane it was used one commercial membrane and two self-made membranes in real oil-water emulsion filtration and all three parallel cells were in use. Appendix III represents the tables of pure water fluxes before and after real oil-water emulsion filtration and cleaning.
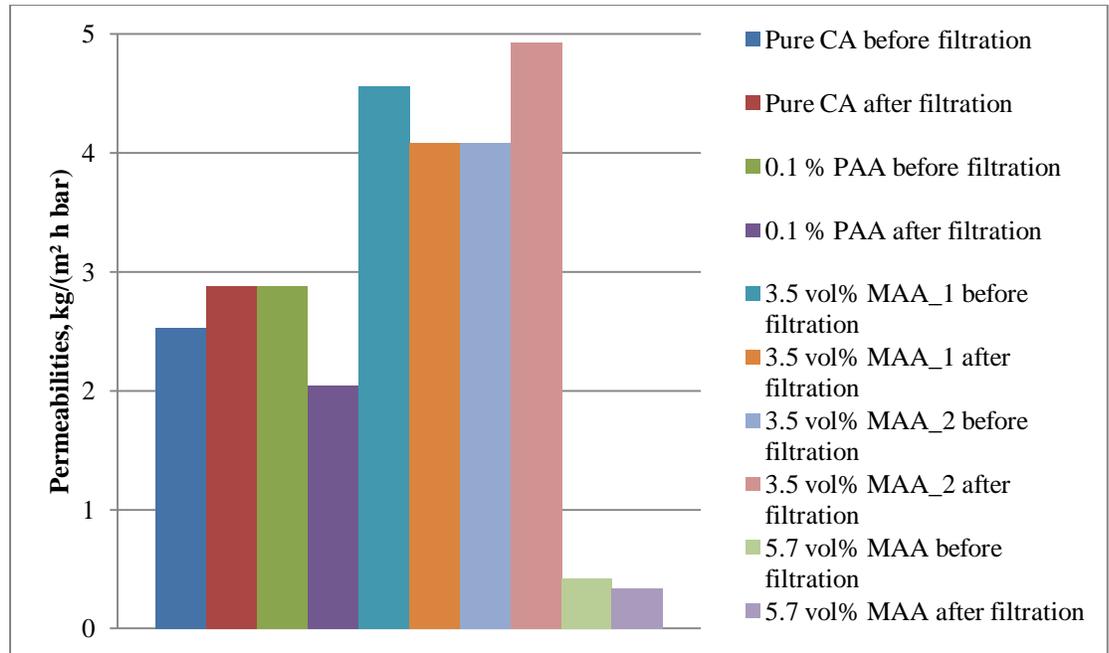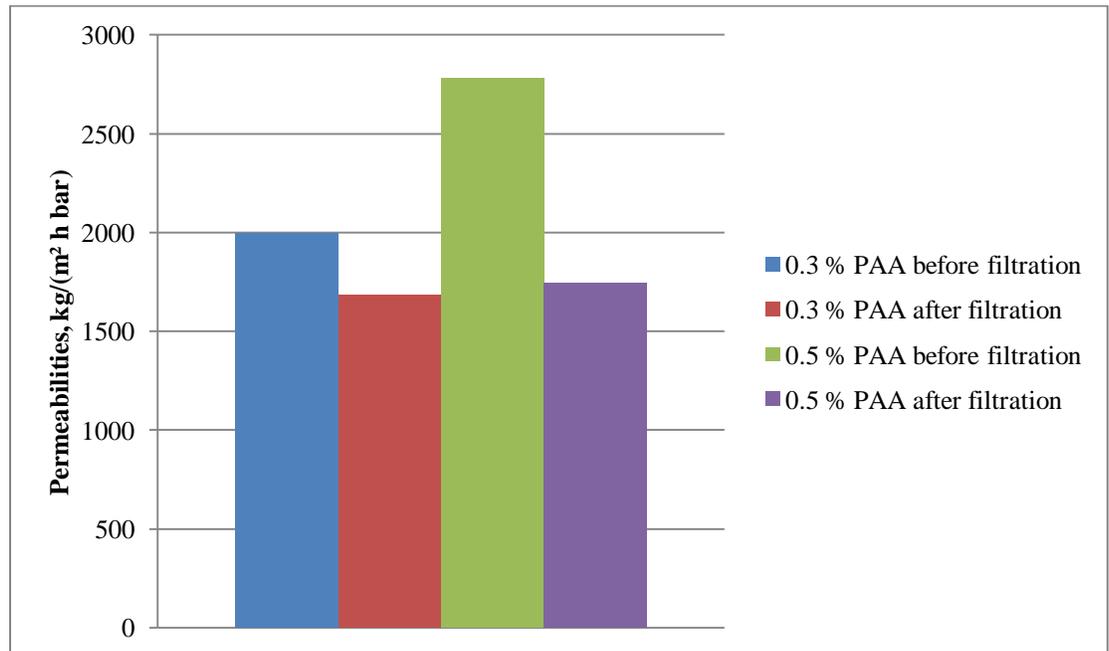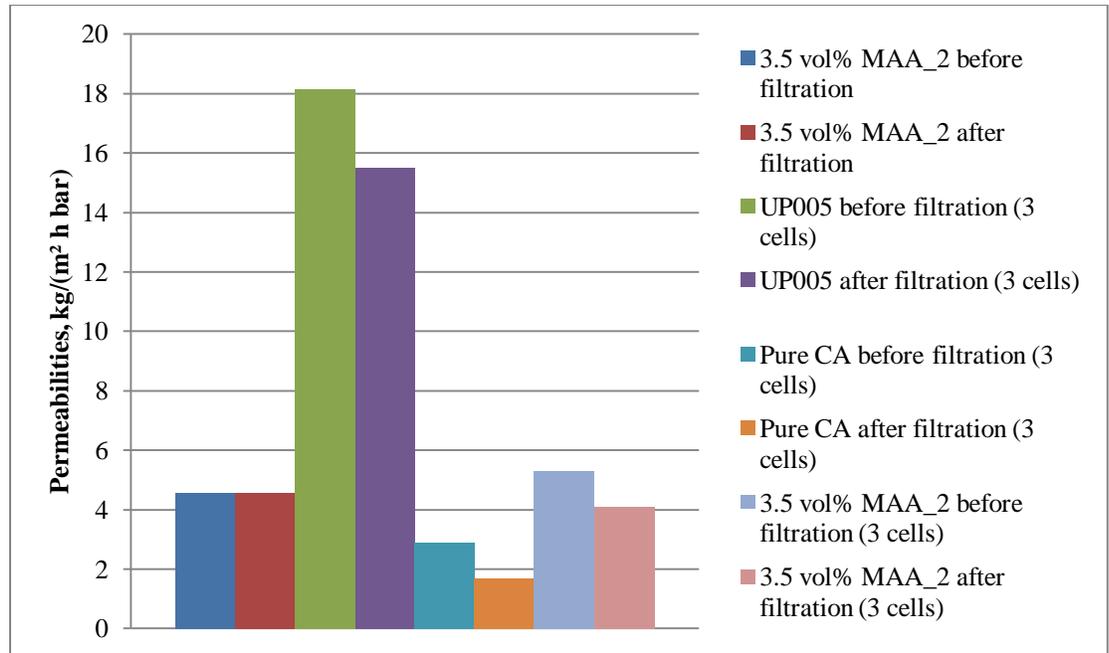
Figure 11.   Pure water permeabilities before and after real oil-water emulsion filtration (T = 22 ± 1 °C, p = 1-3 bar, one cell: FR = 1.4 m/s, Re = 2900, 3 cells: FR = 0.45 m/s, Re = 970).

Real oil-water emulsion pressure-normalized fluxes are shown in Figure 12. The tables of the real oil-water emulsion filtration measurements can be seen in Appendix IV.
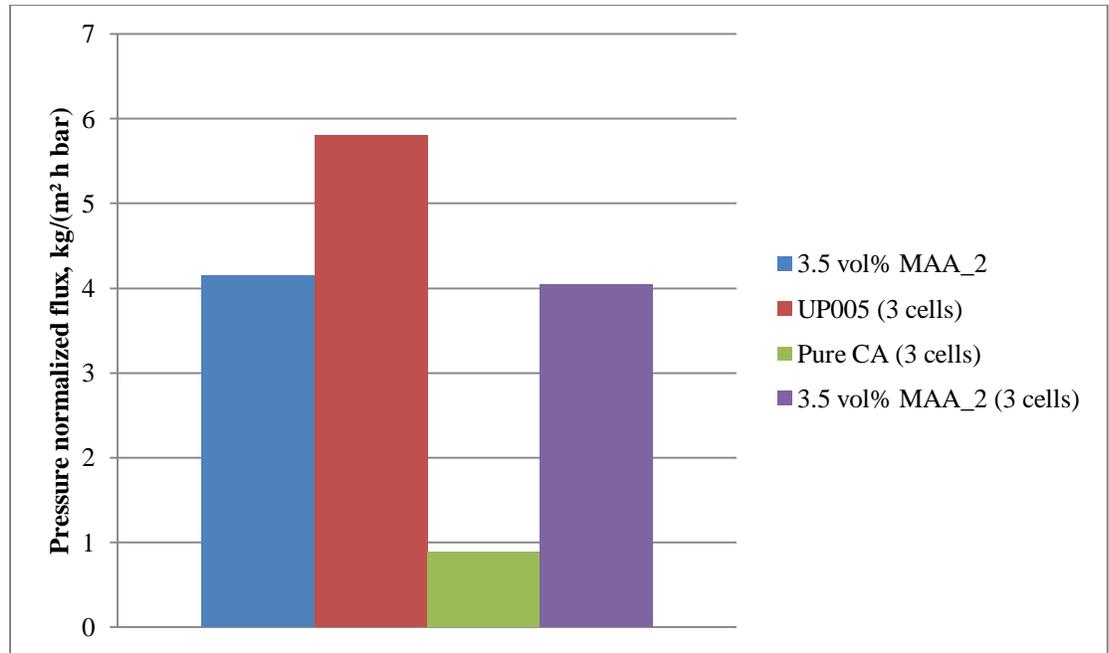
Figure 12.   Real oil-water emulsion pressure-normalized fluxes (T = 24 ± 2 °C, p = 3 bar, one cell: FR = 1.4 m/s, Re = 2900, 3 cells: FR = 0.45 m/s, Re = 970).

From the Figure 11 it can be seen that the UP005 membrane has much higher pure water permeability than pure CA and 3.5 vol% MAA_2 membranes. Also the real oil-water emulsion pressure-normalized flux is higher of the UP005 membrane (Figure 12) but the difference is not as high as in pure water fluxes. In real oil-water emulsion filtration can also be seen that 3.5 vol% MAA membrane has higher permeabilities and pressure-normalized fluxes than pure CA membrane.

Table V represents FRR- and DR-values of different membranes in real oil-water emulsion filtration.

Table V.   FRR-and DR-values to different membranes of real oil-water emulsion.

	FRR, %			DR, %
Membrane	1 bar	2 bar	3 bar	3 bar
3.5 vol% MAA_2	100	89.5	100	5.74
UP005 (3 cells)	58.5	72.7	76.0	70.1
Pure CA (3 cells)	143	81.0	77.4	64.1
3.5 vol% MAA_2 (3 cells)	124	91.1	90.2	17.3

Table V shows that DR-values are very high to UP005 and pure CA membranes but FRR-values are rather good for pure CA membrane but low for UP005 membrane which means that pure CA membrane can be cleaned better than UP005 membrane. When three cells were used, the filtration conditions were different than when only one cell was used. Flow rate in cell is smaller and it can cause the higher fouling. That can be seen from Table V from 3.5 vol% MAA_2 DR-values. DR-value is higher when three cells were used. The difference in FRR-values is not as big, so the membrane can be still cleaned. FRR- and DR-values show, that self-made membranes have better properties than commercial membrane.

Figure 13 represents the difference of feed solution and permeate in real oil-water emulsion filtration with 3.5 vol% MAA_2 membrane.

Figure 13.   Real oil-water emulsion filtration with 3.5 vol% MAA_2 membrane. A is feed solution, B is permeate for first two hour filtration and C is permeate for the last two hour filtration. Filtration conditions: T = 24 ± 2 °C, p = 3 bar, FR = 1.4 m/s, Re = 2900.

Figure 13 shows that permeate are much brighter than feed solution in real oil-water emulsion filtration with 3.5 vol% MAA_2 membrane. The membrane cannot retain the color from the solution but it can be seen that permeate is cleaner than feed

solution. It seems that permeate is oil free so this filtration could be used to concentrate the oil to retentate. Thus it can be reduced the volume of oil solution which needs treatment.

Figure 14 indicates the difference of feed solution and permeates in real oil-water emulsion filtration when three different membranes are used.
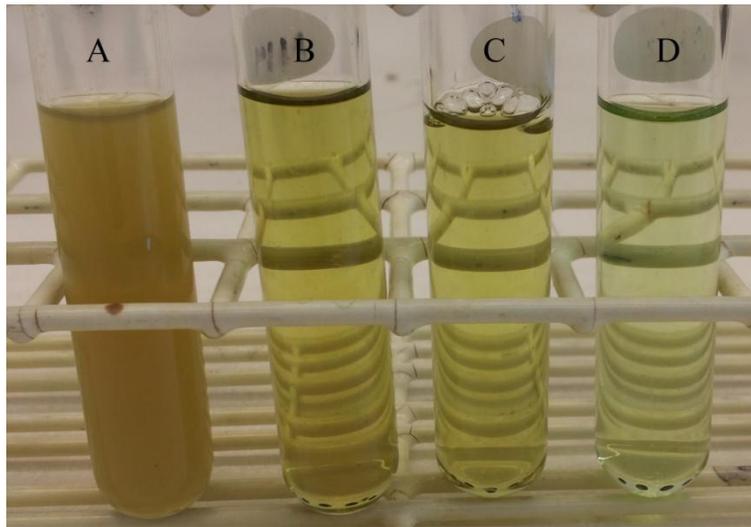
Figure 14.   Real oil-water emulsion filtration with three different membranes. A is feed solution, B is permeate of 3.5 vol% MAA_2 membrane, C is permeate of pure CA membrane and D is permeate of UP005 membrane. Filtration conditions: T = 24 ± 2 °C, p = 3 bar, FR = 0.45 m/s, Re = 970).

Pure CA and 3.5 vol% MAA_2 membrane has quite same color permeates but UP005 membrane permeate is brighter and the color is lighter as can be seen from Figure 14. From that it can be assumed, that UP005 membrane retains some compounds better than two other membranes and permeate is cleaner. That can be due the membrane fouling which causes pore blocking. After filtration and cleaning two self-made membranes seemed as cleaned as before filtration. UP005 membrane was white before filtration but after filtration and cleaning the filtration area was brown.

7.2   pH and conductivity

pHs and conductivities of the feed samples are represented in Table VI and Table VII.

Table VI.   pHs and conductivities of the feed of synthetic oil-water emulsion in filtrations with different membranes.

Membrane	pH	Temperature, °C	Conductivity, µS/cm	Temperature, °C
Pure CA	10.16	21.2	753.9	21.9
0.1 % PAA	10.10	21.2	770.5	22.3
0.3 % PAA	9.93	21.0	741.4	21.7
0.5 % PAA	10.14	21.3	768.1	21.3
3.5 vol% MAA_1	9.94	21.2	756.5	21.6
3.5 vol% MAA_2	9.97	21.1	722.8	21.2
5.7 vol% MAA	9.91	21.1	749.2	21.6

Table VII.   pH and conductivity of the feed of real oil-water emulsion with 3.5 vol% MAA_2 membrane filtration.

Membrane	pH	Temperature, °C	Conductivity, mS/cm	Temperature, °C
3.5 vol% MAA_2	9.10	20.8	4.112	21.1

Table VI shows that synthetic oil-water emulsion is basic and its conductivity is much higher than pure water conductivity (under 1 µS/cm) in room temperature. Real oil-water emulsion is also basic (Table VII). The conductivity of real oil-water emulsion is over five times higher than synthetic oil-water emulsion. The basic pH in synthetic oil-water emulsion can occur due to surfactant SDS. There is also some surfactant in real oil-water emulsion but it is not known so it cannot be said that pH depends on that. Real oil-water emulsion may contain some amines for corrosion inhibitor and that can affect to conductivity. Because the real oil-water emulsion composition is not known the difference in conductivities between synthetic and real oil-water emulsions cannot be explained.

7.3　Zeta potential

The zeta potentials of the membranes are represented in Figure 15.
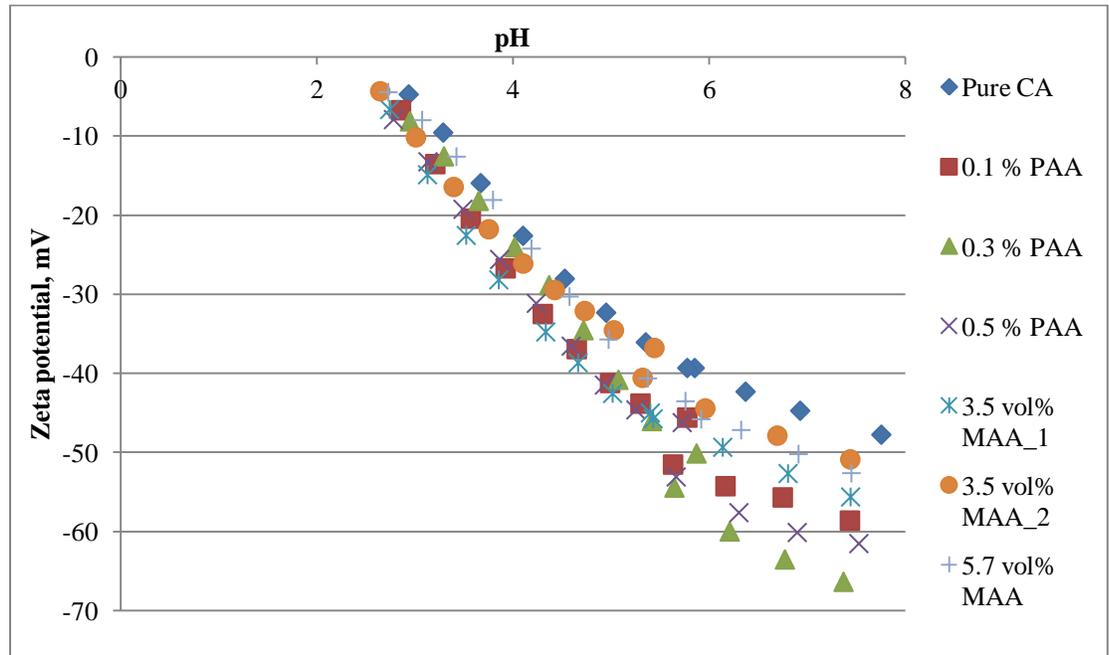
Figure 15.　　The zeta potentials of membranes in surface directions in room temperature.

Figure 15 shows that the zeta potentials of all membranes are negative in pH range 3-8. The differences in zeta potentials are bigger in neutral pH than in acidic pH. It can be seen that pure CA membrane has the least negative zeta potential at whole pH range and the membranes which have PAA have the most negative zeta potentials in pH 7. Figure 15 shows that any kind of modification makes CA membranes more negative which was aim of this study. The filtrations were made about at pH 10 but the zeta potential was able to measure only to pH 8. The zeta potential differences at pH 10 might be even bigger between pure CA and modified membranes. That can explain the better FRR- and DR-values of modified membranes compared to pure CA membrane. Elimelech *et al.* (1994) measured zeta potential to CA membrane using 1 mM NaCl as electrolyte at pH range of 3-11. The zeta potential was negative at all pH range but it wasn't as negative as in this study. At pH 6 the zeta potential was about -20 mV so it was twice smaller than at this study. [Elimelech *et al.* 1994] That

can be explained with different pretreatment methods of sample. Also the membrane was different even though it was prepared from same polymer.

7.4   Contact angle

The mean contact angles of membranes are shown in Figure 16. The contact angles for all six droplets are shown in Appendix V.
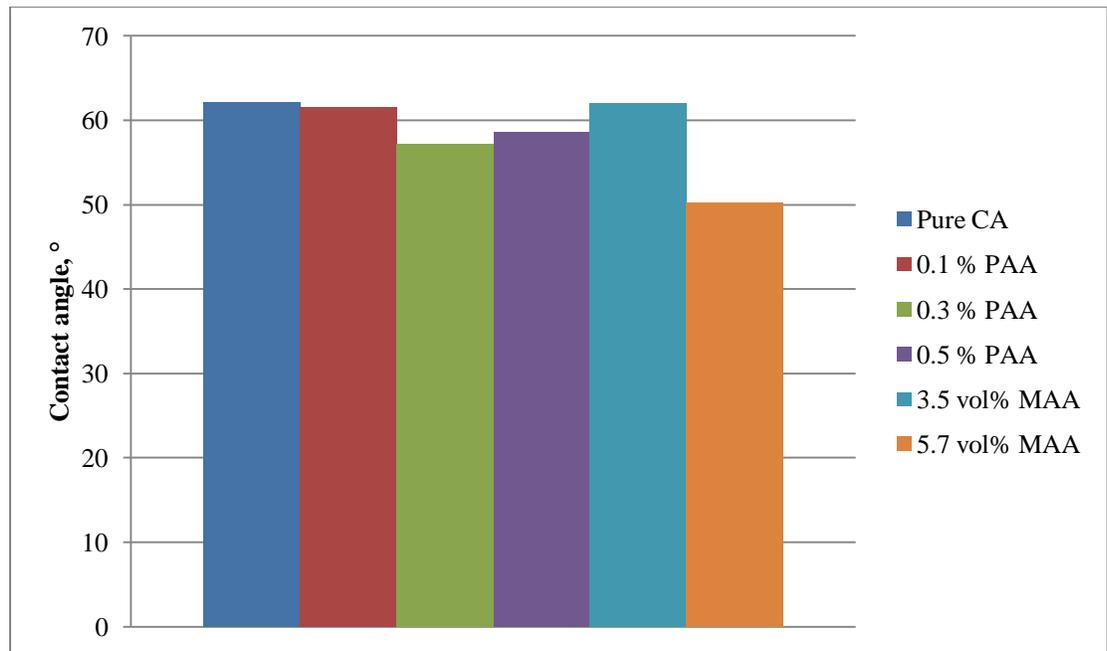
Figure 16.   Deionized water contact angles of membranes with sessile drop method (T = 23 ± 1 °C, RH = 50 ± 2 %).

Figure 16 shows that all membranes are hydrophilic because their contact angles are under 90°. The most hydrophilic membrane is 5.7 vol% MAA. Its contact angle is about 50°. The contact angles of membranes which have PAA are a little more hydrophilic than pure CA membrane. 3.5 vol% MAA membrane contact angle is almost same as pure CA membrane even though the 3.5 vol% MAA membrane was much better at filtrations than any other membrane. Chen *et al.* (2009b) measured to pure CA membrane the static water contact angle 54° so at their study the CA membrane was more hydrophilic than at this study. Also Jayalakshmi *et al.* (2014) measured more hydrophilic CA membrane than at this study. Their result was 43.7° so it was even more hydrophilic than at Chen *et al.* (2009b) study. Shibutani *et al.*

(2011) measured to CA membrane a slightly bigger water contact angle (66°) than at this study, so the contact angle can vary very much depending on different things. The differences may be due to different substitution rates of OH groups in cellulose acetate.

8   Conclusions

The aim of this study was to develop polymeric membrane with low fouling in oily wastewater filtration. Pure CA membrane had low fouling but also low pressure-normalized flux and pure water permeability in synthetic oil-water emulsion filtration. With free radical polymerization method it was successfully made a membrane which had higher pressure-normalized flux and pure water permeability and lower fouling than CA membrane.

Mixing the CA and PAA made the membrane properties worse than pure CA membrane. The fouling parameters were poor for the 0.1 % PAA and the 0.5 % PAA membranes in synthetic oil-water emulsion filtration. The 0.3 % PAA membrane had quite good FRR- and DR-values, but because the filtration time was only few minutes in the 0.3 % PAA and the 0.5 % PAA filtration, the results are not as reliable as they are for other membranes. The 0.1 % PAA membrane had good retention but low flux and permeability, so it is not usable for practical oil-water separation. The 0.3 % PAA and the 0.5 % PAA membranes showed no retention for oily waters oil. The polymers may not have been completely dissolved in DMF and there can be large pores in membranes and therefore the membrane cannot retain any compounds.

Membranes which contain PAA had lower contact angles than pure CA membrane or surface modified membranes. PAA makes membrane more negatively charged. The difference in contact angles was not big so the PAA membranes were not much more hydrophilic than pure CA membrane. The 5.7 vol% MAA membrane had distinctly lowest contact angle, so it can be assumed that higher amount of MAA makes membrane more hydrophilic than smaller amount of MAA because the 3.5 vol% MAA membrane contact angle was almost same as pure CA membrane.

The 3.5 vol% MAA membrane had the best properties in synthetic oil-water emulsion filtration. The 3.5 vol% MAA, pure CA and commercial UP005 membranes were tested also with real oil-water emulsion. The UP005 membrane had the best flux and permeability but strongest fouling ability. The bigger flux contributes the fouling so that's why UP005 has the strongest fouling ability. Pure CA membrane and the 3.5 vol% MAA membrane both had high FRR-values but pure CA membrane had high DR-value and lower flux and permeability. So the 3.5 vol% MAA membrane was the best membrane at this study also to real oil-water emulsion filtration.

At this study the best results were obtained with surface modified membrane. The amount of MAA was deciding factor to membrane properties. It was only tried two amounts of MAA and the smaller amount was better. Although the retention of 5.7 vol% MAA membrane was very high it was not good membrane for this purpose because of very low flux and high fouling. The pure CA membrane had good antifouling properties but it has lower flux, so the 3.5 vol% MAA membrane was the best membrane in oil-water emulsion separation. In the future it could be tested different amounts of MAA in surface modification and in that way prepare even better membrane to oil-water emulsion separation. Different concentrations of CA in polymer solution could also be tested.

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APPENDIXES

APPENDIX I   Pure water flux measurements before and after synthetic oil-water emulsion filtration and cleaning

APPENDIX II   Synthetic oil-water emulsion flux measurements

APPENDIX III   Pure water flux measurements before and after real oil-water emulsion filtration

APPENDIX IV   Real oil-water emulsion flux measurements

APPENDIX V   Contact angles for six droplets

PURE WATER FLUX MEASUREMENTS BEFORE AND AFTER SYNTHETIC OIL-WATER EMULSION FILTRATION AND CLEANING

Pure CA before synthetic oil-water emulsion filtration

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, (kg/m² h)	Pressure, bar	Temperature, °C
1-4	0.1	3.0	0.03	1.9	1	21
5-9	0.2	4.0	0.05	2.9	1	21
average		3.5	0.04	2.4	1	
1-4	0.3	3.0	0.1	5.8	2	21
5-9	0.4	4.0	0.1	5.8	2	21
average		3.5	0.1	5.8	2	
1-4	0.4	3.0	0.1	7.7	3	22
5-9	0.5	4.0	0.1	7.2	3	22
average		3.5	0.1	7.5	3	

Pure CA after synthetic oil-water emulsion filtration and cleaning

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-4	0.1	3.0	0.03	1.9	1	20
5-9	0.1	4.0	0.03	1.4	1	21
average		3.5	0.03	1.7	1	
1-4	0.2	3.0	0.07	3.8	2	21
5-9	0.3	4.0	0.08	4.3	2	21
average		3.5	0.07	4.1	2	
1-4	0.4	3.0	0.1	7.7	3	22
5-9	0.5	4.0	0.1	7.2	3	22
average		3.5	0.1	7.5	3	

0.1 % PAA before synthetic oil-water emulsion filtration

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-4	0.2	3.0	0.07	3.8	1	21
5-9	0.3	4.0	0.08	4.3	1	21
average		3.5	0.07	4.1	1	
1-4	0.4	3.0	0.1	7.7	2	21
5-9	0.5	4.0	0.1	7.2	2	21
average		3.5	0.1	7.5	2	
1-4	0.5	3.0	0.2	9.6	3	22
5-9	0.7	4.0	0.2	10	3	22
average		3.5	0.2	9.9	3	

0.1 % PAA after synthetic oil-water emulsion filtration and cleaning

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-4	0.1	3.0	0.03	1.9	1	20
5-9	0.1	4.0	0.03	1.4	1	21
average		3.5	0.03	1.7	1	
1-4	0.1	3.0	0.03	1.9	2	21
5-9	0.2	4.0	0.05	2.9	2	21
average		3.5	0.04	2.4	2	
1-4	0.3	3.0	0.1	5.8	3	21
5-9	0.4	4.0	0.1	5.8	3	21
average		3.5	0.1	5.8	3	

0.3 % PAA before synthetic oil-water emulsion filtration

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-4	210	3.0	71	4100	1	20
5-9	280	4.0	70	4100	1	20
average		3.5	71	4100	1	
1-4	330	3.0	110	6300	2	20
5-9	440	4.0	110	6300	2	21
average		3.5	110	6300	2	
1-4	420	3.0	140	8100	3	21
5-9	560	4.0	140	8100	3	21
average		3.5	140	8100	3	

0.3 % PAA after synthetic oil-water emulsion filtration and cleaning

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-4	170	3.0	56	3200	1	20
5-9	230	4.0	56	3200	1	21
average		3.5	56	3200	1	
1-4	260	3.0	86	5000	2	21
5-9	350	4.0	87	5000	2	21
average		3.5	87	5000	2	
1-4	340	3.0	110	6600	3	21
5-9	460	4.0	120	6600	3	22
average		3.5	120	6600	3	

0.5 % PAA before synthetic oil-water emulsion filtration

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-4	300	3.0	100	5800	1	20
5-9	400	4.0	100	5800	1	20
average		3.5	100	5800	1	
1-4	470	3.0	160	9000	2	20
5-9	620	4.0	150	8900	2	20
average		3.5	160	8900	2	
1-4	590	3.0	200	11000	3	20
5-9	790	4.0	200	11000	3	20
average		3.5	200	11000	3	

0.5 % PAA after synthetic oil-water emulsion filtration and cleaning

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-4	110	3.0	38	2200	1	20
5-9	150	4.0	38	2200	1	21
average		3.5	38	2200	1	
1-4	200	3.0	68	3900	2	21
5-9	270	4.0	68	3900	2	21
average		3.5	68	3900	2	
1-4	290	3.0	98	5600	3	21
5-9	400	4.0	99	5700	3	22
average		3.5	98	5700	3	

3.5 vol% MAA_1 before synthetic oil-water emulsion filtration

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-4	0.2	3.0	0.07	3.8	1	21
5-9	0.3	4.0	0.08	4.3	1	21
average		3.5	0.07	4.1	1	
1-4	0.5	3.0	0.2	9.6	2	21
5-9	0.6	4.0	0.2	8.7	2	22
average		3.5	0.2	9.1	2	
1-4	0.7	3.0	0.2	13	3	22
5-9	0.9	4.0	0.2	13	3	22
average		3.5	0.2	13	3	

3.5 vol% MAA_1 after synthetic oil-water emulsion filtration and cleaning

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-4	0.2	3.0	0.07	3.8	1	20
5-9	0.3	4.0	0.08	4.3	1	20
average		3.5	0.07	4.1	1	
1-4	0.4	3.0	0.1	7.7	2	21
5-9	0.5	4.0	0.1	7.2	2	21
average		3.5	0.1	7.5	2	
1-4	0.6	3.0	0.2	12	3	21
5-9	0.9	4.0	0.2	13	3	21
average		3.5	0.2	12	3	

3.5 vol% MAA_2 before synthetic oil-water emulsion filtration

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-4	0.3	3.0	0.1	5.8	1	22
5-9	0.4	4.0	0.1	5.8	1	22
average		3.5	0.1	5.8	1	
1-4	0.6	3.0	0.2	12	2	22
5-9	0.7	4.0	0.2	10	2	22
average		3.5	0.2	11	2	
1-4	0.7	3.0	0.2	13	3	22
5-9	1.0	4.0	0.3	14	3	22
average		3.5	0.2	14	3	

3.5 vol% MAA_2 after synthetic oil water emulsion filtration and cleaning

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/m²h	Pressure, bar	Temperature, °C
1-4	0.2	3.0	0.1	3.8	1	21
5-9	0.3	4.0	0.1	4.3	1	21
average		3.5	0.1	4.1	1	
1-4	0.5	3.0	0.2	9.6	2	22
5-9	0.6	4.0	0.2	8.7	2	22
average		3.5	0.2	9.1	2	
1-4	0.7	3.0	0.2	13	3	22
5-9	1.0	4.0	0.3	14	3	22
average		3.5	0.2	14	3	

5.7 vol% MAA before synthetic oil-water emulsion filtration

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-4	0.02	3.0	0.01	0.38	1	21
5-9	0.04	4.0	0.01	0.58	1	21
average		3.5	0.01	0.48	1	
1-4	0.04	3.0	0.01	0.77	2	21
5-9	0.07	4.0	0.02	1.0	2	22
average		3.5	0.02	0.89	2	
1-4	0.07	3.0	0.02	1.3	3	22
5-9	0.09	4.0	0.02	1.3	3	22
average		3.5	0.02	1.3	3	

5.7 vol% MAA after synthetic oil-water emulsion filtration and cleaning

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-4	0.01	3.0	0.003	0.19	1	20
5-9	0.03	4.0	0.01	0.43	1	20
average		3.5	0.01	0.31	1	
1-4	0.03	3.0	0.01	0.58	2	21
5-9	0.05	4.0	0.01	0.72	2	21
average		3.5	0.01	0.65	2	
1-4	0.05	3.0	0.02	1.0	3	21
5-9	0.07	4.0	0.02	1.0	3	21
average		3.5	0.02	1.0	3	

SYNTHETIC OIL-WATER EMULSION FLUX MEASUREMENTS

Pure CA

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-5	0.4	4	0.1	5.8	3	21
6-10	0.4	4	0.1	5.8	3	21
55-59	0.5	4	0.1	7.2	3	24
60-65	0.5	5	0.1	5.8	3	24
110-120	1.0	10	0.1	5.8	3	24
125-130	0.5	5	0.1	5.8	3	25
165-170	0.5	5	0.1	5.8	3	25
175-185	1.1	10	0.1	6.3	3	25
210-215	0.5	5	0.1	5.8	3	25
220-225	0.5	5	0.1	5.8	3	25
230-234	0.4	4	0.1	5.8	3	25
235-240	0.5	5	0.1	5.8	3	25
average			0.1	5.9	3	

0.1 % PAA

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-5	0.4	4	0.1	5.8	3	21
6-10	0.3	4	0.1	4.3	3	21
55-59	0.3	4	0.1	4.3	3	23
60-65	0.4	5	0.1	4.6	3	24
110-114	0.2	4	0.1	2.9	3	25
115-120	0.3	5	0.1	3.5	3	25
165-170	0.4	5	0.1	4.6	3	25
175-185	0.7	10	0.1	4.0	3	25
210-215	0.3	5	0.1	3.5	3	25
220-225	0.4	5	0.1	4.6	3	25
230-234	0.3	4	0.1	4.3	3	25
235-240	0.3	5	0.1	3.5	3	25
average			0.1	4.2	3	

0.3 % PAA

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
0.5-2	180	1.5	120	6800	3	20

0.5 % PAA

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
0.5-1.5	140	1	140	7900	3	20

3.5 vol% MAA_1

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-5	0.9	4	0.2	13	3	21
6-10	0.9	4	0.2	13	3	21
55-59	0.8	4	0.2	12	3	24
60-65	1.1	5	0.2	13	3	24
112-120	1.7	8	0.2	12	3	24
121-125	0.8	4	0.2	12	3	24
172-180	1.7	8	0.2	12	3	24
181-185	0.8	4	0.2	12	3	25
230-234	0.8	4	0.2	12	3	25
235-240	1.1	5	0.2	13	3	25
average			0.2	12	3	

3.5 vol% MAA_2

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-10	2.2	9	0.2	14	3	21
55-65	2.5	10	0.3	14	3	24
115-120	1.2	5	0.2	14	3	25
121-125	1.0	4	0.3	14	3	25
175-185	2.5	10	0.3	14	3	25
230-240	2.4	10	0.2	14	3	25
average			0.2	14	3	

5.7 vol% MAA

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-10	0.1	9	0.01	0.64	3	21
55-65	0.1	10	0.01	0.58	3	24
115-125	0.1	10	0.01	0.58	3	25
175-185	0.1	10	0.01	0.58	3	25
230-240	0.1	10	0.01	0.58	3	25
average			0.01	0.59	3	

PURE WATER FLUX MEASUREMENTS BEFORE AND AFTER REAL OIL-WATER EMULSION FILTRATION AND CLEANING

3.5 vol% MAA_2 before real oil-water emulsion filtration

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-4	0.2	3.0	0.1	3.8	1	21
5-9	0.3	4.0	0.1	4.3	1	21
average		3.5	0.1	4.1	1	
1-4	0.5	3.0	0.2	9.6	2	21
5-9	0.6	4.0	0.2	8.7	2	21
average		3.5	0.2	9.1	2	
1-4	0.7	3.0	0.2	13	3	22
5-9	0.9	4.0	0.2	13	3	23
average		3.5	0.2	13	3	

3.5 vol% MAA_2 after real oil-water emulsion filtration and cleaning

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-4	0.2	3.0	0.1	3.8	1	21
5-9	0.3	4.0	0.1	4.3	1	21
average		3.5	0.1	4.1	1	
1-4	0.4	3.0	0.1	7.7	2	22
5-9	0.6	4.0	0.2	8.7	2	22
average		3.5	0.1	8.2	2	
1-4	0.7	3.0	0.2	13	3	23
5-9	0.9	4.0	0.2	13	3	23
average		3.5	0.2	13	3	

UP005 before real oil-water emulsion filtration (3 cells)

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-4	1.0	3.0	0.3	19	1	22
5-9	1.4	4.0	0.4	20	1	22
average		3.5	0.3	20	1	
1-4	1.9	3.0	0.6	37	2	22
5-9	2.6	4.0	0.7	38	2	22
average		3.5	0.6	37	2	
1-4	2.9	3.0	1.0	56	3	23
5-9	3.9	4.0	1.0	56	3	23
average		3.5	1.0	56	3	

UP005 after real oil-water emulsion filtration and cleaning (3 cells)

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-4	0.6	3.0	0.2	12	1	21
5-9	0.8	4.0	0.2	12	1	21
average		3.5	0.2	12	1	
1-4	1.3	3.0	0.4	25	2	21
5-9	2.0	4.0	0.5	29	2	21
average		3.5	0.5	27	2	
1-4	2.1	3.0	0.7	40	3	22
5-9	3.1	4.0	0.8	45	3	22
average		3.5	0.7	43	3	

Pure CA before real oil-water emulsion filtration (3 cells)

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-4	0.1	3.0	0.03	1.9	1	22
5-9	0.1	4.0	0.03	1.4	1	22
average		3.5	0.03	1.7	1	
1-4	0.3	3.0	0.1	5.8	2	22
5-9	0.3	4.0	0.1	4.3	2	22
average		3.5	0.1	5.0	2	
1-4	0.4	3.0	0.1	7.7	3	23
5-9	0.5	4.0	0.1	7.2	3	23
average		3.5	0.1	7.5	3	

Pure CA after real oil-water emulsion filtration and cleaning (3 cells)

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-4	0.1	3.0	0.03	1.9	1	21
5-9	0.2	4.0	0.1	2.9	1	21
average		3.5	0.04	2.4	1	
1-4	0.2	3.0	0.1	3.8	2	21
5-9	0.3	4.0	0.1	4.3	2	21
average		3.5	0.1	4.1	2	
1-4	0.3	3.0	0.1	5.8	3	22
5-9	0.4	4.0	0.1	5.8	3	22
average		3.5	0.1	5.8	3	

3.5 vol% MAA_2 before real oil-water emulsion filtration (3 cells)

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-4	0.2	3.0	0.1	3.8	1	22
5-9	0.3	4.0	0.1	4.3	1	22
average		3.5	0.1	4.1	1	
1-4	0.6	3.0	0.2	12	2	22
5-9	0.7	4.0	0.2	10	2	22
average		3.5	0.2	11	2	
1-4	0.7	3.0	0.2	13	3	23
5-9	1.1	4.0	0.3	16	3	23
average		3.5	0.3	15	3	

3.5 vol% MAA_2 after real oil-water emulsion filtration and cleaning (3 cells)

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-4	0.3	3.0	0.1	5.8	1	21
5-9	0.3	4.0	0.1	4.3	1	21
average		3.5	0.1	5.0	1	
1-4	0.5	3.0	0.2	9.6	2	21
5-9	0.7	4.0	0.2	10	2	21
average		3.5	0.2	9.9	2	
1-4	0.7	3.0	0.2	13	3	22
5-9	0.9	4.0	0.2	13	3	22
average		3.5	0.2	13	3	

SYNTHETIC OIL-WATER EMULSION FLUX MEASUREMENTS

3.5 vol% MAA_2

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-10	1.9	9	0.2	12	3	22
55-65	2.2	10	0.2	13	3	24
115-120	1.1	5	0.2	13	3	25
121-125	0.9	4	0.2	13	3	25
175-185	2.1	10	0.2	12	3	25
230-240	2.1	10	0.2	12	3	25
average			0.2	12	3	

UP005 (3 cells)

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-10	3.0	9	0.3	19	3	22
55-65	3.1	10	0.3	18	3	25
115-125	3.0	10	0.3	17	3	26
145-155	3.0	10	0.3	17	3	26
175-185	2.9	10	0.3	17	3	26
205-215	2.9	10	0.3	17	3	26
230-240	2.9	10	0.3	17	3	26
average			0.3	17	3	

Pure CA (3 cells)

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-10	0.4	9	0.04	2.6	3	22
55-65	0.4	10	0.04	2.3	3	25
115-125	0.5	10	0.1	2.9	3	26
145-155	0.6	10	0.1	3.5	3	26
175-185	0.5	10	0.1	2.9	3	26
205-215	0.4	10	0.04	2.3	3	26
230-240	0.4	10	0.04	2.3	3	26
average			0.05	2.7	3	

3.5 vol% MAA_2 (3 cells)

Sampling time, min	Weight, g	Time, min	Flow, g/min	Flux, kg/(m² h)	Pressure, bar	Temperature, °C
1-10	1.9	9	0.2	12	3	22
55-65	2.1	10	0.2	12	3	25
115-125	2.1	10	0.2	12	3	26
145-155	2.1	10	0.2	12	3	26
175-185	2.1	10	0.2	12	3	26
205-215	2.1	10	0.2	12	3	26
230-240	2.1	10	0.2	12	3	26
average			0.2	12	3	

CONTACT ANGLES FOR SIX DROPLETS

Membrane	Contact angle, °						Average, °
Pure CA	52.13	61.39	70.97	64.89	64.69	59.11	62.2
0.1 % PAA	58.19	63.70	70.05	61.52	57.52	58.58	61.6
0.3 % PAA	63.82	57.68	50.26	52.44	62.55	56.86	57.3
0.5 % PAA	64.33	57.08	53.74	58.69	64.40	53.53	58.6
3.5 vol% MAA	60.90	62.59	58.19	57.91	65.05	67.19	62.0
5.7 vol% MAA	49.46	48.56	47.65	52.27	51.76	52.20	50.3