



Preparation of Nanofibrous Membranes for Oil/ Water Separation

Diplomová práce

Studijní program: N3106 – Textile Engineering
Studijní obor: 3106T017 – Clothing and Textile Engineering
Autor práce: **Evren Boyraz**
Vedoucí práce: Fatma Yalcinkaya, MSc. Ph.D.





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Master thesis

Study programme: N3106 – Textile Engineering
Study branch: 3106T017 – Clothing and Textile Engineering
Author: **Evren Boyraz**
Supervisor: Fatma Yalcinkaya, MSc. Ph.D.





Master Thesis Assignment Form

Preparation of Nanofibrous Membranes for Oil/ Water Separation

Name and Surname: **Evren Boyraz**
Identification Number: T17000323
Study Programme: N3106 Textile Engineering
Specialisation: Clothing and Textile Engineering
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Rules for Elaboration:

- 1) In the first part of work, student will carry out detailed literature review and research on preparation of nanofiber membranes, membrane technology for the separation of oily water and, the possibility of surface treatment of nanofiber membranes for hydrophilic/oleophobic.
- 2) Various polymeric nanofiber layers will be produced in various area weights using Nanospider Technology. Prepared layers will be form a composite structure to enhance mechanical strength.
- 3) The surface morphology, porosity, pore size, hydrophilicity, permeability of the membranes and mechanical strength tests will be run. At least, two type of oil will be used for separation test. The liquid separation efficiency and the selectivity of the membranes will be evaluated. Test will be done using a custom-made dead-end separation unit. The successful membranes will be carried to a cross-flow device.
- 4) The results will be summarized and analysed with respect to mechanical properties, performance, efficiency, selectivity and applicability in microfiltration technology.

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List of Specialised Literature:

1. Richard W. Baker, Membrane Technology and Applications, Third Edition, John Wiley & Sons, Ltd, DOI: 10.1002/9781118359686, 2012.
2. Seeram Ramakrishna, Kazutoshi Fujihara, Wee-Eong Teo, Teik-Cheng Lim, Zuwei Ma, An Introduction to electrospinning, World Scientific, 2005.
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4. Takeshi Matsuura, Synthetic Membranes and Membrane Separation Processes, CRC Press, ISBN 9780849342028, 1993.
5. Banchik, Leonardo David, Advances in membrane-based oil/water separation, doctoral thesis, Massachusetts Institute of Technology, Department of Mechanical Engineering, 2017.
6. Wan Thiam Teik, Separation of Oil in Water Emulsion by Tangential Flow Microfiltration Process, doctoral thesis, National University of Singapore, 2014.
7. Asmund Bryne Retterstol, Micro-Nano enhanced surfaces for investigation of oil-water separation, master thesis, Norwegian University of Science and Technology, Department of Energy and Process Engineering, 2015

Thesis Supervisor:

Fatma Yalcinkaya, MSc. Ph.D.

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Ing. Jana Drašarová, Ph.D.
Dean

Liberec 4 February 2018



Ing. Blanka Tomková, Ph.D.
Head of Department

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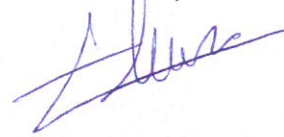
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Abstract

Due to increased environmental awareness and strict regulations, it is necessary to apply new methods to separate oils from industrial wastewaters, sea, ocean waters, and oil spill mixtures. In this thesis, a comprehensive study is presented on the oily wastewater separation by nanofibrous membrane including surface modification. The research developments, oily wastewater separation, improving membrane strength, the performance of permeability, self-cleaning and the membrane properties are also discussed.

Abstrakt

Kvůli zvýšenému povědomí o životním prostředí a přísným předpisům je nutné aplikovat nové metody separace olejů z průmyslových odpadních vod, mořských, oceánských vod a ropných směsí. V této práci je prezentována komplexní studie o separaci olejové odpadní vody nanovláknennou membránou včetně povrchové úpravy. Výzkumný vývoj, separace olejové odpadní vody, zlepšení pevnosti membrány, výkonnost propustnosti, samočisticí vlastnosti a membránové vlastnosti jsou také diskutovány.

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LIST OF SYMBOLS

Symbols	Long Name	Units
p	trans membrane pressure	Pa
PUR	polyurethane	
PA6	polyamide 6	
PAN	polyacrylonitrile	
PVDF	polyvinylidene fluoride	
PET	polyethylene terephthalate	
σ	standard deviation	
SEM	scanning electron microscope	
θ_c	contact angle	
H ₂ O	water	
OH ⁻	hydroxide anion	
KOH	potassium hydroxide	
NaOH	Sodium hydroxide	
Pa	Pascal	
Temp	temperature	C ⁰
MF	microfiltration	
UF	ultrafiltration	
NF	nanofiltration	
RO	reverse osmosis	
FO	forward osmosis	

nm	nanometer	nm
TiO ₂	titanium dioxide	
Gsm	gram per square meter	g/m ²
μm	micrometer	μm
Fe ³⁺	ferric ion	
Al ³⁺	aluminum ion	
F	membrane flux	Lm ⁻² h ⁻¹
k	membrane permeability	Lm ⁻² h ⁻¹ bar ⁻¹
t	hour	h
A	active membrane area	m ²
V	total volume of permeate	L

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1. INTRODUCTION

Industrial or domestic use water contains oil, water, energy, organics, phosphates, nitrogen, cellulose, rare earth, and other resources. Recovering the water, energy, nutrients and other valuable materials which are in the wastewater is a crucial opportunity and new opportunities [1].

The total amount of water is 1 billion 400 million km³ ($1 \text{ km}^3 = 1 \text{ billion m}^3$) in the world. About 97.5% of this water is salt water, and the rest is 2.5% fresh water. But in recent years, existing water resources have been depleted and contaminated due to industrialization and population growth rate [2].

In Europe, the industry of food manufacturing wastes approximately about 5 m³ of water per person, per day. As well, with as far as 1.3 billion tonnes of food wasted yearly, 250 km³ of water is lost per year worldwide [3].

The untreated wastewater discharging to the seas and oceans affect roughly 45,000 km² marine ecosystem, fishing, livelihoods and food chains [3].

The southern states of the United States, southern Europe, North Africa, the Middle East, and Australia face the danger of water scarcity which affects at least 11% of the European population and 17% of the European Union field [2].

It is predicted that the industrial water treatment technologies market will increase by 50% in 2020. North Africa, Middle East countries, Pakistan, India and North China are expected to suffer from water shortage in 2025 [3].

By 2025, industrial water consumption is supposed to be 1.4 times, domestic water consumption is 1.5, water consumption for agricultural activities is 3189 km³ / year, and net water consumption will increase by 1.2 times 2152 km³ / year [4].

By 2030, global energy is expected to increase by 40% and water demand by 50% [3].

Nowadays, renewable freshwater resources are decreasing day by day in the world. Amount of resources of renewable freshwater are shown in Table 1.1.

Table 1.1. Renewable freshwater resources (in million cubic metres) [5].

GEO/TIME	2008	2009	2010	2011	2012	2013	2014	2015	2016	*LTAA
Belgium	29.485	26.224	27.567	24.047	29.829	25.848	26.544	:	:	28.887
Bulgaria	:	:	:	:	74.630	70.865	115.306	82.073	:	72.576
Czechia	49.105	59.046	68.329	49.000	54.812	57.336	51.420	41.643	:	54.653
Denmark	33.742	31.588	:	:	:	:	:	:	:	38.485
Germany (until 1990 former territory of the FRG)	269.000	280.000	300.000	257.000	272.000	276.000	257.000	249.000	:	278.000
Estonia	:	:	:	30.371	38.917	25.719	:	:	:	29.018
Ireland	98.950	105.506	74.010	89.439	92.120	83.886	97.855	105.541	:	87.632
Greece	:	:	:	:	:	:	:	:	:	115.000
Spain	305.174	425.690	337.988	246.633	422.482	263.371	:	344.073	:	346.527
France	562.080	474.837	502.397	428.158	516.008	578.552	567.709	429.730	:	500.770
Croatia	:	:	:	66.680	62.618	61.108	85.551	62.330	:	62.330
Italy	262.290	272.026	306.883	:	:	:	:	:	:	241.105
Cyprus	1.648	3.745	2.570	3.348	4.737	1.770	2.358	2.904	:	3.029,81
Latvia	47.873	47.927	54.298	42.132	48.495	40.641	:	:	:	42.701
Lithuania	43.398	46.871	55.033	44.977	51.598	43.152	41.198	38.517	:	44.886
Luxembourg	2.411	2.156	1.918	1.508	:	:	:	:	:	2.030
Hungary	56.451	58.311	92.535	39.153	45.384	62.031	70.680	51.429	:	55.707
Malta	158,2	214,99	162,13	186,77	164,08	151,54	159,37	175,14	:	177,2
Netherlands	32.924	29.896	32.451	31.397	34.987	30.497	31.678	35.308	:	31.618
Austria	85.243	96.576	88.872	83.256	:	:	:	:	:	98.000
Poland	200.207	211.370	248.797	215.247	195.767	210.119	199.957	155.713	:	193.963
Portugal	52.684	45.418	79.650	70.535	:	:	:	:	:	82.164
Romania	158.000	156.000	201.750	119.290	148.798	162.799	197.196	152.358	:	150.941
Slovenia	36.444	33.588	35.827	23.127	30.156	34.848	39.897	:	:	31.746
Slovakia	40.049	41.715	59.104	31.790,60	34.848,60	42.348	46.806	35.241,10	:	37.352
Finland	255.938	192.638	215.684	254.903	273.591	221.166	:	:	:	222.000
Sweden	357.745	340.066	335.750	381.114	397.478	311.389	337.479	379.573	:	342.157
United Kingdom	316.187	284.961	231.974	:	:	:	:	:	:	287.607
Liechtenstein	:	:	:	:	:	:	:	:	:	:
Norway	:	:	296.366	465.153	379.740	397.998	357.169	444.104	:	470.671
Switzerland	58.563	55.425	59.183	49.767	61.785	65.295	64.698	60.198	:	61.207
North Macedonia	12.999	14.528	20.930	:	:	:	:	:	:	19.533
Albania	29.458	37.218	51.134	20.569	43.050	30.615	37.172	32.711	48.810	:
Serbia	46.758	59.320	71.407	37.504	49.968	53.569	80.300	54.451	:	57.226
Turkey	396.064	633.671	568.961	519.083	695.171	547.042	641.600	637.800	:	503.100
Bosnia and Herzegovina	29.813	36.268	47.302	21.121	31.675	36.222	45.366	29.389	:	:
Kosovo (under United Nations Security Council Resolution 1244/99)	:	:	928,8	536,5	647,5	702,8	802,7	684,4	836,5	:

*LTAA : Long term annual average

The water use by economic sectors (public water supply, 2015 (million m³)) are shown in the Table 1.2 [6].

Table 1.2. Consumption of the water by economic sectors.

	All NACE activities and households	of which:		of which:	Services	Households
		Agriculture, forestry and fishing	Industry and construction	Manufacturing		
Belgium ⁽¹⁾	567.9	8.9	93.5	-	-	-
Bulgaria	380.9	3.5	74.1	31.5	44.6	258.6
Czech Republic	481.3	7.5	42.5	-	109.2	322.0
Denmark	-	-	-	-	-	-
Germany ⁽²⁾	4 233.3	6.0	606.3	418.0	80.5	3 540.5
Estonia ⁽²⁾	49.8	0.3	7.9	7.8	-	-
Ireland ⁽¹⁾	669.0	-	-	-	-	-
Greece	1 182.1	35.1	94.4	73.4	31.8	1 020.8
Spain ⁽⁴⁾	3 669.3	25.5	403.6	353.7	812.2	2 428.1
France ⁽²⁾	3 622.0	-	-	-	-	3 388.0
Croatia	-	-	91.1	-	-	179.6
Italy ⁽²⁾	5 232.2	-	-	-	-	-
Cyprus	79.7	-	2.0	1.9	-	77.7
Latvia	73.8	0.4	4.7	0.8	0.4	68.3
Lithuania	101.2	0.1	9.6	9.2	22.8	68.6
Luxembourg	-	-	-	-	-	42.2
Hungary	443.4	1.2	58.8	6.3	47.5	335.9
Malta	27.7	0.2	2.8	2.0	6.0	18.8
Netherlands ⁽⁴⁾	1 067.9	41.9	141.3	130.8	101.4	783.3
Austria ⁽²⁾	587.0	-	-	-	-	381.0
Poland	1 595.1	-	31.4	18.7	160.8	1 236.5
Portugal ⁽⁴⁾	-	-	-	-	-	-
Romania	774.2	1.6	203.2	-	70.5	498.9
Slovenia	112.0	3.1	9.4	9.3	20.8	78.5
Slovakia	288.1	-	-	-	-	-
Finland	-	-	-	-	-	-
Sweden	-	-	-	-	-	-
United Kingdom ⁽¹⁾	3 968.0	120.0	345.0	263.0	601.0	2 902.0
Iceland ⁽⁴⁾	-	0.0	0.0	0.0	0.0	63.0
Norway ⁽⁴⁾	-	24.0	90.0	-	50.0	366.0
Switzerland ⁽²⁾	808.0	41.2	80.0	76.5	141.8	544.0
Albania	280.2	-	-	-	75.0	12.0
Former Yugoslav Republic of Macedonia ⁽⁴⁾	-	-	31.6	11.4	-	244.6
Serbia	423.2	-	17.7	14.4	88.2	317.3
Turkey ⁽⁴⁾	3 681.8	23.9	111.8	44.4	1 046.1	2 500.0
Bosnia and Herzegovina ⁽²⁾	140.1	1.5	12.6	-	14.3	109.3
Kosovo	120.0	58.5	6.7	4.7	4.6	50.4

⁽¹⁾ 2011.

⁽²⁾ 2012.

⁽³⁾ 2013

⁽⁴⁾ 2014

⁽⁵⁾ 2010

The reuse of wastewater have been brought to the agenda because of the increase in the ratio of industry and population, difficulties in water supply, increase in water wages.

The benefits of recycling wastewater can be listed as follows;

- It is a reliable source of water under the necessary controls and conditions.
- Allows less energy consumption.
- Recovering the treated wastewater prevents the deterioration of surface water quality.
- Reduces consumption of water resources and causes less consumption.

Areas of use of recovered wastewater;

- ♦ Using an industrial process water,
- ♦ Agricultural irrigation, park and garden irrigation,
- ♦ Artificial feeding of groundwater.

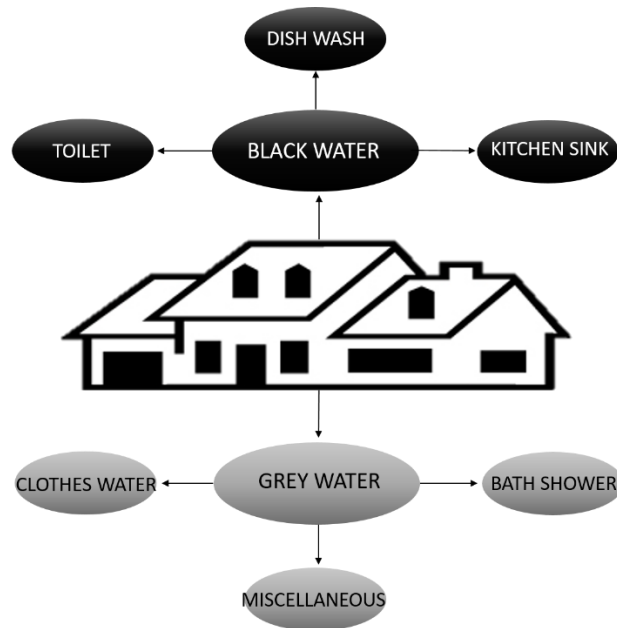


Figure 1.1. Domestic wastewater treatment

In general, land and water pollution occurs when wastewater is spilled or leaked. Groundwater contamination or other problems may arise as a result of not adequately designed or constructed wells. The reason could be due to the breakage of a pipe, explosion of the well, or other problem.

Most wastewater should be disposed of in a way far away from humans, plants, and animals. Because even small concentrations of wastewater chemicals can be toxic to plants, people and soil. Unfortunately, some untreated oil wastes are discharged into rivers, lakes, streams or sea. The wastewater mixed with sand and chemicals is pumped underground to release the oil and gas contained therein. Then the wastewater mixed with groundwater returns to the earth by creating a large amount of salty and toxic waste. These waters, which are then returned to the earth, are directly affected by human health as a result of irrigating food crops or using them for any process.

One of the most severe issues that threaten human life and ecology system is the oil-water emulsion emitted into the soil from domestic wastewater. Thus, there is a huge

demand to produce a separation system for the oil-water emulsion that has high efficiency, low fouling properties and is easy to apply and manage.

2. THEORITICAL PART

2.1. Oily Wastewater

Generally, the following problems arise due to oily wastewater pollution:[7] (a) Affecting water sources, drinking water etc., (b) putting human health endanger, (c) pollution of the atmosphere, (d) affecting crop production, (e) harming nature.

Oily wastewater occurs after many industrial processes such as food, ship, oil refinery, petrochemical, leather, and metal finishing. The oils, and greases (FOGs) in the wastewater must be cleaned and removed before reusing the water in a closed circuit operation or discharged into sewer systems and to the surface waters. The oil is in the form of an oil-water emulsion in the enterprises which is trying to comply with the discharge limits. The range of discharging limit for mineral and synthetic oils and grease is 10–15 mg/L, and those of animal and vegetable origin for 100–150 mg/L [8].

Thanks to increased environmental awareness and strict regulations, it is necessary to apply new methods to separate oils from industrial wastewater, sea and ocean water, and oil spill mixtures.

To produce clean water, the estimation of the current global market value is about 59\$ billion, and it is expected that it will increase over the next 8 years. Therefore the oily wastewater separation is essential and valuable [9].

2.1.1. Categorization of Oil Present in Wastewaters

The origin of oils in wastewaters can be mineral, animal or vegetable. According to the physical form of oil, content is mostly classified into four categories.

- 1- **Free (floating) oil:** it comes up quickly to the water surface under settled conditions.
- 2- **Dispersed oil:** they are fine droplets without surfactants stabilized by their electrical charges

3- Emulsified oil: the distribution of emulsified oil is similar to dispersed oil, but it is more stable because of using surfactants.

It is also categorized when the diameter of the droplet is higher than 150 μm is free oil, between 20-150 μm is dispersed oil and smaller than 20 μm is emulsified oil [8].

2.2. Treatments of Oily Wastewater

Different techniques are used for the treatment of wastewater. The most common processes are such as membrane process (microfiltration and ultrafiltration), chemical destabilization (conventional coagulation) and electrochemical destabilization (electrocoagulation). Biological processes are less used because they contain biocides (heterocyclic sulfur and nitrogen compounds) to prevent industrial fluids from degrading. If the waste is contaminated with soluble compounds and cannot be removed by other techniques, distillation can be an attractive alternative, although it is expensive [10].

2.3. Conventional Treatment Method

2.3.1. Flotation

Flotation is discharged into the water in the shape of very small bubbles. Small air bubbles adhere to the oil particles floating in the water. Because of the density difference between the floating density of oil and water, water stays in the bottom, and the scum layer is separated from the water. In the flotation method, the advantages are producing less sludge and separation efficiency. The treatment of oily wastewater has big potential. Flotation dissolved air flotation, flotation, and jet impeller flotation methods are generally the most used methods. But there are some disadvantages. The problem of repairing and device manufacturing, besides high energy consumption. The dissolved air flotation and flotation impeller stay a long time.

In the flotation method, there are multiple parameters such as bubble size, bubble rising velocity, bubble formation frequency, etc. affecting efficiency. In flotation, oil removal is more than 90%, and in dissolved air flotation, oil removal is more than 90% [7].

2.3.2. Coagulation

Hydrolyzed metal salts such as Fe^{3+} and Al^{3+} are added as coagulant reagents in the chemical destabilization process. The electrochemical method contains the generations of coagulants by electrolytic oxidation of appropriate anode material such as iron or aluminum.

The coagulants promote the dispersion of the emulsion, the reduction of the surface charge of the droplets and the separation of the oil droplets, followed by the separation of the aqueous and oily phases by conventional precipitation or dissolved air flotation.

The attachment of adsorbing macromolecules to more than one droplet at a time (bridging flocculation) is the main destabilization mechanism. To be promoted of destabilization by non-adsorbing polymers are by the mechanism of depletion flocculation (that cause a weak attraction between the oil droplets). Electrically charged species as reagents in the mechanism can be electrically coupled with the electrically charged electrical fields on the droplet surface (by attractive electrical forces). Some authors have reported the elimination of oil from emulsified effluents by the adsorption properties of growing metal hydroxides (iron and aluminum hydroxides) which form nuclei of particles to adsorbing macromolecules causing the bridging flocculation. With the adsorption layers of the anions and cations arranged around the core, the core forms a particle with a small positive charge. This particle is a metal hydroxide and has very high ability to adsorb oil droplets. Coagulation method is very costly, it can cause secondary pollution of the water bodies [10].

2.3.3. Biological treatment

Biological treatment is the dissolution of water using microbial metabolism, and colloidal organic pollutants are transformed into stable harmless substances. It is used commonly in methods of biological filter and activated sludge. The activated sludge in the aeration tanks is concentrated on the surface of the microorganisms to separate the organic matter, using the current state vector as adsorption purifying microorganisms. The micro-organisms hold on to the filter. During the adsorption of organic pollutants, the wastewater from above passes down the filter surface and is decomposed by microorganisms.

In the treatment of large-scale heavy petroleum wastewater, biotreatment system has the potential [7].

2.4. Membrane Technology

A membrane can be described as a barrier, which separates two phases and limits the transport of many chemicals selectively. The types of membranes are homogeneous, heterogeneous, symmetric or asymmetric in structure, solid or liquid and also can carry a positive or negative charge or be neutral or bipolar [11].

The membrane separation efficiency is entirely dependent on the membrane itself and is more efficient than the conventional methods.

The method of separation is straightforward. The membrane does double duty for separation. First is being a semi-permeable layer between two phases and second is transportation between two phases. Essentially, the filter catches suspended solids or other substances that are in the emulsion and will let the water get through the membrane [12]. The process is generally performed at atmospheric conditions. An alternative, efficient and advantageous method for oil-water separation is membrane separation processes. The membrane technology is one of the most effective methods for the separation of oil-water wastewater or emulsions, which are commonly used in food processing, pharmaceutical, desalination, and fuel cell industries.

In comparison to chemical treatment and other treatments, the membrane separation method has higher efficiency, consistent effluent quality and lower consumption of energy. Due to many reason above, membrane technology is the most valid way to separate oily wastewater [13].

Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are the pressure-driven membrane processes. Fundamentally, the processes are similar. The critical difference between them is the membranes pore size as shown in Figure 2.1 [12].

The thickness of the membrane can vary as small as 10 microns to a few hundred micrometers, and pore size is over than 50 nm [12, 14].

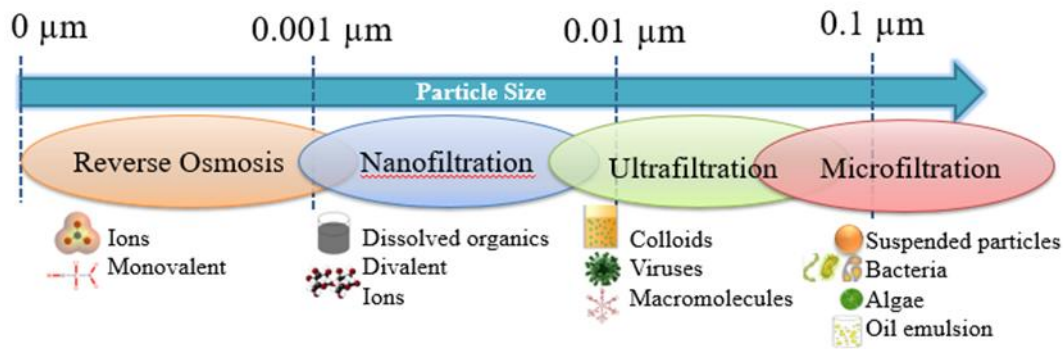


Fig 2.1. Filtration type depending on particle size (reproduced [14]).

For microfiltration (MF) and ultrafiltration (UF), the basic mechanism is the sieving mechanism which is the rejection of molecules whose size is greater than pores [15]. In molecular sieving, the smallest molecule will permeate, and the larger molecules will be retained. Therefore, when the pore size is comparable to the molecular dimensions, the molecular sieving dominates transport mechanism. The molecule dimensions are generally described with the Lennard-Jones (L-J) radii or the van der Waals radii. A shape factor should also be included. Because of separation by molecular sieving, it is not a satisfactory way of stating the molecular size. By increasing temperature, the separation selectivity will normally decrease because of increased diffusion rate for permeating components. The importance of sorption will be minor [16].

When the membranes are in contact with the water-electrolyte solution, they are charged. Origination of membrane charge is from fixed functional groups in the membrane material, or it can be by adsorption of ionic compounds. Negatively charged of polymer membranes are generally above pH 4-6 and positively charged of polymer membranes are below that pH. When low cut-off membranes are used at low salt concentration, the membrane charge affects membrane efficiency. Membrane charge also affects the flux. The common expectation is, both flux and retention are better when electrostatic repulsive forces are present. The fouling is slightly lower when electrostatic repulsion is stronger at pH 7 than at pH 5.5. A strongly charged membrane might be fouled more than a less charged membrane when cationic and anionic additives are used. To the surface of a negatively charged membrane, cationic polymeric retention aids can be bound and cause fouling. The rate of precipitation and fouling are affected by salt, pH, macromolecules and small particles in the range of 1 nm to 1 μm . By softening the water and adjusting pH, the stability can be improved [17,

18]. Because of coagulation and flocculation treatment, colloids are removed from waters. It affects colloidal stability. It sometimes improves the efficiency of filtration [15]. The process of the membrane separation is given in Figure 2.2.

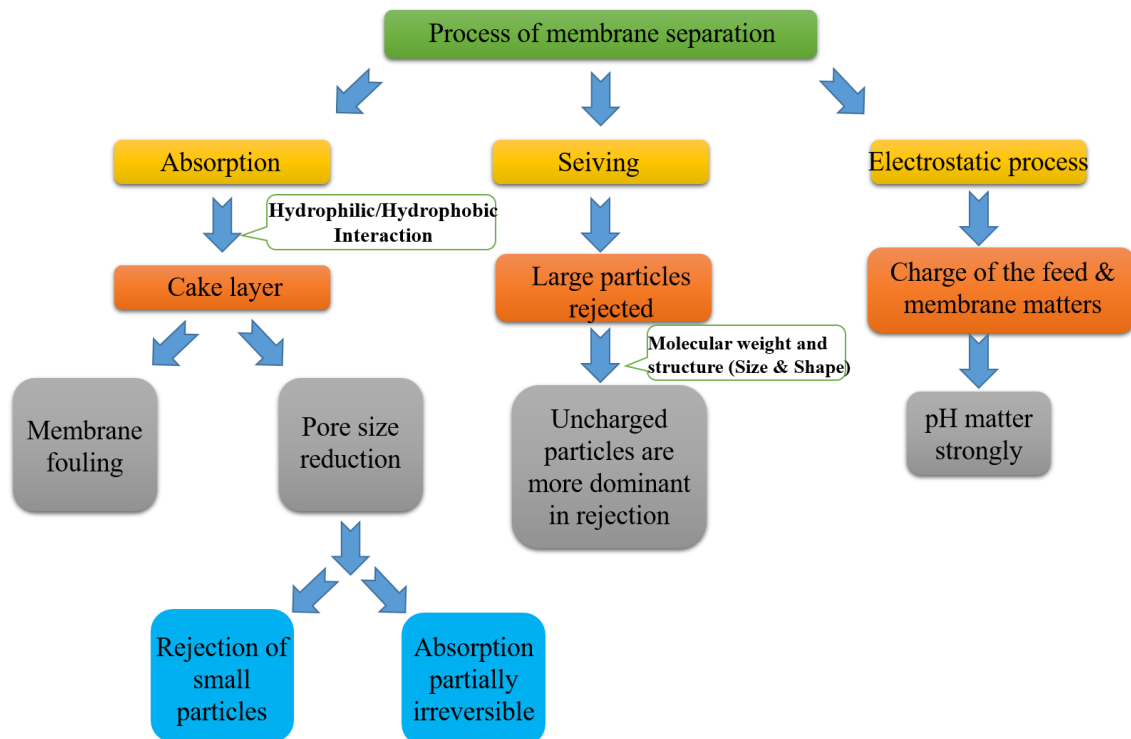


Figure 2.2. Process of membrane separation (reproduced [12]).

The membrane is a thin interface which moderates the permeation of chemical species in contact with it. The interface is, completely uniform in composition and structure or we can also name it molecularly homogeneous, or the interface may be chemically or physically heterogeneous. For example, it contains holes or pores of measurable dimensions or consisting of some form of layered structure [19].

The main types of membrane are shown in the picture, and they are classified as;

- Isotropic membranes
 - Microporous membranes
 - Nonporous, dense membranes
 - Electrically charged membranes
- Anisotropic membranes
- Ceramic, metal and liquid membranes

2.5. Types of Membranes

2.5.1. Isotropic Membranes

2.5.1.1. Microporous Membranes

In point of structure and function, the microporous membrane is very similar to a conventional filter. The pore distribution is randomly, highly voided, interconnected and it has a rigid structure. The reason for the difference than the conventional filter, pores are extremely small and in diameter of 0.01–10 μm . The rejected particles by the membrane are all particles larger than the largest pores. Partially rejected particles are smaller than the largest pores but larger than the smallest pores. The particles passing through the membrane are much smaller than the smallest pores. Therefore, by microporous membranes, solutes separation is mainly dependent on molecular size and pore size distribution. Generally, by microporous membranes, it is possible to separate effectively only molecules that differ considerably in size using by ultrafiltration and microfiltration.

2.5.1.2. Nonporous, Dense Membranes

Non-porous dense membranes are composed of a dense film through which permeants are transported by diffusion under a pressure, concentration or propulsive force of the electrical potential gradient.

The relative transport rate in the membrane determined by the diffusivity and solubility in the membrane directly which affects the separation of the various components of a mixture. Accordingly, if the permeant concentrations in the membrane material (solubilities) differ significantly, nonporous, dense membranes can separate permeants of similar size. To perform the separation, most gas separation, pervaporation, and reverse osmosis membranes use dense membranes. To improve the flux, these membranes usually have an anisotropic structure.

2.5.1.3. Electrically Charged Membranes

Electrically charged membranes may be dense or microporous, but are most generally very finely microporous, with the pore walls carrying fixed positively or negatively charged ions. Membranes with positively charged fixed ions that bind the anions in the surrounding fluid are called anion exchange membrane. Likewise, the cation exchange

membrane is called a membrane containing negatively charged ions. With charged membranes, the separation is basically by the exclusion of ions of the same charge as the fixed ions of the membrane structure and to a much lesser extent by the pore size. The charge and concentration of the ions in the solution affect the separation. In solutions of high ionic strength, the selectivity decreases. For processing electrolyte solutions in electrodialysis, electrically charged membranes are used.

2.5.2. Anisotropic Membranes

The transport rate of a species through a membrane is dependent on the thickness, and it is inversely proportional to the thickness of the membrane. In membrane separation processes, high transport rates are requirable for economic reasons. Thus, the membrane should be as thin as possible. The production of mechanically strong, defect-free films is limited to about 20 μm thicknesses in conventional film production technology. One of the main inventions of membrane technology for the last 40 years was the development of new membrane production techniques to produce anisotropic membrane structures. Anisotropic membranes compose of an extremely thin surface layer and a much thicker, porous support. The layer of surface and its substructure can be formed in a single operation or separately. The layers are usually made from different polymers in composite membranes. The substructure functions as mechanical support. Only the surface layer determines the main separation properties and permeability rates of the membrane. The advantages of the higher fluxes provided by anisotropic membranes are so great. Therefore, a lot of commercial separation processes use such membranes.

2.5.3. Ceramic, Metal, and Liquid Membranes

The interest in membranes formed from less traditional materials has increased in recent years. Ceramic membranes with a special microporous membrane class are used for ultrafiltration and microfiltration applications where solvent resistance and thermal stability are required. For the separation of hydrogen from gas mixtures, dense metal membranes, particularly palladium membranes are being considered. Also for carrier-facilitated transport processes, supported liquid films are being developed. Figure 2.3. shows the cross section of all membrarne types.

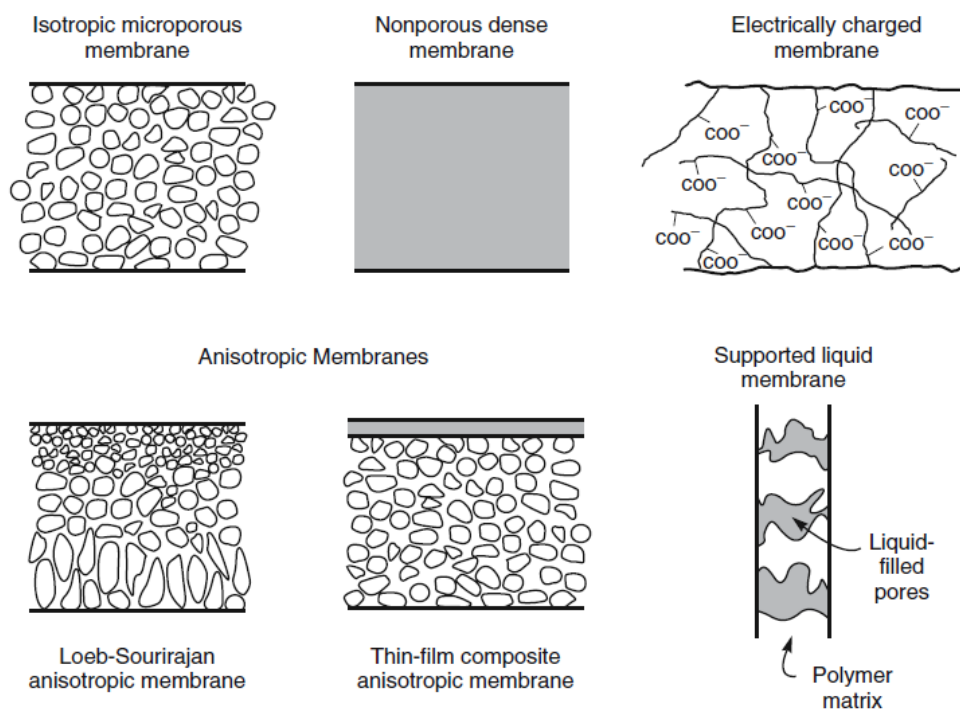


Figure 2.3. Types of membranes [20].

2.6. Membrane Technology for Oil Separation

In general, the treatment of oily wastewater is done by several conventional processes based on physical processes (such as adsorption, flotation, and coagulation).

The adsorption method, which can remove most of the pollutants and recover almost all of the wastewater, has been widely used in the treatment of oily wastewater. The disadvantage of this method is that adsorbents replaced after a relatively short period of operation or need to be removed. It is because of the saturation of the adsorbents with a high concentration of waste. There is also an additional cost for replacement and regeneration is unfavorable for long-term operation.

Due to its high processing capacity and separation efficiency, the flotation method is used. However, high energy consumption and long processes are the disadvantages of the flotation method.

Coagulation is another method used for the removal of emulsified and dissolved oil and some non-biodegradable organic compounds that are present in the wastewater. The disadvantages of coagulation are high cost, long-time process, and sludge production. Electrochemical methods have been used to increase the interest in flotation and coagulation. However, the efficiency of electrocoagulation and electroflotation methods

depends on the structure of the oily wastewater, the voltage and current parameters in the system and the types of anodes and the alignment of the electrodes.

It has been recognized that membrane technology, which is simple and high efficiency, is more useful and promising than traditional methods to remove oil droplets, especially below 10 μm . For decades, many membrane processes such as asymmetric polymeric membranes, which normally involve only single-stage flat sheet casting or hollow fiber spinning, are widely used. The advantages and disadvantages of using various membrane technologies are shown in Table 2.1 [21].

Table 2.1. Advantages and disadvantages of membrane technology.

Membrane technology	Advantages	Disadvantages
Reverse osmosis (RO)	High oil removal (99%) e.g., treat saline oily waste	High pressure requirement
	Removes dissolved contaminants	Membrane fouling issues by oil&grease
	High quality effluent	
Forward osmosis (FO)	High oil removal	Concentration polarization issues
	Low membrane fouling	
	Low or no hydraulic pressures requirement	
	The equipment used is very simple	
Nanofiltration (NF)	Higher oil removal, large organic molecule (e.g., surfactant), hardness removal and divalent salts removal	Higher energy consumption than FO
	Consumes lower energy in comparison with RO processes	
	Compact module	
Microfiltration (MF)	Micron and nano-sized particulates (e.g., emulsified oil/grease)	Membrane fouling
	Compact modules	
	Low energy cost	
	No degradation due to heating	
	No extra safety considerations as in high voltage demulsification	
Ultrafiltration (UF)	Effective in the removal of oily microemulsions	Low flux
	Superiority of low energy consumption and high efficiency	Membrane fouling by property of extremely hydrophobicity
	No chemical preparation involved	

The expectations from the membranes which are used as membrane distillation are being hydrophobic and porous with pore sizes which have the range from some nanometers to few micrometers [14, 22].

For practical applications, the types of membrane modules are hollow fiber, spiral wound, and plate. High packing density, good control of concentration polarization and membrane fouling, low cost and also cost-efficient production are the key factors for an efficient membrane module. Nanofibers seem a good alternative for the membrane process, considering that the properties of the efficient membrane [14].

2.7. Nanofibers in Oil Separation

Fibers with a diameter range around 100-1000 nm are generally classified as nanofibers. Compared to conventional fibers, nanofibers are with higher porosity, lower density, higher surface area to volume ratios and smaller pore size, offer an opportunity for use in a wide variety of applications including composite, filtration, protective clothing, composite materials, biomedical application (tissue engineering, scaffolds, bandages, and drug release systems), electronic applications, sensors, design of solar sails and flexible photocells. The applications of nanofibers are; catalyst and enzyme carriers (chemical reactions, enzyme for biological processes), wound healing (anti-bacterial), reinforcements, electronic and optical nanodevices, protective clothing, energy generation and storage (supercapacitors, batteries, fuel cells, photovoltaic cells, separators, hydrogen-storage, piezoelectric power), microreactors, release control, tissue engineering scaffolds (muscles, bones, cartilages, skins, blood vessels, neural tissues, others), environmental applications (filtration (gas and liquid), desalination, noise reduction, adsorption (heavy metal ions and organic compounds), insect repellent/blocking) and sensors (physical applications, chemical applications, biological applications) [23]. As industrial products, the most advanced and most used nanostructures are filtration, purification materials, and components. These nanostructures can indeed specify efficiency of higher filtration and lower pressure than a conventional filter. Besides, it is easy to clean, enabling customers to significantly extend the life of filters, thus reducing maintenance costs. Currently, water filters such as wastewater treatment and desalination, and energy storage as battery separators are potential products ready to market [23].

Nowadays nanofibers attract great attention due to the technique and resultant products, and simple process of electrospinning. It is possible to have a variety of materials in electrospinning and unique features of the obtained. To treat oily wastewaters, membranes are developed based on nano-porous structures.

Electrospun nanofibers as filter have high flux due to their extremely porous structure. Therefore, electrospun nanofibers as a filter which have high hydrophilicity are an excellent alternative for the oil/water separation [24]. Via bio-inspired mineralization, Xu's group developed a super-hydrophilic membrane to be used for the oily wastewater separation [25]. In oil/water emulsion separation, the properties such as; high porosity, interconnected porous structure, controllable pore size, and large surface area to volume ratio make the electrospun nanofiber membrane attractive [25]. But the oil of oil/water mixtures causes membrane fouling which is the main drawback in the application of membrane filtration. Moreover, low contact and adhesion between the fibers cause poor mechanical strength of electrospun nanofibers [26]. According to applications, used nanofibers are shown in Table 2.2.

Table 2.2. Polymeric nanofibers and their applications [14].

Nanofibers	Application
CS, PVA, cellulose acetate, and PUR/copper oxide	Air filtration
CS/PCL, collagen, gelatin, PCL, and poly(L-lactide-co-glycolide)	Tissue engineering
Cellulose, PA6, PVDF, PAN, PVDF/PAN, PVDF, PUR, and polypropylene	Membrane for water purification
Gelatin, silk, PCL, CS-PEO, PA6, and dextran	Biomedical applications
PVA and PA6	Acoustics
PVA, polyvinyl butyral, PUR, and PAN	High-performance apparels
PVDF	Piezo applications

CS: chitosan; PEO: polyethylene oxide; PA6: polyamide 6; PVDF: polyvinylidene fluoride; PUR: poly-urethane; PVA: polyvinyl alcohol; PCL: polycaprolactone; PAN: polyacrylonitrile.

2.8. Membrane Fouling and Surface Modification

Membrane fouling not only reduces water flux and separation efficiency but also reduces the membrane life and increases the cost [27–30]. To minimize the membrane

fouling, and to optimize the hydrodynamic conditions of the membrane, different methods have been tried, such as, surface modification. It has been achieved that the surface modification increases the hydrophilicity of the membrane also reduces organic foulant adsorption on the membrane [31–33].

The main purpose of the surface modification is increasing membrane surface's hydrophilicity; thereby, the membrane performance improves. The surface modification via chemical reaction or physical absorption is some of the solutions to prevent surface fouling. Decreasing the adsorption of oil droplets on the membrane surface is the most important issue for oily wastewater separation. Adsorption of other organic molecules, such as surfactants cause the membrane fouling. But it is generally overlooked. The organic contaminants cause the membranes to be polluted and blocked. It is difficult to remove contaminations, and membrane life reduces. For this reason, improved anti-fouling performance and efficiency of the membranes are desirable [34].

Chemical surface modification introduces hydrophilic polymers such as poly(ethylene glycol) methyl ether methacrylate, poly(2-hydroxyethyl methacrylate), poly(acrylic acid) or zwitterionic polyelectrolyte or small molecules onto membrane surfaces via the formation of covalent bonds. During the monitored cleaning process, the hydrophilic materials form compact hydrated layers to prevent fouling of the oil droplets on the membrane surfaces and to make the easy oil removal [35].

An extensive research was done about surface grafting of filtration membranes by Jiang and co-workers. Via an acrylate reaction, they grafted a low surface free energy molecule pentadecafluorooctanoic acid onto the surface of an aminated polyacrylonitrile ultrafiltration membrane, as a result an excellent antifouling property was obtained [36].

Another approach to modifying the membrane is via physical absorption. Onto a polyamide reverse osmosis membrane, Freeman and co-workers deposited dopamine via physical absorption. There was not any obvious change in the hydrophilicity of membrane, but a higher flux for oil/water separation was exhibited by the reverse osmosis membrane which was coated by the polydopamine layer [37].

The surface modification of the hydrophilic layer on nanofibrous ultrafiltration membranes was reported by Chu and co-workers to get high flux for oily wastewater emulsion separation [38–41]. The membrane exhibited excellent high flux and anti-

fouling property performance because of high porosity, thin, and smooth barrier layer of the membrane [35].

The properties of PVDF membranes are better than other organic membranes. For instance; good mechanical property, thermostability, chemical stability, and impact resistance properties allow using PVDF membranes in many fields such as microfiltration, ultrafiltration, membrane bioreactor, membrane distillation, gas separation and stripping [34]. Against a wide range of harsh chemicals such as halogens and oxidants, inorganic acids (apart from fuming sulphuric acid), as well as aromatic, aliphatic and chlorinated solvents, PVDF has excellent chemical resistance [42]. Dehydrofluorination, where the carbon-carbon double bond formed as a result of the removal of the hydrogen-fluoride (HF) units from the polymer, is the chemical reaction between PVDF and NaOH [43–45]. By several studies, it has been proved that PVDF is weak to a caustic environment [43, 46–49]. Brownish discoloration has been reported in PVDF exposed to sodium hydroxide (NaOH) solution [46, 47]. The color changing of PVDF from white to brown and then to black color is depending on the degree of the dehydrofluorination [42].

Characterization and hydrolyzation of the polyacrylonitrile fiber (PAN) by alkaline hydrolysis were studied by Xue and co-workers which was about improving water absorption and increasing the antistatic performance [50]. Polyacrylonitrile (PAN) fiber is hydrophobic, and it has some disadvantages, e.g., low moisture-absorbency and electrostatic tendency. The fiber surface energy is low. It has a large water contact angle. Therefore, it is difficult to wet the fiber. The hydrophobic groups which the fiber matrix contains are limiting the transmission and storage of the water is difficult [50]. The main purpose of hydrolysis is the conversion of the polar nitrile groups to the carboxylic group in the PAN. After hydrolysis, the nitrile group ($-C\equiv N$) which is in polyacrylonitrile fiber, converted to the carboxyl group ($-COOH$) which in NaOH aqueous solution [50]. The internal structure of the fiber is not severely damaged, and minimal damage to its strength can occur. Because hydrolysis of the polyacrylonitrile fiber occurs on the surface of the fiber. After hydrolyzation, the properties of the hydrolyzed fiber such as weight, moisture absorption, and chemical reactivity are increased [50].

2.8.1 Self-cleaning

In almost all membrane process, the most important and general problem is fouling. The problem which is because of irreversible deposition materials on the surface of the membrane is defined as fouling, and it causes flux to decline. Both the quantity and quality of products and membrane life are affected by membrane fouling. Because of fouling, separation performance always reduces [52].

The adsorption of organic pollutants on the membrane surface causes in severe fouling because of hydrophobic nature and low surface energy of materials. Therefore, it is good to improve hydrophobicity to decrease fouling and increase the flux of membranes. Nowadays, the hydrophobic membranes can be changed to the strongly hydrophilic membranes by applying Al_3O_4 , SiO_2 , Fe_3O_4 , ZrO_2 , TiO_2 inorganic particles into the membrane. Because of its photocatalytic and super- hydrophilic effects, TiO_2 is prevalently used for membrane modification [51].

The surface coating is by self-assembly of TiO_2 particles via coordinance bonds with OH functional groups of polymer on the membrane do not create only photocatalytic property but also increases the hydrophilicity of the membrane [52].

Anderson et al. researched and the possibility of binding of photocatalytic TiO_2 functionalization with membrane separation [53]. Then the result of research triggered the preparation of TiO_2 -embedded membranes [54, 55]. For example, Damodar et al. used blending different amounts of TiO_2 and they prepared modified polyvinylidene difluoride (PVDF) membranes. Later, they investigated anti-bacterial, photocatalytic, and anti-fouling properties of the membrane. As a result of the additional TiO_2 , they found that the pore size and hydrophilicity of the membrane was affected and that even the water permeability of the PVDF / TiO_2 membrane increased. Additionally, under the UV light exposure, PVDF/ TiO_2 membranes exhibited anti-bio and -organic fouling abilities [56].

3. OBJECTIVE

Using today's technology, cleaning of oily wastewater is expensive and energy-cost; there is a need for new research to identify novel approaches to clean water at lower cost, using less energy, and minimizing the impact on the environment. Membrane technologies have been used industrially and one of the most important industrial market water treatment. The demand for an effective membranes is: high permeability,

high rejection, low fouling, easy to clean, easy to use, chemical and mechanically strong and low cost. Considering the effective membrane properties, nanofiber technology is promising for the separation technology. The greatest advantages of using nanofibers in separation technology are that;

- (a) High surface area of the nanofibers allows rapid adsorption of particles from the wastewater such as microorganisms or hazardous molecules.
- (b) Highly porous and narrow pore size of the nanofibers allow high permeability and selectivity.
- (c) Surface can be modified easily.
- (d) Large variety of the polymeric solution can be used for preparation of nanofibers.
- (e) The high interconnected and asymmetric structure of the nanofibers may reduce the fouling.

Based on the reasons listed above, various nanofiber webs were selected for this thesis. The selection of the various nanofibers was done according to; easy to electrospun, low cost, repeatable and even web surface. The selected nanofibers were PVDF, PAN, PA6 and PUR.

The objective of this thesis was to develop a facile method which was developed to functionalize nanofibrous to produce a versatile and effective self-cleaning membrane for separation of oil/water emulsion to protect the environment.

The specific objectives of the thesis are that:

1. Enhancement of the mechanical properties of nanofibers to use in water domain area.
2. Development of the membranes that can selectively separate water from oil/water emulsion.
3. Development of highly permeable self-cleaned membranes.
4. Development of anti-bacterial self-cleaning membrane using TiO₂ nanoparticles.

4. EXPERIMENTS

4.1. Materials and Methods

4.1.1. Polymers and Nanofibers

Different density of nanolayers such as PVDF, PAN, PA6, and PUR were obtained from the Institute of Advanced Technology and Innovation at the Institute of Nanomaterials, Liberec Technical University (TUL). Nanofibers were prepared using NS-1S500U Nanospider (Elmarco, Czech Republic) under the controlled conditions. Preparation conditions are not given. Samples and their abbreviations are shown in Table 4.1.

Table 4.1. Abbreviation of the samples.

Sample numbers	Material	Gsm [g/m ²]	Modification
S_1	PVDF	3	-
S_5	PVDF	1	-
S_8	PAN	3	-
S_9	PAN	1	-
S_10	PA6	3	-
S_11	PA6	1	-
S_12	PUR	3	-
S_13	PVDF	3	NAOH
S_14	PVDF	3	NAOH+TiO ₂
S_15	PVDF	3	KOH
S_16	PVDF	3	KOH+TiO ₂
S_17	PAN	3	NAOH
S_18	PAN	3	NAOH+TiO ₂
S_19	PAN	3	KOH
S_20	PAN	3	KOH+TiO ₂

PVDF: A special polymer, PVDF, is used in applications which requires the highest purity, resistance to solvents, acids, and hydrocarbons. It is compatible with the FDA (U.S. Food and Drug Administration) and absolutely non-toxic. Therefore for food products, it can be used in repeated contact. The glass transition temperature of PVDF is about -35 °C and it is often 50-60% crystalline. The melting point of PVDF is around 177 °C. It is insoluble in the water. The structural formula of PVDF is shown in Figure 4.1 [57]. More details are given in section 2.8. The chemical formula of the PVDF is;

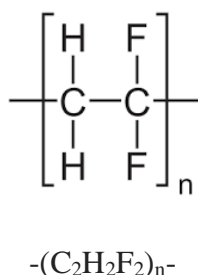


Figure 4.1. Chemical formula of PVDF

PAN: The linear formula of polyacrylonitrile (PAN) is $(\text{C}_3\text{H}_3\text{N})_n$ and is a synthetic, semicrystalline organic polymer resin. Nearly all PAN resins are copolymers, and they are made from monomers mixtures with acrylonitrile as the main monomer. To produce a large variety of products, it is a versatile polymer. Under the normal conditions, it does not melt although it is thermoplastic. Before melting, it degrades. It melts above 300 °C when the rates of heating are 50 degrees per minute or above [58]. It is insoluble in the water. The structural formula of PAN is shown in Figure 4.2 [59]. More details are given in section 2.8. The chemical formula of the PAN is;

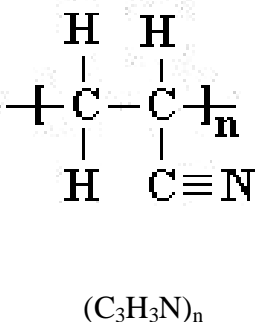


Figure 4.2. Chemical formula of PAN

PUR: Polyurethane (PUR and PU) is organic units polymer composed and joined by carbamate (urethane) links. Mostly polyurethanes are thermoset polymers that when it is heated, it does not melt. But there are also thermoplastic polyurethanes [60]. They can be hard and rigid or soft and flexible [61]. The resistivity of PU to water, oil & grease is high. Therefore it remains stable in the water/oil/grease (with minimal swelling) [62]. The formula of PUR is shown in Figure 4.3.

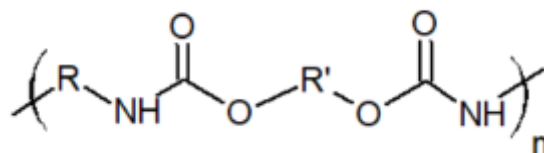


Figure 4.3. Chemical formula of PUR [61].

PA6: Polyamide 6 or Nylon 6, is semi-crystalline polyamide and it has a chemical formula $(\text{C}_6\text{H}_{11}\text{NO})_n$. Nylon 6 fibers have high elasticity, luster, and tensile strength. They are highly resistant to abrasion and chemicals. Fibers can absorb up to 2,4% of water. But that decreases the tensile strength. Nylon 6 has a glass transition temperature around 47 °C. The melting point of Nylon 6 is 215 °C [63]. The structural formula of Nylon 6 (PA6) is shown in Figure 4.4.

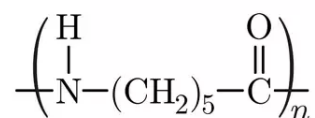


Figure 4.4. Structural formula of Nylon 6 [64].

4.1.2. Lamination of Nanofibre Webs

Samples were cut into A4 size (210 x 297 mm²). 12 g/m² of the copolyester adhesive web and 120 g/m² of polyethylene terephthalate spunbond nonwoven were used as a supporting layer (the information of the supplier is not given). For the lamination process, heat-press equipment (Pracovni Stroje, Teplice, Czech Republic) was used which is in the laboratory of the Institute of Advanced Technology and Innovation at the Institute of Nanomaterials, Liberec Technical University (TUL). There are two metallic hot plates such as upper and lower plates are used under pressure in this equipment. Between the two hot plates, the nanofibers, polyethylene terephthalate spunbond and copolyester adhesive web were placed. Polyethylene terephthalate spunbond and copolyester adhesive web were as a supporting layer. To protect the

contacting between multilayer nanofibrous membranes and hot plates, two silicon layers were used. The pressure was applied for 3 minutes. First 2 minutes, 30 kN was applied to the membrane. The last 1 minute, 50 kN was applied to the membrane in the lamination process. During this process, the heat was 130 °C.

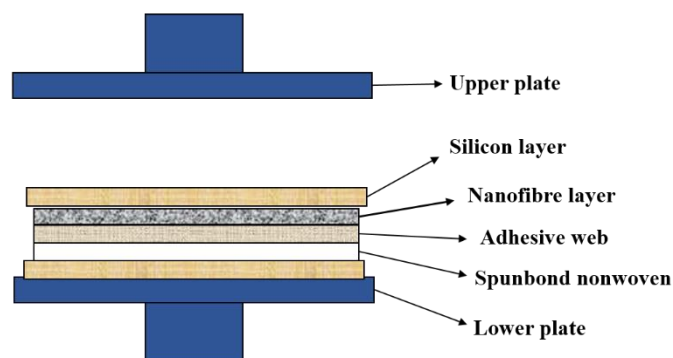


Figure 4.5. Lamination process (reproduced [26]).

4.1.3. Characterization

Surface morphology of the membranes was done using a scanning electron microscope (SEM, Vega 3SB, Brno, Czech Republic). Image-J program (free online program) is used to determine fiber diameters. The maximum, average and the minimum pore sizes are determined by a bubble point measurement device which was working with capillary flow porometry theory and developed in the laboratory of the Institute of Advanced Technology and Innovation at the Institute of Nanomaterials, Liberec Technical University (TUL). The water contact angle of the samples is measured using a Krüss Drop Shape Analyzer DS4 (Krüss GmbH, Hamburg, Germany), at five different points, using distilled water (surface tension 72.0 mN.m^{-1}) on the clean and dry samples at room temperature. The air permeability of all multilayer nanofibrous membranes is tested using an SDL ATLAS Air Permeability Tester (@200 Pa and 20 cm^2 , South Carolina, US). At least three measurements are taken for each sample. Bursting strength test was done using a custom-made equipment. In this experiment, between two rings the sample was placed. The sample size was 45 mm in diameter. Pressurized water was fed to the membrane from the bottom side. By using a pressure controller which is connected to the computer, the hydrostatic pressure was measured. The hydrostatic pressure was gradually increased until the nanofiber layer burst, and in that time on the screen, the pressure value decreased very sharply. Maximum pressure value was recorded as the burst strength of the membrane

4.1.4. Surface Modification

The aim to make surface modification is to promote self-cleaning property of the membranes. The permeability and flux of the membrane decline rapidly due to the membrane fouling which causes performance reduction and shorten the operation time. The main reason for the membrane fouling is because oil droplets block the pore size of the membrane and/or adsorption of the surfactant. Two polymeric membranes were selected among the others (S_1 and S_8) due to their better performance and mechanical properties. Modification was done in two steps. At first step, hydrophilic hydroxyl or carbonyl groups were introduced using the alkaline solution for the PVDF and PAN. Then, treated PVDF and PAN membranes were modified with titanium dioxide (TiO₂) nanoparticles.

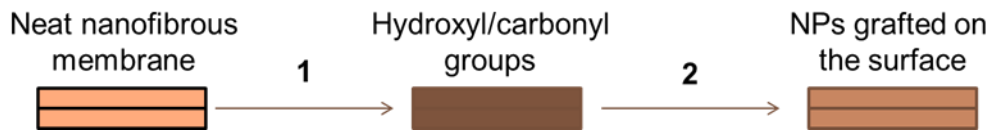


Figure 4.6. Surface modification of nanofibrous membranes.

The potassium hydroxide (KOH), sodium hydroxide (NaOH), and isopropyl alcohol (IPA) were purchased from PENTA s.r.o (Prague, Czech Republic) Selected membranes were S_1 and S_8. It was tested that 10M, 20M and 30M of NaOH. Results indicated that 30M of NaOH has quicker and regular modification. For this aim 30M of NaOH in distilled water were mixed on the magnetic stirrer until the NaOH salt was dissolved in the distilled water. Samples were kept in NaOH solution for 48 hours. Then samples were taken out, and washed many times with distilled water and kept in distilled water until used. The process of NaOH surface modification is shown in Figure 4.7.

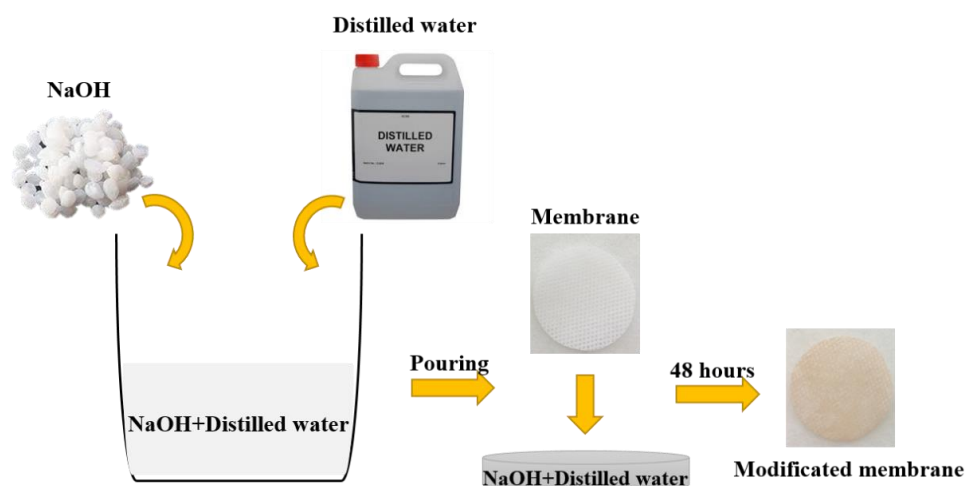
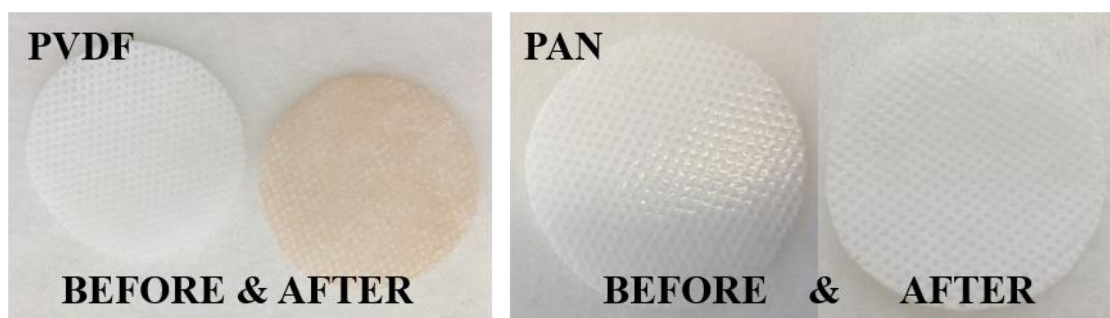


Figure 4.7. Process of surface modification



The PVDF and PAN membranes are shown before modification and after modification in Figure 4.8.

Figure 4.8. PVDF and PAN (S_1 and S_8) membranes before modification and after modification with NaOH

Another modification was done using KOH. For KOH modification, 20 mL IPA and 2gr KOH were mixed on the magnetic stirrer until the particles of KOH were dissolved in isopropyl alcohol. Samples were kept for 1 hour in KOH+IPA solution. It was observed that longer period destroyed the supporting layer. Then samples were taken out, and washed many times with distilled water and kept in distilled water until used. The process of KOH surface modification is shown in Figure 4.8.

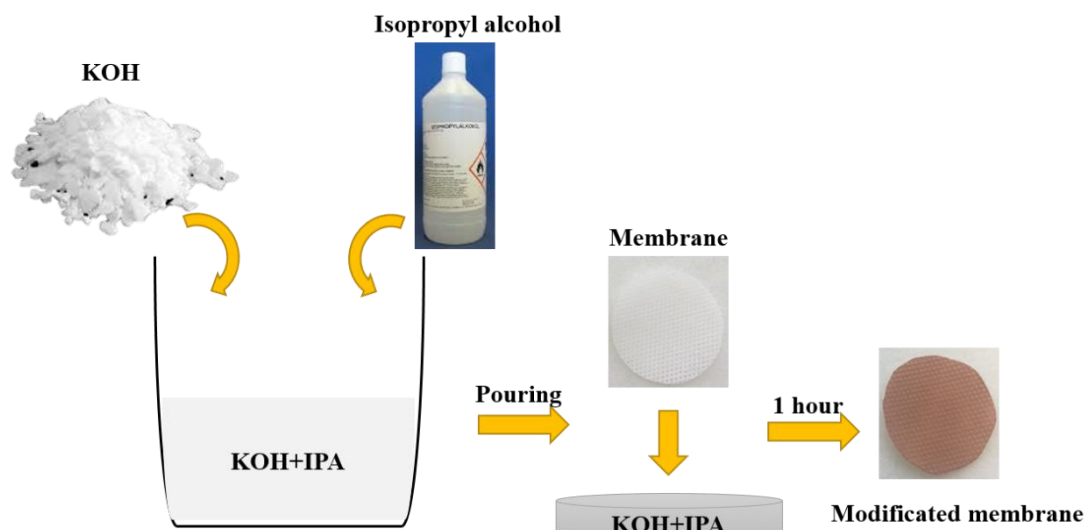


Figure 4.9. The process of KOH surface modification

The PVDF membrane is shown before modification and after modification in Figure 4.10

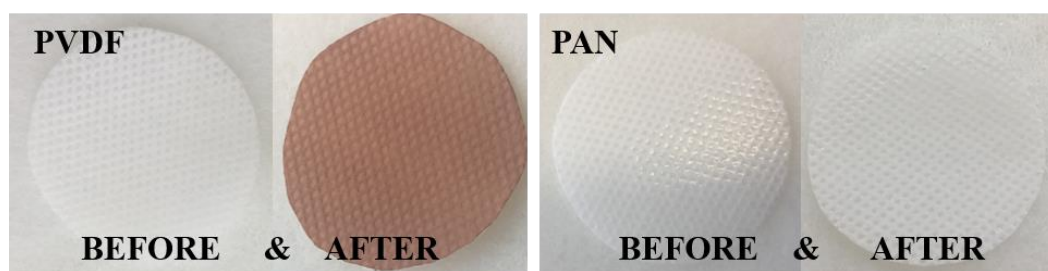


Figure 4.10. PVDF and PAN membranes (S_1 and S_8) before modification and after modification with KOH

The second modification step was done using Titanium(IV) oxide nanoparticles. Titanium(IV) oxide nanoparticle (21 nm particle size) was purchased from Sigma-Aldrich Chemie GmbH and used for the self-cleaning property to both membranes (modified with NaOH and KOH). 40 mL distilled water was mixed with 0.5 gr TiO_2 , and the membranes were dipped to the TiO_2 solution and left for 24 hours. After 24 hours, the membranes were taken from solution and cleaned with distilled water. All membranes which were modified with TiO_2 were also cleaned via ultrasonic cleaning for 1 minute to remove extensive nanoparticles on the surface of the membrane.

4.1.5. Emulsion Preparation

To prepare oily wastewater emulsion, 100 mL of Vita D'or (Czech Republic) sunflower oil was mixed with 100 mL of distilled water in ratio 1:1 v/v. The red water soluble/oil insoluble food coloring was dropped into the emulsion to see separation performance and behavior of the membrane. 2 gr of Triton X-100 (Sigma-Aldrich Corporation) was also dropped into the emulsion to get better stability of oil droplets diameter. After that, the emulsion was mixed by magnetic stirrers (Heidolph Instrument GmbH&Co.KG, Germany). Before mixing and after mixing of the emulsion is shown in Figure 4.11.

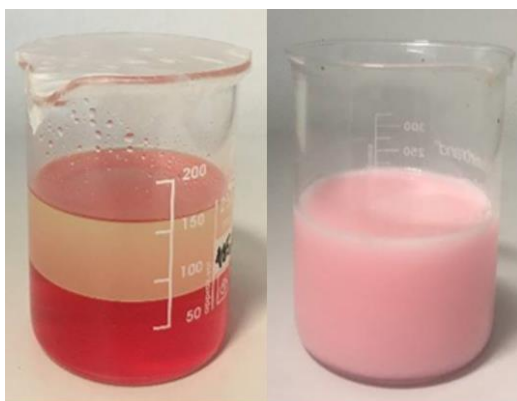


Figure 4.11. Emulsion before and after mixing

The characterization of the emulsion was checked by using Levenhuk C800 NG microscope digital camera. The average of oil droplet diameter was $1058.02 \text{ nm} \pm 345.39 \text{ nm}$. It was checked after a few weeks and observed that the average drop size was the same. The image of the oil droplets are shown in Figure 4.12.

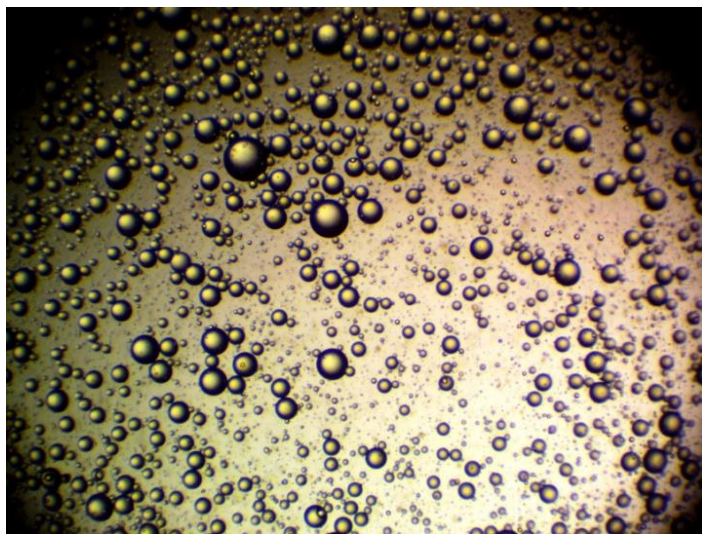


Figure 4.12. Oil droplets in the emulsion

4.1.6. Separation Test

Separation of oily wastewater emulsion is done using an Amicon® Stirred Cell 50mL (EMD Millipore Corporation, USA). The separation process is shown in Figure 4.13. Low of pressure was applied to the system (0.02 bar) using by a vacuum pump which purchased from VACUUBRAND GMBH + CO KG, Germany. Amount of feed solution was 15mL for each test. The active membrane diameter was 4.5 cm. The pressure was controlled by using handheld pressure-meter which purchased from GMH-GREISINGER s.r.o. (Czech Republic), and permeate was collected. To determine self-cleaning property, the same membrane was used at least 3 times. First 15 mL of distilled water was used as feed (1. Water circulation), then 15 mL of emulsion was used as feed (1. Circulation of emulsion). Then process was repeated at least three times with water and emulsion circulation.

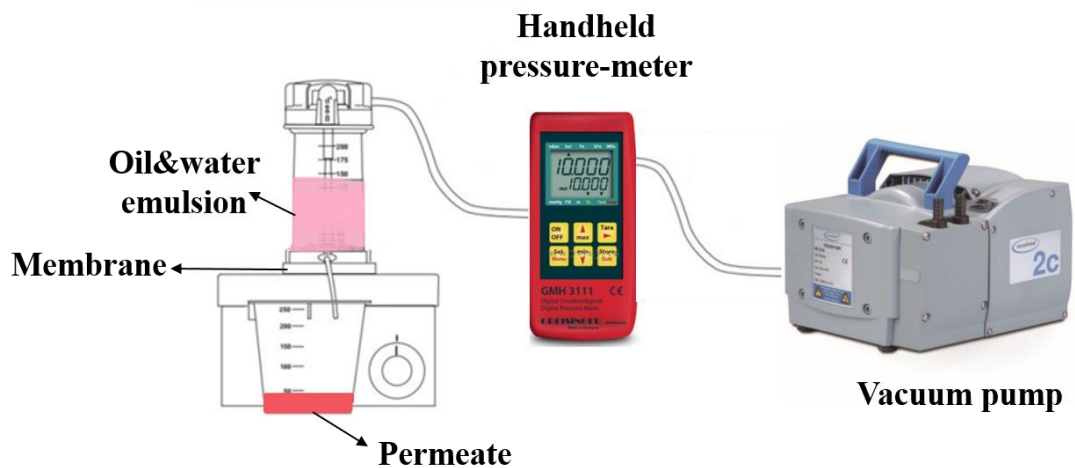


Figure 4.13. Separation process

The membranes flux (F) and permeability (k) were calculated according to equations;

$$F = \frac{1}{A} \frac{dV}{dt} \quad k = \frac{F}{p}$$

where t is the filtration time (hour), A is the active membrane area (m^2), p is the transmembrane pressure (bar), V is the total volume of the permeate (L). Selectivity was determined by observing the color of permeate and it was checked under the microscope which was purchased from Levenhuk Company (USA).

5. RESULTS and DISCUSSION

5.1. Surface Morphology (SEM)

Images of surface morphologies of the samples were taken using a SEM images. To compare the all unmodified polymeric nanofiber webs, it was found that S_11 has the lowest fiber diameter while S_12 has the highest (Appendix Figure 1A – 12A). There are plenty of reason behind it. For instance the properties of the polymeric solution or the system/process parameters are the main reason for that plays role on the fiber diameter. After modification process, it was observed that diameters were slightly increased. The reason could be swelling of nanofibers in alkaline solution. Figure 5.1 showed that the titanium particles are visible on the surface and distributed very well. Fiber diameter distributions are given in Appendix Figure 1A – 12A.

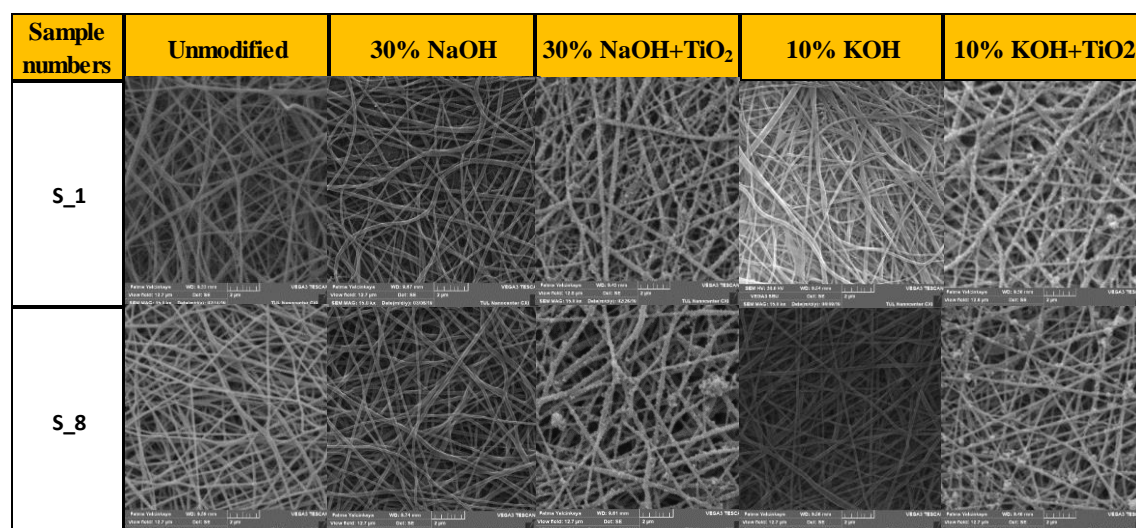


Figure 5.1. Surface morphology of samples

5.2. Pore Size

The pore size and operating conditions (pH, temperature, etc.) of the membranes play a huge role on the selectivity, filtration flux, membrane fouling, and solute rejection. In Figure 5.2, the mean of sample pore sizes are shown. In Figure 5.3, the mean of sample diameters are shown. Pore size measurement was done only for the dry unmodified samples. Modified samples were kept in wet condition. According to previous experiences, when the nanofiber dried after wet form, possible crackings were observed which might effect the pore size measurements.

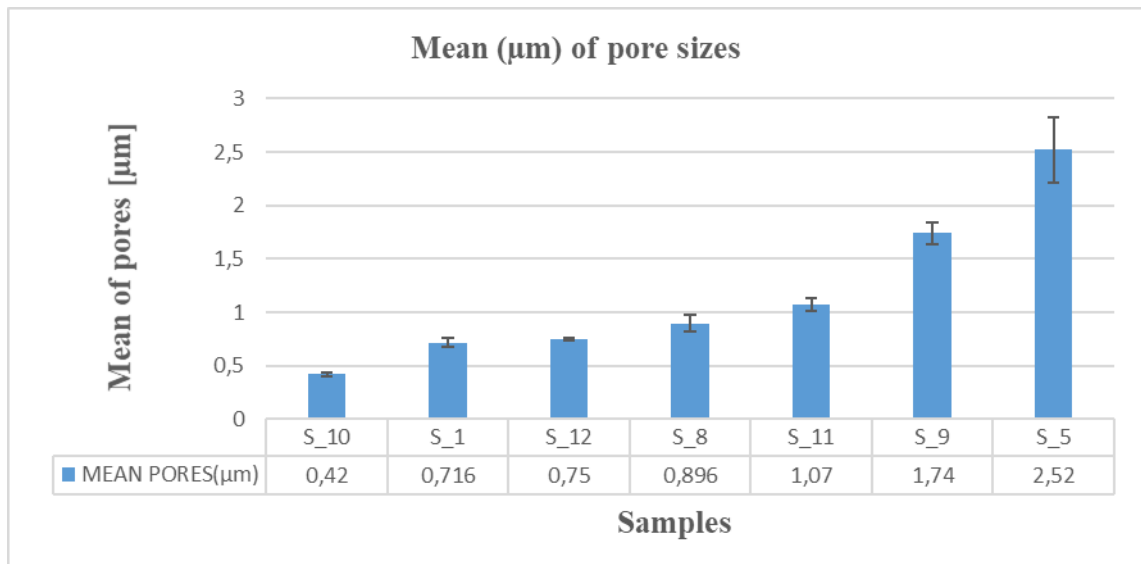


Figure 5.2. Mean of pore sizes.

According to obtained results, it was found that pore size had different result in different polymer and different gsm. The biggest pore sizes were from sample S_5 and the smallest pore sizes were from S_10. For example; S_5 is a PVDF sample which had 1 gsm. S_1 was also PVDF sample which had 3 gsm. When the results of mean of pore sizes were compared, it was observed that in lower gsm, membranes had bigger pore sizes.

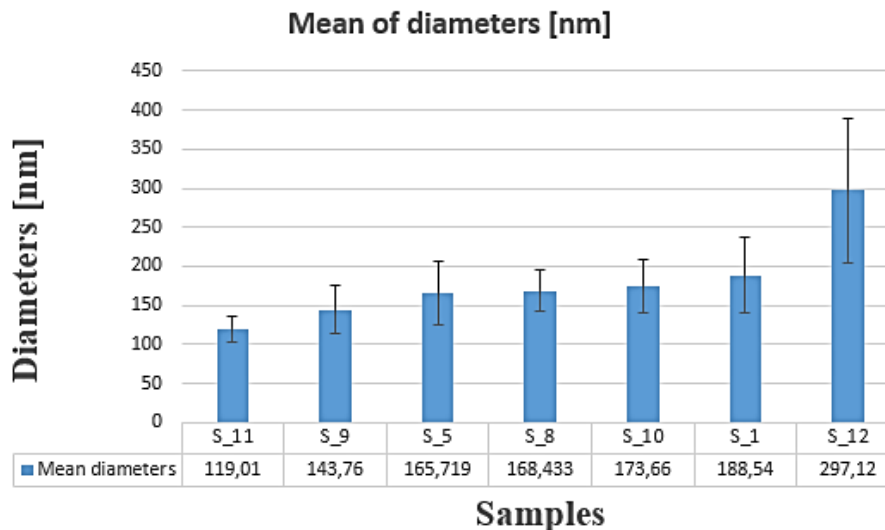


Figure 5.3. Mean of diameters.

Sample diameters are given in Figure 5.3. The biggest diameters were obtained from S_12 and the smallest diameters were obtained from S_11. According to Figure 5.2 and Figure 5.3, they indicate that when the diameters of the nanofibers increases, the pore

size are getting to be smaller. Also, in higher area density (gsm), the diameters were bigger and the pore sizes were smaller.

5.3. Air Permeability

Generally, it is expected that lower gsm induces higher permeability. The main aim to measure the air permeability is to test the lamination process. If the lamination process is not proper, the adhesive can cover all the pores of the nanofibers. Therefore for each membrane, the air permeability test was done. According to results of air permeability, lamination process did not blocked the pores of the nanofiber web.

The air permeability results are shown in Figure 5.3 as a comparison of the samples in different gsm.

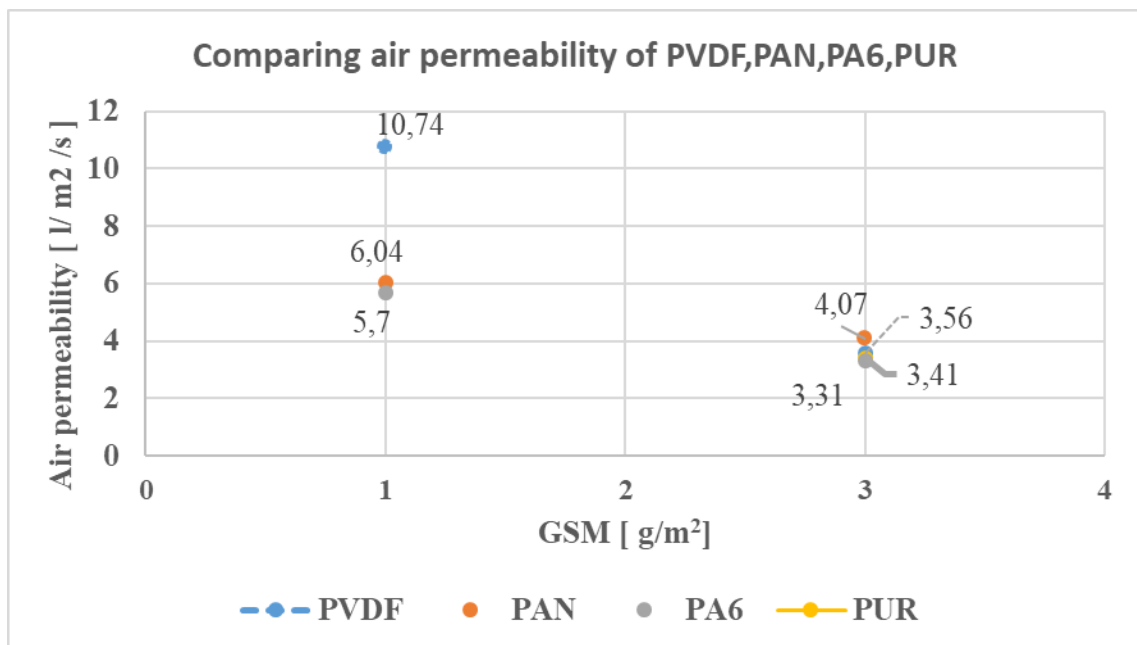


Figure 5.3.Comparison of the air permeability of each unmodified sample.

From the results, it was obtained for all the samples that in higher gsm, it has less permeability. It is very well know that compact structure cause to decrease in air permeability.

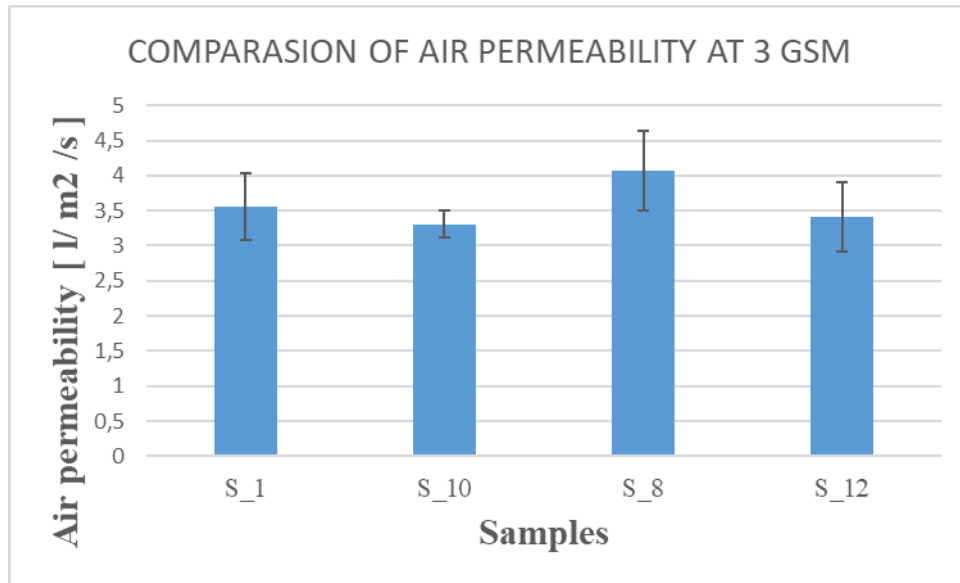


Figure 5.4. Comparasion of air permeability at 3 gsm.

In Figure 5.4, the samples were compared at the same gsm. More or less, all the samples showed similar air permeability. S_8 had the highest permeability and S_10 had the lowest permeability.

5.4. Strength (Delamination)

Bursting test was run to control the adhesion between the supporting layer and the nanofibers. By this method, the quality of the lamination can be determined. The Figure 5.5 shows the samples before and after bursting test. Nanofiber layer removed from supporting layer and created a protrusion. At least three measurements were taken for each membrane and the results are shown in Figure 5.6.

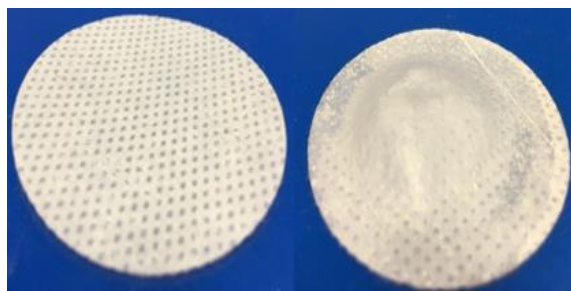


Figure 5.5. The multilayer nanofibrous membrane before and after the test

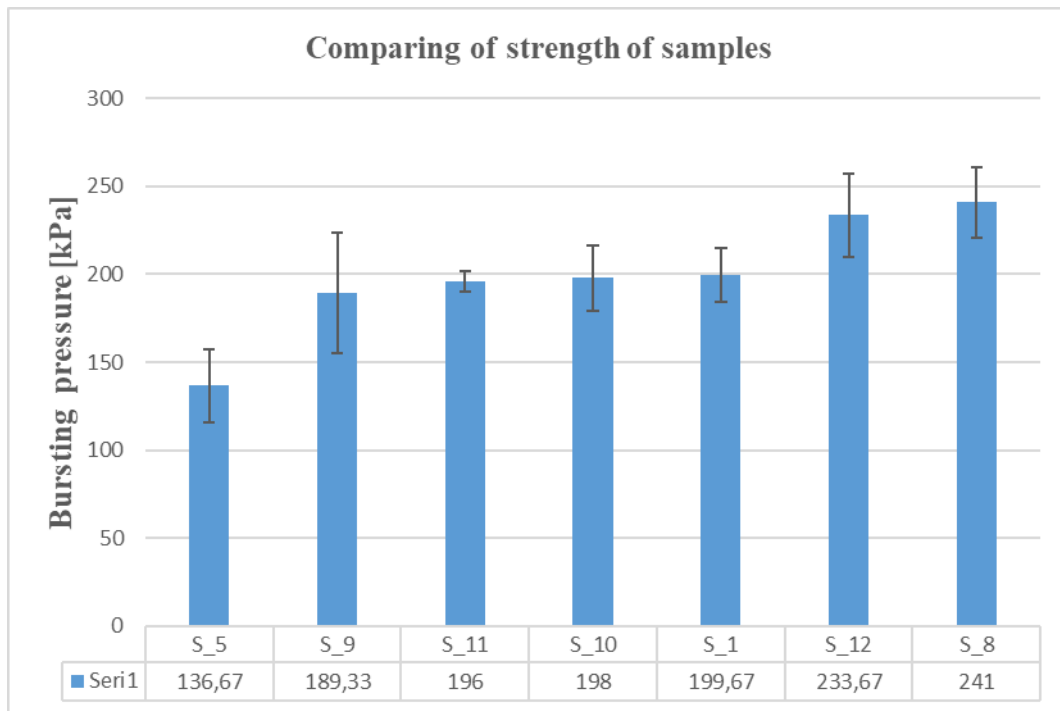


Figure 5.6. Bursting test of the membranes

The gsm is effecting the thickness of the layer. Higher gsm yields to higher thicknes of the web. The results indicated that higher gsm procures higher strength. The reason could be better adhasion of the thicker layer on the support and the better mechanical strength of the thicker layers due to interconnected fiber bundles compared to that lower thickness. During the lamination, the adhesive web overs the surface of the nanofibers and gives a strong athesion. If the nanofiber layer has very low thickness (such as 1 gsm), it will easily damage and break from the surface. Therefore 3 gsm of each sample showed better resistance to bursting.

5.5. Contact Angle

The membranes which show contact angle less than 90° can be catagorized as hydrophilic membranes. The membrane wettability catagories are shown in Table 5.1. Water contact angle (CA) of membranes were measured for the modified and unmodified samples. Moreover, the CA was measured before and after separation test. It was assumed that once the membrane contact with oil/water emulsion, the CA characteristics changed due to surfactant and the oil contaminations in the emulsion. The contact angle results were shown in Table 5.2. Results indicated that all the membranes before modification showed hydrophilic properties. The reason could be due to lamination process. The surface hydrophobicity is related with the surface

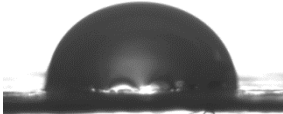
roughness. Under heat and pressure, the surface of the web can be changed. Moreover, the adhesive web has hydrophilic characteristics which might effect the surface of the nanofiber web too. The CA of the membranes changed after separation due to the surfactant effect.

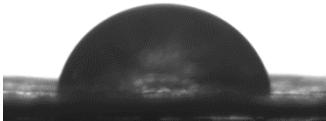
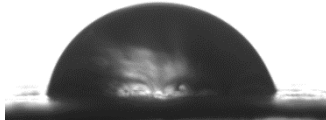
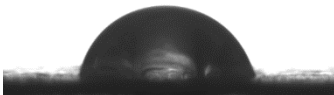
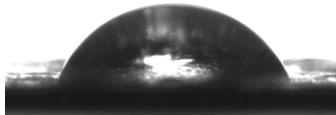
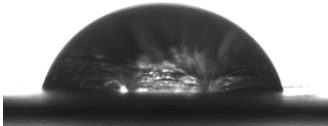
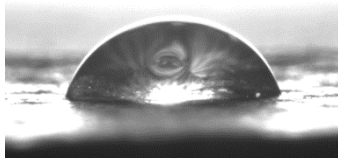
Apparently, modification process improved the hydrophilicity and the membranes became superhydrophilic. Surprisingly, S-14 and S-18 showed CA higher than zero. These two membranes were modified with NaOH+TiO₂. Moreover, the sample S-20 shifted from superhydrophilic to hydrophilic characteristics. The separation test showed this membrane had oil droplets in permeate which might cause oily membrane surface and decrease in wettability.

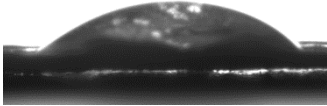
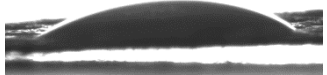
Table 5.1. Membrane categories according to wettability.


Condition	Nature	Effect
$\theta_c = 0$	Superhydrophilic	Complete wetting
$\theta_c < 90^\circ$	Hydrophilic	Water droplets spread up
$\theta_c \geq 90^\circ$ ($90^\circ - 120^\circ$)	Hydrophobic	Incomplete wetting
$\theta_c > 150^\circ$	Superhydrophobic	Repelled, no wetting

Table 5.2. Contact angle results

Sample	CA before separation	CA after separation	Image
S_1	$89,41 \pm 4,69$	$35,32 \pm 8,72$	

S_8	$78,86 \pm 3,92$	$69,8 \pm 1,5$	
S_10	$78,92 \pm 1,63$	0	
S_12	$77,2 \pm 3,55$	$65 \pm 7,01$	
S_5	$71,23 \pm 1,31$	$62,4 \pm 2,17$	
S_9	$73,93 \pm 2,61$	$39,9 \pm 3,47$	
S_11	$78,56 \pm 2$	$56,5 \pm 0,48$	

S_13	0	0	
S_14	$39,43 \pm 3,02$	0	
S_15	0	0	
S_16	0	0	
S_17	0	0	
S_18	$19 \pm 6,65$	0	
S_19	0	0	

S_20	0	$43,85 \pm 4,3$	*The image of CA after separation 
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5.6. Permeability

Decreasing of permeability was observed depending on the repeating of circulations as shown in Figure 5.7. There are several possible causes of reduction in permeability during filtration. The first reason is the concentration polarization, which is a consequence of the membrane selectivity. While the emulsion passes through the membrane, the solute is retained by the surface of the membrane with a relatively high concentration. Also, due to membrane fouling and concentration polarization, the hydrophilicity of the membrane is reduced during filtration. Other reason may be related to membrane pores compression/collapse; therefore it causes a reduction in permeability. Effective factors in membrane permeability are the operating conditions such as feed pressure, temperature, pH, flow rate, etc. [66–68]. After the repeating of the circulations, the water flux decreased due to membrane fouling which was because of oil droplets and additives effect.

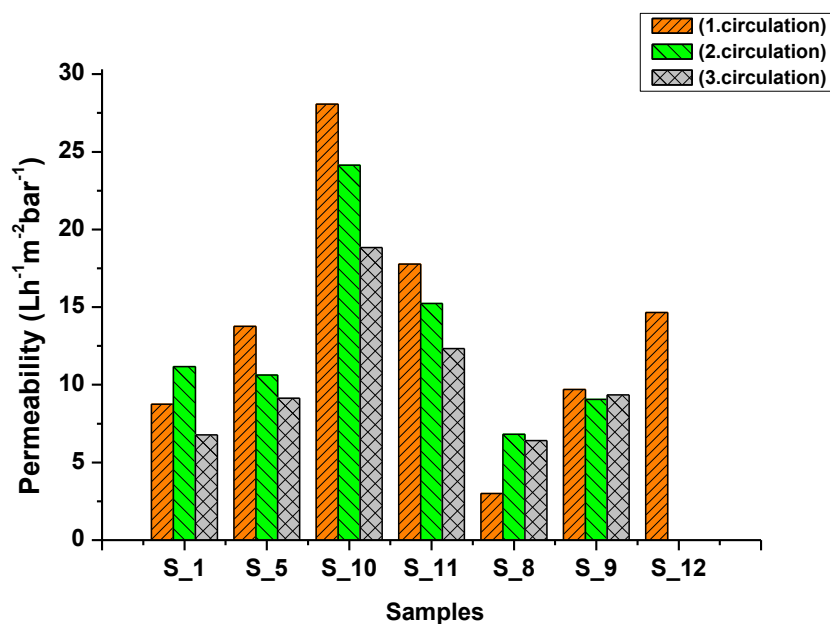


Figure 5.7. Emulsion permeability of the samples

PVDF, PAN, PA6, and PUR were tested, and from those samples, 2 samples were chosen to improve their emulsion permeability via surface modification. Considering the properties of polymers, air permeability and strength results S_1 and S_8 were found to be more advantageous.

PUR (S_12) nanofibers were not chosen due to low performance and fouling problem. Eventhough S_10 nanofibers showed very good permeability but it was not chosen. PA6 are not resistance to some acids, and long term using underwater can cause decomposition of the PA6.

5.6.1. First Modification

The permeability performance of PVDF (S_1) with NaOH and KOH modification is shown in Figure 5.8.

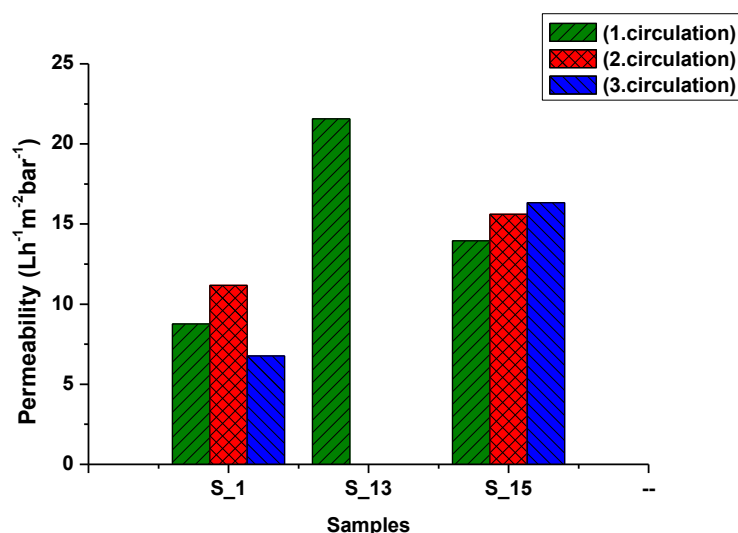


Figure 5.8. Permeability performance of PVDF

The performace of S_1 was decreasing after second circulation because of fouling problem (Figure 5.8). Therefore surface modification was applied to the membrane to increase hydrophilicty. Even hydrophilicty increased, the surface modification with NaOH decreased the permeability performance of S_13. The membrane hydrophilicity increased with the KOH modification, thereupon permeability performance increased.

The permeability performance of PAN (S_8) with NaOH and KOH modification is shown in Figure 5.9.

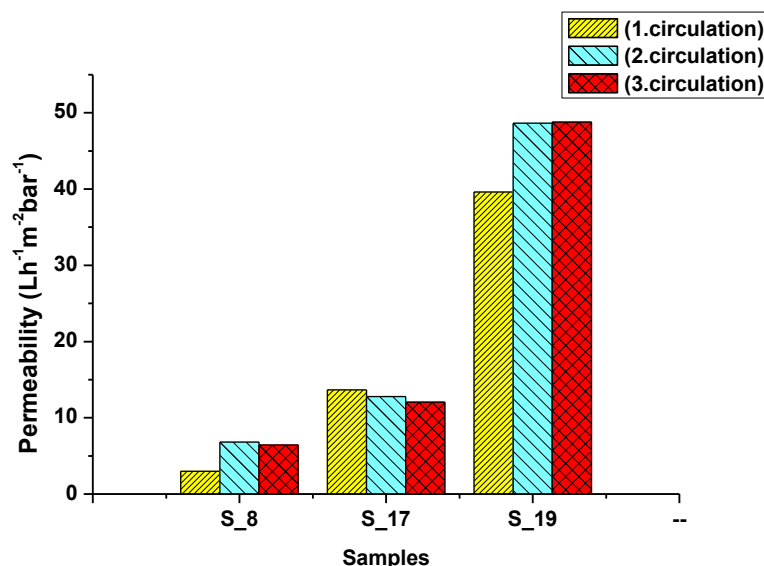


Figure 5.9. Permeability performance of PAN

The sample S_8 showed very low permeability. After alkali solution treatment, a remarkable increment in permeability was achieved. The treated membrane S_17 with NaOH had better hydrophilicity than S_8 thanks to carboxyl group($-\text{COOH}$) but the membrane still had fouling problem. The treated membrane S_19 with KOH had better hydrophilicity and performance than S_8 and S_17. Eventhough the 1 gsm sample (S_9) showed good permeability after 3 circulation, it was not chosen for the modification. The low gsm samples are mechanically not resistance. They could damage under alkaline solution. Moreover, with high gsm there is a better chance to have more hydrophilic active group on the membrane surface.

For both samples, the results indicated that surface modification with NaOH and KOH, hydrophilic hydroxyl groups on PVDF and carbonyl groups on PAN increased the hydrophilicity. As a result of first modification, membranes showed anti-fouling properties.

5.6.2. Second Modification

After NaOH and KOH modification, treated PVDF and PAN membranes were modified with titanium dioxide (TiO_2) nanoparticles to give self-cleaning and anti-bacterial properties. The results are shown in Figure 5.10 and Figure 5.11.

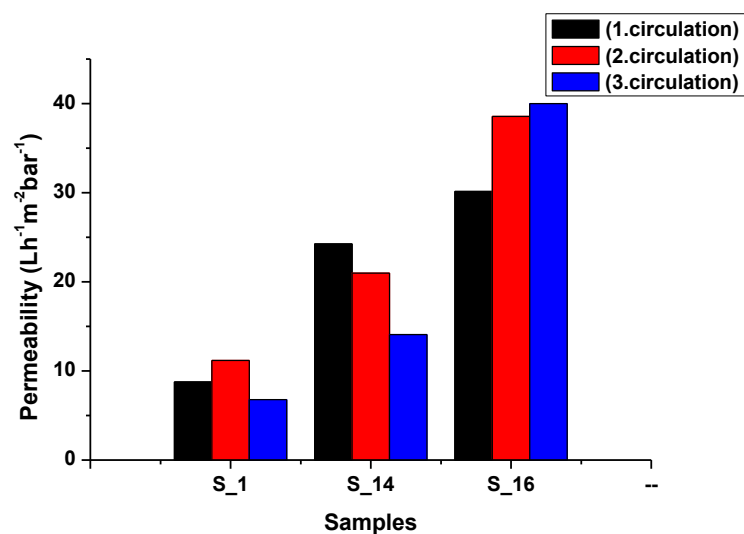


Figure 5.10. Permeability performance of treated PVDF with TiO₂

The Figure 5.10 shows the results of treated PVDF membranes with TiO₂. The sample S_14 is the membrane which was already treated with NaOH, the second modification was applied with TiO₂. It was expected that self-cleaning property will be applied to the membrane and performance will increase. Although the particles of TiO₂ were well distributed on the fiber surfaces, the fouling problem occurred and the permeability performance decreased. The sample S_16 which was already treated with KOH and then second modification was applied with TiO₂. The self-cleaning property was obtained and the permeability performance increased (Figure 5.10).

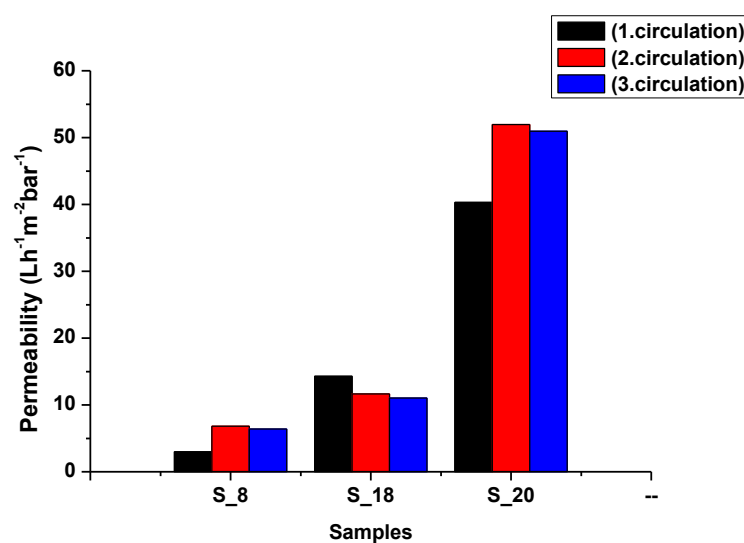


Figure 5.11. Permeability performance of treated PAN with TiO₂

The Figure 5.11 shows the results of treated PAN membranes with TiO_2 . The sample S_18 which was already treated with NaOH, the second modification was applied with TiO_2 . It was expected that self-cleaning property will be applied to the membrane and performance will increase. Although the particles of TiO_2 were distributed on the fiber surfaces, aggregation was observed. It was obtained from permeate that the membrane did not only filtrate the water from emulsion but also some oil droplets were in the permeate. The sample S_20 which was already treated with KOH, the second modification was applied with TiO_2 . The TiO_2 particles were not well distributed on the fiber surfaces, aggregation was observed. It is shown in Figure 5.11 that S_20 had better performance and self-cleaning property. But in the permeate, there were oil droplets which means that the selectivity was bad. The reason could be due to aggregated TiO_2 nanoparticles on the surface of the S_18 and S_20 which might change the surface morphology and wettability. Therefore the samples of PAN such as S_18 and S_20 are not good candidate for oil/water separation. From Figure 5.11, it seems that they had good performance, but weren't able to separate oil.

After all the results were compared, the best result was obtained by the combination of PVDF + KOH + TiO_2 which has a number as S_16. Both permeability performance and self-cleaning increased.

5.7. Selectivity

Depending on used membranes and surface modification, the selectivity of membranes was different and it is shown in Table 5.3. The feed solution was the same for all samples. It is shown from Table 5.3 that after separation of oily wastewater, permeate was obtained. For example; normally PVDF is hydrophobic and oleophilic. But after circulating with emulsion, the selectivity of PVDF changed. PVDF changed to hydrophilic/oleophobic characteristic. After treating the membranes with NaOH and KOH, the hydrophilicity increased. But for S_18 and S_20, selectivity was not good because there was still oily wastewater in permeate.

Table 5.3. The selectivity of membranes

Samples	Feed solution	Permeate
S_1	Oil+ Water	Water
S_5	Oil+ Water	Water
S_8	Oil+ Water	Water
S_9	Oil+ Water	Water
S_10	Oil+ Water	Water
S_11	Oil+ Water	Water
S_12	Oil+ Water	Water
S_13	Oil+ Water	Water
S_14	Oil+ Water	Water
S_15	Oil+ Water	Water
S_16	Oil+ Water	Water
S_17	Oil+ Water	Water
S_18	Oil+ Water	Oil+ Water
S_19	Oil+ Water	Water
S_20	Oil+ Water	Oil+ Water

6.CONCLUSION

In this thesis, properties of nanofibrous membranes such as; pore size, air, and emulsion permeability and selectivity, contact angle, strength, surface modification, and self-cleaning of membranes were discussed. The porous structure, hydrophilicity, the performance of membrane permeability, self-cleaning or anti-fouling are crucial factors for the oily wastewater separation. PVDF, PAN, PA6, and PUR nanofibrous membranes were tested in different densities (gsm). It was found that higher diameter induces smaller pores which affects the selectivity of the membrane. Moreover, the 3 gsm samples had better mechanical strength than 1 gsm.

Permeability performance of PUR was so low and after first circulation of emulsion, the fouling problem occurred. Due to decomposition of PA6 in long term application under water, this polymer was not selected for further steps. It is well know that in the presence of water, the entanglement and bonding between macromolecules of polyamide decreases. The reason is the water acts as plasticizer. As a result, strength of

the polyamide polymer reduces. Due to these reasons, PVDF and PAN were selected for further step.

Normally, PVDF membranes are separating oil from the oily wastewater because PVDF has hydrophobic and oleophilic nature. Contrary in our experiment, during the emulsion separation, the PVDF membranes showed hydrophilic and oleophobic characteristics. The membrane behaviour has been changed. The reason might be due to surfactant which increases the hydrophilicity of the membranes. It was found that remarkable progress has been made via the surface modification of the membranes for separation of oily wastewater. The permeability results showed that PVDF membranes showed extraordinary flux and permeability after surface modification with alkaline solutions and with TiO_2 . The membrane hydrophilicity increased due to increase in hydroxyl groups on the membrane surface. Therefore, the membrane showed the self-cleaning or anti-fouling property. Additionally, SEM images indicated that TiO_2 nanoparticles were attached on the PVDF surface and distributed very well without any aggregation. Oppositely, the TiO_2 nanoparticles were aggregated on PAN membranes which might play a role on the membrane hydrophobicity. Modified PAN membranes only with alkaline solution showed high water permeability. The SEM results indicated that the PAN nanofibers diameters were slightly increased after surface modification. The reason was due to swelling of the PAN nanofibers under alkaline solution. It can be conclude that modified PVDF nanofibrous membrane showed the best efficiency and antifouling property compared to others. PVDF membrane is promising for separation technology.

As a future work, it is suggested to continue on;

- measurement of the membrane life-span,
- measurement of long-term efficiency of the membrane,
- measurement of anti-bacterial efficiency,
- controlling the secondary pollution (can be from membrane or nanoparticles),
- proper cleaning process of the membranes without any damage.

7. REFERENCES

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8. APPENDIX

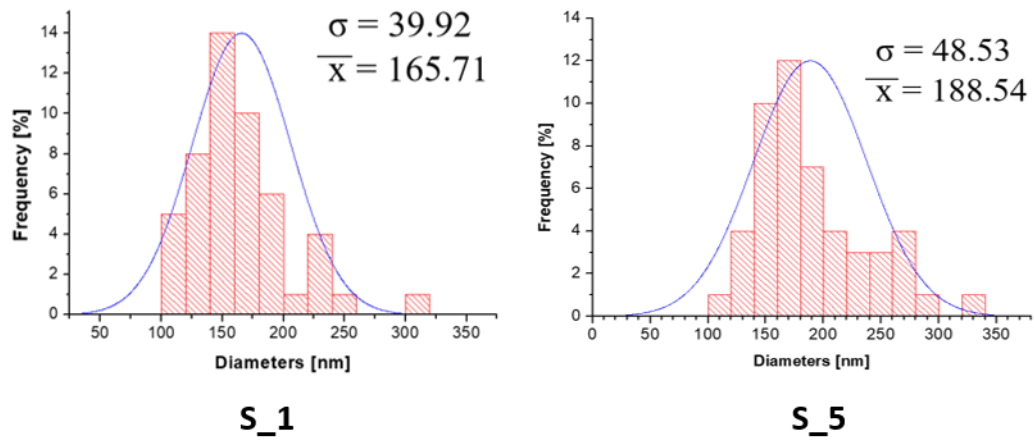


Figure A1. Fiber diameter of S₁ and S₅.

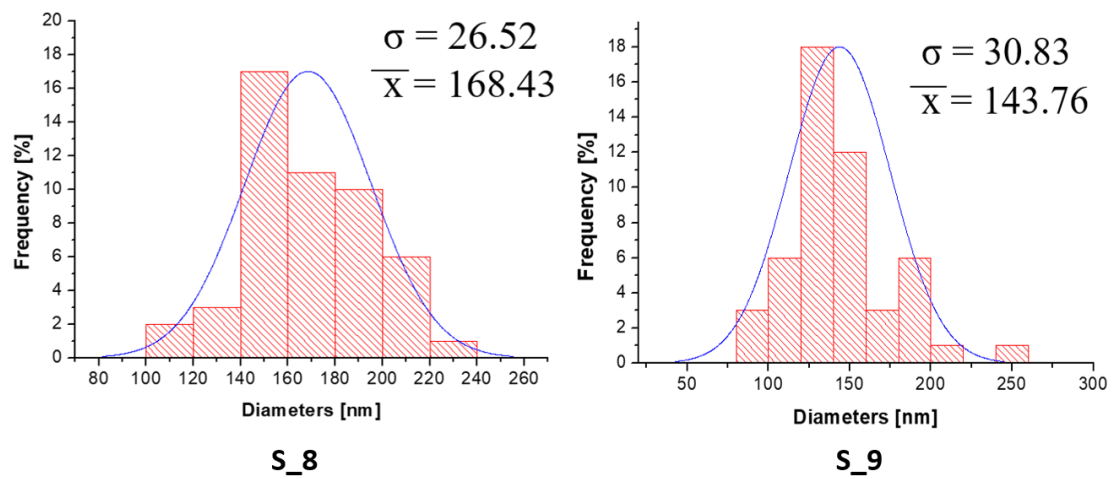


Figure A2. Fiber diameter of S₈ and S₉.

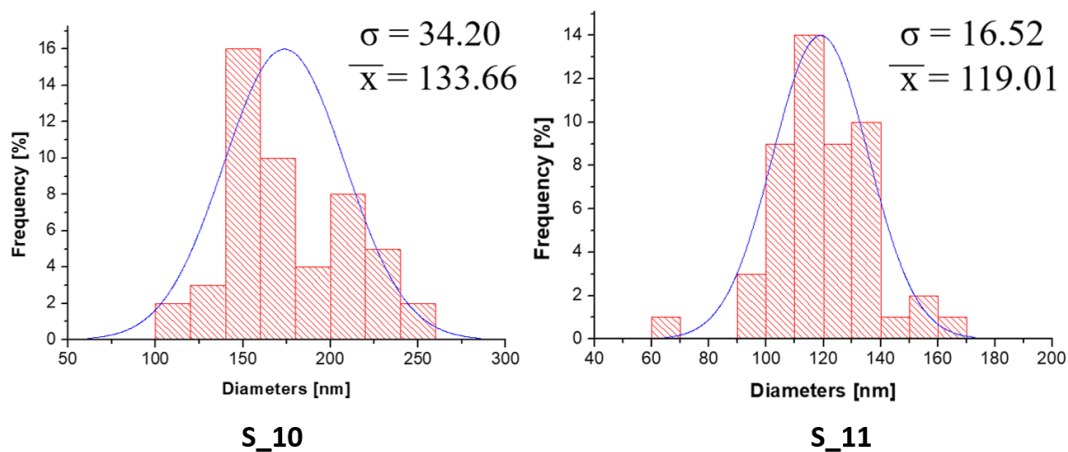


Figure A3. Fiber diameter of S₁₀ and S₁₁.

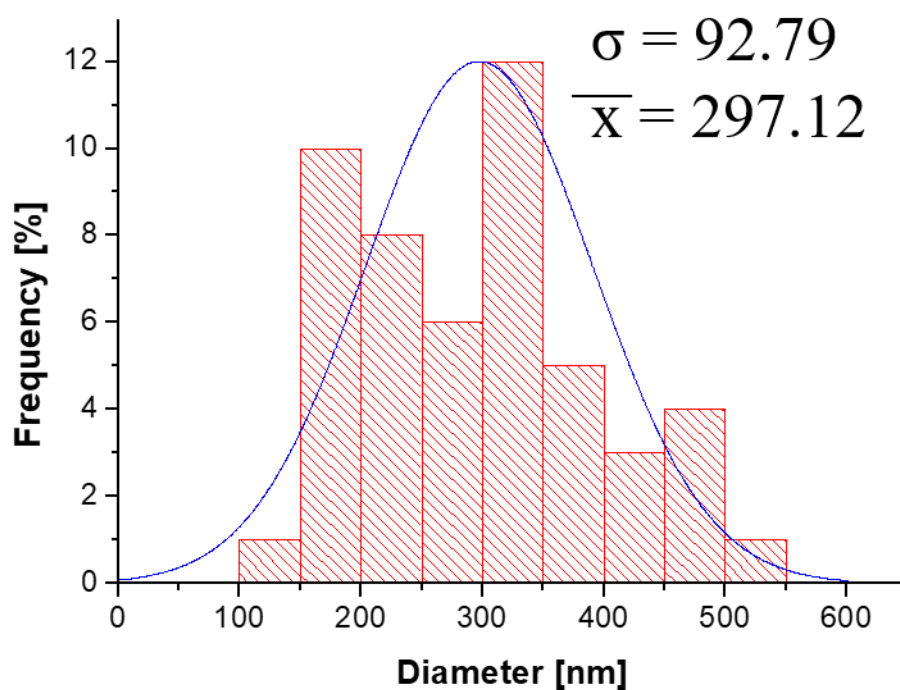
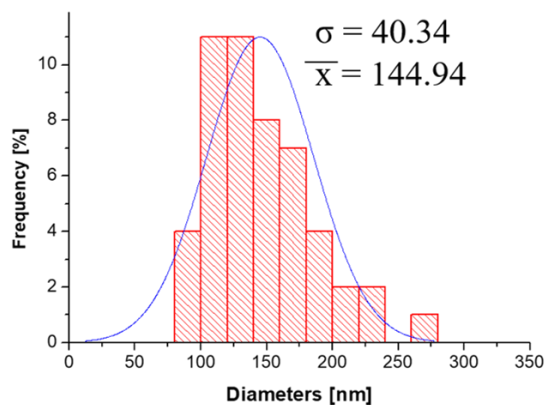
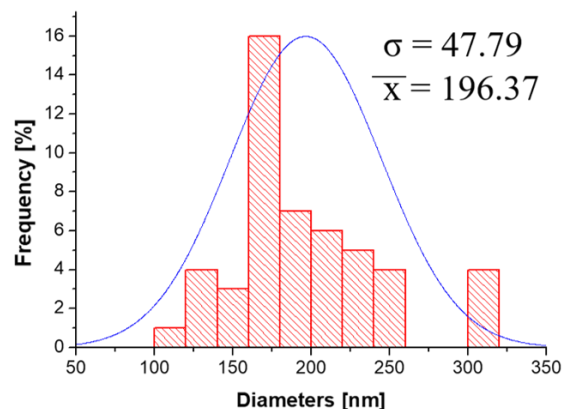


Figure A4. Fiber diameter of S₁₂.

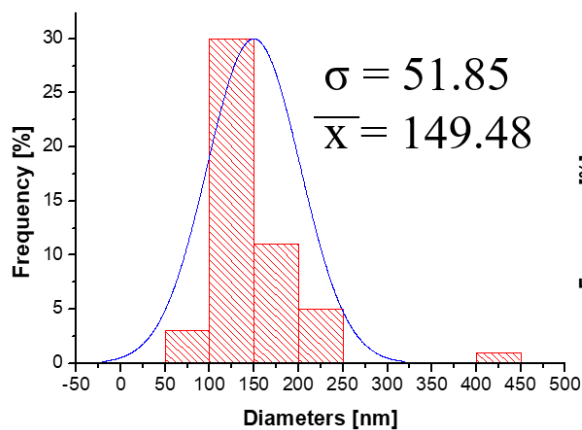


S_13

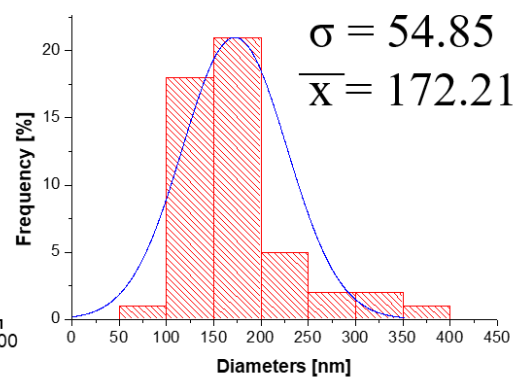


S_14

Figure A5. Fiber diameter of S_13 and S_14.

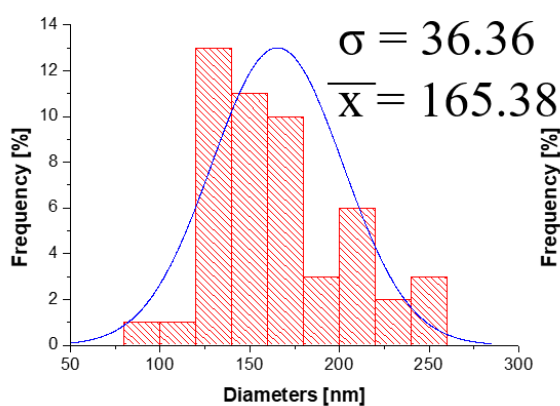


S_15

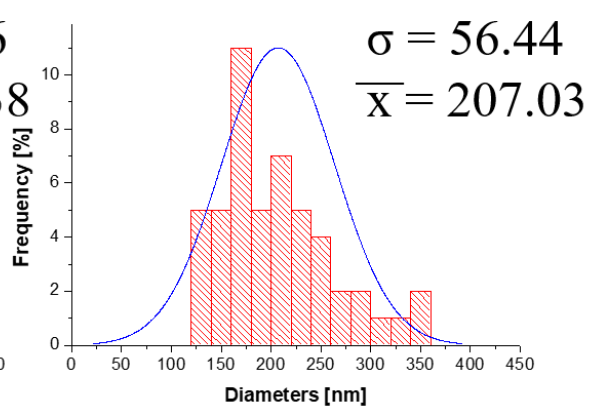


S_16

Figure A6. Fiber diameter of S_15 and S_16.



S_17



S_18

Figure A7. Fiber diameter of S_17 and S_18.

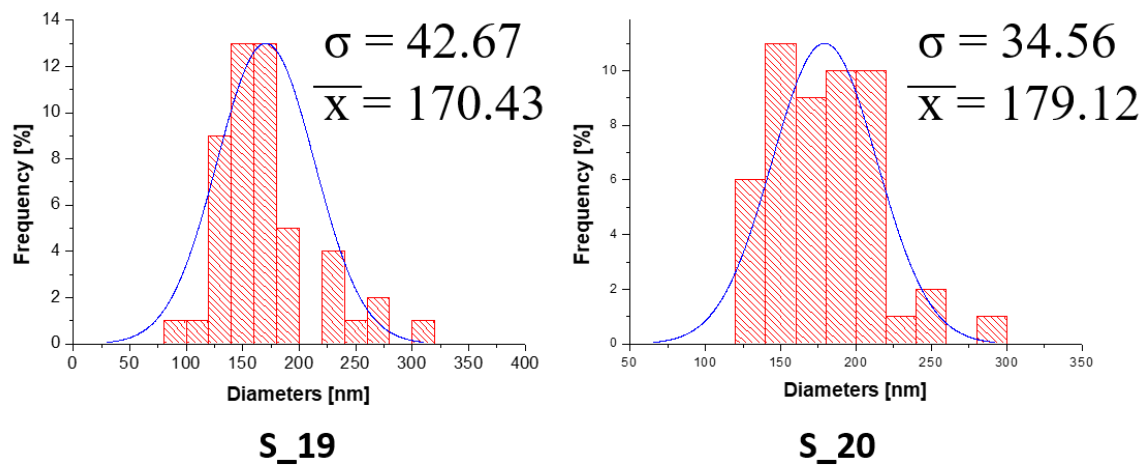


Figure A8. Fiber diameter of S_19 and S_20.

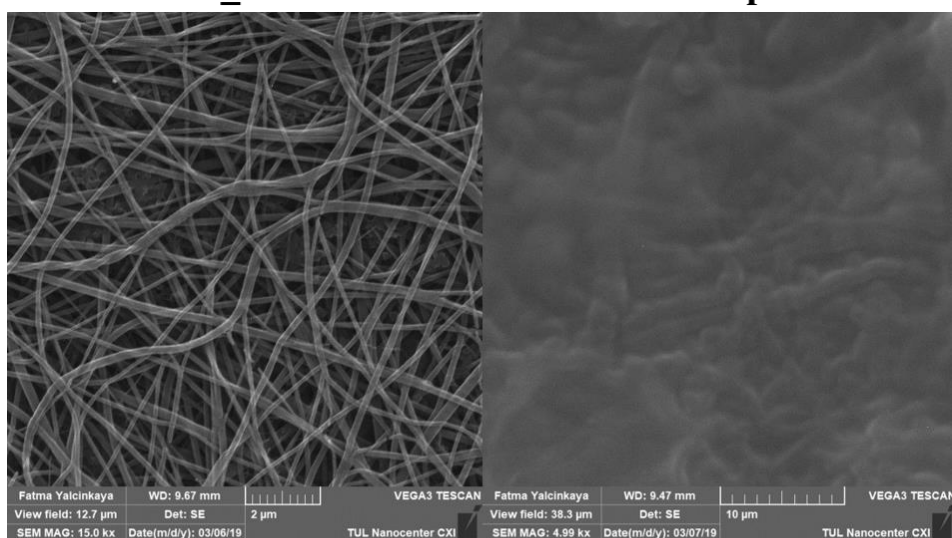
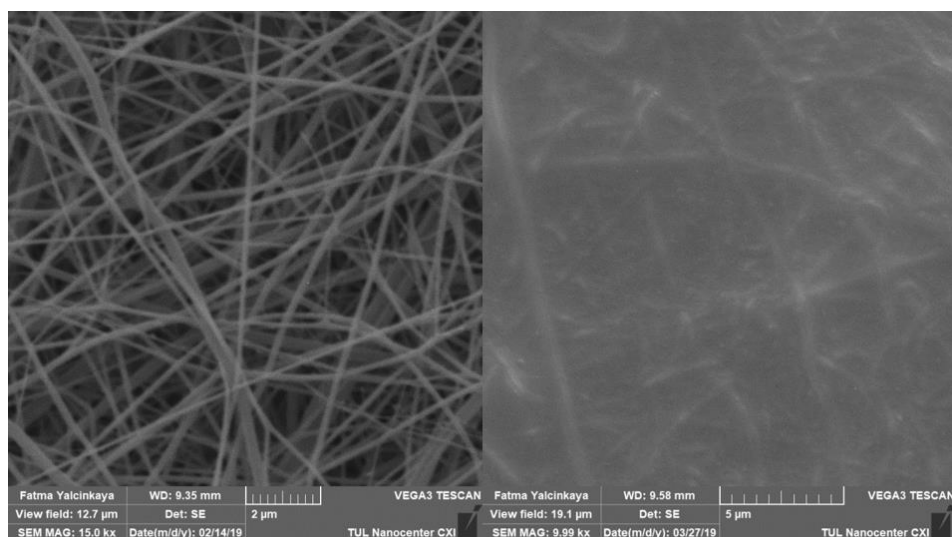
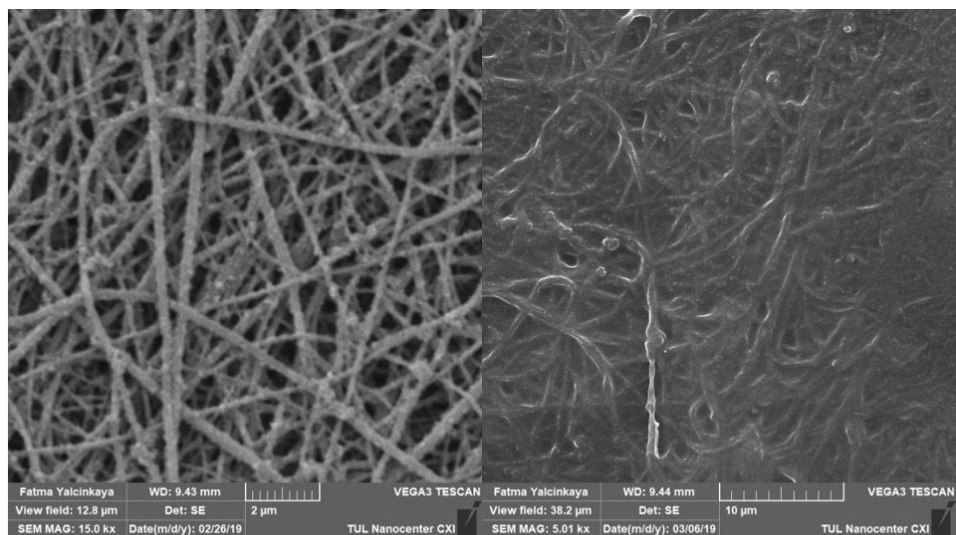
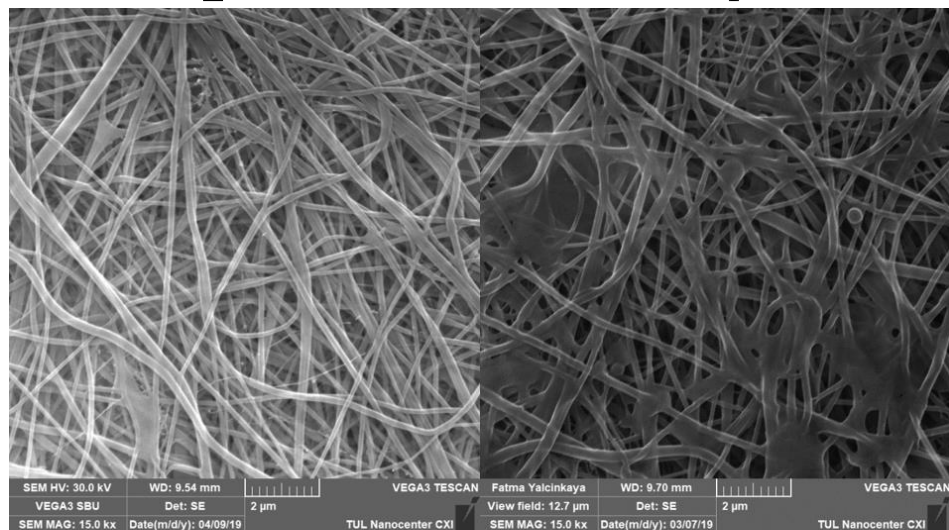


Figure A9. SEM images of S_1 and S_13.



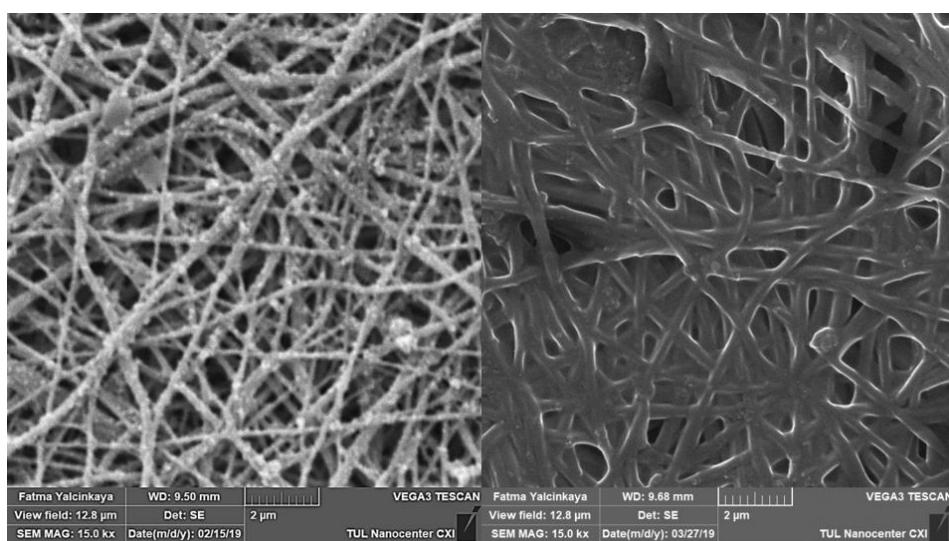
S_14

After separation



S_15

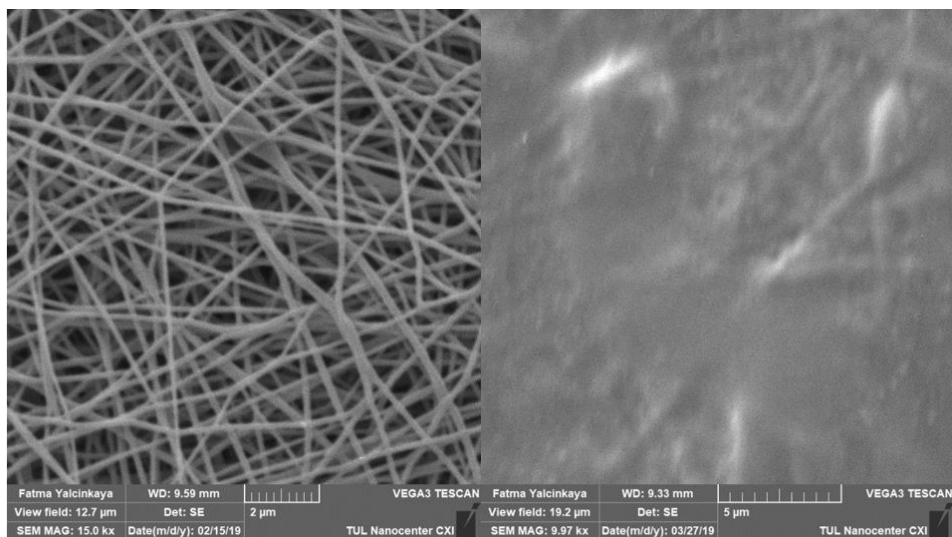
After separation



S_16

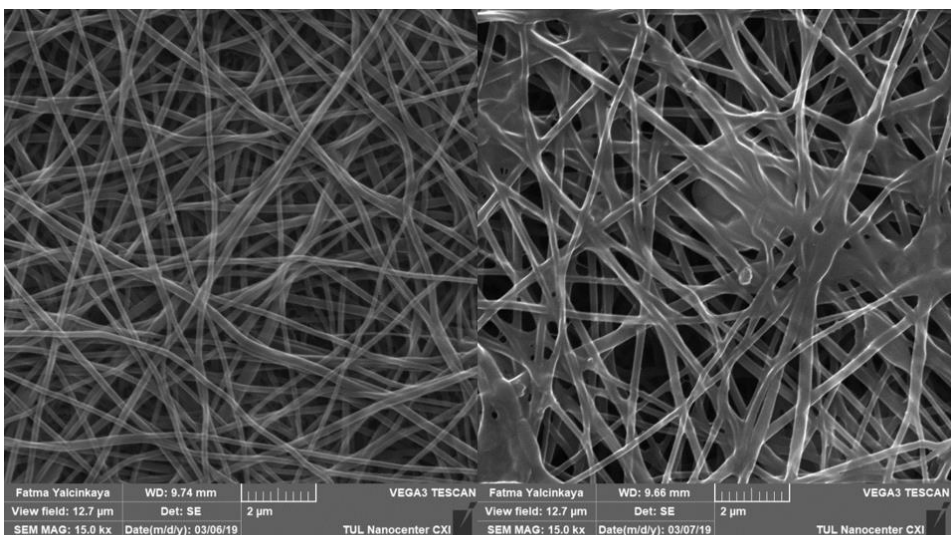
After separation

Figure A10. SEM images of S_14, S_15, and S_16.



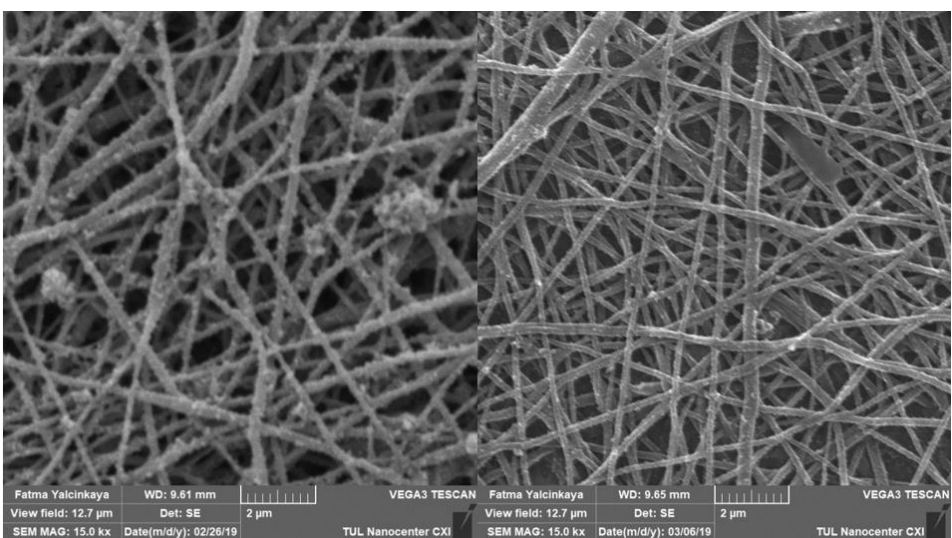
S_8

After separation



S_17

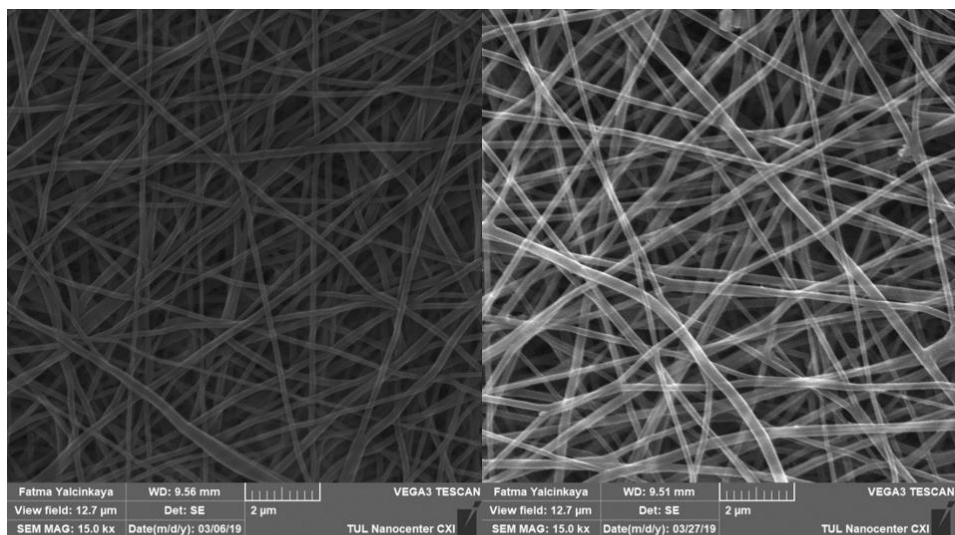
After separation



S_18

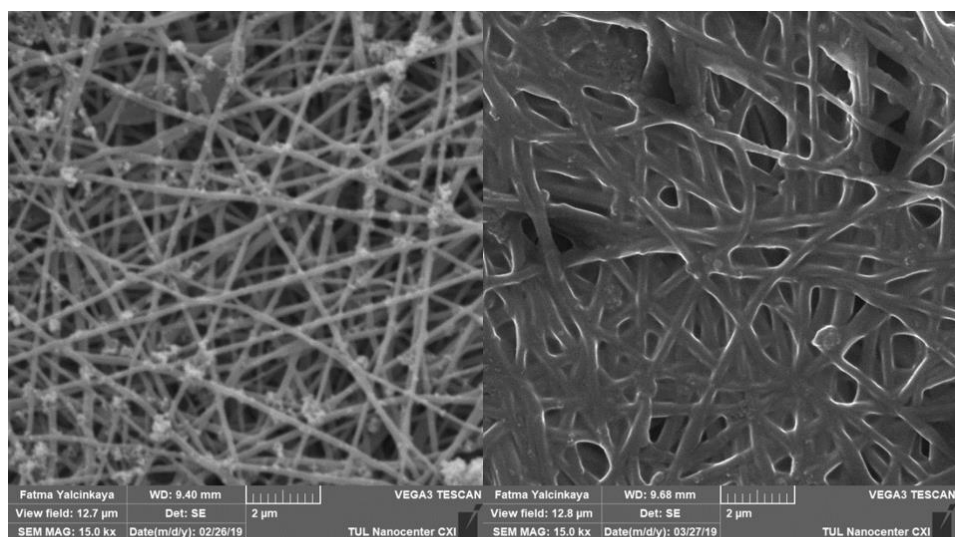
After separation

Figure A11. SEM images of S_8, S_17, and S_18.



S_19

After separation



S_20

After separation

Figure A12. SEM images of S_19 and S_20