

Lappeenranta – Lahti University of Technology LUT
School of Engineering Science
Master's Programme in Chemical and Process Engineering

Heini Issakainen

**ASSESSMENT AND IMPROVEMENT OF WASTEWATER SYSTEM IN PILOT
PLANT**

Master's thesis

Examiners: Professor Antti Häkkinen
D.Sc Teemu Kinnarinen

TIIVISTELMÄ

Lappeenrannan – Lahden teknillinen yliopisto LUT
LUT School of Engineering Science
Master's programme in Chemical and Process Engineering

Heini Issakainen

Pilot-tehtaan jätevesijärjestelmän tarkastelu ja kehittäminen

Diplomityö

2019

89 sivua, 55 kuvaa, 15 taulukkoa, 1 liite

Tarkastajat: Professori Antti Häkkinen
D.Sc Teemu Kinnarinen

Hakusanat: Jätevesi, Jäteveden käsittely, COD, öljy, muovi

Diplomityön tarkoitus oli tutkia parhaita ja tehokkaimpia suodatusmetodeja muoviyrityksen jätevesille. Erityisesti Pilot-tehtaan jätevedessä on havaittu saasteita. Suurimmat saasteiden aiheuttajat ovat olleet muovipartikkeleja, öljyä ja orgaanista materiaalia.

Kirjallisuusosassa käsiteltiin erilaisia tekniikoita jäteveden puhdistamiseksi. Muovipartikkelien ja muun kiinteän materiaalin erotukseen parhaita tekniikoita olivat hiekkasuodatin ja ilmastettu kellutusallas. Öljyn ja orgaanisen materiaalin erotukseen parhaat erotustekniikat olivat keraamiset membraanit tai aktivoituhiili adsorptiokolonne. Kirjallisuusosassa esiteltiin myös kolme mahdollista prosessivaihtoehtoa jätevesien suodatukseen.

Kokeellisessa osassa tarkoituksena oli puhdistaa jätevettä kaksivaiheisessa suodatuksessa. Ensimmäinen erotusosa oli vakuumsuodatin, jossa käytettiin Outotecin kolmea erilaista suodatuskangasta. Toisessa suodatusvaiheessa käytettiin hydrofiilisiä selluloosamembraaneja. Jätevesinäytteitä otettiin 11 päivältä maaliskuun ja toukokuun välisenä aikana.

Vakuumsuodatuksella erotettiin keskiarvallisesti 74 % kiintoaineista jätevedestä. Öljyä ja orgaanista materiaalia erotettiin keskiarvallisesti 32% ja 20%. Jätevedestä erotettiin kiintoaineet ja värin aiheuttavat molekyylit mutta silti suuret määrät orgaanista materiaalia ja öljyä jäivät jäteveteen. Johtopäätöksenä oli, että suuri osa orgaanisesta materiaalista on liunneena jäteveteen. Selluloosamembraani ei erottanut öljyä ja orgaanista materiaalia jätevedestä ja ei ole suositeltava tekniikkavaihtoehto Pilot-tehtaan jätevesijärjestelmään. Jatkossa keraamisia membraaneja tai aktiivihiiliadsorptiota tulisi kokeilla öljyn ja orgaanisen materiaalin erotuksessa.

ABSTRACT

Lappeenranta – Lahti University of Technology LUT
LUT School of Engineering Science
Master's Programme in Chemical and Process engineering

Heini Issakainen

Assessment and improvement of wastewater system in Pilot plant

Master's thesis

2019

89 pages, 55 figures, 15 tables, 1 appendix

Examiners: Professor Antti Häkkinen
D.Sc Teemu Kinnarinen

Keywords: wastewater, wastewater treatment, COD, oil, plastic

Aim of this master's thesis was to study most efficient separation methods for wastewater produced by plastic company. Especially, there has been contaminants in Pilot plant wastewater. The main contaminants in wastewater are known to be plastic, oil and organic matter.

In the literature part possible techniques for contaminant removal were studied. For solid and plastic separation best separation techniques were rapid sand filter and dissolved air flotation. For oil and organic matter best separation techniques were ceramic membranes or activated carbon adsorption. Three different process configurations were presented for wastewater purification.

In the experimental part the objective was to separate contaminants from wastewater as effectively as possibly in two step separation. First separation step was vacuum filtration where three different filtration cloths from Outotec were used. In second filtration step hydrophilic cellulosic membranes were used. Wastewater samples were taken during March – May over 11 days.

On average 74 % of solids were separated in vacuum filtration and oil and organic matter separation efficiencies were 32 and 20 % respectively. Even though color and solids were separated from wastewater, there was still high organic matter and oil amounts left in wastewater. In conclusion, most of the organic carbon is dissolved in the water. Cellulosic membrane filtration did not separate organic matter and oil and therefore it is not suggested as a technique for wastewater treatment in Pilot plant. In further studies ceramic membrane or activated carbon adsorption should be studied for oil and organic matter separation.

ACKNOWLEDGEMENTS

First, I would like to thank my examiners Antti Häkkinen and Teemu Kinnarinen for their help and guidance throughout this project. In addition, special thanks to the company and Pilot plant employees who have supported me and gave me this interesting subject in the first place.

I want to also thank Jouni and my family for supporting me through everything in my personal life. Last but not least, I would like to thank my kemistiperhe for the amazing years while studying. I could not have asked for better friends to share all the late hours and group works with. Thank you all!

Heini Issakainen

Porvoo 24.7.2019

Contents

1	Introduction.....	1
2	LITERATURE PART.....	2
3	Wastewater at Pilot plant	2
3.1	Minimizing contaminated wastewater	4
3.2	Contaminants.....	6
3.2.1	PP and PE.....	7
3.2.2	Organic matter and oil	9
3.2.3	Wastewater legislation.....	11
3.2.4	Results.....	12
3.3	Separation systems	13
3.3.1	Pilot plant.....	13
3.3.2	Finland	15
3.3.3	Austria.....	17
4	Wastewater treatment	18
5	Solid-liquid separation.....	21
5.1	Coagulation and flocculation	23
5.2	Fine screens and micro screens	25
5.3	Sedimentation and flotation	25
5.4	Filtration.....	28
5.4.1	Sand filter.....	29
5.4.2	Disc filter	31
5.5	Membranes	32
6	Oil and organic matter separation.....	36
6.1	Flotation	37
6.2	Membranes.....	40

6.3	Adsorption.....	43
7	Selection of the separation methods	45
8	EXPERIMENTAL PART.....	49
9	Materials and methods	49
9.1	Materials.....	49
9.2	Filtration.....	50
9.2.1	Vacuum filtration.....	51
9.2.2	Membrane filtration	52
9.3	Analysis.....	54
10	Equations	57
11	Results and discussion	58
11.1	Total suspended solids.....	59
11.2	Membrane filtration.....	61
11.3	Chemical oxygen demand	63
11.4	Oil amount	69
12	Error analysis	75
13	Conclusions.....	77
14	References.....	81

ABBREVIATIONS

Al_2O_3	Aluminum oxide
API	American petroleum institute
BAT	Best available technology
BAT-AEL	Best available technology-associated emission levels
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
CTAC	Cetyltrimethylammonium chloride
CWW BAT	Common wastewater best available technology
DAF	Dissolved-air flotation
GC	Gas chromatography
HDPE	High density polyethylene
$\text{K}_2\text{Cr}_2\text{O}_7$	Potassium dichromate
$\text{K}_2\text{S}_2\text{O}_8$	Potassium persulfate
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
MBR	Membrane bioreactor
MDPE	Medium polyethylene
MF	Microfiltration
$\text{Mn}_2(\text{SO}_4)_3$	Manganese(III)sulfate
MP	Microplastic
O_2	Oxygen
P&ID	Piping and instrumentation diagram
PAC	Polyaluminum chloride
PE	Polyethylene
PP	Polypropylene
TiCl_3	Titanium(III)chloride
TiCl_4	Titanium tetrachloride
TiO_2	Titanium dioxide
TSS	Total suspended solids
UF	Ultrafiltration

SYMBOLS

A	Filtration area, m ²
a	Mass of filter paper before filtration, mg
b	Mass of filter after wastewater filtration, mg
C_{c40}	Standard n-tetracontane (c40) amount, mg/l
$C40\ peak$	N-tetracontane (C40) peak area from gas chromatography, -
C_f	COD/oil amount after filtration, ppm
C_i	Initial COD/oil amount, ppm
C_{oil}	Oil amount, mg/l
J	Flux, l/m ² h
t	Filtration time, h
V	Filtered permeate volume, m ³
v	Wastewater sample amount, ml
TSS	Total suspended solids, mg/l
E	Filtration efficiency, %

1 Introduction

Plastic pollution in oceans and in other bodies of water is a growing concern. Plastics are ending up in oceans from overpopulated areas where there are tourists, shipping and other industrial activities. (Cocca et al., 2018) Plastic pollution is most efficiently stopped from the source as early as possible. In plastic producing company it is part of company targets to achieve goal zero in plastic emissions.

In the plastic company considered in this thesis, there are contaminants being washed away by rain or washing to the wastewater treatment. There are improvement opportunities in the wastewater treatment system, especially in the Pilot plant. To minimize the emissions from Pilot plant and plastic site the wastewater system was assessed and different techniques were studied.

Objective of the master's thesis was to study what are the most efficient separation methods for wastewater in Pilot plant. The main contaminants in wastewater are known to be suspended solids, oil and organic matter. In the literature part wastewater treatments in site are presented and the possible techniques for solids, oil and organic matter removal were studied.

In conclusion, for solid and plastic separation best separation techniques were rapid sand filter and dissolved air flotation. For oil and organic matter separation ceramic membranes or activated carbon adsorption are the best techniques. Three different process configurations were suggested. Two of the process configurations were for site wide wastewater system. One option was only for Pilot plant wastewater system.

In the experimental part the objective was to separate total suspended solids, organic matter and oil contaminants from wastewater as effectively as possibly. Two step separation was chosen for the experiments. First separation step was vacuum filtration where three different filter cloths from Outotec (ARTOT20, ARTOS11 and MAROS21) were used. In experimental study ceramic membranes were not available for use in small laboratory scale. Instead in second filtration step hydrophilic cellulosic membranes were used (RC70PP and UC100).

It was concluded that even though 74 % of solids were separated in vacuum filtration the organic carbon and oil amount did not decrease significantly. In one out of 11 days samples

organic matter was decreased below 500 ppm that was the selected limit in filtrations. Oil and organic matter separation efficiencies were 32 and 20 % on average. Initial wastewater had brown-yellow color in it caused by humic acids. Humic acids were filtered in separation steps making filtrate colorless. Even though color and solids were filtered there was still high organic matter and oil amounts. In conclusion, most of the organic carbon is dissolved in the water. Cellulosic membrane filtration was unable to separate organic matter and oil and therefore is not suggested as a result for wastewater treatment in Pilot plant.

2 LITERATURE PART

In the literature part the wastewater treatment in the plastic site and Pilot plant is explained in detail. The contaminants that are measured in plastic factories are presented in chapter 3. In the same chapter is also shown the legislations and limit values for contaminants that are applied to Finnish waters. In chapter 4 is presented basic principles of wastewater treatment. Solid separation techniques for plastics are presented in chapter 5. Oil and organic matter separation are shown in chapter 6. Chapter 7 is the conclusions from the literature part.

3 Wastewater at Pilot plant

In the Pilot plant plastics are made in two lines: polyethylene (PE) and polypropylene (PP) line. Plastic processing happens with polymerization of ethylene/propylene in the presence of catalyst. Catalyst stays in the polymer and is not removed from the product. Polymerization happens in multiple reactors to create bi- & tri modal plastic polymer which is transformed to plastic by adding multiple different additives. In the end of the process, polymer powder and additives are extruded to pellets. Plastic pellets are the final product of the process.

Pilot plant makes test runs based on laboratory scale research. In the Pilot plant the critical points of the process are often tested intentionally. This increases the shutdown frequency at the plant. During the shutdown of the process, equipment that has been plugged is often washed with high pressure. Opening the equipment and washing creates more exertion to the wastewater system. Even though the process is much smaller than the large scale plants, the washing times per year are much more frequent than in large scale. Capacity of Pilot plant is about 200 kg/h altogether and in large scale plants capacity is about 30 tons/hour.

Wastewater systems in Pilot plant are separated into two separate systems. There is more contaminated water system that treats the water coming from the polymerization area. In the polymerization area there are regularly openings of the process equipment and use of water in washing. Water from polymerization area goes to oil water well. The other system treats the rainwater. Water from pelletization goes to the rainwater system.

Water from pelletization used to go to oil water well. In the 1990s there was practical problem with this system. The well was too small and got full very quickly. Because of the small size, there was often flooding in pelletization area. To fix this problem pelletization water was lead to rain water well instead of oil water system. The handling of oil and catalyst, which are used in polymerization, is also done in the pelletization building. The handling area is equipped with an enclosed drain.

In Figure 1 the overall layout of the wastewater collection wells in the Pilot plant is shown. As seen in Figure 1 most of the waters in the process go to oil water treatment. In the figure is shown how the wells are placed in the process area, and dashed lines with arrows show how the wastewater transfers.

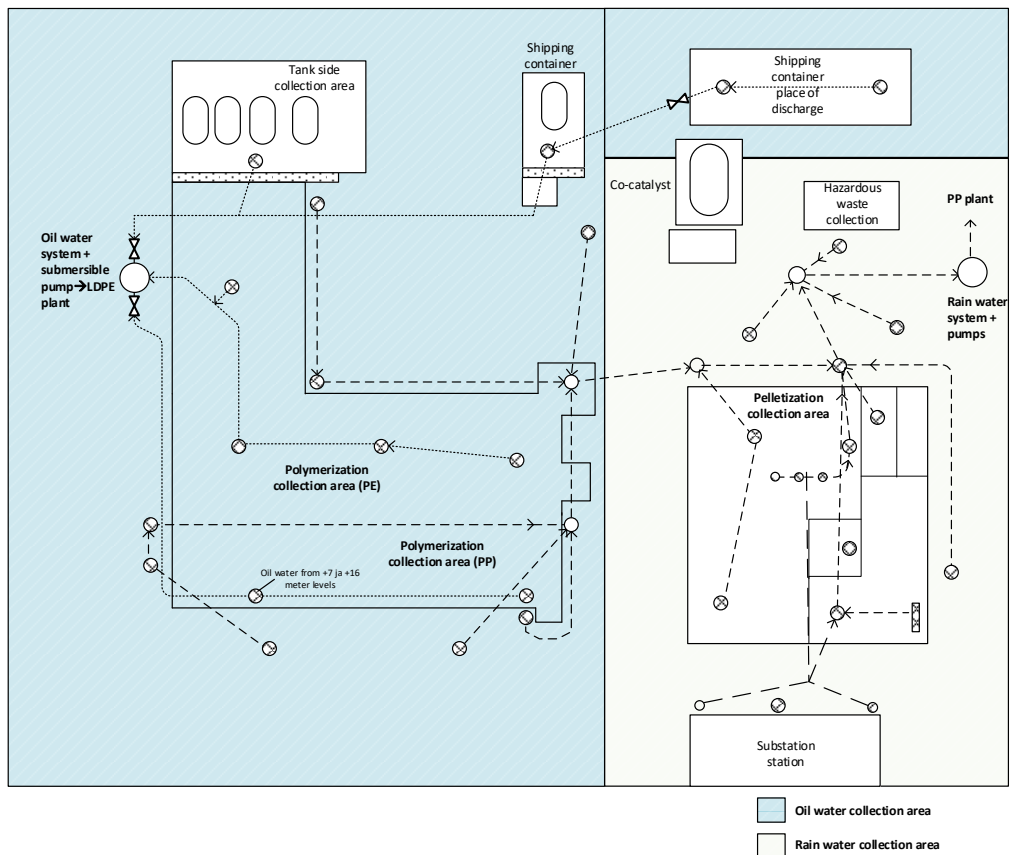


Figure 1 Wastewater collection well system in Pilot plant. Blue area shown is the oil water system and light green is rain water system.

3.1 Minimizing contaminated wastewater

IPIECA (2010) has reviewed the wastewater management used in petroleum refining. According to IPIECA (2010) best practices for minimizing contaminated wastewater treatment are to minimize process collection area, treatment of “first flush”, minimize solids in storm-water and cover process area. Oily water system is the contaminated water system in the plant. The rain water system in Pilot plant is assumed as non-contaminated wastewater.

IPIECA (2010) presents best practices for minimizing the amount of contaminated wastewater. Minimizing contaminated wastewater is beneficial because contaminated water needs more separation steps than non-contaminated water. By minimizing contaminated water amount, the water treatment equipment capacity is smaller. And by optimizing equipment size, the costs of wastewater system can be decreased.

Separation of two systems is usually done by curbing. Treatment with the “first flush” method means that when raining/washing happens the initial wastewater is more contaminated. This is because pollutants on pavement get washed away with first flush. In addition, solids (polymer & pellets) and oil stuck in sewer system detach with the first flush. After first flush, the rest of the wastewater does not need as much processing steps as the contaminated water. After the first flush, wastewater is directed to non-contaminated treatment. (IPIECA, 2010)

Minimizing solids like sand or grit in wastewater is important because according to IPIECA (2010) 0.5 kg of solids creates 4.5 kg of oil sludge when hydrocarbons are present. Oil sludge burdens the separation process. The source of solids are unpaved areas covered with gravel. Covering process area is done to minimize the amount of rainwater that comes into contact with pollutants. This is especially practical with pump stations, heat exchanges and separation drums. (IPIECA, 2010)

In Table 1 is shown how the IPIECA (2010) best practices are used in the plant now and how the methods could be improved at the plant.

Table 1 IPIECA (2010) best practices applied to oil water system in Pilot plant at the moment and development possibilities.

	Minimize process collection area	Treatment of first flush
At the moment	<ul style="list-style-type: none"> • Separation of oil water system and rain water system but pelletization water might go to rainwater system 	<ul style="list-style-type: none"> • Not applied at Pilot plant
Development	<ul style="list-style-type: none"> ➤ Pelletization water should be lead to oil water system ➤ Rain water would not need separation steps 	<ul style="list-style-type: none"> ➤ Very hard to apply in practical use at Pilot plant
	Minimize solids in stormwater	Cover process area
At the moment	<ul style="list-style-type: none"> • Process areas are made of concrete and there is little grit on the pavement • Grit, Sand and pellets are brushed regularly from the pavement • There are some areas in the sides of the process area that are not concrete. 	<ul style="list-style-type: none"> • Pelletization area is covered • Small part is covered in polymerization area • With rain/washing water all oil, polymer and pellets end up from polymerization to oil water system
Development	<ul style="list-style-type: none"> ➤ Concrete everywhere in the process area 	<ul style="list-style-type: none"> ➤ Rooftop to the whole polymerization area so that rainwater does not end up in the floors to wash away ➤ Does not help with washing water

For the non-contaminated wastewater there are two best practices according to IPIECA (2010): re-use and retention. Non-contaminated wastewater can be possibly re-used in petroleum processes for example as fire water and utility water. Retention of non-contaminated is done in for example pond to decide if the water can be discharged or should it be re-used.

3.2 Contaminants

In Pilot plant there are some contaminants that have been detected to end up in wastewater system. From the production there are PP (polypropylene) and PE (polyethylene) ending up in wastewater system in both pellet and powder form. There are several ways how the amounts of plastic to wastewater treatment are minimized at the moment. At the plant, pavement is cleaned regularly to maintain cleaning standards and to minimize the amounts of pellets and powder in wastewater. There are screens in each of the drains at the plant. The

screens capture pellets and some of the powder that can be brushed to recycling. The screens do not capture smaller powder particles and therefore they end up in wastewater treatment. In addition, there has been testing of “canvas” while washing happens at the plant. “Canvas” are placed on pavement to prevent the polymer powder from going to oil water system with washing water. There has been problems with the functionality of the “canvas”. When “canvas” is used during washing, there is flooding happening in the area and water does not seem to be permeating “canvas”.

There have been results of high COD and oil index in the wastewater. Signifying that from the process area there is organic matter and oils going to wastewater treatment. Oils and organic matter are supposed to be removed partly at Pilot plants own well and rest is to be separated later in water treatment as described in chapter 3.3. Metals have also been detected in the wastewater measurements.

3.2.1 PP and PE

Polyethylene and polypropylene made in Pilot plant are thermoplastic low pressure plastics. Pilot makes HD- (high density), MD- (medium density) and LLD- (linear low density) polyethylene. LDPE (low density polyethylene), which is made in high pressure process is not made in Pilot. Differences between the PE plastics are shown in Figure 2. MDPE structure is between LDPE and HDPE. As seen in Figure 2 density of polymer is controlled with comonomer which creates branched structure. Comonomers used in Pilot are 1-butene and 1-hexene. Branched polymers have lower density. (Jeremic, 2014)

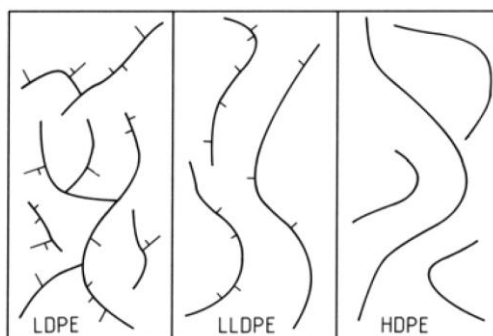


Figure 2 Molecular structures of LDPE (low density polyethylene), LLDPE (linear low density polyethylene) and HDPE (high density polyethylene). (Jeremic, 2014)

The polypropylene polymerization process differs from the polyethylene because of the additional carbon atom in propylene. Branching of the methyl group happens in three main

ways shown in Figure 3. Different structures of polypropylene differ the properties of plastic. The properties of PP plastic can be modified also with comonomer like ethylene. (Gahleitner and Paulik, 2014)

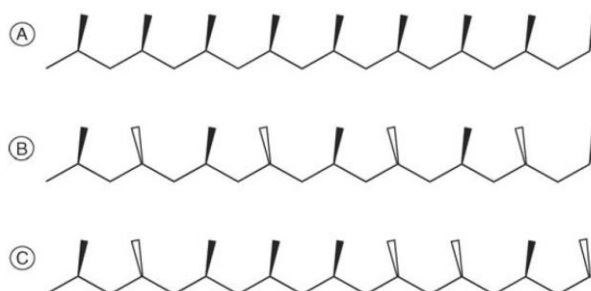


Figure 3 Different polypropylene types. A: Isotactic B: Syndiotactic C: Atactic. The shown black and white sticks are methyl groups located on different sides of hydrocarbon chain. (Gahleitner and Paulik, 2014)

Catalysts are very important in the polymerization process to control properties of plastics. Catalysts used in Pilot plant are mainly coordinative Ziegler-Natta or Single-site catalysts. Ziegler-Natta catalyst are made of TiCl_4 and TiCl_3 (Kawai and Fujita, 2009). Single-site catalysts used in Pilot plant are metallocenes. Metallocenes are organometallic compounds with two cyclopentadienyl ligands (Jeremic, 2014). In the Pilot plant catalyst is activated with cocatalyst, triethylaluminium. The catalyst stays in the product after processing.

The properties of PP and PE are very different depending on the catalyst used and the process conditions. In the Table 2 is shown the bulk densities and particle size distribution in Pilot plant. The values in Table 2 are the minimum and maximum on average polymer powder processed in Pilot plant. The values are averages from final product. Final polymer powder is extruded into pellets. The size of average pellet is 3 mm.

Table 2 Properties of final polymer powder in Pilot plant.

	PP, final	PE-LD, final
Bulk density, kg/m³	370 - 550	370 - 500
Density, kg/m³	850 - 940	910 - 935
Particle size distribution, mm	0.1 - 4,0	0.1 – 4.0

During polymerization there is possibility that optimum particle size is not reached. With unsuccessful polymerization powder particle size is much smaller causing problems to product and process. Small particles are called fines. The size of the fines is in the range of 75-500 μm . Overall, the range of solids ending up in the pavement and from there to waste water system are by particle size minimum of 75 μm and maximum of 3 mm.

Plastic particles below 5 mm in particle size have been defined as microplastics (Felsing et al., 2018), (Sun et al., 2019), (Gatidou et al., 2019), (Prata et al., 2019). This is based on the fact that below 5 mm plastics can be consumed by organisms. Meaning that all particle emissions from Pilot plant are microplastics. Macroplastics are the plastic particles above 5 mm. In more described definition of plastics, mesoplastics are 1-5 mm, microplastics are 0.1 μm – 1 mm and nanoplastics are below 0.1 μm plastic particles. For microplastics, < 5 mm definition is more commonly used. (Wagner and Lambert, 2018) TSS (total suspended solids) values from Pilot are mainly from microplastics. TSS is measured by filtering the solids from water and measuring the dry weight of solids.

3.2.2 Organic matter and oil

Oxygen demand is common testing method for measuring if water has organic pollution. COD (Chemical Oxygen Demand) is one of the commonly used water testing parameters and measures organic matter amount in water. (Boyles, 1997) Organic matter means all carbon based material including both organic and inorganic compounds that contain carbon. Organic matter in water constitutes of dissolved and non-dissolved matter. The distinction between the two is done in using filter with 0.1 – 0.7 μm pore size. The dissolved material goes through filter. (Mostofa et al., 2013) Microplastics amounts are part of the COD amount.

Organic matter amount is determined by the amount of oxidant that reacts with the sample (U.S EPA, 2001). Organic matter reacts with oxidant to carbon dioxide and water. In the COD measurements both organic and inorganic molecules react with oxidant. COD is measured most often using either $\text{K}_2\text{Cr}_2\text{O}_7$ (Potassium dichromate) or $\text{Mn}_2(\text{SO}_4)_3$ (manganese(III)sulfate) as oxidant. COD is used for frequent monitoring of water quality and overall the water treatment efficiency. It is good for overall testing, because toxic materials do not affect tests. COD measurement have couple of disadvantages: chloride ions interfere with

analysis and some organic compounds are not oxidized completely making analysis inaccurate. (Boyles, 1997)

TOC (Total organic carbon) and BOD (Biochemical oxygen demand) are also measured often in water treatment applications. TOC measures the total organic carbon amount in water sample. TOC measurements do not show the inorganic carbon amount. For TOC measurements heat, O_2 and $K_2S_2O_8$ can be used for oxidation. TOC has the same problem that COD measurement has. Some organic compounds cannot be oxidized completely.

BOD is measured in test method that uses microorganisms for oxidation. Standard BOD test lasts 5 days and is therefore longer lasting than COD (maximum 3 hours) and TOC (maximum 1 hour). BOD testing is mainly used when wastewater treatment plant is modelled and biological treatment is planned. BOD testing method has some major disadvantages in addition to the long measurement time. BOD testing is very sensitive to toxic materials that harm the microorganism. In addition, microorganisms cannot oxidize everything in wastewater. (Boyles, 1997)

In the plastic laboratory COD and oil index are measured regularly from the wastewater at each of the plants. Also, the overall COD amount going to sea is measured separately. COD is measured with potassium dichromate with closed tube method. The testing of COD is done according to standard ISO 15705. Oxidizing organic matter with dichromate ions ($Cr_2O_7^{2-}$) can be considered complete. Meaning that in the end organic matter is oxidized to CO_2 and H_2O . Pyridine is exception which does not oxidize completely with dichromate (Boyles, 1997). Dichromate ions react to Cr^{3+} ions. Cr^{3+} ion concentration is measured by photometric Hach DR 6000. The measurement equipment is spectrophotometric working in visible light area. In the plastic laboratory the COD measurements are done during the same day as the sample has been taken and therefore is not pretreated. With pretreatment the wastewater sample can be stored in refrigerator and in dark for maximum of five days. Pretreatment of sample is done by adding sulfuric acid so that pH is 2.

Hydrocarbon oil index is measured in plastic laboratory according to standard ISO 9377-2. The measurement used in laboratory is very similar to Wüst (2000) measurements. In the oil index the oils between n-decane ($C_{10}H_{24}$) and n-tetracontane ($C_{40}H_{82}$) are measured. In the

measurement water is extracted with an extracting agent. After extraction polar substances are removed by magnesium silicate. In the end hydrocarbon oil index is based on GC measurements. The method is good when concentrations of oil are above 0.1 mg/L. (Wüst, 2000)

3.2.3 Wastewater legislation

Wastewaters in plastic plants in Finland are regulated by European Union and Finnish legislation. In the European Union level the requirements come from best available techniques (BAT) reference document for common waste water and waste gas treatment/management systems in chemical sector (2016) document (Brinkmann et al., 2016). The document prepared by Brinkmann et al. (2016) is based on industrial emissions directive 2010/75/EU. There are several BAT – associated emission levels (BAT –AELs) that apply to wastewater emissions. The BAT-AELs are shown in Table 3. BAT-AELs are values for pollutants that leaves the installation. Referencing to the values that are released to the sea.

Table 3 BAT-associated emission levels in wastewaters. (Edited from Brinkmann et al., 2016)

Parameter	BAT-AEL (yearly average)	Conditions
Total Organic Carbon (TOC)	10-33 mg/L	BAT-AEL applies if the emission exceeds 3.3 tons/year
Chemical Oxygen Demand (COD)	30-100 mg/L	BAT-AEL applies if the emission exceeds 10 tons/year
Total Suspended Solids (TSS)	5.0-35 mg/L	BAT-AEL applies if the emission exceeds 3.5 tons/year
Total Nitrogen (TN)	5.0-25 mg/L	BAT-AEL applies if the emission exceeds 2.5 tons/year
Total Inorganic Nitrogen (N _{inorg})	5.0-20 mg/L	BAT-AEL applies if the emission exceeds 2.0 tons/year
Total Phosphorus (TP)	0.50-3.0 mg/L	BAT-AEL applies if the emission exceeds 300 kg/year
Absorbable Organically Bound Halogens (AOX)	0.20-1.0 mg/L	BAT-AEL applies if the emission exceeds 100kg/year
Chromium (Cr)	5.0-25 µg/L	BAT-AEL applies if the emission exceeds 2.5 kg/year
Copper (Cu)	5.0-50 µg/L	BAT-AEL applies if the emission exceeds 5.0 kg/year
Nickel (Ni)	5.0-50 µg/L	BAT-AEL applies if the emission exceeds 5.0 kg/year
Zinc (Zn)	20-300 µg/L	BAT-AEL applies if the emission exceeds 30 kg/year

Wastewater treatment in Finland is regulated by environmental protection act (27 June 2014/527). The environmental regulations and permits are applied according to environmental protection act. Each of the plastic plants have their own environmental permit. The overall approved amount of oily hydrocarbons going to the sea from plastic factories in Finland is 50 kg/month. Pilot is one of four plastic plants in site (Finland).

Hurley et al. (2019) described national legislation on microplastics in a memo. Most of the legislation and initiatives in microplastic restriction are concentrating on microbeads used in cosmetics. The plastic problems and microplastics have received a lot of negative media attention and therefore it is likely that legislations are to be made for EU wide in coming years. At the moment, for example in France, products containing microbeads are banned. The concentration is at the moment in microbead banning but legislation in plastics is probable to move into stricter rules. (Hurley et al., 2019)

3.2.4 Results

BAT-AEL regulated values presented in chapter 3.2.3 allow 30-100 ppm limit for COD if the emission values exceed 10 tons/year. Environmental permit allows 50 kg/month of carbon emissions in water to be released to Baltic Sea. From Pilot plant water goes to follow-up treatment where the water is released to Baltic Sea. In the treatment the Pilot wastewaters are mixed with other factories wastewaters and are diluted in the process. The wastewater contaminant emissions have been changing drastically between two weeks' time. The samples are taken every two weeks. Overall, the results have been high, especially COD concentration.

Oil amounts in wastewater have increased in the years 2018 and 2019. Oil concentrations have been high but the COD amounts are much larger. The oil and COD do not correlate with each other. It is to be noted that TSS resulting from PE and PP increase the COD amounts. In addition, other chemicals and soil ending up in treatment results in COD amount. The objective of wastewater treatment is to separate COD and oil as early in the process as possible.

Metal analyses are not part of regular testing in plastic factories. Metals were analyzed in a separate campaign where extra samples were taken in once a week in four week period in November 2018. Analyses were done according to CWW BAT standards. In the results it

was found that especially Zinc levels were high in Pilot wastewater compared to other plants wastewaters. It is not known where the large zinc amount is coming to the wastewater since zinc is not used in the process. There is suspicion that the zinc is coming from the soil around the process area.

In the same campaign TSS was measured. TSS is not measured at the Pilot plant regularly from the oil water well. During the campaign TSS was measured on four different days and the average value was 167 mg/L. TSS values varied during that time from 42 mg/L to 296 mg/L. In Figure 4 is shown a wastewater sample taken from oil water well. As seen in Figure 4 there are small solid particles floating on the surface. There are also some particles from soil which are at the bottom. Overall, it is obvious there are contaminants in the wastewater that are not separated in oil water well. Water from Figure 4 goes to further treatment after Pilot plant.



Figure 4 Wastewater sample from oil water well in January 2019.

3.3 Separation systems

In the Finnish plastic factories there is separation system in the four plants and a separation system for the location wide wastewater system. From the location wide system water is released to the Baltic Sea after cleaning and separation steps. In this chapter Pilot, location wide system and system in Austria are described.

3.3.1 Pilot plant

Pilot plant is separated into two wastewater systems: Oil water and rain water. These two systems are presented in detail under chapter 3. Oil water system has more contaminants than rain water system and therefore needs further treatment. In Figure 5 is shown the PI&D

picture of the oil water well. All the wastewater from oil water system ends up in oil water well as shown in Figure 5. Oil water well works as a one separation step in water treatment. It is designed so that lighter components than water are floating. In the well light components including pellets, powder and lighter oils float on surface. Water is pumped from bottom with submersible pump. Separation is based only on the density difference of different components. When there is a lot of polymer powder on the top layer, it is collected away from well. Wastewater sample is taken from the pump line after oil separation.

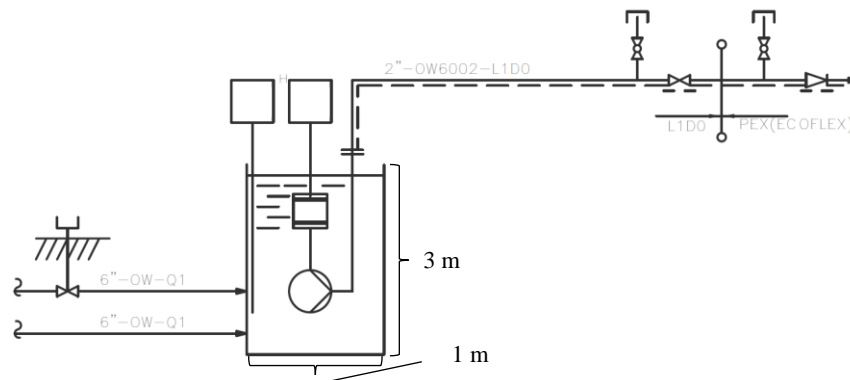


Figure 5 Oil water well in Pilot plant.

It is assumed that most of the oils in the area have density lower than water. In plastic plants propylene glycol is used as heat transfer fluid. The density of propylene glycol is 1.045-1.055 g/mL at 20 °C (DOW Suomi Oy, 2016) which is higher than water density at 20 °C, 0.998 g/mL (Pubchem.ncbi.nlm.nih.gov, 2019). This makes the density based separation difficult when there is both oils with higher and lower density compared to water.

In the well there is level measurement instrument to alarm when the surface of water is at high level. When the alarm goes off, operator turns on the submersible pump. In normal conditions pump is set to pump water for 15 minutes when turned on. If there is heavy rain/washing, the pump can be turned on for hours at a time. The water is pumped through a line to further water treatment in utilities area.

Whole well volume is 2.4 m³ and the capacity of pump is 15 m³/h. Water surface is never at the top of well at 3 meters shown in Figure 5. There are also some structures of pipes and the well structure is not completely cylindrical making the real volume smaller than 2.4 m³. The pump works always at full capacity, 15 m³/h. In normal conditions when pump is 15 minutes on and working in theoretical full capacity, 3.8 m³ of wastewater is pumped to further treatment. Whole well is empty after 9.6 minutes of pumping. There is no level alarm

when the surface of water is at low level. Meaning that when pump is on for 15 minutes water with all the contaminants goes to further treatment without any or very little separation done in Pilot plant.

There is a flow meter in the line after pump which is not shown in PI&D figure. The flow meter shown values are used in the calculation of monthly amount of wastewater leaving Pilot plant. There is monthly report done in the plastic factories about the amounts of pollutants in wastewater. COD amounts measured by laboratory are multiplied with the amount of wastewater leaving each of the plants.

In Pilot plant the flow transmitter has been showing unreliable results. Transmitter has been showing too large amounts. The monthly average has been calculated from daily averages. The monthly values from 2018 have been changing in the range of 36-11 000 m³/month. The range is too wide for the wastewater usage in Pilot plant making the values unreliable. If there would have been 11 000 m³ wastewater usage in December (2018) the pump would have been turned on about 100 times/day. This has not happened especially during the winter months. At least from the past year 2018 the volumetric calculations for wastewater in Pilot have been too high. This has led to too high load values from Pilot during that time. The reason for too large values was found to be ultrasound flow measurement which should be on the water phase at all times to work properly. As seen in Figure 5 the flow measurement is on vertical pipe. According to new calculations the wastewater amount in Pilot is below 100 m³/month.

3.3.2 Finland

From the Pilot oil water well wastewater is pumped to further treatment in utilities area. Water treatment for plants 3, 4 and Pilot is shown in Figure 6. As seen in Figure 6 Pilot oil water goes to the first step of the water treatment and rain water to second part. First step is collection well, also called API separation. In the API separator oil is separated in a system where water passes at low velocity horizontally and oil rises to the surface of water and is skimmed from the surface. API is meant for bigger oil particles in the size range of 150 µm and larger. (Kundu and Mishra, 2017)

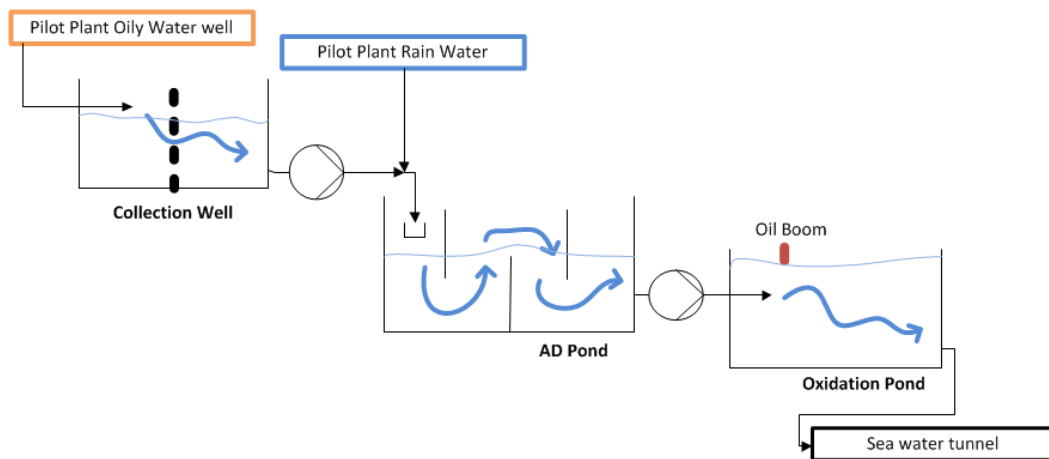


Figure 6 Water treatment unit for Plants 3, 4 and Pilot plant.

After collection well, water is pumped to AD-pond. Between the collection well and AD-pond there is equalization basin which equalizes the flow amounts. Rain water from Pilot plant is fed to equalization basin. AD-pond is also called flotation basin and the P&ID of the pond is shown in Figure 7. In the AD-pond there are also vertical walls where water goes above or below wall and the solid particles float and accumulate behind the walls. There is no aeration in flotation basin. The separation in flotation basin is based on the gravitational forces. Solid particles and oil are removed mechanically from the surface. From AD-pond the water is pumped to oxidation pond. In the oxidation pond (pond 3) there is oil boom that stops the oils that are lighter than water.

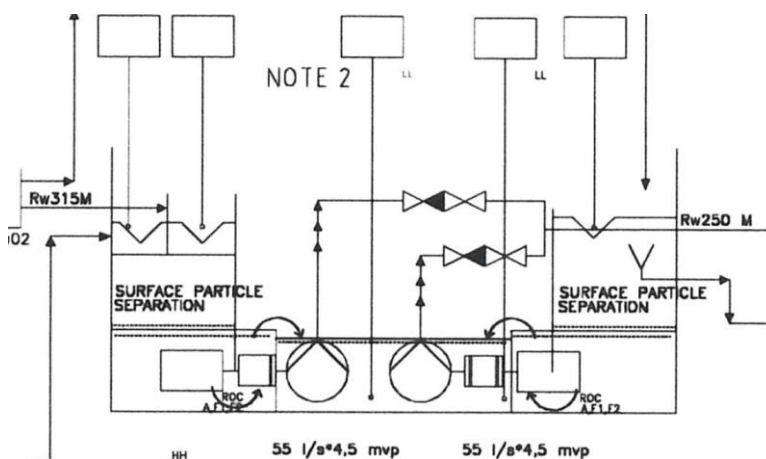


Figure 7 AD-pond, also called flotation basin.

In the Finnish location there is wastewater system for all the wastewaters leaving to sea. In Figure 8 is shown the overall picture how the wastewaters are collected in the utilities area

and released to the sea. Sanitary waters have their own system which is not shown in Figure 8. Plant 2 has its own wastewater separation. In the future the pond 3 is going to be left as a reserve pond and the water will go through new filtering system after pond 1.

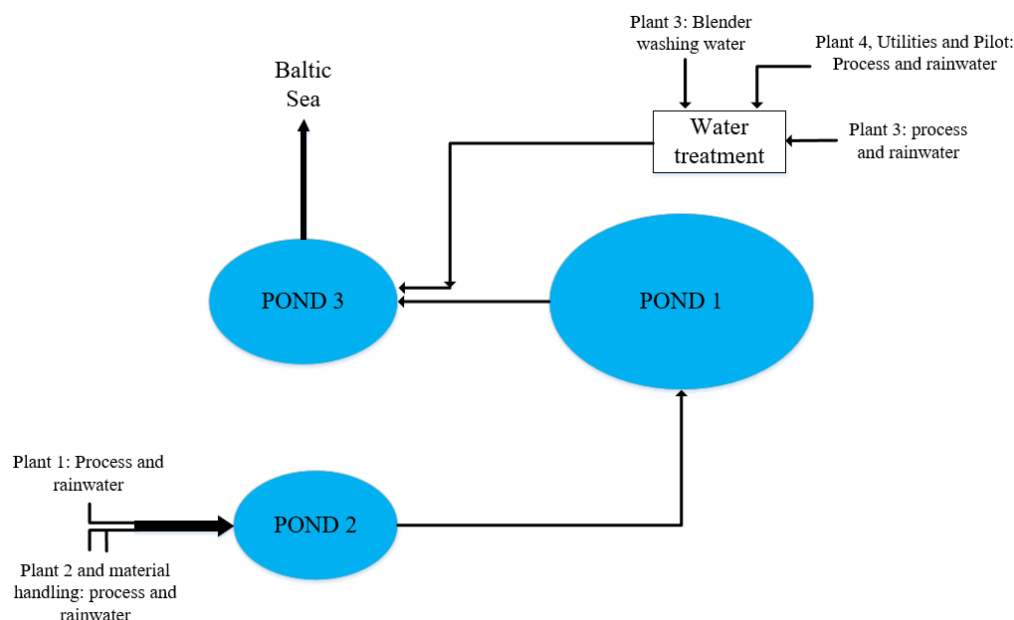


Figure 8 Wastewater system in Finnish plastic plants.

3.3.3 Austria

In the Austria site there is a different kind of wastewater treatment system than in Finland. In Austria site there are more plastic factories than in Finland and the system is bigger. There are treatment units in each of the plants and unified treatment plant where all the waters are directed. From the unified treatment plant, water is directed to river.

Overall, there are couple fundamental differences when comparing the Austrian and Finnish systems. In Finnish site there is much more retention volume available because there are three ponds in water treatment. Finnish system has 20 000 m³ retention volume when in Austria site there is about 3000 m³ of retention volume. Because of this, the retention time in Finland is 72 hours compared to 6 hours in Austria. The main difference between systems lies in microbial biomass. In Austria wastewater plant microbial biomass needs to be taken into account opposed to Finnish system where there is next to no biomass in used water. The difference is caused by the source of process water. In Finland, river water which is purified is used in process and in Austria groundwater without purification is used.

There is another Pilot plant in Austria that uses same technology as in Finland, but has only PP line. There is wastewater treatment unit in Austrian Pilot. In the unit, process waters are lead to filter and to collection well. With collection well the amount of water to further processing can be controlled. From the collection well, water is lead to a coarse particle separation and there to fine separation. Coarse and fine separators are basins where there is filter at outlet. Final step is coalescing filter.

In the Austrian location wastewater treatment there are retention basins that act as a final separator in the wastewater system after release. In addition to the location wide system Austria is considering investment to a disc filter and sandfilter.

4 Wastewater treatment

Traditionally wastewater treatment is categorized into four different steps. These steps are shown in Figure 9. In Figure 9 is shown below the step name: object of the step, what it separates and the treatment technology type used. The types used in wastewater treatment depend on the contaminants present in influent. (Stuetz and Stephenson, 2009)

In the preliminary treatment gross solids are removed. Preliminary treatment is more often used in municipal wastewater treatment where there can be rocks and trash in the wastewater. For the preliminary treatment physical separation methods like screens and grit removal are used. Screens are used for removal of floating objects and gross particles. Separation happens in bar or mesh. Coarse screens are removing objects with size of 6 – 150 mm (Tchobanoglous et al., 2003). Grit removal is based on gravity and separates dense particles on some applications with density of 2500 kg/m^3 . (Stuetz and Stephenson, 2009)

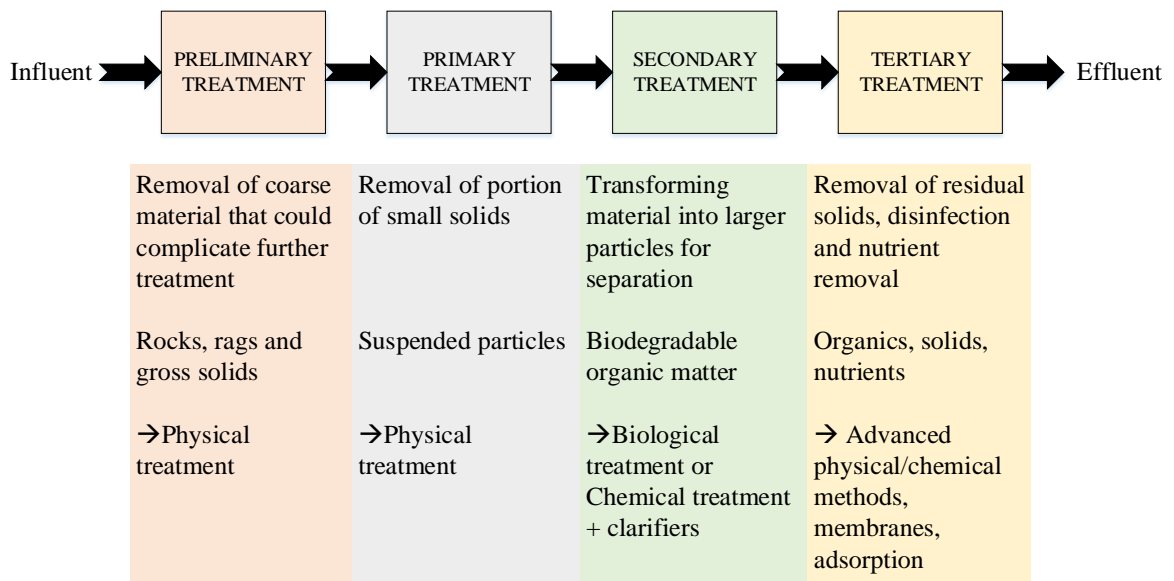


Figure 9 Wastewater treatment steps. (Edited from Tchobanoglous et al., 2003)

Primary separation uses also physical separation methods in removing the smaller solid particles. There are also screens for fine and microsized particles. Fine screening removes small particles and micro screening removes fine solids, floatable matter and algae. Fine screens separate solids with size of below 6 mm. Microscreens separate particles with size of below 50 μm . In the primary treatment only portion of organic matter and suspended solids are separated. It is possible to use more advanced primary treatment to remove more of contaminants. In advanced primary treatment filtration or chemical addition is used in addition to physical separation. (Tchobanoglous et al., 2003)

In the secondary treatment biodegradable organic matter and suspended solids are removed including disinfection. It is possible to also separate nutrients (nitrogen and phosphorus) in secondary treatment. The most common secondary treatment in municipal wastewater treatment is activated sludge treatment. In activated sludge treatment micro-organisms are used for the degradation of pollutants in wastewater. In tertiary treatment residual suspended solids are removed often using filtration or microscreens. Disinfection is usually part of tertiary treatment. Disinfection and removal of pathogens is done with UV radiation, ozone, chlorine compounds or chlorine dioxide. (Tchobanoglous et al., 2003)

Overall the separation of contaminants is usually done in certain order. The removal sequence of contaminants is the following:

1. Gross suspended solids
2. Organic matter and colloids
3. Suspended matter
4. Dissolved organic matter
5. Dissolved salts
6. Dissolved gases
7. Microbiological contaminants. (Stuetz and Stephenson, 2009)

In the plastic factories there are no dissolved salts, gases or microbiological contaminants (5-7) in wastewater. First gross suspended solids are separated, meaning microplastics. In wastewater treatment at plastic plants organic matter and colloids needs to be separated. After that, dissolved organic matter should be separated.

In Figure 10 is shown possible treatment technologies for the major pollutants in wastewater. In the Pilot plant and plastic factories the major pollutants are organic matter (COD), Suspended solids (TSS), oils and metals. These are circled in Figure 10. As seen in Figure 10 there are multiple possibilities for the separation of each contaminant. The primary applications for the contaminant separation and in (X) is shown the secondary applications.

It is to be noted that when choosing the wastewater treatment technique to Pilot plant, there are many factors which affect the selection. The system needs to be small enough that it can fit to limited space in Pilot plant. System needs to be efficient enough to remove suspended solids, organic matter and oil in the water in cost efficient way.

Technique	TSS	BOD COD TOC	Refractory COD/TOC	AOX EOX	N total	NH ₄ -N (NH ₃)	PO ₄ -P	Heavy metals	Sulphides	Sulphate	Phenols	Oil	Acids, alkalis
Neutralisation	(X)							(X)					X
Grit separation	X												
Coagulation/flocculation	X	X ^{(b),(8)}						X	X			X ^(b)	
Sedimentation	X	(X) ^(f)						(X) ^(f)	X ^(f)				
Flotation	X	X ^(f)						(X) ^(f)				X	
Filtration	X	(X) ^(f)						(X) ^(f)					
Microfiltration (MF)/ Ultrafiltration (UF)	(X) ^(f)	(X) ^(8,9)						X				X	
Oil-water separation	X	X										X	
Hydrocyclone	X												
Electrocoagulation	X	X						X					
Chemical precipitation			X				X	X		X			
Crystallisation							X	X					
Chemical oxidation (pre)		X	X	X					X		X		
Wet oxidation with hydrogen peroxide (pre) ^(*)		X	X	X	X						X		
Wet air oxidation (pre) ^(*)		X	X	X							X		
Chemical reduction								X ^(f)					
Chemical hydrolysis		X		X									
Nanofiltration (NF)/Reverse Osmosis (RO)		X	X	X	X	X	X	X			X		
Electrodialysis			X										
Electrolysis													
Adsorption		X ^(f)	X	X	X	X		X			X	X	
Ion exchange		(X) ^(f)						X		X			
Extraction		X	X	X							X		
Pertraction		X	X	X							X		
Distillation/rectification		X	X	X									
Evaporation ⁽⁸⁾		(X) ^(f)		X	X	X	X	X					
Pervaporation		X ^(f)	X ^(f)	X ^(f)									
Stripping		(X) ^(f)		X	X	X		X	X ^(f)		X		
Waste water incineration (FT) ^(*)		X	X	(X) ⁽⁸⁾	X	X		(X) ^(b)			X	X	
Anaerobic treatment		X		(X) ^(b)	(X) ^(b)			X ^(f,m)		X			
Biological removal of sulphur compounds/heavy metals								X	X	X			
Aerobic treatment		X		(X) ^(b)	X	X	X	(X)	X		X		
Nitrification/denitrification					X	X							
Enhanced biological phosphorus removal							X						
Phosphorus removal by chemical precipitation							X						
Retention ponds	X	X											
Sand filters	X												

(*) Only solid. (b) Undissolved organic content. (c) Finely dispersed and low concentration. (d) Ionic organic species. (e) Non-volatile organic content. (f) Volatile organic content. (g) Special incinerator equipment required. (h) Only biodegradable part. (i) Undissolved heavy metal compounds. (j) Transferred to ash or waste water originating from incinerator. (k) In combination with sulphate precipitated as sulphides. (l) Transferred to sludge. (m) Colloids. (n) Ammonia. (o) Hydrogen sulphide. (p) Some macromolecules. (q) Side effect of ammonia or nitrate removal. (r) Side solubilisation. (s) Cr(VI). (*) Includes nitrification/denitrification and one-step nitrogen removal process of Annamox type. (**) Including colour agents, surfactants, nitrocompounds, chloro compounds, phenols. (*) Techniques applicable on concentrated effluents [148, Degremont SUEZ 2007].
NB: (FT) = used as a final treatment technique; (pre) = used in particular as a pretreatment, for example before final biological treatment; X = primary application; (X) = secondary application.
Source: [227, CWW TWG 2009]

Figure 10 The most common contaminants in wastewater and the possible techniques for separation of each pollutant. (Brinkmann et al., 2016) Bolded columns are the contaminants of interest in the plastic factories.

5 Solid-liquid separation

In the wastewater at the plastic factories there are pellets and polymers powder that need to be removed in the solid-liquid separation stage. As previously determined polymer powder has smaller particle size than pellets. Most of the pellets in the plants are removed by screens in the drains before they end up in the wastewater system. Therefore, in the solid-liquid separation, polymer powder separation from water is researched further. Particle size of polymer powder is usually 1 mm but can be as small as 75 µm. In Figure 10 above is shown the possible techniques for removal of TSS from wastewater. In the list it is shown that neutral-

ization, grit separation, coagulation/flocculation, sedimentation, flotation, filtration, micro-filtration/ultrafiltration, oil/water separation, hydrocyclone, electrocoagulation, retention ponds and sand filters can be used for TSS separation.

There are many different separation methods for suspended solids. Most of them still are not feasible solutions for removal of plastic powder and microplastics. In the choosing of mechanical solid-liquid separation there are two main principles where to choose from: Sedimentation or filtration. Sedimentation is based on gravity difference between phases and there is very little possibilities for process control. The sedimentation can be enhanced by centrifugal force or by increasing the mass of particles in flocculation. In Figure 11 is shown the main differences between the two principles. (Svarovsky, 2000)

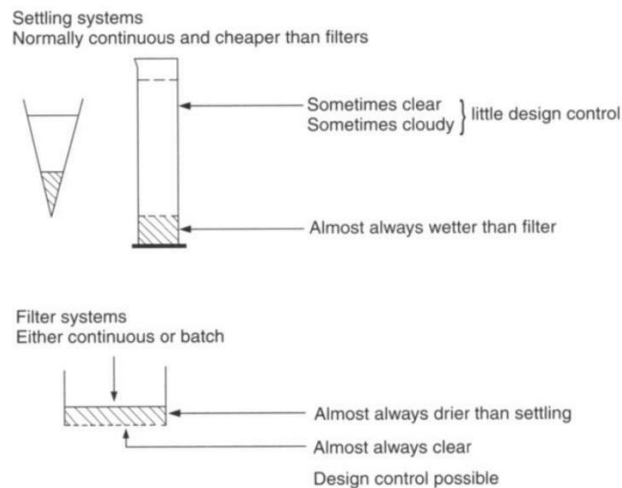


Figure 11 Illustration of differences of settling and filtration. (Svarovsky, 2000)

As seen in Figure 11 filter systems are more advanced because design control can be applied and filtration residue is drier. Filter systems are not as suitable to continuous production. Sedimentation system works in continuous process well and tend to be cheaper option than filters. In the separation treatment it is recommended to use both sedimentation and filter to make process practical and reliable. Sedimentation unit is usually first to reduce the amount of water to filters. Microfiltration/Ultrafiltration membranes can only be used for finely dispersed suspended solids in low concentrations. (Svarovsky, 2000) Tchobanoglous et al. (2003) defines that fine and micro screens can also been used in removal of small particles.

5.1 Coagulation and flocculation

Coagulation and flocculation are both separation technologies where particle sizes are increased. Therefore, they are usually used as pretreatment before particle separation. With the increase of particle size, more efficient flotation of particles and settling can be achieved. Particle clusters achieved by coagulation are usually 1 mm by size. (Svarovsky, 2000)

Coagulation is based on destabilization of colloidal particles. Destabilization is done by adding coagulants that changes the electrical balance between particles. This is done by inverting, reducing or by neutralizing electrical repulsion of particles. Principle of electric forces on particles is shown in Figure 12a. Coagulation is based on reducing the repelling forces on the particle by chemicals. (Ranade and Bhandari, 2014)

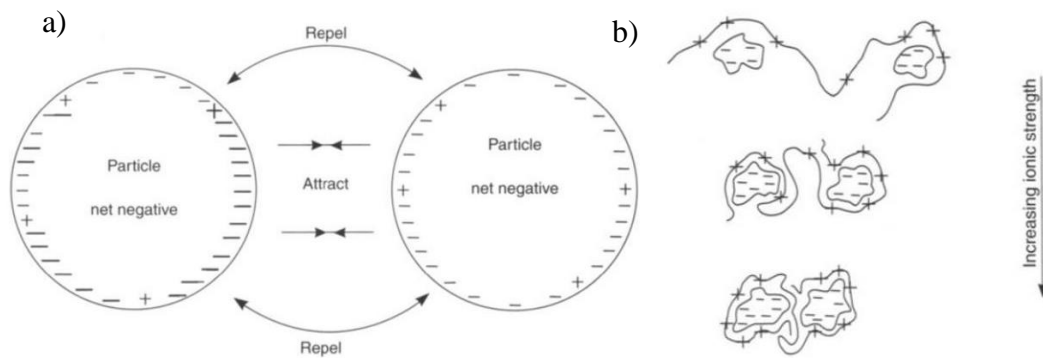


Figure 12 a) Electric difference on particles. b) Flocculation with cationic polyelectrolytes for negatively charged particles. (Svarovsky, 2000)

Coagulation is commonly used in industrial wastewater treatment and has been proven to be effective in removing color from wastewaters. The most effective result has been achieved with dissolved solids and charged matter. Both inorganic and organic compounds can be used. Most common inorganic coagulants are aluminium salts, ferric and ferrous salts and lime. Organic coagulants used are cationic polymers or anionic and non-ionic polymers. (Ranade and Bhandari, 2014)

Flocculation uses synthetic polyelectrolytes with high molecular weight to interconnect colloidal particles into large flocs that can be maximum of 10 mm in size. Flocculation differs from coagulation by the different chemicals used and the size of particles, Figure 12b. The dosage of the coagulant chemical and the type is very essential. The type and amount used depends on factors like pH, solid concentration, particle size distribution, surface chemistry and electrolyte content. (Svarovsky, 2000)

There are some major disadvantages in using coagulation/flocculation in wastewater treatment. With coagulation/flocculation chemicals are used in large amounts. In the treatment a lot of sludge is produced and the sludge disposal costs a lot. Organic coagulants are more efficient than inorganic coagulants in the treatment. When the treatment is more efficient, less sludge is produced. With less sludge to dispose and handle, the treatment process becomes less expensive. In addition, inorganic coagulants are pH sensitive and work in specific pH range. It is preferred to use organic coagulants because of the disadvantages with inorganic coagulants. (Ranade and Bhandari, 2014)

Coagulation/flocculation cannot be used in itself as only treatment method. The treatment can work as a pretreatment of solid-liquid separation. The coagulation/flocculation treatment step should be designed together with filtration or other separation step after coagulation/flocculation. Depending on the separation method used there are different requirements from coagulation/flocculation. For example in gravity based filtration large and loosely packed flocks are needed. (Svarovsky, 2000)

Ma et al. (2019) researched PE microplastic removal in drinking water application with coagulation. In the research first there was coagulation step with Al- and Fe-based salts. Al-based salts had better coagulation results than Fe-based salts. After coagulation there was sedimentation and ultrafiltration membrane steps. Smaller PE plastics created better results with less fouling on the membrane. Tests were done with microplastics sized $d < 0.5$ mm, $0.5 < d < 1$ mm, $1 < d < 2$ mm, $2 < d < 5$ mm and polyvinylidene fluoride membrane with a molecular weight cutoff of 100 kDa. Best removal efficiency (27%) was with $d < 0.5$ mm PE particles and Al-based salt. (Ma et al., 2019)

Herbort et al. (2018) researched agglomeration with trichlorosilane-substituted Si derivatives. After agglomeration the size of particles changed from 300 μ m to 2-3 cm. The industrial scale test is shown in Figure 13. The removal of agglomerated particles was done easily by sand traps. (Herbort et al., 2018)

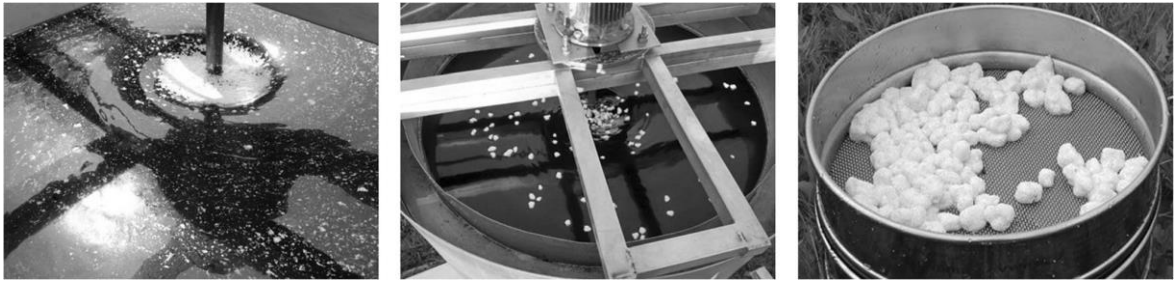


Figure 13 Agglomeration process when 100 mg of PE and PP microplastics are in 2000 L water tank in $T=10-28\text{ }^{\circ}\text{C}$, $\text{pH}=5-6$ with mixing and 24 h process time. (Herbort et al., 2018)

5.2 Fine screens and micro screens

In fine screens (0.2-6 mm) there are typically three types used for preliminary treatment of municipal wastewater: static, rotary drum or step type. Step screen model in municipal water treatment is shown in Figure 14. When the fine screens have been used to replace primary treatment in municipal wastewater treatment the removal percentages have varied a lot. In fixed parabolic screen with 1.6 mm sized openings 5-30 % TSS can be removed. In rotary drum screen with 0.25 mm sized openings 25-45 % TSS can be removed. (Tchobanoglous et al., 2003) It is to be noted that the values are for municipal wastewater that is very different from industrial wastewater. It is not described further what kind and sized suspended solids are present in municipal wastewater.



Figure 14 Example of a step screen used in municipal solid removal. (Huber Technology)

5.3 Sedimentation and flotation

Sedimentation is used as primary treatment in municipal wastewater treatment to separate settleable solids and floating material. In average 50 – 70 % of suspended solids are removed

in sedimentation pond. In the municipal treatment 25- 40 % of BOD is removed at the same time in sedimentation. There are two types of sedimentation tanks used: rectangular and circular. (Tchobanoglous et al., 2003) In Figure 15 is shown the circular sedimentation tank and in Figure 16 is shown the rectangular sedimentation tank.

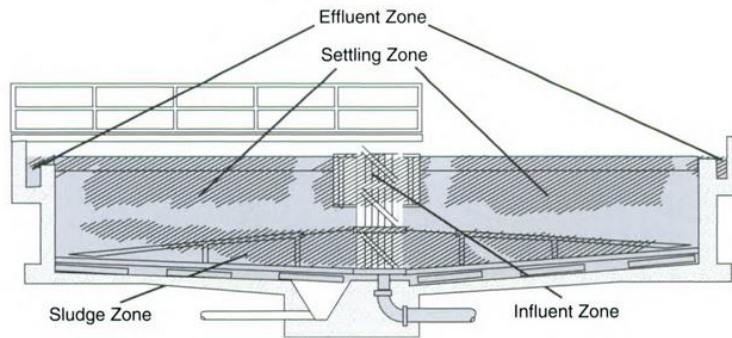


Figure 15 Circular sedimentation tank. (Pizzi, 2005)

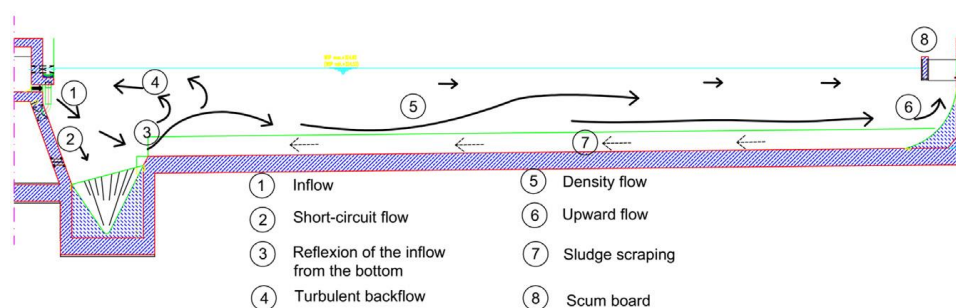


Figure 16 Rectangular sedimentation tank. (Kiss and Patziger, 2018)

Sedimentation is based on the gravitational force of suspended particles. Suspended particles are removed from the bottom of the tank. For the enhancing of sedimentation coagulation/flocculation agents are often introduced to the water before sedimentation unit. And because plastics float on water the coagulation step is necessary. In the rectangular sedimentation there are sludge collectors which move the sludge on bottom to the sludge collection. There is also sludge collection in circular sedimentation tank. For the suspended solids usual removal efficiency in sedimentation tank is 65 % after 6 hours when there is 100-200 mg/L in the inlet wastewater. But it is to be noted that 43 % removal efficiency can be reached in 1 hour. (Tchobanoglous et al., 2003) Sedimentation technology can also remove microplastics but operational conditions need more optimization to increase removal efficiency. Hydraulic retention time is the most important parameter. (Sun et al., 2019)

Flotation is used in wastewater treatment to separate suspended matter. Floating is more suitable for microplastic removal. Most common technique for flotation in wastewater treatment is dissolved-air flotation (DAF). In the DAF air is injected to water which is under pressure and pressure is released during process. Air bubbles attach to the particles and with buoyant force bubbles bring the particles to the surface. In flotation denser particles than water can be brought to the surface. Particles are removed from the surface by skimming. (Tchobanoglous et al., 2003)

DAF system is shown in Figure 17. In DAF the inflowing water is first pressurized so that air dissolves. When the inflow goes to the flotation tank it goes through pressure reducing and the feed is released to the tank forming small bubbles. Small bubbles bring solids and oil to the surface where it can be collected. Flotation tank model resembles rectangular sedimentation tank model. (Rocha e Silva et al., 2018)

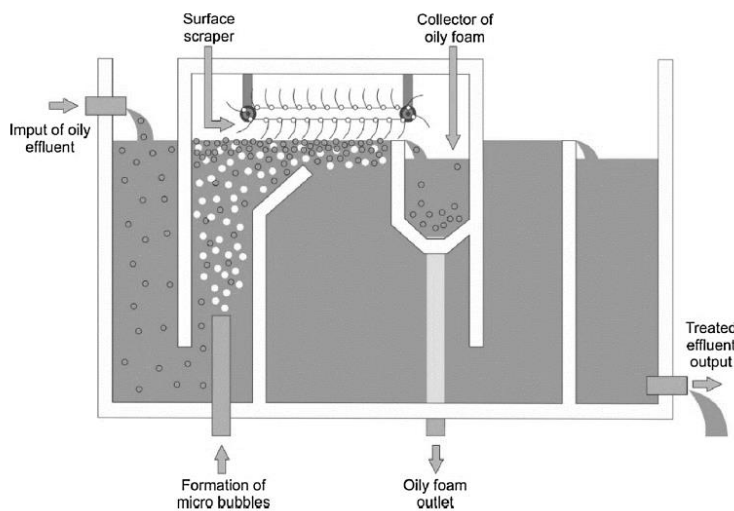


Figure 17 DAF separation system. (Rocha e Silva et al., 2018)

DAF is used in municipal wastewater mainly to concentrate the amount of biosolids and is often used in industrial waste reduction. (Tchobanoglous et al., 2003) In Talvitie et al. (2017) DAF system microplastics were removed with the efficiency of 95 % when in feed there were 2.0 microplastic pieces/liter. To enhance the DAF system flocculation agent polyaluminum chloride (PAC) was added at amount of 40 mg/L. (Talvitie et al., 2017) In addition, DAF can separate oil. Al-Shamrani et al. (2002) concluded that with addition of coagulants >99 % oil removal efficiency can be achieved. Coagulants used were aluminum and ferric

sulphates. DAF could possibly remove both microplastics and oil in Pilot wastewater in one step.

Other flotation technique is dispersed air flotation which differs from DAF so that aeration happens in atmospheric pressure. Structure of dispersed air flotation tank is circular where there is impeller in the middle and air is fed to impeller together with water, creating bubbles. Dispersed air flotation is more often used in industrial applications to remove suspended solids and emulsified oil. Dispersed air flotation is especially for high-volumes of wastewater. Compared to DAF, dispersed air flotation has lower capital cost, smaller size and is able to remove free oil and suspended solids. There are also some disadvantages: high power requirements and only hydraulic control. (Tchobanoglous et al., 2003)

5.4 Filtration

In Figure 18 is shown the basics of the filtration system. Pressure difference is essential so that fluid moves through the filter media. Pressure difference can be achieved by pressure, vacuum, gravity or centrifugal. There are two main categories for filters: Surface filters and depth filters.

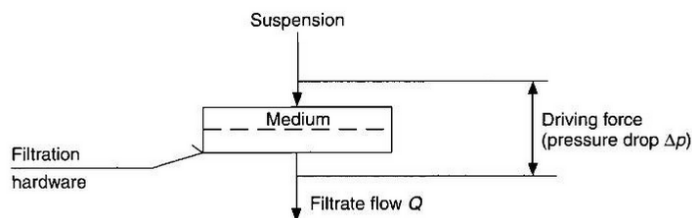


Figure 18 Illustration of the basic filtration system. (Svarovsky, 2000)

Surface filters are made of thin filter medium. On top of the filter medium a cake made of solids is formed. This type of filtering is called cake filtration. With depth filters cake formation on top of the medium is undesired. The separation is based on the fact that particles attach inside the medium and not on top. The working principle described can be seen in Figure 19. (Svarovsky, 2000)

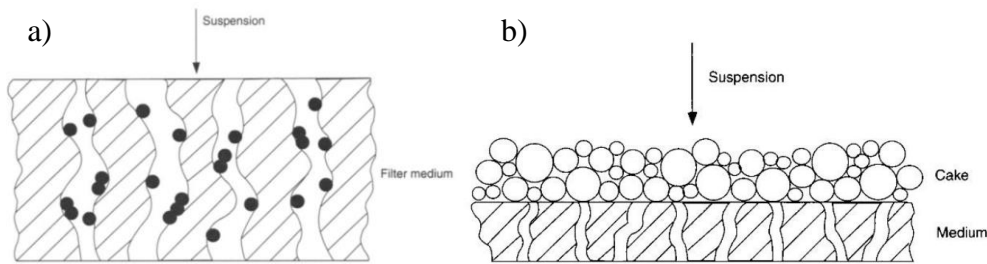


Figure 19 a) Depth filtration principle, b) Surface filtration principle. (Svarovsky, 2000)

In the surface filtration the cake formed on top acts itself as a filter medium to separate even smaller particles. Surface filters are used for separation treatments where solids amounts are more than 1 % by volume. It is essential for working of surface filters that there is enough solids in the feed. For the depth filter, particles are smaller than the openings in the medium. Depth filters are meant for treatment where there is less than 0.1 % (volume) of solids in the liquid. The openings are longer than in surface filtration medium. Depth filtration is based on electrostatic forces and forces between molecules. (Svarovsky, 2000)

Suspended solid amount in Pilot wastewater is in the range of 40-300 mg/L. The mix of TSS is both PE and PP and averagely the density of TSS is about 900 kg/m^3 . With average density of 900 kg/m^3 volumetric percentage of TSS in Pilot wastewater is 0.004 - 0.03 %. Therefore, depth filtration would be better option for Pilot plant because the amount of solids is less than 0.1 volume-%.

5.4.1 Sand filter

Sand filters are commonly used depth filters in the wastewater treatment. There are two main types of sand filtration: slow and rapid. Slow sand filtration is usually used instead of rapid filtration in small water systems. In the slow sand filtration filter media is sand with grain size of 0.25 - 0.35 mm. Slow sand filter is shown in Figure 20. (Spellman, 2014) In the rapid sand filter the grain size is usually 0.4 – 1.2 mm (Rowe and Abdel-Magid, 1995). Christensen (2003) summarises that in a bed of 0.6 – 0.75 m deepness, 0.4 -0.6 mm sand sizes are used. Because the sand particles are bigger in rapid filter, the suspension moves more quickly through the filter. Rapid sand filters are more often used in industry because the capacity of rapid sand filters is bigger. (Spellman, 2014)

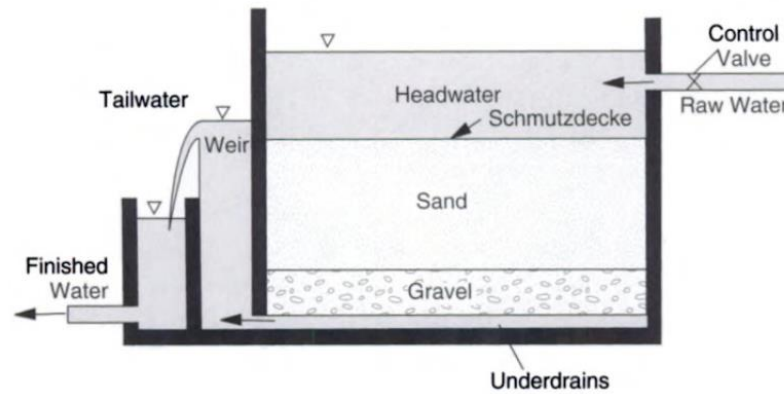


Figure 20 Slow sand filter basic principle. (Christensen, 2003)

In the rapid sand filters the medium is made of different layers of sands from fine to coarse (Christensen, 2003). Slow sand filter media are made of same kind of sand (Christensen, 2003). The slow sand filters have capacity of 170 – 570 litres per day and m^2 of filter media area. In the rapid sand filter the capacity of 614 litres per minute and m^2 of filter media area can be achieved. In the rapid sand filters the regeneration of filter happens with backwashing. In backwashing water is sprayed up the filter (opposite direction) and at the same time top of the media is agitated. Backwashing usually spends 3-7% of the water produced by the water treatment. (Spellman, 2014)

In the rapid sand filters the different types of media are placed so that on top is the coarsest material and on bottom the fines (usually heaviest). In the rapid filter the coarser suspended particles are separated on top and rest is separated in the bottom of the filter where there is finer sand. In the slow filters backwash is not used. In the selection of sand for specific application some considerations need to be done. If sand is too fine for the application, the flow of water is resisted because the system is blocked quickly. With too fine sand backwashing needs to be done more often. If the sand is too coarse, contaminants are not eliminated in the filter. In addition, it is important that hard sand is used in the filter because backwashing strains the medium and therefore softer sand can break during backwashing. (Christensen, 2003)

As previously discussed the amount of wastewater from Pilot plant is below 2400 litres when the well is full. At times when washing is happening the pump is on for hours at a time. During washing the amount of wastewater leaving Pilot plant can be maximum of 15 000

litres per hour. Therefore, rapid sand filter is preferred option for Pilot plant instead of slow filter.

Talvitie et al. (2017) researched microplastic removal from wastewater with advanced treatment methods. Talvitie et al. (2017) examined microplastic removal with rapid sand filter in Turku Kakolanmäki wastewater treatment plant. The rapid filter was using gravel with size of 3-5 mm on top in 1 m length of the bed. The rest of the bed, 0.5 m, was quartz with grain size of 0.1-0.5 mm. Talvitie et al. (2017) were able to separate 97 % of microplastics in wastewater. There were 0.7 microplastic pieces per liter of wastewater in the feed. In the outlet there was only 0.02 microplastic pieces per liter left. In the sand filtration microplastics got stuck between sand grains and adhered to the surface of sand particles. Talvitie et al. (2017) suggests that addition of coagulation could improve the sand filtration. It is to be noted that in Pilot plant the amount of microplastics is larger than 0.7 microplastic pieces per liter. TSS is on average 167 mg/L in Pilot wastewater and it is assumed that most of the TSS is plastics.

5.4.2 Disc filter

Disc filter is based on surface filtration. With disc filter Talvitie et al. (2017) separated 40.0 – 98.5 % of the microplastics from wastewater. Talvitie et al. (2017) used Pilot scale disc filter in Helsinki Viikinmäki wastewater treatment. Two tests were made on different sized filter mediums: 10 μm and 20 μm . In the 20 μm disc filter 98.5 % removal efficiency was detected when inlet amount of microplastic was 2 microplastics/liter. In the 10 μm disc filter and 0.5 microplastics/liter inlet the removal efficiency was only 40 %.

In Figure 21 is shown disc filter where there are four discs on the use. Discs in filter have the filter cloths where the separation happens. These clothes can be filter or membrane material. In the disc filter feed inlet is to the middle of discs and through suction device filtered water flows out. There is sludge collection pipe for the separated solids. In the disc filters the amount of discs can be chosen between 2 – 20 discs in designing (Jiang et al., 2014). In disc filters it is possible to have continuous backwashing.

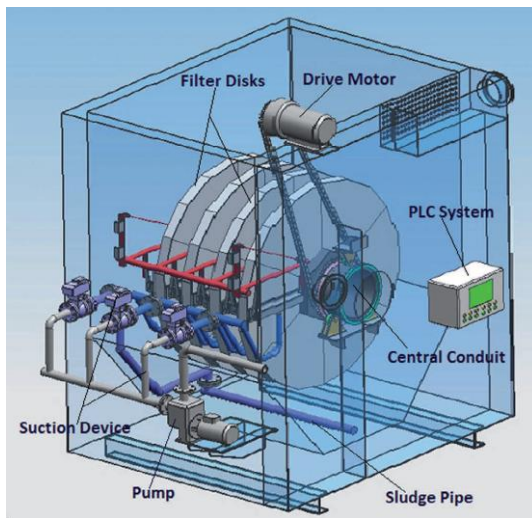


Figure 21 Disc filter. (Jiang et al., 2014)

In Talvitie et al. (2017) research disc filter consisted of two discs. In each of the discs there were 24 filter panels. In the Pilot system used in the research, coagulants were used in dosages of 3 mg/l altogether in wastewater increasing the separation. The removal was based on physical separation and cake forming. Cake was removed with high pressure backwashing when water level rose to certain level. Water level increase signaled that the cake had formed too thick and water was not getting through the filtration medium. (Talvitie et al., 2017)

5.5 Membranes

Membrane is thin “skin” which can separate certain small particles while permeating certain particles through the membrane. Membranes have many advantages and their utilization has been increasing in the separation technology. The main advantages are that they are easy to handle, have low energy requirements and no addition of chemicals is needed (Padaki et al., 2015). The membrane material can vary a lot by its morphology. As seen in Figure 22 the material can have pores or be dense. In the porous material there can have dense top layer and holes at the bottom and therefore be asymmetric. (Nunes and Peinemann, 2006), (Mulder, 1997)

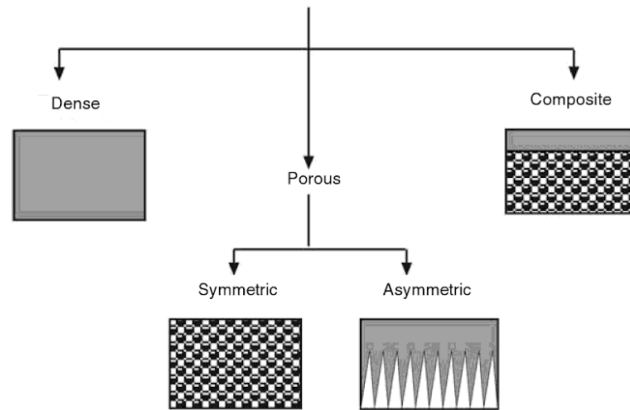


Figure 22 Different membrane material choices. (Nunes and Peinemann, 2006)

Membranes can also be classified by the driving force that the separation is based on. Driving force in membrane separation can be based on pressure, temperature, concentration or electrical potential difference. (Mulder, 1997) Membranes based on pressure difference are more often used in industrial applications. There are four main types of pressure driven membranes used: Microfiltration, ultrafiltration, nanofiltration and reverse osmosis. Figure 23 shows differences in separation between pressure driven membranes. Microfiltration is the most suitable membrane separation technique for microplastics (Figure 23). (Cui and Muralidhara, 2010)

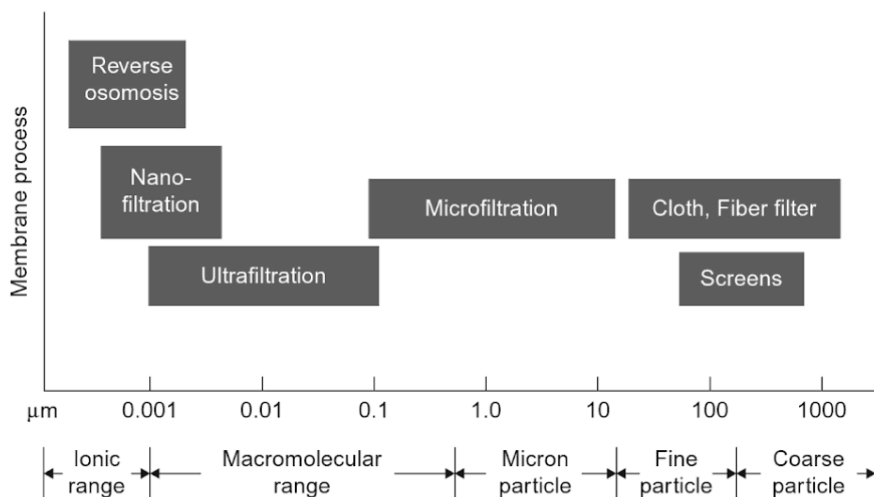


Figure 23 Membranes suitable for different sized molecules and ions. (Cui and Muralidhara, 2010)

In microfiltration symmetric or asymmetric membranes can be used. In the symmetric membrane thickness of the material is 10-150 μm and in asymmetric material the thickness is only 1 μm . The pressure applied to microfiltration membrane is very low, below 2 bars. Pore

sizes in membrane are usually 0.05-10 μm . (Mulder, 1997) Most of the contaminants ending up in Pilot wastewater are 1 mm particles of polymer powder.

Fouling is the main problem in membrane usage and important consideration in the design of membrane system. Fouling means accumulation of constituents from the feed stream on the surface or the pores of membrane. To prevent fouling right kind of membrane need to be chosen and pretreatment designed. (Tchobanoglous et al., 2003)

In Figure 24, 1) is shown different ways how fouling can happen. Fouling can be reflected as decline of flux. Flux is the amount permeating through membrane. Membrane fouling can be reduced with backflushing, Figure 24, 2). With each backflushing time the maximum flux is always smaller than before backflushing. When complete blocking happens, the whole pore is blocked by larger particles. Smaller particles can coat the insides of pores resulting in standard blocking. In intermediate and cake filtration, layer of particles builds on top of the membrane. In both cases there is still permeating happening but in cake filtration the cake narrows the pores sizes. The last oil layer blocking (e) is not official fouling mechanism but is proposed by Dickhout et al. (2017). In the oil layer blocking the particles do not block the holes but instead continuous layer of oil blocks pores. (Dickhout et al., 2017)

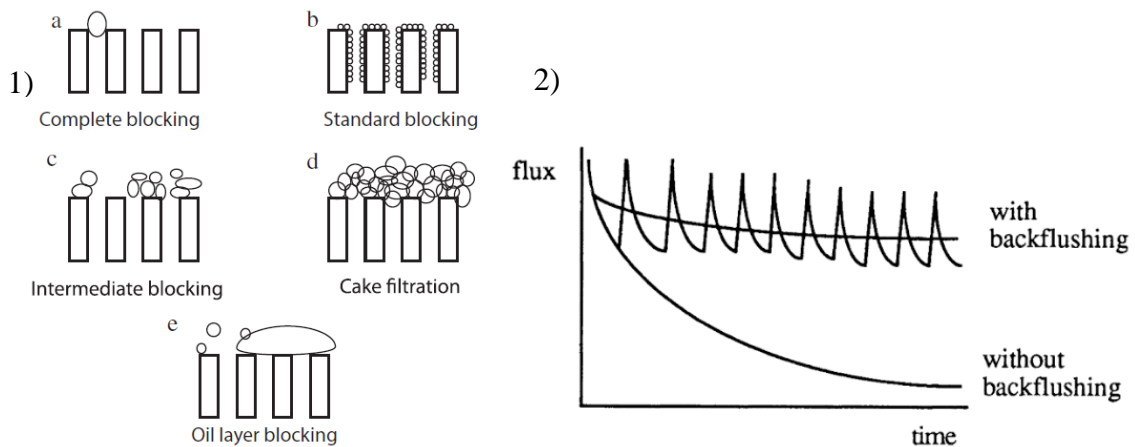


Figure 24 1) Fouling mechanisms happening on the membrane. (Dickhout et al., 2017)
2) Backflushing impact on the flux over time. (Mulder, 1997)

Membrane bioreactors (MBR) are often used in municipal wastewater treatment plants. Talvitie et al. (2017) and Lares et al. (2018) researched microplastic separation in membrane bioreactors in municipal wastewater treatment plant. In MBR reactor membrane is attached to the reactor complex. MBR is often used in secondary wastewater treatment where there is activated sludge system with membrane. The working principle is based on the fact that

while reaction is going membrane separates products at the same time. Separation of product at the same time as reaction happens increases the productivity according to Le Chatelier's principle by shifting reaction to right side. Two different types of MBR are shown in Figure 25. (Figoli and Criscuoli, 2017)

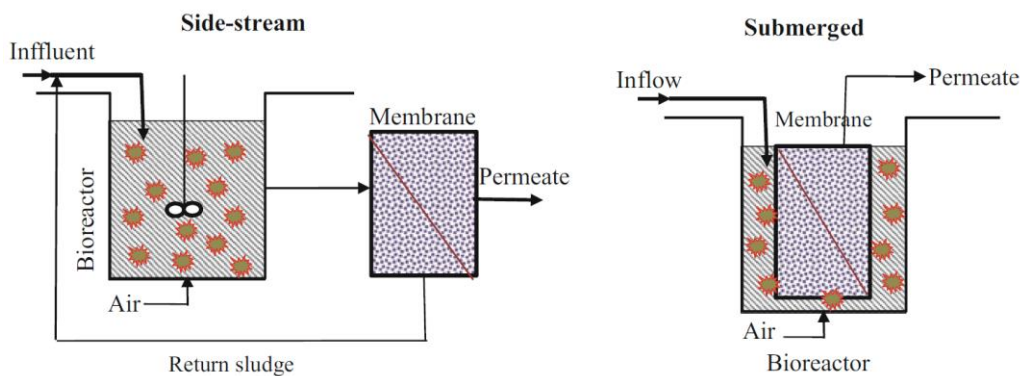


Figure 25 Membrane bioreactor (MBR) two configurations. On left side: Side-stream MBR, on right side: Submerged MBR. (Figoli and Criscuoli, 2017)

In the side-stream MBR, separation is based on pressure driven filtration separate to the reactor. In comparison, submerged MBR is based on vacuum driven filtration happening inside reactor in dead-end mode. In the side-stream MBR there is a need for recycle back to the reactor which increases energy consumption. In side-stream MBR capacity is larger (50-150 L/m²h) than in submerged MBR.

Talvitie et al. (2017) separated microplastics with efficiency of 99.9 % in MBR when feed amount was 6.9 microplastics/liter. Research was made in Mikkeli wastewater treatment plant where submerged MBR was used with ultrafiltration. Ultrafiltration membrane had pore sizes of 0.4 μm and the capacity was 40-90 L/h with hydraulic retention time of 20-100 hours.

Lares et al. (2018) used same MBR equipment in Mikkeli as Talvitie et al. (2017) and during three month period of sampling during October 2016-January 2017 researched microplastic removal. Lares et al. (2018) concluded that overall microplastics were separated with 99.4 % efficiency in ultrafiltration even during the winter months. Gurung et al. (2017) researched membrane fouling in winter months and concluded that cold weather accelerated fouling and cleaning frequency increased. In municipal wastewater treatment MBR with ultrafiltration is used for separation of other contaminants than microplastics. Michielssen et al. (2016)

researched that best possible removal of microplastics would be when granular sand filtration and membrane filtration are united.

6 Oil and organic matter separation

Yu et al. (2017) reviewed oil treatment methods for petroleum and oil industry. The main technologies that were reviewed in the article were flotation, coagulation, membranes and biological treatment. In addition, combined technologies and advanced oxidation processes were discussed. Previously mentioned techniques are especially for petroleum and oil industry wastewater. (Yu et al., 2017) In the oil and COD removal a lot of same techniques as for suspended solids are presented from oil and COD removal perspective. In Figure 26 is shown the three main ways that oil can be in wastewater.

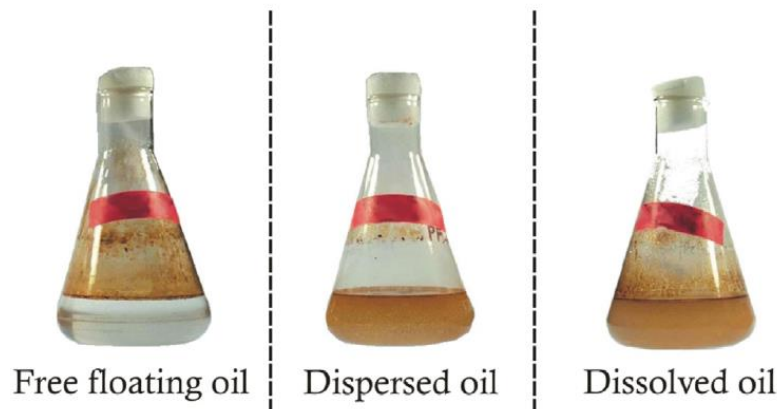


Figure 26 Three categories of oil in wastewater based on size of oil droplets. (Otitoju et al., 2016)

When comparing Figure 26 to Figure 4 of wastewater in Pilot, by appearances the Pilot wastewater seems to be containing more dispersed or dissolved oil than free floating oil. The differences between the three categories are in the oil droplet sizes. Free floating oil droplet size is $>150\ \mu\text{m}$, dispersed oil droplet size is $20\text{-}150\ \mu\text{m}$ and in dissolved oil droplet size is $< 20\ \mu\text{m}$. As previously discussed in chapter 3.3.2 the API separator at Finnish site separates only the $>150\ \mu\text{m}$ free oil droplets. In Figure 27 is shown the different sizes of oil drops and the possible separation methods for each size. Dissolved oil is same as emulsified and soluble oil.

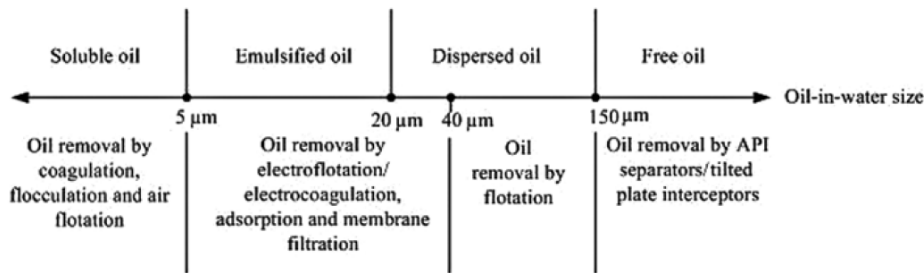


Figure 27 Different oil types and the separation methods. (Kundu and Mishra, 2017)

As concluded before all the COD in Pilot wastewater is not resulting only from oil and microplastics amounts. The COD amounts results in all the carbon in the wastewater. The sources of carbon in COD are not known. COD can be resulting from oil, suspended solids, chemicals, soil and some other unknown factors.

6.1 Flotation

Flotation is the one of the conventional oil removal methods. Flotation, DAF and jet impeller flotation can be used for oil and organic matter separation. Flotation technologies are mature and the separation of oil is stable and good. In flotation un-settleable small particles can be removed (Saththasivam et al., 2016). The main disadvantage is that usually high energy consumptions are needed in flotation and to produce small bubbles. Especially it is not cost effective to create bubbles that are smaller than oil droplets. In addition, usually coagulant is needed so that dissolved oil can be removed. (Saththasivam et al., 2016) (Yu et al., 2017)

The separation efficiency is best when more gas is used and when the bubble sizes are small. Flotation is able to reduce oil amount from 1000 ppm to 10 ppm. (Saththasivam et al., 2016) Yu et al. (2017) reviewed the removal efficiencies of oil and COD from wastewater, Table 4. Zhu and Zheng (2002) removed oil with 81.4 % efficiency. In addition the suspended solid separation was 69.2 % in the same study. Hamia et al. (2007) added DAF to activated carbon treatment and the removal rate increased from 64 % to 92.5 %.

Table 4 Oil and COD separation efficiencies in flotation. (copy from Yu et al., 2017)

Flotation type	Treatment effect	References
Flotation	Oil removal is more than 90 %	Wang (2007)
Peeling flotation	Oil removal is 81.4 %	Zhu and Zheng (2002)
DAF	COD removal rate is 92.5 %	Hamia et al. (2007)
DAF	Oil removal is more than 90 %	Al-Shamrani et al. (2002)

Flotation efficiency can be enhanced with the use of coagulants. In Table 5 is shown different cases where flotation and coagulants are used together. In addition, there is one DAF and electro-flotation process where coagulation is not used. In Table 5 is shown what kind of oils are separated in the process, what process conditions are used and the separation efficiency. In most of the methods the microbubbles were created with pressure, in electroflotation methods the bubbles are created with electric DC.

Table 5 Review of coagulation and flotation technique separation. (Copy from Van le et al., 2012)

Process	Application	Emulsified oil		Microbubbles			Oil concentration	
		Method	Size, um	Method	Size, um	Optimum conditions	Influent, mg/l	Removal %
Coagulation and DAF	Emulsion oil contain n-octane, non-ionic surfactant Tween 80	Ultrasonic	2-6	Pressure	30-120	pH 6, Ferric chloride 100 mg/l, Sodium oleate 50 mg/l	500	95
Coagulation and DAF	Non-ionic surfactant (Span 20) 0.3 % oil and deionized water	Mixing	-	Pressure	-	pH 8, Aluminium sulfate 100 mg/l, pH 7, Ferric sulfate 120 mg/l	1630	>90
Coagulation and DAF	Mixing lubrication oil, cooking oil, ghee and mixture of all	Mixing	-	Pressure	-	pH 5-6, Alum 2.5 mg/l, Polymer 1.25 mg/l	50-500	85
Flocculation and electro-flotation	Cutting oil (80% mineral oil, 10 % surfactants, 10 % others	-	-	Electric DC	-	pH 8.6, Aluminium sulfate 200 mg/l, Ferric sulfate 200 mg/l	10000-40000	99
On-line flocculation-flotation	Synthetic emulsion oil	-	10	Pressure	-	pH 6, Polyacrylamide 2 mg/l, Ferric hydroxide 50 mgFe/l	695	>90
DAF	Synthetic emulsion oil from dehydrated and degassed crude oil	Mixing	0.4-100	Pressure	-	pH 6-9, Sodium dodecyl sulfonate 10 mg/l, Polyaluminium chloride 30 mg/l, Polyacrylamide 15 mg/l	100	>90
Electro-flotation	Crude oil	Mixing	-	Electric DC	-	pH 4.72, Salinity 4 mg/l	50	94
Coagulation and modified induced air flotation	Synthetic emulsion from palm oil, tap water and anionic surfactant	Mixing	-	Pressure	-	pH 8, Alum: 800-1400 mg/l	10000	94-97

As seen in Table 5 the efficiencies in coagulation-flotation systems are often over 90 % depending on the influent concentration. In flocculation-electroflotation the feed concentration was over 10 000 mg/L and the efficiency was 99 %. In coagulation-DAF system where feed amount is 50-500 mg/L the efficiency is less, 85 %. (Van le et al., 2012) There are differences between the processes but when there is less contaminants in wastewater it is harder to get high efficiency values.

In the study Van le et al. (2012) evaluated three systems: flotation without coagulant, flotation with polyaluminium chloride (PAC) coagulant and flotation with cetyltrimethylammonium chloride (CTAC) as cationic surfactant. The feed oil concentration was 1000 mg/L of dissolved oil. Best removal efficiency was detected with flotation with PAC with 90 % efficiency. With CTAC the removal efficiency was 82 % with 0.5 mg/L. It was noted that with pH reduction to 3-4 the flotation without coagulant efficiency increased from 10 % to 70%. It is to be noted that when using coagulants more chemicals are inserted to wastewater. 50 mg/L PAC was added to wastewater. (Van le et al., 2012) In Pilot plant wastewater amount is below 100 m³/month and therefore needed PAC amount would be maximum of 5 kg/month for Pilot wastewaters.

6.2 Membranes

In the oil separation microfiltration (MF) and ultrafiltration (UF) membranes have been proven to be efficient separation methods. MF has higher initial flux than ultrafiltration because of the larger pore size. On the other hand, UF has smaller pore size and separates oil more efficiently. (Otitoju et al., 2016) Advantages, disadvantages and efficiency of the two types of membranes are considered in this chapter. Overall, Yu et al. (2017) summarizes that usually only one membrane is not good and efficient solution to oil separation. In oil separation either a combination of different membranes or combining membrane separation to conventional wastewater treatment methods is best option for oil removal.

Table 6 shows different studies made on oil separation with membranes. As seen in Table 6 high oil removal efficiencies were achieved with MF, UF and dynamic membrane. In the Hua et al. (2007), Salahi et al. (2013) and Sarfaraz et al. (2012) researches COD and TOC (total organic carbon) removal efficiencies were studied. COD and TOC amounts represent oil separation in the researches. (Yu et al., 2017) When oily waters are researched it is assumed that most of the carbon has been in oil form in the wastewater.

Table 6 Review of membrane technologies for oil, COD and TOC separation. (copy from Yu et al., 2017)

Membrane separation technology type	Treatment effect	References
UF	Oil content is below 1 mg/l	Yu et al. (2006)
MF	Oil removal is 97 %	Song et al. (2006)
Dynamic membrane	Oil removal is 99 %	Yang et al. (2011)
MF	TOC removal is 92.4 %	Hua et al. (2007)
MF	Oil removal is 99 %	Cui et al. (2008)
Nano-porous membrane	COD removal is 76.9 %	Salahi et al. (2013)
Nano-porous membrane-powdered activated carbon	TOC removal is 71.5 %	Sarfaraz et al. (2012)

MF is usually preferred option for oil separation because the fouling is not as much of a problem as in UF. As seen in Table 6 the MF applications have also high efficiencies. Song et al. (2006) used low cost MF membrane with pore size of 1 μm , $p= 1000$ kPa and flow rate of 0.1 m/s. As a result, oil amount in permeate was less than 10 mg/L and the overall removal efficiency was 97%. (Song et al., 2006) Hua et al. (2007) removed TOC with ceramic MF membrane with 50 nm pore size and efficiency of 92.4 %. Cui et al. (2008) separated oil with efficiency of 99 % with NaA zeolite MF membrane. In Cui et al. (2008) research permeate had less than 1 mg/L oil concentration with relatively high capacity of 85 L/m²h.

Ceramic membranes have been researched a lot for oil separation because of their good properties compared to polymeric membranes. Ceramic membranes have often asymmetric structure with visible top layer and they are less hydrophobic than polymeric membranes. Hydrophilicity is desired property in water treatment membranes because with hydrophilic membrane water permeates more easily and non-polar contaminants like oil are rejected. Often Al₂O₃ or TiO₂ materials are used in ceramic membranes. (Ihksan et al., 2017) Dickhout et al. (2017) concluded that ceramic membranes are most often used in oil separation applications because of their resistance to high temperatures, chemicals and effective cleaning methods. In addition, ceramic membranes are reliable and have high operation safety (Ihksan et al., 2017). The durability and hydrophilicity of ceramic membranes makes them good option for industrial applications.

Das et al. (2017) prepared kaolin based ceramic MF membranes. Membranes prepared were low in cost. In the study best separation efficiencies were achieved when feed oil concentration was high and pressure low. Best separation efficiencies (95 %) were achieved when 250 mg/L oil feed amount was separated with 138 kPa pressure difference. With 100 mg/L to 150 mg/L feed oil amount the removal efficiency was 75-90 %. (Das et al., 2017)

UF membranes can separate oil at high efficiencies but the main problem in operation is the fouling. Fouling is one of the main reasons for industries not to use UF membranes. (Munirasu et al., 2016) In Table 7 is shown review of ultrafiltration membranes combined with different technologies in industry.

Table 7 Separation efficiencies with ultrafiltration combined with different technologies.

Membrane	Oil	COD	Other	Flux, L/m ² h	Reference
UF (PES + PVP)	99.7	83	TSS: 100%	84	(Salahi et al., 2015)
Ceramic UF+ disc filter	> 99 %	> 98%	-	198-250	(Ebrahimi et al., 2013)
Ceramic UF+ coagulant	-	-	Turbidity: 99%, TOC: < 20 %	120	(Loganathan et al., 2015)
UF +MF, MF+MF	-	-	Turbidity: 97- 100%, TOC: 10-17 % TSS: 100%	Max. 60 kg/m ² h	(Jiang et al., 2013)

Salahi et al. (2015) used polyethersulfone (PES 17 wt-%) and of polyvinylpyrrolidone (PVP 2.5 wt-%) mix in polymeric membrane for process water treatment. PVP was added to the PES to increase hydrophilicity and in conclusion high removal rates were achieved. Ebrahim et al. (2013) researched ceramic (Al₂O₃) disc membranes with both micro- (0.2 µm) and ultrafiltration (7 nm). In the research similar results were achieved with both MF and UF membrane in a disc filter. In the usage of disc filter, two rotational speeds were used 1200

and 1800 rpm. Study concluded that higher speed flux is higher (250 L/m²h) and the fouling decreased.

Loganathan et al. (2015) researched coagulation as a pretreatment method for UF membrane. High turbidity removal rates were detected and flux was higher because of pretreatment. Jiang et al. (2013) studied MF and UF and two MF combined in water treatment. TSS and Turbidity removal was almost the same for all combinations. The differences came from TOC removal and flux. MF & UF combination removed 17 % of TOC compared to 10 % of two MF membranes. Two MF (1.4 µm and 0.2 µm) membranes had the best flux values (60 kg/m²h), 3.5 times bigger than MF & UF. The price of UF is double the price of MF membrane. Therefore, for industrial application it would be more cost efficient for oil separation to use two MF membranes in series rather than UF membrane. It is estimated that the cost of two MF membranes unit in water treatment would be 4.3 euros/m³ wastewater treated. (Jiang et al., 2013) On the other hand MF is not able to remove dissolved oil as efficiently as UF (Saththasivam et al., 2015). If most of the oil in Pilot wastewater is dissolved then UF is better choice.

In Pilot high removal efficiency is required for oil removal because the selected limit for releasing oily water is 4 ppm. With separation efficiency of 90 % (e.g Das et al., 2015) the required below 4 mg/L oil contamination is not reached in Pilot plant if the feed oil concentration is more than 40 mg/L. In Pilot plant, the oil amounts have been maximum of 135 mg/L. This means that overall the separation efficiency need to be > 90 %. High removal efficiency needs to be taken into account when choosing separation method. One step MF membrane is not often efficient enough on its own. Therefore, MF combined with conventional technique or other MF membrane could be more efficient solution for the plant. In addition, COD which is not suspended solids or oils need to be taken into account. Membranes have high removal efficiency for other carbon constituents too.

6.3 Adsorption

Adsorption is a phenomenon where contaminants are accumulated or concentrated on the adsorbing particles. Adsorption happens because of the surface reactions. Surface reactions are a result from forces within phase or surface boundaries. Surface tension at the liquid phase surface is a result of attractive forces between liquid molecules. Liquid has smaller attractive forces for the solute (contaminant) than for each other. Therefore, the solvent that

decreases surface tension is concentrated on the surfaces. For wastewater applications, adsorption often happens in solid-liquid phases but adsorption can happen between other phases as well. (Cecen and Aktas, 2012)

Activated carbon is the most commonly used adsorbent in industrial applications because of the porous structure and large specific surface area (Kundu and Mishra, 2017). Adsorption is used as a tertiary or advanced treatment step. Activated carbon adsorption is used as a method to separate refractory organics.

Activated carbons are porous carbonaceous adsorbents. Activated carbon can remove by porous surface large amounts of aromatics, phenolics, hydrocarbons, ketones, esters, ethers and alcohols. (Cecen and Aktas, 2012) Rajak et al. (2018) separated oil with 98 % efficiency by using activated charcoal from saw-dust adsorption. The adsorption of oil with activated carbon was modelled best with Freundlich isotherm.

Adsorption capacity for one cycle with activated carbon is 0.25-0.87 kg COD/kg carbon adsorbent. After cycle, regeneration happens by using steam, high temperature or solvent extraction. In wastewater application thermal regeneration is often used. (Ranade and Bhandari, 2014) There are many advantages in adsorption process in addition to high removal efficiency. Adsorption is capable to process varying flow rates and contaminant amounts. Adsorption process is mature process which has flexibility in design and operation. The effluent from adsorbent process is usually so clean that it can be reused. (Sharma and Sanghi, 2013)

There are still many things that need to be developed when using adsorption. Adsorbents used need to be developed towards cost effective solutions in a way that they are more tailor made for specific contaminants. The regeneration needs more efficient solutions because with every cycle the capacity decreases. The main disadvantage in adsorption is that the used adsorbent is hazardous waste and therefore the reusing should be developed. In addition, adsorbents are still expensive and the process has high capital cost. (Ranade and Bhandari, 2014)

Adsorption is also efficient method for metal removal. In Pilot wastewater there were metals in wastewater. Especially zinc levels were too high. In Figure 28 is shown different activated carbon adsorbents and the removal efficiencies of the methods. Activated carbon is cheaper

than many other adsorbent but still activated carbon from coal is expensive. Therefore activated carbon is acquired from cheaper options. (Renu et al., 2017)

Adsorbent derived from	Metal concentration (mg/L)	Optimum pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorbent capacity (mg/g)	Removal per cent (%)
Acrylonitriledivinylbenzene copolymer	30	2	Freundlich	420	0.6	101.2	80%
<i>Syzygium jambolanum</i> nut carbon	20–100	2	Langmuir	240	5	–	100%
Green alga <i>Ulva lactuca</i>	5–50, 5–250	1	Langmuir	40	2	10.61 112.36	98%
Jatropha wood	30–100	2–10	Langmuir	360	0.6–2	106.4–140.8	–
Tamarind wood	10–50	6.5	Langmuir Freundlich	40	2	–	28%
<i>Pterocladia capillacea</i>	5–100	1	Langmuir	120	3–10	66	100%
<i>Zizania caduciflora</i>	10–50	2–3	Freundlich	48	0.8	2.7	84.8%
Prawn shell	25–125	–	Langmuir Freundlich	31.4	–	100	98%

Figure 28 Chromium separation by activated carbon adsorbents derived from cheaper alternatives. (Renu et al., 2017)

7 Selection of the separation methods

The main contaminants in plastic factories are plastics in the form of polymer and pellets, oil and organic matter. Organic matter results in high COD results. Plastics and oil are also organic matter but do not result the whole COD amount measured. All the plastic in Pilot can be classified as microplastics because they are below <5 mm in size (Felsing et al., 2018), (Sun et al., 2019), (Gatidou et al., 2019), (Prata et al., 2019). It can be assumed that almost all the TSS is result of microplastics in wastewater.

In Table 8 is shown summary of the chapter 5 where suspended solids separation was studied. In Table 8 average separation efficiency, advantages and disadvantages are listed for each technology. Coagulation, screens and sedimentation are not good selections for microplastic separation. Coagulation is used mainly as a pretreatment technology but could enhance the next separation step. Screens are used mainly for large amount of municipal suspended solids and are not suitable for microplastics. Sedimentation is not suitable because most of the suspended solids at plastic factories do not sediment without chemical addition.

Table 8 Comparison between separation methods for solid separation.

Technology	Average separation efficiency	Advantages	Disadvantages
Coagulation	27 % of MP (d<0.5 mm) (Ma et al., 2019)	+ Increase of particle size → simple separation in next step	- Chemical usage - Cannot be used alone - Extra step to separation - Pre-treatment method
Micro- & fine screens	25-45 % municipal TSS (Tchobanoglous et al., 2003)	+ Large amounts can be handled + Mature technology	- No research in MP removal
Sedimentation	50-70 % of municipal TSS (Tchobanoglous et al., 2003)	+ Mature technology + Large volumes can be processed	- Land usage - No research for MP
Flotation	95 % MP in DAF (Talvitie et al., 2017)	+ MP and oil removal in same operation + Mature technology + Large volumes can be processed	- A lot of energy needed for creating small bubbles - Land usage
Filtration	97 % MP in rapid sand filter (Talvitie et al., 2017)	+ High efficiency + Relatively cheap	- Backwashing needed
Membranes	99.4 MP with UF membrane (Lares et al., 2018)	+ High Efficiency + Can remove MP and other contaminants efficiently + Small area is needed	- Fouling - Cold weather accelerates fouling

Membrane separation can separate efficiently solid particles in micro and nanoscale. The main disadvantage and problem in membrane technology is fouling. In the wastewater in Particle sizes of MP can vary from 75 μm to 3 mm and the membranes separate particles < 10 μm . Membrane however is considered expensive compared to other solid-liquid separation techniques.

Flotation (DAF) and filtration (rapid sand filter) could possibly be the best possible separation techniques for Pilot wastewater MP removal. Both techniques have high removal efficiency of MP. There is already flotation pond in Finnish site water treatment system. With

updating the pond or replacing the flotation pond with DAF the system efficiency could increase drastically. Flotation can separate MP, oil and organic matter. Filtration and especially depth filters are possible choice for the MP separation. Depth filters are usually cheaper option than flotation but since there is already flotation pond in treatment, the enhancements could be cost-effective compared to filters.

In Table 9 is shown oil and organic matter separation technologies. Flotation can be used for removal of solids and oils. DAF has high removal efficiency for oil but dissolved oil separation is not efficient without coagulant. Membrane separation and adsorption are more advanced separation technologies for oil and COD removal. They are also more expensive alternatives. MF membranes are two times less expensive than UF membranes (Jiang et al., 2013). UF membranes are more efficient in removing dissolved oil and smaller particles but are more prone to fouling. It was concluded that two MF membranes in series might be a good choice for oil and COD separation. Ceramic MF membranes are best suited for oil and COD removal with good separation and less fouling in operation.

Table 9 Comparison of separation methods for oil and COD.

Technology	Average separation efficiency	Advantages	Disadvantages
Flotation	>90 % oil DAF (Al-Shamrani et al., 2002)	+ Low maintenance cost + Moderate equipment cost	-Dissolved oil removal not efficient - A lot of energy needed for microbubbles
Flotation+ coagulation	90-99 % oil DAF +coagulant (Van le et al., 2012)	+ Dissolved oil removal increases with the use of coagulant	- Sludge disposal - Chemicals addition
Membrane	97-99 % oil MF (Yu et al., 2017)	+ High efficiency + Small area is needed	-Fouling -Cost
Adsorption	80-100 % activated carbon (Renu et al., 2017)	+ High efficiency + Can separate metals	-Adsorbents and process expensive - Adsorption model needs to be known

Adsorption with activated carbon is efficient way for oil separation, COD reduction and can also separate some of the metals. Adsorption treatment has high capital cost. Membranes

and adsorption are usually used as tertiary treatment. The most efficient way of using membranes and adsorption is to separate solids before to decrease fouling and regeneration.

In Figure 29 is shown three possible processes for wastewater system. The first system is for the case where the wastewater is purified at the Pilot plant. With first system it is assumed that after wastewater has been purified it can be released straight to sea and it is not profitable to mix it with other plants wastewater in flotation pond.

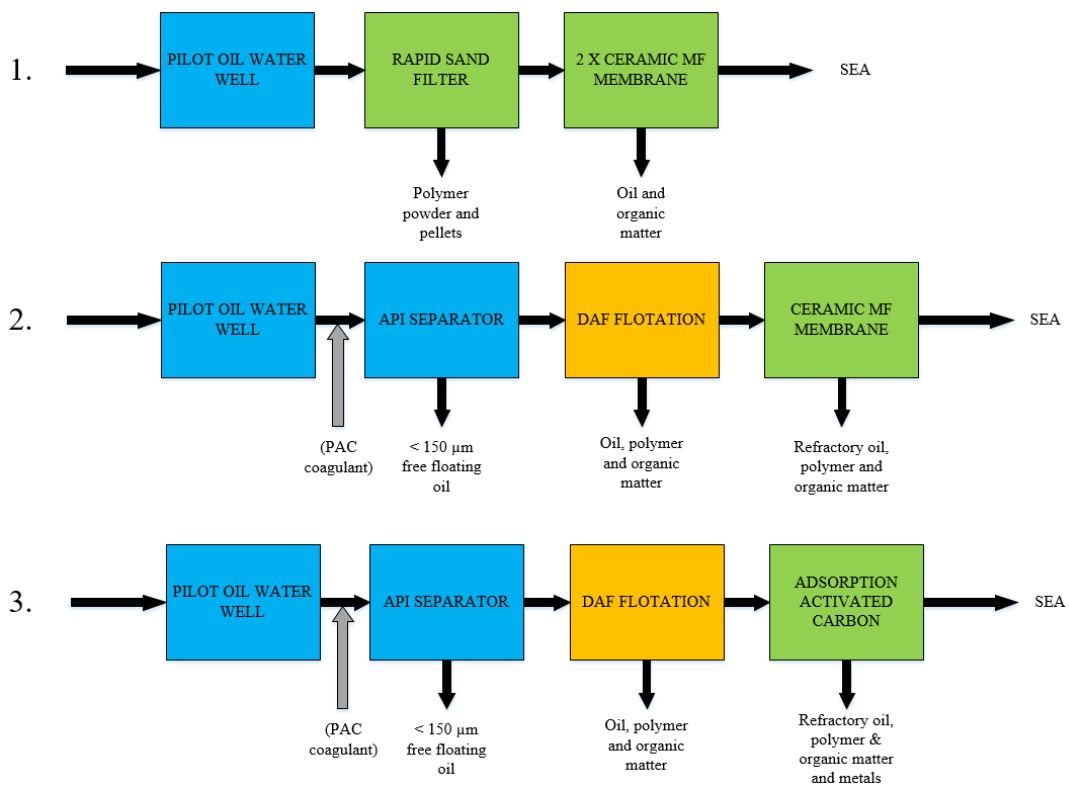


Figure 29 Three possible configurations of the wastewater treatment. Blue = old system, Green = New system, Yellow = Enhancement to old system.

Second and third system are the same except that the last step can be either adsorption or membrane unit. In both of the systems there would be no added separation unit in Pilot. Coagulant addition is on grey because it could be added as an extra step to make API and flotation more efficient. In the systems old flotation unit would be enhanced by adding aeration or replacing it with DAF unit. After membrane/adsorption unit water could be released to the sea. Fourth possible option would be adding filter to the Pilot plant for solid separation and then leading rest of the wastewater through enhanced location wide system.

8 EXPERIMENTAL PART

In the experimental part objective was to filtrate wastewater in two steps and analyze the difference after filtrations. First filtration step was vacuum filtration where the objective was to separate solid material from wastewater. Membrane separation step objective was to separate oil and other organic matter. Three different filtration cloths were used in first separation. In second separation step two different cellulose membranes were used. COD, oil and TSS were analyzed before and after separations. Filtration experiments were done for samples taken from Pilot plant wastewater well on 11 days (19.3, 27-28.3, 8.4, 17-18.4, 25.4, 13-14.5, 22-23.5).

9 Materials and methods

In materials and methods chapter chemicals and methods for filtrations and analyzing methods are introduced.

9.1 Materials

In the Table 10 the chemicals used in experimental part are shown. In the oil amount analysis florisil and sodium sulfate were used in sample preparation. Decane, n-tetracontane, diesel and mineral oil were used in standard preparation for oil analysis. N-Pentane was used for oil extraction from water in oil analysis. Sulfuric acid was added to some of the wastewater samples for preservation.

Table 10 Chemicals used in the sample preservation and analysis.

Chemical	Molar mass, g/mol	Company	Lot number	Other information
Florisol Activated MgO ₃ Si	100.39	Sigma-Aldrich	BCBW0450	Coarse powder, 60-100 mesh, pretreatment: 16h in 140 °C
Decane C ₁₀ H ₂₂	142.29	Sigma-Aldrich	MKBN8296V	Purity ≥ 99%
Diesel no-additives	-	-	-	-
Mineral oil no-additives	-	-	-	-
N-Tetracontane C ₄₀ H ₈₂	563.10	ACROS Organ- ics	A015146701	Purity 98 %
N-Pentane CH ₃ (CH ₂) ₃ CH ₃	72.15	Baker Grade	-	-
Sodium sulfate Anhydrous Na ₂ SO ₄	142.04	J.T Baker	1428601833	
Sulfuric acid H ₂ SO ₄	98.08	-	-	Concentration 4.5 mol/l

9.2 Filtration

Filtration and analysis steps used are shown in Figure 30. As seen from Figure 30 COD, oil amount and TSS were measured before and after steps. In vacuum filtration three filtration cloths were used: ARTOT20, ARTOS11 and MAROS21. Filter cloths are made by Outotec. The air permeating flux through filter cloths were measured with flow transmitter where 2 cm air column was formed in water. Air column represented the pressure difference. Air fluxes are shown in Figure 30. ARTOT20 was the tightest of the cloths.

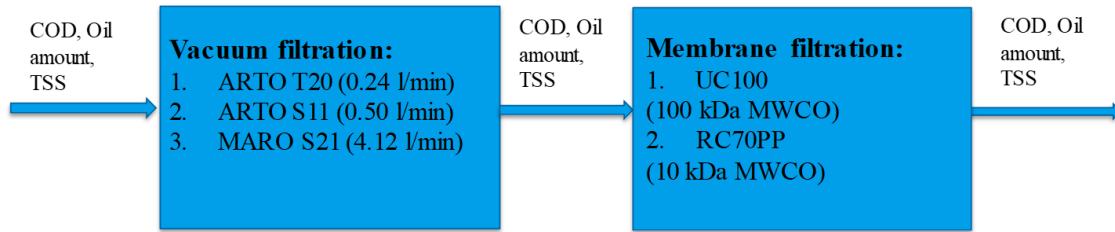


Figure 30 Filtration and analysis plan.

Membranes used in second separation step were cellulose membranes. Membranes were chosen because of the hydrophilic nature of cellulose. Ultrafiltration cellulose membranes are made from two parts: structural and cellulose part. Cellulose part is making the membrane more hydrophilic. Ceramic membranes cannot be tested in small laboratory scale. UC100 membrane from Microdyn Nadir GmbH has 100 kDa molecular weight cutoff (MWCO) value. RC70PP membrane from Alfa Laval has 10 kDa MWCO. MWCO means lowest molecular weight where 90 % of solute is retained (Luis, 2019).

Wastewater samples were taken from oil water well in Pilot always at 7:30 am. When taking samples the wastewater line was recycled back to the well in order to make the samples homogeneous. Samples were taken in 3-5 one liter glass bottles. Some of the wastewater samples were preserved with addition of sulfuric acid so that pH was approximately 2. Sulfuric acid was added 10 ml per liter of sample. Most of the samples were treated with sulfuric acid. Sulfuric acid was not added to some of the samples for comparison. Sulfuric acid addition was done at the site and transferred to the filtration location. During transfer, the samples were at room temperature for one day. After transfer all samples were stored in freezer.

9.2.1 Vacuum filtration

Vacuum filtration was carried out with equipment (Bühner vacuum filter) shown in Figure 31. Before filtration samples were melted to 20-25 °C temperature. During the experiment, initial wastewater was poured out on the feed tank shown in Figure 31. Feed tank was in normal air pressure and temperature. Vacuum was turned on and hand valve was opened. Filtrate poured to the container on scale where it was collected. Filtration cloths were reusable and could be washed with water. Filtration cloths were washed with water between each of the filtrations. Samples were taken before and after filtration.

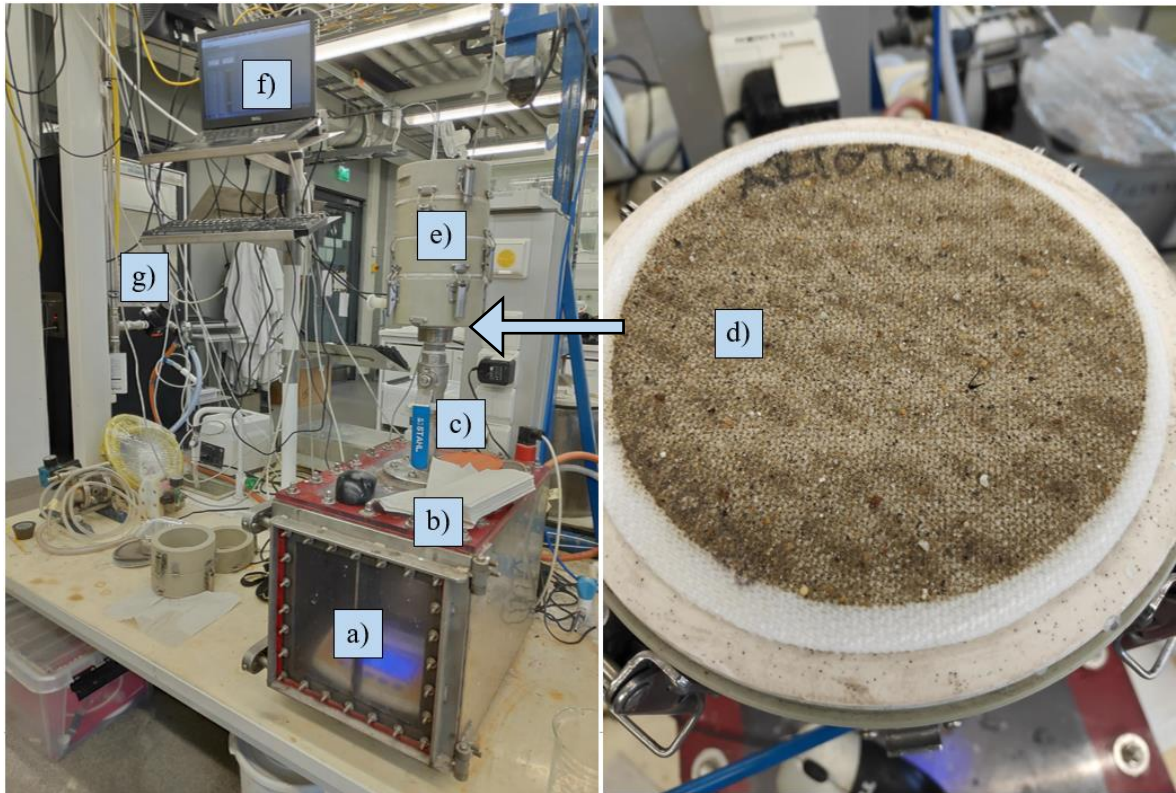


Figure 31 Bühner vacuum filtration equipment. A) Scale where filtrate is collected b) Vacuum box c) Hand valve d) Filtration cloths (after filtration) e) Wastewater feed tank f) Data collection system pressure and weight of filtrate g) pressure controller

The amount of feed slurry varied between 500-1300 ml. Each of the samples were filtered with three different filtration cloths.

9.2.2 Membrane filtration

Membrane separation for vacuum filtered wastewater was executed in dead-end Amicon laboratory scale filtration equipment. Amicon equipment can be seen in Figure 32.

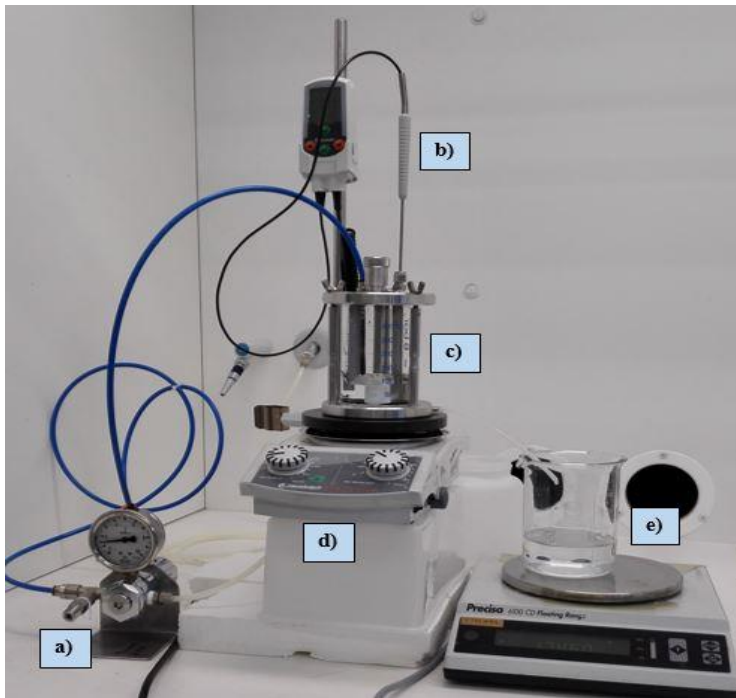


Figure 32 Amicon dead-end filtration unit. a) pressure controller, b) temperature meter, c) filtration tank, d) mixer (Heidolph MR Hei-Standard), e) Scale (Precisa 3100 CD Floating range)

Membranes (UC100 and RC70PP) were stored in fridge before cutting for preservation. Membranes were prepared by cutting them to 76 mm diameter circles to fit the Amicon equipment. After cutting, membranes were put into deionized water and ultrasound equipment for an hour. Ultrasound was stopped and deionized water changed couple of times during the procedure. Ultrasound removes glycol layer that the membranes have been layered with for preservation purposes. After ultrasound treatment membranes were stored in deionized water in fridge for maximum of seven days.

After pretreatment of membranes they were used on bottom of filtration tank. Filtration tanks size was 250 ml and therefore the feed amount was 250 ml in every filtration. Mixing speed in tank was 250 rpm in every experiment. Temperature in filtrations were 20-25 °C. Before actual filtration, the membrane was pressurized to 3 bars with deionized water. After pressurizing, deionized water flux experiment was conducted.

Water flux determination was carried out at four different pressures (1, 1.5, 2.0, 2.5 bar). Permeate mass information was collected after 1 minute of filtering at each pressure. After ionized water flux determination, wastewater was filtered. Flux determination for

wastewater was conducted in the same way as for deionized water. During wastewater filtration, permeate sample was collected during 2 bar flux. With RC70PP 15-25 g wastewater was permeated before sample collection. With UC100, 50-60 g wastewater was permeated before sample collection. Around 200 ml of filtered wastewater permeate was collected. Around 50 ml of concentrate stayed in filtration tank and was collected for sample in some filtrations. Fouling was tested by deionized water flux after wastewater filtration. In between the filtrations membrane was washed with water. Membrane filtration fluxes are shown in APPENDIX I.

9.3 Analysis

Total suspended solids were analysed using Büchner funnel. Filter paper used in Büchner was Glass Microfiber Filter GF/A 1.6 μm (Diameter 90 mm, Whatman). In the analysis 250 ml of wastewater was filtered through Büchner. After the tests, the filtration paper was in oven (105 °C) for an hour. Papers were put in desiccator for ½ hour before weighing. Weight was measured on a scale with accuracy of 0.01 mg.

Chemical oxygen demand was analysed using COD tubes (Merck Spectroquant). Commercial tubes have reagents ($\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4) and catalyst (Ag_2SO_4) already in them. Tubes oxidize the organic material injected changing the color of the liquid. Two kinds of tubes were used: <1500 mg/l and <15 000 mg/l. To the 1500 mg/l tubes 2 ml of sample was added. To 15 000 mg/l 200 μl of sample was added. After addition of sample, tubes were put in 150 °C COD reactor (Hach) for two hours. Before the COD measurement, samples were cooled down for ½ hour. Spectrophotometer (HACH DR/2010) with 620 nm wavelength was used for measurement of the samples. Deionized water was used as a zero sample.

Oil amount was analysed with method that was adjusted from standard SFS-ENISO9377-2 (Standards Finland, 2001). Gas chromatography was used as an analysis equipment for samples. Gas chromatography equipment is shown in Figure 33. Detector used in the analysis was flame ionization detector. Carrier gas used was hydrogen from laboratory scale hydrogen generator and make-up gas used was nitrogen.

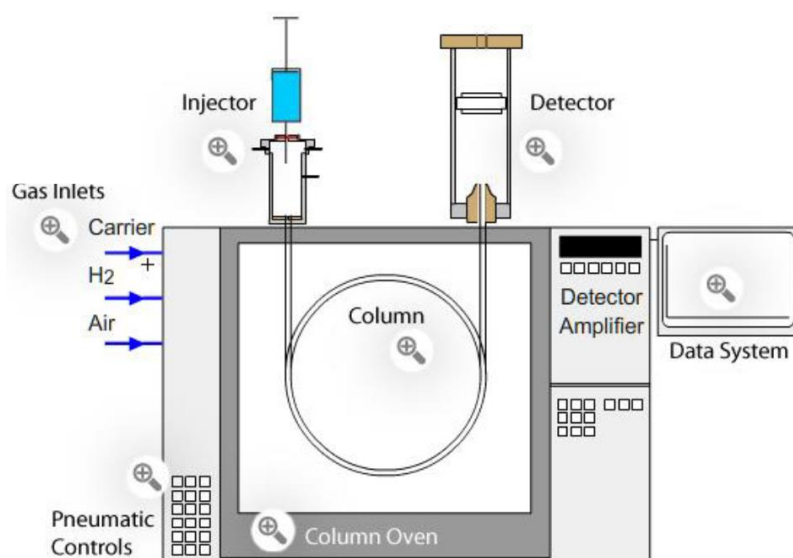


Figure 33 Gas chromatography equipment. (CHROMacademy, 2019)

Column specifics can be seen from Table 11. Oil analysis was run with method where the initial temperature is 31 °C where the temperature is ramped up by 10 °C at a time to 360 °C.

Table 11 Gas chromatography column information

Column	HP-1/SIMDIST
Length, m	15
Diameter, mm	0.53
Film, μm	0.15
Temperature limits, °C	-60 - 320
Part number	19095Z-221
Serial number	USB482713B

There were two standards used in oil analysis: standard A and standard B. In standard A mineral oil and diesel were mixed with n-pentane. In standard B decane (C₁₀) and n-tetracontane (C₄₀) were mixed with n-pentane. C₁₀ and C₄₀ were used as limit peaks and oil amount was measured from the peaks between limits. The concentrations of used standards are shown in Table 12. As seen from Table 12 standard B has two different concentrations. Standard B was prepared two times between analyses. The different concentrations have been taken into consideration in calculations.

Table 12 Standard A and B concentrations. Standard B was prepared two different times therefore two mixes have different concentrations.

Standard A	
Mineral oil, mg/l	275
Diesel, mg/l	263
Standard B	
1. C10 mg/l	645
1. C40, mg/l	525
2. C10, mg/l	1752
2. C40, mg/l	500

Calibration samples were run with each of the analysis. Calibration samples were mix of standard A and B in different rates. Standards A/B were mixed in five different rates: 0.3, 0.4, 0.6, 0.7 and 0.8. In Figure 34 is shown standard mixes and standard B as a baseline.

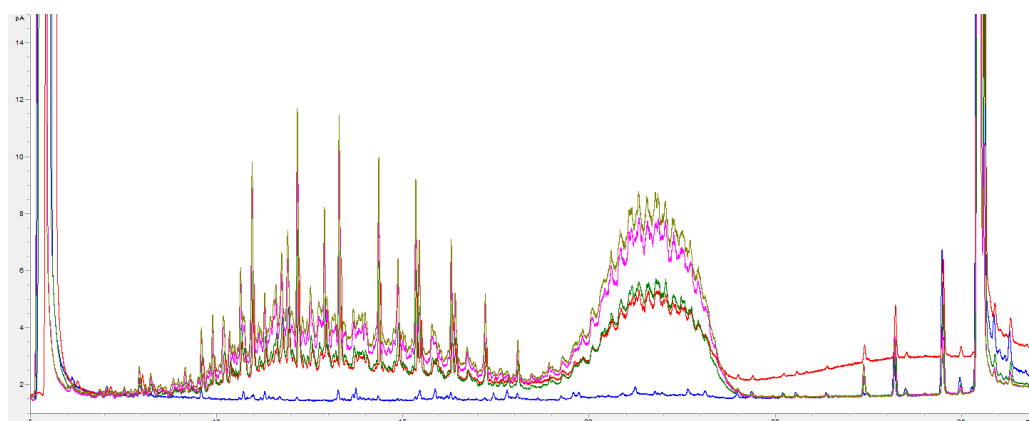


Figure 34 Standard graphs from gas chromatography (Hewlett Packard GC system HP6890 system). Blue=standard B, Red=0.3, Dark green=0.4, Pink=0.6, Light green=0.7.

Samples were prepared by adding 100 μ l of standard B to 4 ml of wastewater sample. Oil was extracted from water by 4 ml n-pentane. Extraction was done in test tubes that were shaken in 400 1/min rotary shaker for 45 minutes. After extraction clear phase difference was formed and the top layer containing pentane and oil was removed. Florisil (5mg) and Na_2SO_4 (5mg) were added to the extracted pentane and oil phase. Florisil removes polar substances from sample (Standards Finland, 2001). After one hour time samples were analysed.

10 Equations

TSS was calculated using equation 1.

$$TSS = \frac{(b-a)*1000}{v}, \quad (1)$$

where	<i>TSS</i>	total suspended solids, mg/l
	<i>b</i>	mass of filter after wastewater filtration, mg
	<i>a</i>	mass of filter paper before filtration, mg
	<i>v</i>	wastewater sample amount, ml

Fluxes from membrane filtrations were calculated using equation 2.

$$J = \frac{V}{A \cdot t}, \quad (2)$$

where	<i>J</i>	Flux, l/m ² h
	<i>A</i>	Filtration area, m ²
	<i>t</i>	Filtration time, h
	<i>V</i>	Filtered permeate volume, m ³

Filtration efficiencies were calculated with equation 3.

$$E = \frac{C_i - C_f}{C_i}, \quad (3)$$

where	<i>E</i>	Filtration efficiency, %
	<i>C_i</i>	Initial COD/oil amount, ppm
	<i>C_f</i>	COD/oil amount after filtration, ppm

Oil amounts were calculated using equation 4.

$$C_{oil} = \frac{k \cdot C_{c40}}{\frac{c40 \text{ peak}}{oil \text{ peak}} - b}, \quad (4)$$

where	C_{oil}	Oil amount, mg/l
	C_{c40}	Standard n-tetracontane (c40) amount, mg/l
	C40 peak	N-tetracontane (C40) peak area from gas chromatography, -
	Oil peak	Oil peak area from gas chromatography, -
	k	Slope of standard graph, -
	b	Intercept of standard graph, -

11 Results and discussion

TSS, COD and oil amount were analyzed from initial and filtered samples. Separation efficiency of both filtration steps were evaluated. Some of the samples did not contain sulfuric acid and the effect of sulfuric acid addition was evaluated. In Figure 35 is shown five sample bottles taken on same day. In bottles a, b and c sulfuric acid was added so that pH was 2. In bottles d and e no sulfuric acid was added. As seen from Figure 35 when sulfuric acid is added and pH is decreased, color of wastewater changes. Before sulfuric acid was added to wastewater all five samples had the same color. Molecules creating the color precipitate during pH change.

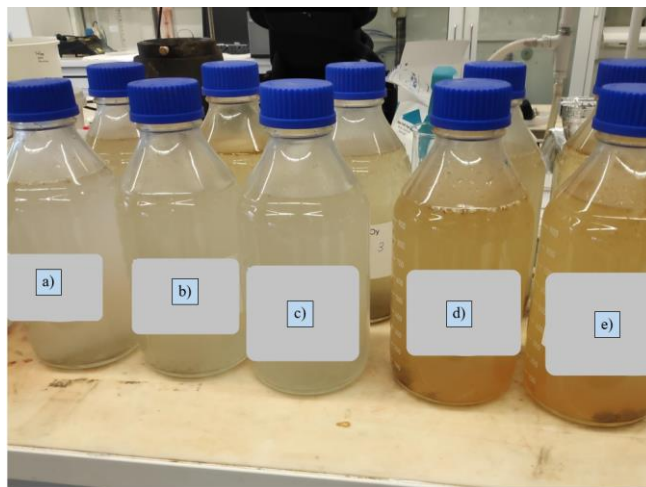


Figure 35 Initial wastewater samples taken in 23.5 2019. 10 ml of sulfuric acid (4.5 mol/l) has been added to liter of sample in a), b) and c) bottles. No sulfuric acid has been added to d) and e) bottles.

Standards Finland (2001) specifies that the yellow-brown color in ground water are caused by humic substances and at low pH they are precipitated. Humic substances are organic macromolecules from soil (Ghabbour and Davies, 2014). Humic substances can be categorized to three groups: humic acids, fulvic acids and humin. Humic acid creates dark brown and gray black colors to wastewater. Fulvic acid creates light and darker yellow colors and has lower molecular weight than humic acids. It has been studied that humic acids precipitate when pH decreases. Fulvic acids remain dissolved in the wastewater upon pH modification. (Stevenson and Olsen, 1989) It is to be concluded that shown color change in Figure 35 is caused by humic acid precipitation.

11.1 Total suspended solids

TSS was measured for the initial wastewater and filtrate samples after vacuum filtration. The objective of vacuum filtration was to separate solid particles (soil and plastic). TSS results were calculated using equation 1. TSS results for samples taken in March and April are shown in Figure 36. As seen from Figure 36 there is very little solid separation in samples taken in 19.3.2019, 8.4.2019 and 18.4.2019. In 17.4.2019 and 25.4.2019 separation is more efficient. In 25.4.2019 separation efficiency is 95-98 %. In 17.4.2019 there is initial sample with and without sulfuric acid addition. As seen from Figure 36 solid amount is slightly smaller in the sample where no sulfuric acid is added. This is in contrary to results in Figure 37 and Figure 38.

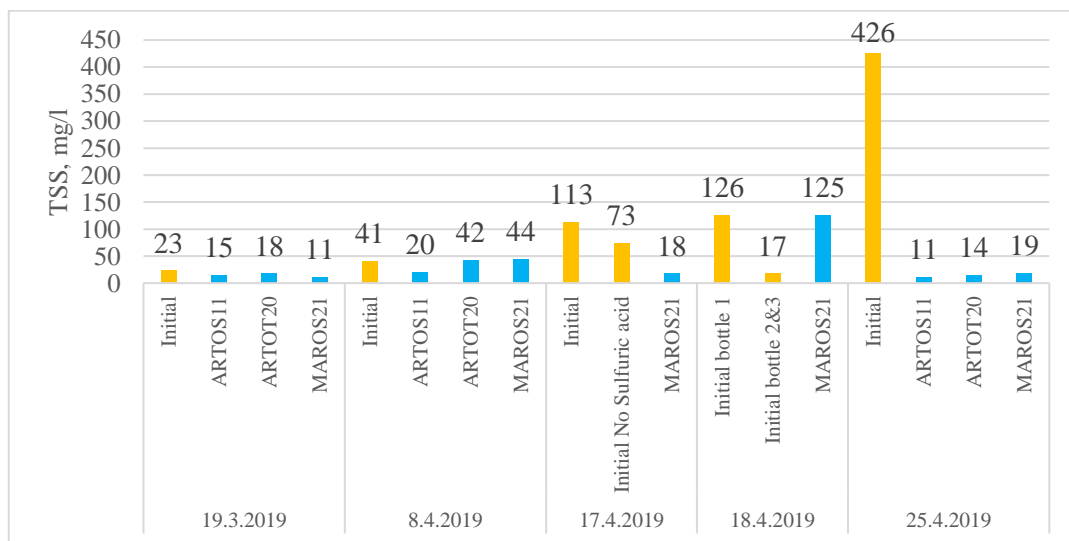


Figure 36 TSS results from March and April samples. On yellow there are the initial samples before filtration. On blue are samples after vacuum filtration. Büchner paper: Glass Microfiber Filter GF/A 1.6 μm , diameter 90 mm, $T_{\text{water}}=20\text{-}25\text{ }^{\circ}\text{C}$.

Samples were taken in 3-5 different bottles from one day. It was noted that by appearance the different sample bottles looked different in 18.4.2019. The TSS difference between bottle 1 and bottles 2 and 3 were measured. As seen in Figure 36 difference between sample bottles was significant (108 mg/l). The difference can be even more significant. Before filtration steps sample bottles were mixed to make initial sample homogeneous.

In Figure 37 is shown TSS results from 13-14.5.2019. As seen from the figure separation efficiency is better than in March and April varying between 89-97 %.

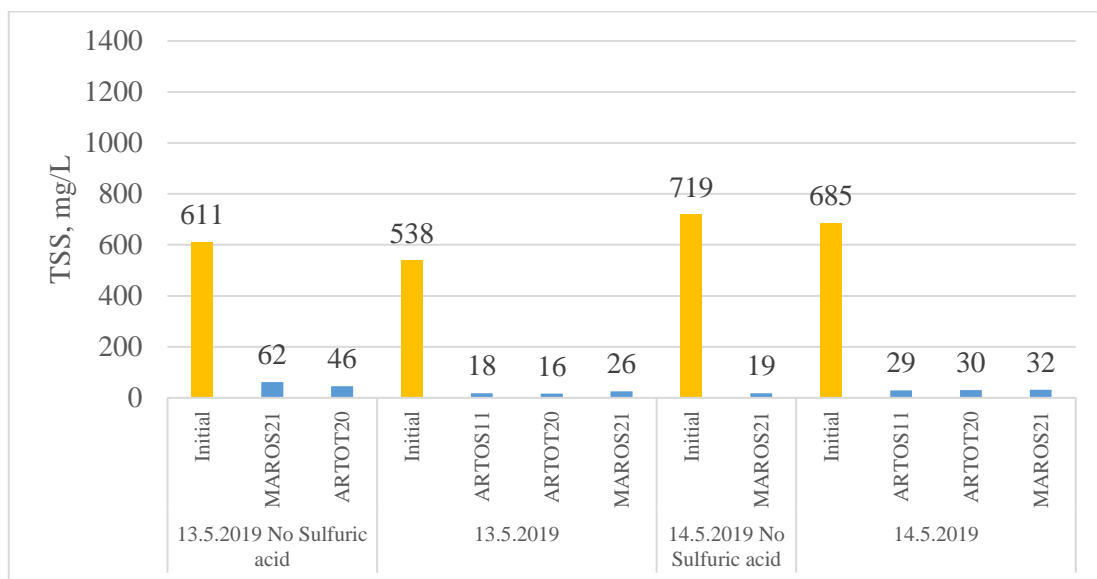


Figure 37 TSS results from 13.5 and 14.5 samples. On yellow there are the initial samples before filtration. On blue is samples after vacuum filtration. Büchner paper: Glass Microfiber Filter GF/A 1.6 μ m, diameter 90 mm, $T_{\text{water}}=20-25$ °C.

In Figure 37 and Figure 38 it can be seen that when no sulfuric acid is added to the initial sample the TSS is larger. Wastewater not containing sulfuric acid reaches same or slightly lower TSS values after filtration. This indicates that humic acid can be separated with filtration cloths.

It is to be noted that according to the BAT-AEL (chapter 3.2.3) maximum value for TSS was 35 mg/l. Even though separation efficiency is high, the objective is not reached in all the filtrations. Especially in 22-23.5.2019 (Figure 38) the initial TSS was so high that the objective is not reached in most of the filtrations. Overall, the initial TSS amounts vary from 17 mg/l to 1333 mg/l. As it can be seen Figure 38 the wastewater samples properties can change a lot in one day. In Figure 31 d it can be seen that all the solids are not plastic but rather soil and sand.

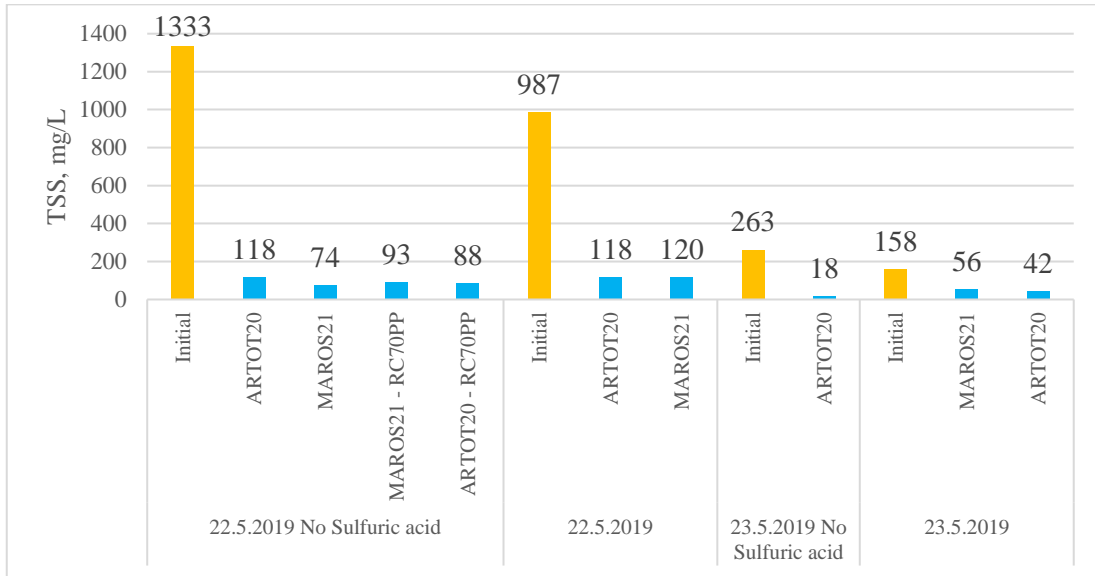


Figure 38 TSS results from 22.5 and 23.5 samples. On yellow there are the initial samples before filtration. On blue is samples after vacuum filtration. Büchner paper: Glass Microfiber Filter GF/A 1.6 μm , diameter 90 mm, $T_{\text{water}}=20\text{-}25\text{ }^{\circ}\text{C}$.

11.2 Membrane filtration

In the membrane filtration fluxes for each of the filtration were measured. Flux values were calculated using equation 2. On some of the filtrations fouling of membrane was analyzed by measuring flux for deionized water after wastewater filtration. In Figure 39 is shown one example of fluxes with RC70PP membrane. As seen from the figure no fouling can be detected since the flux is same before and after wastewater filtration. If the pores of membrane would be fouled the flux would decrease.

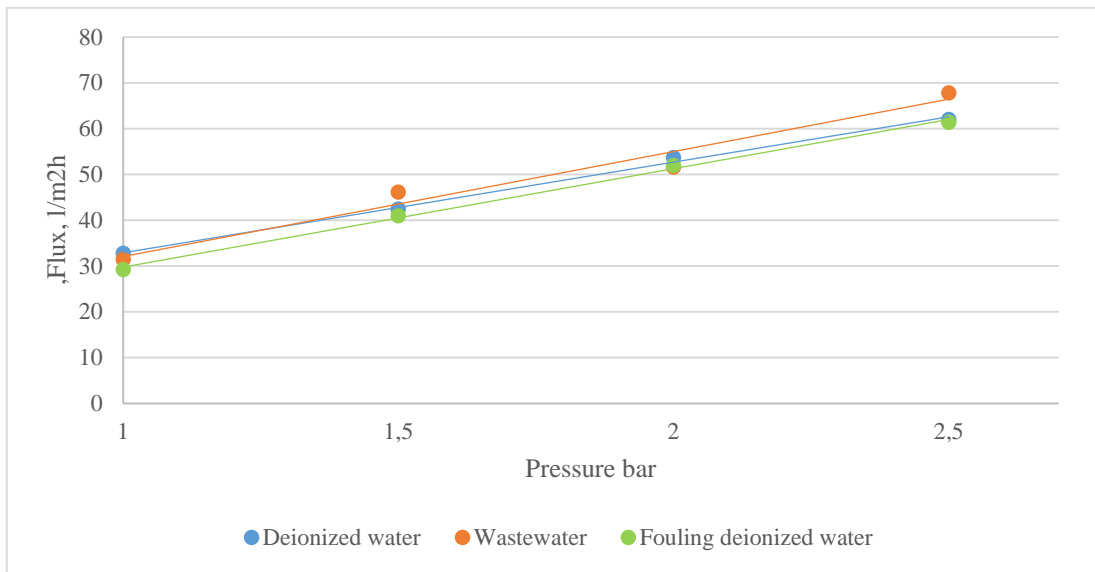


Figure 39 Fluxes of deionized water before and after wastewater filtration with RC70PP membrane. Wastewater filtered was 18.4.2019 ARTOS11. After wastewater filtration membrane was washed with deionized water. $T_{\text{water}}=22-25\text{ }^{\circ}\text{C}$, mixer speed was 250 rpm, $A_{\text{membrane}}=45.4\text{ cm}^2$.

In Figure 40 is shown one example of fluxes with UC100 membrane. With UC100 membrane no fouling could be detected since the deionized water fluxes are same before and after wastewater filtration. No fouling was detected in membrane separation. Flux for RC70PP was 30 L/m²h and UC100 150 L/m²h.

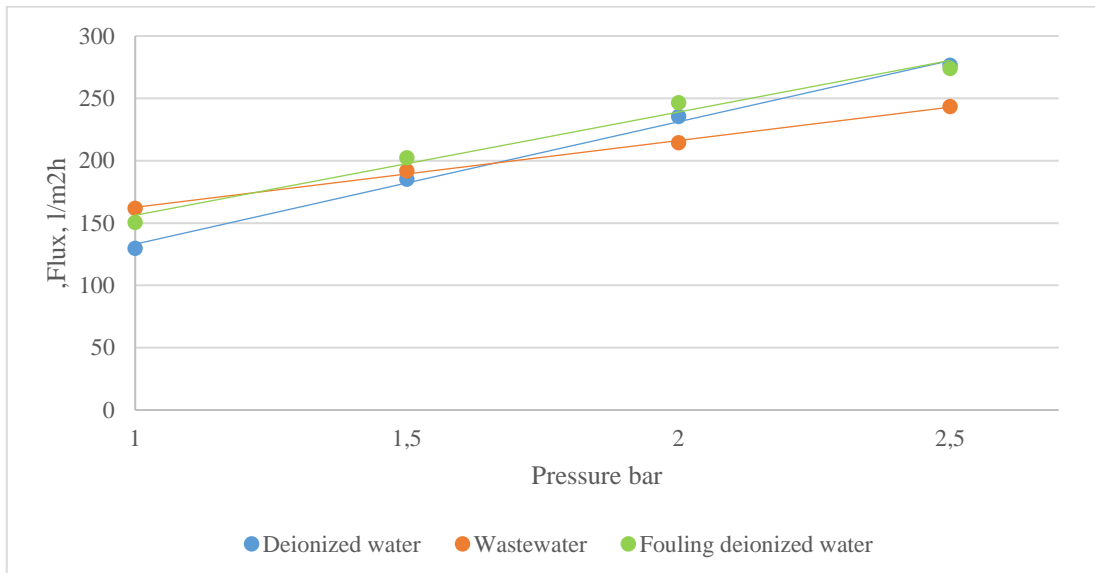


Figure 40 Fluxes of deionized water before and after wastewater filtration with UC100 membrane. Wastewater filtered was 14.5.2019 ARTOT20 (No sulfuric acid). After wastewater filtration membrane was washed with deionized water. $T_{\text{water}}=22-25\text{ }^{\circ}\text{C}$, mixer speed was 250 rpm, $A_{\text{membrane}}=45.4\text{ cm}^2$.

In Figure 41 is shown figures of wastewater before and after membrane filtration. Additionally, the membrane is shown on right (d) after filtration. As seen from the left side of Figure 41 yellow-brown color of wastewater is filtered to concentrate in membrane filtration. Color from membrane could be cleaned easily with water.

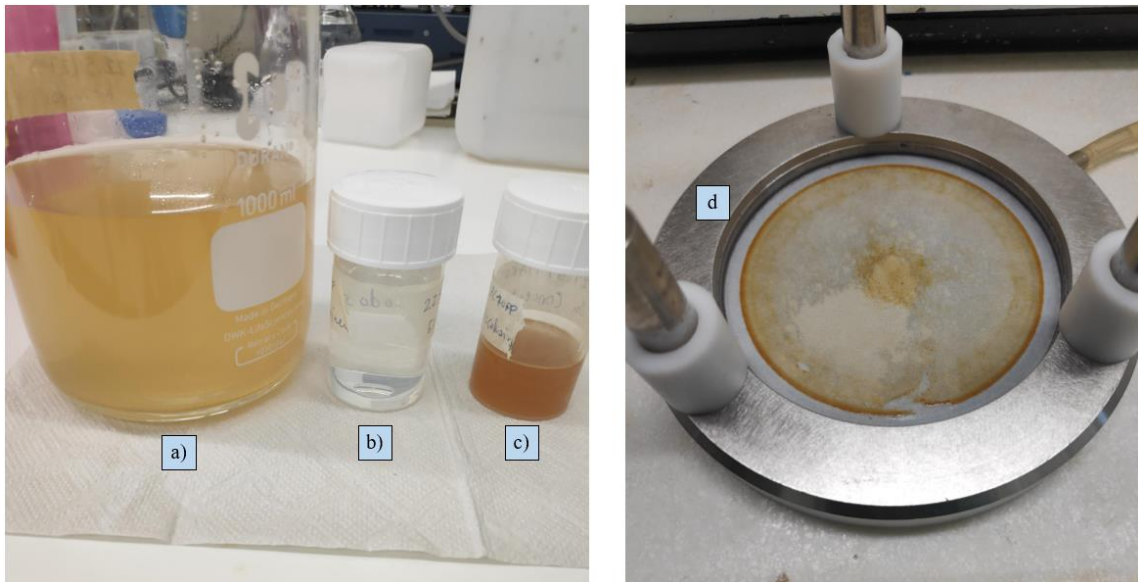


Figure 41 Before and after figures of membrane filtrations of samples taken in 22.5.2019 (No sulfuric acid). a) Sample after first filtration (ARTOT20) b) Permeate sample after second filtration (ARTOT20 – RC70PP) c) Concentrate sample in second filtration (ARTOT20 – RC70PP) d) Membrane after second filtration. $T_{\text{water}}=22-25\text{ }^{\circ}\text{C}$, mixer speed was 250 rpm, $A_{\text{membrane}}=45.4\text{ cm}^2$.

11.3 Chemical oxygen demand

COD was analyzed from samples before and after each filtration. In Figure 42 is shown COD results of samples taken in March. As seen in Figure 42 carbon material is not filtered in first or second filtration on 19.3.2019 and 27.3.2019 samples. There is some carbon matter separated in 28.3.2019 samples. As seen from Figure 42 COD decreases after first separation. Most separation happens with ARTOT20 where separation efficiency is 70 % compared to ARTOS11 (40%) and MAROS21 (53 %). After membrane separation COD amount is larger. Some of the difference can be explained by sample preservation. Sample analysis results are affected by the long preservation in freezer. It is to be noted that according to BAT-AELs maximum limit for COD is 100 ppm. The wastewater from Pilot goes to further treatment therefore the Pilot limit was chosen to be 500 ppm. In March all the initial samples COD are under 500 ppm.

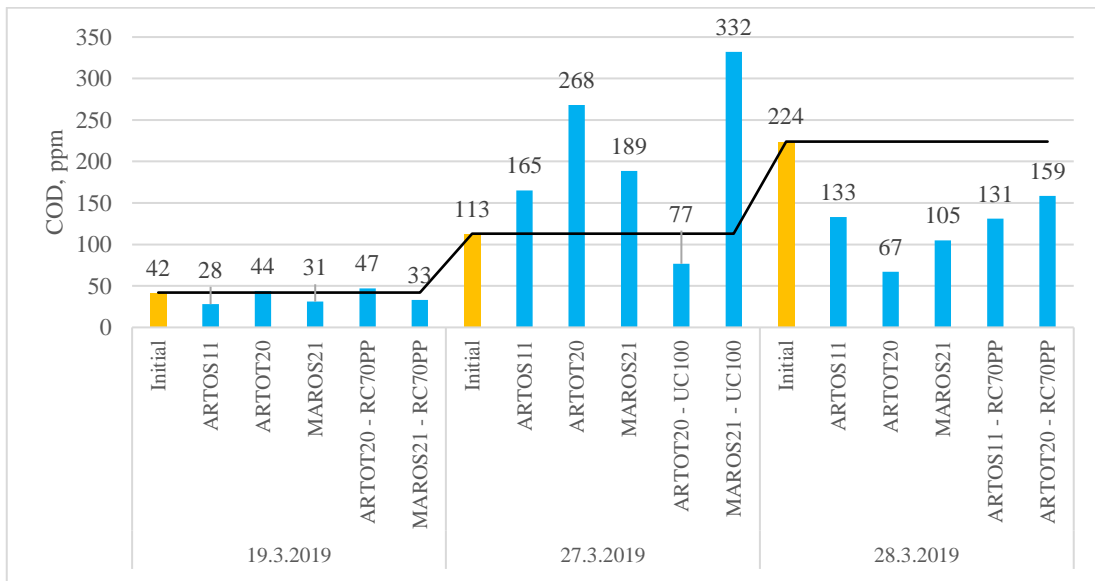


Figure 42 COD results of samples taken in March. On yellow there are the initial samples before filtration. On blue is samples after first or second filtration. Black line is the initial amount where blue samples are compared to. COD test tubes 1500 mg/l and 15 000 mg/l: Merck Spectroquant. COD tubes were 2 h in 150 °C Hach COD reactor.

In Figure 43 is shown COD results of samples taken in 17-18.4.2019. As seen from Figure 43 none of the filtrations are able to decrease COD under 500 ppm. No significant separation of organic matter was detected. Initial samples (17.4.2019) with and without sulfuric acid have 500 ppm difference.

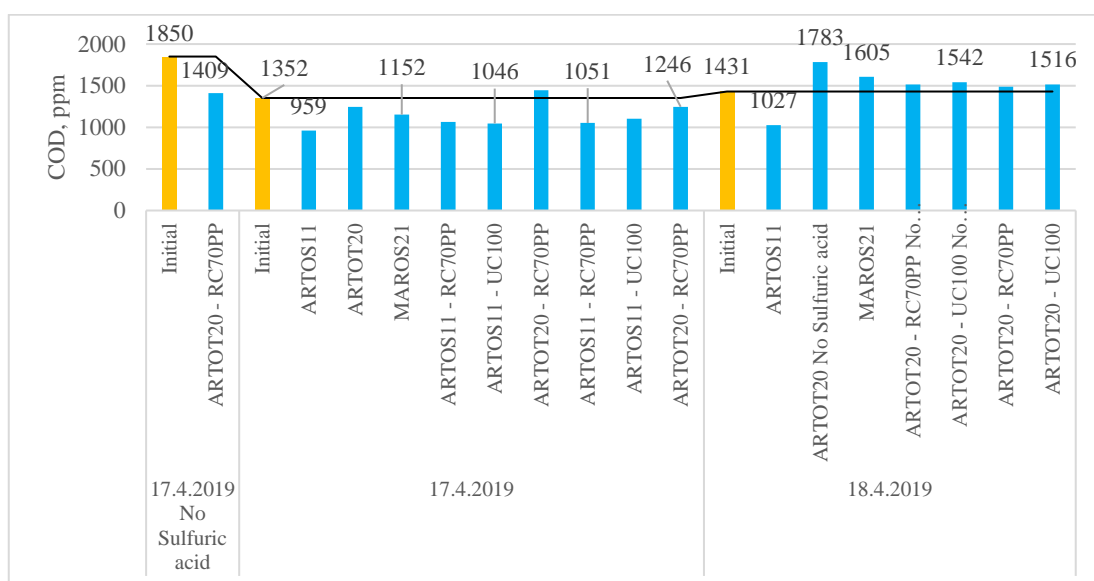


Figure 43 COD results of samples taken in 17-18.4.2019. On yellow there are the initial samples before filtration. On blue is samples after first or second filtration. Black line is the initial amount where blue samples are compared to. COD test tubes 1500 mg/l and 15 000 mg/l: Merck Spectroquant .COD tubes were 2 h in 150 °C Hach COD reactor.

In Figure 44 is shown COD results of 8.4.2019 and 25.4.2019. As seen from Figure 44 separation efficiency is larger but the amounts separated are not big. COD amount of samples are under 500 ppm in initial situation.

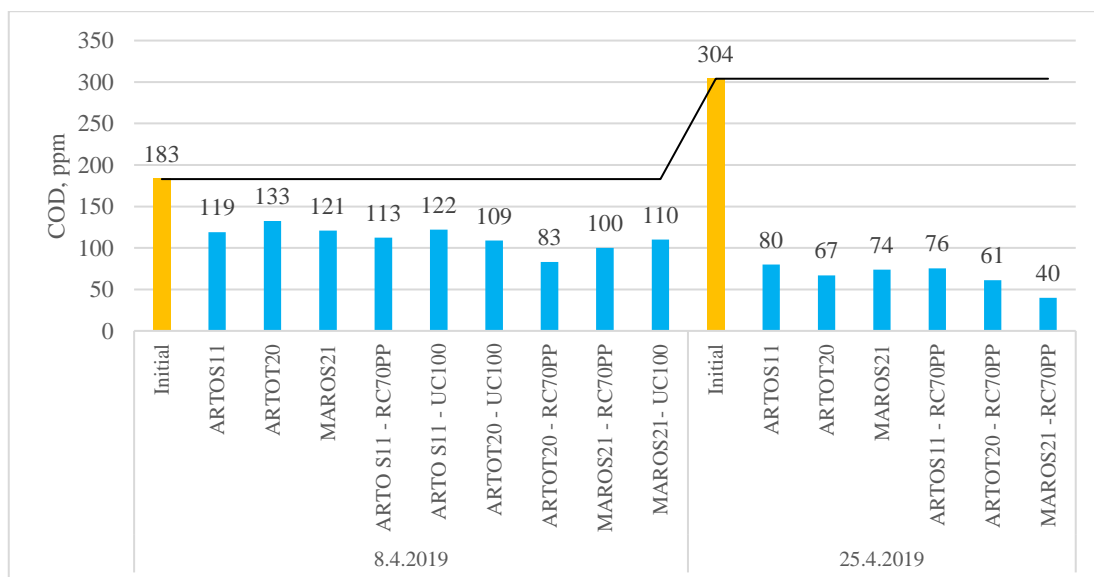


Figure 44 COD result of samples taken in 8.4.2019 and 25.4.2019. On yellow there are the initial samples before filtration. On blue is samples after first or second filtration. Black line is the initial amount where blue samples are compared to. COD test tubes 1500 mg/l and 15 000 mg/l: Merck Spectroquant .COD tubes were 2 h in 150 °C Hach COD reactor.

In Figure 45 is shown COD results from samples taken in 13.5.2019. As seen from Figure 45 all the filtration samples are under 500 ppm COD. The separation efficiency was 76 % on average for COD.

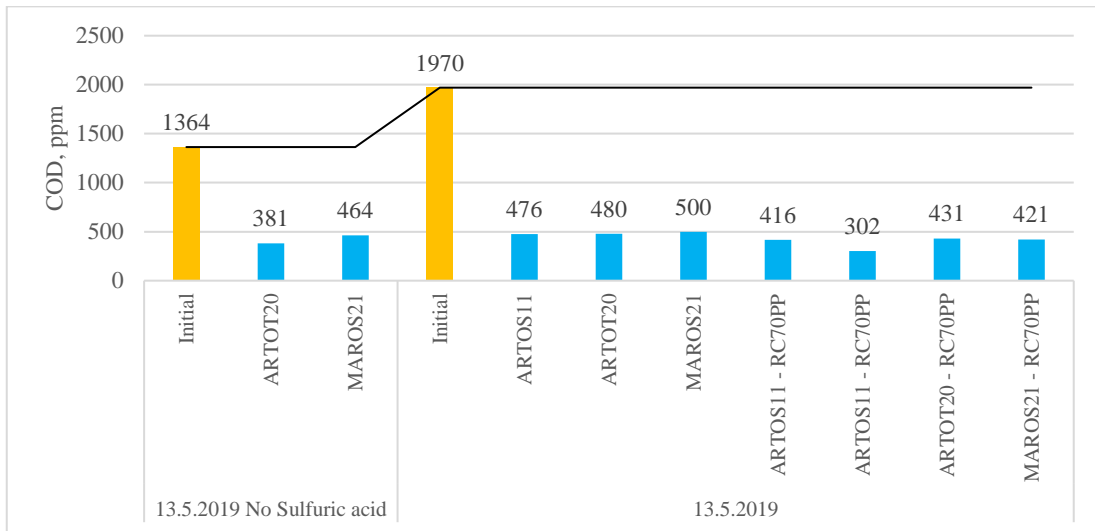


Figure 45 COD results of sample taken 13.5.2019. On yellow there are the initial samples before filtration. On blue is samples after first or second filtration. Black line is the initial amount where blue samples are compared to. COD test tubes 1500 mg/l and 15 000 mg/l: Merck Spectroquant .COD tubes were 2 h in 150 °C Hach COD reactor.

In Figure 46 shown COD results from samples taken in 14.5.2019 and 18.5.2019. As seen from Figure 46 14.5.2019 filtration decreases COD. In average COD decreases in samples where sulfuric acid was not added by 880 ppm, in samples where sulfuric acid was added the average decrease of COD was 2330 ppm.

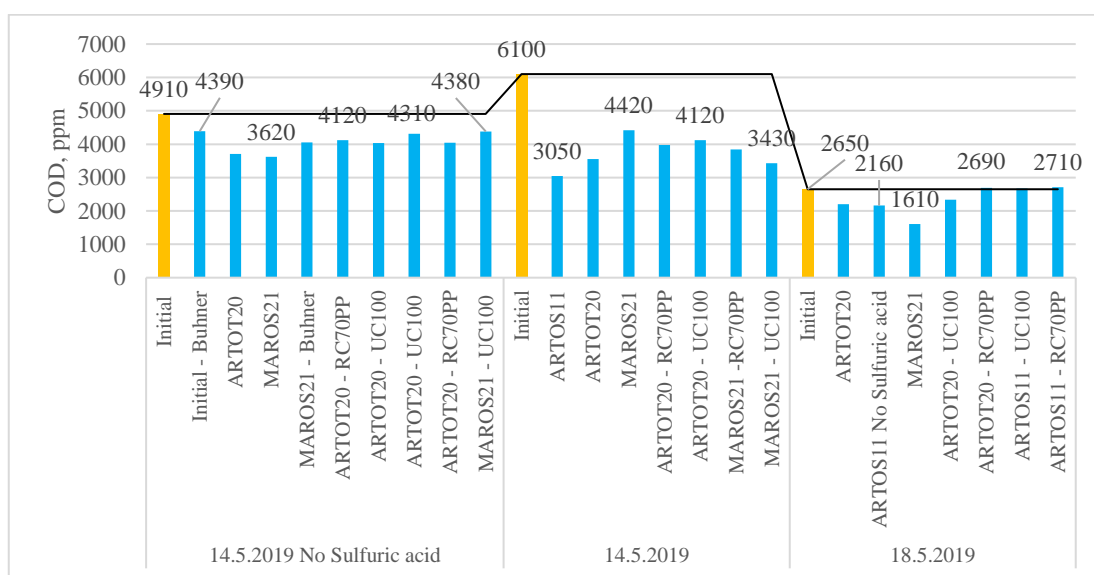


Figure 46 COD results of samples taken in 14.5.2019 and 18.5.2019. On yellow there are the initial samples before filtration. On blue is samples after first or second filtration. Black line is the initial amount where blue samples are compared to. COD test tubes 1500 mg/l and 15 000 mg/l: Merck Spectroquant .COD tubes were 2 h in 150 °C Hach COD reactor.

In Figure 47 is shown COD results from samples taken in 22.5.2019 and 23.5.2019. As seen from the Figure 47 in 22.5.2019 there was exceptionally large amount of COD in wastewater. COD amount is not decreased with filtration even though TSS was separated efficiently.

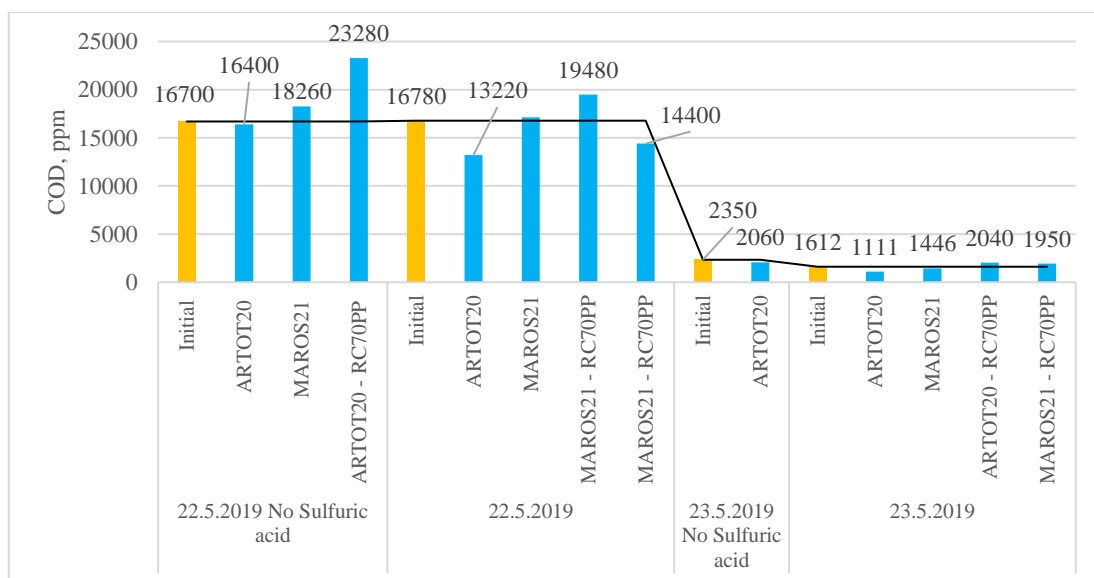


Figure 47 COD results of samples taken in 22-23.5.2019. On yellow there are the initial samples before filtration. On blue is samples after first or second filtration. Black line is the initial amount where blue samples are compared to. COD test tubes 1500 mg/l and 15 000 mg/l: Merck Spectroquant .COD tubes were 2 h in 150 °C Hach COD reactor.

In 22-23.5.2019 the COD amount did not decrease during filtration. In Figure 41 is shown how all the color in 22.5.2019 has been filtered. Even though the humic acids and solids have been successfully filtered the COD values decrease minimally. In conclusion, the main chemicals influencing in high COD values are dissolved and colorless. There was next to no difference between ARTOT20, ARTOS11 and MAROS21 vacuum filtration cloths in filtration efficiency. There was next to no difference between vacuum and membrane filtration efficiencies.

In Table 13 is shown summary of filtration efficiencies from different samples. Filtration efficiency has been calculated using Equation 3. As seen from Table 13 some days average values are negative. This means that COD has increased during filtration. There is no clear reason for this, but most likely it is caused by preservation of samples. Long preservation time and freezing of samples changes the results. Most COD amount was filtered in average 2330 ppm in 14.5.2019 filtration. Best filtration efficiency was 78 % in 25.4.2019 and 13.5.2019. Concentrate samples were taken in membrane separation and are compared to filtrate. Concentrate contains all the contaminants that are not filtered through membrane. As seen from the Table 13 the values are very small and are similar to the results shown in Figure 42-Figure 47 where membrane separation reduces COD not at all or very little.

Table 13 Summary of the average COD decrease after filtration values and filtration efficiencies. Average decrease of COD and filtration efficiency values are from both vacuum and membrane filtration. Average difference between concentrate and filtrate samples are averages from membrane separation. COD test tubes 1500 mg/l and 15 000 mg/l: Merck Spectroquant .COD tubes were 2 h in 150 °C Hach COD reactor.

Sample	Average decrease of COD in filtration, ppm	Average filtration efficiency, %	Average difference between concentrate - filtrate, ppm
19.3.2019	5	13	9
27.3.2019	-93	-82	-
28.3.2019	105	47	53
8.4.2019	71	39	62
17.4.2019 No sulfuric acid	441	24	-85
17.4.2019	206	15	-
18.4.2019	-65	-5	-
25.4.2019	238	78	47
13.5.2019 No sulfuric acid	941	69	-
13.5.2019	1538	78	17
14.5.2019 No sulfuric acid	880	18	-
14.5.2019	2330	38	142
18.5.2019	310	12	-70
22.5.2019 No sulfuric acid	-2613	-16	210
22.5.2019	720	4	-
23.5.2019 No sulfuric acid	290	12	-
23.5.2019	-25	-2	-659
AVERAGE	311	20	-88

11.4 Oil amount

In Figure 48 is shown standard graphs from three different analysis measurements. Standards were prepared in same concentrations for all analysis measurements but the peak response changed. Sample oil amounts were calculated using equation 4 with respective standard graph.

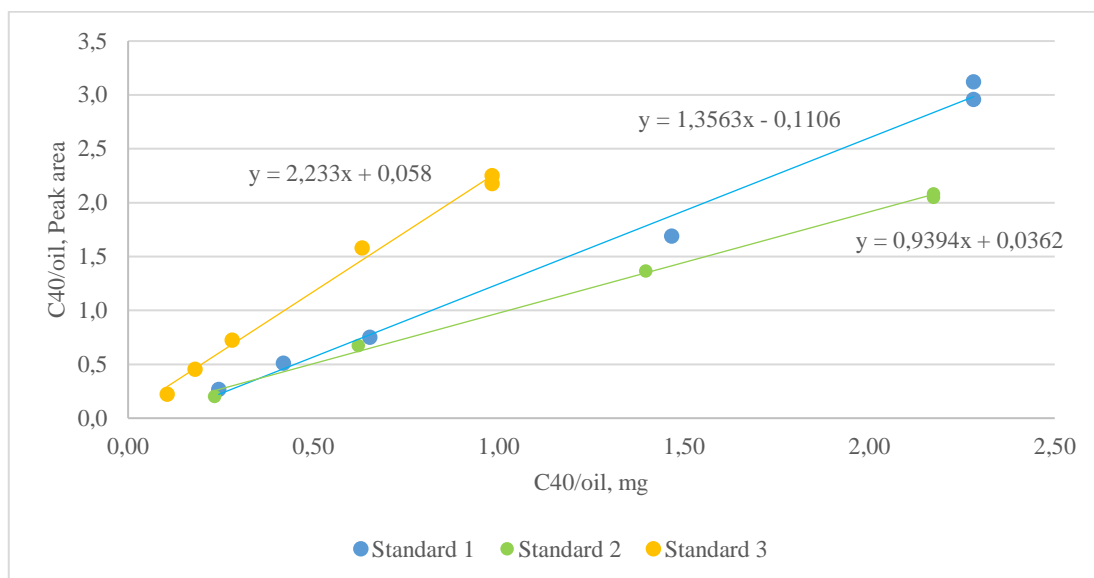


Figure 48 Standards graphs that were prepared from standard A / standard B rates of 0.3, 0.4, 0.6, 0.7 and 0.8. C10=decane and C40=n-tetracontane. Gas chromatography column: HP-1/SIMDIST.

In Figure 49 is shown examples of three different oil samples compared to 0.6 standard. As seen from Figure 49 the peaks on blue graphs differentiate between different samples. In samples a and b, the peaks are closer to C40 end of the spectrum. In sample c the largest peak area is large and close to C10 end of spectrum. In sample a, there are a lot of separate peaks. In sample b there is one broad peak. Most of the samples were represented by a and b samples shown in Figure 49.

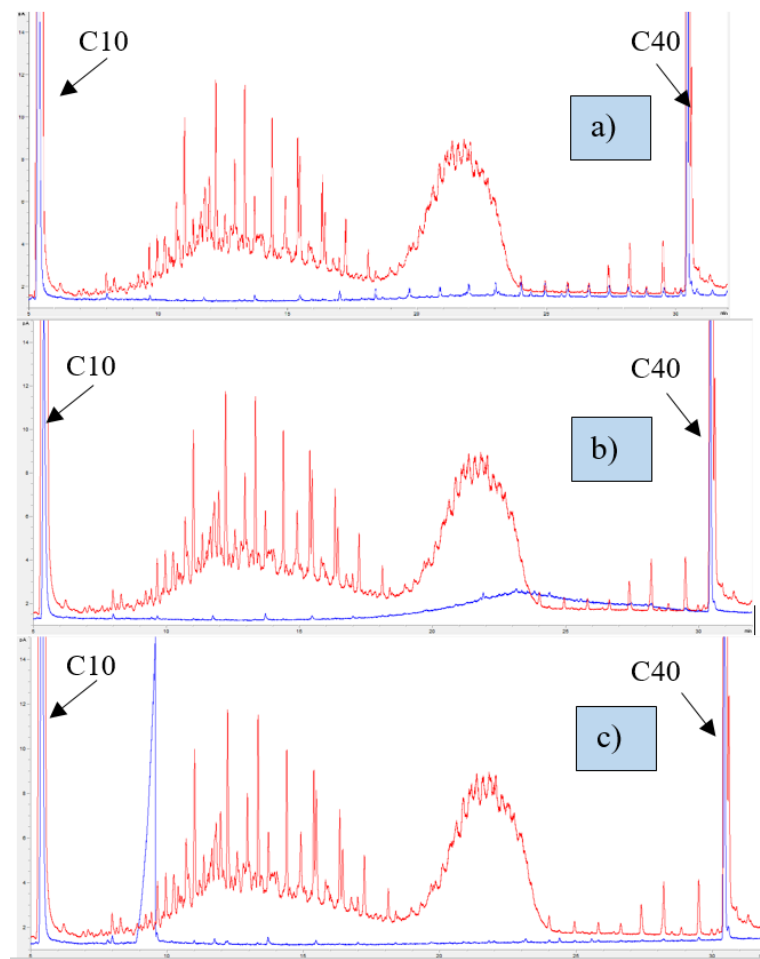


Figure 49 Three different oil samples compared to 0.6 standard. On blue: a) 28.3 ARTOT20 – RC70PP concentrate (0.061 mg/l) b) 23.5 MAROS21 – RC70PP concentrate (0.22 mg/l) c) 22.5 MAROS21 – RC70PP. On red = 0.6 standard A (diesel & mineral oil)/standard B (C10 & C40). Gas chromatography column: HP-1/SIMDIST.

In Figure 50 is shown oil results from samples taken in 19.3.2019 and 27-28.3.2019. As seen from Figure 50 the oil amount do not decrease during filtrations. In 19.3.2019 and 27.3.2019 samples the oil amount is larger in filtrate. Same could be detected in COD values of the same samples in Figure 42.

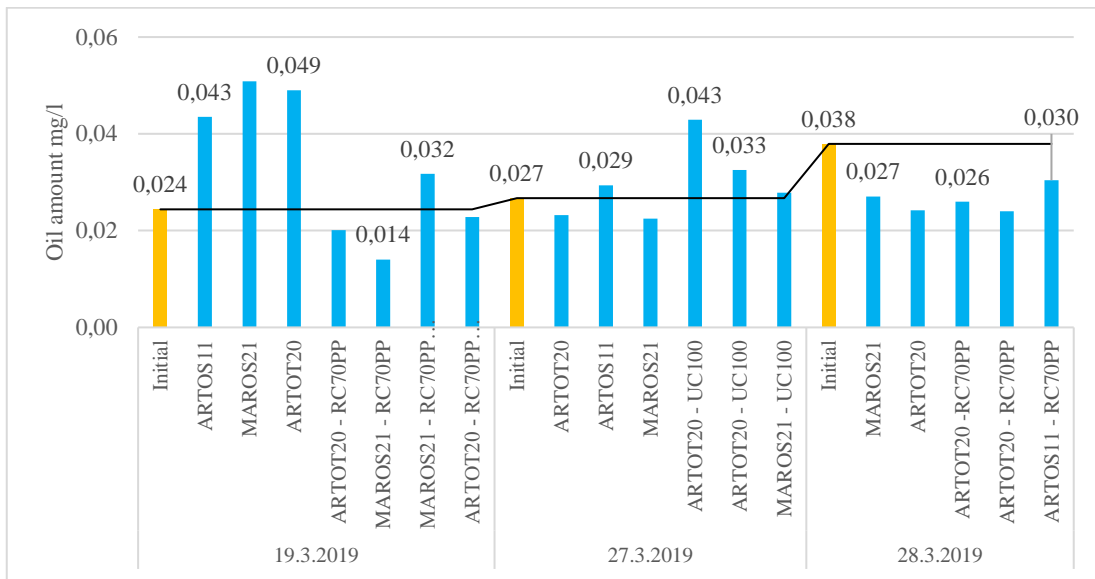


Figure 50 Oil amount results of before and after filtration of samples taken in 19.3.2019 and 27-28.3.2019. Yellow: Initial samples, Blue: Filtration samples, Black line: Initial amount where filtration samples are compared to. Gas chromatography column: HP-1/SIMDIST.

In Figure 51 is shown the oil results from samples taken in 17-18.4.2019. As seen from the figure the separation efficiency is very low. Best separation efficiencies are achieved when filtrating 18.4.2019 (No sulfuric acid) but as seen from values same oil separation is achieved by vacuum and membrane filtration.

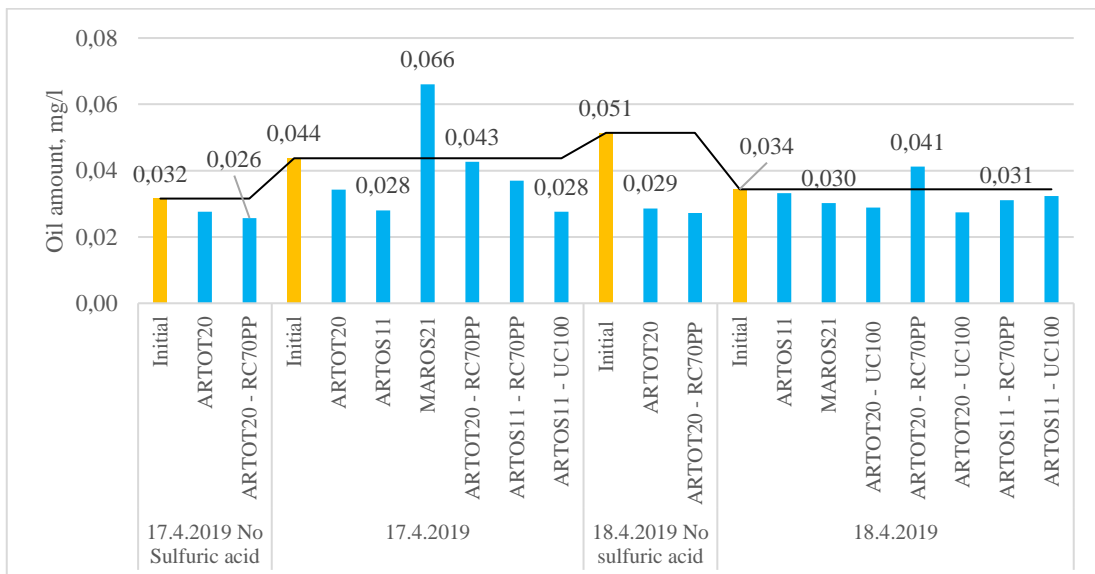


Figure 51 Oil amount results of before and after filtration of samples taken in 17-18.4.2019. Yellow: Initial samples, Blue: Filtration samples, Black line: Initial amount where filtration samples are compared to. Gas chromatography column: HP-1/SIMDIST.

In Figure 52 is shown the oil results from samples taken in 8.4.2019 and 25.4.2019. In 25.4.2019 taken samples oil is separated with 74 % filtration efficiency. In 25.4.2019 COD

was also filtered efficiently (78 %). The separation efficiencies are same in oil and COD reduction. It can be concluded that at least in 25.4.2019 organic material in sample is carbon chain between C10 - C40.

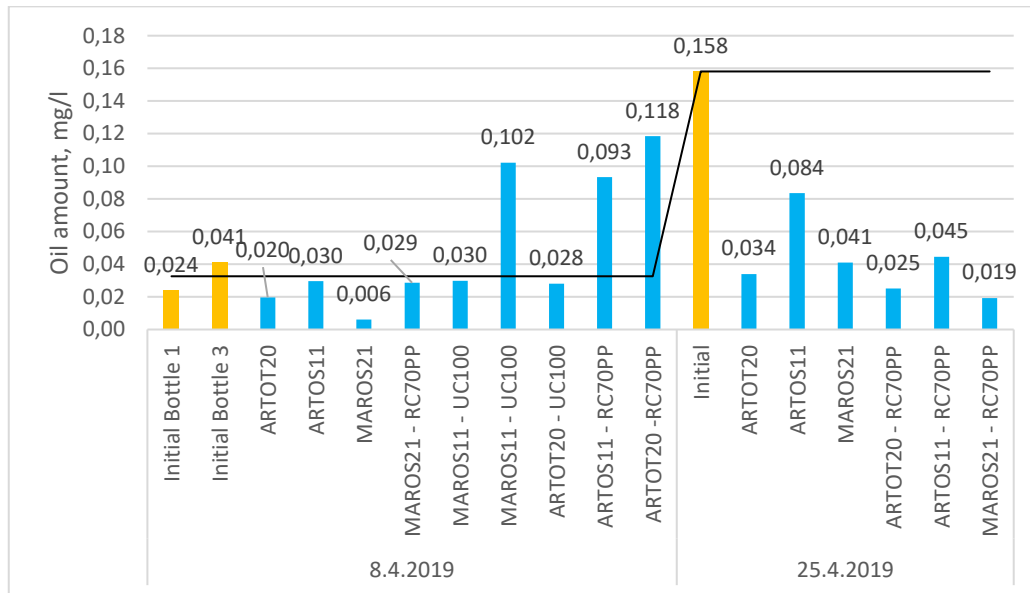


Figure 52 Oil amount results of before and after filtration of samples taken in 8.4.2019 and 25.4.2019. Yellow: Initial samples, Blue: Filtration samples, Black line: Initial amount where filtration samples are compared to. Gas chromatography column: HP-1/SIMDIST.

In Figure 53 is shown the oil results from samples taken in 13-14.5.2019. As seen from Figure 53 much higher separation efficiency can be detected in these filtrations. No clear reason was detected. Filtration efficiency varied on average between 56-67 % (Table 14). No significant constant difference can be detected between vacuum and membrane separation in oil separation.

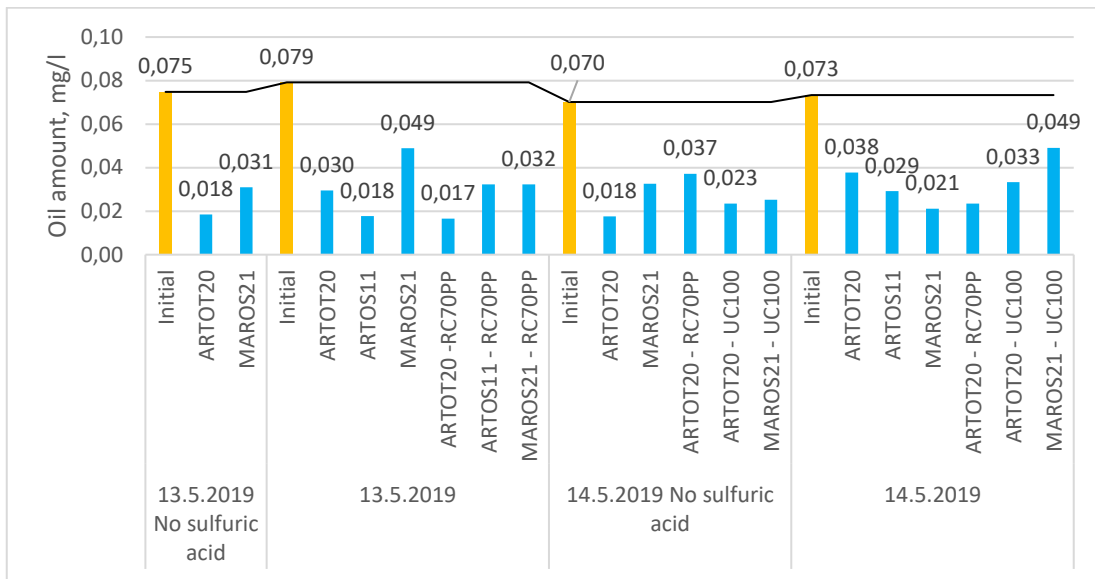


Figure 53 Oil amount results of before and after filtration of samples taken in 13-14.5.2019. Gas chromatography column: HP-1/SIMDIST.

In Figure 54 is shown the oil results from samples taken in 22-23.5.2019. As seen from Figure 54 22.5.2019 initial sample contained most oil.

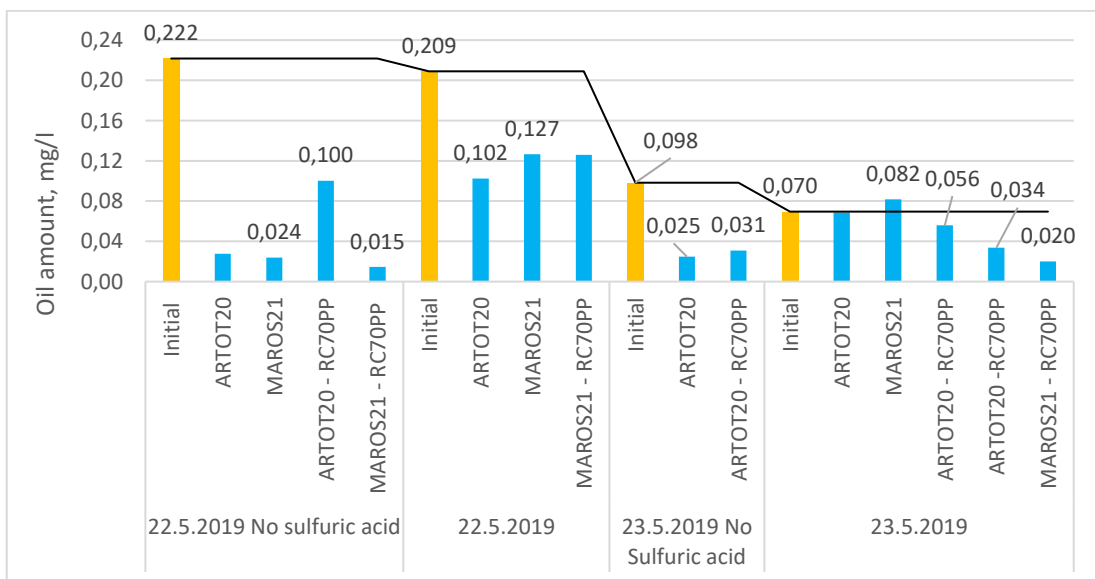


Figure 54 Oil amount results of before and after filtration of samples taken in 22-23.5.2019. Gas chromatography column: HP-1/SIMDIST.

In 22.5.2019 (No sulfuric acid) separation efficiency for oil was high on average (81%) and filtrate oil amounts were very small. Oil and COD results on 22.5.2019 (No sulfuric acid) are very different. COD amounts were larger after filtration resulting in negative filtration efficiency. Biggest difference between oil and COD was detected in 22.5.2019 (No sulfuric acid).

When comparing initial samples with and without pH reduction, very little difference between samples can be detected. Humic acid chemical formula can differ a lot depending on soil but the average carbon amount is C22 (Stevenson and Olsen, 1989). This means that humic acids are shown in oil analysis where carbon is measured between C10-C40.

Table 14 is shown summary of average separation of oil amount and separation efficiency between different sampling days. On average oil could be separated 0.04 mg/l with average separation efficiency of 32 %.

Table 14 Summary of the average decrease of oil after filtration and filtration efficiencies. Average decrease of oil and filtration efficiency values are from both vacuum and membrane filtration. Gas chromatography column: HP-1/SIMDIST.

	Average decrease of oil in filtration, mg/l	Average filtration effi- ciency, %
19.3.2019	-0,009	-36
27.3.2019	-0,003	-11
28.3.2019	0,012	31
8.4.2019	-0,018	-55
17.4.2019 No sulfuric acid	0,005	16
17.4.2019	0,004	10
18.4.2019 No sulfuric acid	0,023	46
18.4.2019	0,003	9
25.4.2019	0,117	74
13.5.2019 No sulfuric acid	0,050	67
13.5.2019	0,050	63
14.5.2019 No sulfuric acid	0,043	61
14.5.2019	0,041	56
22.5.2019 No sulfuric acid	0,180	81
22.5.2019	0,091	43
23.5.2019 No sulfuric acid	0,071	72
23.5.2019	0,018	25
AVERAGE	0.040	32

12 Error analysis

Wastewater samples were tested to find out if freezing affected TSS and COD values. According to the SFS-ENISO9377-2 ideally samples should be analysed the same day as sample was taken. If analysis would be done later the wastewater should be acidified so that water pH is 2. With acidification the sample can be stored in fridge temperature (+ 4 °C) for

maximum of five days. (Standards Finland, 2001) Because the experimental part was executed in two different locations, filtration experiment could not be done within five days. Therefore, freezing of samples was chosen to be the preservation method. To analyse the effect that freezing has on wastewater samples, freezing tests were conducted. Freezing tests were done in company laboratory where TSS and COD were measured from samples before and after two weeks of freezing period. Samples were acidified before measuring. Results of the test are shown in Figure 55.

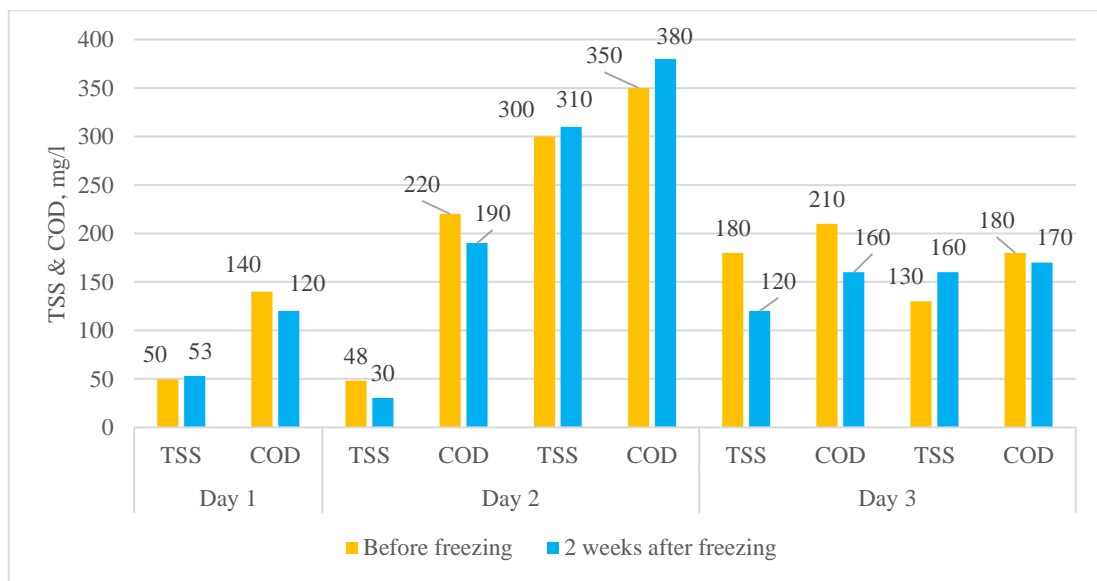


Figure 55 Freezing test made in company laboratory from three days samples that were acidified (pH=2). Day 1: 6.2.2019, day 2: 12.2.2019 (2 sample bottles), day 3: 13.2.2019 (2 sample bottles). Sample analysis before freezing was done in same day as sample was taken. Wastewater was frozen for two weeks and analysis was repeated.

As seen from the freezing results the COD and TSS have random dispersion. No definite conclusion can be made that TSS and COD would increase or decrease as a result of freezing. On average TSS changed 24 mg/l before and after freezing. Percentage differences were between 7-36 %. TSS change is large compared to the sample taken in 19.3.2019 where initial TSS was 23 mg/l. On average TSS of all samples (initial and filtered) in experimental part was 153 mg/l.

COD changed by 28 mg/l before and after freezing. Percentage differences were between 8-55 %. COD change is not that significant because the COD values in samples were much larger on average. On average COD of all samples (initial and filtered) in experimental part was 2772 mg/l. Wastewater samples were in the freezer 1-3 months and they were frozen and melted multiple times causing inaccuracy to COD and TSS results.

For the preservation of samples the pH was reduced for sample preservation. The effect of pH reduction was evaluated by not adding sulfuric acid to some of the samples. The COD values of initial samples with and without sulfuric acid changed on average by 623 ppm. This causes inaccuracy to the results.

Oil analysis results were conducted in experimental part based on the same standard that company laboratory uses. However, for the experimental part the method was modified to meet resources at the University. The oil results from experimental part can be compared to each other but cannot be compared to the company produced oil results. In 17.4.2019 company's laboratory result for oil index was 10 mg/l and from experimental part oil amount was on average 0.038 mg/l. In 15.5.2019 the laboratory result for oil index was 52 mg/l and the average value from initial samples of 14.5.2019 was 0.072 mg/l. Rate between company laboratory oil results was 0.19 when comparing 10 mg/l to 52 mg/l. Rate between oil results in experimental part was 0.52 when comparing 0.038 mg/l to 0.072 mg/l. The rate between results is different and therefore, the results cannot be compared to each other linearly. In modified analysis method lower sample amount was used (4 ml compared to 1 liter). Extraction in smaller sample amount wasn't good enough which resulted in lower oil results.

Sample taking accuracy was also considered. Samples are taken after line flushing to one liter glass bottles. In normal operation one bottle of sample is delivered to laboratory for measurement. For the experimental part 3-5 bottles of sample were taken. In 18.4.2019 samples TSS varied between two bottles from 17 to 123 mg/l (Figure 36). In Figure 55 is shown two different results for TSS and COD in day 2 and 3. The results are from different sample bottles. As seen from Figure 55, especially day 2, there is a big difference between TSS values in different sample bottles. The inaccuracy between sample bottles creates error to the results evaluated in Pilot plant. In the experimental part different sample bottles were mixed to eliminate the error in filtration.

13 Conclusions

Plastic pollution in oceans and in other bodies of water is growing concern. Plastics are ending up in oceans from overpopulated areas where there are tourists, shipping and other industrial activities. (Cocca et al., 2018) Plastic pollution is most efficiently stopped from the source as early as possible. In plastic producing company it is part of company targets to achieve goal zero in plastic emissions.

Objective of the master's thesis was to study what are the efficient separation methods for wastewater in Pilot plant. The main contaminants in Pilot wastewater are known to be suspended solids, organic matter and oil. In the literature part different technologies for plastic, organic matter and oil filtration from wastewater were studied. In conclusion, three different process configurations were suggested. One process configuration was chosen to be studied in experimental part.

In the experimental part the objective was to separate TSS, COD and oil contaminants from wastewater as effectively as possibly. Two step separation was chosen for the experiments. According to literature part rapid sand filter was considered best option for solid separation. Ceramic membranes were considered best option for oil and organic matter separation. These equipment were not available in laboratory and slightly different equipment were used. First separation step was vacuum filtration where three different filtration cloths from Outotec (ARTOT20, ARTOS11 and MAROS21) were used. In experimental study ceramic membranes were not available for use in small laboratory scale. Instead in second filtration step hydrophilic cellulosic membranes were used (RC70PP and UC100).

In Table 15 is shown summary of the average amounts of TSS, COD and oil that could be separated with two part separation. TSS separation efficiency was high compared to COD and oil separation.

Table 15 Average filtration amounts and efficiencies for TSS, COD and oil.

	TSS	COD	Oil
Average filtration amount, mg/l	440	311	0.04
Average filtration efficiency, %	74	20	32

It was concluded that even though 74 % of solids were separated by vacuum filtration, the COD and oil were not separated. By estimate most of the suspended solids were from soil and sand. Meaning that smaller portion of suspended solids were created by plastic. Plastic in the wastewater did not affect the COD values. In filtrations there was next to no difference between vacuum filtration cloths separation efficiencies. In one out of 11 days samples COD was decreased below the 500 ppm selected limit in filtrations.

Initial wastewater had brown-yellow color in it. For sample preservation most of the samples were acidified to pH 2. The acidification made color resulting molecules to precipitate. It was concluded that humic acid was the main cause to color in wastewater. Humic acids were detected in oil analysis with other oil constituents. Humic acids were filtered in separation steps making filtrate colorless. Even though color and solids were removed by filtration there was still high COD and oil amounts. In conclusion, most of the carbon is dissolved in the water.

In addition, sample reliability was analysed. It was concluded that sample contaminant values varied between different bottles taken at the same time. Sampling line should be flushed more. Load of contaminants in Pilot plant has been calculated from volumetric flow and the sample that is taken every two weeks. The volumetric flow is not analysed daily basis. Meaning that since the results can change daily from 2300 ppm to 17 000 ppm (22.5 and 23.5), the monthly load value is not reliable. The samples should be taken more often to monitor the load values in a reliable way.

Oil amounts measured in experimental part cannot be compared to company measured oil amounts because the analysis method was different. Oil results were compared to each other and 32 % oil removal was achieved by filtration. There was no difference between vacuum filtration and membrane filtration in filtration efficiency. Cellulosic membrane filtration was unable to separate COD and oil and therefore is not suggested as a method for wastewater treatment in Pilot plant.

Other suitable technologies discussed in the literature part should be further studied for Pilot wastewater. In the literature part it was concluded that depth filtration was suitable choice for solid separation because Pilot wastewater suspended solid amount was below 0.1 volume-%. In the Finland wastewater system investment has been made to surface filtration equipment instead of depth filtration. Rapid sand filters have been proven to be economical and effective as a depth filtration system for solid separation.

Dissolved organic matter in wastewater should be analyzed further to know exact chemicals present in wastewater. In the experimental part ceramic membranes were not studied. As concluded in literature part ultrafiltration ceramic membranes were good for oil separation because of their hydrophilicity, durability and high separation efficiency. In addition, acti-

vated carbon adsorption is mature and efficient technology for oil separation. It is also possible to remove metal ions through adsorption. DAF is not able to separate dissolved oil efficiently without coagulant and therefore is not optimal method.

14 References

Act 2014/527. Environmental protection act. Accessed 30 January 2019. Retrieved from <https://www.finlex.fi/fi/laki/ajantasa/2014/20140527#L1>

Al-Shamrani, A., James, A. and Xiao, H. (2002). Destabilisation of oil–water emulsions and separation by dissolved air flotation. *Water Research*, 36(6), pp.1503-1512.

Boyles, W. (1997). *The Science of Chemical Oxygen Demand: Technical Information Series, Booklet No. 9*. 15th ed. Hach company.

Brinkmann, T., Giner Santonja, G., Yükseler, H., Roudier, S. and Delgado Sancho, L. (2016). Best available techniques (BAT) reference document for common waste water and waste gas treatment/management systems in the chemical sector. Luxembourg: Publications Office of European Union.

Cecen, F. and Aktas, Ö. (2012). *Activated carbon for water and wastewater treatment*. Weinheim: Wiley-VCH, pp.1-500.

Ghabbour, E. and Davies, G. (2014). *Understanding Humic Substances*. Cambridge: Elsevier Science, pp.1-20.

Christensen, M. (2003). *Principles and Practices of Water Supply Operations: Water treatment*. 3rd ed. American Water Works Association, pp.1-250.

CHROMacademy (2019). *Theory and instrumentation of GC introduction*. CHROMacademy, pp.2-10.

Cocca, M., Pace, E., Errico, M., Gentile, G., Montarsolo, A. and Mossotti, R. (2018). *Proceedings of the International Conference on Microplastic Pollution in the Mediterranean Sea*. Cham: Springer International Publishing, pp.1-25.

Cui, J.Y., Zhang, X.F., Liu, H.O., Liu, S.Q., Yeung, K.L., (2008). *Membr. Sci.* 325, 420–426.

Cui, Z. and Muralidhara, H. (2010). *Membrane technology: A practical guide to membrane technology and application in food and bioprocessing*. 1st ed. Oxford: Elsevier Ltd., pp.100-200.

Dickhout, J., Moreno, J., Biesheuvel, P., Boels, L., Lammertink, R. and de Vos, W. (2017). Produced water treatment by membranes: A review from a colloidal perspective. *Journal of Colloid and Interface Science*, 487, pp.523-534.

DOW Suomi Oy (2016). *Käyttöturvallisuustiedote DOWCAL 200 Heat Transfer Fluid*. 8th ed. Helsinki: DOW Suomi Oy, p.6.

Ebrahimi, M., Schmitz, O., Kerker, S., Liebermann, F. and Czermak, P. (2013). Dynamic cross-flow filtration of oilfield produced water by rotating ceramic filter discs. *Desalination and Water Treatment*, 51(7-9), pp.1762-1768.

Felsing, S., Kochleus, C., Buchinger, S., Brennholt, N., Stock, F. and Reifferscheid, G. (2018). A new approach in separating microplastics from environmental samples based on their electrostatic behavior. *Environmental Pollution*, 234, pp.20-28.

Figoli, A. and Criscuoli, A. (2017). *Sustainable Membrane Technology for Water and Wastewater Treatment*. Singapore: Springer Nature, pp.1-400.

Gahleitner, M. and Paulik, C. (2014). Polypropylene. *Ullmann's Encyclopedia of Industrial Chemistry*, [online] 1. Available at: https://doi.org/10.1002/14356007.o21_o04.pub2 [Accessed 21 Jan. 2019].

Gatidou, G., Arvaniti, O. and Stasinakis, A. (2019). Review on the occurrence and fate of microplastics in Sewage Treatment Plants. *Journal of Hazardous Materials*, 367, pp.504-512.

Gurung, K., Ncibi, M. and Sillanpää, M. (2017). Assessing membrane fouling and the performance of Pilot-scale membrane bioreactor (MBR) to treat real municipal wastewater during winter season in Nordic regions. *Science of The Total Environment*, 579, pp.1289-1297.

Hamia, M.L., Al-Hashimi, M.A., Al-Doori, M.M., (2007). *Desalination* 216, 116–122.

Herbort, A., Sturm, M. and Schuhen, K. (2018). A new approach for the agglomeration and subsequent removal of polyethylene, polypropylene, and mixtures of both from freshwater systems – a case study. *Environmental Science and Pollution Research*, 25(15), pp.15226-15234.

Hua, F.L., Tsang, Y.F., Wang, Y.J., Chan, S.Y., Chua, H., Sin, S.N., (2007). *Chem. Eng.* 128, 169–175.

Huber Technology (n.d.). Screening considerations: A guide to selection. [ebook] Huntsville: Huber Technology, p.14. Available at: <http://huberforum.net/considerations> [Accessed 19 Feb. 2019].

Hurley, C., Janssen, J., Schreuder, M., Simonin, I., Zeng, J. and Zhong, W. (2019). Memo on national legislation and initiatives banning microplastics. Leiden: Universiteit Leiden, pp.1-10.

Ikhsan, S., Yusof, N., Aziz, F. and Misdan, N. (2017). A review of oilfied wastewater treatment using membrane filtration over conventional technology. *Malaysian Journal of Analytical Science*, 21(3), pp.643-658.

IPIECA (2010). Petroleum refining water/wastewater use and management. 1st ed. [ebook] London: IPIECA. Available at: http://www.savetexaswater.org/bmp/industrial/doc/Refining_Water_Best_Practices.pdf [Accessed 11 Jan. 2019].

Jeremic, D. (2014). Polyethylene. *Ullmann's Encyclopedia of Industrial Chemistry*, [online] 1. Available at: https://doi.org/10.1002/14356007.a21_487.pub3 [Accessed 21 Jan. 2019].

Jiang, J., Liu, Z. and He, Y. (2014). Development Trend: Rotary fibre disk filtration in the treatment of oilfield wastewater. *Filtration + Separation*, 51(1), pp.32-34.

Kawai, K. and Fujita, T. (2009). *Metal Catalyst in Olefin Polymerization*. Ed. Guan, Z. Berlin: Springer.

Kiss, K. and Patziger, M. (2018). On the accuracy of three dimensional flow measurements at low velocity ranges in municipal wastewater treatment reactors. *Flow Measurement and Instrumentation*, 64, pp.39-53.

Kundu, P. and Mishra, I. (2017). Treatment and reclamation of hydrocarbon-bearing oily wastewater as a hazardous pollutant by different processes and technologies: a state-of-the-art review. *Rev Chem Eng*, 35(1), pp.73-108.

Lares, M., Ncibi, M., Sillanpää, M. and Sillanpää, M. (2018). Occurrence, identification and removal of microplastic particles and fibers in conventional activated sludge process and advanced MBR technology. *Water Research*, 133, pp.236-246.

Li, L., Xu, G., Yu, H. and Xing, J. (2018). Dynamic membrane for micro-particle removal in wastewater treatment: Performance and influencing factors. *Science of The Total Environment*, 627, pp.332-340.

Loganathan, K., Chelme-Ayala, P. and Gamal El-Din, M. (2015). Effects of different pre-treatments on the performance of ceramic ultrafiltration membrane during the treatment of oil sands tailings pond recycle water: A Pilot-scale study. *Journal of Environmental Management*, 151, pp.540-549.

Luis, P. (2018). *Fundamental Modeling of Membrane Systems: Membrane and Process Performance*. Amsterdam: Elsevier Inc.

Ma, B., Xue, W., Hu, C., Liu, H., Qu, J. and Li, L. (2019). Characteristics of microplastic removal via coagulation and ultrafiltration during drinking water treatment. *Chemical Engineering Journal*, 359, pp.159-167.

Michielssen, M., Michielssen, E., Ni, J. and Duhaime, M. (2016). Fate of microplastics and other small anthropogenic litter (SAL) in wastewater treatment plants depends on unit processes employed. *Environmental Science: Water Research & Technology*, 2(6), pp.1064-1073.

Mostofa, K., Yoshioka, T., Mottaleb, M. and Vione, D. (2013). *Photobiogeochemistry of organic matter*. Berlin: Springer-Verlag Berlin Heidelberg.

Mulder, M. (1997). *Basic principles of membrane technology*. 2nd ed. Dordrecht: Kluwer Academic Publishers, pp.1-500.

Munirasu, S., Haija, M. and Banat, F. (2016). Use of membrane technology for oil field and refinery produced water treatment—A review. *Process Safety and Environmental Protection*, 100, pp.183-202.

Nollet, L. (2000). *Handbook of water analysis*. Marcel Dekker Inc.

Nunes, S. and Peinemann, K. (2006). *Membrane technology in the chemical industry*. 2nd ed. Weinheim, Germany: Wiley, pp.1-300.

Otitoju, T., Ahmad, A. and Ooi, B. (2016). Polyvinylidene fluoride (PVDF) membrane for oil rejection from oily wastewater: A performance review. *Journal of Water Process Engineering*, 14, pp.41-59.

Padaki, M., Surya Murali, R., Abdullah, M., Misdan, N., Moslehyani, A., Kassim, M., Hilal, N. and Ismail, A. (2015). Membrane technology enhancement in oil–water separation. A review. *Desalination*, 357, pp.197-207.

Pizzi, N. (2005). Water treatment operator handbook. [Denver, Colo.]: American Water Works Association, pp.60-100.

Prata, J., da Costa, J., Duarte, A. and Rocha-Santos, T. (2019). Methods for sampling and detection of microplastics in water and sediment: A critical review. *TrAC Trends in Analytical Chemistry*, 110, pp.150-159.

Pubchem.ncbi.nlm.nih.gov. (2019). Water. [online] Available at: <https://pubchem.ncbi.nlm.nih.gov/compound/962#section=Solubility> [Accessed 12 Feb. 2019].

Rajak, V., Kumar, S., Thombre, N. and Mandal, A. (2018). Synthesis of activated charcoal from saw-dust and characterization for adsorptive separation of oil from oil-in-water emulsion. *CHEMICAL ENGINEERING COMMUNICATIONS*, 205(7), pp.897-913.

Ranade, V. and Bhandari, V. (2014). Industrial wastewater treatment, recycling and reuse. 1st ed. Oxford: Butterworth-Heinemann, pp.1-500.

Renu, Agarwal, M. and Singh, K. (2017). Heavy metal removal from wastewater using various adsorbents: a review. *Water reuse and desalination*, 07.4, pp.387-419.

Rocha e Silva, F., Rocha e Silva, N., da Silva, I., Ferreira Brasileiro, P., Luna, J., Rufino, R., Santos, V. and Sarubbo, L. (2018). Oil removal efficiency forecast of a Dissolved Air Flootation (DAF) reduced scale prototype using the dimensionless number of Damköhler. *Journal of Water Process Engineering*, 23, pp.45-49.

Rowe, D. and Abdel-Magid, I. (1995). Handbook of wastewater reclamation and reuse. Boca Raton: CRC Press.

Salahi, A., Mohammadi, T., Mosayebi Behbahani, R. and Hemmati, M. (2015). Asymmetric polyethersulfone ultrafiltration membranes for oily wastewater treatment: Synthesis, characterization, ANFIS modeling, and performance. *Journal of Environmental Chemical Engineering*, 3(1), pp.170-178.

Salahi, A., Noshadi, I., Badrnezhad, R., Kanjilal, B., Mohammadi, T.,(2013). J. Environ. Chem. Eng., <http://dx.doi.org/10.1016/j.jece.2013.04.021>.

Sarfaraz, M.V., Ahmadpour, E., Salahi, A., Rekabdar, F., Mirza, B.,(2012). Chem. Eng. Res. Des. 90, 1642–1651.

Saththasivam, J., Loganathan, K. and Sarp, S. (2016). An overview of oil–water separation using gas flotation systems. Chemosphere, 144, pp.671-680.

Sharma, S. and Sanghi, R. (2013). Wastewater reuse and management. Dordrecht: Springer Science, pp.1-500.

Song, C.W., Wang, T.H., Pan, Y.Q., (2006). Sep. Purif. Technol. 51, 80–84.

Spellman, F. (2014). Handbook of water and wastewater treatment plant operations. 3rd ed. Boca Raton: Taylor and Francis Group, LLC, pp.1-600.

Standards Finland (2001). Water quality. Determination hydrocarbon oil index. Part 2: Method using solvent extraction and gas chromatography. SFS-EN ISO 9377-2. Finnish Environment Institute. SFS.

Stevenson, F. and Olsen, R. (1989). A simplified representation of the chemical nature and reactions of soil humus. J.Argon.Educ, 18(2), pp.1-5.

Stuetz, R. and Stephenson, T. (2009). Principles of water and wastewater treatment processes. London: IWA, pp.45-165.

Sun, J., Dai, X., Wang, Q., van Loosdrecht, M. and Ni, B. (2019). Microplastics in wastewater treatment plants: Detection, occurrence and removal. Water Research, 152, pp.21-37.

Svarovsky, L. (2000). Solid-Liquid separation. 4th ed. Oxford: Butterworth-Heinemann.

Talvitie, J., Mikola, A., Koistinen, A. and Setälä, O. (2017). Solutions to microplastic pollution – Removal of microplastics from wastewater effluent with advanced wastewater treatment technologies. *Water Research*, 123, pp.401-407.

Tchobanoglous, G., Burton, F. and Stensel, H. (2003). *Wastewater engineering treatment and reuse*. 4th ed. The McGraw-Hill Companies, Inc., pp.10-1200.

U.S EPA (2001). *Methods for collection, storage and manipulation of sediments for chemical and toxicological analyses: Technical manual*. Washington, D.C.: United States Environmental Protection Agency, Office of Water.

Van Le, T., Imai, T., Higuchi, T., Doi, R., Teeka, J., Xiaofeng, S. and Teerakun, M. (2012). Separation of oil-in-water emulsions by microbubble treatment and the effect of adding coagulant or cationic surfactant on removal efficiency. *Water science and Technology*, pp.1036-1043.

Wagner, M. and Lambert, S. (2018). *Freshwater microplastics: Emerging Environmental Contaminants?*. Cham: Springer Nature, pp.1-100.

Wang, T.Y., Zhou, H.G., Bi, Y., Tang, Y.A., (2007). Improve the efficiency of the sewage settling tank degreasing with flotation. *Technol.Supervision Pet. Ind.* 1, 18–20.

Wüst, B. (2000). *Measuring Hydrocarbon Oil Index according to ISO 9377-2 (DIN H53)*. Waldbronn: Agilent Technologies.

Yang, T., Ma, Z.F., Yang, Q.Y., (2011). *Desalination* 270,50–56.

Yu, L., Han, M. and He, F. (2017). A review of treating oily wastewater. *Arabian Journal of Chemistry*, 10, pp.S1913-S1922.

Yu, S.L., Lu, Y., Chai, B.X., (2006). *Desalination* 196, 76–83.

Zhu, D.H., Zheng, Z.H., (2002). Application of MAF Air Flotation Technology in Refinery Wastewater Treatment. *Environ. Prot. Petrochem. Ind.* 25, 16–18.

APPENDIX LIST

APPENDIX I Pure water and wastewater fluxes from membrane filtrations

APPENDIX I

Membrane fluxes with deionized water and wastewater are shown in Figure 56 - Figure 99.

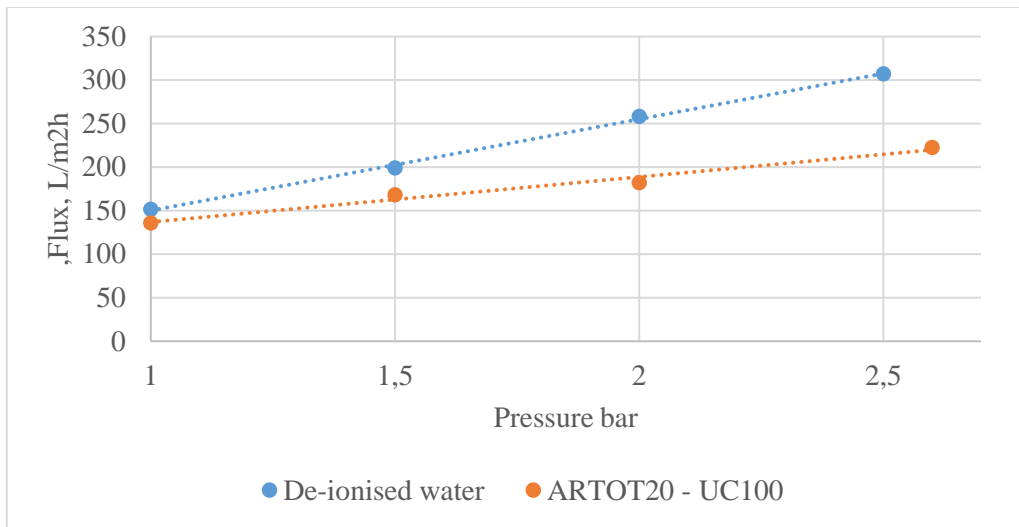


Figure 56 27.3 sample ARTOT20 - UC100. $T_{\text{water}}=20-22$ °C, mixer speed 250 rpm.

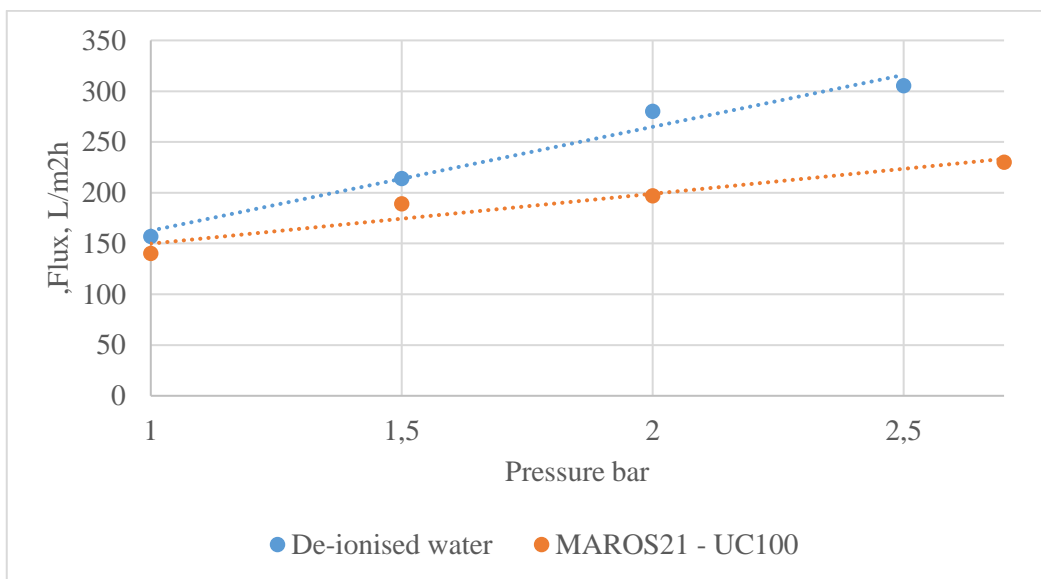


Figure 57 27.3 sample MAROS21 - UC100. $T_{\text{water}}=21-23$ °C, mixer speed 250 rpm.

APPENDIX I

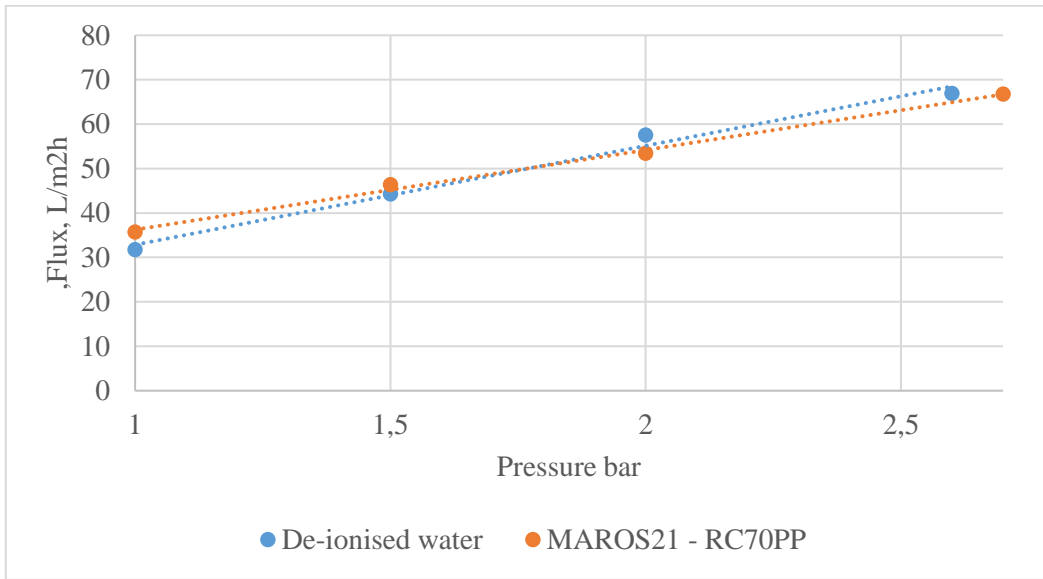


Figure 58 8.4 sample MAROS21 – RC70PP. $T_{\text{water}}=22-23$ °C, mixer speed 250 rpm.

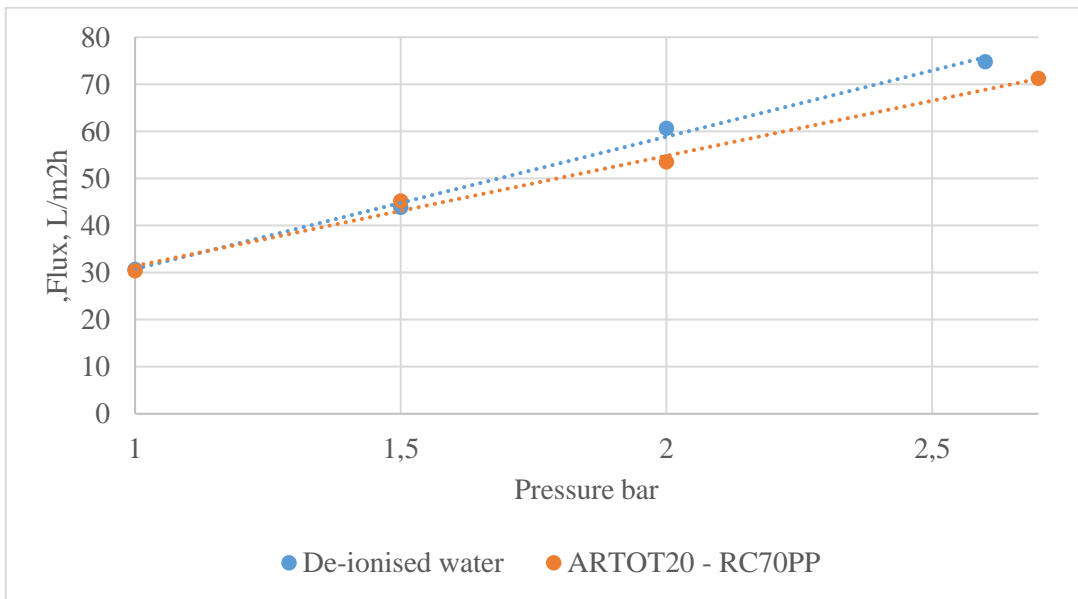


Figure 59 8.4 sample ARTOT20 – RC70PP. $T_{\text{water}}=22-23$ °C, mixer speed 250 rpm.

APPENDIX I

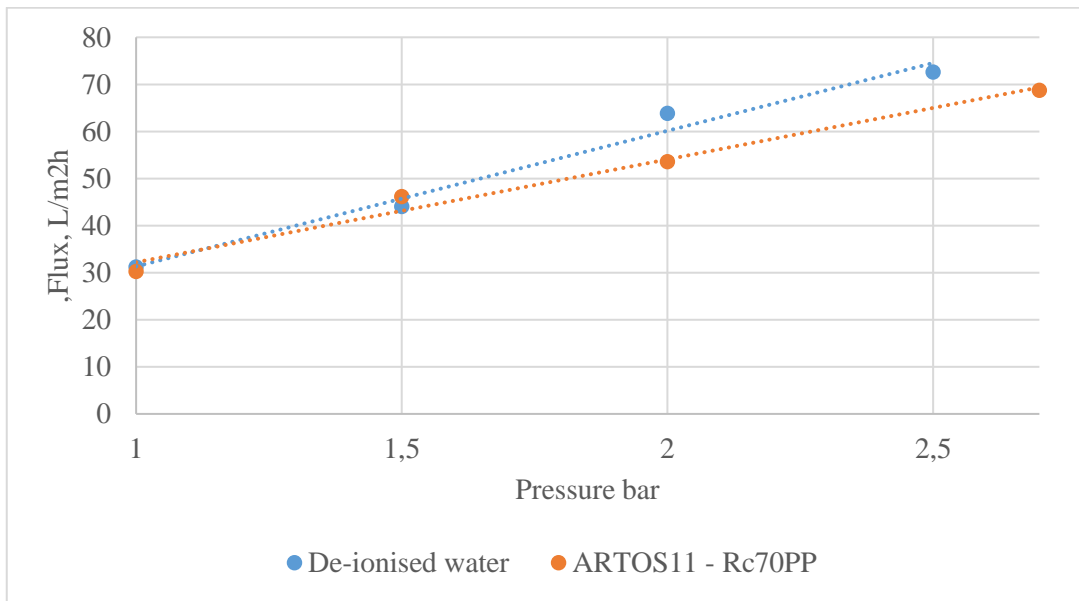


Figure 60 8.4 sample ARTOS11 – RC70PP. $T_{\text{water}}=22-23\text{ }^{\circ}\text{C}$, mixer speed 250 rpm.

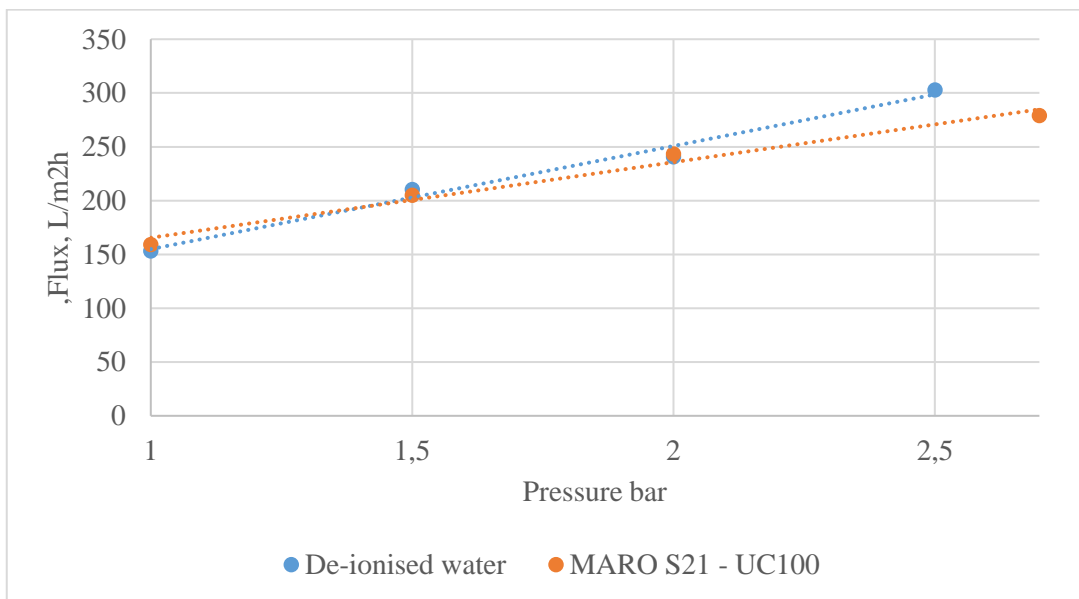


Figure 61 8.4 sample MAROS21 – UC100. $T_{\text{water}}=21-23\text{ }^{\circ}\text{C}$, mixer speed 250 rpm.

APPENDIX I

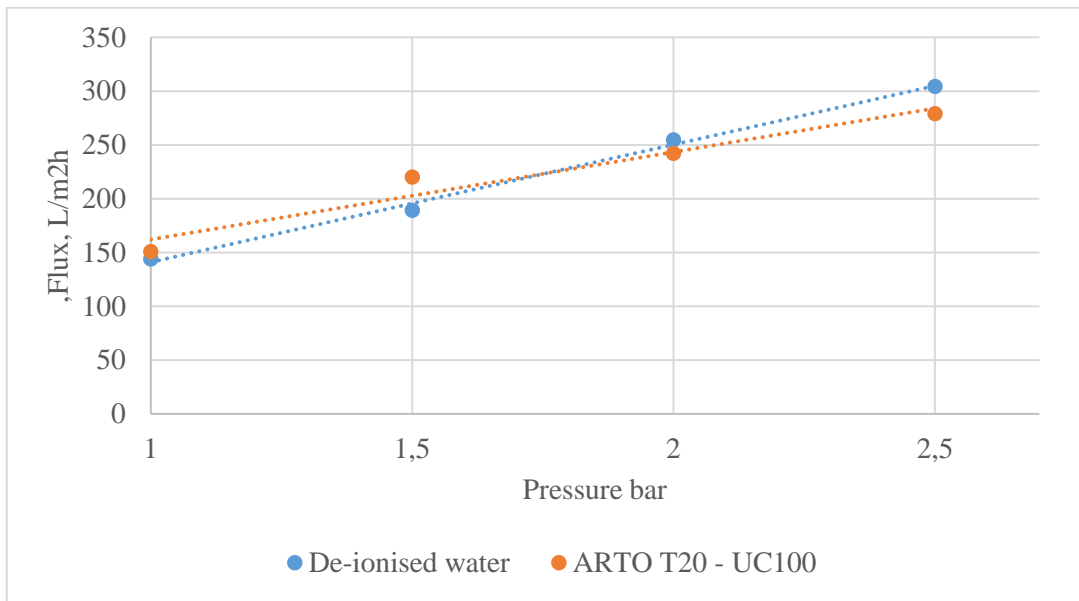


Figure 62 8.4 sample ARTOT20 – UC100. $T_{\text{water}}=21-23\text{ }^{\circ}\text{C}$, mixer speed 250 rpm.

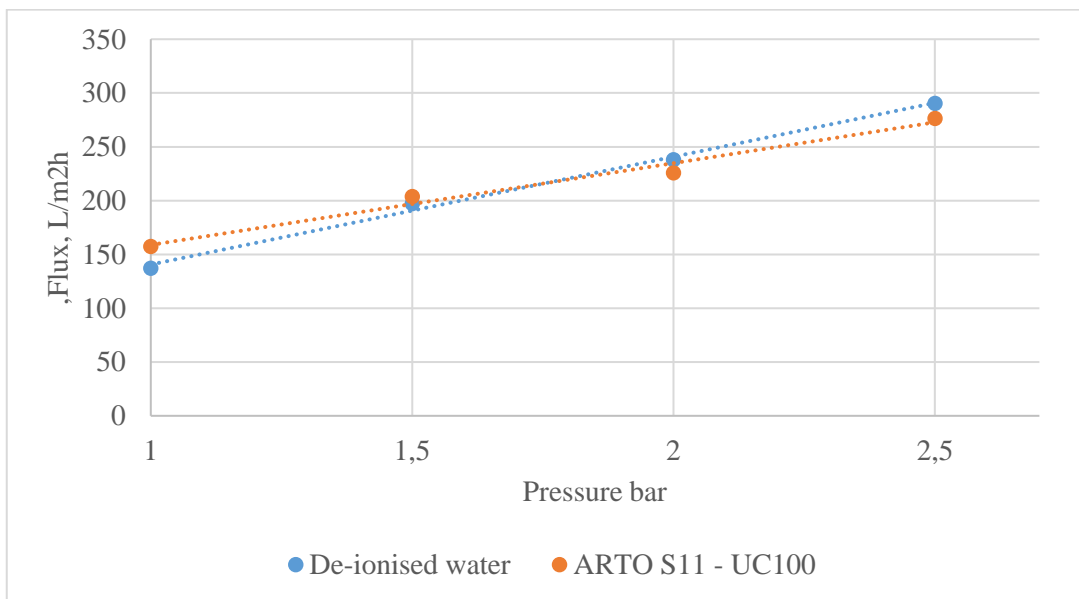


Figure 63 8.4 sample ARTOS11 – UC100. $T_{\text{water}}=21-23\text{ }^{\circ}\text{C}$, mixer speed 250 rpm.

APPENDIX I

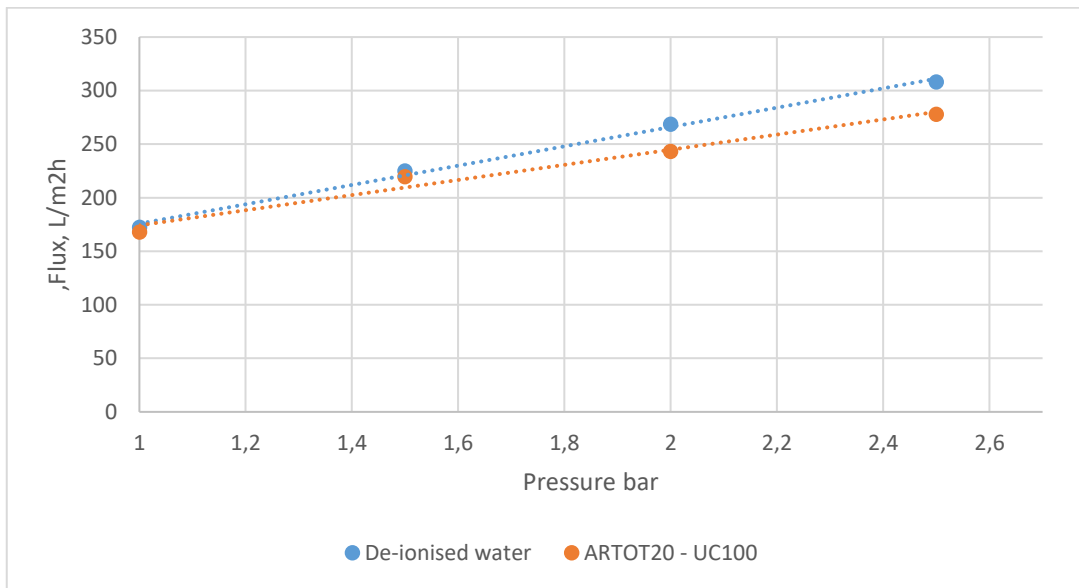


Figure 64 18.4 sample ARTOT20 – UC100. $T_{\text{water}}=21-25\text{ }^{\circ}\text{C}$, mixer speed 250 rpm.

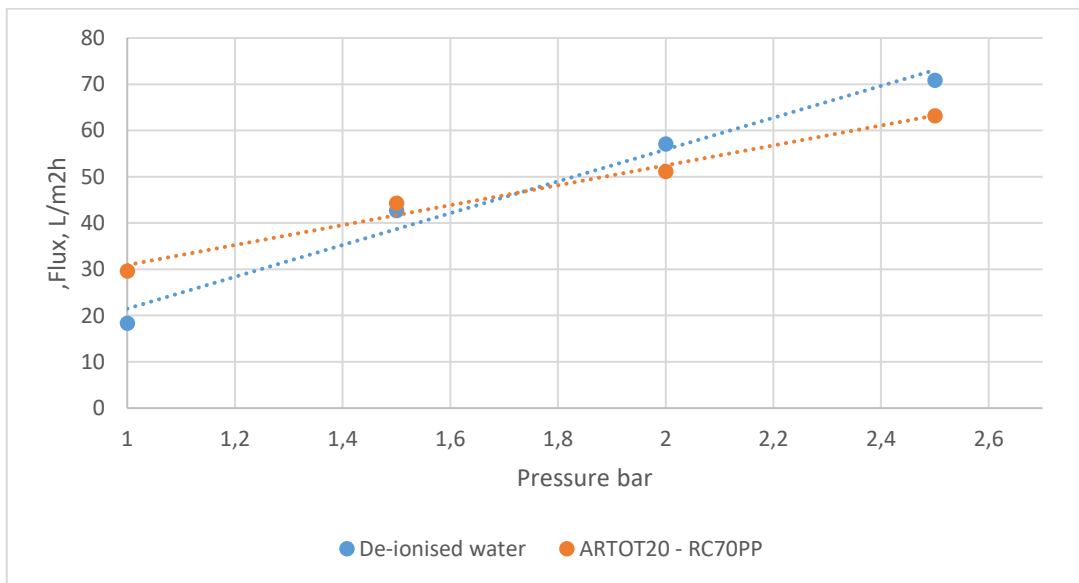


Figure 65 18.4 sample ARTOT20 – RC70PP. $T_{\text{water}}=21-25\text{ }^{\circ}\text{C}$, mixer speed 250 rpm.

APPENDIX I

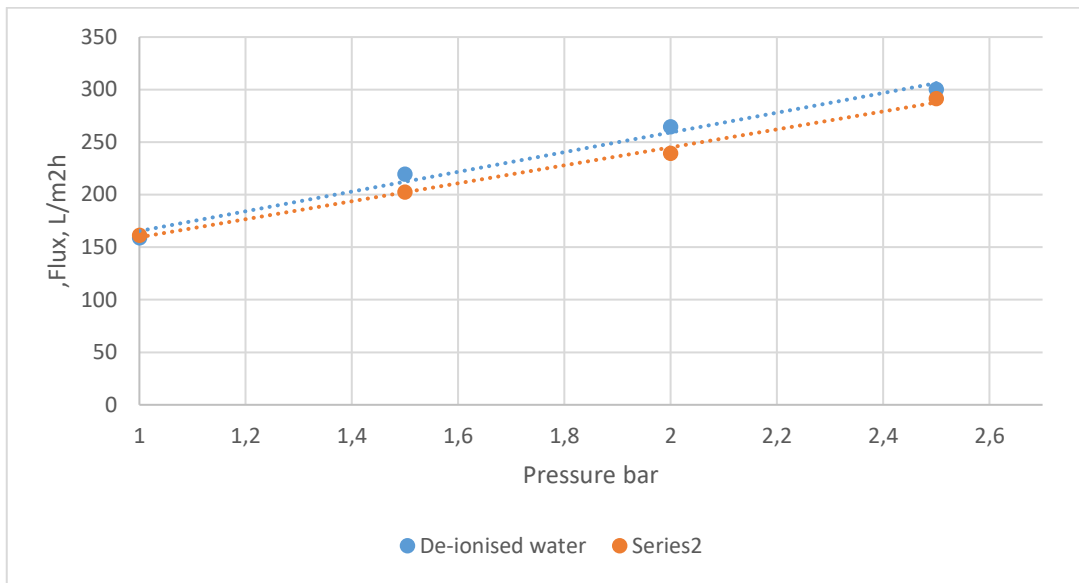


Figure 66 18.4 sample ARTOT20 – UC100. $T_{\text{water}}=21-23$ °C, mixer speed 250 rpm.

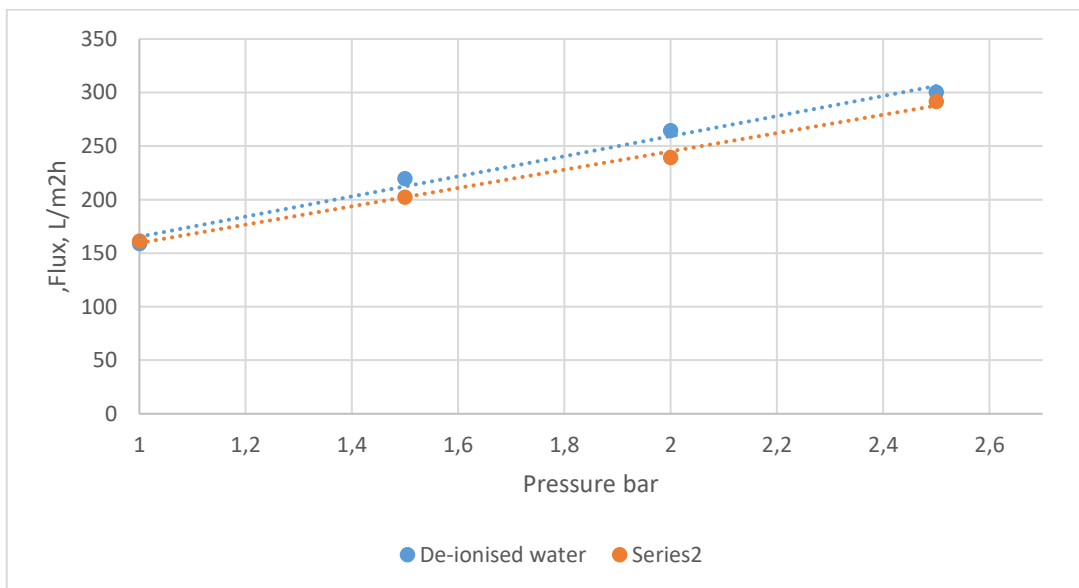


Figure 67 18.4 sample ARTOT20 – RC70PP. $T_{\text{water}}=21-24$ °C, mixer speed 250 rpm.

APPENDIX I

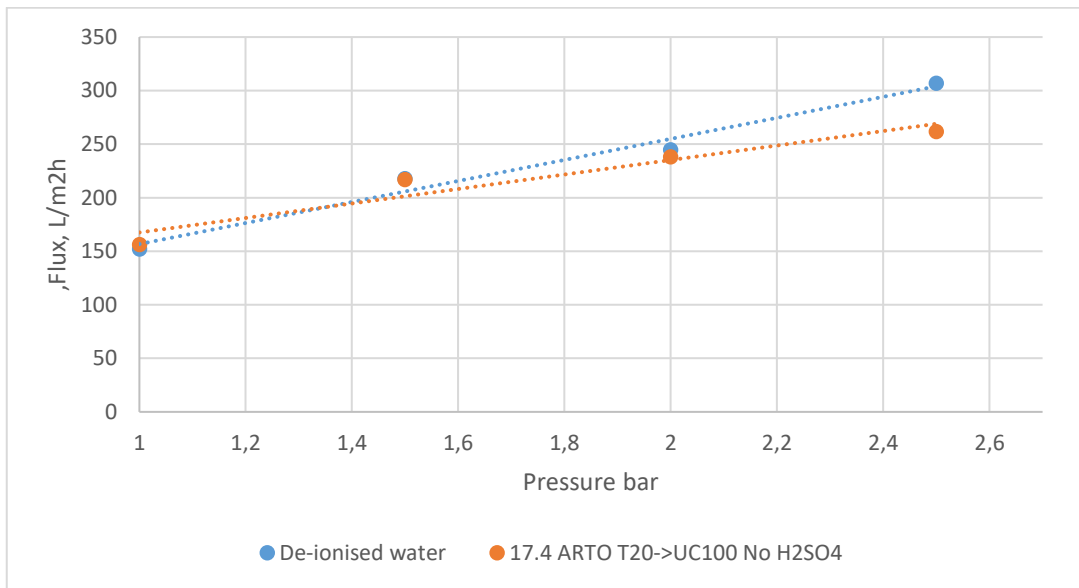


Figure 68 17.4 sample ARTOT20 – UC100 No H2SO4. T_{water}=21-24 °C, mixer speed 250 rpm.

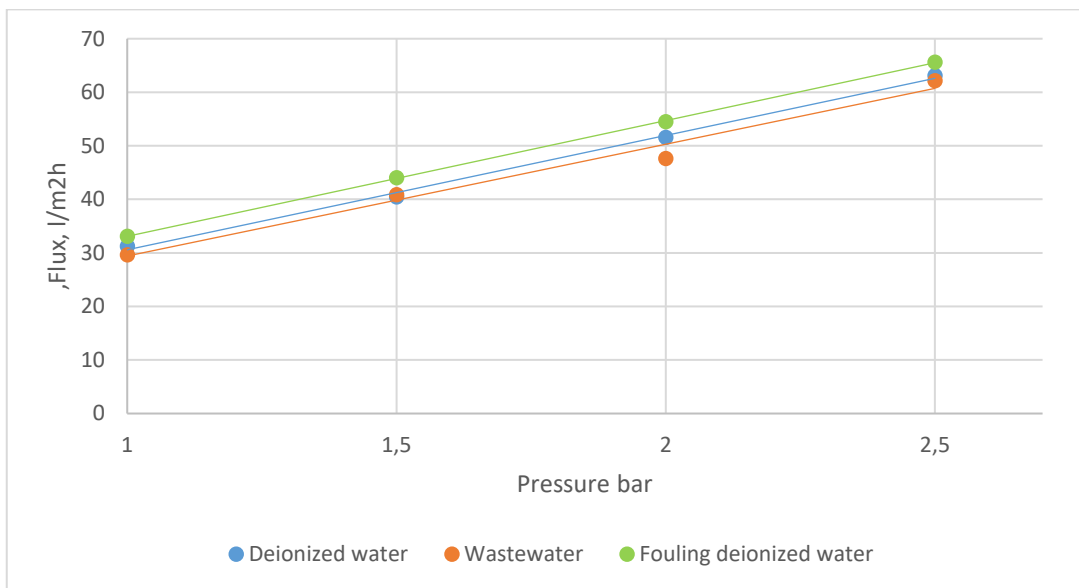


Figure 69 17.4 sample ARTOT20 – RC70PP No H2So4. T_{water}=21-24 °C, mixer speed 250 rpm.

APPENDIX I

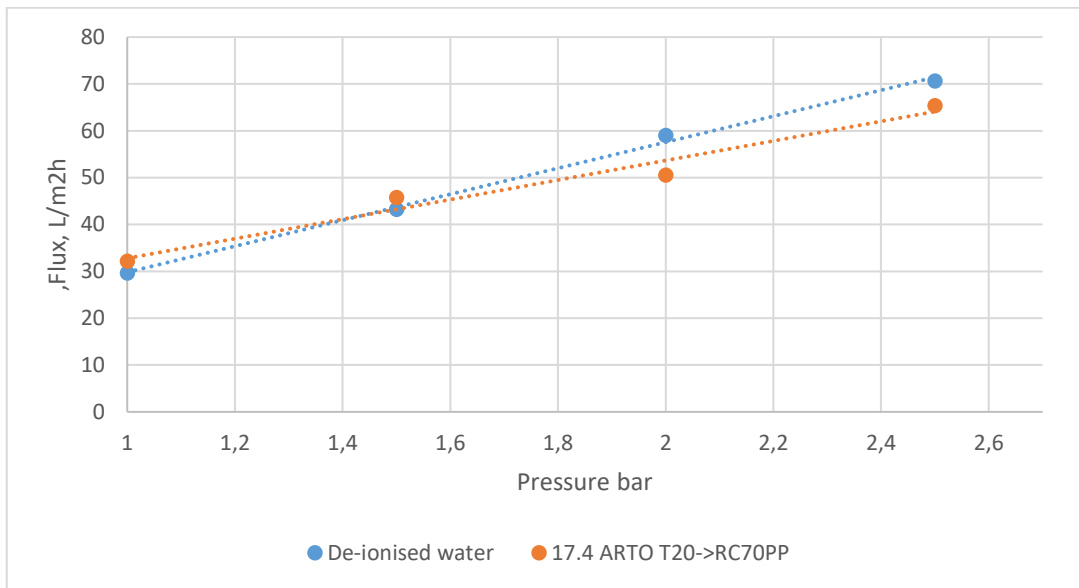


Figure 70 17.4 sample ARTOT20 – RC70PP. $T_{\text{water}}=23\text{ }^{\circ}\text{C}$, mixer speed 250 rpm.

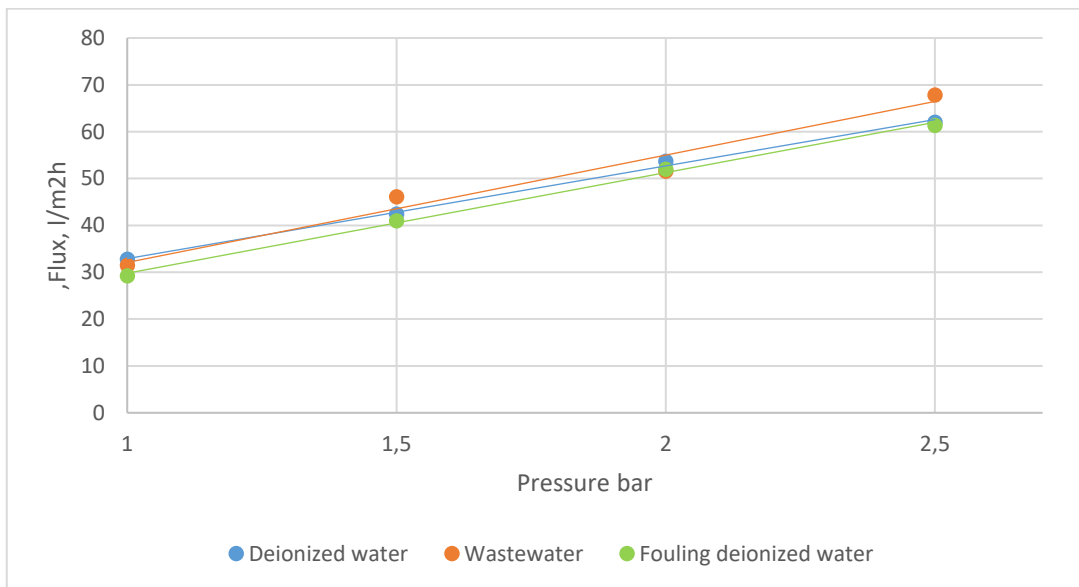


Figure 71 18.4 sample ARTOS11 – RC70PP. $T_{\text{water}}=22\text{-}25\text{ }^{\circ}\text{C}$, mixer speed 250 rpm.

APPENDIX I

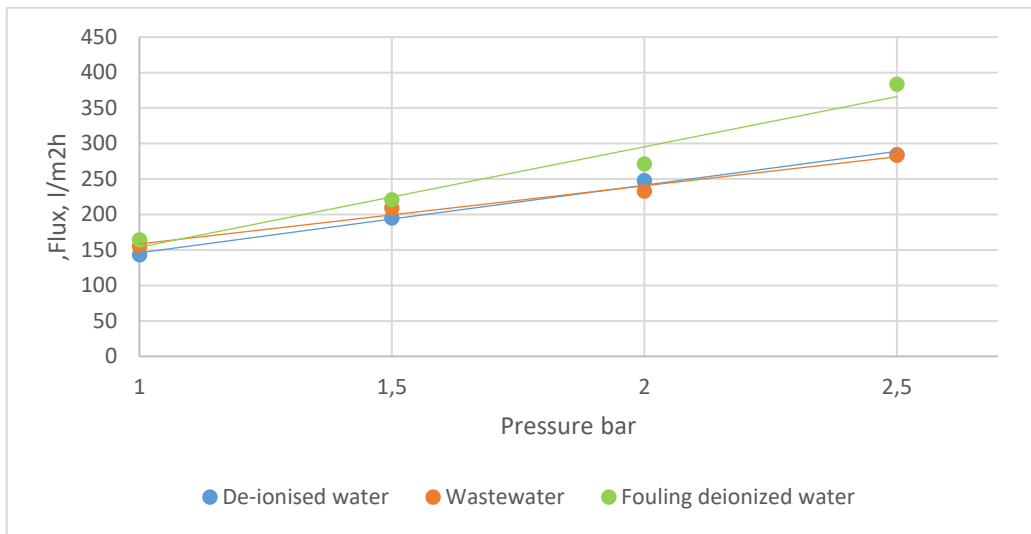


Figure 72 18.4 sample ARTOS11 – UC100. $T_{\text{water}}=22-25^{\circ}\text{C}$, mixer speed 250 rpm.

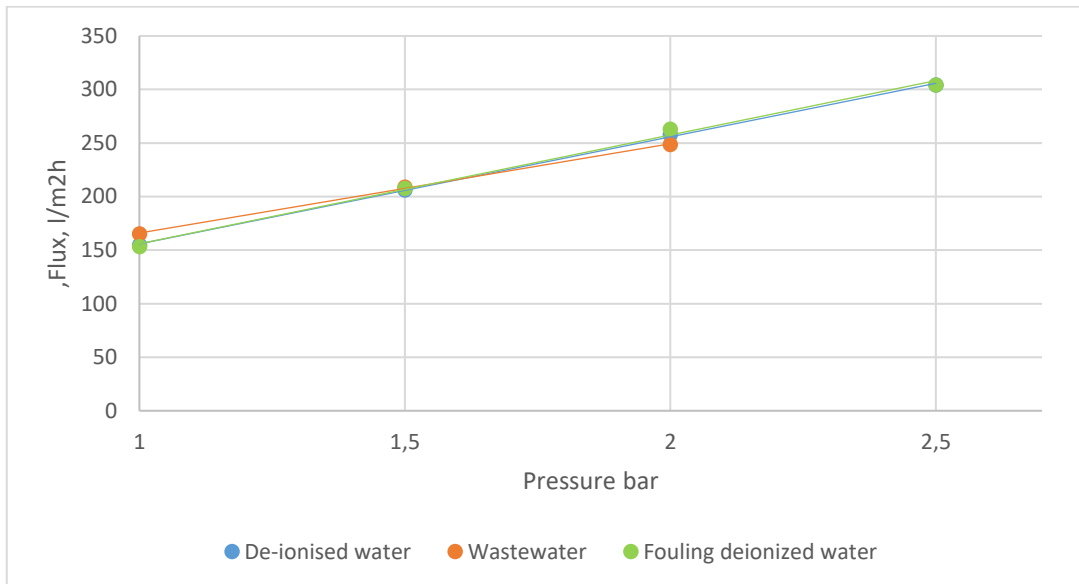


Figure 73 18.4 sample ARTOS11 – UC100. $T_{\text{water}}=22-25^{\circ}\text{C}$, mixer speed 250 rpm.

APPENDIX I

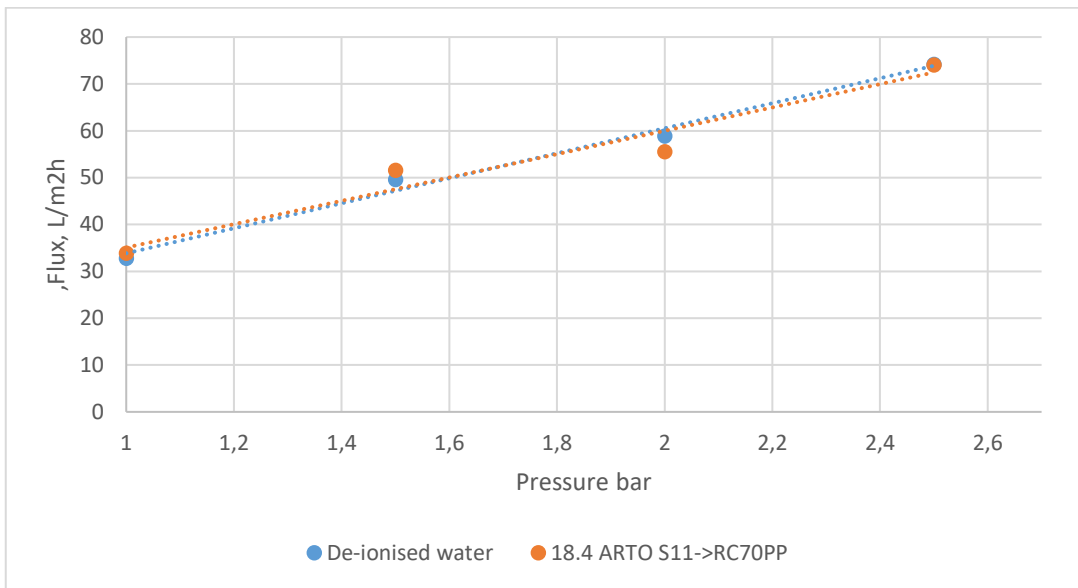


Figure 74 18.4 sample ARTOS11 – RC70PP. $T_{\text{water}}=22-25^{\circ}\text{C}$, mixer speed 250 rpm.

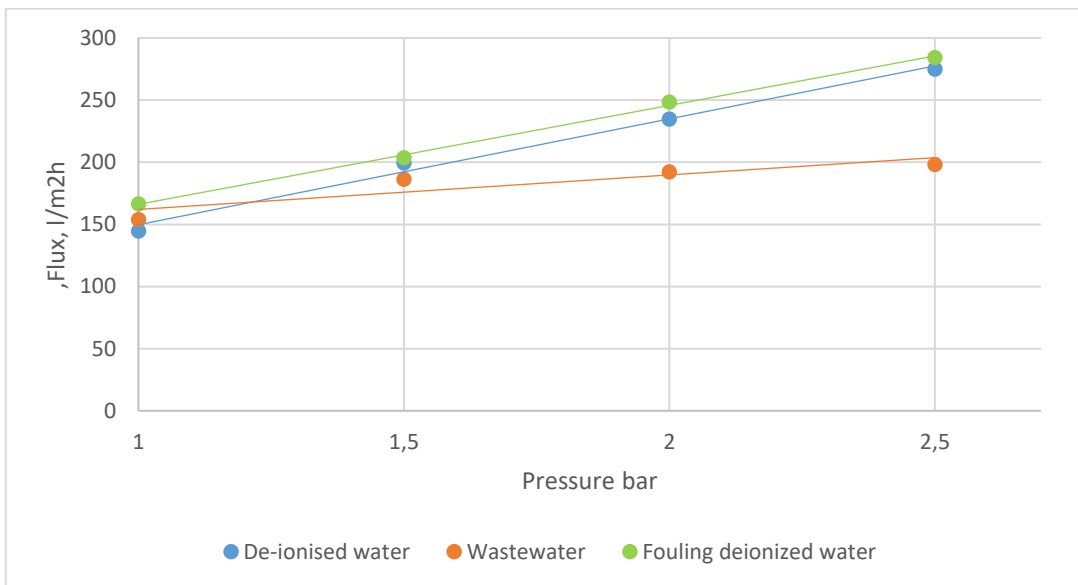


Figure 75 14.5 sample MAROS21 – UC100 No H₂SO₄. $T_{\text{water}}=22-24^{\circ}\text{C}$, mixer speed 250 rpm.

APPENDIX I

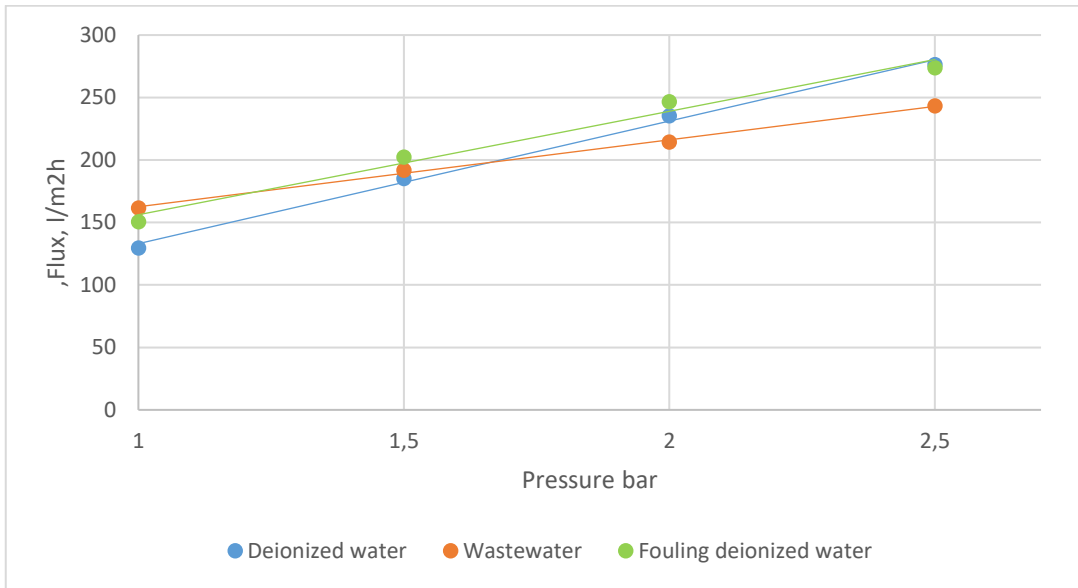


Figure 76 14.5 sample ARTOT20 – UC100 No H₂SO₄. T_{water}=22-24°C, mixer speed 250 rpm.

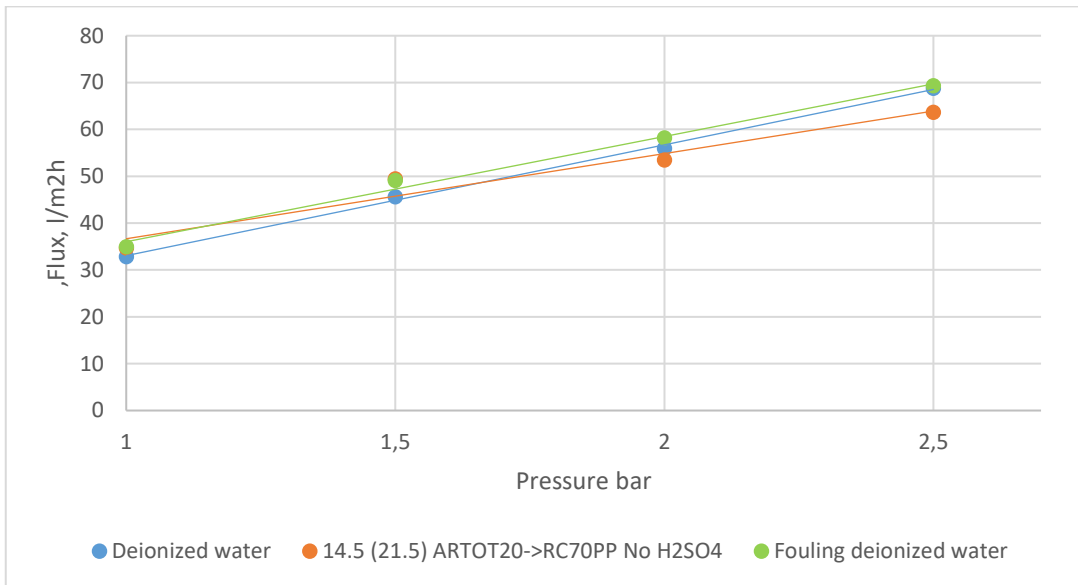


Figure 77 14.5 sample ARTOT20 – RC70PP No H₂SO₄. T_{water}=22-24°C, mixer speed 250 rpm.

APPENDIX I

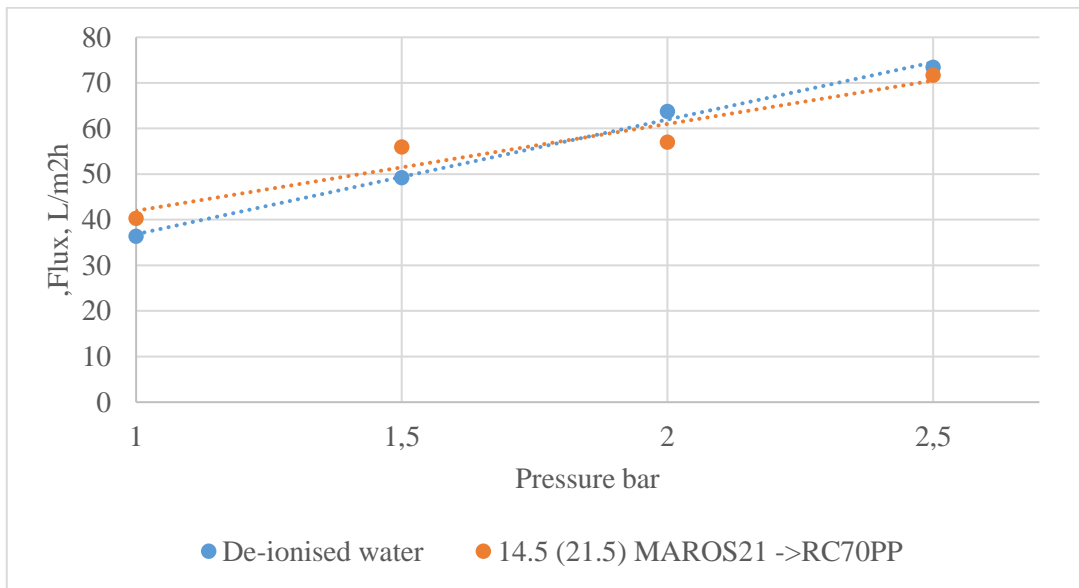


Figure 78 14.5 sample MAROS21 – RC70PP. $T_{\text{water}}=22-24^{\circ}\text{C}$, mixer speed 250 rpm.

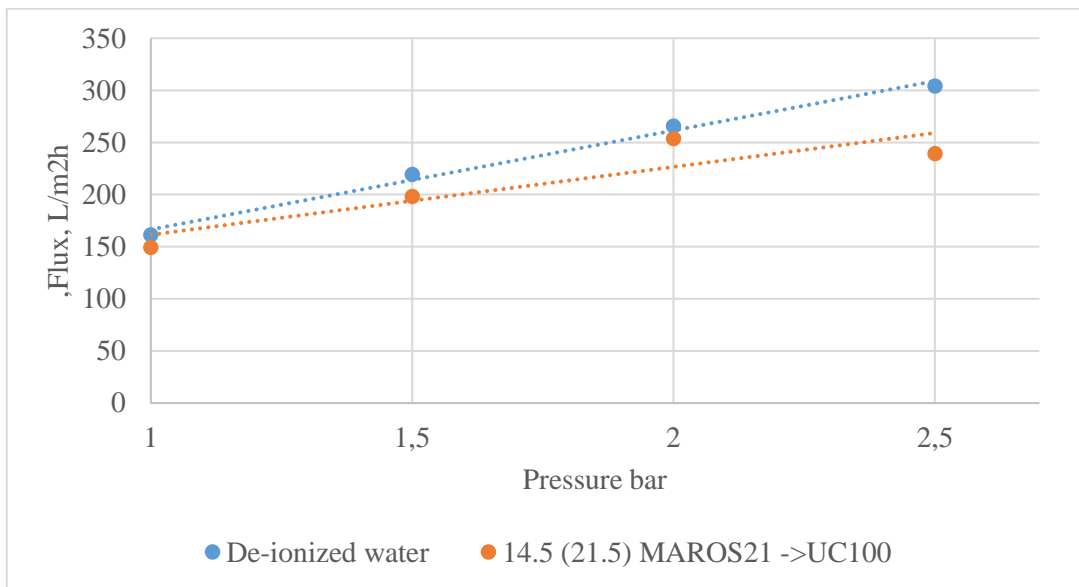


Figure 79 14.5 sample MAROS21 – UC100. $T_{\text{water}}=22-24^{\circ}\text{C}$, mixer speed 250 rpm.

APPENDIX I

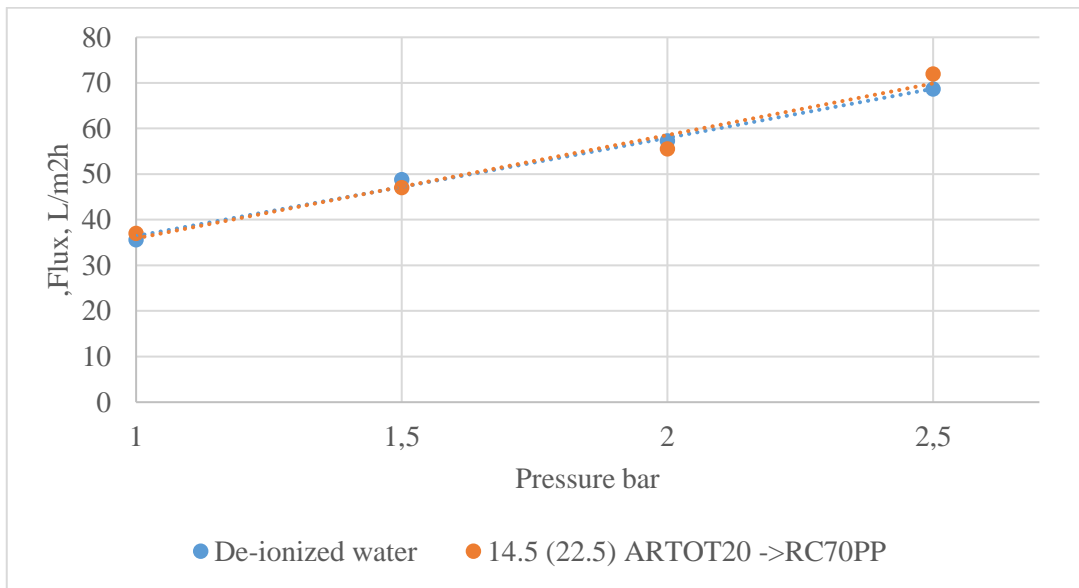


Figure 80 14.5 sample ARTOT20 – RC70PP. $T_{\text{water}}=22-24^{\circ}\text{C}$, mixer speed 250 rpm.

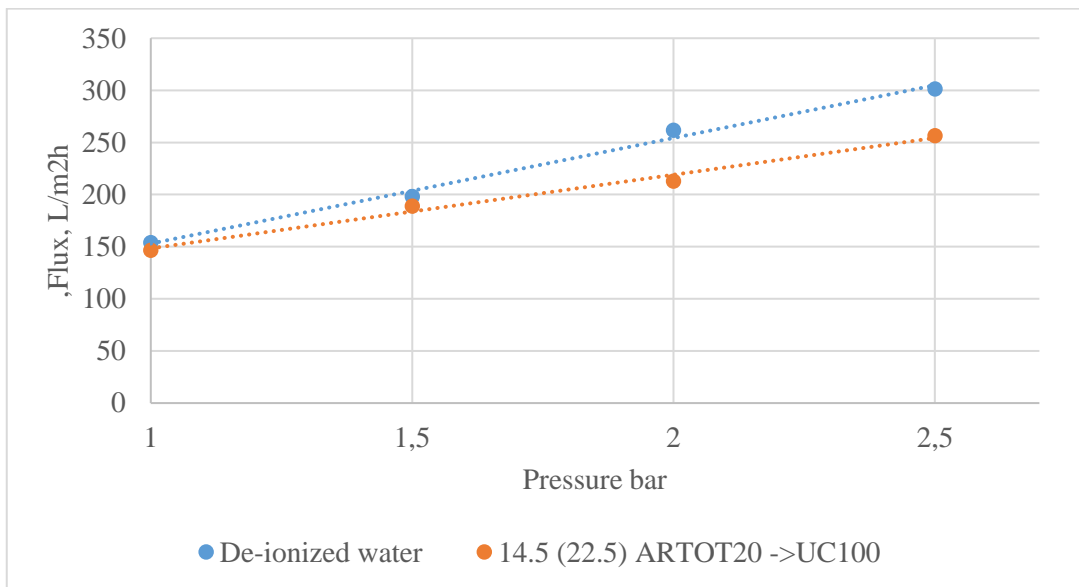


Figure 81 14.5 sample ARTOT20 – UC100. $T_{\text{water}}=22-23^{\circ}\text{C}$, mixer speed 250 rpm.

APPENDIX I

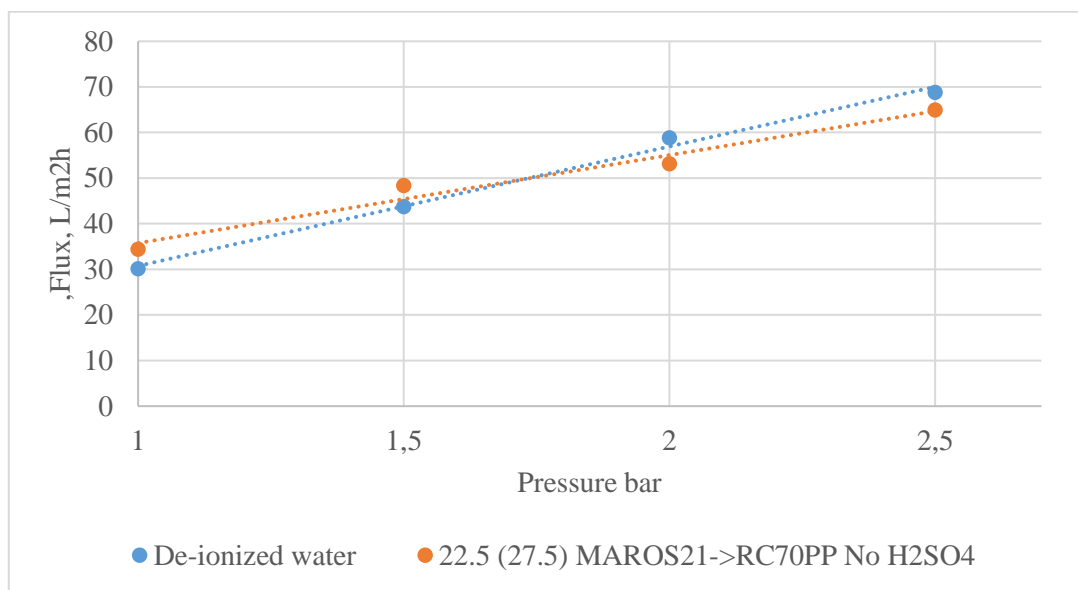


Figure 82 22.5 sample MAROS21 – RC70PP No H₂SO₄. T_{water}=22-23°C, mixer speed 250 rpm.

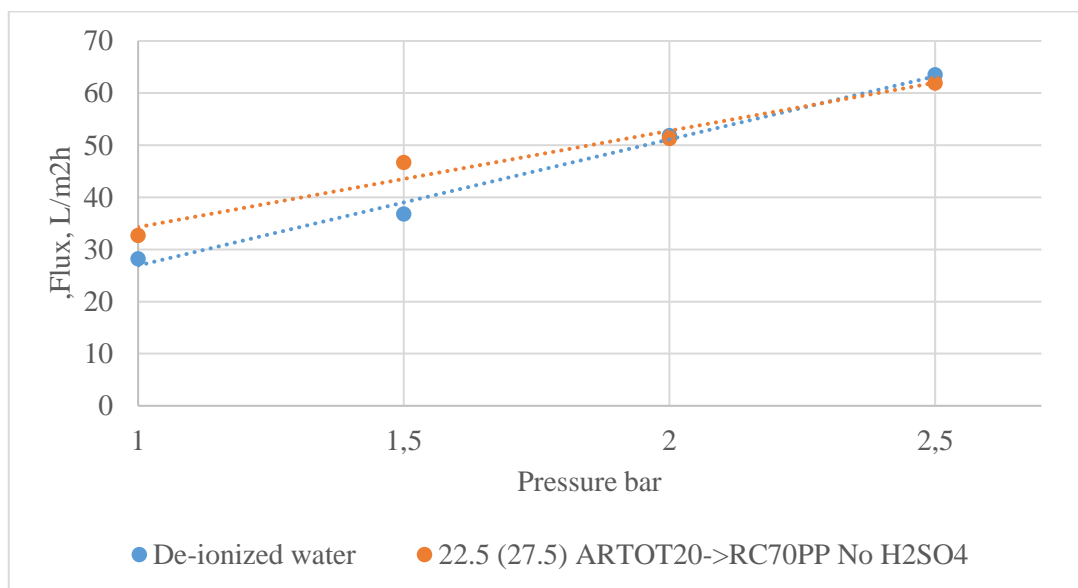


Figure 83 22.5 sample ARTOT20 – RC70PP No H₂SO₄. T_{water}=22-23°C, mixer speed 250 rpm.

APPENDIX I

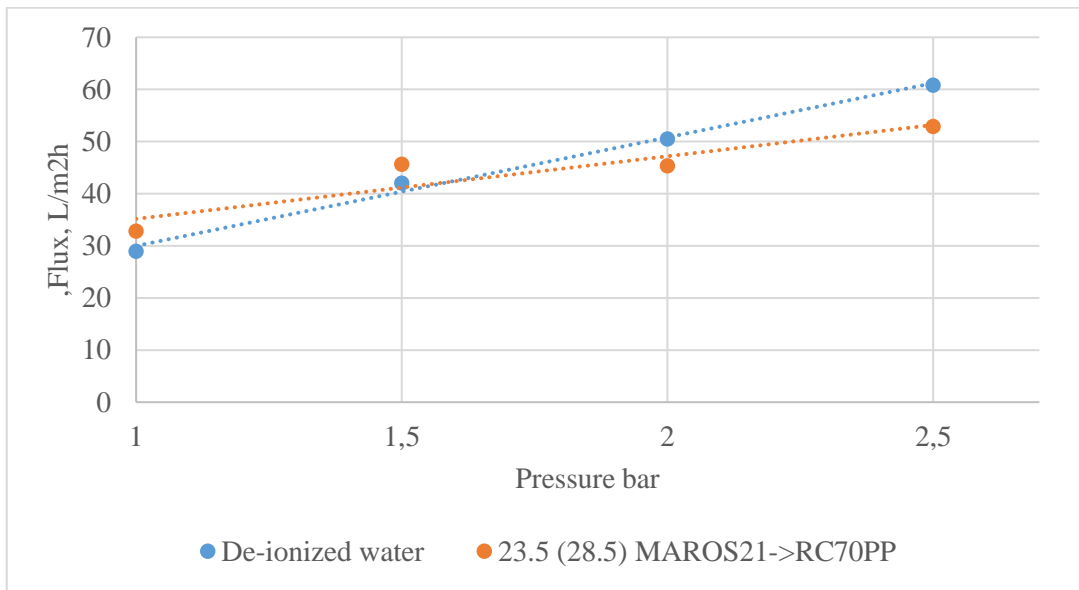


Figure 84 23.5 sample MAROS21 – RC70PP. $T_{\text{water}}=22-23^{\circ}\text{C}$, mixer speed 250 rpm.

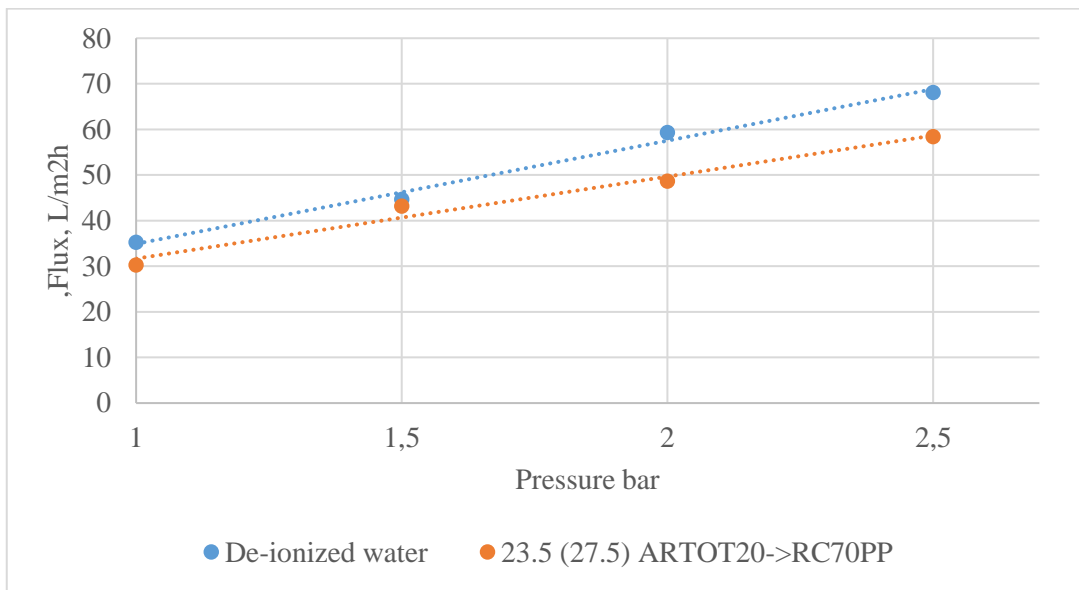


Figure 85 23.5 sample ARTOT20 – RC70PP. $T_{\text{water}}=22-23^{\circ}\text{C}$, mixer speed 250 rpm.

APPENDIX I

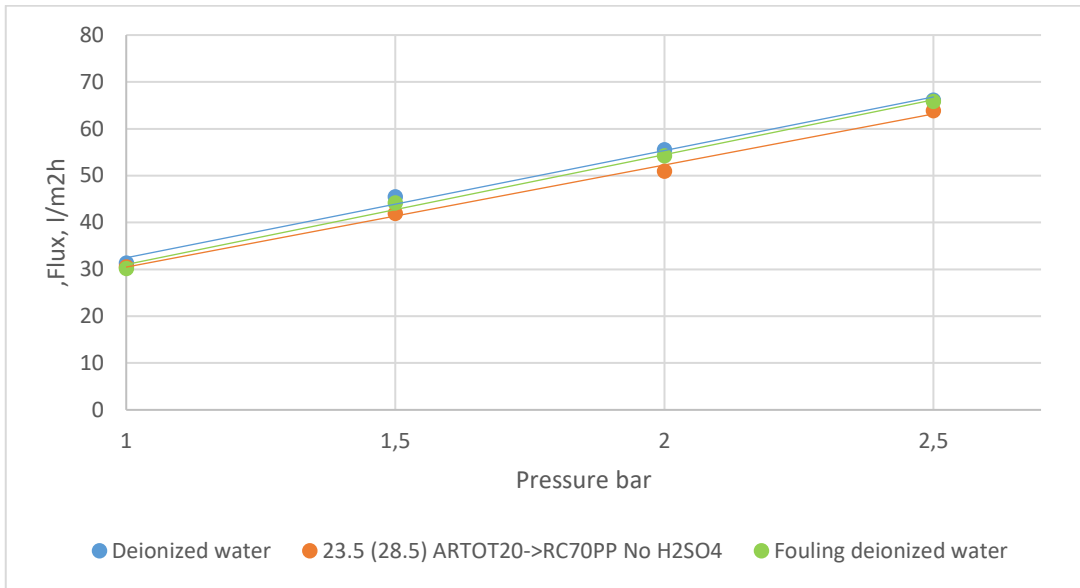


Figure 86 23.5 (28.5) ARTOT20->RC70PP No H₂SO₄. T_{water}=22-23°C, mixer speed 250 rpm.

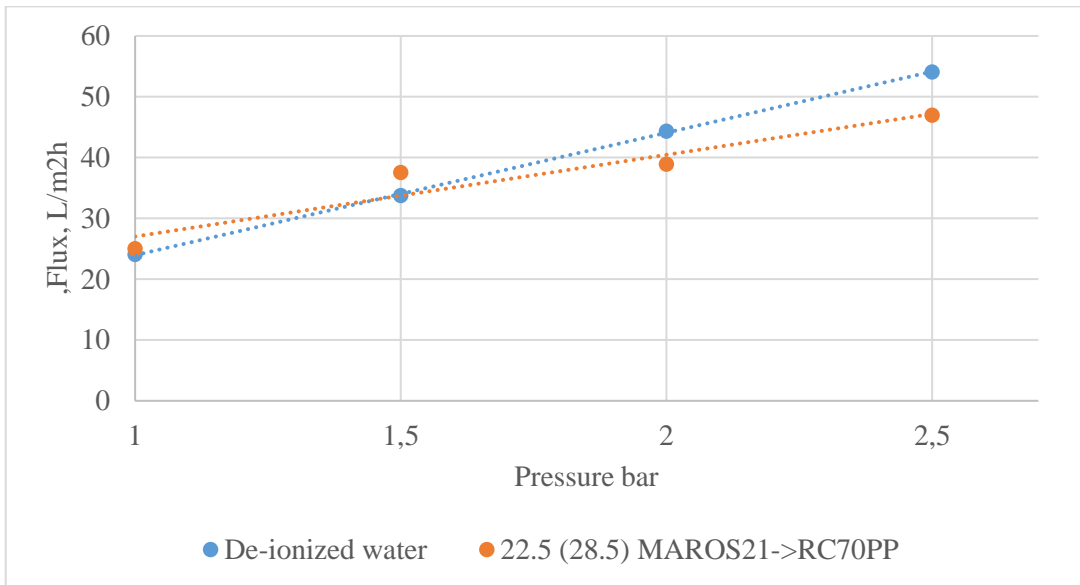


Figure 87 22.5 (28.5) MAROS21->RC70PP. T_{water}=22-23°C, mixer speed 250 rpm.

APPENDIX I

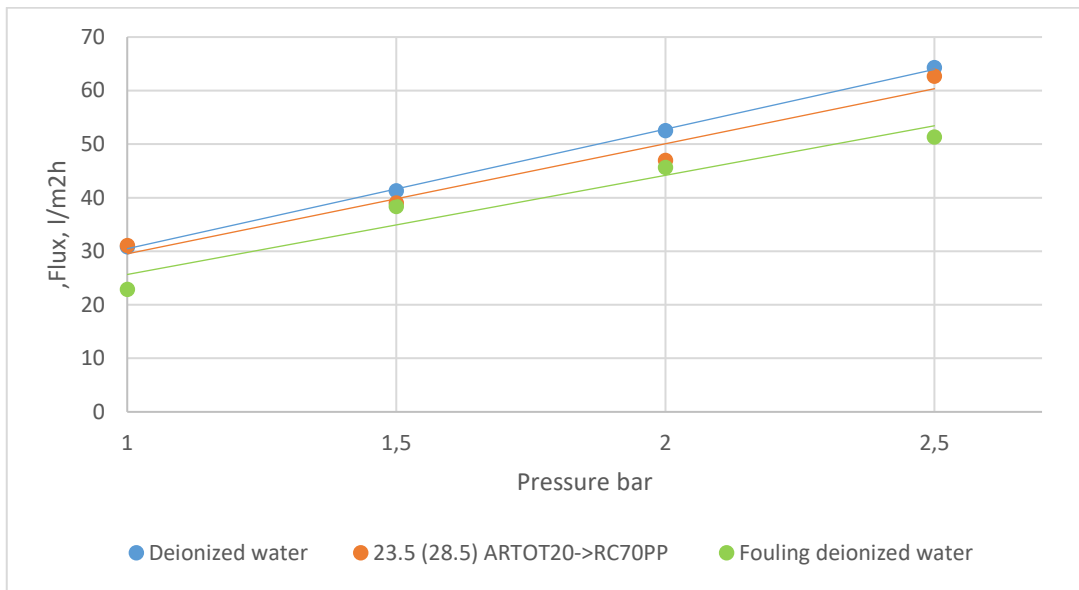


Figure 88 23.5 (28.5) ARTOT20->RC70PP. T_{water}=22-23°C, mixer speed 250 rpm.

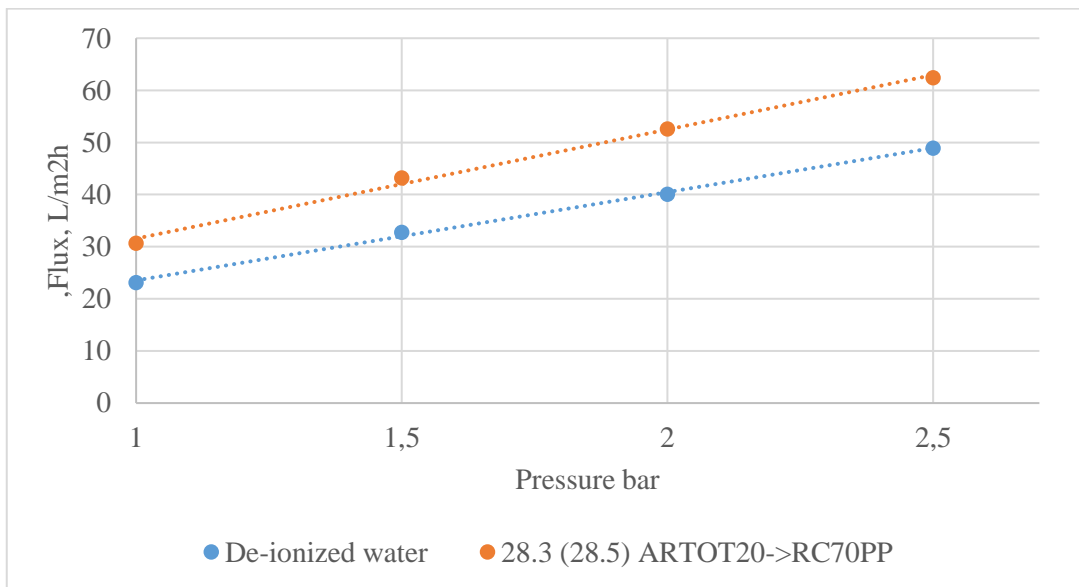


Figure 89 28.3 (28.5) ARTOT20->RC70PP. T_{water}=22-23°C, mixer speed 250 rpm.

APPENDIX I

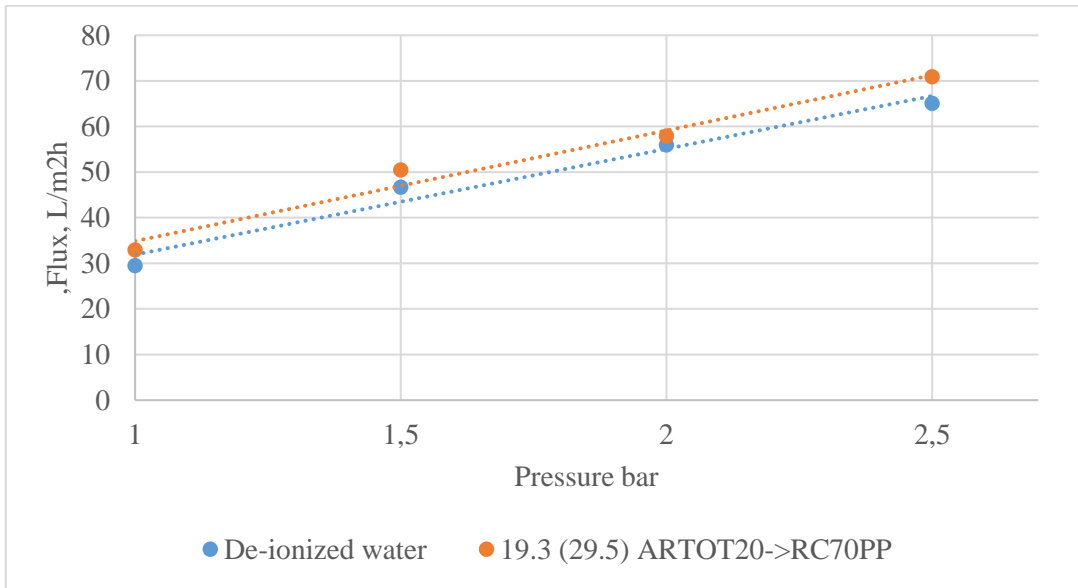


Figure 90 19.3 (28.5) ARTOT20->RC70PP. T_{water}=22-23°C, mixer speed 250 rpm.

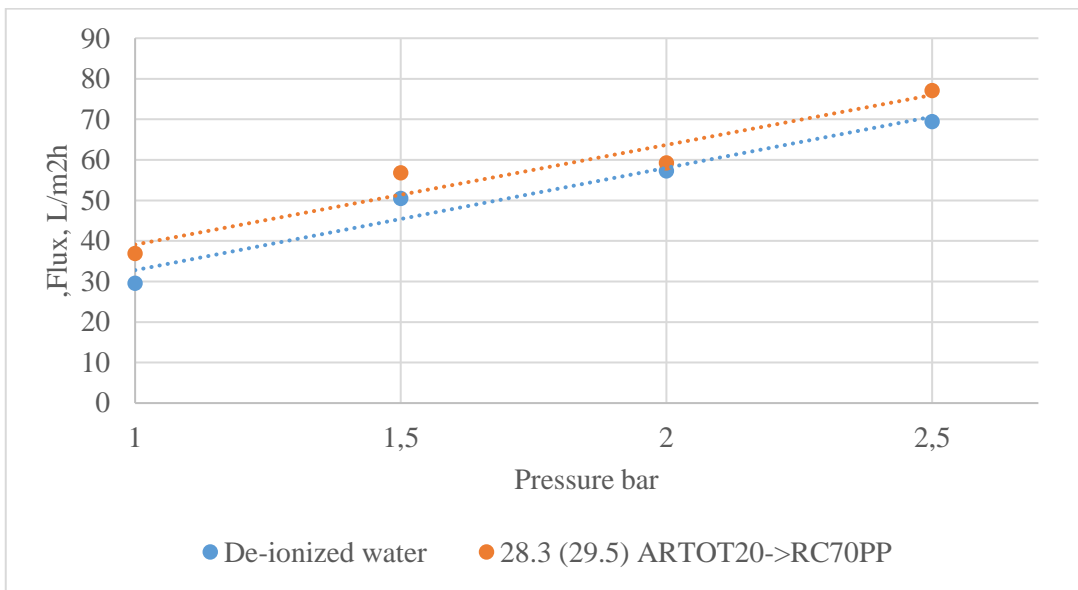


Figure 91 28.3 (28.5) ARTOT20->RC70PP. T_{water}=22-23°C, mixer speed 250 rpm.

APPENDIX I

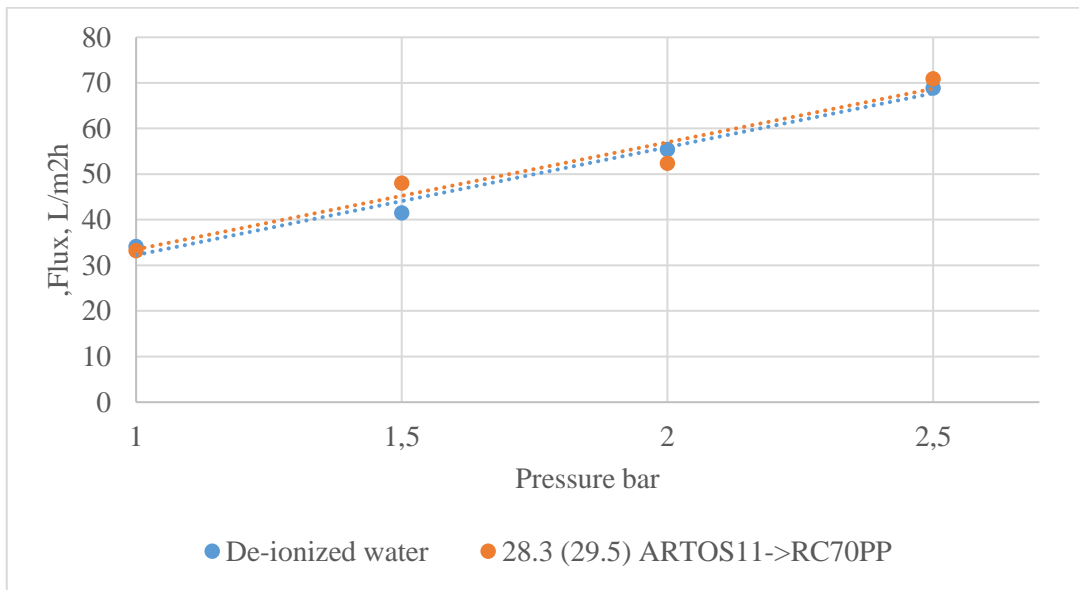


Figure 92 28.3 (29.5) ARTOS1->RC70PP. T_{water}=22-23°C, mixer speed 250 rpm.

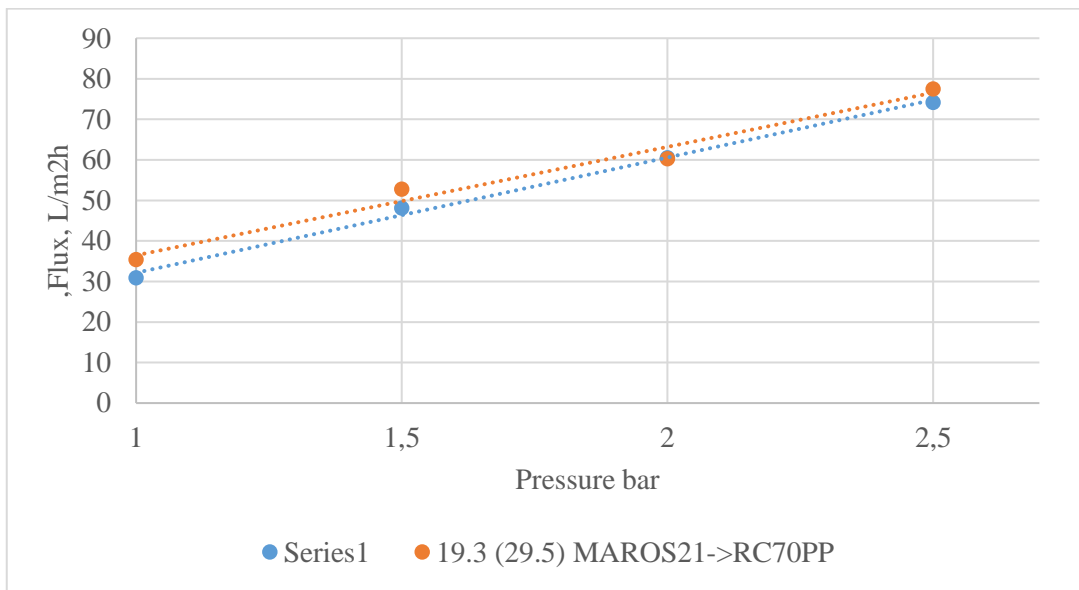


Figure 93 19.3 (29.5) MAROS21->RC70PP. T_{water}=22-23°C, mixer speed 250 rpm.

APPENDIX I

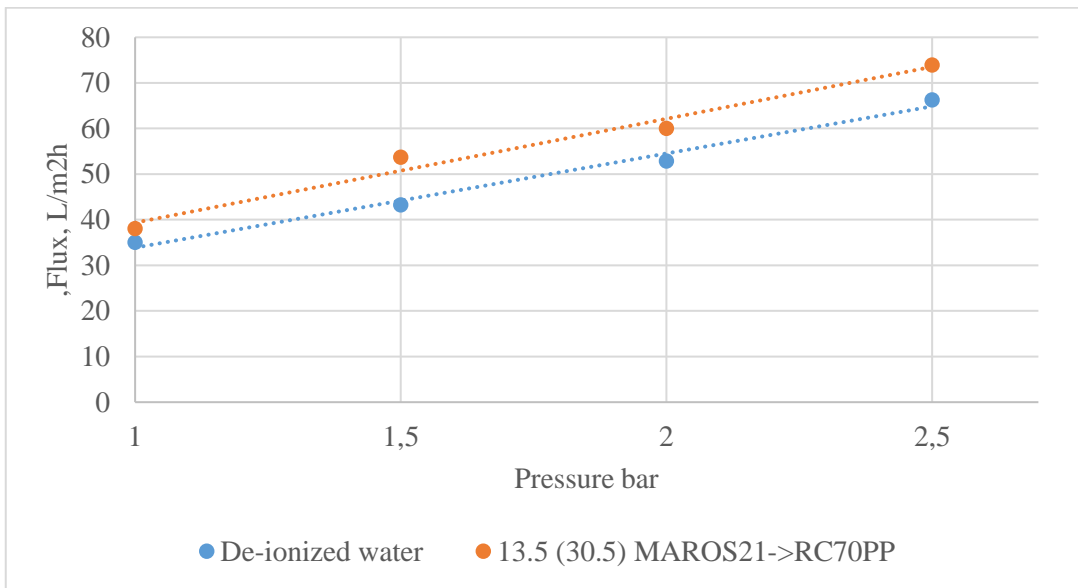


Figure 94 13.5 (30.5) MAROS21->RC70PP. T_{water}=22-23°C, mixer speed 250 rpm.

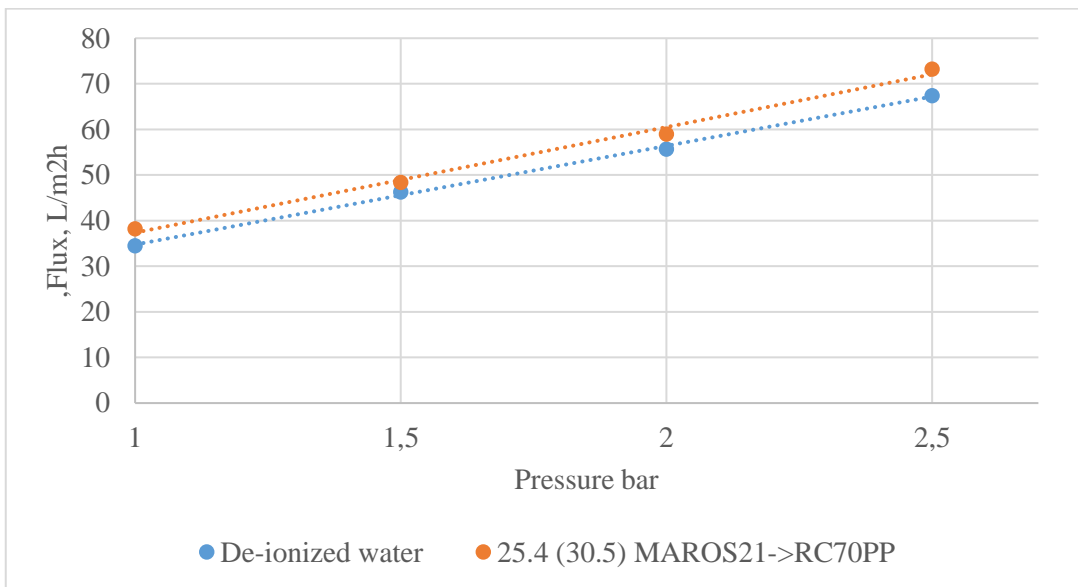


Figure 95 25.4 (30.5) MAROS21->RC70PP. T_{water}=22-23°C, mixer speed 250 rpm.

APPENDIX I

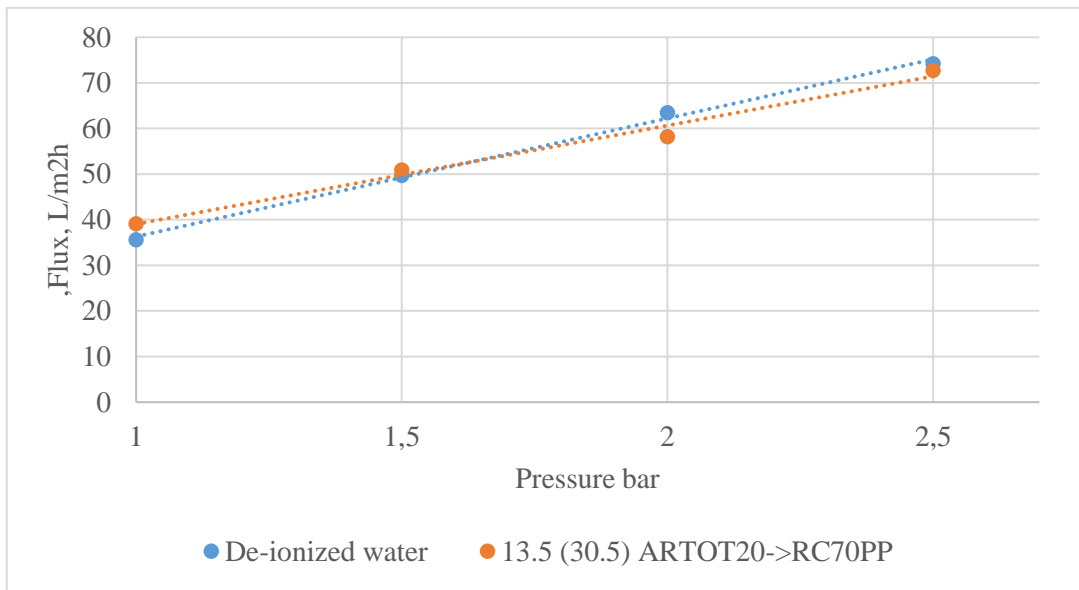


Figure 96 13.5 (30.5) ARTOT20->RC70PP. T_{water}=22-23°C, mixer speed 250 rpm.

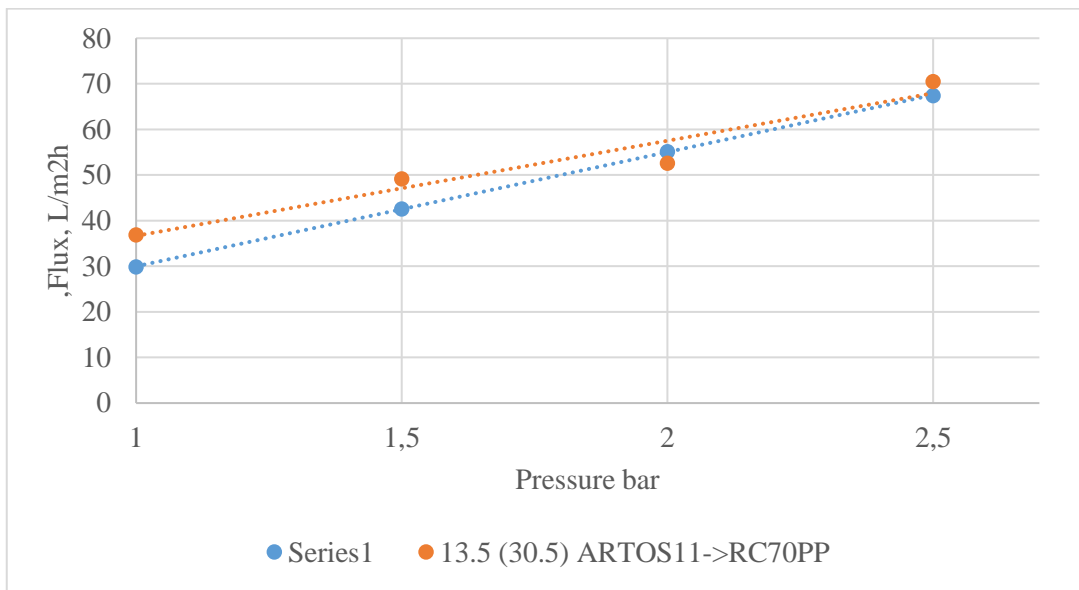


Figure 97 13.5 (30.5) ARTOS11->RC70PP. T_{water}=22-23°C, mixer speed 250 rpm.

APPENDIX I

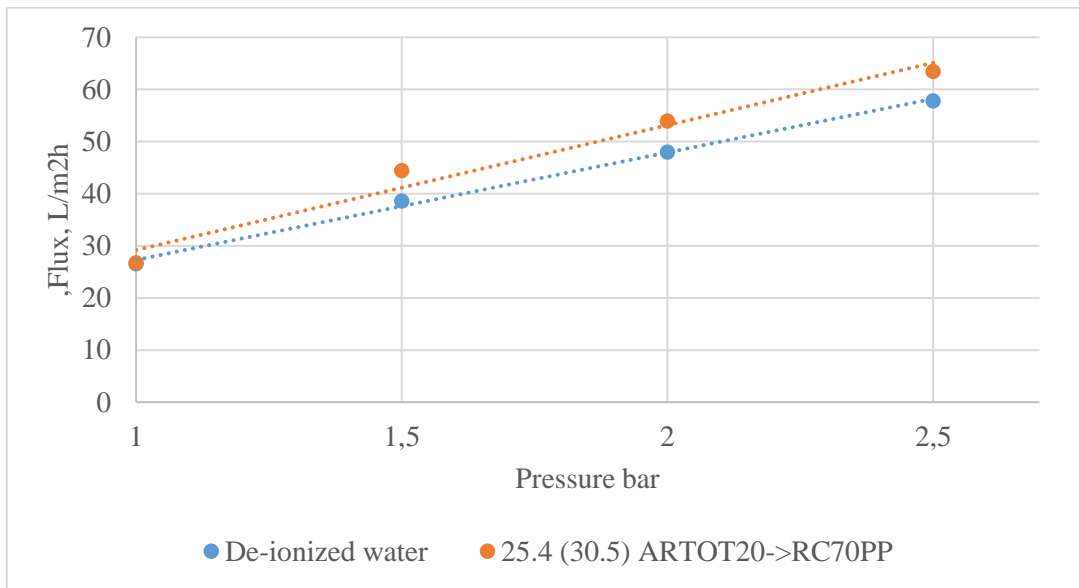


Figure 98 25.4 (30.5) ARTOT20->RC70PP. T_{water}=22-23°C, mixer speed 250 rpm.

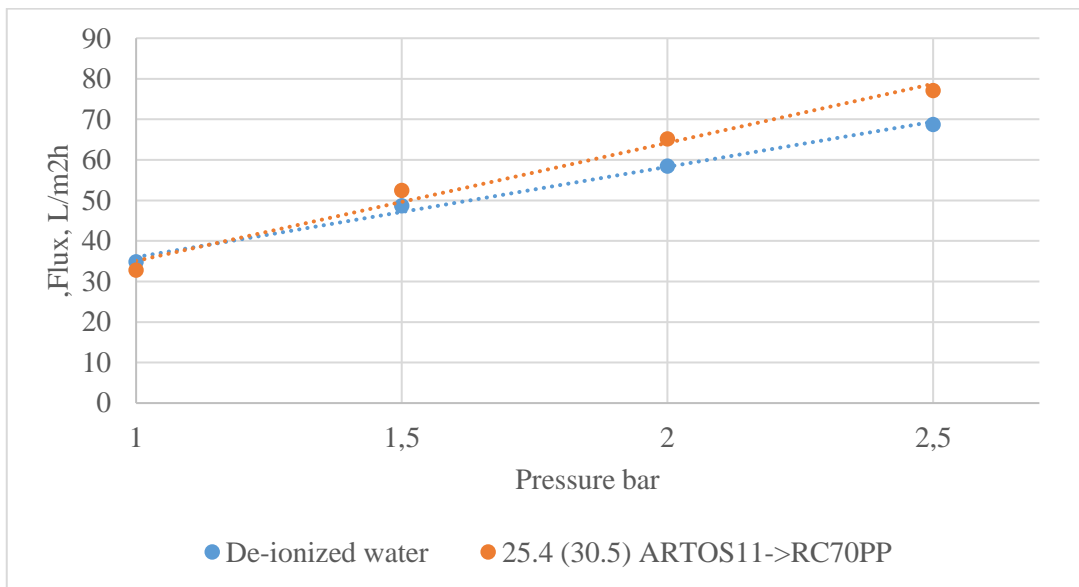


Figure 99 25.4 (30.5) ARTOS11->RC70PP. T_{water}=22-23°C, mixer speed 250 rpm.