

Lappeenranta-Lahti University of Technology LUT

LUT School of Engineering Science

Master's programme in Chemical Engineering and Wastewater Treatment

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**PURIFICATION OF WASTEWATERS FROM OIL REFINING PLANT WITH
MEMBRANE TECHNOLOGY**

Examiners: Professor Mika Mänttari

Associate professor Mari Kallioinen

Supervisor: Junior researcher Anastasia Gafiullina

ABSTRACT

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Purification of Wastewaters from Oil Refining Plant with Membrane Technology

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The aim of this master's thesis was to improve wastewater treatment quality at the oil refinery by developing an effective membrane treatment procedure which would reduce biological and chemical oxygen demand (BOD and COD) and concentrations of pollutants in the wastewater to meet the effluent quality requirements.

In the literature part of the thesis, oily wastewater sources, amounts, and composition along with different treatment techniques focusing on membrane processes were discussed. Additionally, main sources of oily wastewater and existing wastewater treatment process at the refinery were reviewed.

The experimental part of the thesis focused on the evaluation of the treatment efficiency of different membrane processes. The wastewater contained high BOD, COD, and total organic carbon (TOC). Ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes were used for wastewater treatment. The effect of operating conditions on membrane retention and flux was studied using the Taguchi method. Two combinations of multistage membrane processes were tested and compared to achieve the required wastewater treatment quality. The effect of recovery rate on membrane retention was studied to estimate how much the feed solution could be concentrated to reduce the amount of produced concentrates. Different pretreatment methods were tested to enhance membrane process performance.

Both tested multistage membrane processes demonstrated high treatment performance, reduced COD of the wastewater by 83% and 87% and achieved 73% and 74% water recovery, respectively. COD of the effluent was reduced below the target value. There was a potential to increase water recovery. The main limiting factor was fouling and concentration polarization in UF. Combination of powdered activated carbon (PAC) and UF treatment mitigated the effect of fouling.

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ABBREVIATIONS

AC	Activated carbon
AEL	Associated emission levels
BAT	Best available techniques
BOD	Biological oxygen demand
BTEX	Benzene, toluene, ethylbenzene and xylene
COD	Chemical oxygen demand
D	Dialysis
DF	Dilution factor
ED	Electrodialysis
FO	Forward osmosis
GAC	Granulated activated carbon
GS	Gas separation
IAF	Induced air flotation
IEP	Isoelectric point
MD	Membrane distillation
MF	Microfiltration
MTBE	Methyl tert-butyl ether
MWCO	Molar mass cut-off
NF	Nanofiltration
PAC	Powdered activated carbon
PV	Pervaporation
PWF	Pure water flux
RO	Reverse osmosis
TDS	Total dissolved solids
TFC	Thin-film composite
TOC	Total organic carbon
TSS	Total suspended solids
UF	Ultrafiltration
UV	Ultraviolet radiation
WW	Wastewater
WWTP	Wastewater treatment plant

1 Introduction

The petrochemical industry has a significant footprint on the environment. Oily wastewaters are one of the largest waste streams produced by the petroleum and petrochemical industries. Other industries such as chemical, metal, automotive, and food also generate significant amounts of oily wastewaters. It is a mixture of oil-water emulsions, different dissolved organic and inorganic compounds which are the major pollutants to the water environment. Due to increasing environmental concerns and regulations, the discharge of wastewater in recent years has been decreasing. Wastewater must undergo treatment through different physical, chemical, and biological methods. However, conventional treatment methods have limited capabilities at removing small emulsified oil particles and dissolved constituents and sometimes can even cause secondary pollution (chemical treatment). Membrane filtration is an effective and promising technology for oily wastewater treatment. There is a trend of membrane technologies replacing and/or enhancing conventional treatment methods due to its cost-effectiveness and small footprint. Therefore, the aim for future development is the optimization of current methods and the introduction of novel technologies and combinations for oily wastewater treatments in order to comply with effluent treatment and discharge standards.

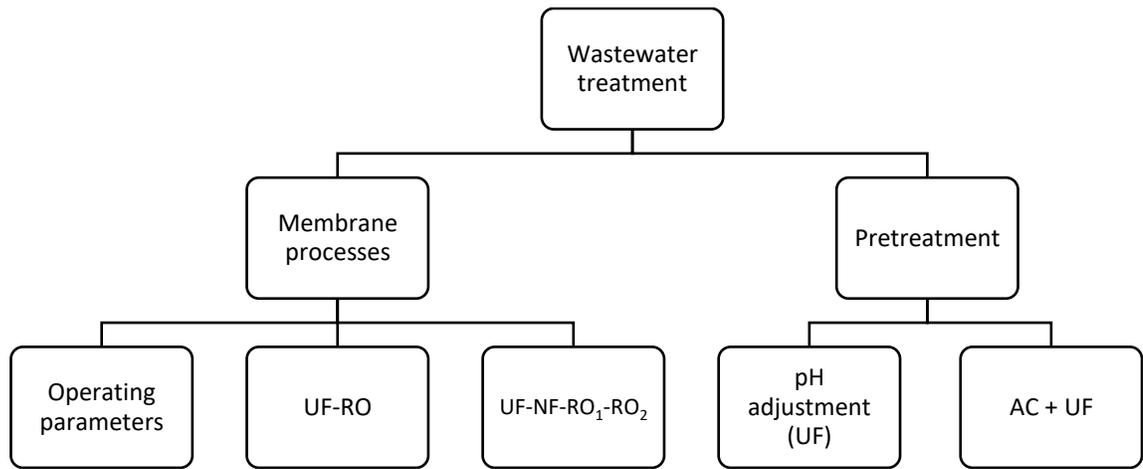
STR Tecoil is a used lubricating oil re-refinery, producing high quality base oils. The annual capacity is 70 000 tons of used lubricating oil for an output of 50 000 tons of base oil. The plant also produces bitumen and fuel oils as side products. Used lubricating oil is mainly collected in North-Western Europe and countries around the Baltic Sea. Feedstocks suitable for regeneration are mineral oil-based engine, gear, turbine, hydraulics, and compressor lubricants. The feedstock usually contains small amounts of water due to fuel combustion in engine, condensation of humidity, rain and snow melting. Wastewater is produced in the oil re-refining process. It consists of water in the feedstock (removed in de-watering step), stripping steam, recycle gas wash water, vacuum condensates, and steam from the vacuum system. STR Tecoil has a wastewater treatment plant (WWTP) and sends the effluent to the municipal sewage treatment plant for additional treatment and disposal. However, effluent quality after WWTP is not satisfactory. It has high BOD, COD, and phenols concentration which increases treatment costs.

This study discusses different oily wastewater treatment techniques, their combinations, benefits and drawbacks focusing on membrane technology. Additionally, the existing WWTP at the re-refinery and its treatment quality are reviewed. The primary objective of this work is to design an effective treatment procedure based on membrane technology which could minimize emissions from the plant

and reduce BOD of the produced wastewater below 2000 mg/L to meet the effluent quality requirements and potentially replace the existing multistage wastewater treatment process.

Figure 1.1 shows the structure of the experimental part of this work. It focuses mainly on the membrane wastewater treatment processes and studies pretreatment techniques to improve the performance of the main method. UF and RO are primary treatment processes. This work determines optimal operating conditions and their effect on UF and RO utilizing the Taguchi method, compares the effectiveness of UF-RO and UF-NF-RO₁-RO₂ combinations and studies the effect of recovery rate on membrane performance. pH adjustment and activated carbon (AC) treatment of the feed before UF are studied as pretreatment methods for the membrane process to improve the performance and minimize fouling.

Figure 1.1. Experimental strategy.



LITERATURE PART

2 Oily wastewater

2.1 Sources

Oily wastewater is a by-product of oil and gas, maritime, metal, textile, automotive and food industries, oil and gas extraction being the largest source (Mondal, 2008). Global onshore and offshore production rates of wastewaters are estimated at approximately 250 million barrels per day (Dal Ferro, Smith, 2007). In oil and gas extraction water is mixed with chemicals, e.g., solvents, demulsifiers, and injected into the well under high pressure to increase recovery level where it comes into contact with crude oil. In the petrochemical industry, oily water is produced during crude desalting and water washing where water comes into contact with crude oil. Steam is widely used at different stages of oil processing where it comes into direct contact with different fractions of hydrocarbons and various substances, e.g. distillation, hydrotreatment, visbreaking, catalytic cracking, hydrocracking (**Table 2.2**). Also, rainwater falling onto the site can be polluted due to entry to containment systems (Pascal et al., 2015). Main types of wastewaters from refineries and their annual amounts are listed in **Table 2.1**. In the automotive industry water usually enters the lubricating oil when it is in the engine's fuel combustion compartment, by condensation of air humidity and the possibility of coolant leakage (Toms, Toms, 2010). Large volumes of lubricants and coolants, which are mainly composed of stabilized oil-in-water, are used in the metal industry for grinding, drilling, rolling, etc. The quality of these lubricants and coolants deteriorate with operation, requiring replacement which leads to the production of oily wastewater. Bilgewater accumulates in ships because materials leak, spill, are washed off the deck and drain into the bilge compartment of ships (Stamper, 2008).

Table 2.1. Wastewater volumes produced by 41 refinery plants in Europe (Pascal et al., 2015).

Type of wastewater	Volume discharged, million m ³ /yr
Wastewater from the process	0.55 – 10
Wastewater from cooling	0 – 212
Potentially contaminated rainwater	0.09 – 2.3
Total wastewater	0.54 – 65

2.2 Classification

The oil is a mixture of hydrocarbons most of which are not soluble in water (Ekins, 2007). The form in which oil can exist in water depends on oil/water ratio, mixing intensity, temperature, total dissolved solids (TDS), pH, salinity, etc. (Tansel, 1995). Polar organic compounds (low and medium carbon ranges), benzene, toluene, ethylbenzene and xylene (BTEX), phenols, organic acids, and low-molecular-weight aromatics are soluble in water. Dispersed oil is a suspension of small oil droplets in the water and consists of PAHs (polyaromatic hydrocarbons) and heavy alkyl phenols (Fakhru'l-Razi, 2009). Oil-in-water can be found in 4 forms:

- free-floating oil (separate layer) with oil droplet size $>150\ \mu\text{m}$,
- unstable (dispersed) oil-in-water emulsion with droplet size $20\text{-}150\ \mu\text{m}$,
- highly stable (emulsified) oil-in-water emulsion with droplet size $<20\ \mu\text{m}$,
- dissolved oil with oil particle size $<5\ \mu\text{m}$ (Cheryan, 1998, Kundu, Mishra, 2018a)

Figure 2.1 shows three main forms in which oily wastewater can be found.

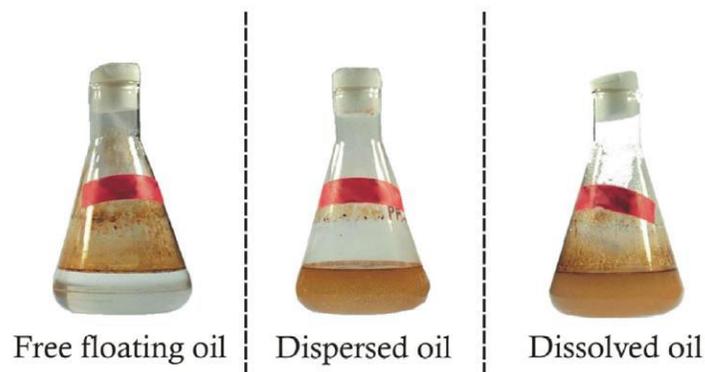


Figure 2.1. Three types of oily wastewater based on oil-in-water droplet size (Otitoju, Ahmad & Ooi, 2016)

2.3 Composition

Oily wastewater is a mixture of organic and inorganic components. Generally, depending on the type of regeneration process and the raw material used process waters contain dissolved and solid metals, chlorinated compounds, phenols, and other organic compounds as well as dissolved, dispersed, emulsified and free-floating oil. **Table 2.2** links water pollutants groups and their main sources at the refinery. **Table 2.3** provides a detailed composition of typical refinery untreated wastewater.

Table 2.2. Main water pollutants generated at the refinery and their sources (Pascal et al., 2015).

Water pollutant	Sources									
	Distillation	Hydrotreatment	Visbreaking	Catalytic cracking	Hydrocracking	Lube oil	Spent caustic	Ballast water	Sanitary blocks	Rain
Oil	+	+	+	+	+	+	+	+		+
H ₂ S	+	+	+	+	+	+	+			
NH ₃ (NH ₄ ⁺)	+	+	+	+	+	+			+	
Phenols	+		+	+			+	+		
Organic compounds (BOD, COD, TOC)	+	+	+	+	+	+	+	+	+	+
CN ⁻ , (CNS ⁻)			+	+			+	+		
Total suspended solids (TSS)	+		+	+			+	+	+	

Table 2.3. Typical oil refinery untreated annual average wastewater composition (Pascal et al., 2015).

Parameter	Average, mg/L	Maximum, mg/L
TOC	100	250
COD	300-500	1000
BOD	80-150	300
TSS	20-60	200
HOI (Hypoiodous acid)	40-50	100
Nitrogen	25	50
Ammonium-N	12-15	30
Phosphate	5	20
Cyanide	0-3	5
Sulphide	5	10
Phenols	12	25
MTBE (methyl tert-butyl ether)	0-3	15
Fluoride	0-30	60
BTEX	5	10
PAH-16	0.1	0.5
Heavy metals	1	2

2.4 Wastewater specifications

European Union laws regulate industrial wastewater collection, handling, treatment, and discharge. Wastewater flow, pH and temperature must be monitored continuously at key locations, e.g. influent

to pretreatment and final treatment. Also, emissions to water (TOC, COD, TSS and total nitrogen) should be monitored at plants specializing in the refining of mineral oil and gas. According to the Industrial Emission Directive (IED) 2010/75/EU, individual emission limit values for the plant must be based on the Best Available Techniques – associated emission levels (BAT-AELs). **Table 2.4** shows direct emission levels for wastewater discharge based on BAT. These AELs apply only when certain minimal emissions are exceeded.

Table 2.4. BAT-AEL direct emission levels to a receiving water body (Brinkmann et al., 2016).

Parameter	BAT-AEL, mg/L (average per year)	Minimal emission level when BAT-AEL is applied, t/yr.
COD	30-100	10
TOC	10-33	3.3
TSS	5-35	3.5
Total phosphorus (P)	0.5-3	0.3
Total nitrogen (N)	5-25	2.5
Total inorganic nitrogen (N _{inorg})	5-20	2

3 Conventional treatment methods

When managing oily wastewater three-step approach is utilized (Brinkmann et al., 2016):

1. Minimization of water use and wastewater production
2. Treatment and reuse
3. Discharge

Oily wastewater must undergo treatment before discharge to meet onshore and off-shore regulations. For reuse, it also must be treated to meet high quality requirements. General water treatment objectives (Fakhru'l-Razi, 2009) are:

1. TSS removal
2. De-oiling
3. Removal of soluble organics
4. Desalination
5. Softening
6. Removal of dissolved gases
7. Disinfection

There is a great variety of wastewater treatment techniques. The suitable treatment method is selected based on the type of pollutants present in the wastewater and their particle sizes (Hua, 2007). The treatment methods can be classified to physical, chemical, and biological. Also, combinations of different methods can be applied for a better treatment quality (Yu, L., Han & He, 2017)

Oily wastewater treatment usually is a three-step process as shown in **Table 3.1**. In primary treatment, free-floating oil and suspended solids are removed by gravity separation. The solids settle down while free-floating oil rises to the surface where it is usually collected by skimming. Separation can be enhanced by centrifugation. In secondary treatment, suspended solids which were not removed by sedimentation, dispersed oil, and organic matter is removed. Suspended solids and dispersed oil are often removed by coagulation and/or flocculation with flotation. Activated sludge treatment is used to remove organic matter. In tertiary treatment, residual TSS, emulsified and dissolved oil, nutrients, and inorganic salts are removed. TSS and emulsified oil can be effectively removed by membrane filtration. Carbon adsorption is applied for oil and hydrocarbons removal. Usually, disinfection is applied at this stage to remove nutrients. Inorganic salts are removed by RO. (Tchobanoglous, Burton & Stensel, 2003, Coca-Prados, Gutiérrez & Benito, 2013)

Table 3.1. Stages in oily wastewater treatment (Tchobanoglous, Burton & Stensel, 2003, Coca-Prados, Gutiérrez & Benito, 2013).

	Primary treatment	Secondary treatment	Tertiary treatment
Pollutants removed	TSS Free-floating oil	TSS Dispersed oil Organic matter	TSS Emulsified oil Dissolved oil Nutrients Inorganic salts
Method of treatment	Physical	Physical Chemical Biological	Membrane Physical Chemical
Unit operation, process	Sedimentation Centrifugation Skimming	Coagulation Flocculation Flotation Activated sludge	Membrane filtration Adsorption Disinfection RO

3.1 Physical treatment

Physical treatment methods are based on the application of physical forces and they were the first treatments methods to be implemented. Physical treatment methods can be applied at all treatment stages but commonly it is used for preliminary and primary treatment (screening, sedimentation, centrifugation, etc.). **Table 3.2** summarizes some common oily wastewater physical treatment methods, their applications and the equipment.

Table 3.2. Common physical oily wastewater treatment methods (Tchobanoglous, Burton & Stensel, 2003).

Method	Application	Device
Screening	Removal of solids and small particles	Screen
Flocculation	Increasing particle size to enhance sedimentation	Flocculator
Sedimentation	Removal of settleable solids	Clarifier
Skimming	Removal of free-floating oil	API separator Corrugated plate interceptor (CPI) Parallel plate interceptor (PPI)
Flotation	Acceleration of gravity separation	Dissolved air flotation (DAF) Induced air flotation (IAF)
Membrane filtration	TSS, colloids, dissolved organic and inorganic matter removal	MF, UF, NF, RO
Adsorption	Removal of organic and inorganic pollutants, taste and odour	Adsorber

3.1.1 Gravity separation

Gravity separation followed by skimming is the most common primary method for removing free-floating oil from wastewater (Cheryan, 1998). API separators, corrugated plate interceptors (CPI), parallel plate interceptors (PPI) are applied as a pretreatment method based on the oil-water density difference but it is only effective for oil droplets larger than 150 μm (Schultz, Thomas E., 2005). The free-floating-oil layer is removed by skimming and the sediment layer from the bottom is removed by a scraper (Coca-Prados, Gutiérrez & Benito, 2013).

3.1.2 Flotation

Smaller oil particles can be removed by gas flotation. Gas flotation accelerates gravitational separation by injection of fine gas bubbles into the water phase containing immiscible oil droplets so that the bubbles attach themselves to the droplets, thus increasing the density difference between two phases. There are two major methods of introducing gas to the liquid phase – induced gas flotation (IGF) and dissolved gas flotation (DGF). Typically, air is used for gas flotation (IAF, DAF). Demulsifiers and coalescer can be added before flotation to destabilize emulsion and increase oil droplets size resulting in improved separation efficiency (Moosai, 2003).

3.1.3 Sand filtration

Sand filters are often used as a pretreatment or secondary treatment step in the wastewater purification process. Sand filters are effective with low concentration oil-water emulsions (less than 50 mg/L), while for higher concentrations combination with coagulation proven to be more efficient (Almojjly et al., 2018). The oil removal efficiency is highly influenced by the hydrophobicity of the filter media. Several studies show that the hydrophobicity of the filter media surface can be increased by superhydrophobic coatings, thus increasing adsorption capacity and oil removal performance (Liu, J. et al., 2018). This separation method proved to be inexpensive, non-toxic, environmentally friendly but faces the same problems as other conventional filters do – clogging, decrease in performance over time, frequent washing.

3.1.4 Adsorption

Adsorption is a conventional and widely used tertiary wastewater treatment method based on the accumulation of pollutants on the adsorbent surface due to hydrophobic electrostatic interactions between them (Nam et al., 2014). Organic compounds of oily wastewater (and some heavy metals) adhere to porous media surfaces of adsorbents (Worch, 2012). In oily wastewater treatment, natural (clay minerals, zeolites, oxides, and biopolymers) and engineered (activated carbon, polymeric and oxidic adsorbents, molecular sieves) are used.

In industrial wastewater treatment applications activated carbon (AC) is the most commonly used adsorbent because of the porous structure, high specific surface area, and low price (Kundu, Mishra, 2018b). AC is used to remove organic and inorganic (nitrogen, sulphides, and heavy metals) compounds, taste, and odour. Usually, the surface of AC is hydrophobic, so hydrophobic compounds

are adsorbed better than hydrophilic (Mansour et al., 2018). The pore structure of AC is characterized by three types of pores:

- macropores (>25 nm)
- mesopores (1-25 nm)
- nanopores (<1 nm)

Molecules enter AC media through macropores and are transported through mesopores to micropores where adsorption happens (Yu, F. et al., 2016). The adsorption intensifies with an increase in internal surface area. Adsorbate molecule size also positively affects adsorption as long as molecules are able to enter the adsorbent pore system. Increased temperatures lead to lower adsorption (exothermic process). High-molecular-weight non-polar organic molecules and aromatic compounds have a high affinity towards AC. Competitive adsorption is observed in multicomponent systems leading to a decrease in adsorption of a certain compound compared to single-component adsorption (Tchobanoglous, Burton & Stensel, 2003).

AC comes in two forms: granulated activated carbon (GAC) with particle size 0.5-4 mm and powdered activated carbon (PAC) with particle size <40 μm (Tchobanoglous, Burton & Stensel, 2003). When treated with GAC, wastewater passes through an AC bed in a contactor. PAC can be used in combination with biological treatment (Lesage, Sperandio & Cabassud, 2008), chemical precipitation (Mueller et al., 2003), DAF (Hami, Al-Hashimi & Al-Doori, 2007), and membrane filtration (Yang, Chen & Xing, 2011). After AC is saturated, it requires regeneration of its adsorptive capacity. Regeneration procedure involves oxidation (typically thermal) and removal of adsorbed pollutants from the adsorbent. Adsorption is simple and reliable wastewater treatment method, it has low energy consumption, can be operated in both continuous and batch modes, is not sensitive to toxic pollutants and does not produce any toxic by-products, can be reused multiple times after regeneration. On the other hand, AC is expensive to produce and regenerate, it requires periodic replacement due to adsorption capacity decrease with each regeneration cycle and small adsorbent loss during operation and regeneration. (Tchobanoglous, Burton & Stensel, 2003)

3.2 Chemical treatment

Chemical treatment methods are based on the application of chemical reactions and are usually implemented in combination with physical and biological processes for secondary treatment. **Table 3.3** summarizes some common oily wastewater chemical treatment methods and their applications. In

combination with primary treatment methods, chemical processes can achieve complete secondary treatment of raw wastewater. The main drawbacks of chemical treatment are:

- net TDS increase in effluent
- high sludge production
- these processes often require the use of toxic chemicals which can cause secondary pollution

Table 3.3. Common chemical oily wastewater treatment methods (Tchobanoglous, Burton & Stensel, 2003).

Method	Application
Coagulation	Destabilization of pollutants to enhance their aggregation
Precipitation	Removal of TSS, BOD, phosphorus, heavy metals, hardness
Neutralization	pH adjustment
Stabilization	Corrosion control
Oxidation	BOD, COD, and ammonia removal, the elimination of bacterial growth and odours
Ion exchange	Removal of organic compounds, ammonia, and heavy metals
Disinfection	Removal of odours, control of slime growth, destruction of microorganisms

3.2.1 Chemical coagulation

The purpose of chemical coagulation is to destabilize the emulsion by forming larger flocs that can be better separated by flotation or other physical separation methods. Usually, inorganic salts are used as coagulants while flocculants are organic polymers (Coca-Prados, Gutiérrez & Benito, 2013). Usually, coagulation is applied as a primary treatment step before gravity separation or flotation. If properly applied, coagulation can be effective, but it has some drawbacks:

- the process is very sensitive to change in influent quality, thus require customization and close control
- the process produces high amounts of sludge
- the large footprint of the equipment

- corrosion problems caused by influent acidification
- increased TDS in the effluent

3.2.2 Chemical precipitation

Chemical precipitation is a wastewater treatment method based on dissolved pollutants changing to solid form. Commonly used chemicals are:

- lime or sodium hydroxide (hydroxide precipitation)
- sodium sulfide or biosulfide (sulfide precipitation)
- ferrous or zinc sulfate (cyanide precipitation)
- calcium carbonate or carbon dioxide (carbonate precipitation)

After precipitation, solids are separated. Chemical precipitation has low capital cost and is easy to operate. However, the operating costs are high due to the consumption of chemicals and sludge disposal which is produced in large amounts during the process. (Vaccari et al., 2005)

3.2.3 Chemical oxidation

In the chemical oxidation process, oxidizing agents (ozone, chlorine, chloride dioxide, hydrogen peroxide, oxygen, permanganate) are introduced to change the chemical composition of pollutants present in the wastewater. Chemical oxidation with chlorine, ozone, and hydrogen peroxide can be applied to reduce BOD and COD but the reaction rate is too slow for industrial-scale application. To effectively oxidate complex organic components, advanced oxidation methods are applied. It is typically based on the generation of hydroxyl free radicals which are strong oxidants (oxidation potential 2.8 V) and degrade compounds that cannot be oxidized by conventional oxidants (Tchobanoglous, Burton & Stensel, 2003). Different combinations of ozone, hydrogen peroxide and ultraviolet radiation (UV) are applied in advanced oxidation processes.

3.2.4 Fenton process

The Fenton reagent with hydrogen peroxide is often used for removal of a broad range of organic contaminants. The Fenton process is considered one of the most effective oxidation processes. Its principle is also based on the production of hydroxyl radicals. This method is described as cost-effective and simple to implement, it does not create toxic by-products. Fenton process requires only continued stirred tank reactor (CSTR) where oxidant, catalyst, and wastewater are mixed and the reaction takes place, a settler for sludge removal, and a neutralization vessel. The drawbacks of the

process are high sludge production and difficulties associated with hydrogen peroxide handling. It is also difficult to determine optimal dosages for cost-effective treatment. (Bhuta, 2014)

3.2.5 Ion exchange

Ion exchange is mostly applied in domestic water softening but it can also be applied for wastewater treatment. This method is based on the replacement of dissolved pollutants in the solution by harmless ions of different species coming from the resin. Typical ion exchange materials are naturally occurring zeolites and synthetic organic exchange resins or phenolic polymers. The process is operated in a similar way to adsorption, it can be operated in batch or continuous modes. After ion exchange resin is saturated it requires regeneration. (Tchobanoglous, Burton & Stensel, 2003, Yargeau, 2012)

3.3 Biological treatment

Biological wastewater treatment is the use of bacteria or other microorganisms to remove pollutants by incorporating them. Biological wastewater treatment is effective and widespread, especially in the chemical processing industry. It can also be applied for oily wastewater treatment (Zhao et al., 2006, Liu, G. et al., 2013) Bacteria and microorganisms have the ability to consume different wastewater components to provide energy for metabolism and growth.

Biological treatment has low capital and operating costs comparing to chemical oxidation processes. It is possible to oxidize a wide variety of organic compounds, remove some inorganic compounds, e.g. ammonia and nitrogen, and reduce aquatic toxicity with biological treatment (Schultz, Thomas, 2005). On the other hand, the process is susceptible to temperature and composition changes in the influent, it produces sludge which requires additional treatment. The influent requires pretreatment if it contains pollutants which are toxic to microorganisms.

4 Membrane separation technology

4.1 Fundamentals

A membrane is a selective barrier allowing the passage of certain constituents while retaining pollutants in the feed solution (Cheryan, 1998). Membrane technology is a promising and widely applied method for oily wastewater treatment. It has an extended operating range allowing for dissolved constituents (approx. from 0.1 nm to 0.1 μm) separation (Tchobanoglous, Burton & Stensel, 2003). Membrane technology has higher efficiency, low energy consumption and operational costs compared with other conventional physical and chemical treatment methods (Gryta, 2001).

4.1.1 Classification

Membrane processes are classified according to the nominal size of the separation (**Figure 4.1**), driving force, membrane material, and separation mechanism. Typically applied membrane processes are (Strathmann, Giorno & Drioli, 2006):

- microfiltration (MF)
- ultrafiltration (UF)
- nanofiltration (NF)
- reverse osmosis (RO)
- gas separation (GS)
- pervaporation (PV)
- dialysis (D)
- electrodialysis (ED)
- membrane distillation (MD)
- forward osmosis (FO)

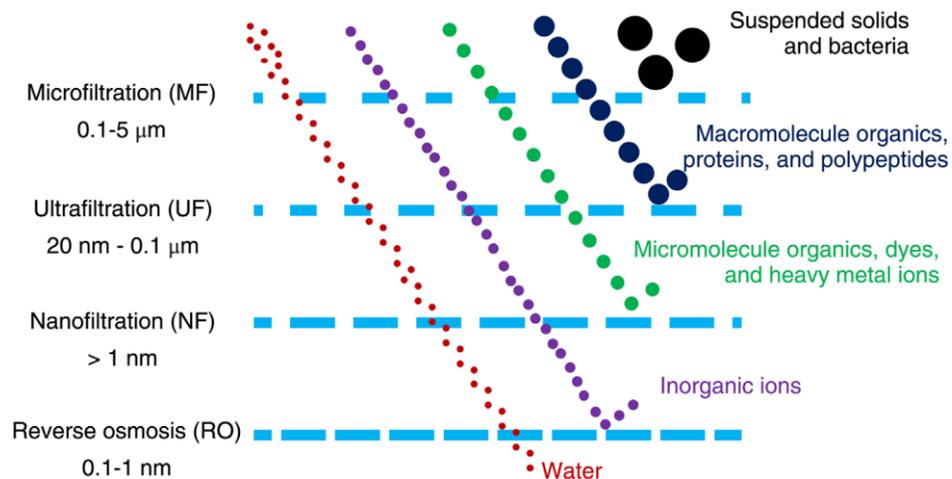


Figure 4.1. The rejection size distribution of membrane processes (Jiang et al., 2018).

Membrane processes can be classified into four groups based on the driving force (Strathmann, Giorno & Drioli, 2006):

- hydrostatic pressure difference (MF, UF, NF, RO, GS)
- concentration gradient (D, PV, FO)
- electrical potential (ED)
- temperature difference (MD)

The driving force for the most common membrane separation technologies is hydrostatic pressure difference (MF, UF, NF, RO). Dialysis is based on concentration difference, and electro dialysis involves electromotive force and ion-selective membranes to separate charged ionic species.

4.1.2 Separation mechanisms

Two main transport mechanisms in pressure-driven membrane separation are:

- sieving through a porous membrane
- diffusion through a non-porous membrane

Sieving mechanism is based on the convective flow of constituents through membrane pores under transmembrane pressure (TMP) (**Figure 4.2b**). The separation is based on size exclusion and described by Darcy's Law. Mostly occurs in MF and UF. Separation in diffusion mechanism is based on different solubility and diffusivity of constituents into membrane media. Concentration gradient influences the solution and diffusion of molecules into the non-porous membrane (**Figure 4.2a**). This type of transport is described by Fick's Law (NF, RO). (Strathmann, Giorno & Drioli, 2006)

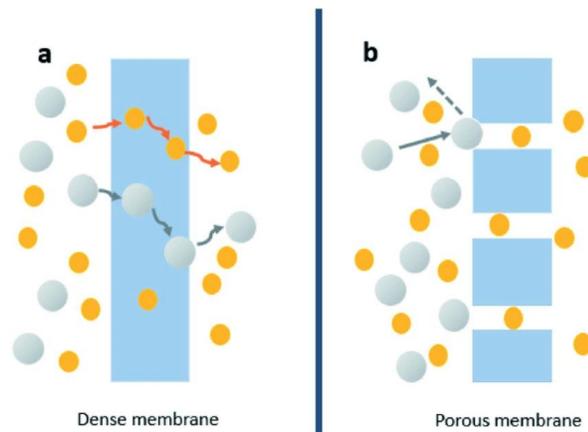


Figure 4.2. Membrane transport mechanisms (Lyu et al., 2018).

The diffusion mechanism in a non-porous membrane (a), the sieving mechanism in a porous membrane (b).

4.1.3 Materials and structures

The material from which membranes are prepared can be organic or inorganic (**Figure 4.3**). Inorganic membranes show high mechanical strength, are resistant to high temperatures and have narrow pore size distribution allowing to use it in acidic solutions, organic solvents, solutions with high bacterial growth and in other harsh conditions. Contrary, organic material has a shorter service life and

demonstrates lower separation efficiency compared to inorganic but it has a lower price (Kim, J., Van der Bruggen, 2010).

Common membrane materials can be classified as:

- ceramics
- polymers
- glass
- metals
- liquids

Typically, organic materials are used in membranes designed for water treatment, including polypropylene, cellulose acetate, aromatic polyamides, and thin-film composite (TFC) (Tchobanoglous, Burton & Stensel, 2003). **Table 4.1** lists materials used to prepare different types of membranes.

Table 4.1. Typical materials used for membrane preparation (Tchobanoglous, Burton & Stensel, 2003, Vigneswaran et al., 2012)

Process	Materials used for membrane preparation
MF	Polycarbonate, modified polyethylene and polypropylene, nylon, carbon composites, cellulose nitrate, stainless steel with ceramic coating,
UF	Ceramics, regenerated cellulose, polyacronitrile, polyvinyledene fluoride, polyvinyl alcohol
NF	Polyacronitrile, silicone, polyvinyl alcohol, cellulose acetate
RO	Polyamide, cellulose acetate, polyimide and TFCs of other polymers

The membrane structure can be symmetric or asymmetric (**Figure 4.3**). In symmetric membranes, the structural and transport properties are constant while in asymmetric it varies over the entire cross-section of the membrane. Asymmetric membranes usually consist of thin skin (0.20-0.25 μm) supported by a porous bed (100 μm) (Tchobanoglous, Burton & Stensel, 2003), have high flux, mechanical stability, and are usually applied in UF and RO. Symmetric membranes are mostly used for dialysis and electro dialysis.

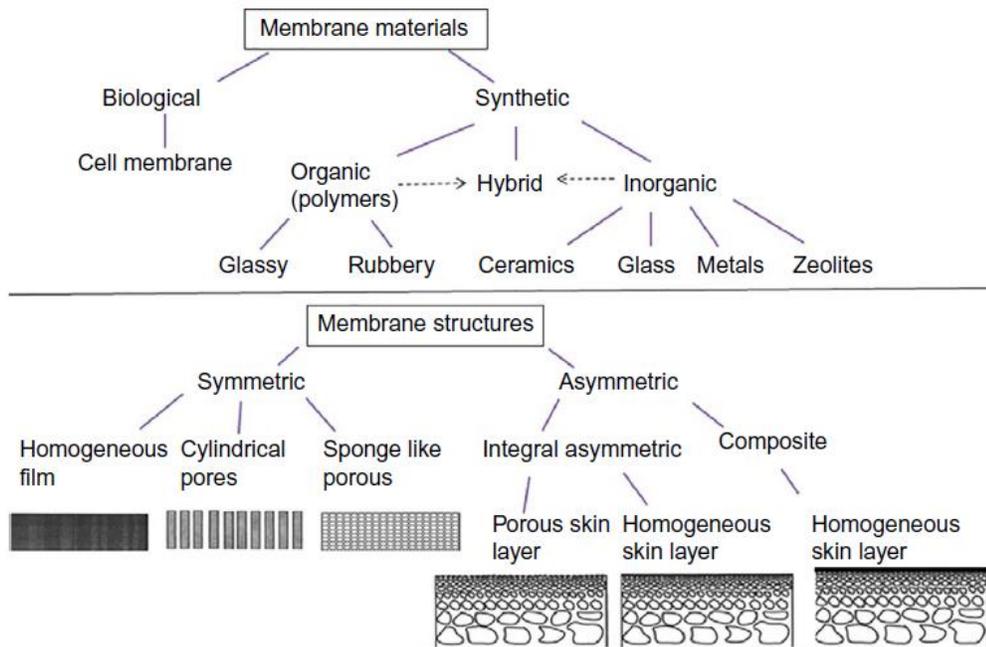


Figure 4.3. Membrane classification based on material and structure (Gohil, Choudhury, 2019).

4.1.4 Membrane properties

Molecular weight cut-off (MWCO) is the molecular weight (in Daltons) which is 90% retained by the membrane. The ability of UF membranes to reject macromolecules is based on their molecular weight (molar mass). For this reason, MWCO is mainly used for UF characterisation. To achieve a good separation molar mass of two solutes must differ by a factor of ten, and MWCO of the membrane must be at least one-half of the solute to be retained (Singh, 2015).

Membrane hydrophilicity is important membrane surface property. Multiple studies show that hydrophilic surface increases membrane performance by reducing fouling (Kim, D., 2004, Xiao, 2011, van der Marel et al., 2010). Hydrophilicity/hydrophobicity can be estimated from the contact angle of the membrane surface. When the contact angle is $< 90^\circ$, then a membrane is hydrophilic, if the contact angle $> 90^\circ$, it is hydrophobic (**Figure 4.4**) (Law, 2014).



Figure 4.4. Liquid droplet profile on hydrophobic (left) and hydrophilic (right) surfaces (Bălțatu et al., 2018).

The surface charge of the membrane has an effect on fouling (Zhan et al., 2004, Xiao, 2011). The membrane has to be neutrally charged or have the same charge as the constituents in the feed (Mulder, 1996). Opposite charges attract each other which can lead to increased adsorptive fouling and/or concentration polarization. Study shows that protein adsorption on the membrane surface can be effectively reduced by enhancing the repulsive electrostatic force (Zhan et al., 2004). Positive membrane surface charge can enhance demulsification significantly while negative charge increases antifouling properties (Wu, 2018).

4.1.5 Operating modes

Membrane filtration can be operated in two modes: dead-end (direct) where the feed solution is filtered through the membrane perpendicularly and cross-flow (tangential flow) where the feed flows parallel to the membrane surface (**Figure 4.5**). In dead-end filtration, solids and retained constituents accumulate on the surface of the membrane forming a cake layer which increases the resistance to mass transfer through the membrane and, as a result, negatively affects flux (**Figure 4.5a**). In cross-flow filtration, retained constituents are swept by the flow over the surface of the membrane and recirculated into the feed solution. Therefore, membrane flux can be maintained at a higher level compared to dead-end mode. On the other hand, the cross-flow mode requires more energy to sustain high CFV for sufficient mixing. (Vigneswaran et al., 2012)

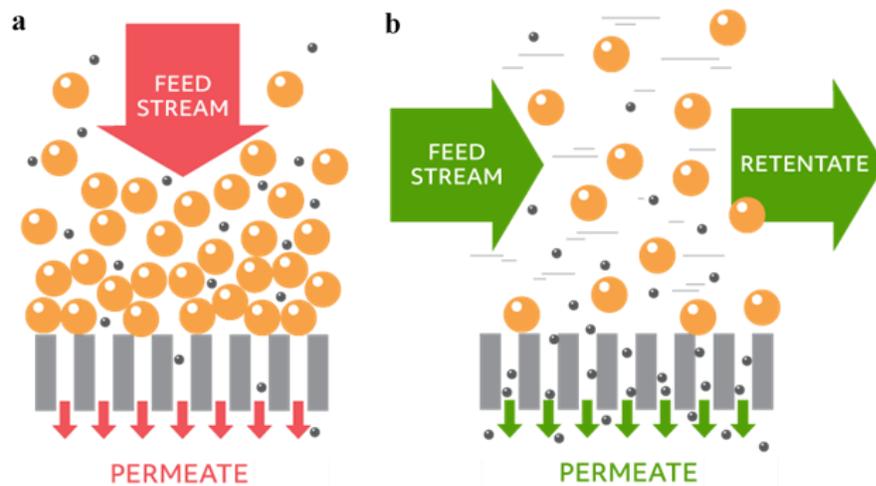


Figure 4.5. Membrane filtration operating modes (FORMULATRIX, 2019). Dead-end (a), cross-flow (b).

4.1.6 Configurations

To be operated, membranes must be installed in membrane modules which provide pressure support for the membrane, have feed, permeate, and retentate ports. Stirred dead-end cells are often used for

small-scale laboratory applications but it cannot be used in industrial processes. The main membrane configurations for wastewater treatment, their parameters and applications are listed in **Table 4.2**.

Table 4.2. The main membrane configurations and their parameters (Strathmann, Giorno & Drioli, 2006, Vigneswaran et al., 2012, Jiang et al., 2018).

Module	Packing density, m ² /m ³	Membrane price	Energy consumption	Flow	Fouling control*	Application
cartridge	800-1000	cheap	low	laminar	- -	dead-end MF
plate-and-frame (flat sheet)	400-800	moderate	low-moderate	laminar	+	MF, UF, NF, RO, D, ED
tubular	20-100	very expensive	high	turbulent	++	NF, NF, UF, RO
hollow fibre	2000-5000	very cheap	low	laminar	++	RO, GS
spiral-wound	800-1200	cheap	moderate	laminar, turbulent	+	UF, NF, RO, GS
capillary	600-1200	cheap	low	laminar	++	MF, UF, D

* (-) poor, (- -) very poor, (+) good, (++) very good

4.2 Applications

4.2.1 Water treatment

Membrane technology has a broad range of applications in different fields. One of the main fields where membrane technologies are utilised is water treatment. Water treatment includes:

- desalination of water
- industrial water purification
- wastewater treatment

Membranes are used for desalination of water and purification of potable and industrial water (boiler, cooling, process, and ultrapure water) production from seawater or brackish water. ED is widely used for this application along with UF, NF, RO (Strathmann, Giorno & Drioli, 2006).

Wastewater can be classified as inorganic, containing inorganic salts and heavy metals, hardness, COD, and ammonia nitrogen, and organic with high COD (>2000 mg/L), fats, cellulose, carbohydrates, proteins and other organic compounds. RO, MD, FO, and also NF as a pretreatment method for RO are applied for inorganic wastewater treatment (Jiang et al., 2018).

Oily wastewater, textile and cooking wastewaters are considered as organic. For oily wastewater treatment, different membrane processes are applied (MF, UF, NF, RO, MD, FO, MBR) (Strathmann, Giorno & Drioli, 2006, Jiang et al., 2018). Multilevel membrane processes (MF, UF, NF, RO) are applied for effective removal of surfactants, dye, and inorganic salts from textile wastewaters while NF, RO, and MBR are used to treat highly toxic cooking effluents (Jiang et al., 2018).

Increasing environmental concerns and the development of new and low-cost membranes drive progress in the field of environmental engineering. Membrane technology replaces more and more conventional separation technologies, especially in light of the need to remove resistant organic constituents and operating pressures for membrane processes going down.

4.2.2 Other applications

Apart from water treatment, membrane technologies are well established in a number of different industries. Membrane technologies are often applied in (Strathmann, Giorno & Drioli, 2006):

- chemical industry for gas and solvent separation, chemicals recovery from wastewater,
- food and beverage industry for juice, dairy and milk, wine and beer processing,
- pharma and biotech industries for a wide range of different applications.

4.3 Pressure-driven membrane processes

Pressure-driven membrane processes operate based on the transmembrane pressure (TMP) gradient. The feed solution is circulated through the membrane under pressure and divided into two streams: retentate (concentrate) and permeate (**Figure 4.6**). Permeate is usually collected at atmospheric pressure.

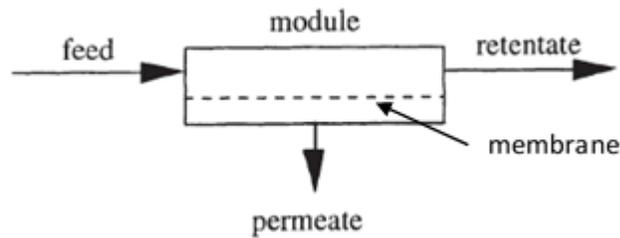


Figure 4.6. Schematic representation of a membrane process (Mulder, 1996).

Table 4.3 presents the main operating characteristics of pressure-driven membrane processes.

Table 4.3. Characteristics of pressure-driven membrane processes (Cardew, Le, 1998, Tchobanoglous, Burton & Stensel, 2003, Strathmann, Giorno & Drioli, 2006).

	Operating range, μm	TMP, kPa	Flux, $\text{L}/\text{m}^2\cdot\text{d}$	Recovery, %	MWCO, Da
MF	0.08-2.0	7-100	405-1600	90-99.99	-
UF	0.005-0.2	70-700	405-815	80-98	>1000
NF	0.001-0.01	500-1000	200-815	50-95	400-500
RO	0.0001-0.001	850-7000	320-490	30-90	<200

4.3.1 Microfiltration

Microfiltration is a pressure-driven process. The principle of MF is shown in **Figure 4.7**. Usually, symmetric macroporous MF membranes are made of polypropylene, acrylonitrile, nylon, and polytetrafluoroethylene. The separation of particles is accomplished by size exclusion (particles larger than 100 nm are rejected) (Gohil, Choudhury, 2019). Mass transport in MF takes place by convective flow through the pores and is described by Darcy's law (Strathmann, Giorno & Drioli, 2006, Vigneswaran et al., 2012).

The pore size in microfiltration is >50 nm (macropores). Typical operating range is 0.08-2.0 μm , operating pressure 7-100 kPa, rate of flux 405-1600 $\text{L}/\text{m}^2\cdot\text{d}$ (**Table 4.3**). Typical applications are water purification, TSS removal during pretreatment for UF, NF, RO, MD, and sterilization. (Tchobanoglous, Burton & Stensel, 2003, Strathmann, Giorno & Drioli, 2006)

Microfiltration membranes have a smaller footprint and treatment chemicals requirement comparing with conventional units and it can be easily automated. This is the least expensive type of membranes. (Tchobanoglous, Burton & Stensel, 2003)

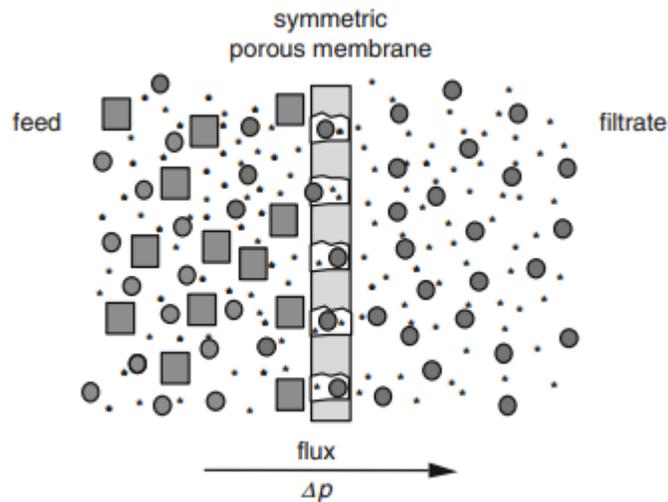


Figure 4.7. Principle of MF (Strathmann, Giorno & Drioli, 2006).

4.3.2 Ultrafiltration

Ultrafiltration is also a pressure-driven process. The principle of UF is shown in **Figure 4.8**. The separation of particles is accomplished by size exclusion. UF membranes are made from cellulose acetate or aromatic polyamides (Tchobanoglous, Burton & Stensel, 2003) and have an asymmetric structure with the smallest pores situated on the feed side of the membrane (Strathmann, Giorno & Drioli, 2006). Mass transport in UF takes place by convective flow through the pores and is described by Darcy's law (Strathmann, Giorno & Drioli, 2006, Vigneswaran et al., 2012).

The pore size in ultrafiltration is 2-50 nm (mesopores). Typical operating range is 5 nm - 2.0 μm , operating pressure 70-700 kPa, rate of flux 405-815 $\text{L}/\text{m}^2\cdot\text{d}$ (**Table 4.3**). At high TMP membrane flux is high and the retention approaches its maximum while at very low TMP the retention is zero (Strathmann, Giorno & Drioli, 2006).

UF membranes retain components with molecular weight from 5000 to couple million Da (colloids and proteins, TSS, organic matter) (Strathmann, Giorno & Drioli, 2006, Jiang et al., 2018). Ultrafiltration (UF) membranes have similar application field as MF. Typical applications are TSS removal and membrane disinfection during pretreatment for NF and RO, organics removal. UF may require pretreatment, which increases the overall footprint, it produces concentrate which must undergo additional treatment. (Tchobanoglous, Burton & Stensel, 2003)

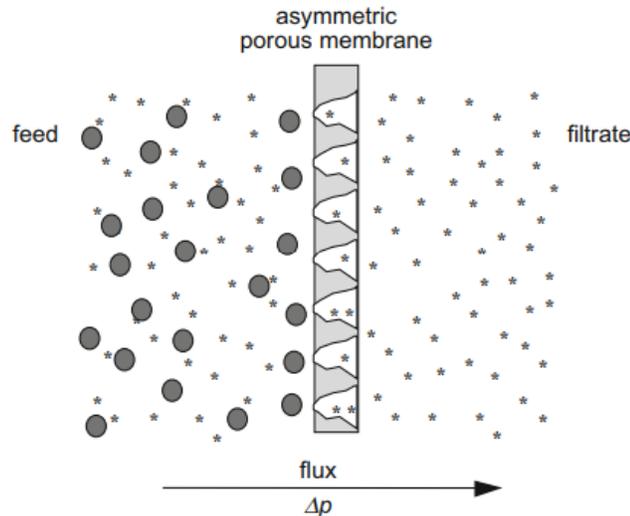


Figure 4.8. Principle of UF (Strathmann, Giorno & Drioli, 2006).

4.3.3 Nanofiltration

Nanofiltration is similar to UF and RO. NF has a high rejection of organic compounds compared to UF and is operated at low pressures comparing to RO. The principle of NF is shown in **Figure 4.10**. The pore size in NF is <2 nm (micropores). Size exclusion is the separating mechanism for large molecules and colloids. (Vigneswaran et al., 2012)

The mass transfer through NF membrane is defined by two mechanisms: diffusion (Fick's law) and Donnan exclusion. For diffusion to take place, TMP has to overcome osmotic pressure. For Donnan exclusion, the permeability of charged particles is affected by electrostatic interactions between these particles and the membrane surface. **Figure 4.9** explains schematically how salt rejection and flux are influenced by TMP and feed concentration (Strathmann, Giorno & Drioli, 2006, Jiang et al., 2018).

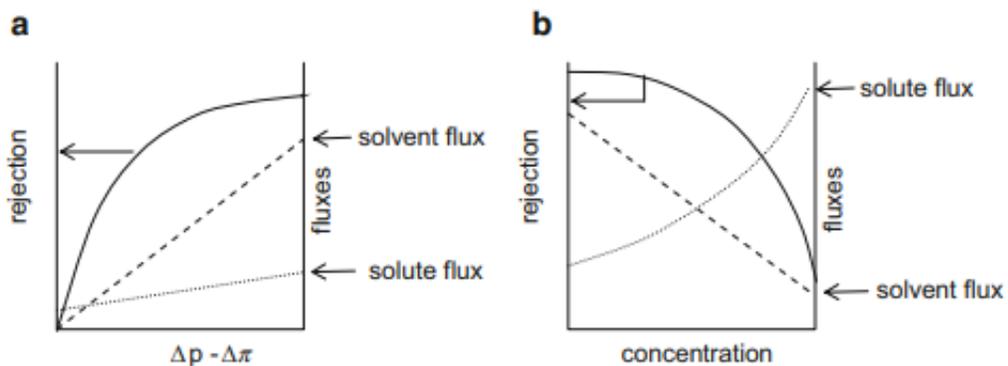


Figure 4.9. Positively charged NF membrane rejection and flux of salt as a function of hydrostatic and osmotic pressure difference (a) and the feed concentration (b) (Strathmann, Giorno & Drioli, 2006).

Typical operating range for NF is 0.001-0.01 μm , operating pressure 500-1000 kPa, rate of flux 200-815 $\text{L}/\text{m}^2\cdot\text{d}$ (**Table 4.3**). Nanofiltration is used for removal of low-molecular-weight dissolved constituents from wastewater. It can remove synthetic organic compounds, some hardness, heavy metals, nitrates, bacteria, viruses (can be applied for membrane disinfection) (Tchobanoglous, Burton & Stensel, 2003).

Typical NF applications are effluent reuse and wastewater softening. In effluent reuse, NF is used to treat prefiltered with MF effluent for indirect potable reuse applications and disinfection. In wastewater softening, NF is used to reduce the concentration of multivalent ion contributing to hardness. NF and RO require a very high-quality feed for efficient operation, so the feed solution must undergo pretreatment before. Usually, pretreatment may include chemical clarification combined with MF and/or UF to remove colloidal material, filtration with cartridge filters (5-10 μm) to remove residual TSS, disinfection by chlorine, ozone, or UV to limit bacteria activity, oxygen exclusion to prevent oxidation of iron, manganese, and H_2S , removal of chlorine and ozone, removal of iron and manganese to decrease scaling potential, and pH adjustment (4.0-7.5). (Tchobanoglous, Burton & Stensel, 2003)

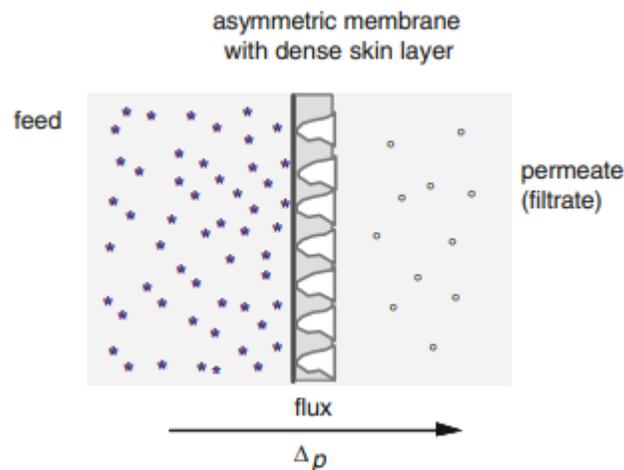


Figure 4.10. Principle of NF (Strathmann, Giorno & Drioli, 2006).

4.3.4 Reverse osmosis

Reverse osmosis (RO) is an occurrence of flow through a semipermeable membrane from more concentrated to the less concentrated region when the pressure gradient opposite in direction and exceeding osmotic pressure is applied (**Figure 4.11**). The principle of RO is shown in **Figure 4.12**. Mass transport in RO is described by the solution-diffusion model. Solute passage through pores and pinholes can be neglected. (Strathmann, Giorno & Drioli, 2006)

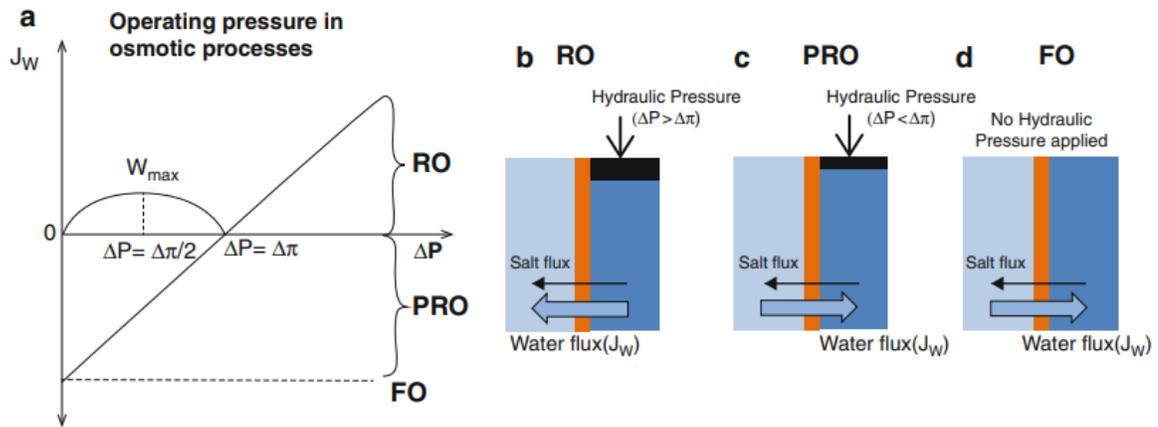


Figure 4.11. Illustration of the osmotic phenomenon (Klaysom, Vankelecom, 2016)
 a) effect of TMP on solvent flux through semipermeable layer from the more concentrated solution to the less concentrated solution, b) RO, c) pressure retarded osmosis (PRO), d) FO

RO membranes have an asymmetric structure and a dense skin layer on the feed solution side. The typical pore size in RO is 0.1-1 nm, operating pressure 850-7000 kPa, rate of flux 320-490 L/m²*d (Table 4.3).

The main RO application is water desalination. In wastewater treatment, it removes residual dissolved constituents after MF or UF. It can remove biodegradable and synthetic organics, hardness, colour, heavy metals, nitrates, sulphates, dissolved constituents, bacteria, and viruses. It is evident that RO cannot provide a sufficient barrier to dissolved gases and some low-molecular-weight organic molecules (Bellona et al., 2004). Due to economic reasons, commercial membranes are not truly semi-permeable but rather utilize membrane-solute interactions with additional diffusion limitations (chemical functional groups) to increase solute rejection at lowest possible pressures (Ozaki, Li, 2002). Rejection of trace organics by RO is affected by pH, solute and membrane surface charges, molecular weight and geometry of the solute, polarity and hydrophobicity (Ozaki, Li, 2002).

Typical applications are effluent reuse, desalination and purification of water, two-stage treatment for high-pressure boiler use. Although RO can exclude the smallest molecules and even ions, it requires advanced pretreatment of feed, extremely high operating pressures, and has a low flux. RO faces a problem of particulate and colloidal fouling. Another problem is the precipitation of inorganic salts. It produces concentrates which must be disposed of. All these problems contribute to the high costs of RO compared to conventional treatment methods. (Tchobanoglous, Burton & Stensel, 2003)

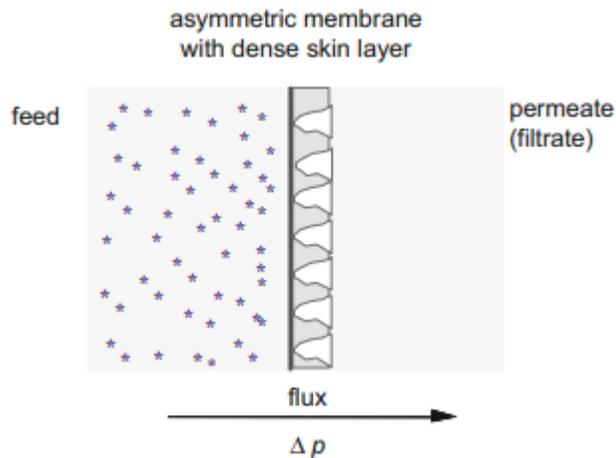


Figure 4.12. Principle of RO (Strathmann, Giorno & Drioli, 2006).

4.4 Hybrid membrane processes

Often, to obtain the specified effluent quality it is not enough to use only one treatment method or one type of membrane operation. Industrial wastewaters are usually highly concentrated, tend to contain high TSS, have high viscosities and osmotic pressures. Oily wastewaters have complex composition, contain a broad range of dissolved hydrocarbons and components with various molar mass. Furthermore, these types of influents can cause severe fouling of the membranes without a proper pretreatment procedure. (Coca-Prados, Gutiérrez & Benito, 2013)

Hybrid membrane processes can be a great solution to acquire sufficient treatment quality. Membrane processes can be combined with other treatment methods (integrated membrane process) or combinations of multiple membrane processes (multistage or dual membrane process) can be used to increase treatment performance or mitigate negative effects like fouling. Membrane processes can be easily integrated into treatment existing systems with conventional unit operations, chemical or biological treatment. (Coca-Prados, Gutiérrez & Benito, 2013)

Often, when the wastewater contains high TSS and/or free-floating oil, physical treatment (sedimentation, skimming, DAF) is applied as a pretreatment step before membrane process to minimize the effect of fouling and improve process performance. For example, effluent from API separator can be used as a feed solution for UF (Salahi, Abdolhamid et al., 2009). DAF can be used as an effective pretreatment technique for MF, UF, NF or RO reducing fouling and extending membrane life (Al-Zoubi, Al-Thyabat & Al-Khatib, 2009). DAF was used in combination with MF and RO (Çakmakce, Kayaalp & Koyuncu, 2008). Coagulation and flocculation is a common chemical

pretreatment method before a membrane process. Combined demulsification and RO process was able to remove more than 99% of COD, oil, and turbidity from highly concentrated oil/water solution (Zhang et al., 2008). Combination of chemical coagulation, MF and RO removed 92% of COD from oil gas produced water (Çakmakce, Kayaalp & Koyuncu, 2008). Membrane bioreactor (MBR) is based on a combination of an activated sludge process in a continuously stirred tank reactor (CSTR) with a membrane separation process (Coca-Prados, Gutiérrez & Benito, 2013).

Sorption processes can be integrated with membrane processes via filtration/sorption before membrane separation or as a polishing step after membrane filtration. PAC is often being used for the treatment of oily wastewaters. PAC has a large specific area, it is able to adsorb low-molecular-weight organics, and it demonstrates high affinity towards hydrophobic components (Coca-Prados, Gutiérrez & Benito, 2013). Another benefit of PAC and membrane combination that PAC can be added directly to the feed circulation loop without changing the design of the process (Mohammadi, Esmaelifar, 2005). On the other hand, PAC is expensive and requires regeneration. Application of hybrid PAC-UF combination can increase COD, TOC, and phenols removal, minimize fouling and increase flux compared to single UF process (Mohammadi, Esmaelifar, 2005). PAC can also be applied as a polishing step after MF (Abbasi, Reza Sebzari & Mohammadi, 2011), UF (Dong, 2011), and NF (Hilal et al., 2005) processes.

Combinations of multiple membrane processes are applied in oily wastewater treatment to obtain high-quality water effluents. Usually, a combination of two membrane processes is being used. **Table 4.4** demonstrates oily wastewaters treatment quality by different dual membrane processes via COD reduction.

Table 4.4. Treatment quality of different dual membrane processes.

	Membranes	Influent COD, mg/L	Reduction, %	Reference
MF-UF	-, MW	1861	92	(Çakmakce, Kayaalp & Koyuncu, 2008)
MF-NF	MV020, NF270	2165	77-88	(Ozgun et al., 2013)
MF-RO	-, ST10	1861	88	(Çakmakce, Kayaalp & Koyuncu, 2008)
UF-NF	UC010, NF270	2165	75-85	(Ozgun et al., 2013)
UF-RO	-, AG	1861	97	(Çakmakce, Kayaalp & Koyuncu, 2008)
UF-RO	-	11460	97	(Latif Ahmad, Ismail & Bhatia, 2003)
UF-RO	PAN, PA	124	98	(Salahi, Abdolhamid et al., 2011)
NF-RO	NF270, XLE	600	99	(Kurt et al., 2012)

MF-RO, UF-RO, MF-NF combinations were used for the treatment of highly polluted wastewater from oil and gas production well (Çakmakce, Kayaalp & Koyuncu, 2008). Performances of MF-NF, UF-NF, MF-RO, and UF-RO hybrid membrane processes were studied with wastewater produced by oil and gas production well at different TMP (Ozgun et al., 2013). Palm oil mill effluent with high COD, oil and grease, and BOD was treated with UF-RO combination (Latif Ahmad, Ismail & Bhatia, 2003). Performance of UF-RO combination was studied at different operating conditions using effluent from API separator as a feed solution (Salahi, Abdolhamid et al., 2011). Textile dye wash wastewater was treated with pilot-scale NF-RO system (Kurt et al., 2012).

4.5 Fouling and concentration polarization

The constituents in the feed stream can deposit and accumulate on the membrane which is called fouling. During the operation at constant TMP membrane flux constantly decreases due to fouling while mass transfer resistance increases. Fouling is one of the biggest limitations of membrane technology affecting pretreatment needs, cleaning requirements, operating conditions, costs, and performance. Fouling can be reversible or irreversible. The flux of the membrane affected by irreversible fouling cannot be restored by physical cleaning. Reversible fouling can be controlled by process parameters (TMP, CFV) while irreversible fouling is more relevant to membrane surface characteristics (hydrophilicity/hydrophobicity, surface roughness, surface charge, pore size, etc.) (Huang, Ras & Tian, 2018). There are four main types of fouling distinguished (Jiang et al., 2018):

- inorganic fouling
- organic fouling
- scaling and colloids fouling
- biofouling (attachment of biological material to the membrane surface)

The main fouling mechanisms are (Tchobanoglous, Burton & Stensel, 2003):

- absorption (particles smaller than pore size)
- pore blockage (particles larger or equal to pore size)
- cake layer formation (occurs at high concentrations)

Adsorption can occur at different concentrations and affects UF, NF, RO membranes. Pore blockage is significant at low pressures and concentrations. Cake layer forms due to concentration polarization. Because the retained components in UF and MF have a high-molecular-weight they diffuse back to

the bulk of the solution slowly. Since mass transport of solute towards the membrane is greater than backflow to the bulk of the solution the concentration near to the surface increases and after it exceeds the solubility of the constituents, they start to precipitate forming a cake layer. When a solid cake layer is formed, the flux becomes independent from the TMP. This cake layer on the surface of the membrane can act as a permeable membrane and reject low-molecular-weight components not retained by the membrane (Strathmann, Giorno & Drioli, 2006).

The concentration polarization is a reversible process based on diffusion. It occurs when the material retained by the membrane accumulates near to the membrane surface to the point where concentration gradient between the bulk of the feed solution and the concentrated solution near the membrane surface is established which leads to backflow of the accumulated material. A higher concentration of the solute leads to an increase in osmotic pressure which is inversely proportional to the membrane flux according to **Figure 4.11**. The feed solution in RO typically has high osmotic pressure, so an increase in concentration causes the reduction of flux at constant TMP. To make things worse, the leakage of the pollutants to the permeate side is also increased which consequently reduces the retention of the membrane. The flux reduction due to concentration polarization is a major problem for NF and RO. (Strathmann, Giorno & Drioli, 2006)

Fouling in oily wastewater treatment is considered more complex than scaling. Oil droplets can wet the membrane surface changing its properties or deform and coalesce forming oil films on the membrane surface. Small oil particles can enter membrane pores which is difficult to clean. **Figure 4.13** illustrates main oil fouling models in oily wastewater treatment. Fouling in oily wastewater filtration is affected by (Huang, Ras & Tian, 2018):

- surface interactions (affinity of the oil droplets and the membrane)
- pore size (pore size should be smaller than oil droplet size to have a good sieving effect)
- surface structure (roughness)
- surface charge (membrane surface and oil droplets should have opposite charges)
- surfactants (can be adsorbed on the surface of the membrane or change its wettability)
- salts (salt can promote coalescence of oil droplets or deformation and their passage through pores)
- operating conditions (turbulence, cross-flow configuration)

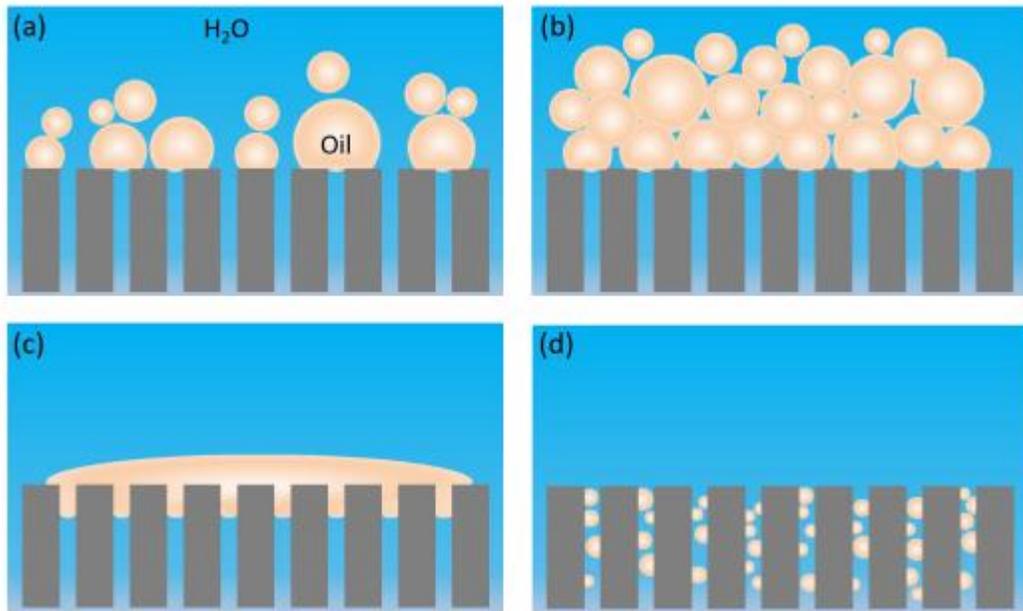


Figure 4.13. Oil fouling models (Huang, Ras & Tian, 2018).

- a) partial pore blockage, b) cake layer deposition, c) oil film on the membrane surface, d) internal oil fouling

Membrane fouling can be controlled by (Jiang et al., 2018, Strathmann, Giorno & Drioli, 2006):

- membrane modification
- optimization of devices
- optimization of operating parameters
- pretreatment of the feed solution
- membrane cleaning

4.6 Cleaning

Successful membrane operation requires good fouling management. Periodic cleaning can effectively restore productivity (**Figure 4.14**) allowing further use of the unit. There are two types of cleaning: physical cleaning (flushing, backwashing, mechanical scouring) and chemical cleaning. Flushing involves decreasing the feed stream pressure, which causes an increase in reject flow sweeping settled and consolidated solids. Backwashing involves feeding wash water in the opposite direction to the operational. Although this method is more effective it also consumes approx. 10% of the production and can damage supported membranes. Mechanical scouring of the surface can be applied in some cases but can damage the membrane too. (Tchobanoglous, Burton & Stensel, 2003)

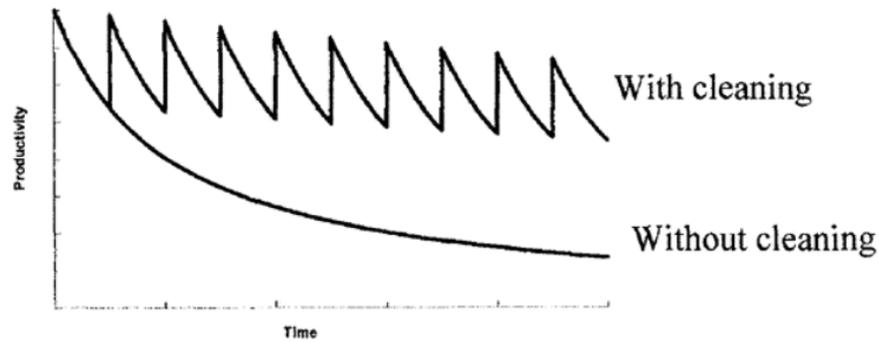


Figure 4.14. Effect of cleaning on productivity (Cardew, Le, 1998).

Physical cleaning methods restore the performance but cannot provide full recovery. After each cleaning procedure, the fouling occurs at a higher rate. Although chemical cleaning is less desirable and has problems connected with secondary pollution, sometimes it is the only fouling remedy left. Acids or bases (HNO_3 and NaOH), oxidants, enzymes, and detergents are usually used (sometimes in combination or in series) for chemical cleaning (Strathmann, Giorno & Drioli, 2006).

5 Wastewater treatment plant

The wastewater treatment plant (WWTP) at the re-refinery collects process water from different stages of the process. Main oily wastewater sources are:

- 1) De-watering
- 2) Vacuum condensates
- 3) Recycle gas wash
- 4) Steam used in vacuum system

Collected oily wastewater undergoes multiple physical and chemical treatment processes at the WWTP. The main stages of the WWTP are:

1. Sour water stripping
2. Neutralization
3. IAF
4. Chemical oxidation
5. Coagulation
6. DAF
7. Sand filtration

Process waters are collected in the oil-water separator where free-floating oil is separated by gravity and sold as a by-product. The wastewater leaving the separator contains emulsified and dissolved hydrocarbons along with other pollutants. Volatile compounds, mainly hydrogen sulphide, ammonia, and light hydrocarbon fractions are removed from the wastewater by stripping with low-pressure steam. Emulsified oil is removed from the wastewater by IAF. Prior to IAF, the wastewater is neutralized by the pH adjustment. Volatile organic compounds present in the wastewater are decomposed by the chemical oxidation. Oil traces in the wastewater are precipitated by chemical coagulation with prior pH adjustment for optimal precipitation and subsequent flocculation. Precipitated particles are then separated from the wastewater by the combination of flocculation and DAF. Sand filtration is applied as a final wastewater purification step. Effluent from WWTP is sent to the municipal sewage plant for additional treatment.

6 Objective statement

Table 6.1 comprises quality requirements for the effluent set by the municipal sewage treatment plant, untreated oily wastewater parameters before WWTP and effluent parameters after WWTP.

Table 6.1. Effluent quality requirements, wastewater parameters before and after WWTP.

Parameter	Quality requirements	Water before the treatment	Water after the treatment
Temperature, °C	max 40	max 60 (30-47)	max 49, 35
pH	6-9	9.2 (8.4-9.7)	8 (6.7-9.3)
TSS, mg/L	250	13-18	14.7 (3.2-27)
BOD, kg/day	150	-	-
Sulphates (SO ₄), mg/L	400 total	11-240	628 (290-1100)
Thiosulphate, -sulphides, sulphates, mg/L	sulphates	130-270	775 (480-1500)
Total nitrogen (N), mg/L	50	170-270	372 (130-490)
Total phosphorous (P), mg/L	8	0.21	0.546 (0.25-1)
Phenol, mg/L	10	65.9 (11.7-147)	43.2 (15.3-82.4)
Ammonium (NH ₃), mg/L	40	310	290-300
Arsenic (As), mg/L	0.1	-	0.033
Silver (Ag), mg/L	0.1	-	<0.00020
Mercury (Hg), mg/L	0.01	-	0.0014
Copper (Cu), mg/L	0.5	-	0.0036
Chromium (Cr), mg/L	0.5	-	<0.0030
Cadmium (Cd), mg/L	0.01	-	<0.00020
Zinc (Zn), mg/L	2	-	<0.005
Nickel (Ni), mg/L	0.5	-	<0.0030
Lead (Pb), mg/L	0.5	-	<0.0010
Magnesium (Mg), mg/L	300	0.45	0.45-0.6
Formaldehyde (water), mg/L	0.5	0.66	4.3 (0.59-14)
Tin (Sn), mg/L	2	-	<0.0010

Wastewater samples before and after WWTP are collected by the STR Tecoil laboratory three times a week for pH, COD, and phenols concentration measurements. Additionally, a comprehensive wastewater analysis is carried out by the external laboratory once a month (**Table 6.1**). Daily measurements show that after WWTP, COD and phenols concentration of the wastewater decrease on average by 14% and 31%, respectively. However, this is not enough to meet the quality requirements set by the municipal sewage treatment plant. Performance of the existing WWTP is unsatisfactory, thus it requires modification or replacement.

The most problematic parameters are BOD, COD, and phenols concentration of the wastewater. The limit for BOD is set to 150 kg/day which depending on the amount of produced wastewater is equal to approx. 2000 mg/L. The primary objective of this work is to design an effective treatment procedure based on membrane technology which could minimize emissions from the plant and reduce BOD of the produced wastewater below the specified limit to meet the effluent quality requirements and potentially replace the existing multistage wastewater treatment process. Since it usually takes from 5 to 7 days (depending on the method) to measure BOD of the wastewater sample (Merck, 2019), COD was used as a target parameter in this work. Because the limit for COD of the effluent was not initially determined by the quality requirements, the target COD was estimated at 3600 mg/L according to the COD/BOD ratio of 1.8.

EXPERIMENTAL PART

7 Aims and content of the work

The main objectives of this work were to design an effective treatment procedure which would reduce chemical oxygen demand (COD) of the oily wastewater produced by STR Tecoil re-refinery below 3600 mg/L and estimate how much the wastewater could be concentrated during the treatment process to reduce the amount of produced concentrate. The requirement for total organic carbon (TOC) was not set but it was also used to assess water treatment quality and membrane retention along with COD.

COD, TOC, conductivity, and turbidity of the wastewater provided by the company were measured. Ultrafiltration (UF) was tested with raw wastewater as a feed solution. Reverse osmosis (RO) performance was tested with raw wastewater, UF permeate, and RO permeate as feed solutions. Optimal operating conditions (temperature, transmembrane pressure (TMP) and cross-flow velocity (CFV)) and their effect on UF and RO were determined using the Taguchi method based on COD retention and flux of the membranes. The multistage approach was applied to obtain high COD and

TOC removal. Combinations UF-RO and UF-NF-RO₁-RO₂ were tested and compared. Experiments were carried out in the pilot cross-flow filtration system up to 95% recovery rates to reduce the amount of concentrate produced in the process. To determine how much the feed solution could be concentrated the effect of recovery rate on treatment quality was studied. pH adjustment and activated carbon (AC) treatment were tested as pretreatment steps before UF to increase membrane performance and minimize fouling. The effect of pH adjustment as a pretreatment step before UF on COD retention and flux was studied. The effect of the pH on COD and TOC removal by granulated activated carbon (GAC) and powdered activated carbon (PAC) treatment was studied. The effect of PAC dosage and adsorption time on COD removal was studied. Two combinations of PAC treatment and UF were tested.

8 Materials

8.1 Wastewater

Untreated oily wastewater was provided by STR Tecoil re-refinery. The wastewater was characterised as alkaline, contained dissolved and dispersed oil that caused high COD, TOC and turbidity levels. Among organoleptic parameters, yellowish colour (**Figure 8.1**) and pungent odour were registered. According to **Table 6.1**, the most significant pollutants were COD and biological oxygen demand (BOD) caused by organic and inorganic compounds, nitrogen, and sulphur compounds. The detailed composition of the wastewater can be found in **Appendix I**.



Figure 8.1. Photo of a raw oily wastewater (WW) sample.

Table 8.1 shows the parameters of the oily wastewater measured in the LUT laboratory. High Cod and TOC was probably caused by dissolved hydrocarbons (Sadeghian, 2010).

Table 8.1. Raw oily wastewater parameters measured in LUT laboratory.

pH	9.4 - 9.6
COD, mg/L	11000-13000
TOC, mg/L	3000-4000
Conductivity, $\mu\text{S}/\text{cm}$	939
Turbidity, NTU	2520

8.2 Chemicals

Both 35% HCl (VWR, 7647-01-0) and 99% NaOH (compressed in pellets, VWR, 1310-73-2) were used to prepare both 1 M and 0.1 M solutions to adjust the pH of the oily wastewater.

P3-ultrasil 110 alkaline, liquid detergent for membrane filtration plants was used for the cleaning of the cross-flow filtration set-up between experiments.

8.3 Membranes

The membranes used in the experiments were flat sheet RC70PP ultrafiltration (UF), NF270 nanofiltration (NF), and SW30 reverse osmosis (RO) membranes. **Table 8.2** lists the main parameters of the membranes used in this study.

Table 8.2. The main parameters of the studied membranes.

Type	Name	pH	Operating TMP, bar	Operating temp., $^{\circ}\text{C}$	MWCO, Da	Reference
UF	RC70PP	1-10	1-10	5-60	10000	(Alfa Laval, 2018)
NF	NF270	2-11	<41	<40	150-300	(Dow, 2019b), (Racar et al., 2017)
RO	SW30	2-11	<69	<45	Dense	(Dow, 2019a)

The RC70PP membranes provided by Alfa Laval Corporate AB are composed of regenerated cellulose acetate layer on top of polypropylene support. RC70PP membrane was chosen because it showed high flux and retention, low fouling tendency in multiple studies due to the hydrophilic surface of the membrane (Chen, 2013, Issakainen, 2019, Macedo, Duarte & Fragoso, 2015). Hydrophilic membranes are often used for wastewater treatment applications since water easily permeates these membranes while non-polar constituents like oil are rejected (Haynes, Lide & Bruno, 2016).

The N270 and the SW30 membranes were provided by Dow-Filmtec. The NF270 membranes are composed of a semi-aromatic polyamide thin-film on top of an asymmetric polysulfone microporous 50 nm support backed by 200 nm polyester non-woven fibres (Freger, Gilron & Belfer, 2002). It has 40-60% calcium and < 3% magnesium passage (Dow, 2019b). It showed 65% retention of TOC and more than 75% retention of inorganic compounds (SO₄, Ca, K, Mg, Na, Cu, Zn) (Orecki, Tomaszewska, 2007). The NF270 membrane is hydrophilic and has a negative surface zeta potential (at pH 4 and higher). It has low fouling potential and demonstrates high retention of organic components (90% for glucose) and high flux (125 L/m²*h) (Mänttari, Pekuri & Nyström, 2004).

The SW30 membranes are composed of ultrathin polyamide top layer, microporous polysulfone interlayer, and a polyester base. The SW30 membranes are designed to sustain high pressures required to achieve 99.4% salt rejection (Dow, 2019a). SW30 membrane was selected for low fouling tendency due to hydrophilic surface, high TOC, nitrogen, and conductivity retention (Tomaszewska, Orecki & Karakulski, 2005, Masse, 2014).

8.4 Adsorbents

Granulated activated carbon (Norit, GAC830W, 7440-44-0) and powdered activated carbon (Norit, SAE 2, 7440-44-0) were used to test COD and TOC removal efficiency from oily wastewater.

8.5 Filters

Schleicher & Schuell grade 589/2 circle 40.5 mm filter papers with retention range of 4-12 µm were used to separate spent adsorbent from treated wastewater after adsorption experiments.

9 Methods

9.1 Experimental setup

9.1.1 Cross-flow filtration set-up

The filtration experiments with feed volumes ranging from 2.5 L to 20 L and up to 95% recovery were carried out using the pilot cross-flow system (**Figure 9.1**). The feed solution was circulated by the Hydra Cell G03 diaphragm pump P1 from 2 L feed tank to the membrane pressure chamber. Feed solution temperature in the tank was controlled by the LAUDA Proline RP 855 thermostat. Cross-flow velocity (CFV) was measured by rotameter FI and controlled by changing motor rotation frequency. The pressure was adjusted by the needle valve V2 installed after the membrane pressure

chamber. The pressure was measured by the digital pressure meter PT installed before the needle valve. The volume of pipes and pump was approx. 0.5 L making the total feed volume in the apparatus approx. 2.5 L. Rectangular membrane pressure chamber was used. The active membrane surface area was 100 cm². The permeate was collected while retentate was being recycled back to the feed tank. The permeate weight as a function of time was recorded using precision balances Precisa 8200D connected to the computer. The drain was used to collect feed samples and empty the tank.

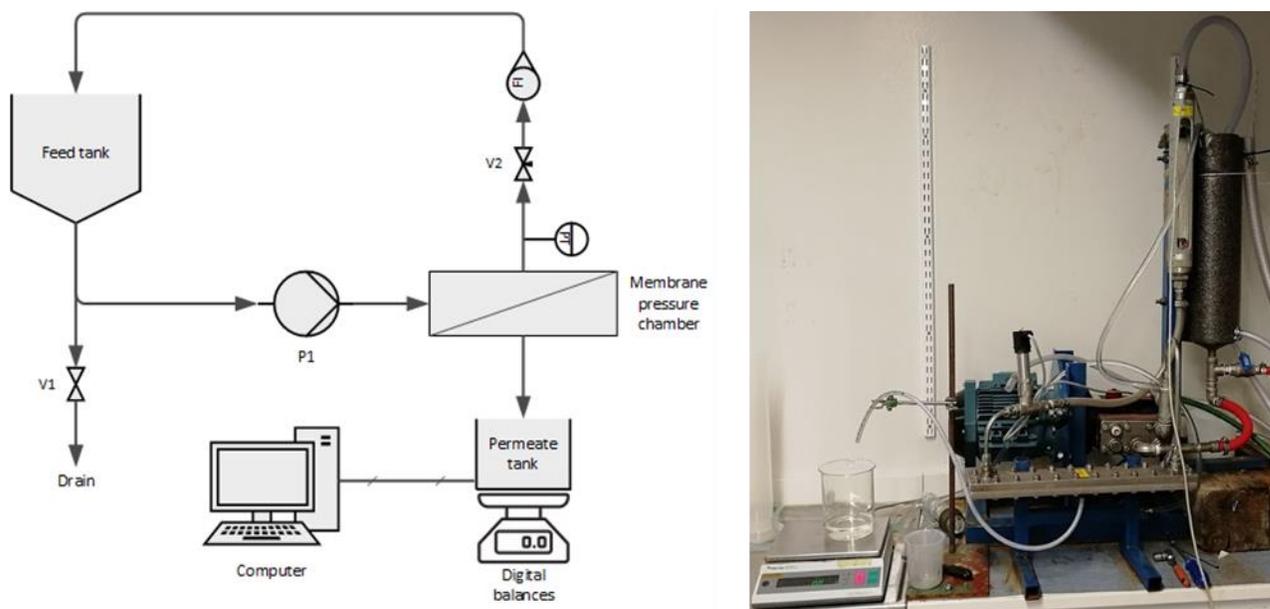


Figure 9.1. Schematic view (left) and the photo (right) of the experimental setup used to perform cross-flow filtration experiments.

9.1.2 Dead-end filtration set-up

The experiments to study the effect of pH of the raw wastewater on UF and UF of PAC treated effluents were conducted in the dead-end filtration unit. The dead-end filtration experiments were carried out using the 400 mL Amicon stirred cell. The experimental setup is shown in **Figure 9.2**. The Amicon stirred cell was connected to the pressurized nitrogen tank, pressure in the cell was controlled by the valve V1 and displayed by the pressure gauge PT. The temperature was controlled by the heater integrated into the magnetic stirring unit (Heidolph, Hei-Standart). The active membrane surface area was 38 cm². Mass of the collected permeate was measured during the filtration using precision balances Precisa 2200C connected to the computer.

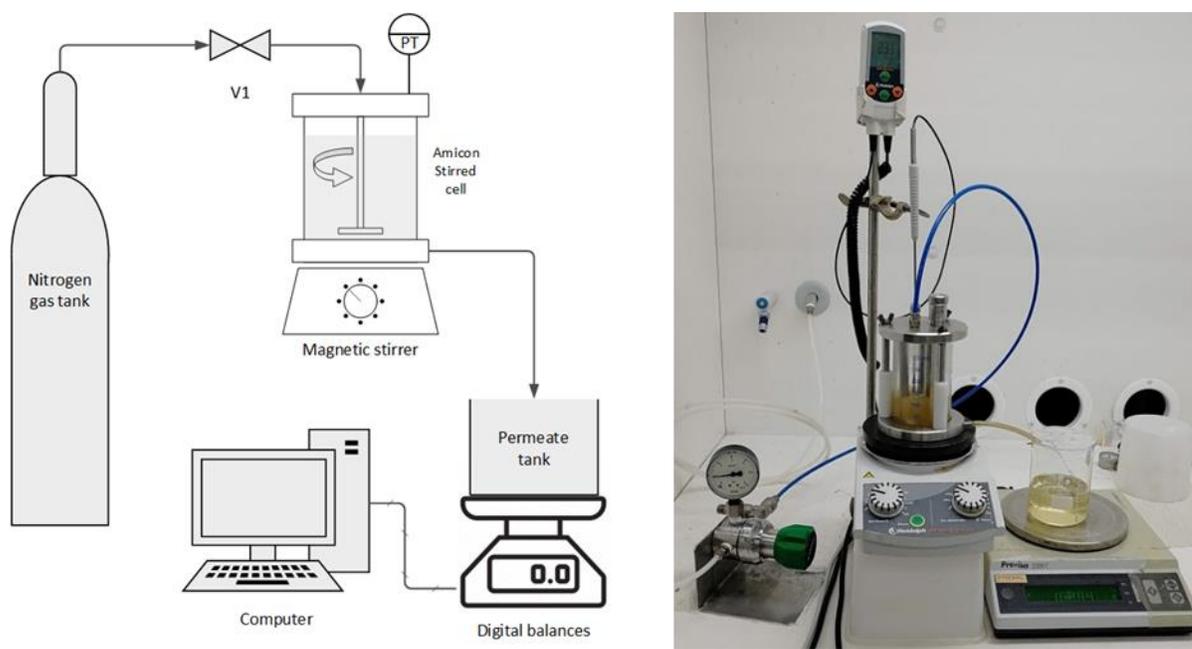


Figure 9.2. Schematic view (left) and the photo (right) of the experimental setup used to perform dead-end filtration experiments.

9.2 Experimental procedure

9.2.1 Membrane preparation

Before use, membranes were soaked in DI water overnight at 4 °C for removal of preservative glycol layer. Before the experiments, membranes were again washed with DI water, installed in the filtration unit and compacted with water (tap water in the cross-flow unit, DI water in dead-end unit) to avoid any structural changes in membranes and obtain steady flux during the experiments. TMP was increased gradually during compaction. The RC70PP, NF270, and SW30 membranes were compacted at 5, 10, and 45 bar, respectively for 30 min. At the end of the compaction procedure, the permeate sample was taken for TOC analysis to make sure that preservative was completely removed.

9.2.2 Cross-flow filtration experiments

The main parameters of all cross-flow filtration experiments conducted during this study are summarized in **Table 9.1**, where V_f is the total feed solution volume.

Flat sheet rectangular membranes were placed in the pressure chamber, installed in the cross-flow filtration system (**Figure 9.1**) and compacted with water. Pure water flux before the filtration (PWF_0) was measured after compaction. Initial feed volume was 2.5 L, 2 L of which was accounted for the feed tank and 0.5 L was in the pipes and the pump. The feed solution was circulated for 2 min without

the application of pressure before the experiment to ensure complete homogenization of the feed solution in case there was some water left in the system after the compaction. Initial feed sample was collected from the feed tank at the beginning of the experiment. The fresh feed solution was being added in 0.5 L portions during experiments to maintain constant feed level in the tank. During filtration, permeate and feed samples were collected, membrane flux was monitored and recorded. At the end of the experiment, the remaining concentrate was drained from the tank and the system was flushed with water. Pure water flux after the filtration (PWF_1) was measured and compared with previously measured PWF_0 to evaluate irreversible membrane fouling. PWF values at different TMP can be found in **Appendix II**. Tap water was used for compaction, flushing, and PWF measurements in the cross-flow filtration unit. Between the experiments, the system was cleaned with 1% P3-ultrasil 110 solution for 30 min at 40 °C and flushed with water.

Table 9.1. List of the cross-flow filtration experiments and experimental conditions.

No	Experiment	Trials	Feed	V_f , L	T, °C	TMP, bar	CFV, m/s
1	UF	1	Raw WW	5	25	3	3
2	RO1	1	Raw WW	2.5	25	40	4
3	RO2	1	UF perm.	4.5	25	30	3
4	RO3	1	RO perm.	3	25	40	5
5	Taguchi UF	9	Raw WW	2.5	25,30,35	1,3,5	2,3,4
6	Taguchi RO	9	UF perm.	2.5	25,30,35	20,30,40	3,4,5
7	1 st stage UF	1	Raw WW	11	25	5	4
8	2 nd stage RO	1	1UF perm.	7	25	30	4
9	1 st stage UF	1	Raw WW	20	25	3	4
10	2 nd stage NF	1	1UF perm.	19	25	8	4
11	3 rd stage RO	1	2 NF perm.	15	25	30	4
12	4 th stage RO	1	3RO perm.	12.5	25	30	4
13	pH+UF	1	WW (pH 7)	3.5	25	5	4

9.2.3 Ultrafiltration

UF was carried out with raw wastewater to test the performance of RC70PP membrane, estimate what level of treatment could be achieved by UF solely and acquire the feed solution for RO and other experiments.

9.2.4 Reverse osmosis

Performance of RO was tested with 3 types of feed: raw wastewater, UF permeate, and RO permeate to test the treatment process at different feed solution concentrations and compositions to evaluate how much COD and TOC could be retained by SW30 membrane. A new membrane was used for each experiment.

The first RO experiment (№2) was carried out with raw oily wastewater as a feed solution. The second RO experiment (№3) was carried out with UF permeate obtained during the UF experiment (№1) described in section 9.2.3 as a feed solution. TMP was reduced from 40 to 30 bar to mitigate the effect of fouling. The feed solution was diluted by approx. 0.5 L of water (dilution factor $DF=1.125$) which was in the tubes and the pump, so the feed concentration was lower than the initial concentration of collected UF permeate. The third RO experiment (№4) was carried out with RO permeate as a feed solution from the previous RO experiment (№3). The feed solution was diluted by approx. 0.5 L of water which was in the tubes and the pump. TMP was increased back to 40 bar because the feed concentration was low after the treatment with UF and RO, and the feed solution was also diluted ($DF=1.2$).

9.2.5 Effect of operating conditions on UF and RO

Taguchi method was used to determine the optimal operating conditions and their effect on the UF and RO cross-flow filtration based on COD retention and flux. Taguchi method is widely used to determine optimal conditions and predict response values (Idris et al., 2002). It is based on the statistical technique introduced in the 1920s by Fisher and improved by Taguchi in the 1940s (Taguchi, Chowdhury & Wu, 2005). The Taguchi method uses an orthogonal array to study the effect of multiple factors on the response with a small number of experiments.

For the first step, factors had to be chosen. Based on the literature, temperature, TMP, CFV, pH, and oil concentration were usually studied (Hesampour, Krzyzaniak & Nyström, 2008, Salahi, A., 2011, Nadjafi, 2018). The pH affects the emulsion stability (Fujii, Okada & Furuzono, 2007, Sawain et al., 2009), while temperature, TMP, CFV directly affect membrane retention and permeability (Hesampour et al., 2009). Thus, three factors (temperature, TMP, and CFV) were chosen to study at three levels each to recognize any non-linearity in the response (Hesampour et al., 2009).

L_9 orthogonal array was used to create an experiment plan (**Table 9.2**). Numbers in columns 3-4 represent levels, not the actual parameter values. This experimental plan was used for both UF and

RO. 9 trials were carried out for each membrane while in conventional full factorial experiment design it would require $3^3 = 27$ trials to study three factors at three levels (Wahyudin et al., 2017). Minitab 17 software was used to design the plan of experiments and analyse the results during this study.

Table 9.2. The design of experiments for the L_9 array.

Trial	T	TMP	CVF
1	1	1	1
2	1	2	2
3	1	3	3
4	2	1	2
5	2	2	3
6	2	3	1
7	3	1	3
8	3	2	1
9	3	3	2

Factors and corresponding numerical values of the levels for determination of the optimal conditions for UF and RO are presented in **Table 9.3**. The temperature range was selected from 25 to 35 °C because according to BAT specifications the maximum water effluent temperature should be 40 °C. If implemented in industry, most probably this process will be carried out in that temperature range. CVF range for UF was chosen from 2 to 4 m/s because the minimal flow velocity at which turbulent flow was possible in cross-flow filtration system was 2 m/s. For RO, CFV was increased to sustain the high pressure required to conduct RO. TMP range was selected based on (Chen, 2013, Sun et al., 2014, Issakainen, 2019) and (Al-Bastaki, 2003, Tomaszewska, Orecki & Karakulski, 2005, Karakulski, 2006) for UF and RO, respectively.

Table 9.3. Factors and their levels for determination of optimal operating conditions for UF and RO.

Membrane	UF			RO			
	Factor	T, °C	TMP, bar	CVF, m/s	T, °C	TMP, bar	CVF, m/s
Level 1		25	1	2	25	20	3
Level 2		30	3	3	30	30	4
Level 3		35	5	4	35	40	5

Raw oily wastewater was used as a feed solution for the UF trials (experiment 5) while the UF permeate collected from experiment 1 was used as a feed solution for the RO trials (experiment 6). 250 mL of permeate was collected during each trial. Permeate and feed solution samples were taken

after each trial. Then, the collected permeate was returned to the feed tank to maintain the concentration of the feed solution the same during different trials.

9.2.6 Combination of UF and RO

The combination of UF and RO was applied to achieve high total COD and TOC removal and reduce the COD of the collected permeate below 3600 mg/L threshold. To reduce fouling during RO, pretreatment of the feed solution should be applied (Baker, 2004). Multiple studies showed that a combination of UF and RO can potentially demonstrate 95% and higher COD and TOC removal (Salahi, Abdolhamid et al., 2009, Abbasi, 2013). The raw untreated wastewater was used as a feed solution for the UF while its permeate was used as a feed solution for the RO as shown in **Figure 9.3**. **Figure 9.3** shows the design of the dual membrane process and TMP at which experiments were carried out. These parameters were based on optimal operating conditions determined by the Taguchi method described in section 9.2.5. From 0.5 to 1 L of feed was lost between stages because the water left in the system after compaction and PWF measurement had to be washed out with the feed solution to prevent dilution.

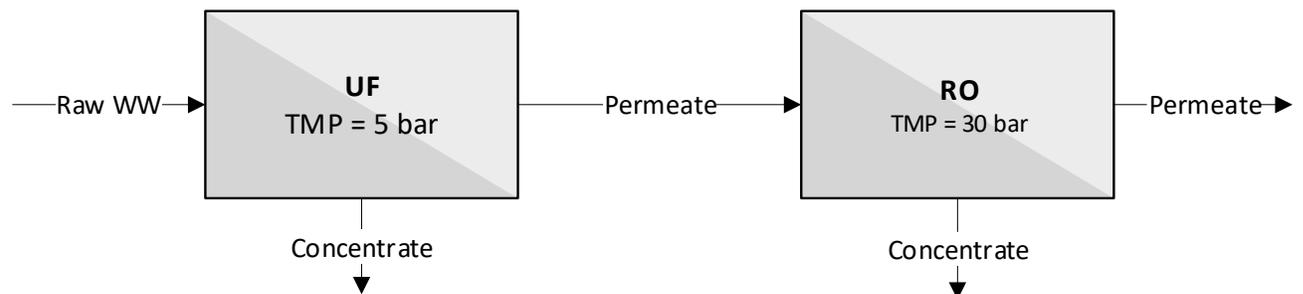


Figure 9.3. Design of the two-stage UF-RO treatment process (experiments 7,8).

9.2.7 Combination of UF, NF, and RO

The combination of UF, NF, and two RO stages in series was applied to improve the performance and increase the total COD and TOC removal compared to UF-RO combination. NF was applied as an additional treatment step before RO. The raw untreated wastewater was used as a feed solution for the UF while its permeate was used as a feed solution for the next step and so on. **Figure 9.4** shows the design of the multistage membrane process and TMP at which each experiment was carried out. These parameters were based on optimal operating conditions determined by the Taguchi method (section 9.2.5). TMP at which UF was conducted was reduced from 5 bar to 3 bar to mitigate the effect of fouling. From 0.5 to 1 L of feed was lost between stages because the water left in the system after compaction and PWF measurement had to be washed out with the feed solution to prevent dilution.

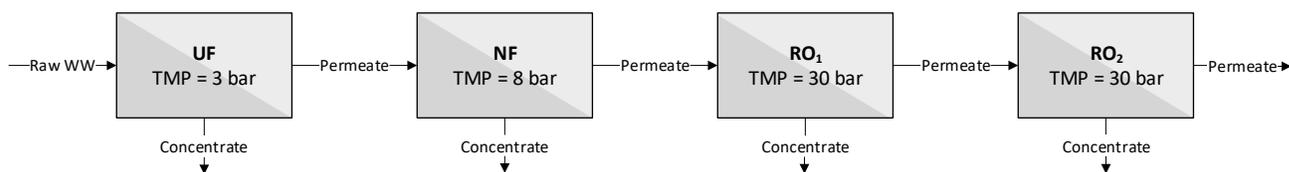


Figure 9.4. Design of the multistage UF-NF-RO₁-RO₂ treatment process (experiments 9-12).

9.2.8 Dead-end filtration experiments

The main parameters of dead-end filtration experiments conducted during this study are summarized in **Table 9.4**, where V_f is the total feed solution volume.

Flat sheet membrane “coupons” were placed in the stirred Amicon cell (**Figure 9.2**) and compacted. PWF_0 was measured after compaction. The feed solution was poured into the cell and mixed for 1 min without the application of pressure before each trial to ensure complete homogenization of the feed, in case there was some water left in the cell after compaction. The feed solution sample was collected from the cell before filtration started. Membrane flux was monitored and recorded during the experiments. Permeate and concentrate samples were collected after filtration, and the cell was rinsed with DI water. PWF_1 was measured and compared with PWF_0 to evaluate membrane fouling. Compaction, rinsing, and PWF measurements were done with DI water.

Table 9.4. List of the dead-end filtration experiments and experimental conditions.

Experiment	Trials	Feed	V_f , mL	T, °C	TMP, bar	rpm
14	pH+UF	5	pH+WW	300	25	1 250
15	PAC+UF	2	PAC+WW	250	25	5 250

9.2.9 Effect of pH on UF performance

A total of five trials were conducted for wastewater samples with pH adjusted to 3, 5, 7, 9.4 (raw WW, no adjustment), and 11 to study the effect of pH on the COD retention and flux of RC70PP membrane (experiment 14). Wastewater samples were collected before and after the pH adjustment to determine if the COD of the samples changed. A new membrane was used for each trial.

An additional UF experiment (№13) in the cross-flow unit was conducted with wastewater adjusted to 7 pH as a feed solution. The operating parameters can be found in **Table 9.1**.

9.2.10 Effect of pH on AC performance

The main parameters of activated carbon (AC) treatment experiments are summarized in **Table 9.5**, where m_f is the feed solution mass, t_{ads} is the adsorption time.

Table 9.5. List of the AC experiments and experimental conditions.

Experiment	Trials	Feed	m_f , g	AC dosage, g/L	t_{ads} , h	T, °C	
16	Blank	5	Raw WW	150	21	24	28
17	GAC	5	Raw WW	150	21	24	28
18	PAC	5	Raw WW	150	21	24	28
19	PAC dose	5	Raw WW	300	3.5-49	24	28
20	PAC time	6	Raw WW	300	21	2-20	26
21	UF+PAC	1	UF perm.	300	21	24	26

The wastewater treatment efficiency of GAC and PAC was compared based on COD removal at different pH values (experiments 16-18). Each trial included three consequent steps: pH adjustment, adsorption, and vacuum filtration to separate spent AC from the treated solution.

Three sets each containing five wastewater samples (150 g) with pH adjusted to 3, 5, 7, 9.4 (raw wastewater, no pH adjustment), and 11 were prepared. Wastewater samples were collected before and after pH adjustment to determine if COD of the samples changed.

Wastewater samples were mixed with AC in 300 mL glass beakers. The AC dosage was 21 g/L. GAC was added to the first set (experiment 17) and PAC was used with the second (experiment 18). The third set was blank (experiment 16) meaning that no adsorbent was added to the wastewater samples to determine how much COD was removed by activated carbon (AC) and how much COD reduced due to agitation and vacuum filtration with paper filters. AC experiments were conducted for 24 h at 28 °C and 250 rpm. A total of 15 trials were carried out. Agitation was provided by IKA EOA 5 multi-place magnetic stirrer and the temperature was controlled by AKA EH 2 thermostat. Beakers were covered with Parafilm to prevent evaporation during experiments.

The third step was the spent AC separation from wastewater after the experiment. The separation was done by vacuum filtration using S&S grade 589/2 filter papers. The supernatant was collected while AC was left on the filter surface and discarded. Blank set was also filtered through filter paper because it could potentially contribute to COD reduction. Samples of collected supernatants from every trial

were collected. Additionally, the pH of collected samples was measured to determine if there was any change in pH after adsorption.

9.2.11 Effect of PAC dosage and adsorption time

Effect of PAC dosage on raw oily wastewater treatment quality based on COD reduction was studied during the experiment 19. Five wastewater solutions of 300 g each were mixed with different PAC doses in 500 mL glass beakers. PAC dosages were 3.5, 7, 21, 35, 49 g/L. These dosages corresponded with 1, 2, 6, 10, and 14 g of PAC added to each solution sample. Adsorption trials were carried out at 28 °C and 250 rpm for 24 h. Experiments followed the procedure described in section 9.2.10. Samples were collected before the adsorption and after separation of the spent PAC.

Effect of PAC adsorption time on raw oily wastewater treatment efficiency based on COD reduction was studied during the experiment 20. Six wastewater solutions of 300 g each were mixed with PAC in 500 mL glass beakers. The PAC dosage was 21 g/L. Adsorption trials were carried out for 2, 4, 8, 12, 16, 20 h at 26 °C and 250 rpm. Experiments followed the three-step procedure described in section 9.2.10. Samples were collected before the adsorption and after separation of the spent PAC.

9.2.12 Combination of PAC and UF

Two combinations of PAC treatment and UF were tested:

1. PAC (3.5 and 49 g/L) and UF (RC70PP)
2. UF (RC70PP) and PAC (21 g/L)

Combination of PAC treatment and UF could potentially improve the COD and TOC reduction, mitigate membrane fouling, consequently increasing membrane flux (Mohammadi, Esmaelifar, 2005, Yang, Chen & Xing, 2011). In the first combination, two samples of supernatants of 300 g each collected during the experiment 19 described in section 9.2.11 were filtered with RC70PP membrane at 5 bar (experiment 15 in **Table 9.4**). The first sample was treated with 3.5 g/L of PAC (minimal PAC dose) and the second with 49 g/L of PAC (maximum PAC dose) for 24 h. The second combination was 300 g sample of the RC70PP permeate mixed with 21g/L PAC dose for 24 h without pH adjustment, as described in section 9.2.10 (experiment 21).

UF experiments were carried out at 25 °C and 250 rpm. The feed solution volume was 250 mL.

9.3 Analyses

The equipment used for COD, TOC, conductivity, turbidity and colour measurements is listed in **Table 9.6**. All measurements were done at room temperature.

Table 9.6 Equipment used for measurements.

Parameter	Equipment
pH	Metrohm 744 pH meter
COD	Spectroquant COD cell tests, Hatch DR2010 spectrophotometer
TOC	TOC analyser Shimadzu TOC-L/CPH
Conductivity	Consort C3010 multi-parameter analyser
Turbidity	Hatch DR2010 spectrophotometer
Colour	Hatch DR2010 spectrophotometer

The parameters measured in each test are summarised in **Table 9.7**. As can be seen, the efficiency of the treatment was estimated mainly based on the value of COD and TOC parameters. In addition, conductivity, turbidity and colour were measured during multi-stage filtration (UF-RO and UF-NF-RO₁-RO₂). pH was measured during pH effect and AC experiments.

Table 9.7. Measurements conducted with samples collected during the experiments.

	Experiment	COD	TOC	Conductivity	Turbidity	Colour	pH
Cross-flow filtration							
1	UF	yes	no	yes	yes	no	no
2	RO	yes	yes	no	no	no	no
3	RO	yes	yes	yes	no	yes	no
4	RO	yes	yes	no	no	no	no
5	Taguchi UF	yes	no	no	no	no	no
6	Taguchi RO	yes	no	no	no	no	no
7	1 stage UF	yes	yes	yes	yes	no	no
8	2 stage RO	yes	yes	yes	yes	no	no
9	1 stage UF	yes	yes	yes	yes	no	no
10	2 stage NF	yes	yes	yes	yes	yes	no
11	3 stage RO	yes	yes	yes	yes	yes	no
12	4 stage RO	yes	yes	yes	no	yes	no
13	pH+UF	yes	yes	no	no	no	yes
Dead-end filtration							
14	pH+UF	yes	no	no	no	no	yes
15	PAC+UF	yes	no	no	no	no	
Adsorption							
16	Blank	yes	yes	yes	no	no	yes
17	GAC	yes	yes	yes	no	no	yes
18	PAC	yes	yes	yes	no	no	yes
19	PAC dose	yes	no	no	no	no	no
20	PAC time	yes	no	no	no	no	no
21	UF+PAC	yes	no	no	no	no	no

9.4 Calculations

Flux indicates the amount of permeate passing through a membrane in relation to its surface area and time.

$$J = \frac{m}{A \cdot t} \quad (1)$$

where J – permeate mass flux, kg/(m²*h)

m – permeate mass, kg

A – active surface area of the membrane, m²

t – filtration time, h

The retention (refers to solute) indicates what part of the feed stream is rejected by the membrane.

Equation 2 is used to calculate the retention of cross-flow and dead-end filtration.

$$R = \frac{C_f - C_p}{C_f} = 1 - \frac{C_p}{C_f} \quad (2)$$

where C_f – initial feed solution concentration, mg/L

C_p – collected permeate concentration, mg/L

The recovery rate refers to water and indicates what portion of the feed solution passes through the membrane.

$$r = \frac{V_p}{V_f} \quad (3)$$

where V_p – collected permeate volume, L

V_f – feed solution volume, L

The spot retention describes “true” retention of the membrane at a given TMP and feed solution concentration assuming an infinitely small volume change ($r \rightarrow 0$) (Strathmann, Giorno & Drioli, 2006).

$$R_i = 1 - \frac{C_{pi}}{C_{fi}} \quad (4)$$

where C_{fi} – current feed solution concentration, mg/L

C_{pi} – momentary concentration of the permeate coming out from the membrane, mg/L

Mixing cup concentration is a concentration of an entire collected and mixed permeate up to a given recovery rate (Strathmann, Giorno & Drioli, 2006).

$$\bar{C}_i = \frac{C_f}{r} [1 - (1 - r)^{1-R_i}] \quad (5)$$

where r – recovery rate

C_f – initial feed solution concentration, mg/L

R_i – spot retention of the membrane

The pure water flux reduction (FR_{PWF}), is a measure of irreversible fouling of the membrane. It is calculated by equation 6 (Mänttari, Pekuri & Nyström, 2004).

$$FR_{PWF} = 1 - \frac{PWF_1}{PWF_0} \quad (6)$$

where FR_{PWF} - pure water flux (PWF) reduction, %

PWF_1 - PWF after filtration, kg/(m²*h)

PWF_0 - PWF before filtration, kg/(m²*h)

The S/N is a signal-to-noise ratio and it is used as a measure of the quality characteristics of the choice. It is calculated by equation 7.

$$\frac{S}{N} = 1 \log_{10} \frac{1}{MSD} \quad (7)$$

where *MSD* - mean square deviation

The equilibrium adsorption capacity was calculated by equation 8.

$$q_e = \frac{C_i - C_e}{m} V \quad (8)$$

where C_i – initial COD, mg/L

C_e – equilibrium concentration, mg/L

m – adsorbent mass, g

V – the volume of the solution, mL

10 Results and discussions

Table 10.1 lists cross-flow experiments and their main results (collected permeate volume, recovery, COD and TOD of the total collected permeate, and retention for both COD and TOC).

Table 10.1. List of experimental results for the cross-flow experiments.

№	Experiment	Feed	V_p, L	r, %	COD, mg/L	TOC, mg/L	R_{COD}, %	R_{TOC}, %
1	UF	Raw WW	4	80	9625	-	14	-
2	RO1	Raw WW	0.375	15	937	379	93	88
3	RO2	UF perm.	2.5	56	1440	1001	83	63
4	RO3	RO2 perm.	1.5	50	196	47	79	63
7	1 st stage UF	Raw WW	9.5	86	10400	2296	15	23
8	2 nd stage RO	1UF perm.	6	86	2030	538	80	80
9	1 st stage UF	Raw WW	19.0	95	10693	2794	13	17
10	2 nd stage NF	1UF perm.	18.0	95	9290	2402	11	8
11	3 rd stage RO	2NF perm.	13.5	90	4658	1293	49	48
12	4 th stage RO	3RO perm.	11.3	90	1647	507	65	56

Figure 10.1 shows UF and RO fluxes as functions of time during cross-flow UF and RO with different feed solutions (experiments 1-4).

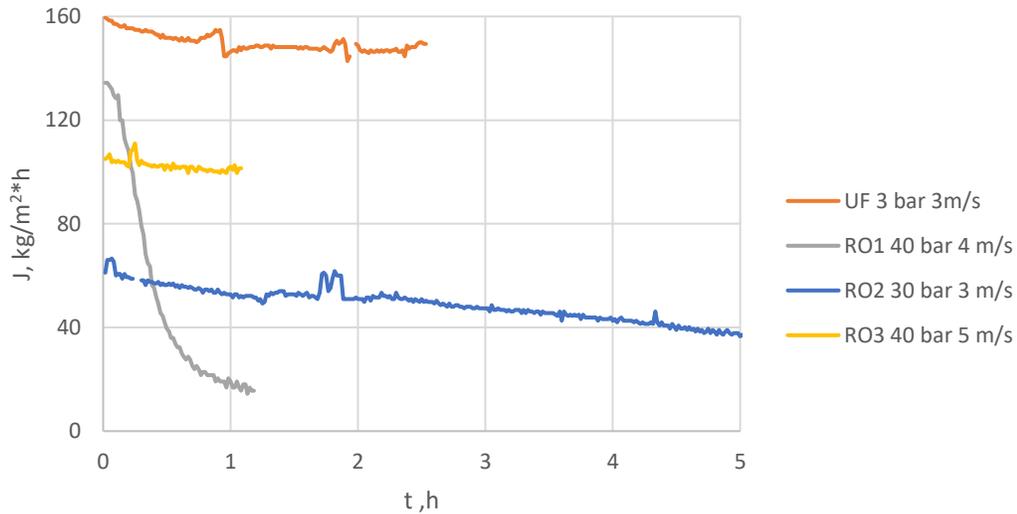


Figure 10.1. UF and RO fluxes as a function of time (experiments 1-4).

10.1 Ultrafiltration

The results of UF are presented in **Table 10.1**. RC70PP membrane showed only 14% COD retention. According to (Baker, 2004) retention of UF membranes is determined by the shape and size of molecules to be retained. Globular molecules are retained much better by UF membranes than linear, water-soluble molecules. Linear and low-molecular-weight molecules can pass through membrane pores. This might explain the low retention of UF. Also, the wastewater contains ethanol (**Appendix I**) which is miscible with water and many organic solvents (Haynes, Lide & Bruno, 2016). Potentially, it could also have negatively affected the retention. UF removed 99.9% of turbidity but did not affect conductivity as it can only retain particles and high-molecular-weight components from the solution, while conductivity is mostly derived by total dissolved solids (TDS). **Figure 10.1** shows UF flux as a function of time. RC70PP membrane maintained high and stable flux, it decreased by 7% during filtration. Fluctuations of the membrane flux on the graph at approx. 60, 115, and 150 min correspond with times when the feed level in the tank was low.

10.2 Reverse osmosis

The main results of the three RO experiments (№ 2-4) are summarized in **Table 10.1** (recovery, COD and TOC of the total collected permeate, and membrane retention).

During experiment 2, SW30 showed 93% and 88% COD and TOC retention, respectively, COD was reduced below 1000 mg/L, but only 15% recovery rate was reached (**Table 10.1**). According to **Figure 10.1**, the RO was carried out only for 70 min, but the membrane flux decreased by 88%. The membrane was significantly affected by fouling and was completely plugged after the experiment ($PWF_1 = 0$). Probably, a gel/cake layer deposited on the surface of the membrane since the raw wastewater contained high concentrations of high-molecular-weight inorganic and organic compounds and dissolved oil (Baker, 2004).

During experiment 3, the retention was lower (83% for COD and 63% for TOC) and the COD of the total collected permeate was higher (1440 mg/L) than in the previous experiment (**Table 10.1**). RO reduced conductivity by 84% (conductivity of the collected permeate was 121 $\mu\text{S}/\text{cm}$). The possible reason for lower retention in experiment 3 compared to experiment 2 was that gel/cake layer might have acted as an additional barrier and retained some of the constituents. Membrane flux gradually decreased during experiment 3 by 43% (**Figure 10.1**), there was no sudden drop in flux. Because most of the pollutants causing fouling were probably removed by the UF, the effect of fouling on the SW30 membrane was less significant.

During experiment 4, COD retention slightly decreased to 79% while TOC retention did not change compared to the previous experiment. Membrane flux decreased only by 4% during the experiment (**Figure 10.1**), and after flushing the membrane with water, PWF fully recovered, meaning that the membrane was not affected by irreversible fouling.

It can be concluded that RO could not be operated with raw wastewater and required pretreatment of the feed solution to minimize the concentration of pollutants which contributed to fouling. RO demonstrated slightly lower retention of TOC. It might be explained by the fact that commercial RO membranes cannot provide a sufficient barrier to low-molecular-weight organic molecules like ethyl acetate, ethylene glycol, formaldehyde and 2-butanone (Košutić, Kunst, 2002, Bellona et al., 2004). Retention of the RO slightly decreased with each treatment step because apparently, gel/cake layer depositing on the membrane surface during operation might have acted as an additional barrier to pollutants especially for organic components since plugged SW30 membrane during experiment 2 showed 25% higher TOC retention than two following RO stages. Event though UF, RO1, and RO2 were done in sequence, it should not be viewed as a single process since the feed solution was diluted before both RO stages and the total treatment efficiency or water recovery of such combination cannot be correctly determined.

10.3 Effect of operating conditions on UF and RO

Table 10.2 comprises the experimental set for experiment 5, COD retention and flux values (response), and calculated S/N ratios for each trial (S/N₁ is for retention and S/N₂ is for flux). The calculated S/N ratios show how much the temperature, TMP, and CFV affected the response in each trial. In this study “the larger the better” approach was used because the intention was to maximize retention and flux.

The retention of UF varied from 16% to 20% for different trials. The membrane flux changed from 53 kg/m²*h during trial 1 to 193 kg/m²*h during trial 9. Trials 3 and 9 demonstrated the highest S/N₁ and S/N₂ ratios which corresponded with the highest TMP of 5 bar, approx. 20% COD retention, and flux of 193 kg/m²*h. Also, the S/N₁ ratio of the third trial was higher than of the ninth, indicating that CFV had a higher influence on retention than temperature.

Table 10.2. Summary of factors, responses, and S/N ratios for the UF (experiment 5).

Trial	T, °C	TMP, bar	CFV, m/s	R _{COD} , %	S/N ₁	J, kg/m ² *h	S/N ₂
1	25	1	2	16.6	24.42	53.5	34.56
2	25	3	3	16.3	24.27	131.4	42.37
3	25	5	4	20.3	26.17	192.7	45.70
4	30	1	3	16.4	24.28	63.1	35.99
5	30	3	4	19.1	25.61	152.6	43.67
6	30	5	2	18.0	25.12	152.7	43.67
7	35	1	4	17.1	24.65	67.8	36.63
8	35	3	2	17.6	24.90	134.0	42.54
9	35	5	3	19.6	25.86	193.4	45.73

Figure 10.2 shows how much in comparison each factor affects the S/N ratios and consequently COD retention and flux of the UF process. Effect of TMP on retention and flux is the highest. At high TMP the retention of UF approaches maximal values (Strathmann, Giorno & Drioli, 2006). An increase in CFV from 3 to 4 m/s also had a strong positive effect on retention. Probably, an increase in CFV intensified turbulence which reduced the concentration polarization layer positively affecting the retention. CFV did not significantly affect flux. Temperature affected retention and flux insignificantly compared to TMP and CFV. The small positive effect of an increase in temperature on retention might be explained by higher diffusion of substance from concentration polarization layer to the bulk of the feed solution due to increased solubility. However, higher solubility might also

increase the passage of pollutants through the membrane reducing the retention and thus minimizing the total positive effect. Higher temperature will not increase the treatment efficiency substantially but will increase energy consumption.

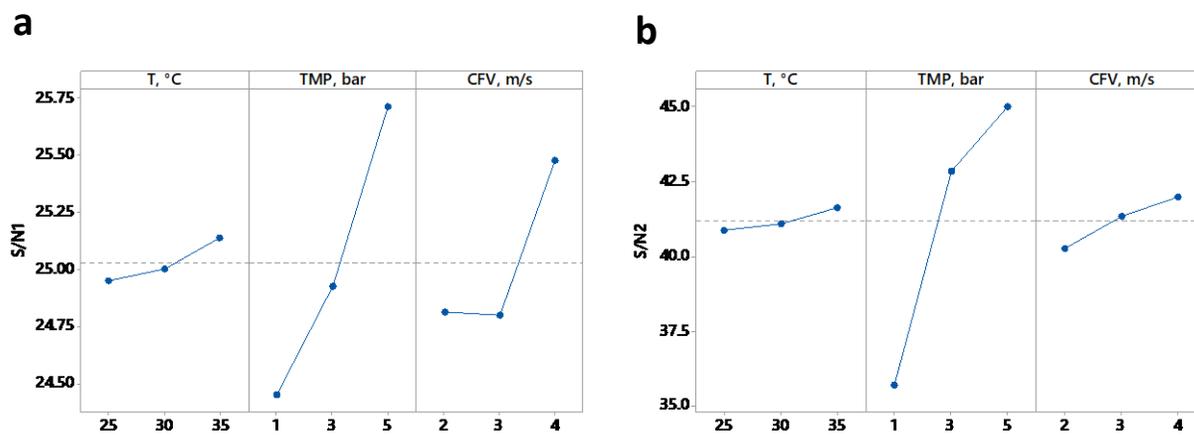


Figure 10.2. Effect of temperature, TMP, and CFV on a) S/N_1 (retention), b) S/N_2 (flux) ratios for the UF (experiment 5).

Table 10.3 comprises the experimental set for experiment 6, COD retention and flux values (response), and calculated S/N ratios for each trial (S/N_1 is for retention and S/N_2 is for flux). The retention of RO varied from 86% to 90% during different trials. The membrane flux changed from 36 kg/m²*h during trial 1 to 82 kg/m²*h during trial 6. Trials 3 and 6 showed the highest S/N_1 ratio which also corresponded with the highest TMP. The highest S/N_2 ratio was registered during trial 9 where RO was operated at the highest temperature and TMP.

Table 10.3. Summary of factors, responses, and S/N ratios for the RO (experiment 6).

Trial	T, °C	TMP, bar	CFV, m/s	R _{COD} , %	S/N_1	J, kg/m ² *h	S/N_2
1	25	20	3	86.5	38.74	35.7	31.06
2	25	30	4	89.4	39.02	53.9	34.63
3	25	40	5	90.1	39.09	71.8	37.13
4	30	20	4	86.0	38.69	41.4	32.34
5	30	30	5	89.1	39.00	63.8	36.10
6	30	40	3	90.2	39.10	82.2	38.30
7	35	20	5	77.4	37.77	50.0	33.99
8	35	30	3	87.8	38.87	72.4	37.19
9	35	40	4	89.4	39.03	97.7	39.80

Figure 10.3 shows how much in comparison each factor affects the S/N ratios and consequently COD retention and flux of the RO process. An increase in temperature demonstrated a negative effect on retention while it positively affected flux. An increase in temperature might have promoted transport of solute through the membrane due to increased solubility (Strathmann, Giorno & Drioli, 2006). TMP had the highest effect on retention and flux. With an increase in TMP, rejection and flux also increased. Increase in TMP from 30 to 40 bar increased retention only by 1% thus it was not practical to operate RO at 40 bar. Probably, the retention of the SW30 membrane approached the maximum value at 30 bar and a further increase in pressure did not lead to a significant increase in rejection (Strathmann, Giorno & Drioli, 2006). CFV demonstrated almost no effect on flux. With an increase in CFV from 3 to 4 m/s there was almost no effect on retention observed but when CFV was further increased from 4 to 5 m/s retention reduced by 3%.

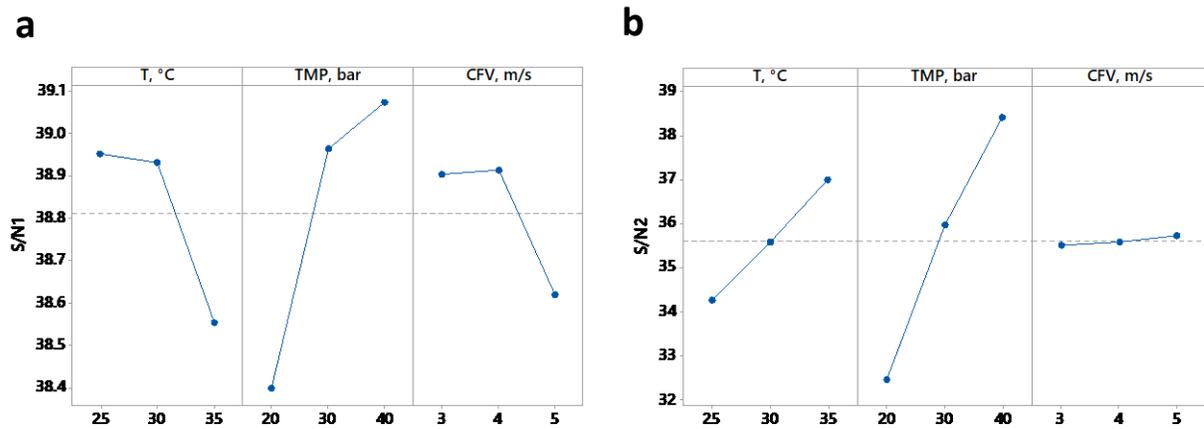


Figure 10.3. Effect of temperature, TMP, and CFV on a) S/N₁ (retention), b) S/N₂ (flux) ratios for the RO (experiment 6).

The selected optimal conditions were 25 °C, 5 bar, 4 m/s for UF and 25 °C, 30 bar, 4 m/s for RO. Changes in operating parameters contributed only to 4% change in retention for both UF and RO. Even though retention and flux were studied, fouling must be considered too when selecting optimal operating parameters because it might have a serious effect on membrane performance in the long run, especially for UF since it is used as the first treatment step. Unfortunately, flux was not assessed during these trials due to short filtration time and only 10% recovery rate. If serious fouling occurs in the following experiments TMP should be changed since it directly affects fouling (Strathmann, Giorno & Drioli, 2006).

10.4 Combination of UF and RO

Figure 10.4 shows the design and the main results of the UF-RO process – a combination of UF and RO in series. The total recovery rate was 74%. The total retention was 83% of both COD and TOC. UF-RO combination allowed to reduce COD of the wastewater below the target value (3600 mg/L) down to 2030 mg/L. Characteristics of the initial feed and the effluent can be found in **Table 10.4**.

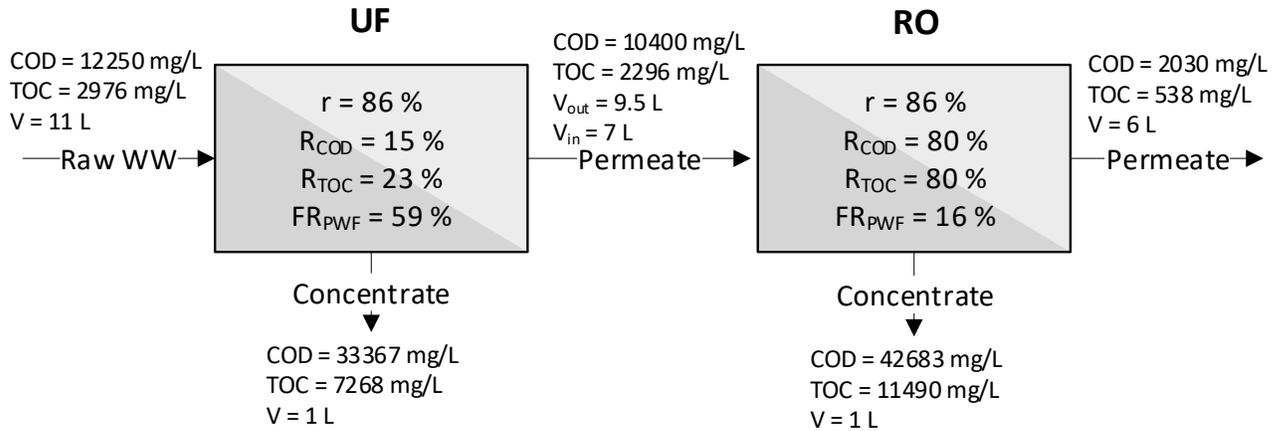


Figure 10.4. Design and main parameters of a two-stage UF-RO process (experiments 7,8).
 V_{out} – UF permeate volume, V_{in} – RO feed solution volume.

According to **Figure 10.4**, the UF showed 15% COD and 23% TOC retention, it removed 99.7% of turbidity but did not decrease conductivity as it can only retain particles and high-molecular-weight constituents from the solution while conductivity is mostly derived by ions. The difference in COD and TOC rejection indicate that organic components are better rejected by UF than inorganic. Possibly, high-molecular-weight components in the feed solution which are best retained by the UF are predominantly organic which could explain the higher TOC retention.

The RO stage demonstrated considerably higher retention (80% for both COD and TOC) compared to UF. It also reduced the conductivity by 85%. If concentrates from both stages had been mixed, the COD and TOC of the acquired solution would be 38025 mg/L and 9379 mg/L, respectively.

Table 10.4. Comparison of WW characteristics before and after UF-RO treatment.

Parameter	Before treatment	After treatment	Target	Reduction, %
COD, mg/L	12250	2030	3600	83
TOC, mg/L	2976	538	-	83
Conductivity, $\mu\text{S}/\text{cm}$	747	134	-	82
Turbidity, NTU	2330	2	-	100

It can be seen from **Figure 10.5**, that RO permeate was clear and transparent, while UF permeate had a slightly yellowish colour potentially indicating the presence of dissolved oil in the collected permeate sample.

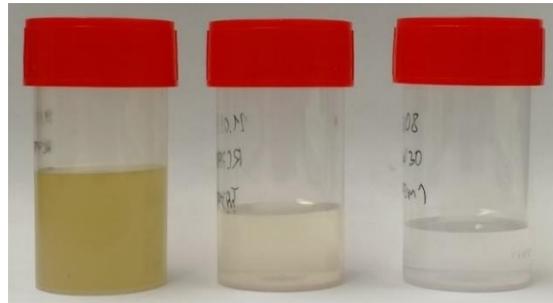


Figure 10.5. Samples from different stages of the UF-RO process.
From left to right: raw WW, UF permeate, RO permeate.

Figure 10.6 shows the momentary permeate COD and the spot retention (equation 4) as a function of recovery of UF stage. Horizontal grey and red dashed lines represent the COD of the initial feed solution (raw wastewater) and the target COD (3600 mg/L), respectively. Momentary permeate COD was stable during the filtration even though the COD of the feed solution increased with an increase in recovery rate. The spot retention gradually increased during filtration. It may be explained by the gel/cake layer formation on the surface of the membrane during the filtration which acted as an additional barrier for solute and gradually increased the retention of the membrane compensating for an increase in the feed concentration (Jermann et al., 2009).

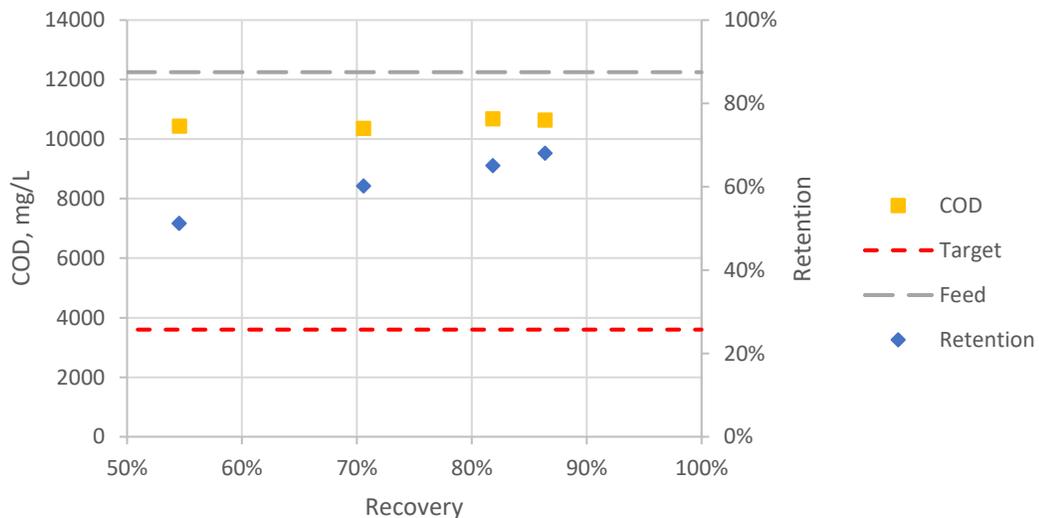


Figure 10.6. Momentary permeate COD and spot retention as a function of recovery of UF stage (UF-RO combination).

Performance of UF stage is represented by momentary permeate COD because mixing cup permeate COD could not be calculated by equation 5 due to fouling which affected the performance of the UF membrane. The recovery rate of the UF stage was 86% but it could potentially be increased for further reduction of the produced concentrate amount without a significant increase in the collected permeate concentration.

Figure 10.7 shows the calculated mixing cup permeate COD and the spot retention (equation 4) as a function of recovery of RO stage. The spot retention of RO (91%) did not change with an increase in recovery rate meaning that the concentration of the permeate increased with an increase in the concentration of the feed solution. The mixing cup permeate COD was calculated from the spot retention values by equation 5 and determined the COD of collected permeate up to a given recovery rate. Horizontal grey and red dashed lines represent the COD of the initial feed solution and the target COD (3600 mg/L), respectively. The large dot on the graph represents the COD of the total collected permeate (2030 mg/L) at 86% recovery. It can be estimated from the curve of the calculated mixing cup permeate COD that the recovery rate of RO stage could potentially be increased up to 95% thus reducing the amount of produced concentrate without exceeding the COD limit for the collected permeate.

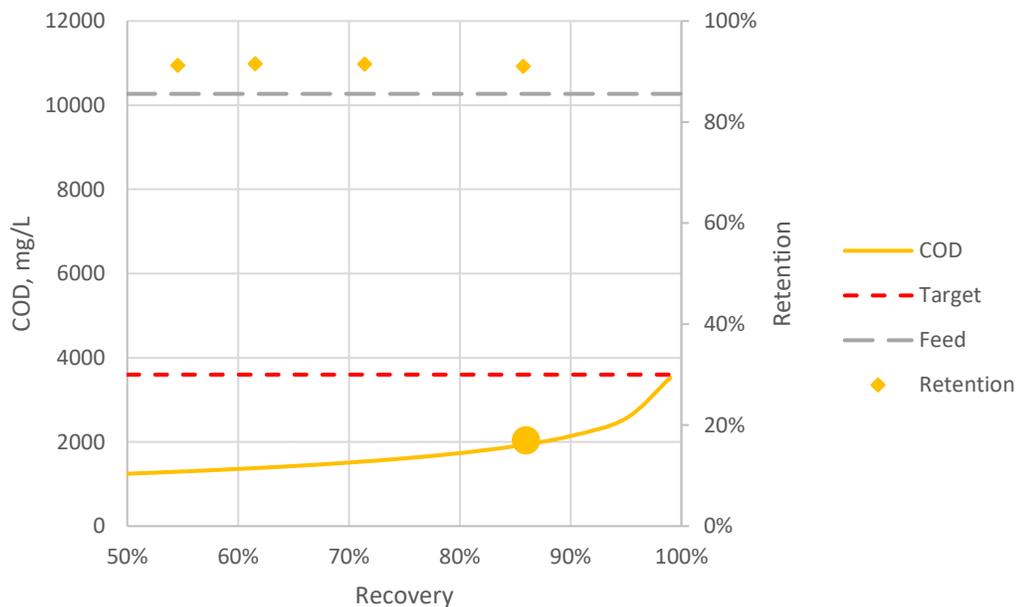


Figure 10.7. Calculated mixing cup permeate COD and spot retention as a function of recovery rate (UF-RO combination).

Figure 10.8 shows UF and RO fluxes as a function of time. UF flux decreased by 89% during filtration while the PWF reduction (equation 6) was 59% indicating that the membrane was highly affected by irreversible fouling. After 10 h of filtration, UF flux was equal to RO flux. As the first stage, UF was more affected by fouling and concentration polarization than RO. In RO, the retained solutes are dissolved salts and low-molecular-weight pollutants while UF retains colloids and macromolecules. These high-molecular-weight components have significantly lower diffusion coefficients than constituents in the RO feed solution (Baker, 2004). For this reason, diffusion from the concentration polarization layer to the bulk of the solution is lower during UF compared to RO which can lead to precipitation and/or gel/cake layer formation on the surface of the membrane (Strathmann, Giorno & Drioli, 2006).

Flux decreased by 58% during RO while PWF reduction was 16% indicating that the membrane was less affected by fouling compared to UF because most of the constituents contributing to fouling were removed by UF stage.

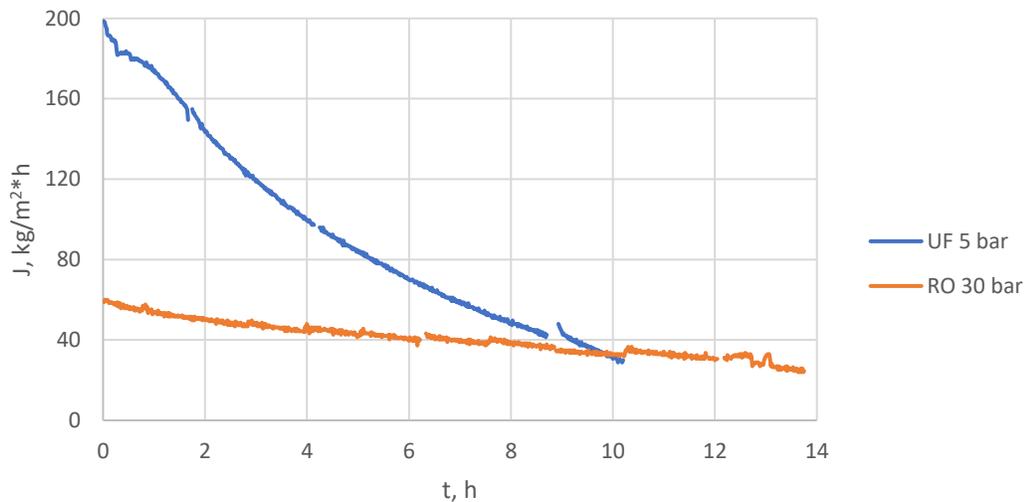


Figure 10.8. Membrane fluxes as a function of time (UF-RO combination).
CFV = 4 m/s, r = 86%

Overall, UF-RO combination showed good treatment performance and reduced the COD of the wastewater below the specified limit. There is a potential to increase the recovery rate for both stages up to 95% thus achieving the total recovery of 90%. The main limitation was severe fouling at UF stage. To minimize the effect of fouling UF should be carried out at lower TMP (3 bar) and/or additional pretreatment of the wastewater before UF should be applied.

10.5 Combination of UF, NF, and RO

Figure 10.9 shows the design and the main results of the UF-NF-RO₁-RO₂ process – a combination of UF, NF, and two RO stages in series. The total recovery rate was 73% and the total retention was 87% and 85% of COD and TOC, respectively. UF-NF-RO₁-RO₂ combination allowed to reduce COD of the wastewater below the target value (3600 mg/L) down to 1647 mg/L. Characteristics of the initial feed and the effluent can be found in **Table 10.5**.

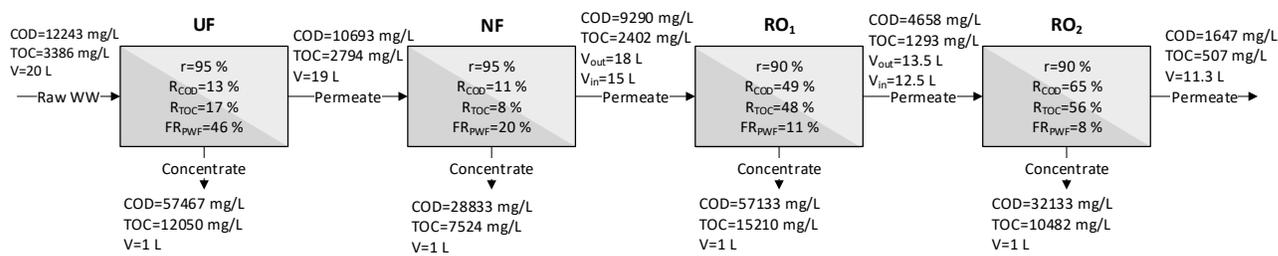


Figure 10.9. Design and main parameters of the UF-NF-RO₁-RO₂ treatment process (experiments 9-12).

V_{out} – permeate volume, V_{in} – feed solution volume.

According to **Figure 10.9**, the UF showed 13% COD and 17% TOC retention, it removed 99.4% of turbidity but did not decrease conductivity. The NF demonstrated 11% COD and 8% TOC retention because probably most of the constituents that could be removed from the wastewater by the NF were already retained by the UF. The NF removed 32% of conductivity (the total collected permeate conductivity was 611 $\mu\text{S}/\text{cm}$), 92% of residual turbidity and 72% of colour.

The first RO stage (RO₁) demonstrated 49% and 48% retention of COD and TOC, respectively. The COD of the RO₁ total collected permeate was 4658 mg/L. The RO₁ removed 62% of conductivity (the total collected permeate conductivity was 231 $\mu\text{S}/\text{cm}$) and 80% of residual colour.

Table 10.5. Comparison of WW characteristics before and after UF-NF-RO₁-RO₂ treatment.

Parameter	Before treatment	After treatment	Target	Reduction, %
COD, mg/L	12243	1647	3600	87
TOC, mg/L	3386	507	-	85
Conductivity, $\mu\text{S}/\text{cm}$	901	90	-	90
Turbidity, NTU	2470	-	-	100
Colour, PtCo	-	5	-	-

The second RO stage (RO₂) was used to reduce the COD of the wastewater under the specified limit of 3600 mg/L. The RO₂ showed 65% and 56% retention of COD and TOC, respectively. It removed 63% of conductivity (the total collected permeate conductivity was 90 µS/cm) and residual colour. The COD of the RO₂ total collected permeate was 1647 mg/L.

If concentrates from all stages had been mixed, the COD and TOC of the acquired solution would be 43904 mg/L and 11317 mg/L, respectively.

It can be seen from **Figure 10.10**, that NF and both RO permeates were clear and transparent, while the UF permeate had a slightly yellowish colour and turbidity indicating the presence of dissolved oil.



Figure 10.10. UF-NF-RO₁-RO₂ process samples.

From left to right: raw WW, UF permeate, NF permeate, RO₁ permeate, RO₂ permeate.

Figure 10.11 shows the momentary permeate COD and the spot retention (equation 4) as a function of recovery of UF stage. Horizontal grey and red dashed lines represent the COD of the initial feed solution (raw wastewater) and the target COD (3600 mg/L), respectively. Momentary permeate COD of the UF was stable during the filtration even though the COD of the feed solution increased with an increase in recovery rate. The spot retention gradually increased during the filtration. It may be explained by the gel/cake layer formation on the surface of the membrane during the filtration which acted as an additional barrier for solute and gradually increased the retention of the membrane compensating for an increase in the feed concentration (Jermann et al., 2009).

The recovery rate of the UF stage was 95% but it could potentially be increased for further reduction of the produced concentrate amount without a significant increase in the collected permeate concentration.

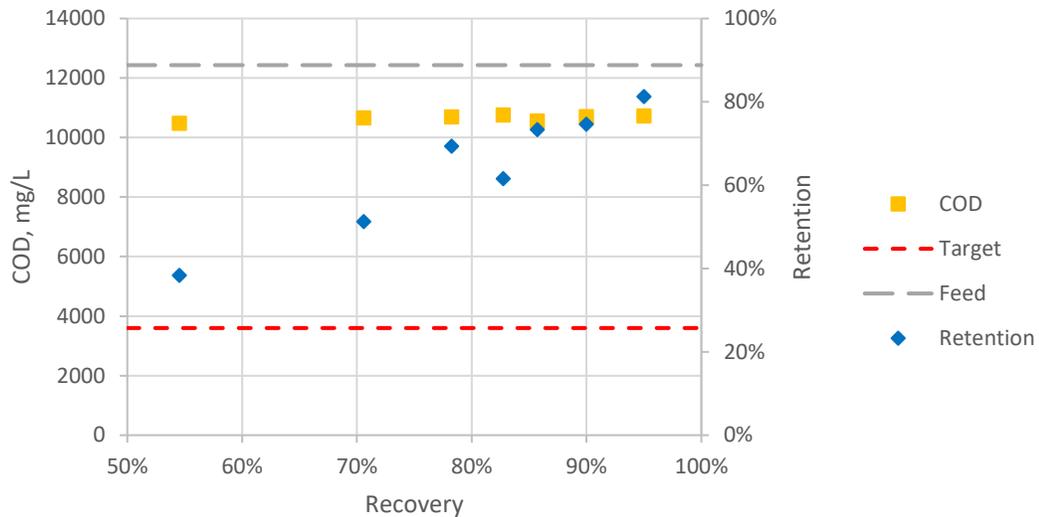


Figure 10.11. Momentary permeate COD and spot retention as a function of recovery of UF stage (UF-NF-RO₁-RO₂ combination).

Figure 10.12 shows the calculated mixing cup permeate COD (equation 5) and the spot retention of the COD (equation 4) as a function of recovery of NF, RO₁, and RO₂ stages. Horizontal grey and red dashed lines represent the COD of the initial feed solution (UF permeate) and the target COD (3600 mg/L), respectively. The large dots on the graph represent the COD of the total collected permeate from NF, RO₁, and RO₂ stages at certain recovery rates.

The spot retention of NF varied between 40% and 60% during filtration. After 90% recovery, the retention decreased and the momentary permeate COD became higher than the COD of the initial feed solution (UF permeate).

The spot retention of RO₁ (approx. 83%) and RO₂ (approx. 88%) did not change significantly with an increase in recovery rate meaning that the concentration of the permeate increased with an increase in the concentration of the feed solution. The recovery rate for both RO₁ and RO₂ was 90% but, based on the mixing cup concentration curves, it could be potentially increased up to 95% without a severe increase in the COD of the collected permeate thus meeting the quality requirement for the effluent (3600 mg/L). An increase in recovery rate for RO₁ and RO₂ stages from 90% to 95% would lead to total recovery rate of 77% (NF stage recovery should not be increased above 90%). Potentially, three stages instead of four could be used to produce the effluent with COD below 3600 mg/L, but only if both NF and RO recovery rates were below 90%.

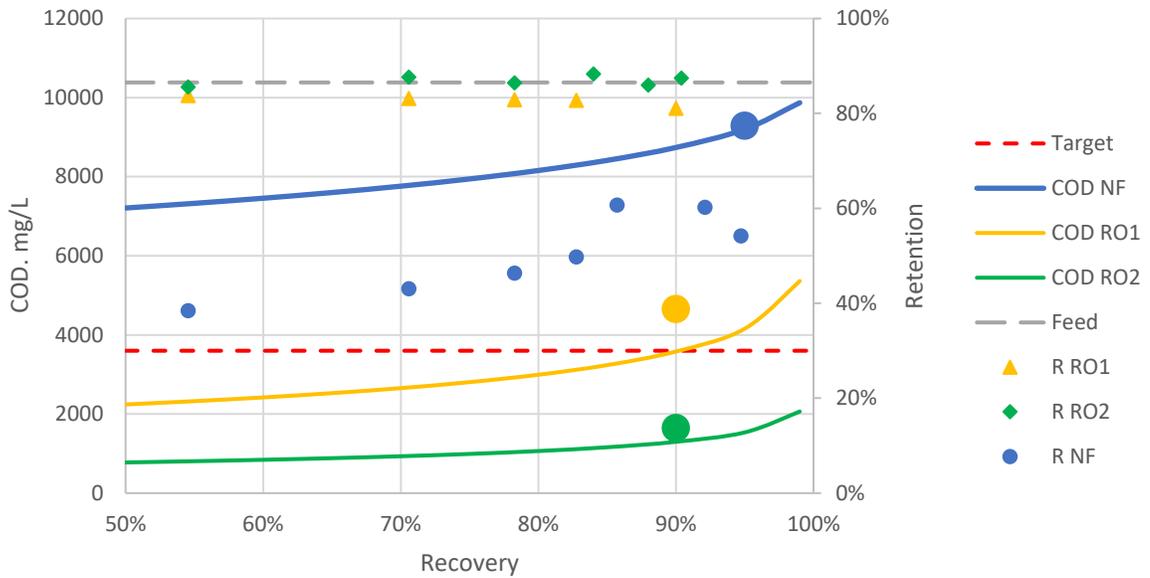


Figure 10.12. Calculated mixing cup permeate COD and spot retention (R) as a function of recovery rate for NF, RO₁, and RO₂ stages (UF-NF-RO₁-RO₂ combination).

Figure 10.13 shows UF, NF, RO₁, and RO₂ fluxes as a function of time. UF and NF showed high fluxes. UF flux decreased by 34% during filtration while PWF reduction was 46%. Changing TMP from 5 to 3 bar allowed to reduce the effect of fouling and increase average flux without a decrease in retention. At 5 bar flux decreased below 40 kg/m²*h after 10 h of filtration, while after filtration for 15h at 3 bar the flux still was approx. 100 kg/m²*h. However, this is not enough for effective continuous operation. NF flux decreased by 37% during filtration, and PWF reduction was 20%.

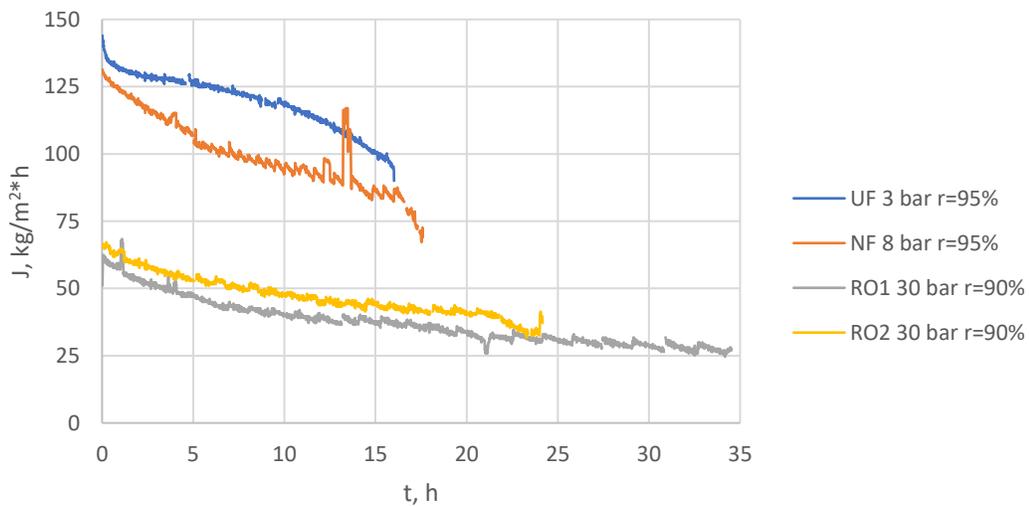


Figure 10.13. Membrane fluxes as a function of time (UF-NF-RO₁-RO₂ combination).
CFV = 4 m/s.

Both RO₁ and RO₂ flux decreased by approx. 50% while PWF reduction was only 11% and 8%, respectively, indicating that the effect of fouling on both RO stages was insignificant.

Although UF-NF-RO₁-RO₂ combination showed good wastewater treatment quality and reduced the COD of the wastewater below the specified limit, it did not show a considerable increase in the quality of the effluent compared to UF-RO process which would justify the use of four stages instead of two. Potentially, 3 stages (UF-NF-RO) could be used but at lower recovery rates. Introduction of NF stage did not improve the treatment quality as it was expected. Both RO stages demonstrated lower retention after NF stage compared to the UF-RO combination.

10.6 Effect of pH on UF performance

After the pH adjustment of the feed solution, precipitation was observed at pH 3 and 5. The precipitation in the sample with the pH adjusted to 3 was higher than at 5 pH, also the turbidity slightly decreased. As a result of pH adjustment to 3 and subsequent precipitation, COD of the wastewater decreased by 9%. COD of the other five samples did not decrease (**Figure 10.14**). This indicates that when pH was changed to acidic, solid and oil particles became unstable and precipitated or/and coagulated. Multiple studies have shown that oil-in-water becomes unstable at pH values below 5 (Fujii, Okada & Furuzono, 2007, Sawain et al., 2009). The reason for this might be the fact that by shifting pH to the acidic side we introduced positive charges which neutralized the negative zeta potential of charged particles thus decreasing the stability of oil and causing precipitation/coagulation (Almojjly et al., 2018).

Figure 10.14 compares the contribution of pH adjustment and UF to the total COD reduction at different pH values. It can be seen that the UF retention was the highest (16%) at neutral conditions and decreased when it shifted to acidic or alkaline. After filtration at pH 3, the permeate COD was slightly higher than the initial feed concentration (10620 vs 10494 mg/L). This small increase might be explained by a measurement or dilution error, so the retention can be assumed to be zero. It might be because all the constituents which could be retained by UF were already separated by precipitation and/or coagulation after the pH adjustment. Another possible reason is that at acidic conditions at pH 3 and lower some polymers were able to pass through membrane pores because their form and charge were changed due to introduction of positive charges (Baker, 2004).

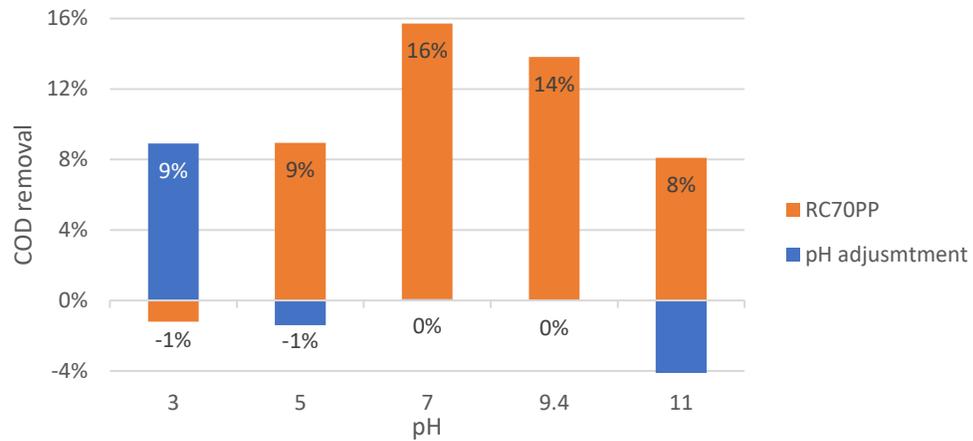


Figure 10.14. Effect of pH on COD removal by UF and pH adjustment (experiment 14). Negative values indicate increase in COD.

Figure 10.15 shows the UF flux at five studied pH values. The flux was the highest at pH 3, while pH 5 and 11 showed the lowest flux. A possible explanation for high flux at pH 3 is that precipitated particles did not contribute to the fouling of the membrane since the flux stabilized at $45 \text{ kg/m}^2\cdot\text{h}$ and did not decrease further. At pH 7 and 9.4 (no pH adjustment) flux was slightly higher than at pH 5 and 11. Variations of flux at pH 9.4 were caused by changes in TMP during filtration. After stabilizing, flux was at the same level as at pH 7. UF at pH 7 and 9.4 demonstrated the best performance, COD retention at pH 7 was only by 2% higher compared to retention at pH 9.4.

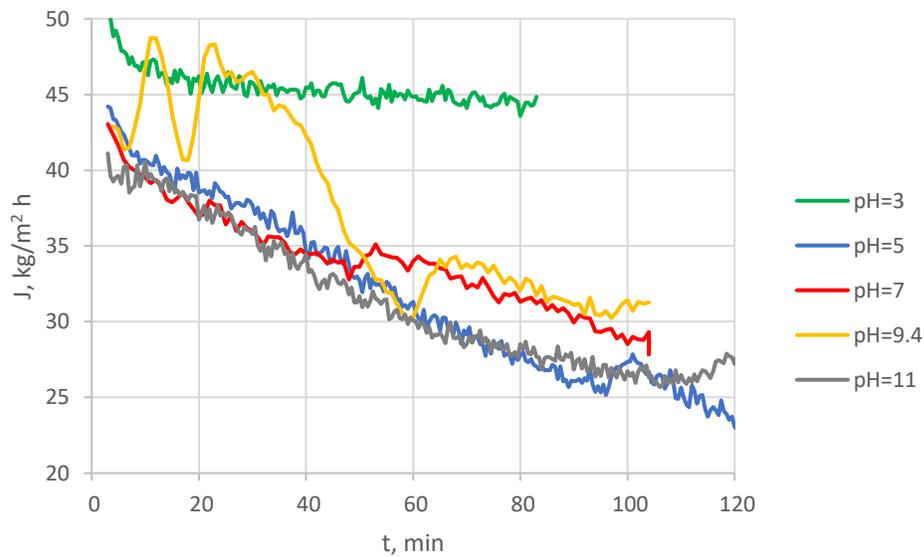


Figure 10.15. UF fluxes as functions of time recorded at different pH (experiment 14).

Usually, the membrane surface is negatively charged at pH values higher than the isoelectric point (IEP) and becomes positive at pH lower than IEP. Positive surface charge of the membrane lowers electrostatic rejection of the membrane which is often associated with higher fouling and concentration polarization. IEP for cellulose acetate membranes were determined to be at 4.2 (Freger, Gilron & Belfer, 2002). Low COD retention at pH=5 can be explained by the increased passage of molecules due to lower electrostatic rejection while flux also decreased because the membrane became more susceptible to fouling.

During the additional confirmation UF cross-flow experiment (№13), 2 L of permeate was collected at 57% recovery rate. The total COD and TOC retention, in this case, was 16%. In comparison, during experiment 7 conducted at the same conditions, but without pH adjustment of the feed solution, the COD and TOC rejection at the same recovery rate was 15% and 23%, respectively. **Figure 10.16** compares UF membrane flux during the cross-flow filtration of the wastewater adjusted to pH 7 and raw wastewater (pH = 9.6). It can be seen that UF flux is higher with raw wastewater compared to UF at neutral conditions.

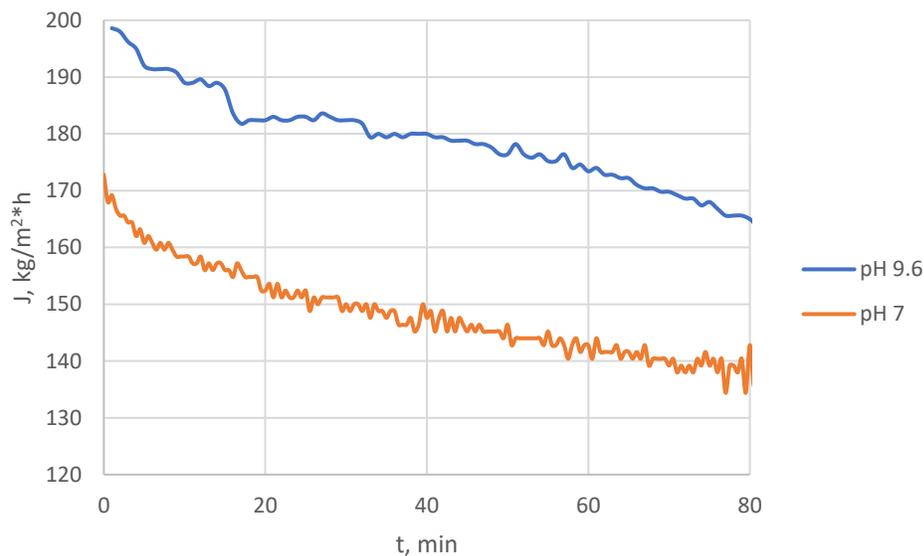


Figure 10.16. UF membrane flux as a function of time. pH 7 vs pH 9.6

It can be concluded that pH adjustment of the feed to neutral can improve the performance of the UF, but this effect is insignificant and could potentially be caused by other factors. The pH adjustment to 3 can precipitate some constituents from the wastewater and mitigate the fouling but the total COD reduction, in this case, is lower compared to UF at neutral conditions.

10.7 Effect of pH on AC performance

Figure 10.17a demonstrates COD reduction efficiency at different pH by GAC and PAC (experiments 17 and 18) in comparison to blank trials (experiment 16) where no adsorbent was added to the wastewater. COD reduction achieved with PAC was on average 7-8% higher than that obtained by GAC. COD reduction was not influenced by pH. It might be due to the hydrophobic nature of contaminants present in the wastewater (Nam et al., 2014). From 12 to 15% of COD was removed by blank trials where no adsorbent was added. This might be the effect of pH adjustment, agitation for 24 h at room temperature and vacuum filtration. In fact, it can be noted that the COD reduction was slightly higher (15%) at the pH of 3 and 5 where coalescence was observed during the pH adjustment.

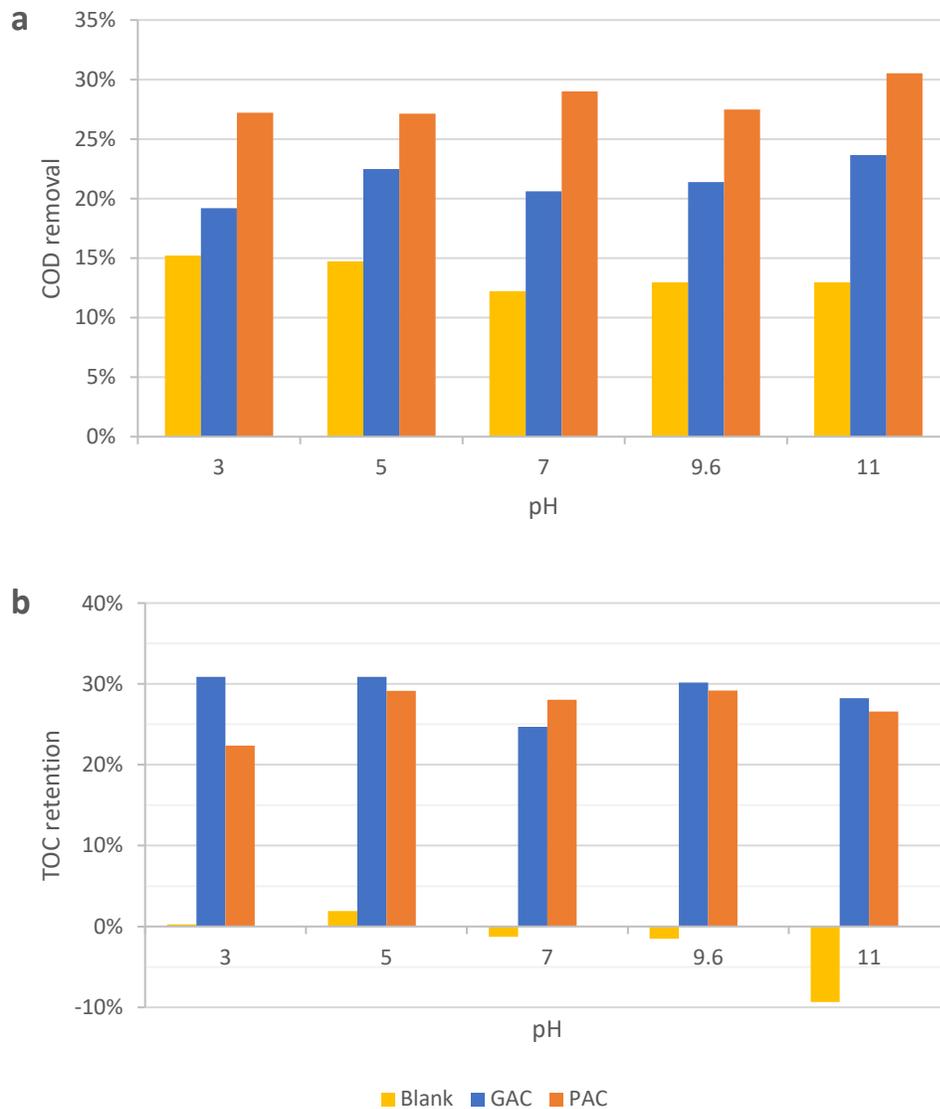


Figure 10.17. Comparison of COD (a) and TOC (b) removal of AC at different pH.

TOC reduction by GAC and PAC at five studied pH values is presented in **Figure 10.17b**. The results were compared with the blank experiments carried out without AC. TOC reduction by GAC varied from 25 to 31% while PAC demonstrated slightly lower removal efficiency (22–29%). Blank trials showed a reduction close to zero and at pH=11 TOC increased by 9%. Low TOC removal compared to 12-15% COD removal by blank trials indicated that pH adjustment, agitation and vacuum filtration removed some of the inorganic pollutants while organic components were not affected. There was no significant effect of pH on TOC removal observed. However, it was noted that for blank trials TOC slightly reduced in acidic conditions while in alkaline it increased.

10.8 Effect of PAC dosage and adsorption time

According to **Figure 10.18**, experiments 19 and 20 were carried out to study the effect of PAC dosage (a) and adsorption time (b) on COD removal and the equilibrium adsorption capacity. Wastewater COD reduction by PAC ranged from 17% to 42% depending on the dosage.

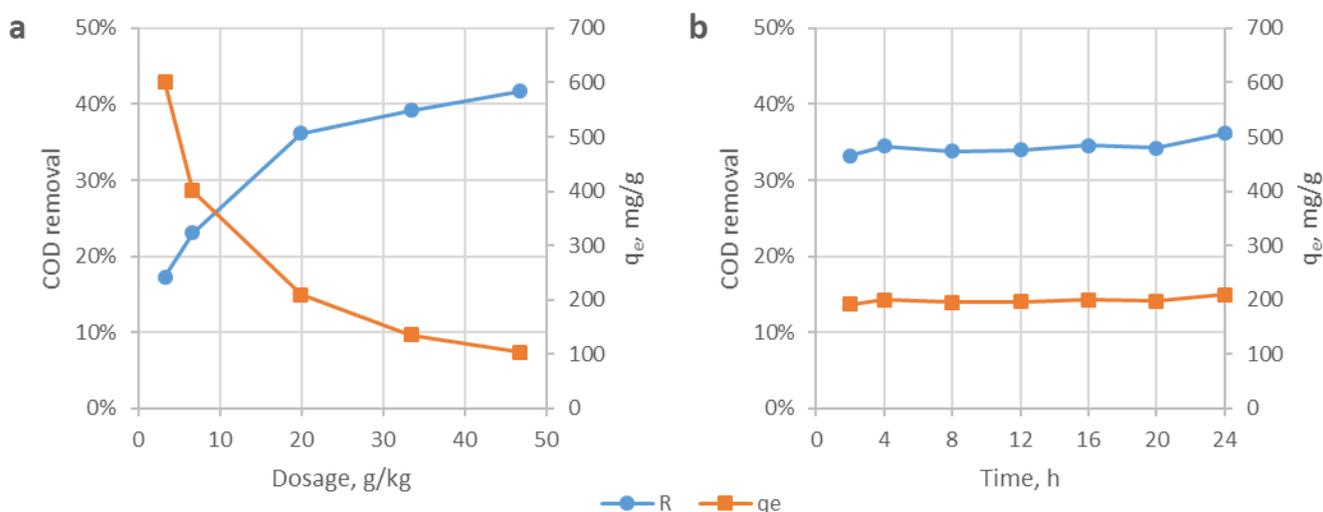


Figure 10.18. Effect of PAC dosage (a) and adsorption time (b) on COD removal and equilibrium adsorption capacity.

Figure 10.18a shows that with an increase in PAC dosage COD removal also increased while equilibrium adsorption capacity decreased. There was a limited amount of pollutants that could be adsorbed by PAC. When more PAC was added almost all available constituents were adsorbed without PAC reaching the state of saturation.

Figure 10.18b demonstrates that COD removal and equilibrium adsorption capacity did not change with adsorption time indicating that adsorption equilibrium time was less than 2 hours.

10.9 Combination of PAC and UF

According to **Table 10.6**, retention of the RC70PP membrane after treatment of the feed solution with PAC was significantly lower because most constituents were removed by PAC. However, it prevented the membrane from fouling. The same membrane was used for both trials (experiment 15) but PWF was not affected. Contrary, PWF of the UF membrane decreased more than twice after the filtration of raw wastewater. Even the lowest dosage of PAC (approx. 0.3 wt.%) completely mitigated the fouling in UF and increased the total COD reduction compared to single UF treatment.

Table 10.6. Results of combined UF and PAC treatment experiments.

No	Combination	R _{ads} , %	R _{mem} , %	R _{tot} , %	FR _{PWF} , %
15	PAC (3.5 g/L) + UF	17	6	22	0
	PAC (49 g/L) + UF	42	3	43	0
21	UF + PAC (21 g/L)	26	14	37	59

11 Conclusions

The primary objective of this work was to design an effective oily wastewater treatment procedure based on membrane technology which could minimize emissions from the STR Tecoil re-refinery and reduce BOD of the produced wastewater below 2000 mg/L to meet the effluent quality requirements and potentially replace the existing wastewater treatment plant. Since BOD measurements are often time-consuming, COD was chosen as a target parameter to assess the wastewater treatment quality. The target value of 3600 mg/L of COD was selected based on the COD/BOD ratio of the wastewater.

The raw oily wastewater provided by the company contained 11000-13000 mg/L of COD and 3000-4000 mg/L of TOC, dissolved oil, high-molecular-weight components, inorganic salts, and low-molecular-weight organic components.

UF, as the first raw oily wastewater treatment step, demonstrated 14% COD retention and high flux but was severely affected by fouling. RO could not be operated with raw wastewater as a feed solution and could be applied only after prior treatment with UF. Then RO demonstrated 83% COD retention and was not significantly affected by fouling.

Multistage membrane approach was utilized to achieve the required treatment quality since the raw oily wastewater was highly contaminated. Two combinations were studied, tested and compared:

UF-RO and UF-NF-RO₁-RO₂. UF-RO combination provided 83% reduction of COD. The COD of the effluent was 2030 mg/L. UF-NF-RO₁-RO₂ combination removed 87% of COD and the effluent COD was 1647 mg/L. Both combinations demonstrated good treatment performance and reduced the COD of the wastewater below 3600 mg/L threshold. In both cases, the UF stage had a high flux but suffered from fouling caused by high-molecular-weight organic components present in the feed solution. On the other hand, this fouling layer acted as an additional barrier increasing the retention of the membrane. UF required an additional pretreatment to reduce fouling. Reducing the TMP from 5 to 3 bar allowed to cut down the effect of fouling in UF. NF demonstrated 9% COD retention and did not substantially decrease COD. Both combinations produced concentrates with COD exceeding 40000 mg/L. Production of these concentrates could be minimized by increasing the recovery rate. Based on calculated mixing cup permeate concentrations, it was estimated that the recovery rate of each separate stage could be increased up to 95% without a significant decrease in the effluent quality. Although, UF-NF-RO₁-RO₂ combination showed slightly higher total COD reduction than UF-RO it was less effective because it had four stages instead of two and lower potential for total water recovery rate increase.

pH adjustment of the feed solution before UF caused slight precipitation at 3 pH but did not considerably improve the wastewater treatment performance. In neutral conditions, UF showed less than 2% increase in retention. Also, the effect of pH was studied on the performance of the wastewater treatment with AC. Overall, pH did not have a considerable effect on UF either on AC treatment.

Combination of PAC and UF increased the total COD reduction compared to single UF and mitigated the fouling. The total COD reduction varied from 22% to 43% depending on the PAC dosage. Even the lowest PAC dosage completely diminished the effect of fouling on RC70PP membrane.

In conclusion, the UF-RO combination showed good wastewater treatment performance and effluent quality. It has a potential for improvement by reducing the TMP of UF stage to minimize fouling and increasing the recovery rate to reduce the amount of produced concentrate. Also, there is a potential to apply PAC treatment before UF-RO combination with a condition that PAC could be effectively removed by UF before RO to prevent it from plugging the RO membrane. Small doses (<0.1 wt%) of PAC can be added directly to the UF circulation loop to increase COD and BOD removal and prevent the membrane from fouling without PAC forming a cake layer on the membrane surface (Mohammadi, Esmaelifar, 2005).

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APPENDICES

Appendix I. The detailed composition of the untreated wastewater

Table 1. Results of a comprehensive raw WW analysis carried out by the independent laboratory.

Parameter	Value
T, °C	max 60, (30-47)
pH	9.2 (8.4-9.7)
TSS, mg/L	13-18
BOD 7-ATU, mg/L	>3700
Sulphates (SO ₄), mg/L	11-240
Tiosulphate, -sulfides and sulphates, mg/L	130-270
Total nitrogen (N), mg/L	170-270
Total phosphorous (P), mg/L	0.21
Phenol, mg/L	65.9 (11.7-147)
Formaldehyde (water), mg/L	0.66
Alkalinity (HCO ₃), mg/L	560
Alkalinity (CO ₃), mg/L	500
Fluoride (F), mg/L	2.1
CO ₂ (free), mg/L	<1.0
Electrical conductivity, mS/m	170
Total phosphate (PO ₄), mg/L	<0.03
Ammonium NH ₄ , mg/L	310
Nitrate (NO ₃), mg/L	<1.0
Total hardness (Ca + Mg), mmol/L	0.15
SiO ₂ , mg/L	2.5
HC's (C ₁₀ -C ₄₀), mg/L	4.7-99
Middle distillates HC's (C ₁₀ -C ₂₁), mg/L	3-51
Heavy HC's (C ₂₁ -C ₄₀), mg/L	1.7-48
Barium (Ba), mg/L	<0.0020
Boron (B), mg/L	60
Bromine (Br), mg/L	0.16
Kalium (K), mg/L	0.36
Calsium (Ca), mg/L	5.3
Magnesium (Mg), mg/L	0.45
Natrium (Na), mg/L	2
Iron (Fe), mg/L	0.22
Strontium (Sr), mg/L	0.01
VOC:	
Toluene, µg/L	18
Ethylenebenzene, µg/L	6
m+p-Xylene, µg/L	23
o-Xylene, µg/L	13

Styrene, µg/L	<0.5
n-Propyl benzene, µg/L	2
Isopropyl benzene, µg/L	0.8
n-Butyl benzene, µg/L	1
Sec-Butylbenzene, µg/L	4
2-ethylene toluene, µg/L	4
3-ethylene toluene, µg/L	6
4-ethylene toluene, µg/L	3
p-Isopropylene toluene, µg/L	<0.5
1,2,3-trimethylene benzene, µg/L	12
1,2,4-trimethylene benzene, µg/L	20
1,3,5-trimethylene benzene, µg/L	3
1,2,3,5-tetramethylene benzene, µg/L	9
1,2,4,5-tetramethylene benzene, µg/L	6
Naphthalene, µg/L	32
MTBE (methyl tert-butyl ether), µg/L	7
TAME (tertiary amyl methyl ether), µg/L	5
TAAE (tertiary amyl ethyl ether), µg/L	0.6
ETBE (ethyl tertiary butyl ether), µg/L	1
Cyclohexane, mg/L	1
Heptane, µg/L	380
Octane, µg/L	1000
Nonane, µg/L	3900
Decane, µg/L	31
Acetone, mg/L	0.9
Methylene ethylene ketone, mg/L	<0.2
Methanol, mg/L	14
Ethanol, mg/L	24
Propanol, mg/L	0.6
Isopropanol, mg/L	8
n-Butanol, mg/L	1
2-Butanol, mg/L	4
Isobutanol, mg/L	0.6
Tert-Butanol, mg/L	0.03
Bensin C5-C10, mg/L	0.53
Octamethylenecyclotetrasiloxane D4, µg/L	400

Appendix II. Pure water fluxes

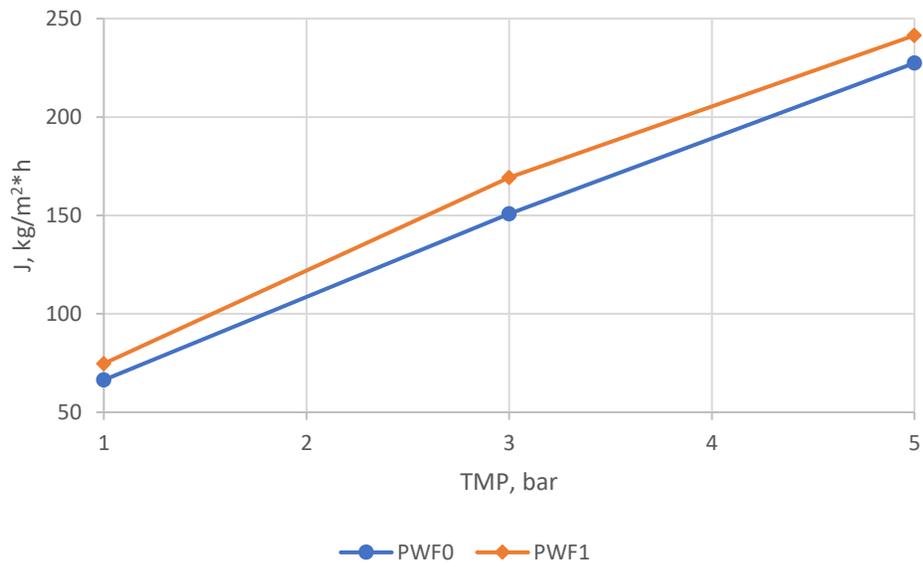


Figure 1. PWF of RC70PP membrane before and after cross-flow UF of raw WW (experiment 1).

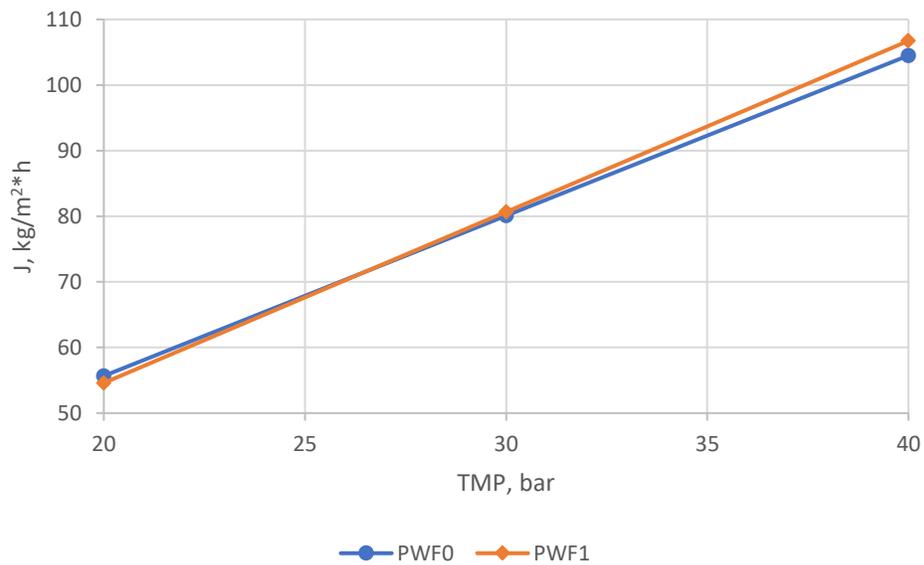


Figure 2. PWF of SW30 membrane before and after cross-flow RO of SW30 permeate (experiment 4).

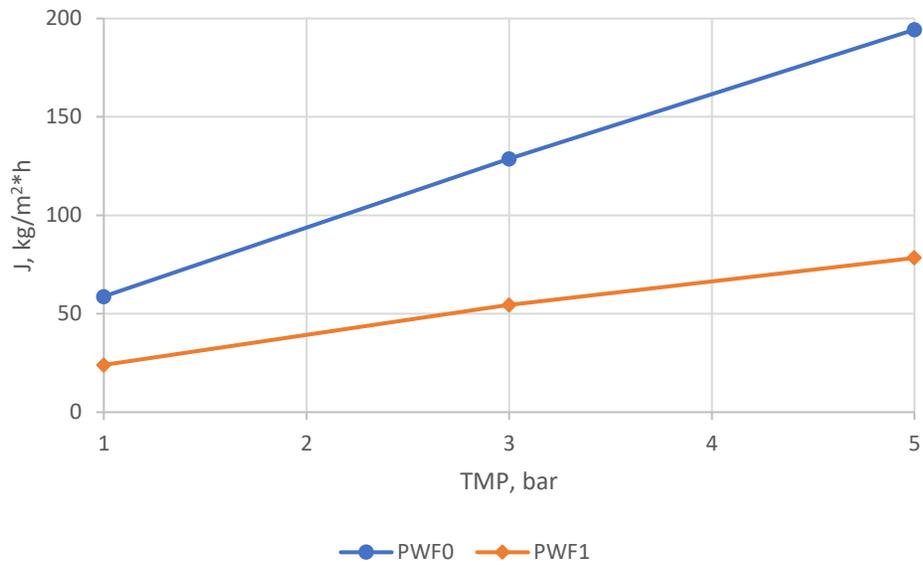


Figure 3. PWF of RC70PP membrane before and after cross-flow UF of raw WW (experiment 7).

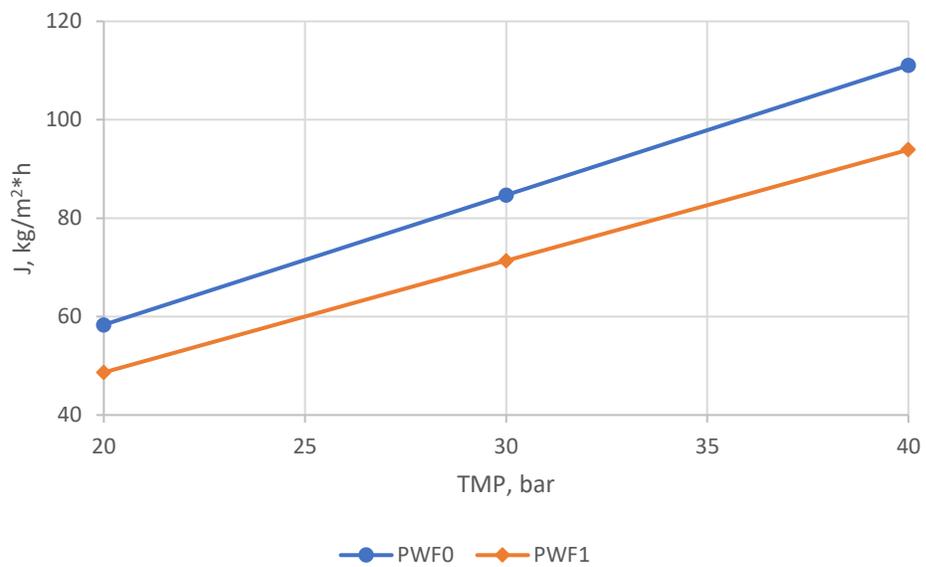


Figure 4. PWF of SW30 membrane before and after cross-flow RO of UF permeate (experiment 8).

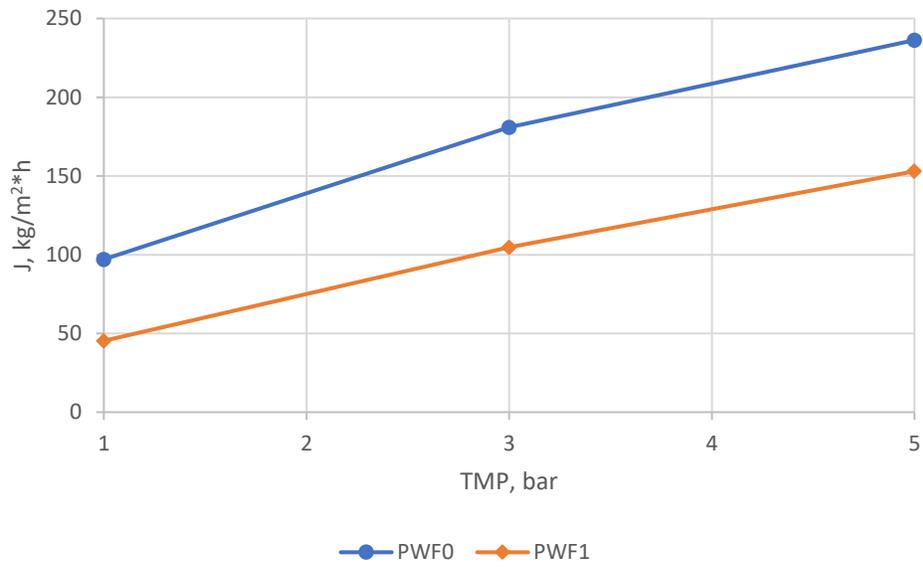


Figure 5. PWF of RC70PP membrane before and after cross-flow UF of raw WW (experiment 9).

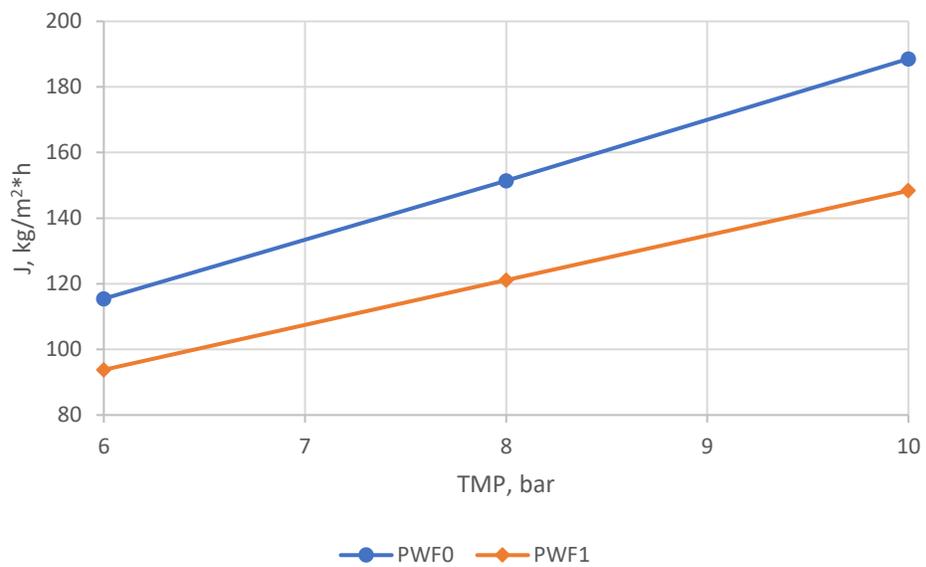


Figure 6. PWF of NF270 membrane before and after cross-flow NF of UF permeate (experiment 10).

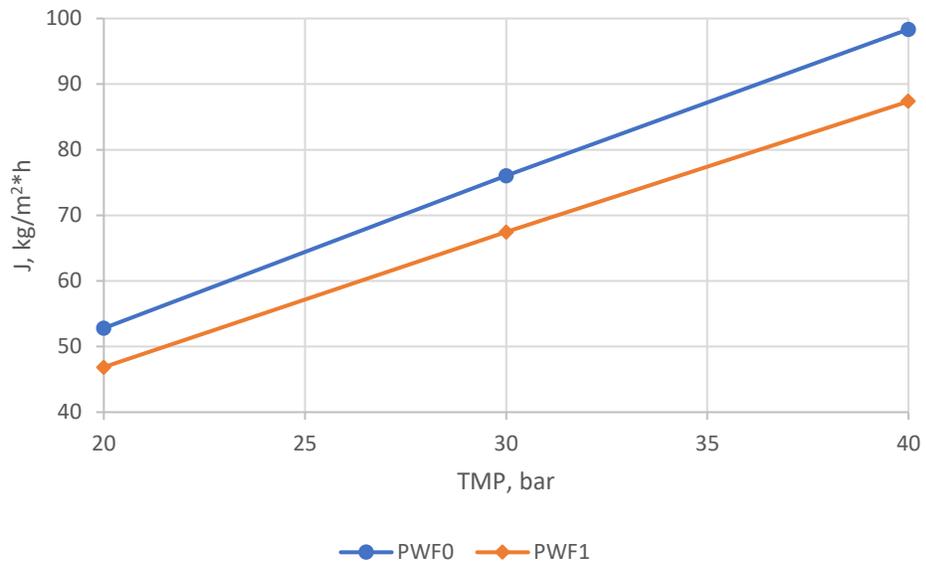


Figure 7. PWF of SW30 membrane before and after cross-flow RO of NF permeate (experiment 11).

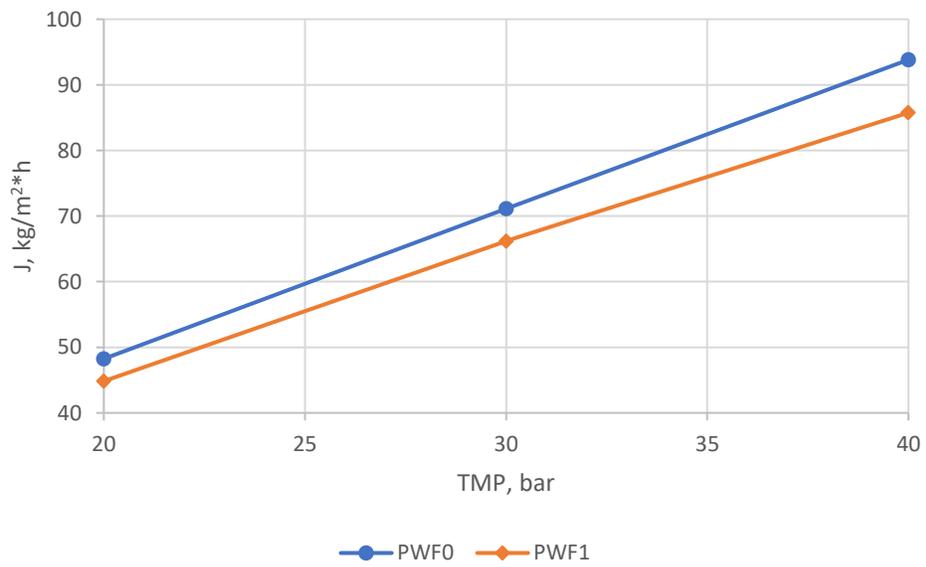


Figure 8. PWF of SW30 membrane before and after cross-flow RO of RO permeate (experiment 12).

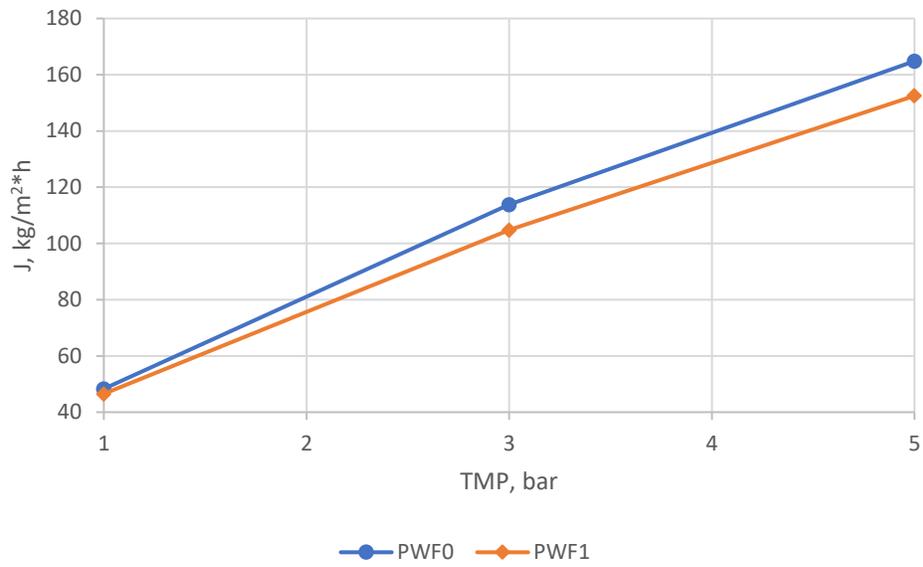


Figure 9. PWF of RC70PP membrane before and after cross-flow UF of WW adjusted to pH 7 (experiment 13).

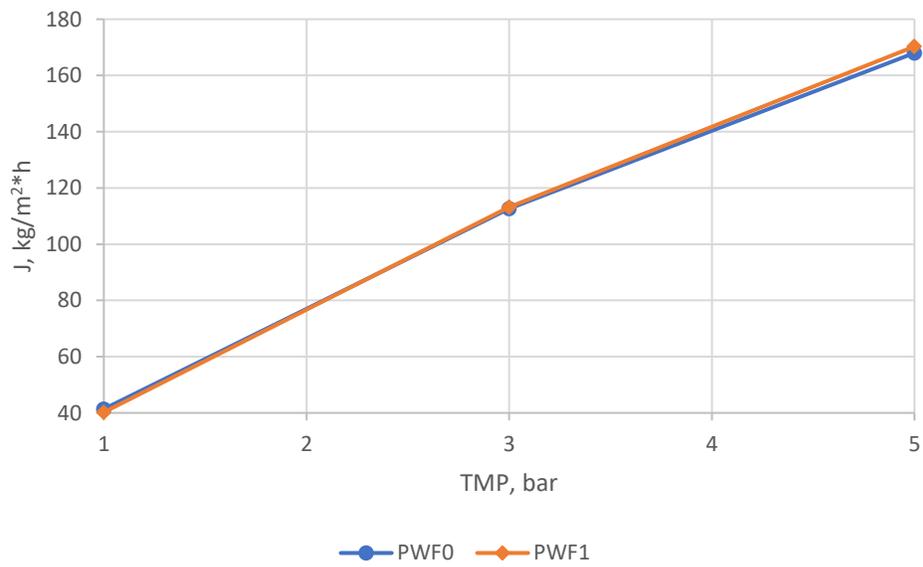


Figure 10. PWF of RC70PP membrane before and after dead-end UF of WW adjusted to pH 7 (experiment 14).

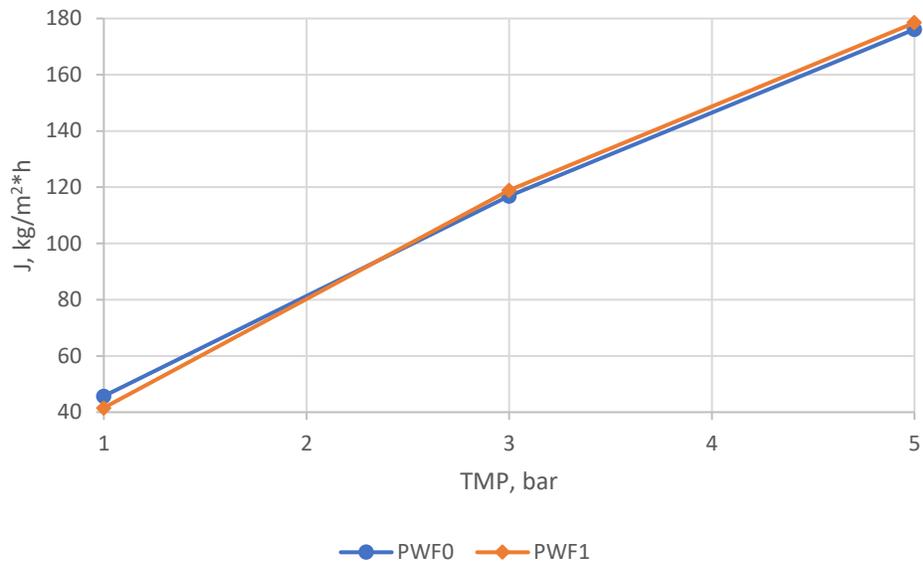


Figure 11. PWF of RC70PP membrane before and after dead-end UF of raw WW (pH 9.4) without pH adjustment (experiment 14).

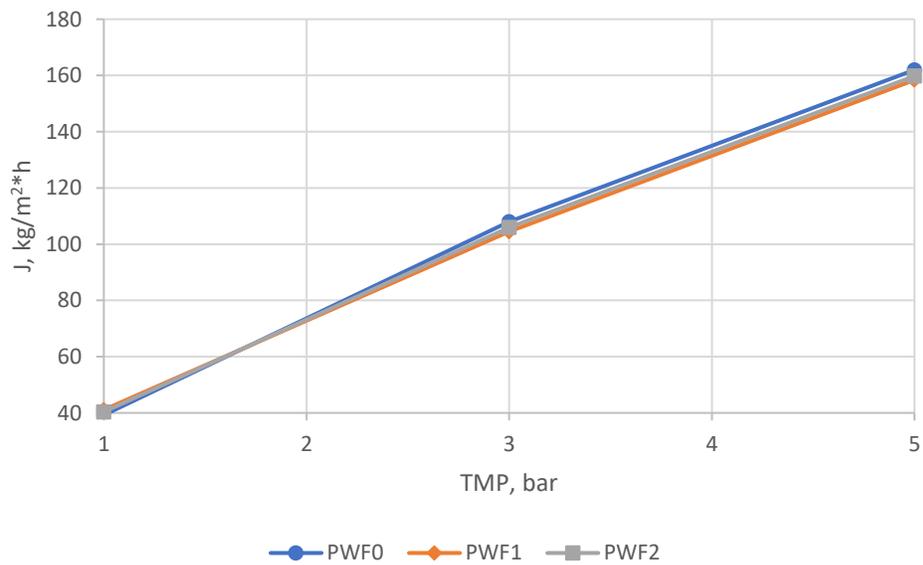


Figure 12. PWF of RC70PP membrane before and after dead-end UF of two PAC treated samples (experiment 15). PWF0 – initial, PWF1 – after filtration of the sample treated with PAC (3.5 g/L), PWF2 – after filtration of the sample treated with PAC (49 g/L).