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YAĞ-SU EMÜLSİYONLARININ ULTRAFİLTRASYON İLE AYIRILMASI

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ULTRAFILTRATION OF OIL - WATER EMULSIONS

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PREFACE

Ultrafiltration of oil-water emulsions is a very promising application. Although it is a new subject for Turkey, this application has already draw great attention in the world and seems to be one of the areas that will see the greatest growth in the immediate future.

I especially wish to acknowledge my supervisior Assoc. Prof. Dr. Birgül Tantekin-Ersolmaz who has introduced me to the field of membrane technology, for her scientific guidance.

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February 1998 Berna Yoğurtçugil

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NOMENCLATURE

ΔP	: Transmembrane pressure difference
ΔT	: Temperature gradient
ΔE	: Electrical potential gradient
J	: Flux
A	: Membrane area
m	: Total mass of the permeate
t	: Time
K	: Hydrodynamic permeability of the membrane
$\mathcal{R}$	: Retention (rejection)
$\mathcal{R}^*$	: True retention
C_p	: Permeate concentration
C_f	: Feed concentration
C_m	: Concentration at the membrane-solution interface
C	: Concentration at the boundary layer at a certain difference from the membrane
C_g	: Gel concentration
r	: Pore radius
Δx	: Length of the channel
x	: Distance from the membrane surface
D	: Diffusion coefficient
k_m	: Mass transfer coefficient
δ_m	: Boundary layer thickness
J_{lim}	: Limiting membrane flux
$\Delta\Pi$	: Osmotic pressure difference
M_w	: Molecular weight
T	: Temperature
R	: Gas constant
$B_2, B_3, \ldots$	: Virial coefficients
R	: Resistance
R_m	: Membrane resistance
R_c	: Cake layer resistance
μ	: Viscosity
V_1, V_2, V_3	: Valves
J_{pwf}	: Pure water flux
FD	: Flux decline
FR	: Flux recovery

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SUMMARY

ULTRAFILTRATION OF OIL-WATER EMULSIONS

Contamination of water sources by discharging industrial effluents containing waste oils is a problem arising from metal working and finishing industries. Such industries generate wastewaters as oil in water emulsions containing ionic and nonionic surfactants. Discharging of these wastewaters is strictly regulated all over the world. Classical oil-water emulsion breaking system is chemical treatment which involves first the acidification and coagulation and subsequent separation of oil by air floatation, centrifugation, filtration or suitable agglomeration techniques. These processes are expensive and at the same time inadequate to meet the new environmental regulations. Ultrafiltration utilizing suitable membranes can be used to concentrate the oil in the oily wastewaters which can either be reused in the industry or discharged into public waterways with no harmful effect on the environment.

The objective of this study is to investigate the potential use of several membranes in treating oil-water emulsions by ultrafiltration and to understand the behaviour of these membranes under various operating conditions. Commercially available membranes supplied from PCI Membrane System Ltd. are used to separate oil-water emulsions prepared with cutting oils utilizing an Armfield ultrafiltration/reverse osmosis unit. Effect of different operating pressures and feed flow rates are investigated in terms of permeate flux and retention (rejection) values. Fouling, one of the most important phenomena in ultrafiltration of oil-water emulsions treatment is also determined in terms of pure water fluxes. Different cleaning methods are applied to both new and fouled membranes and cleaning effenciency is investigated.

It is shown that oil-water emulsions can be separated succesfully via ultrafiltration generating permeates with oil content below discharge limits of 1988-Water Pollution Control Regulation when a suitable membrane is used. Highest retention values has been obtained for polyethersulphone membranes with a MW cut-off value of 4000. Polysulphone membranes with a MW cut-off value of 8000 showed the lowest retention producing permeates not suitable for direct discharge indicating high pore density and wide pore size distribution. Polyacrylonitrile and polyethersulphone membranes with a MW cut-off value of 25000 has exhibited suitable retention values at some feed flow rate and pressure difference values. Polyethersulphone (MW cut-off 25000) and polysulphone (MW cut-off 8000) membranes seems to be highly fouled and show considerable flux decline after emulsion experiments as determined by pure water flux measurements. Both acid and caustic cleaning has not been succesfull in cleaning the fouled membranes used in separation of oil-water emulsions.

ÖZET

YAĞ-SU EMULSİYONLARININ ULTRAFİLTRASYON İLE AYIRILMASI

Evsel ve endüstriyel atıkların çevreye yayılması ile oluşan kirlilik, hava, toprak ve su kalitesinin korunabilmesini önemli bir sorun haline getirmiştir. İnsanoğlu yaşamı, endüstriyel uygulamaları ve tarımsal faaliyetleri için temiz suya ihtiyaç duyar. Aynı zamanda, bu temiz su ihtiyacına rağmen, tarımsal, evsel ve endüstriyel atık suları ve çöplük alanlarındaki sızıntı sularını, su kaynaklarına deşarj ederek söz konusu yeraltı ve yerüstü kaynaklarını sürekli kirletmektedir.

Su kalitesinin korunması ve doğan problemlerin ortadan kalkması için hem kullanılan sular hem de deşarj edilen akımlar özellikleri ve amaçlarına uygun olarak arıtılmalıdır. Özellikle endüstriyel atık sular, dayanılmaz kokusu ve görüntüsü olan, yangın gibi bazı güvenlik tehlikeleri oluşturabilen ve su kaynaklarındaki oksijen miktarının azalmasına yol açan değişik konsantrasyonlarda yağlı maddeler içermektedir. Bu yağlı atık sular, petrol rafinerileri, metal ve metal işleme, gıda, tekstil, boya, yüzey kaplama ve yapıştırıcı, yağ, sabun, ve deterjan, mürekkep ve deri endüstrileri ile benzin istasyonlarında taşıtların yıkanması ve sanayi tipi çamaşırhaneler tarafından oluşturulmaktadır. Özellikle metal işleme sanayiinde uygulanan pek çok işlemde soğutma ve aynı zamanda koruma amaçlı yağ emülsiyonları büyük miktarlarda kullanılmakta ve bu oldukça kararlı emülsiyonları içeren akımlar deşarj edilerek çevre kirliliğine büyük katkılarda bulunmaktadırlar.

Çevre sorunlarının öneminin artması hem dünyada hem de Türkiye'de çevre kanunlarının oluşturulmasına sebep olmuştur. Türkiye'de "1988- Su Kirliliği Kontrolü Yönetmeliği"ne göre metal işleme sanayiinde maksimum deşarj edilebilir yağ ve gres miktarı 20 mg/l'dir. Özellikle orta ve küçük ölçekli işletmelerde kontrollerin artması ve böylece mevcut kanunların uygulanabilmelerinin sağlanması doğanın ve insan sağlığının daha fazla zarar görmesini engelleyecektir.

Yağlı atık sularda yağ, serbest halde veya mekanik dispersiyonlar, kimyasal emülsiyonlar, çözünmüş yağ ve yağ ile ıslanmış katılar şeklinde bulunabilir. Mevcut yağlı atık su ayırma yöntemlerinin içinden uygun olanın seçiminde en önemli faktör, yağın atık sularda bulunduğu hal, emülsiyonlaşma derecesi ve şekli ile konsantrasyonudur. Genel olarak yağlı atık su arıtım yöntemleri ağırlık esasına göre ayırma, kimyasal olarak emülsiyonu kırma ve membran prosesleri ile biyolojik arıtım ve adsorpsiyon olarak sıralanabilir. Ağırlık esasına göre ayırma, en basit ve sık

kullanılan yöntem olup, ayırma özgül ağırlık farklılıklarına dayanarak sağlanır ve API (American Petroleum Institue) separatörleri, koaleserler, hava ile yüzdürme ve santrifüj gibi işlemleri kapsar. Bu yöntemler serbest haldeki yağları ve yağ ile ıslanmış katıları ayırır. Kimyasal olarak emülsiyonu kırma, membran proseslerine göre daha eski bir yöntem olup, emülsiyonun genellikle asit ile kırılması ve koagülasyonu ve bunu takiben flokulasyonu gibi basamakları içerir. Bu yöntem ile bazı yağ-su emülsiyonlarını ve mekanik dispersiyonları ayırabiliriz. Bir membran ayırma prosesi olan ultrafiltrasyon ise çok dayanıklı yağ-su emülsiyonlarını ayırabilen fiziksel bir ayırma metodudur. Burada seçici geçirgen olan membranın gözeneklerinden sürücü güç olan basınç farkı yardımıyla su molekülleri geçerken, yağ ve katkı maddeleri gibi makromoleküller geri çevrilmektedirler. Membran proseslerinde, kimyasal olarak emülsiyon kırmada olduğu gibi ilave işlemlere ihtiyaç duyan akımlar ortaya çıkmaz. Atık suya uygun, doğru özelliklerde membranın seçilmesiyle bu yöntem çok avantajlı hale gelebilir. Günümüzde yağlı atık suların arıtılması için membran üreten pek çok firma vardır ve bu yöntem gün geçtikçe daha çok işletme tarafından tercih edilmektedir.

Gözenekli ve asimetrik yapıya sahip ultrafiltrasyon membranları, membranın alıkoyacağı varsayılan makroçözünenin molekül ağırlığı demek olan, "ayrılabilen molekül ağırlığı" ile sınıflandırılırlar. Ayrılabilen molekül ağırlığı kaba bir şekilde membranın gözenek büyüklükleri hakkında fikir verir.

Bir uygulama için membranın davranımını belirleyen ve incelenmesi gereken iki özellik geçen akımın akısı ve geri çevirme oranıdır. Geri çevirme oranı membranın ayırma kapasitesini ve geçen akımın saflığını belirtir ve aşağıdaki gibi ifade edilir:

$$\mathcal{R} = 1 - \frac{C_p}{C_f}$$

Burada $\mathcal{R}$ geri çevirme oranı, C_p geçen akım konsantrasyonu, C_f ise kalan akım konsantrasyonudur. Birim zamanda, birim alandan geçen madde miktarı olarak tanımlanan akı, sürücü güç olan basınç farkı ile orantılıdır. Saf su akısı bu duruma göre şöyle belirtilebilir:

$$J = K.\Delta P$$

Burada oran sabiti K, membranın direncinin (R_m) hesaplanabildiği hidrodinamik geçirgenlik, J, saf su akısı, ΔP ise basınç farkıdır. Akı, uygulanan basınç farkının artmasıyla orantılı olarak önce artacak, ancak bir noktadan sonra artması duracaktır. Yani basınç farkı ne kadar arttırılırsa artsın, akı değeri değişmeyecektir. Bu değere akının sınır değeri denir ve konsantrasyon polarizasyonu ile kirlenme/tıkanma

nedeniyle gerçekleşir. Konsantrasyon polarizasyonu, çözünen maddelerin membran yüzeyinde daha yoğun olarak bulunması; kirlenme ise, bu çözünen maddelerin membranda birikmesidir. Kirlenme gözeneklerin tıkanması, çözünenlerin gözeneklerde adsorplanması veya bir jel katmanının membran yüzeyinde oluşmasıyla olur. Akının sınırlandığı bu bölge için değişik yaklaşımlarla akı modelleri oluşturulmuştur. Bu modellerden başlıcaları film modeli, jel modeli, direnç modeli ve osmotik basınç modelidir.

Bu tezin amacı, kararlı yağ-su emülsiyonlarının ultrafiltrasyonla ayrılmasının araştırılmasıdır. Metal işleme sırasında oluşan yağlı atık suları temsilen bir çözünebilir yağ olan Klora bor yağı yaklaşık %3.9 konsantrasyonunda olacak şekilde seyreltilerek model yağ-su emülsiyonları hazırlanmıştır. PCI Membrane Systems Ltd'dan temin edilen dört farklı ticari ultrafiltrasyon membranı yağ-su emülsiyonlarını ayırmak için Armfield FT18 ultrafiltrasyon-ters ozmoz ünitesinde incelenmiştir. Bu dört membran ES625, AN620, ES404 ve PU608 kodlu ve sırasıyla polietersülfon, poliakrilonitril, polietersülfon ve polisülfondan yapılmış tüp şeklinde membranlardır. Üretici firma olan PCI Membrane Systems Ltd'den edinilen bilgilere göre kullanılan bu dört membranın ayrılabilen molekül ağırlıkları ES625 için 25000, ES404 için 4000, AN620 için 25000 ve PU608 için 8000dir.

Ultrafiltrasyon ünitesinde, geçen akımın besleme tankına gönderilmesiyle sağlanan sabit besleme konsantrasyonunda çapraz akış durumunda ayırma deneyleri yapılmıştır. Membranların ayırma özellikleri olan geçen akım akısına ve geri çevirme oranına, basınç farkı ve besleme akış hızının etkileri incelenmiş ve membranların kirlenme davranımları araştırılmıştır. Geri çevirme yüzdesinin hesaplanması için bilinmesi gereken yağ konsantrasyonlarının belirlenmesinde ise türbidimetri ve gravimetrik yöntem kullanılmıştır. Bunun için öncelikle membranların bünyelerindeki koruma çözeltilerinin değişik temizleme yöntemleriyle uzaklaştırılması sağlanmış ve membranların karakterize edilmeleri için saf su akıları belirlenmiştir. Değişik operasyon koşullarında (basınç farkı ve besleme akış hızı) membranların davranımları (geçen akım akısı ve geri çevirme yüzdesi olarak) incelendikten sonra kirlenme etkilerinin belirlenmesi için tekrar saf su akıları ölçülmüş ve daha sonra membranlar farklı yöntemlerle temizlenmiştir. Temizlemenin etkisine akı geri kazanımı değeri incelenerek bakılmıştır.

$$\text{Akı Geri Kazanımı} = \frac{J_{pwf,temizlenmiş}}{J_{pwf,kirli}}$$

Asidik veya kostik temizleme yöntemlerinin bu koruma çözeltilerinin uzaklaştırılmasındaki başarısının incelenmesi için saf su akıları ölçülerek karşılaştırılmıştır. Asidik yıkamada nitrik asit çözeltisi, kostik yıkamada ise Henkel P3 Ultrasil 10'a sodyum hidroksit ilave edilmesi ile hazırlanan çözeltiler kullanılmıştır. AN620 membranı için kostik yıkama sodyum lauryl sülfat (SLS) ilave edilmiştir.

Asidik yıkamanın PU608 membranın yapısının bozulmasına yol açtığı görülmüştür. Hem bu membran hem de ES404 için öntemizleme işlemleri istenilen sonuçları vermemiş, koruma çözeltilerinin asidik veya kostik yıkama yardımıyla uzaklaştırılması yeterince verimli olmamıştır. Bunun yanında benzer ön yıkama AN620 ve ES625 membranlarında akıda artışlara sebep olmuştur. Diğer iki membran için daha uygun yıkama yöntemleri geliştirilmelidir.

Yeni membranların saf su akıları ve ayrılabilen molekül ağırlığı değerleri karşılaştırılarak karakterizasyonları yapılmıştır. ES625 ve AN620 en büyük gözenekli iki membran olmalarına rağmen oldukça farklı saf su akısı değerlerine sahiptirler. AN620 membranının daha düşük saf su akısı göstermesi, gözenek yoğunluğunun az olmasıyla açıklanabilir. PU608 ayrılabilen molekül ağırlığı değerine oranla daha fazla akıya sahiptir. Bu davranış benzer şekilde gözenek yoğunluğunun yüksek olmasıyla açıklanabilir. ES404 daha yoğun yapısıyla en düşük akı değerlerini vermektedir.

Yukarıda da belirtildiği gibi değişik operasyon koşullarında yani değişik basınç farkı (4-10 bar) ve besleme akış hızı (9-30 l/dak) değerlerinde, emülsiyon ayrımının etkinliğini incelemek için geçen akım hızı ve geri çevirme oranları bulunmuş ve incelenmiştir. Bunun için her deney parametresinde yatışkın hale ulaşıldıktan sonra minimum 10 ölçüm yapılmış ve verilerin tekrarlanabilirliği sağlanmıştır. Bundan sonra her koşul için ortalama bir değer hesaplanmış ve değerlendirmeler buna göre yapılmıştır.

ES404 her koşulda yüksek geri çevirme oranları göstermiştir. Geçen akımdaki yağ konsantrasyonu deşarj limitlerinin altındadır. Diğer membranlarla karşılaştırıldığında gözenek özelliğinden dolayı daha düşük akı değerlerine sahiptir. Daha yüksek basınçlarda çalışılarak bu membranın verimliliği arttırılabilir. ES625 bazı basınç ve besleme akış hızı değerlerinde deşarj edilebilir kalitede geçen akımlar vermektedir. Bu membran 6 bar ve 30 l/dak'da hem uygun geri çevirme oranına hem de oldukça yüksek akıya sahiptir. AN620, poliakrilonitril membran ise ES625 'e benzer özellikleri 6 bar ve 15 l/dak'da veya 10 bar ve 30 l/dak'da göstermektedir. PU608 membranıysa ayrılabilen molekül ağırlığı değerine göre yüksek gözenek yoğunluğundan kaynaklanabilecek yüksek akı değerlerine sahip olsa da, çok düşük geri çevirme oranları göstermektedir. PU608 membranın gösterdiği düşük geri çevirme oranının, dolayısıyla yüksek yağ geçirgenliğinin nedeni membranın gözenek boyutu dağılımının yüksek olması olabilir. Daha kesin bulgular için cryo-SEM gibi metodlar yardımıyla yüzey özelliklerinin incelenmesi yalnızca bu membran için değil aynı zamanda diğerleri içinde yararlı olabilir.

Membranlar karşılaştırıldığında özellikle ES625'in geçen akım akısının, besleme akış hızının düşmesiyle diğer memranlara oranla çok daha fazla düşüş gösterdiği görülmektedir. Bu durum membranın konsantrasyon polarizasyonundan etkilendiğini göstermektedir. Hidrofilik bir yapıya sahip olan AN620 ise düşük besleme akış hızlarında en yüksek geçen akım akısına sahip membran olarak gözükmektedir.

Emülsiyon deneylerinden sonra ise kirlenme ve temizlemenin düşüş gösteren akı değerlerine etkisi incelenmiştir. Bütün membranların akılarında emülsiyon ayrımından sonra düşme görülmüştür. Başta ES625 olmak üzere AN620 hariç bütün membranlar kirlenmeden çok etkilenmiş ve fazla akı azalması göstermişlerdir. AN620'nin hidrofilik yapısı, akıda bu düşmenin görülmemesine sebep olmaktadır. Kirlenme daha az olduğu için hem asidik hem de kostik temizleme bu membranda çok iyi sonuçlar göstermektedir. ES625'in temizleme ile düşen akı değerini önemli ölçüde kazanabildiği görülmüştür. Yine de hem ES625 hem de diğer iki membran olan ES404 ve PU608 için daha verimli temizleme yöntemleri araştırılmalıdır. Kirlenmenin nasıl bir mekanizma ile gerçekleştiği önem taşımaktadır ve bu yolda yapılacak araştırmalar akı geri kazanım limitlerinin daha iyi anlaşılmasına yardım edecektir.

CHAPTER 1

INTRODUCTION

In recent decades, over population and increasing level of industrialization resulted in environmental pollution in terms of soil, water and air sources [1]. Water quality preservation became a major problem arising from contamination by discharging domestic wastewater and industrial effluents into the environment. The need of protecting the quality of water sources in the world forced us to standardize the discharging methods of wastewaters into the environment. Therefore, varying regulations according to regions were adapted and applied to different industrial sectors [2].

In Turkey, an environmental law was prepared in 1983 and followed by some changes in 1988. Considering these changes, a new "Water Pollution Control Regulation" was published in order to protect all water sources in Turkey and ensure their effective use. Although the existence of plants in Turkey which has water treatment facilities to process wastewaters before discharge is a promising fact, the number of such plants is still below the desired level. One of the most important environmental problems in Turkey is the direct discharge of domestic and industrial effluents to water sources. The "Water Pollution Control Regulation" forbids direct discharge of wastewaters and mandates application of feasible technologies as treatment methods [3].

Among several methods that can be used in wastewater treatment, membrane processes have promising potential due to their low energy consumption, improved separation properties, continuous operation under mild conditions and compactness. Pressure driven processes like microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, and pervaporation and electrodialysis are the membrane processes

that offer many opportunities in treating the food processing, dairy, agricultural, textile, pulp and paper, power plant, electroplating, petrochemical, metal working and finishing wastes. Membrane technology can be implemented in the field of environment not only as cleaning technology but also as clean technology since the regulatory focus is now shifting from end-of-pipe treatment to pollution prevention and resource recovery [2].

Oily wastewaters are almost the common waste in aforementioned industries. Especially in metal working industry, large amounts of wastewaters containing stable oil-water emulsions are generated during several mechanical operations such as grinding, rolling, cutting, drawing, etc. The use of enormous quantities of cutting oils and drawing oils in metal working industry has resulted in a difficult oily wastewater disposal problem. These oils are usually mineral oils combined with a variety of ionic and nonionic surfactants. The cutting oil is usually diluted for use as coolant during metal working. The drawing oil sticking to the surface of the metal parts is removed by subsequent rinsing with water.

Classical methods to treat stable oil-water emulsions involve first destabilization of the emulsion by acidification and coagulation and subsequent separation of oil by air floatation, centrifugation, filtration or suitable agglomeration techniques. These processes are not only expensive but also are generally inadequate to meet the new environmental requirements of practically negligible oil content in the final effluents. Ultrafiltration utilizing suitable membranes can be used to concentrate oil in the oily wastewaters which can either be reused in the industry or discharged into public waterways with no harmful effect on the environment. The concentrated oil resulting from ultrafiltration can either be upgraded, reutilized, or incinerated with no additional fuel [4].

The objective of this study is to investigate the potential use of several membranes in treating oil-water emulsions by ultrafiltration and to understand the behavior of membranes under various operation conditions. The organization of the thesis is as follows: Membrane processes and ultrafiltration are summarized briefly in Chapter 2.

The sources of oily wastewaters, related environmental regulations and methods used in treating oily wastewaters are presented in Chapter 3. Chapter 4 covers the experimental setup and the method applied in this study, whereas Chapter 5 covers the results and discussion. Finally, conclusions and recommendations are presented in Chapter 6.

CHAPTER 2

MEMBRANE PROCESSES AND ULTRAFILTRATION

2.1. MEMBRANE PROCESSES

Membrane processes are becoming competitive separation technologies in many ways although they had appeared during the last three decades. Main advantages of membrane processes over conventional separation technologies are less energy consumption, no requirement of additives, easy up-scaling, continuous separation as well as being suitable for hybrid processes that can be carried out under mild conditions. There are still some drawbacks that have to be mentioned like flux decline, limited life time of the membrane and sometimes low selectivity [1,5].

In all membrane processes membrane is the main part of the system which can be defined as a thin barrier, between two bulk phases, that permits transport of some components while retaining others under a driving force. A schematic drawing that represents a typical membrane separation process is shown in Figure 2.1 [5].

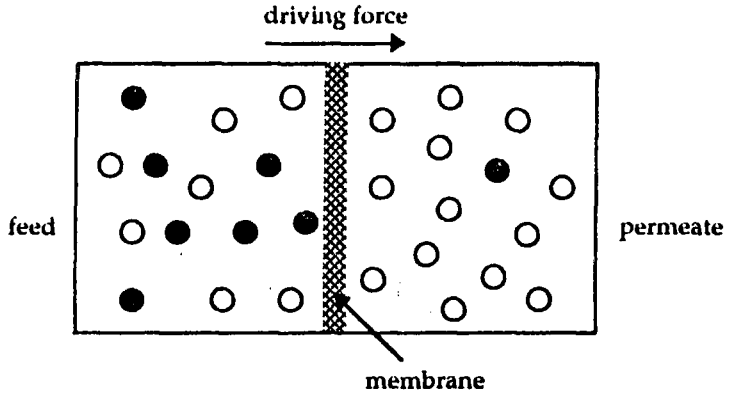


Figure 2.1. Schematic drawing illustrating a membrane separation process [6].

Classification of membrane processes can be made according to the driving force or on the basis of separation mechanism. A general overview and the classification of membrane processes are summarized in Table 2.1. If size is the separation mechanism, membranes act as filters which separate components in a feed solution because of a difference in solute size. Membranes can also act as barriers in which feed materials selectively are dissolved and transported through the membrane which has been mentioned as affinity in Table 2.1 [6, 7].

Table 2.1 Overview of membrane processes [6].

Membrane process	driving force	feed state	permeate state	separation mechanism
microfiltration (MF)	ΔP	liquid	liquid	size
ultrafiltration (UF)	ΔP	liquid	liquid	size
nanofiltration (NF)	ΔP	liquid	liquid	size / affinity
reverse osmosis (RO)	ΔP	liquid	liquid	size / affinity
piezodialysis (PD)	ΔP	liquid	liquid	affinity
gas separation (GS)	ΔP	gas	gas	affinity / size
pervaporation (PV)	ΔP	liquid	gas	affinity
dialysis (D)	ΔC	liquid	liquid	size
osmosis (O)	ΔC	liquid	liquid	affinity
liquid membranes	ΔC	liquid	liquid	chemical nature
electrodialysis	ΔE	liquid	liquid	charge
thermo-osmosis	ΔT, Δp	liquid	liquid	vapor pressure
membrane distillation (MD)	ΔT, Δp	liquid	liquid	vapor pressure

The driving force that is necessary for the transport through the membrane may be a transmembrane pressure gradient (ΔP), a concentration or activity gradient (ΔC or Δa), an electrical potential gradient (ΔE), or a temperature gradient ΔT. The first four processes mentioned in Table 2.1, microfiltration, ultrafiltration, nanofiltration and reverse osmosis utilize a hydrostatic pressure difference as the driving force [5].

Microfiltration, ultrafiltration and reverse osmosis differ principally in the size of the particles separated by the membrane. Ultrafiltration begins (MF ends) at the point where the size of the solute particle is 10-fold greater than the size of the solvent molecules. In reverse osmosis solutions of low MW and high concentration are treated where osmotic pressure is appreciable, whereas ultrafiltration treats solutions that have high MW and low concentration so that osmotic pressure is negligible [8]. Pressure-driven membrane processes are summarized in Table 2.2.

Unlike pressure-driven processes, in electrodialysis charged membranes are used to separate ions from aqueous solutions under the driving force of an electrical potential difference. Anion and cation exchange membranes allow anions and cations, respectively. The chief function of the ED process is the removal of inorganic ions, which leave bacteria, viruses and neutral organics in the dilute stream. The principal application of electrodialysis is the desalting of brackish groundwater [2,9].

Table 2.2. Comparison of pressure-driven liquid phase membrane processes [5]

Process	Pore size (nm)	Materials retained	Materials passed	Pressure (bar)
MF	> 50	particles (bacteria, yeasts etc)	water, salts macromolecules	< 2
UF	1-100	macromolecules, colloids, lattices solutes MW > 10000	water, salts, sugars	1-10
NF	= 1	solutes MW >500,di- and multivalent ions	water, sugars, monovalent ions	5-20
RO	not relevant	all dissolved and suspended solutes (salts, sugars)	water	15-80

Basic principle of gas separation is passing of a mixed feed gas at an elevated pressure across the surface of a membrane that is selectively permeable to one component of the feed. Gas separation systems with polymeric membranes is a developing process which already has current applications like separation of hydrogen from nitrogen,

argon and methane in ammonia plants, the production of nitrogen from air and the separation of carbondioxide from methane in natural gas operations [9].

Pervaporation is a membrane process in which a liquid mixture contacts one side of a membrane and the permeate is removed as a vapor from the other side by the difference in partial pressure between the liquid feed solution and the permeate vapor. The low vapor pressure existing on the permeate side can be achieved by employing a carrier gas on using a vacuum pump. It is used to separate mixtures of dissolved solvents. Dehydration of organic solvents, removal of organic components from water and separating of some non-aqueous mixtures are the main application of pervaporation [6].

The other membrane processes mentioned in Table 2.1 are mostly in the development stage and they will not be discussed here since they are beyond the scope of this thesis. Interested readers should refer to the excellent reviews in the literature on membrane processes [6,9,10,11,12,13,14].

Module configuration has a direct effect on the efficiency of membrane systems. An ideal module should ensure a sufficient flow rate so as to limit as much as possible the formation of concentration polarization layers and to avoid dead spots. It should be as compact as possible with easy membrane replacement, easy cleaning, good chemical compatibility, pressure resistance, low cost and high packing density. There are four different configurations with different advantages and disadvantages.

Plate and frame module design has its origins in the conventional filter-press. Membrane feed spacers and product spacers are layered together between two end plates. Prefiltration is often needed for this type of module and membrane replacement is difficult. These units are also expensive and leaks caused by the many gasket seals are a serious problem.

In tubular modules the membrane is inserted into a tubular support or cast directly onto its internal surface. The pressure support is a perforated stainless steel or fiber-

glass tube. This type of modules are now used in applications where the benefit of resistance to membrane fouling because of good fluid hydrodynamics overcomes the problem of their high capital cost.

Although there is a number of spiral-wound module design, the first and simplest one consists of a membrane envelope wound around a perforated central collection tube. The wound is placed inside a tubular pressure vessel and feed is circulated axially down the module across the membrane envelope, permeating into it and exiting via the collection tube. In spiral-wound modules generally prefiltration is necessary, leak detection is difficult and covers high area per module. They are much more commonly used in low pressure or vacuum gas separation applications.

The hollow fiber module consists of fibers which feed under high pressure, flows over the outside surface of them. The permeated stream then flows out through the base of the fibers and is collected as product. The advantages of this configuration is a large membrane area per unit volume and the possibility of operating with pressure for flushing the module. In hollow fiber modules prefiltration is necessary and the strength of the fibers limits operating pressures [10,11].

2.2 ULTRAFILTRATION

2.2.1 General

Ultrafiltration is a pressure driven membrane process that can be grouped with microfiltration, reverse osmosis and nanofiltration. In all of these processes, the liquid being treated is circulated under pressure in contact with a membrane through which some molecules pass and some others retain [11]. Ultrafiltration separates macromolecules (like proteins) where reverse osmosis separates low MW solutes (salt) and macrofiltration separates particles (bacteria, yeasts). The separation mechanism is in fact a sieving mechanism in which molecules are distinguished according to their size and shape in both micro and ultrafiltration. In reverse osmosis,

the chemical affinities of the solute molecules also play an important role in separation. Furthermore, the osmotic pressure effects are important, where it is negligible in ultrafiltration and microfiltration which results in lower operating pressures for ultrafiltration [6,12].

Most ultrafiltration processes operate in cross flow mode that is tangential filtration. The dead end flow mechanism exists only in laboratory devices and in a few industrial applications [12]. Ultrafiltration will be discussed in detail in the following sections.

2.2.2 Historical Development

Ultrafiltration first appeared at the end of the last century and was for a long time used as a concentration and purification technique in laboratory preparations. These membranes were away from maintaining chemical and mechanical resistance and high permeability which is required for industrial applications. In the early 1960's Loeb and Sourirajan's development of the first asymmetric reverse osmosis membranes with reasonably high water flux and excellent salt rejection was the major technological breakthrough. Ultrafiltration using asymmetric membranes is a result of research in developing reverse osmosis membranes for specific applications. Although the cellulose acetate membranes had a fairly low resistance to chemical attack, their sufficiently high hydraulic permeability made industrial application of ultrafiltration worthwhile. After it was found that other more inert polymers could be used in determining the asymmetric structure instead of cellulose acetate, commercially available ultrafiltration membranes became available. One recent development has been the appearance of inorganic membranes capable of withstanding high temperatures and pressures [7, 8].

2.2.3 Ultrafiltration Membranes

Ultrafiltration membranes have asymmetric structure where a porous top layer exist on a porous support. The top layer thickness in ultrafiltration membrane is generally less than 1 μ [5].

Membranes used in ultrafiltration are generally polymeric although some inorganic (ceramic) membranes are also being used. Polysulphone, polyethersulphone, polyvinylidene fluoride, polyacrylonitrile, cellulosics, polyimide and aliphatic polyamides are some of the polymers that are used to prepare ultrafiltration membranes. These polymeric ultrafiltration membranes are often prepared by immersion - precipitation process. For this purpose, a polymer solution is cast as a thin film and immersed in a coagulation bath that contains a non-solvent for the polymer. Solvent starts to diffuse out of the homogeneous liquid polymer film, whereas non-solvent diffuses into the film. Due to the presence of the non-solvent, phase separation takes place in the polymer film and the polymer precipitates as a solid phase to form a porous asymmetric membrane structure [5,6].

Although the properties of the membranes must be specific for each application, general requirements from every membrane is high retention, high flux and a long life. This is strongly related with the membrane properties that generally depends on preparation method [11].

Ultrafiltration membranes are typically rated by molecular weight cut-off (MW cut-off), a convenient but fictitious value giving the molecular weight of a hypothetical macrosolute that the membrane will just retain and is given in Daltons. A convention to define MW cut-off was set by Amicon in the 1960s as the molecular weight of the globular protein which is 90% retained by the membrane. Although this is an upper molecular weight limit for solute passage as the "90% point"is quite arbitary and there are some complications about proteins, the marker (like adsorption or different molecular shapes), the membrane could have transport capacity above the cut-off [9,11,13].

2.2.4 Flux and Retention (Rejection)

An important property of an ultrafiltration membrane is its flux, which is defined as the permeate mass (or volume) flow through the membrane per unit time and per unit membrane area and can be shown as

$$J = \frac{1}{A}\frac{dm}{dt} \qquad (2.1)$$

where m is the total mass of the permeate during a time t, and A is the membrane area [7].

Fluid flow through microporous membranes in ideal situation (where membrane has uniformly distributed equally sized pores, there is no fouling and concentration polarization) can be described with Hagen-Poiseuille law for stream-line flow through channels. One form of the model useful in ultrafiltration assuming laminar flow, constant density, steady state conditions, newtonian fluid and negligible end effects is

$$J = \frac{\varepsilon r^2 P}{8\mu\Delta x} \qquad (2.2)$$

where J is the flow through the membrane, r is the mean pore radius, P is the applied transmembrane pressure, μ is the viscosity of the fluid permeating the membrane, Δx is the length of the channel and ε is the surface porosity of the membrane. It is difficult to get independent measurements of ε, r and Δx for use in this form of equation but these characteristics are incorporated in the membrane permeability. According to the model, flux is directly proportional to the applied pressure and inversely proportional to the viscosity. The flux of pure water at room temperature per unit pressure drop is

$$J = K.\Delta P. \qquad (2.2)$$

where K, the proportionality constant is the hydrodynamic permeability of the membrane [14,15].

Another important characteristic of a membrane is selectivity. This can be expressed as the retention or rejection which is defined as

$$\mathcal{R} = 1 - \frac{C_p}{C_f} \qquad (2.3)$$

where the ratio of the permeate to retentate or feed concentration, C_p/C_f is the sieving coefficient. When solutes are completely retained by the membrane the membrane has a retention of $\mathcal{R}$=1.

2.2.5 Concentration Polarization and Fouling

Ultrafiltration is a pressure driven process and the flow of solvent through the membrane increases linearly with pressure. However, during actual ultrafiltration, only at low pressure range and for moderated pressures a non-linear relation is observed. The linear region is called the filtration region as shown in Figure 2.2. At high pressure range the permeate flux remains constant with transmembrane pressure increase which is called the limiting flux region. This decline of flux in time leads to a loss of performance of the process. The reason for this flux decline is related to the concentration polarization and fouling phenomena [16].

During a separation process, while solute is retained by the membrane, solvent will permeate through the membrane under a driving force. The retained solute therefore, tends to accumulate at the surface of the membrane due to a convective transport causing a reduction in the driving force, due to an increase in the osmotic pressure of the feed solution or the formation of a gel layer in front of the membrane. The increased concentration at the membrane surface will be counterbalanced by a back

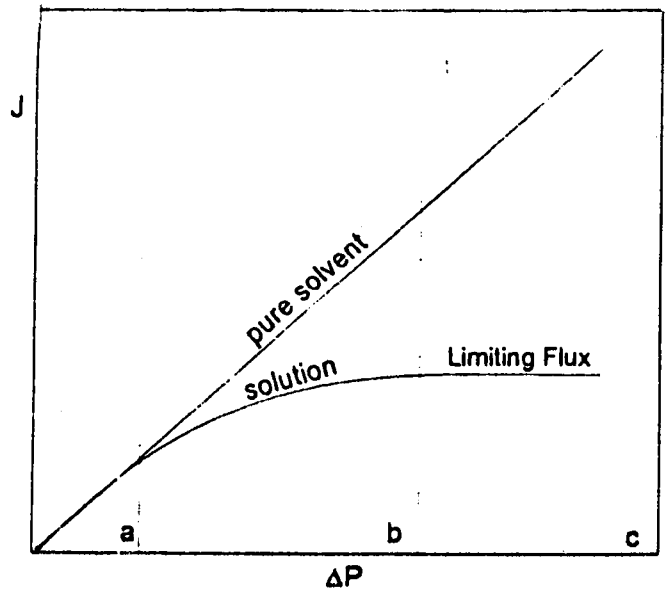


Figure 2.2. Ultrafiltration sketch: permeate flux (J) versus transmembrane pressure difference (ΔP). Three distinct regions: (a)filtration,(b)non-linear,(c)limiting flux [16].

diffusion in to the bulk and consequently a concentration gradient is formed in the boundary layer. This phenomenon which is shown schematically in Figure 2.2 is called concentration polarization and constitutes a supplementary barrier opposing resistance to the passage of the solvent [7].

It should be noted here that the retention defined by the Equation (2.3) is the observed retention. In order to take into account the effect of concentration polarization, a true rejection coefficient ($\mathcal{R}^*$) is defined as

$$\mathcal{R}^* = 1 - \frac{C_p}{C_m} \qquad (2.4)$$

where C_m is the concentration at the membrane-solution interface.

Concentration polarization is reversible and will disappear when the driving force is removed. Concentration polarization results in rapid flux decline and eventually in adsorption, precipitation or gelation of the solutes on the membrane surface

(blocking) can occur. This long- term flux decline is known as fouling and contrary to concentration polarization can be irreversible.

Fouling is defined as the deposition of retained particles or solutes on the membrane. This includes adsorption, pore narrowing, pore blocking and cake formation which represent different fouling mechanisms as seen in Figure 2.3. Different types of fouling may occur depending on the ratio between the solute diameter and the pore diameter of the membrane. In ultrafiltration generally the pores are very small in comparison to the solute diameter so the formation of a cake layer is favorable. If pores are of about the same size as the solutes, complete or partial pore blocking can occur. In the first few seconds of ultrafiltration, this mechanism plays an important part. The biggest pores get plugged, resulting a steep flux decline. Internal fouling of the membrane structure leads to pore narrowing [7, 8].

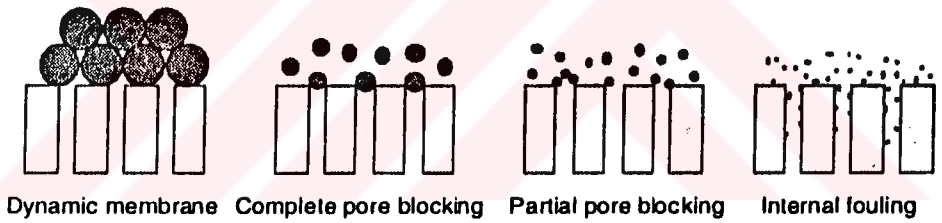


Figure 2.3. Different fouling mechanisms [7]

It is known that largest molecular weight compounds in the multicomponent feed mixtures can block the largest membrane pores resulting in a steep flux decline in the first few seconds of filtration. Apart from this, these largest molecular weight compounds can act as seeds are catalysts for the formation of a cake layer on top of the actual membrane resulting in lower fluxes. Removing large molecular weight compounds from feed by prefiltration will improve the permeate flux.

Membrane fouling depends on a lot of factors which can be divided into feed solution, membrane and process related factors.

Membrane related factors are either material related like hydrophobicity and charge or structure related like roughness, pore size, pore size distribution and porosity. The first fouling on a membrane is usually due to the interacts between the feed solute and the membrane material. It is known that hydrophobic materials show a stronger interaction with most solutes than hydrophilic materials. Therefore hydrophilic membranes have a lower fouling tendency and higher permeate fluxes compared to hydrophobic membranes. Hydrophilic membranes usually have limited thermal and chemical stability so modified (with chemical reaction, UV-irradiation, adsorption coating etc.) hydrophobic membranes are generally used. The presence of charge affects flux and retention behavior of membranes because of electrostatic repulsion and attraction.

If the membrane roughness increases, the flux decline and the degree of fouling is also observed. Extreme surface roughness hinders the formation of a complete cake layer because solutes have to fill and bridge irregularities on the surface. In general the membrane fouling is more severe with increasing pore size because of degree of internal fouling increases. At the same time initial permeate fluxes increase and initial retention decrease with increasing pore size. Due to the low porosities of ultrafiltration membranes, solvent will have to follow streamlines to the opening of isolated pores and this will cause high local polarization and fouling effects at the pore entrances.

The extent of membrane fouling is also affected by process related factors such as temperature, transmembrane pressure and cross-flow velocity. Increasing the temperature generally leads to an increase in the flux due to a lowering of the viscosity and an increase in the diffusivity while decreases retention because of an increase in concentration. In general increasing the transmembrane pressure results in an increase in the permeate flux. However, if the solubility limits of the solutes during filtration is reached, a gel or cake layer is formed. If pressure is increased when a gel or cake layer is established a temporary flux increase causes the gel or cake to thicken which results again in a decrease of the flux to its original value. This is the limiting flux phenomena as described earlier. Increasing the cross-flow velocity, the last

process related factor, results in a flux improvement owing to a reduction in concentration polarization and fouling.

It can be concluded here that to prevent or diminish flux decline suitable membranes and suitable conditions should be chosen for a specific application considering the factors described above [7].

2.2.6 Flux Models

During ultrafiltration and microfiltration due to concentration polarization and fouling, flux decline is observed as described in Section 2.2.5. In the literature, there are several models describing this observed flux decline and there are several reviews in the literature concerning these flux models [7, 14, 16, 17, 18] and a short summary of some of these models will be presented in this section. There are many other models developed in the literature to describe the anomalies between the calculated fluxes and experimental fluxes but will not be reviewed here.

2.2.6.1 Film model

Concentration polarization with low molecular weight solutes without precipitation at the membrane surface can be mathematically described by the so-called film model as schematically shown in Figure 2.4. It is assumed that a laminar boundary layer is established adjacent to the membrane surface in which longitudinal mass transport is negligible. Therefore mass transport within the boundary layer (film) can be regarded one dimensional. A steady state situation is reached as a result of the balance between convective transport of solutes towards the membrane surface and diffusive back transport of retained solutes into the feed solution.

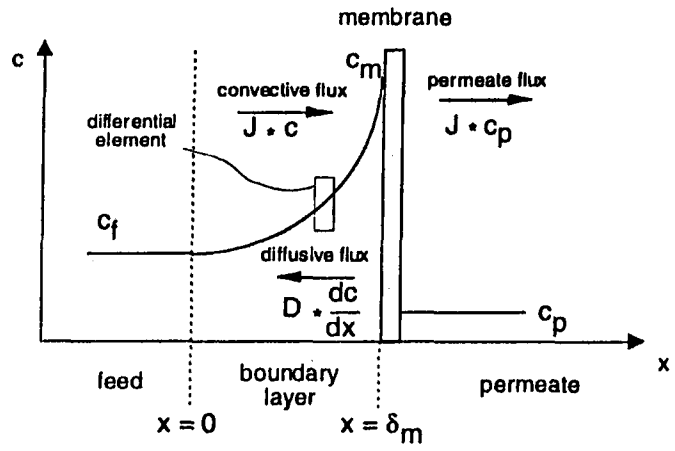


Figure 2.4. Schematic drawing of the concentration profile in the feed solution and in the permeate, illustrating the concentration polarization phenomenon and the convective and diffusive transport terms [7].

A material balance for the solute in a differential element of the film is given by Equation (2.5)

$$J \cdot C = D\frac{dc}{dx} + J.C_p \qquad (2.5)$$

where C is the concentration in the boundary layer at a certain distance from the membrane surface (n/m^3), C_p is the concentration of the permeate (n/m^3), x is the distance from the membrane surface (m), D is the diffusion coefficient (m^2/s), J is the convective flux (m/s). Both the diffusion coefficient and the convective flux are assumed constant. This equation is integrated over the boundary layer in which concentration build up is assumed to take place with the boundary conditions, $C = C_f$ (feed concentration) at $x = 0$ and $C = C_m$ (concentration at the membrane surface) at $x = \delta_m$. After integration,

$$J = k_m \ln\left(\frac{C_m - C_p}{C_f - C_p}\right) \qquad (2.6)$$

is found as the film model relation in which

$$k_m = \frac{D}{\delta_m} \qquad (2.7)$$

Here C_m is the concentration at the membrane surface, $C_{f\ is}$ the uniform bulk concentration, k_m is the mass transfer coefficient, δ_m is the thickness of the boundary layer.

The film model can be used to study the effect of some characteristic filtration parameters on the permeate flux during reverse osmosis where fouling is not a serious problem. If the cross-flow velocity increases, the model predicts higher fluxes, because of an increase in the mass transfer coefficient. A temperature rise increases the diffusion coefficient and as a result flux increases. These can be observed in practice.

There are some drawbacks of this model. For example, the concentration at the membrane surfaces is not limited contrary to the fact that all solutes have an upper solubility limit. Other simplifications are the assumption of a steady state situation, no mass transport parallel to the membrane surface due to concentration or density gradients and a fully developed velocity profile in the turbulent flow regime [7].

2 2.6.2 Gel Model

In ultrafiltration, simple film model is not applicable because of a low diffusive back transport of macromolecules into the feed solution and a high transmembrane flux compared to reverse osmosis. If the diffusive back transport can not counterbalance the convective transport towards the membrane surface, the solute concentration at the membrane surface exceeds its solubility or gel concentration and this will result in formation of a gel layer on the membrane surface as shown in Figure 2.5.

As the gel layer is formed, increasing the transmembrane pressure will first result in an temporary increase in flux but as the solute deposition and thickening also increase, the flux will decrease to its original value. This is again the limiting flux phenomena and means that the transmembrane flux will be independent of the transmembrane pressure as the gel layer is formed. The gel model can be expressed by

$$J_{lim} = k_m . \ln\left(\frac{C_g}{C_f}\right) \qquad (2.8)$$

where J_{lim} is the limiting membrane flux, k_m is the mass transfer coefficient, C_g is the gel concentration, C_f is the concentration in the feed solution.

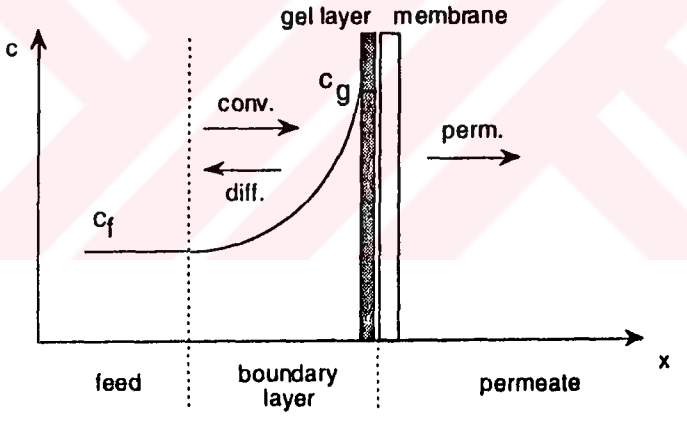


Figure 2.5. Schematic drawing illustrating the concentration polarization with solutes which form a gel layer [7].

This model, known as gel model has been used by many researches in dead-end and cross-flow filtration. A drawback of this model is that it can not be applied to solutes which do not precipitate or gelate [7].

2.2.6.3 Osmotic pressure model

The flux behavior of solutes which do not show gel formation can be described by an osmotic pressure model. The osmosis pressure difference across the membrane has been neglected in the previous models because macromolecular weight solutes have a very low osmotic pressure contrary to low molecular weight solutes. The effect of osmotic pressure can no longer be neglected due to accumulation of solutes near the membrane. The basis for the osmotic pressure model is the flux equation:

$$J = K.(\Delta P - \Delta \Pi) \qquad (2.9)$$

Here ΔP is the transmembrane pressure, $\Delta \Pi$ is the osmotic pressure difference over the membrane and equal to $(\Pi_m - \Pi_p)$ and K is the hydrodynamic permeability.

The magnitude of the osmotic pressure depends on the type of the solute and on the concentration at the membrane surface. The relation between these parameters is expressed in the Van't Hoff equation for dilute solutions:

$$\Pi = \frac{RT}{M_w}\left(C + B_2C^2 + B_3C^3 + \ldots\right) \qquad (2.10)$$

in which C is the concentration of solutes, M_w is the molecular weight of solutes, T is the temperature, R is the gas constant and B_2 and B_3 are the second and third virial coefficients specific for the kind of the solute respectively.

The osmotic pressure model also predicts the occurrence of a limiting flux. As the transmembrane pressure increases, the accumulation on the membrane surface also increases which leads to an increase in the osmotic pressure difference counteracting the transmembrane pressure. These two counteracting phenomena leads to a limiting flux. A drawback of this phenomena is, in most cases, osmotic pressure is negligible in ultrafiltration and microfiltration [7].

2.2.6.4 Resistance Model

The flow through porous media such as UF membranes can be characterized by Darcy's law [16]:

$$J = \frac{\Delta P}{\mu R} \tag{2.11}$$

where J is the membrane flux (m/s), ΔP is the transmembrane pressure (Pa), μ is the solution viscosity (kg/m.s), R is the resistance (1/m).

The resistance, *R* is the sum of several resistances which are assumed to be additive and independent of each other. Reversible and irreversible resistances can be distinguished. A well-known model based on the resistances in series approach is the cake layer model :

$$J = \frac{\Delta P}{\mu\left(R_m + R_c\right)} \tag{2.12}$$

Here R_m is the membrane resistance and R_c is the cake layer resistance.

This theory assumes that the diameter of the solutes is larger than the pore diameter of the membrane so that no internal fouling can occur and a cake layer can be formed on top of the membrane. Membrane resistance can be obtained from experiments with pure solvent. This resistance can be assumed constant if no modifications in the membrane characteristics are observed during the ultrafiltration process. There are many approaches to calculate the cake layer resistance which are discussed in detail in the literature [7, 16].

2.2.7 Applications of Ultrafiltration

Some advantages like recovery of high-value products, recycling of the permeate, pollution control and energy savings when the permeate that can be recycled is hot make ultrafiltration a very attractive process. The main applications of ultrafiltration are summarized in Table 2.3.

In addition to the applications presented in Table 2.3, one possible application is phase separation on the end of solvent extraction process which in spite of extensive studies in the last years, is not fully solved [19].

Table 2.3 Applications of ultrafiltration [11]

Industry	Existing	Emerging
Metal finishing	Electropaint Oil/water emulsions	Spray paint
Metal working	Oil/water emulsions	Spent lubricating oils
Dairy	Whey proteins, Milk	Protein hydrolysis
Pharmaceutical	Enzymes, Vaccines Plasma proteins, Antibiotics Pyrogens	Membrane reactors
Food	Potato starch, Egg white Gelatin, Juice clarification	Blood (abattoirs) Vegetable oils
Textile	Sizing chemicals Indigo, Wool scouring	
Pulp/paper	Lignin compounds	
Chemicals	Waste latex In-process latex	In-process and waste polymers
Leather working		Tannery wastes
Sewage	Sewage treatment for buildings	Municipalities
Water	Water purification -for various industries -for RO pretreatment	

In other potential applications, ultrafiltration can be combined with other processes and this will convert ultrafiltration from being a simple concentration process to a process capable of fractionation [11].

CHAPTER 3

OILY WASTEWATERS

3.1 SOURCES AND PROPERTIES OF OILY WASTEWATERS

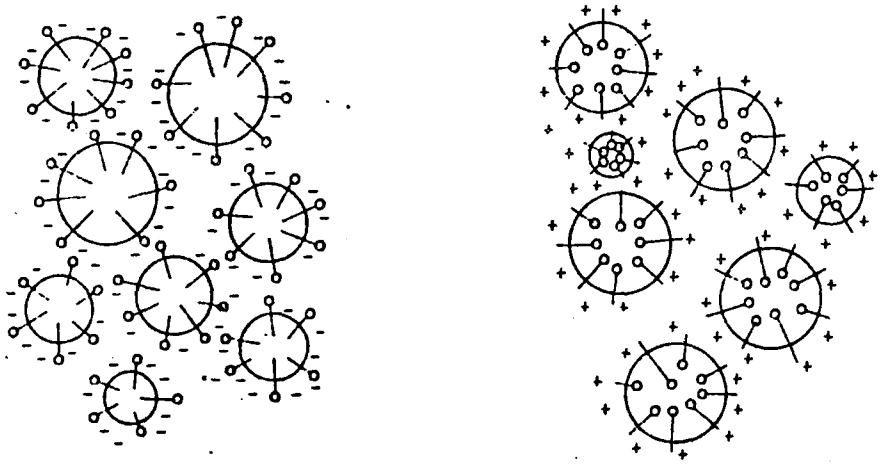
Many industries produce large volumes of oily wastewaters that need to be treated before discharge to municipal sewage systems. Oil discharged into the environment have deleterious effects. Oily waste discharges may have toxic effect on marine life and cause undesirable taste in fish, as well as causing undesirable appearance. Oils also have more serious effects like creation of potential fire hazard and consumes dissolved oxygen necessary to forms of life in water and limits oxygen transfer due to the blanketing of the surface by the thin oily film [20].

Oils is the general name given to various liquid products such as vegetable oils, mineral oils and light hydrocarbons which may be present in wastewaters as free oil mechanical or chemical emulsions, dissolved oil or oil-wet solids. Free oil rises quickly to the water surface when given a short settling period. Mechanical dispersions are distributions of fine oil droplets ranging in size from microns to fractions of a milimeter and having stability due to electrical charges and other forces but not due to the presence surface active materials. Chemically stabilized emulsions are distributions of oil droplets similar to mechanical dispersions but they have additional stability due to chemical interactions typically caused by surface active agents present at oil-water interface. Dissolved oil is that which is truly dissolved in a chemical sense plus that oil is dispersed in such fine droplets that removal by normal physical means is impossible. The oil that adheres to the surface of particulate materialsis referred to as oil-wet solids [20,21].

Petroleum refining, metals manufacturing and machining, and meat and food processing are the three major industries which produce oily waste. Other industries that have potential oily wastewater problem are, textiles, paints, surface coatings and adhesives, oils, fats and waxes, soaps and detergents, dyes and inks, transportation operations and the leather industry.

Much of the oil released from industries and residences is emulsified by detergents and soaps used for removing oil [22]. Furthermore, especially the metal working industry, uses and discharges enormous quantities of lubricating and cutting oils which are used for a variety of reasons such as improving tool life, reducing work piece thermal deformation, improving surface finish and flushing away chips from the cutting zone. These cutting oils are emulsions of oil droplets in water, prepared by diluting a so-called soluble oil to the desired extent with water. When formulating a cutting oil, one or more emulsifiers must be chosen that will disperse components such as mineral oil, chlorinated paraffin, sulfurized lard oil and numerous secondary ingredients. This choice of the emulsifier is determined by the chemical nature, ionic nature, hydrophilic-lipophilic balance (HLB) and quantity used [22,23,24].

An emulsion is a colloidal dispersion and is defined as an opaque, heterogeneous system which consists of two immiscible liquid phases, usually an 'oily' phase and a 'water' phase, in which one of the phases is dispersed as droplets in the other phase. Two types of emulsions are commonly found, oily wastewater (oil emulsified in water or O/W emulsions) and waste oil emulsions (water emulsified in oil or W/O emulsions) as shown in Figure 3.1. Water-in-oil emulsions are viscous, concentrated substances formed when oil comes into contact with water and solids. Metal particles and other solids may be coated with surfactants in such a manner that they are prefentially wetted by the oil rather than the water. In circumstances where agitation is present, the water becomes dispersed in the oil as a fine emulsion and these small water droplets together with the oil-coated solids maintain the stability of the emulsion. Oil-in-water or oily waste emulsion in which oil is dispersed in the water phase, contain any of various types of oil in a wide range of concentrations and will be the main concern in this thesis.



(a) Oil in water emulsion

(b) Water in oil emulsion

Note: Emulsifier molecule shown in simplified form: o—
Water soluble end ↗ ↖Oil soluble end

Figure 3.1. Chemical stabilization of emulsions by surfactants having hydrophilic and lipophilic groups [22].

Oil-water emulsion stability is maintained by physical and chemical mechanisms. One stabilizing mechanism is ionization by addition of surface-active agents such as organic materials and cleaners which usually carry an electrical charge and seek out the oil/water interface of the emulsified interface of the emulsified droplet. Here the accumulated charges cause the emulsion to be stabilized through repulsion of the commonly charged droplets. Non-ionic surfactants can also stabilize an emulsion, since these molecules are bifunctional, one end soluble in water and the other in hydrocarbon, so the molecule bridges the interface and stabilizes it. Most emulsifiers are surfactants having either anionic or nonionic polar groups and disperse oil droplets in the water phase because they have an affinity for both water and oil because of their both hydrophilic and lyophilic groups. Fine, solid particles may also stabilize an emulsion if they are of correct size and abundance. Friction between the oil and water phases created by mechanical or physical agitation can also lead to stabilization [22].

3.2 WASTEWATER DISCHARGE REGULATIONS

After the industrial revolution, environmental pollution became an important problem for the world which led to the development of environmental laws and discharge standards.

The Federal Clean Water Act of 1977 (CWA) mandates the regulation of the discharge of pollutants from nonpoint sources, point sources or contaminated storm waters to any waters of the U.S.A. The CWA directs the U.S. EPA to regulate industrial discharges and municipal treatment plants. EPA has the authority to enforce the National Pollution Discharge Elimination System (NPDES), which requires that all industrial and municipal wastewater and contact storm water comply with permit limitations. The EPA has authorized most states to manage the NPDES program for discharges in their jurisdiction. But in U.S. the regulatory requirements do vary from state to state and from one local jurisdiction to another. In Tennessee, for example, the discharge is regulated under an NPDES permit and here NPDES water quality based limitations for oil and grease permits an average discharge value of 26 mg/l and daily maximum value is 52 mg /l . Also, again in U.S. according to the local limits developed by the Washington State King County Department of Metropolitan Services, the non-polar (petroleum based like motor oil, diesel oil, axle grease) FOG (fat, oil and grease) concentrations must not exceed 100 mg/l [25,26].

In the literature, a discharge value for oil, according to the 1980 Marine Discharge Standards and to the discharge standards of MARPOL (International Maritime Organisation) 75/78, is recorded as 15 mg/lt [18,27].

In order to be able to use efficiently and preserve the water sources in Turkey, Water Pollution Control Regulations (Su Kirliliği Kontrolu Yönetmeliği) has been arranged on 4.9.1988. According to this regulation, 16 industrial sectors covering different industries are formed and discharge limitations of each industry is given in terms of composite sampling (2 and 24 hours). Composite sampling is taken samples in predetermined intervals over a selected time period. During inspection of waste

streams of industries, 2 hours-composite sampling values are taking into consideration and in metals sector, in metal working industries this maximum allowable discharge value of oil and grease is 20 mg/lt [3].

3.3 TREATMENT METHODS OF OILY WASTEWATERS

3.3.1 General

In many industrial effluents, oils are present either in a free state or as highly stable and unstable emulsions. The appropriate treatment technology can be selected once oil droplet size distribution, emulsification state and concentration of oil in the wastewater is known. Although a number of physical and chemical wastewater treatment technologies including gravimetric separation, chemical emulsion breaking, membrane separation are used for the removal of oil, the most important point is applying the most suitable technology. Free oil can be readily removed by gravity separation which includes mechanical separation devices that use gravitational forces as the driving force. Unstable oil-water emulsions like mechanical emulsions can be mechanically or chemically broken rather than gravity separated. Highly stable emulsions like dissolved oil or chemical emulsions require more sophisticated treatment methods like chemical emulsion breaking or membrane processes. Biological treatment and carbon adsorption are two other alternative treatment methods which can remove trace quantities of oil. Biological treatment systems are only effective if suitable pretreatment and high dilution can be achieved and carbon adsorption require large capital investment for carbon inventory and regeneration. These two techniques did not find widespread use and will not be discussed here. This section will give a brief overview of gravimetry separation, chemical emulsion breaking and membrane processes [14,20,22,].

3.3.2 Gravity Separation

Gravity separation is the simplest form of wastewater treatment. It can be used to remove floating oils which are large enough to settle out. Gravimetric techniques include simple American Petroleum Institute (API) separators as well as enhanced techniques such as coalescence, air flotation and high speed centrifugation. These techniques separate free (unemulsified or dispersed) oil from the water on the basis of differences in specific gravity [26].

API separators are designed to remove oil droplets down to 150 microns in size. The typical effluent concentrations achieved are greater than 100 ppm. API separators are difficult to cover for smell reduction purpose, must be cleaned out periodically and sludge removal from the bottom is impractical [21,22].

Coalescing plate interceptors (CPI) are typically designed to remove droplets down to 60 microns. They can attain effluent concentrations down to 10 to 20 ppm. CPIs' coalescing plates which have improved efficiency by helping small oil drops to touch each other and grow large enough to rise quickly.

In a flotation unit, air is dissolved under pressure (40 - 70 psig) in the liquid to be treated. As the pressure is released, small bubbles (10 - 100 microns in diameter) form and make the particle rise to the surface. There it combines with other particles or float and can be removed by mechanical skimmers. Flotation systems are capable of removing droplets down to 5 microns. They are usually used for secondary treatment and can produce effluent concentrations of 1 to 25 ppm [25,28].

Centrifuges enhance separation by placing wastewater under high acceleration and mostly used for off-shore applications. The effluent concentrations that centrifuges produce are down to 70 ppm. Their main disadvantage is high energy and maintenance requirements [22].

3.3.3 Chemical Emulsion Breaking

Chemical emulsion breaking is one of the most widely used industrial wastewater treatment methods. In breaking emulsions, the stabilizing factors must be neutralized to allow the emulsified droplets to coalesce. In fact, all potentially applicable methods of chemical treatment involve destabilizing or breaking the oil emulsion to allow some type of gravimetric or physical separation to be effective.

The treatment is normally divided into two steps:

1. Coagulation: This is the destruction of the emulsifying properties of the surface active agent or neutralization of the charged oil droplet.
2. Flocculation: This is agglomeration of the neutralized droplets into large, separable globules.

The effectiveness of a chemical to destabilize an emulsion is dependent on the emulsifier and the emulsified oil. Anionic emulsions can often be destabilized by pH depression using an acid (normally sulfuric acid). Chemical coagulating agents, such as iron or aluminum salts, can be used in place of acid, with the additional benefit that these aid in agglomeration of the oil droplets. However, the aluminum or iron forms hydroxide sludges that are difficult to dewater. Acids generally break emulsions more effectively than coagulant salts but the resultant acidic wastewater must be neutralized after oil/water separation. Organic demulsifiers (polyamines, polyacrylates and their substituted copolymers) are extremely effective emulsion breaking agents, giving more consistent results and producing better effluent quality [22,26].

Chemical treatment results in a sludge in which dirt, floc and trapped water remained with the oil phase. This sludge always require further stabilization before disposal. The water phase from chemical treatment needed additional treatment to meet environmental standards for discharge into a sewer which is the main drawback of this treatment method [14]

3.3.4 Membrane Processes

Membranes offer a simple and reliable approach for solving most oily wastewater problems based on oil in water emulsions. As membranes are selective barriers, oil in water emulsions break by passing of water through the pores of the membrane while rejecting oil, additives and dirt contaminants. Membrane processes can be classified as physical treatment methods which results in many advantages such as being simple, reliable, no requirement of chemical addition [22].

In membrane processes, a water phase that can usually be discharged to a sewer with no posttreatment and an oil phase which can be incinerated, upgraded or reutilized are produced [14].

Ultrafiltration is a membrane process that is commonly used in treatment of oil water emulsions arising from several different industries. As more complex cutting oil formulas (an important source of oil contamination in water) are developed which can not be destabilized by traditional chemical emulsion breaking method, ultrafiltration became more popular. In spite of all these advantages, ultrafiltration may not be feasable because of regular cleaning requirements and periodically replacement due to plugging depending on the characteristics of both the wastewater and membrane itself. It is known that many commercially available membranes are used for oily wastewater treatment in many industries effectively [29].

3.4 REVIEW OF STUDIES ON ULTRAFILTRATION OF OIL-WATER EMULSIONS

This section will give a brief overview of the studies in the literature concerning ultrafiltration of oily wastewaters. Sources of oily wastewater vary from metal cutting, metal rolling and drawing to car and truck wash, industrial laundries. Studies under the title of oily wastewaters or oil-in-water emulsions include all of these oils that have different backgrounds. In most of these studies, a model feed solution

formulation is chosen either as a commercially available soluble oil or laboratory prepared emulsion.

The early studies involve application of cellulosic membranes for treating oily waters in various configurations. Later studies of development of suitable membranes for oil-in-water emulsions are mostly patented work. Harris et al. in their studies with turbine lubricating oil and bilge oil, showed that noncellulosic tubular membrane provide higher flux than the cellulosic types and permeates containing less than 10 mg/l oil could be obtained even in the presence of detergents [30].

Bhattacharyya et al. studied the ultrafiltration characteristics of oil-nonionic detergent-water systems with non-cellulosic tubular membranes. The water flux characteristics and fouling behavior are explained in terms of mathematical models [18].

Kutowy et al. developed tubular cellulose acetate reverse osmosis membranes for oily wastewaters' ultrafiltration treatment which were commercialized as Electrohome ultrafiltration modules with high rejection capabilities. The development program, specification and typical performance of these membranes are discussed in their paper in detail [31].

One of the later studies was done by Pia Lipp et al. to determine the factors affecting both flux and rejection. In this study, coalescing in the polarized layers and even within the membrane was proved. However, oil rejections were high enough and permeate flux generally followed gel polarized film model. Fouling was observed and most easily reversed when cellulosic membranes were used [32].

Cleaning of ultrafiltration membranes is generally an important concern of researchers studying ultrafiltration of oily wastewaters. Lindau et al. investigated influences of different types of cleaning agents on polysulphone ultrafiltration membranes which were used in ultrafiltration of oily wastewater treatment. The influence of five different cleaning agents on the fluxes were investigated. It was shown that the acidic

cleaning agents had the ability to dissolve inorganic deposits on the membrane, and hence for oil-water emulsions this cleaning resulted in time dependent flux. Alkaline cleaning agents dissolved organic deposits and had a positive effect on the membrane itself [33].

One of the recent studies involve the investigation of ultrafiltration and microfiltration in treating lube oil and heavy fuel oil in water emulsions in terms of Reynolds number, transmembrane pressure and feed concentration. In this study, Re de Paolini et al. found out that ultrafiltration performed better than microfiltration in separating this kind of oily emulsions [34].

Recently, Balkacem et al. developed a model for calculating the steady state flux of organic ultrafiltration membranes in the case of treatment of cutting oil emulsions. The model gives the resistance of polarization layer in terms of the pressure drop across the membrane, the velocity of the feed fluid in the membrane module, the viscosity and the density of the emulsion. The model gives a basis for estimating the optimal parameters for ultrafiltration operations [35].

Finally, Karakulski et al. studied treatment of bilge water with a hybrid ultrafiltration and photocatalytic processes. Ultrafiltration experiments using different membranes indicated that ultrafiltration is suitable for the treatment of bilge water. Further treatment is done with the photocatalytic process which results in complete decomposition and conversion of organic pollutants into organic materials. Karakulski et al's work shows that applications of ultrafiltration can be broadened by hybrid processing [27].

CHAPTER 4

EXPERIMENTAL

4.1 MATERIALS

4.1.1 Membranes

In this study four commercially available ultrafiltration membranes were used for characterization of their performance in treating oil-in-water emulsions. These tubular membranes were supplied by PCI Membrane Systems Ltd. and the specifications of these membranes obtained from the manufacturer are presented in Table 4.1.

Two polyethersulphone membranes with different pore sizes, one hydrophilic polyacrylonitrile membrane with a relatively high molecular weight cut-off value and a tighter membrane made from polysulphone are the membranes that are chosen for our application from PCI's large product range.

The polyacrylonitrile used for AN620 membranes is said to be resistant in its' bulk form to most common organic solvents such as alcohols, ethers, ketones, esters, aliphatic and aromatic hydrocarbons and chlorinated hydrocarbons. This polymer however swells or dissolves when in contact with highly polar substances and concentrated solutions of some organic salts like dimethylacetamide, dimethylformamide, dimethylsulphoxide and ethylenecarbonate.

Polysulphone and polyethersulphone polymers are resistant to aliphatic hydrocarbons (n-hexane, n-pentane, cyclohexane), aromatic hydrocarbons (benzene and toluene), aliphatic alcohols (methanol, ethanol, isopropanol, n-propanol, n-butanol, n-pentanol, isobutanol, cyclohexanol), aromatic alcohols (benzyl alcohol, phenol), some ethers

(diethyl ether, di-sopropyl ether), glycols (ethylene glycol, di-ethylene glycol, glycerol) and some halogenated hydrocarbons (Freon TF and Genosolu D), formaldehyde, kerosene, turpentine and vegetable oils.

4.1.2 Chemicals

Oil-in-water emulsions are prepared by adding a certain amount of water to Klora brand cutting oil, a soluble oil used as cutting fluid which contains mineral oil, emulsifiers and additives.

Chemicals which are used in determination of oil concentration by partition-gravimetric method are sodium sulphate, anhydrous crystal (Carlo Erba), n-hexane (Atabay), methylterbutylether (Merck), HCl (Carlo Erba).

In acid cleaning of membranes, nitric acid (Carlo Erba) solutions and in caustic cleaning of membranes P3 Ultrasil 10 (Henkel) and sodium lauryl sulphate (Zohar Detergent Factory) are used. Membranes are preserved in 0.25%sodium metabisulphite (Carlo Erba) solutions.

4.2 EQUIPMENT

The Armfield FT18 reverse osmosis-ultrafiltration unit designed specifically for laboratory scale testing is used in conducting ultrafiltration experiments. A schematic illustration of the unit is presented in Figure 4.1. The unit is designed to operate in the crossflow mode in a continuous manner. Feed solution, placed in feed tank, is circulated through the membrane module which contains two tubular membranes in series. The total membrane area is 0.024 m^2. The tubular membranes are 1.25 cm in diameter and 32 cm in length. The retentate leaving the module passes

Table 4.1. Specification of PCI Tubular Membranes

Membrane Code	Material	MW Cut-off	Hydro-phillicity[1]	Solvent Resistance[2]	Normal Operating Pressure (bar)	Maximum Operating Pressure (bar)	Normal Operating Temp. (°C)	Maximum Operating Temp. (°C)	Operation pH Range	Maximum pH Range (cleaning)
ES 625	Polyether sulphone	25.000	2	++	6	15	10-60	80	2-11	1.5-12
ES 404	Polyether sulphone	4.000	2	++	10-20	30	10-60	80	2-11	1.5-12
AN 620	Polyacrylo nitrile	25.000	5	+++	6	10	10-50	60	2-9	2-10
PU 608	Poly sulphone	8.000	2	++	6	6	10-60	80	2-11	1.5-12

[1] 1 low, 5 high
[2] + low, +++ high

through a back pressure valve (V1) which is used to create the desired system pressure together with the bypass valve V2 and a plate heat exchanger and is recycled back to the feed tank while the permeate, the material passing through the membrane, drains by gravity into the permeate tank. This design can be changed in order to maintain constant feed concentration by also returning the permeate into the feed tank. The flowrate through the membrane is adjusted to 9 l/min, 15 l/min,18 l/min and 30 l/min by changing both the motor speed and position of two triple plunger positive displacement pumps. Work done on the fluid by the pumps causes an increase in temperature in time. This temperature increase is controlled by pumping the fluid through a plate and frame heat exchanger.

Four semi-conductor temperature sensors that measure the temperatures at different points are installed into the system. System pressure is detected by a pressure sensor. Both temperature and pressure values are indicated digitally on the controle console.

4.3 PREPERATION OF EMULSIONS

Oil water emulsions to model the oily waste waters generated in the metal working industry are prepared by diluting a soluble cutting oil to the desired extent with water. Oily waste waters from the metal finishing industry generally vary in oil concentration from 0.5 to 10 vol. %. The manufacturer of the cutting oil recommends a dilution of 1:20 oil / water for use as a cutting fluid. The oil-water emulsion used as the feed solution for the ultrafiltration experiments contains 3.9 vol. % cutting oil in distilled water.

4.4 EXPERIMENTAL PROCEDURE

Two tubular membranes are first inserted into the module, sealed and carefully placed to its place on the unit. The feed tank is filled with oil-water emulsion of the appropriate concentration. The cooling water supply of the heat exchanger is opened

and the flow of cooling water is adjusted with a variable area flowmeter in order to maintain the required temperature since the temperature increases due to the friction between the unit and the circulated fluid. Before starting the pumps, V1 and V2 valves which are used in establishing the required system pressure difference must be fully opened. Appropriate feed flow rate is adjusted by first changing the number of pumps in use. After feed solution is sent to the module and no leakage is observed the speed of the pumps in use is adjusted. The pressure difference is set by turning V1 back pressure valve clockwise and closing V2 by-pass if required.

In all experiments conducted in thesis, the permeate was recycled back to the feed tank as well as the retentate to keep the concentration in the close loop constant. In order to characterize the membranes before and after emulsion filtration experiments,

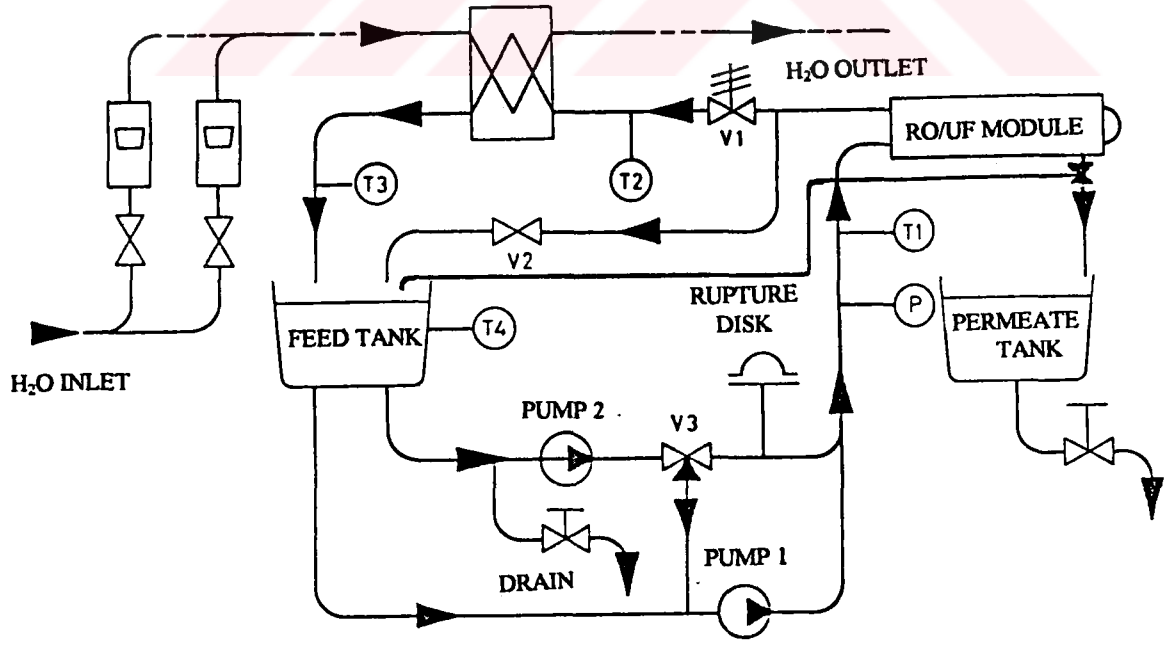


Figure 4.1. Schematic drawing of Armfield FT18 RO/UF unit.

pure water fluxes are determined at a transmembrane pressure of 6 bar, 30 l/min for about 30 minutes to two hours. The flux recovery value is calculated as the ratio of the pure water flux after and before the emulsion filtration experiments.

The permeate flux is measured throughout the whole experiment and 4 samples of permeate are taken to determine the oil concentration. The oil concentration in the feed tank is also measured at different time intervals in order to calculate the retention and also to check if there is any increase that may occur because of permeate sampling. At the end of the experiment, the shutdown of the equipment is done by doing the reverse of the start-up procedure.

4.5 DETERMINATION OF OIL CONCENTRATION

There are several methods which can be used in determination of oil concentration such as refractometry, total organic carbon measurements, partition-infrared and partition-gravimetric methods and turbidity measurements.

Refractometers are only capable of giving a general idea about concentration but not suitable for qualitative determination.

In total organic carbon measurements, organic carbon is converted to carbondioxide by catalytic combustion or wet chemical oxidation and the CO_2 formed is measured. Data based on total carbon content do not differentiate between oil, surfactants and other additives in the sample.

There are five different methods recommended for oil and grease in "Standard methods for the examination of water and waste water" [36] but only three of them may be suitable for liquid samples. These are the partition-gravimetric method, partition-infrared method and Soxhlet method. In all of these methods, "oil and grease" is defined as any material recovered as a substance soluble in the solvents, so the determined concentration will be the concentration of these soluble materials in

the solvent. The Soxhlet method is ruled out at the first step as it is the method of choice when the levels of nonvolatile greases may challenge the solubility limit of the solvent. The other two methods, the partition-gravimetric and partition-infrared, are suitable for use in this study.

Partition-gravimetric method is a very common method and it has been chosen for the determination of feed concentration in this study. However, for low levels of oil (~10mg/l) this method do not provide the required precision.

Turbidimetry is recommended in the literature for low levels of oil concentration. Turbidity refers to the characteristic optical properties of dispersions and may be taken as the ratio of light reflected to that incident upon a dispersion. A limitation to turbidimeter measurements, is that the concentration must not exceed 100 mg/l but under this value a calibration of turbidity reading as a function of oil concentration is linear and gives results with high precision. This is the method of choice for our permeate oil concentration determination. Since partition-gravimetric method is chosen for the feed concentration determination and turbiditimetry is chosen for the permeate concentration measurements, these two methods will be discussed here in more detail.

4.5.1 Partition-Gravimetric Method

A sample with a known volume, is first acidified with HCl to pH 2 or lower and than extracted with 30 ml of solvent (80% n-hexane and 20% methyl-tetrabutylether) for 3 subsequent times. In each step, solvent layer is collected in a tared distilling flask passing through a funnel containing Na_2SO_4. After combing all extracts and rinsing solvent, the solvent is distilled out and the flask is cooled in a desiccator and weighted. The oil concentration is determined according to the formula given below :

$$\text{mg oil and grease} / \text{l} = \frac{\text{Total gain in weight}}{\text{ml sample}} x1000 \qquad (4.1)$$

4.5.2 Turbidimetry

The turbidimeter used in the study is Jenway 6035 model and the standard solution of 5 NTU turbidity is supplied from Jenway Ltd. company. Turbidity values are given in NTU. A calibration curve is prepared by measuring turbidity of oil-in-water emulsion of known concentrations as shown in Figure 4.2.

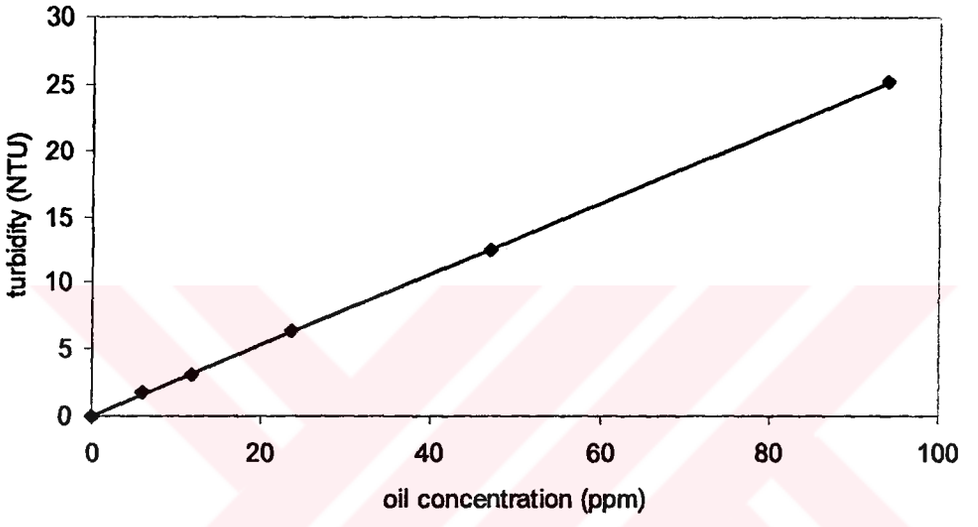


Figure 4.2. Calibration of turbidity measurement as a function of oil concentration (Klora cutting oil) in water.

4.6 EXPERIMENTAL PARAMETERS

During all experiments, feed concentration and temperature are assumed to be kept constant. Temperature during all experiments were between 21-28°C and in each experiment, at the first minutes a steep increase is observed because of friction. But later, the heat exchanger manages to keep the temperature constant at a certain level. An oil concentration of 3.9 % vol. is kept constant for the feed in all experiments.

The parameters investigated are membrane material, pressure and feed flow rate: Four membranes made from three different materials are tested. Feed flow rate values are limited with the module configuration. Two pumps operating together or only one

at high or low speed results in feed flow rates of 9 l/min, 15 l/min, 18 l/min and 30 l/min. Feed flow rates are chosen 9 l/min, 15 l/min and 30 l/min in this study. The maximum pressure difference that can be applied with ultrafiltration-reverse osmosis unit is 55 bar. As ultrafiltration operates at low pressures, generally below 10 bar; three different pressures 4 bar, 6 bar and 10 bar are chosen in this study. However, there is an upper pressure limit of 6 bars for one of the membranes used, namely PU608 polysulphone membrane, therefore only, 4, 5 and 6 bars are used for this particular membrane.

4.7 MEMBRANE PRESERVATION AND CLEANING

Membranes are preserved in a 0.25% v/v solution of Proxel GXL (by Zeneca Biocides) plus 18% v/v of Glycerol (98% reagent grade) provided by PCI Membrane Systems Ltd., the manufacturer of the membranes. According to their instructions, 0.25% w/w solution of sodium metabisulphite can also be used and this method is chosen for membrane preservation in our studies.

According to the instructions of PCI Membrane Systems Ltd., a standard clean should be given to each membrane before first use for removal of this preservation liquid. As concentration polarization and fouling are the two phenomena that limit the performance of ultrafiltration membranes, the membranes should be cleaned regularly to get back their initial separation quality.

A list of cleaning agents suitable for each membrane is provided by the manufacturer. Although more than one cleaning procedure is available to each membrane, appropriate one must be chosen for each application.

Acid cleaning with nitric acid or Henkel P3 Ultrasil 75 to give a solution of pH 1.8 is suitable for all of the membranes. Although acid or caustic cleaning is appropriate to each membrane, different cleaning procedures must be applied according to membranes properties. ES625, ES404, PU608 membranes are cleaned by

recirculating 0.25% Henkel P3 Ultrasil 10 plus sodium hydroxide solution for about one hour at 50-55°C. This solution has a pH of 12 which is over the tolerance pH limit of AN620 (pH<10). Caustic cleaning of AN620 is done by either circulating only 0.08% Henkel P3 Ultrasil 10 solution or circulating 0.08%Henkel P3 ultrasil 10 plus 0.25% sodium lauryl sulphate (SLS) as adviced by the manufacturer. The effect of cleaning is investigated for both initial (before first use) cleaning and after-use cleaning in terms of pure water fluxes.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 PURE WATER FLUX

Membranes are produced with differing pore sizes, pore densities and pore size distributions and can be characterized by measuring pure water flux through the membrane. The membranes used in this study are first characterized by their pure water fluxes.

A preservation liquid is present in the structure of each PCI membrane which has to be removed before initial use. The preservation liquid that the manufacturer uses is a mixture of Proxel GXL and glycerol. Removal of this preservation liquid will directly effect the flux and performance of the membranes. From different cleaning methods which are adviced by the manufacturer, first, acid cleaning is applied to each membrane. After the effect of acid cleaning is determined by comparing the pure water flux values of the membranes before and after cleaning, the membranes are again preserved in sodium metabisulphite solution for further investigation. Furthermore, membranes were also given a suitable caustic cleaning and pure water flux values are compared to those of acid cleaning to determine the effect of cleaning methods in removing the preservation liquid. The pure water flux values obtained are presented in Table 5.1. All pure water flux values are measured at 28°C, 30 lt/min. feed flow rate and 6 bar pressure difference for about two hours.

ES625 polyethersulphone (PES) membrane with a MW cut-off value of 25000 presented the highest pure water flux. The other PES membrane ES404 with a MW cut-off value of 4000 gave a pure water flux value almost on third of the PES membrane with the higher MW cut-off. This seems to be logical since lower MW cut-

Table 5.1 Pure water fluxes of untreated and treated new membranes

			Pure Water Flux (l/min*m2)		
Membrane	Material	MW Cut-off	Untreated	Pretreated with acid cleaning⊗	Pretreated with caustic detergent
ES625	Polyethersulphone	25000	4.20	5.03	*4.45
ES404	Polyethersulphone	4000	2.03	1.72	*1.92
AN620	Polyacrylonitrile	25000	0.92	0.99	**0.74 ***0.98
PU608	Polysulphone	8000	4.43	0.33	*3.03

*: method 1: 0.25% Henkel P3 Ultrasil 10 plus 0.1% sodium hydroxide

**: method 2: 0.08% Henkel P3 ultrasil 10

***: method 3: 0.08% Henkel P3 Ultrasil 10 plus 0.25% SLS

⊗: 3 ml/l of 70% nitric acid solution

off value means smaller pores in the membrane. Pure water flux values obtained for the polyocrylonitrile (PAN) membrane AN620 is the lowest in Table 5.1, although PAN is a hydrophilic polymer and this membrane has a high MW cut-off value (25000) same as ES625. Pore size is not the only factor determining the flux, pore density is also important. AN620 has a lower pore density and this may be the reason for the low pure water flux value. Polysulphone PU608 (8000 MW cut-off) membranes gave relatively high pure water flux values compared to ES625 which has a higher MW cut-off value (25000) and again this may be due to higher pore density of PU608 membranes or PU608 may have a broader pore size distribution

Acid pretreatment has improved pure water flux values of ES625 and AN620 which means that removal of preservation liquid is accomplished. ES404 membrane showed a slight decrease in its pure water flux value with acid cleaning whereas PU608 showed a considerably decreased pure water flux value with acid cleaning. This important decrease in pure water flux of PU608 membrane means that acid pretreatment causes changes in the membrane material and different cleaning methods should be used. Caustic cleaning is another method which is adviced by the manufacturer. After preservation of membranes again, suitable caustic cleaning methods are applied to each membrane.

Generally ES625, ES404 and AN620 did not exhibit major differences in pure water flux values between acid cleaning and caustic cleaning. Pretreatment was able to improve pure water fluxes of ES625 and AN620. For ES625, acid pretreatment seems to be a better choice while for AN620 two types of cleaning (acid cleaning and SLS added caustic cleaning) have nearly the same influence. For ES404, pure water fluxes for treated membranes are slightly lower than those of untreated membranes. For PU608, although the pure water flux value after caustic cleaning was higher than the pure water flux value after acid cleaning, the highest pure water flux value for this membrane has been obtained when this membrane is used as received without any further cleaning. Obviously both cleaning methods are not suitable for PU608 and flushing with pure water gives much better results in term of pure water flux value.

As addition of SLS has improved pure water flux of AN620 in caustic cleaning, pure water flux values of other membranes may be improved by addition of SLS which can be a subject for further investigations.

5.2 SEPARATION OF OIL-WATER EMULSIONS

5.2.1 Typical Results

Permeate flux and permeate oil concentration for each membrane are determined at constant temperature and feed concentration for different transmembrane pressures and feed flow rate values. Typical results obtained in these experiments are presented in Figures 5.1, 5.2, 5.3 and 5.4.

In Figure 5.1 and 5.2. permeate fluxes are presented as a function of time at constant feed flow rate for different transmembrane pressure (TMP) values and at constant TMP for different feed flow rate values respectively. Permeate fluxes flactuate a little at the beginning of all experiments but a steady state value is reached in a short while and stayed fairly constant throughout the rest of the experiment. This mean value is taken as the characteristic permeate flux of the membrane for emulsion filtration experiments.

The permeate concentration change in time at constant feed flow rate and constant TMP are presented in Figures 5.3 and .5.4 respectively. In all experiments permeate oil concentration is slightly higher at the beginning of the experiment but reaches to a lower mean value at longer times. The slight decrease in permeate concentration may be due to the concentration polarization phenomena.

The mean permeate concentration values are used to calculate retention values

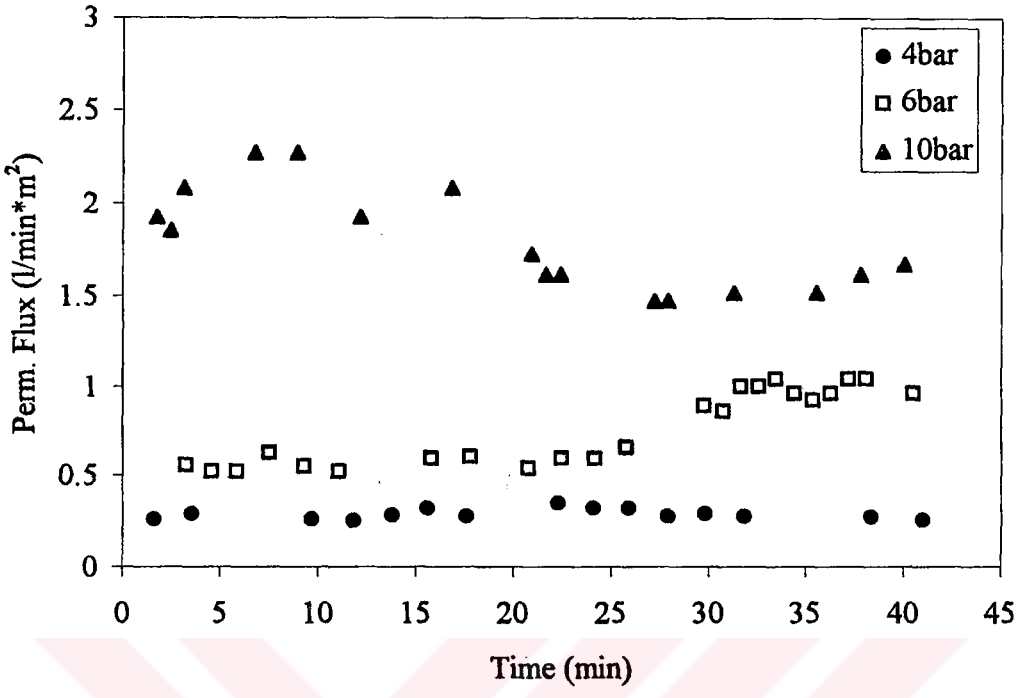


Figure 5.1 Permeate flux versus time values at constant feed flow rate of 30 l/min for three different transmembrane pressure differences.

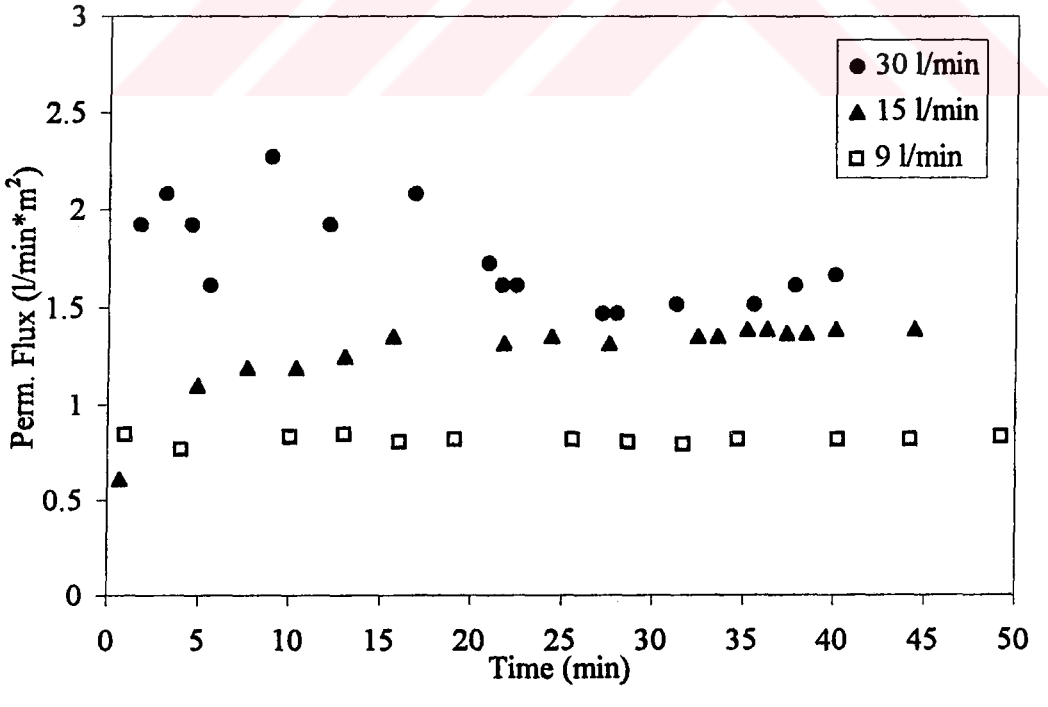


Figure 5.2 Permeate flux versus time values at constant transmembrane pressure difference of 4 bar for three different feed flow rates.

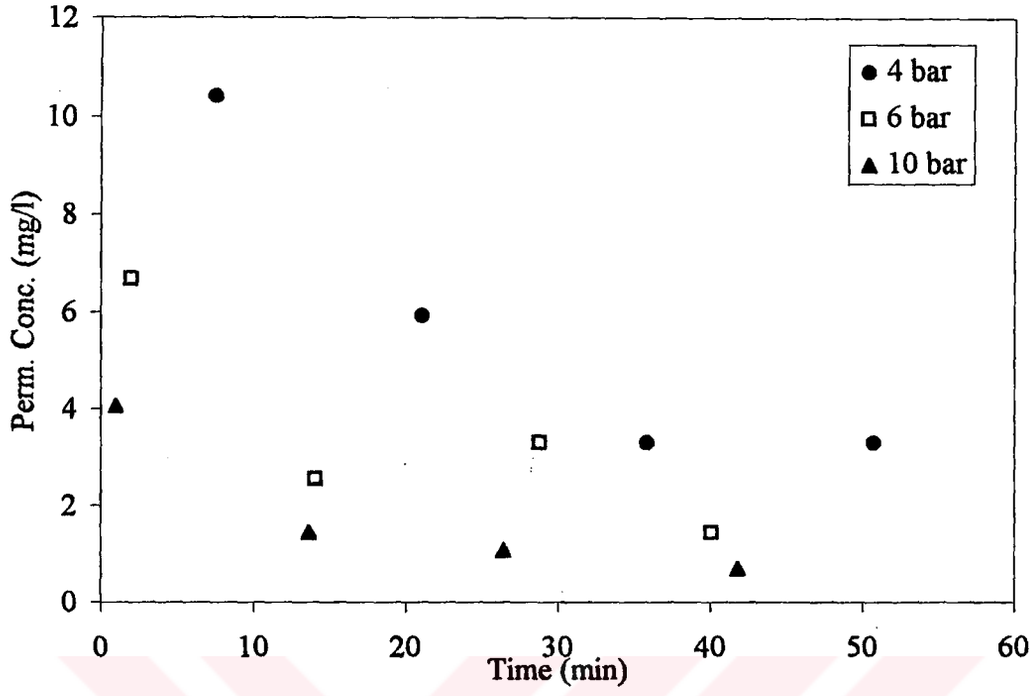


Figure 5.3 The permeate concentration versus time at constant feed flow rate of 30 l/min for three different transmembrane pressures.

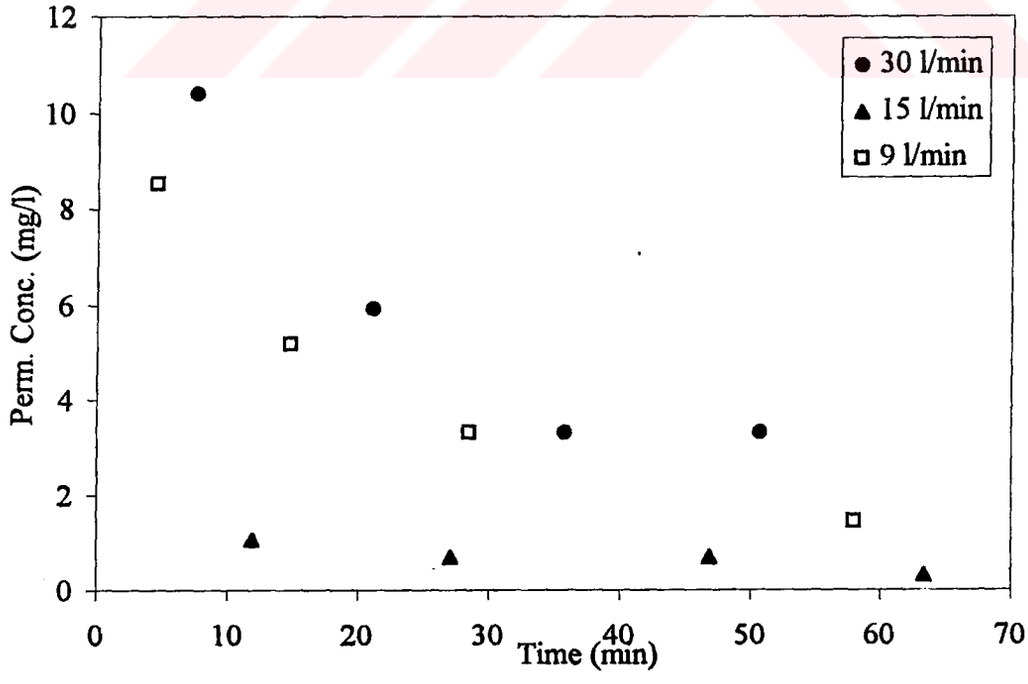


Figure 5.4 The permeate concentration versus time at a constant transmembrane pressure difference of 4 bar for three different feed flow rates.

according to the following equation:

$$\% R = 100 (1- C_p/C_f). \quad (5.1)$$

where R is retention (%), C_p is mean permeate concentration (ppm) and C_f is the feed concentration (ppm).

5.2.2 Effect of pressure difference and feed flow rate

Figure 5.5 presents, the permeate flux as a function of pressure difference at different feed flow rates for each membrane. An increase in permeate flux is expected with increasing pressure difference until the limiting flux is reached. All membranes exhibit an increase in permeate fluxes with increasing pressure difference. The rate of flux increase, however, generally decreases as the pressure difference is increased indicating that a limiting value will be reached.

For all membranes, except ES404, higher feed flowrates generally results in higher flux values due to enhanced mass transfer and hence a thinner polarized layer. ES404 is the membrane that has the lowest MW cut-off and probably flow rates used were not high enough to remove or sweep away the polarized layer. A linear increase can be observed in permeate flux of ES404 membrane with increasing pressure difference indicating that limiting flux region has not been reached yet.

PU608 shows a linear increase with increasing pressure difference like ES404 but has higher permeate fluxes due to its pore characteristics. Although it seems is that working at higher pressures may improve permeate flux, there is an upper operating pressure limit of 6 bar for this membrane as recommended by the manufacturer. The unusual increase at 30 l/min may be due to experimental error since at high feed flow rates determination of permeate flux is rather difficult.

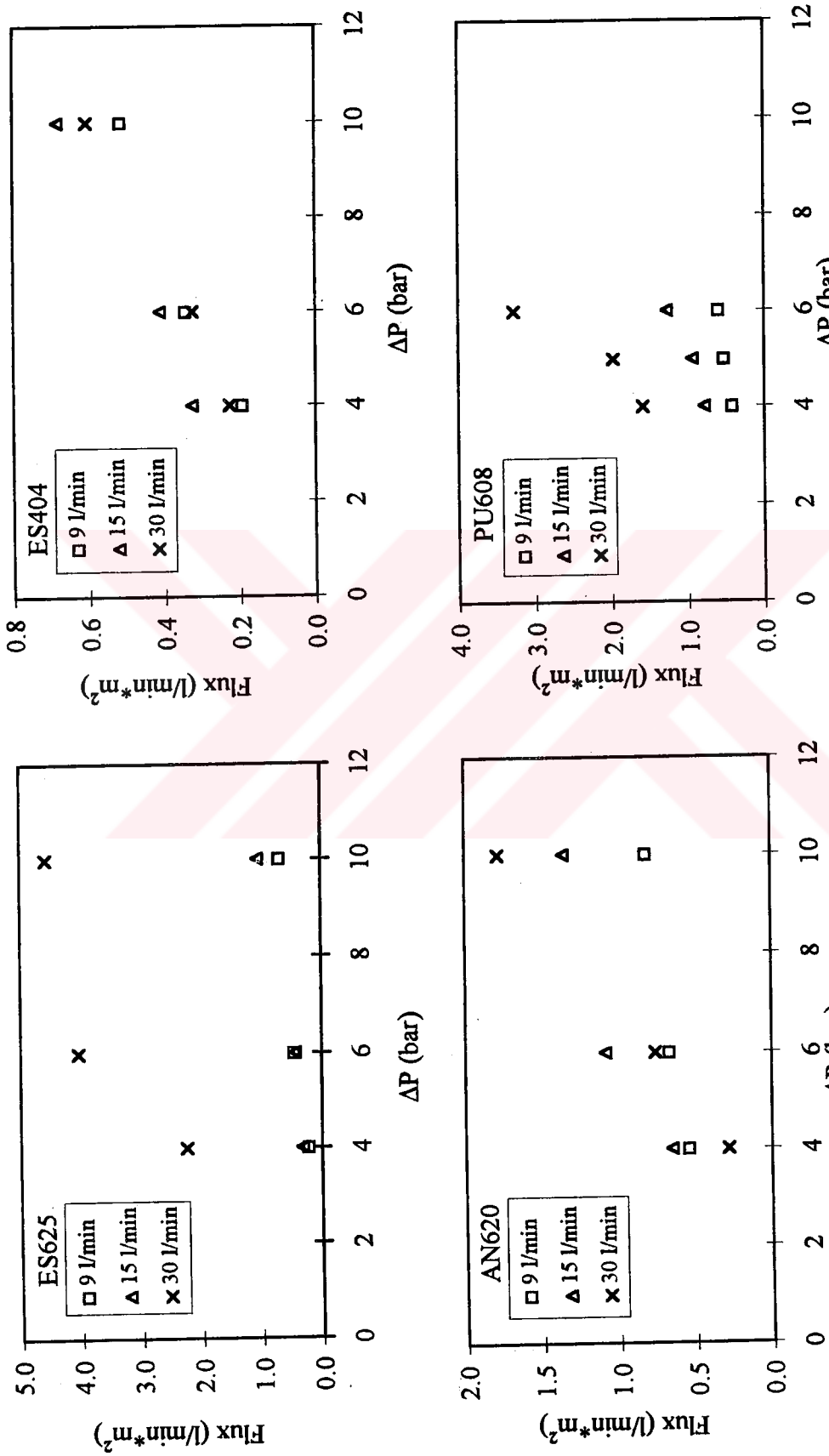


Figure 5.5 Effect of transmembrane pressure difference on permeate flux at different feed flow rates

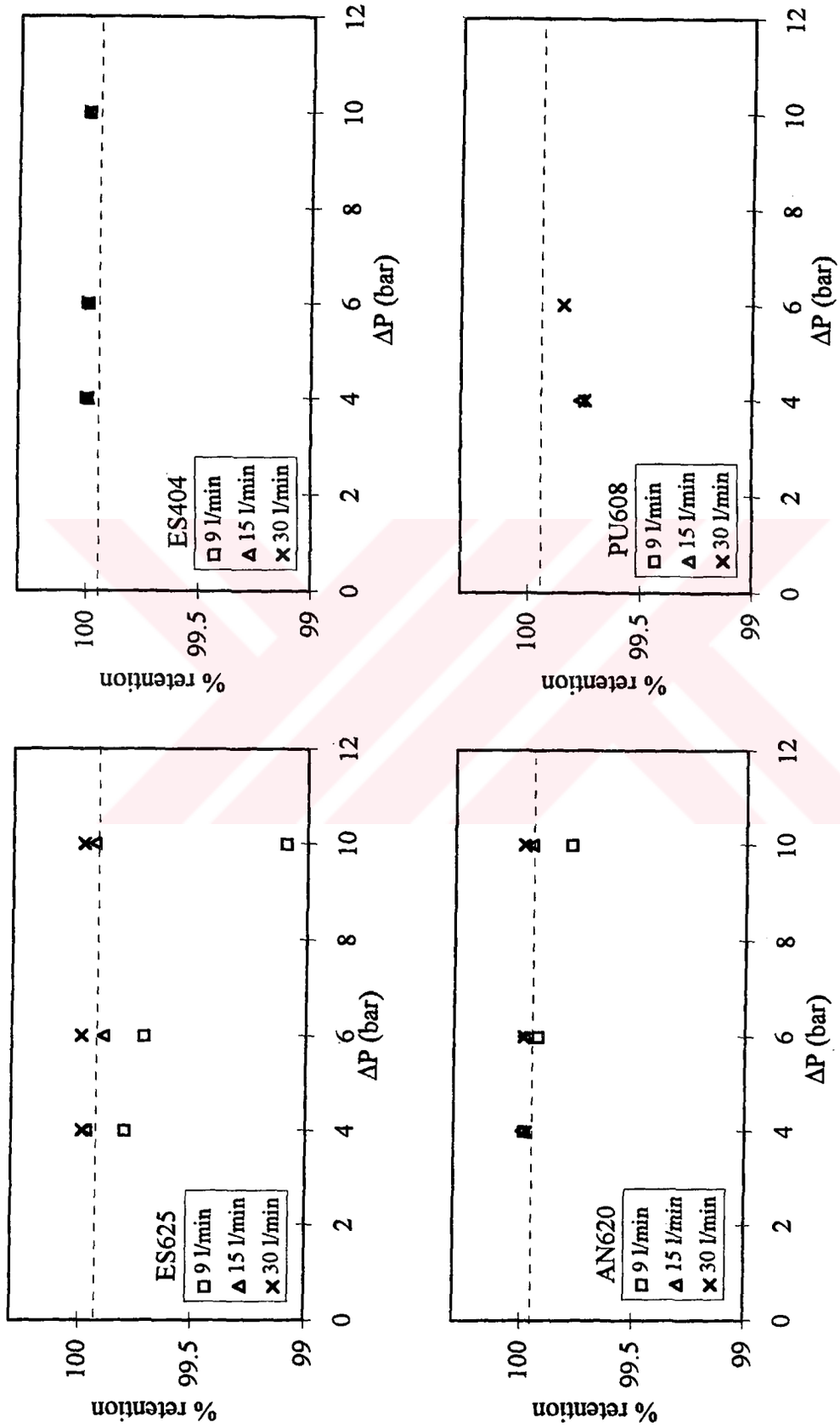


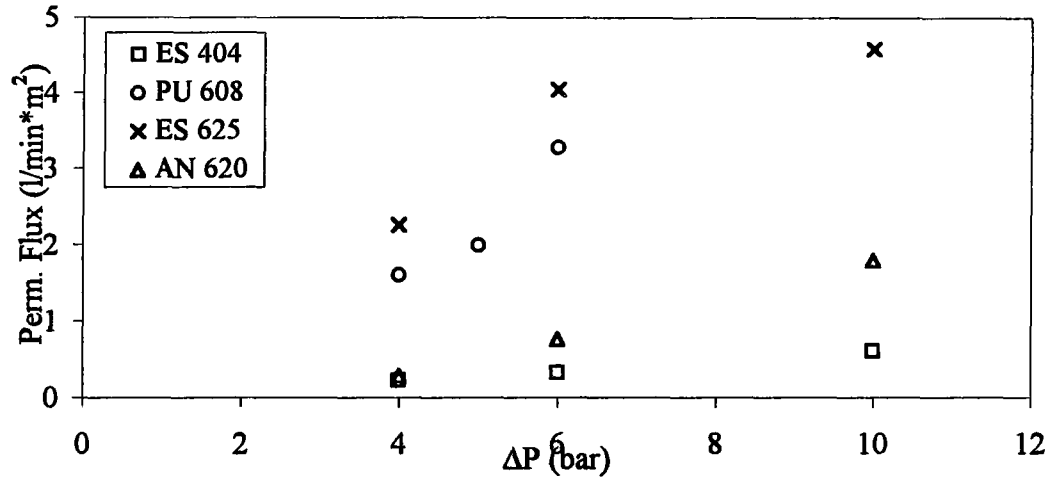
Figure 5.6 Effect of pressure difference on retention (%) at different feed flow rates

AN620 membrane exhibits a linear increase with increasing pressure difference at 30 l/min flow rate. However at the other two feed flow rates, 9 and 15 l/min, increasing pressure difference beyond 6 bars does not increase in permeate flux which means that the limiting flux value is reached. The same limiting flux phenomena is also observed for ES625.

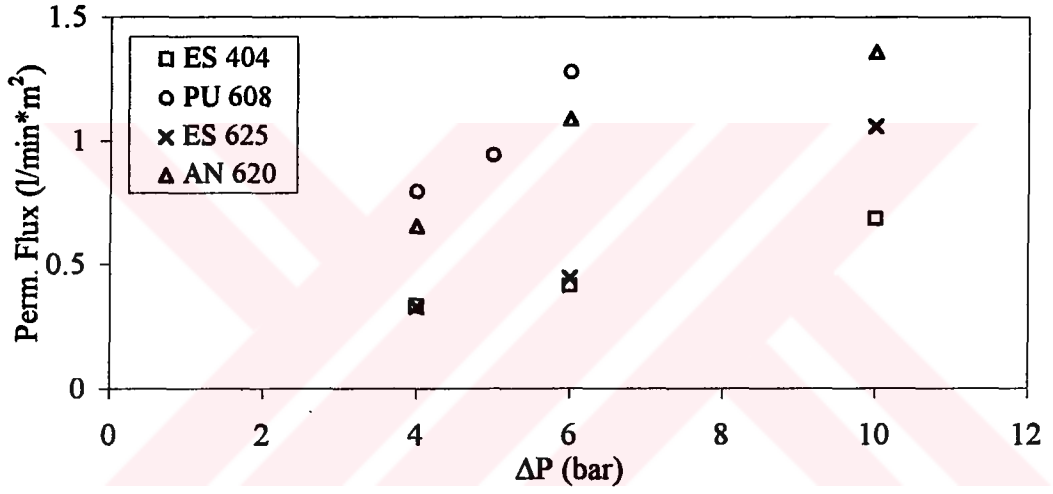
In Figure 5.6, the retention behaviour of four membranes are presented as a function of pressure difference at three different feed flow rate values. The horizontal line shows the retention value calculated according to 20 mg/l the upper discharge limit of oil and grease in Turkey. Membranes having retention (%) values above this line is desired. ES404 is the only membrane that exhibits the desired retentions at every feed flow rate and pressure difference values tested. Other membranes let oil pass into the permeate resulting in lower retentions at some conditions. There are some missing data points in the retention plot of PU608 membranes. These missing data points are due to very high oil concentrations which are over the range of turbidimeter and far away from discharge standarts. The oil contamination in the permeate has been noticable with naked eye in these experiments. Other two membranes ES625 and AN620 have high oil concentrations and low retentions especially at lower (9 l/min) feed flow rates. This is related to the concentration polarization phenomena.

Although PU608 has relatively lower MW cutoff, it has the lowest retentions which means that this membrane can not be used for oil-water emulsion separation. AN620 and ES625, two membranes with 25000 MW cut-off is suitable, according to discharge standarts, at high feed flow rate values. ES625 can be used at approximately 30 l/min and 6 bars where AN620 can be suitable at 10 bars and 30 l/min or 15 l/min and 6 bars. Long term behaviour should also be investigated for more definitive conclusions. Also effective cleaning and flux recovery should be investigated in determining the right membrane.

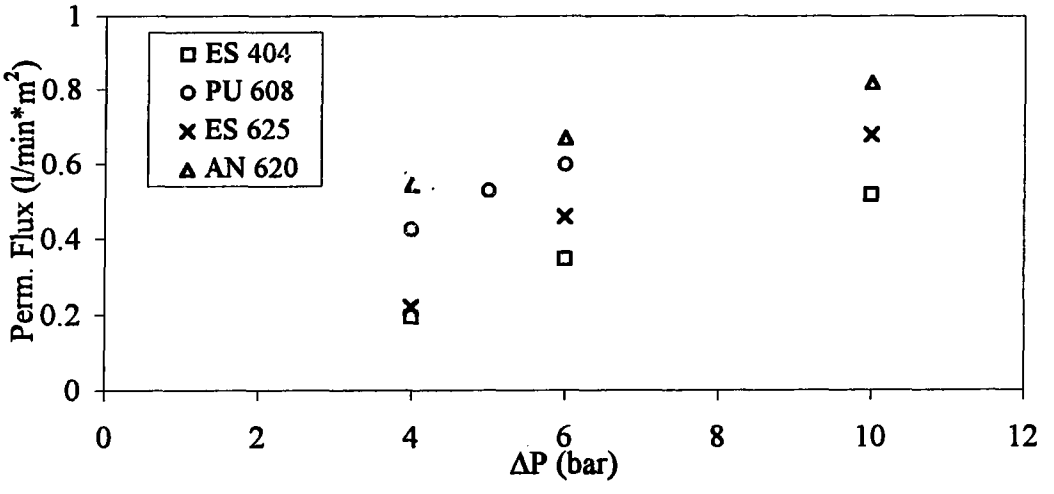
A comparison of membranes can also be made by plotting the same data in a different manner as shown in Figures 5.7 and 5.8. Figure 5.7 and 5.8 presents the permeate



(a)

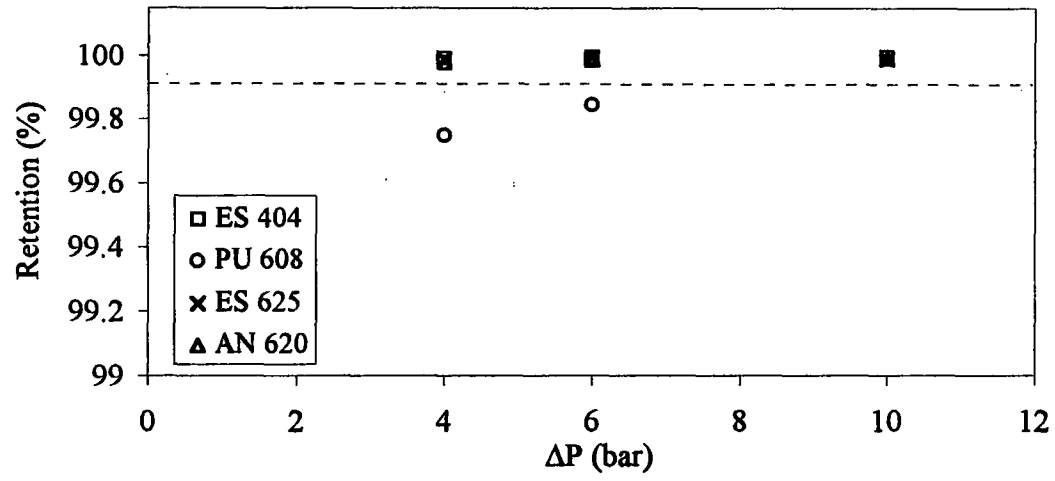


(b)

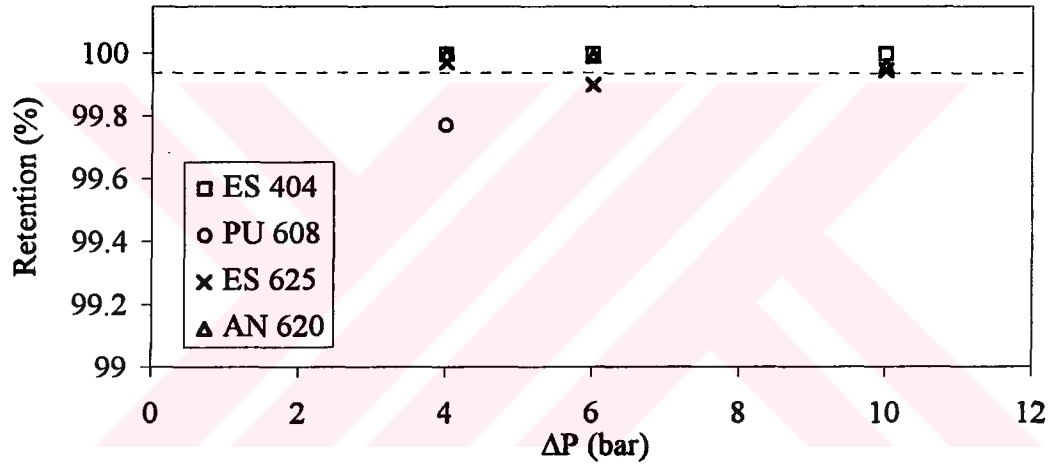


(c)

Figure 5.7 The effect of pressure on permeate flux at (a) 30 l/min, (b) 15 l/min and (c) 9 l/min feed flow rates



(a)



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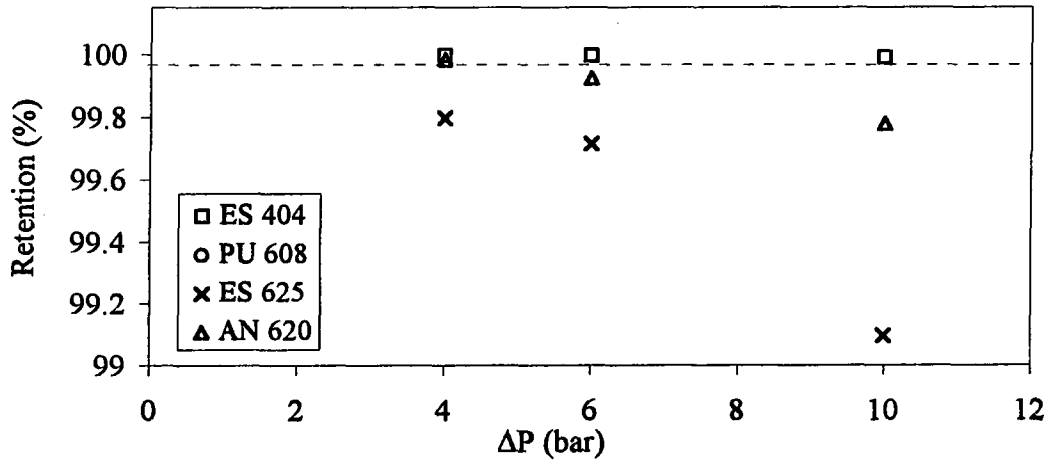


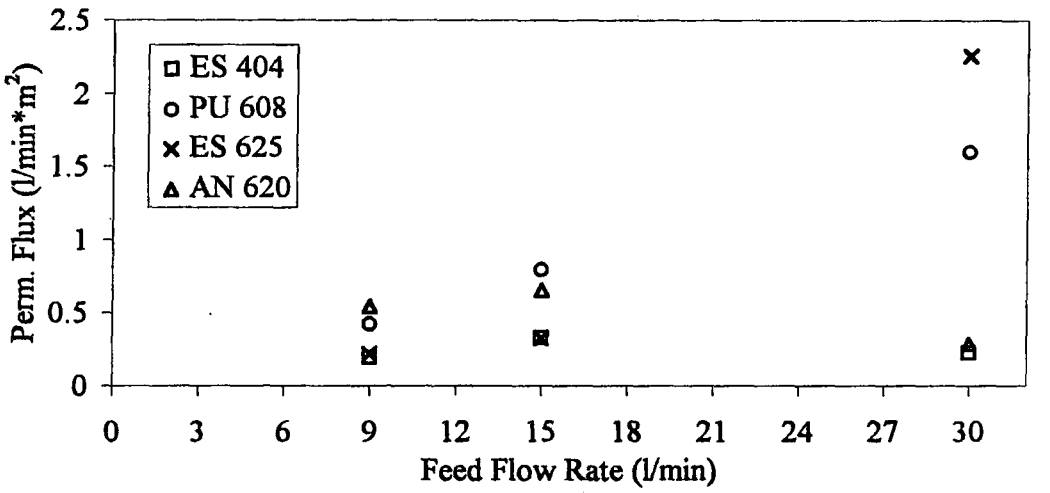
(c)

Figure 5.8 The effect of pressure on retention (%) at 30 l/min (a), 15 l/min (b) and 9 l/min (c) feed flow rates

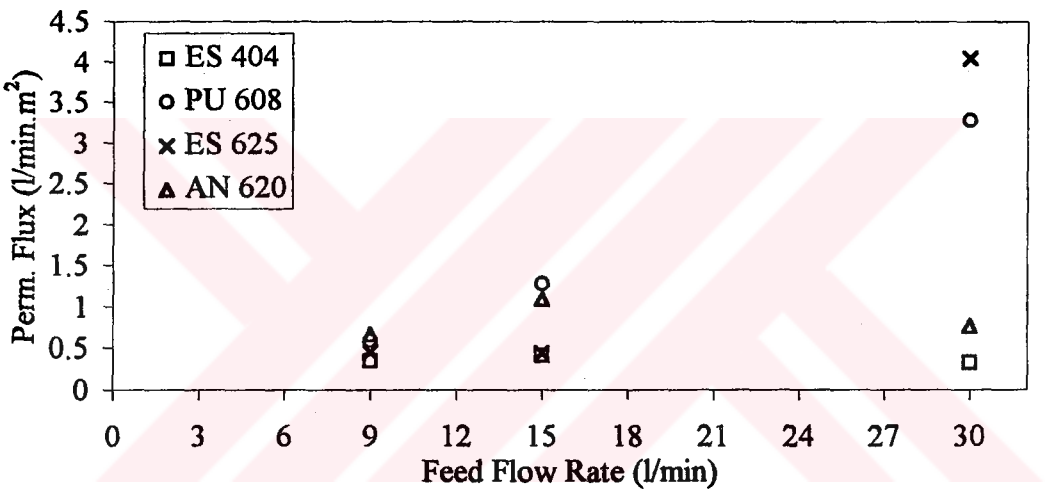
flux and retention (%) values of the four membranes tested in this study as a function of pressure difference respectively.

The highest flux value is obtained for ES625 and the lowest flux value is obtained for ES404. This is expected as ES404 is the membrane with the smallest MW cut-off and ES625 is the membrane with the biggest MW cut-off. AN620, although has MW cut-off value of 25000, showes fluxes lower than PU608 and ES625 because of its lower pore density. The plot in Figure 5.7 (a) is for 30 l/min, the highest feed flow rate, so fouling effects are less. In the other two plots in Figure 5.7 (b) and (c) again ES404, the membrane with the smallest MW cut-off gives lower permeate fluxes as expected. However in case of ES625 polyethersulphone membranes, exhibit lower fluxes when feed flow rate is decreased to 15 l/min and 6 l/min. This unexpected decline may be due to fouling. AN620 becomes the membrane with the highest permeate flux at lower feed flow rates indicating that AN620 membranes are not fouled. This membrane is very hydrophillic compared to the other membranes and hydrophillicity may be the reason of not being fouled. Although PU608 has lower MW cut-off than ES625 and AN620, the passage of oil through PU608 is higher. This may be due to swelling of the polymer or due to wider pore distribution.

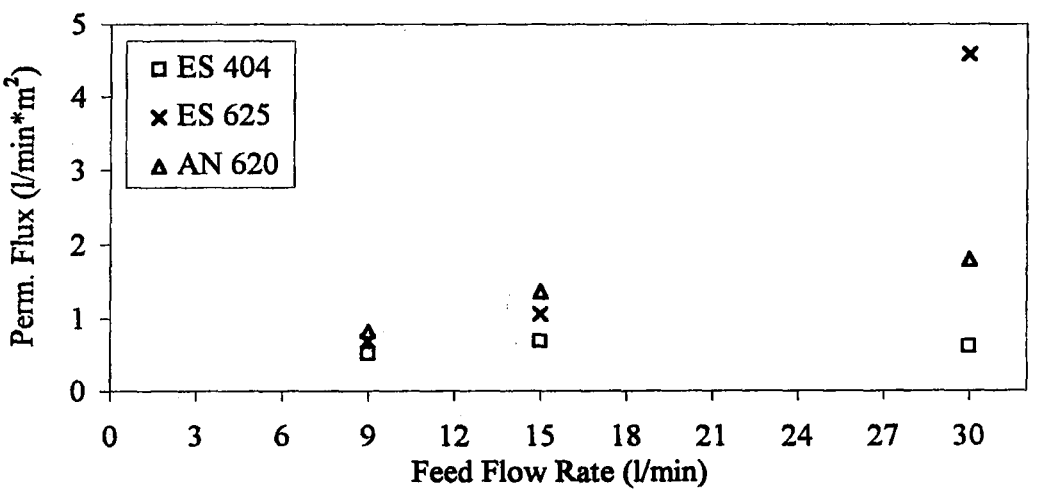
Effect of feed flow rate can also be understood better by plotting the same data in a different manner. Figure 5.9 and 5.10 shows permeate flux and retention (%) values for the four membranes tested as a function of feed flow rate respectively. As the feed flow rate increases, an increase in the permeate flux at constant pressure difference is also observed in these plots for all membranes. An increase with feed flow rate increases the turbulance and reduces the thickness of the concentration polarization layer which results in a flux increase.



(a)

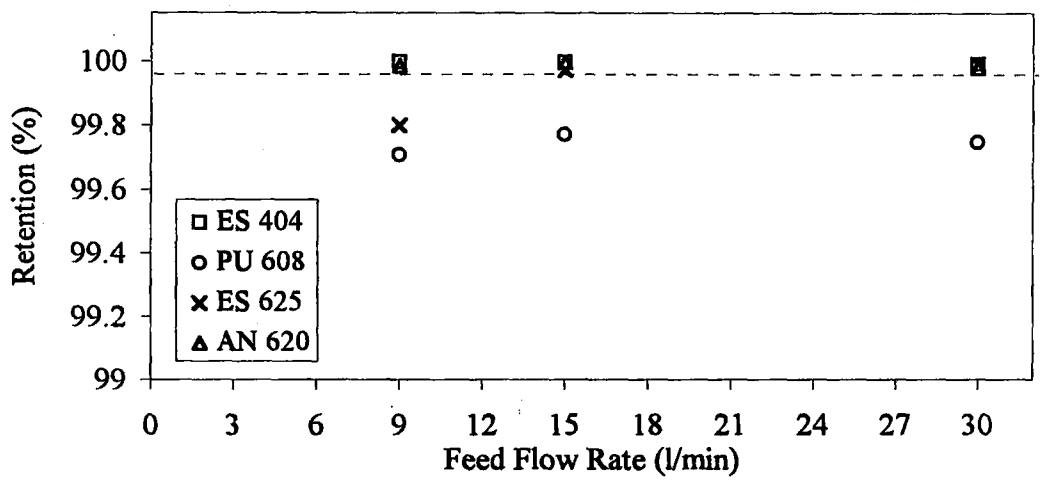


(b)

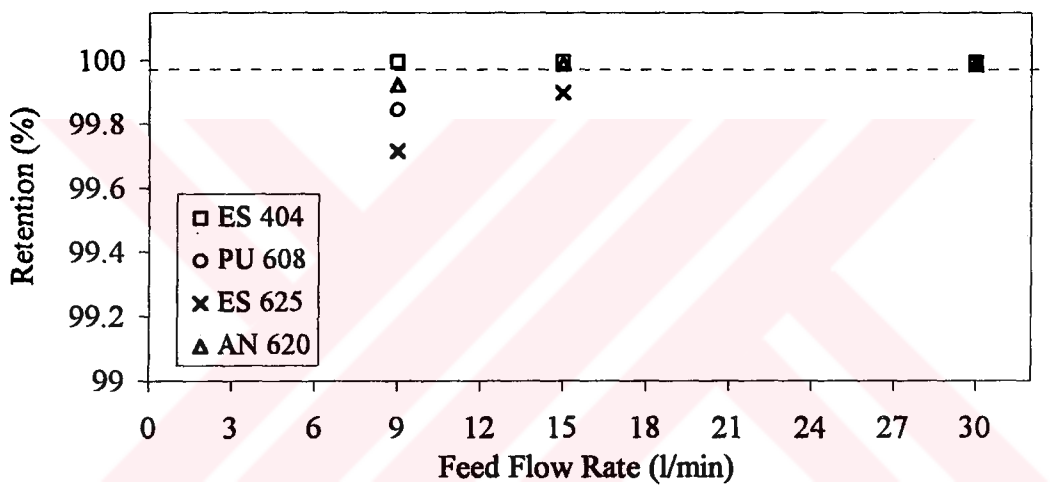


(c)

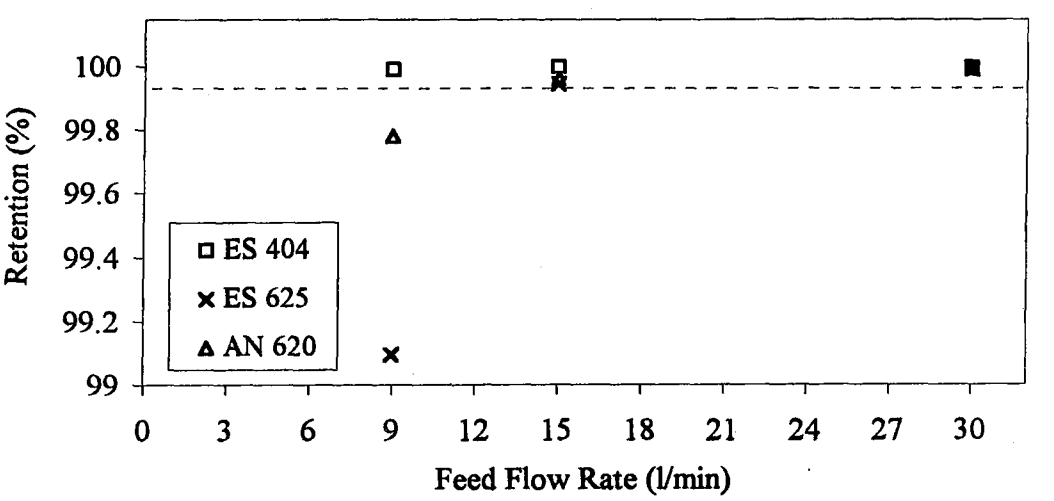
Figure 5.9 The effect of feed flow rate on permeate flux at 4 bar (a), 6 bar (b) and 10 bar (c) pressure differences



(a)



(b)



(c)

Figure 5.10 The effect of feedflowrate on retention (%) at 4 bar (a), 6 bar (b), and 10 bar (c) pressure differences

5.3 FOULING OF MEMBRANES

Fouling of membranes are determined in terms of pure water fluxes measured before and after emulsion filtration experiments. Although fouling includes different mechanisms like pore narrowing, cake layer formation, pore blocking and adsorption, the fouling analysis in terms of pure water fluxes will not differ between these mechanisms and is a macroscopic approach to fouling as mostly done in the literature. Fouling can be overcome by adopting cleaning procedures. The efficiency of a cleaning procedure is generally evaluated by pure water flux measurements although this comparison gives no information on the surface properties of the membrane.

Pure water flux values of ES625, ES404, AN620 and PU608 membranes before and after emulsion experiments are used to calculate flux decline values as follows:

$$\text{Flux decline (FD)} = \frac{J_{pwf,after}}{J_{pwf,before}} \qquad (5.1)$$

Similarly flux recovery value can be calculated using pure water flux values before and after cleaning procedure as follows:

$$\text{Flux Recovery (FR)} = \frac{J_{pwf,cleaned}}{J_{pwf,uncleaned}} \qquad (5.2)$$

Flux decline values of all membranes and the effect of acid and caustic cleaning on the flux recovery of fouled membranes are presented in Table 5.2.

All membranes showed flux loss after emulsion experiments. This phenomena is more prominent for ES625 where there is an important decrease in pure water flux resulting in a very low flux decline value indicating high fouling. Although AN620 has a lower initial flux, it has the highest flux recovery which means that fouling is less effective for this membrane. AN620 polyacrylonitrile membrane is hydrophillic. This property favors passage of water while avoiding oil-membrane interactions.

It has been concluded in section 5.1 that acid cleaning damages PU608 polysulphone membrane so this type of cleaning is omitted for PU608. Acid cleaning has decreased the pure water fluxes of each membrane except AN620. As there is little fouling for AN620 membrane, acid cleaning does not make much difference.

Caustic cleaning improved all fluxes except ES404 as this type of cleaning has ability to clean organic materials. Caustic cleaning with the addition of sodium lauryl sulphate (SLS) is preferred for all membranes. Addition of SLS results in improved fluxes as shown in Table 5.3.

Table 5.3 Effect of SLS addition in caustic cleaning

Membrane	Pure water flux after caustic cleaning ($l/min*m^2$)	Pure water flux after SLS added caustic cleaning ($l/min*m^2$)
ES625	0.07	1.25
ES404	0.04	0.16
PU608	0.13	0.51

Both acid and caustic cleaning results in nearly the same flux recoveries for AN620. The highest flux recovery between the other three membranes belongs to ES625 which is followed by AN620 and PU608 with nearly the same flux recovery values. Both caustic and acid cleaning of ES404 caused even more decline in pure water flux compared to the flux value after emulsion experiments indicating that ES404 is damaged by both cleaning procedures.

Table 5.2 Fouling of membranes

Membrane	$J_{pwf,\ new}$ ($l/min*m^2$)	$J_{pwf,after}$ ($l/min*m^2$)	$\frac{J_{pwf,after}}{J_{pwf,\ new}}$	$J_{pwf,acid\ clean.}$ ($l/min*m^2$)	$J_{pwf,caustic\ clean}$ ($l/min*m^2$)	$FR_{acid\ clean}$	$FR_{caustic\ clean}$
ES625	5.03	0.04	0.008	0.02	1.25	0.50	31.25
ES404	1.72	0.33	0.19	0.02	0.16	0.06	0.48
AN620	0.99	0.75	0.76	0.8	0.83	1.13	1.07
PU608	4.43	0.47	0.11	-	0.51	-	1.09

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Four commercially available ultrafiltration membranes are used in this thesis to separate oil-water emulsions of 3.9 vol % oil concentration. Furthermore, the effect of pressure difference and feed flow rate on the flux and retention values of the membranes has been investigated.

This study has demonstrated that oil-water emulsions can be separated succesfully generating permeates with oil content below discharge limits (20 mg/l) of 1988-Water Pollution Control Regulation when a suitable membrane is used.

Highest retention values has been obtained with polyethersulphone membrane with a MW cut-off value of 4000 which is the lowest cut-off value within the membranes used. Polysulphone membranes with a MW cut-off value of 8000 shows the lowest retention values producing permeates of undesired quality, although its MW cut-off value is fairly low indicating high pore density and wide pore size distribution.

Polyethersulphone and polyacrylonitrile membranes with the same MW cut-off value (25000) exhibited different flux values because of differences in their pore densities. On the contrary polysulphone membrane (8000 MW cut-off) gives high fluxes considering its MW cut-off value indicating high pore density. The polyethersulphone membrane with 4000 MW cut-off value is a tighter membrane and hence it has relatively lower fluxes.

Polyethersulphone membrane with a MW cut-off value of 25000 and the polysulphone membrane of 8000 MW cut-off value are the two membranes which are highly fouled and exhibit considerable flux decline. Polyacrylonitrile membrane (MW cut-off 25000) is less influenced from fouling and has exhibited vey little flux decline.

Acid cleaning affects membrane structure of the polysulphone membrane and damages it. Polysulphone and polyethersulphone membrane (MW cut-off 4000) are the membranes that both acid and caustic cleaning has not been succesfull while caustic cleaning seems to improve the flux properties of polyacrylonitrile (MW cut-off 25000) and polyethersulphone (MW cut-off 25000) to a certain extent. Better cleaning methods for both new and fouled membranes needs to be found. Addition of sodium lauryl sulphate to caustic cleaning may be worthwhile to try.

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