CERAMIC MICROFILTRATION MEMBRANE DESIGN TOWARDS OIL REMOVAL IN METAL INDUSTRY WASTEWATER STREAMS

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ABSTRACT

CERAMIC MICROFILTRATION MEMBRANE DESIGN TOWARDS OIL REMOVAL IN METAL INDUSTRY WASTEWATER STREAMS

Increasing water scarcity is an important threat to the whole world. The use of too much water during the production processes and the insufficient level of reuse of this water and the increasing quantities of oil containing waste generated in many industrial activities cause dangerous consequences for the environment. Highly concentrated oil-in-water emulsions are very harmful for aquatic life, soil, atmosphere and human health. Traditional treatment methods are not effective in the removal of emulsified oil droplets which have less than 20 μm of droplet size. Ceramic micro/ultrafiltration membranes have been explored and developed in recent years due to their superior advantages in oil containing water treatment/purification.

The aim of this MSc study was to produce tubular ceramic supports and microfiltration membranes for the removal of oil from stable oil in water emulsions used as metal cutting fluids. The prepared metal cutting fluids were fed to the crossflow filtration system and the effects of experimental parameters such as transmembrane pressure (TMP), crossflow velocity (CFV) and oil content on membrane performance/permeate flux were investigated. The single/double layered coatings on the support surfaces were formed in the preparation of the microfiltration membranes by using stable 0.4 μm α-alumina suspensions. The 1 layer and 2 layers containing microfiltration membranes were heavily fouled and very low permeate fluxes were obtained in an hour of treatment. This was attributed to the formation of a thin oil layer on the microfiltration membrane surfaces. The reduction of the total suspended solids (TSS) and turbidity were determined as ~100 %. A stable permeate flux with a lower extent of membrane fouling and concentration polarization was obtained with 1% oil content and the support membrane and TMP=2 bars.

ÖZET

METAL ENDÜSTRİSİNDE ATIKSULARIN YAĞDAN ARINDIRILMASINA YÖNELİK SERAMİK MİKROFİLTRASYON MEMBRAN TASARIMI

Artan su kıtlığı tüm dünya için bir tehdit oluşturmaktadır. Sanayide aşırı su kullanımı, yetersiz geri dönüşüm ve yüksek yağ konsantrasyonlu su atıkları çevre için tehlikeli sonuçlar doğurmaktadır. Yüksek yağ konsantrasyonlu su emilsiyonları su yaşamı, toprak, atmosfer, insan sağlığı için oldukça tehlikelidir. 20 µm ve altı boyutta küçük yağ parçacıklarını uzaklaştırmak için kullanılan geleneksel metotlar yeterince verimli olmamaktadır. Son yıllarda, yağlı su arıtımındaki avantajlarından dolayı seramik mikro/ultrafiltrasyon membranları keşfedilmiş ve geliştirilmiştir.

Bu yüksek lisans tezinin amacı seramik destekli boru şeklindeki membran üretimini ve mikrofiltrasyonunu çalışmaktır. Hazırlanan metal kesme sıvısı çapraz akım filtrasyon sistemiyle beslenmiş ve transmembran basıncı, çapraz akım hızı ve yağ içeriği gibi deneysel parametreler incelenmiştir. Destek katmanı üzerindeki tek ve çift katlı kaplamalar 0,4 µm α-alumina kullanılarak hazırlanmıştır. 1 saat süreli deneyde MF membranının 1 katmanı ve 2 katmanı tıkanma ve düşük süzüntü akışı gözlenmiştir. Toplam askıda katı madde ve bulanıklığın azalması %100 olarak belirlendi. Düşük membran tıkanıklığına sahip sabit süzüntü akımı ve konsantrasyondaki polarizasyon %1 yağ içeriğine sahip destek membranda elde edilmiştir ve ve transmembran basıncı 2 bar olarak bulunmuştur.

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TMP. :	Trans Membrane Pressure
CFV :	Cross-Flow Velocity
min :	Minute
g :	Gram
L :	Liter
h :	Hour
rpm :	Revolution per minute

CHAPTER 1

INTRODUCTION

The treatment processes used in water reuse and recovery has gained vital importance due to the increasing levels of freshwater use in various industrial activities. The use of satisfactory levels of freshwater is essential for a healthy human survival all over the globe. Although water is the primary source of life, only a very low fraction of water present on earth can be classified as drinkable water with a very nonuniform distribution around the globe. The discharge of oily water to the freshwater sources and sea is the most serious environmental problem facing humankind. The oily water is a danger for aquatic life. Fatty acids and some organic compounds disarrange the oxygen transfer chain by covering the surface of seawater. The discharged oily wastewater streams contaminate drinkable/underground water and in the long term may give a serious damage to the terrestrial life cycle. The environmental protection rules ban the direct release of oily wastewater to the freshwater sources.

Industrial companies have been forced to remove organic pollutants from oily wastewater streams. Traditional methods like flotation, skimming gravity and coagulation have been commonly used in the first stage of wastewater treatment. These treatment methods can’t provide the desired increasing environmental purification requirements. The emerging membrane treatment processes may help in obtaining the desired refinement of oily wastewater. Generally, the membrane treatment processes are based on the utilization of droplet size in oil-water emulsions. The traditional methods can only utilize density differences whereas membrane technologies can separate smaller oil droplets even under 20 micrometers in size. The membrane-based technologies thus offer an ecofriendly solution to this major treatment problem.

A membrane accomplishes separation by acting as a selective barrier between two different phases. The undesired or desired components can be removed in one of these two phases. The history of membrane technologies related studies can be traced back to the second half of 20. Century where the pioneering research had been conducted on inorganic membranes. Although the primary scientific membrane studies started in the middle of 1700s, scientific research started in the 1940s for industrial separation applications.

The first inorganic membranes were used in the 1960s in the separation of uranium isotopes (Gillot, 1991). Inorganic membranes were further classified as symmetric and asymmetric membranes based on their different structures.

The first milestone in the membrane applications was the development of asymmetric inorganic membranes in the 1960s. After this discovery, modern membrane technology became increasingly attractive to scientists and industrialists. Inorganic membranes are generally made of ceramic materials and the nature of these phases depend on their advantages in the respective application. Ceramic based membranes are the most useful and common inorganic membranes since they have several advantages such as corrosion resistance, thermal and chemical stability. There are three main layers of inorganic (ceramic) asymmetric membranes. The top layer has the smallest pore size and is formed on an interlayer which is supported by a thicker support layer responsible from the mechanical integrity of the whole structure. The top selective layer mainly is responsible from the separation because the top layer has the smallest pore size. A long useful lifetime durability is one of the requirements for a membrane system. This problem is solved by using the support layer which provides the necessary mechanical strength needed for the asymmetric ceramic membrane constructs. The nature and properties of asymmetric ceramic membrane layers differ based on their thickness and pore size as shown in Table 1.1(De Vos & Verweij, 1998).

Table 1. 1. Asymmetric ceramic membrane properties. (Source: De Vos & Verweij, 1998)

Layer	**Top (Selective)**	**Intermediate**	**Support**
Material	SiO2	γ -Al_2O_3	α-Al_2O_3
Thickness	30 – 200 nm	10^3- $4*10^3$ nm	$2*10^6$nm
Pore Diameter	0.3 – 0.8 nm	2- 5 nm	80-120 nm

Inorganic ceramic membrane supports can be shaped by slip casting, pressing, tape casting and extrusion methods (Drioli & Giorno, 2010). Alumina is the most commonly used material due to its chemical stability and strength in the support preparation processes.

There are a couple of membrane based techniques which can be used in various applications along with the inorganic microfiltration ceramic membrane based methods. Nanofiltration (NF) is a method which necessitates the application of pressures in between ultrafiltration (UF) and reverse osmosis (RO). The NF membrane can separate nanosized species from liquid solutions. The use of NF method for the separation of 200-1000 Da polyvalent molecules was reported in a recent research article (Lu, Chen, Chen, Qiu, & Fan, 2016). The NF membrane can successfully separate organic impurities from liquids. The NF membranes can be classified in two main groups as organic polymeric and inorganic ceramic membranes based on membrane material (Van Gestel et al., 2002). Ceramic NF membranes have significant advantages since they have superior mechanical, chemical, thermal stability compared to their polymeric counterparts.

Membranes must have a set of properties for achieving the desired separation process. The stability of membrane pore sizes/structure especially have a critical role in the separation applications. Neodymium and zirconium can be used as dopants for the development/design of the nanostructure. Also titania and titania based materials can be used for the prevention of pore growth. The addition of ZrO_2 was reported to control the pore growth in TiO_2 based membranes where the membrane pore size decreased to 3.6 nm compared to the 4.5 nm in the undoped membranes (Sekulić, Magraso, ten Elshof, & Blank, 2004).

The nanoscale membrane separation processes necessitates the presence of very small pores about 1 nm in size. Nanoporous TiO_2-ZrO_2 mixed-oxide membranes can be prepared in the above pore sizes due to the delayed/controlled crystallization and nucleation processes during nanostructure development (Aust, Benfer, Dietze, Rost, & Tomandl, 2006). SiO_2-ZrO_2 membranes on the other hand may also have beneficial properties because they can be used at higher temperatures. This composition can be utilized due not only to pore size control ability of silica but also desirable properties of zirconia in aqueous media (Puthai, Kanezashi, Nagasawa, & Tsuru, 2016). Farsi and coworkers' recent article reports the experimental work carried out on the preparation of microporous NF membranes in the SiO_2-TiO_2 mixed-oxide system in the similar pore size range (Farsi et al., 2017). The two well known sol-gel processes classified as polymeric sol-gel route and colloidal sol-gel route have been commonly used for the formation of selective layers in all these reported research on inorganic ceramic membrane preparation. The major difference between these sol-gel processes is the fact that polymeric sol-gel route usually generates microporous structures whereas colloidal sol-gel route usually fabricates mesoporous membrane structures (Aust et al., 2006).

The main application area of the synthetic membranes is the purification/filtration and the the separation of unwanted components from wastewater streams and the recycle of clean/reusable filtrate streams. Both microfiltration and ultrafiltration ceramic membranes can be utilized for the separation of very small oil droplets from oily wastewater streams (Abadi, Sebzari, Hemati, Rekabdar, & Mohammadi, 2011). The most effective working parameters such as temperature, pH, transmembrane pressure (TMP), and cross-flow velocity (CFV) were investigated in the above article. These are commonly known factors with a direct influence on the efficiency of the feed solution filtration. The highlighted desired terms are high permeate fluxes and high oil removal efficiencies along with the ability to control and maximize these through the control of the processing parameters for a specific membrane structure. Micro and ultrafiltration ceramic membrane performances have certain limits due to concentration polarization effect and membrane fouling problems. However, scientists have developed some techniques to solve these problems. A nano-coating modification that may enhance the hydrophilicity of the MF membrane surfaces was discovered to be the first of a number of solutions in overcoming membrane fouling problems. There are three most useful membrane phases like γ-Al_2O_3, ZrO_2 and TiO_2 used in these solutions. Hydrophilicity of the membrane surfaces may be increased by using γ-Al_2O_3, ZrO_2 and TiO_2 coatings which may decrease the adherence capacity of very small oil droplets to the surface (Zhou, Chang, Wang, Wang, & Meng, 2010).

The aim of this study was to investigate the effect of different parameters on oil removal from metal industry cutting fluids by ceramic microfiltration membranes. The necessary membrane design/structure was also analysed which was a strong function of the metal cutting fluid composition/stability/droplet size.

CHAPTER 2

MEMBRANES

Ceramic inorganic membranes have several significant advantages when compared with their polymeric counterparts. They have a longer lifetime and much higher thermal/mechanical/chemical stability. They are dirt-repellent and washable, have a high throughput volume with minimized fouling problems and control and design of their pore size/structure may be much easier than organic membranes. All ceramic inorganic membranes possess these advantages and ceramic membranes with various properties can be designed and prepared. On the other hand, since ceramic membranes are brittle, they must be prepared in special configurations on suitable supports so that they are able to have a long trouble-free lifetime. Relatively lower energy requirements, small footprint and eco-friendly behavior, easy operation conditions and the use of lower levels of chemicals makes ceramic membranes the best choice for the treatment of wastewaters despite these disadvantages related to restricted geometries and brittle behavior (van Rijn, 2004).

Membranes can be divided into two groups as polymeric or inorganic based on material. Although polymeric membranes can be used commonly in many different applications, their thermal and pH stability are significantly lower than inorganic membranes. The use of polymeric membranes although is very common nowadays they are less preferable than ceramic membranes in industrial applications involving higher temperatures and corrosive streams. The membrane material is the most important factor for the efficiency of an operation. The separation and operating conditions are defined in Table 2.1. Inorganic membranes can work even at high temperatures and at extra pH. The polymeric membranes are generally more sensitive than inorganic membranes in process applications where organic solvents and other cleaning agents are involved. The thermal stability, mechanical strength and pH stability of inorganic membranes are significantly higher so that inorganic membranes can work at high transmembrane pressures. Multi-layered inorganic membranes generally have higher permeation capacities than their polymeric equivalents and through the relatively easier control of their thin selective layer pore structures also molecular level species separation may become possible. These selective ceramic membrane layers are generally made of zirconia, titania, silica, and alumina. The high temperature heat treatment and processing conditions/expenses are very important in the pore structure control and in determining the ceramic membrane prices which are usually higher than polymeric membranes currently.

Table 2. 1. Commonly used membrane materials and their properties. (Source:Hsieh, 1996).

Material	**Application(s)**	**Approximate maximum working temperature (^oC)**	**pH range**
Cellulose acetates	RO, UF, MF	50	3 – 7
Aromatic polyamides	RO, UF	60 – 80	3 – 11
Fluorocarbon polymers	RO, UF, MF	130 – 150	1 – 14
Polyimides	RO, UF	40	2 – 8
Polysulfone	UF, MF	80 – 100	1 – 13
Nylons	UF, MF	150 – 180	
Polycarbonate	UF, MF	60 – 70	
Polyvinyl chloride		120 – 140	
PVDF	UF	130 – 150	1 – 13
Polyphosphazene		175 – 200	
Alumina (gamma)	UF	300	5 – 8
Alumina (alpha)	MF	>900	0 – 14
Glass	RO, UF	700	1 – 9
Zirconia	UF, MF	400	1 – 14
Zirconia (hydrous)	DM(RO, UF)	80 – 90	4 – 11
Silver	MF	370	1 – 14
Stainless steel (316)	MF	>400	4 – 11

2.1. History of Inorganic Membranes

The fundamental membrane scientific research had historically been initiated with the invention of osmosis phenomena and the term osmosis was used for the first time towards membrane separation in 1748. Abbe Nolet carried out experiments on semi-permeable membranes for water separation and filtration. Fick synthesised the first artifical membrane made of nitrocellulose in 1855. Bechold conducted research on how to control the pore diameter and measure the pore size following the pioneering membrane research. He also had used the term ultrafiltration fort he first time (Tamimi, 2013) Sir Thomas Graham had noticed that the metalic palladium hydrogen absorption capacity was wery effective for gas separation membrane applications in 1866.

A German company successfully fabricated the first commercial membrane in 1927. Reverse osmosis entered to the dictionary of the membrane processes in 1931 which was utilized for desalination (separation of salt from water) of seawater. In 1940s, the membrane processes was able to filtrate/separate microorganisms and small particles from liquid and gasous streams. Scientists had developed a membrane process which was able to generate salt-free water at high fluxes through desalination of sea water in 1960.

Scientific research was concentrated on decreasing membrane thickness and increasing membrane flux. Souriarjan and Loeb developed cellulose acetate membranes by using annealing method to decrease membrane thickness. Acording to their studies, the increase in pore size of the the membrane decreased the rejection of the salt and the flux was increased with increasing temperature. The following most important development emerged from Souriarjan and Loeb's research on the asymmetric membrane concept (Tamime 2013). The discovery of nanofiltration and reverse osmosis membranes/ techniques gave an acceleration in industrial applications in the 1980s. Scientists and industry were heavily interested in inorganic ceramic membranes due to their superior properties and benefits.

Nanofiltration (NF) is the most useful innovative membrane separation and filtration process developed to satisfy the increasing industrial separation operations along with microfiltration (MF), ultrafiltration (UF) and reverse osmosis (RO). NF is one of the most useful separation methods which can be classified into three groups as loose RO, intermediate RO/UF and tight UF membrane. Scientists conducted research on preparing a lower priced membrane material with maximum filtration/separation abilities and performance. The worldwide extensive research have shown that zirconium oxide and titanium oxide based selective layers were the best materials commercially applicable in microfiltration, ultrafiltration and nanofiltration membrane based separation applications.

2.2. Classification of Membranes

Inorganic membranes can be classified according to their structure, pore size, operation principle and driving force. There are several classification methods based on different properties of membranes. The most important classification is based on structure of membrane as symmetric and asymmetric. The structure is important for separatioın because symmetry of membrane is very important in the determination of the flux. Symmetric membranes can be divided into three main groups as the homogeneneous films, those with cylindirical pores and sponges. Asymmetric membranes can be classified as integral asymmetric and composite. Asymmetric membrane is very useful for seperation because it have several different layers and they increase the selectivity. The thickness of the top selective layer formed on porous layers on the support is critical in obtaining desired permeate flux levels and is usually very thin. Asymmetric membranes are generally used in microfiltration, nanofiltration, ultrafiltration and reverse osmosis due to their stability and higher flux values.

Table 2. 2. Microfiltration (MF) Ultrafiltration (UF) Nanofiltration (NF) Reverse osmosis (RO).

Filtration	**Driving Force**	**Feed content**	**Permeate Stream content**	**Particle size**	**Removed Species in Retantate Stream**	**Pressure Trans Memrane**
(MF)	Pressure or vacuum	Suspended solids, water	Dissolved solutes, water	0.1-10 µm	Suspended solids, bacteria	1-3 bar
(UF)	Pressure	Water, large molecules	Water, Small molecules	10-100 nm	Colloids, polysaccharides, proteins	2-10 bar
(NF)	Pressure	Disassociated acids, water	Water, Undissociated acids	1-10 nm	Viruses, multivalent ions	6-10 bar
(RO)	Pressure	Water, solutes	Water	0.1-1 nm	Monovalent ions	10-70 bar

MF, UF, NF and RO use trans membrane pressure difference as driving force. As shown in Table 2.2, water-based solutions are separated as permeate and retentate streams. The most common MF application is used for liquid purification and sterilization in metal industry. UF membranes are used especially for metal enrichment such as uranium and some biological separations. RO is different than others in terms of permeability. This process allows only water transport. Therefore, it is used for desalination and in metal industry. NF membranes are used for metallic ion separation and desalination. The most significant factor is the pore size in determining the membrane function and capacity.

Also, membranes are separated based on being dense/porous and pore size. Metallic membranes and solid electrolyte membranes are very common examples for dense membranes. Porous membranes are composed of selective top and intermediate layers on supports which usually are designed to have micron sized pores. Another classification is based on being natural or synthetic. Synthetic membranes can be divided in two subgroups as polymeric and ceramic membranes. There are several classifications of membranes due to the difficulty in the identification of various properties of membrane types.

2.3. Classification of inorganic membranes

The classification and characterization of membranes is generally based on pore size, driving force, operation mode, structure and morphology. They can be identified as MF, UF, RO and NF based on pore structure. Driving force or the working principle based classification groups them as membranes operating with concentration gradient, pressure or electrical potential differences. Crossflow filtration and dead-end filtration are two major types based on operation mode. Structure and morphology difference based groups are basically known as dense or porous membranes (Hsieh, 1996).

There are two main operation modes known as dead-end and crossflow filtration mode for membrane filtration as shown in Figure 2.1. In the dead-end filtration, the feed enters the membrane upright where the targeted pollutants and solids are accumulating and retained on the membrane surface. When the layer becomes denser with filtration time, the permeation through the membrane will face more resistance, and the flux decreases gradually.

In the crossflow filtration, the feed flows parallel to the membrane surface. While only a small part of the water penetrates from the membrane under the applied pressure, the rest circulates into the feed water tank. Since the formed cake layers on the surface are swept by the flow, the accumulation of pollutants on the membrane surface is significantly reduced in crossflow filtration. Higher permeate fluxes compared to dead end filtration is commonly obtained due to the lower level of cake resistance. Crossflow filtration requires higher pressures and energy to keep the flow at a comparatively high speed which can stated as a disadvantage of this mode of operation.

The permeate flow rate decreases during filtration due to the accumulation of a filter cake which is known to cause membrane fouling. The fouled membrane should be cleaned with chemical and physical cleaning or backwashing to remove cake components stuck or trapped inside the pores or surface of the membrane. The membrane can be used for different filtration processes after cleaning. Cross flow filtration requires less cleaning time compared to dead-end filtration which makes it possible to obtain more stable fluxes and longer filtering operation periods.

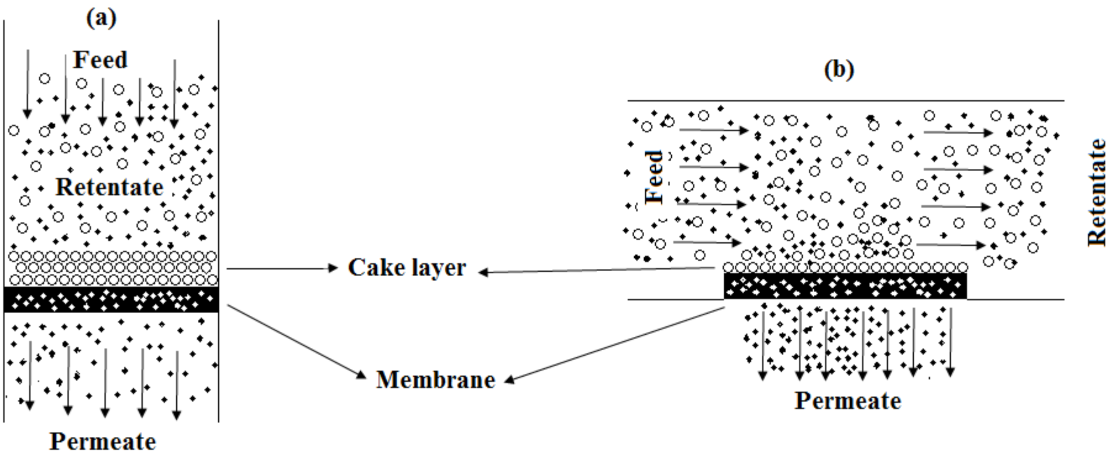

Figure 2. 1. (a) Schematic diagram of a dead-end filtration mode. (b) Schematic diagram of a crossflow filtration mode.

2.4. Materials for membranes

Membranes can be prepared from organic, inorganic or composite materials. Membrane materials must be chosen based on the intended application and both advantages and disadvantages of the material choice have to be considered. These materials can be listed based on application. Aromatic polyamides, cellulose acetates, polyamides, fluorocarbon polymers, polycarbonate glass, nylons polyvinyl chloride, polysulfone, alumina and zirconia can be used in ultrafiltration membrane production. Stainless steel and silver can be used only as microfiltration membranes (Cheryan, 1998).

Polymeric membranes are currently heavily used in industrial applications due to economical reasons which is an output of their major advantages in terms of material cost and ease of fabrication. Chemical properties of polymeric membrane give rigidity and stereoregularity to chains. Therefore, polymeric membrane becomes stable and energetically unfavorable and this property makes membranes easy to prepare. Cellulose acetate has a wide application range. Naturally, it prevents one of the most important problems which is membrane fouling by courtesy of its hydrophilic tail. Phase inversion, track etching and coating are the methods of preparation of polymeric membranes. The methods utilized depend on membrane polymeric materials.

Inorganic membranes can be divided into three groups as structural, operation mode and size. The most popular material is ceramics based in order to prepare porous membranes. The ceramic structures becomes resistant to harsh conditions such as high concentration of corrosive chemicals and high temperatures after proper heat treatment processes. Ceramic membranes are usually made of alumina (Al_2O_3), zirconia (ZrO_2), titania (TiO_2) and silica (SiO_2) which are known to be the main commonly used metal oxides in high technology ceramic components.

2.4.1. Structural Based Classification

Membranes can be classified as dense (nonporous) and porous membranes based on the nature of the pore structure. The principle mass transport mechanism is through ionic/atomic diffusion in nonporous membranes. Diffusion acts as a driving force and it can be based either on a concentration or pressure gradient. Separation and filtration capacity have direct proportion with membrane materials and their diffusivity. Permeability is the distinctive measure of diffusivity.

Porous membranes are composed of multilayer structures as support and intermediate/top layers. Ceramic membranes are the best representative membrane types for porous membranes. Separation capacity is based on both permeability and adsorption ability. The selectivity is provided by the distribution and size of the pores.

Also, inorganic membranes can be classified based on distribution of layers as symmetric (isotropic) and asymmetric as shown in Figure 2.2. Symmetric membranes are formed by the regular placement of certain selectable layers on top of each other so that it is isotropic. This homogenous structure gives the membrane the necessary mechanical strength. The permeate flux decreases with increasing layer thickness.

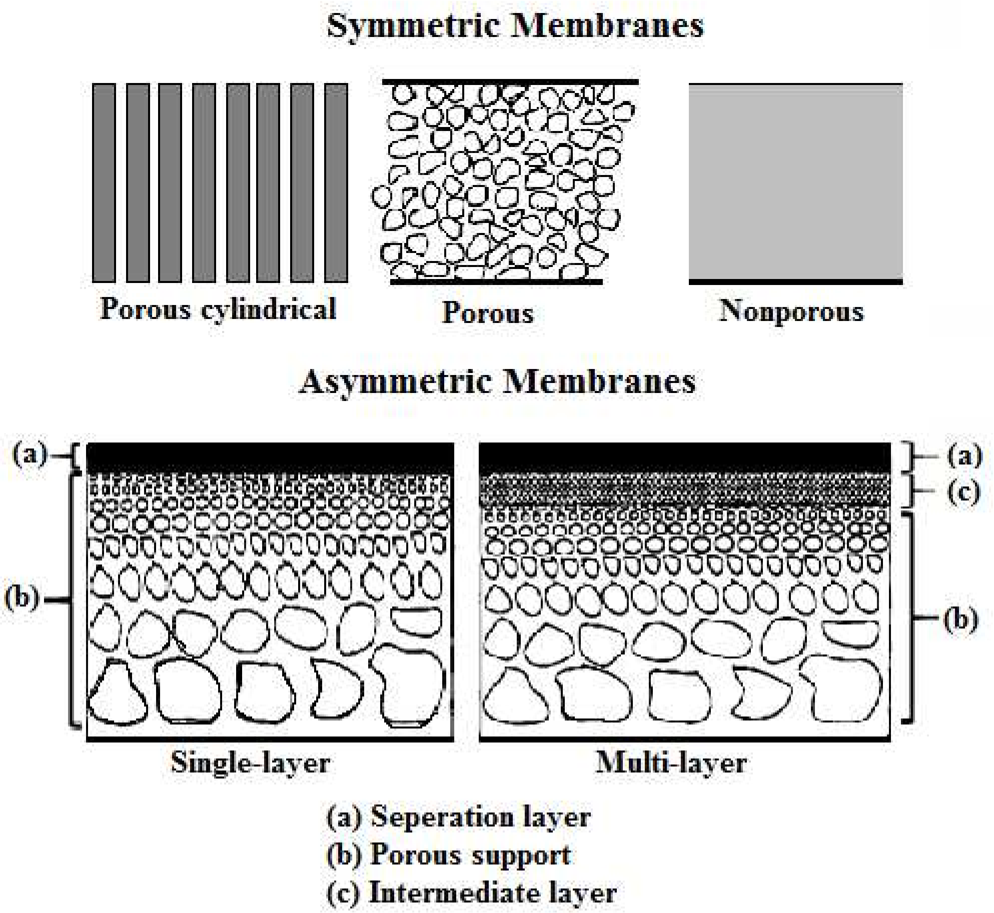

Figure 2. 2. Schematic representation of symmetric and asymmetric membrane structures.

Asymmetric membranes exhibit heterogeneous distribution of certain layers. The membrane layers have a porous structure and their pore sizes become gradually smaller with the smallest pores being present in the top layer. The largest pores are present in the support which provides the mechanical strength of the whole membrane. Intermediate-layers are commonly prepared by sol-gel method application for obtaining gradually decreasing pore size and maximum selectivity. Top layer is the thinnest layer. The drying and thermal treatment conditions must be optimized in designing the best membrane layer structures during the preparation of the various selective layers and the supports.

It is commonly accepted that asymmetric membranes present higher mechanical strength and permeate fluxes and they are convenient structures for the treatment and filtration/purification of wastewater streams. Research in the last decades have proven that asymmetric membranes are more commonly used and are more easily innovated for the solution of challenging separation problems.

2.4.2. Size Based Classification

The presence of a transmembrane pressure difference is the driving force for separation operations in membrane filtration. Membranes are classified as MF, NF, UF and RO according to their pore sizes in pressure driven membrane processes (Figure 2.3).

MF has the largest pore size (50nm-5micrometer) with about 0,5-3 bar transmembrane pressure difference. It is capable of separating suspended materials and colloids such as bacteria and protozoa. This technique is used as prefiltration for wastewater, dye, food and beverage industry and bacteria removal.

UF membranes have pore sizes in the 5-100nm range with 0,5-5 bar transmembrane pressure differences. It is used in food, beverage and pharmaceutical industrries and removal of oil droplets from water. NF membranes have 1-10nm pore sizes with 5-25 bar operation pressures. It can be used for filtration/separation of salt and sugar from aqueous solutions.

Reverse osmosis membranes have 1nm or smaller pore sizes with 10-70 bar operation pressures. It can remove all suspended and unwanted colloids in food and beverage industries and desalinate salty waters (Rjin, 2004).

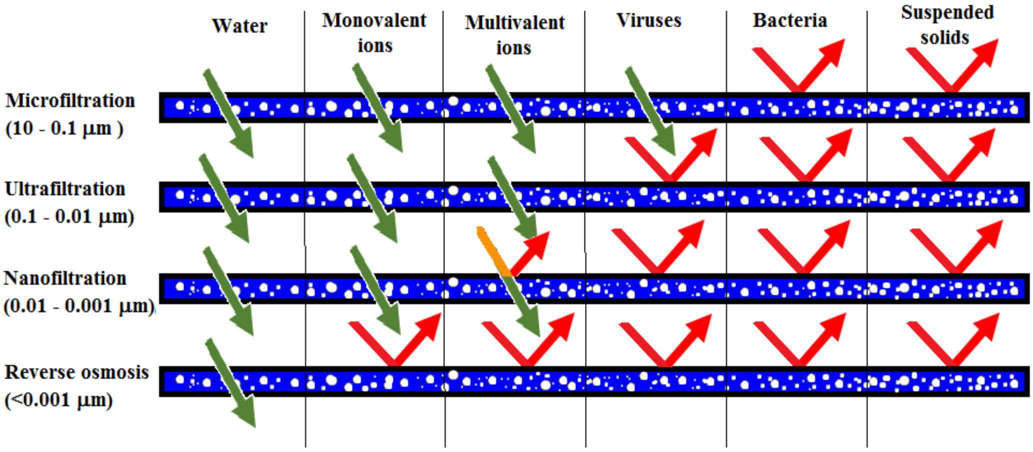

Figure 2. 3. Separation processes of membranes.

2.5. Ceramic Membranes

Although the development and applications of membranes have been conducted with polymeric membranes, ceramic membranes gained an accelerating significance and interest in the last couple of decades. The advantages of ceramic membranes discussed earlier increased the interest by the industry and ceramic membranes now has a wide range of applications in metal industry, biotechnology, and petrochemical industries. The most common application is wastewater treatment.

Polymer suspension and catalysts recovery, asphalt and its product recovery by deasphalting of petroleum residues, recycling and recovery of salt water, recovery of coloring matter such as stains and pigments, recovery of organic solvents, liquid oil and ethanol processing such as separation of ethanol-water mixtures and purification of waste lubricating oil, treatment of polluted water that includes dangerous pollutants for environment such as heavy metals, oils and solids at petrochemical plants, elimination of heavy metal precipitates, elimination of dichloroethane emulsions in vinyl chloride during monomer production, elimination of aromatic and paraffinic compounds, precipitates and dusts from wastewater from gel removal from photoresist are the major application areas of separation processes in chemical and petrochemical industries. They are briefly used for product recovery, separation, and cleaning (Luque, Gómez and Álvarez, 2008; Hsieh, 1996a).

Segregated lignosulfonate, COD decreasing of bleach plant residue, paper covering and whitewater treatment in paper product process from paper machines, coloring matter or chemical elimination waste water, polyvinyl alcohol treatment from waste streams, recovery of water from primary and secondary wool residue during rinsing process, stain and size removal, water recovery for recycling to obtain high qualified filtered water, dye bath recovery are the major purposes of use in textiles, pulp and paper industry (Luque, Gómez and Álvarez, 2008; Hsieh, 1996

Adjustment of antibiotics, amino acids, enzymes, proteins, vitamins, , biopolymers and organic acids, and plant extracts in terms of concentration, segregate, purification, sterilization, filtration, concentration, and dehydrate of biomass and algae, blood and blood plasma filtering, vaccine production, alginates process and other excipients, elimination of fat emulsions and salt, fermentation broth purification and concentration of beneficial living organism such as yeast, concentration of bacterial suspensions, treatment of polysaccharide during fermentation process, endotoxin elimination, aqueous stream by-product recovery, cleaned-in place (CIP) and sterilize water that does not include any pyrogen and bacteria. Pharmaceutical active agents and beneficial living organism concentration and filtration are the major separation processes in pharmaceutical, cosmetic, and biotechnology related industries can be conducted by using ceramic membrane processes (Luque, Gómez and Álvarez, 2008; Hsieh, 1996a).

Elimination and reusing of heavy oil such as grease oil and recovery of oil and water mixture, elimination of oil and grease and pollutants such as suspended solids, treatment and filtration of heavy metals, wastewater treatment during grinding process, recovery of wastewater form glass production process and glass fiber production, first washing and true washing machine tanks and oily wastewater treatment are the most common reasons to use ceramic membranes as a separation process (Luque, Gómez and Álvarez, 2008; Hsieh, 1996a).

Purification and stabilization of fermented products such as soy sauce wine, beer, vinegar, cider by alcoholic fermentation process, production and concentration of fruit juice such as apple, cranberry, pears, peaches, carrots, elimination of harmful living organism such as bacteria and other microorganisms, adjustment of concentration of juices, elimination of microorganisms from milk and milk product, filtration and segregate of milk and whey ingredients, concentration adjustment of whey proteins, removal of salt form whey, milk protein, raw or pasteurized whole milk normalization, removal of salt and lactose from dairy products, concentration of pasteurized milk, pH adjustment concentration of milk, isolation and purification of soybean protein, concentration and adjustment of animal and plant products, color concentration and purification, dehydration of products, separation and purification of drinking water, sugars and starches processing, treatment of product from beer and cider tank bottoms and yeast from beer tank bottoms are the most common and major usage area of separation and filtration process in food, dairy and beverages (Luque, Gómez and Álvarez, 2008; Hsieh, 1996a).

First treatment with reverse osmosis, wastewaters and drinkable water treatment, elimination of pollutants such as dusts, suspended solids, emulsified oil removal, renewable oils, elimination of pharmaceuticals and harmful chemical compounds in agriculture such as pesticides, elimination and separation of dangerous microorganisms, separation of heavy metals and gray water recovery, reusing process of water in swimming pools, isolation of the discharged sewage plants and sewer overflow recovery, digester water recovery, amplifying wastewater with oil under a defined vacuum, landfill leachate steps, wastewater recovery for radioactive harms, waste recycling in zero-waste plant, COD, BOD, and suspended solids degradation, elimination of turbidity from green water, a liquid waste during olive oil process, refinement of wastewater from washing operations in dairy industry such as textile, food and beverage, produced water from oil source recovery, textile industry wastewaters recovery, water with heavy metals, oils and suspended solids in petrochemical plants recovery, precipitated heavy metal solids elimination, COD reduction of bleach plant waste, coloring matter or chemical elimination from waste streams, polyvinyl alcohol filtration for textile industry in waste streams, color matter and pigment washing, fat emulsions elimination, reusing and removal of grease oil by degreasing and oily wastewater recovery and wastewater treatment from waste streams are the most important application areas of membranes in separation and filtration processes in water ,wastewater, recycling in environmentally related areas (Luque, Gómez and Álvarez, 2008; Hsieh, 1996a).

2.5.1. Comparison of advantages and disadvantages of ceramic membranes

The comparison between organic and inorganic membranes can be made in terms of their resistance to mechanical, thermal and chemical effects. The wastewater may include very strong and aggressive chemicals which can cause degradation or corrosion. Ceramic membranes are durable to any mixture with a pH in the range of 0-14. Thus, ceramic membranes basically are not affected the concentration or pH of mixture/solution. For example, ozone and chlorine gases are very corrosive but, they are necessary for cleaning the membrane as prewashing. The chemical stability of ceramic membranes makes this process to be conducted relatively easily.

These membranes are thermally stable and can withstand temperatures up to several hundred ºC. Some of the limitations for ceramic membrane systems apply only to the gaskets and other module materials and not necessarily to the ceramics based membrane. In all cases consideration should be given to the type of ceramic material used.

Inrganic (ceramic) membranes has special operation conditions in order to create an optimum positive barrier for wastewater treatment as well as other microfiltration and ultrafiltration membrane products. Mechanical strength is important to apply any treatment which is used in increased oil droplets or suspended solids. The pressure or flux of wastewater mixture may cause to dilapidation. Therefore, the dilapidation resistance increases the membrane life span due to characteristics of ceramic materials. Ceramic membranes have great toleration ability to cross flow due to low TMP for a defined flux.

Ceramic membranes can remove disinfection by-product (DBP) from wastewater by appropriate coagulation and with or without flocculation thanks to microfiltration and ultrafiltration process. The separation and then removing ability is the most wanted ability for a membrane. Ceramic membranes can filter unwanted solids even at 98% removal rate by forming a barrier. Ceramic membranes are barriers against suspended solids or unwanted droplets in wastewater. Also, the separation time is important due to commercial concerns. Ceramic membrane can present a very rapid process alternative for the separation of suspended solids and oils.

Polymeric membrane has a drying time during preparation method. Otherwise, drying time is not necessary for ceramic membranes. This qualification enables for reusage of a ceramic membrane after wastewater treatment. Reusage is important in terms of energy minimalizing, economically admissible and time saving. Due to the materials for ceramic membrane, it is very eco-friendly because of zero waste generation management. Generally, ceramic membrane is composed of harmless elements such as aluminum.

Energy requirement is one of the biggest problems nowadays. Energy requirement of wastewater treatment process necessitates higher expenses. This problem can be solved by ceramic membranes because life spans are better than polymeric membranes. Ceramic membrane processes can guarantee higher energy efficiency and lower cost by minimization in cleaning process, reduction of chemicals and filtration ability.

Ceramic membranes have several advantages however considering all these economical parameters and last developments in polymeric membrane technology, ceramic membranes are a bit falling into disrepute.

Although, ceramic membrane has a durable life cycle, in some cases degradation can be possible. For example, higher concentration of chemical attack of fluoric acid and by the time thermal shock may causes to frazzle. Even under these conditions, ceramic membranes are able to restore and renew themselves.

Operation method choice may constitute a risk. Usually, ceramic membranes are resistant to be frozen, except cold thermal shock or sudden change in temperature. Whether membrane preparation process do not occur properly, ceramic membranes can suffer a loss from infiltrated wastes such as suspended solids in feed or powdered on membrane surface due to their components of construction and fabrication methods.

Luckily, ceramic membranes are usually resistant to harsh conditions like abrasion or corrosion.

CHAPTER 3

OIL CONTAINING WATER AND METAL CUTTING FLUIDS

Recent developments in petrochemical, metal, textile, and food industries cause increasing waste product streams. According to data, the oily wastewater production is one of the abundant of side products. It leads to scientists give importance to this topic. Especially in metal industry, high amount of oily wastewater is formed because of metalworking such as aluminum rolling hot and cold rolling and can fabrication. Food industry has the second major percent of high level of concentration of oily wastewater products. For food and beverage production due to processing very high amount of oily wastewater such as palm oil production. With the upsurge in wastewater production and environmental pollution, waste treatment methods are accelerated. There are several treatment methods such as primary and secondary treatment which aim to reuse of high amount of wastewater in industry. In spite of all working, they could not obtain a positive result because oil and grease have heavy pollution. Also, this kind of oily waste are called hazardous oily waste depends on working process. The high amount of oil contents poses a danger for environment because they usually include non-recycled waste which is lethal for especially aquatic living beings and also all living organisms. Oily water can contain both organic and inorganic compounds due to chemical structure. Aliphatic, aromatics, phenols, Nitrogen Sulphur Oxygen (NSO) and some other hydrocarbons compose the organic side of an oil and they become very dangerous for the environment as surfactants and fatty acids.

There are very wild range of oily waste products. For example, during metalworking the cleaning of alkaline and acid cause to high amount of heavy oil production. Also, food and beverage industry such as floor cleaning is one of the most waste producers. During petrochemical working process, for both free and emulsified oily production, oily waste is formed which has difficult treatment methods such as petroleum drilling and refining.

Even very small amounts of oily water might be hazardous for the living organisms because oily wastewater disturb groundwater resources chemical structure and contents by coating the surface. Both living organism and aquatic life are dramatically affected because of discharging of oxygen transportation mechanism and pollution on the surface. Aquatic living organism cannot be utilized oxygen directly on the air. For their respiration oxygen must be dissolved in the water. If oil covers the surface, oxygen cannot dissolve so, aquatic organism will be death. Also, there is a limit for oil content in the water for balance of food chain. If the concentration arrives the critical point, it will be lethal for aquatic living beings. There are not only aerobic creatures but also aerobic creatures under water. The concentration stability is important for conservation of food chain balance and sustainable aquatic life and aquatic living conditions. The discharging in the aquatic life cause to negative effects on crop production. Since the underground water is polluted, there might be leakage up to soil and crops. After a while later, the oily wastewater coats the soil and it ensures the crops. It might be very dangerous for crops and plants due to its heavy oil contents. It affects the plants negatively because it bans the plants to arrive healthy nutrient and clean water. If the soil cannot be cleaned, the plants and crops growing cannot continue normally. At the end, contamination risk and pathogens which are creatures dangerous or directly lethal for human reveals such as cholera.

Nowadays, an application which provides to determine the limit of oil content of waste is accepted in different countries all around the world to protect the environment and prevent the discharge of oily water directly on the environment. The limit is defined the discharge criteria of oily wastewater which includes oil contents commonly in the 10 to 15 mg/l range (Lu et al. 2016). China is accepted 10 mg/l content as discharge criteria (Yu, Han, and He 2013). Otherwise, some countries limited the application for only under 5 mg/l of oil content as discharge criteria (Lu et al. 2016).

In machining process, heat that generated by internal and external friction causes some negative events such as metal surface cutting edge. In this operation with metal cuttıng fluıds, the machining counts as most important factors that adversely affect the mechanic and tool life (Çakır & Kılıçkap, 2001; Çakır, Kıyak, & Altan, 2004). The heat generated in the cutting zone is very important in terms of surface quality, cutting forces, chip conformation and tool life span of the work piece because almost all the energy that was used in machining converts into heat (Çakır, Kıyak, & Altan, 2004; Yamane, Narutaki, & Hayashi, 1996). This heat accumulation can be dangerous for operation. During machining, fluids that are enriched with synthetic chemical addition and water-soluble coolant are used to eliminate heat-induced negative effects and increase production efficiency (Nguyen & Zhang, 2003). However, cutting fluids are very useful in several terms, cutting fluid produce waste that are harmful to the environment because waste treatment is expensive and they contain dangerous chemicals (Nguyen & Zhang, 2003).

3.1. Tasks of Metal Cutting Fluid

A good metal cutting fluid have some defined properties. It should provide lubricity even under high pressure and prevents metal adhesion due to its lubricity property between surfaces. It should ban the temperature increase to eliminate surface friction. It should remove chips and dust or wastes from the cutting area. It should avoid the heat during chip removal. It should protect the metallurgical properties of the workpiece (Hamrock, Schmid, & Jacobson, 2004; Bastian, 1951).

3.2. Metal Cutting Fluids

Cutting fluid is a special type of cooling medium and greasing agent and it serves as stamping and machining in metalworking processes. Their general purpose is that facilitate metal working fluid process due to solubility properties that usually include a chlorine, boron free and high mineral oil content. They are usable for varies of fluid such as neat cutting fluid, metalworking coolant neat cutting oil, metal grinding fluid grinding fluid, metal machining fluid to provide high performance in a different types of water.

There are three kinds of cutting fluid as synthetic, semi synthetic and solubles. Firstly, synthetic, includes fully synthetic grinding and machining fluid, general purpose, multi metal, and synthetic metalworking fluid. Secondly, semi synthetics includes high oil semi synthetic, high performance semi synthetic metalworking coolant, high oil semi synthetic for aluminium alloys, high performance semi synthetic metalworking coolant, and premium semi synthetic metal working coolant. Lastly, solubles includes general purpose soluble metal working fluid and high performance soluble metal working fluid.

Metal cutting fluid is proper for application in small and medium general machine operation due to high performance even varies of materials, obtain stable product and relatively low and reasonable cost. Low – medium alloy steels and aluminium alloys are easy to handle and non-staining by metal cutting fluid.

Metal cutting fluid systems are becoming more popular nowadays because the environmental concerns about pollutant and recycling. The requirement to extend the life of the fluid before elimination cause usage of long lasting substances such as metal cutting fluid. Briefly, advantages of metal cutting fluid systems contain longer fluid last, reasonable disposal costs, clean operation environment and reducing tool maintenance.

- Metal cutting fluids is easy to manage multi metal convenient and they are the best method for small to medium machining process by presenting great potential for compatible product.
- Products are stable in the end of the process with metal cutting fluids. They maintain clean operation conditions by showing low scamming output in hard water environments.
- They eliminate low foam with antifoams and reduce operation costs by performing low foam output in soft water environment.
- They provide effective biocide system to prevent bacterial degradation and extend coolant life.
- Included minerals make system better to work. Boron free, chlorine, phenol and nitrite free is used for residue characteristics reducement and environmental compatibility in waste treatment.

There are two types of greasing agent mechanisms that have lubricating effect on metal cutting. Firstly, boundary lubrication have the thin fluid film to separate and keep the contact with surfaces. Secondly, extreme pressure lubrication, in which a thin solid layer of a salt such as iron sulfide is formed on the tool surface to provide lubrication.

The most common method of application is flooding applied in a machining operation because it has a steady stream system that affects directly to the operation. However there are several popular methods such as fluid hole delivery, mist application, through the tool, and manual application.

In metal cutting fluids, dry machining step is machine shops that cause some problems inherent in the use of cutting fluids. Cutting fluids become open to contamination over time because environment has a variety of contaminants such as tramp oil, garbage and small living organism. The long usage of contaminated cutting fluids can be hazardous for human health and they cannot efficient perform of their lubricating function as well as fresh and clean cutting fluids.

Also, higher temperature than limit cause overheating the tool and absence of chip removal benefits that are provided by cutting fluids in grinding and milling are major problems in dry machining process (John, Bhattacharya, & Raynor, 2004; D'souza, de Man, & de Man, 1991).

3.2.1. Pure Cutting Oils

Pure cutting oils are mineral-based, synthetic or vegetable oils that are used alone or by forming a compound with polar, chemical active substances without mixing with water. Pure cutting oils include a few amount of materials. If it had considered that there is no water in the environment, water could not affects adversely. Cutting performance efficiency can be increased with addition of polar additives and chemical active EP under high pressure additives of pure cutting oils such as mineral oil, vegetable oil, and synthetic esters. Vegetable oils are the most innocuous oils than other cutting oils because they have limited waste production capacity. Although they are more expensive than mineral oils, used vegetable oils are easier to remove. Also, they are more advantageous than mineral oils and they provide hydrodynamic lubrication. Because they form compounds with lubricating additives, they are very useful in heavy cutting operations that are difficult to process (Byers, 2016).

3.2.2. Water-Miscible Cutting Oils

Water-miscible oils are most common cutting fluids in metal cutting bacuse to emulsify the oil with water, special additives are added to the oil. Operation efficiency is increased by emulsifying the oil in water. The oil globules are well dispersed in the water during the continuous phase. Cooling the water cutting toolswith coolant is increased the life of the cutting tool. In such cutting oils, dilution rates are between 1-20% depending on the metal cutting operation, and this rate is generally around 5%. The change in the pH of the emulsions causes corrosion on the workpiece, so corrosion inhibitors are added into the mixture (Byers, 2016). Water-miscible cutting oils contain 60-90% vegetable oil surfactants and other additives and in some cases they may include mineral and synthetic oil. Metal cutting fluid is used by mixing concentrated oil with water. When the concentrated oil is mixed with water, surfactants allow the oil to be dispersed in water and an oil in water emulsion is prepared. Surfactants reflect heat and provide the liquid a milky and opaque appearance.

3.2.3. Semi Synthetic Cutting Fluids

Such cutting fluids, like water-miscible cutting oils, are water-based and are prepared by emulsifying vegetable or mineral oils in proportions varying between 5-20%. They are oil in water micro emulsions during water is in continuous phase and oil is in dispersed phase. The high amount of surfactants in semi-synthetic cutting fluids become the oil globules very small. Semi-synthetic fluids normally are transparent, but they can also appear opaque. Emulsion particle sizes range from 0.1-0.01 µm (Byers, 2016).

3.2.4. Synthetic Cutting Fluids

Synthetic cutting fluids are water-based and do not contain mineral oil. Particle size in synthetic coolant is 0.003 µm. They generally consist of rust preventive additives and water soluble chemical lubricants. The cooling capacity and lubricating properties of synthetic cutting fluids are very good. These cutting fluids are preferred in high temperature and high speed metal cutting processes due to their high cooling ability. Rust inhibitors and oil additives are added to synthetic cutting fluids to give the properties of oil-based cutting fluids. They have ethanolamine to prevent corrosion and keep the pH value constant in the content. They contain phosphates and borates for water softening, soaps and wetting agents for lubrication, phosphorous, chlorinated and sulfur compounds for chemical lubrication, chemical additives found in synthetic cutting fluids (Byers, 2016).

CHAPTER 4

EXPERIMENTAL

4.1. Materials

Tubular alumina support preparation basically was conducted by using four main materials. The main component is a mixture of commercial α-alumina (α- Al2O3) powders with reported average particle sizes of 0.5, 1.3 and 5.2 µm (CL 4400 FG, CT 1200 SG, CT 3000 SG, Almatis). Commercial boehmite (AlOOH) powders were used as inorganic binders. Hydroxypropyl methylcellulose was used as a polymeric binder and glycerin as plasticizer in the preparation of cakes used for extruding tubular supports. Materials that were used in this work are tabulated in Table 4.1 along with their trade names and basic properties.

Dolapix was used for dispersing α-alumina powders and the preparation of well dispersed suspensions for microfiltration selective layer preparation. Polyvinyl alcohol (PVA) was used for improving the green strength of selective membrane layers. Defoamer was also added in low levels to the stable colloidal sols for gas bubble elimination during microfiltration layer preparation.

Table 4. 1. Materials used in the experimental work.

Materials	**Property**
0.18 µm alumina 0.5 µm alumina 1.3 µm alumina 5.2 µm alumina	99.8 % purity, Sumitomo 99.8 % purity, CT 3000 SG, Almatis 99.8 % purity, CT 1200 SG, Almatis 99.8 % purity, CL 4400 FG, Almatis
Boehmite (AlO(OH))	99.8 % purity, Disperal and P2
Hydroxypropyl methycellulose (HPMC)	Methocel F4M, The Dow Chemical Company
Glycerin ($C_3H_8O_3$)	99.5 % purity, Merck
Polyvinyl alcohol (PVA)	80 % hydrolyzed, MW= 9000-100000 g/mol, Aldrich

Dolapix CE 64	Eurokimya
Defoamer	Dağlar Kimya
Nitric Acid, HNO_3	65 %, MW=63.01 g/mol, d=1.39 g/cm^3, Merck

Deionized water was used in all stages of the experimental work and in the preparation of metal cutting fluids used in the filtration experiments.

4.2. Method

Selective layer coating/formation is one of the major steps of membrane preparation. The selective layer properties determine the membrane separation capacity and affects water filtration directly. Support layers of membranes of tubular α-alumina ceramics were coated with MF selective layers. The coating must be prepared on a layer by layer basis in the inner surfaces of the supports for the formation of the asymmetric porous membrane structure. The slip casted thin selective layer films must be dried, and heat treated properly for the formation of a final crack-free membrane selective layer. This operation is applied for all layers because the stabilization of the previous layer is essential before the preparation of the following selective layer. The desired thermal/chemical/mechanical stability of the ceramic membrane with the designed separation abilities and a long lifetime necessitate the proper application of these processing steps to be conducted for all the membrane layers.

4.3. Preparation of Tubular Multi-Channel Alumina Supports

Supports with high mechanical / chemical / thermal stability and smooth inner surfaces are an important requirement for the formation of flawless thin selective layers. Organic binder, three different α-alumina powders (to optimize pore structure and mechanical properties), in reported average sizes of 0.5, 1.3 and 5.2 μm, methocel and inorganic binder boehmite were mixed in a ball mill for 2 hours. These powders were hand kneaded while adding the water / glycerin liquid mixture. A screw extruder was used to obtain a homogeneous paste and was fed to the piston extruder which was moved forward to form tubular ceramic supports with 16/25 mm (inner / outer) diameter and 200 mm length in dimensions. Extruded multichannel 7-hole (5 mm diameter 7 holes) tubular ceramic supports were also extruded with a new die. The pictures of both dies used in tube extrusion are given in the Appendix in Figures A1 and A2. The extruded soft tubular supports were dried for a day at room temperature on a rotating cylindrical bed to partially remove water. The tubular supports were further dried in an oven at 100ºC overnight. The high temperature heat treatment schedule involved organics removal and inorganic binder phase transformation (conversion of boehmite to γ-alumina) step in the 250-350°C range and a final heat treatment at 1525 ° C for 1 hour (Yılmaz 2016).

4.4. Preparation of Tubular Alumina Supports

The desired supports must have a high mechanical/chemical/thermal stability and smooth inner surfaces. These physical properties are important for defect free thin selective layer formation. The mixture components and their proportions have a crucial role in support preparation which is schematically given in Figure 4.1. The pore structure and mechanical properties optimization is very critical in tubular support preparation. The balance between organic binder and the main support phase which is the α-alumina powder mixture must be well-adjusted also for optimized paste rheological properties. The final support is formed mainly from three different α-alumina powders with average particle sizes of 0.5, 1.3 and 5.2μm. This α-alumina powder mixture, organic binder and the boehmite used as an inorganic binder were mixed in a ball mill for at least 2 h. The mixture was used for making a paste by hand while adding a water/glycerin liquid mixture. The hand-formed paste was homogenized by using a screw extruder. The prepared paste batch was about 5000 grams in weight. The feeding of the paste to the piston extruder forms the tubular ceramic supports 200 mm in length and 16/25 mm inner/outer diameter in size. Extruded tubular ceramic supports dried at room temperature for a day on a roller machine to decrease the water content. 250-350 ºC is necessary for the organic component removal. Final heat treatment was conducted at 1525ºC for 2 hours.

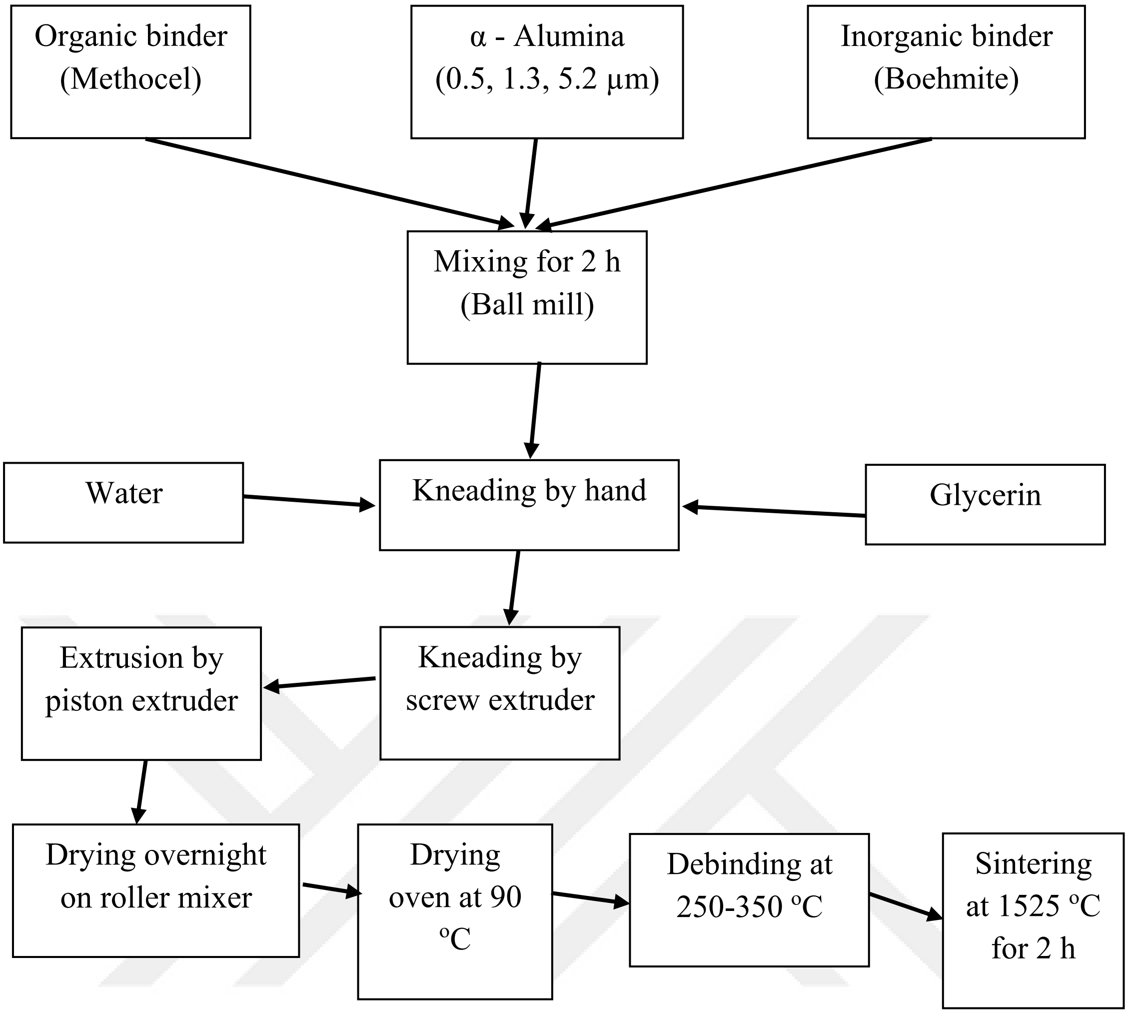

Figure 4. 1. Flowchart of α-Alumina support preparation.

4.5. Preparation of MF1 layers

MF layers are coated on the inner surfaces of the supports by using stable well-dispersed 0.5 µm α-alumina powder suspensions/colloidal sols. This coating has a smaller powder particle/pore size compared to the support and must be heat treated at lower temperatures for the preparation of a porous selective layer. MF layer preparation involves a series of preparation steps. The careful design of the order of these steps is important for forming a durable porous thin layer with sufficient mechanical integrity/strength.

PVA is a commonly used binder and it improves the mechanical strength of the dried ceramic structures. PVA is added to the water used for forming the suspensions. 7 wt. % 0.5 µm α-alumina powder was added to the PVA-water solution and stirred at constant speed. Dolapix was a good dispersing agent which was added for the prevention of the agglomeration of the α-alumina powder. Defoamer was used to eliminate foams/bubbles which may cause in air bubble entrapment in the dip coating step. Ultrasonic bath treatment was applied to the suspension for 2 hours to aid in forming a well-dispersed colloidal sol and this suspension left to rest overnight. The few large particles were expected to settle at the bottom of the suspension and the suspension at the upper of the bottle was used for dip/slip coating of the MF layers. The bottom of the tubular ceramic supports were sealed with a cylindrical silicone rubber piece and slip/dip coating was conducted by pouring the suspension into the hollow tube for 10 min. The tubes were further slowly drained out for the formation of a microfiltration layer with smooth surfaces. The coted wet α- alumina supports were dried at room temperature overnight. The MF coating undergoes a heat treatment process with the following steps. Firstly, furnace (Carbolite CWF 1300) was heated up to 110 °C with a rate of 2 °C/min, from 110 °C to 1000 °C at 2.5 °C/min and furnace reached 1200 °C at 2 °C/min. This temperature was hold for 60 min and then cooled to room temperature.

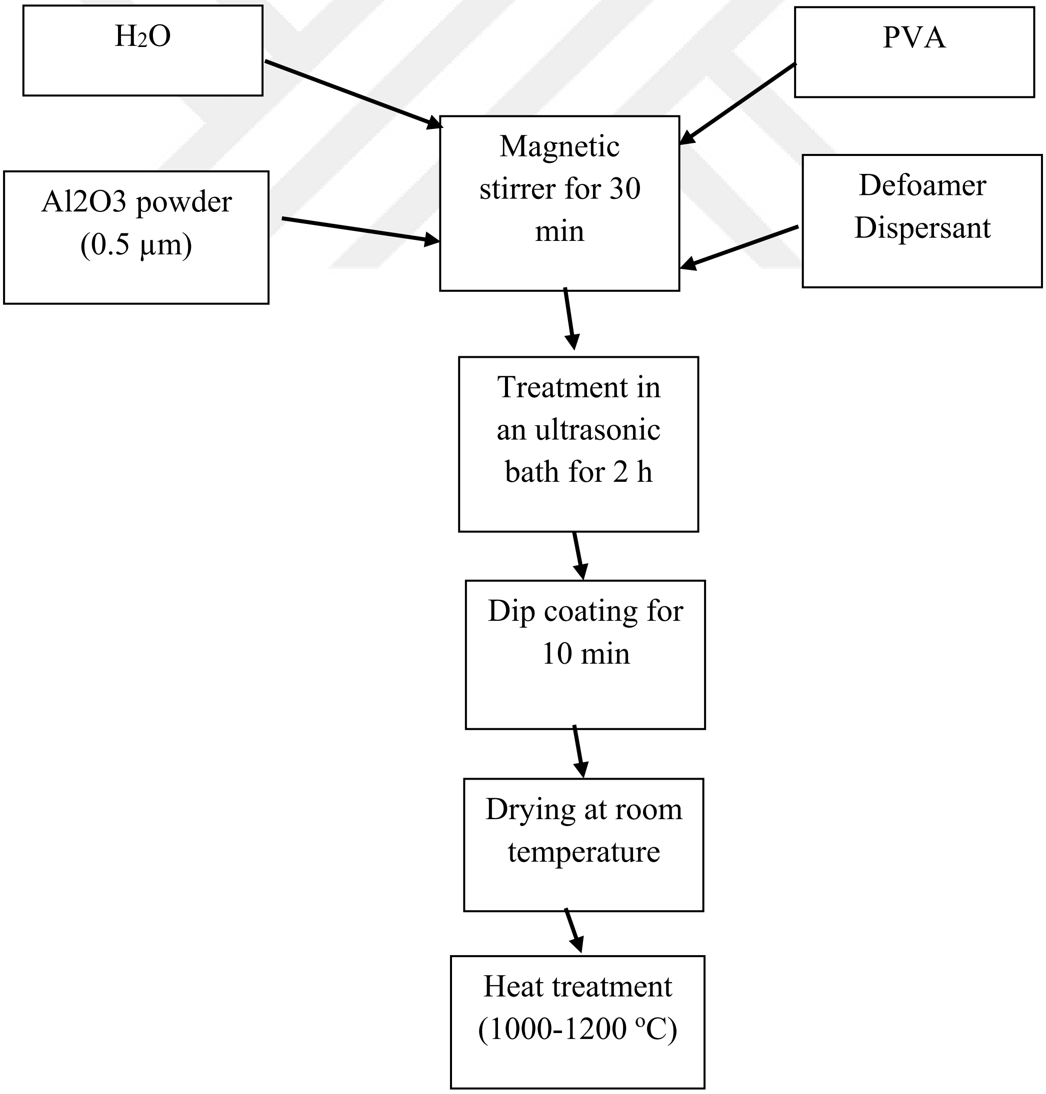

Figure 4. 2. Flowchart of microfiltration membrane preparation.

4.6. Preparation of MF2 layers

MF2 was formed by reapplying the suspension prepared in MF1 as a second layer to the inner surface of heat treated MF1 coated tubes. The base of the tubular ceramic support was wrapped with a silicone rubber, filled with stable suspension and left for 10 minutes. A small hole was made in the silicone rubber using a needle where the excess suspension was slowly discharged drop by drop while creating a soft coating surface. Microfiltration layer coated α-alumina tubes were vertically dried at room temperature to remove water. The MF coating was heat treated according to the following schedule: furnace (Carbolite CWF 1300) heated from 110 ° C to 1000 ° C at 2.5 ° C / min at a speed of 2 ° C / min and the furnace reached 1200 ° C at 2 ° C / min. This temperature was kept for 60 minutes and then cooled to room temperature.

4.7. Preparation and Characterization of Emulsions

Emulsion was prepared using metal cutting fluid and distilled water. The oil content was fixed at 0.5 and 1 by weight %. Metal cutting fluid (PO Bor Yağ) was added to the water and mixed for 2.5 minutes using a blender to form a well-mixed and stable emulsion. The mixer was used at high speed and transferred to the feed tank.

4.8. Filtration Experiments

A cross flow filtration system present in the laboratory was used fort he filtration experiments which is shown in Figure 4.3. Tubular membrane structure was placed into the stainless-steel membrane module. The retantate oily wastewater was fed back to the feed tank. CFV was altered and regulated from control panel as F notation. CFV values corresponding to each F value are tabulated in Table 4.1. Four different F values (15, 20, 25 and 40 respectively) were used in this work for the filtration experiments. TMP was set up to a defined valve and TMP was measured with gauge readings. 1, 2, 3 and 4 bar TMP values were used for different filtration conditions. Permeate was recorded after every testing and flux was calculated based on membrane surface area and permeate fluxes were plotted as a fuction of filtration time.

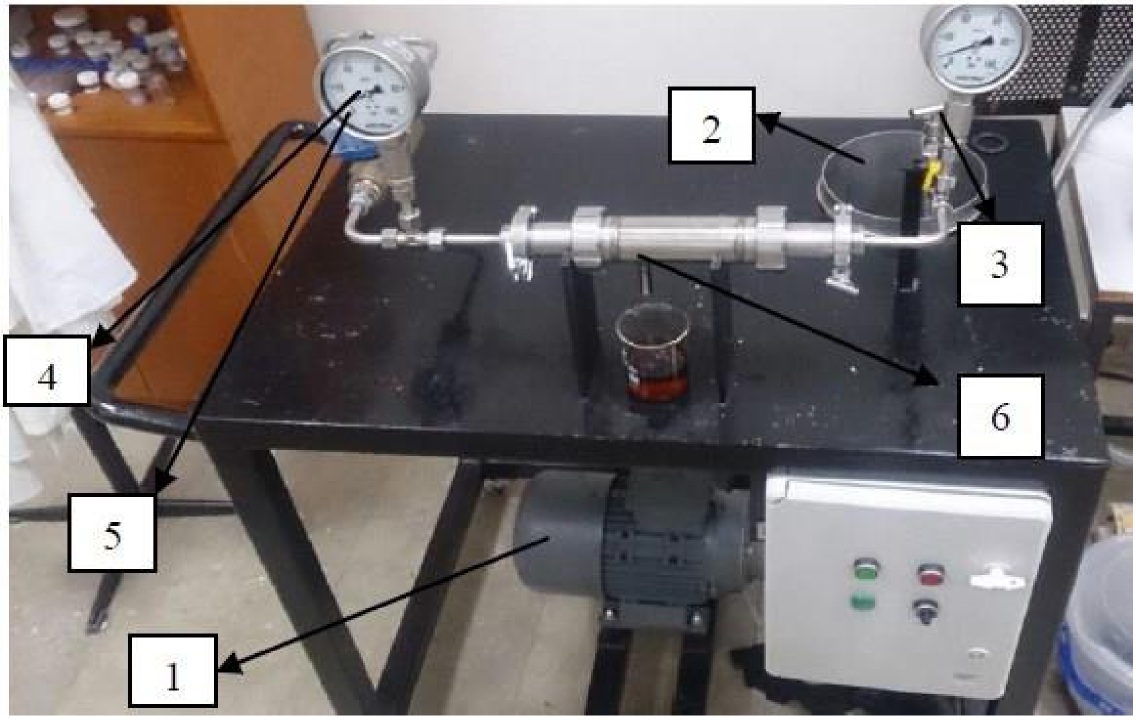

Figure 4. 3. The filtration set-up (1-pump, 2-feed tank, 3- recycle, 4-gauge, 5-flowmeter, 6-cross-flow membrane module).

Table 4. 2.The CFV and TMP levels used in the experiments.

F value	CFV(m/sec)	TMP(bar)	Conc.%
15	0.40 - 0.45	1,2,3,4	0.5
20	0.55 - 0.60	1,2,3,4	0.5 , 1
25	0.70 - 0.75	1,2,3,4	0.5
40	1 – 1.1	1,2,3,4	1.5

CHAPTER 5

RESULTS AND DISCUSSION

The ceramic membrane preparation in the last 6-7 years in the İYTE Chemical Engineering Department Laboratories have been conducted by forming hollow tubular supports 25 mm in outer diameter, 16 mm in inner diameter which are about 20 cm in length. The paste properties, procedures for required paste rheological properties have been investigated and extrusion steps with a piston extruder have been identified. The current MSc. Research was initially planned to be conducted with multichannel (7 circular channels) supports with original dimensions. The initial attempts with the developed paste formulations failed in the preparation of crack-free dried/heat treated supports. The paste formulation was modified through changing various component amounts/ratios and the rheology of the prepared pastes was characterized by using a capillary rheometer. These results will be given and briefly discussed in the first section of this chapter. The multichannel support preparation studies continued along the year 2020. The main body of the work conducted in metal cutting fluid filtration is conducted by using hollow tubular supports. The preparation of several multichannel supports was achieved by the end of the year. The cracks forming on the walls of the surrounding the circular channel in the middle of the tube was concluded to be due to the drying stresses caused during water removal from the soft extruded support. The drying conditions must be optimized in future research. The pictures of the two extrusion die along with supports are given in Figures A1 to A3 in the APPENDIX.

5.1. Reology of ceramic paste

Capillary die piston type extruder with length and diameter (L / D = 1) was used in the experimental part of the paste modification/characterization studies. The sample pastes were extruded using a mechanical tester (Testometric SN 500-526) mounted with a 100 kN load cell at 5 mm / min extrudate speeds. Each batch was prepared approximately in about 100 grams and kneaded with the help of an agate mortar and pestle for 30-45 minutes. Each experiment was repeated three times and the results were plotted by taking the average of three trials. The overall compositions of the pastes on a volumetric percentage basis are given in Table 5.1 and the compared values are marked with colors.

Table 5. 1. The compositions of the 15 pastes investigated in paste modification work.

Number of experiment	Volume %							
	Alumina [µm]			Polymeric Additive	Inorganic Additive		Glycerol	Water
	5,2	1,3	0,5	F4M	Boehmite	P2		
1	68,02	8,06	3,15	2,0153164	1,904474	0	1,733172	15,11487
2	67,34	7,98	3,12	2,99281724	1,885475	0	1,715882	14,96409
3	66,67	7,90	3,09	3,95100751	1,866851	0	1,698933	14,81628
4	66,02	7,83	3,06	4,89045383	1,848592	0	1,682316	14,67136
5	65,38	7,75	3,03	5,81170089	1,830686	0	1,666021	14,52925
6	64,75	7,68	3,00	6,71527245	1,813124	0	1,650038	14,38987
7	66,24	7,85	3,07	1,96261224	2,782003	0	3,375693	14,71959
8	66,86	7,92	3,10	1,98098257	1,872029	0	3,40729	14,85737
9	66,86	7,92	3,10	1,98098257	0	1,87	3,40729	14,85737
10	66,24	7,85	3,07	1,96261224	0	2,78	3,375693	14,71959
11	65,63	7,78	3,04	1,94457948	0	3,68	3,344677	14,58435
12	64,23	7,61	2,98	6,6603235	1,798287	0	2,454805	14,27212
13	63,70	7,55	2,96	6,60626652	1,783692	0	3,246508	14,15629
14	62,24	7,38	2,89	6,45399226	1,742578	0	3,171676	16,13498
15	60,83	7,21	2,82	6,30857967	1,703317	0	3,100216	18,02451

The force vs. distance traveled by piston curves/data were obtained by using mechanical test device model analysis. Extrusion force raw data at same velocity (5 mm/min) and L/D ratio (1) can be seen in Figures 5.1 to 5.7. The force increases initially and levels out at a certain value at the plateou in these capillary rheometry curves. The polymer content was increased from the original 2 vol% level to about 6.7 vol% level in the first six pastes. As the amount of F4M (methocel) in the mixture was increased the force level applied to exit the capillary die piston extruder increased as seen in Figure 5.1 where the force varied in about the 450-900 N range. The regular pastes were prepared and tubular supports were extruded by using the piston extruder. The dried/heat treated supports all had cracks in the walls of the middle hole in 7 channel supports.

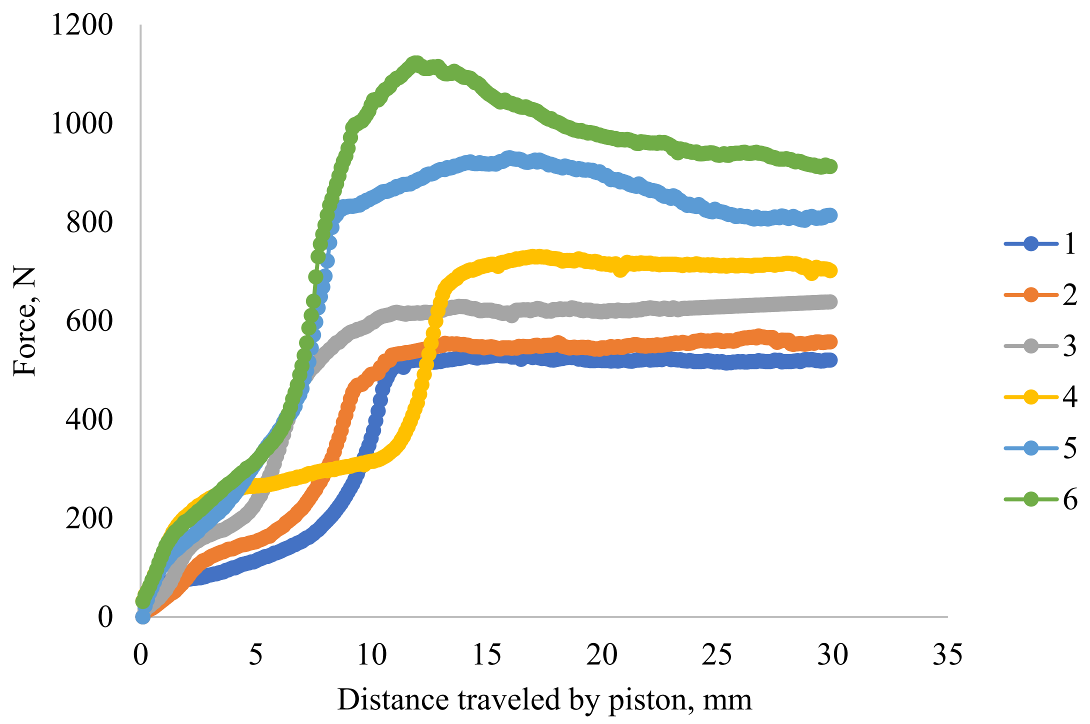

Figure 5. 1. Effect of Polymeric Additive (F4M).

Figure 5.2 compares the effect of the amount of water on the alumina paste rheology. As can be seen from the graph, as the amount of water in the mixture increased, the amount of force applied to exit the capillary die piston extruder decreased in the 300-800 N range. The dried multichannel tubes had similar cracks in the middle of the tubes.

The inorganic binder was replaced with P2 boehmite and the force-distance behaviour of the pastes were characterized and they are given in Figure 5.3. The plateau force varied in the 300-600 N range. The nanosized nature of the P2 boehmite decreased the extrusion force and was expected to yield crack-free multichannel tubes. Similar cracks unfortunately were observed in the dried/heat treated tubes.

The P2 boehmite decreased the extrusion force and increasing the glycerol twice decreased the force by about 100% (Figure 5.7). Due to the large number parameters effective on paste rheology and the materials limitations (Since 5 kg paste batches being necessary for a real piston extrusion) the modification trials were ended at a certain stage. The crack formation was observed/concluded to be related with the drying conditions applied in the laboratory. Several crack free multichannel tubular supports were finally prepared in December 2020. The pictures of these tubes are given in Figure A3 in the Appendix.

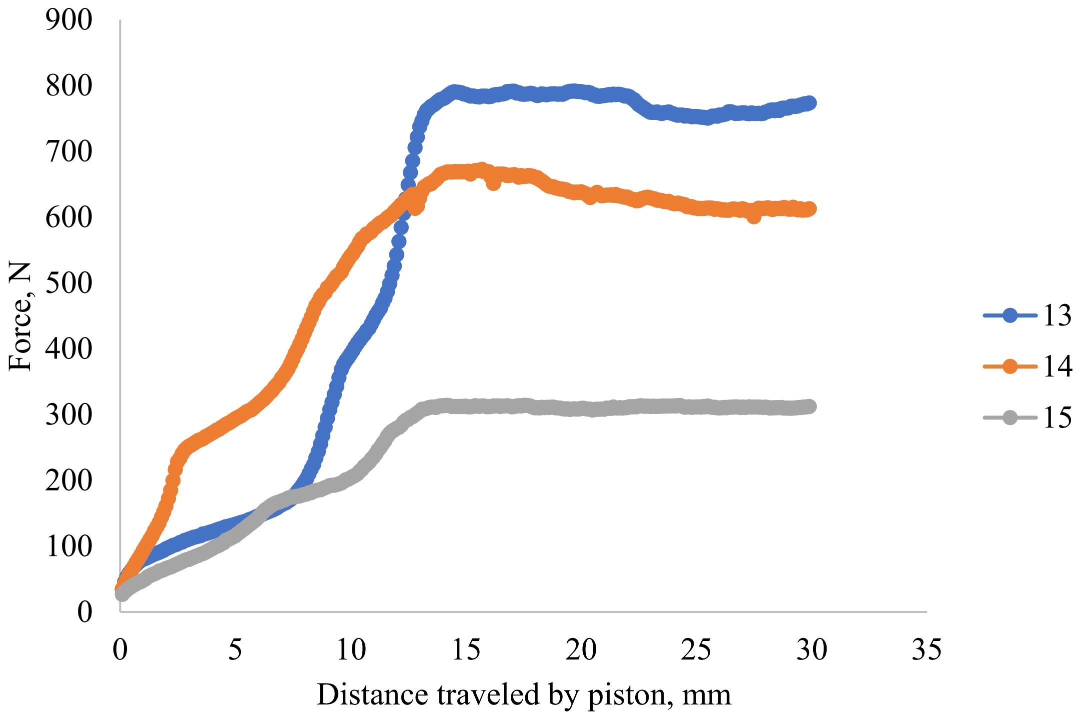

Figure 5. 2. Effect of water.

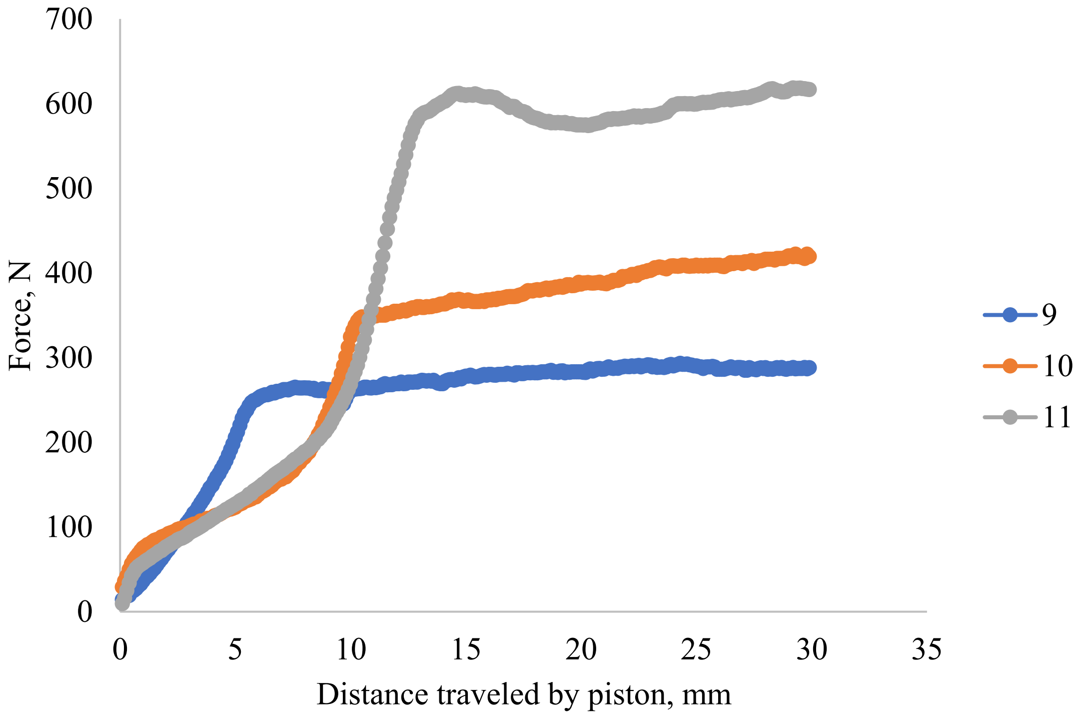

Figure 5. 3. Effect of Inorganic Additive(P2).

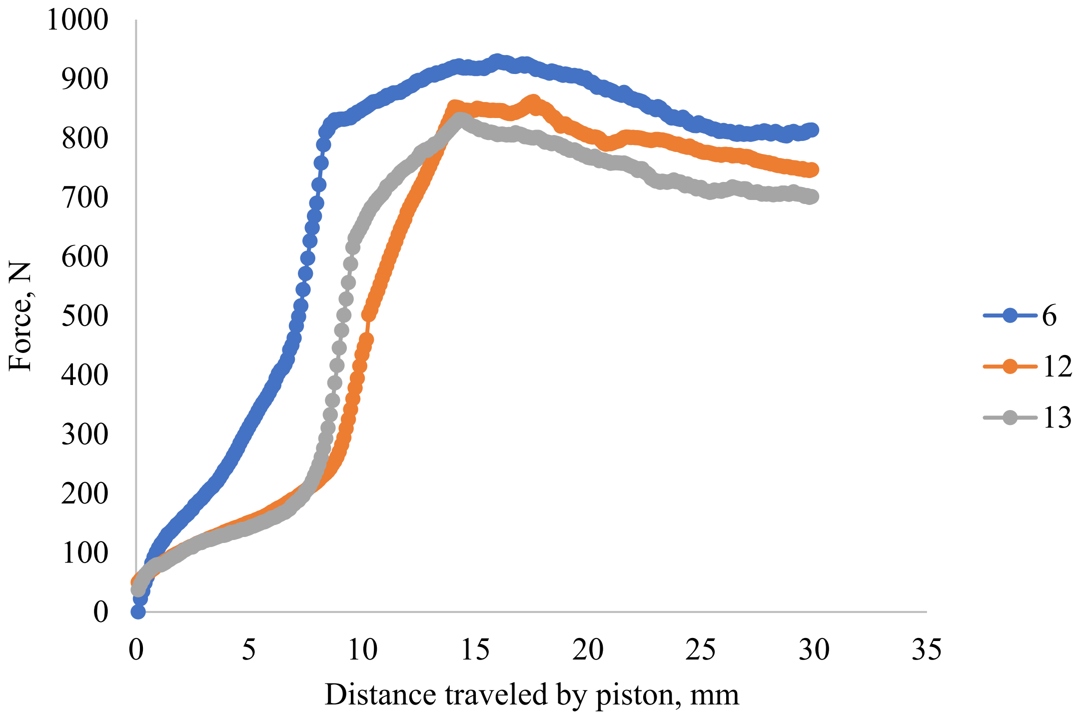

Figure 5. 4. Effect of Glycerol content.

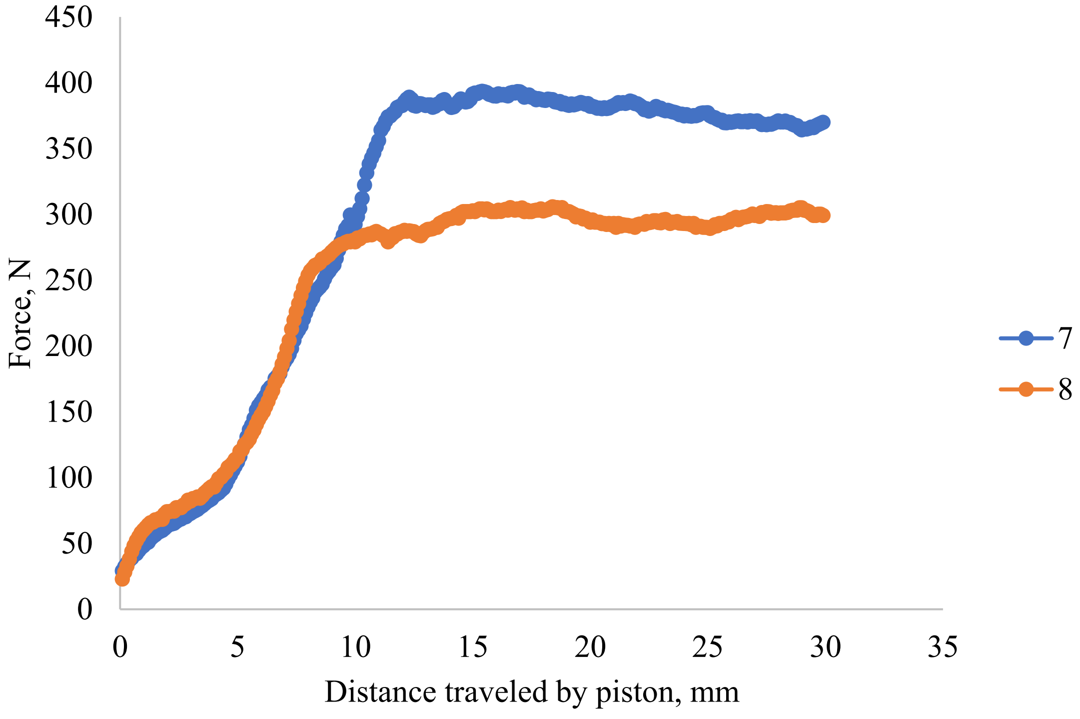

Figure 5. 5. Effect of Inorganic Additive (Boehmite).

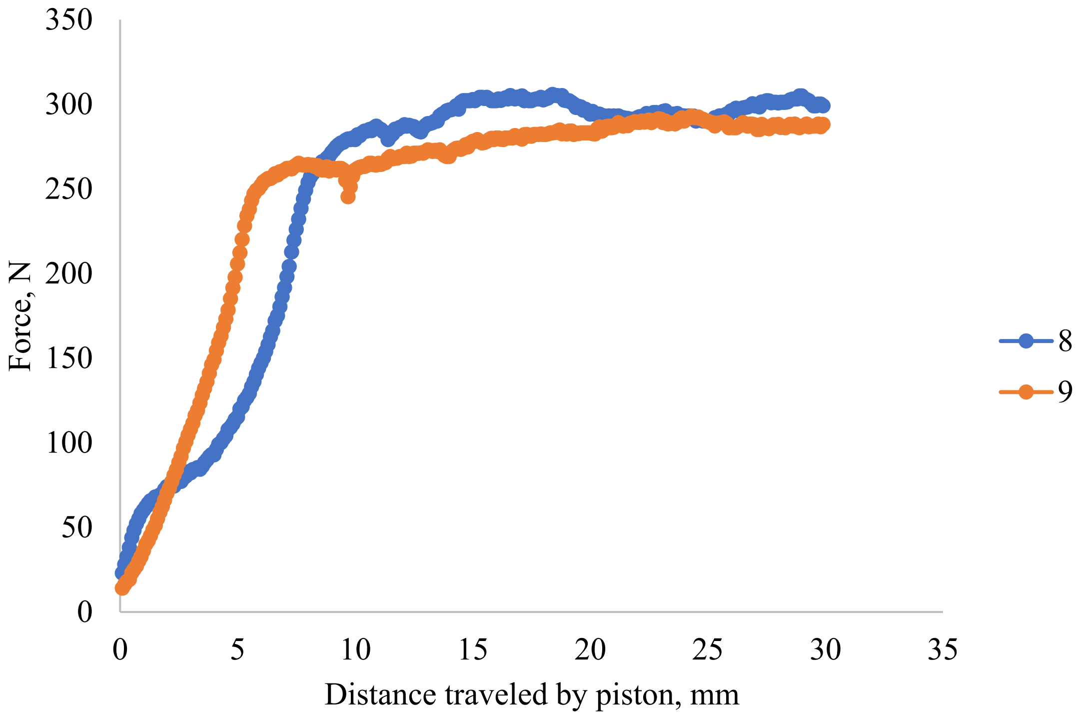

Figure 5. 6. Effect of difference between Inorganic Additive of Boehmite and P2

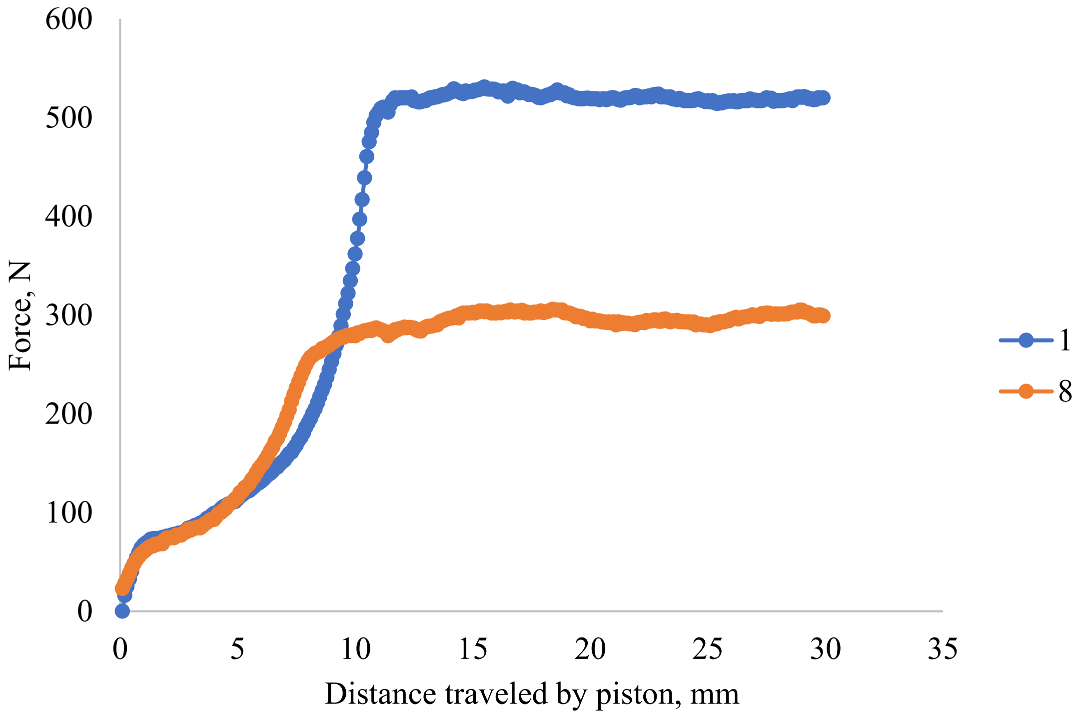

Figure 5. 7. Effect of Glycerol content.

5.2.Filtration experiment with support

Determination of pure water permeability through a membrane is the first step in the evaluation of the performance of a membrane separation process. Pure water fluxes at various trans-membrane pressures (TMP) and for several crossflow velocities (CFV) were first measured. Permeate fluxes determined during the filtration experiments were then compared with the pure water fluxes. Pure water permeabilities do not only act as a basis of comparison but they also provide information on the fouling of membranes during filtration experiments along with the permeate fluxes measured at the onset of the filtration.

Pure water fluxes through ceramic tubular supports prepared in this study were evaluated at four different TMP values (1, 2, 3 and 4 bar) and for three different cross-flow velocities (F=15, 20 and 25). Stabilities of pure water fluxes were also determined by monitoring the fluxes for approximately 3 hours. Pure water fluxes of the ceramic support for CFV of F=15 evaluated at TMPs of 1, 2, 3 and 4 bar are shown in Figure 5.8. Water fluxes for 1, 2, 3 and 4 bar were found to be around 450, 850, 1100 and 1400 L/m2·h, respectively. Except only slight deviations, pure water fluxes of the ceramic support stayed almost constant at all TMPs. Pure water fluxes of the support membrane increased as the pressure increased from 1 to 4 bar for CFV of F=15 as it was expected.

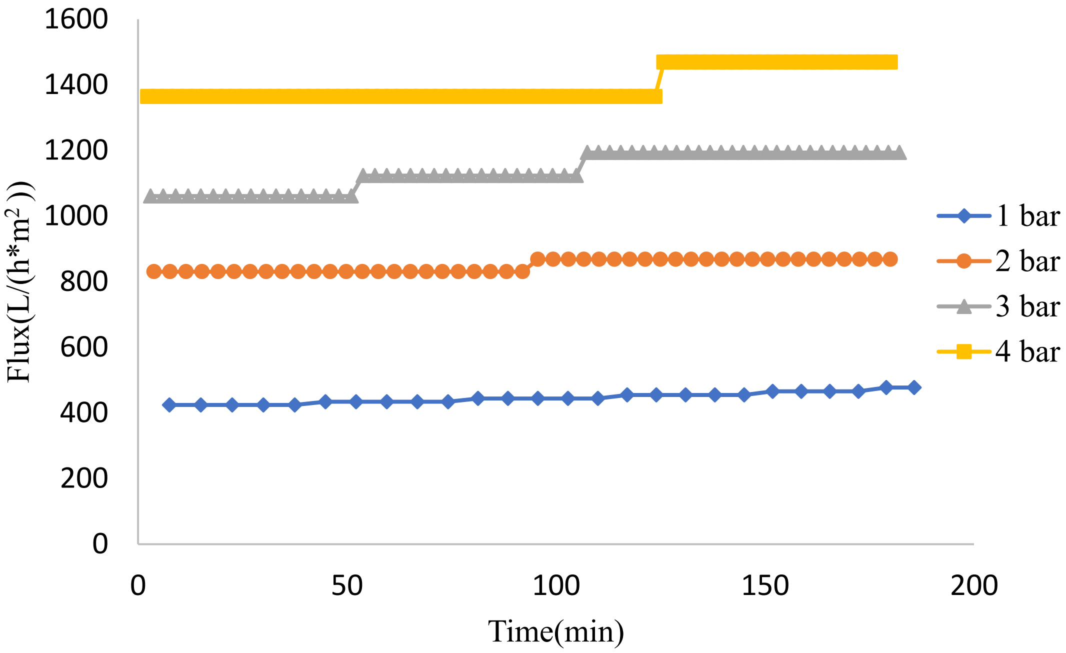

Figure 5. 8. Effect of TMP on pure water flux of the support (F=15).

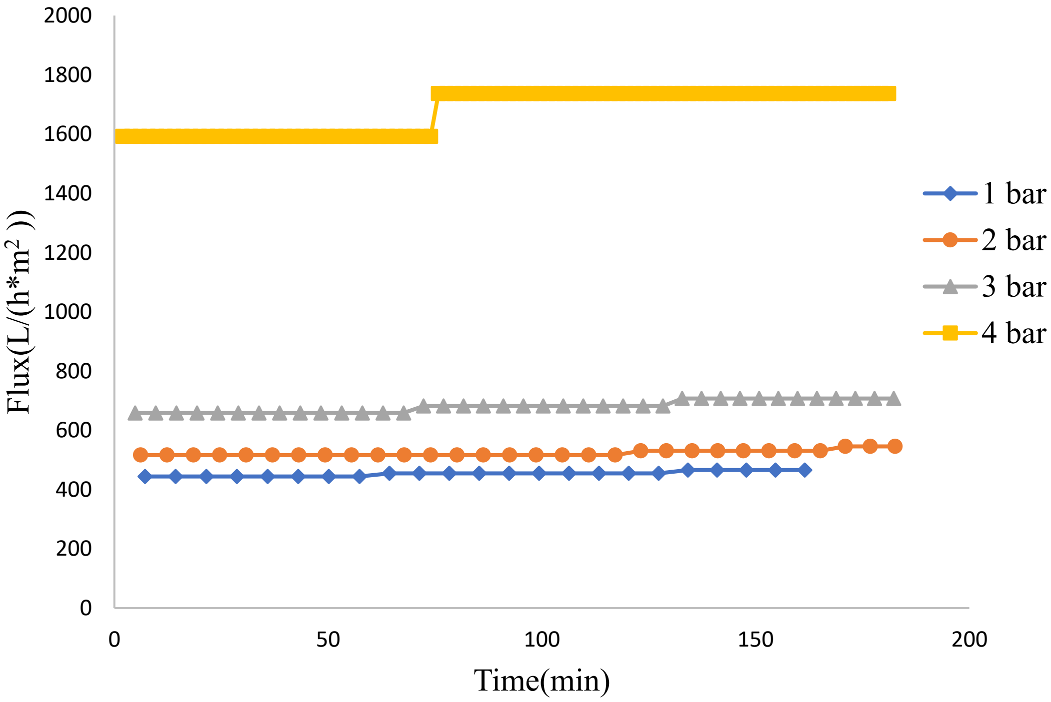

Figure 5. 9. Effect of TMP on pure water flux of the support (F=20).

The results of water permeability experiments performed for CFV of F=20 are given in Figure 5.9. Pure water fluxes were measured to be ~ 450, 525, 680 and 1700 L/m^2·h for 1, 2, 3 and 4 bar. Pure water fluxes were approximately 600, 1300, 1500 and 1700 L/m^2·h for CFV of F=25 at 1, 2, 3 and 4 bar, respectively (Figure 5.10). In all filtration experiments performed for CFV of F=15, 20 and 25, TMP increase resulted in water permeability increase. When permeate values obtained for CFV values of F= 15 and F=20 was compared, increase of CFV from 15 to 20 did not increase water flux at 1, 2 and 3 bar. Increase of CFV however increased water permeability at 4 bar. The effect of CFV on the permeate flux can be clearly observed when the water fluxes measured for F=25 are compared to those measured for F=15 at similar TMP values, increase in CFV increases water flux. Increase in TMP at constant CFV increases water permeability through the support membranes.

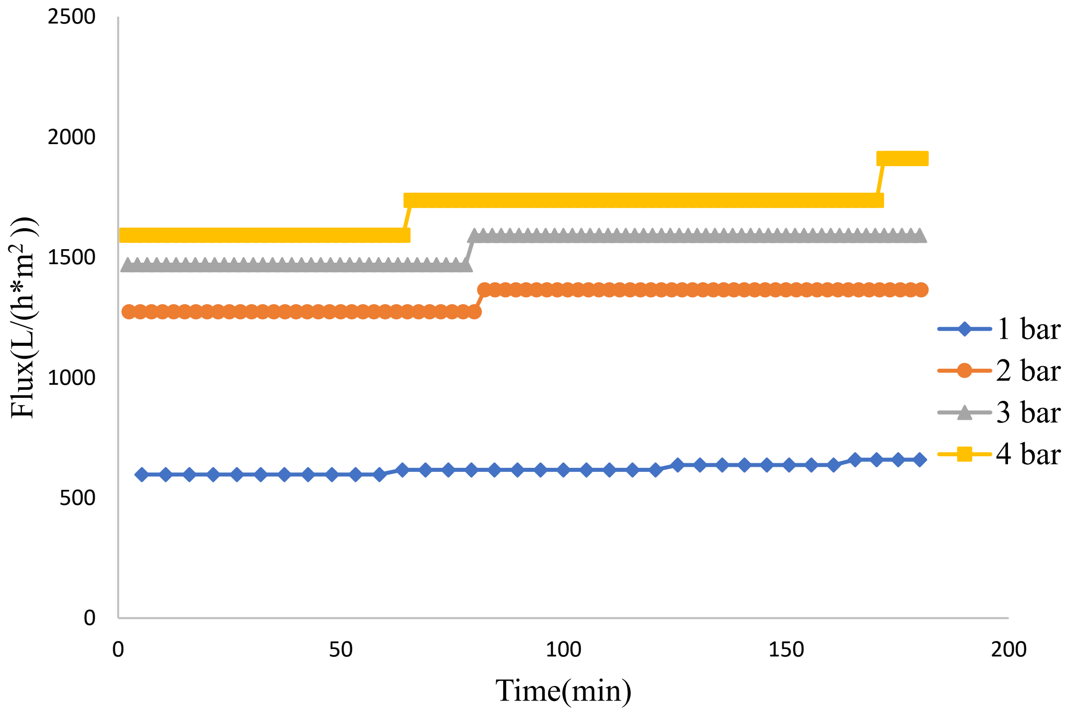

Figure 5. 10. Effect of TMP on pure water flux of the support (F=25).

Ceramic tubular supports were used for the treatment of oily wastewaters prepared by diluting metal cutting fluid with water. Wastewaters containing metal cutting fluid in two different concentrations (0.5 and 1 wt. %) were prepared. Performances of tubular ceramic supports in the treatment of 0.5 % oily wastewaters were evaluated for CFV values of F=15, 20 and 25 at 1, 2, 3 and 4 bar. Figure 5.11 shows the flux decline and the percent oil retention during the filtration of 0.05 wt. % oily water for CFV of F=15 at 1 bar TMP. Permeate flux was measured to be ~ 70 L/h·m^2 at the initial stages and decreased to 46 L/h·m^2 at the end of the filtration. Oil removal efficiency initially measured as 99 % decreased to 92 % at the end of filtration suggesting the oil leakage through the membrane.

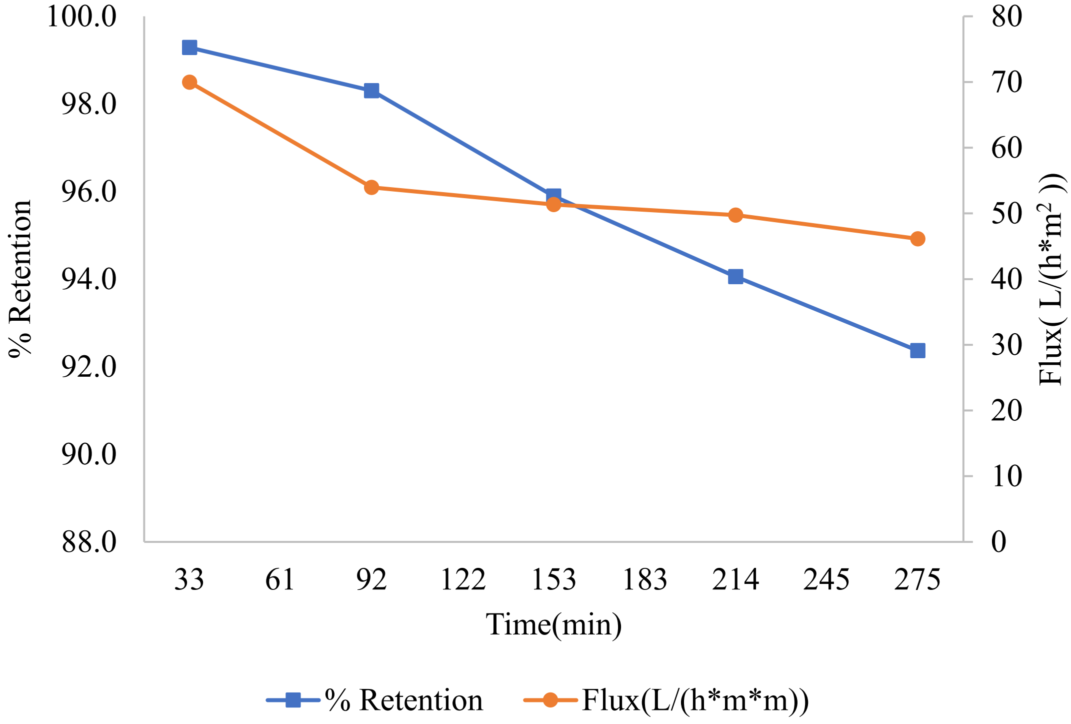

Figure 5. 11. Effect of 1 bar of TMP on oily water flux of the support and % retention (F=15).

Increasing TMP to 2 bar increased permeate fluxes as shown in Figure 5.12. Initial permeate flux which was measured to be 191 L/h·m^2 was higher than the initial permeate flux observed in the filtration of oily water at TMP of 1 bar. Similar to the permeate flux change observed at 1 bar, permeate flux at 2 bar was gradually decreased and measured to be 99.5 L/h·m^2 at the end of the filtration. Time dependent behavior of oil removal efficiency observed at 2 bar however was totally opposite of that observed at 1 bar. Oil removal percentage was 91 % at the early stages of the filtration. It gradually increased in the course of filtration and reached 96 % at the end.

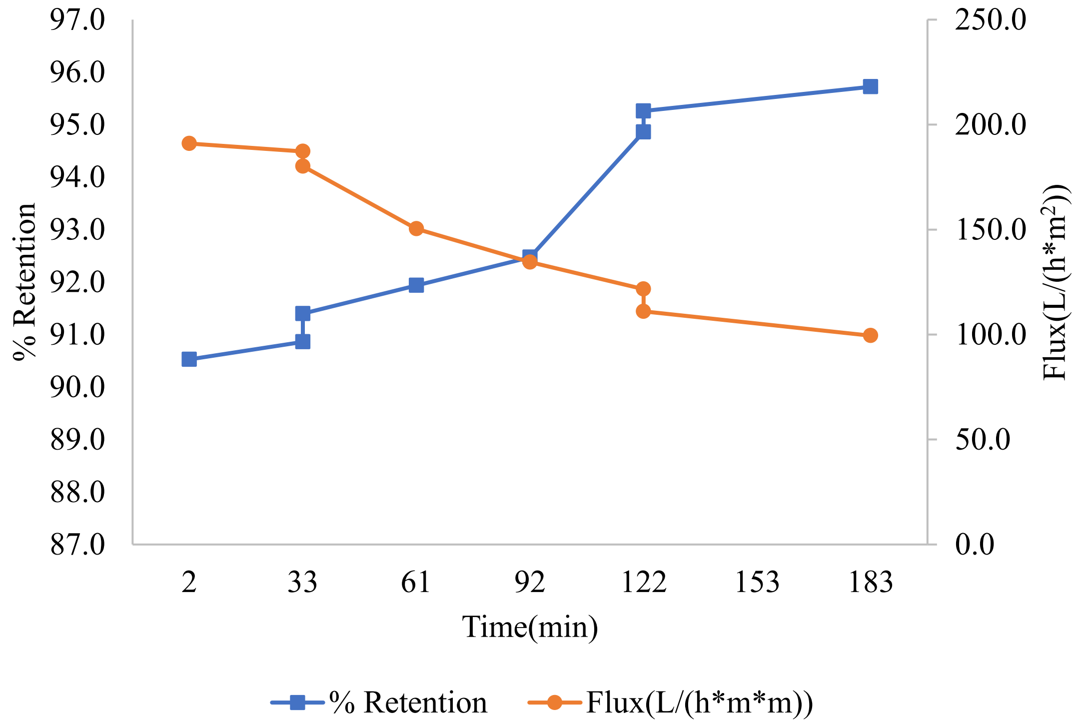

Figure 5. 12. Effect of 2 bar of TMP on oily water flux of the support and % retention (F=15).

When TMP was increased to 3 bar, permeate fluxes measured however were found to be similar to those obtained at 1 bar. Permeate flux was initially measured to be 91 L/h·m^2 and decreased to 54 L/h·m^2 at the end of filtration (Figure 5.13). Percent oil removal was ~86 % at the initial stages and reached ~97 % throughout the filtration.

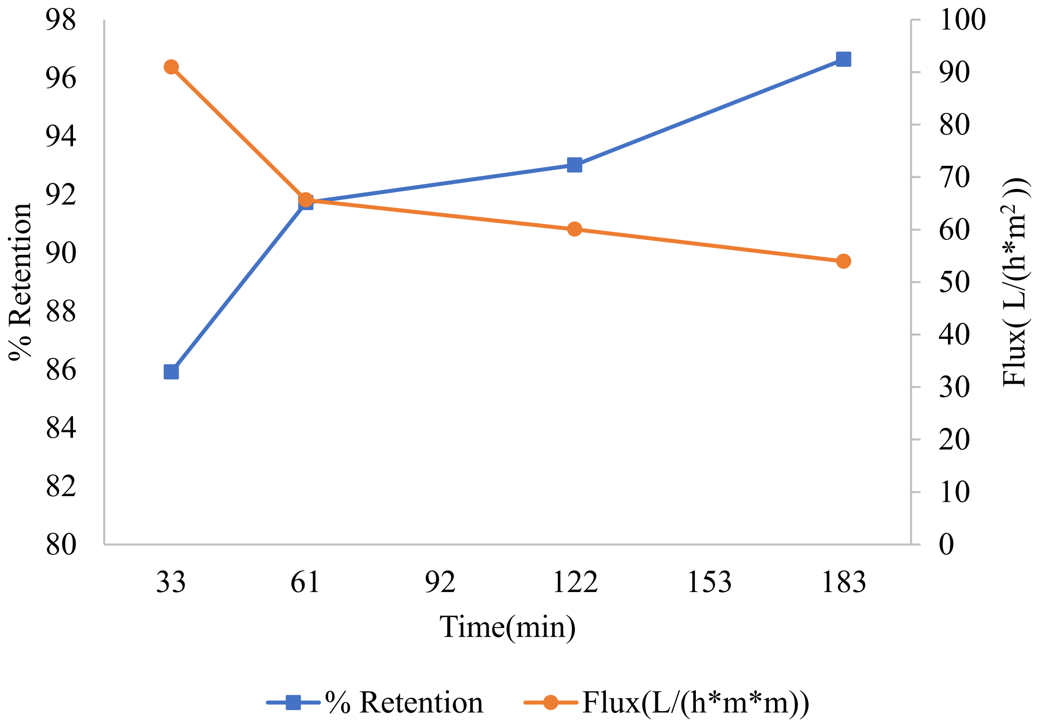

Figure 5. 13. Effect of 3 bar of TMP on oily water flux of the support and % retention (F=15).

The effects of 4 bar on the permeate flux and oil removal efficiency in the filtration of 0.05 wt. % oily water are shown in Figure 5.14. Initial and final permeate fluxes were measured to be 69 and 54 L/h·m2, respectively while corresponding oil removal percentages were determined as 91 and 94 %.

All trans-membrane pressures except 2 bar resulted in somewhat closer initial fluxes and similar final fluxes. This suggested that the increase in TMP for CFV of F=15 did not cause significant increase in permeate flux. Initial permeate flux observed at 2 bar was 2-3 fold higher than those observed at 1, 3 and 4 bar. The final permeate flux measured at 2 bar was almost two fold of those measured at other TMPs. In all filtration experiments but that performed at 1 bar, oil removal efficiency increased in the course of the filtration. Oil removal percentage was initially at least 86 % and increased to over 94 % at the end of filtrations. Filtration performed at 1 bar however yielded 99 % initial oil recovery and oil removal percentage gradually decreased to 92 % at the end of filtration.

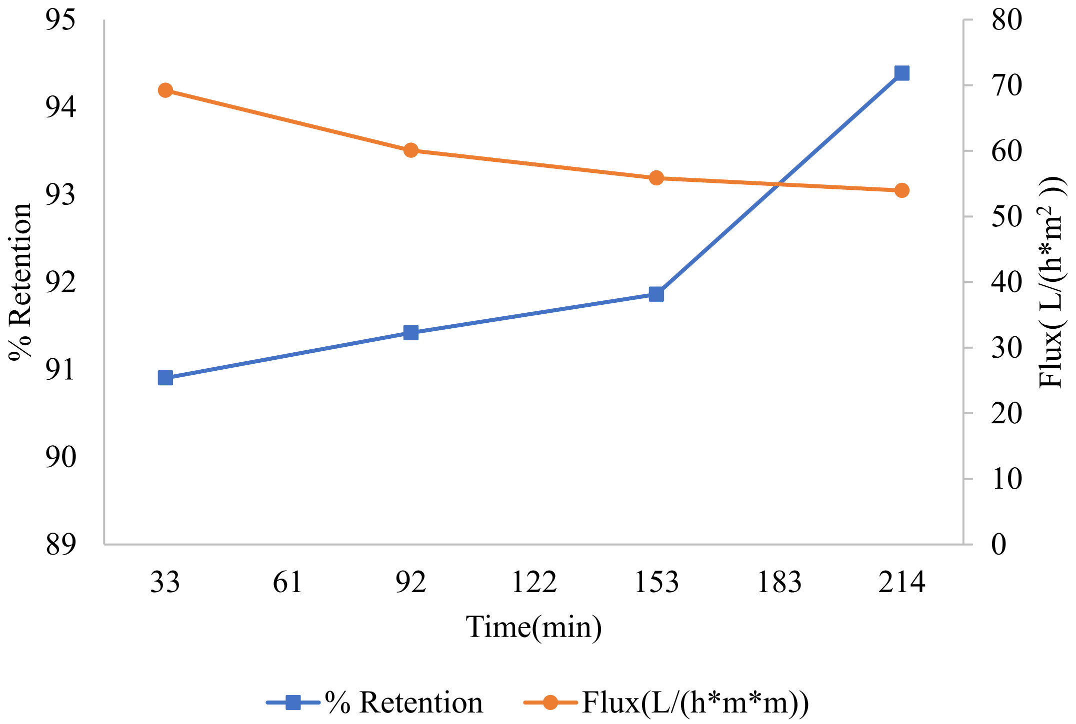

Figure 5. 14. Effect of 4 bar of TMP on oily water flux of the support and % retention (F=15).

The results of the filtration experiments performed at 1,2, 3 and 4 bar for CFV of F=20 are given in Figures 5.15, 5.16, 5.17 and 5.18, respectively. As it is inferred from Figure 5.15, permeate flux slightly decreased from 69 to 41 L/h·m2 whereas oil removal percentage increased from 79 to 99 % at 1 bar. At 2 bar (Figure 5.16), similar to initial permeate flux observed at 2 bar for CFV of F=15, initial permeate flux was 175 L/h·m^2 and greater than those observed at other TMP values. These higher initial fluxes observed at 2 bar both for F=15 and F=20 and higher final flux observed for F=20 might have been possibly due to instability of oil in water emulsions in oily water prepared and accumulation of certain fraction of oil on the surface of water inside the feed tank. Permeate flux at the end of filtration at 2 bar however reached the similar final flux values observed at other pressures. This might be due to the fact that higher pressure might have homogenized oily water during the filtration.

Oil retention was measured to be 86 % at the early stages of filtration and almost 100 % removal was observed at the end of filtration (Figure 5.16).

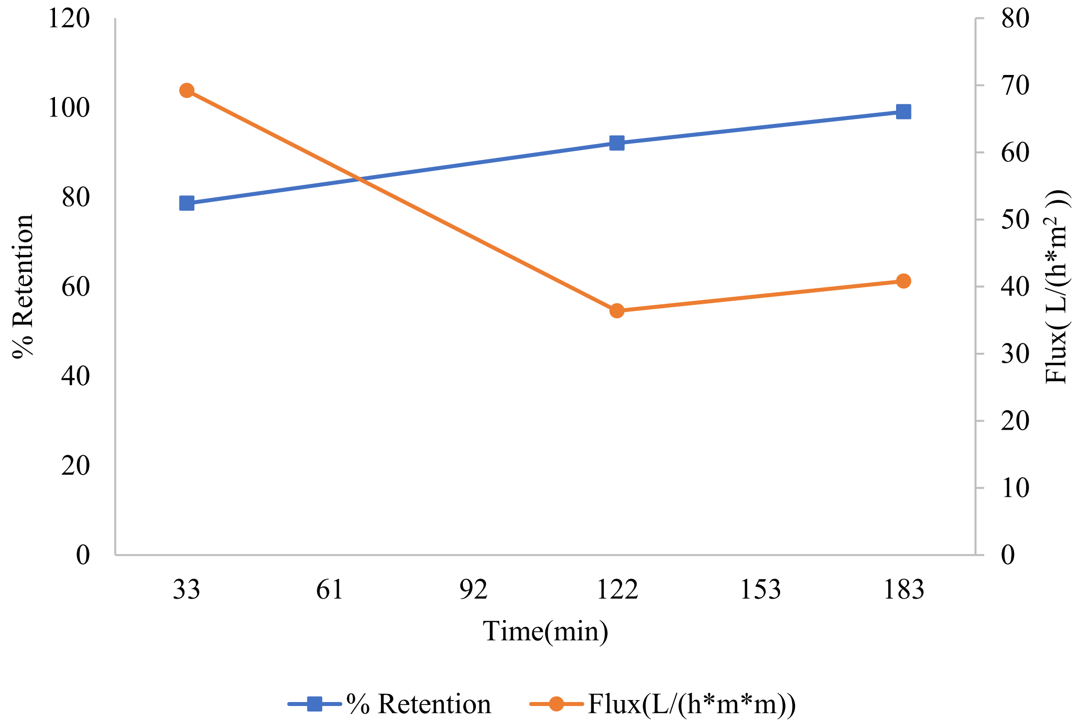

Figure 5. 15. Effect of 1 bar of TMP on oily water flux of the support and % retention (F=20).

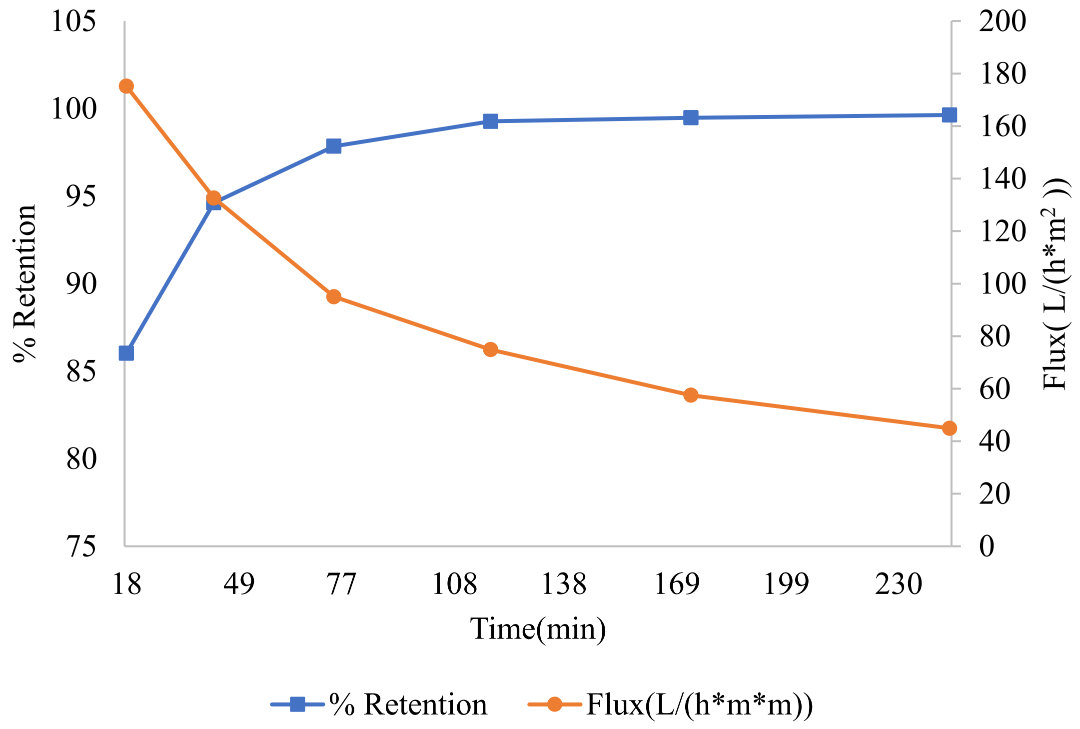

Figure 5. 16. Effect of 2 bar of TMP on oily water flux of the support and % retention (F=20).

Filtration experiments performed at 3 and 4 bar TMP exhibited similar initial (~ 65 L/h·m2) and final permeate fluxes (~ 57 L/h·m2) (Figures 5.17 and 5.18).Initial and final oil retention percentages were 97 % and 100 %, respectively in the filtration experiment performed at 3 bar. Oil removal percentages were measured to be equal or greater than 99 % at 4 bar.

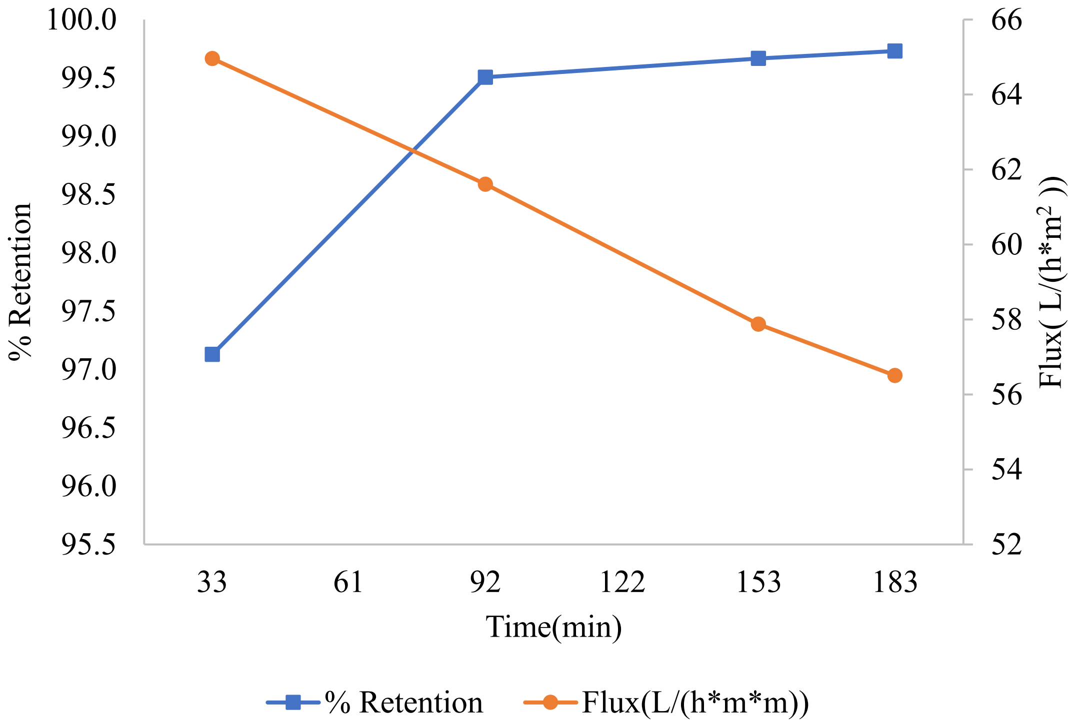

Figure 5. 17. Effect of 3 bar of TMP on oily water flux of the support and % retention (F=20).

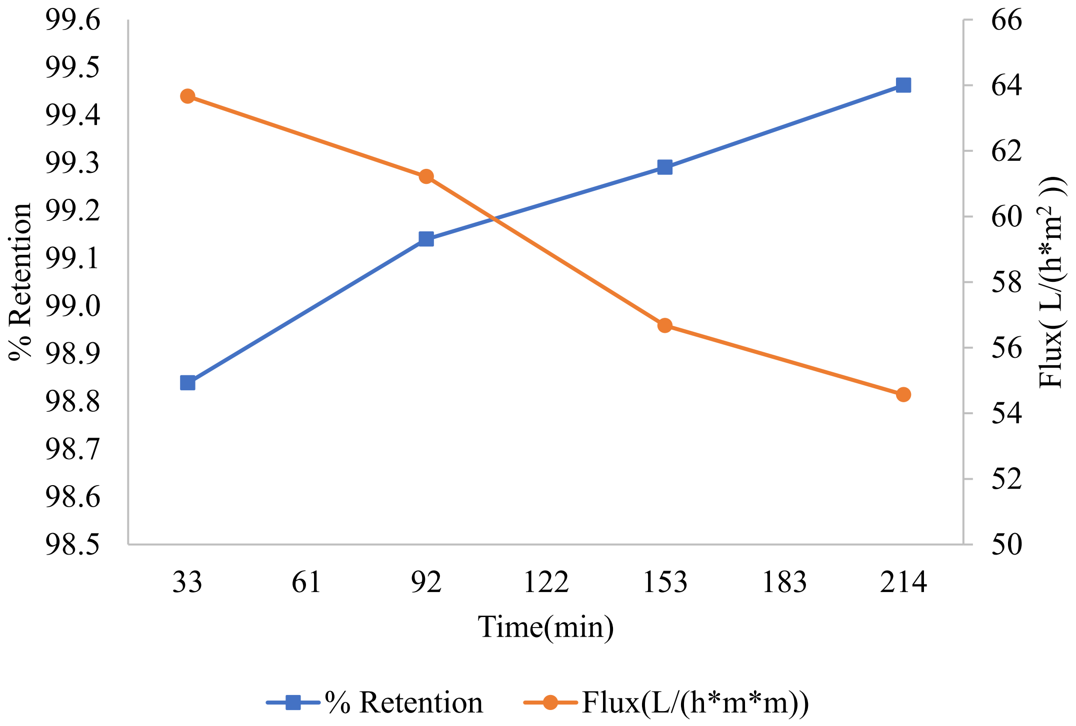

Figure 5. 18. Effect of 4 bar of TMP on oily water flux of the support and % retention (F=20).

Time dependent changes in permeate fluxes and oil retention percentages during the filtration of 0.5 wt. % oily water using tubular ceramic supports where CFV was adjusted to F=25 are shown in Figures 5.19, 5.20, 5.21 and 5.22. Figures 5.19, 5.20, 5.21 and 5.22 present the results of the filtration experiments performed at TMP= 1, 2, 3 and 4 bar, respectively. Similar fluxes were obtained at all trans-membrane pressures applied. Initial fluxes were found to be 45, 40, 57 and 60 L/h·m^2 whereas final fluxes were 30, 35, 44 and 47 L/h·m^2 at 1, 2,3 and 4 bar, respectively. These results together with the permeate fluxes measured for CFV of F=15 and F=20 show that the increase in TMP does not increase the permeate flux in the filtration of oily water. Initial permeate fluxes measured in all experiments were much lower than pure water fluxes of the support membranes. These suggest that oil in the oily water restricts the transport of water through the membrane by adsorbing on the inner surface of the membrane and/or clogging the membrane pores. Oil removal percentages were greater than 98 % at all TMP values for CFV of F=25.

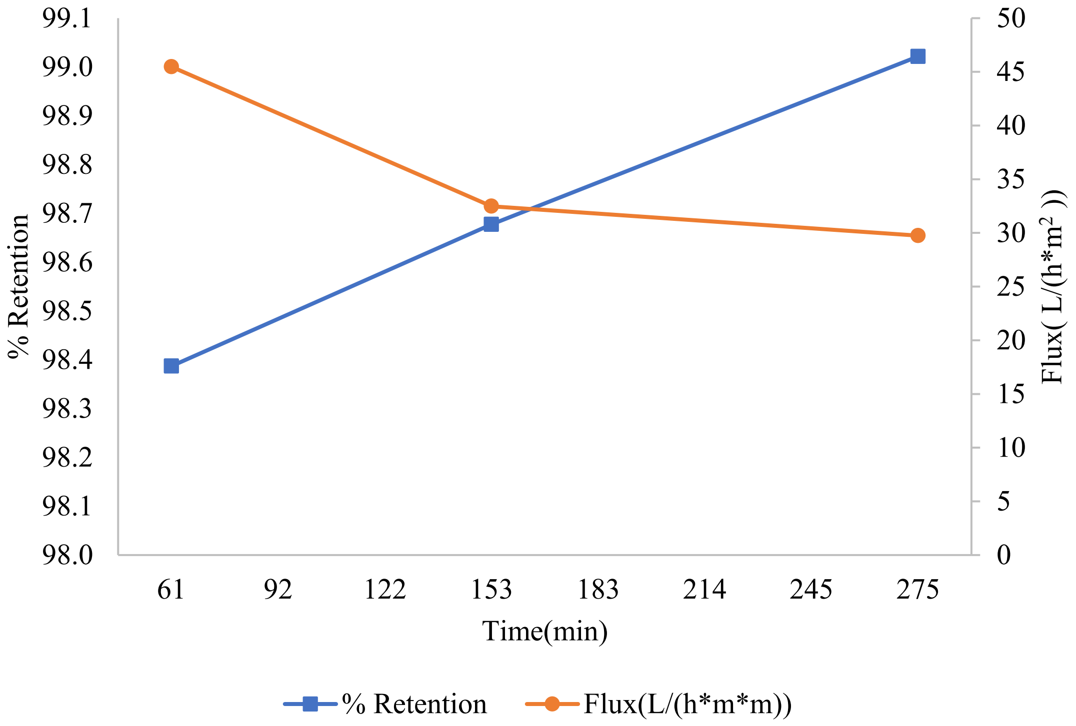

Figure 5. 19. Effect of 1 bar of TMP on oily water flux of the support and % retention (F=25).

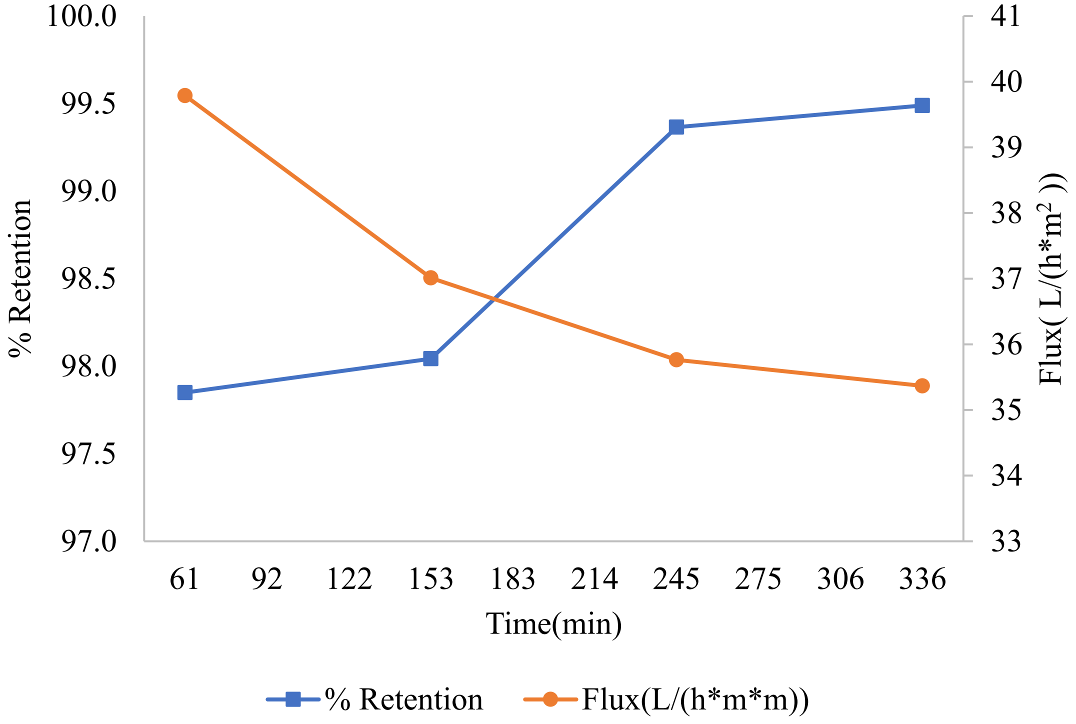

Figure 5. 20. Effect of 2 bar of TMP on oily water flux of the support and % retention (F=25).

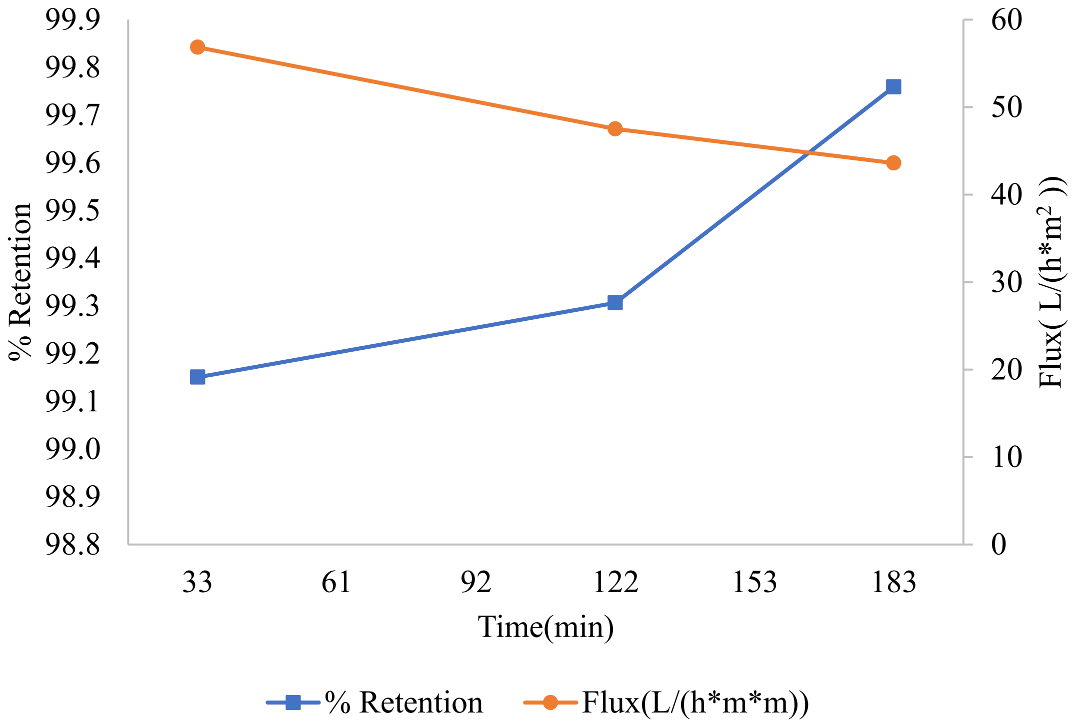

Figure 5. 21. Effect of 3 bar of TMP on oily water flux of the support and % retention (F=25).

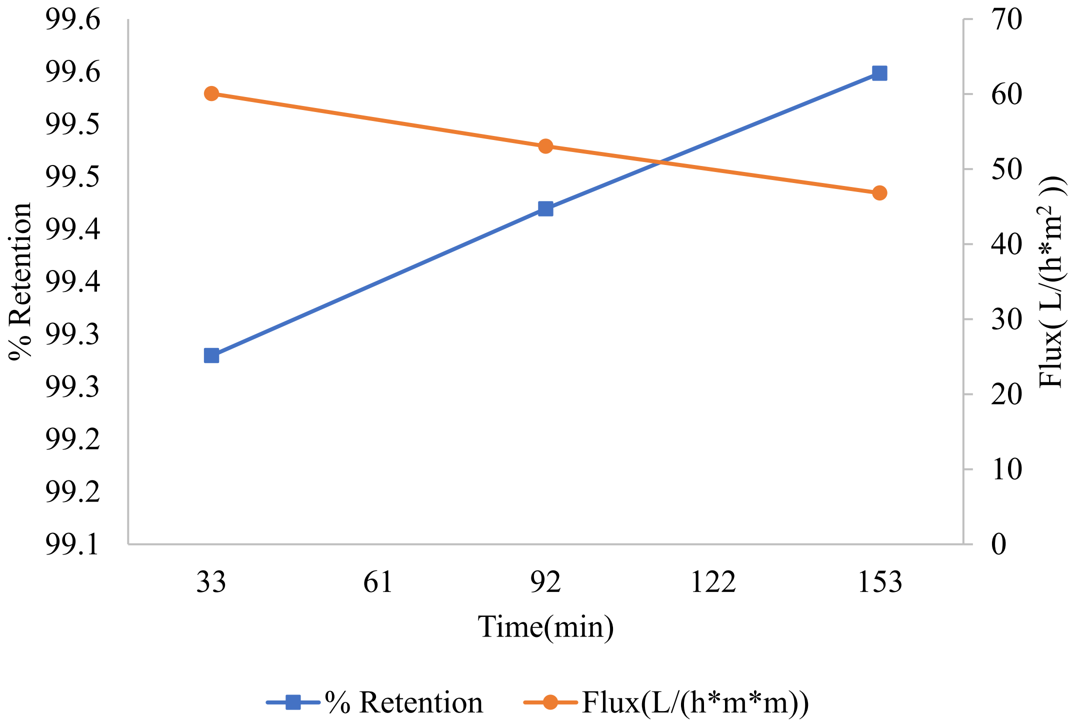

Figure 5. 22. Effect of 4 bar of TMP on oily water flux of the support and % retention (F=25).

The effect of oil concentration on the performance of tubular ceramic supports for the treatment of oily water was evaluated by preparing oily water containing 1 wt. % cutting fluid. Filtrations were performed at 1,2,3 and 4 bar TMPs for CFV of F=20. Permeate flux was measured to be 210 L/h·m^2 at the onset of filtration and logarithmically decayed to 65 L/h·m^2 after 3 hours filtration (Figure 5.23). Oil retention was almost 100 % in the first 1.5 hours and decreased to 98 % at the end of filtration (Figure 5.23).

When TMP was increased to 2 bar, initial flux was increased to 378 L/h·m^2 (Figure 5.24). Permeate flux measured at the end of the filtration was also increased when compared to final flux observed at 1 bar. Oil retention was 99 % at the beginning; it reached almost 100 % after 5 minutes of filtration and decreased to 96 % at the end of the filtration.

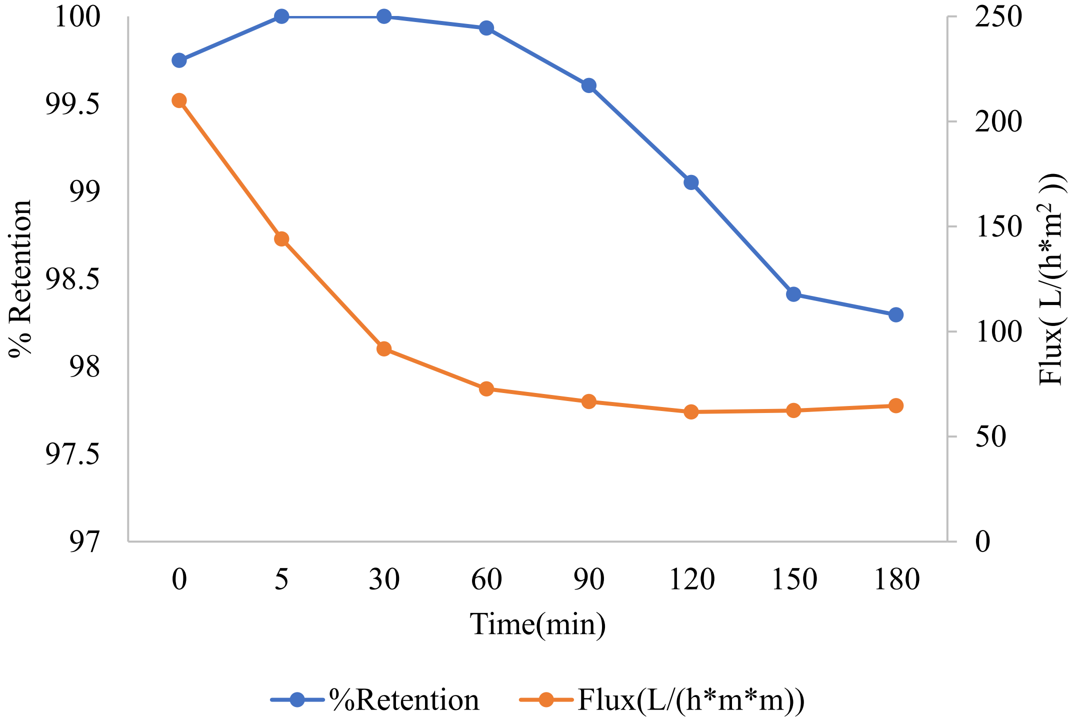

Figure 5. 23. Effect of 1 bar of TMP on 1% oily water flux of the support and % retention (F=20).

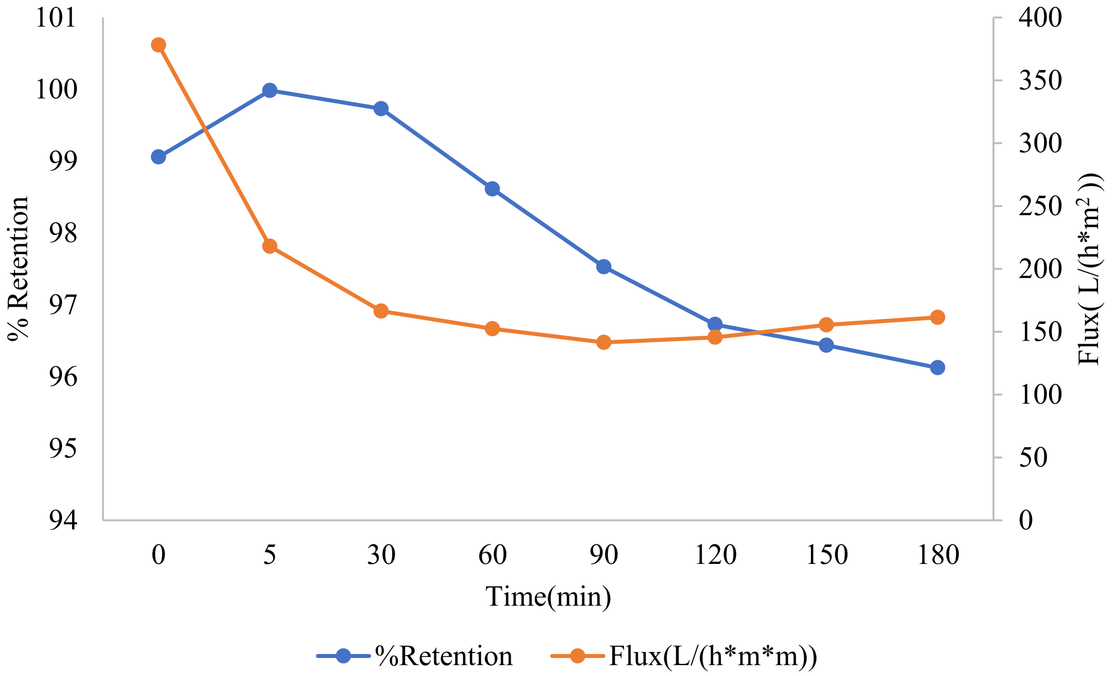

Figure 5. 24. Effect of 2 bar of TMP on 1% oily water flux of the support and % retention (F=20).

Initial permeate fluxes were observed to be 532 and 622 L/h·m^2 in the filtration experiments performed at TMP values of 3 (Figure 5.25) and 4 bar (Figure 5.26), respectively. Permeate flux was decreased to 281 L/h·m^2 at the end of filtration at 3 bar whereas final permeate flux was measured to be 265 L/h·m^2. Oil retention percentages were initially equal to almost 100 % at both TMPs. Oil retention at 3 bar was gradually decreased to 96 % until 90 minutes and increased to 99 % after 180 minutes of filtration at 3 bar. Oil retention at 4 bar exhibited similar behavior. Oil retention which was initially measured to be ~ 100 % decreased to 96 % after 60 minutes and rose back to 99 % at the 150th minutes of filtration. Oil retention decreased slightly to 98 % at the end of filtration.

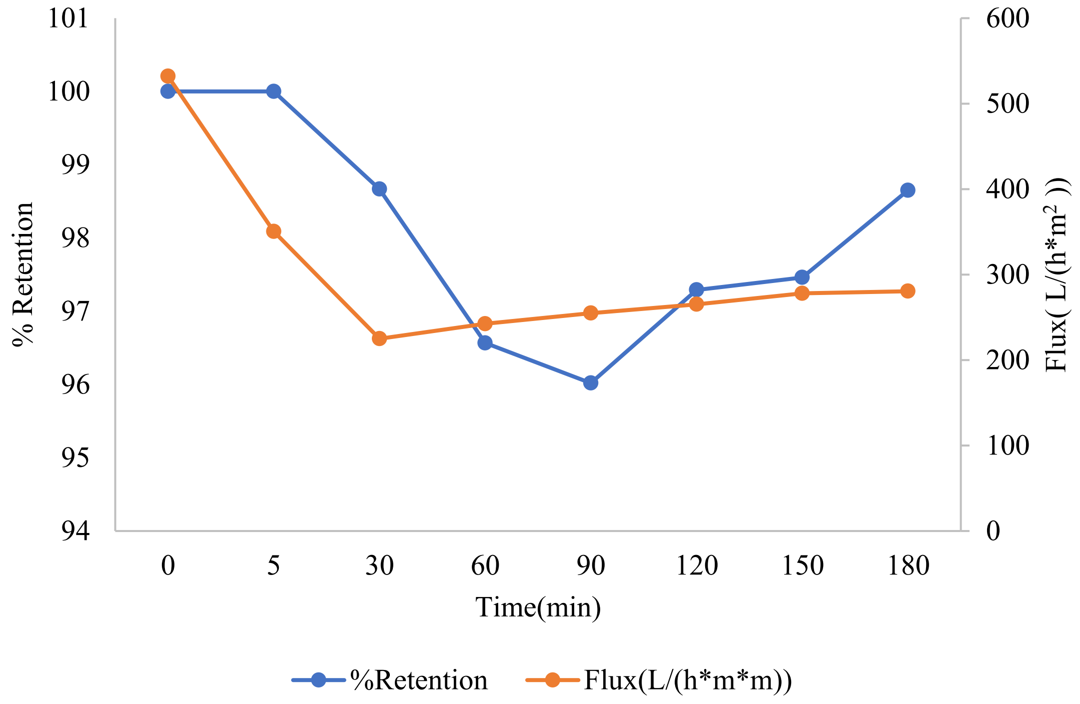

Figure 5. 25. Effect of 3 bar of TMP on 1% oily water flux of the support and % retention (F=20).

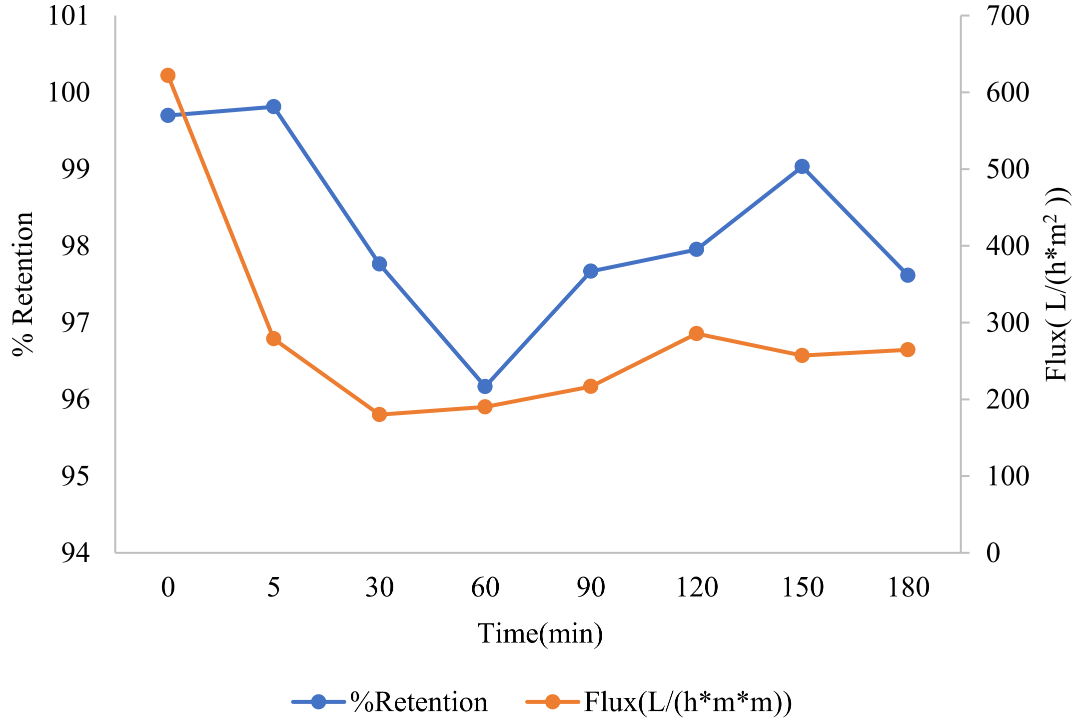

Figure 5. 26. Effect of 4 bar of TMP on 1% oily water flux of the support and % retention (F=20).

Although the permeate fluxes measured at 1, 2, 3 and 4 bar for CFV of F= 20 during the filtration of 1 wt. % oily water showed that increasing TMP resulted in the increase in permeate fluxes, permeate fluxes were much more higher than those observed in the filtration of 0.5 wt. % oily water. They were indeed closer to the pure water fluxes measured for CFV of F=20. Collection of oil over the surface of water in the feed tank following the disruption of oil in water emulsions during the filtration is more likely the reason for higher fluxes obtained using 1 wt. % oily water. Increasing metal cutting fluid concentration increases the oil concentration in water and the number of oil in water emulsions. Although oily water is homogenized during preparation, oil phase separates from water easily when the number of oil in water emulsion is large once they are disrupted. These results either in the complete phase separation or decrease in the number of oil in water emulsions. Separation of oil from aqueous phase in the tank at least lead to the flow of aqueous phases containing lower amounts of oil emulsions through the membrane. When no or insufficient amount of oil is present in the aqueous phase, membranes do not completely foul and permeate fluxes closer to pure water fluxes can be obtained.

5.2. Filtration experiment with MF1

Pure water permeation fluxes of ceramic MF 1 membranes were measured at 1, 2, 3 and 4 bar for CFV of F= 15, 20 and 25. Figure 5.27 shows that pure water fluxes of MF1 membrane at all TPM values for F=15 were stable during 180 minutes permeability experiments. Water fluxes of 382, 707, 796 and 909 were obtained at 1, 2, 3 and 4 bar, respectively. As it is inferred from Figure 5.27, greater the trans-membrane pressure, higher the pure water flux was.

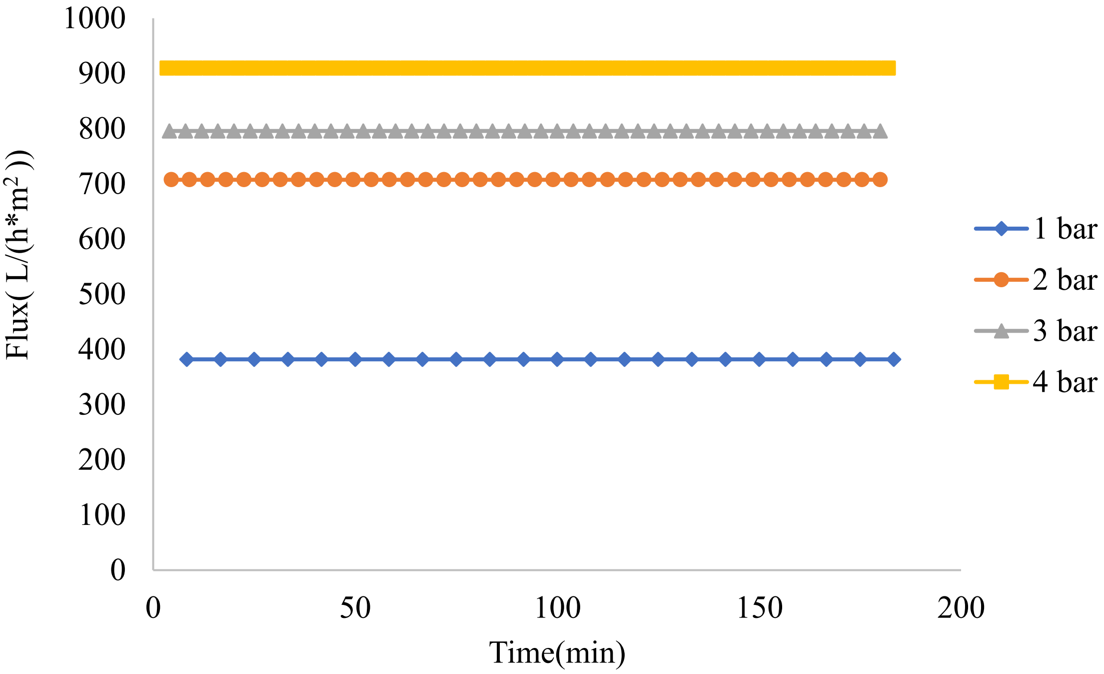

Figure 5. 27. Effect of TMP on pure water flux of the MF1 (F=15).

When water permeability fluxes were measured for CFV of F=20, water fluxes obtained at 1 (107 L/h·m^2) and 2 bar (490 L/h·m^2) for F=20 (Figure 5.28) were found to be lower than those observed for F=15. Permeate fluxes obtained at 3 and 4 bar were 1061 and 1273 L/h·m^2, respectively and greater than those obtained at 3 and 4 bar for CFV of F=15. Water fluxes obtained for CFV of F=25 are shown in Figure 5.29. Pure water permeability values at 1, 2, 3 and 4 bar were 502, 1123, 1273 and 1469 L/h·m^2, respectively. Water permeability experiments showed that increase in TMP results in the increase of pure water flux for all cross-flow velocities employed. Increasing cross-flow velocity from 15 to 25 yielded increase in water permeability except 1 and 2 bar TMP values for F=20.

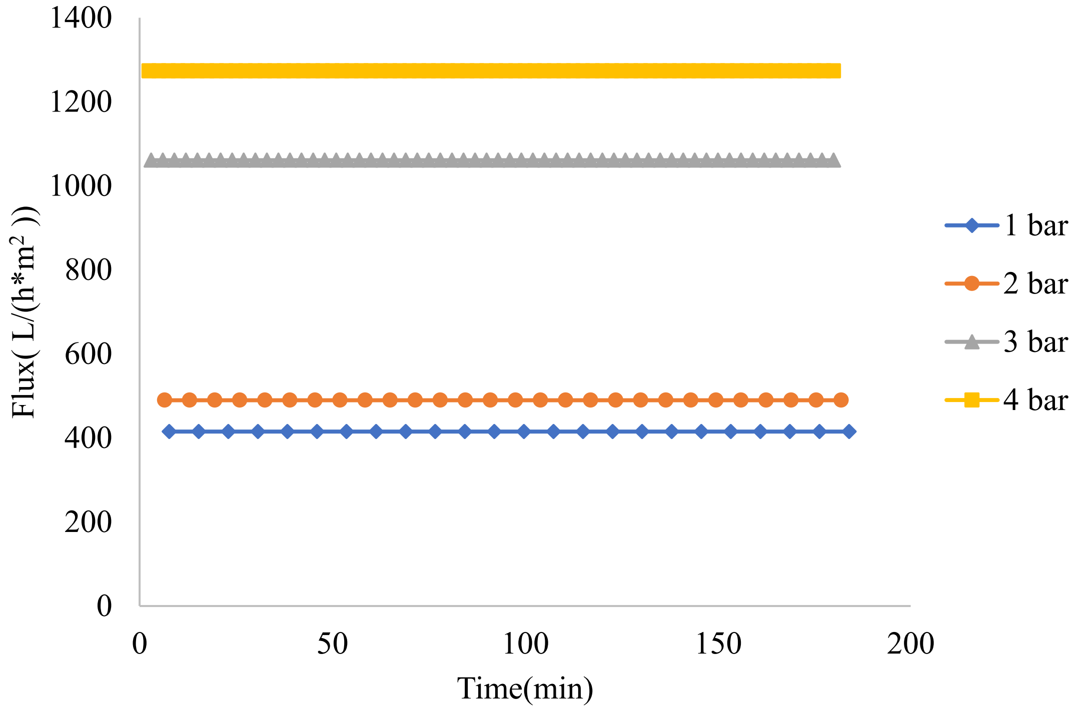

Figure 5. 28. Effect of TMP on pure water flux of the MF1 (F=20).

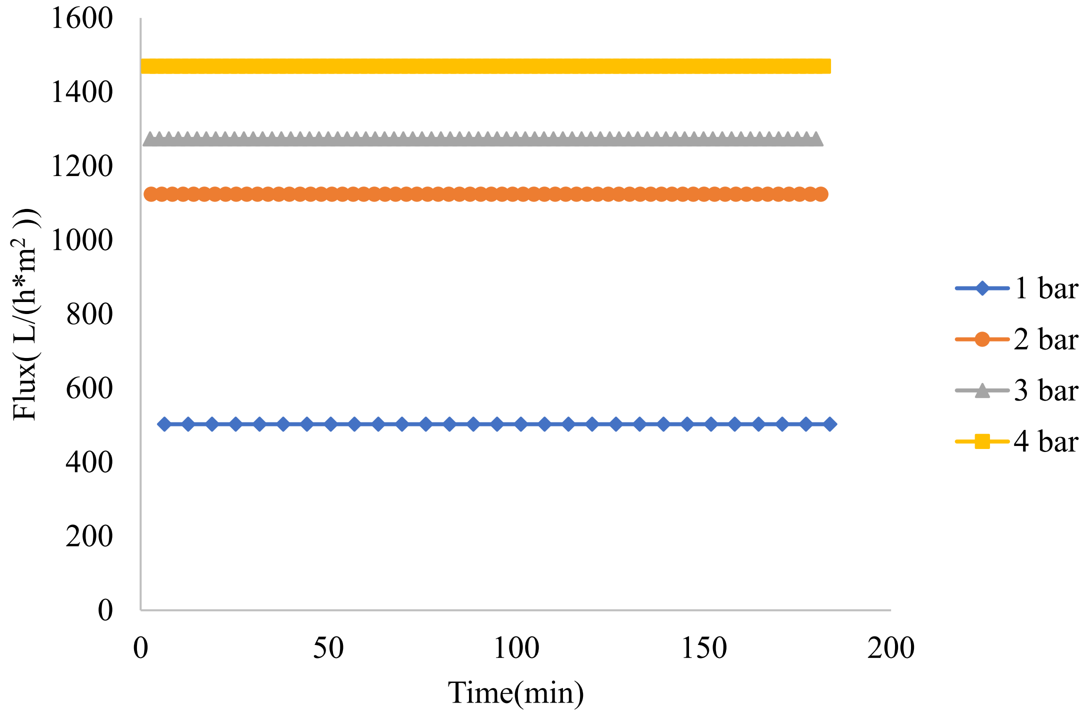

Figure 5. 29. Effect of TMP on pure water flux of the MF1 (F=25).

Permeate flux and percent oil retention monitored throughout the filtration of 0.5 % oily water using MF1 membrane at TMP of 1 bar and CFV of F=15 are given in Figure 5.30. Permeate fluxes were measured to be 148 L/h·m^2 and 13 L/h·m^2 at the beginning and end of the filtration, respectively. Percent oil retention was initially measured as ~100 % and stayed constant throughout the filtration.

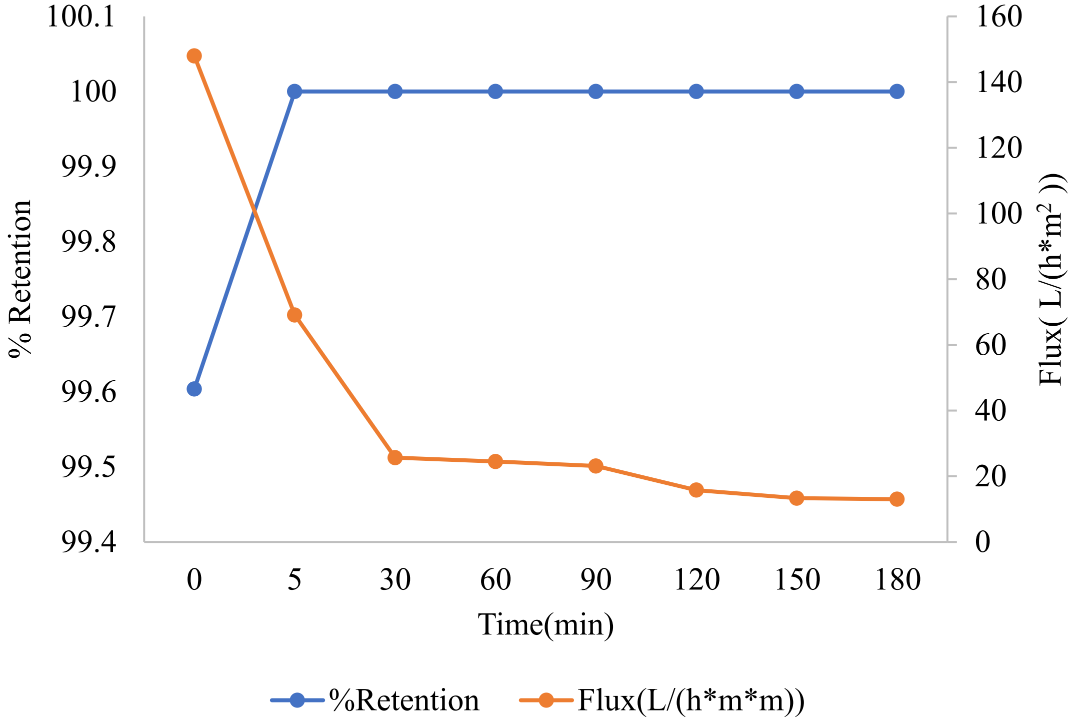

Figure 5. 30. Effect of 1 bar of TMP on 0.5 % oily water flux of the MF1 and % retention (F=15).

Initial permeate fluxes were 190 and 195 L/h·m^2 and reduced to 10 and 4 L/h·m^2 at the end of filtrations at 2 and 3 bar, respectively (Figures 5.31 and 5.32). Oil retention percentage was ~100 % at both pressures. When TMP was adjusted to 4 bar, initial flux was measured to be 292 L/h·m^2 and fell down to 5 L/h·m^2 (Figure 5.33). Oil removal percentage was greater than 99 % during filtration.

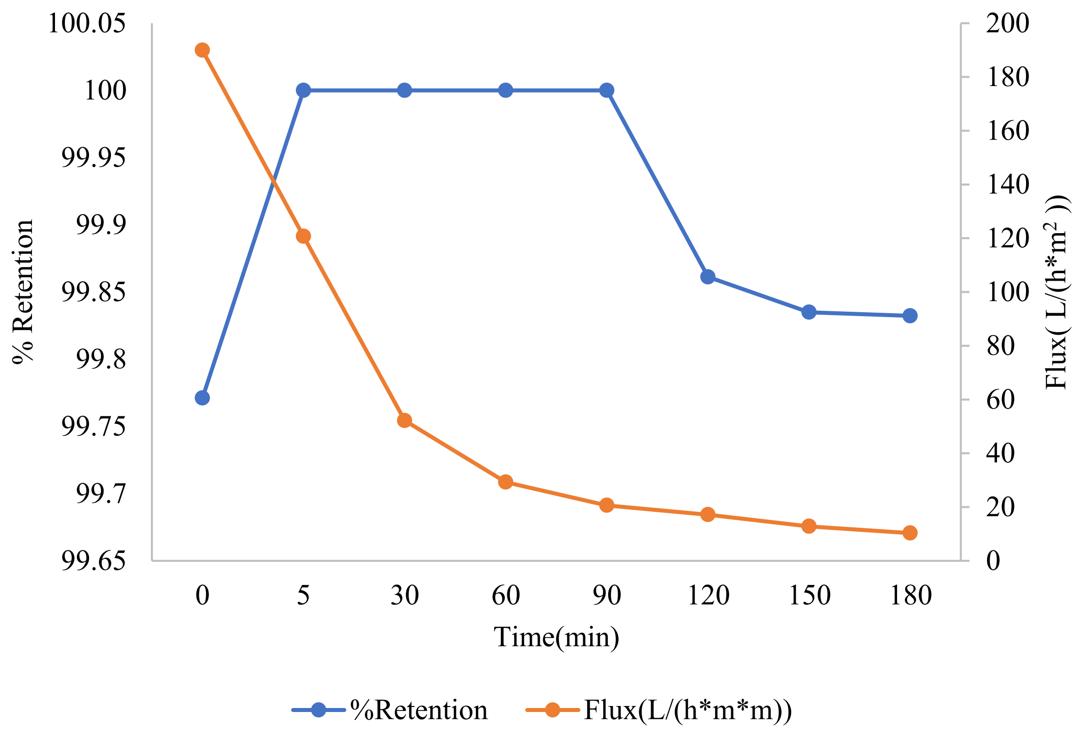

Figure 5. 31. Effect of 2 bar of TMP on 0.5 % oily water flux of the MF1 and % retention (F=15).

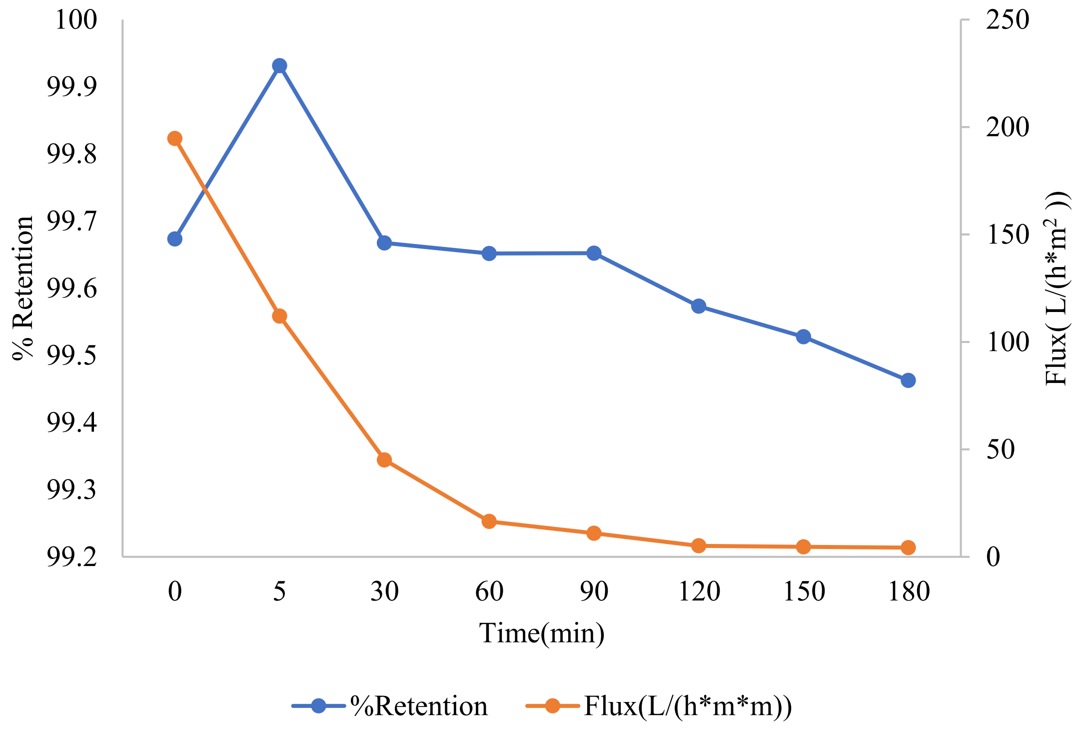

Figure 5. 32. Effect of 3 bar of TMP on 0.5 % oily water flux of the MF1 and % retention (F=15).

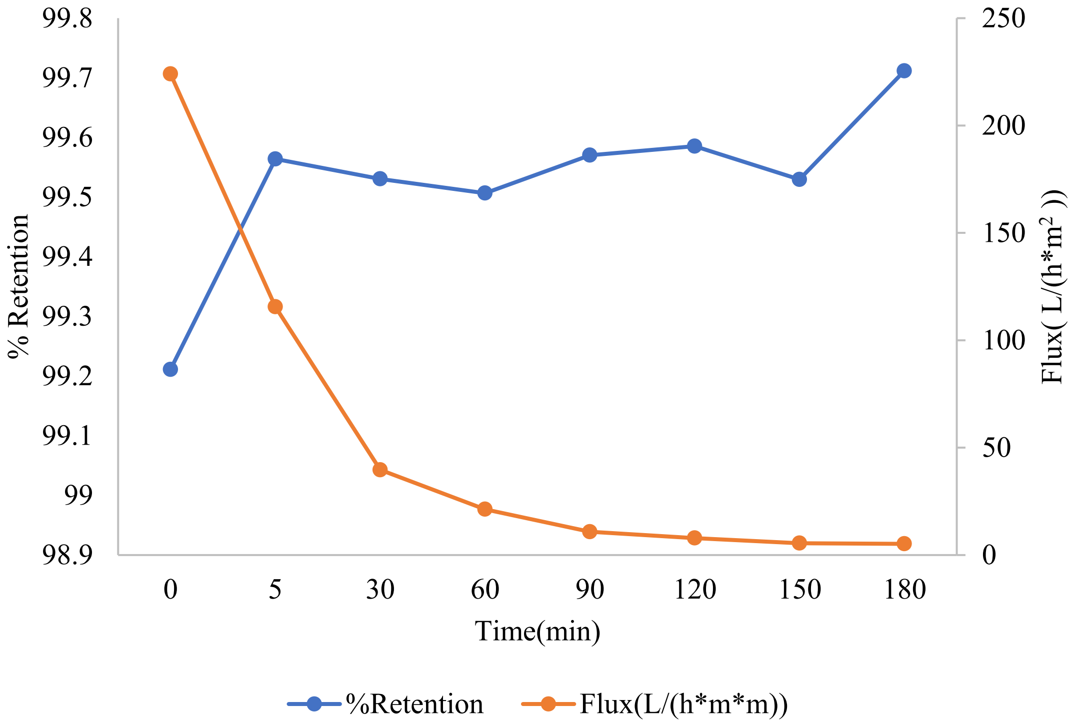

Figure 5. 33. Effect of 4 bar of TMP on 0.5 % oily water flux of the MF1 and % retention (F=15).

The results of the filtration experiment where cross-flow velocity was adjusted to F=20 are given in Figure 5.34. Permeate flux initially measured as 135 L/h·m^2 and decreased to 1.5 L/h·m^2 at 1 bar. Initial and final permeate fluxes were 200 L/h·m^2 and 17 L/h·m^2, respectively at 2 bar (Figure 5.35). Further increase of TMP to 3 bar yielded initial permeability of 195 L/h·m^2 (Figure 5.36) similar to that obtained at 2 bar. Final permeate flux was 3 L/h·m^2 at the end of the filtration at 3 bar. Initial permeate flux was increased to 292 L/ h·m^2 when TMP was increased to 4 bar (Figure 5.37). At the end of the filtration, permeate flux was measured to be 7 L/h·m^2. Oil removal percentages were found to be greater than 99 % during the filtration experiments performed at all TMP values applied.

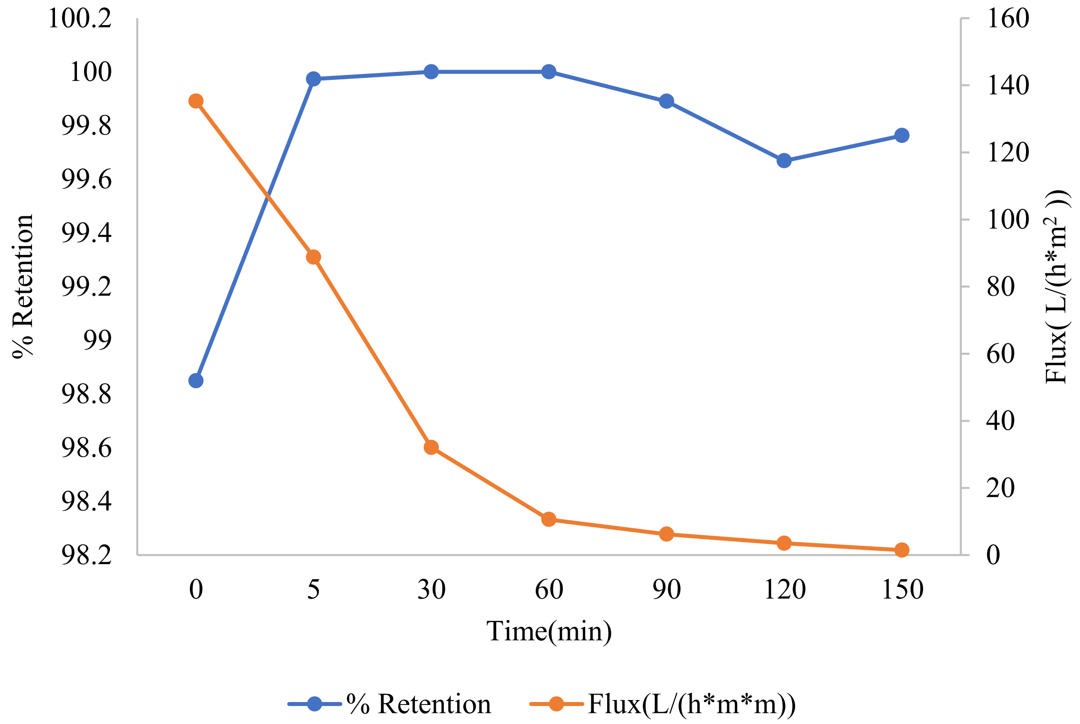

Figure 5. 34. Effect of 1 bar of TMP on 0.5 % oily water flux of the MF1 and % retention (F=20).

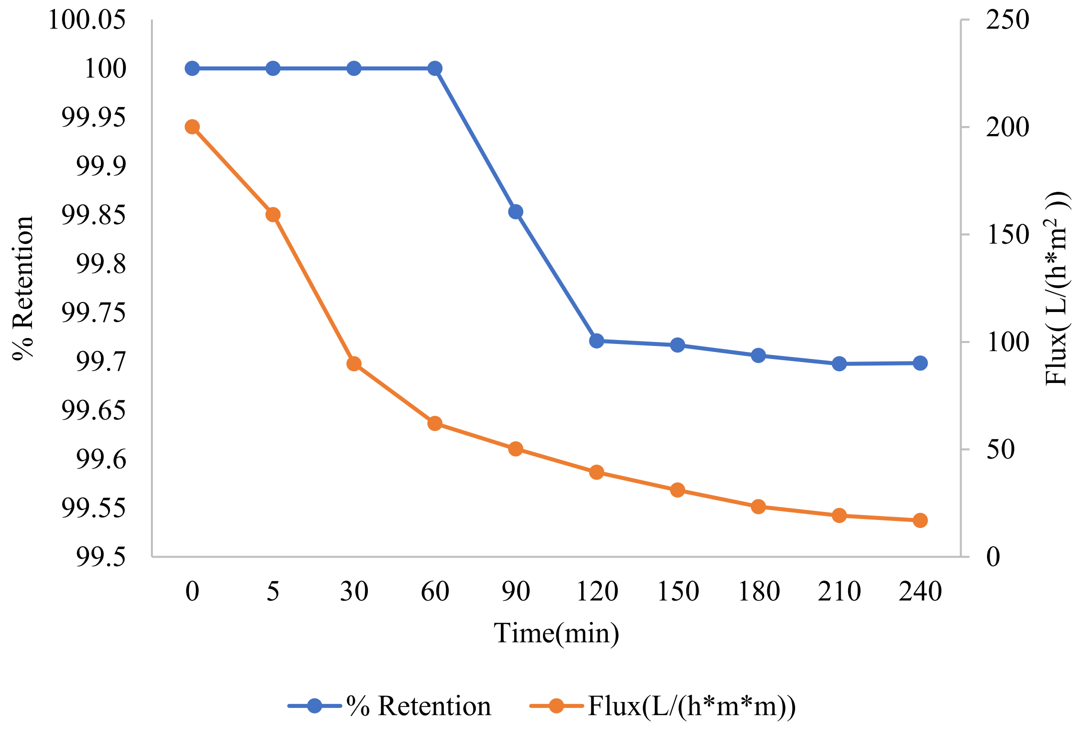

Figure 5. 35. Effect of 2 bar of TMP on 0.5 % oily water flux of the MF1 and % retention (F=20).

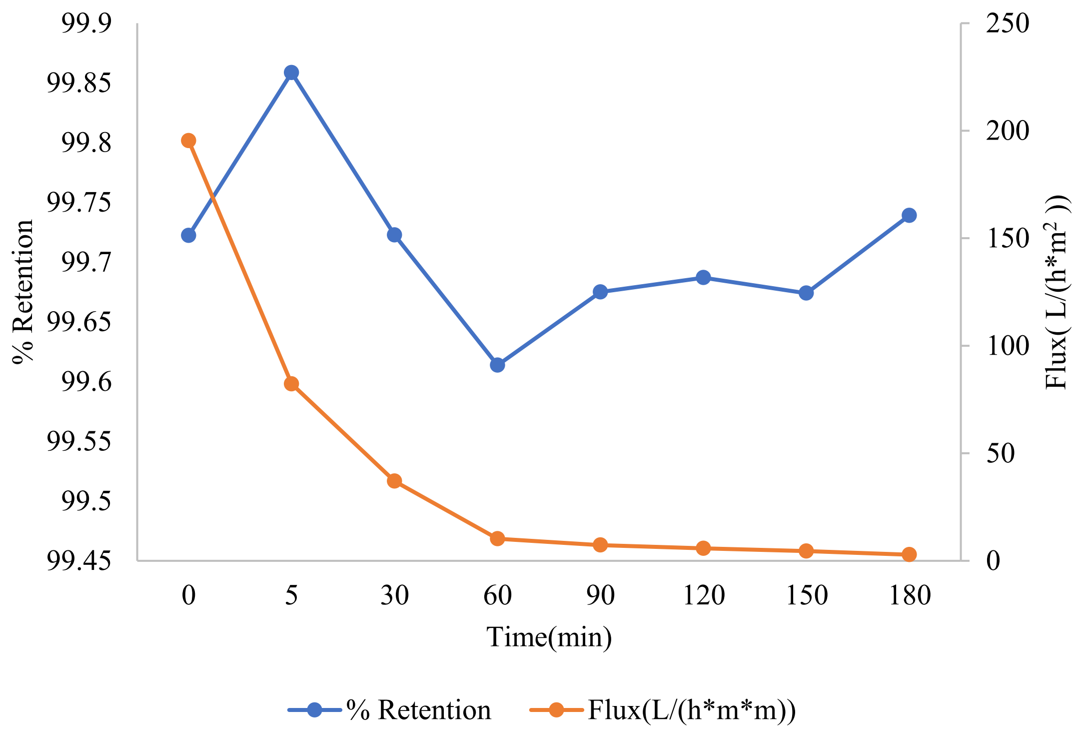

Figure 5. 36. Effect of 3 bar of TMP on 0.5 % oily water flux of the MF1 and % retention (F=20).

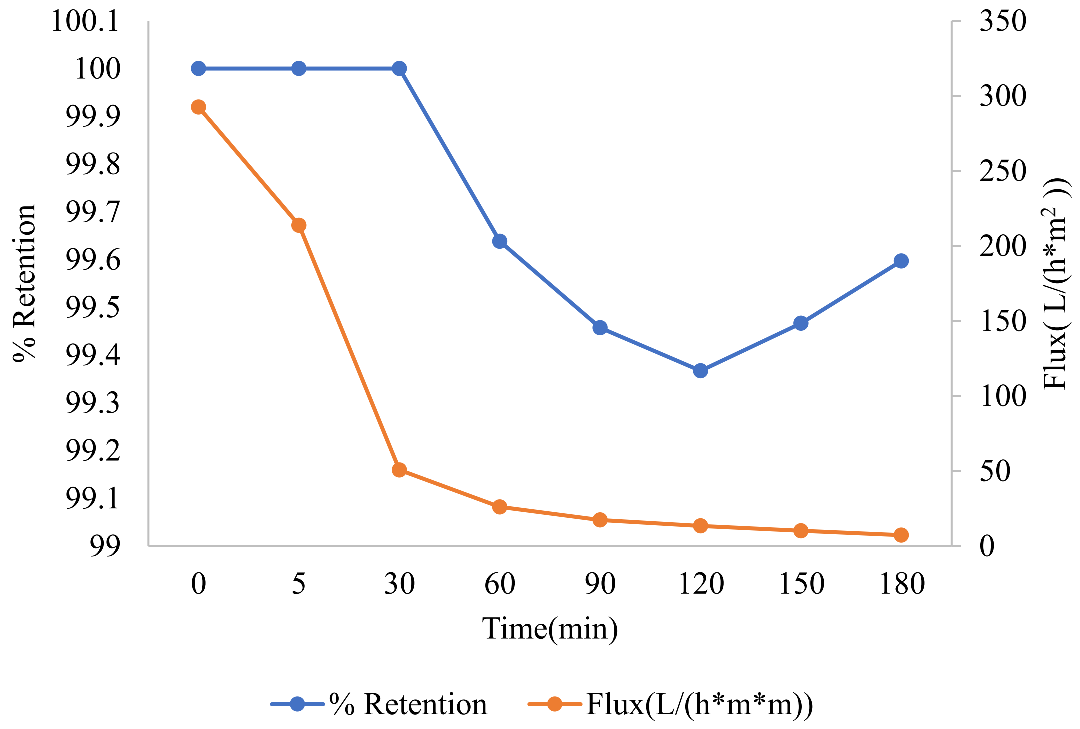

Figure 5. 37. Effect of 4 bar of TMP on 0.5 % oily water flux of the MF1 and % retention (F=20).

The results of the experiments performed at 1, 2, 3 and 4 bar TMP values when CFV was F=25 are shown in Figures 5.38, 5.39, 5.40 and 5.41. Permeate fluxes observed at the beginning of filtrations were 123, 147, 163 and 290 L/h·m^2 at 1, 2, 3 and 4 bar, respectively. Final fluxes however ranged between 6 and 21 L/h·m^2. Oil removal was however ~ 100 % at 1, 2 and 3 bar and greater than 99 % at 4 bar.

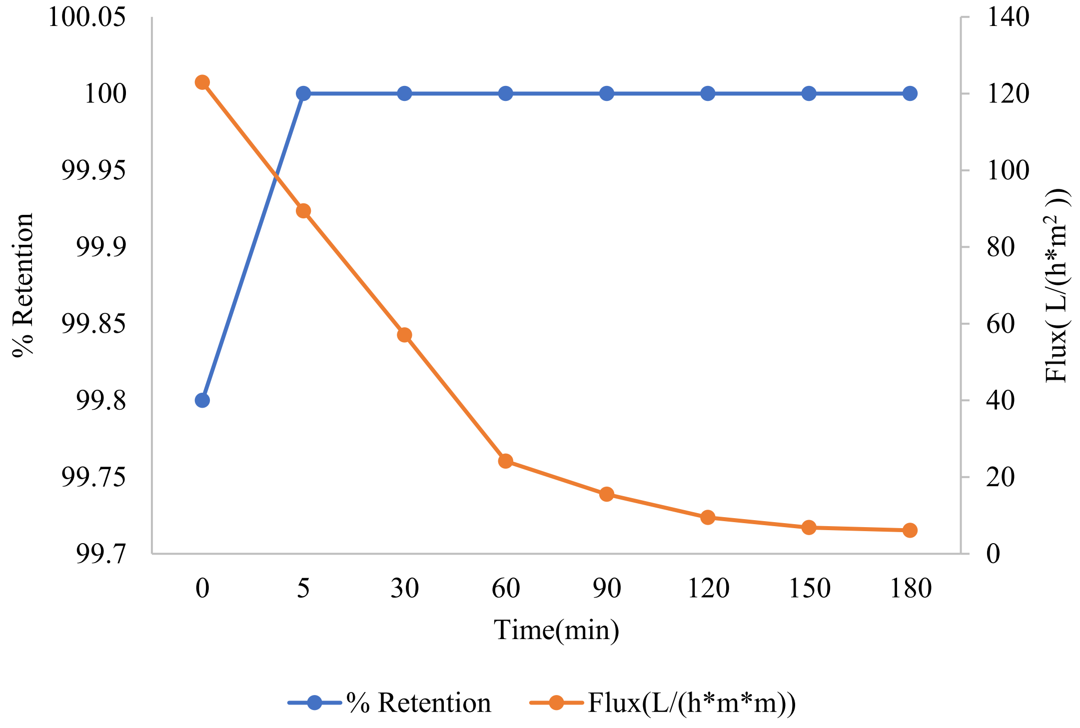

Figure 5. 38. Effect of 1 bar of TMP on 0.5 % oily water flux of the MF1 and % retention (F=25).

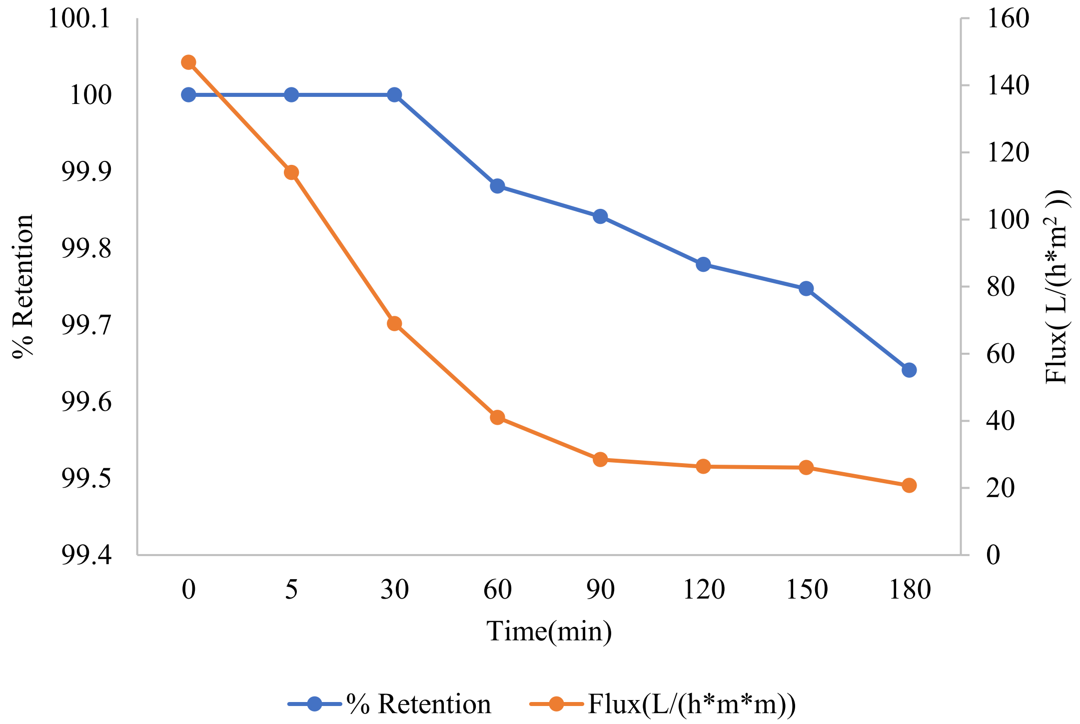

Figure 5. 39. Effect of 2 bar of TMP on 0.5 % oily water flux of the MF1 and % retention (F=25).

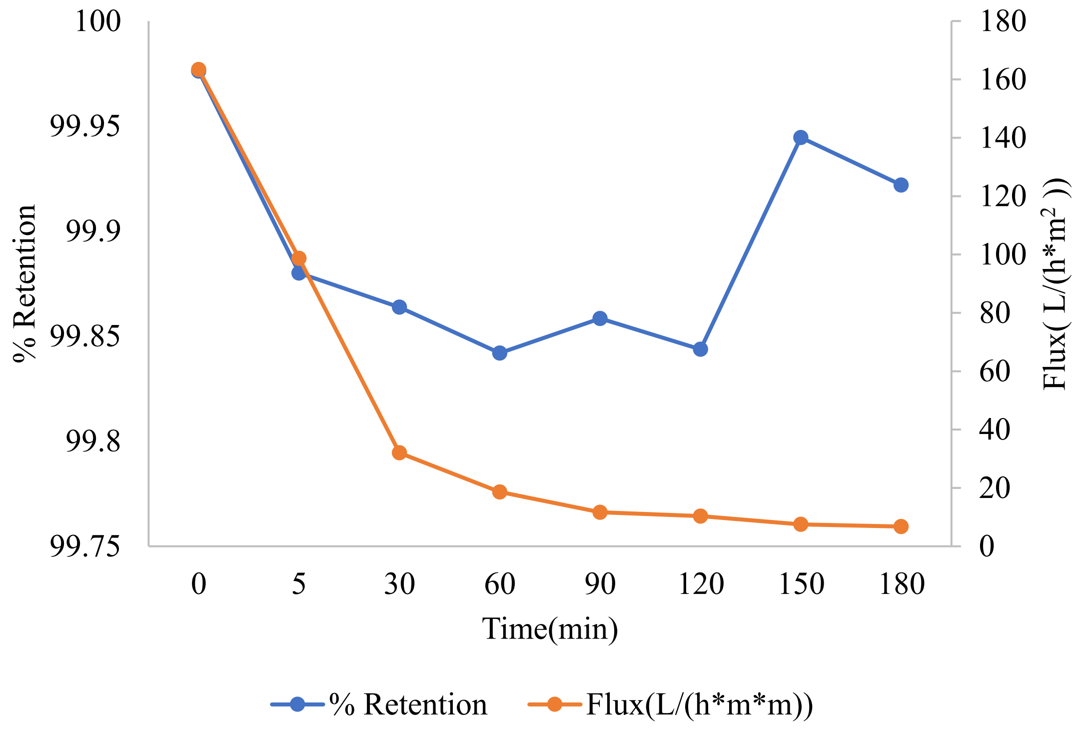

Figure 5. 40. Effect of 3 bar of TMP on 0.5 % oily water flux of the MF1 and % retention (F=25).

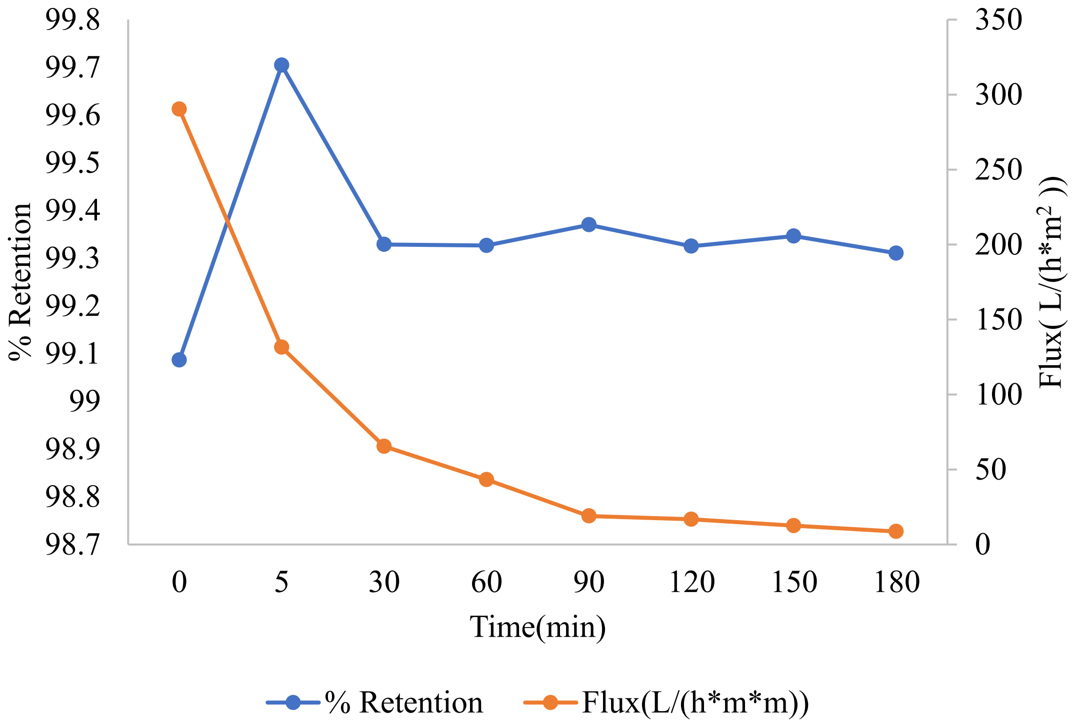

Figure 5. 41. Effect of 4 bar of TMP on 0.5 % oily water flux of the MF1 and % retention (F=25).

A relatively higher cross-flow velocity (F=40) was selected and applied in the filtration of oily water using MF1 ceramic membranes. It was not possible to adjust TMP to 1 and 2 bar since this CFV value resulted in TMP built-up greater than 2 bar without any pressure adjustment. Filtration experiments were therefore performed only at 3 and 4 bar. Permeate flux was initially 149 L/h·m^2 at 3 bar (Figure 5.42) and lower than permeate fluxes obtained at same TMPs for lower CFV values. Initial water permeability at 4 bar was 315 L/h·m^2 (Figure 5.43) and greater than that obtained at 3 bar. Permeate fluxes measured at the end of filtrations at 3 and 4 bar were 15 and 86 L/h·m^2, respectively. Initial permeate fluxes measured at all TMP for all CFV values indicated that increase in TMP increases permeate flux yet increasing CFV do not cause increase in water permeability. Lower final fluxes indicate the fouling of the MF1 membranes in the filtration of oily water. The observation that increase in CFV did not increase permeate flux points out the fouling of the membrane pores or insufficiency of CFV in the removal of fouling cake layer on the internal surface of the membrane.

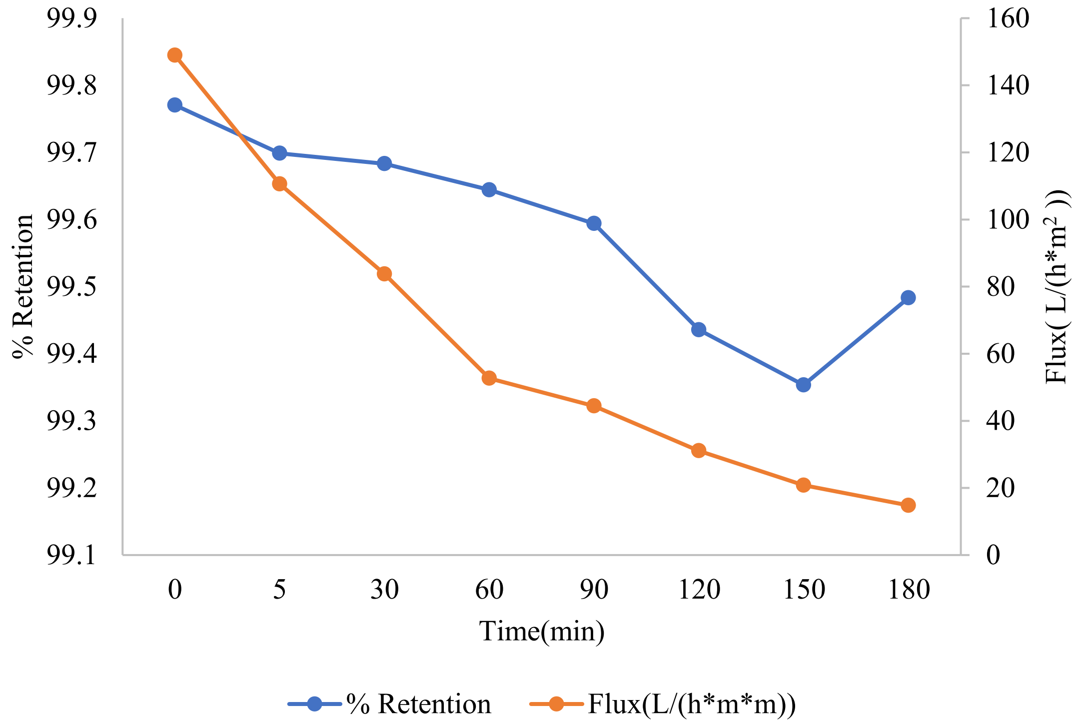

Figure 5. 42. Effect of 3 bar of TMP on 0.5 % oily water flux of the MF1 and % retention (F=40).

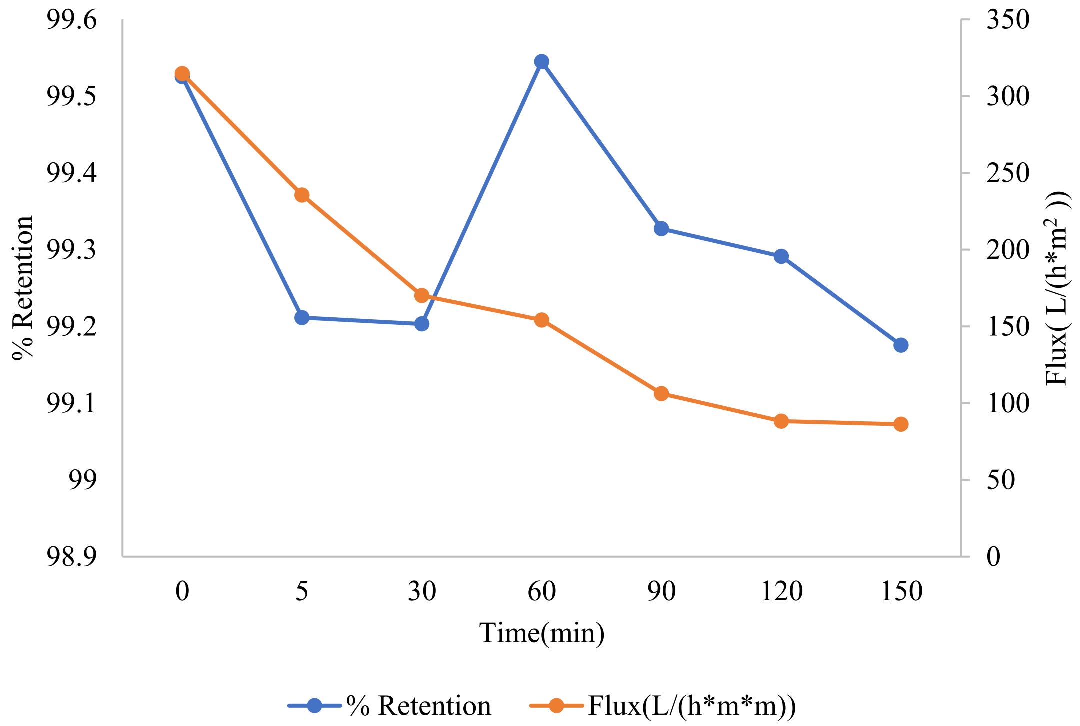

Figure 5. 43. Effect of 4 bar of TMP on 0.5 % oily water flux of the MF1 and % retention (F=40).

MF1 membranes were also used in the filtration of oily water containing 1 wt. % cutting fluid. Filtration experiments were performed at 1, 2, 3 and 4 bar for only CFV of F=20. As shown in Figures 5.44, 5.45, 5.46 and 5.47, initial permeate fluxes were 75, 186, 187 and 313 L/h·m^2 results at 1, 2, 3 and 4 bar, respectively. Final fluxes ranged between 2 and 33 L/h·m^2. Oil retention percentages were found to be around 99 % or greater at 1, 2 and 3 bar. Oil retention was ~100 % at the beginning of the filtration at 4 bar however it was measured to be 95 % at the 30th and 60th minutes. It increased thereafter and stayed at ~99 % until the end of the filtration.

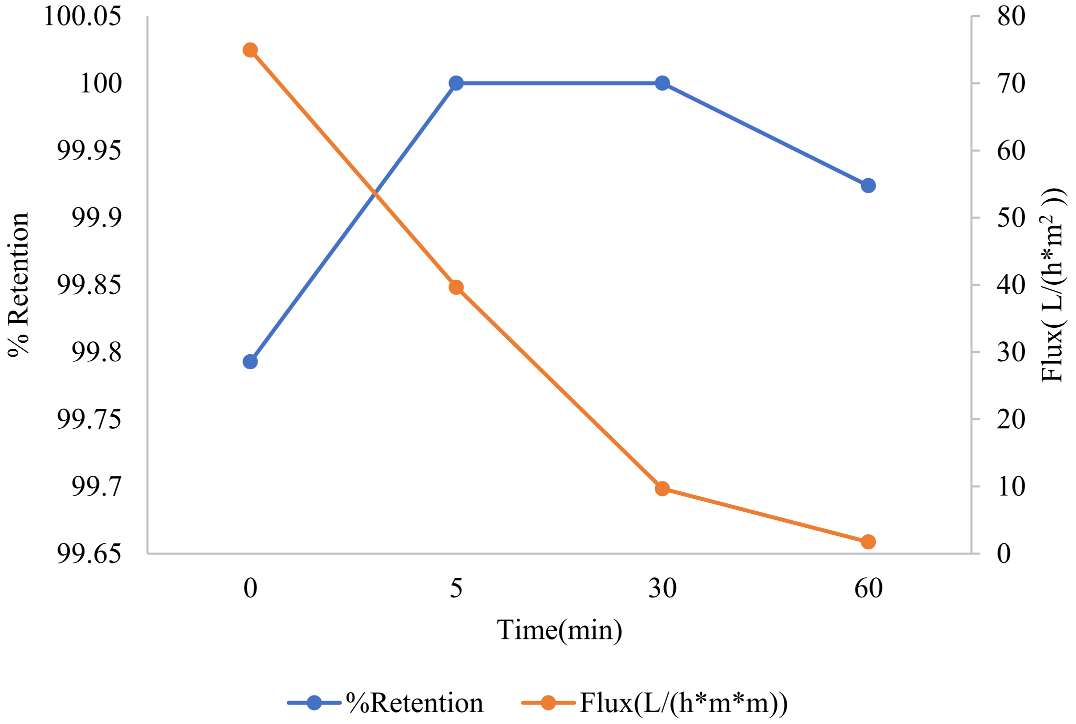

Figure 5. 44. Effect of 1 bar of TMP on 1 % oily water flux of the MF1 and % retention (F=20).

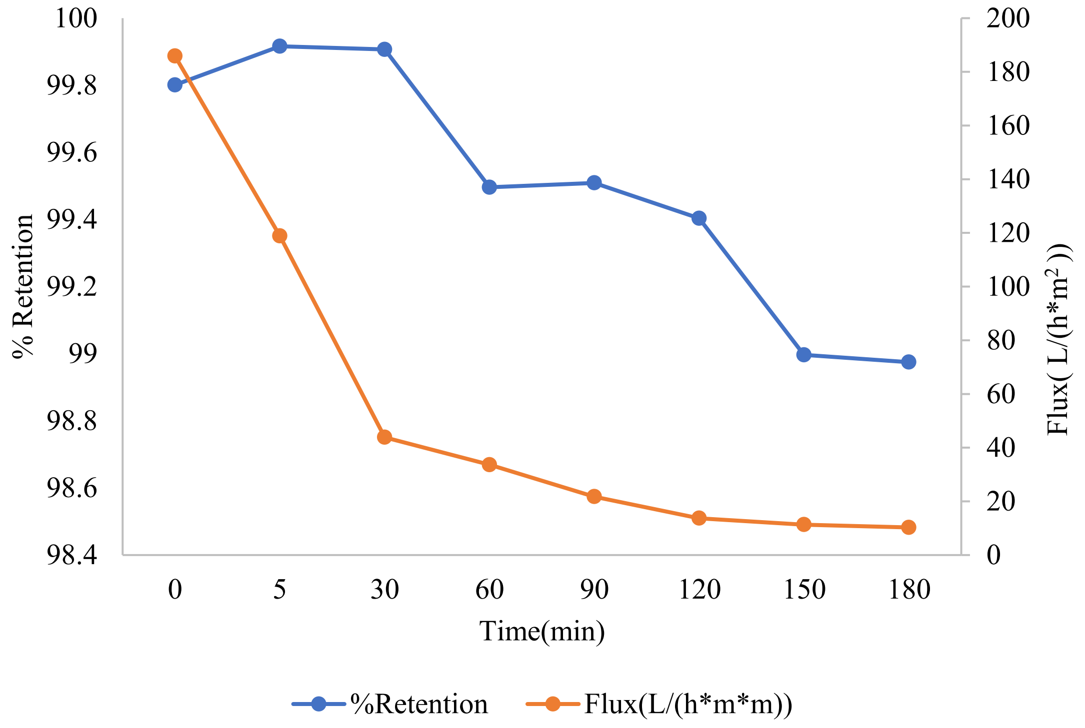

Figure 5. 45. Effect of 2 bar of TMP on 1 % oily water flux of the MF1 and % retention (F=20).

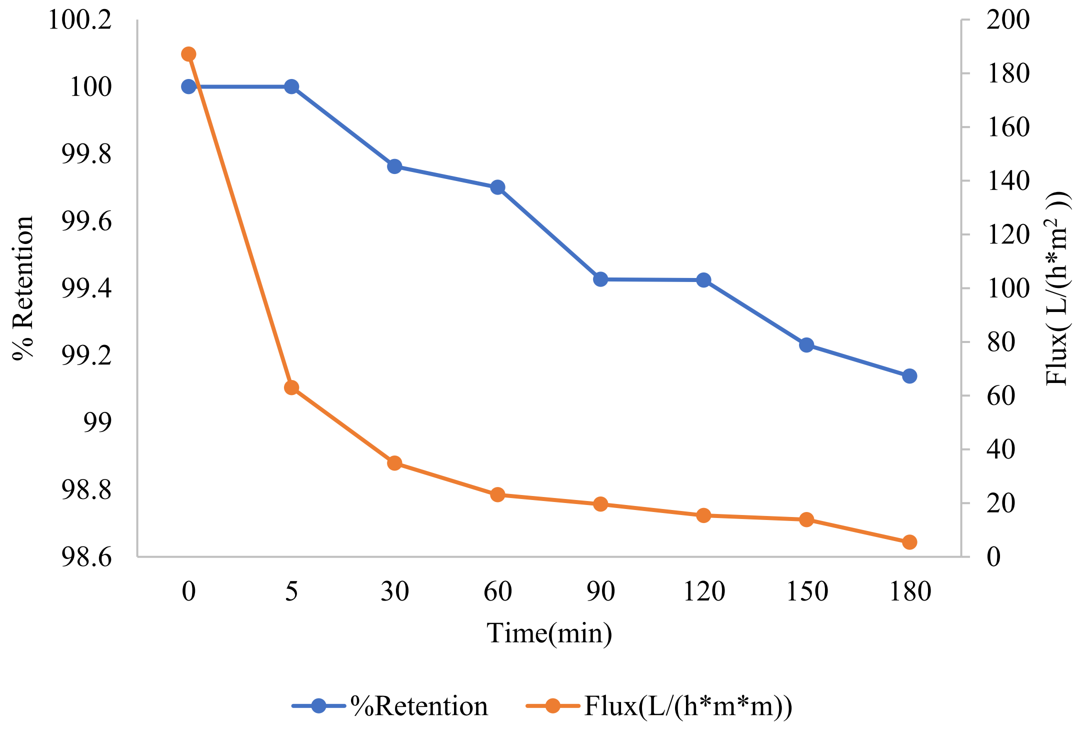

Figure 5. 46. Effect of 3 bar of TMP on 1 % oily water flux of the MF1 and % retention (F=20).

When the results of the filtration experiments by MF1 mebranes using 1 wt. % oily were compared with the results of those performed using 0.5 wt. % oily water, it can be seen that similar permeate fluxes at the same TMP values were obtained. In the filtration experiment performed at 1 bar using 1 wt. % oily water, permeate flux decreased to ~2 L/h·m^2 after 60 minutes filtration. Permeate flux measured at 60th minute was 11 L/h·m2. Permeate flux similar to that obtained using 1 wt. % oily water had been obtained after 150 minutes for 0.5 wt. % oily water. This shows that increase in oil concentration in the water causes early fouling of the membrane at 1 bar for CFV=20. When permeate fluxes obtained at the same intervals were compared, fluxes obtained in the filtration of 1 wt. % oily water were lower at 1 and 2 bar and higher at 3 and 4 bar than those counterparts obtained in the filtration of 0.5 wt. % oily water. These findings suggest that membrane fouling due to increased oil concentration reduces the permeate flux at TMP values of 1 and 2 bar and the decrease in the permeate flux due to membrane fouling is compensated by the increase of TMP to 3 and 4 bar.

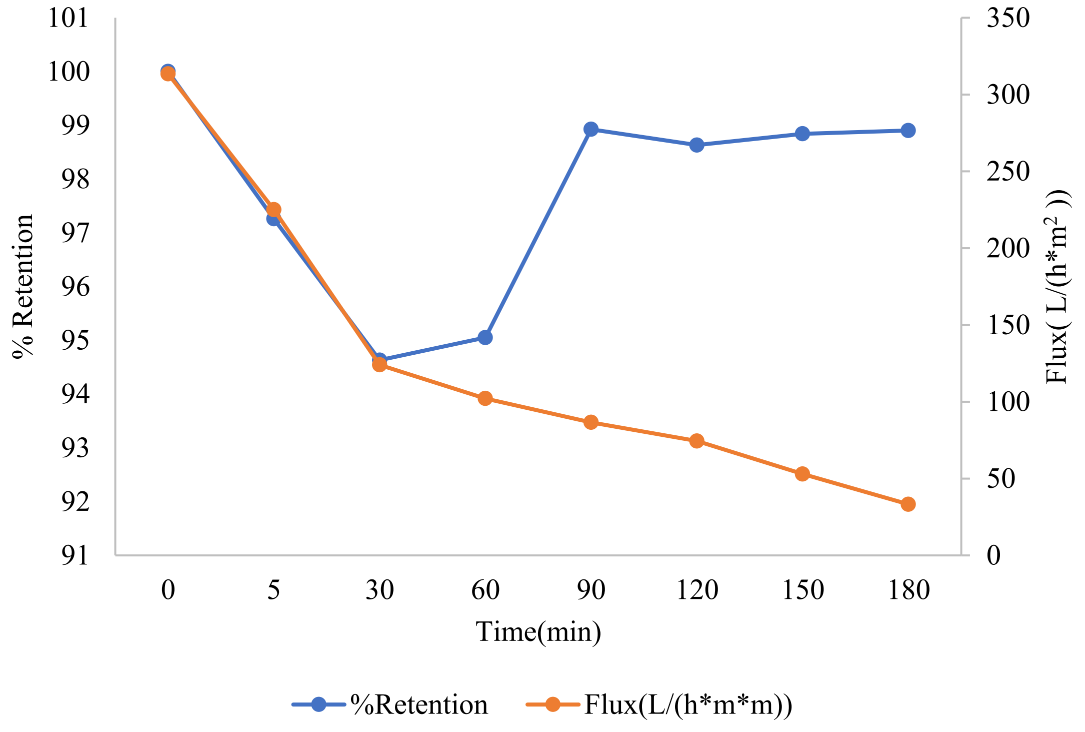

Figure 5. 47. Effect of 4 bar of TMP on 1 % oily water flux of the MF1 and % retention (F=20).

5.3. Filtration experiment with MF2

Second type of ceramic tubular microfiltration membranes (MF2) was prepared and evaluated in the treatment of oily water in this study. Pure water permeability of MF2 membranes were evaluated at 1, 2, 3 and 4 bar TMPs for CFV of F=15, 20 and 25. Water permeability values of MF2 membrane are given in Figure 5.48 for F=15, Figure 5.49 for F=20 and Figure 5.50 for F=25. Pure water permeability fluxes were found to be 318, 382, 466 and 659 L/h·m^2 at 1, 2, 3 and 4 bar for F=15 (Figure 5.48).

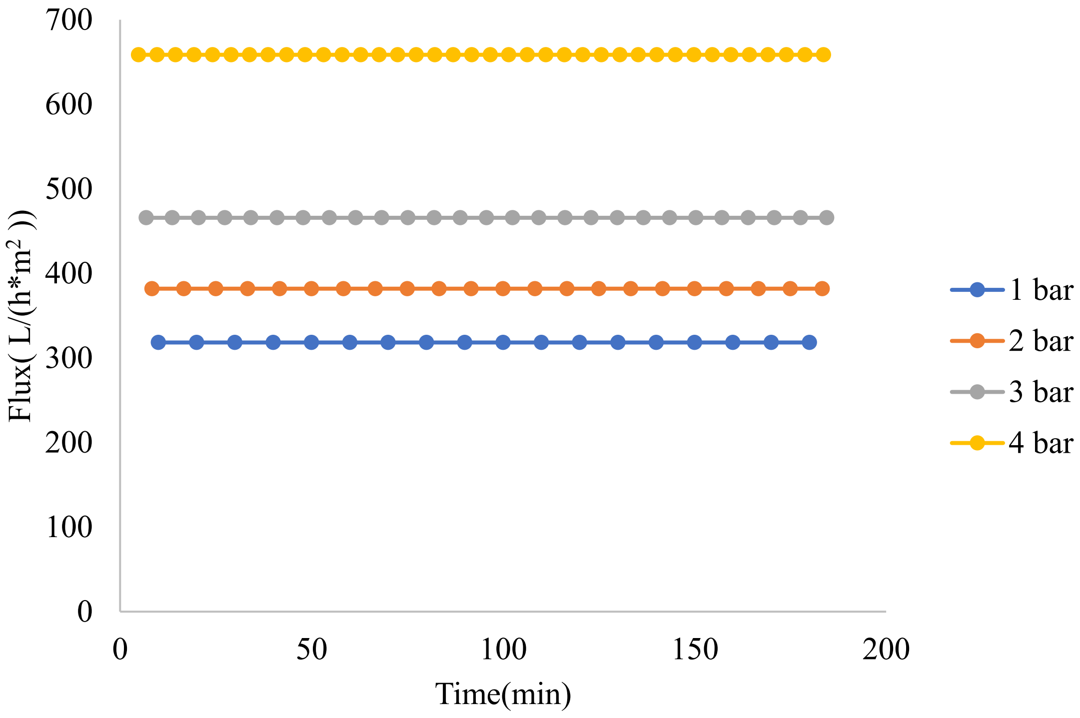

Figure 5. 48. Effect of TMP on pure water flux of the MF2 (F=15).

Pure water fluxes were 360, 415, 490 and 735 L/h·m^2 for F=20 (Figure 5.49) and 398, 516, 579 and 868 L/h·m^2 for F=25 (Figure 5.50) at 1, 2, 3 and 4 bar, respectively. These results show that both increase in TMP at constant CFV and increase in CFV at constant TMP increase water permeation through MF2 membrane. TMP however seems to have more profound effects on the permeate flux than CFV. TMP of 4 bar, especially, results in the higher increase in water permeability of MF2 membranes with respect to 1, 2 and 3 bar (Figures 5.48,.5,49 and 5.50).

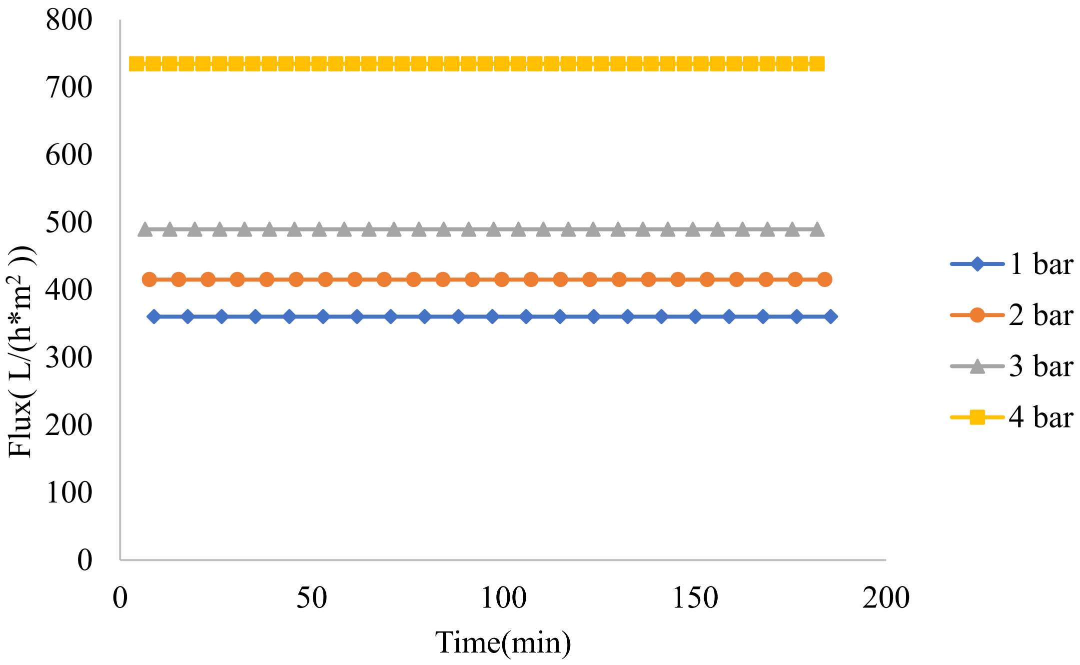

Figure 5. 49. Effect of TMP on pure water flux of the MF2 (F=20).

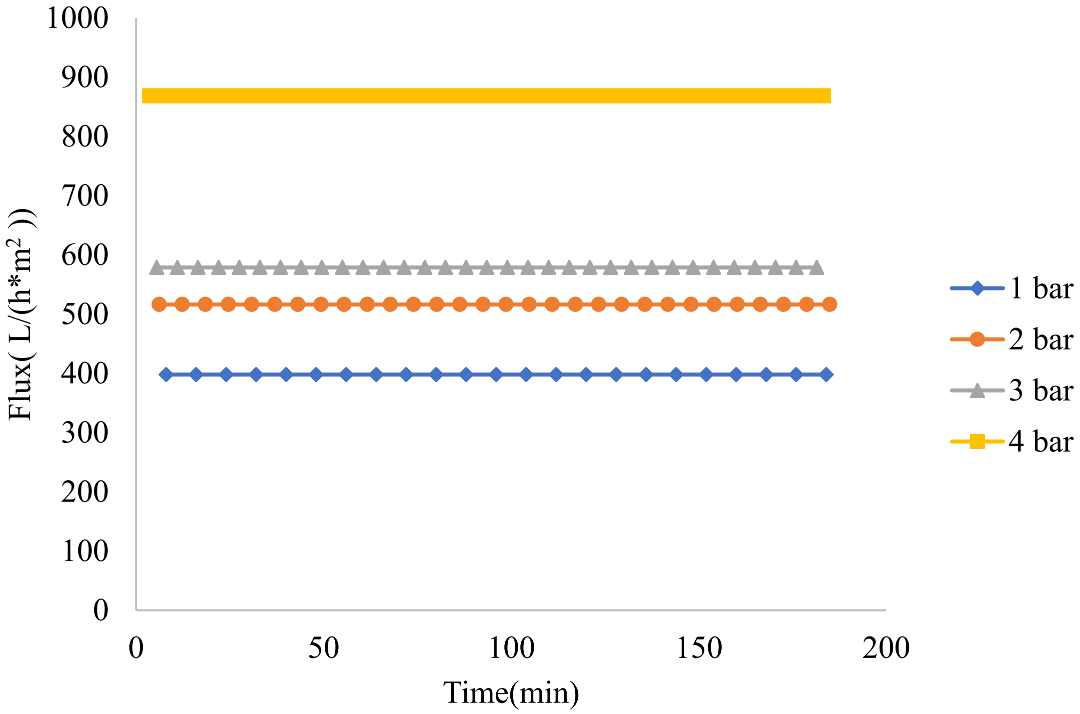

Figure 5. 50. Effect of TMP on pure water flux of the MF2 (F=25).

Comparison of pure water permeation fluxes of MF1 and MF2 membranes showed that water fluxes of MF2 membrane was lower than their counterparts of MF1 membrane. This indicates that MF2 membranes had pores smaller than the pores of MF1 so that the water permeability of MF2 was lower than MF1 membranes.

Filtration experiments were performed using MF2 membranes at 1, 2, 3 and 4 bar for CFV values of F=15, 20, 25 and 40. Figures 5.51 and 5.52 show the changes in permeate flux and oil retention percentage throughout the filtration at 1 and 2 bar, respectively for F=15. Permeate fluxes were measured as 47 L/h·m^2 at the beginning and reached 15 L/h·m^2 at the end of the filtration. Increase of TMP from 1 bar to 2 bar did not exhibited any increase in the permeate flux. Oil retention percentages were found to be 100 % at both TMP values.

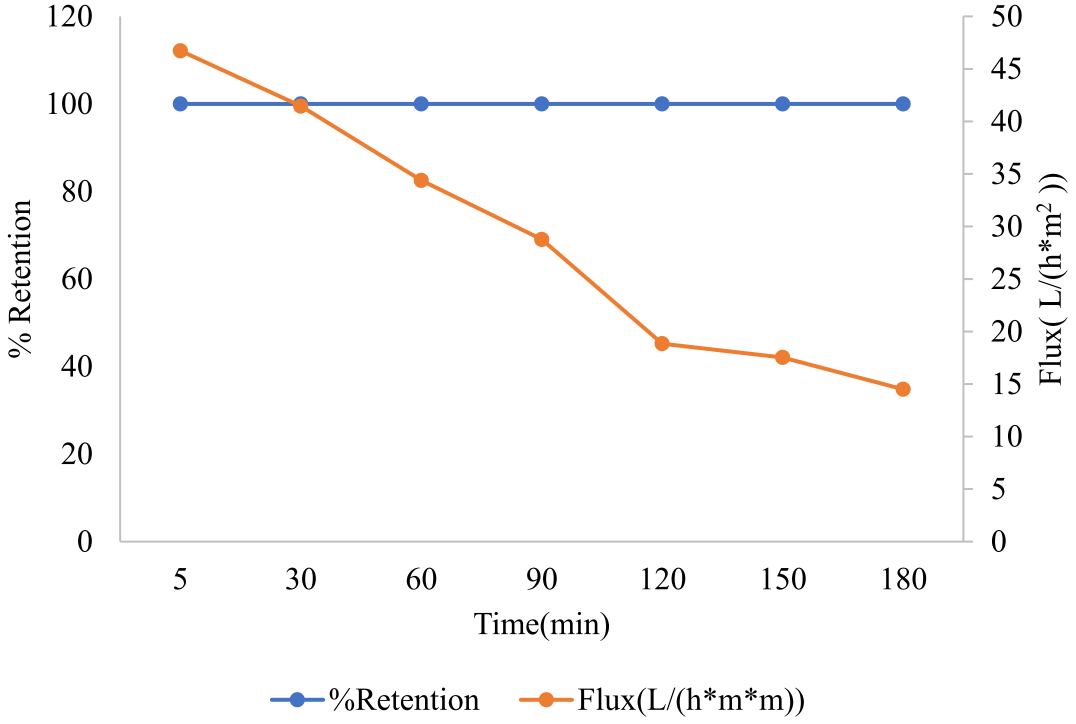

Figure 5. 51. Effect of 1 bar of TMP on 0.5 % oily water flux of the MF2 and % retention (F=15).

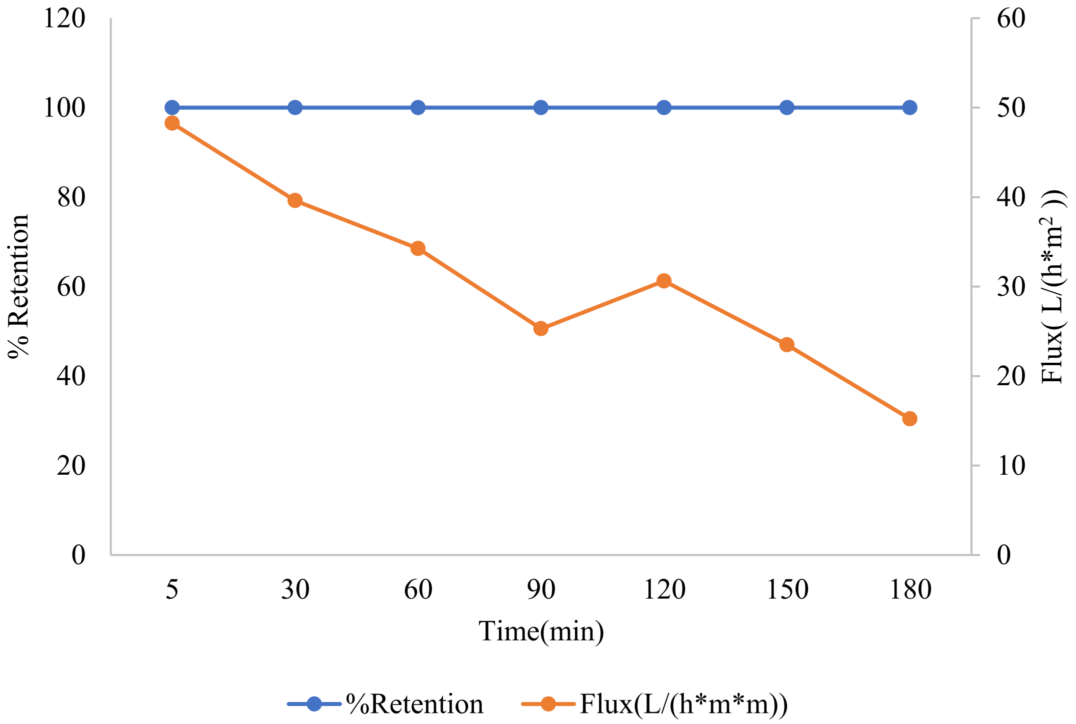

Figure 5. 52. Effect of 2 bar of TMP on 0.5 % oily water flux of the MF2 and % retention (F=15).

Increasing TMP to 3 bar (Figure 5.53) almost doubled initial permeate flux (89 L/h·m^2). Final permeate flux obtained was 22 L/h·m^2. Further increase in TMP to 4 bar also increased initial flux (119 L/h·m^2) and final flux measured (24 L/h·m^2) was similar to that obtained at 3 bar. Although the initial fluxes were different, final permeate fluxes reached similar values at the end of filtration experiments due to membrane fouling. Oil retention percentages were ~100 % also at 3 and 4 bar.

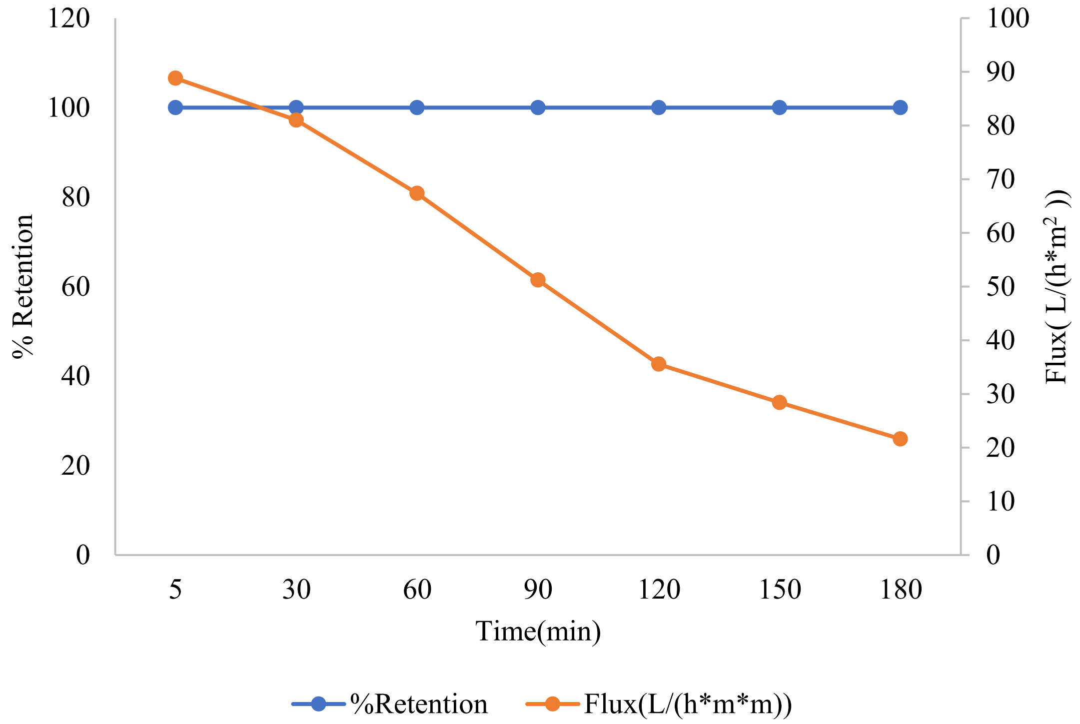

Figure 5. 53. Effect of 3 bar of TMP on 0.5 % oily water flux of the MF2 and % retention (F=15).

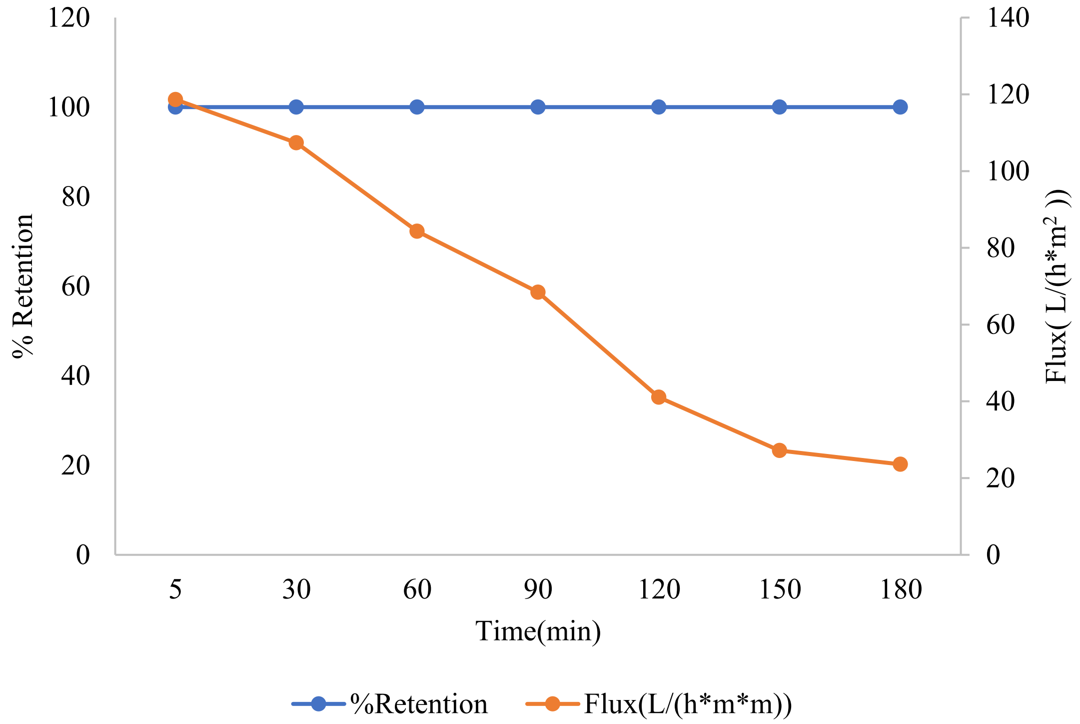

Figure 5. 54. Effect of 4 bar of TMP on 0.5 % oily water flux of the MF2 and % retention (F=15).

Adjusting cross-flow velocity of oily water to F=20 did not increase permeate fluxes obtained at each TMP. The results of the experiments at 1, 2, 3 and 4 bar for CFV of F=20 are presented in Figures 5.54, 5.55, 5.56 and 5.57, respectively. Initial permeate fluxes were measured to be 51, 45, 71 and 87 L/h·m^2 while final fluxes were 8, 4, 3 and 3 L/h·m^2 at 1, 2, 3 and 4 bar, respectively. Oil removal percentages were monitored as 100 % during the filtration experiments where TMP values were adjusted to 1, 2 and 3 bars. Oil retention was almost equal to 100 % at the 5th minutes of filtration and decreased to 99.4 % and stayed constant thereafter.

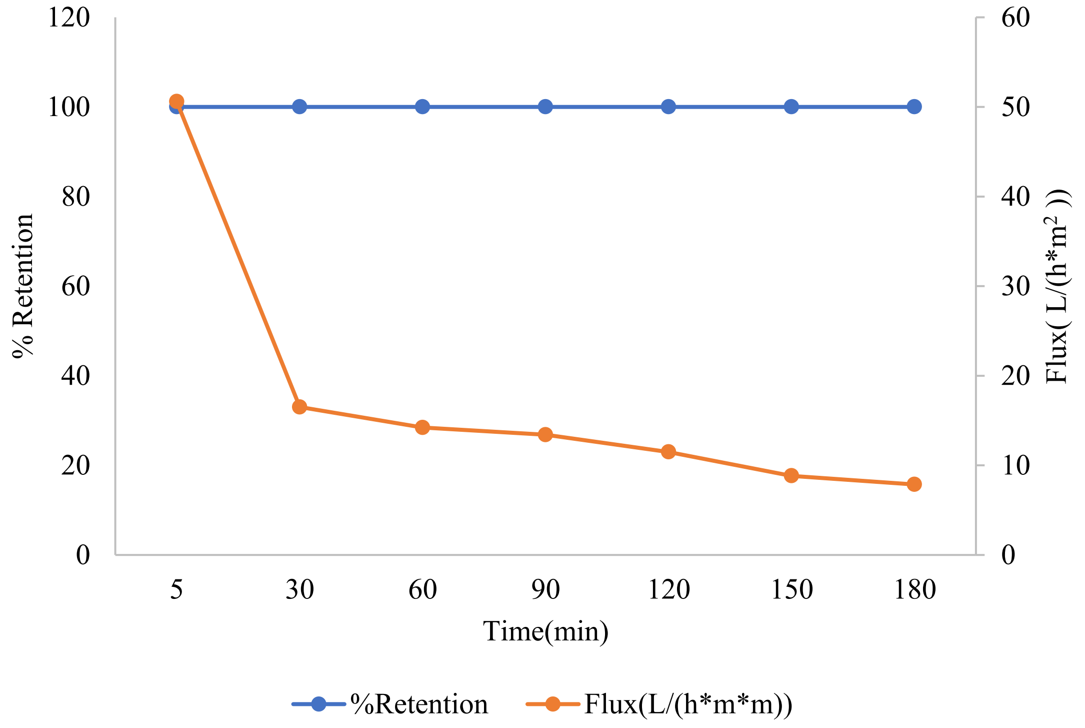

Figure 5. 55. Effect of 1 bar of TMP on 0.5 % oily water flux of the MF2 and % retention (F=20).

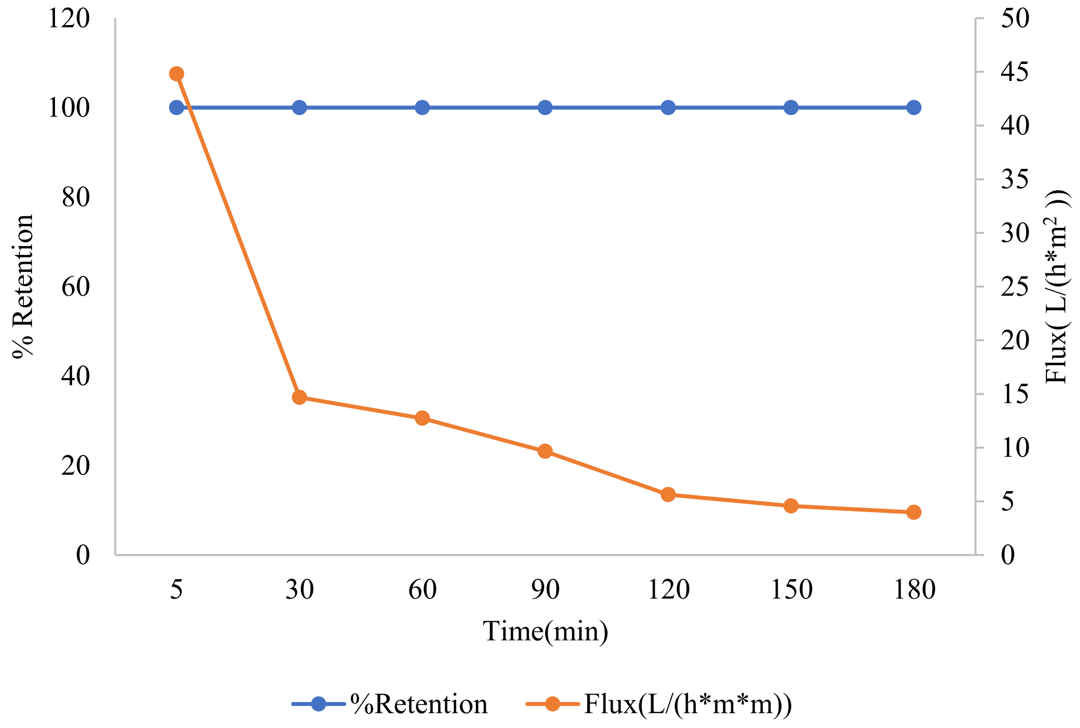

Figure 5. 56. Effect of 2 bar of TMP on 0.5 % oily water flux of the MF2 and % retention (F=20).

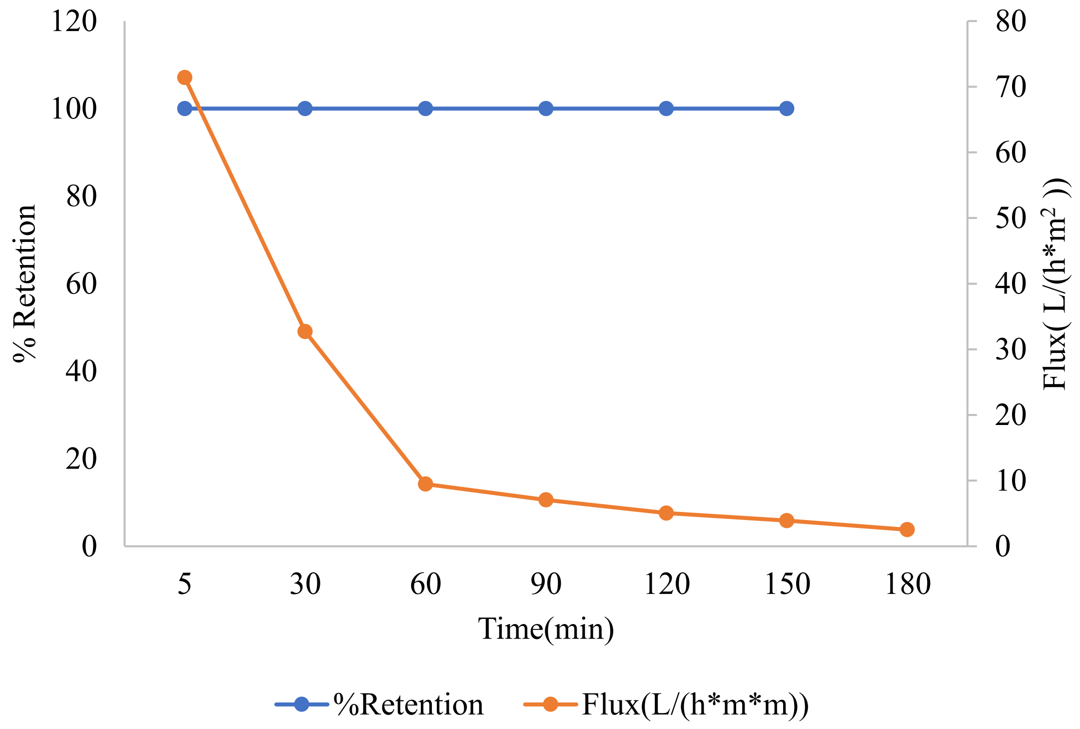

Figure 5. 57. Effect of 3 bar of TMP on 0.5 % oily water flux of the MF2 and % retention (F=20).

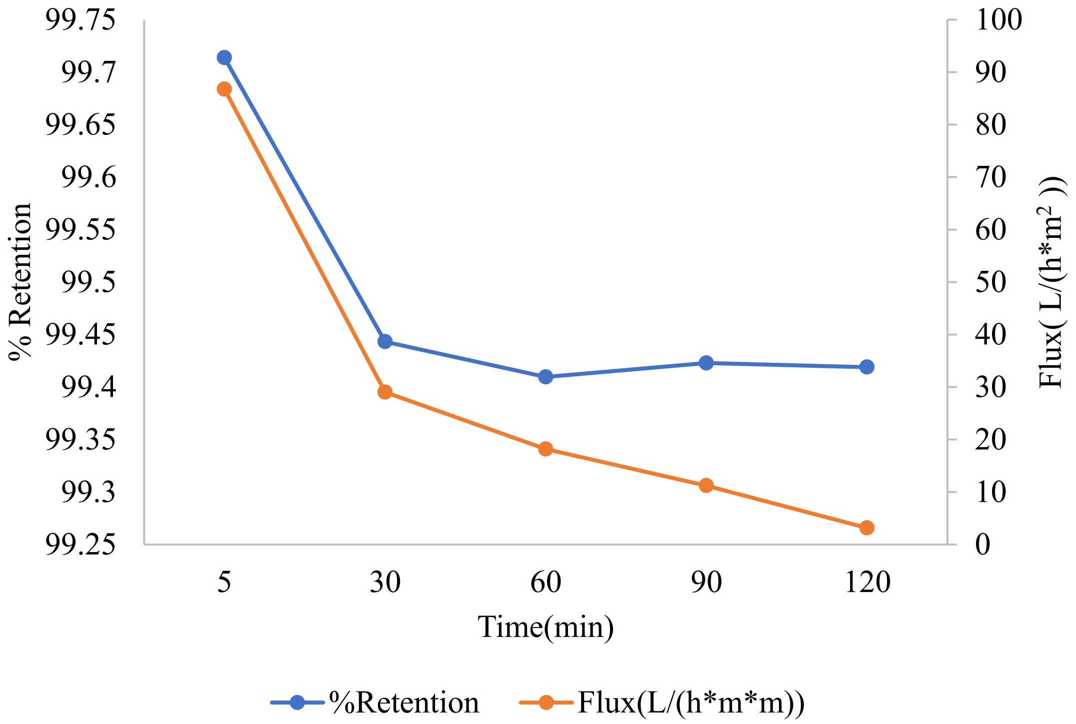

Figure 5. 58. Effect of 4 bar of TMP on 0.5 % oily water flux of the MF2 and % retention (F=20).

Initial permeate fluxes observed in the filtration experiments for CFV of F=25 were similar or lower than permeate fluxes at corresponding pressures for CFV=20. As shown in Figures 5.59, 5.60, 5.61 and 5.62, inital fluxes were measured as 53, 46, 50 and 75 L/h·m^2 at 1, 2, 3 and 4 bar, respectively. At the end of all filtration experiments, final fluxes decreased and found to be in the range of 3-11 L/h·m^2.

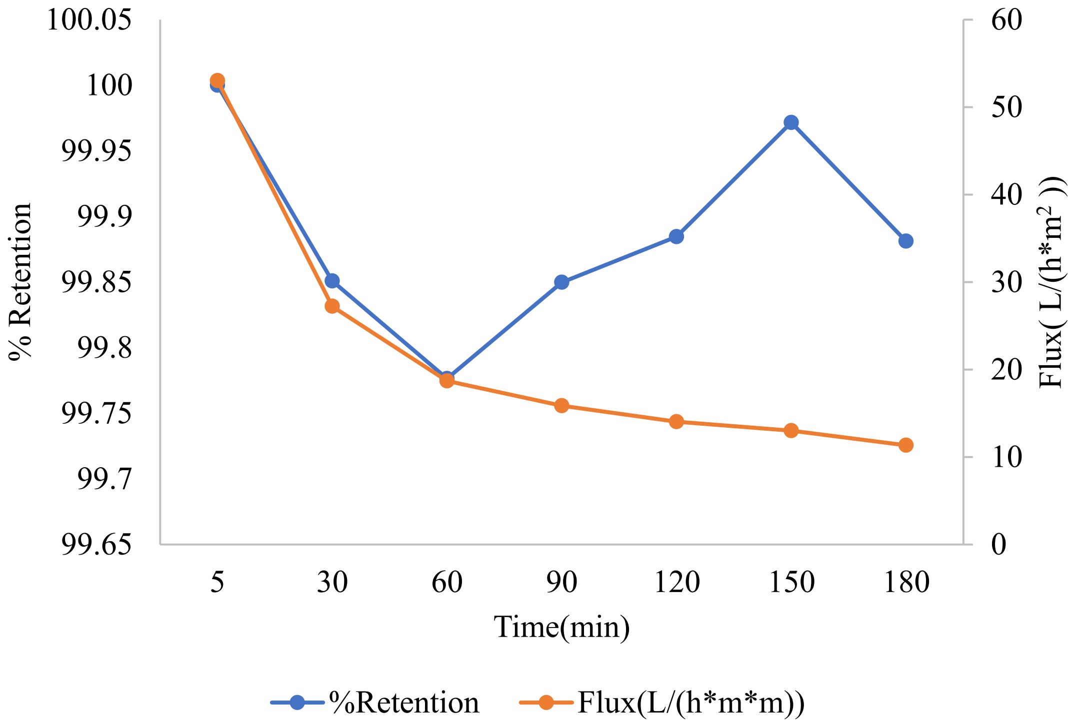

Figure 5. 59. Effect of 1 bar of TMP on 0.5 % oily water flux of the MF2 and % retention (F=25).

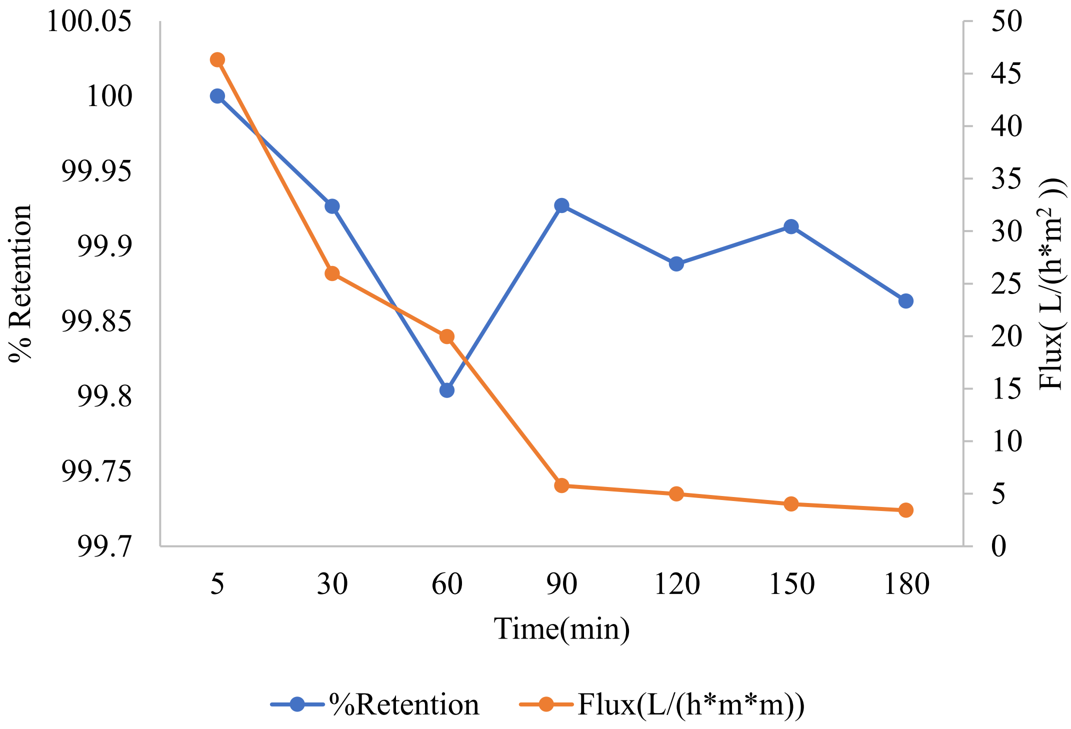

Figure 5. 60. Effect of 2 bar of TMP on 0.5 % oily water flux of the MF2 and % retention (F=25).

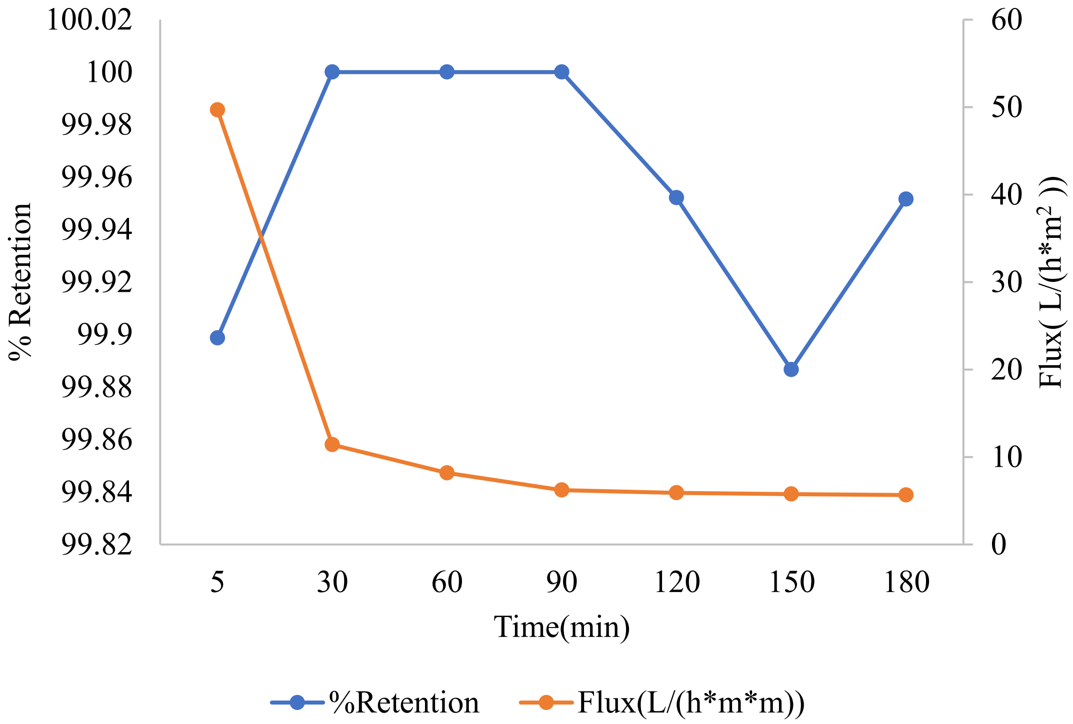

Figure 5. 61. Effect of 3 bar of TMP on 0.5 % oily water flux of the MF2 and % retention (F=25).

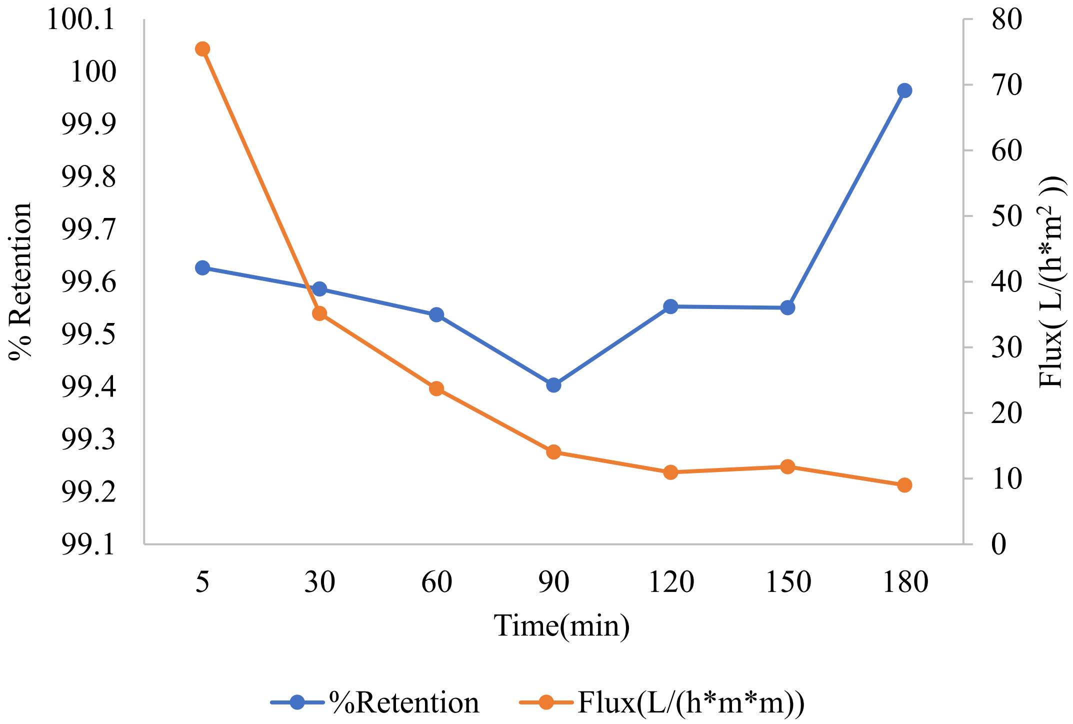

Figure 5. 62. Effect of 4 bar of TMP on 0.5 % oily water flux of the MF2 and % retention (F=25).

Microfiltration of 0.5 % oily water could be performed only at 2, 3 and 4 bar TMPs for CFV of F=40 since the pressure was greater than 1 bar without any adjustment by a needle valve. Initial permeate fluxes were similar at all trans-membrane pressure values applied. Permeate flux at 2 bar was initially found to be 88 L/h·m^2 and it decreased to 26 L/h·m^2 at the end. Initial fluxes observed at 3 and 4 bar were 79 and 99 L/h·m^2, respectively. Permeate flux was decreased to 13 L/h·m^2 at 3 bar and 23 L/h·m^2 after 120 minutes of filtration. In all experiments, oil retention was found to be 100 %.

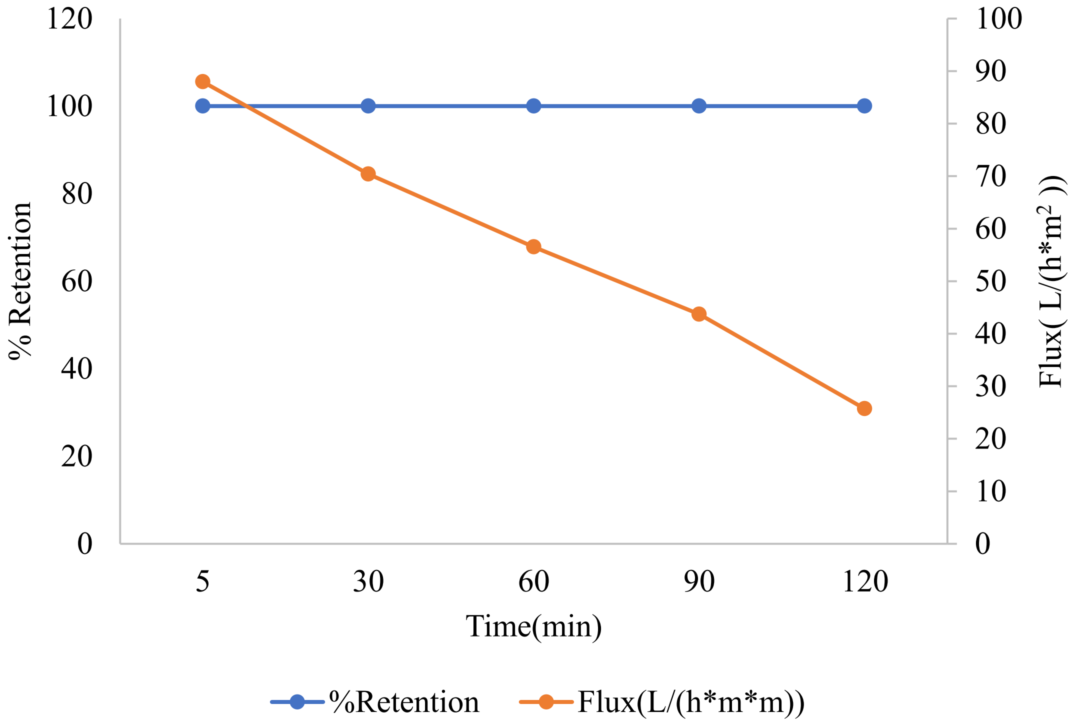

Figure 5. 63. Effect of 2,2 bar of TMP on 0.5 % oily water flux of the MF2 and % retention (F=40).

When the initial permeate fluxes measured at all TMP values for all CFVs, increase in CFV in general did not result in the increase of permeate flux suggesting the formation of cake layer strongly adsorbed onto the internal surface of the membrane or clogging of the membrane pores with oil droplets. Oil retentions greater than 99 % state that the formation of strongly adsorbed cake layer is more likely than clogging the pores with oil droplets since higher pressures would have pushed oil droplets and oil retention would be lower.

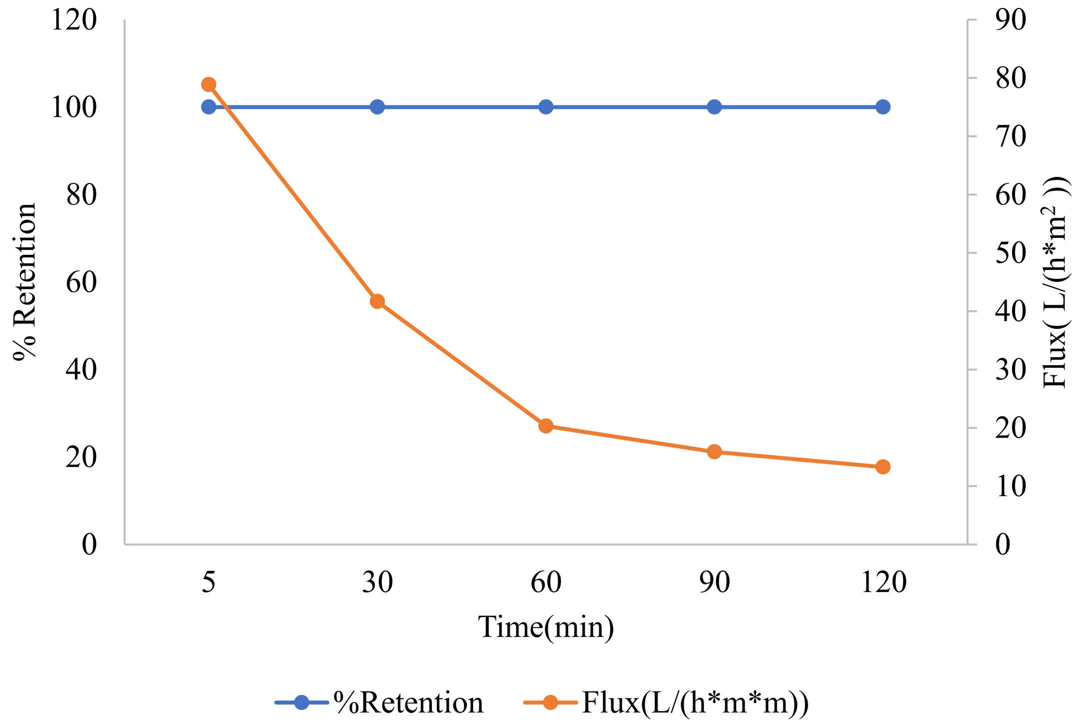

Figure 5. 64. Effect of 3 bar of TMP on 0.5 % oily water flux of the MF2 and % retention (F=40).

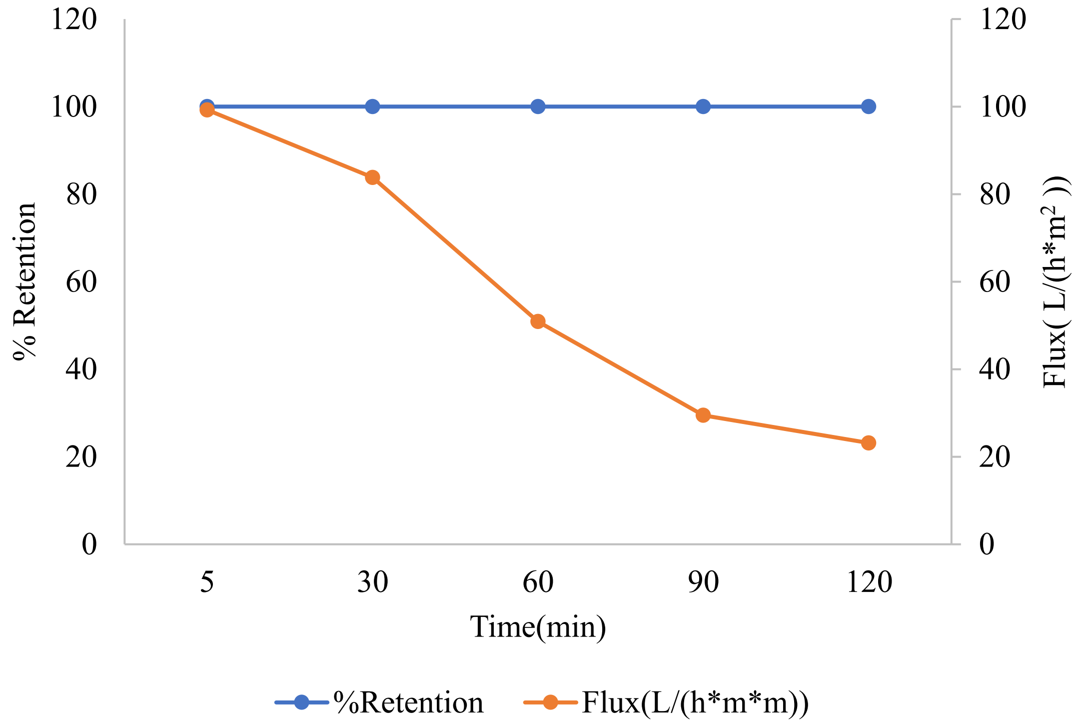

Figure 5. 65. Effect of 4 bar of TMP on 0.5 % oily water flux of the MF2 and % retention (F=40).

CONCLUSIONS

The uncontrolled discharge of oil-in-water emulsions are very harmful for aquatic life, soil, atmosphere, and human health. Traditional treatment methods are not effective in the removal of emulsified oil droplets which have less than 20 μm of droplet size. Metal cutting fluids are heavily used for metal polishing/cutting/shaping operations for cooling and lubrication purposes. They are used in industry with a wide range of production capacities. The small and medium sized industrial companies send these contaminated waste emulsions to centralized treatment centers. A treatment scheme involving ceramic membranes may present an efficient solution to this important problem.

The aim of this MSc study was to produce tubular ceramic supports and microfiltration membranes for the removal of oil from stable oil in water emulsions used as metal cutting fluids. The prepared metal cutting fluids were fed to the crossflow filtration system and the effects of experimental parameters such as transmembrane pressure (TMP), crossflow velocity (CFV) and oil content on membrane performance/permeate flux were investigated. The single/double layered coatings on the support surfaces were formed in the preparation of the microfiltration membranes by using stable 0.4 μm α-alumina suspensions. The 1 layer and 2 layers containing microfiltration membranes were heavily fouled and very low permeate fluxes were obtained in an hour of treatment. This was attributed to the formation of a thin oil layer on the microfiltration membrane surfaces. The reduction of the total suspended solids (TSS) and turbidity were determined as ~100 %. A stable permeate flux with a lower extent of membrane fouling and concentration polarization was obtained with 1% oil content and the support membrane and TMP=2 bars. Major implication of this work is the design of a treatment operations may be a solution to the metal cutting waste fluid handling/reuse. This process must include a settling tank for the removal of unstable section of the oil present in the fluid. The stable low oil content emulsion can be fed to a support and microfiltration ceramic membranes for complete oil recovery.

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APPENDIX

Figure A 1. Pictures of the dies used in multichannel and hollow tube extrusion.

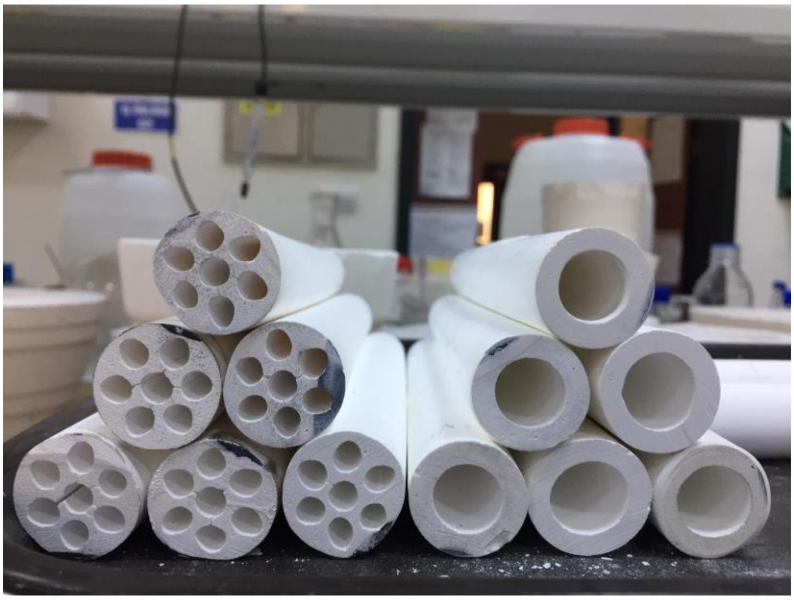

Figure A 2. Multichannel and hollow tubular ceramic supports.