



Surface Modified Nanofiber Membranes: Characterization and Application

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3. Sutherland KS, Chase G. Filters and filtration handbook. Elsevier; 2011 Apr 18.
4. Baker RW, Cussler EL, Eykamp W, Koros WJ, Riley RL, Strathmann H. Membrane separation systems—A research and development needs assessment. USDOE Office of Energy Research, Washington, DC (USA). Office of Program Analysis; USDOE Membrane Separation Systems Research Needs Assessment Group (USA); 1990 Apr 1.
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Abstract

Separation of oily wastewater, especially emulsified oil / water mixtures, is a worldwide problem due to the large amount of oily wastewater generated in many industrial processes and everyday life. For the treatment of oily wastewater, membrane technology is considered to be the most efficient method due to its high separation efficiency and relatively simple operation process.

PVDF membranes are used to separate the oily water emulsion. Measurements were made on a dead end device designed in our laboratory. Membranes are coated with Ti-Ag nanoparticles and since nanoparticle synthesis is a green method. As a result of the experiments made, the best flux recovery and permeability results were obtained from PVDF-OH / 0.1 mMol and PVDF-OH/1 mMol NPs membranes.

Membrane technology that minimizes the damage to the environment has been accepted as useful and promising.

Keywords: Membrane, nanoparticles, wastewater, PVDF

Abstrakt

Oddělení olejové odpadní vody, zejména emulgovaných směsí olej / voda, je celosvětovým problémem kvůli velkému množství olejové odpadní vody vytvářené v mnoha průmyslových procesech a každodenním životě. Pro čištění olejových odpadních vod je membránová technologie považována za nejúčinnější metodu díky své vysoké účinnosti separace a relativně jednoduchému provoznímu procesu.

K oddělení emulze olejové vody se používají PVDF membrány. Měření byla prováděna na slepém zařízení navrženém v naší laboratoři. Membrány jsou potaženy nanočásticemi Ti-Ag a protože syntéza nanočástic je zelená metoda. Na základě provedených experimentů byly nejlepší výsledky regenerace a propustnosti toku získány z PVDF-OH / 0,1 mMol a PVDF-OH / 1 mMol NPs membrán.

Membránová technologie, která minimalizuje poškození životního prostředí, byla přijata jako užitečná a slibná.

Klíčová slova: Membrána, nanočástice, odpadní voda, PVDF

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LIST OF SYMBOLS

Symbols	Long Name	Units
PVDF	Polyvinylidene fluoride	
SEM	Scanning Electron Microscopy	
H ₂ O	Water	
OH ⁻	Hydroxide anion	
KOH	Potassium hydroxide	
NaOH	Sodium hydroxide	
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	
TiAg	Titanium Silver	
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

Water is essential natural resources in our life. Changing climatic conditions and world conditions with the increasing population will put even the richest countries in terms of water stress in the coming years [1]. The arid parts of North Africa and approximately half of the European countries face water scarcity. Even industrialized countries such as the USA are developing highly innovative technologies for water conservation and treatment, exhibiting the challenge of depleted water reservoirs as more water is drawn from the refilled. Of the 600 largest cities in China, 550 are facing water shortages because even the largest rivers are extremely polluted, and not to mention the treatment of drinking water, even their use for irrigation, should be neglected [2].

A group of leading climate impact researchers has shown that climate change increases possible regional and global water scarcity. They estimate that 2 °C of global warming above current temperatures will bring about 15% of the global population to face a severe decrease in water resources and increase the number of people living in absolute water scarcity by at least 40% compared to the impact of population growth alone [2].

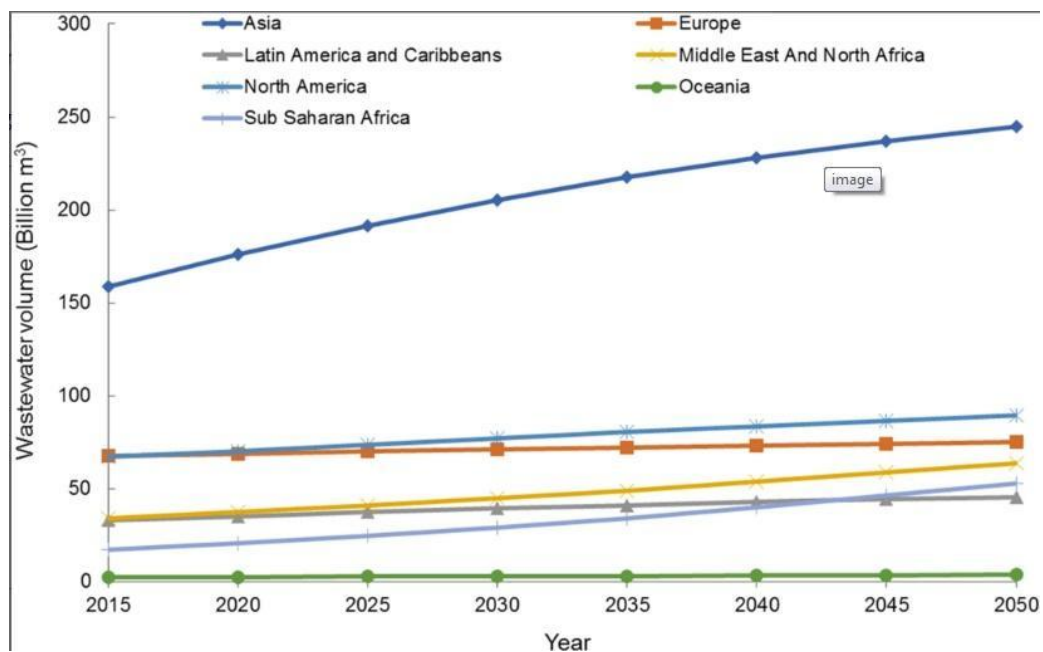


Figure 1.1 Wastewater production across regions in 2015 and predicted until 2050

The area with direct and indirect wastewater irrigation was recently estimated at 36 million hectares, of which 29 million hectares are exposed to direct and indirect use of untreated wastewater [3]. A significant part of this land is close to urban areas.

Data from coastal cities flowing into the sea were excluded. These estimates are based on modeling studies and are considered wastewater in both diluted and undiluted forms with a crop density of 1.48 [3]. Estimates will point to an irrigation potential of 42 million hectares of undiluted wastewater, given the same crop density and including coastal cities.

As some of the wastewater is discharged into the oceans, not all municipal wastewater is collected, and competition for land increases around cities, it may take decades to reach planned use for full-scale wastewater collection, treatment, and irrigation, or for other purposes where natural water supply is limited. Flux recovery rate of samples after using kitchen oil [3].

Due to the expected increase in the urban population in the coming years, there will be a rising need for water supply in urban areas compared to increasing wastewater volumes. The estimates show that global wastewater production is expected to reach 470 billion m³ in 2030 by the end of the Sustainable Development Goals period, a 24% increase over current wastewater creation; and, it will be expected to reach 574 billion m³ by 2050 which will increase 51% above the current level as shown in Figure 1.1 [4]. The scenarios put forward an opportunity to address the water scarcity in dry lands through agriculture, aquaculture, agroforestry/landscaping, aquifer replenishment and direct collection, purification, and purposeful use of wastewater, suggesting that more wastewater will be available in the coming years [3].

There is a lot of concern expressed about the global environment and its effects on people. These concerns are related to doing anything with climate change and possible human causes; ongoing hunger in vast regions of an otherwise wealthy world; or the transformation of illegal consumption into a sustainable expansion, large areas of the world begin to note the need to make parallel changes in their environment and the way life is conducted; especially in energy consumption and freshwater supply [3].

The general importance of environmental protection justifies mentioning here because filtering has an important role to play in most programs trying to achieve this protection. Environmental protection legislation has been in place in the US and Europe for several decades, but the beneficial effects are only just beginning to emerge [3].

Similar processes exist in other developed regions, but developing countries have tough decisions to allow enlargement to relax, to satisfy or rein their people’s natural desire for higher living standards, to give sustainability a chance [4].

Market forces imposed by environmental legislation are an important driving force for the filtration market. The legislation calls for the minimization of waste and the continuous higher standard treatment of inevitable waste streams, both of which are well received by existing and emerging types of filtration equipment [4].

The separation industry itself can make a useful contribution to energy savings, all filters need some kind of driving force, especially in high-pressure membrane systems, and the design of filter systems to minimize energy demands is an important feature of the development of such systems [3–5].

It is estimated that the industrial water treatment technologies market will increase by 50%. In 2025, North Africa, Middle Eastern countries, Pakistan, India, and Northern China are expected to experience water shortages. It is assumed that industrial water consumption is will increase by 2025 [6].

Domestic water consumption will increase by 1.4 times, water consumption for agricultural activities 3189 km³/year it is expected that net water consumption will increase by 1.2 times 2152 km³/year. The expected world’s energy demand is to increase by 40% and water demand by 50% by 2030. Today, renewable freshwater resources are decreasing day by day in the world [5, 6].

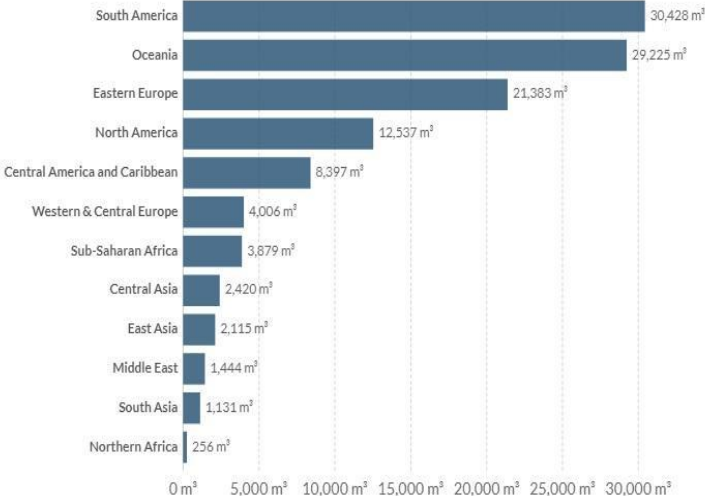


Figure 1.2 Per capita renewable freshwater resources, 2015

Average renewable freshwater resources per capita are measured in cubic meters per person. Renewable internal freshwater resources refer to the amount of inland freshwater from inlet river basins and recharge groundwater aquifers. Figure 1.2 [5] shows the average per capita renewable freshwater resources measured in cubic meters per person per year.

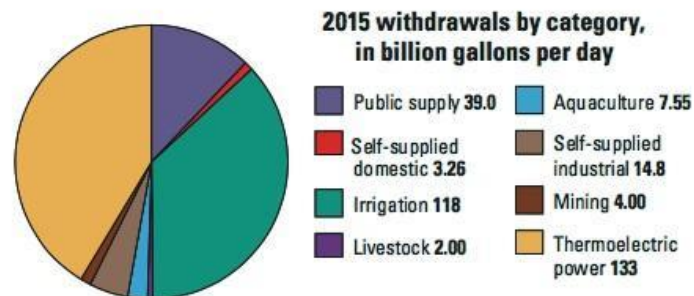


Figure 1.3 2015 water-use withdrawals by category

The three largest categories, shown in Figure 1.3 [6], were thermoelectric power, irrigation, and public supply, which cumulatively accounted for 90% of the total.

The wastewater reuse method can be used to supply water for both industrial and community applications [7].

The ability to reuse water has positive benefits, such as increasing water resources or managing nutrients in treated wastewater. These benefits include [8];

- Improved agricultural production;
- Reduced energy consumption;
- Reuse of treated wastewater and nutrient loads falling into receiving waters.

Water reuses are mostly non-potable uses, such as car washes, toilet flushes, cooling water for power plants, water used for concrete mixing, irrigation for artificial lakes, water used for golf courses, and water used in public parks [9].

Water contamination is observed often as a result of human activities. Lakes, rivers, oceans, and groundwater make up bodies of water. Water pollution occurs when pollutants enter the natural environment [10, 11]. Surface water and groundwater pollution are types of water pollution.

Various chemicals and pathogens and physical parameters are among the causes of water pollution. Contaminants may contain organic and inorganic substances [12, 13].

Wastewater must be removed from people, animals, and plants because even small amounts of wastewater chemicals can be toxic to plants, humans, and soil. Unfortunately, some unrefined petroleum waste is dumped into rivers, lakes, or the sea [13].

Wastewater mixed with sand and chemicals is pumped underground to release oil and gas from it. Wastewater mixed with groundwater then returns to the soil, creating a large amount of saline and toxic waste. These waters, which eventually return to the soil, directly affect human health as a result of irrigation of food crops or use for any process [13].

The oil-water emulsion released from domestic wastewater to the soil is one of the most serious issues that endanger human life and the ecological system. Therefore, there is a great demand to produce oil-water emulsion separation systems. For this; a method with high efficiency, low fouling properties, and easy to apply and manage is required [14].

2. THEORETICAL PART

In this chapter of the thesis, membrane technology, membrane separation history, advantages of membranes in separation, membrane fouling phenomena, surface modification of the membranes for anti-fouling properties, nanofibers in membrane technology, advantages of nanofibers and nanomaterials in membrane technology and the aim of work will be explained.

2.1 Oily Wastewater

With the development of the industry, there is an increase in the amount of oil used, despite various technical and managerial developments; too much oil cannot be prevented from flowing into the water and causing pollution. The treatment of oily wastewater sources in the oil industry is extensive [15].

The effects of oily wastewater pollution are seen in the following ways [15]:

1. Affects drinking water and groundwater resources, endangering water resources,
2. Endangers human health,
3. It creates atmospheric pollution,
4. Badly affects crop production,
5. Destroys the natural landscape and possibly even results in the compounding of oil-burning safety issues that arise.

Today, in the field of environmental engineering problems, there is an urgent need for oily wastewater treatment [15].

Table 2.1 Sources of oily effluents

Industrial Process	Oil Concentration (mg/L)
Petroleum refining	20-4000
Metal processing and finishing	100-20000
Copper wire drawing	1000-10000
Edible oil refining	4000-6000
Car washing	50-2000
Aircraft maintenance	500-1500
Leather processing (tannery effluents)	200-40000
Wool scouring	1500-12500

Oily wastewater occurs after many industrial processes as shown in Table 2.1 [16]. Oils and greases in wastewater are generally classified as hazardous waste and must be disposed of. Oily wastewater is usually in an emulsified form, inverse emulsions, total dissolved solids, or suspended solids. For emulsion-type oily wastewater, the oil droplets are dispersed throughout the water. Water is in the continuous phase and is the dispersion medium while the oil is in the dispersion phase. Oil must be removed from the water to meet the discharge requirements of the water. The oily wastewater in inverse emulsions, which is the opposite of emulsions, contains water droplets dispersed within the oil droplets. Here, water is a byproduct of oil production, must be separated from the oil. Total dissolved solids type oily wastewater, with small particles scattered all over. The main feature can be given that the particles cannot be filtered with the filter paper. As a result, the particles will collapse under the influence of gravity, but this is a time-consuming method. Suspended solids consist of particles in water, similar to a colloidal suspension. Suspended solids typically float in water rather than disperse. Because the particles are larger, they can be filtered much more easily, but coagulants and flocculants are sometimes still needed to speed up the process [17].

2.1.1 Classification of Oil in Wastewater

The source of oils in wastewater can be mineral, animal, or vegetable. According to the physical form of the oil, it is mostly divided into four categories [14].

- a) Free (floating) oil: it rises to the water surface rapidly in settled conditions.
- b) Dispersed oil: they are fine oil droplets, but they do not contain surfactants stabilized by electrical charges.
- c) Emulsified oil: the dispersion of emulsified oil in water is more stable due to the use of surfactants; otherwise it is similar to dispersed oil.
- d) Soluble oil:

When the diameter of the droplet is higher than 150 μm it is categorized as free oil, between 20-150 μm dispersed oil, and when smaller than 20 μm as emulsified oil [14].

2.2 Treatment of Oily wastewater

Different techniques are used for the purification of water from oil. The most common techniques are known as membrane filtration, chemical destabilization, and electrochemical destabilization. Biological processes are used less frequently as they contain biocides to prevent the degradation of industrial fluids [14].

Distillation, although expensive, can be an attractive alternative if the waste is contaminated with soluble compounds and cannot be removed by other techniques [14].

2.3 Conventional Treatment Techniques of Oily Wastewater

2.3.1 Gravity separator

Free oils in water normally exist either as a floating mass or in the form of oil droplets larger than 150 μm . Free oil can be separated with the spillway in the tank, weight separator, and skimmer. The gravity separator consists of an empty container that allows liquids to be held for a long time. This will help settle under gravity and form two separate layers. As shown in Figure 2.1 [18], proper hydraulic design and longer holding time increase separation efficiency [19].

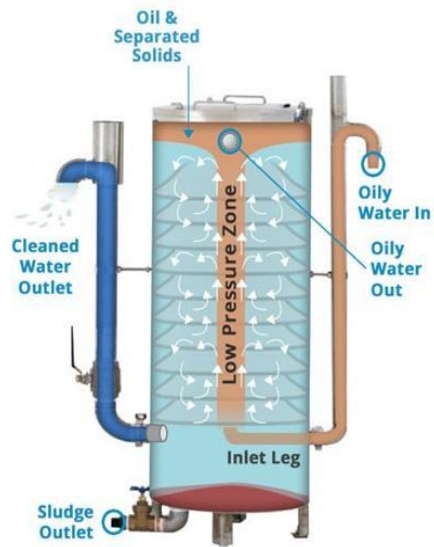


Figure 2.1 Gravity Separator

2.3.2 Flotation

The flotation technique applies a process similar to the gravity separation concept to remove oil and grease from wastewater, as oil is lighter than water [20].

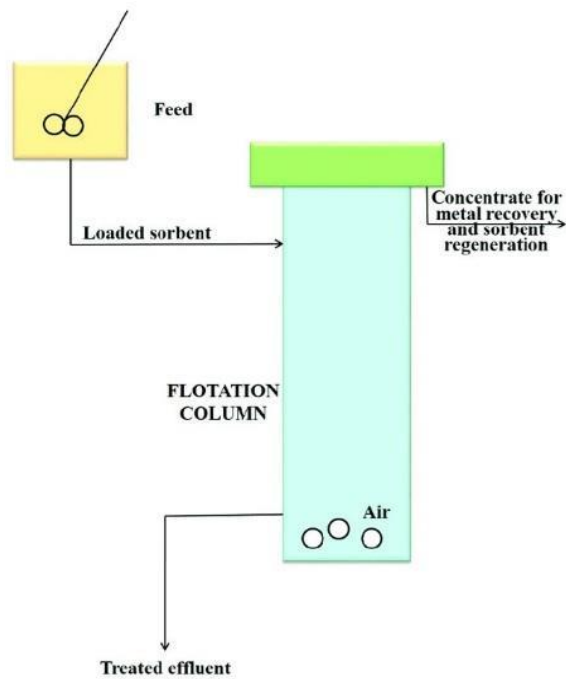


Figure 2.2 Scheme of a counter-current dispersed-air flotation rig

The flotation technique consists of four basic steps [20]:

1. Forming air bubbles,
2. The effective connection between oil droplets and gas bubbles,
3. Gas bubbles sticking to oil droplets,
4. Rising of the air-oil combination.

The successful flotation process allows an effective bonding of the oil droplets with the gas bubbles until the surface of the flotation cell is covered by bubbles [20].

Flotation can be carried out in rectangular/cylindrical mechanically stirred vessels or flotation columns. The mechanical bowl is equipped with a stirrer and air diffuser at the bottom of the mixing tank to deliver air and aid in the mixing process. In flotation columns, air diffusers are used under a long column to deliver air while exhausting the slurry from the top of the column [19]. The process is shown schematically in Figure 2.2 [20].

Advantages of the flotation technique [20];

- Less sludge generation,
- Separation efficiency,
- Treatment of oily wastewater has great potential,
- Flotation dissolved air flotation, buoyancy, and jet impeller flotation techniques are generally the most used techniques.

However, there are some disadvantages [20];

- High energy consumption,
- The problem of repair and device manufacturing.

Multiple parameters affect efficiency in the flotation technique, such as bubble size, bubble rise velocity, bubble formation frequency. Oil removal is more than 90 % in flotation and oil removal is more than 90 % in dissolved air flotation [15].

2.3.3 Coagulation

In the chemical destabilization process, hydrolyzed metal salts such as Fe^{3+} and Al^{3+} are added as coagulation reagents. The electrochemical method involves coagulant generations by electrolytic oxidation of the appropriate anode material [21].

Coagulants allow the dispersion of the emulsion, the reduction of the surface charge of the droplets, and the separation of the oil droplets, after which they support the separation of the aqueous and oily parts by predictable precipitation or dissolved air flotation [21].

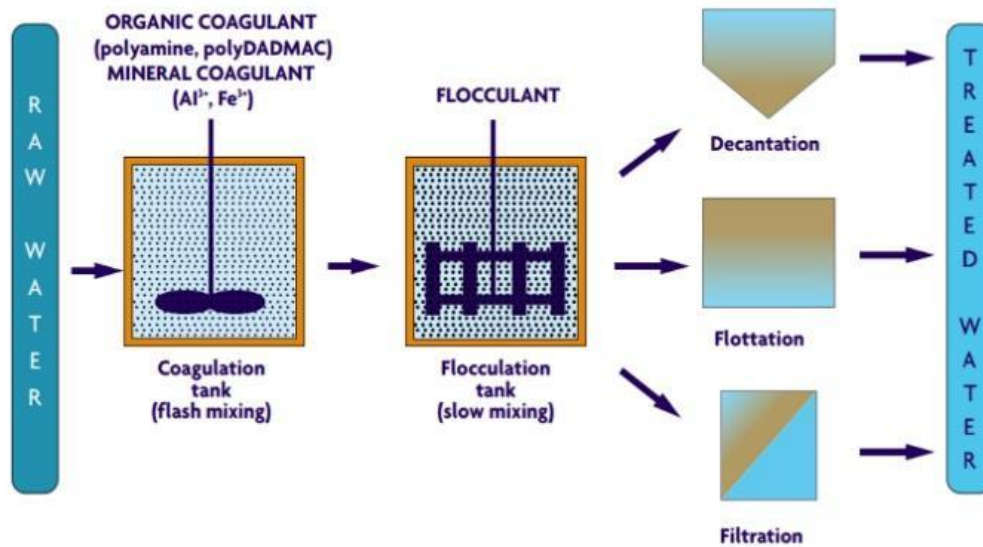


Figure 2.3 Physical and chemical process involved in Coagulation-Flocculation

The main destabilization mechanism is the binding of adsorbing macromolecules to more than one droplet at a time. Supporting destabilization by non-absorbent polymers is also a depletion flocculation mechanism. The process showed schematically in Figure 2.3 [21]. Electrically charged species as reagents in the mechanism can be electrically coupled to electric fields on the droplet surface [21].

Some scientists have investigated that the oil is eliminated from the emulsified wastewater by the adsorption properties of the growing metal hydroxides forming the particle nuclei and the adsorption properties to the adsorbing macromolecules that cause bridging flocculation. The core forms a small positively charged particle with adsorption layers of anions and cations placed around the core. This particle is a metal hydroxide and its ability to adsorb oil droplets is very high. The disadvantages of the coagulation method are that the cost is very high and it can cause secondary contamination of water bodies [22].

2.3.4 Biological Treatment

Biological treatment is the conversion of colloidal organic pollutants into stable harmless substances by dissolving water using microbial metabolism. It is widely used in biological filter and activated sludge methods [23].

Activated sludge in aeration tanks concentrates on the surface of microorganisms to separate organic matter using the current state vector as adsorption purifying microorganisms. Microorganisms cling to the filter. The biological treatment process is shown schematically in Figure 2.4 [23].

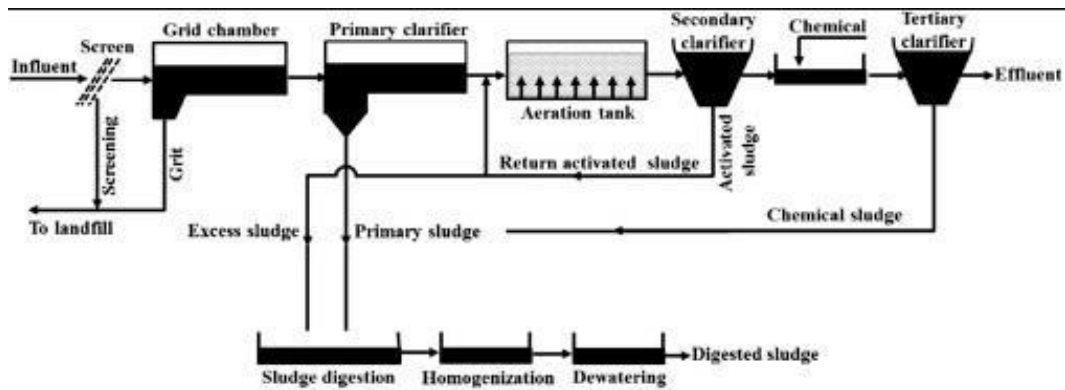


Figure 2.4 Biological treatment process

The wastewater that comes during the adsorption of organic pollutants passes through the filter surface and is decomposed by microorganisms. In the treatments of large-scale, heavy oily wastewater, a bio-treatment system has great potential [15].

2.4 Membrane Technology and History

The membrane allows some substances to pass while stopping others, so it is a selective barrier. These substances can be molecules, ions, or other tiny particles [24].

A membrane [24];

- Can be homogeneous or heterogeneous,
- Can be symmetrical or asymmetrical,
- Can be solid or liquid,
- Can bear a proton or electron charge,
- Can be neutral or bipolar,

Transport across a membrane can be affected by convection or diffusion of individual molecules [24].

Membrane technology has evolved into a fundamental separation technology, with numerous applications [24].

Application areas of membranes [25–28];

- Water and wastewater treatment,
- Domestic and industrial wastewater treatment and reuse,
- Obtaining drinking water from salty and brackish water,
- Separation and removal of organic materials,
- Production of industrial process water,
- Bacteria separation and removal,
- Gas separation processes,
- They have wide application areas such as the recovery of precious metals from water, wastewater, and liquid solutions.

Advantages of membrane technology [25];

- It works without the addition of chemicals,
- Lower energy requirement,
- Easy to use,
- Well-regulated process execution.
- High performance

Disadvantages of membrane technology [25–28];

- Fouling problem
- Membranes should be changed regularly
- Polluted water production because of backwashing.
- High cost for membrane production.
- As the processes increases, the permeability decreases
- Use of more modules because of used low flux.

In membrane separation, the efficiency is entirely dependent on the membrane itself and is currently more efficient than conventional techniques.

The membrane material composition and its corresponding surface chemistry are determined by its interaction with water, and thus its wettability, or in other words, its behavior against water [25–28].

- Hydrophilicity is a water-loving and interesting material property. Hydrophilic means “water-loving” and such materials easily adsorb water. Hydrophilic materials have high surface tension values. The surface chemistry of these materials allows a water film or coating to form on the membrane surface. The characterizations of hydrophilic materials are adopted by the presence of active groups capable of forming “hydrogen bonds” with water.
- Hydrophobicity compared to hydrophilic materials, there is an opposite or water-loving, irrelevant reaction to water interaction. There is little or no adsorption as the hydrophobic material tends to “cordon” with water and water surfaces. The hydrophobic material has low surface tension values do not contain surface chemistry active groups to form “hydrogen bonds” with water.

A greater charge density at the membrane surface correlates with greater membrane hydrophilicity generally. Polysulfone, cellulose acetate, ceramic and thin-film composite membranes used for water treatment and wastewater recovery generally have a negative surface charge. Hydrophobic compounds and particles tend to aggregate or form groups to form colloidal particles. Therefore, in practice, the surface chemistry and hydrophobic properties of the membranes are used by transforming them into hydrophilic properties by various methods [29].

Separation is quite simple: the membrane regulates the transport between the two phases and acts as a semi-permeable layer between these two phases. Specifically, the filter will capture suspended solids and other matter while allowing water to flow through the membrane. There are a variety of methods to allow substances to enter a membrane. Membranes are more effective in generating process water from groundwater, surface water, or wastewater. Membranes are now in competition for conventional techniques in water treatment [29].

An alternative, efficient and advantageous method for oil-water separation: membrane separation processes. These processes are usually carried out under atmospheric conditions. While membrane technology is widely used in the food processing, pharmaceutical, desalination, and fuel cell industries, they are also serve as one of the most efficient methods for separating oil-water wastewater or emulsions [29].

The membrane separation method has higher efficiency, consistent waste quality, and lower energy consumption compared to chemical treatment and other treatments. For many reasons such as these, membrane technology is the most viable way to separate oily wastewater [29].

Membrane separation depends on three basic principles such as adsorption, sieving, and electrostatic phenomenon [29].

The adsorption mechanism has been associated with solute and membrane hydrophobic interactions. These interactions cause a reduction in pore size resulting in further rejection.

Figure 2.5 [17] shows the basic principle of membrane separation.

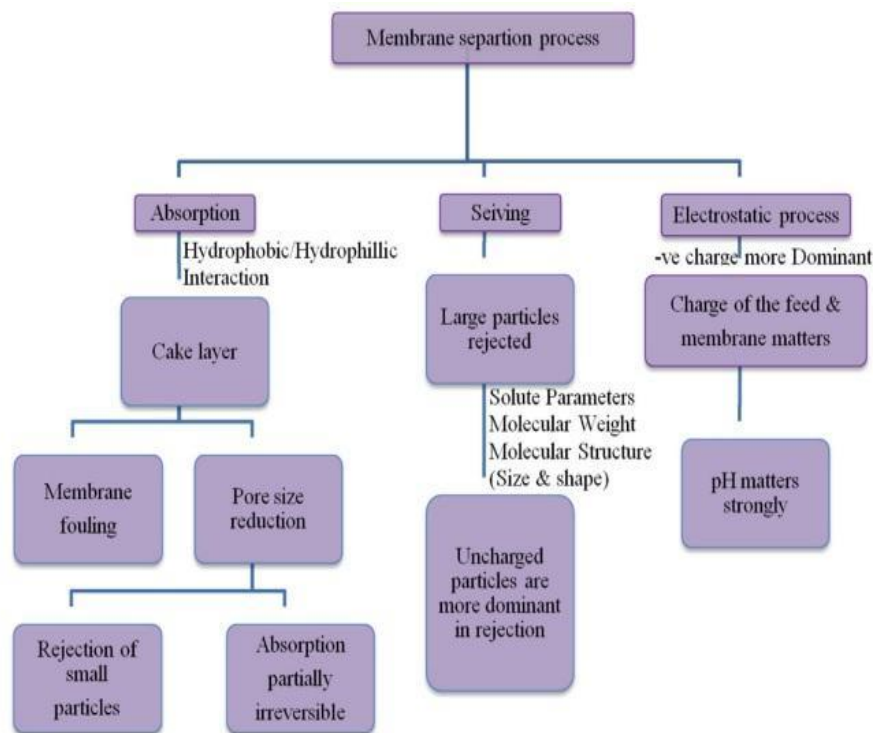


Figure 2.5 Basic principles of membrane separation

The development of membrane science and technology had a long history in laboratory work before its first major industrial application in the 1960s [30]. Major events are listed in Table 2.2 (adapted from refs. [31–34]). “Osmosis”, the oldest recorded membrane phenomenon, was discovered by accident in 1748 by Abbe Nollet [35]. Eighty years later, the observation of hydrogen gas escaping from broken jars by Doebereiner in 1823 [36] prompted Thomas Graham to study gas diffusion in 1833 [37] and later proposed Graham’s law of gas diffusion in 1866 [38]. Adolf Fick formulated the phenomenological laws of diffusion in 1855 [39] and soon became the important rule defining diffusional transport in membranes.

Semi-permeable membranes were first made to measure the osmotic pressure of the solution, which led to the classical solution theory, by Traube in 1867 [40] and used by Pfeffer (1877) [41], which led to the classical solution theory- Van’t Hoff’s osmotic pressure equation

(1887) [42]. This landmark work was awarded the first Nobel Prize in chemistry in 1901 [43]. Zsigmondy in 1907-1920 [44], ultrafine particle filters or early micro filters and ultrafilters.

Shortly thereafter, in the 1920s the Reverse Osmosis (RO) prototype was observed and studied with cellophane or cellulose-nitrate membranes by Michaelis (1926) [30], Manegold (1929) [45], and McBain (1931) [46].

The foundation of electrodialysis membranes and modern membrane electrodes was created in the 1930s by Teorell and Meyer [47] from their work on transport over neutral and constant-charged membranes. In the late 1950s, electrodialysis, Microfiltration (MF), and ion change membranes were researched and used on a lab scale and tested drinking water safety in Europe [30].

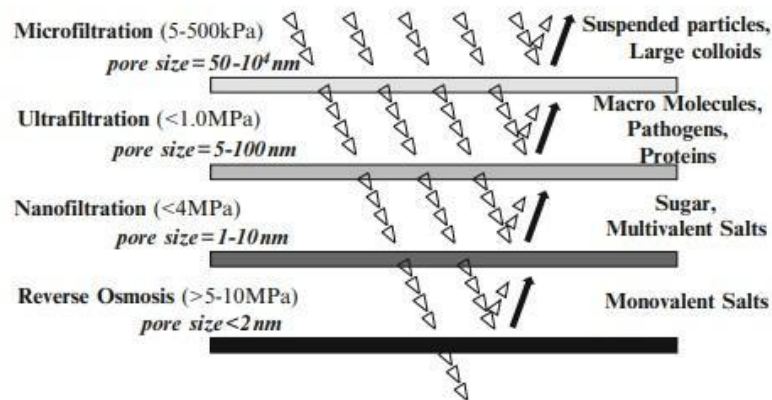


Figure 2.6 Filtration types depending on particle size

The first commercial facility to use electrodialysis and ion change membranes from the production of drinking water from a saline source began operations in 1954 [30]. One of the milestones in the industrial application of membranes was the production of faultless, high flux, anisotropic RO, asymmetric cellulose acetate (CA) membranes by Loeb and Sourirajan in 1962 [48]. By 1980 RO, Ultrafiltration (UF), MF, and Electrodialysis (ED) had found applications in large-scale facilities around the world. In the 1980s [49], commercial pervaporation (PV) systems and industrial membrane gas separation (GS) processes were developed [49].

It is generally accepted that wide industrial applications of membrane processes have started from the 1960s [31–34].

Membrane separation processes, which are becoming a suitable alternative method for oil-water separation, mainly consist of MF, UF, nanofiltration (NF), and RO pressure-operated processes. As shown in Figure 2.6 [19], the surface pore sizes that define the applications of the membranes are fundamental differences but conceptually similar processes [19].

Table 2.2 Historical development of membranes (pre-1980s)

Year	Development	Scientists
1748	“Osmosis”, permeation of water through pig bladders	Abbe’ Nollet
1833	The law of diffusion of gases	Thomas Graham
1855	Phenomenological laws of diffusion	Adolf Fick
1860–1880s	Semi-permeable membranes: osmotic pressure	M. Traube (1867), W. Pfeffer (1877), J.W. Gibbs (1878), J.H. Van’t Hoff (1887)
1907–1920	Microporous membranes	R. Zsigmondy
1920’s	The prototype of reverse osmosis	L. Michaelis (1926), E. Manegod (1929), J.W. McBain (1931)
1930’s	Electrodialysis membranes, modern membrane electrodes	T. Teorell (1935), K.H. Meyer and J.F. Sievers (1936)
1950’s	Electrodialysis, microfiltration, and hemodialysis, ion-exchange membranes	Many
1963	Defect-free, high-flux, anisotropic reverse osmosis membranes	S. Loeb and S. Sourirajan
1968	Basics of pervaporation	P. Aptel, and J. Neel
1968	Spiral-wound RO module	J. Westmorland
1977	Thin-film composite membrane	J. Cadotte
1970–1980	Reverse osmosis, ultrafiltration, microfiltration, electrodialysis	Many
1980’s	Industrial membrane gas separation processes	J.M.S. Henis and M.K. Tripodi (1980)
1989	Submerged membrane (bioreactor)	K. Yamamoto

Membrane filtration can be operated in two models: dead-end and cross-flow as shown in Figure 2.7 [21].

In dead-end mode, the entire feed system is transported vertically to the membrane so that entrained particles and other components accumulate and sediment on the membrane surface, while in a cross-flow process, the feed stream moves parallel to the membrane surface and only part of the feed stream passes through the membrane under driving pressure. Moving the

feed stream tangentially to the membrane surface can result in much higher permeation flows as the flow continuously removes the trapped material [50].

Besides, backwash, ultrasonic vibration, or periodic flow can also be used to remove the sedimentary material from the membrane surface. The membrane lifespan can be prolonged. However, the cross-flow mode requires more complex equipment compared to the dead-end mode, and also the operating cost of the cross-flow mode is higher than the dead-end mode due to the energy required circulating the feed stream [51].

Dead end mode tends to be used in the water/wastewater industry for dilute nutrients such as surface waters or secondary wastes. Periodic backwashing is required to control cake build-up and contamination [50, 51].

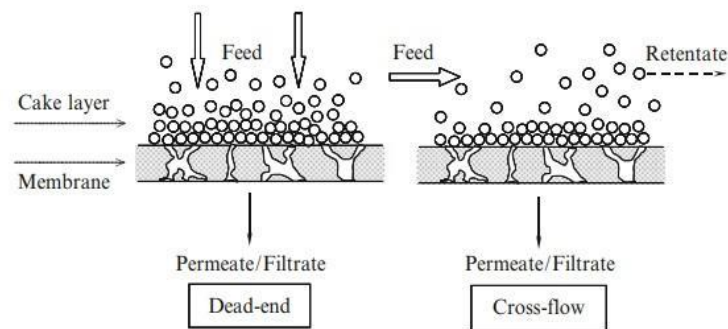


Figure 2.7 Schematics of dead-end and cross-flow filtrations

2.5 Membrane Morphology

The membrane is a thin interface that attenuates the penetration of chemical species in contact with it. The interface is completely uniform in composition and structure, or it can be called molecularly homogeneous, or the interface can be chemically or physically heterogeneous. For example, it contains measurable size pores or holes or consists of some form of the layered structure [52].

The main types of membrane morphologies are classified as follows [52];

- Isotropic membranes,
 - Microporous membranes,
 - Non-porous dense membranes,
 - Electrically charged membranes,

- Anisotropic membranes,
- Ceramic, metal, and liquid membranes.

2.5.1 Isotropic membranes

This type of membrane can be examined in three groups as microporous membranes, non-porous dense membranes, and electrically charged membranes [52].

2.5.1.1 Microporous membranes

The microporous membrane is very similar in structure and function to a conventional filter. The pore distribution of these membranes is random, the membrane pores are highly hollow, the pores are interconnected and the membrane has a rigid structure. The reason it differs from a conventional filter is that pores are extremely small and are 0.01-10 μm in diameter. The particles rejected by the membrane are all larger than the largest pores. Partially rejected particles are smaller than the largest pores but larger than the smallest pores. Particles passing through the membrane are much smaller than the tiniest pores. Therefore, solute separation with microporous membranes mainly depends on molecular size and pore size distribution. In general, with Microporous membranes, it is possible to effectively separate only molecules that differ significantly in size using UF and MF [53–55].

2.5.1.2 Non-porous, Dense Membranes

Non-porous, dense membranes consist of a dense film in which permeates are transported by diffusion, under pressure or repulsive force of the electrical potential gradient [53].

The relative transport rate established by the diffusivity and solubility in the membrane directly influences the separation of the various components of a mixture. Thus, if the permeable concentrations in the membrane material differ considerably, non-porous, dense membranes can separate similarly sized permits [54].

Most gas separation, pervaporation, and RO membranes use dense membranes to achieve separation. The membranes usually have an anisotropic structure to improve flux [53–55].

2.5.1.3 Electrically Charged Membranes

These types of membranes are also called ion exchange membranes. They are often very fine microporous, their pore walls carry positively or negatively charged ions [55].

An anion exchange membrane is a membrane fixed with positively charged ions. The opposite is true for the cation exchange membrane. Separation is achieved mainly by

excluding ions with the same charge as fixed ions on the membrane structure which is affected by the charge and concentration of ions in the solution. This type of membrane is used for processing electrolyte solutions in electrodialysis [53–55].

2.5.2 Anisotropic Membranes

The membrane should be very thin as possible as it can be because high transport rates are required in the membrane separation process for economic reasons. In conventional membrane production technology, the production of a mechanically strong, fault-free membrane with a thickness of approximately 20 μm is very limited. The goal of developing new membrane manufacturing techniques was to create anisotropic membrane structures, which is discovered more than 40 years. An extremely thin surface layer and a much thicker, porous support layer form anisotropic membranes. The surface layer and the support layer can be formed in one operation or separate operations. In composite membranes, layers are usually made of different polymers. The support layer acts as mechanical support. Only the surface layer of the membrane determines the basic separation properties and permeability rates. The advantage of anisotropic membranes is the higher flux provided. For this reason, many commercial separation processes use such membranes [53–55].

2.5.3 Ceramic, Metal, and Liquid membranes

The interest in membranes made of conventional materials has declined in recent years. Therefore, ceramic membranes are classified as special microporous membranes and are used for UF and MF applications where solvent resistance and thermal stability are required. Dense metal membranes (especially Palladium membranes) are used to separate Hydrogen from gas mixtures. Besides, reinforced liquid films are being developed for carrier facilitated transport processes Figure 2.8 [52] shows all membrane morphology types [53–55].

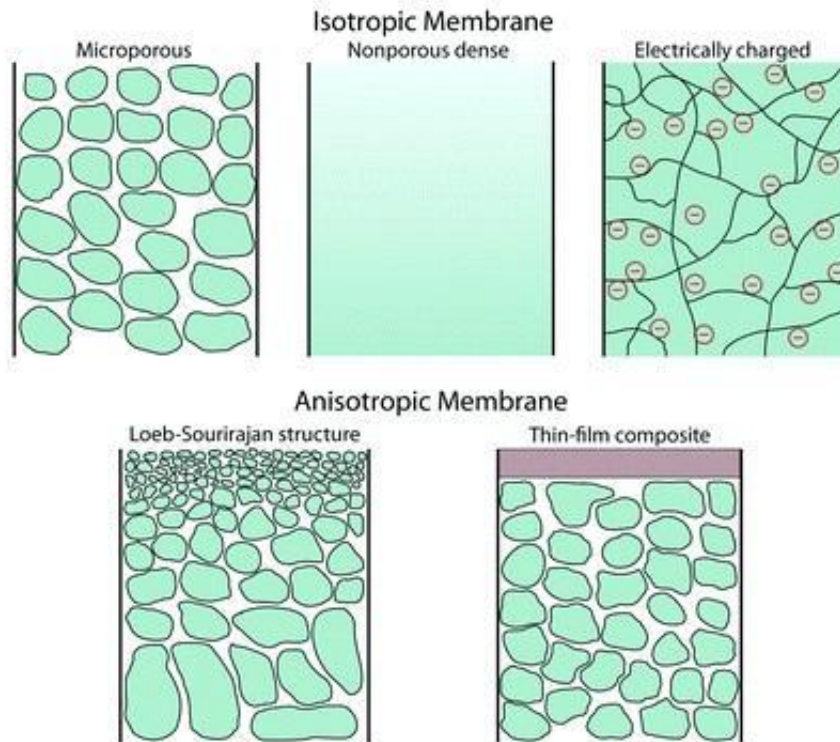


Figure 2.8 Membrane morphologies

2.6 Advantages of Membranes in Separation

In this section advantages of membranes in separation will be expressed in more detail [14].

Membrane technology covers all engineering approaches transporting substances between two phases with the help of permeable membranes. Generally, membrane technology is used to separate gaseous or liquid streams in mechanical separation [14].

Membrane technology is becoming more and more important in wastewater treatment. With the help of UF / MF, it is possible to separate particles, colloids, and macromolecules so that the wastewater can be reused in this way [14].

Almost half of the market is used in medical fields such as artificial kidneys to decompose toxic substances through hemodialysis and as an artificial lung to produce bubble-free oxygen in the blood. In the field of environmental protection, the importance of membrane technology is increasing. Membrane technologies, advantages, and disadvantages are shown in Table 2.3 [14].

The advantages brought by such wide usage areas are as follows [25, 54, 56];

- Since membrane processes can be separated on a molecular scale to such a scale that particles can be seen, this means that a large number of separation needs can be fulfilled by membrane separation processes.
- Membrane separation processes commonly do not require a phase change to make a separation (except pervaporation). Therefore, energy requirements will be low unless a large amount of energy has to be used to increase the feed stream pressure to pass the penetrating components through the membrane.
- Membrane processes offer a very simple flow chart. Compared to many other processes, there are no moving parts (except compressors or pumps), complex control schemes, and very little auxiliary equipment. Therefore, they can offer a simple, direct-to-operate, low-maintenance process option.
- Membranes can be produced with extremely high selectivity for the separation of various compounds. Generally, the values of these selectivities are much higher than typical values for relative volatility for distillation processes.
- Hence the huge amount of polymeric and inorganic material can be used as membranes; the control of selectivity is easier.
- Membrane processes can recover small but valuable components from a mainstream without significant energy costs.
- Membrane separation processes are potentially better for environmental protection, as the membrane approach requires the use of relatively simple and harmless materials.

Table 2.3 The list of advantages and disadvantages of various membrane technologies

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 and grease
	High-quality effluent	
Forward Osmosis (FO)	High oil removal	Concentration polarization issues
	Low membrane fouling	
	Low or no hydraulic pressures required	
	The equipment used is very simple	
Nanofiltration (NF)	Higher oil removal, large organic molecule, 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 module	
	Low energy Cost	
	No degradation due to heating	
	No extra safety elements	
Ultrafiltration (UF)	Effective in the removal of oily microemulsions	Low flux
	The superiority of low energy consumption and high efficiency	
	The superiority of low energy consumption	Membrane fouling by property of extremely hydrophobicity
	No chemical preparation involved	

2.7 Membrane Fouling Phenomena

Membrane fouling is a condition in which small particles or dissolved macromolecules are deposited or adsorbed in membrane pores or on the membrane surface, resulting in clogging of membrane pores or narrowing of membrane pores as shown in Figure 2.9 [58]. Membrane fouling can cause severe flux drops and severely affect the quality of the produced water. Serious contamination may require intensive chemical cleaning or membrane replacement. This will increase operating costs significantly. Membrane fouling is thought to occur in three manners [57–59]:

- Pore plugging,
- Pore narrowing
- Cake formation.

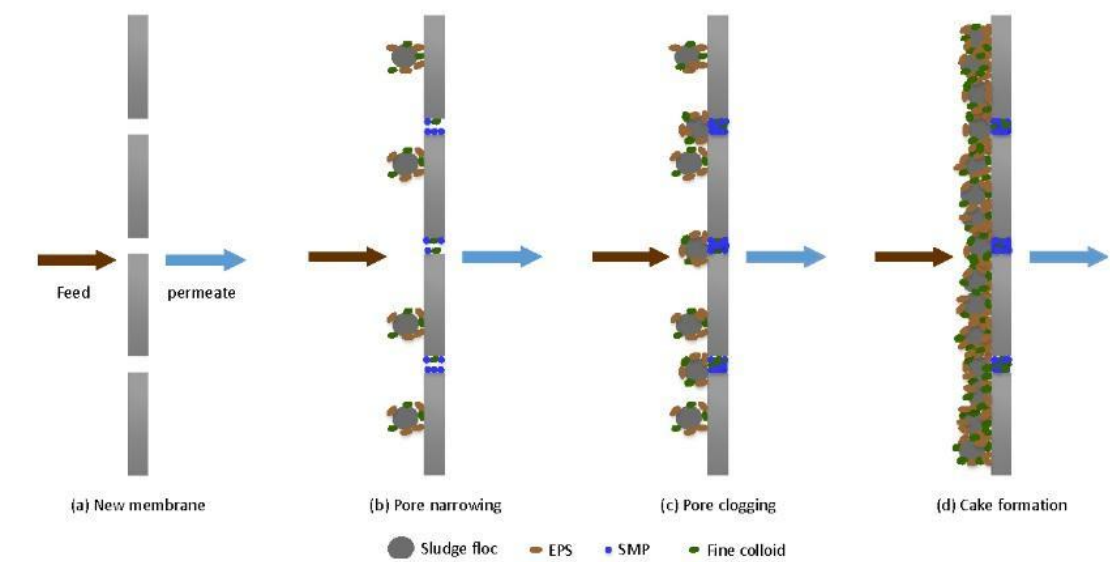


Figure 2.9 Mechanisms of membrane fouling

Membrane fouling directly affects membrane flow and has been extensively studied by many researchers. In general, membrane fouling management can be accomplished through the following two strategies [60–62]:

- To reduced the contamination rate
- Cleaning the dirty membrane.

To reduce the fouling, membrane fouling can be controlled by pre-treatment of incoming fluid, optimization of operational conditions, and modification of membrane properties [60–62].

Adjusting the pH of the inlet water can have a significant effect on membrane fouling because extreme pH conditions damage membrane performance and life as well as biological properties. Removal of excess inorganic species such as Mg, Al, and Ca also reduces membrane fouling because the interaction between these inorganic species and polymers significantly affects the formation and density of the cake layer [60–62].

2.8 Surface Modification of the Membranes for Anti-Fouling Properties

The surface modification method has been tried to minimize membrane fouling and optimize the hydrodynamic conditions of the membrane. The effect of surface modification was found to increase the hydrophilicity of the membrane and also lower the adsorption of organic pollutants on the membrane an example with PVDF nanofiber membrane shown in Figure 2.10 [63–65].

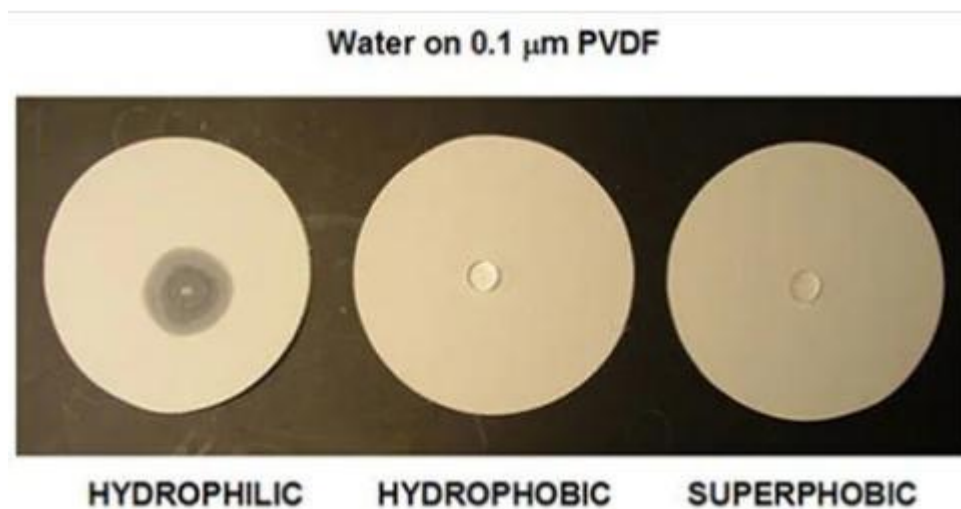


Figure 2.10 Hydrophilicity of a PVDF Nanofiber Membrane with and without Surface Modification

Increasing the hydrophilicity of the membrane surface is the main purpose of surface modification. This increases the membrane performance. Some solutions to prevent surface contamination; it is a surface modification by chemical reaction or physical absorption. The process is shown in Figure 2.11 [66].

The most important issue in the separation of oily wastewater is to reduce the adsorption of oil droplets on the membrane surface. Membrane fouling is caused by the adsorption of other organic molecules such as surfactants. However, this is often neglected. Organic pollutants cause contamination and clogging of the membranes [67].

Contaminants are difficult to remove and contaminants shorten membrane life. Therefore, improved antifouling performance and efficiency of the membranes are desirable [67].

Surface modification of synthetic membranes can be performed by the following methods [68];

- By mixing or adding other components to the main polymeric material,
- By coating the membrane surface with another polymer,
- Changing the membrane surface by a chemical reaction,
- By radiation through high energy particles and,
- By other techniques.

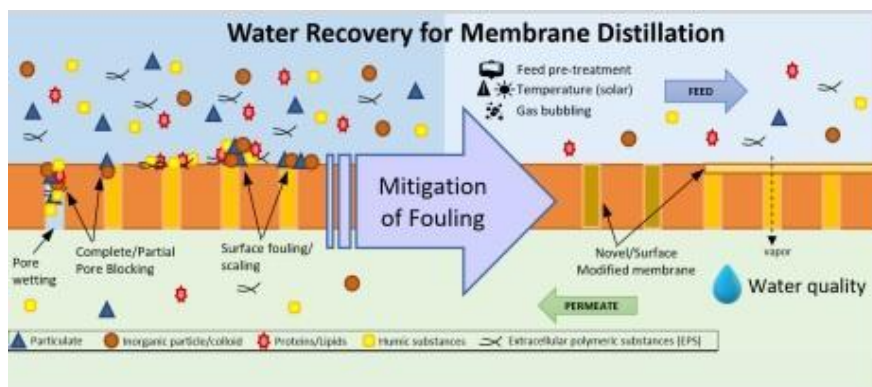


Figure 2.11 Membrane Distillation for Water Recovery.

2.8.1 Surface Modification by Mixing or Adding Other Components to the Main Polymeric Material

The main purpose of surface modification is to change hydrophobic surfaces to hydrophilic or hydrophilic surfaces in a hydrophobic direction. To make hydrophobic membranes hydrophilic, a wetting agent such as surfactants can be added to a polymeric solution for casting. Typically, such surface modification is only temporary and membranes cannot be subjected to repeated wetting and drying procedures without loss of wettability [69].

Another membrane casting method is based on the incorporation of hydrophilic cross-linkable monomers into a hydrophobic polymer casting solution. A semi-crystalline polymer with hydrophilic surface properties is formed upon casting [69].

Membranes produced with surface modifying molecules have proven useful in water treatment through UF due to reduced fouling [69].

2.8.2 Surface modification by Coating the Membrane Surface with Another Polymeric Solution

The membrane surface can be modified by touching the surface of one side of the membrane with a different polymer solution. After the solvent has evaporated, a thin layer of polymer is left on top of the polymer membrane. It can also be applied after some treatments. There are many techniques of coating the surface layer with different layers of polymer [70].

Moya described a process for a porous or non-porous substrate coated with a polymeric composition with hydrophilic functional groups suitable for filtration application [70].

The invention provides a porous or non-porous membrane from a fluorine-containing polymer substrate, preferably perfluorinated, cross-linked, or branched fluorocarbon, surface modified as compared to the unmodified substrate [70].

2.8.3 Surface Modification by Chemical Reaction

The surfaces of polymeric membranes can also be changed by chemical reactions [70].

Scientist Noh found a method for chemically modifying the surface of PTFE materials that allows improving the biocompatibility of materials. The method was to get the membrane in a mixture of hydrogen compound, a cyclic compound, and an organic solvent. During the reaction, fluorine will be extracted and the surface will change from hydrophilic to hydrophobic and the membrane will be composite [71].

2.8.4 Surface Modification by Radiation

Polymer surfaces can be altered both chemically and physically when exposed to high-energy particles [72].

Kozlov and Wilson found a method for porous membrane surface modification by radiation-assisted polymerization [72].

Koh et al. found a method to modify the polymer membrane surface by the ion-assisted reaction. In this process, the pore size on the membrane surface can be controlled according to the irradiation dose and the type of ion beam, resulting in water penetration or electrolyte conduction [72].

2.8.5 Surface Modification by Other Techniques

Sikdar et al. invented adsorbent-filled pervaporation membranes used to extract volatile organic compounds from wastewater [73].

2.9 Nanofibers in Membrane Technology

Fibers that have a diameter in the nanometer range are called nanofibers. Many types of polymers were converted into nanofibers of 50 to 1000 nanometers in diameter; compare to conventional fiber spinning, nanofibers are several orders of magnitude [74].

Properties of nanofibers are as follows [74];

- Large specific surface area
- High porosity
- Small pore size
- Diameter range (50-1000) nm

The materials that nanofibers can be obtained from are explained below [74];

- Polymer solutions or melts,
- More than 30 polymers electrospun including polyethylene oxide, DNA, polyaramids, and polyaniline,
- These fibers can be made from various organic or biological polymers,
- Polyvinyl alcohol, polystyrene, polyacrylonitrile, but also peptide amphiphiles or cellulose.

Nanofiber application areas [74];

- Air and liquid filters,
- Wound dressings,
- Tissue engineering,
- Surface modifications

- Sound absorbing materials,
- Etc.

There are various methods to produce nanofibers. Some of these methods are template synthesis, melt blowing, freeze-drying, and phase separation, etc. [74].

The most widely used technique is electrospinning. What is essential for this process is a high voltage electrical field containing positive and negatively charged ends [74].

The polymer is loaded into the extruder at one end of this area and is quickly drawn and stretched at the opposite electrically charged end, creating an ultra-fine mesh of nanofibers that is electrospun directly onto a support layer. The process of electrospinning is shown in Figure 2.12 [75].

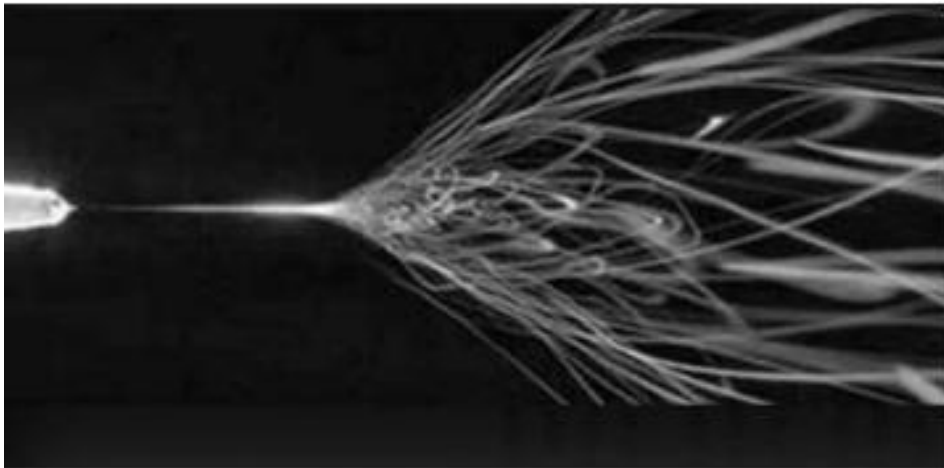


Figure 2.12 Electrospinning process

Industrially the most advanced and most used nanomaterials are filtration, purification materials, and components. These nanomaterials can achieve higher filtration and lower pressure efficiency than conventional filters [75].

Besides, it is easy to clean, significantly extending the life of the filters, reducing upkeep costs. Presently, water filters for wastewater treatment and desalination are ready-to-market products [75].

Today, nanofibers are of great interest due to the technique and the resulting products, and the simple electrospinning process. In electrospinning, it is possible to have various materials and unique properties of the obtained. Membranes based on nanoporous structures are developed to treat oily wastewater [75].

As a highly hydrophobic filter, electrospun nanofibers are therefore an excellent alternative for separating oil/water emulsion. The following properties in oil/water emulsion separation make the electrospun nanofiber attractive [76]:

- High porosity,
- Interconnected porous structure,
- Controllable pore size,
- Large surface area/volume ratio.

Table 2.4 Nanofibers and their application areas.

Nanofibers	Application
Chitosan, polyvinyl alcohol, cellulose acetate, and Polyurethane/Copper oxide	Air filtration
Chitosan/Polycaprolactone, collagen, gelatin, Polycaprolactone, and Poly(L-lactide-co-glycolide)	Tissue Engineering
Cellulose, Polyamide 6, Polyvinylidene fluoride, Polyacrylonitrile, Polyvinylidene fluoride/ Polyacrylonitrile, Polyurethane ad polypropylene	Membrane for Water purification
Gelatin, silk, Polycaprolactone, Chitosan-Polyethylene oxide, Polyamide 6, Dextran	Biomedical applications
Polyvinyl alcohol and Polyamide 6	Acoustics
Polyvinyl alcohol, Polyvinyl Butyral, Polyurethane and Polyacrylonitrile	High-performance apparels
Polyvinylidene fluoride	Piezo applications

As filters, electrospun nanofibers have a very high flux, which can be attributed to their extremely porous structure [76].

However, the oil component in oil/water emulsion causes membrane fouling, which is the main disadvantage in membrane filtration application. Also, the low contact and adhesion between the fibers cause the electrospun nanofibers to have poor mechanical strength. The use of the nanofibers according to the application areas is shown in Table 2.4 [76–78].

2.9.1 Advantages of Nanofibers and Nanomaterials in Membrane Technology

Electrospun nanofiber membranes offer uniquely desirable properties for creating membrane materials, including high specific surface area, interconnected pore sizes, high porosity, and easy modification that makes them advantageous over traditionally prepared membranes.

Very porous nanofiber membranes are produced from electrospinning techniques from a wide variety of materials for water treatment applications, including MF, NF, UF, RO, oil/water separation, membrane distillation, and bioseparation [79].

It has been investigated that the electrospun nanofibers' structural properties such as fiber diameter, thickness, porosity, and pore size greatly affect membrane performance [79].

Membrane fouling was found to be a critical problem during filtration processes due to the high flow of electrospun nanofiber membranes and was effectively reduced by surface modifications of electrospun nanofiber membranes using appropriate antifouling materials/coatings. Therefore, making electrospun nanofiber membranes by layering, coating, polymerizing, and blending electrospun nanofibers in different configurations is the most important step that enables them to be used in various water treatment applications [80].

Membrane technologies are used industrially and are one of the most important water treatment techniques in the industrial market. An effective membrane requires high permeability, high rejection, low contamination, easy to clean, easy to use, chemically and mechanically strong, and low cost [79].

Given its effective membrane properties, nanofiber technology is promising for separation technology. The biggest advantages of using nanofibers in separation technology are as follows [79, 80];

- The high surface area of nanofibers allows rapid adsorption of particles from wastewater such as microorganisms or hazardous molecules.
- The highly porous and narrow pore size of nanofibers allows high permeability and selectivity.
- The surface of the nanofibers can be easily changed.
- A wide variety of polymeric solutions can be used in the preparation of nanofibers.
- The highly interconnected and asymmetrical nature of nanofibers can reduce fouling.

2.10 Aim of This Thesis

In this study, Polyvinylidene fluoride (PVDF) nanofiber membranes were used to separate oily wastewater. PVDF polymer is highly hydrophobic and oleophilic. Herein, it was planned to change the wettability of PVDF membranes using the surface modification technique. The resulting membranes showed oleophobic/hydrophilic properties.

Commercial nanoparticles (NPs) have been used in previous studies [81, 82]. In this study, an environmentally friendly modification method was used through laser irradiation synthesis.

Membranes were characterized and their separation performance was compared. The characterization will be made for membrane and feed/permeate water.

For this purpose;

- Both low and high viscosity oils were tested.
- Membrane characterizations were made.
- The flux, permeability, and recovery of the membrane were calculated for the membrane fouling resistance property.

The characterization method includes;

- SEM (Scanning Electron Microscopy)
- Optical microscope
- Filtration device for permeability and flux measurement
- Litron lasers; LDY300 PIV series with diode pump, double cavity
- Contact angle
- Pore size

The expected results from the tests performed are as follows;

- Hydrophilic/oleophobic PVDF membranes
- Fouling resistance membranes
- High selectivity and permeability.

3. EXPERIMENTAL PART

3.1 Material and Methods

3.1.1 Polymers and Nanofibers

PVDF nanofibrous surfaces were acquired from the Institute of Advanced Technology and Innovation at the Institute of Nanomaterials, Technical University of Liberec (TUL). Nanofibers were prepared under controlled conditions by using NS-1S500U Nanospider (Elmarco, Czechia). Preparation conditions are not mentioned here. Samples are shown in Table 3.1.

Table 3.1 Sample Names and Surface Modifications

Sample Name	Mass per Unit Area (Gsm)	Surface Modification
PVDF	3	No Modification
PVDF-OH	3	KOH + IPA
PVDF-OH + 0.001 mMol NPs	3	KOH + IPA and NPs
PVDF-OH + 0.01 mMol NPs	3	KOH + IPA and NPs
PVDF-OH + 0.1 mMol NPs	3	KOH + IPA and NPs
PVDF-OH + 1 mMol NPs	3	KOH + IPA and NPs
PVDF-OH + 10 mMol NPs	3	KOH + IPA and NPs

3.1.1.1 Polyvinylidene Fluoride (PVDF)

In membrane domain applications, it is required the highest purity and resistance to solvents, acids, and hydrocarbons membranes. For this aim, a special polymer, PVDF was used. It is non-toxic. Therefore, it can be used for food products repeatedly in contact. The glass transition temperature of PVDF is about -35°C and is usually 50-60 % crystalline. PVDF has a melting point of around 177°C . It is insoluble in water. The structure and chemical formula of PVDF is shown in Figure 3.1 [83].

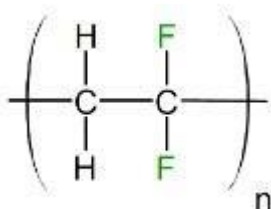
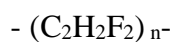


Figure 3.1 PVDF Structure



3.1.2 Surface Modification

PVDF membrane is highly hydrophobic and oleophilic before surface modification. The purpose of the surface modification is to make the membranes hydrophilic, increase permeability and to improve the fouling resistance properties of the membranes.

Due to membrane contamination, the permeability and flux of the membrane rapidly decrease, resulting in poor performance and this contamination is shortening the membrane's operation time. The main cause of membrane contamination is oil droplets clogging the membrane's pore size and/or adsorption of surfactant.

Electrospun nanofibers were collected on silicone paper and laminated with a heat press (PracovniStroje, 70 Teplice, Czech Republic), where a spun-bonded nonwoven fabric with an adhesive mesh was used as the backing layer.

Surface modification was done in two steps. In the first step, hydrophilic hydroxyl groups were introduced using an alkaline solution for PVDF. In the next step, the treated PVDF membranes were modified with Ti-Ag (Titanium-Silver) nanoparticles (NPs). Process is shown in Figure 3.2 [14].



Figure 3.2 Surface modification process of membranes

The surface of the membranes was modified by immersion in a 1.4 M solution of potassium hydroxide (KOH, Fluka) in isopropyl alcohol (IPA, Fluka) for 1 hour at room temperature. It has been observed that a long time destroys the supporting layer.

Samples were taken and washed several times with distilled water and kept in distilled water until use. Immersion in KOH solution enabled dehydrofluorination of the PVDF membrane, as well as allowing the bonding of decoration NPs with OH groups. Depending on the degree of dehydrofluorination, the color of the sample is getting darker samples used for separation after 1st modification shown in Figure 3.3.

Ti-Ag NPs were synthesized with a 0.025 mm thick Ti foil, chosen as a solid target because the ablation energy threshold was too low for fs pulses, and the liquid medium includes a solution of silver nitrate in deionized water. The entire surface of the Ti foil was irradiated and then the solid target was removed from the glass beaker and the membrane is placed inside in a vertical position.

The recently produced nanocolloid was magnetically stirred for 2 hours to ensure the maximum number of NPs fixed on the membrane, and 10 minutes of ultrasonication was performed to get rid of the NPs that were not properly attached.



Figure 3.3 PVDF membrane before and after first step surface modification

3.1.3 Emulsion Preparation

The oil/ water system chosen was the emulsion type, with two of the oil types most used in this field served as the basis of the emulsion; sunflower kitchen oil from the market (100% Glodplus) whose psychochemical properties are not well controlled but widely used, and n-hexane (purity is 99.0 %, Penta sro), an oil with well-known psychochemical properties. Preparation of each emulsion was done by mixing 400 ml of deionized water with 0.4 ml of nonionic surfactant Triton X100 (laboratory grade, Sigma-Aldrich) and 1 ml of the matched oil. The mixtures were stirred overnight at 600 rpm until a uniform emulsion was obtained. An optical microscope was used to measure emulsion uniformity and drop sizes (Axio Imager M2, Carl Zeiss) where the mean oil droplets diameter was $6.2 \pm 2.9 \mu\text{m}$ for kitchen oil and $2.0 \pm 0.7 \mu\text{m}$ for n-hexane.

3.1.4 Separation Tests

The oil/water separation performance of each sample was evaluated with a custom-built gravity-powered filtration unit. The emulsion was used to feed the filtration unit open top and the feed level was kept 30 cm above the membrane (Diameter is 20 mm) as shown in Figure 3.5. The emulsion filtration test was repeated 10 times (10 cycles) without changing the membrane to evaluate the fouling resistance of the sample.

All samples were filtered 30 ml of deionized water before emulsion testing and between cycles.



Figure 3.4 Custom made Dead-End Filtration Device Scheme

Membrane flux (F) and permeability (k) are calculated according to the equations;

$$F = \frac{1}{A} \frac{dV}{dt}$$

$$k = \frac{F}{p}$$

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 permeate (L).

Fouling of the sample was determined by the difference between permeability values in the first (k_i) and last filtration cycle (k_f).

3.1.5 Anti-fouling property of the Samples

The anti-fouling properties of modified membranes were tested with a solution of oil-water emulsion at 0.03 bars and room temperature. First, DI water was filtered through the membrane for at least 30 min and the average water flux was recorded as J_0 . Then the emulsion was filtered through the membrane, and the average water flux was recorded as J_f . The membrane was not cleaned between each cycle, and then the operation was repeated. The antifouling performance evaluation for each membrane was operated with 10 cycles. Normalized flux was used to determine the anti-fouling properties of the sample during 10 cycles.

The normalized flux has been calculated in each cycle by using the formula:

$$\text{Normalized flux (\%)} = \frac{J_f}{J_0} \times 100$$

The flux recovery rate (FRR) is also used to determine membrane fouling resistance. The flux recovery rate of membranes is calculated by the following equation;

$$FRR = \frac{J_{wt}}{J_{w0}} \times 100$$

Where J_{w0} is the DI water flux before filtration of oil-water emulsion, J_{wt} is the DI water flux after oil-water emulsion separation. The FRR was calculated for 10 cycles of each membrane during 14 min test.

3.1.6 Characterization

The surface morphology of the membranes was examined by scanning electron microscopy (SEM) using a microscope (Vega3 SB, Tescan) operated at an acceleration voltage of 30 kV. The pore size of the membranes was determined by the bubble point method using a pore size analyzer (Porometer 3G, Anton Paar GmbH). Finally, the wettability of the sample was determined by the contact angle in the air using a drop shape analyzer (DSA30E, Krüss GmbH).

Droplets in air consisted of deionized water and measurements were taken at six different points on the dry surface of the sample at room temperature.

4. RESULTS AND DISCUSSION

4.1 Surface Morphology (SEM)

Images of the surface morphologies of the samples were taken using SEM images. The chemical composition of the NPs has a critical effect on the decoration of the membrane, where those with a larger Ag content appear to be more tightly bound to the surface of the membrane. As the hydroxyl groups are functionalities used to immobilize particles, samples with a larger Ag content are expected to bind more strongly to the membranes.

This is due to the stronger covalent bonding between Ag and OH groups, as opposed to the weakening of hydrogen bonding around Ti oxides when the membrane is exposed to water with OH groups. SEM images of the membranes with and without NPs are shown in Figure 4.1. It seems that fiber diameter slightly increased after modification. The reason could be due to swelling of the fibers. A similar result has been observed in previous work [81]. It was found that alkaline treated PVDF membranes showed a slight increase in fiber diameter.

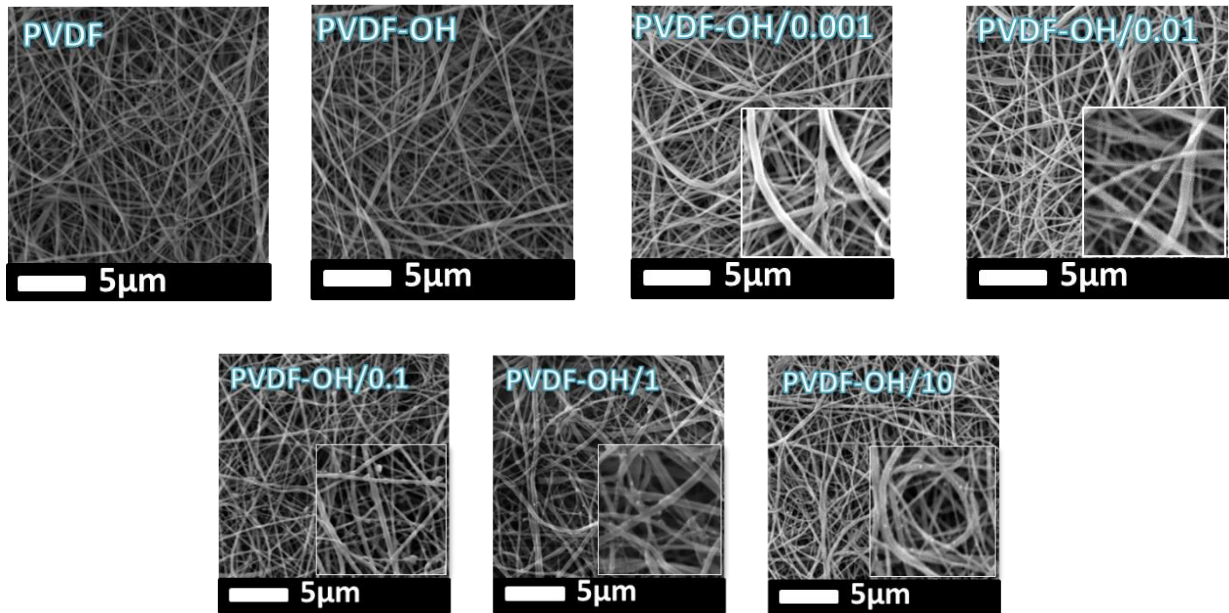


Figure 4.1 SEM image analysis of the membranes with fiber diameters, PVDF=155 nm, PVDF-OH=173 nm, PVDF-OH/0.001=184 nm, PVDF-OH/0.01=167 nm, PVDF-OH/0.1=150 nm, PVDF-OH/1=176 nm, PVDF-OH/10=162 nm.

The NPs has been observed on the membrane surface with higher magnification of SEM images. More particles were detected for the samples PVDF-OH/0.1, PVDF-OH/1, and PVDF-OH/10 due to higher amount of particle.

4.2 Contact Angle

Membranes that show a contact angle of less than 90° can be categorized as hydrophilic membranes. Membrane wettability categories are shown in Table 4.1 the water contact angle (WCA) of the membranes was measured for modified and unmodified samples. Also, WCA was measured before and after the separation test. It is assumed that when the membrane comes into contact with the oil/water emulsion, the WCA properties change due to the surfactant and oil contamination in the emulsion. Contact angle results are shown in Figure 4.2. Positively charged surface is attracted by the polar molecules of water, the hydrophilicity of the materials increases. Herein, higher amount of Ag^+ adsorbed on the surface of the membrane increased the hydrophilicity. This effect can only be seen in the PVDF-OH/0.1mM NPs example, and this besides providing hydrophilicity, makes the membrane surface oleophobic regardless of the type of oil.

In contrast, higher amount of NPs appear to be disadvantageous for breaking the surface tension of the water droplet by providing many low contact areas. A larger NPs charge provides a greater number of low contact areas and eventually makes the membrane both hydrophobic and oleophobic.

Table 4.1 Membrane Wettability Conditions

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

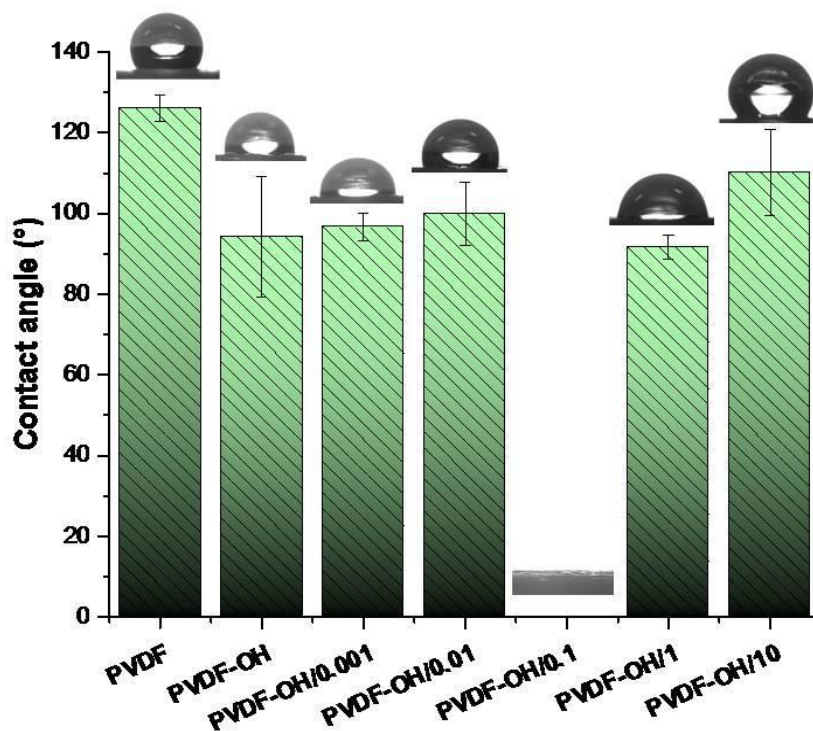


Figure 4.2 Contact angle measurements of the samples

4.3 Pore Size

Variations in the pore size of membranes are shown in Table 4.3. Compared to unmodified PVDF, modified membranes have a slightly lower pore size. The reduction in pore size may be due to microstructural shrinkage of the membrane caused by the dehydrofluorination process through modification. The average pore size did not change significantly. However, the effect of the modification is more pronounced at the maximum pore size. Pores shrink almost 4 times. The narrow pore size is an advantage for the selectivity of the membrane.

Table 4.2 Pore size of the modified and unmodified membranes

Membrane	Average pore size (μm)	Maximum pore size (μm)
PVDF	0.40 ± 0.1	2.40 ± 0.1
PVDF-OH	0.37 ± 0.1	0.82 ± 0.1
PVDF-OH/0.001	0.34 ± 0.1	0.74 ± 0.1
PVDF-OH/0.01	0.32 ± 0.1	0.61 ± 0.1
PVDF-OH/0.1	0.34 ± 0.1	0.51 ± 0.1
PVDF-OH/10	0.38 ± 0.1	0.59 ± 0.1

4.4 Oil/Water Separation Tests

4.4.1 Kitchen oil/Water Emulsion Separation

The kitchen oil permeability of the samples was calculated according to the formula given in chapter 3.1.4. The graphics are shown in Figures 4.3, 4.4, 4.5, 4.6, 4.7, 4.8, 4.9.

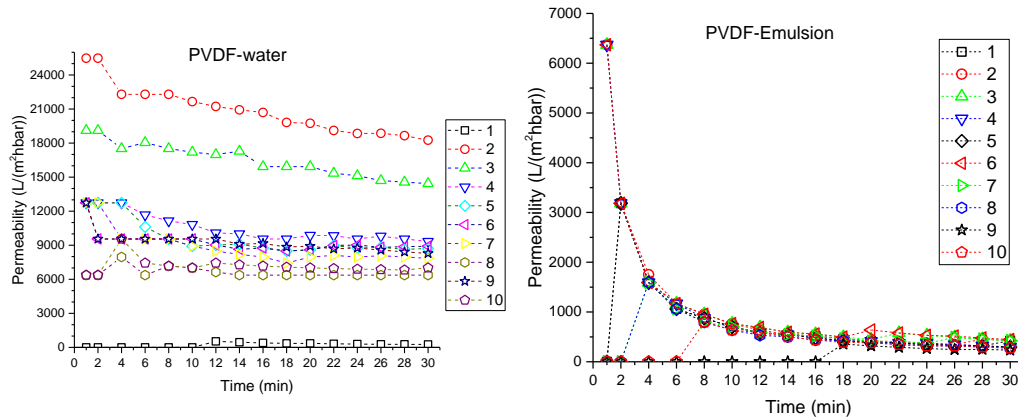


Figure 4.3 PVDF membrane DI water and kitchen oil permeability.

PVDF membranes are quite hydrophobic which not allows the water to pass through the membranes. As is indicated in Figure 4.3, there was zero permeability for the pristine PVDF membrane. As soon as membrane contact with emulsion, which includes the surfactant, membrane surface hydrophilicity changed. A similar result has been submitted by Safari et al. [84]. They found that adding 2% surfactant improves membrane flux around 38-fold. However, after the 2nd cycle, membrane pure water and emulsion permeability decreased in each cycle due to fouling. In the last two cycles (9 and 10), emulsion permeability has been stopped at the beginning of the filtration experiment.

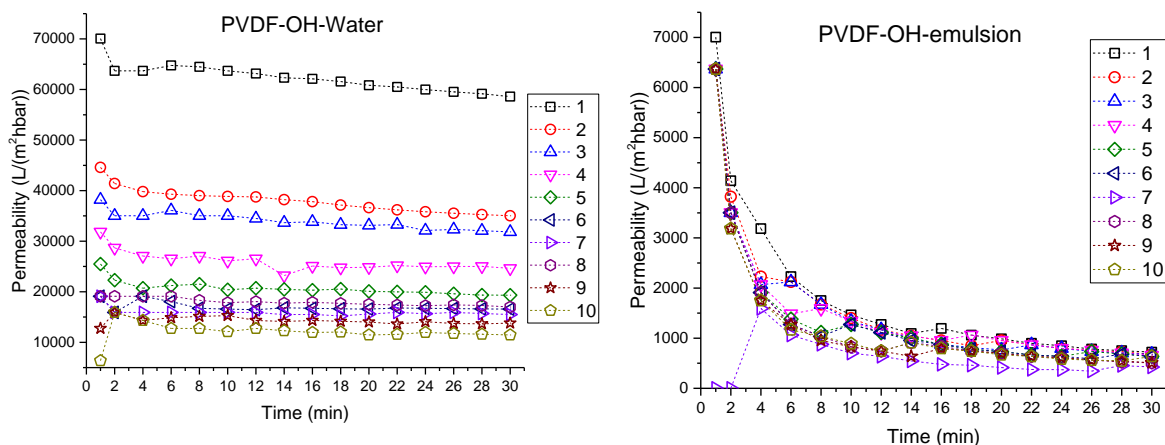


Figure 4.4 PVDF-OH membrane DI water and kitchen oil permeability.

Adding -OH group on the membrane surface increases the membrane hydrophilicity. Compare to the pristine PVDF membrane, PVDF-OH showed enormous pure water permeability. However, a visible decrease in membrane permeability has been observed in each cycle due to membrane fouling. The membrane had to be stopped after the 7th cycle, kept in DI water, and continued the next day. Our results indicated that resting membrane overnight helped to improve membrane permeability slightly. Compared to the pristine PVDF membrane, PVDF-OH showed almost double emulsion permeability after 10 cycles.

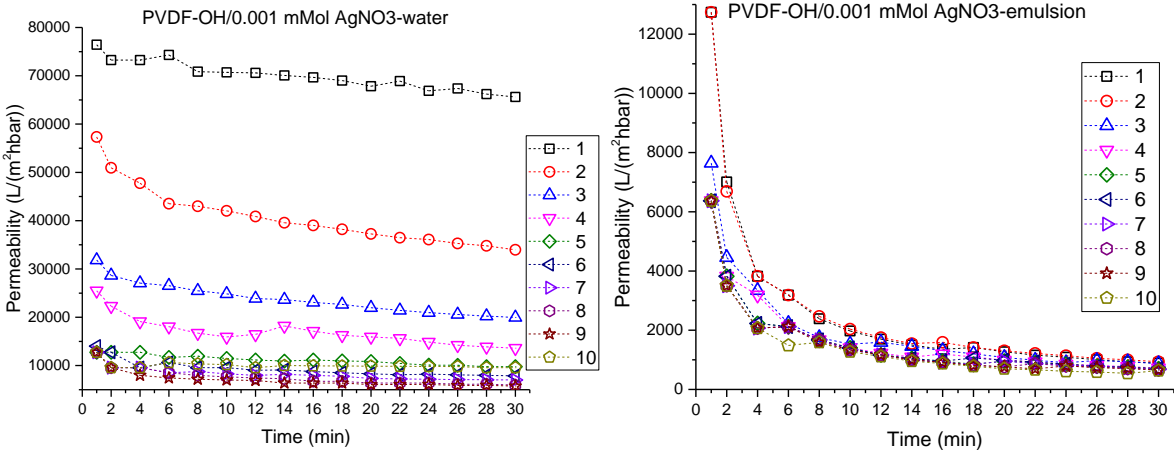


Figure 4.5 PVDF-OH/0.001 mMol NPs membrane DI water and kitchen oil permeability.

Grafting NPs on the membrane surface improved the membrane pure water and emulsion permeability compared to pristine PVDF membrane. However, the decline in the pure water permeability after the first two cycles has been observed due to membrane fouling. On the other side, emulsion permeability decline was observed at the beginning of the experiment but after 10 min of filtration, it became more stable. During the 10 times emulsion cycle, the membrane showed almost the same emulsion permeability. We can say that NPs helps to keep membrane permeability stable during 10 cycles.

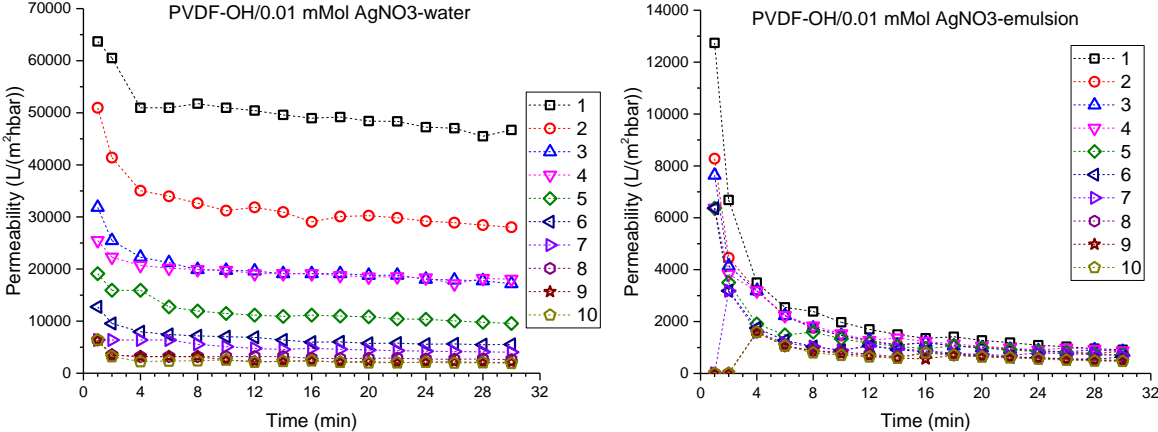


Figure 4.6 PVDF-OH/0.01 mMol NPs membrane DI water and kitchen oil permeability.

As in Figures 4.4, 4.5, and 4.6, membrane pure water permeability declined in time due to fouling. On the other hand, emulsion permeability showed a similar value during 10 cycles.

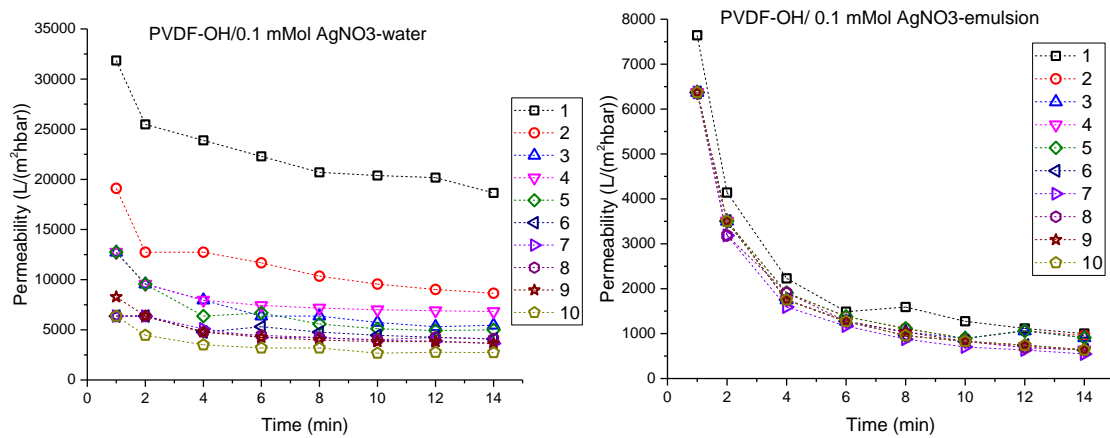


Figure 4.7 PVDF-OH/0.1 mMol NPs membrane DI water and kitchen oil permeability.

Interestingly, the emulsion permeability of the PVDF-OH/0.1 showed almost the same permeability from the first minute will end during 10 cycles. It seems that this membrane has a very consistent and stable permeability.

The water contact angle of this membrane showed zero. The reason was explained above. A highly hydrophilic membrane shows similar permeability during 10 cycles.

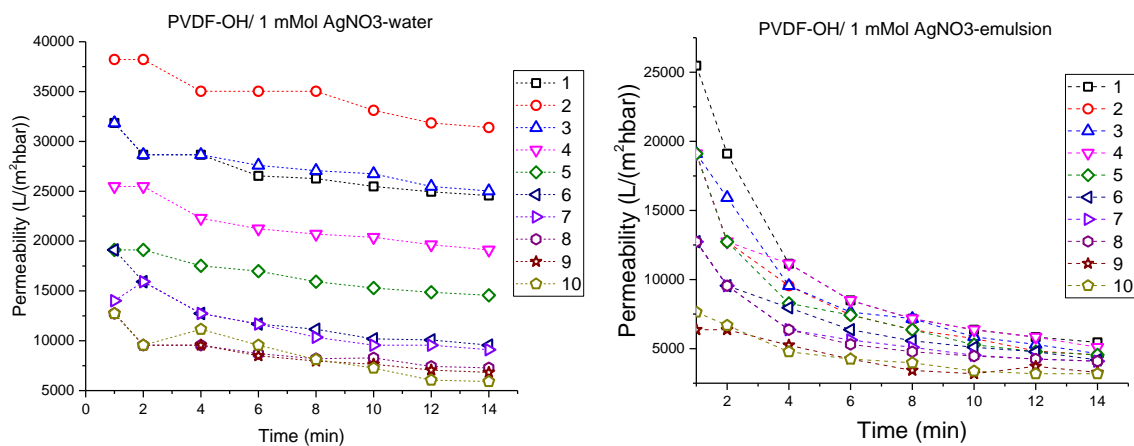


Figure 4.8 PVDF-OH/1 mMol NPs membrane DI water and kitchen oil permeability.

PVDF-OH/1 membrane showed higher emulsion permeability compared to other modified membranes but also different permeability in each cycle. It seems like the membrane is fouling in time. The high concentration of NPs amount can help the increase in permeability but fouling is inevitable.

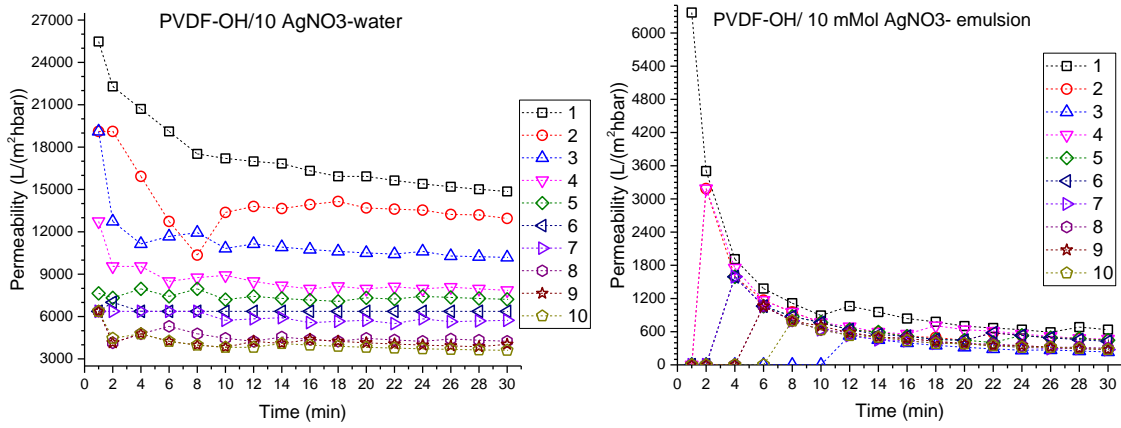


Figure 4.9 PVDF-OH/10 mMol NPs membrane DI water and kitchen oil permeability

Increasing concentration of NPs may cause aggregation of particles and create bigger particle sizes. The main reason for different membrane behavior of PVDF-OH/10 compared to fewer amounts of NPs might be due to size of NPs changes because of aggregation and also the concentration of NPs. There are not such good bounds between membrane surface and the NPs. Probably, NPs are released from the membrane surface and an excessive amount of NPs blocked the membrane pores which might cause fouling during 10 cycles.

Oil rejection was controlled using optical microscopy and no oil droplets have been observed in permeate.

4.4.2 n-Hexane / Water Emulsion Separation

n-Hexane permeability of the samples was calculated according to the formula given in chapter 3.1.4. The graphics are shown in Figures below;

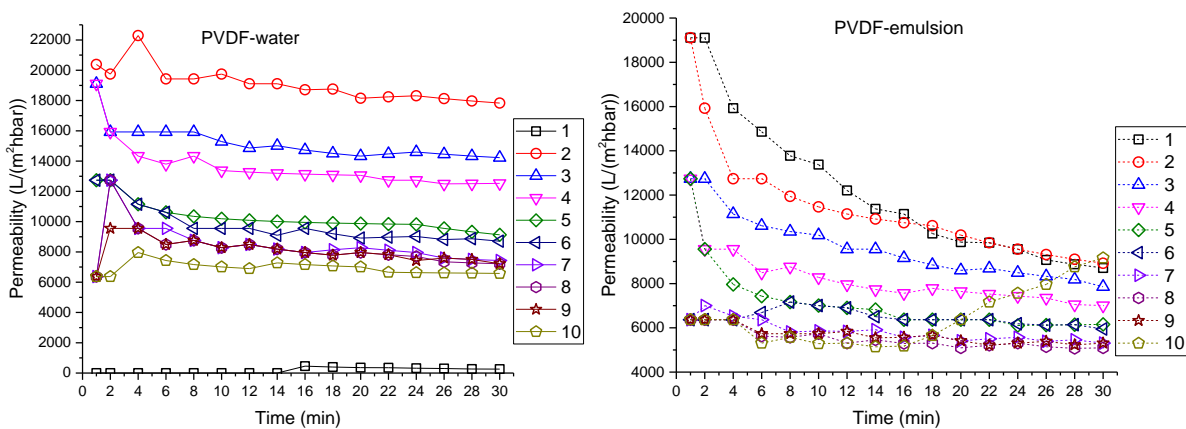


Figure 4.10 PVDF membrane DI water and n-Hexane permeability.

Hexane is low viscositic oil which is changed between 34.27–54.66cP [85]. The PVDF is hydrophobic and has almost zero pure water permeability.

After contacting with emulsion which consists of surfactant, the membrane became more hydrophilic and pure water permeability increased drastically. However, due to fouling, the pure water, and emulsion permeability decreased in each cycle.

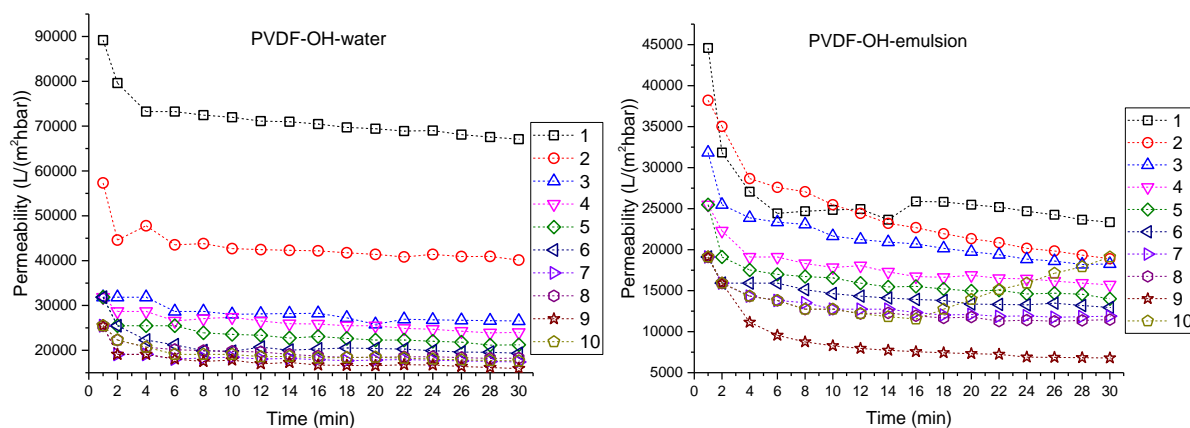


Figure 4.11 PVDF-OHmembrane DI water and n-Hexane permeability.

After alkaline treatment (Figure 4.11), the pure water and emulsion permeability of the membranes increased almost double the times compared to the pristine PVDF membrane. A similar result has been observed for the separation of kitchen oil/water emulsion. Membrane fouling has been observed in each cycle due to blocking of the pores and forming a cake layer on the membrane surface.

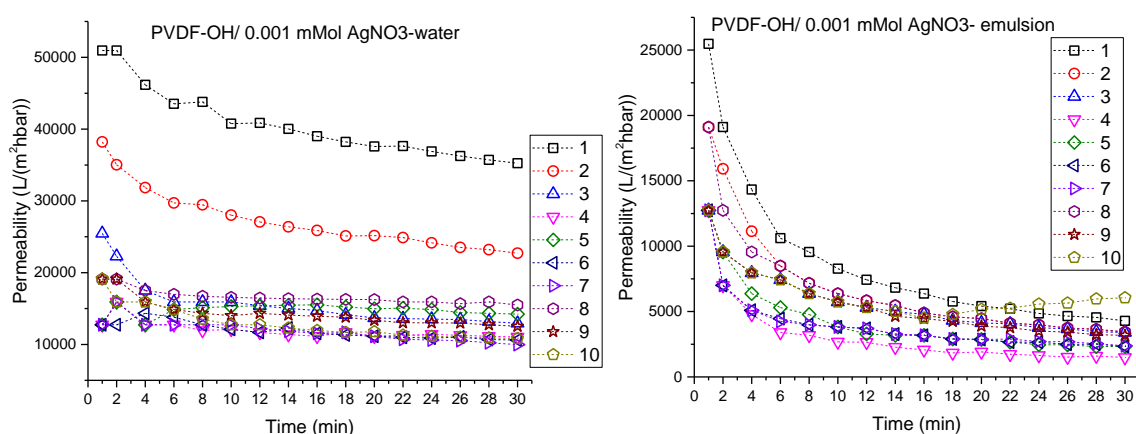


Figure 4.12 PVDF-OH/0.001 mMol NPsmembrane DI water and n-Hexane permeability

Adding NPs slightly improved fouling resistance as shown in Figure 4.12. During the first two cycles, membrane permeability decreased, then permeability continued stable during 10 cycles.

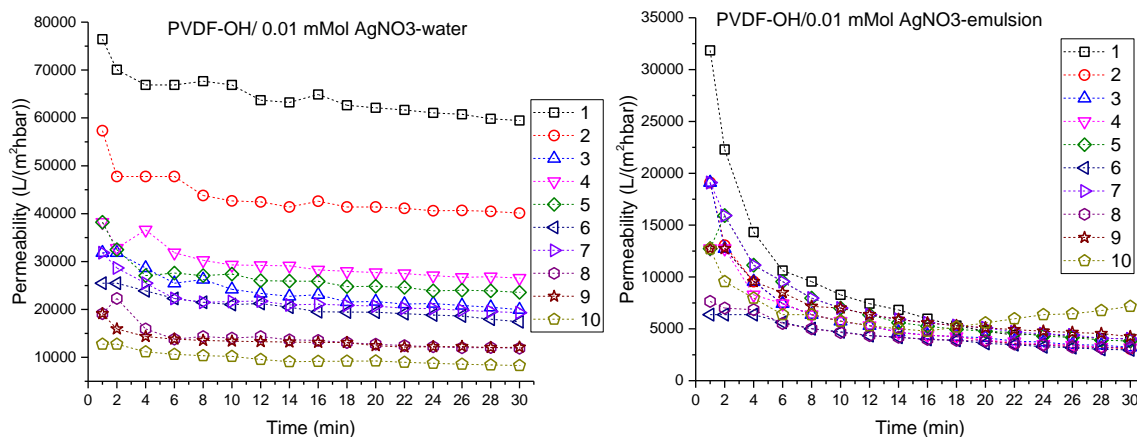


Figure 4.13 PVDF-OH/0.01 m Mol NPs membrane DI water and n-Hexane permeability

Unlike the membrane PVDF-OH/0.001, the pure water permeability of PVDF-OH/0.01 decreased in each cycle. On the other hand, emulsion permeability showed a similar tendency during 10 cycles.

At the beginning of each cycle, the permeability decreased and in time it reached a steady-state form. Probably, beginning of each cycle, a cake layer was formed and when the thickness of the cake layer reached a steady-state thickness, the permeability kept constant.

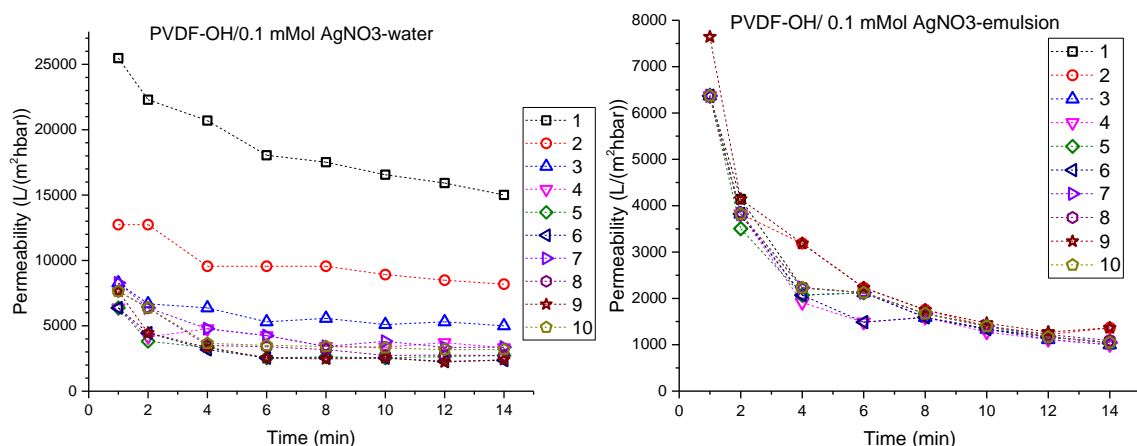


Figure 4.14 PVDF-OH/0.1 m Mol NPs membrane DI water and n-Hexane permeability

Very consistent emulsion permeability has been achieved by using PVDF-OH/0.1 membranes. Similarly, the same result has been observed using kitchen oil/water emulsion. PVDF-OH/0.1 membrane had the maximum hydrophilicity among the other membranes and showed the same emulsion permeability during 10 cycles.

Even the overall permeability is lower than other membranes (such as PVDF-OH/0.01), the membrane showed better fouling resistance.

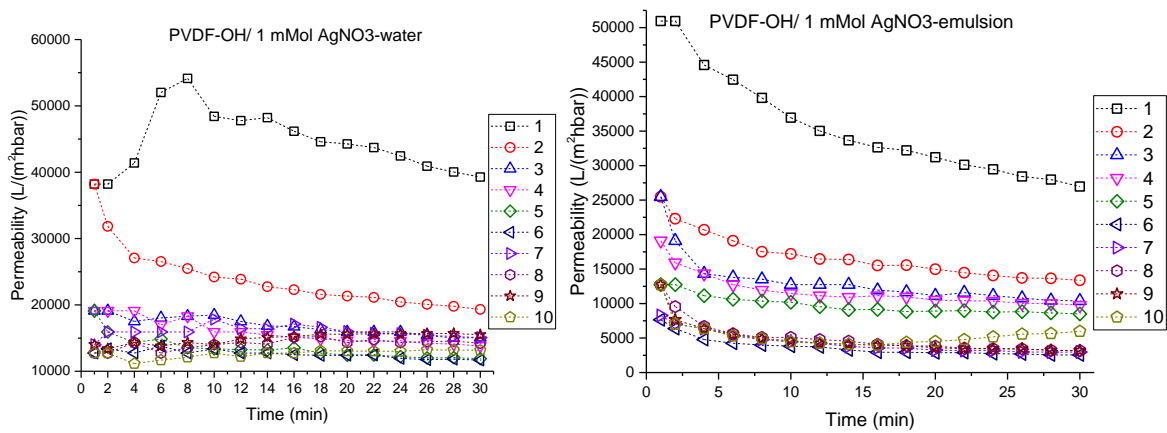


Figure 4.15 PVDF-OH/1 mMol NPs membrane DI water and n-Hexane permeability

PVDF-OH/1 membrane showed higher emulsion permeability at the first cycle compared to other modified membranes but also different permeability in each cycle. It seems like the membrane is fouling in time.

The high concentration of NPs can help the increase in permeability but fouling is inevitable. As similar in kitchen oil/water emulsion separation, possibly particles aggregated, separated from the membrane surface, and blocked the membrane pores.

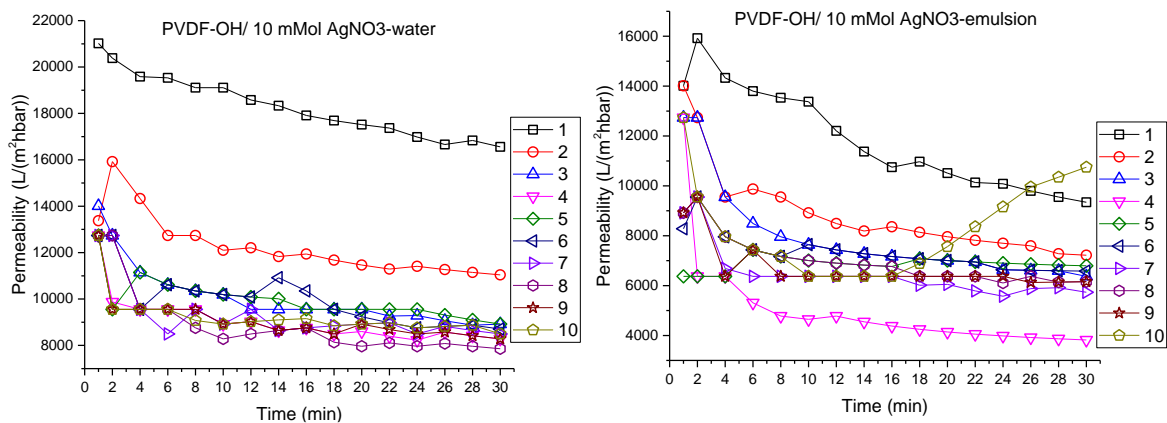


Figure 4.16 PVDF-OH/10 mMol NPs membrane DI water and n-Hexane permeability

Separation of n-hexane/water emulsion showed similar results as kitchen oil/water for the membrane PVDF-OH/10. Increasing concentration of NPs may cause aggregation of particles and create bigger particle size which causes reduction of the membrane permeability in time. After the 5th cycle, the filtration was stopped and continued the next day. Resting overnight in the distilled water helped to clean the membrane from excessive particles which were not attached properly.

Oil rejection was controlled using optical microscopy and no oil droplets have been observed in permeate.

4.5 Anti- Fouling Properties of Membranes

There are several methods to measure the fouling resistance of the membranes. The first one is calculating normalized flux and the second is calculating flux recovery rate. Normalized flux was measured using the differences between the pure water flux in between each cycle before and after contact with oil. It means water flux after each cycle (contaminated membrane) was compared with the very first water flux of clean membrane. The highest normalized flux with a stable value in each cycle is an advantage. It means the membrane is not contaminated so much, or after contamination, it kept stable permeability. Normalized flux was calculated based on the average flux of pure water during 14 min filtration. The reason to select 14 min is that we observed in 14 min, flux getting stable.

The pristine membrane has not been counted for anti-fouling calculation due to zero permeability of water for clean membranes.

Antifouling performances of the samples were calculated using normalized flux according to the given formulas in 3.1.5 and shown in Figure 4.17.

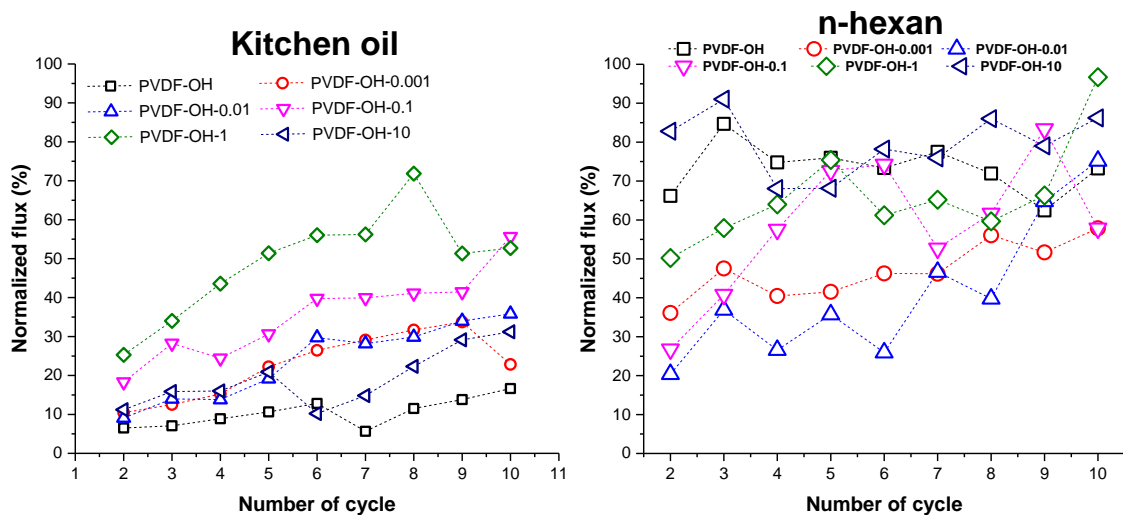


Figure 4.17 Normalized flux of samples during 10 cycles.

Based on the calculation of normalized flux, it can be concluded that;

- Membranes used for kitchen oil emulsion showed max. normalized flux around 70% and min. 5 %. Among all membranes, only PVDF-OH/0.1 and PVDF-OH/1 showed higher normalized flux.
- Membranes used for n-hexane oil emulsion showed max. normalized flux around 95% and min. 20 %. Except for the PVDF-OH/0.001 and PVDF-OH/0.01, almost all membranes showed high normalized flux.

The main reason for differences in normalized flux for both oils is due to the type of oil and its properties. Probably, both oils had different droplet sizes after mechanical mixing due to their viscosities.

Flux recovery rate is another evaluation method for determining the fouling resistance. Flux recovery rate is calculated according to formulas given in 3.1.5 during 10 cycles of using the same membrane without any cleaning. FRR calculation is very similar to normalized flux which means that depends on the contaminated membrane's pure water flux and clean membrane's pure water flux. However, FRR was evaluated for 14 min, not average flux was considered. Results are shown in Figure 4.18 for n-hexane and Figure 4.19 for kitchen oil.

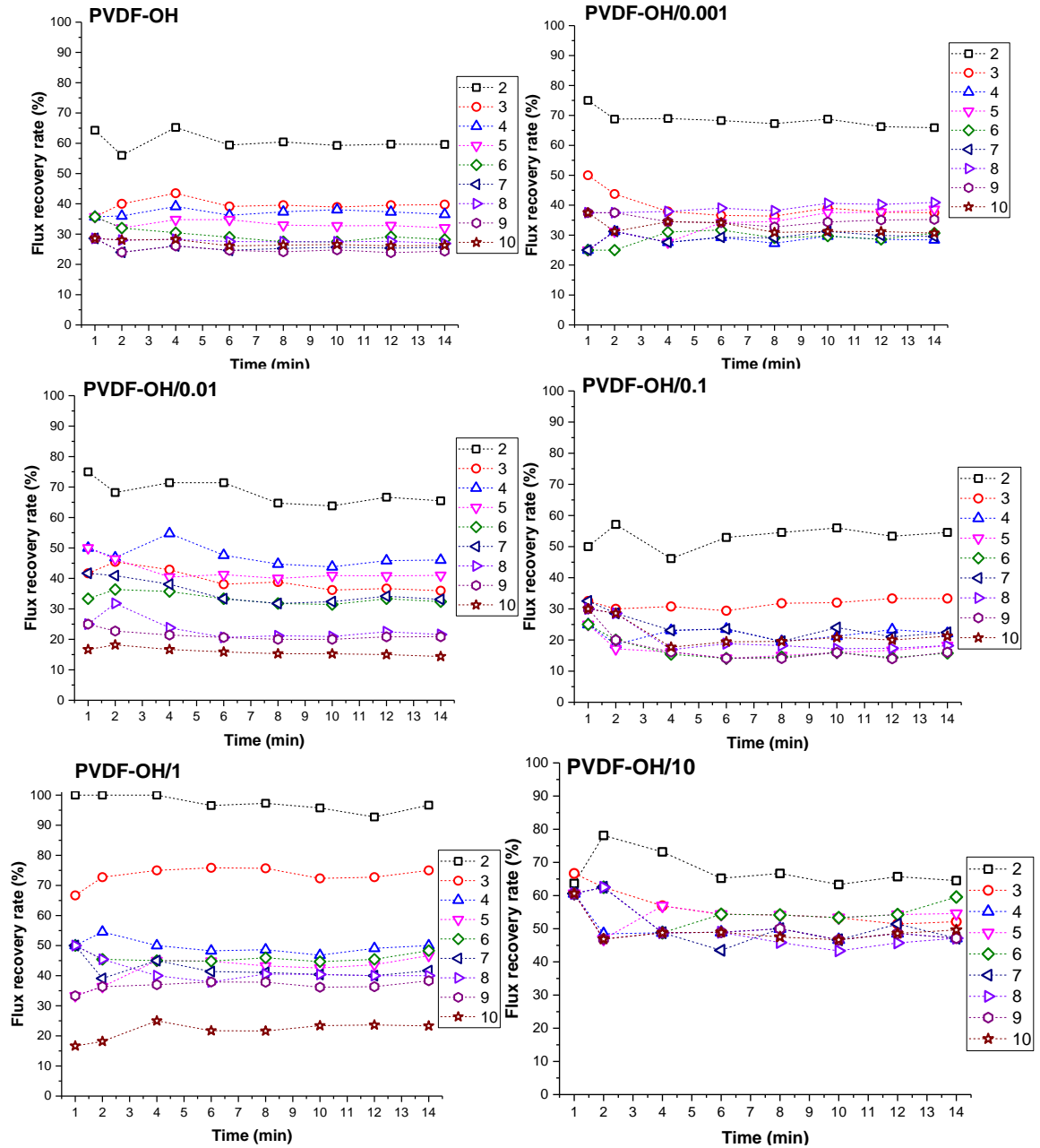


Figure 4.18 Flux recovery rate of samples after using n-Hexane.

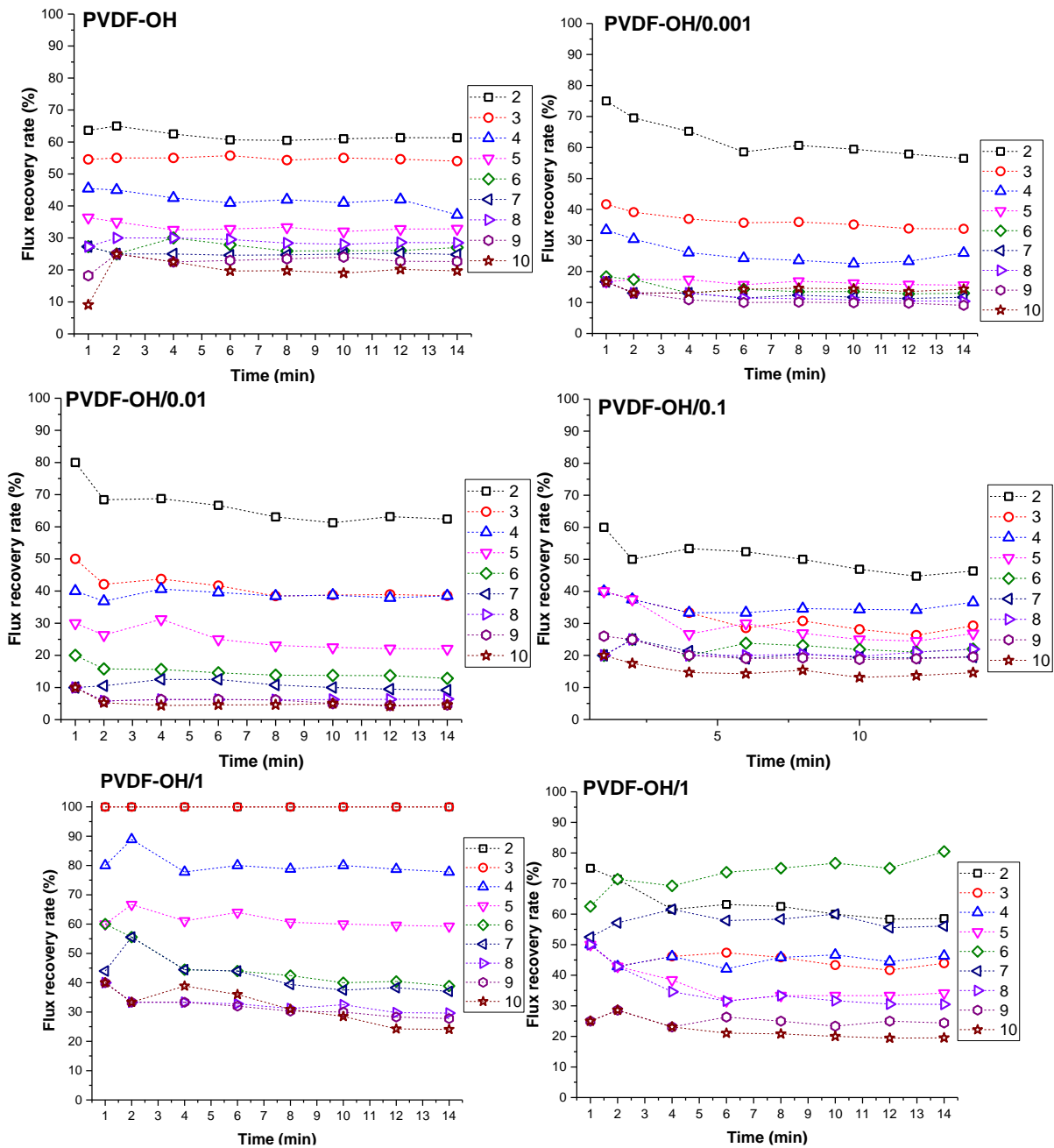


Figure 4.19 Flux recovery rate of samples after using kitchen oil.

FRR results can be concluded that;

- For the n-hexane, oil emulsion: for all membranes, the first cycle showed very good FRR during 14 min. Then all membranes started to foul and FRR decreased in each cycle. PVDF-OH/0.001, PVDF-OH/0.1, and PVDF-OH/10 showed similar FRR during 10 cycles after the 2nd cycle was completed.
- For the kitchen oil emulsion: Unlike the hexane oil emulsion separation, all membranes showed decreased FRR during 10 cycles.

- In summary, highly selective membranes with high permeability have been prepared for oil separation. However, none of the membranes achieved 99.99 % FRR or normalized flux during 10 cycles of filtration. It is very challenging to achieve such high values. On the other hand, we suggest remarkable improvement on fouling resistance property for the pristine PVDF using modification with a different number of NPs.

All the modified samples reject the oil droplets from the emulsion. Previous experiments prove that using Ag nanoparticles on PVDF nanofiber surface rejection rate kept over 96 % even at a different pore size of the membranes [86]. We can say that, using modified membranes, membrane permeability and fouling resistance improve considerably with high rejection of oil droplets.

5. CONCLUSION

The properties of nanofibrous membranes were discussed in this study, including pore size, emulsion permeability, and flux recovery, contact angle, surface modification, and membrane self-cleaning. For oily wastewater separation, porous structure, hydrophilicity, membrane permeability, performance, self-cleaning, and fouling prevention are all critical factors. In this research, PVDF, PVDF-OH, PVDF-OH / 0.001mM NPs, PVDF-OH / 0.01mM NPs, PVDF-OH / 0.1mM NPs, PVDF-OH / 1mM NPs and the PVDF-OH / 10mM NPs were tested.

Normally PVDF membranes separate oil from oily wastewater because PVDF has hydrophobic and oleophilic nature. Oppositely in this experiment, PVDF membranes showed hydrophilic and oleophobic properties during emulsion separation. Membrane behavior has been changed. This may be due to the surfactant which increases the membrane's hydrophilicity. It has been found that considerable progress has been made through surface modification of membranes for the separation of oily wastewater. Permeability results showed outstanding flux and permeability after surface modification of PVDF membranes with alkaline solutions and TiAg NPs.

Since TiAg NPs have high demand properties for the improvement of membranes used for the recovery of clean water from oily contaminated sources, their effect on setting oily water emulsions by modifying PVDF membranes with them has been studied. Results show that Ag is mostly present on the surface of NPs and provides the optimizing qualities for membranes.

On the one hand, this basic composition enables optimum loading that provides ideal wettability to prevent the long-term passage of oil droplets through filtration membranes, regardless of oil viscosity or droplet size. On the other hand, these NPs can contribute to the anti-fouling properties of the membrane by converting them into catalyst structures for the degradation of organic contaminants commonly found in wastewater while providing self-cleaning properties.

Overall, the current work brings new insights into the efficient design of specialized nanomaterials for the improvement of membranes and lays the groundwork for future developments in truly cleaning oily wastewater.

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