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**Ceramic Membrane Technology Applied to Oily
Wastewater Separation**

Candidate for Doctor of Philosophy

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Department of Civil and Structural Engineering

The Hong Kong Polytechnic University

July 2006



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Wastewater Separation**

HUA Feng Lin

A thesis submitted in partial fulfillment of the requirements for
the Degree of Doctor of Philosophy

Department of Civil and Structural Engineering

The Hong Kong Polytechnic University

CERTIFICATE OF ORIGINALITY

I hereby declare that this thesis entitled “Ceramic Membrane Technology Applied to Oily Wastewater Separation” is original and has not been accepted for the award of any other degree or diploma. It does not contain any material, partly or wholly, published or written by others, except those references quoted in the text.

HUA Feng Lin

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ABSTRACT

Hong Kong has also been working rigorously to improve its water quality since the 1980s. The implementation of the first stage of the Harbour Area Treatment Scheme (HATS) has resulted in great improvement in the water environment in Victoria Harbour which was one of the most seriously polluted areas in Hong Kong. According to the report of the Drainage Services Department (DSD) in 2003, the trade effluent surcharges collected from the restaurant industry reached as high as 72.4% of surcharges collected from all trade types. One of the main reasons was due to the ineffectively control of oil concentrations in wastewater under the existing oil-trap method.

Membrane separation is becoming a promising technology for the 21st century. Membrane separation technology has several advantages such as stable effluent quality, no chemicals addition, small area occupied, a high volume concentration ratio achieved.

The main work presented in this thesis includes: 1) the examination of the feasibility of ceramic membrane in treating restaurant oily wastewater; 2) the proposal of the filtration resistance model and development of non-stable prediction models for permeate flux and cumulative volume of permeate.

On the feasibility research of ceramic membrane filtration, the effects of wastewater (feed solution) nature and operating conditions on the ceramic membrane filtration are identified. The contributions in this part of research are:

1. To understand membrane characterization by operating the filtration process under various separation conditions using pure water as feed solution;
2. To identify the effect of transmembrane pressure (TMP), crossflow velocity (CFV), oil concentration, temperature, salt concentration and pH on the permeate flux and permeate quality, and the influence of salt concentration and pH on the size and zeta potential of emulsion droplet as well.
3. To compare the effect of membrane cleaning under different chemical cleaner, and propose a protocol for membrane cleaning.
4. To design a plan for oily wastewater treatment with ceramic membrane technology.

On the mechanism research of ceramic membrane separation, filtration resistances and four kinds of separation mechanism are reviewed. A new method to observe the variation of various resistances under different operating

conditions is proposed. Models for predicting permeate flux and cumulative volume of permeate are developed. The contributions in this part of research are:

1. A new method to calculate the filtration resistances is proposed according to the different permeate fluxes determined in the various stages of the filtration process. The variations of filtration resistances under different operating conditions are presented.

2. Non-stable prediction models for permeate flux and cumulative volume of permeate are developed using one set of experimental data, and are verified using another set of experimental data. The results show good correlation between experimental data and predicted data.

3. The factor which has significant effect on the filtration process is identified using the sensitivity analysis method.

This research has provided a theoretical basis and practical evidence for the application of ceramic membrane on the oily wastewater treatment. These experimental results will be of benefit to process design of oily wastewater treatment system, and contribution to the reduction of water pollution.

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LIST OF ABBREVIATIONS

λ	= the ratio of solute size to membrane pore size
μ	=viscosity
μ_T	=viscosity at T°C
μ_0	=viscosity at 0°C
ρ	=density
ω	=angular velocity
A.C.	=alternating current
ANOVA	=analysis of variation
APF	=adsorptive particulate flotation
BOD ₅	=biological oxygen demand
C_{ave}	=the average oil concentration in the permeate
C_f	=concentration in the feed solution
C_{feed}	=oil concentration in the feed solution
C_g	=concentration in the membrane surface
C_p	=concentration in the permeate stream
C_t	=oil concentration at time t
CF	=concentration factor
CFV	=crossflow velocity
COD	=chemical oxygen demand
CONC	=oil concentration
d	=diameter
d_s	=the solute diameter
d_p	=pore diameter of the membrane
D.C.	=direct current
DA	=demulsifying activity

DAF	=dissolved air flotation
DLVO	=Derjaguin-Landau-Verwey-Overbeek
DSD	=Drainage Services Department
ECF	=electrolytic coagulation/flotation
EDTA	= ethylenediaminetetraacetic acid
HATS	=Harbour Area Treatment Scheme
I	=ion strength
IAF	=induced air flotation
$J(t)$	=permeate flux at time t
J_{ave}	=the time-average permeate flux
J_i	=the initial pure water flux for a given membrane,
J_f	=the final pure water flux for the membrane that has been cleaned
and	
J_p	= the pure water flux before the fouled membrane cleaned,
J_w	=the steady-state wastewater flux,
MF	=microfiltration
min	=minute
MPa	=million Pascal
NF	=nanofiltration
O/W	=oil in water
P	=pressure
PHC	=petroleum hydrocarbons
Q_f	=the volume of the initial feed solution
Q_p	=the permeate volume
R	=rejection
R_a	=adsorptive resistance
R_{ap}	=adsorptive and pore blocking resistances
R_c	=concentration polarization resistance

R_{cg}	=concentration polarization and gel-layer resistances
R_g	=gel-layer resistance
R_m	=membrane resistance
R_{ir}	=irreversible resistance
R_p	=pore blocking resistance
R_t	=total resistance
Re	=Reynolds number
RO	=reverse osmosis
S.D.	=standard deviation
SA	=sensitivity analysis
SS	=suspended solid
TMP	=transmembrane pressure
TOC	=total organic carbon
UF	=ultrafiltration
VR	=volume reduction
V_t	=permeate volume at time t
W/O	=water in oil
WFR	=water flux recovery
Y	=recovery

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CHAPTER ONE

INTRODUCTION

1.1 Water Environment in Hong Kong

Hong Kong has a land area of 1104 km² and a population of nearly 7 million (Hong Kong Census and Statistics Department, 2005). About two thirds of Hong Kong's population resides around the Victoria Harbour, resulting in a population density of 1000 residents per hectare. Population growth, concentrated economic activities, and a lack of measures of pollution control in the past have resulted in severe environmental problems. In the beginning of 1990s, only 10% of wastewater received secondary treatment, 40% was screened and macerated, the remaining 50% entered the coastal waters either directly or indirectly via stream without any treatment. These had led to deterioration of aquatic and marine ecological system, closure of beaches, occurrences of red tides, bioaccumulation and contamination of seafood (Chua *et al.*, 1995; Hong Kong Environmental Protection Department, 1992).

Currently, out of all 2.5 million cubic meters of wastewater generated each day, 98% of them have been treated. The deterioration in water environment is efficiently controlled in the whole territory (Hong Kong Environmental Protection Department, 2004). However, as described in the Drainage Services Department report (Hong Kong Drainage Service Department, 2004), the trade effluent surcharges (TES) collected from restaurant industry reached as high as 72.4% of surcharges collected from of all trade types, while water consumption only accounted for 16.4% (Hong Kong Food and Environmental Hygiene Department, 2004). This revealed the restaurant wastewater is one of the main pollution sources. Restaurant wastewater contains high content of oil and grease (Table 1.1) (Chen et al., 2000a). This causes a lot of problems during pipeline conveyance and biological treatment. Over time, grease deposits get larger as more grease and other solid material builds up. They reduce the capacity of sewer pipes and cause sewage overflows, offensive odour and an unhealthy environment. In addition, after reaching the municipal wastewater treatment works, they can be neither easily decomposed biologically nor simply treated by other conventional means. Excess oily wastes will inhibit natural biological activities in the treatment plant, in the worst scenario, requiring the plant to re-seed their bacterial colonies with a selected, specially adapted product to re-activate the system. Lastly, as oil floats on water surface, it deters oxygen transferring from air to water. This will result in deterioration of water quality

Table 1. 1 Characteristics of restaurant wastewaters.

Parameters	Chinese restaurant	Western restaurant	American fast food	Permission standards
pH	6.62-7.96	6.94-9.47	6.30-7.23	6-10
COD, mg/L	292-3390	912-3500	980-4240	3000
BOD ₅ , mg/L	58-1430	489-1410	405-2240	1200
Oil & grease, mg/L	120-712	53-2100	158-799	100
SS, mg/L	13-246	152-545	68-345	1200

and affect the growth of aquatic lives.

According to the regulation of the waste water discharges under the “Water Pollution Control Ordinance”, restaurants owners are required to ensure their discharges meet statutory standards. Moreover, imposing stringent regulation to the effluent is the main trend in the future. It is very urgent to take measures to treat the oily wastewater effectively.

1.2 Oily Wastewater and Current Treatment Technology

The study on industrial oily wastewater separation has been conducted for several decades. So far, there are several techniques for oily wastewater separation and treatment. Typical ones for separation of oily wastewater include physical methods, chemical methods and biological methods. The detailed information is described in Section 2.2 – 2.4.

Membrane separation of liquids has enjoyed increasing popularity over the last 30 years and is becoming a promising technology for the 21st century (Porter, 1972; Lee *et al.*, 1984; Lipp *et al.*, 1988; Akay *et al.*, 2002; Melnyk *et al.*, 2005).

Membrane technology has shown several advantages:

1. The technology is more widely applicable across a wide range of industries. The quality of the effluent is more uniform regardless of influent variations.
2. Membrane technology can be used in-process to allow recycling of selected waste streams within a plant.
3. Membrane separation can obtain a high volume concentration ratio. No extraneous chemicals are needed, making subsequent oil recovery easier.

4. Membrane equipment occupies a smaller space, which fits for operation in the limited space.
5. Energy costs are lower compared to thermal treatments.
6. The membrane separation process can be highly automated and does not require highly skilled operators.

Investigation of the membrane separation processes for oily water treatment has been started since 1970s. There were a number of reports on membrane application, particularly in ultrafiltration (UF) and reverse osmosis (RO) (Lee *et al.*, 1984; Chiang and Cheryan, 1987; Daiminger *et al.*, 1995; Cho *et al.*, 2000; Qdais and Moussa, 2004; Kim and Lee, 2006). In those studies, most membranes were made up of organic materials. Organic membranes are sensitive to both polar and chlorinated solvents, as well as highly oil fraction. Applications of inorganic ceramic membrane are becoming popular (Anderson *et al.*, 1987; Hyun and Kim, 1997; Cheryan and Rajagopalan, 1998; Saminario *et al.*, 2002; Velasco *et al.*, 2003), however, few studies have reported on the oily wastewater with ceramic membrane filtration.

1.3 Objectives

The main objective of this research is to study the feasibility of the use of ceramic membrane for oily wastewater treatment and to propose the resistance model and non-stable prediction models. The specific objectives of this study are summarized as follows:

- 1) To understand characteristics of membrane filtration process.
- 2) To identify the effect of transmembrane pressure (TMP), crossflow velocity (CFV), oil concentration and temperature on the permeate flux and permeate quality.
- 3) To conduct restaurant wastewater treatment by ceramic membrane.
- 4) To design protocol for membrane cleaning.
- 5) To identify the effect of salt concentration and pH on the separation process and stability of emulsion droplets.
- 6) To propose the modeling of filtration resistance.
- 7) To develop the modeling of permeate flux and cumulative volume of flux.

1.4 Organization of the Thesis

This thesis is divided into eight chapters. The present chapter includes introduction of water environment in Hong Kong, current oily wastewater treatment technology, and objectives of this study. A detailed literature review is presented in Chapter Two. Chapter Three introduces the methodology of this research. Chapter Four studies the membrane filtration characteristics using distilled water as feed solution. Chapter Five concentrates on the study of factors that affect the microfiltration process of oily wastewater. Chapter Six investigates the effect of salt and pH on the stability of emulsion droplet as well as filtration process. Chapter Seven develops the models on filtration resistances, permeate flux and cumulative volume of permeate. Finally, Chapter Eight gives general conclusions of this study.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

2.1.1 Status of Oil Phase

Oil and water are immiscible fluids. That is, when mixed they do not go into solution or form a third and unique chemical compound. When a small amount of oil is mixed with a much large amount of water, a portion of the oil is suspended in the form of small droplets.

Oily wastewaters are often placed into three broad categories according to the distribution of the oil phase as follows: free-floating oil; unstable oil-water emulsions; stable oil-water emulsions. Oil may be combined with water in any of the following forms (Fleischer, 1984; Cardew and Le, 1998):

1. Primary Dispersion: Droplets above 50 micron diameter. These have a significant rising velocity in water and will be separated by gravity devices.

2. Secondary Dispersion: Droplets in the range of 3~50 micron diameter. These have progressively smaller rising velocities and may only be separated by special media arrangements designed to affect the surface energies of the droplets.
3. Mechanical Emulsions: Droplets below 3 micron. These are unlikely to be separated by physical processes. Separation may be facilitated by the addition of certain chemicals.
4. Chemical Emulsions: Droplets less than 2 micron diameter on which surfactants are adsorbed and create a potential barrier inhibiting the coalescence process. Separation is able only by chemical means.
5. Microemulsions: Thermodynamically stable colloidal dispersion. Coalescence would produce an increase in free energy, and hence does not occur. Such dispersions are created by using an amphiphatic molecule.
6. Dissolved Hydrocarbons (including oil): Some oils, particularly the lighter fractions will be soluble in water and cannot be separated by physical methods.

Oil dispersions are often not homogenous, but may comprise a mixture of several of the above types of dispersions.

2.1.2 Movement of Oil Droplets

By assuming that these droplets are spherical, rigid, non-interacting and suspended in a vortex free fluid their behaviour can be described by simple equation known as Stokes' Law. According to Stokes' Law when a droplet of oil is placed in water, the buoyancy of the lighter oil causes it to rapidly accelerate upward. As the droplet accelerates, the drag force also increases rapidly. These forces are so large that the droplet quickly reaches a terminal velocity. For all practical purposes, the acceleration distance and time are so small that they can be ignored. The terminal velocity is given by the following expression:

$$V = (\rho_p - \rho_l) g d^2 / 18\mu \quad (2.1)$$

where V is the velocity of sedimentation; ρ_p is the density of particle; ρ_l is the density of liquid; d is the diameter of particle; μ is the viscosity of the liquid; g is gravitational force. The behavior described by the above Eq. (2.1) has some very important consequences, including: Although V depends on the factor $(\rho_p - \rho_l)$, in a liquid of low uniform density, d^2 is generally the more important factor, expect for very dense or very light particles; A particle will settle down if $\rho_p > \rho_l$ and if $\rho_p < \rho_l$ then V will be negative and the particle will float up through the liquid rather than sediment.

2.2 Physical Separation Methods

2.2.1 Gravity Settling Separation

Gravity separation utilizes the difference in specific gravity between the particle and water. An ideal settling basin can be defined as a tank in which settling occurs in the same manner as in a quiescent settling container of the same depth. The basin consists of four zones (Figure 2.1). The inlet zone is a region where the incoming suspension is distributed uniformly over the cross section of the tank. In the settling zone the particles settle at the same rate as they would be in a quiescent fluid. The direction of fluid flow is horizontal and the fluid velocity is constant at all points in the settling region. At the outlet zone, the clarified liquid is collected uniformly over the cross section of the basin. The solids collect in a sludge zone at the bottom of the tank. All particles reaching the sludge zone are permanently removed from the suspension.

2.2.1.1 Oil Gravity Separator

Gravity type separators are the most common devices employed in oily

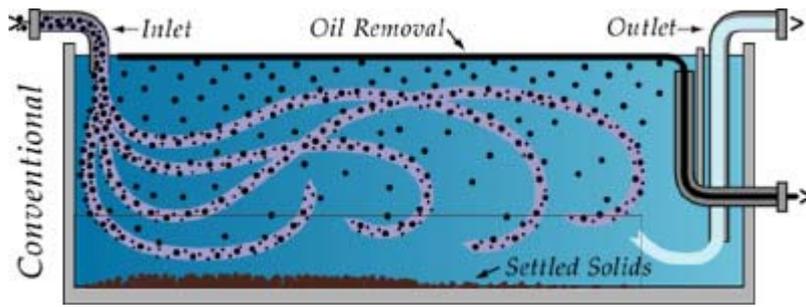


Fig.2. 1 Oil gravity separator.

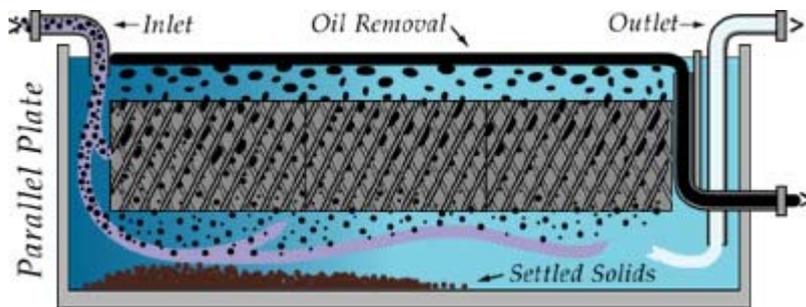


Fig.2. 2 Parallel plate for oil coalescing.



Flow Range 1-5200 GPM

Fig.2. 3 Pan American Environmental oil/water separator.

wastewater treatment. The treatment process normally involves retaining the oil waste in a holding tank and allowing gravity separation of the oily material, which is then skimmed from the wastewater surface. Theoretically, the separation process in gravity separators can be predicated by Stoke's law, but turbulence and short-circuiting are common. Thus, in practice, the effectiveness of a gravity separator depends upon proper hydraulic design, and design period of wastewater retention. Longer retention times allow better separation of the floatable oils from the water. The influence of retention time on separator efficiency for a refinery wastewater is reported by Wallace *et al.* (1965). Short detention times of less than 20 minutes resulted in less than 50% oil-water separation, while more extended holding periods improved oil separation from the waste stream.

2.1.1.2 Mechanical Coalescence Separator

Oil droplet size is such a very important factor in separator performance. Separation efficiency increases with the increase of the oil droplet size. Small droplets are difficult to be separated. Under this circumstance, one modified method of coalescing media plates is often proposed in order to produce larger oil droplets (Figure 2.2). This design, when designed properly (or even

improperly) provides a certain tank length, width and depth that provide a wide, quiet spot in the pipeline to give oils time to rise.

Oil droplets rise a short distance before encountering the oleophilic, coalescing media plates inside the separation chamber as opposed to rising a great distance in gravity separation. Upon impinging on the plates the oils coalesce (gather) into larger droplets until the droplet buoyancy is sufficient to pull away from the media and raise the water's surface. By using the coalescing media, the size of the tank is reduced and a higher performance is attained than by gravity separation.

One example of industrial application is Pan American Environmental Oil/water Separator (Figure 2.3). This separator provides a laminar flow path that creates a quiescent zone to facilitate the impact with and attachment of oils to the media surface by reducing waste stream turbulence and velocity. This control of the waste stream creates a more ideal environment for oil removal. Due to oil typically being lighter than water, oil droplets rise over the coalescing plate. As the oil droplets rise up the plate they will coalesce or come together with other droplets, creating progressively larger droplets.

American Petroleum Institute (API) separator utilizes the mechanical equipment to promote coalescence to form larger oil droplet through the change of state of fluid motion, then larger droplet rise to the surface and is separated. Usually, the API separator is a rectangular trough with 3-10 ft wide, and 50-150 ft long. It is the standard for many industries. The circular separator has the advantage of taking up less space. The parallel-plate separator can be more compact. But each of these separators can be designed to remove all droplets larger than 0.015 cm in diameter.

Gravity settling separator relies on gravity to separate the phases, and therefore requires longer processing times. In some cases settling does not occur even after extended periods simply because the force of gravity is insufficient to separate the oil and water. The maximum obstacle of application of this method owes much to spending long time, occupy large space, and obtain low efficiency.

2.2.2 Centrifugal Separation Method

Centrifugation process is widely used in separating liquids of different density, thickening slurries, or removing solids. Centrifugation breaks oil emulsions by

separating the oil and water phases under the influence of centrifugal force. The principles of centrifugation are the same as gravity sedimentation separation, but an additional force is involved due to the radial acceleration imposed on the particles by the rotating centrifuge basket. The particles experience a radial centrifugal force moving them away from the axis of rotation. The centrifugal force (F) is expressed as in Eq. (2.2):

$$F = m\omega^2r \quad (2.2)$$

where F is magnitude of the centrifugal force; m is effective mass of the particle; ω is angular velocity; r is distance of the particle from the axis of rotation.

Centrifuges are traditionally classified into three groups according to the maximum speed they can achieve. Low-speed centrifugals generally have a maximum speed up to 7 000 rpm, high-speed centrifugals - up to 21 000 rpm and ultracentrifugals above 21 000 rpm. Centrifugation is best applied to oily sludge and is generally not used in treatment of the typical dilute oily waste stream, unless the volume is small.

Beccari *et al.* (1999) carried out laboratory-scale treatment of olive oil mill effluents. They found centrifugation turned out to be preferable for small volumes of separated phase. In another treatment process (Chalmers, 1972), a

mobile heating plus centrifugation process applied to treat an oily waste at 45 m³/week. In the separation process, magnesium chloride was added, the waste was heated to 95 °C for 3 - 15 minutes, and centrifuged. Oil concentration reduced from initial levels of 2 000 - 4 000 mg/L to effluent values of 22 - 89 mg/L.

Centrifuges will not of themselves break a stable emulsion. Used with chemical demulsifiers they are effective in a variety of commercial applications. As a whole, centrifuges are not as widely used for oil/water separation as some other methods. They are justified where there is a relatively low-volume, high-value material to recover or where rapid separation is necessary.

2.2.3 Air Flotation

Dissolved air flotation (DAF) is a process for removing suspended particles from liquid by bringing the particles to the surface of the liquid. Air is dissolved at high pressure in a saturator, and microbubbles are formed when water is released in the flotation cell at atmospheric pressure. The microbubbles become attached to the particles increasing their buoyancy and allowing them to rise to the surface. The production of microbubbles is considered to be important as the

rising velocity of the bubbles is less than for larger bubbles (De Rijk and Van Der Graaf, 1994). This ensures a longer residence time in the flotation tank allowing more opportunities for collisions between bubbles and particle. Three operating configurations of DAF systems exist (Rykaart and Haarhoff, 1995):

(a) Full-flow pressure flotation, where the influent is pressurised and then released in the flotation tank where the bubbles are formed. This is commonly used for particles, which do not need flocculation but require large volumes of air bubbles.

(b) Split-flow pressure flotation, where part of the influent are pressurised and directly introduced to the flotation tank. This is employed in applications where suspended particles are susceptible to the shearing effects of pressure pump, also where suspended particles are at low concentration and thus have a low air requirement.

(c) Recycle-flow pressure flotation, where a portion of treated wastewater is pressurised and recycled to the flotation tank. This is generally employed where coagulation and flocculation are needed and the flocculated particles are mechanically weak. Recycle-flow pressure flotation is used more often than the

others for applications including oil removal (Zouboulis and Avranas, 2000; Al-Shamrani *et al.*, 2002).

Air flotation is commonly employed as an alternative to destabilization of an oily emulsion, to separate the oil and water (Stricklank, 1980). Shamrani *et al.* (2002a) reported the results of separation of oil from water by DAF. In their experiment, synthetic industrial effluent was prepared by stabilising low concentrations of oil in aqueous dispersion with a non-ionic surfactant (Span 20) and DAF was used to clarify this wastewater. Results indicated that a saturator efficiency of about 90% was achieved and it was found that increasing the working pressure of saturator had less effect in the separation of oil droplets than increasing recycle ratio. Optimum conditions for separation are obtained with an air to oil ratio of 0.0075 corresponding to a recycle ratio of 10%. They found an inversion of the oil droplets charge even at very low polyelectrolytes concentration, however, it was ineffective in enhancing the separation. In contrast, when aluminum sulphate was used it was found that it is important to decrease the magnitude of zeta potential in order to decrease electrostatic repulsion so that the emulsion was destabilised prior to flotation.

Tansel and Pascual (2004) studied the operational variables of the DAF process on removal efficiency of petroleum hydrocarbons (PHC) from water sources contaminated with fuel oils. The operational variables of the DAF process were

compared for both batch and continuous modes of operation by a factorial analysis. The factorial analysis of the experimental results showed that for the batch mode of operation, all four operational variables investigated (i.e., detention time, influent PHC concentration, coagulant use, and source water type) had a significant effect on PHC removal. However, for the continuous DAF runs, the only variable that was significant at the 95% confidence level was the run time. The coagulant use did not have a significant effect on PHC removal efficiency.

Another way of air flotation is induced air flotation (IAF). In IAF a rotor forces the liquid through the dispenser orifice, creating a negative pressure that draws air down into the liquid, generating the desired small air bubbles. IAF has also been used extensively in the removal of stable oily emulsions (Strickland, 1980; Bennett, 1988; Belhateche, 1995). IAF utilizes bubbles between 40 -1 000 μm in size and turbulent hydrodynamic conditions. The process has low retention times, normally < 5 minutes. Conversely, DAF employs micro-bubbles (30 - 100 μm), and quiescent regimes. IAF normally represents a lower capital investment and smaller space requirements than does DAF. However, in DAF, retention times are higher (20-60 minutes), this process is inefficient when treating high volume effluents and high flow-rates.

Air flotation combined with adsorbents was studied to improve removal efficiency. In the adsorptive particulate flotation (APF) process contaminants are adsorbed (and/or absorbed) onto the surface of a particulate carrier and both are separated attached to rising bubbles. Feris *et al.* (2004) reported that high separation values were found for oil droplets—emulsified in water by APF (IAF or DAF) using mineral particles or coal wastes as carrier. Treated solutions had very low content of oil, lower than emission limits.

Chemical flocculating agents such as salts of iron and aluminum, with or without organic polyelectrolytes, are particularly helpful in improving the effectiveness of the air flotation process. In industrial application of DAF, 60 - 80% of oil removal was achieved by direct air flotation, and 90% removal upon addition of chemical coagulant (Quigley and Hoffman, 1966; Schuldt and Suffoletta, 1975; Shamrani *et al.*, 2002b; Meyssami and Kasaeian, 2005).

Although air flotation presents high efficiency in the oily wastewater separation, strict control of operating conditions and elaborate fabrication of treatment facility is needed. Sometimes, chemical pre-treatment is often needed in order to improve the performance of contaminant removal.

2.2.4 Heat Treatment Methods

Heating is a common demulsification method. The demulsification is achieved by heating the oil/water emulsion to high temperature. The explanation of heat treatment probable is that this accelerates any chemical reaction that may be going on, changes the nature of the interfacial film and reduces the viscosity so that conditions favorable to demulsification are produced. The oil density decreases faster than the density of the water (oils have a larger coefficient of expansion than water). Elevated temperature also increases the solubility of the surfactants in both the oil and water phases, thus weakening the interfacial film (Lissant, 1986), thus allowing the coalescence (Vega and Delgado, 2002).

As a modification of heat treatment, freeze-thaw (F/T) method was tested recently. When emulsions freeze, the lipid droplets become progressively concentrated into the freeze concentrate phase thereby coming into close contact with one another in the unfrozen aqueous channels between ice crystals. The concentration of the lipid droplets in these narrow channels could promote aggregation, flocculation and/or coalescence during the freeze-thaw process (Komatsu *et al.*, 1997; Saito *et al.*, 1999).

Jean *et al.* (1999) employed freeze/thaw method to separate oil from oily sludge. The freeze/thawed sludge comprised three distinct layers, an oil layer at the top, a sediment layer at the bottom and a water layer locating in between. The method could separate over 50% of its oil content. However, ultra-fast freezing is not beneficial for oil separation.

Another report on this method was from Chen and He (2003). They used the oil sludge generated from the pretreatment step of the used lubricating oil re-refinery and contained complex and tight water/oil emulsion with water content varying from 38% to 77% (wt). Centrifuging or gravitational settlement at elevated temperature did not show significant effects on water separation, and the usage of inorganic chemicals and the typical demulsification agents from oil fields gave satisfactory results neither. However, freeze/thaw method removed near 90% of water. The demulsification was achieved due to the expelling of surfactant molecules from the ice lattices during freezing and the forming of surfactant micelles during thawing. An optimal freezing temperature was found to be around the point where water droplets were all frozen, about -40 °C, and the best thawing conditions found were either in ambient air or in water bath at a temperature below 20 °C. Sufficient freezing time was required for the removal of water to reach its maximum value (He and Chen, 2002).

In the works of Xia *et al.* (2003) and Rajakovic and Skala (2005), method of the combined use of F/T and microwave radiation (MWR) for separation of water-in-oil emulsion was study. They have proved that MWR is a very effective method for demulsification of oil-in-water (O/W) emulsion. The results from their experiment indicated the optimal demulsification was achieved at -40 °C for 20 hours during freezing period. This long time was necessary because the inner part of emulsion has to be completely frozen and surfactants expelled from the ice lattices, parallel with new micelles forming (Rajakovic and Skala, 2004). Three sets of thawing procedure were applied in their experiment. They are: in ambient air at 20 °C for 5 hours, in water bath at 40 °C for 5 hours and in microwave oven for 3.5 minutes. Compared with water bath and ambient air, MWR was the most efficient thawing procedure.

As a whole, heating the oil-water emulsion is not generally recommended when light fuels such as gasoline, jet fuel, kerosene, and other solvents are present and could result in a fire hazard. Another deficient is long time required during freezing process.

2.2.5 Electrical Treatment Methods

Electrical separation is a simple and effective method for treating water and wastewater. It has been tested successfully to treat potable water, textile wastewater, chemical fiber wastewater and urban wastewater (Matsui *et al.*, 1980; Vik *et al.*, 1984; Lin and Peng, 1996; Lin and Chen, 1997; Lin and Lin, 1998; Mostefa and Tir, 2004). Four processes utilize electricity for the destabilization and separation O/W and water-in-oil (W/O) emulsion: electrostatic coalescence, electrooxidation, electroflotation and electrocoagulation.

Electrical coalescence are based on one of the two mechanisms, the forces exerted on particles having net charges, and the forces between neutral particles resulting from their acquiring induced dipoles on an A.C. or D.C. field. More early as 1911, Cottrell (1911) observed that emulsions coalesce more quickly when subjected to an electric field than gravity alone. The petroleum industry uses electrostatic coalescence to separate brine emulsified in crude oil. When a D.C. field is applied, water molecules orient and move in the direction of the applied field. When an A.C. field is applied, motion occurs in the direction of maximum field strength (dielectrophoresis mechanism) (Pohl, 1951). Pearce (1954) applied an electric field to a 10% water-in-oil emulsion, he observed

under a microscope that the water molecules form chains of droplets that are oriented along the direction of the applied field. This chain formation and elongation of water droplets can also disturb the thin film between droplet surfaces and lead to coalescence (Kriechbaumer and Marr, 1985).

Effects of the dispersed phase hold-up, the applied voltage and the frequency on the phase separation rate were studied by Mori *et al.* (1994). The separation rate was larger for lower initial hold-up of the dispersed phase. When the initial hold-up was less than 40%, the coagulation stage preceded the coalescence stage and the separation rate decreased. The separation rate increased approximately with the second order of the applied voltage. It also increased with frequency and tended to become constant at frequencies in the range of 1000 to 2000 Hz. The water content of the separated oil phase decreased with increase in frequency.

Israilides *et al.* (1997) treated olive oil wastewater (OOW) by using electrooxidation method (Figure 2.4). In their experiment, using Ti/Pt as anode and Stainless Steel 304 as cathode, sodium chloride 4% (w/v) as an electrolyte was added to the wastewater and the mixture was passed through an electrolytic cell. Due to the strong oxidizing potential of the chemicals produced (chlorine, oxygen, hydroxyl radicals and other oxidants) the organic pollutants were wet

oxidized to carbon dioxide and water. After 1 and 10 h of electrolysis at 0.26 A/cm², total COD was reduced by 41 and 93%, respectively, total TOC was reduced by 20 and 80.4%, and total phenolic compounds were reduced by 50 and 99.4%. However, the mean energy consumption was 1.273 kWh per kg of COD removed and 12.3 kWh per kg of COD removed for 1 and 10 hours, respectively. These results strongly indicated that this electrolytic method of total oxidation of OOW only could be used as an oxidation pretreatment stage for detoxification of the wastewater.

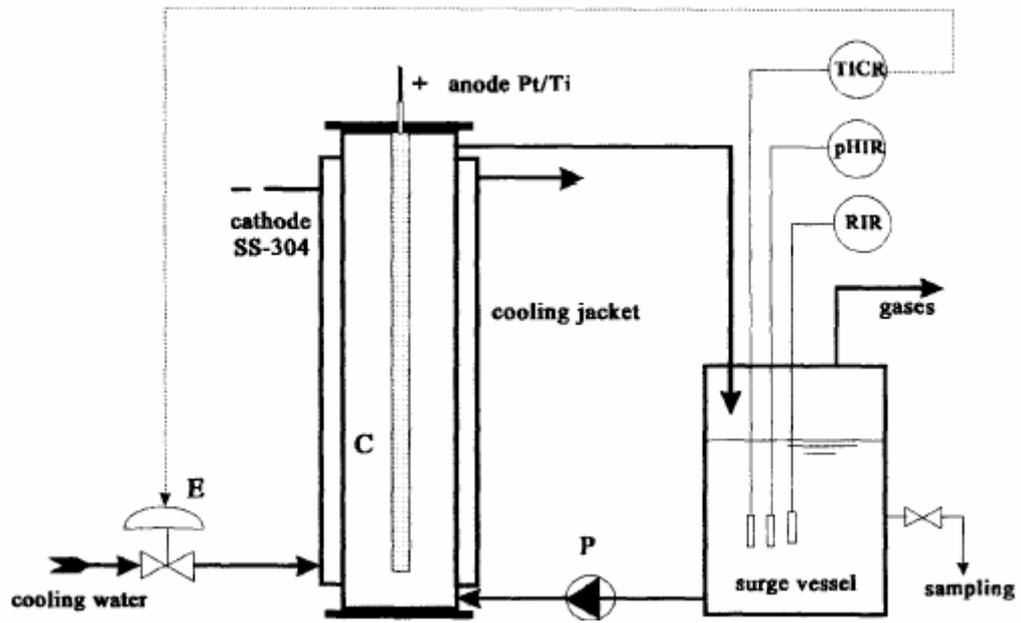


Fig.2. 4 Olive oil wastewater treatment using electrochemical method.

Electroflotation technology is an alternative to air flotation to induce small gas bubbles formed at both electrodes through the electrolysis of water to oxygen and hydrogen gas. Applications, at an industrial scale, have been in the area of removal of light colloidal systems such as emulsified oil from water, ions, pigments, ink and fibers from water (Cottrell, 1976; Renk, 1988; Zabel, 1992; Zouboulis *et al.*, 1992). The disadvantages of this method are the low throughput, the emission of H₂ bubbles, electrode costs and maintenance and the voluminous sludge produced. The recent development of lead dioxide electrodes has improved the economics of the electroflotation process.

The electrocoagulation process utilizes consumable electrodes such as iron and aluminum (Pouet and Grasmick, 1995). Voltage applied to the system oxidizes the electrode to release a metallic coagulant such as the ferrous ion, aluminum ion. The waste stream requires sufficient conductivity for cell operation and to prevent passivation of the electrode material. Restaurant wastewater treatment by electrocoagulation was studied by Chen *et al.* (2000a, 2004).

The electrocoagulation unit mainly consists of an electrochemical reactor and a separator. Effluent from the electrocoagulation unit was sampled after steady state operation was achieved. The removal efficiency of oil and grease was range from 84.1 to 99%. They found the removal efficiency of oil content was

obviously affected by the electrode material and charge loading. Aluminum electrodes are preferred for this application than iron, this is because the effluent with aluminum electrodes was found very clear and stable, whereas the effluent with iron electrodes appeared greenish first, and then turned yellow and turbid resulted from the oxidation of ferrous. Furthermore, the yellow fine particles of $\text{Fe}(\text{OH})_3$ is difficult to settle and be separated in the subsequent operations. Results from their experiment showed electrocoagulation is almost a feasible process for treat the oily wastewater.

Xu and Zhu (2004) also studied treatment of refractory oily wastewater by using electrocoagulation process. The removal efficiency of oil and COD under optimum condition exceeded 95% and 75%, respectively, as the current density was 10 - 14 A/m^2 and reaction time was between 20 and 30 min. The optimal electrode distance was determined to be 10 mm for this equipment in consideration of the treatment cost and efficiency together. The COD and oil removal efficiency descended with increasing electrode distance. The pH effect on the performance of the electrocoagulation process was not very significant in the range of 3 - 10. Conductivity had little effect on the treatment efficiency. Addition of extra salts (e.g., sodium chloride) could save the power consumption significantly.

An electrolytic coagulation/flotation (ECF) system has been also reported using reversible polarity aluminum electrodes (Matis, 1980; Renk, 1988; Pouet and Grasmick, 1995; Chen *et al.*, 2000b). Herein, aluminum ions are released from the anodes, inducing coagulation, and hydrogen bubbles are generated at the aluminum cathodes, enabling flotation of the flocs. Bulk water passes through the reactor and is treated by the coupled coagulation/ flocculation process. In such a process, the electrocoagulation mainly plays the role of destabilizing and aggregating the fine particles, and the electroflotation is responsible for floating the flocs formed in the effluent of the electrocoagulation unit. The advantages of this process are both short retention time and dried sludge produced.

2.2.6 Microwave and Acoustic Separation Methods

Microwaves radiation (MWR) is electromagnetic energy (frequency range from 300 MHz to 300 GHz). It is a nonionizing radiation that causes molecular motion by migration of ions and rotation of dipoles. After exposing the emulsion to the EM field, molecular rotation and ionic conduction due to the penetration of EM into the emulsion are responsible for the internal heating. Thus, MWR results in the acceleration of separation of emulsion (Chanami *et al.*, 2000).

The research of microwave technology on the separation of emulsion wastewater has been conducted for a long time. The concept of microwave heating of emulsion was first suggested by Klaila (1983) and Wolf (1986). Fang *et al.* (1988, 1995) successfully tested in the field and laboratory operations for the demulsification of oil-in-water by using microwave heating technology (Figure 2.5).

The experiment of demulsification of W/O emulsions by MWR (Chan and Chen, 2002) exhibited that both the demulsification rate and the separation efficiency increased with the increase in droplet size and the concentrations of the carrier and acid. However, they decreased with the increase in surfactant concentration and the volume ratio of the oil-phase to aqueous phase.

Acoustic wave can induce agglomeration of particles which can then be recovered by conventional physical screening or gravity driven methods (Frank *et al.*, 1993; Allman and Coakley, 1994; Gupta and Feke, 1995, 1998; Hill and Feke, 2000). An U.S. Patent (Megal, 1969) described an acoustic or shock-wave technique. The O/W emulsion was introduced near the bottom of a tank which was equipped with a steel diaphragm which was made to vibrate at audio frequencies (15-500 Hz). Oil was removed from the top of the tank; water was drawn off from the bottom.

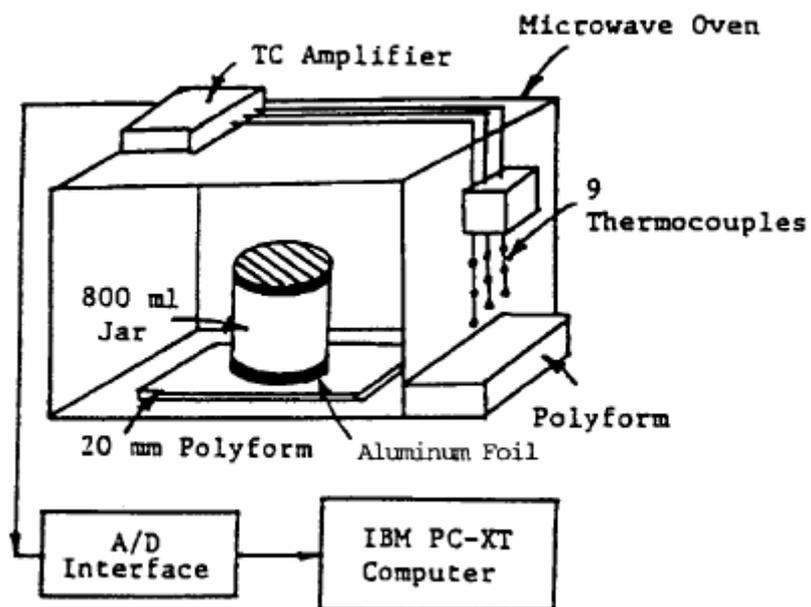


Fig.2. 5 Microwave separation of oil-in-water.

Ultrasonic liquid treatment uses high frequency energy to cause vibration in liquids to produce physical or chemical effects (Kuttruff, 1991). In spite of the fact that ultrasonic has strong dispersive effects on liquid emulsions, depending on the wavelength and intensity, ultrasonic can be applied in coagulation of emulsion. Ultrasonic field causes oil droplets to coalesce and/or to be transported to the internal surfaces of the chamber where the oil phase accumulates, and clarified water flows out from the chamber (Stuckart, 1992).

Stack *et al* (2005) conducted the investigation of ultrasonic separation of oil-in-water. They studied the role of the pH, conductivity, temperature, ultrasound intensity and duration, and electrolysis voltage, current, and duration. The results showed that conductivity was the most significant factor; however interactions among the eight study variables were more important than individual factors.

Sonication experiments were also carried out by Tech Sonic Company at an intensity of 30 W/cm^2 and frequency of 22 kHz. A comparison of the influence of the ultrasonic and mechanical mixing on demulsifying activity (DA) of different demulsifiers is shown in Table 2.1. From the table, a higher efficiency of ultrasonic technology is seen: DA values are about two or three times higher for each demulsifier.

Pangu and Feke (2004) developed a novel method for recovering the oil phase from aqueous emulsions. The method applies a low-intensity, resonant ultrasonic field within a rectangular chamber, which is optionally filled with a highly porous medium. Oil droplets dispersed in water have negative acoustic contrast factor and thus are driven to the pressure antinodes of the standing wave field under the influence of acoustic radiation forces. Subsequent coalescence and/or wetting onto the internal surfaces of the chamber occur. The oil collection was found to be sensitive to the natural affinity between the oil and the porous medium. Out of the three media studied, the polyester mesh was found to be the best in terms of the percentage oil collection while the bed of glass beads performed the poorest. The oil collection was found to be highly sensitive to the residence time of the emulsion in both the porous medium and acoustic field.

Table 2. 1 Comparison of effect under ultrasonic and mechanical mixing.

Demulsifier	Mechanical mixing		Ultrasonic mixing	
	Dose, mg/L	DA, %	Dose, mg/L	DA, %
Neftenol ST	100	15	100	65
	300	36	300	86
Neftenol D-NF	200	54	200	90
Diproxamin 157-65 M	100	16	100	75
Repon 4V	100	22	100	92
Separol WF-41	100	40	100	90
	200	55	200	95
Demulsifier 343k	100	33	100	89
DS 1618S	100	42	100	78
	300	51	300	94

2.3 Chemical Methods

Chemical methods are probably the most widely used technique for breaking up emulsion. They operate on the principle of removing the barriers that hinder coalescence. The demulsification mechanism of demulsifiers is quite complicated (Patterson, 1985; Sjoblom *et al.*, 1990; Li and Zhen, 1998). The process of coalescence can be divided into three distinct stages: the collision of the droplets, the thinning of the film between the droplets, and the final breaking of the film to achieve a single droplet (Hazlett, 1988). To accomplish this, however, it is necessary to weaken or remove the interfacial film. This is usually accomplished through the use of chemical demulsifiers (Eley *et al.*, 1988; Schramm, 1992), which may displace the indigenous species because of their higher interfacial activity. Chemical treatment of oily wastewater is generally conducted in two steps. First, a demulsifier is added to break down the stable oil emulsion. After destabilization, a flocculant is then added to coagulate and flocculate the destabilized emulsion.

2.3.1 pH Adjustment

pH adjusting is a widely used demulsification procedure. It may decompose the emulsifying agent (i.e. alkali soap is degraded by an acid), change the electrokinetic potential at the oil/water interface or change the degree of negative surface charge (Lobo *et al.*, 2005). At low pH, Becher (2001) reported that the emulsion particles were found to carry a small positive charge. As pH was increased, the charge reversed to negative. Acids/bases affect the interfacial properties of the adsorbed layers on the droplet surfaces and increase the coalescence rate of dispersed droplets (Demetriades *et al.*, 1997).

Several types of destructible or splittable surfactants have been reported in the literature and patents (Ono *et al.*, 1990; Galante *et al.*, 1998a, b). A common property of the surfactants is that their surfactant characteristics can be easily destroyed by adjusting pH, which affects the droplet size and the emulsion stability, and thus, is convenient for demulsification treatments.

A laboratory study by Chen *et al.* (2000) was conducted to evaluate the effect of pH on the stability of oil-in-water emulsions stabilized by a commercial splittable surfactant Triton SP-190 by comparison with the results obtained by a common surfactant Triton X-100. They found that the addition of inorganic

acids did not significantly affect the stability of emulsions stabilized by Triton X-100, but had a profound influence on the stability of emulsions stabilized by Triton SP-190. Moreover, the droplet size of a Triton X-100-stabilized emulsion and its dynamic interfacial activity were insensitive to acids. However, at lower pH the droplet size of the emulsions stabilized by Triton SP-190 was considerably increased. From the dynamic interfacial tension measurements the dynamic interfacial activity of Triton SP-190 at the oil/water interface was found to be strongly inhibited by the addition of acids, resulting in a slower decreasing rate of dynamic interfacial tension. The results demonstrated that the dramatic destabilization of Triton SP-190-stabilized emulsions could be realized by the use of acids, which evidently changed the interfacial properties of the surfactant and resulted in a higher coalescence rate of oil droplets.

2.3.2 Inorganic Salts

Oil-in-water emulsions are stabilized mainly by electrostatic interactions and/or adsorption of macromolecules or solids particles at the interface. The ionic strength of the continuous medium has a strong influence on the zeta potential of the oil droplets, and this parameter controls the electrostatic interactions, thereby influencing the emulsion stability (Rios *et al.*, 1998). It was reported that

increased salt (electrolyte) concentration decreased the emulsion stability as a result of change of zeta potential. Zeta potential is a close approximation to the surface potential (double layer charge). Changes in the double layer charge can be demonstrated by adjusting the electrolyte concentration. By making the appropriate adjustment to electrolyte concentration, the zeta potential can be reduced to a point of zero point charge (ZPC). At ZPC, demulsification will proceed at the greatest rate since the repulsive forces will be effectively reduced to have no charge.

Amritharajah and Mills (1982) identified three mechanisms for coagulation by aluminum sulphate (alum) in the emulsion: sweep coagulation of insoluble Al(OH)_3 trapping colloids while settling, adsorption-destabilization (zeta potential modification) by charged hydro-metal complexes (Al(OH)_4^-) on the colloid or double layer compression by Al^{3+} . They also assumed, for practical purposes, that coagulation was a function of alum dosage and pH.

Chemical coagulation followed by gravity sedimentation is employed in a number of industries (Cheremisinoff, 1987). Coagulation with alum (35 mg/L) followed by sedimentation reduces API separator refinery effluent oil from initial levels of 50-100 mg/L to a final effluent oil content consistently less than 15 mg/L. Following chemical destabilization of oily emulsion, air flotation is

commonly employed as an alternative to sedimentation, to separate the oil and water.

Song *et al.* (1998) studied the synergistic effect of salt and ozone treatment on the demulsification. They found the demulsification efficiency was at least 40% higher than the only salt or ozone treatment and other conditions such as pH and the initial emulsion concentration did not critically affect the demulsification efficiency. They explained the salt could destabilize the oil-water interface, making the emulsifiers readily oxidized, and allowing acceleration of the demulsification reaction. Actually, none of these materials is really a specialized demulsifying chemical. They serve to neutralize the charge on the oil drops or to help the oil drops to clump together.

2.3.3 Organic Agents

Organic agents, usually high-molecular-weight polymers derived from ethylene, propylene, vinyl, vinylidene, vinyl-acetate, and similar polymers, are widely used as effective demulsifying agents in petroleum industry (Jaffrin *et al.*, 1997; Nemtoi *et al.*, 2000; Ghimici *et al.*, 2001; Deng *et al.*, 2005; Kang *et al.*, 2006).

Larson *et al.* (1994) found butanol was an effective demulsifying agent. They noted that addition of n-butanol to some microemulsion formulations caused spontaneous demulsification. The rate of demulsification was related to the butanol concentration and temperature and inversely proportional to the surfactant concentration. Butanol appeared to weaken the water-surfactant interactions. This weakening of the thin surfactant film which separated droplets in the aggregates aided the coalescence processes.

Zaki (1997), in his study, compared the influence of heating the emulsion and/or adding a chemical demulsifier. Although heating to 50 °C caused some water separation of the 90% (vol.) oil-content emulsion, even after prolonged heating (6 hours) complete water separation did not occur. This demulsifier was an alkyl phenol-formaldehyde ethoxylated-propoxylated demulsifier. Different doses of the demulsifier were tested for demulsification of the 90% (vol.) Geisum-crude-oil-in-water emulsion, namely, 20, 40, 60, 80 and 100 mg/L with respect to the total emulsion volume. It was found that heating the emulsion at 50 °C without addition of the demulsifier, did not cause complete separation of water. Furthermore, complete water-separation was achieved by the following demulsifier concentrations: 60, 80 and 100 mg/L with an increasing rate of separation as the demulsifier concentration was increased.

Demulsification of emulsions by addition of chemicals is known to be effective (Lissant, 1986). The disadvantage of chemical additives is chemical treatment is very specific. Laboratory based feasibility tests on the wastewater samples are usually required before effective formulations for the demulsifying and flocculating agent can be chosen. The solid/sludge will require disposal eventually. The use of coagulant salts is most common in industrial wastewater treatment, with oil removal by sedimentation or floatation. Polymer may be added to enhance demulsification or flocculation. It has been emphasized that coagulation with aluminum or iron salts is generally effective for demulsifying oily waste. However, the aluminum or iron precipitate hydroxides sludge, which may prove difficult to dewater. Acids generally cleave emulsions more effectively than do coagulant salts, but are more expensive, and the resultant acidic wastewater must be neutralized after oil-water separation. Organic demulgators are extremely effective demulsifying agents, but due to their high cost they are considered impractical at high rinse water flow rates

2.4 Biological Treatment Methods

Many microbes existing naturally in the environment can biodegrade almost every organic compound (Pritchard *et al.*, 1992; Atlas, 1995; Swannell *et al.*, 1996; Venosa *et al.*, 1996; Swannell *et al.*, 1999). But the rate of natural biodegradation is not fast enough to prevent an organic compound from becoming a potential pollutant. This could be attributed to a number of factors: microbial population density, amount and availability of nutrients and complexity in biodegradation pathways. The techniques to isolate and optimize conditions to increase the effectiveness of naturally occurring microbes have been reported in the literature (Zaidi and Mehta, 1995; Hickey and Smith, 1996; Becker *et al.*, 1997; Zaidi and Imam 1999; Eckenfelder, 2000).

2.4.1 Factors that Affect Treatment Process

Fats and oils removal by aerobic and anaerobic microorganisms have been documented by several researchers (Nunn, 1986; Ratledge, 1992; Lalman and Bagley, 2000). As can be expected, this process is extremely temperature dependent, with total microbial degradation rates ranging from nearly 80% at 25

°C to none at 4 °C (Ludzack & Kinkead, 1956; Ludzack *et al.*, 1957; Gray *et al.*, 2000). The process of bio-treatment is also affected by the provision of nutrient substances (Hozumi *et al.*, 2000). Oxygen availability appears to play an important role and, together with temperature and nutrient requirements, may control degradation rates (Ludzack *et al.*, 1957, Young, 1979). The biological processes require an appropriate BOD/COD ratio. When the raw wastewater has a BOD/COD value lower than 0.2, it necessitates a proper pretreatment to improve BOD/COD ratio before the biological step (Azbar and Yonar, 2004).

2.4.2 Conventional Biological Process

The feasibility of a biological augmentation approach to eliminate oil and grease in the wastewater of a large bakery was tested by Keenan and Sabelnikov (2000). They devised a long scheme for the wastewater treatment as following several parts: included pH adjustment and mixing–aeration systems, an external biological reactor system for production and periodic injection of the appropriate bacteria to the treatment tank, and a biological filter. Oil and grease concentration in the bakery waste dramatically decreased from approximately 1 500 mg/L to less than 30 mg/L.

Azbar and Yonar (2004) successfully treated vegetable oil refining industry wastewater (VORW) using a combination of physicochemical and biological methods. They used two different pretreatment flow schemes before biological reactor. One consisted of an air floatation unit, chemical treatment and extended aeration activated sludge tank, while the other applied the DAF process with chemical addition before the biological reactor. The overall percentage removal of COD, TSS, and Oil&Grease was 92 - 96, 83 - 98 and 93 - 95%, respectively.

Biotreatment appears to be one of the simple and cost-effective technologies. However, biological treatment methods for O/W separation are characterized by long residence times. The residence times are required for both the growth and establishment of bacterial colonies, and the interaction between the bacteria and the oily wastewater. On the other hand, surveys have shown that the foams are associated with a dominance of the sludge biomass by the filamentous microbes- *N. amarae*, *Rhodococcus* or *M. parvicella* (Goddard and Forster 1987; Forster, 1992). *N. amarae* is known to have the ability to utilize straight chain alkanes, to produce surface active compounds and to have a hydrophobic surface. *M. parvicella*, which is the main foam-forming species, has been shown both to utilize and to store oleate. This would confer a significant degree of hydrophobicity to cell surfaces. Long-chain saturated fatty acids were less degradable due to lower dispersion (Matsui *et al.*, 2005). Therefore, the cost

effective degradation of oil and grease by microorganism may occur under certain specific conditions such as lower oil/grease concentration, suitable environment and special race of microorganism.

2.4.3 Specific Enzymes and Microorganisms

Several enzymes and microorganisms are being exploited to carry out fat- and oil-degrading activities (Tan and Gill, 1987; Tano-Debrah *et al.*, 1999). The inoculum (designated as the JAT inoculum) with a mixed-culture of 15 bacterial isolated from various fatty wastewater samples was used. All isolates with a well-demonstrated ability to degrade fats and oils. Biodegradative tests with the inoculums on samples of eight different fats and oils showed that several fats and oils could be degraded by the organisms in the culture with pH ranging from 4.5 to 9.5 and temperature ranging from 20 to 25 °C.

Twedell *et al.* (1978) reported the use of mutant bacterial enhanced oil and grease removal during periods of high influent concentration. Batch reactor studies indicated that an initial concentration of 400 mg/L of oil, the mutant population could achieve 61% reduction within 12 hours and 95% reduction within 72 hours.

Wakelin (1997) identified the effect of the growth of a range of pure and mixed cultures on the removal of fats, oil and grease using vegetable oils, lard and 'grease' from a fast-food restaurant grease-trap. The effectiveness of these cultures was assessed in terms of their grease-removal efficiency, the biomass production and yield coefficients. The pure cultures were *Acinetobacter* sp., *Rhodococcus rubra*, *N. amarae* and *M. parvicella* and these were compared with a mixed culture isolated from a grease trap, MC1, and with activated sludge. *Acinetobacter* was the most effective of the pure cultures, typically removing 60–65% of the fatty material whose initial concentration had been 8 000 mg/L. The effectiveness of the mixed culture, MC1, was variable, with the removal efficiency ranging from 29% for rapeseed oil to 73% for the restaurant grease. The activated sludge gave a more consistent removal, which was generally better than 90%. However, there was a lag phase of about 1 day in every case. Acclimatised activated-sludge did not exhibit a lag phase and also achieved a high (> 90%) removal efficiency. The absence of a lag phase resulted in faster growth and fat removal.

2.4.4 Thermophilic Microorganisms

Reimann *et al.* (2002) developed a new, high performance process for fat degradation using an aerobic thermophilic microorganism isolated from an Icelandic hot spring. This microorganism grows optimally at a temperature of 65 °C. This offers the advantage in that it allows the process to be performed at higher temperatures, since the enzymes are thermoactive, and simultaneously, the substrate – wastewater containing oil/grease in this case – becomes bioavailable in crucial quantities. Wastewater with an average concentration of COD of 4 500 mg/L, lipid concentration of 500 mg/L used in experiment was from spiced oil production. As the continuous fermentation of wastewater reached stable condition, the oil/grease degradation reached a value of 50% with HRT at 6.5 hours and cell density around 2×10^8 cell/mL.

2.4.5 Bio-agents

Formula IV oil eating-microbes developed and sold by Biotech 2000, Inc., have been reported by the company to be quite effective at biodegrading oil and grease. It is said the Formula IV microbes supposedly need only water and oxygen to thrive and biodegrade the oil and grease at ambient conditions.

An experiment was carried out to identify the effect of the bio-agent named “Biowash”. The different dosages of Biowash were used in various oil concentration solutions. Samples were analyzed at different time during the test. The results were presented in the Table 2.2. As could be seen, it was necessary to keep long reaction time longer than 6 hours in order to obtain better oil removal efficiency. High dosage of Biowash was more efficient to increase the removal efficiency. Actually, the most disadvantages of bio-agents are high cost and long retention time of wastewater.

Table 2. 2 Oil concentrations at different reaction time (unit: mg/L).

Dosage of Biowash	Initial concentration	T = 2 hrs	T = 6 hrs	T = 24 hrs	T = 48 hrs
25	20	9 (55)*	3 (85)	6 (70)	0.4 (98)
25	40	27 (33)	11 (72)	12 (70)	0.6 (98)
50	40	29 (28)	13 (68)	7 (82)	0.5 (99)
100	150	123 (18)	74 (50)	45 (70)	9.4 (94)

* Value in the parenthesis is removal efficiency.

2.5 Membrane Separation Technology

2.5.1 Introduction

2.5.1.1 Membrane Separation

Membrane technology is devoted to the separation of the minutiae of particles ranging from bacteria to atoms (Gill and Bansal, 1973; Cooper, 1980; Crespo and Boddeker; 1994; Judd and Jefferson, 2003; Farahbakhsh and Smith, 2004). The membrane filtration processes considered here are pressure driven separation processes, where the driving force is a pressure difference across the membrane. There are four membrane processes which are pressure driven force:

Microfiltration (MF): MF is the membrane filtration process with the least restrictive membrane type. Its uses include bacteria and pigment removal, and removal of other particulates with particle sizes in the submicron range.

Ultrafiltration (UF): UF can remove bacteria and viruses, and can separate macromolecules like sugars and proteins, as well as colloidal silica and pyrogens.

Nanofiltration (NF): The membranes used in NF operate on a solution diffusion principle, diffusing monovalent ions through the membrane, rather than blocking ions from passing through the membrane because of pore size like in MF or UF. NF is useful for color removal, sugar and dye removal or for removing THM precursors and hardness or sulfate from a water supply.

Reverse osmosis (RO): RO is operated with the tightest membrane type available. The organic and inorganic molecules are separated from a feed solution by a solution diffusion process. Typically, RO membranes are used to separate aqueous salts and ions with a molecular weight less than 200.

A precise definition for the various technologies is frequently given in terms of size, and/or molecular weight (see Table 2.3). The reality though is that there is no key principle separating one technology from another. However, the terminology is more than just one of semantics. Thus, the boundaries should not be regarded as rigidly defined, but as an indicator of technology differences. In keeping with the different uses the various membrane technologies are characterized in different ways. MF membranes are characterized in terms of pore size, while UF membranes are normally described in terms of a molecular weight cut-off (MWCO). As might be expected the operating parameters for

Table 2. 3 Characteristics of membrane filtration process.

Process technology	Separation principle	Size range	MWCO	Usual objective
MF	Size	0.05 ~ 10 μm	-	Removal of suspended solids, including bacteria, cysts and spores, <i>etc.</i>
UF	Size, charge	1 ~ 50 nm	>1000	Removal of both large, dissolved solute molecules and suspended colloidal particles, including proteins, viruses, <i>etc.</i>
NF	Size, charge, affinity	~ 1 nm	200-1000	Removal of multivalent ions and certain charged or polar molecules, such as sugars, pesticides, <i>etc.</i>
RO	Size, charge, affinity	< 1 nm	<200	Removal of inorganic ions, salts and sugars.

these filtration processes vary drastically, with MF processes offering a high recovery of feed at low pressure, while RO offers lower recoveries at much higher pressures (see Table 2.4).

Membrane filtration processes are increasingly being applied for treating oily wastewater (Faibish and Cohen, 2001a, b; Hoffman, 2003). Out of the three broad categories of oily wastewater, free oil is readily removed by mechanical separation devices which use gravitational force as the driving force, unstable oil/water emulsions can be mechanically or chemically broken and then gravity separated. The stable oil/water emulsions are difficult to be separated by conventional methods. Membrane separation methods are most useful with stable oil/water emulsions (Cheryan, 1998).

2.5.1.2 Membrane Modules

A useful membrane process requires the development of a membrane module containing large surface areas of membrane. In much of the early laboratory work membranes were used in the form of flat sheets, but for industrial applications of any scale the membrane has to be suitably housed in a manageable unit. The structure of such a device has been a continual challenge,

Table 2. 4 Typical operating parameters and membrane materials used for pressure driven process.

Process technology	Materials	Typical operating range	
		TMP, MPa	Recovery, %
MF	Polymers, ceramics, metals	0.05 - 0.2	90 - 99.99
UF	Polymers, ceramics	0.1 - 0.5	80 - 98
NF	polymers	0.3 - 1.5	50 - 95
RO	polymers	1 - 6	30 - 90

which requires balancing the economic costs of a unit versus performance factors and operational factors, e.g. cleaning, replacement. There are four types of membrane modules (Madsen, 1977; Rautenbach and Dahm, 1987; Noble and Stern, 1995): plate and frame, spiral-wound, hollow-fibre, and tubular.

1. Plate and frame module

In the early days, membranes were made as simple flat sheets. When the high pressures required present considerable engineering in order to avoid leakage, Plate and frame module were developed. One of the attraction of these devices are that are easy to disassemble, sanitise, and replace the membrane sheets. However, the down-side is that disassembling and re-assembling is a very labour intensive and time-consuming. Moreover, a practical difficulty was ensuring that during re-assembly all parts were positioned correctly so that water tight seals are made. Despite these problems, in small scale, high added value applications, such as pharmaceuticals, and development work, these plate and frame devices are a useful tool.

2. Spiral-wound module

Compared to other membrane packages, the most noticeable difference is the complexity of the design. A typical element is made from up to 11 different materials. Until fairly recently each element had to be hand made. The

spiral-wound module is one of the most favoured for the applications of gas separation and RO. Despite its complex internal design, it is easy to use, and is available in a large number of formats with different materials. In addition, spirals have a reasonably high membrane area per unit volume which means the size of the pressure vessels and associated pipework and frames are less, giving an additional economic and practical benefit. The major disadvantage of the spiral device is a thicker feed spacer when the spiral device is applied in ultrafiltration, this means there is a reduction in membrane area for a given size device.

3. Hollow-fibre module

The basic design of a hollow-fibre module is a bundle of fibres sealed at each end by an epoxy resin plug, and the whole element encased in PVC, or acrylic tube or a fibre re-inforced plastic. The large commercial gas separation units use small hollow-fibres less than 100 microns in thickness, and extending over several metres in length. RO element also uses small fibres but is usually shorter (1 to 2 m). UF and MF use hollow - fibres larger than 200 microns to meet the hydraulic and fouling demands. In concept, the hollow fibre format is probably the most appealing, providing a very high surface area per unit volume, with no spacers or meshes needed to support the membrane. However, the membrane permeability is significantly lower than that used in spiral or plate and frame

designs, and this alleviates some of the advantage that derives from the high specific surface area. The major practical difficulty with the module is the fineness of spaces between the fibres which means that they are vulnerable to fouling.

4. Tubular module

Tubular modules have the largest dimensions of all membrane devices. To some extent, they are an extension of the hollow-fibre type with diameters ranging up to 25 mm. However, tubular modules differ from hollow-fibre devices in that the membrane is invariably supported along its length and packed in an array which might contain from 1 to 100 tubes. The membrane is usually cast on the inside of a rigid porous tube. The feed flows down the centre of the tube, and permeate flows through the walls where it is channeled to a side-pot.

Tubular membranes are widely used in food applications because of their capability of handling difficult rheological systems, or fluids which contain large suspended solids (which might be inconvenient to remove), or present difficult fouling problems. Although tubular membranes have relatively low surface area per unit volume their simplicity means that they are easy to clean. The large diameter of the tubes means the liquid hold up is high. The tubular

membrane format means that no prefiltration is required despite the feed turbidity.

The use of the various membrane modules varies with application and technology (Belfort, 1988). Some important factors that drive selection are summarized in Table 2.5. Besides, the criteria for the selection of a module type for a defined application are the membrane packing density, given in m^2/m^3 . This defines the effective membrane area installed per volume of a module. Examples for average values for different modules are: 10 000 m^2/m^3 for hollow fibre, 1 000 m^2/m^3 for spiral wound, 200 m^2/m^3 for disc tube and 40 m^2/m^3 for tubular modules. The packing density is the main indicator for the degree of pretreatment necessary for the different modules in order to achieve a safe and trouble-free long term operation. A high membrane packing density means a high degree of pretreatment required. The advantage of ceramic membranes additionally offers the possibility of forming multichannel membrane elements which enlarge the treatment capacity.

Table 2. 5 Factors that influence the choice of membrane module.

Membrane availability	Hold-up	Flexibility	Fouling
Ease of cleaning	Maintenance	Suspended solids content	Hygiene
Serviceability	Dissolved solids concentration	Feed viscosity	Cost
Polarization	Pressure drop	Replacement cost	experience

2.5.1.3 Applications of Microfiltration Technology

The beginnings of MF could be traced back into 19th century with the synthesis of nitrocellulose in 1845 by Schoenbein (Cardew and Le, 1998). Fick then used ether-alcohol solutions of the same (collodion) to form the first nitrocellulose membranes in 1855. Even today, the most common polymers used in MF membranes are mixed esters of cellulose-including cellulose nitrate (Porter, 1990; Crespo and Boddeker, 1993; Caetano *et al.*, 1995; Baker, 2004).

In the first quarter of the 20th century, researchers like Bechhold, Bigelow, Gemberling, Schoep, Brown, Zsigmondy, Bachmann made significant advances in the methodology of casting and regulating pore size. It is astonishing that during that period the technology of controlling pore size and microstructure was developed to such a high degree of sophistication before understanding the mechanism of membrane formation. At last, the first commercial production of membrane known as “Zsigmondy Membranefilter” was produced, but sales were largely confined to the laboratory market.

The first important application of these membranes emerged during World War II. German water supplies were often devastated or contaminated by bombing

raids. A more efficient method for detecting *coliform* or pathogenic bacteria was needed. Conventional culturing techniques at that time in liquid or gel-like nutrient media could take up to 96 hours to obtain a final result. Mueller developed the membrane for filtering and culturing bacteria. In less than 24 hours of incubation (37 °C), the colony would be readily visible and countable by the naked eye.

In 1950, Goetz improved production methods to make membranes with higher flow rates and more uniform pore size. He also imprinted grid-lines on his filters to facilitate counting of the bacteria colonies. Based on Goetz's developments, the Lovell Chemical Company in 1954 sold its membrane manufacturing facility to the newly organized Millipore Corporation, producing the Goetz membranes on a commercial scale.

Generally speaking, the use of MF membranes was confined to very small-scale industrial applications till mid-1960s. The introduction of pleated membrane cartridges by Gelman in the 1970s was an important step forward and made possible the use of MF membranes in large-scale industrial applications. In the 1960s and 1970s, MF became important in biological and pharmaceutical manufacturing. Investigation of the membrane separation processes for oily water treatment also started in 1970s. Beginning in 1990s the first MF/UF

system began to be installed to treat municipal drinking water obtained from surface water.

Koltuniewicz and Field (1996) studied on the separation of oil from oily waters. The results showed that the ceramic membranes demonstrated better performance. The permeate flux was higher and more stable.

Effect of pore size on separation mechanism of microfiltration of oily water, using porous glass tubular membrane was conducted by Ohya et al (1998). The filtration mechanism in the first stage can be explained by three types of blocking models such as the complete type for pore size 0.27 μm , the intermediate type for pore size 0.75 μm and the standard type for pore size 1.47 μm . The second stage can be also explained by the cake filtration model. The oil rejection is found to decrease with time initially, but is soon stabilized at a constant level. This was explained by the comparison among the average pore size, the pore size distribution of used membrane and the droplet distribution of the feed emulsion.

Mohammadi et al (2003) studied the effects of transmembrane pressure (7-15.5 bar), oil concentration (0.3-5%), temperature (20 – 50 $^{\circ}\text{C}$), crossflow velocity (0.95-1.55 m/s) on the permeation flux. Models of complete blocking filtration, intermediate blocking filtration, cake filtration and standard blocking filtration were compared with experimental data. The results showed that experimental data was consistent with the intermediate blocking filtration model.

2.5.2 Characteristic of Membrane Process

2.5.2.1 Operating Model

There are two operating model for membrane filtration: the dead-end mode, and the cross-flow mode (Figure 2.6). In the dead-end mode, the feed is pumped directly towards the filter. There is one stream entering the filter module and only one stream (the permeate) leaving the filter. Such operation is normally restricted to either low-solids water, as for cartridge filtration of boiler feed water or ultrafiltration for apyrogenic pure water production. In the cross-flow mode, the feed is pumped across or tangentially to the membrane surface. In this mode of operation, there is one stream entering the module and two streams- the retentate and the permeate leaving the module (Ho and Sirkar, 1992). The benefit is that particles/solutes that would otherwise accumulate at the membrane surface are moved along, achieving a steady-state distribution of particles or solutes at the interface, rather than the continually developing one that is seen in the dead-end mode. The consequence of cross-flow is that in continuous operation the permeate flux through the membrane tends to

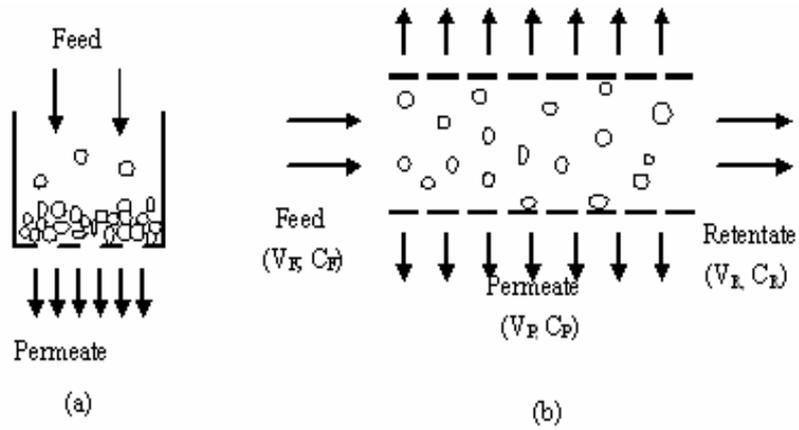


Fig.2. 6 (a) Dead-end filtration, (b) Crossflow filtration.

a constant while in dead-end filtration mode the permeate flux continues to fall. If the feed contains relatively high solids and/or if the solids need to be recovered easily, cross-flow is advantageous in that it limits the buildup of the solids (“cake”) on the membrane surface. The solids are kept in suspension in the flowing feed stream, resulting in less cake buildup and less cake resistance on the membrane, thus resulting in a higher average flux during operation (Cheryan, 1998).

2.5.2.2 Transmembrane Pressure (TMP)

In MF process, the pressure gradient across the membrane would force solvent and smaller species through the pores of the membrane, while large molecules/particles would be retained. The flux through a membrane can be expressed as:

$$Flux = \frac{\text{net driving force}}{\text{viscosity} \times \text{total resistance}} = \frac{\Delta P}{\mu(R_m + \sum R_i)} \quad (2.3)$$

where, ΔP is the TMP; R_m is the membrane resistance; R_i is the various resistances except membrane's; μ : viscosity of feed solution.

In practice of MF application, the pressure on the permeate side of the membrane is usually regarded as zero. Therefore, the feed side pressure of the

membrane, the mean value of the inlet and outlet of the membrane module, is approximately the net driving force.

A typical flux versus TMP relation is shown in Figure 2.7. When the membrane system is operated below the critical pressure, the flux is positive proportional to pressure. As pressures greater than the critical pressure, the flux changes unobvious due to the significant increasing of resistance. Thus, critical pressure is defined as the operating pressure at which the pressure-controlled permeate flux becomes pressure-independent.

2.5.2.3 Efficiency Evaluation

MF is primarily used for clarifying liquid. It is necessary to quantitatively estimate the relative degree of purification in a MF process or, conversely, to calculate the amount of membrane processing required attaining a certain degree of concentration, separation, or purification.

1. Flux

Productivity is determined by the amount of membrane and its permeate flux.

The volumetric rate of flow of permeate through a membrane is referred to as

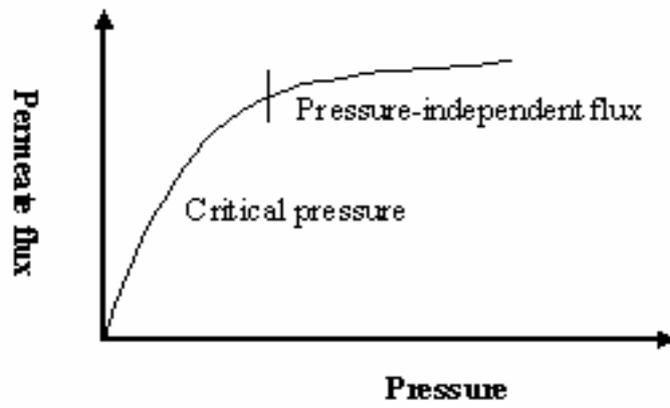


Fig.2. 7 Permeate flux as a function of transmembrane pressure.

permeate flux. The flux is expressed in terms of unit membrane area and is defined as given below:

$$Flux = \frac{\text{Permeate volume collected}}{\text{membrane area} \times \text{time}} \quad (2.4)$$

This means that it takes SI units of $\text{m}^3/(\text{m}^2 \text{ s})$, or simply m/s . In some cases, the productivity is usually quoted as a flux (production rate per unit area). Thus, from the required production rate, membrane area required for the separation can be calculated.

2. Rejection (R)

Rejection relates to the solute quantity that permeates or is retained by a membrane. Solute rejection by a membrane is usually defined as the reduction in the feed concentration across the membrane. At any point in the filtration process, the apparent rejection (instantaneous rejection), R_a , of a membrane is given by:

$$R_a = 1 - \frac{C_P}{C_F} \quad (2.5)$$

where, C_F is instantaneous solute concentration in the permeate stream; C_P is instantaneous solute concentration in the feed or retentate stream.

Actually, the concentration of the solute will be higher near the membrane surface compared to the bulk of the liquid because of concentration polarization

and cake fouling. Hence, the real value of rejection, R_r , should be calculated as shown below:

$$R_r = 1 - \frac{C_p}{C_g} \quad (2.6)$$

where C_g represent the solute concentration on the membrane surface.

3. Recovery

Batch membrane filtration experiments can be performed in two ways: recycle mode and recovery mode. In the recycle mode, the permeation and the concentrate streams are returned to the original feed reservoir. This configuration is used in research so as to monitoring the permeation at different operating conditions, whereas recovery mode is usually applied in the industries and wastewater treatment. The permeation is collected in a separate reservoir while the concentrate is returned to the feed reservoir. The fraction of the feed which is treated is known as the recovery, Y , and is defined as the fraction of the feed that passes through the membrane,

$$Y (\%) = \frac{Q_p}{Q_F} \times 100 \quad (2.7)$$

where Q_p the permeate volume, Q_F the volume of the initial feed solution.

4. Volume reduction (VR) and concentration factor (CF)

In the wastewater treatment, much attention is paid to the quality of the permeation and the degree of VR achieved. The CF achieved is often a critical measure of performance. These factors are not independent, but linked to how much water is recovered from the feed. Indeed, for batch operation

$$VR = \frac{V(\text{final})}{V(\text{initial})} \quad (2.8)$$

Thus, a system with 80% recovery represents an 80% reduction in feed volume. As water is removed from a feed, the rejected components become concentration. A mass balance shows that the concentration factor (CF), the rejection (R), and the recovery are linked via

$$CF = \frac{C(\text{final})}{C(\text{initial})} = 1 + R \left(\frac{Y}{1 - Y} \right) \quad (2.9)$$

If the membrane is ideal (i.e. R = 1), this equation can be simplified as

$$CF = \frac{1}{1 - Y} \quad (2.10)$$

2.5.3 Application of Membrane Separation Technology

Application of membrane processed within the industrial sector is widespread and well established in many instances. MF and UF are both widely used in industries of juice, wine and beer to clarify, concentrate and stabilize the product (Gan *et al.*, 2001; Urkiaga *et al.*, 2002; Matta *et al.*, 2004; Vaillant *et al.*, 2005).

MF processes are also applied in refining vegetable oil and recovering volatile fatty acid (Pioch *et al.*, 1998; Hafidi *et al.*, 2005; Kim *et al.*, 2005). Water supply industry uses MF combining with flocculation for purifying drink water (Bottino *et al.*, 2001; Han *et al.*, 2002; Meier-Haack *et al.*, 2003; Schlichter *et al.*, 2004) and removing natural organic matter (Thiruvengkatachari *et al.*, 2002; Koh *et al.*, 2005). Membrane technologies are also used for treatment of industrial wastewater to remove dissolved organic material (Rozzi *et al.*, 1999; Cassano *et al.*, 2001; Noor *et al.*, 2002; Kang and Choo, 2003), heavy metal (Brandhuber and Amy, 1998; Ellis *et al.*, 2000; Blöcher *et al.*, 2003; Mavrov *et al.*, 2003), and nutrient substances (Ghyoot *et al.*, 1999; Lesjean *et al.*, 2002).

Investigation of the membrane separation processes for oily water treatment has been started since 1970s (Porter, 1972; Lipp *et al.*, 1988; Park *et al.*, 2001). From then on, membrane processes such as MF, UF, NF and RO are increasingly being applied for treating oily wastewater. There were a number of studies on this field (Field *et al.*, 1994; Kim *et al.*, 1998; Saminario *et al.*, 2002; Velasco *et al.*, 2003; Mohammadi and Esmaelifar, 2004). Flux obtained from membrane filtration is mainly affected by characteristics of membrane (material, pore size, hydrophilic/hydrophobic), characteristics of feed solution (temperature, oil content, oil droplet size, concentration, pH, salt concentration) and operating parameters (TMP, CFV) (Hlavacek, 1995; Koltuniewicz and

Field, 1996; Reed *et al.*, 1997; Ohya *et al.*, 1998; Hu *et al.*, 2002; Mohammadi *et al.*, 2003). The comparisons among membrane technology, physical, chemical and biological separation technology are summary in Table 2.6. These researches indicated that membrane technology could be emerged as one of the most promising alternatives to separate oily wastewater. However, most of these researches on oily wastewater treatment use polymer membrane. Few are concerned with inorganic membrane.

Although the development of ceramic membranes could be traced backed into 1940s, ceramic membranes were developed as a by-product of nuclear research in the early stage. In 1980s, a ceramic membrane with effective area of 4 millions square meters was mainly used in microfiltration and ultrafiltration in the liquid separation. In the later stage, membrane separation technology can be applied to industry (Kijseoglu *et al.*, 1990; Vickers *et al.*, 1995; Scholz and Fuchs, 2000). It was successfully applied to milk and beverage industries (Strohwalder and Ross, 1992; Pafylis *et al.*, 1996; Guerra *et al.*, 1997). Alumina membranes exhibit unique physical and chemical properties that are only partially or not shown by organic membranes. Compared to polymeric membrane, the inorganic membrane has a series of special characteristics (Cheryan, 1998):

1. Inert to common chemicals and solvents: very few chemicals will bother these membranes. It can also tolerate strong doses of chlorine (up to 2 000 mg/L).
2. Wide temperature limits: some inorganic membranes can be operated as high as 350 °C. Routine sterilization by steam or hot water (e.g. 125 °C) is expected with all inorganic membranes.
3. Wide pH limits: most manufactures will specify pH ranges of 0.5 to 13. Its ability to tolerate acids and alkalis is better.
4. Pressure limits: considering the nature of the membrane, it can endure high pressure (up to 10 bars).
5. Extending operating lifetimes: Unlike polymeric membranes, whose membrane life is most affected by the frequency and nature of cleaning, inorganic membranes appear to be tolerate frequent aggressive cleaning regimes.
6. Backflushing capability: Unlike spiral-wound and polymeric tubular membranes, most tubular inorganic membranes are well suited for backflushing and backpulsing.

Today they are used in a wide range of fluid processing applications for water treatment, food, beverage, chemical, petroleum and pharmaceutical production.

Therefore, this research possesses a profound significance for providing a practical and theoretical base for oily wastewater treatment.

Table 2. 6 Comparison of several characteristics under various separation and treatment methods.

Parameters	Physical methods	Chemical methods	Biological methods	Membrane method
Oil status	Free-floating oil, unstable oil-water emulsions	Unstable oil-water emulsions	Unstable and stable oil-water emulsions	Unstable and stable oil-water emulsions
Efficiency	Fair but unstable	Good and stable	Fair and stable	Good and stable
Operating and maintenance	Simple/complex	Complex	Complex	Simple
Facility size	Small-middle	Middle	Large	Small
By-product	Concentrated oil or sludge	Sludge	Sludge	Concentrated oil

CHAPTER THREE

METHODOLOGY AND MATERIALS

3.1 Introduction

3.1.1 Composite Complexity of Oily Wastewater

Attentions to application of vegetable oil in industries have been arisen during the last decade as vegetable oils are renewable resources and environmentally friendly non-toxic fluids (Padavich and Honary, 1995; Rhee, 1996; Graboski and McCormick, 1998). Most of the lubricants originate from petroleum stock, which is toxic to environment and difficult to dispose. Vegetable oils are considered to be potential candidates to substitute conventional mineral oil-based lubricating oils and synthetic esters (Asadauskas *et al.*, 1996). Volumes of lubricants, especially used in engine oils and hydraulic fluids, have the highest need for biodegradable lubricants as a result of requirement of resource conservation and environmental protection (Bagley *et al.*, 1998; Erhan and Asadauskas, 2000; Adhvaryu *et al.*, 2005).

Although vegetable oils have reputation of a low-cost candidate for the biodegradable replacement of mineral oils due to their high inherent biodegradability (Battersby *et al.*, 1992; Randles and Wright, 1992), vegetable oil in its natural form has limited use as industrial fluids due to poor thermal/oxidation stability (Becker and Knorr, 1996), low temperature behavior (Asadauskas and Erhan, 1999). Modifications on vegetable oil have to be done in order to industrial applications. These modification maybe make use of acids, alkali, salt and organic additives. Thus, the compositions of oily wastewaters from modification process become much complex. Based on these considerations, some separation tests were conducted under the conditions of various pH and salt concentrations.

3.1.2 Experiment Design

Firstly, membrane characterizations were determined with distilled water under various TMP, temperature, pH and salt concentrations. Secondly, the influences of variables such as TMP, CFV, oil concentration, temperature, pH and salt concentration on membrane filtration of oily wastewater were studied. Thirdly, membrane cleaning tests and restaurant wastewater treatment were carried out.

Finally, the effect of pH and salt concentration of the feed solution on the size and zeta potential of oil droplets and performance of MF were investigated.

3.2 Experimental Procedures

3.2.1 Membrane Selection

Commercial alumina membrane elements usually come in three configurations (Baker, 2004): disks, tubes and honeycomb monoliths. The use of disks has been limited to medical and pharmaceutical applications, while tubes and monoliths are used industrially for various applications such as removal of bacteria from wine and beer fermentation, oil-water separation, fruit juice concentration, milk processing, etc.

The ceramic membrane used in this research was provided by Nanjing Tianye Membrane Separation Technology Limited Company. It was an aluminum oxide ($\alpha\text{-Al}_2\text{O}_3$) membrane. Two kinds of pore size of membranes, with the average pore sizes of 50 nm, 100 nm, were chosen in this study according to the purpose and acquirement (high permeate flux and acceptable permeate quality) of the oily wastewater separation. The dimensions of the ceramic membrane are 425 mm length, 30 mm diameter with 19 lumens which with 4 mm diameter. Thus, the effective area was 0.10 m^2 . The membrane outlook is shown in Figure 3.1.

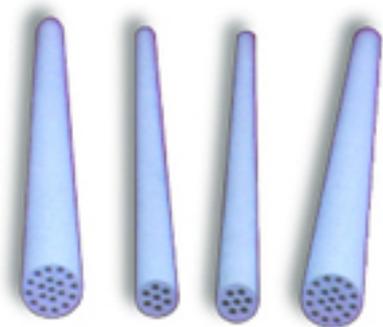


Fig.3. 1 The ceramic membrane outlook.

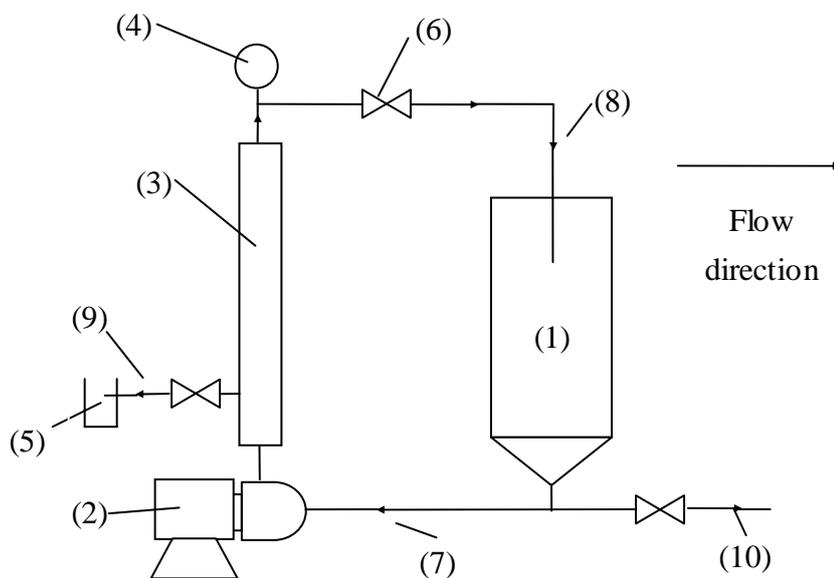


Fig.3. 2 Schematic view of ceramic membrane separation unit.

(1) feed tank; (2) pump with its adjustor ; (3) membrane module; (4) pressure gauge; (5) sample bottle; (6) control valve; (7) feed solution; (8) retentate; (9) permeate; (10) discharge.

3.2.2 Preparation of Feed Solution

Refined corn oil is primarily triacylglycerols (TAG), with very residual free fatty acids (FFA) and trace material. The various combinations of TAG of corn oil give it an average molecular weight of about 900 grams per mole (Watson *et al.*, 1987). Physical properties of corn oil such as density and melting point are highly dependent on the composition of the oil. The chain length and degree of saturation among the chains alters the melting point, and the melting point increases with the increase of chain length.

In this study, the various oil concentrations of oily emulsions were prepared by emulsifying 4 - 32 gram of pure canola oil (Hop Hing) in 1400 mL of distilled water with 0.2 gram of surfactant, polyoxyethylene (20) sorbitan trioleate (Tween 80[®], Wako), using a homogenizer (Chicago) at 4000 rpm for 20 minutes, then diluted to 16 litres. In order to investigate the effect of ionic strength on the performance of the membrane filtration, NaCl concentrations in the feed solution were adjusted to 0.001, 0.005, 0.01, 0.05 mol/L, respectively. In order to investigate the influence of pH on the membrane filtration, pH value of feed solution were controlled at four different levels with 2 mol/L HCl and 2 mol/L NaOH.

3.2.3 Operation of MF Process

The experimental setup is schematically shown in Figure 3.2. The feed tank was filled with total 16 litres of oily emulsion. The feed solution was pumped by means of a circulatory pump into the ceramic module. The By throttling the pump motor-power adjustor and control valve, TMP and CFV were independent regulated from 0.10 to 0.30 MPa and from 0.21 to 1.68 m/s, respectively. The permeation sample was collected each 5 min interval, and the sample volume was measured. Several millimetre of permeation was remained for determination of TOC later, the rest sample was returned to the feed tank. A mini-water cooler was used to prevent the elevation of temperature due to cycling of feed solution.

Before each filtration performance, the experimental setup was rinsed with a distilled water or oil-free solution which was at the same pH and salt concentration as the feed solution. After each test the membrane was first washed with hot water, then cleaned with cleaner, and finally rinsed with distilled water (The details were presented in 3.2.4.1).

3.2.4 Membrane Cleaning

Cross-flow filtration is helpful in slowing down membrane fouling but does not eliminate it. Therefore, all membrane-based filtration processes require some form of periodic cleaning to remove the foulants. Membrane cleaning may involve the removal of external foulants deposited on the membrane surface as well as foulants embedded within the membrane pore (Leenaars and Burggraaf, 1985). Inorganic membrane materials have advantages of chemically inert in strongly alkaline or basic solutions and unattacked by organic solvents or oxidizing agents even at high temperatures.

3.2.4.1 Normal cleaning

After each operation of MF process, the membrane was cleaned. The procedure was as follows: Firstly, the oily wastewater was drained from the system, and then rinsed the system with circulating hot tap water (40 °C) for 15 minutes. After this, the system was washed by circulating 2% NaOH solution for 2 hours in order to restore the membrane permeability. Finally, the system was rinsed using tap water until neutral permeate reached. The water flux of the membrane was checked again after cleaning to ensure a difference of less than 10% to the

water flux before next filtration, allowing a high reproducibility for the test. Further membrane cleaning would go on, if needed. Although the pure water permeate flux after membrane cleaning changed from time to time for a used membrane, a difference of less than 10% of the water flux was ensured for each group test.

3.2.4.2 Fouling and Cleaning

The initial pure water permeate flux (J_i) of the membrane was first determined before membrane separation. Then, membrane filtration of oily wastewater was conducted. Periodic permeate flux (J_w) measurements were made until it reached a steady state. In the next step, the procedure of membrane cleaning was conducted.

Membrane cleaning was carried out by using five different chemicals. They were: acidic solution (HNO_3 , 0.2 mol/L), alkaline solution (NaOH , 0.5 mol/L), oxidant agent (NaOCl , 0.01 mol/L), chelating agent (EDTA , 0.2 mol/L) and surfactant (tween-80). The membrane cleaning procedure was adapted from a previous study (Elmaleh and Abdelmoumni, 1997). Firstly, the oily wastewater was drained from the system. The membrane was then washed by circulating a

solution of chemical agent for 1 hour in order to restore the membrane permeability. Finally, the system was rinsed using tap water and the washing procedure was completed by rinsing with deionised water until the permeation reached neutral. The permeate flux (J_f) was measured using distilled water after every cleaning operation. The cleaning efficiency was evaluated with water flux recovery (WFR) (Sayed Razavi *et al.*, 1996). WFR was defined as:

$$WFR = \frac{J_f - J_w}{J_i - J_w} \times 100 \quad (3.1)$$

3.3 Calculation and Analytical Methodology

3.3.1 Flux

The permeate flux (J) is calculated by dividing the permeation volume by the product of effective membrane area and the sampling time.

$$\text{Permeate flux} = \frac{\text{Permeate volume collected}}{\text{membrane area} \times \text{time}} \quad (3.2)$$

Time-average permeate flux is the value of total permeate flux over the time of the filtration run, it is defined as:

$$J_{ave} = \frac{1}{t} \int_0^t J(t) dt \quad (3.3)$$

where J_{ave} is the time-average permeate flux, t is the filtration time, $J(t)$ is the instantaneous flux.

3.3.2 Oil Rejection

The average oil concentration (C_{ave}) in the permeate is defined as follows:

$$C_{ave} = \frac{1}{\sum_t V_t} \int_0^t V_t C_t dt \quad (3.4)$$

where V_t is instantaneous permeate volume, C_t is oil concentration in the instantaneous permeate, t is operational time.

The average oil rejection is calculated by:

$$\text{Oil rejection} = \left(1 - \frac{C_{ave}}{C_{feed}} \right) \times 100\% \quad (3.5)$$

Because low oil concentration in the permeate could not be determined precisely. Therefore, oil rejection was evaluated in the way of TOC removal in this study.

3.3.3 Chemical Analyses

3.3.3.1 Determination of Oil and Grease, COD and TOC

In this study, EPA Method 1664 (EPA, 1999) was used for the analysis of oil and grease. This method determines the amount of n-Hexane extractable material using n-Hexane as extraction solvent. The procedure for n-Hexane extractable material involved acidifying a 1 litre sample to a low pH followed by extraction with n-Hexane. COD was measured by means of the Closed Reflux Titrimetric Method (EPA, 1999). Total organic carbon (TOC) was measured using a total organic carbon analyzer (TOC 5050, Shimadzu Corporation, MD)

Conversion of COD, TOC and oil concentration

The Method 1644 for determining the oil and grease is more precise at high concentration than at low concentration. When the oil concentration in the permeation is determined with this method, the large determination error of the method will occur. Therefore, it is inappropriate to compare the removal efficiency of oil and grease. The method for determining COD appears always appropriate whether high or low concentration of oil and grease. However, it is time-exhausted. Besides, many chemicals need to be consumed during the COD determination process, which results in discharge with acidic, heavy metal wastewater. TOC is a typical parameter that represents the organic pollution. It can be easily determined with special instrument. Based on the consideration of above reasons, a relationship was set up among the three parameters through experiment, that is, 1 mg/L Oil and grease = 2.32 mg/L COD = 0.814 mg/L TOC.

3.3.3.2 pH Determination

The pH meter should be calibrated before use. The major procedures of pH determination are as follows:

- 1, Rinse the electrode with distilled water and blot dry gently.
- 2, Place the electrode into the sample. The sample of pH is adjusted with 2

mol/L NaOH solution or 2 mol/L HCl solution to target value. Stir until the reading is steady and note the reading.

3, Rinse electrode between measuring different samples.

3.3.3.3 Zeta Potential Determination

Zeta potential was determined with Zetasizer 2000/3000 (Malvern Instruments Ltd.). The basic steps of a measurement include: 1, power up 2, sample preparation 3, setup specific sample details 4, run a measurement 5, examine results 6, saving and reporting. This equipment measures the distribution of electrophoretic mobilities and hence Zeta potentials of droplets in liquid suspension using an optical technique. Samples of suspension are injected into a measuring cell and after measurements have been made the output from the instrument include the average Zeta potential and its standard deviation. The Zeta potentials reported here were calculated from the average of at least five separate injections per sample. Once a suitable sample is prepared, simply inject the sample into the cell from the sample entry port. It is advisable to suck the sample gently into the syringe, to avoid producing bubbles, and to hold the 10 mL syringe vertically to expel any air in the top, before injecting into the instrument.

3.3.3.4 Size Measurement

Size of droplet was determined using the same instrument as the determination of zeta potential. The most distinction of operation is the sample entry port. Samples are poured into a measuring cell. Bubbles are not allowed to attach the cell wall. The outer surface of the cell must keep transparent and dry.

3.3.3.5 Viscosity Determination

The coefficient of dynamic viscosity μ is defined as the shear force per unit area (or shear stress τ) required dragging one layer of fluid with unit velocity past another layer a unit distance away from it in the fluid. The common viscometer used is the Brookfield viscometer. The unit consists of a rotating rod connected to the motor by a torsional spring. Various cylindrical bobs of different diameters can be attached to the rod. The suspended bobs can be turned over a range of rotational velocities. The stress on the bob generated by motion through the liquid at a known rotational velocity is measured by the deflection of the torsional spring. Before the determination, the instrument must be calibrated with standard liquid provided by the instrument supplier. The experimental procedures are to: Select an appropriate rotating rod, and then connect the rod to

the motor. Add the solution into the beaker to a target level, and select an appropriate rotational velocity. Press on the button and write the data from the indicator. Find the factor value from the table according to the rod type and rotational velocity. The viscosity is given out by factor value time indicator data. The bubble attached the rod could result in measurement error. This situation should be excluded during the test. Selecting an appropriate rotating rod and rotational velocity is very important for obtaining experimental data. Summary of analytical methods of different parameters were present in Table 3.1.

3.3.4 Data Analysis

The one-way ANOVA was used to test any significant difference in COD removal efficiencies in the effluent among various operating conditions, including TMP, CFV, oil concentration, pH and salt concentration at the 95% confidence level. All statistical analyses were performed using SPSS^R for Window Release 10.1. The means and standard deviations of the data were analyzed using Microsoft Excel 2000 software on a personal computer.

Table 3. 1 Summary of analytical methods of different parameters.

Parameter	Technique	Methods
Oil & grease	gravimetric	EPA 1664
TOC	Combustion infrared	SM 6420C
COD	Closed reflux	EPA 5220C
pH	Thermo Orion 720	SM 4500H
Zeta potential	Zetasizer 2000/3000	
Particle size	Zetasizer 2000/3000	
Viscosity	Brookfield viscometer	

CHAPTER FOUR

MEMBRANE CHARACTERIZATIONS

4.1 Introduction

Corundum, or $\alpha\text{-Al}_2\text{O}_3$, is the most thermodynamically stable phase and is formed at temperature greater than 1 050 – 1 100 °C (Knozinger and Ratnasamy, 1978). In the $\alpha\text{-Al}_2\text{O}_3$ configuration, the oxygen ions are in hexagonal closest packing with aluminum ions in two-thirds of the octahedral interstices, and each aluminum ion is coordinate with six oxygen atoms and each oxygen atom has four aluminum atoms for nearest neighbors (Morterra *et al.*, 1976).

This chapter is designed to illustrate the basic properties and characteristics of alumina membrane during the MF separation process. Many research revealed the MF process was influenced by the operational parameters and feed solution characteristics (Laine *et al.*, 1989; Braghetta, 1995; Iritani *et al.*, 1999; Jones and O'Melia, 2001). The experiments in this chapter were carried out with $\alpha\text{-Al}_2\text{O}_3$ ceramic membrane of pore size 50 nm and 100 nm, and the distilled water was used as feed solution.

4.2 TMP

For many membrane separations, such as microfiltration and ultrafiltration, the permeate flux was dependent directly on the applied transmembrane pressure (Güell and Davis, 1996; Song, 1998). Figure 4.1 presents the results of the permeate flux obtained from α -alumina membrane with 50 and 100 nm of pore size under the different TMP. It can be seen that the permeate flux increases with the increase of TMP. This was because there was not any concentration polarization and membrane fouling formed during the clear water (solute-free) filtration process, the filtration resistances were nothing but membrane resistance.

According to the Eq. (2.3), the permeate flux was positively proportional to the TMP. Therefore, good linear correlation is shown between the permeate flux and TMP in Figure 4.1. Figure 4.1 also illustrates that the line slope from 100 nm membrane is larger than that of 50 nm membrane. This indicated the influence of TMP on the permeate flux was more sensitive for 100 nm membrane than for the 50 nm membrane. This was because that membrane with a larger pore size had a low resistance. As a result, a high permeate flux was obtained under the same TMP.

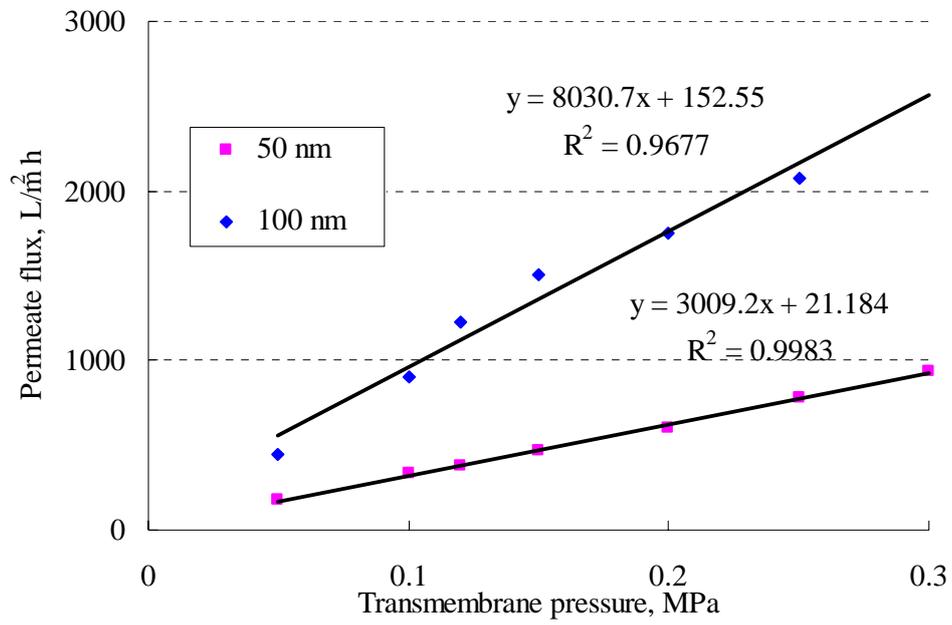


Fig.4. 1 Effect of TMP on the permeate flux (20).

4.3 Temperature

Figure 4.2 illustrates the effect of temperature on the permeate flux. It could be found that the effect of temperature on permeate flux was quite obvious. As the water temperature raised from 15 to 40 °C, the permeate flux increased from 289 to 468 L/(m² h) for 50 nm membrane, and from 774 to 1206 L/(m² h) for 100 nm membrane. The permeate flux was almost linearly increased as the temperature increasing. The effect of increasing the temperature of a fluid was to reduce the cohesive force while simultaneously increasing the rate of molecular interchange. The former effect tended to cause a decrease of shear stress, while the latter caused it to increase. The net results was that liquids showed a reduction in viscosity with increase of temperature (Cheryan, 1998)

$$\mu_T = \mu_0 / (1 + AT + BT) \quad (4.1)$$

where μ_T is the viscosity at T °C, μ_0 is the viscosity at 0 °C, and A, B are constants depending on the liquid. For water, A = 0.03368, B = 0.000221. According to the Eq. (2.3), the reduction of viscosity resulted in the increasing of the permeate flux. However, increasing temperature increased osmotic pressure, according to Darcy's law, which resulted in the decrease of permeate flux. Meanwhile, increasing temperature also increased diffusivity, and as a result increases permeate flux. As a whole, the bilateral effect of temperature

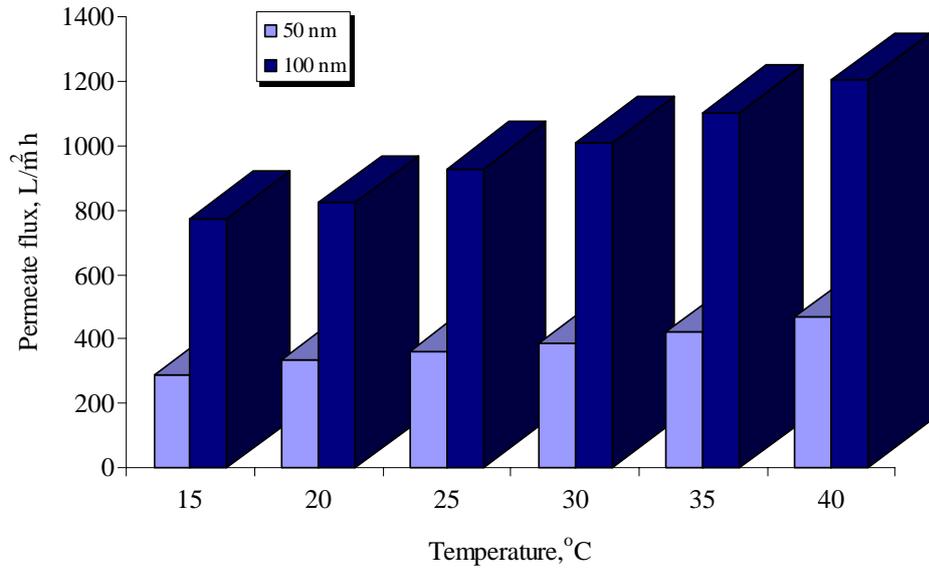


Fig.4. 2 Effect of temperature on the permeate flux (0.1MPa).

was positive, and its intensity depended on the solute of the feed solution and membrane type used in the filtration process. In the case of dilution aqueous solution, the permeate flux was increased by a factor 2 by raising the temperature from 20 - 50 °C (Bhave and Fleming, 1988). The viscosity dependence of permeate flux could be strongly nonlinear (Zydney and Colton, 1986).

The significance of temperature on the filtration process is profound. A high value of flux will reduce the membrane area requirements and can result in a lower cost. Hence, in some situations, the increased energy costs associated with the higher operating temperature have to be considered to achieve an optimum balance between the increased operating costs and lower capital costs.

4.4 pH Value

pH value of feed solution is a very important factor that significantly affects separation performance (Ohmori and Glatz, 1999). Figure 4.3 shows the variation of permeate flux of 100 nm membrane under different pH value. The permeate flux was high when the pH value of solution was low. As the pH increased from 4 to 8, the permeate flux decreased from 510 to 440 L/(m² h), and the permeate flux almost became stable after pH higher than 8. This was because many inorganic membranes such as Al₂O₃, ZrO₂, SiO₂ and TiO₂ consisted of charged particles whose zeta potential values were influenced by the pH value of the solution. Metal oxide membranes, in the absence of specially adsorbed ions, are expected to have a positive zeta-potential at low pH and a negative zeta-potential at high pH. The pH at which the transition from positive to negative occurs is called the iso-electric point. For example, the iso-electric points of Al₂O₃, ZrO₂ and TiO₂ are known to be around pH values of 6.5 - 9, 4 - 5 and 5 - 6, respectively (Nazzal and Wiesner, 1994; Huisman *et al.*, 1998). As a result of the interactions between the membrane surface and solutions filtered (such as by adsorption), changes in zeta potential. Surface charge and the related distribution of ionic species near pore surfaces within the matrix of the membrane can have a significant effect on the permeability of the

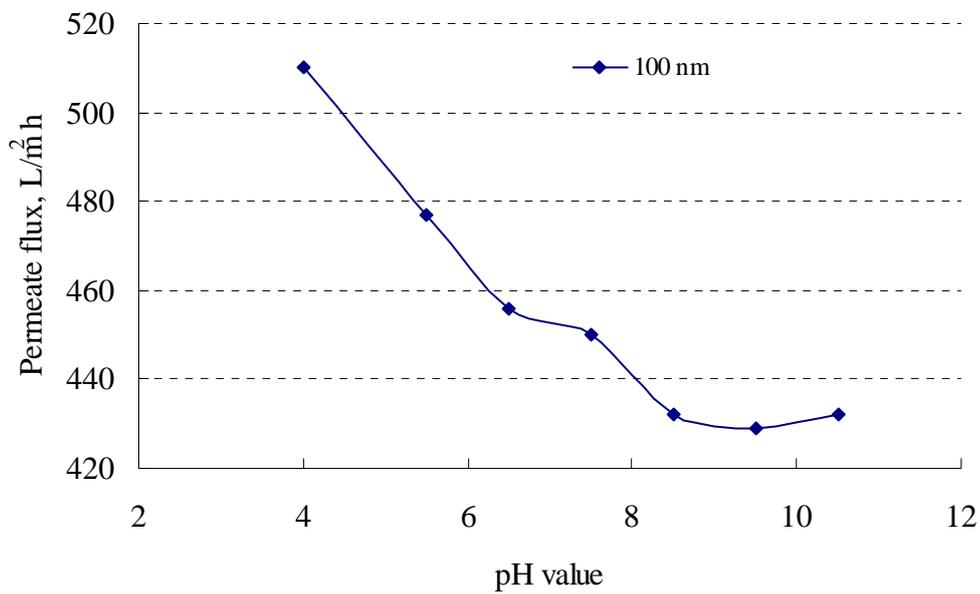


Fig.4. 3 Effect of pH on the permeate flux (0.1MPa).

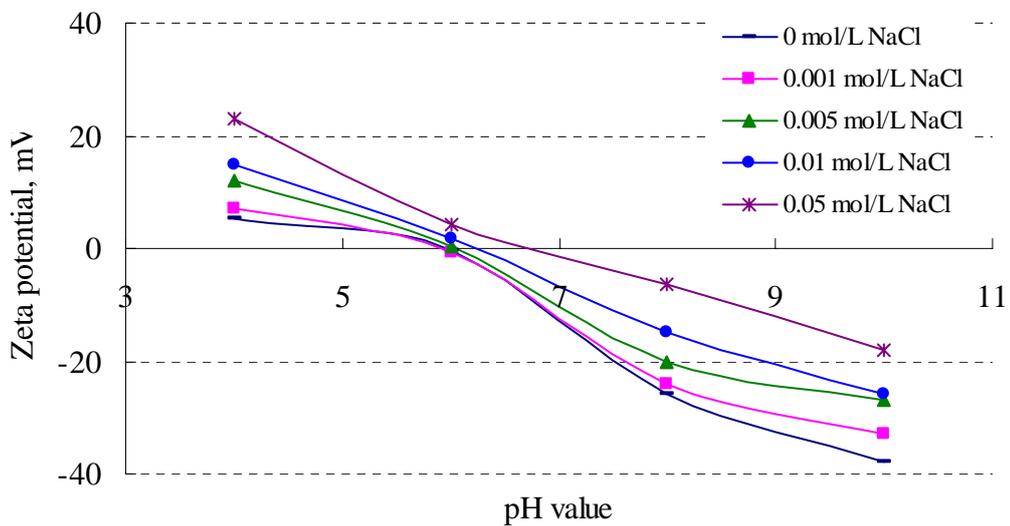


Fig.4. 4 Effect of pH on the zeta potential of α -alumina particles.

membrane and adsorptive fouling (Ohmori1 and Glatz, 1999).

In order to identify the surface charge of the membrane, measurements of zeta potential were carried out with α -alumina (Al_2O_3) particles. These Al_2O_3 particles were made of the same material and had the same chemical and physical treatment as particles that constitute the active layer of the microfiltration membrane. Zeta potential measurement of α - Al_2O_3 particles were done in dilute suspensions containing 100 mg/L particles. The pH was adjusted to the target value by adding HCl or NaOH. The value of the zeta potential under various pH and salt concentrations is shown in Figure4.4.

Zeta-potentials as increasing the pH will first result in a decrease in the absolute value to zero (the iso-electric point), and then an increase in the absolute value. A negative sign is then added to the values obtained above the iso-electric point. The iso-electric point of the α - Al_2O_3 particles was obtained as about pH 5.8. From the Figure4.4, we observed that the surface charge on the α -alumina particles was dependent strongly on the pH of the solution in which they were immersed. This was because the α -alumina particles possess groups were able to gain or lose a proton, H^+ . These amphoteric groups dissociated as hydrolysis products including $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3$ and $\text{Al}(\text{OH})_4^-$. These products were either negatively or positively charged as above or below the iso-electric

point. These results were almost coincided with those commonly found in the literature (Huisman *et al.*, 1998).

Since the sizes of hydrated ions of Al_2O_3 and H_2O are smaller under low pH than that under high pH, the steric resistance under low pH is low when water molecules pass through the membrane (Pashley and Karaman, 2004). Therefore, high permeate flux obtained under low pH conditions.

4.5 Salt Concentration

The results of permeate flux under different salt concentration are shown in Figure 4.5. From the figure, increasing the salt concentration from 0.001 to 0.05 mol/L led to an increasing in permeate flux. The physical explanation of the observed phenomena was as follows. Upon increasing the salt concentration, the Debye length (κ^{-1}) decreases. Therefore the ‘effective’ pore size increases and approaches the real pore size; the water flux increases accordingly. A similar explanation was given by Huisman *et al.* (1997). They supposed that the apparent viscosity μ_a in a cylindrical pore is related to the zeta-potential of the pore surface as

$$\kappa^{-1} = \sqrt{\frac{\varepsilon_0 \varepsilon k T}{1000 N_A e^2 \sum_i c_i z_i^2}} \quad (4.2)$$

$$\frac{\mu_a}{\mu_0} = \left(1 - \frac{8\beta(e\zeta/kT)^2 (1-G)F}{(\kappa r)^2}\right)^{-1} \quad (4.3)$$

where ε_0 the permittivity of vacuum, ε the static dielectric constant of the medium, k Boltzmann constant, T the absolute temperature, N_A Avogadro’s number, e the elementary charge, c_i the concentration of ion i , z_i the valency of ion i , μ_0 the bulk viscosity of the electrolyte solution, ζ the zeta-potential of the capillary surface, κ the Debye constant, and r is the capillary radius. G the ratio

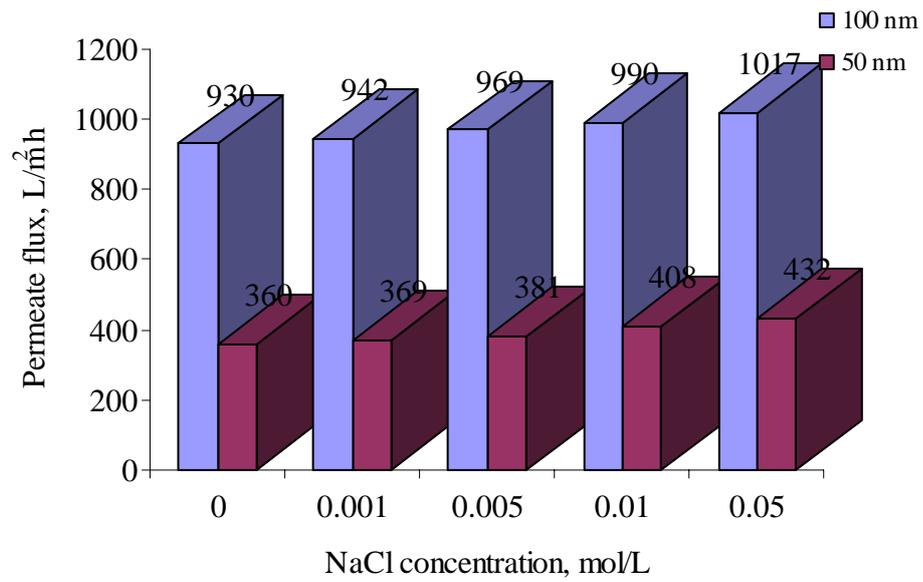


Fig.4. 5 Permeate flux under various salt concentration (0.1MPa).

of the mean electrostatic potential across the pore to the zeta potential, and F a factor used to correct Smoluchowski's equation for effects of high zeta potential and fine capillaries, both are dependent on ζ and on κr , and can be determined from graphs given by Levine *et al.* (1975). For large values of κr , $G \approx 0$ and $F \approx 1$. β is a dimensionless parameter that depends solely on electrolyte properties, given by:

$$\beta = \frac{\varepsilon^2 k^2 T^2 \kappa^2}{16 \pi^2 \mu \lambda e^2} \quad (4.4)$$

where λ is the conductivity of the electrolyte. Increasing the salt concentration increases the dimensionless parameter κr , so that the right-hand side of Eq. (4.4) approaches unity. Therefore the apparent viscosity decreases and approaches the bulk viscosity. However, at very high salt concentrations (>0.1 mol/L) the flux decreased again, since high salt concentrations cause notable increases in the bulk viscosity (Huisman *et al.*, 1998).

Figure 4.6 shows the synchronous effect of pH and salt on the permeate flux. Under the lowest pH value (pH = 3.8), the permeate flux was obvious high whether the salt concentration was low or high. Under other pH conditions, the effect of salt conditions on the permeate flux was obvious when the salt concentration changed at a range of low value. Under the highest salt concentration (0.05 mol/L), the permeate flux were almost the same values

among the pH at 5.8 – 9.8. It could be concluded that the influence from pH on permeate flux was predominant. The effect of salt on permeate flux was obvious only at pH of 5.8 – 9.8.

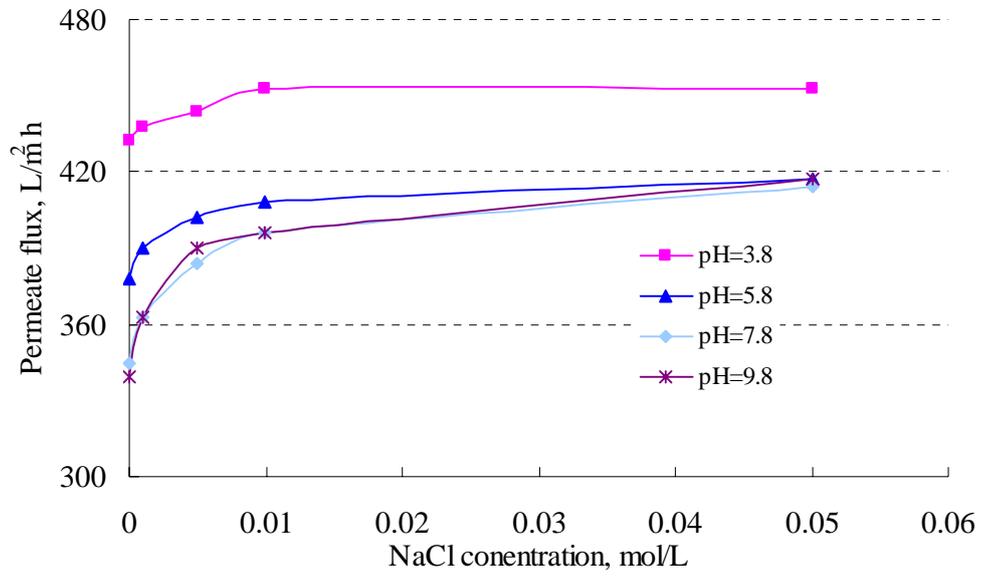


Fig.4. 6 Effect of pH and salt concentration on the permeate flux (0.1MPa, 50 nm).

4.6 Summary

This chapter describes membrane characterizations under various conditions. First of all, it is doubtless that the pore size of the membrane is the one the most important factors that affect the permeate flux. The large pore size of the membrane generates high permeate flux. Secondly, the permeate flux depends strongly on the applied TMP. When the feed solution is the pure water, the filtration resistance is only the membrane resistance. The permeate flux increased linearly with increase of TMP. Thirdly, the high permeate flux is obtained when the temperature of feed solution is high as a result of low viscosity. Finally, the influence of pH and salt concentration on the permeate flux is related to the composite and structure of the membrane materials. The changes of electric charge and effective pore size of the membrane resulted from the variations of pH and salt concentration can result in the difference in permeate flux. Both acidic and saline condition are helpful to increase the permeate flux when the feed solution is clear water (solute-free).

The influence of CFV on the permeate flux is related to the solute, colloid and particles of the feed solution. Therefore, for clear water, the influence of CFV on the permeate flux can be neglected.

CHAPTER FIVE

MEMBRANE FILTRATION PROCESS

5.1 Introduction

The size of oil droplet and the viscosity of feed solution have significant influence on filtration performance. The determination of oil droplet size and viscosity of artificial oily wastewater were done and the results were presented in this chapter. On the other hand, MF process is affected by many factors such as CFV, TMP, oil concentration and temperature of feed solution. In order to identify their influences, series of experiments were carried out in this study (Table 5.1). As the removal efficiency of membrane separation needs to be considered in real case application, TOC concentration in the permeate flux was determined. As membrane cleaning was very important to improve membrane separation capacity, the effects of different cleaners on membrane cleaning were compared as well. The most effective membrane cleaning method was proposed in the chapter. Experiment of real restaurant wastewater with ceramic membrane separation was performed in the laboratory. The suggestion on process design of the restaurant wastewater treatment system was proposed.

Table 5. 1 Summary of experimental conditions.

Pore size of membrane, nm	TMP, MPa	CFV, m/s	Oil concentration, mg/L	Temperature, °C
50	0.2	0.21 to 1.68	500	20
100	0.2	0.21 to 1.68	500	20
50	0.1 to 0.3	1.68	500	20
100	0.1 to 0.3	1.68	500	20
50	0.2	1.68/	250 to 2000	20
100	0.2	1.68	250 to 2000	20
50	0.2	1.68	500	20 to 40
100	0.2	1.68	500	20 to 40

5.2 Size and Viscosity

5.2.1 Size Distribution

A membrane can be described as a semipermeable barrier between two phases which prevent intimate contact. Both pore size of membrane and solute size play a key role in determining permeability and selectivity of a membrane. The ratio λ was defined as follow:

$$\lambda = \frac{d_s}{d_p} \quad (5.1)$$

where d_s the solute diameter, and d_p pore diameter of membrane. Hence, λ was usually used to indicate the influence of steric factors on the membrane rejection characteristics. As expected, high solute rejection occurred as a result of low high λ value (Leenaars and Burggraaf, 1985; Langer and Schnabel, 1990). The retention of solute for a given diameter membrane may also vary with the nature of pores and membrane material characteristics (Fane and Hodgson, 1990).

For oily water membrane filtration, the size of oil droplet affects permeate quality and permeability. Oil dispersions are often not homogenous, it may comprise of several dispersion types. Figures 5.1-5.2 show typical particle size distributions for oil-water emulsion before and after membrane filtration

process. The size distributions of particles had changed after separation and the average particle size for feed solution was 677.5 nm, while the average size oil droplet in the permeate was 192.8 nm. The determination of distribution of oil emulsion droplet size in the permeate was repeated three times to ensure the reproducibility of the analysis (Figures 5.2 a, b & c). The results indicated good reproducibility during the measurement. Most of the particles in the feed solution were larger than the nominal pore sizes of the membranes, so the permeate would have very low oil concentration. Oil droplet size in the permeate was larger than pore size of membrane because spontaneous coalescence of oil droplet occurred through thin microporous membrane (Daiminger *et al.*, 1995).

5.2.2 Viscosity of the Feed Solution

As mentioned previously, the permeate flux through the membrane can be written as:

$$Flux = \frac{\text{driving force}}{\text{viscosity} \times \text{total resistance}} \quad (5.2)$$

Therefore, the variation of viscosity of the feed solution employed would affect the flux when other operating conditions remained constant. Viscosity is one of

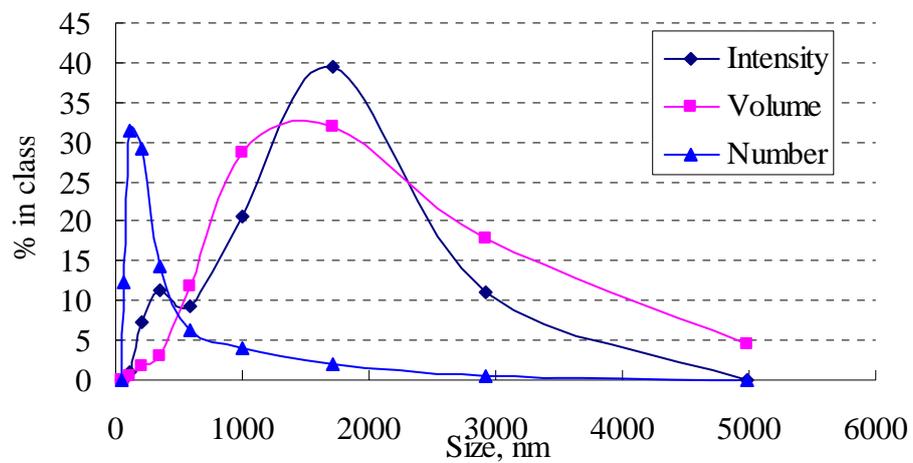


Fig.5. 1 Size distribution of oil droplets in the feed solution.

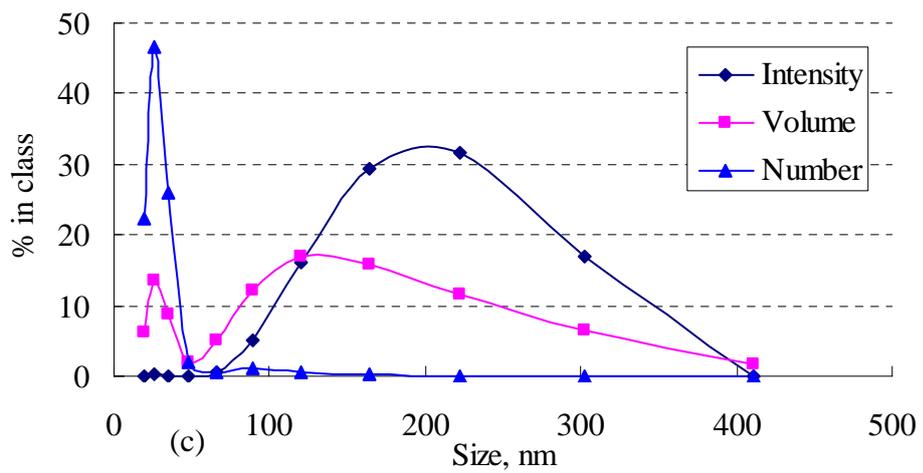
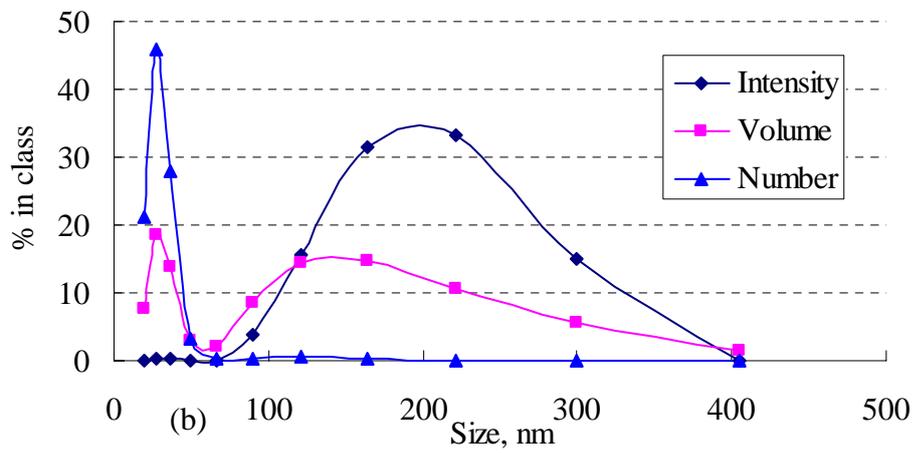
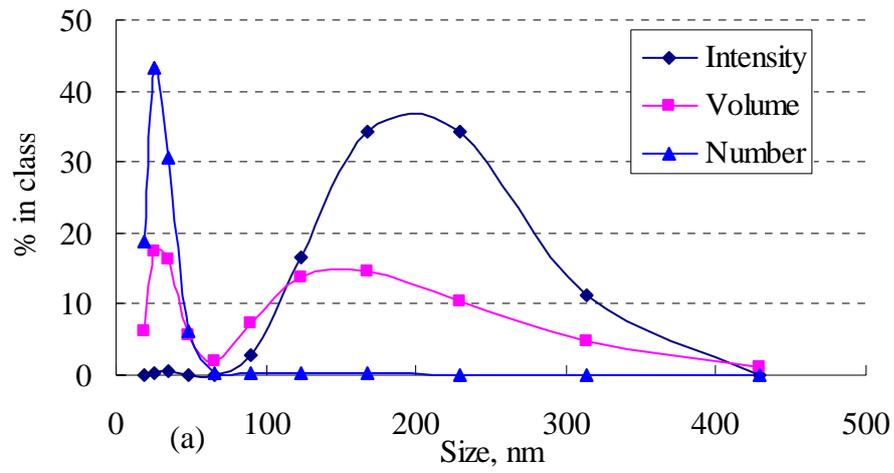


Fig.5. 2 Size distribution of oil droplets in the permeate.

the important properties of the materials. The viscosity of liquids falls with increasing temperature. Pressure has very little effect on the viscosity of water because water molecule has compressed by hydrogen bonding. In order to understand variation of viscosity under various oil concentration conditions, the viscosities of pure water and oil emulsion were determined. Results are presented in Figure 5.3. Pure water had a low viscosity, at 9.87 mPa·s. The emulsions had slightly high values of viscosity. However, when the oil concentration changed from 250 mg/L to 2 000 mg/L, the viscosity among these emulsions had no significantly difference (between 10.82 and 11.16 mPa·s). It was because oil concentration was accounted for no more than 0.2%, its influence on the viscosity was insignificant.

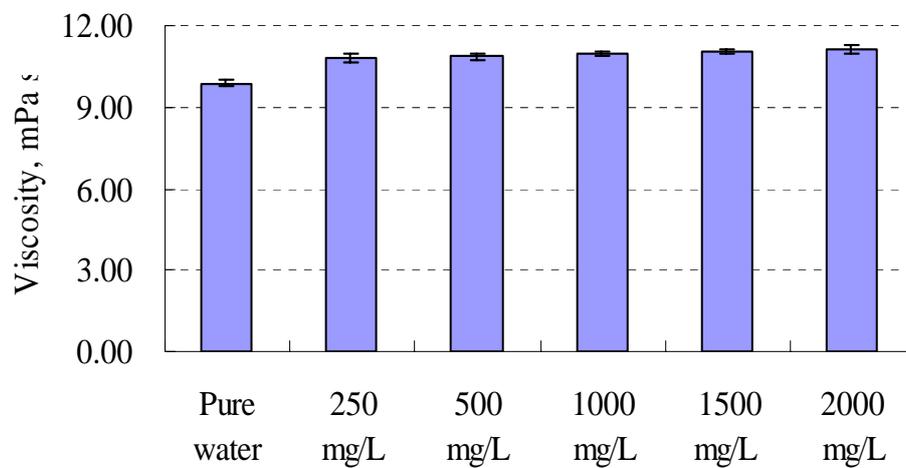


Fig.5. 3 Overview of viscosities under various oil concentrations. Values are means \pm S.D. (n=6)

5.3 Effect of Cross-flow Velocity (CFV)

5.3.1 Filtration Process

To study the effect of CFV on the permeate flux, experiments were carried out under CFV range of 0.21 – 1.68 m/s. Figures 5.4-5.5 show the time dependence of permeate flux with various CFV through the membranes of pore sizes of 50 nm, 100 nm, respectively. The initial permeate flux of membranes with pore sizes of 50 nm and 100 nm were 393 L/(m² h) and 825 L/(m² h), respectively. The permeate fluxes decreased significantly in the early stage of filtration. However, higher CFV produced higher permeate flux at the steady state. The largest permeate fluxes reached 163 L/(m² h) and 202 L/(m² h) at the steady state for membranes with pore size of 50 nm and 100 nm, respectively.

The results of membrane filtration under various CFV conditions are summarized in Table 5.2. At the largest CFV condition, the average permeate fluxes reached 206 and 293 L/(m² h), with the membrane pore size of 50 nm and 100 nm, respectively. The permeate flux at steady state of 100 nm membrane was not much larger as expected than that of 50 nm membrane. This can be explained that fouling in the membrane with large pore is more serious than that in the membrane with small pore. However, the total amount of permeate

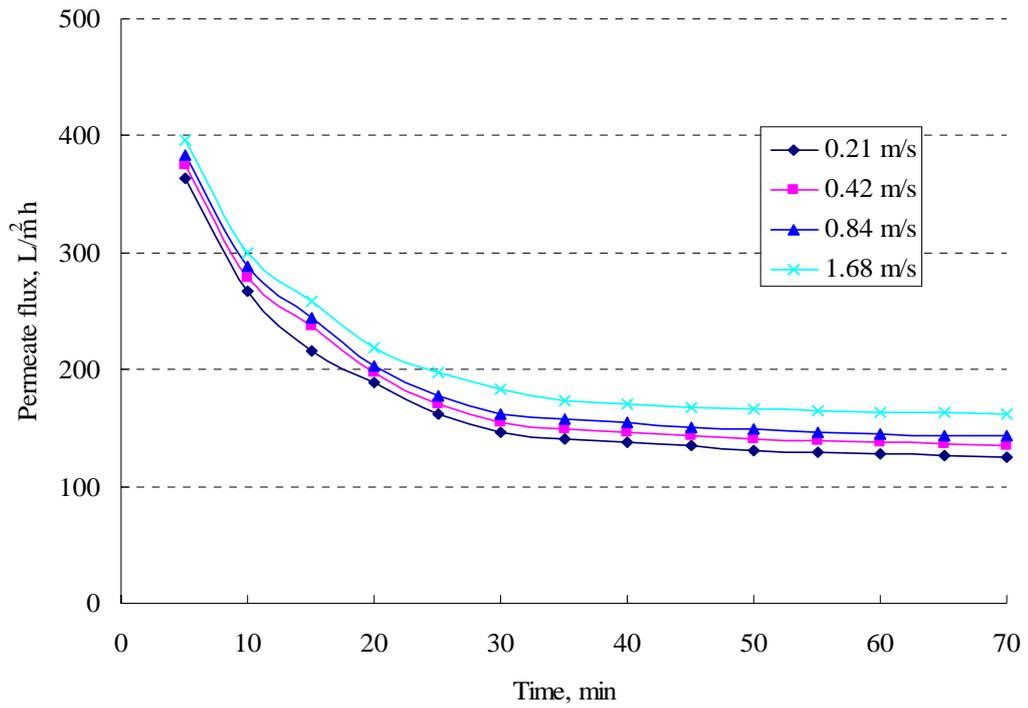


Fig.5. 4 Effect of CFV on permeate flux (0.2 MPa, 500 mg/L, 20 , 50 nm).

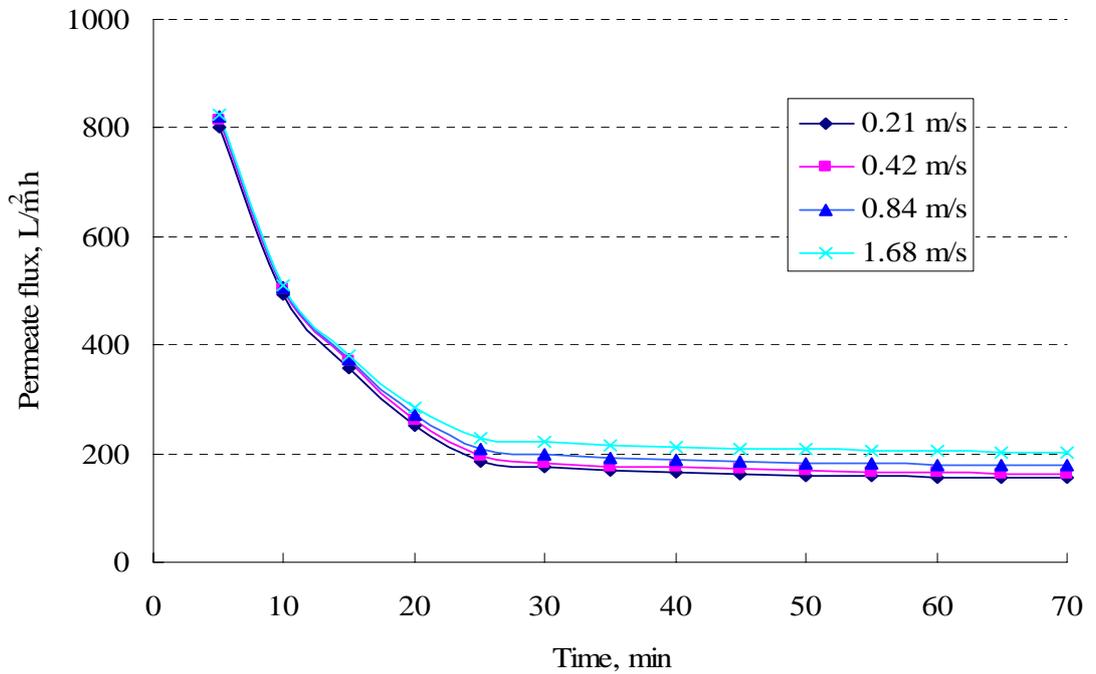


Fig.5. 5 Effect of CFV on permeate flux (0.2 MPa, 500 mg/L, 20 , 100nm).

Table 5. 2 Summary of results of membrane filtration under various CFV values (0.2 MPa, 500 mg/L oil, 20 °C).

Item	50 nm membrane			100 nm membrane		
	Total permeate, L	Steady permeate flux, L/m ² h	Average permeate flux, L/m ² h	Total permeate, L	Steady permeate flux, L/m ² h	Average permeate flux, L/m ² h
0.21	19.95	125	171	29.5	154	253
0.42	21.2	136	182	30.6	162	262
0.84	22.1	143	189	32.1	178	275
1.68	24.1	163	206	34.3	202	294

volume was almost 45% higher in 100 nm membrane than that in 50 nm membrane. This result was coincided with the previous study (Hyun and Kim, 1997).

Although CFV does not impose any influence on permeate flux when pure water is used as feed solution, however, CFV can influence the deposition of solute on the membrane surface. This effect could be evaluated by the Reynolds number.

Reynolds number (Re) is calculated through the following Equation:

$$\text{Re} = \frac{\rho v d}{\mu} \quad (5.3)$$

where ρ the density of the liquid, v the velocity of the liquid, d the diameter of the pipe, and μ the viscosity of the liquid.

The velocity (CFV) is one of most important factors which influence the Reynolds number. With all other conditions unchanged, increasing the CFV results in an increase of Reynolds number. Theoretically, in the straight pipes with constant diameter, flow is turbulent if the Reynolds number exceeds 4 000. Under this condition, the permeate flux will increase as a result of the increase of turbulency and the reduction of concentration polarization. In this research, as CFV value increased from 0.21 to 1.68 m/s, the Reynolds numbers increased from 836 to 6 680, correspondingly. Hence, the turbulent flow occurred under

the highest CFV value, which lessened the concentration polarization and solute deposition. The permeate flux increased as increase of CFV.

High CFV value can increase permeate flux of membrane filtration, however, several cautions must be paid. Turbulent flow may consume TMP of the system, which is likely to result in the decline of permeate flux. Forceful turbulent is not recommended in the MF membrane process. Koltuniewicz *et al.* (1995) reported that CFV exerted a greater effect for the high TMP than that at the low pressure. At lower pressure, the flux was almost independent of CFV changes. Besides, increasing CFV needs to increase power cost. The cost-effectiveness of system must be evaluated. Therefore, the CFV of 1.68 m/s was adopted in the following experiment.

5.3.2 TOC Rejection

Time dependence of TOC concentrations with various CFV is presented in Table 5.3. The average TOC concentrations in the permeate and average TOC removal efficiencies are illustrated in Figure 5.6. TOC concentrations in the permeate were high in the early stage of filtration process. The oil droplets,

Table 5. 3 Summary of TOC concentrations in the permeate under various CFV values (0.2 MPa, 500 mg/L oil, 20 °C), mg/L.

Item	50 nm membrane				100 nm membrane			
	0.21 m/s	0.42 m/s	0.84 m/s	1.68 m/s	0.21 m/s	0.42 m/s	0.84 m/s	1.68 m/s
0-5	12.4	12.1	12.6	13.8	20.3	20.9	20.6	21.5
5-10	10.6	10.9	11	11.4	17.2	18.1	18.3	19.3
10-15	10.1	10.3	9.5	10.1	15.8	15.9	16.7	18.3
15-20	9.5	9.5	8.9	9.3	15.1	15.3	15.8	16.8
20-25	9.3	9.2	9.3	9.2	14.6	14.4	15.2	15.4
25-30	9.3	9.4	9.1	8.9	14.8	13.8	14.3	14.6
30-35	9.6	9.1	8.6	9.2	13.6	14.1	13.6	13.9
35-40	9.2	9.4	8.4	9.3	14.2	13.9	13.7	14.3
40-45	8.9	8.9	8.7	8.8	14.3	14	14.1	14
45-50	9.1	9	9.1	8.5	14.5	14.3	14.4	13.6
50-55	9.2	8.6	8.6	8.4	14.3	14.5	14.2	13.9
50-60	8.6	8.9	8.8	8.8	14.1	13.9	14.3	13.6
60-65	8.8	8.4	8.4	8.5	13.7	14.1	14.2	13.2
65-70	9.1	8.7	8.3	8.7	13.9	14.2	14.3	13.7

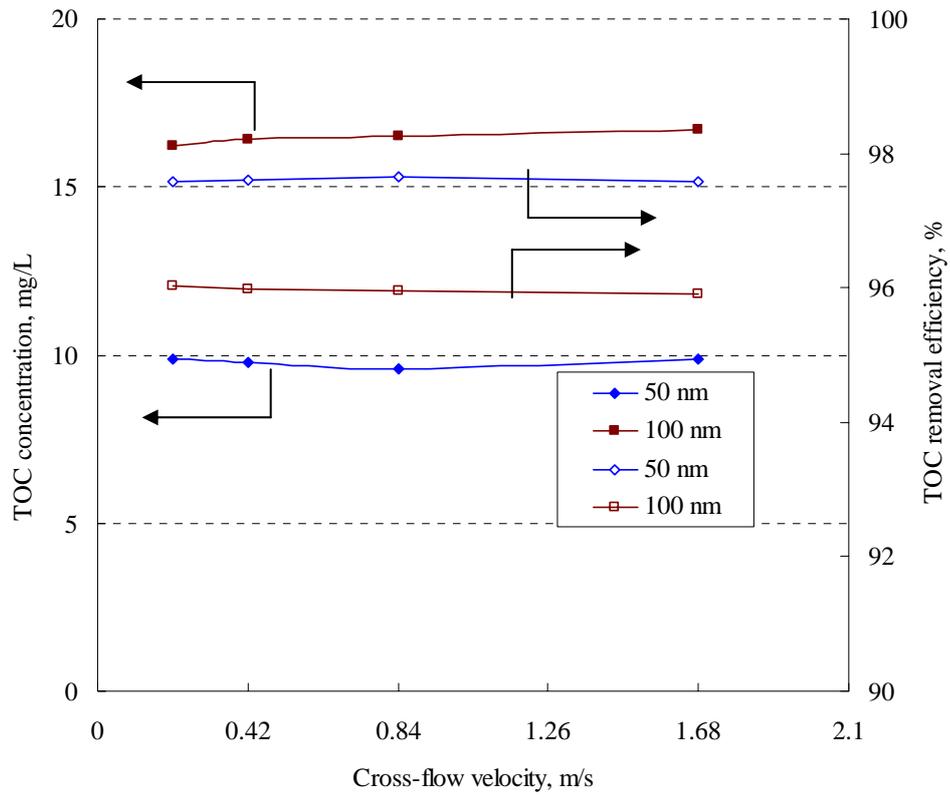


Fig.5. 6 Average TOC concentrations and removal efficiencies in the permeate under various CFV values (0.2 MPa, 500 mg/L, 20).

which were smaller than the average pore size of the membrane, permeated through the membrane and filled the pore entrances of the membrane at the same time. After that, the TOC concentrations remained stable. With membrane of its pore size of 50 nm, the average TOC concentrations in the permeate and average TOC removal efficiencies, under various CFV values, were 9.6 - 9.9 mg/L and 97%, respectively; while with the membrane of its pore size of 100 nm, the average TOC concentrations in the permeate and average TOC removal efficiencies, under various CFV values, were 16.2 - 16.7 mg/L and 96%, respectively. The results indicated the removal efficiencies obtained under these operating conditions were quite satisfactory. The corresponding oil concentrations in the permeate were much lower than permission standard.

For each membrane, the results of one-way ANOVA showed that both the average TOC removal efficiencies and the average TOC concentrations had no significant difference under various CFV values ($p > 0.05$).

5.4 Effect of TMP

5.4.1 Filtration Process

To study the effect of TMP on the permeate flux, experiments were carried out under TMP range of 0.1 – 0.3 MPa. Figures 5.7-5.8 show the time dependence of permeate flux with various TMP through membrane with their pore size of 50 nm, 100 nm, respectively. As could be observed for each membrane, the initial permeate flux had a high value. The permeate fluxes decreased sharply in the early stage of filtration and then decreased slowly to a constant value. The permeate flux value under a steady state was strongly dependent on TMP conditions. Higher TMP resulted in higher permeate flux at the steady state for both membranes. The largest permeate fluxes at their steady state reached 207 L/(m² h) and 236 L/(m² h) under the highest TMP conditions for the membranes with its pore diameter of 50 nm, 100 nm, respectively.

The detailed results of membrane filtration under various TMP are summarized in Table 5.4. At the highest TMP value, the average permeate fluxes reached 283 and 371 L/(m² h), with the membrane pore size of 50 nm and 100 nm, respectively. The permeate flux at steady state of 100 nm membrane was not much larger as expected than that of 50 nm membrane, because fouling in the

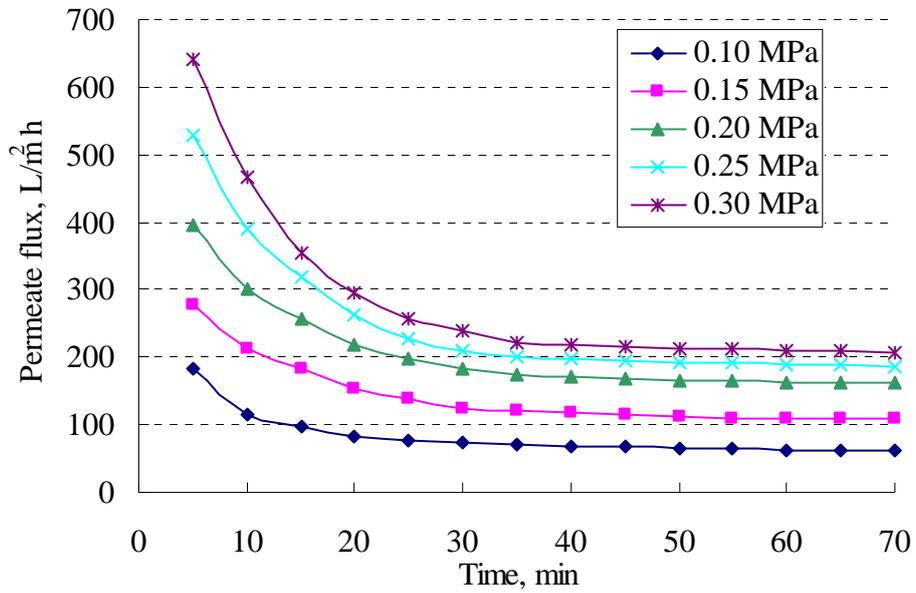


Fig.5. 7 Effect of TMP on permeate flux (1.68 m/s, 500 mg/L, 20 °C, 50 nm).

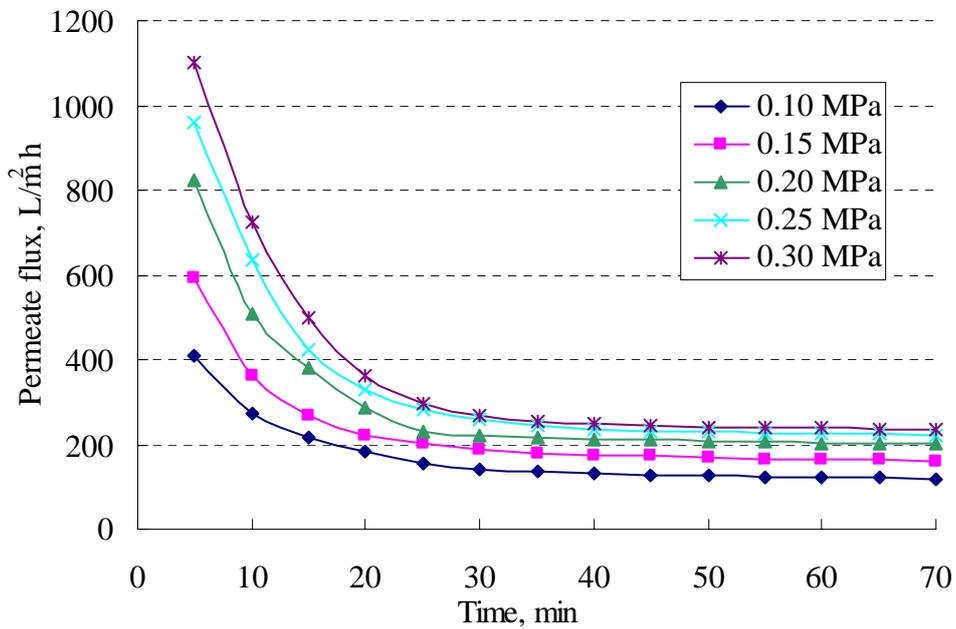


Fig.5. 8 Effect of TMP on permeate flux (1.68 m/s, 500 mg/L, 20 °C, 100nm).

Table 5. 4 Summary of results of membrane filtration under various TMP values (1.68 m/s, 500 mg/L oil, 20 °C).

Item	50 nm membrane			100 nm membrane		
TMP, MPa	Total permeate, L	Steady permeate flux, L/m ² h	Average permeate flux, L/m ² h	Total permeate, L	Steady permeate flux, L/m ² h	Average permeate flux, L/m ² h
0.10	9.6	61	82	19.9	119	170
0.15	16.6	108	142	26.6	162	227
0.20	24.1	163	206	34.3	202	294
0.25	29	187	249	39.3	223	337
0.30	33.3	207	283	43.3	236	371

membrane with large pore size is more serious than that in the membrane with small pore size. From the Table 5.4, it is also found that the increase of permeate flux was obvious when the TMP was increased from a low narrow value. When TMP was larger than 0.2 MPa, the effect of increasing the TMP to improve permeate flux was lessened. It was significantly different from the membrane filtration performance using pure water as feed solution. Under the later circumstance, since no solute existed in the feed stream, there was no membrane fouling existed in the filtration process. The permeate flux always increased proportionally with the TMP applied in the membrane module. However, when solute existed in the feed solution, membrane fouling acted on the filtration process.

When solute is presented in the feed stream, the influence of TMP on the permeate flux has both positive and negative effect. The positive effect was that under higher TMP the droplets (both solvent and solute) passed through the membrane pores rapidly, while the negative effect was that more and more oil droplet accumulated both on the membrane surface and in the membrane pore, which resulted in membrane fouling and decrease of permeate flux. However, the positive effect on the permeate flux was predominant in the range of low TMP conditions, so the permeate flux increased obviously with the increase of TMP. Actually, at low TMP the flux increased almost proportionally with TMP

up to a point commonly described as the “threshold pressure” (Strohwalde and Ross, 1992; Elmaleh *et al.*, 1994; Elmaleh and Ghaffor, 1996). This was characterized as the pressure-controlled regime. Beyond the threshold pressure, the flux increased nonlinearly with TMP due to concentration polarization (Porter, 1990; Lee *et al.*, 2004). Occasionally, a permeate flux decline happened as TMP became excessive (Bhave and Fleming, 1988). Increasing of TMP value will result in the increase in power consumption, meanwhile, membranes been previously used at a higher pressure show increased susceptibility to fouling in the next run (Koltuniewicz *et al.*, 1995). Therefore, 0.2 MPa for TMP was selected in the next experiment.

5.4.2 TOC Rejection

Time dependence of TOC concentrations in the permeate with various TMP conditions are presented in Table 5.5. The average TOC concentrations in the permeate and average TOC removal efficiencies are illustrated in Figure 5.9. TOC concentrations in the permeate were high in the early stage for each membrane filtration process. The oil droplets, which were smaller than the average pore size of the membrane, permeated through the membrane and filled the pore entrances of the membrane at the same time. The same phenomenon

was less obvious in the membrane with its pore diameter of 50 nm due to its small pore size. After that, the TOC concentrations in the permeate became stable. Besides, the TOC concentrations in the permeate were obviously affected by TMP conditions. The high TMP value resulted in high TOC concentrations in the permeate, it was because high TMP deformed oil droplets and the oil droplets passed through the membrane pores rapidly. When the TMP was larger than 0.2 MPa, the influence on TOC was obvious. The average TOC concentrations in the permeate and average TOC removal efficiencies for the membrane with its pore size of 50 nm, under various TMP were reached 7.6 - 30.9 mg/L and 92 - 98%, respectively; while the average TOC concentrations in the permeate and average TOC removal efficiencies for the membrane with its pore size of 100 nm, under TMP were reached 13.5 - 41.8 mg/L and 90 - 97%, respective. High removal efficiencies also achieved under various TMP conditions for both membranes. Although large variations of TOC concentrations in the permeate existed, the corresponding oil concentrations still met the permission standard. However, care should be taken when high TMP value is applied to membrane filtration.

For each membrane, the results of one-way ANOVA showed that both the average TOC concentrations in the permeate and the average TOC removal efficiencies had no significant difference under the TMP of 0.1, 0.15 and 0.2

MPa ($p > 0.05$). However, TOC removal efficiencies decreased rapidly from 98% to 92% for membrane with its pore size of 50 nm, from 96% to 90% for membrane with its pore size of 100 nm, when the TMP increased from 0.2 to 0.3 MPa. This also revealed that TMP higher than 0.2MPa was inappropriate for the sake of high effluent quality.

Table 5. 5 Summary of TOC concentration in the permeate under various TMP values (1.68 m/s, 500 mg/L oil, 20 °C), mg/L.

Item	50 nm membrane					100 nm membrane				
	0.1 MPa	0.15 MPa	0.2 MPa	0.25 MPa	0.3 MPa	0.1 MPa	0.15 MPa	0.2 MPa	0.25 MPa	0.3 MPa
0-5	9.3	10.8	13.8	27.7	43.7	17.2	18.4	21.3	35.6	57.4
5-10	8.6	9.6	11.4	23.4	36.4	15.3	16.1	19.3	29.3	45.8
10-15	8.1	8.9	10.1	21.2	32.1	14.4	15.3	18.3	25.4	38.3
15-20	7.8	8.4	9.3	20.6	30.6	13.7	14.4	16.8	23.6	36.2
20-25	7.4	7.7	9.2	19.2	28.5	13.1	14.1	15.4	22.1	35.5
25-30	7.3	7.2	8.9	19.3	26.9	12.3	13.6	14.6	21.7	35.7
30-35	7.1	7.1	9.2	18.7	25.5	12.4	13.1	13.9	21.8	35.4
35-40	6.6	7.5	9.3	18.3	25.7	11.5	12.7	14.3	21.5	36.1
40-45	6.7	7.6	8.8	18.4	25.9	11.7	12.8	14	21	35.4
45-50	6.9	7.3	8.5	17.9	24.8	11.3	12.4	13.6	21.6	35
50-55	7	7.1	8.4	17.7	25.1	11.6	11.9	13.9	22.3	34.7
50-60	6.7	6.6	8.8	18.1	25.3	11.2	11.8	13.6	21.9	35.1
60-65	6.5	7.2	8.5	18.3	25.7	11.5	12.4	13.2	21.4	35.3
65-70	6.9	7.3	8.7	18.5	24.4	11.4	12.3	13.7	21.7	35.7

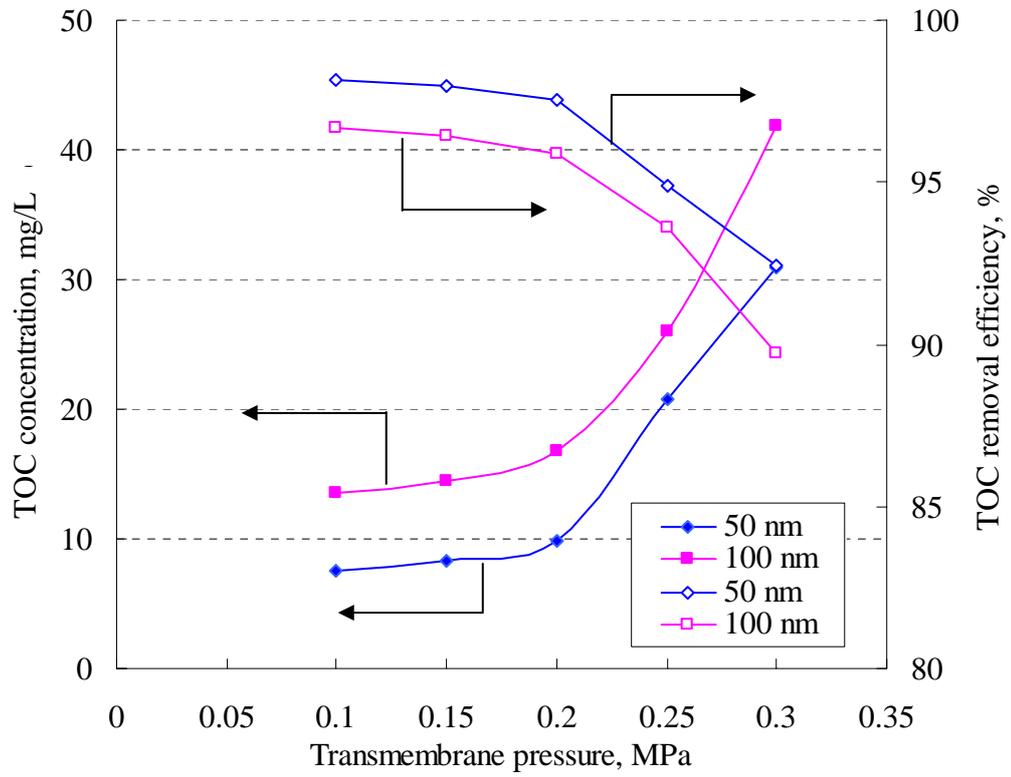


Fig.5. 9 Average TOC concentrations and removal efficiencies in the permeate under various TMP values (1.68 m/s, 500 mg/L, 20 °C).

5.5 Effect of Oil Concentration

5.5.1 Filtration Process

Although the effect of oil concentration on the permeate flux was not apparent as TMP and total resistance in the calculation equation of permeate flux, the influence of oil concentration on filtration process was still obvious. To study the effect of oil concentration on the permeate flux, some experiments were carried out with oil concentration range of 250 – 2 000 mg/L. Figures 5.10 - 5.11 show the time dependence of permeate flux with various oil concentrations through membrane with their pore sizes of 50 nm, 100 nm, respectively. It was found that membrane with pore size of 50 nm had a highest permeate flux of 415 L/(m² h) at the beginning of filtration, while the membrane with its pore diameter of 100 nm had a highest permeate flux 842 L/(m² h) at the beginning of filtration. The permeate fluxes through both membrane decreased sharply in the early stage of filtration and then decreased slowly to a constant value. The permeate flux value under steady state was also related to oil concentration. Low permeate flux at steady state was generated under high oil concentration in the two membranes. The largest permeate fluxes at the steady state of 167 and 208 L/m² h were obtained for the membranes with its pore size of 50 nm, 100 nm, respectively.

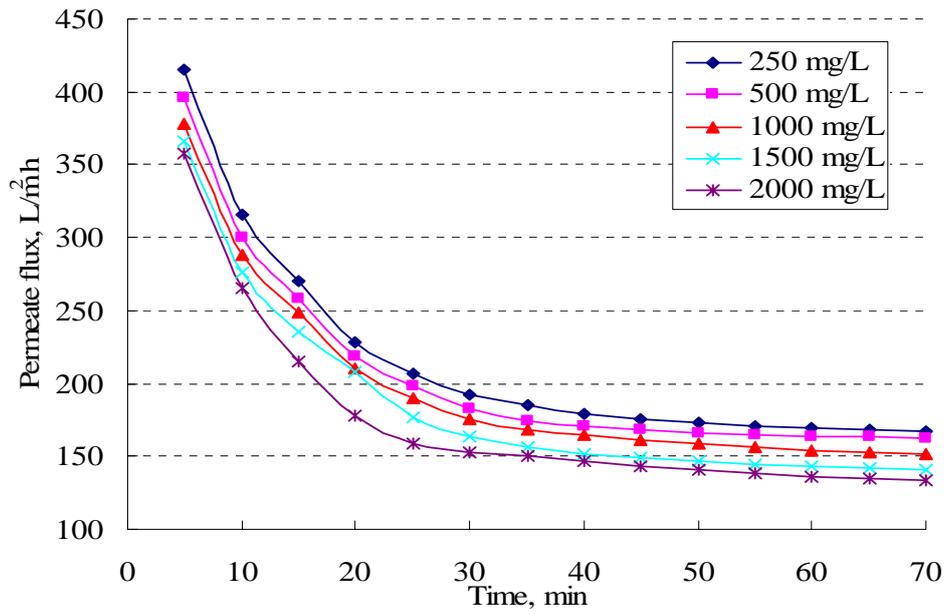


Fig.5. 10 Effect of oil concentration on permeate flux (1.68 m/s, 0.2 MPa, 20 °C, 50 nm).

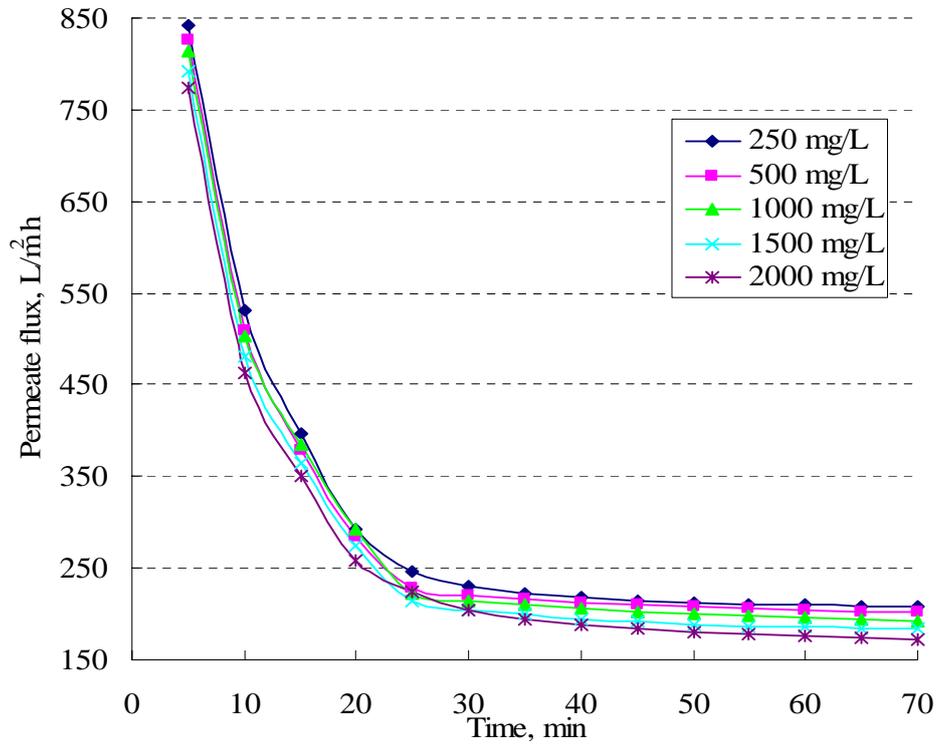


Fig.5. 11 Effect of oil concentration on permeate flux (1.68 m/s, 0.2 MPa, 20 °C, 100 nm).

The detailed results of membrane filtration under various oil concentrations are summarized in Table 5.6. The influence of oil concentration on average permeate flux was small at low oil concentrations. Small variation of steady state permeate flux and average permeate flux was found when the oil concentrations were between 250 and 500 mg/L. As a result, the higher the oil concentration in the feed solution, the lower the permeate flux.

The effect of oil concentration on permeate flux can be classified into two parts. Firstly, oil content would affect the viscosity of the solution. As increasing the oil concentration, the viscosity of the feed solution becomes large. The determination results showed the variation of viscosity was not obvious with an oil concentration range of 250 to 2 000 mg/L. Therefore, this kind of influence could be neglected. Secondly, oil concentration results in membrane fouling. As oil concentration increased, more oil droplet accumulated in the membrane surface and membrane pore as well, which interfered with the water penetration. This is the main reason that resulted in the decrease in permeate flux.

5.5.2 TOC Rejection

Time dependence of TOC concentrations in the permeate with various oil concentrations are presented in Table 5.7. The average TOC concentrations in

Table 5. 6 Summary of results of membrane filtration under various oil concentrations (1.68 m/s, 0.2 MPa, 20 °C).

Item	50 nm membrane			100 nm membrane		
Oil concentration, mg/L	Total permeate, L	Steady permeate flux, L/m ² h	Average Permeate flux, L/m ² h	Total permeate, L	Steady permeate flux, L/m ² h	Average permeate flux, L/m ² h
250	25.2	167	215	35.5	208	304
500	24.1	163	206	34.3	202	294
1000	23	152	197	33.6	193	288
1500	21.7	141	186	32	184	275
2000	20.4	133	175	31	173	266

the permeate and average TOC removal efficiencies are illustrated in Figure 5.12. TOC concentrations in the permeate were also affected by oil concentration in the feed. High oil concentration resulted in high TOC concentration in the permeate. It was because high oil concentration contained large proportion of small oil droplets which could easily pass through the membrane pores. When the oil concentration in feed was larger than 1000 mg/L, the influence on TOC in the permeate was obvious. The average TOC concentrations in the permeate and average TOC removal efficiencies for the membrane with its pore diameter of 50 nm, under various oil concentrations were reached 8.6 - 32.9 mg/L and 96 - 98%, respectively; while the average TOC concentrations in the permeate and average TOC removal efficiencies for the membrane with its pore diameter of 100 nm, under various oil concentrations were reached 13.2 - 52 mg/L and 94 - 97%, respectively. The results showed that the removal efficiencies were always satisfactory. The corresponding oil concentration in the permeate still can meet the discharge standard.

For each membrane, the results of one-way ANOVA showed that the average TOC removal efficiencies had no significant difference with the oil concentration of 500, 1000, 1500 and 2000 ($p > 0.05$). However, obvious difference was existed in the average TOC concentrations of the permeation under different initial oil concentrations.

Table 5. 7 Summary of TOC concentration in the permeate under various oil concentrations (1.68m/s, 0.2MPa, 20 °C), mg/L.

Item	50 nm membrane					100 nm membrane				
	250 mg/L	500 mg/L	1000 mg/L	1500 mg/L	2000 mg/L	250 mg/L	500 mg/L	1000 mg/L	1500 mg/L	2000 mg/L
0-5	10.2	13.8	23.1	38.2	50.3	18.4	21.3	46.7	60.8	71.1
5-10	9.4	11.4	16.5	26.8	35.6	13.9	19.3	32.1	42.3	55.6
10-15	9.1	10.1	13.2	23.2	32.8	12.3	18.3	26.5	38.5	50.1
15-20	8.6	9.3	11.6	22.5	30.4	11.4	16.8	25	35.7	48.3
20-25	8.3	9.2	11.7	22.3	28.4	11.5	15.4	24.6	34.6	45.7
25-30	8	8.9	11.4	22.7	28.2	11.2	14.6	24.4	33.2	44.3
30-35	8.1	9.2	10.9	22.3	27.9	10.9	13.9	23.9	31.4	42.6
35-40	7.8	9.3	11.5	22.1	28.4	11.1	14.3	24.1	30.9	43.5
40-45	7.8	8.8	11.3	21.6	28.5	11.5	14	24	30.3	44.2
45-50	8.2	8.5	11	21.9	28.1	11	13.6	24.7	30.6	44.1
50-55	8.1	8.4	11.2	21.3	28.3	11.4	13.9	24.2	30.4	46.2
50-60	7.6	8.8	11.6	21	28.5	11.7	13.6	24.4	30.4	43.2
60-65	8.3	8.5	11.3	21.3	28.8	11.5	13.2	24.5	30.2	42.8
65-70	8.2	8.7	11.3	21.4	28.2	11.3	13.7	24.3	30.7	43.1

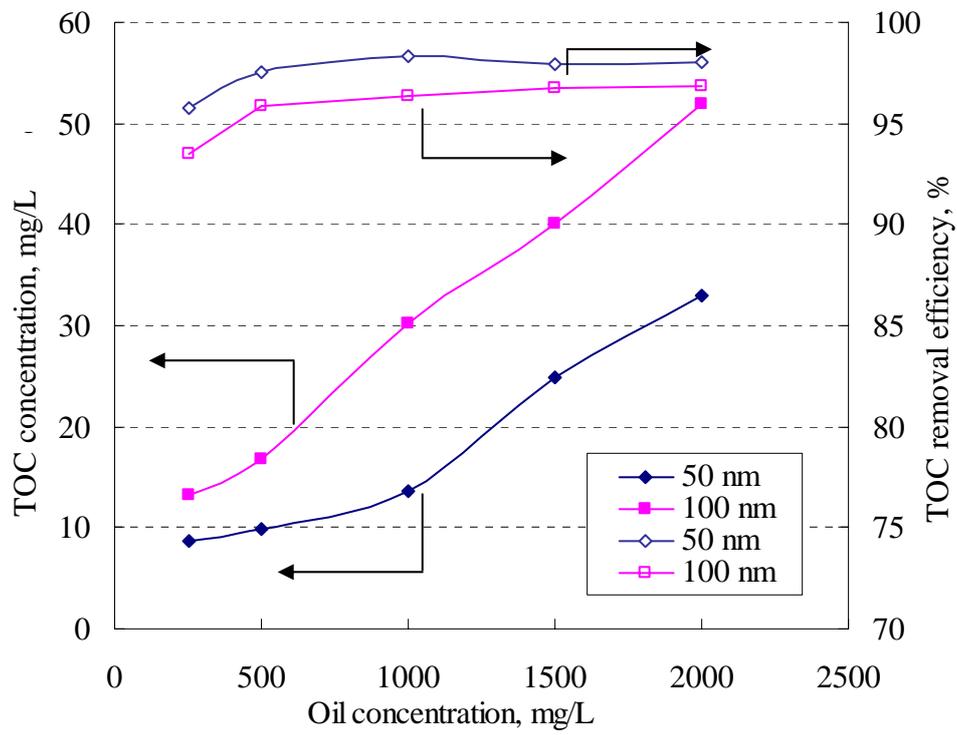


Fig.5. 12 Average TOC concentrations and removal efficiencies in the permeate under various oil concentrations (1.68 m/s, 0.2 MPa, 20 °C).

5.6 Effect of Temperature

5.6.1 Filtration Process

The effect of temperature on flux can be quite significant even within the constraints imposed by the system such as the nature of feed or product. To study the effect of feed temperature on the permeate flux, experiments were carried out under the temperatures of 20, 30, and 40 °C. Figures 5.13-5.14 show the time dependence of permeate flux with various temperatures through membrane with their pore size of 50 nm and 100 nm, respectively. The permeate flux value under steady state was dependent on temperature. High temperature produced high permeate flux at steady state in both membrane. The detail results of membrane filtration under various temperatures are summarized in Table 5.8.

The reason that the permeate flux increased with increase of feed temperature was due to the reduction of viscosity. Although high temperature of a fluid would reduce the cohesive force while simultaneously increase the rate of molecular interchange, the net results show a reduction in viscosity with increasing temperature. According to Eq. (2.3), the permeate flux increased with the decrease of viscosity. Meanwhile, increasing temperature increases

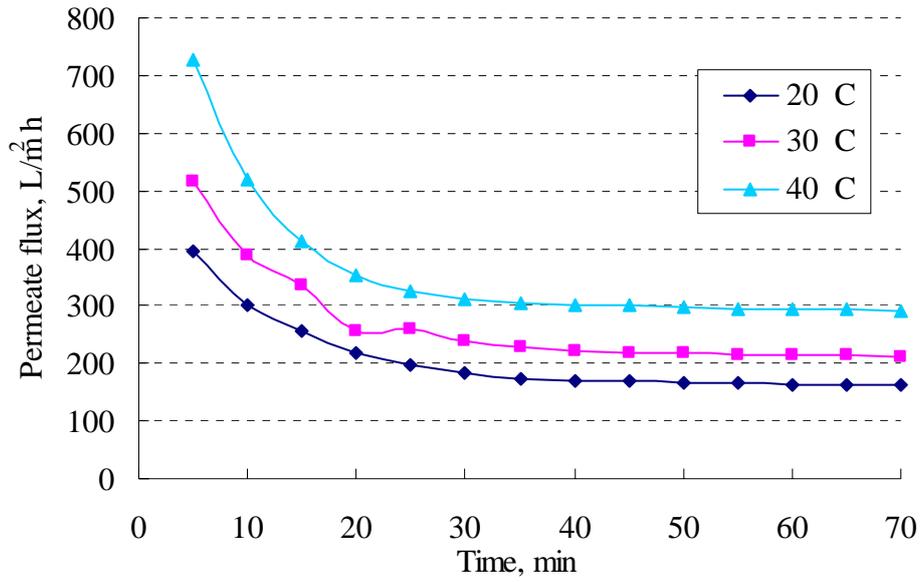


Fig.5. 13 Effect of temperature on permeate flux (1.68 m/s, 0.2 MPa, 500 mg/L, 50 nm).

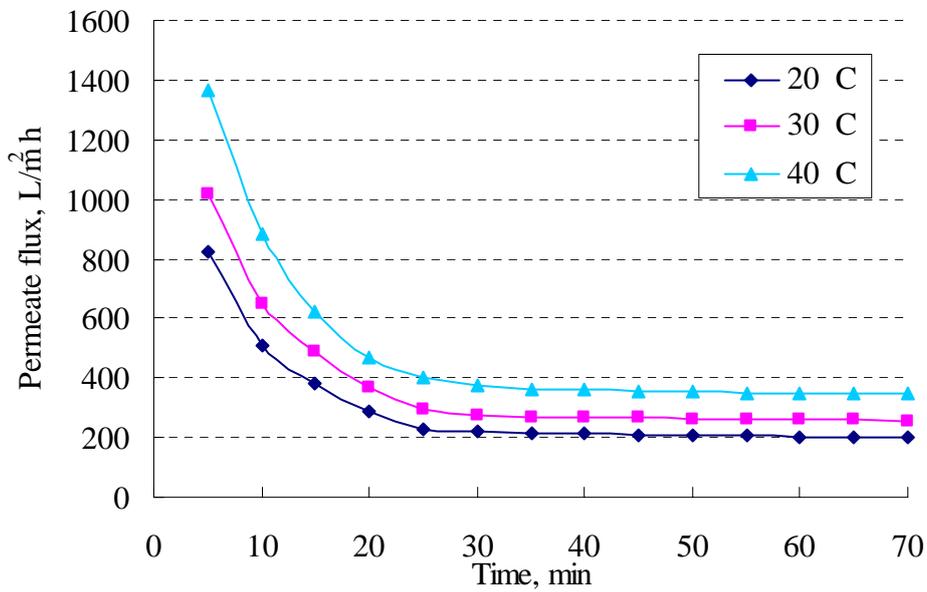


Fig.5. 14 Effect of temperature on permeate flux (1.68 m/s, 0.2 MPa, 500 mg/L, 100 nm).

Table 5. 8 Summary of results of membrane filtration under various temperatures (1.68m/s, 0.2MPa, 500 mg/L).

Item	50 nm membrane			100 nm membrane		
Temperature, °C	Total permeate, L	Steady permeate flux, L/m ² h	Average permeate flux, L/m ² h	Total permeate, L	Steady permeate flux, L/m ² h	Average Permeate flux, L/m ² h
20	24.1	163	206	34.3	202	294
30	31.2	212	267	43.3	257	371
40	41.9	292	359	57.9	346	496

diffusivity, and thus increases permeate flux. In the case of dilution aqueous solution, the permeate flux can be increased by a factor 2 by raising the temperature from 20-50 °C (Bhave and Fleming, 1988).

5.6.2 TOC Rejection

Time dependence of TOC concentrations in the permeate with various feed solution temperature are presented in Table 5.9. The average TOC concentrations in the permeate and average TOC removal efficiencies are illustrated in Figure 5.15. The average TOC concentrations in the permeate and average TOC removal efficiencies for the membrane with its pore size of 50 nm, under various temperatures maintained at 16.7 - 25.9 mg/L and 96.7 - 97.6%, respectively; while the average TOC concentrations in the permeate and average TOC removal efficiencies for the membrane with its pore size of 100 nm, under various temperatures stayed at 13.2 - 52 mg/L and 93.6 - 95.9%, respectively. TOC concentrations in the permeate were affected by temperature. The reason was largely due to high solubility of oil in the water as a result of high temperature of feed solution (Osada and Nakagawa, 1992).

For each membrane, the results of one-way ANOVA showed that the average TOC removal efficiencies had no significant difference under various temperatures ($p > 0.05$), while obvious difference was existed with various average TOC concentrations.

Table 5. 9 Summary of TOC concentrations in the permeate under various temperatures (1.68 m/s, 0.2MPa, 500mg/L oil), mg/L.

Item	50 nm membrane			100 nm membrane		
	20°C	30°C	40°C	20°C	30°C	40°C
0-5	13.8	15.2	19.3	21.3	31.2	38.9
5-10	11.4	12.3	15.6	19.3	23.6	26.3
10-15	10.1	10.6	13.1	18.3	21.1	24.1
15-20	9.3	10.2	12.6	16.8	19.7	22.5
20-25	9.2	10.1	12	15.4	19.4	22.3
25-30	8.9	10.4	11.7	14.6	19.1	21.8
30-35	9.2	9.6	11.5	13.9	19.5	21.4
35-40	9.3	9.3	11.9	14.3	18.6	21.6
40-45	8.8	10.2	12.1	14	18.3	21.4
45-50	8.5	9.1	11.4	13.6	18.5	21.1
50-55	8.4	9.3	11.2	13.9	18.9	21.5
50-60	8.8	9	11.6	13.6	18.4	21.9
60-65	8.5	9.4	11.3	13.2	18.5	21.3
65-70	8.7	9.5	11.1	13.7	18.3	21.2

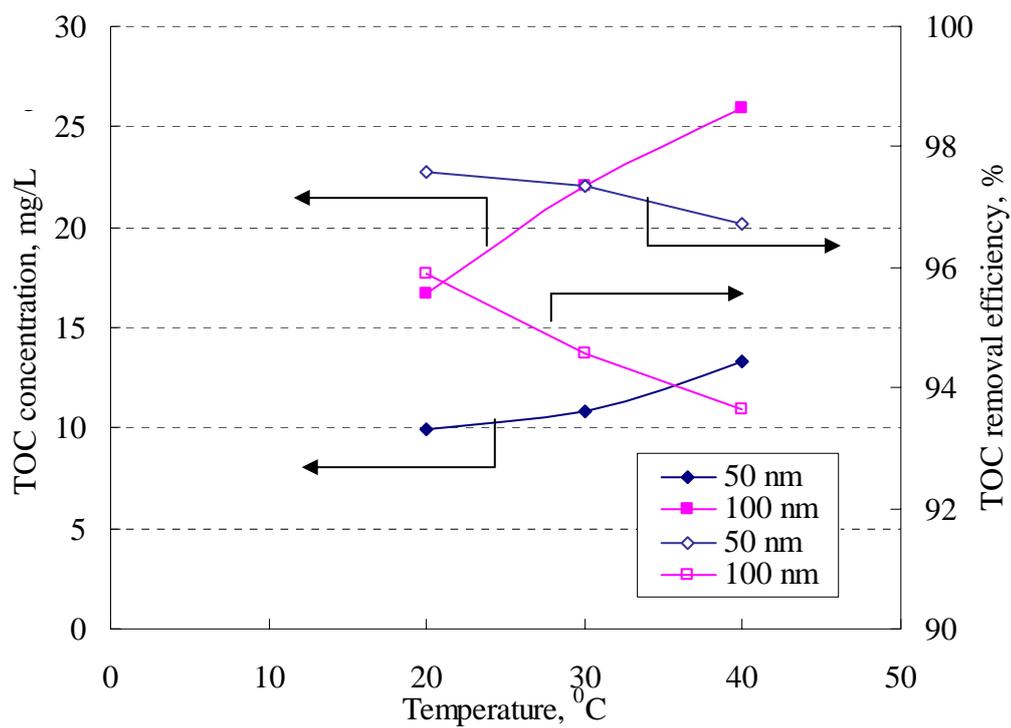


Fig.5. 15 Average TOC concentrations and removal efficiencies in the permeate under various temperature (1.68 m/s, 0.2 MPa, 500 mg/L).

5.7 Membrane Cleaning

Fouling is a major problem in all membrane operations. Fouling can be defined as the irreversible deposition of retained particles, colloids, macromolecules, salts, etc., at the membrane surface or inside the membrane at the pore wall, which causes a continuous flux decline. There is extensive literature on fouling (Matthiasson and Sivik, 1980; Tarnawski and Jelen, 1986; Fane and Fell, 1987). Fouling occurs mainly in MF/UF where porous membranes are used, which is inherently susceptible to fouling. The flux decline in MF can reach over 90% in pure water flux (Bhave, 1991). The fouling behaviour in microfiltration is much more complex compared with ultrafiltration. There are four cases affecting MF membrane (Belfort *et al.*, 1993). Cross-flow filtration is often helpful in slowing down membrane fouling but does not completely eliminate it (Baker *et al.*, 1985). Therefore, membrane cleaning is necessary.

5.7.1 Factors that Affect Cleaning Effectiveness

In order to acquire a cost-effective membrane cleaning, some factors must be taken into consideration before the membrane cleaning starts (Zheng and Wang,

2000; Hoffman, 2003; Baker, 2004).

1) Chemical cleaner: Contrary to the cellulose acetate and polyamide membrane, ceramic/inorganic membrane can withstand high acid, alkali, and chlorine concentration, as well as a wide variety of chemicals.

2) Fluid mechanics: Cleaning solutions should be pumped through the system under turbulent flow conditions, generally at Reynolds numbers greater than 2100. The pressures applied on the membrane filtration should be as low as possible, but fulfilling the requirement of maintaining CFV. High TMP merely serve to re foul the membrane with the foulant.

3) Time: Most chemical cleaners complete their actions within 30-60 minutes. Prolonged cleaning after optimum DURATION may actually cause refouling of the membrane due to filtration effect.

4) Temperature: The temperature of the cleaning solution should be as high as possible, but within the temperature limitations of the membrane. High temperature could increase the chemical reaction rate.

5.7.2 Efficiency Comparison

In this study, membrane cleaning protocol was as follows. Firstly, the fouled 50 nm and 100 nm membranes were cleaned with chemical cleaner for 1 hour at a cross-flow rate of 0.68 m/s and a TMP of 0.1 MPa, then, the system was rinsed tap water until the permeate reached neutral. At last, the permeate flux was measured again using distilled water to identify effect of membrane cleaning.

The results of membrane cleaning with various chemical cleaners are presented in the Table 5.10. WFR for each chemical cleaner is showed in Figure 5.16. A comparison of recovery from membrane cleaning with five chemicals indicated that the most effective chemical agent is NaClO. WFR of membrane cleaning with NaClO was 69% and 75%, for the membranes of 50 nm and 100 nm, respectively. High cleaning efficiency is mostly contributed to oxidant and alkaline (Jin *et al.*, 2000). However, there was some evidences that hypochlorite solution could cause membrane swelling (Kang and Choo, 2003; Lim and Bai, 2003). Hence, hypochlorite was only used with specific membranes that are not susceptible to chlorine damage. Alkalis were also effective cleaning agents from the view of membrane cleaning. The WFR of membrane cleaning with NaOH in this study was 62% and 69%, for the membranes of 50 nm and 100 nm,

Table 5. 10 The cleaning effect of different cleaning agents, L/m² h.

Item	50 nm membrane			100 nm membrane		
	Initial (J _i)	Before cleaning (J _w)	After cleaning (J _f)	Initial (J _i)	Before cleaning (J _w)	After cleaning (J _f)
NaOH, 0.5 mol/L	301	61.3	214	833	108	605
HNO ₃ , 0.2 mol/L	293	59.4	146	821	112	391
NaClO, 0.01 mol/L	290	60.2	219	816	105	641
EDTA, 0.2 mol/L	291	58.9	132	823	108	337
Tween-80	288	59.1	173	814	111	511

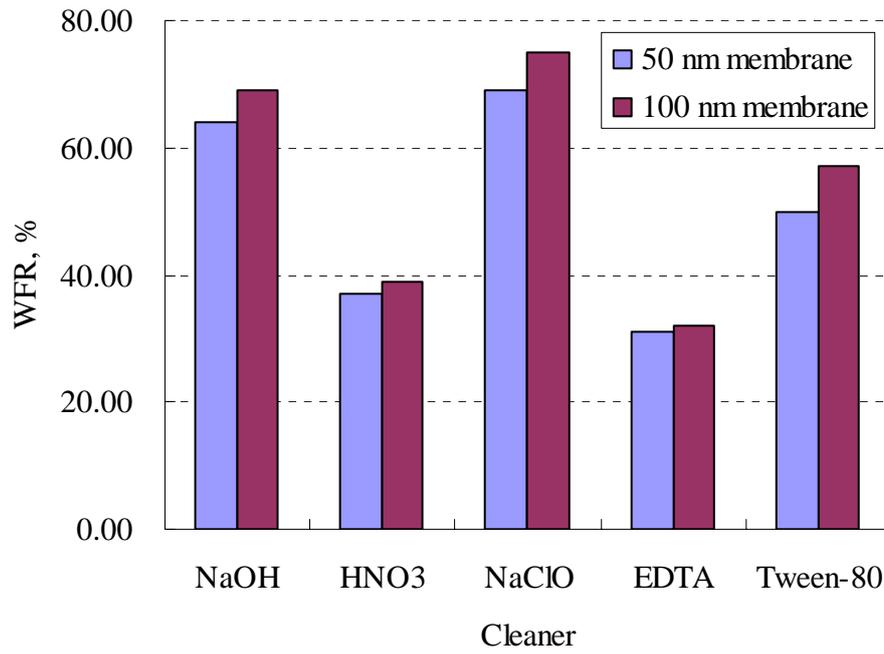
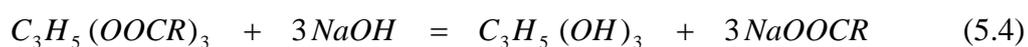


Fig.5. 16 WFR under each chemical cleaner.

respectively. Alkali cleaners for membrane cleaning is followed by different mechanisms, including neutralization of acidic materials (e.g., fatty acids and humic acids), hydrolysis of fats and oils, and dispersion of colloidal material (Kim *et al.*, 1993). Esters are insoluble in acidic media, but they are more soluble under alkaline condition. The hydrolysis reaction is of the general form



However, the reaction product (R-COONa) could become insoluble in acid solution (where they were converted to the corresponding fatty acids) or they formed precipitates in the presence of divalent (e.g., Ca^{2+} , Mg^{2+}) ions. Thus, most alkaline cleaners are needed to use in combination with appropriate chelating agents to remove free metal ions from solution in order to further improve cleaning efficiency.

Acid cleaners are most effective at removing insoluble salts and metal oxides. In both cases, these components are dissolved by reaction with the acid to form a soluble salt (Bedwell *et al.*, 1988). Nitric acid is also an extremely strong oxidant and can cause nitrification of some organic compounds, making it attractive for cleaning many organic and biological foulants (Daufin *et al.*, 1991). However, the cleaning efficiency in this experiment was not satisfied. The reason was explained that the fouling materials were not sensitive to HNO_3 . The complexing agent, EDTA, presented the worst cleaning effect among 5

cleaners used in this research. This was expected as a result of foulants hardly containing metal precipitates. Surfactant (tween-80) had a fair appearance in this experiment. WFR for both membranes was in a range of 50 - 57%. Surfactant function as effective cleaning agents by (1) displacing foulants from the membrane surface due to their strong surface adsorption, (2) emulsifying oils, and (3) solubilising hydrophobic foulants by incorporating them into surfactant micelles. Tween-80, as a typical nonionic surfactant, is stable and effective in both acidic and alkali solutions, and it is not affected by the presence of metal cations.

5.7.3 Membrane Cleaning Process

In fact, membrane fouling rarely occurs by just a single foulant, and the presence of multiple inorganic and organic foulants can severely complicate the choice of an effective chemical cleaning agents. For severely fouled membranes, sequential use of strongly acidic and basic solutions may be necessary, including addition of bleaching agents such as sodium hypochlorite. The addition of complexing agent, wetting agents and/or surfactants also quite often greatly improves the cleaning efficiency. For example, membrane fouling during the UF of milk always involves a combination of proteins and calcium (inorganic)

precipitates. The protein deposits tend to dominate during milk processing. Therefore, the cleaning cycle for the system in this study typically involves an alkaline cleaner that remove proteins followed by an acid cleaner that remove the calcium salts (McCray and Glater, 1985).

In industrial application, membrane filtration processes operate in continuous mode. The re-water flux recovery is one of the important factors that should be considered in deciding membrane cleaning program. Although EDTA had a low WFR, however, its re-water flux recovery was very well, while NaClO had a high WFR but a relatively low re-water flux recovery (Jin *et al.*, 2000). The ideal membrane cleaning process should both have high WFR and high re-WFR, integrated cleaning of membrane would help to achieve this objective. Considering the experimental results and factors mentioned above, the program of membrane cleaning proposed here is sequentially washing the membrane with (1) hot water, (2) sodium hydroxide solution, (3) EDTA solution, sequentially. In order to obtain the high permeate flux, membrane cleaning should be carried out before the permeate flux reaches a steady value.

Backflushing is employed in most cross-flow microfiltration and in some ultrafiltration systems as an effective technique to disrupt or destroy the gel layer or concentration polarization layer. It also helps in preventing particle

penetration into the porous microstructure which will have a detrimental effect on the flux. In order to obtain the best effectiveness, Galaj *et al.* (1984) further proposed that the backflushing preferred frequent, short, high-pressure pulses and should start at the very beginning of the filtration operation. In other words, it is not desirable to do backflushing after the flux has noticeably decreased. Unfortunately, constrained by the experimental conditions, backflushing was not applied to membrane cleaning in the experiment. It was expected when backflushing was in place of hot water in the membrane cleaning program, the effectiveness of membrane cleaning would be better.

The investment of the equipment using membrane separation for oily wastewater treatment has a little higher than other physical methods. However, the membrane separation system is easy to maintain and has lower operating costs. Moreover, the by-product is concentrated oil, which can be reused as industrial raw material. Therefore, this method can be accepted in Hong Kong.

5.8 Application of Ceramic Membrane in Treating Restaurant Wastewater

5.8.1 Experimental Result

The raw oily wastewater for this study was taken from a local restaurant. After the sample was sent to the laboratory, it was placed in quiescent condition for one hour. Then the supernatant was used as the feed solution for ceramic membrane filtration. Separation experiment was operated in the total recycle model, that is, the permeate sample collected in the sample vessel was measured and then returned to the feed tank for recycling. The volume of the feed solution was 16 L. The experiment was carried out with a membrane of 100 nm pore diameter at a pressure of 0.2 MPa, CFV of 1.64 m/s and temperature at 20 °C.

The profile of permeate flux curve with time during the filtration process was similar to the curves obtained with artificial emulsion. The filtration process reached steady state after 40 minutes of operation. The steady permeate flux was 184 L/(m² h). The main difference in membrane separation between real wastewater and artificial emulsion under the same operating condition was that the former reached steady state with lower steady flux in short working time. The reason was that real wastewater might have a higher suspended solid

concentration than the artificial emulsion. The convection of particles on the membrane surface and pore was reached stable in shorter time. The membrane fouling was then faster in real wastewater than that in artificial emulsion. The low flux indicated that serious membrane fouling existed in the real wastewater filtration process.

The oil concentration in the raw wastewater was 284 mg/L, and the average oil concentration in the permeate was 13 mg/L. The oil rejection reached as high as 95%. The removal efficiency was satisfactory.

5.8.2 Process Design

Up to now, there are four approaches that are usually used to design and lay out a MF device (Cheryan, 1998). They are batch operation, single-pass continuous filtration, feed-and-bleed operation, and multistage operations. Batch operations are usually used where the permeate is the required product. A single-pass through the module will result in a very low volume of permeate, and thus, it suits for feed stream with low flow rates. The mode of feed-and-bleed operation, shown schematically in Figure 5.17, merges the batch and the single-pass operations. After reaching the steady state, retentate is bled off the

recirculation loop at a flow rate (V_R). Permeate flow rate is calculated from the following equation:

$$V_P \text{ (L/h)} = J \text{ (L/m}^2 \text{ h)} \times A \text{ (m}^2\text{)} \quad (5.5)$$

and V_R is obtained from the following equation:

$$V_R = V_P - V_F \quad (5.6)$$

where V_F , V_R , and V_P are the flow rate of feed, retentate, and permeate, respectively. The disadvantage of this mode is that the retentate can not be efficiently concentrated for a mid-large scale amount of feed solution.

The mode of multistage operation can overcome the low flux of the feed-and-bleed operation, and maintain its continuous nature. A schematic of a three-stage, multistage recycle device is shown in Figure 5.18. Several individual feed-and-bleed stages are sequentially used in this mode. Only final stage is operating at the highest concentration and low flux, while other stages are operating at lower concentrations with consequently higher flux. Therefore, the total membrane area used in separation should be less than a single-stage feed-and-bleed operation.

Example of estimating the membrane area required for treating oily wastewater using three-stage operation.

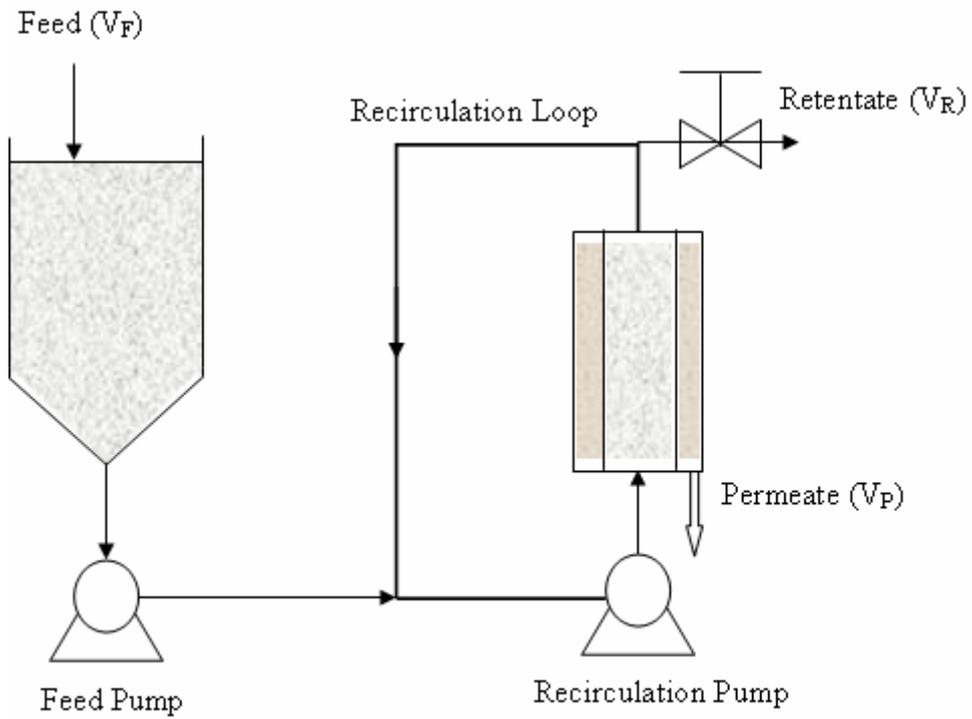


Fig.5. 17 Feed-and-bleed operation

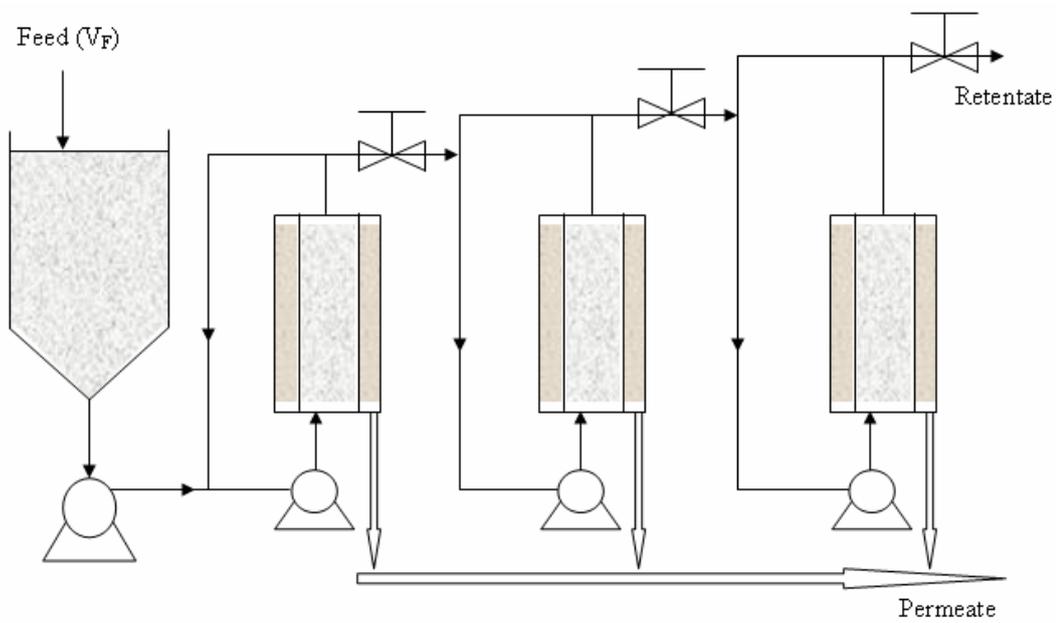


Fig.5. 18 Three-stage filtration

Assume the following conditions were set: 100 nm alumina membrane, TMP: 0.2 MPa; CFV: 1.68 m/s; feed flow rate: 10 m³/d (or 500 L/h); final VCR: 100; oil concentration (raw): 300 mg/L; temperature: 20 °C. The fluxes of the first stage, the second stage and the third stage, at VCR of 10, 50, and 100, is 150, 100, and 25 L/(m² h), respectively. These permeate fluxes at different oil concentration were obtained from this research and previous study (Cardew and Le, 1998). From the Equation (5.6):

$$V_{P1} = 500 - 500/10 = 450 \text{ L/h}$$

From the Equation (5.5):

$$A_1 = 450/150 = 3.0 \text{ m}^2$$

In the second stage, VCR = 50, $V_{P2} = 500/10 - 500/50 = 45 \text{ L/h}$,

$$A_2 = 45/100 = 0.45 \text{ m}^2$$

In the third stage, VCR = 100, $V_{P3} = 500/50 - 500/100 = 5 \text{ L/h}$,

$$A_3 = 5/25 = 0.2 \text{ m}^2$$

Therefore, the total area is $3.0 + 0.45 + 0.2 = 3.65 \text{ m}^2$.

Therefore, 4 m² of membrane area was adequate for a user that discharged 10 m³ of oily wastewater per day. A considerable reduction in membrane area can be achieved using multiple stages. However, due to additional piping, instrumentation, controls and pumps, it may not be economical to go beyond three stages in this particular example.

5.9 Summary

The influence of CFV, TMP, oil concentration and temperature on the MF process of oily wastewater were discussed. Of these parameters, the most crucial factors were TMP and temperature. Increasing TMP values provided high driven force for the filtration that resulted in high permeate flux. However, this effect was valid under a pressure control region. Beyond the crucial point of the pressure, the influence of TMP on the permeate flux could be reduced or showed negative effect. The permeate flux increased as a result of decreased viscosity under the high temperature. High permeate flux was also obtained under high CFV values and low oil concentrations of feed solution. TOC concentrations in the permeate were also affected by the operational parameters. High TOC concentration in the permeate was found under the conditions of high TMP and oil concentration of feed solution.

Membrane fouling had a significant influence on the decline of the permeate flux. Therefore, the effective membrane cleaning was very important to obtain a large permeate flux. The method of membrane cleaning proposed here was the sequentially washing of the membrane with (1) hot water, (2) sodium hydroxide solution, (3) EDTA solution. It was expected when backflushing in place of hot

water rinse in the membrane cleaning, the effectiveness of membrane cleaning would be better.

The experimental results revealed that restaurant wastewater could be effectively treated by MF with ceramic membrane. Oil rejection reached as high as 95% under defined experimental conditions. The mode of three-stage operation was the best option for treating oily wastewater. From the calculation, 4 m² of membrane area was adequate for a user that discharged 10 m³/day of wastewater from restaurant.

CHAPTER SIX

EFFECTS OF pH AND SALT CONCENTRATION ON CERAMIC MEMBRANE SEPARATION

6.1 Introduction

Inorganic ceramic membranes are made of metal oxides. The most common products are Zr, Si and Al oxide membranes. In an aqueous environment these oxides contain hydroxyl groups at the surface which can, depending on the pH, be protonated. As in the case of ZrO_2 membranes the surface will bear $ZrOH_2^+$ groups at pH less than 3.8, and evolve to ZrO^- groups at pH more than 11.4 (Dumon and Barnier, 1992). Therefore, these materials show an amphoteric behaviour under different pH conditions. Meanwhile, these membrane surfaces can serve as ligand adsorption sites for ions or macromolecules (Pifferi and Spagna, 1987). Hence, pH and ion concentration of the feed solution will affect surface charge and the related distribution of ionic species near pore surfaces within the matrix of the membrane, resulting in a significant effect on the permeability and the fouling of the membrane.

The effects of the solution environments on membrane filtration performance have been reported by many authors (Fane *et al.*, 1983; Wakeman and Akay, 1997; Yang *et al.*, 1998; Ohmori and Glatz, 1999; Yuan and Zydney, 1999; Burns and Zydney, 2000; Sousa *et al.*, 2002). Moosemiller *et al.* (1989) reported that the permeation of particle-free electrolyte solutions through γ -Al₂O₃ and TiO₂ membranes was greatest near the isoelectric points of these membranes. Iritani *et al.* (1999) also reported that the average porosity in the filter cake of TiO₂ was maximum and average specific filtration resistance was minimum around the iso-electric pH because the particles flocculated. However, Hoogland *et al.* (1990) reported that the permeate flux was at a minimum near pH 9 when filtering suspensions of SiO₂ on an Al₂O₃ membrane. The highest permeation rates were achieved at pH 2 and pH greater than 10. Nazzal and Wiesner (1994) also studied the effects of pH and salt concentration on the performance of a ceramic microfiltration membrane. They used different types of feed water: particle-free electrolytes, silica suspensions and humic acid solutions. They found the influence of pH and salt on the treatment performance under various feed solutions was significant difference. For the particle-free electrolyte solution, the permeate flux was significantly increased by decrease of pH and increase of salt concentration, respectively. The experiments performed with the silica particles showed that the permeate flux was affected by electroviscous effects and particle deposition on the membrane surface. In contrast, the

filtration flux was insensitive to pH and salt concentration in the presence of humic materials. Jones *et al.* (2001) studied the effect of pH on filtration of humic acid and protein. They reported reversible and irreversible resistances were higher at the isoelectric point (IEP) of the protein and decreased at higher pH values, and humic acid adsorption decreased as pH was increased from 4.7 to 10. Ohmori and Glatz (1999) found that when the pH of the cell slurry was adjusted from 6.3 to 2.0, the resistance was decreased by a factor of 5 indicating that the total flux was improved five times. Meanwhile, they found that the effect of ionic strength was much less. However, Kwon and Vigneswaran (1998) found that the ionic strength of the suspension had a significant effect on critical flux. Faibish *et al.* (1998) studied the effect of electrostatic double layer interaction on permeate flux decline and deposit cake formation in crossflow membrane filtration of colloidal suspensions. The rate of flux decline was strongly dependent on ionic strength and, to a much lesser degree, on solution pH (for the investigated pH range of 6.1-10.0).

All these studies have revealed that the pH and the ionic strength of solution affected permeation rates and flux in different ways. However, there are many conflictions among different researchers. Furthermore, less attention has been paid to the effects of pH and salt on the filtration process for oil-water emulsion separation.

The present study identified the effects of pH and salt (NaCl) on membrane filtration processes for oily wastewater treatment. The experiments of membrane filtration under different pH and salt conditions were carried out. The variations of zeta-potential and size of oil droplets under various pH and salt conditions were determined. It must be mentioned that all membrane separation experiments in this chapter were carried out by a membrane with pore size of 50 nm at oil concentration of 500 mg/L, TMP of 0.15 MPa, CFV of 0.84 m/s and temperature at 20 °C. The pH and salt concentration of feed solution were adjusted either sodium hydroxide or dilute hydrochloride acid and sodium chloride, respectively.

6.2 Effects of pH and Salt Concentration on Zeta Potential and Size of Oil Droplet

6.2.1 Electric Charge

Most substances acquire a surface electric charge when brought into contact with a polar (e.g. aqueous) medium, possible charging mechanisms being ionization, ion adsorption and ion dissolution. This surface charge influences the distribution of nearby ions in the polar medium. Ions of opposite charge (counter-ions) are attracted towards the surface and ions of like charge (co-ions) are repelled away from the surface.

The ionization depends strongly on the pH of solution. Proteins acquire their charge mainly through the ionization of carboxyl and amino groups to give COO^- and NH_3^+ ions under various pH conditions, while ionic substances can acquire a surface charge by virtue of unequal dissolution of the oppositely charged ions which they are composed. For example, with excess I^- ions, the silver iodide particles are negatively charged; and with sufficient excess Ag^+ ions, they are positively charged.

A net surface charge can be acquired by the unequal adsorption of oppositely charged ions. Surfaces in contact with aqueous media are more often negatively charged than positively charged. This is a consequence of the fact that cations are usually more hydrated than anions and so has the greater tendency to reside in the bulk aqueous medium; whereas the smaller, less hydrated and more polarizing anions have the greater tendency to be specifically adsorbed. Oil droplets and suspended in water and in most aqueous electrolyte solutions have negative electrophoretic mobilities (Yoon and Yordan, 1986). This net negative charge is explained in terms of negative adsorption of ions. Surfaces which are already charged usually show a preferential tendency to adsorb counter-ions, especially those with a high charge number. It is possible for counter-ion adsorption to cause a reversal of charge.

6.2.2 Zeta Potential

The zeta potential is a consequence of the existence of surface charge, and can give information on electrical interaction forces between the dispersed particles. Zeta potential is a measure of the magnitude of the repulsion or attraction between particles. According to DLVO theory, the magnitude of the zeta potential gives an indication of the potential stability of the colloidal system. If

all the particles have a large negative or positive zeta potential they will repel each other and there is dispersion stability; however, if the particles have low zeta potential values then there is no force to prevent the particles coming together and there is dispersion instability. Usually, a dividing line between stable and unstable aqueous dispersions is generally taken at either +30 or -30 mV, and effective coagulation has been demonstrated over a range of plus or minus 0.5 mV (Hunter, 1981). Most particles in a polar medium such as water will possess a surface charge. A charged particle will attract ions of the opposite charge in the dispersant, forming a strongly bound layer close to the surface of the particle. Those ions further away from the core particle make up a diffuse layer, more loosely bound to the particle.

The variations of zeta potential of O/W emulsion droplets under different pH and salt concentrations are shown in Figures 6.1-6.6. According to the results, the effect of salt concentration on the zeta potential was significant (Figure 6.1). When salt concentration of the solution was increased from 0.001 to 0.01 mol/L, the zeta potential steeply increased from -33.4 to -8.3 mV. However, when the salt concentration was further increased from 0.01 to 0.05 mol/L, the zeta potential slowly increased from -8.3 to -4.6 mV. The effect of pH on the zeta potential was also significant. When pH of the solution was lower, higher zeta

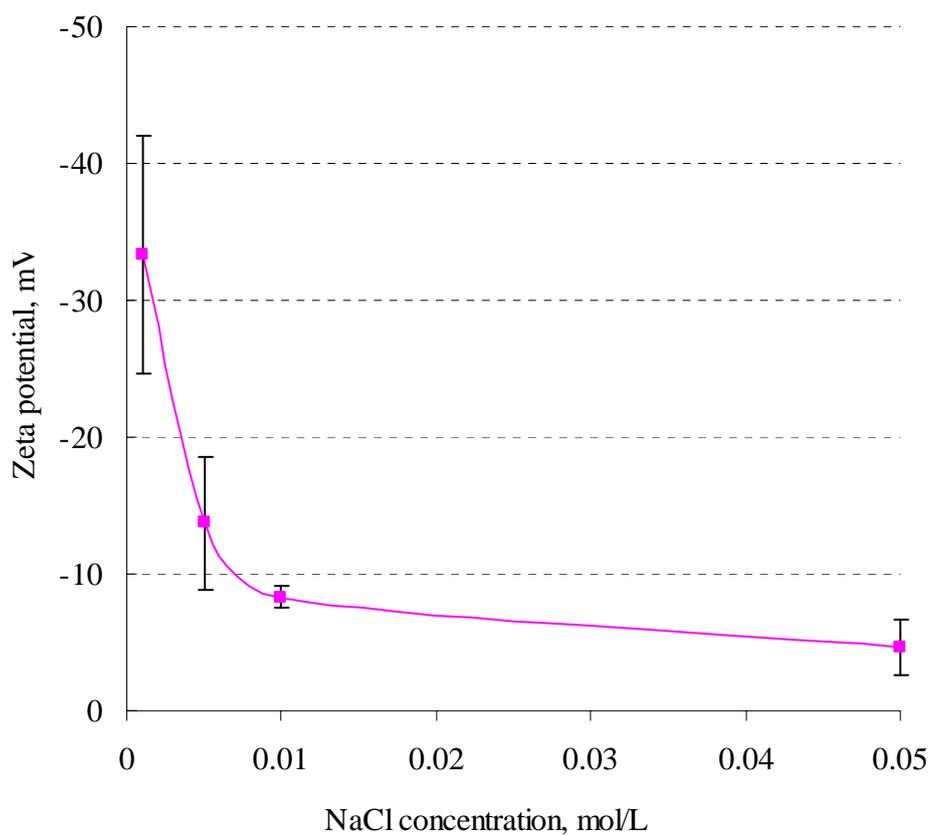


Fig.6. 1 Variations of oil droplet zeta potential over the range of salt concentration. Values are means \pm S.D. (n=5)

potential obtained. The zeta potential was near zero at pH of 3.14, while the zeta potential was -47 mV at pH of 9.88 (Figure 6.2). The change of zeta potential was almost linearly with the variation of pH value. Under the presence of salt, the zeta potential increased with decrease of the pH value. However, the variation of zeta potential arising from the change of pH was not the same situation both in the acidic condition and alkaline condition. The decrease of zeta potential was slowly when the pH increased within the acidic range, while the decline of zeta potential still kept steep under the pH higher than 7 (Figures 6.3-6.6). Comparing to the zeta potential under high salt concentration, the effect of pH was not as significant as salt concentration. These results from the experiments were almost the same as the previous studies (McDonogh *et al.*, 1984; Nazzal and Wiesner, 1994; Mullet *et al.*, 1997; Zhao *et al.*, 2005).

Under the neutral conditions, oil-water emulsion droplets are usually negatively charged and negative zeta potential (Yoon and Yordan, 1986). Under alkaline conditions, emulsion droplets tended to adsorb more negatively charge, and then had lower zeta potential. However, when acid was added to this emulsion, then the surface charge was neutralized. Further addition of acid caused a build up of positive charge. As the salt in different concentrations was added to the O/W emulsion, specific adsorption occurred at the droplets, and the same change of

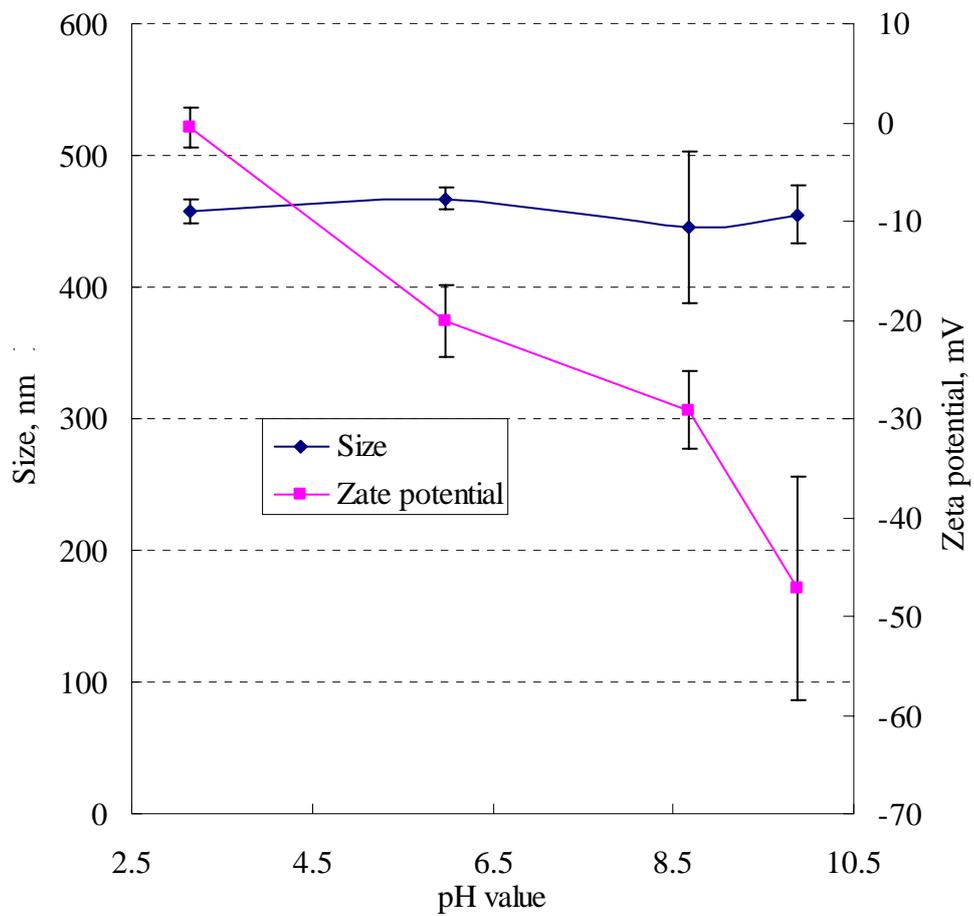


Fig.6. 2 Variations of oil droplet size (n=3) and zeta potential (n=5) over the range of pH. Values are means \pm S.D.

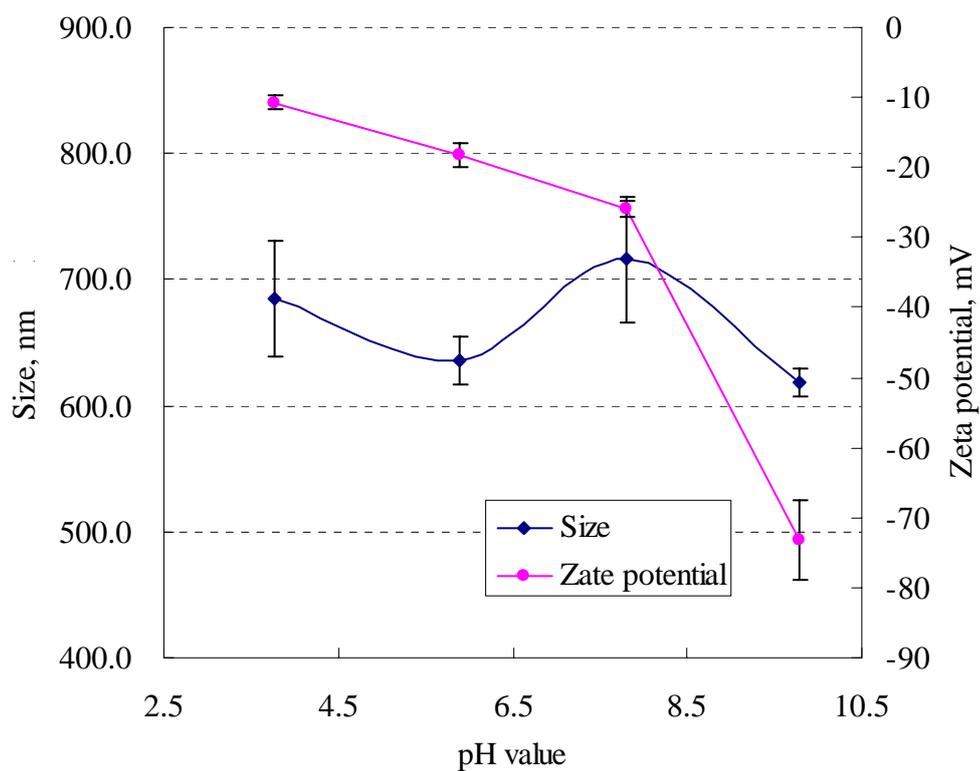


Fig.6. 3 Variations of oil droplet size (n=3) and zeta potential (n=5) over the range of pH (0.001 mol/L). Values are means \pm S.D.

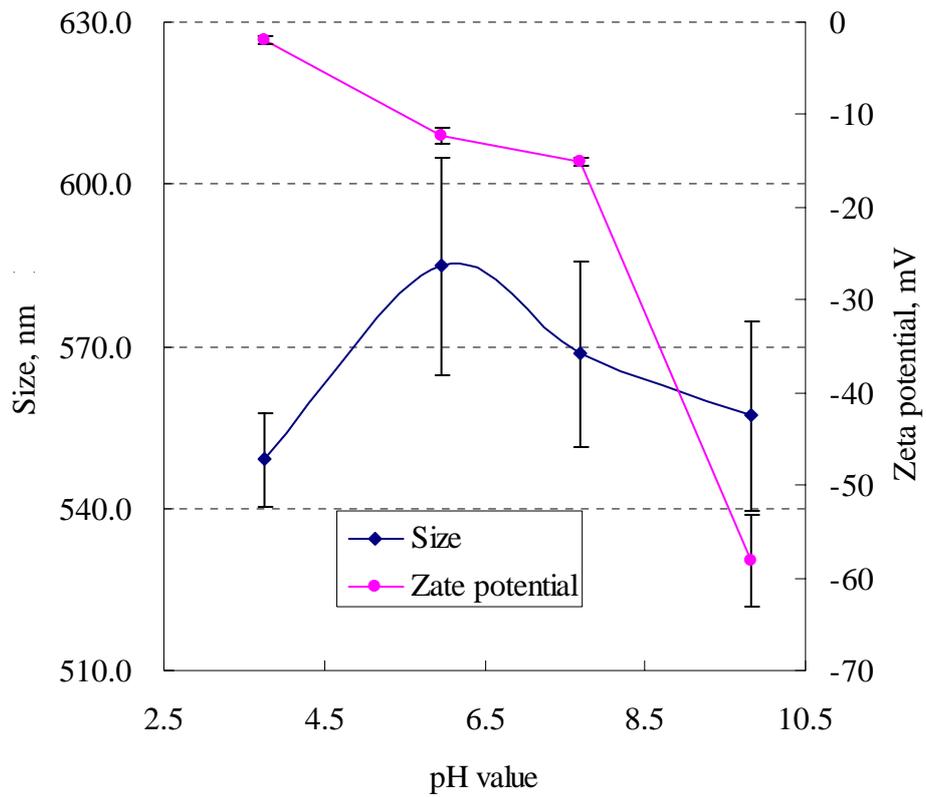


Fig.6. 4 Variations of oil droplet size (n=3) and zeta potential (n=5) over the range of pH (0.005 mol/L). Values are means \pm S.D.

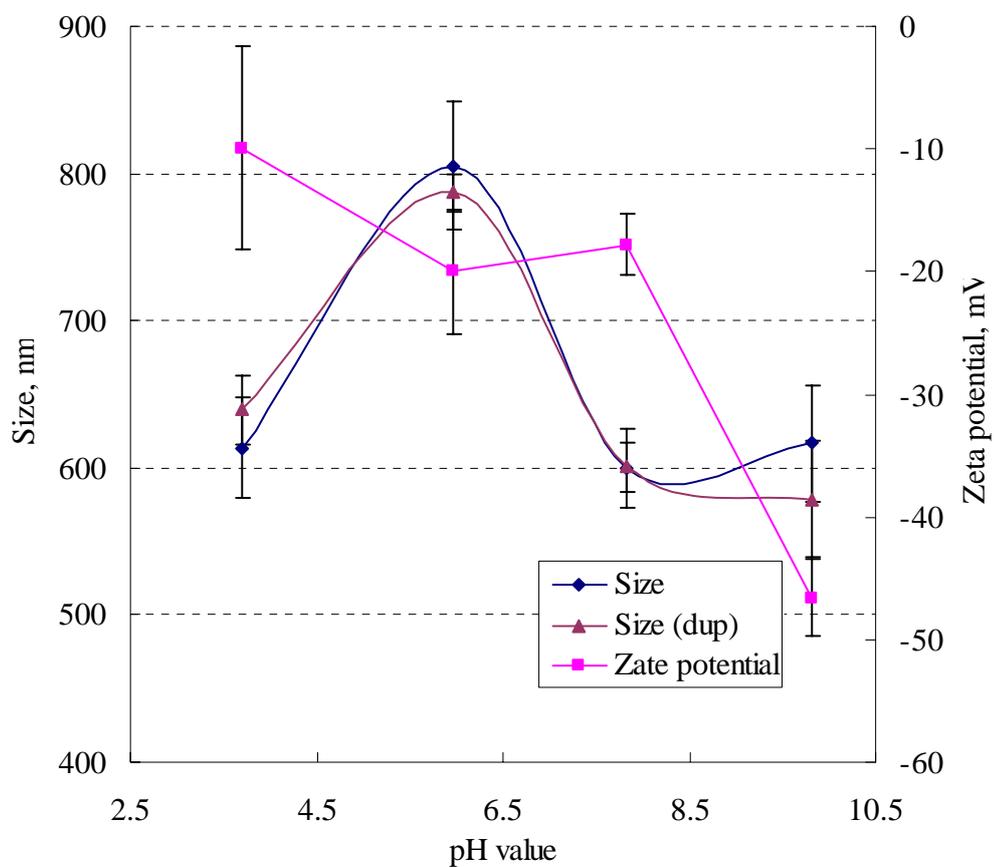


Fig.6. 5 Variations of oil droplet size (n=3) and zeta potential (n=5) over the range of pH (0.01 mol/L). Values are means \pm S.D.

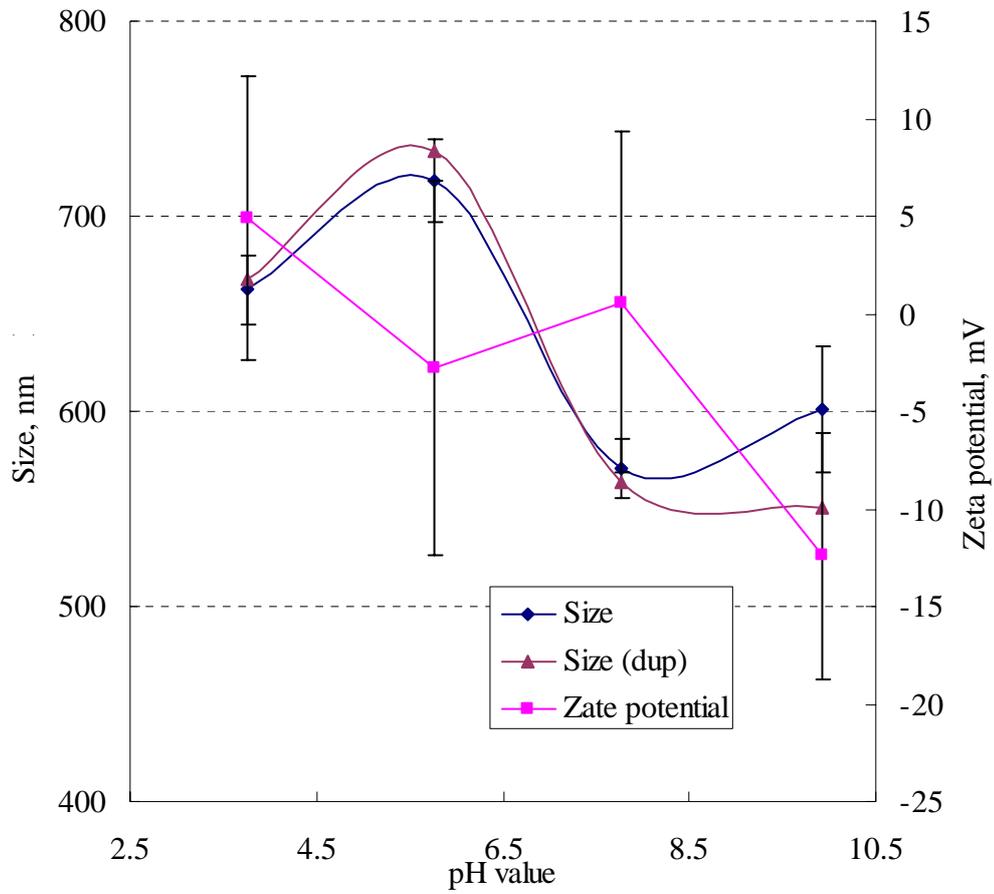


Fig.6. 6 Variations of oil droplet size (n=3) and zeta potential (n=5) over the range of pH (0.05 mol/L). Values are means \pm S.D.

charge conversion happened at emulsion droplets. This resulted in the variation of zeta potential of emulsion droplets.

6.2.3 Size of Oil Droplet

The variations of average size of emulsion droplets under various pH and salt concentrations are shown in Figures 6.2-6.6. The average size of emulsion droplets was not significantly affected under various pH values (Figure 6.2). In the presence of salt in the solution, the average size of emulsion droplets was changed disproportionately (Figures 6.3-6.6), each set of experiment was strictly controlled at a uniform procedure and condition was attempted. However, the average size of droplets seemed to increase under high salt concentration. This could be explained by the coagulation of emulsion droplets under the increase of ionic strength of solution.

6.3 Membrane Filtration Performance

6.3.1 Effect of pH on Membrane Filtration

Figure 6.7 presents the results of membrane filtration experiment at different pH values. The permeate flux decreased rapidly during the first 10 minutes, and then reached a steady state. The permeate flux at the steady state was dependent on the pH value of the feed solution. Higher pH of the solution resulted in a higher steady state flux. The steady state flux at pH of 5.78 reached a maximum value and was 45% greater than that at pH of 3.78. The permeate flux did not obviously change as pH values changed from 5.78 to 9.86. Similar experiments were carried out under the salt concentration of 0.01 mol/L and pH value at 3.75 and 9.86 (Figure 6.8). It was also found that higher permeate flux obtained under higher pH value condition. The results from these two sets are consistent with each other.

The results of permeate flux obtained from the O/W emulsion filtration under different pH values were unexpected since the permeate flux obtained from distilled water as feed solution was increased with the decrease of pH. Zhao *et al.* (2005) also found the steady flux decreased when the pH value increased in a

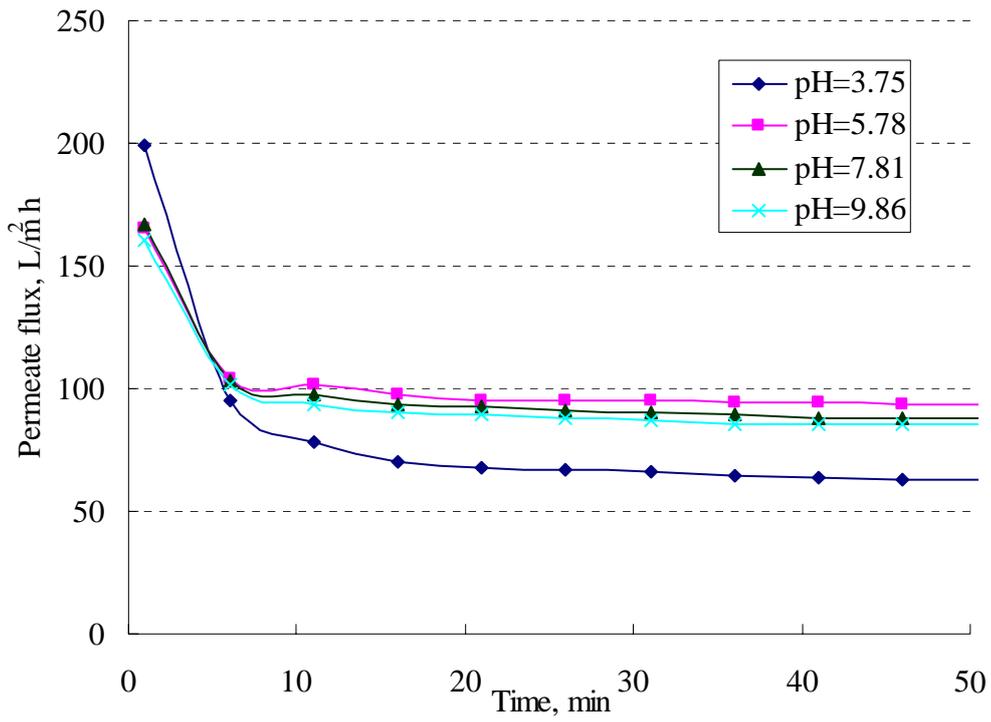


Fig.6. 7 Effect of pH on the permeate flux.

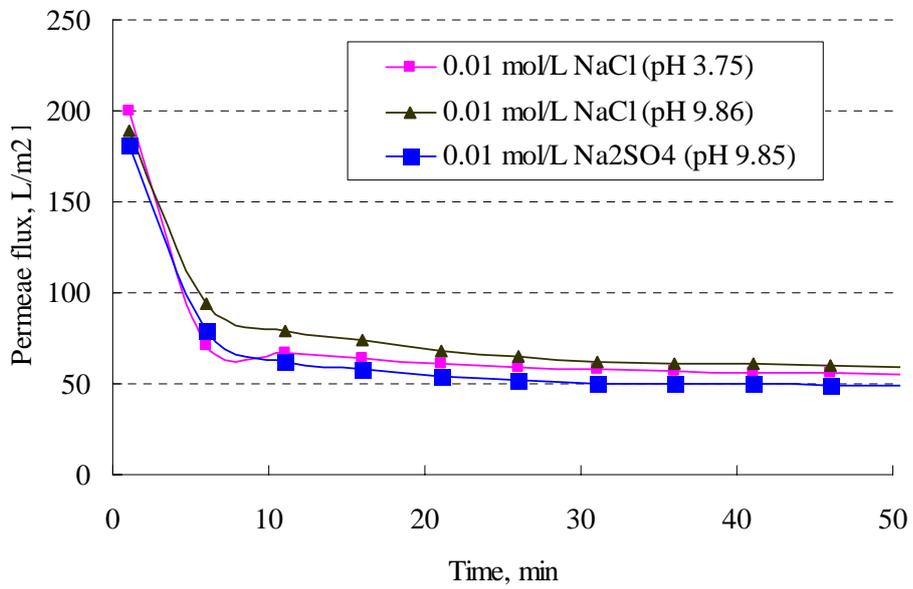


Fig.6. 8 Effect of various pH value and salts on permeate flux.

pH range of 2 to 10. They explained that the TiO_2 particles with high zeta potential tended to disperse at high charge density, resulting in a cake consisting of fine particles. However, Moosemiller *et al.* (1989) reported that alumina appeared to have maximum permeability at pH about 8-10, while the maximum permeability for titania was at pH of 4. They suggested that the maximum permeability was obtained as a result of pH values roughly corresponding to the isoelectric points of the membranes. There was less hydration of the pore walls under such conditions, resulting in higher permeation rates.

The permeate flux of MF process under various pH values was affected not only by the characteristics of membrane but also by the performance of the solute (droplet). From the results of determination, the obvious variation did not exist in average size of droplets under various pH values. Therefore, under low pH value, coagulation of emulsion did not happen although the zeta potential of emulsion droplet was low in absolute value. This is consistent with the stability of the O/W emulsions was more stable at pH of 4 to 6 than that at pH of 6 to 10 (Tambe and Sharma, 1993). Therefore, the high steady flux did not happen under low pH value. However, under high pH value, the emulsion droplet had a high negative charge. The cake layer became more "open" because of the inter-droplet repulsion, and this increased the cake permeability, and thus increased the permeate flux; meanwhile, the inter-droplet repulsion prevented

particle from the depositing so that the thickness of the cake layer decreased (Elzo *et al.*, 1998). These factors resulted in the high steady flux under higher pH value.

Time dependence of TOC concentrations in the permeate under various pH values are presented in Table 6.1. The average TOC concentrations in the permeate and the average TOC removal efficiencies are illustrated in Figure 6.9. The results indicated under various pH values, average TOC concentrations in the permeate and average TOC removal efficiencies were little changed, they were in the range of 9.3 - 13.1 mg/L and 96.6 - 97.7%, respectively. The oil concentrations in the permeate were below the discharge standard. The results of one-way ANOVA showed that the average TOC removal efficiencies had no significant difference among various pH conditions ($p > 0.05$).

Table 6. 1 Time-dependence TOC concentrations under various pH values, mg/L.

Time, min	pH = 3.75	pH = 5.78	pH = 7.81	pH = 9.86
0-1	3.5	0	0	0
5-6	4.5	14.4	12.6	17.4
10-11	5.2	12.9	11.4	14.3
15-16	10.1	11.3	11.1	12.2
20-21	8.7	10.6	11	14.5
25-26	11.5	10.8	10.4	15.2
30-31	12.1	10.3	10.6	14.6
35-36	11.9	9.5	10.3	15.2
40-41	11.8	10.1	10.1	15.6
45-46	11.2	10.4	10.7	16.1
50-51	11.4	10.5	11.3	15.4

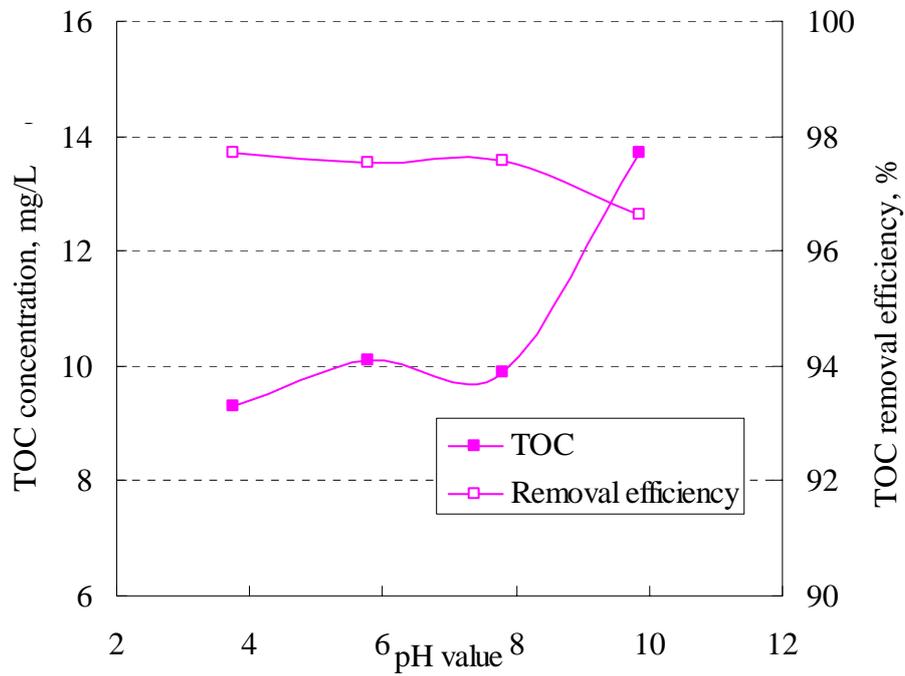


Fig.6. 9 Average TOC concentrations and removal efficiencies under various pH values.

6.3.2 Effect of Salt Concentration on Membrane Filtration

The effect of salt concentration on the permeate flux was studied by carrying with salt concentration at a range of 0 to 0.05 mol/L. Figure 6.10 shows the time dependence of permeate flux under various salt concentrations. The higher salt concentration gave a lower steady flux. The steady flux at high salt concentration (i.e. at $I = 0.05$ mol/L) was only 40% and 45% of that at lower salt concentrations $I = 0$ mol/L and $I = 0.001$ mol/L, respectively. Figure 6.8 illustrates the effect of different anion on the steady flux. It was found that the lower steady flux was obtained under higher valence anion.

The results of the effect of salt concentration on the flux were not similar to our expectation, since the permeate flux was increased with the increase of salt concentration when pure water was used as feed solution. This result was also in contrast to the study of MF of TiO_2 particles by Zhao *et al.* (2005). They found that the increase of ionic strength resulted in a higher steady flux. They explained such results that zeta potential of the TiO_2 particle decreased as the ionic strength increased. More counter-ions could penetrate the compact layer, resulting in a lower charge density in the diffuse layer. Hence, the TiO_2 particles tended to flocculate at high ionic strength. The formation of flocs produced a

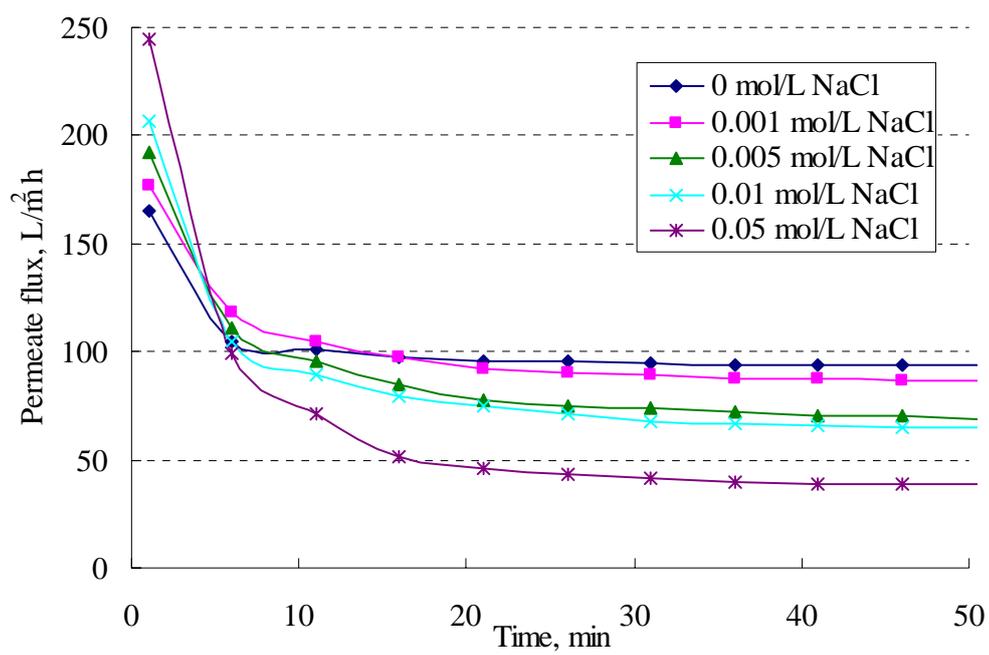


Fig.6. 10 Effect of various salt concentrations on permeate flux.

more permeable cake. As a consequence, the cake resistance was decreased and the permeate flux was raised. Tambe and Sharma (1993) also thought high ionic concentrations surely tended to decrease the thickness of the double layer of emulsion droplets, thereby reducing the electrostatic barrier to coalescence. However, Elzo *et al.* (1998) obtained the opposite results. They found that high permeate fluxes were obtained at low salt concentration with silica particles.

As discussed in chapter 5, the size of oil-water emulsion droplet was not uniform. Some small size of emulsion droplets could become smaller under higher salt concentration since the thickness of the double layer is decreased. Hence, less chance is provided for collision and coagulation for small droplets before they deposited on the membrane surface to form a sealed cake layer. Furthermore, the smaller droplets easily enter the membrane pore or a vacant space of fouling, resulting in the decrease of permeate flux. The effect of various anions on the flux obtained in this study was coincident with the results from Zhao *et al.* (2005). The high zeta potential (absolute value) observed at high valence anions solution due to adsorption on the membrane. This caused greater electroviscous effects and therefore, higher apparent viscosity. As a result, the filtration resistance increased and the permeate flux decreased.

Time dependence of TOC concentrations in the permeate under various salt concentrations are presented in Table 6.2. The average TOC concentrations in the permeate and the average TOC removal efficiencies are illustrated in Figure 6.11. The average TOC concentrations in the permeate and the average TOC removal efficiencies were in the range of 9.6 - 11.1 mg/L and 97.3 – 97.7%, respectively. The results of one-way ANOVA showed that both the average TOC removal efficiencies and average TOC concentrations in the permeation had no significant difference under various salt concentrations ($p > 0.05$).

Table 6. 2 Time-dependence TOC concentrations under various salt concentrations, mg/L.

Time, min	0 mol/L	0.001 mol/L	0.005 mol/L	0.01 mol/L	0.05 mol/L
0-1	0	0	0	0	0
5-6	14.4	13.7	13.4	14.2	11.7
10-11	12.9	12.4	13.1	13.7	11.9
15-16	11.3	11.6	13.2	12.7	11.7
20-21	10.6	10.5	12.5	11.4	11.7
25-26	10.8	11.1	12.3	10.3	10.7
30-31	10.3	10.2	11.8	10	10.3
35-36	9.5	9.8	11.5	9.7	9.7
40-41	10.1	11.2	11.6	9.8	9.3
45-46	10.4	10.7	10.9	9.6	8.6
50-51	10.5	10.5	11.2	9.8	9.1

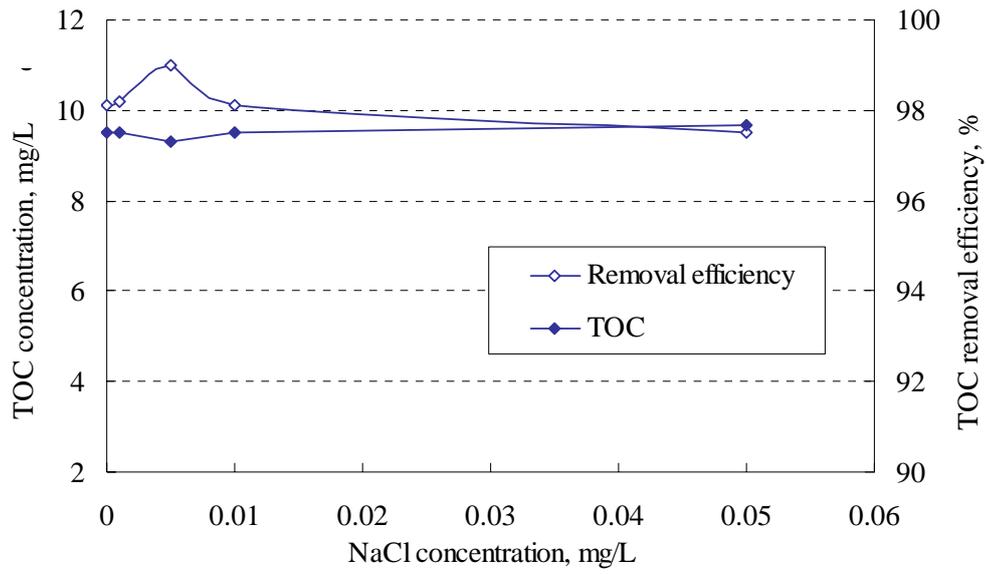


Fig.6. 11 Average TOC concentrations and removal efficiencies under various salt concentrations.

6.4 Summary

The effects of pH and salt concentration on the permeate flux were reported in this Chapter for the membrane filtration process. The MF process using ceramic membrane to treat oily wastewater was significantly affected by the pH value and salt concentration of the feed solution. The low permeate flux was acquired under high salt concentrations and low pH values. It is because pH value and salt concentration of the feed solution gave rise to the variations of zeta potential of oil emulsion droplets. The influence of salt concentration on the zeta potential was significant ($p < 0.5$). When a little of salt concentration increased in low range of salt concentration, zeta potential of oil emulsion droplet increased sharply. However, for the salt concentration of the emulsion bulk larger than 0.01 mol/L, the zeta potential had a gentle increase as the salt concentration increased. The zeta potential of emulsion droplets was tedious increased from -47 mV to near zero as the decrease of pH value from 9.88 to 3.14. Under the presence of salt, the zeta potential was also increased with the decrease of pH value. However, the variation magnitude of zeta potential arising from the change of pH was different in the acidic condition and alkaline condition. The decrease of zeta potential was slowly as pH increasing within the acidic range, while the decline of zeta potential still kept steep after pH higher than 7.

Comparing to the zeta potential under high salt concentration, the effect of pH was less significant. The average size of emulsion droplets was not momentously affected by the variation of pH value. The average size of emulsion droplets was changed disproportionately while in the presence of various salt concentrations. However, the trend of the average size of droplets seemed to increase under higher salt concentrations. It is because the coagulation of emulsion droplets was likely to happen under higher ionic strength of the solution.

Either under various pH values or salt concentrations, low average TOC concentrations in the permeate and high average TOC removal efficiencies were found. Statistic analysis showed that the average TOC concentrations and the average TOC removal efficiencies had no significant difference among various pH values or salt concentrations ($p > 0.05$).

CHAPTER SEVEN

MEMBRANE FILTRATION MECHANISM AND MODEL

7.1 Membrane Filtration Resistances

During the operation of membrane filtration processes, Flux decline under constant operating conditions (TMP, CFV, *etc.*) occurred (Tarnawski and Jelen, 1986; Belfort *et al.*, 1993; Song, 1998). This is because besides the membrane resistance, the process still affected by concentration polarization, adsorption, gel-layer formation and plugging of the pores (Figure 7.1) (Van Den Berg and Smolders, 1990; Jonsson, 1993; Noble and Stern, 1995; Pope *et al.*, 1996; Vyas *et al.*, 2002). All these factors induce additional resistances on the feed side to the transport across the membrane. They are qualitatively described as follows:

7.1.1 Membrane Resistance, R_m

In the ideal case, only the membrane resistance R_m , is involved in membrane filtration process. At a fixed operating pressure, the membrane resistance is a function of viscosity of the feed water (Mehdizadeh *et al.*, 1989). R_m can be

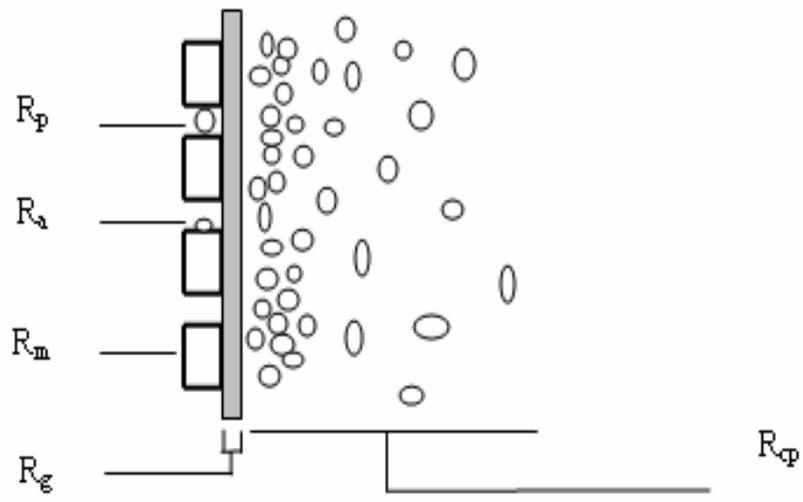


Fig.7. 1 Types of resistances during filtration process.

modeled in terms of the feed water viscosity as shown below:

$$R_m = k_m (\nu)^\alpha \quad (7.1)$$

where R_m is the membrane resistance; ν is the kinematic viscosity of the feed, k_m and α , represent the coefficient and exponent of the membrane resistance correlation, respectively.

7.1.2 Adsorption and Pore Plugging Resistance, R_{ap}

When membrane is in contact with the feed solution, solute molecules will adsorb at the membrane surface due to physico-chemical interactions. Thus, the resistance, R_a , can arise due to adsorption phenomena. With porous membranes it is possible for some solutes to penetrate into the membrane and block the pores, leading to the pore-plugging resistance, R_p . The resistance due to adsorption-pore plugging, R_{ap} is a function of the feed water bulk concentration, molecular size distribution and membrane pore size (or MWCO), feed water pH and ionic strength. Generally, a higher bulk concentration results in enhanced fouling by adsorption and pore plugging. The magnitude of R_{ap} is a strong function of the relative size of the membrane pore and the size of the solute molecule. The behaviour of R_{ap} with respect to the bulk concentration and the

ratio of solute diameter to the diameter of pore can be represented as given below:

$$R_{ap} = k_{ap} (C_f)^m (\lambda)^n \quad (7.2)$$

where k_{ap} is an experimentally determined coefficient; λ is the ratio of solute size to the pore size of membrane; C_f is the bulk concentration m and n are the arbitrary exponents of C_f and λ , respectively.

7.1.3 Concentration Polarization Resistance, R_{cp}

There will be an accumulation of retained molecules near the membrane surface during filtration process. This results in a highly concentration layer near the membrane and this layer exerts a resistance towards mass transfer, i.e., the concentration polarization resistance, R_{cp} . The major factors that influence R_{cp} include bulk concentration, TMP and CFV. Higher bulk concentration often results in a thicker and more compact boundary layer. Higher TMP can cause a greater permeation of solutes across the membrane and thereby result in lower R_{cp} . The effect of the cross-flow velocity on R_{cp} is strongly governed by the chemical constituents of the feed water. The dependence of R_{cp} on the factors can be shown as bellow:

$$R_{cp} = k_{cp} (C_f) (\Delta P)^q (U)^r \quad (7.3)$$

where C_f is bulk concentration; ΔP is transmembrane pressure; U is the cross-flow velocity; k_{cp} is the coefficient; p , q and r are the exponents of C_f , ΔP and U , respectively.

7.1.4 Gel-layer Resistance, R_g

Because polarization phenomena always occur and inherent to membrane separation processes, the concentration of the accumulated solute molecules may become so high that a gel-layer can be formed, which exerts the gel-resistance, R_g . When the membrane system is operated below the critical pressure, the gel-layer resistance is low. As TMP greater than the critical pressure, the thickness and density of the gel-layer increase to an extent where the R_g is significantly greater. R_g can be modeled in terms of the TMP as shown below:

$$R_g = k_g C_f (\Delta P)^s \quad (7.4)$$

where C_f is bulk concentration; ΔP is transmembrane pressure; K_g is the coefficient; s is the exponents of ΔP .

7.1.5 Series Resistance Model

The series resistance (SR) model represents the flux decline due to various fouling mechanisms as serial resistances and has the general form

$$J_w = \frac{\Delta P}{\mu(R_m + R_a + R_p + R_{cp} + R_g)} \quad (7.5)$$

where R_m , R_a , R_p , R_{cp} and R_g represent membrane resistance, adsorption resistance, pore-plugging resistance, concentration polarization resistance and gel-layer resistance, respectively.

7.2 Membrane Filtration Laws

Up to now, membrane fouling remains incompletely understood. It is usually considered that two distinct types of fouling phenomena exist: 1) Macrosolute adsorption, which refers to specific intermolecular interactions between a macrosolute and the membrane that occur even in the absence of any filtration (i.e., in the absence of the hydrodynamic and body forces); 2) Filtration-induced macrosolute/particle deposition, which is over and above that observed in a static system. Hermia (1982) introduced the filtration laws, which aimed to describe fouling mechanism. He considered that flux decline was attributed to four mechanisms: complete blocking, intermediate blocking, standard blocking and cake filtration

7.2.1 Complete Blocking Model

In the complete blocking model, it is assumed that each particle reaching the membrane seals the pore and the particles are not superimposed one upon the other. The blocked surface area is proportional to the permeate volume. The rate of change in the number of open pores is assumed to be directly related to the

rate of particle convention to the membrane surface. Cake formation is assumed to be negligible in this model.

7.2.2 Intermediate Blocking Model

In the intermediate blocking model, the number of blocked pores or surface is also assumed to be proportional to the permeate volume but it is less restrictive. This model assumed that each particle would not block a pore; particles could settle on other particles. It is also assumed that the suspension is perfectly homogeneous, and the second particle layer has an equal probability to settle on the first layer as on the surface which was left free.

7.2.3 Standard Blocking Model

In the standard blocking model, it is assumed the particle is much less than the pore diameter, thus, the particles can enter most pores, deposit on the pore walls, and reduce the pore volume. The pore volume decreases proportionally to filtrate volume due to the deposition of particles on the pore walls. The membrane is also assumed to have a set of pores of constant diameter and length.

7.2.4 Cake Filtration Model

If the particles are bigger than the pores, or if the pore becomes sufficiently clogged, the particles will deposit onto the membrane surface and form a filter cake. In the case of cake filtration, it is assumed that the flux decreases as cake thickness increases, and the cake thickness increase proportionally to filter volume. This model is used to explain for the case of large particles, which can not enter pores, and hence deposit forms a cake on the membrane.

These models can be written in the characteristic form of equations. These equations may be expressed as simple linear equations relating the permeate flow rate (Q), permeate volume (V) and time (t) with the filtration constants for each model (K_b , K_i , K_s , K_c) and Q_0 the initial permeate flow rate as shown in Table 7.1 (Mohammadi *et al.*, 2003).

7.2.5 Results of Model Calculation

In order to identify which kind of model was coincided with the oily wastewater separation, experimental data from two typical MF processes (with TMP of 0.2 MPa, CFV of 1.68 m/s, oil concentration of 500 mg/L, temperature of 20 °C, 50

Table 7. 1 Four different membrane filtration models.

Model	Equation
Complete blocking filtration	$Q = Q_0 - K_b V$
Intermediate blocking filtration	$\frac{1}{Q} = K_i t + \frac{1}{Q_0}$
Standard blocking filtration	$\sqrt{Q} = \sqrt{Q_0} - (K_s \sqrt{Q_0} V/2)$
Cake filtration	$\frac{1}{Q} = \frac{1}{Q_0} + K_c V$

nm and 100 nm, respectively) were selected to regress with four kinds of membrane fouling models.

Figures 7.2-7.5 present the results of regress the data from membrane with pore size of 50 nm to the individual filtration models by plotting the permeate flow rate (Q , $1/Q$ or \sqrt{Q}) against the filtration volume (V) or the filtration time depending on the model. From these figures the filtration process could not be completely and effectively expressed with anyone of models. This demonstrated that the interaction among emulsion droplets, membrane surface, and membrane pores were complex during the filtration process. As shown in the figures, the whole filtration process could be mostly divided into two stages. The first stage (as filtration time < 30 minutes, or permeate flow rate > 350 mL/min, or filtration volume $< 16\ 000$ mL) was expressed by some blocking filtration models, and the second (after first stage) was by cake filtration model. That is, during the initial stage of MF, emulsion droplet with a size range much smaller than that of the pores will pass through the pores. Once within the membrane pores, these droplets may be adsorbed and deposited due to various forces, such as London—van der Waals interaction, electrostatic and hydrodynamic attraction forces, leading to the formation of a colloidal film on the internal pore surface. As the internal surface area of the pores is saturated with these droplets, pore size is reduced. Then accumulation and deposit happened on the external

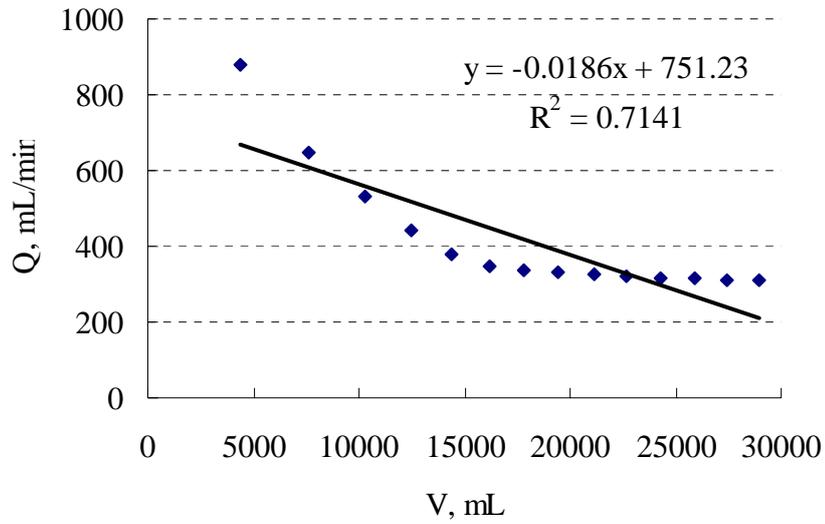


Fig.7. 2 Plotting of Q against V in complete blocking filtration model (50 nm).

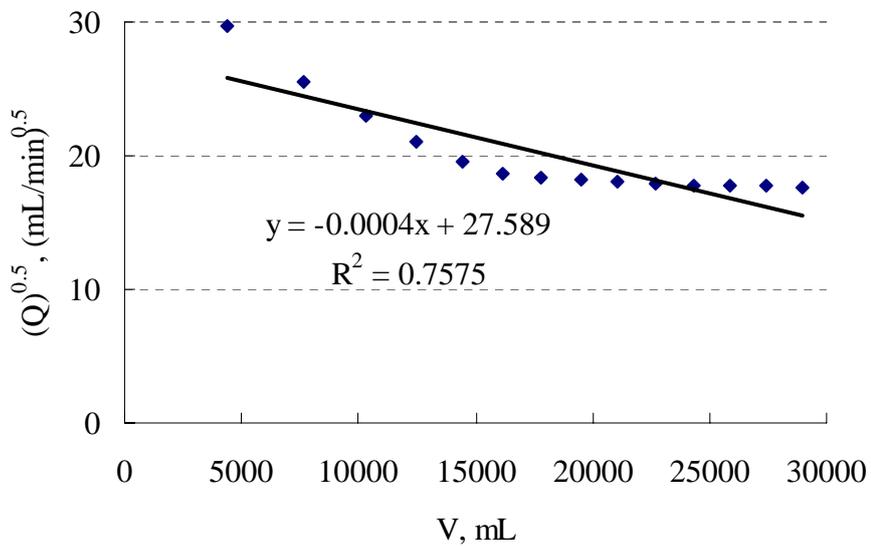


Fig.7. 3 Plotting of $Q^{0.5}$ against V in standard blocking filtration model (50 nm).

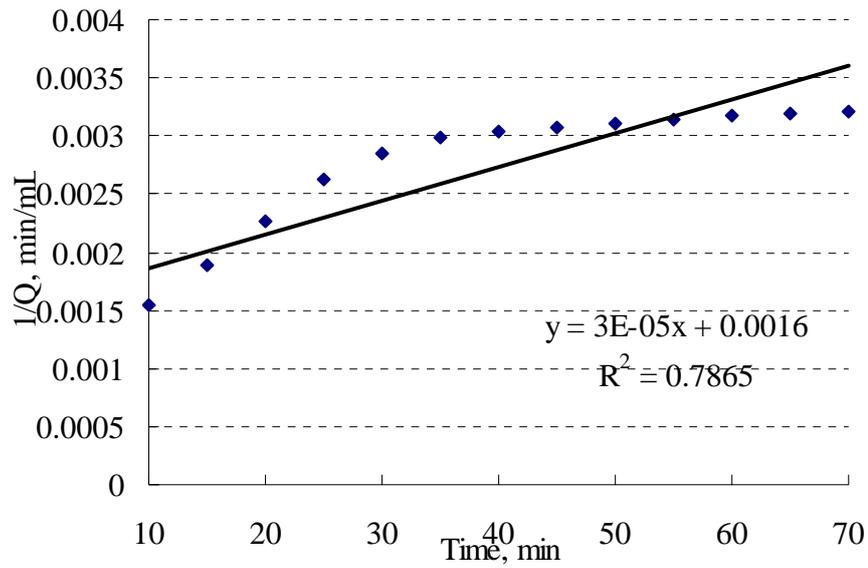


Fig.7. 4 Plotting of $1/Q$ against time in intermediate blocking filtration model (50 nm).

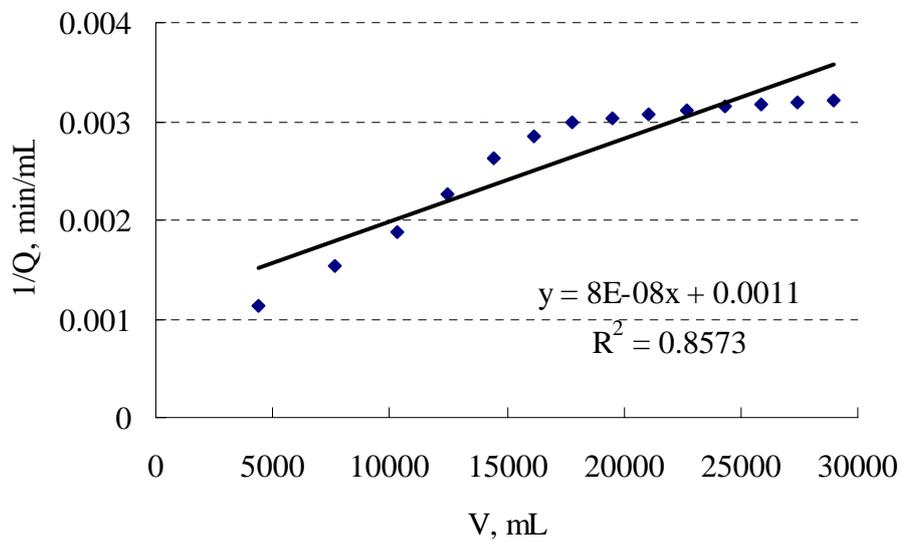


Fig.7. 5 Plotting of $1/Q$ against V in cake filtration model (50 nm).

membrane surface. Deposition of these species at or nearby the pore entrances results in a complete or partial pore blocking, reducing membrane porosity and permeability (Seminario *et al.*, 2002). Subsequently, the accumulated droplets and colloids can form aggregates, whose structures grow in time, leading to the formation of an external film or cake layer on the membrane surface. This result was in accordance with the result obtained by Ohya *et al.* (1998). All mechanisms occurred in a complete filtration experiment either successively or superimposed due to pore and particle size distribution (Bowen *et al.*, 1995).

Figures 7.6-7.9 present the results of regressing the data from membrane filtration with pore size of 100 nm to the individual filtration models by plotting the permeate flow rate (Q , $1/Q$ or \sqrt{Q}) against the filtration volume (V) or the filtration time depending on the model. The results were almost the same as that obtained with the membrane of 50 nm. The whole filtration process could be mostly divided into two stages. The first stage (as filtration time < 25 minutes, or permeate flow rate > 470 mL/min, or filtration volume < 22 000 mL) was expressed by some blocking filtration models, and the second (after first stage) was by cake filtration model. The results were also in accordance with conclusion that under conditions of low TMP and low CFV pore blocking continues to dominate after 20 minutes (Koltuniewicz *et al.*, 1995).

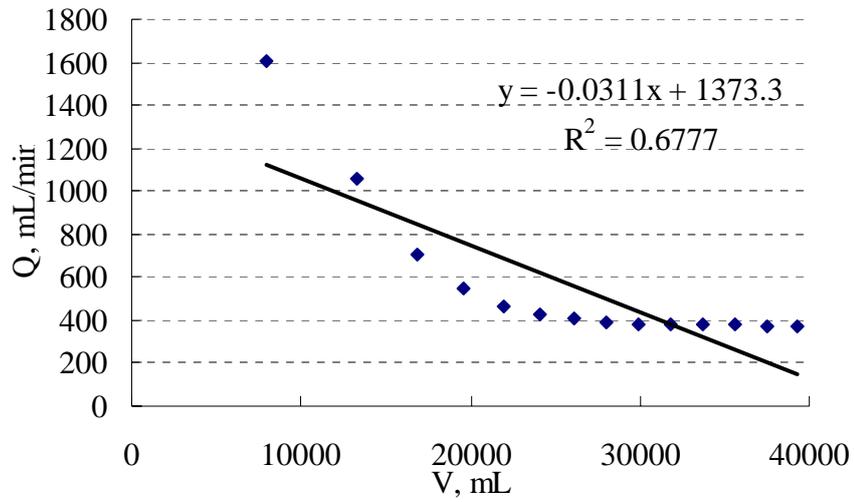


Fig.7. 6 Plotting of Q against V in complete blocking filtration model (100 nm).

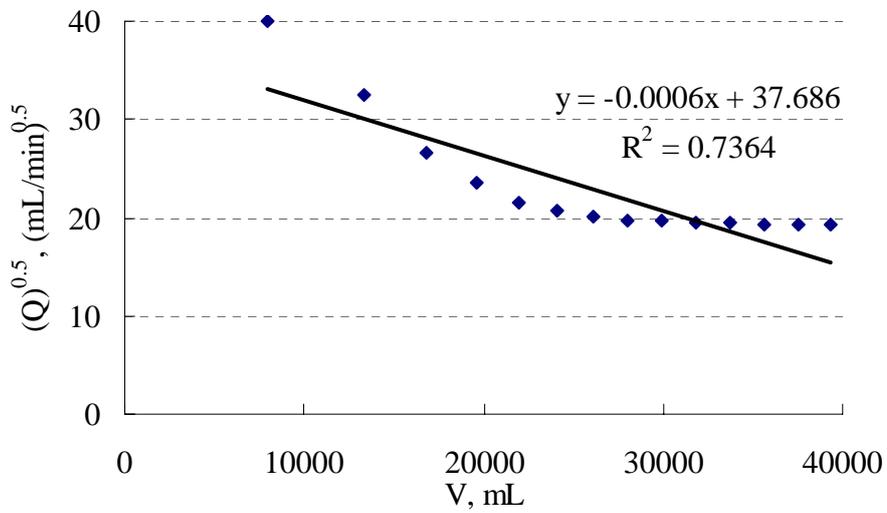


Fig.7. 7 Plotting of $Q^{0.5}$ against V in standard blocking filtration model (100 nm).

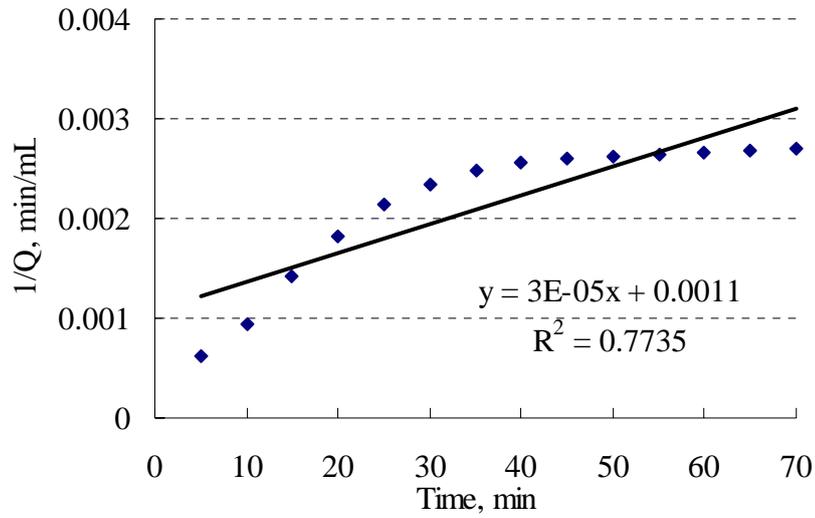


Fig.7. 8 Plotting of $1/Q$ against time in intermediate blocking filtration model (100 nm).

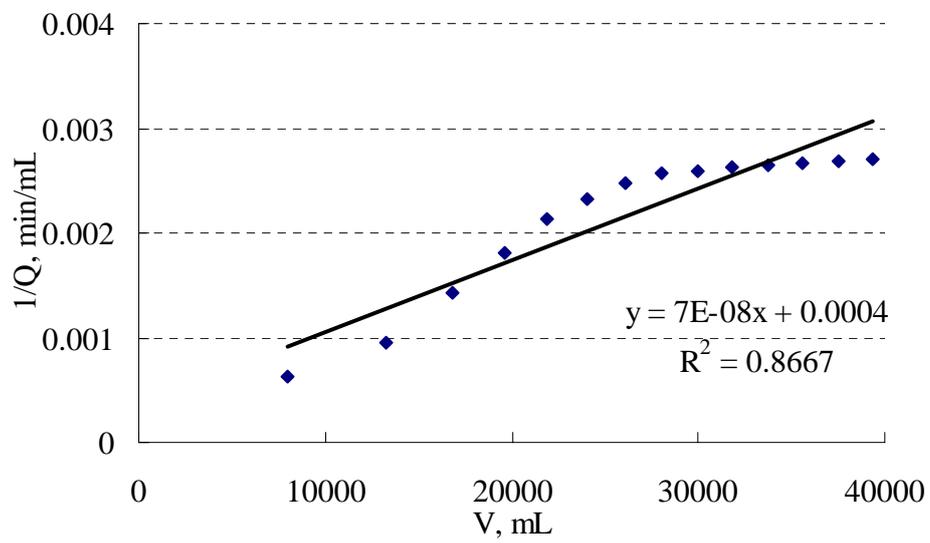


Fig.7. 9 Plotting of $1/Q$ against V in cake filtration model (100 nm).

7.3 Variations of Filtration Resistance

7.3.1 Resistance Calculation

During the MF process, the magnitude of each part of resistance was different under different operational conditions. It was very helpful for us to select an optimal operating condition for MF process. This section described the variations of resistance under various operational conditions.

Total resistance could be integrated and expressed various combined forms (Pouliot *et al.*, 1994; Dal-Cin *et al.*, 1996; Arnot *et al.*, 2000; Mohammadi *et al.*, 2003). In order to determine the variation of each kind of resistance, total resistances (R_t) were reclassified into four parts:

$$R_t = R_m + R_{cg} + R_{ap} + R_{ir} \quad (7.6)$$

where R_m is the membrane resistance which can be calculated from the pure water flux, R_{cg} is the total of the resistance from concentration polarization and gel-layer on the membrane, R_{ap} is the total of the resistance from membrane absorption and pore block and R_{ir} is the irreversible resistance. These resistances can be calculated from flux change under different conditions.

The following fluxes were experimentally measured during membrane separation processes:

J_i : the initial pure water flux for a given membrane,

J_w : the steady-state wastewater flux,

J_p : the pure water flux before the fouled membrane cleaned,

J_f : the final pure water flux for the membrane that has been cleaned and recovered.

The R_m can be calculated using the following Eq. (7.7) with the initial pure water permeability (J_i):

$$R_m = \frac{\Delta P}{\mu \times J_i} \quad (7.7)$$

As the relation exists between the J_i and J_f ,

$$\frac{J_i}{J_f} = \frac{R_m + R_{ir}}{R_m} \quad (7.8)$$

The Eq. (7.8) can be rearranged to calculate R_{ir} :

$$R_{ir} = \left(\frac{J_i}{J_f} - 1 \right) R_m \quad (7.9)$$

As concentration polarization describes the concentration profile of solutes in the liquid phase adjacent to the membrane resulting of the balance between different transport phenomena (generally convection and back diffusion), it disappears as soon as the operating pressure has been released. The gel-layer

resistance formed on membrane also hardly exists when pure water instead of feed solution. The flux loss between J_f and J_p can be attributed to the resistance from membrane absorption and pore block, and the difference between J_s and J_p can be attributed to the resistance from concentration polarization and gel-layer on the membrane. The resistances (R_{cg} , R_{ap}) can be calculated in a similar way.

The results are shown below:

$$R_{ap} = \frac{J_i}{J_f} \left(\frac{J_f}{J_p} - 1 \right) R_m \quad (7.10)$$

$$R_{cg} = \left(\frac{J_p}{J_w} - 1 \right) \left[\left(\frac{J_i}{J_f} - 1 \right) + \left(\frac{J_f}{J_p} - 1 \right) \frac{J_i}{J_f} + 1 \right] R_m \quad (7.11)$$

The relative resistance of each component can be expressed as a function of the total resistances (R_t):

$$R_m (\%) = \frac{R_m}{R_t} \times 100 \quad (7.12)$$

$$R_{cg} (\%) = \frac{R_{cg}}{R_t} \times 100 \quad (7.13)$$

$$R_{ap} (\%) = \frac{R_{ap}}{R_t} \times 100 \quad (7.14)$$

$$R_{ir} (\%) = \frac{R_{ir}}{R_t} \times 100 \quad (7.15)$$

7.3.2 Resistance Variations

7.3.2.1 Variation of Resistance under Various CFV

Fluxes (J_i , J_f , J_p , J_w) under various CFV were determined. The results are listed in Table 7.2. Filtration resistances were calculated with the Eqs. (7.7), (7.9), (7.10) and (7.11). The calculated results of filtration resistances are presented in the Figure 7.10. From the figures, as CFV increased from 0.21 to 1.68 m/s, R_{cg} decreased from 31.3% to 23.1% of total resistance for the membrane with its pore size of 50 nm, while R_{cg} decreased from 24.5% to 18.9% of total resistance for the membrane with its pore size of 100 nm. This indicated that when the CFV increased, the percentage of resistance resulted from the concentration polarization and gel-layer (R_{cg}) decreased. The calculated results were in accordance with the theoretical analysis in Chapter 5.

7.3.2.2 Variation of Resistance under Various TMP

Fluxes (J_i , J_f , J_p , J_w) under various TMP were determined. The results are listed in the Table 7.3. Filtration resistances were calculated with the Eqs. (7.7), (7.9), (7.10) and (7.11). The results of filtration resistances are presented in

Table 7. 2 Results of permeate flux with various CFV values, L/m² h.

Item	Velocity, m/s	J _i	J _w	J _p	J _f
50 nm membrane	0.21	593	125	182	545
	0.42	578	136	194	538
	0.84	584	143	202	527
	1.68	579	163	212	524
100 nm membrane	0.21	1466	154	204	1378
	0.42	1481	162	209	1361
	0.84	1445	178	227	1352
	1.68	1453	202	249	1337

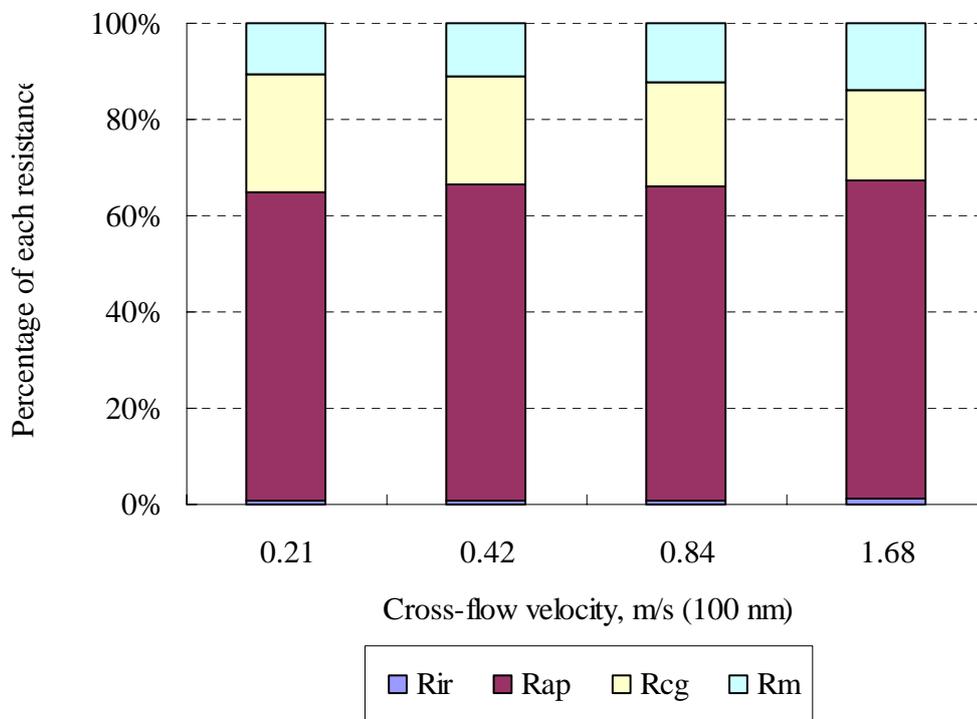
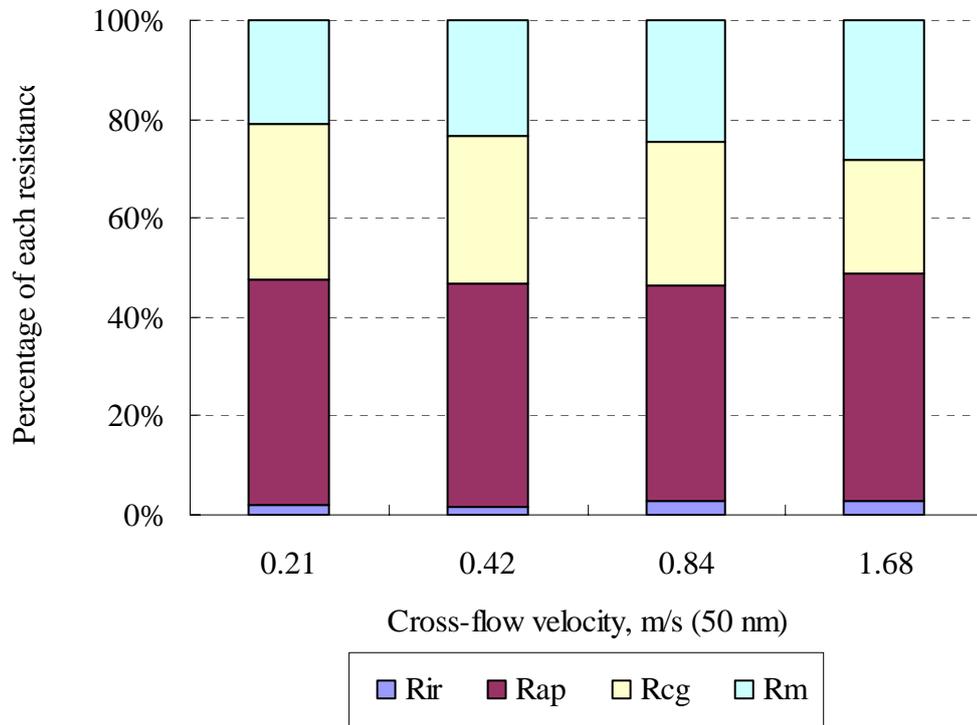


Fig.7. 10 Percentage of various filtration resistances under different CFV values.

the Figure 7.11 with membranes of pore size of 50 nm and 100 nm. Shown in the figures, as TMP increased, the resistance from the concentration polarization and gel-layer (R_{cg}) had a tendency to increase. This conclusion was the same as previous report (Cheryan, 1986). Meanwhile, the irreversible resistance (R_{ir}) was also increased as TMP increased from 0.2 to 0.3 MPa. This effect was more obvious for the membrane with pore diameter of 50 nm than that of 100 nm. This could be explained by the fact that membrane with small pore size was difficult to clean and recover. R_{ir} resulted in irreversible decrease of permeate flux. Furthermore, R_{ir} would shorten the lifespan of the membrane. Therefore, the appropriate TMP for this kind membrane for oil-water emulsion separation should maintain at 0.2 MPa or below.

7.3.2.3 Variation of Resistance under Various Oil Concentrations

Fluxes (J_i , J_f , J_p , J_w) under various oil concentrations were determined. The results are listed in the Table 7.4. Filtration resistances were calculated with the Eqs. (7.7), (7.9), (7.10) and (7.11). The calculated results of filtration resistances are presented in the Figure 7.12 with membranes of pore size of 50 nm and 100 nm. It can be observed the resistance from the membrane adsorption and pore block (R_{ap}) increased obviously as a result of the oil concentration

Table 7. 3 Results of permeate flux with various TMP values, L/m² h.

Item	TMP, MPa	J _i	J _w	J _p	J _f
50 nm membrane	0.1	327	61	82	284
	0.15	450	108	146	403
	0.2	579	163	212	524
	0.25	761	187	249	616
	0.3	914	207	305	669
100 nm membrane	0.1	883	119	161	808
	0.15	1203	162	219	1103
	0.2	1453	202	249	1337
	0.25	1718	223	307	1345
	0.3	2044	236	341	1538

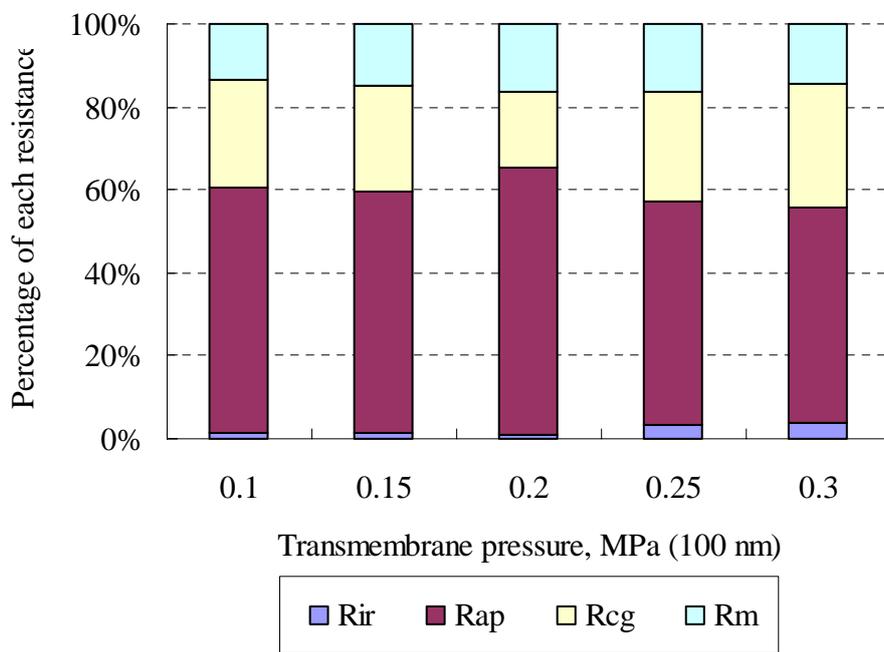
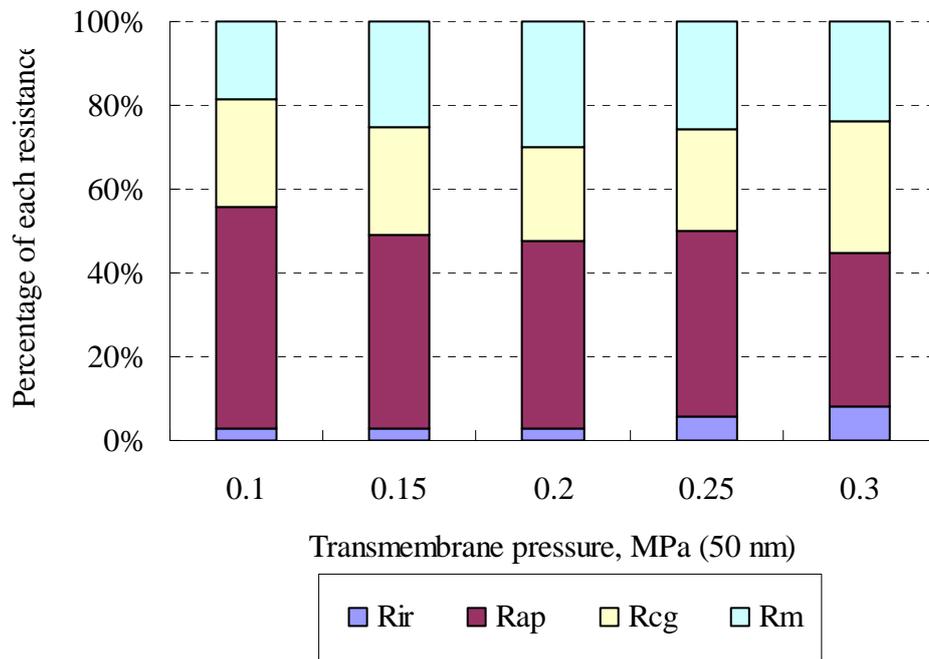


Fig.7. 11 Percentage of various filtration resistances under different TMP values.

increased, especially for the membrane with pore size of 50 nm. The percentage of R_{ap} was 41% at oil concentration of 250 mg/L, while the percentage of R_{ap} was up to 53% at oil concentration of 2 000 mg/L for the 50 nm membrane. The R_{ir} was also increased obviously for the membrane with pore diameter of 50 nm. This was the reasons that there was more oil droplets which were smaller than the membrane pore size existed in the feed solution and entered the membrane pore under the high oil concentration.

Table 7. 4 Results of permeate flux with various oil concentrations, L/m² h.

Item	Oil concentration, mg/L	J _i	J _w	J _p	J _f
50 nm membrane	250	583	167	220	525
	500	579	163	212	524
	1000	578	152	193	517
	1500	571	141	175	498
	2000	588	133	164	473
100 nm membrane	250	1461	208	255	1342
	500	1453	202	249	1337
	1000	1467	193	236	1324
	1500	1471	184	221	1309
	2000	1449	173	209	1296

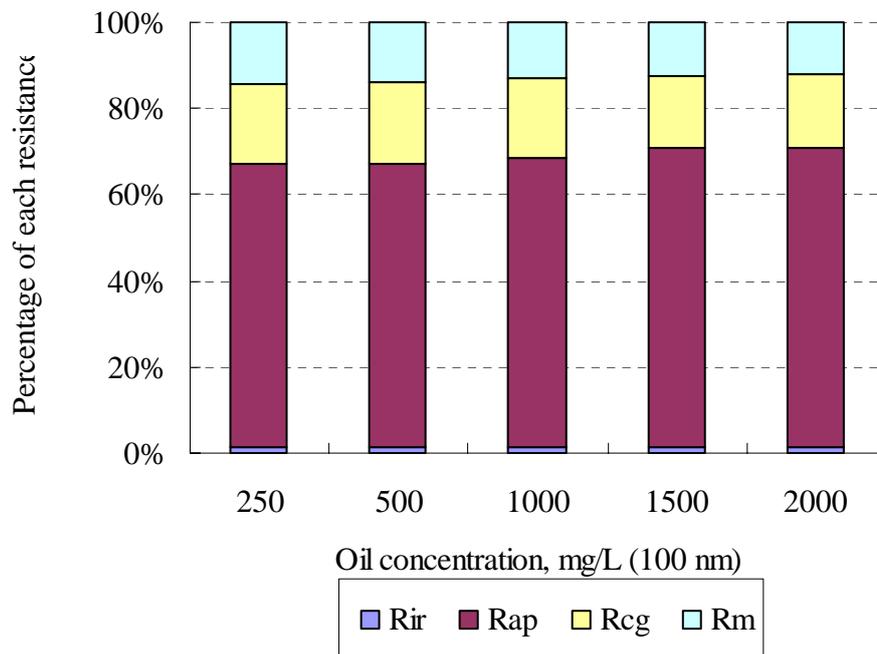
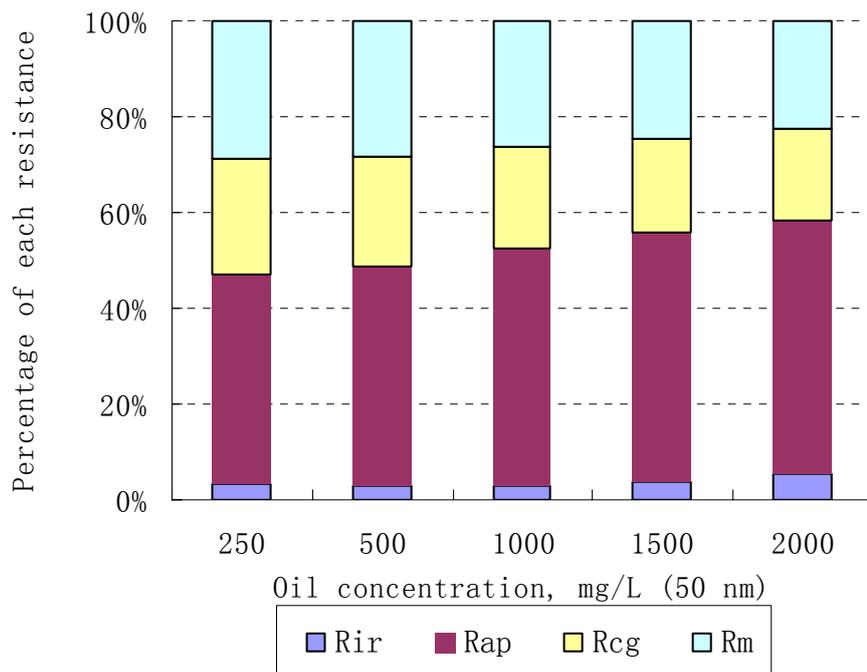


Fig.7. 12 Percentage of various filtration resistances under different oil concentrations.

7.4 Prediction Models

Membrane fouling is responsible for the non-steady state nature of MF processes, as it causes permeate flux decline to occur with time (Visvanathan & Ben Aim, 1989; Todisco *et al.*, 1996; Blanpain-Avet *et al.*, 1999). Therefore, steady-state flux decline models are not capable of accurately describing membrane performance in MF processes, and it is necessary to use non-steady state models.

There were many non-steady state empirical or semi-empirical models in the literature, but most of them were for the description of UF and RO processes (Niemi and Palosaari, 1993; Wang and Song, 1999). Empirical models are more accurate than non-empirical models, although their applicability is restricted to a range assumed by the experimentation. The permeate fluxes obtained from non-empirical models was similar to those experimentally observed only at long time scales (Vela *et al.*, 2006). Hence, it was not accurate to describe the full stages of the filtration process. In this research, prediction model were developed and verified with experimental data.

7.4.1 Prediction Model -Permeate Flux

As analysis in Section 7.1, all kinds of resistances are related to nature of feed solution and operating conditions. The relation among them is very complicated. Actually, they can not express in an empirical formulation. Therefore, it is difficult to develop a perfected non-steady state prediction model for the permeate flux under various CFV, TMP and oil concentrations. Supposing the effect from the TMP on permeate flux is predominant, compared with CFV and oil concentration (CONC). Modeling process is shown as follows:

- 1, Analyze the time-dependence permeate flux curve, find out nonlinear regression between the permeate flux and time, $J = f(t)$;
- 2, Consider the effect of TMP (positive) on the permeate flux, set up nonlinear regression between the TMP and permeate flux, $J = f(t, \text{TMP})$;
- 3, Consider the effect of CFV (positive effect) and CONC (negative effect) on the permeate flux, modify $J = f(t, \text{TMP})$ to $J = f(t, \text{TMP}, \text{CFV}, \text{CONC})$;
- 4, Calibrate the regression equation (largest value of R^2);

5, Verify the model, compare the predicted data with experimental data.

According to the experimental data (CFV = 0.21, 0.42, 1.68 m/s; TMP = 0.1, 0.15, 0.25, 0.3 MPa; CONC = 250, 500, 1 500, 2 000 mg/L), fitted models of non-steady state permeate flux were developed.

For 50 nm membrane

$$J = 4165 \times \text{TMP} \times \left(0.85 + 2.59 \times \sqrt{\frac{\text{CFV}}{\text{CONC}}}\right) \times T^{-0.444} \quad (7.16)$$

$$R^2 = 0.9632$$

For 100 nm membrane

$$J = 7879 \times \text{TMP}^{0.785} \times \left(0.9 + 1.725 \times \sqrt{\frac{\text{CFV}}{\text{CONC}}}\right) \times T^{-0.644} \quad (7.17)$$

$$R^2 = 0.9635$$

where J is permeate flux (L/m² h), TMP is pressure (MPa), CFV is velocity of feed (m/s); CONC is oil concentration (mg/L); t is filtration time (min). Validity of the equation: TMP was at a range of 0.1-0.3 MPa, CFV was less than 1.68 m/s, and oil concentration was less than 2 000 mg/L.

The predicted data by the models (Eqs. (7.16) and (7.17)) are compared with the experimental data under typical conditions. The results are presented in Figures 7.13 - 7.15. In Figure 7.13, experimental and predicted data are obtained at CFV of 0.84 m/s, TMP of 0.2 MPa, and CONC of 500 mg/L. In Figure 7.14,

experimental and predicted data are obtained at TMP of 0.25 MPa, CFV of 1.68 m/s, and CONC of 500 mg/L. In Figure 7.15, experimental and predicted data are obtained at CONC of 1 000 mg/L, CFV of 1.68 m/s, and TMP of 0.2 MPa.

Although slight discrepancies between predicted and experimental data appeared at long time scales ($t > 50$ minutes), this may be due to the fact that the permeate flux almost remain stable after 50 minutes in the experiment, while the permeate flux from model are always decrease with the time. However, good correlation during the full filtration process were showed between experimental and predicted data ($R^2 = 0.9707$ (50 nm), $R^2 = 0.9647$ (100 nm) for CFV of 0.84 m/s; $R^2 = 0.9335$ (50 nm), $R^2 = 0.9598$ (100 nm) for TMP of 0.25 MPa; and $R^2 = 0.9445$ (50 nm), $R^2 = 0.9674$ (100 nm) for CONC of 1 000 mg/L).

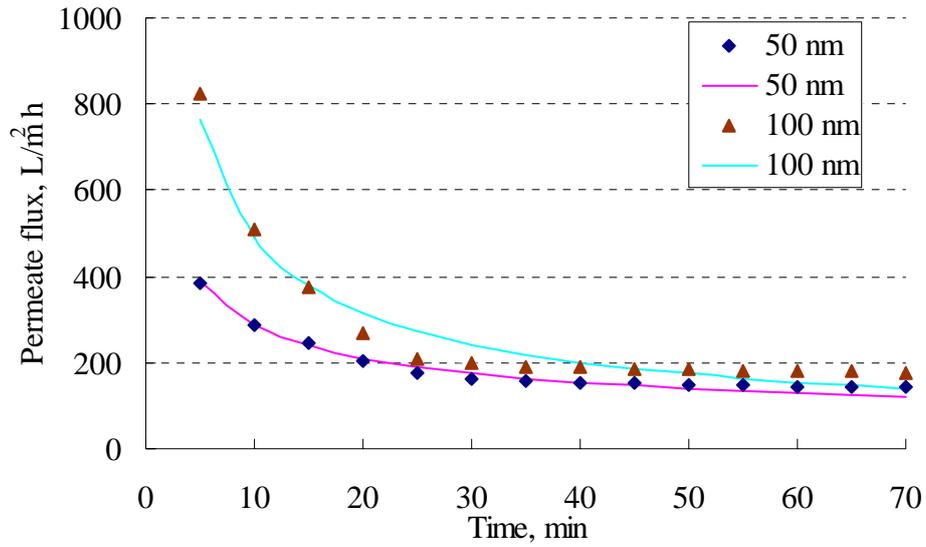


Fig.7. 13 Comparison between experimental results (symbols) and predicted permeate flux (lines) at CFV of 0.84 m/s.

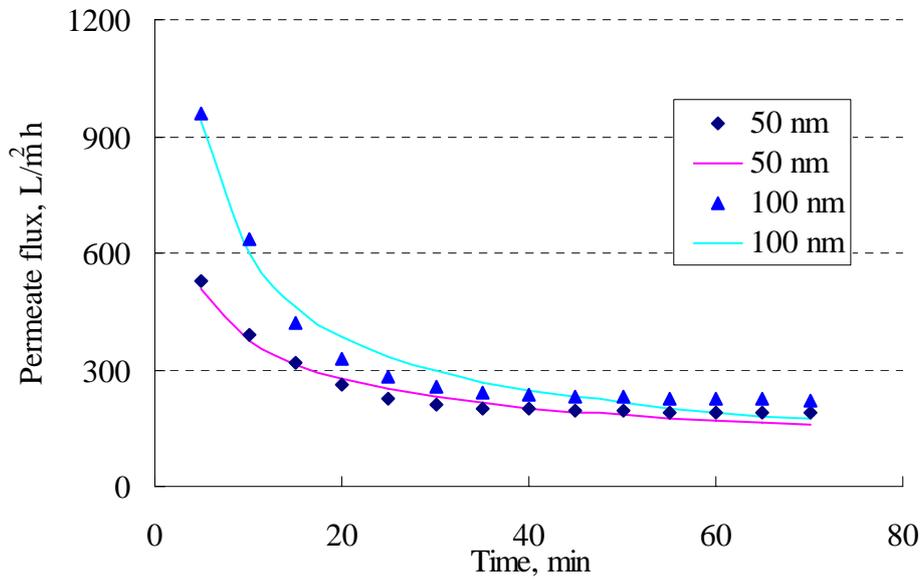


Fig.7. 14 Comparison between experimental results (symbols) and predicted permeate flux (lines) at TMP of 0.25 MPa.

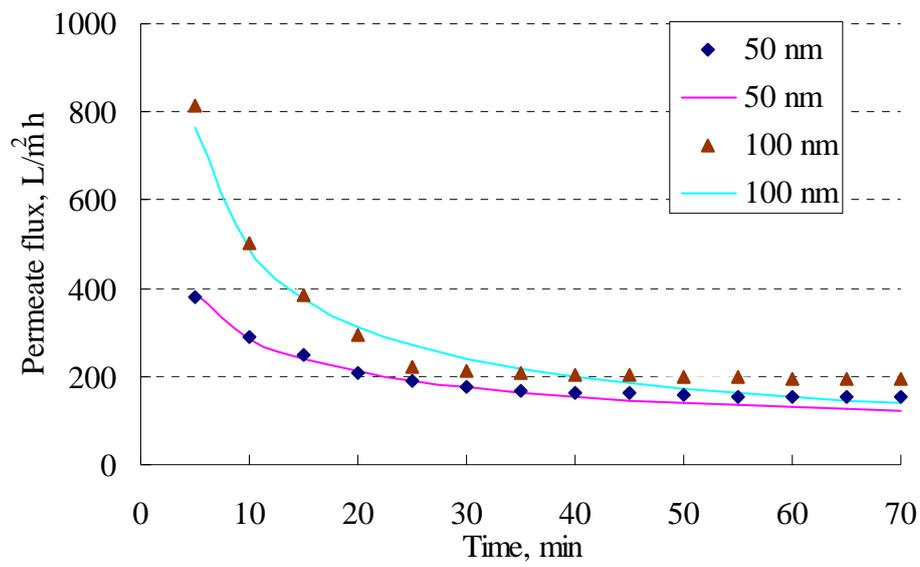


Fig.7. 15 Comparison between experimental results (symbols) and predicted permeate flux (lines) at CONC of 1000 mg/L.

7.4.2 Prediction Model -Cumulative Volume of Permeate

The method and procedure to develop non-steady state cumulative volume is the same as that described in Section 7.41.

According to the experimental data (CFV = 0.21, 0.42, 1.68 m/s; TMP = 0.1, 0.15, 0.25, 0.3 MPa; CONC = 250, 500, 1 500, 2 000 mg/L), fitted models of non-steady state cumulative volume of permeate were developed.

For 50 nm membrane

$$V = 6350 \times TMP \times (0.85 + 1.32 \times \frac{(CFV)^{0.6}}{(CONC)^{0.4}}) \times (T - 0.5)^{0.68} \quad (7.18)$$

$$R^2 = 0.9919$$

For 100 nm membrane

$$V = 9782 \times TMP^{0.75} \times (0.9 + 0.88 \times \frac{(CFV)^{0.6}}{(CONC)^{0.4}}) \times (T - 0.2)^{0.57} \quad (7.19)$$

$$R^2 = 0.9940$$

where V is cumulative volume of permeate (mL), TMP is pressure (MPa), CFV is velocity of feed (m/s); CONC is oil concentration (mg/L); t is filtration time (min). Validity of the equation: TMP was at a range of 0.1-0.3 MPa, CFV was less than 1.68 m/s, and oil concentration was less than 2 000 mg/L.

The predicted data by the models (Eqs. (7.18) and (7.19)) are compared with the experimental data under typical conditions. The results are present in Figures 7.16, - 7.18. In Figure 7.16, experimental and predicted data are obtained at CFV of 0.84 m/s, TMP of 0.2 MPa, and CONC of 500 mg/L. In Figure 7.17, experimental and predicted data are obtained at TMP of 0.25 MPa, CFV of 1.68 m/s, and CONC of 500 mg/L. In Figure 7.18, experimental and predicted data are obtained at CONC of 1 000 mg/L, CFV of 1.68 m/s, and TMP of 0.2 MPa.

Good correlation was showed between experimental and predicted data ($R^2 = 0.9995$ (50 nm), $R^2 = 0.9981$ (100 nm) for CFV of 0.84 m/s; $R^2 = 0.9984$ (50 nm), $R^2 = 0.9963$ (100 nm) for TMP of 0.25 MPa; and $R^2 = 0.9986$ (50 nm), $R^2 = 0.9984$ (100 nm) for CONC of 1 000 mg/L). The predicted data, from either 50 nm membrane or 100 nm membrane, were better coincided with the experimental data during the full filtration process than that of permeate flux.

These models are helpful for users to understand the variation of permeate flux and cumulative volume of permeate during the filtration process, to determine the time for the membrane cleaning, to know the effect of TMP, CFV and CONC on the membrane filtration, and to find the optimal situation for filtration performance.

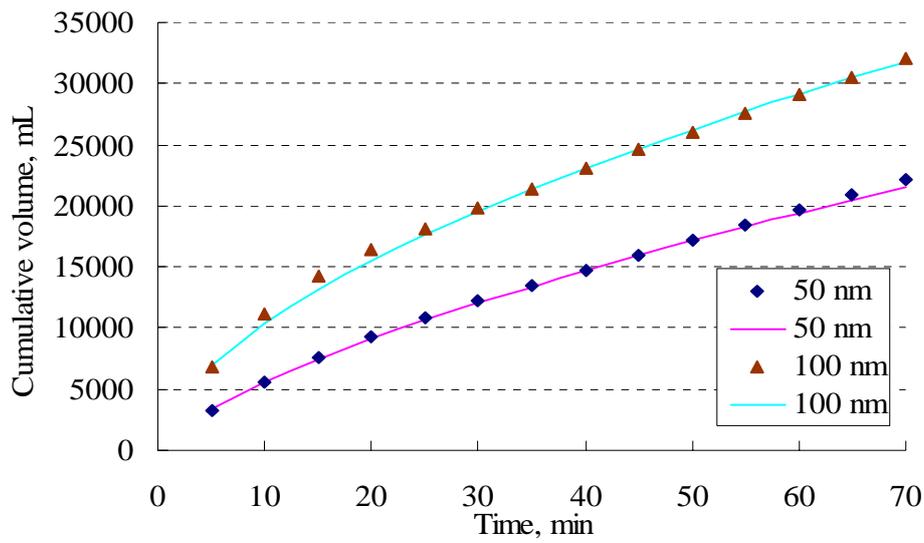


Fig.7. 16 Comparison between experimental results (symbols) and predicted cumulative volume of permeate (lines) at CFV of 0.84 m/s.

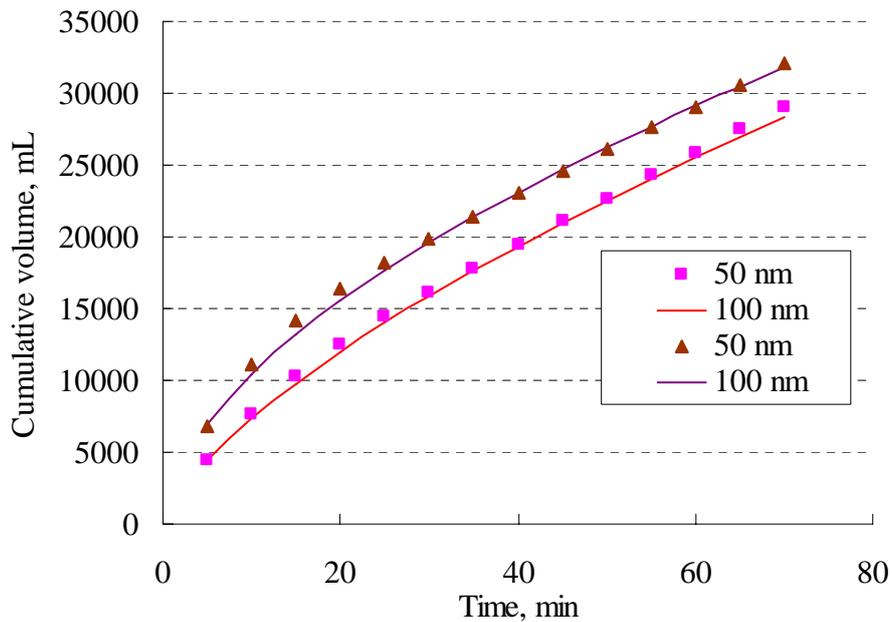


Fig.7. 17 Comparison between experimental results (symbols) and predicted cumulative volume of permeate (lines) at TMP of 0.25 MPa.

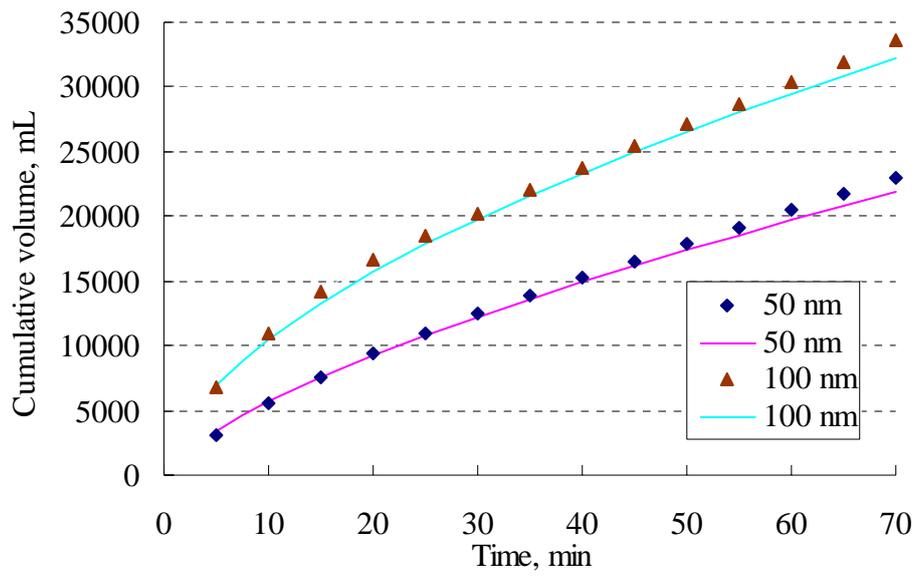


Fig.7. 18 Comparison between experimental results (symbols) and predicted cumulative volume of permeate (lines) at CONC of 1000 mg/L.

7.4.3 Sensitivity Analysis (SA)

A sensitivity analysis is the process of varying model input parameters over a reasonable range (range of uncertainty in values of model parameters) and observing the relative change in model response (Saltelli *et al.*, 1993). The purpose of the sensitivity analysis is to demonstrate the sensitivity of the model simulations to uncertainty in values of model input data. The sensitivity of one model parameter relative to other parameters is also demonstrated. Sensitivity analyses are also beneficial in determining the direction of future data collection activities. Data for which the model is relatively sensitive would require future characterization, as opposed to data for which the model is relatively insensitive. Model-insensitive data would not require further field characterization. Up to now, many different methods have been developed for SA, such as screening methods, local SA methods and global SA methods (Saltelli *et al.*, 2000). Local SA methods is one of the most used methods in the environmental research (Battaglia and Sands, 1998; Van der Peijl and Verhoeven, 1999; Brugnach, 2005).

Three parameters of the prediction model were examined in the parameter sensitivity analysis. Table 7.5 gives the definition and standard operating value

Table 7. 5 Parameters used in SA.

Parameters	Definition	Units	Assigned range	Assigned value
TMP	Transmembrane pressure	MPa	0.1-0.3	0.2
CFV	Cross-flow velocity	m/s	0.21-1.68	0.95
CONC	Oil concentration in the feed stream	mg/L	250-2000	1125
t	Operating time	minute	0-70	35

for membranes of each of these parameters. The relative sensitivities (defined below) of permeate flux and cumulative volume of permeate to variations of each parameter were computed and used to assess the sensitivity of the prediction models to changes in its parameter values.

The relative sensitivity analysis $SA(X; p)$ of an output variable X with respect to a parameter p is the change ΔX in X produced by a change Δp in p relative to the original values of X and p (Brylinsky, 1972), i.e.

$$SA(X, p) = \frac{\Delta X / X}{\Delta p / p} \quad (7.20)$$

The higher the value of SA , the more sensitive a model is to changes in that parameter (Jørgensen, 1988). Relative sensitivity of a variable to a parameter is positive or negative depending on whether an increase in the parameter leads to an increase or a decrease, respectively, in that variable. A relative sensitivity of unity indicates that a percentage change in the value of a parameter will result in the same percentage change in the variable. The accuracies of the sensitivities calculated depend on the parameter change Δp . In the case of nonlinear models, parameter changes that are too large (e.g. > 5%) would damage the assumption of local linearity. If the parameter change is too small, the difference between the original and perturbed solutions is too small and the round-off error is too high. In most cases, a 1% perturbation is a good practical choice (Saltelli *et al.*,

2000). Here, changes were made of +1% and -1% of the assigned values. The individual value and average value of SA was then calculated for each model [Eqs. (7.16), (7.17), (7.18) and (7.19)] and three parameters (TMP, CFV and CONC).

Table 7.6 shows the results of the model SA to parameter changes. It can be seen that the models are most sensitive to changes in TMP. The model was relatively insensitive to changes in values of the other two parameters. This result indicates that of all these three parameters, the influence of TMP on the permeate flux and cumulative volume of permeate is the most significant. Therefore, the selection of a fitting value for TMP during the operation is very important for membrane filtration process. The value of 0.2 MPa for TMP for membrane separation of oily wastewater is recommended.

Table 7. 6 Calculation results of SA.

Parameter		50 nm membrane		100 nm membrane	
		Flux model	Volume model	Flux model	Volume model
TMP	+1%	1.00(+)	1.00(+)	0.81(+)	0.67(+)
	-1%	1.00(+)	1.00(+)	0.76(+)	0.67(+)
	Ave	1.00(+)	1.00(+)	0.785(+)	0.67(+)
CFV	+1%	0.03(+)	0.05(+)	0.03(+)	0.03(+)
	-1%	0.04(+)	0.04(+)	0.02(+)	0.03(+)
	Ave	0.035(+)	0.045(+)	0.025(+)	0.03(+)
CONC	+1%	0.04(-)	0.03(-)	0.02(-)	0.02(-)
	-1%	0.03(-)	0.03(-)	0.03(-)	0.02(-)
	Ave	0.035(-)	0.03(-)	0.025(-)	0.02(-)

(+/-) indicates a positive/inverse relation between the change in the parameter and the change in the flux or volume.

7.5 Summary

During the membrane filtration process, various membrane resistances are responsible for the permeate flux decline. The resistances are related to the interaction between the membrane and solute of feed solution and solutes of feed solution as well. The resistances are also affected by the operating conditions. The series resistance (SR) model presents the correlation of flux, viscosity and total resistances.

Hermia (1982) introduced the filtration laws, which aimed to describe fouling mechanisms such as complete blocking, intermediate blocking, standard blocking and cake filtration. The models are valid for an eligible condition. However, none of these four mechanisms can be selected to completely describe the ceramic membrane filtration process of oil-in-water emulsion. This indicates that resistances and their influence on the permeate flux are very complicated.

The changes of CFV, TMP and oil concentration may result in the change of resistances, which dominate the membrane filtration performance. Each kind of resistance can be calculated by measuring the various permeate flux (J_i , J_w , J_p , J_f) during operation process. When CFV value increased, the percentage of

resistance resulted from the concentration polarization and gel-layer (R_{cg}) decreased. As TMP increased, the concentration polarization and gel-layer (R_{cg}) irreversible resistance (R_{ir}) had a tendency to increase. The membrane adsorption and pore block (R_{ap}) increased obviously as a result of the oil concentration increased. These results contribute to the selection of operating parameters in the MF process.

Non-steady state prediction models of permeate flux and cumulative volume of permeate are developed and verified by experimental data. The results indicate that good correlation exists between the experimental data and predicted data. The models are helpful for users to understand the variation of permeate flux and cumulative volume of permeate under different operating conditions, to determine the time for the membrane cleaning, to understand the effect of TMP, CFV and CONC on the membrane filtration, and to find the optimal situation for filtration performance.

SA indicates that the models are most sensitive to changes of TMP. The model was relatively insensitive to changes of the other two parameters. This result indicates that of all these three parameters (TMP, CFV and CONC), the influence of TMP on the permeate flux and cumulative volume of permeate is the most significant. The selection of a fitting value for TMP during the

operation is very important for membrane filtration process. The value of 0.2 MPa for TMP is recommended.

CHAPTER EIGHT

CONCLUSIONS AND RECOMMENDATIONS

8.1 Concluding Remarks

Membrane filtration process is influenced by the characteristics of membrane material, the nature of solution environment, and operating conditions. The pore size of the membrane is one of the most important factors that affect membrane filtration performance. In addition, as temperature affects the viscosity of the feed solution, high permeate flux is obtained as a result of decrease of viscosity under high temperature. The effects of CFV, TMP, oil concentration, pH and salt concentration on the ceramic membrane MF process are described as follows.

8.1.1 Membrane Characterizations

Under the circumstance of pure water as feed solution, filtration resistance during the filtration process exists only in the form of membrane resistance.

Therefore, the permeate flux increases linearly with the TMP increasing. As the viscosity of feed solution decreases with the increase of temperature, the permeate flux increases with the increase of temperature. The influence of pH and salt concentration on the permeate flux is related to the composite and structure of the membrane materials. The electric charge of the membrane surface and effective pore size of the membrane change as the variations of pH value and salt concentration, which result in the variations of permeate flux. Under acidic and/or saline conditions, high permeate flux is obtained. Since the sizes of hydrated ions of Al_2O_3 and H_2O are smaller under low pH than that under high pH, the steric resistance under low pH is low when water molecules pass through the membrane. Therefore, high permeate flux obtained under low pH conditions. With the presence of salt, the Debye length (κ^{-1}) decreases. Therefore the 'effective' pore size increases and approaches the real pore size, and the water flux increases accordingly.

8.1.2 Oily Wastewater membrane filtration

The factors of CFV, TMP and oil concentration can affect the ceramic membrane filtration processes of oily wastewater. Among these variables, TMP is the most crucial factors. Increasing TMP provides high driven force for the

MF process that results in high permeate flux. However, this influence is valid under pressure control region. Beyond the crucial point of the pressure, the influence of TMP on the permeate flux could be reduced or have a negative effect. High permeate flux is also obtained under high CFV value and low oil concentration of feed solution. This is due to the fact of low membrane adsorption and weak concentration polarization and gel-layer, under high CFV value and low oil concentration. The permeate flux increases as a result of decrease of viscosity under high temperature of feed solution. The permeation quality is also affected by TMP, oil concentration and temperature. High TOC concentrations in the permeation present high TMP, high oil concentration and high temperature of feed solution. As a whole, the oil concentrations of the permeation obtained under whole experimental conditions can meet statutory standard.

The MF process of oily wastewater with ceramic membrane is also affected by the pH value and salt concentration of the feed solution. The low permeate flux is obtained under high salt concentration and low pH value condition. This result is different from the results obtained from pure water as feed solution. The reason is that pH value and salt concentration of the feed solution give rise to the variations of zeta potential of emulsion droplets. The influence of salt concentration on the zeta potential is significant. When a little of salt

concentration increased in low range of salt concentration, zeta potential of oil emulsion droplet had a steep increase. The zeta potential of emulsion droplet was almost linearly increased with the decrease of pH value. The average size of emulsion droplets was not significantly change under the various pH values. Under the presence of various salt concentrations, the average size of emulsion droplets was changed disproportionately. However, the trend that the average size of droplets increased under high salt concentration was perceived. This can be explained by the coagulation of emulsion droplets which is likely to happen as salt concentration is increased.

Membrane fouling is predominantly responsible for the decline of the permeate flux. Effective membrane cleaning is necessary to maintain large permeate flux. The procedure of membrane cleaning proposed here was sequentially washing the membrane with (1) hot water, (2) sodium hydroxide solution, (3) EDTA solution. It is expected that when backflushing with hot water in place of hot water rinse in the membrane cleaning process, the effectiveness of membrane cleaning would be much better.

The experimental results revealed that restaurant wastewater could be effectively treated by ceramic membrane with its pore size of 100 at TMP of 0.2 MPa and CFV of 1.68 m/s. The oil concentration monitored in the raw

wastewater was 284 mg/L, and the average oil concentration in the permeation was 13 mg/L. The oil rejection reached as high as 95%. The removal efficiency was satisfactory. The mode of three-stage filtration operation was the best option for treating oily wastewater. The calculation showed that 4 m² of membrane surfaces were enough for a restaurant that discharged 10 m³/day of wastewater.

8.1.3 Filtration Resistances and Prediction Models

During the membrane filtration process, the filtration resistances are related to the interaction between the membrane and solute of feed solution and solutes of feed solution as well. The resistances are affected by the nature of the feed solution and operating conditions. Hermia (1982) introduced the filtration laws, which aimed to describe fouling mechanisms such as complete blocking, intermediate blocking, standard blocking and cake filtration. The models are only valid under an eligible condition. None of these four mechanisms can be selected to describe the ceramic membrane filtration process of O/W emulsion. This indicates that the resistances and their influence on the ceramic membrane MF process are very complicated.

A new method to identify the filtration resistance variations is proposed in this study. With the measurement of various permeate fluxes (J_i , J_w , J_p , J_f) during the membrane separation process, each kind of resistance can be calculated. When CFV value increased, the percentage of resistance resulting from the concentration polarization and gel-layer (R_{cg}) decreased. As TMP increased, the concentration polarization and gel-layer (R_{cg}) irreversible resistance (R_{ir}) had a tendency to increase. The membrane adsorption and pore block (R_{ap}) increased obviously as a result of the oil concentration increased. The calculated results coincide with the theoretical analysis. These results yield a useful contribution to the selection of operating parameters for the MF process.

Non-steady state prediction models of permeate flux and cumulative volume of permeate are developed according to one group of data obtained from this experiment. The prediction models are also verified with another group of experimental data. The results indicate that good correlation exists between the experimental data and predicted data.

The models are helpful for users to understand the variation of permeate flux and cumulative volume of permeate under various operating conditions, to determine the situation of the membrane cleaning, to understand the effect of

TMP, CFV and oil concentration on the membrane filtration, and to ascertain the optimal situation for filtration performance.

SA indicates that the models are most sensitive to changes in TMP. The model was relatively insensitive to changes of the other two parameters. This result indicates that of all these three parameters (TMP, CFV and CONC), the influence of TMP on the permeate flux and cumulative volume of permeate is the most significant. The selection of a fitting value for TMP during the operation is very important for membrane filtration process.

8.2 Limitations and Future Research

The present study mainly focused on artificial oily wastewater. Considering the complexity of wastewater component and the difference between lab-scale batch experiments and field continuous operation, further field tests are needed to modify the process including when and how long the ceramic membrane should be cleaned.

New methods to calculate the resistance are needed to verify through observing changes happened on the membrane surface and membrane pores by high-tech means. Meanwhile, the prediction models developed in this study are the first step to attempt a description of the filtration process. Therefore, they need to be further verified and improved before they are widely applied.

This research provides a theoretical basis and practical evidence for the application of ceramic membrane on the oily wastewater treatment. It is hoped that these experimental results will be of benefit to process design of oily wastewater treatment system, and contribution to the reduction of water pollution.

RELATED PUBLICATIONS

F. L. Hua, Y. F. Tsang, Y. J. Wang, S. Y. Chan, H. Chua and S. N. Sin,
Performance Study of Ceramic Microfiltration Membrane for Oily
Wastewater Treatment, Chemical Engineering Journal, in press .

F. L. Hua, Y. F. Tsang and H. Chua, Progress in Water Environment Pollution
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wastewater treatment by means of ceramic membrane, Proceedings of the
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Separation of edible oil-water emulsion by ceramic membrane, Desalination,
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APPENDIX I

Standards for effluents discharged into foul sewers leading into Government sewage treatment plants

(All units in mg/L unless otherwise stated; all figures are upper limits unless otherwise indicated)

Determinand	Flow rate (m ³ /day)	≤ 10	> 10 and ≤ 100	> 100 and ≤ 200	> 200 and ≤ 400	> 400 and ≤ 600	> 600 and ≤ 800	> 800 and ≤ 1000	> 1000 and ≤ 1500	> 1500 and ≤ 2000	> 2000 and ≤ 3000	> 3000 and ≤ 4000	> 4000 and ≤ 5000	> 5000
pH (pH units)		6-10	6-10	6-10	6-10	6-10	6-10	6-10	6-10	6-10	6-10	6-10	6-10	6-10
Temperature (°C)		43	43	43	43	43	43	43	43	43	43	43	43	43
Suspended solids		1200	1000	900	800	800	800	800	800	800	800	800	800	800
Settleable solids		100	100	100	100	100	100	100	100	100	100	100	100	100
BOD		1200	1000	900	800	800	800	800	800	800	800	800	800	800
COD		3000	2500	2200	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000
Oil & Grease		100	100	50	50	50	40	30	20	20	20	20	20	20
Iron		30	25	25	25	15	12.5	10	7.5	5	3.5	2.5	2	1.5
Boron		8	7	6	5	4	3	2.4	1.6	1.2	0.8	0.6	0.5	0.4
Mercury		0.2	0.15	0.1	0.1	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Cadmium		0.2	0.15	0.1	0.1	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Copper		4	4	4	3	1.5	1.5	1	1	1	1	1	1	1
Nickel		4	3	3	2	1.5	1.5	1	0.8	0.7	0.7	0.6	0.6	0.6
Chromium		2	2	2	2	1	0.7	0.6	0.4	0.3	0.2	0.1	0.1	0.1
Zinc		5	5	4	3	1.5	1.5	1	0.8	0.7	0.7	0.6	0.6	0.6
Silver		4	3	3	2	1.5	1.5	1	0.8	0.7	0.7	0.6	0.6	0.6
Other toxic metals individually		2.5	2.2	2	1.5	1	0.7	0.6	0.4	0.3	0.2	0.15	0.12	0.1
Total toxic metals		10	10	8	7	3	2	2	1.6	1.4	1.2	1.2	1.2	1
Cyanide		2	2	2	1	0.7	0.5	0.4	0.27	0.2	0.13	0.1	0.08	0.06
Phenols		1	1	1	1	0.7	0.5	0.4	0.27	0.2	0.13	0.1	0.1	0.1
Sulphide		10	10	10	10	5	5	4	2	2	2	1	1	1
Sulphate		1000	1000	1000	1000	1000	1000	1000	900	800	600	600	600	600
Total nitrogen		200	200	200	200	200	200	200	100	100	100	100	100	100
Total phosphorus		50	50	50	50	50	50	50	25	25	25	25	25	25
Surfactants (total)		200	150	50	40	30	25	25	25	25	25	25	25	25

(Enacted 1990)

APPENDIX II

Variation of some properties of water with temperature

Temperature,	Density, kg/m ³	Viscosity, ×10 ⁻³ kg/m s	Kinematic viscosity, ×10 ⁻⁶ m ² /s	Surface tension, ×10 ⁻² N/m
0	999.9	1.792	1.792	7.62
5	1000	1.519	1.519	7.54
10	999.7	1.308	1.308	7.48
15	999.1	1.140	1.141	7.41
20	998.2	1.005	1.007	7.36
25	997.1	0.894	0.897	7.26
30	995.7	0.801	0.804	7.18
35	994.1	0.723	0.727	7.10
40	992.2	0.656	0.661	7.01
45	990.2	0.599	0.605	6.92
50	988.1	0.549	0.556	6.82
55	985.7	0.506	0.513	6.74
60	983.2	0.469	0.477	6.68
65	980.6	0.436	0.444	6.58
70	977.8	0.406	0.415	6.50
75	974.9	0.380	0.390	6.40
80	971.8	0.357	0.367	6.30
85	968.6	0.336	0.347	6.20
90	965.3	0.317	0.328	6.12
95	961.9	0.299	0.311	6.02
100	958.4	0.284	0.296	5.94

APPENDIX III

Points of zero charge for some oxides in water*(Kosmulski, 1997)

Oxide	PZC	Oxide	PZC
Ag ₂ O	11.2	Nb ₂ O ₅	2.8
Al ₂ O ₃	9.1	NiO	10.2
BeO	10.2	PuO ₂	9.0
CdO	11.6	RuO ₂	5.3
CeO ₂	8.1	Sb ₂ O ₅	1.9
CoO	10.2	SiO ₂	2.0
Co ₃ O ₄	7.4	SnO ₂	5.6
Cr ₂ O ₃	7.1	Ta ₂ O ₅	2.8
CuO	9.3	ThO ₂	9.2
Fe ₂ O ₃	8.2	TiO ₂ (rutile)	5.7
Fe ₃ O ₄	6.6	TiO ₂ (anatase)	6.2
HgO	7.3	V ₂ O ₃	8.4
La ₂ O ₃	10.1	WO ₃	0.4
MgO	12.4	Y ₂ O ₃	8.9
MnO ₂	5.3	ZnO	9.2
MoO ₃	2.0	ZrO ₂	7.6

*The PZC for many oxides are somewhat variable. The reasons are that the oxides occur in various crystallo-graphic forms and impurity level.

APPENDIX IV Experimental data

Part One: Viscosity and size distribution

Measured values of viscosity of pure water and various oil concentration solution (20 °C)

unit: mPa·s

Viscosity	1	2	3	4	5	6
Pure water	9.95	10.02	9.70	9.86	9.95	9.73
250 mg/L	10.94	10.62	10.71	10.97	10.87	10.81
500 mg/L	10.87	10.94	10.81	11.03	10.68	10.90
1000 mg/L	10.90	10.94	11.03	10.90	10.97	11.13
1500 mg/L	10.97	11.22	11.03	11.00	11.06	11.13
2000 mg/L	11.03	11.44	11.06	11.25	11.13	11.03

Size distribution of feed solution and permeate solution

Feed solution

size (nm)	intensity	volume	number
40.8	0	0	0
69.6	0	0.1	12.4
118.6	0.9	0.6	31.4
202.3	7.3	1.7	29.1
345.1	11.2	2.9	14.4
588.6	9.4	11.8	6.3
1004	20.6	28.6	3.9
1712.4	39.4	32	2.1
2920.8	11.1	17.9	0.4
4981.7	0	4.4	0

Permeate solution

first

Size(nm)	Intensity	Volume	Number
19	0	6.2	18.8
25.9	0.3	17.4	43.3
35.4	0.6	16.4	30.5
48.4	0.1	5.7	6.2
66	0	2.1	0.3
90.2	2.9	7.3	0.3
123.2	16.5	13.7	0.4
168.2	34.3	14.7	0.2
229.7	34.2	10.4	0.1
313.6	11.2	4.9	0
428.3	0	1.2	0

duplicate one

Size(nm)	Intensity	Volume	Number
19.9	0	7.7	21.3
26.9	0.4	18.5	46
36.3	0.4	13.7	28
49.1	0	3	3.3
66.3	0	2.2	0.2
89.7	3.7	8.4	0.4
121.2	15.7	14.3	0.5
163.9	31.4	14.7	0.2
221.5	33.3	10.7	0.1
299.4	15.1	5.5	0
404.7	0	1.4	0

duplicate two

Size(nm)	Intensity	Volume	Number
19.2	0	6.2	22.4
26.1	0.2	13.6	46.7
35.4	0.1	8.7	26.1
48.1	0	2.1	2
65.4	0.5	5	0.7
88.8	5	12.2	1
120.7	16.2	16.9	0.7
164	29.5	15.7	0.3
222.8	31.6	11.5	0.1
302.8	16.9	6.4	0
411.4	0	1.8	0

Part Two: Pure water as feed solution

Permeate flux under different TMP

50 nm membrane

TMP(MPa)	Permeate, mL/min(20)	Permeate flux,L/(h m ²)	Permeate, mL/min(40)	Permeate flux,L/(h m ²)
0.05	300	180	480	288
0.1	550	330	810	486
0.12	625	375	920	552
0.15	780	468	1040	624
0.2	1005	603	1280	768
0.25	1300	780	1550	930
0.3	1555	933	1850	1110

100 nm membrane

TMP,Mpa	Permeate, mL/min(, 20)			Permeate flux,L/(m ² h)		
0.05	785	745	750	471	447	450
0.1	1535	1500	1510	921	900	906
0.15	2020	2010	2040	1212	1206	1224
0.2	2490	2525	2510	1494	1515	1506
0.25	2895	2915	2910	1737	1749	1746
0.3	3420	3475	3450	2052	2085	2070

Permeate flux under different temperatures

Item	50 nm membrane		100 nm membrane	
	Permeate, mL/min	Permeate flux, L/(m ² h)	Permeate, mL/min	Permeate flux, L/(m ² h)
15	482	289.2	1290	774
20	562	337.2	1375	825
25	604	362.4	1550	930
30	645	387	1680	1008
35	705	423	1840	1104
40	780	468	2010	1206

Permeate flux under different pH

100 nm membrane (used)

pH	Permeate, mL/min	Permeate flux, L/(m ² h)
4	850	510
5.5	795	477
6.5	760	456
7.5	750	450
8.5	720	432
9.5	715	429
10.5	720	432

Permeate flux under different pH and salts

50 nm membrane

NaCl, mol/L	pH=3.8		pH=5.8	
	Permeate, mL/min	Permeate flux, L/(m ² h)	Permeate, mL/min	Permeate flux, L/(m ² h)
0	720	432	630	378
0.001	730	438	650	390
0.005	740	444	670	402
0.01	755	453	680	408
0.05	755	453	695	417
NaCl, mol/L	pH=7.8		pH=9.8	
	Permeate, mL/min	Permeate flux, L/(m ² h)	Permeate, mL/min	Permeate flux, L/(m ² h)
0	575	345	565	339
0.001	605	363	605	363
0.005	640	384	650	390
0.01	660	396	660	396
0.05	690	414	695	417

Item	50 nm membrane		100 nm membrane	
NaCl, mol/L	Permeate, mL/min	Permeate, mL/min	Permeate flux, L/(m ² h)	Permeate flux, L/(m ² h)
0	600	1550	930	360
0.001	615	1570	942	369
0.005	635	1615	969	381
0.01	680	1650	990	408
0.05	720	1695	1017	432

Zeta potential of α -alumina particles vs. the pH of the solution at various NaCl concentrations

pH	Zeta potential,mV				
	0 mol/L	0.001mol/L	0.005mol/L	0.01mol/ L	0.05mol/L
4.0	5.4	7.2	12	15	23
6.0	-0.5	-0.6	0.5	1.6	4.2
8.0	-26	-24	-20	-15	-6.3
10.0	-38	-33	-27	-26	-18

Part Three: Oily water as feed solution

Permeate flux and TOC concentration under various CFV

0.21 m/s CFV, 0.2MPa, 500mg/L oil, 20 , 100nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	1335	801	20.3
10	5-10	820	492	17.2
15	10-15	595	357	15.8
20	15-20	420	252	15.1
25	20-25	310	186	14.6
30	25-30	290	174	14.8
35	30-35	280	168	13.6
40	35-40	275	165	14.2
45	40-45	270	162	14.3
50	45-50	266	159.6	14.5
55	50-55	263	157.8	14.3
60	50-60	260	156	14.1
65	60-65	258	154.8	13.7
70	65-70	257	154.2	13.9

0.42 m/s CFV, 0.2MPa, 500mg/L oil, 20 , 100nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	1360	816	20.9
10	5-10	840	504	18.1
15	10-15	616	369.6	15.9
20	15-20	435	261	15.3
25	20-25	325	195	14.4
30	25-30	303	181.8	13.8
35	30-35	294	176.4	14.1
40	35-40	290	174	13.9
45	40-45	285	171	14
50	45-50	281	168.6	14.3
55	50-55	277	166.2	14.5
60	50-60	275	165	13.9
65	60-65	272	163.2	14.1
70	65-70	270	162	14.2

0.84 m/s CFV,0.2MPa,500mg/L oil,20 ,100nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	1370	822	20.6
10	5-10	845	507	18.3
15	10-15	625	375	16.7
20	15-20	450	270	15.8
25	20-25	345	207	15.2
30	25-30	330	198	14.3
35	30-35	320	192	13.6
40	35-40	315	189	13.7
45	40-45	310	186	14.1
50	45-50	306	183.6	14.4
55	50-55	303	181.8	14.2
60	50-60	300	180	14.3
65	60-65	298	178.8	14.2
70	65-70	296	177.6	14.3

1.68 m/s CFV,0.2MPa,500mg/L oil,20 ,100nm membrane)

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC,mg/L
5	0-5	1375	825	21.3
10	5-10	850	510	19.3
15	10-15	632	379.2	18.3
20	15-20	475	285	16.8
25	20-25	381	228.6	15.4
30	25-30	368	220.8	14.6
35	30-35	360	216	13.9
40	35-40	355	213	14.3
45	40-45	350	210	14
50	45-50	346	207.6	13.6
55	50-55	343	205.8	13.9
60	50-60	340	204	13.6
65	60-65	338	202.8	13.2
70	65-70	336	201.6	13.7

0.21 m/s CFV,0.2MPa,500mg/L oil,20 ,100nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux,L/(h m ²)	TOC,mg/L
5	0-5	1335	801	20.3
10	5-10	820	492	17.2
15	10-15	595	357	15.8
20	15-20	420	252	15.1
25	20-25	310	186	14.6
30	25-30	290	174	14.8
35	30-35	280	168	13.6
40	35-40	275	165	14.2
45	40-45	270	162	14.3
50	45-50	266	159.6	14.5
55	50-55	263	157.8	14.3
60	50-60	260	156	14.1
65	60-65	258	154.8	13.7
70	65-70	257	154.2	13.9

0.42 m/s CFV,0.2MPa,500mg/L oil,20 ,100nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux,L/(h m ²)	TOC,mg/L
5	0-5	1360	816	20.9
10	5-10	840	504	18.1
15	10-15	616	369.6	15.9
20	15-20	435	261	15.3
25	20-25	325	195	14.4
30	25-30	303	181.8	13.8
35	30-35	294	176.4	14.1
40	35-40	290	174	13.9
45	40-45	285	171	14
50	45-50	281	168.6	14.3
55	50-55	277	166.2	14.5
60	50-60	275	165	13.9
65	60-65	272	163.2	14.1
70	65-70	270	162	14.2

0.84 m/s CFV,0.2MPa,500mg/L oil,20 ,100nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	1370	822	20.6
10	5-10	845	507	18.3
15	10-15	625	375	16.7
20	15-20	450	270	15.8
25	20-25	345	207	15.2
30	25-30	330	198	14.3
35	30-35	320	192	13.6
40	35-40	315	189	13.7
45	40-45	310	186	14.1
50	45-50	306	183.6	14.4
55	50-55	303	181.8	14.2
60	50-60	300	180	14.3
65	60-65	298	178.8	14.2
70	65-70	296	177.6	14.3

1.68 m/s CFV,0.2MPa,500mg/L oil,20 ,100nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC,mg/L
5	0-5	1375	825	21.3
10	5-10	850	510	19.3
15	10-15	632	379.2	18.3
20	15-20	475	285	16.8
25	20-25	381	228.6	15.4
30	25-30	368	220.8	14.6
35	30-35	360	216	13.9
40	35-40	355	213	14.3
45	40-45	350	210	14
50	45-50	346	207.6	13.6
55	50-55	343	205.8	13.9
60	50-60	340	204	13.6
65	60-65	338	202.8	13.2
70	65-70	336	201.6	13.7

Permeate flux and TOC concentration under various TMP

0.1MPa,1.68m/s,500mg/L oil,20 ,50nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	303	181.8	9.3
10	5-10	190	114	8.6
15	10-15	160	96	8.1
20	15-20	140	84	7.8
25	20-25	130	78	7.4
30	25-30	125	75	7.3
35	30-35	120	72	7.1
40	35-40	115	69	6.6
45	40-45	112	67.2	6.7
50	45-50	109	65.4	6.9
55	50-55	106	63.6	7
60	50-60	104	62.4	6.7
65	60-65	102	61.2	6.5
70	65-70	101	60.6	6.9

0.15MPa,1.68m/s,500mg/L oil,20 ,50nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	465	279	10.8
10	5-10	352	211.2	9.6
15	10-15	305	183	8.9
20	15-20	255	153	8.4
25	20-25	230	138	7.7
30	25-30	208	124.8	7.2
35	30-35	200	120	7.1
40	35-40	195	117	7.5
45	40-45	190	114	7.6
50	45-50	186	111.6	7.3
55	50-55	183	109.8	7.1
60	50-60	181	108.6	6.6
65	60-65	180	108	7.2
70	65-70	180	108	7.3

0.2MPa,1.68m/s,500mg/L oil,20 ,50nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	660	396	13.8
10	5-10	500	300	11.4
15	10-15	430	258	10.1
20	15-20	365	219	9.3
25	20-25	330	198	9.2
30	25-30	305	183	8.9
35	30-35	290	174	9.2
40	35-40	285	171	9.3
45	40-45	280	168	8.8
50	45-50	277	166.2	8.5
55	50-55	275	165	8.4
60	50-60	273	163.8	8.8
65	60-65	272	163.2	8.5
70	65-70	271	162.6	8.7

0.25MPa,1.68m/s,500mg/L oil,20 ,50nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	880	528	27.7
10	5-10	650	390	23.4
15	10-15	530	318	21.2
20	15-20	440	264	20.6
25	20-25	380	228	19.2
30	25-30	350	210	19.3
35	30-35	335	201	18.7
40	35-40	330	198	18.3
45	40-45	325	195	18.4
50	45-50	321	192.6	17.9
55	50-55	318	190.8	17.7
60	50-60	315	189	18.1
65	60-65	313	187.8	18.3
70	65-70	312	187.2	18.5

0.3MPa,1.68m/s,500mg/L oil,20 ,50nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	1070	642	43.7
10	5-10	780	468	36.4
15	10-15	590	354	32.1
20	15-20	490	294	30.6
25	20-25	430	258	28.5
30	25-30	400	240	26.9
35	30-35	370	222	25.5
40	35-40	365	219	25.7
45	40-45	360	216	25.9
50	45-50	356	213.6	24.8
55	50-55	353	211.8	25.1
60	50-60	350	210	25.3
65	60-65	348	208.8	25.7
70	65-70	345	207	24.4

0.1MPa,1.68m/s,500mg/L oil,20 ,100nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	680	408	17.2
10	5-10	452	271.2	15.3
15	10-15	363	217.8	14.4
20	15-20	303	181.8	13.7
25	20-25	261	156.6	13.1
30	25-30	238	142.8	12.3
35	30-35	225	135	12.4
40	35-40	219	131.4	11.5
45	40-45	214	128.4	11.7
50	45-50	209	125.4	11.3
55	50-55	206	123.6	11.6
60	50-60	203	121.8	11.2
65	60-65	201	120.6	11.5
70	65-70	199	119.4	11.4

0.15MPa,1.68m/s,500mg/L oil,20 ,100nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	985	591	18.4
10	5-10	605	363	16.1
15	10-15	450	270	15.3
20	15-20	370	222	14.4
25	20-25	335	201	14.1
30	25-30	312	187.2	13.6
35	30-35	300	180	13.1
40	35-40	292	175.2	12.7
45	40-45	287	172.2	12.8
50	45-50	282	169.2	12.4
55	50-55	277	166.2	11.9
60	50-60	274	164.4	11.8
65	60-65	272	163.2	12.4
70	65-70	270	162	12.3

0.2MPa,1.68m/s,500mg/L oil,20 ,100nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	1375	825	21.3
10	5-10	850	510	19.3
15	10-15	632	379.2	18.3
20	15-20	475	285	16.8
25	20-25	381	228.6	15.4
30	25-30	368	220.8	14.6
35	30-35	360	216	13.9
40	35-40	355	213	14.3
45	40-45	350	210	14
50	45-50	346	207.6	13.6
55	50-55	343	205.8	13.9
60	50-60	340	204	13.6
65	60-65	338	202.8	13.2
70	65-70	336	201.6	13.7

0.25MPa,1.68m/s,500mg/L oil,20 ,100nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	1602	961.2	35.6
10	5-10	1057	634.2	29.3
15	10-15	704	422.4	25.4
20	15-20	551	330.6	23.6
25	20-25	467	280.2	22.1
30	25-30	429	257.4	21.7
35	30-35	404	242.4	21.8
40	35-40	390	234	21.5
45	40-45	385	231	21
50	45-50	381	228.6	21.6
55	50-55	378	226.8	22.3
60	50-60	376	225.6	21.9
65	60-65	373	223.8	21.4
70	65-70	371	222.6	21.7

0.3MPa,1.68m/s,500mg/L oil,20 ,100nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	1834	1100.4	57.4
10	5-10	1206	723.6	45.8
15	10-15	831	498.6	38.3
20	15-20	603	361.8	36.2
25	20-25	496	297.6	35.5
30	25-30	450	270	35.7
35	30-35	425	255	35.4
40	35-40	412	247.2	36.1
45	40-45	407	244.2	35.4
50	45-50	403	241.8	35
55	50-55	400	240	34.7
60	50-60	397	238.2	35.1
65	60-65	395	237	35.3
70	65-70	393	235.8	35.7

Permeate flux and TOC concentration under various oil concentrations

250mg/L oil, 1.68 m/s, 0.2MPa, 20 °C, 50nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	692	415.2	10.2
10	5-10	527	316.2	9.4
15	10-15	450	270	9.1
20	15-20	380	228	8.6
25	20-25	344	206.4	8.3
30	25-30	320	192	8
35	30-35	308	184.8	8.1
40	35-40	298	178.8	7.8
45	40-45	293	175.8	7.8
50	45-50	288	172.8	8.2
55	50-55	285	171	8.1
60	50-60	282	169.2	7.6
65	60-65	280	168	8.3
70	65-70	278	166.8	8.2

500mg/L oil, 1.68 m/s, 0.2MPa, 20 °C, 50nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	660	396	13.8
10	5-10	500	300	11.4
15	10-15	430	258	10.1
20	15-20	365	219	9.3
25	20-25	330	198	9.2
30	25-30	305	183	8.9
35	30-35	290	174	9.2
40	35-40	285	171	9.3
45	40-45	280	168	8.8
50	45-50	277	166.2	8.5
55	50-55	275	165	8.4
60	50-60	273	163.8	8.8
65	60-65	272	163.2	8.5
70	65-70	271	162.6	8.7

1000mg/L oil,1.68 m/s,0.2MPa,20 ,50nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	630	378	23.1
10	5-10	481	288.6	16.5
15	10-15	415	249	13.2
20	15-20	350	210	11.6
25	20-25	316	189.6	11.7
30	25-30	293	175.8	11.4
35	30-35	280	168	10.9
40	35-40	274	164.4	11.5
45	40-45	269	161.4	11.3
50	45-50	264	158.4	11
55	50-55	260	156	11.2
60	50-60	257	154.2	11.6
65	60-65	255	153	11.3
70	65-70	253	151.8	11.3

1500mg/L oil,1.68 m/s,0.2MPa,20 ,50nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	611	366.6	38.2
10	5-10	460	276	26.8
15	10-15	392	235.2	23.2
20	15-20	347	208.2	22.5
25	20-25	295	177	22.3
30	25-30	272	163.2	22.7
35	30-35	260	156	22.3
40	35-40	253	151.8	22.1
45	40-45	248	148.8	21.6
50	45-50	244	146.4	21.9
55	50-55	241	144.6	21.3
60	50-60	238	142.8	21
65	60-65	237	142.2	21.3
70	65-70	235	141	21.4

2000mg/L oil,1.68 m/s,0.2MPa,20 ,50nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	596	357.6	50.3
10	5-10	442	265.2	35.6
15	10-15	358	214.8	32.8
20	15-20	297	178.2	30.4
25	20-25	264	158.4	28.4
30	25-30	255	153	28.2
35	30-35	250	150	27.9
40	35-40	244	146.4	28.4
45	40-45	238	142.8	28.5
50	45-50	234	140.4	28.1
55	50-55	230	138	28.3
60	50-60	227	136.2	28.5
65	60-65	224	134.4	28.8
70	65-70	222	133.2	28.2

250mg/L oil,1.68 m/s,0.2MPa,20 ,100nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	1403	841.8	18.4
10	5-10	885	531	13.9
15	10-15	660	396	12.3
20	15-20	489	293.4	11.4
25	20-25	412	247.2	11.5
30	25-30	385	231	11.2
35	30-35	370	222	10.9
40	35-40	363	217.8	11.1
45	40-45	358	214.8	11.5
50	45-50	354	212.4	11
55	50-55	351	210.6	11.4
60	50-60	349	209.4	11.7
65	60-65	347	208.2	11.5
70	65-70	346	207.6	11.3

500mg/L oil,1.68 m/s,0.2MPa,20 ,100nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	1375	825	21.3
10	5-10	850	510	19.3
15	10-15	632	379.2	18.3
20	15-20	475	285	16.8
25	20-25	381	228.6	15.4
30	25-30	368	220.8	14.6
35	30-35	360	216	13.9
40	35-40	355	213	14.3
45	40-45	350	210	14
50	45-50	346	207.6	13.6
55	50-55	343	205.8	13.9
60	50-60	340	204	13.6
65	60-65	338	202.8	13.2
70	65-70	336	201.6	13.7

1000mg/L oil,1.68 m/s,0.2MPa,20 ,100nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	1357	814.2	46.7
10	5-10	838	502.8	32.1
15	10-15	642	385.2	26.5
20	15-20	487	292.2	25
25	20-25	370	222	24.6
30	25-30	358	214.8	24.4
35	30-35	349	209.4	23.9
40	35-40	343	205.8	24.1
45	40-45	338	202.8	24
50	45-50	333	199.8	24.7
55	50-55	329	197.4	24.2
60	50-60	326	195.6	24.4
65	60-65	323	193.8	24.5
70	65-70	321	192.6	24.3

1500mg/L oil,1.68 m/s,0.2MPa,20 ,100nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	1320	792	60.8
10	5-10	800	480	42.3
15	10-15	609	365.4	38.5
20	15-20	457	274.2	35.7
25	20-25	357	214.2	34.6
30	25-30	340	204	33.2
35	30-35	334	200.4	31.4
40	35-40	325	195	30.9
45	40-45	319	191.4	30.3
50	45-50	314	188.4	30.6
55	50-55	311	186.6	30.4
60	50-60	309	185.4	30.4
65	60-65	307	184.2	30.2
70	65-70	306	183.6	30.7

2000mg/L oil,1.68 m/s,0.2MPa,20 ,100nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	1291	774.6	71.1
10	5-10	773	463.8	55.6
15	10-15	585	351	50.1
20	15-20	432	259.2	48.3
25	20-25	374	224.4	45.7
30	25-30	340	204	44.3
35	30-35	325	195	42.6
40	35-40	315	189	43.5
45	40-45	307	184.2	44.2
50	45-50	301	180.6	44.1
55	50-55	296	177.6	46.2
60	50-60	292	175.2	43.2
65	60-65	289	173.4	42.8
70	65-70	288	172.8	43.1

Permeate flux and TOC concentration under various temperatures

20 ,1.68 m/s,0.2MPa,500mg/L oil,50nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	660	396	13.8
10	5-10	500	300	11.4
15	10-15	430	258	10.1
20	15-20	365	219	9.3
25	20-25	330	198	9.2
30	25-30	305	183	8.9
35	30-35	290	174	9.2
40	35-40	285	171	9.3
45	40-45	280	168	8.8
50	45-50	277	166.2	8.5
55	50-55	275	165	8.4
60	50-60	273	163.8	8.8
65	60-65	272	163.2	8.5
70	65-70	271	162.6	8.7

30 ,1.68 m/s,0.2MPa,500mg/L oil,50nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	862	517.2	15.2
10	5-10	647	388.2	12.3
15	10-15	559	335.4	10.6
20	15-20	430	258	10.2
25	20-25	434	260.4	10.1
30	25-30	398	238.8	10.4
35	30-35	380	228	9.6
40	35-40	370	222	9.3
45	40-45	365	219	10.2
50	45-50	362	217.2	9.1
55	50-55	358	214.8	9.3
60	50-60	357	214.2	9
65	60-65	355	213	9.4
70	65-70	354	212.4	9.5

40 ,1.68 m/s,0.2MPa,500mg/L oil,50nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	1211	726.6	19.3
10	5-10	863	517.8	15.6
15	10-15	687	412.2	13.1
20	15-20	591	354.6	12.6
25	20-25	544	326.4	12
30	25-30	518	310.8	11.7
35	30-35	508	304.8	11.5
40	35-40	505	303	11.9
45	40-45	500	300	12.1
50	45-50	496	297.6	11.4
55	50-55	493	295.8	11.2
60	50-60	490	294	11.6
65	60-65	488	292.8	11.3
70	65-70	486	291.6	11.1

20 ,1.68 m/s,0.2MPa,500mg/L oil,100nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	1375	825	21.3
10	5-10	850	510	19.3
15	10-15	632	379.2	18.3
20	15-20	475	285	16.8
25	20-25	381	228.6	15.4
30	25-30	368	220.8	14.6
35	30-35	360	216	13.9
40	35-40	355	213	14.3
45	40-45	350	210	14
50	45-50	346	207.6	13.6
55	50-55	343	205.8	13.9
60	50-60	340	204	13.6
65	60-65	338	202.8	13.2
70	65-70	336	201.6	13.7

30 ,1.68 m/s,0.2MPa,500mg/L oil,100nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	1693	1015.8	31.2
10	5-10	1084	650.4	23.6
15	10-15	809	485.4	21.1
20	15-20	615	369	19.7
25	20-25	490	294	19.4
30	25-30	460	276	19.1
35	30-35	451	270.6	19.5
40	35-40	447	268.2	18.6
45	40-45	443	265.8	18.3
50	45-50	438	262.8	18.5
55	50-55	435	261	18.9
60	50-60	432	259.2	18.4
65	60-65	430	258	18.5
70	65-70	429	257.4	18.3

40 ,1.68 m/s,0.2MPa,500mg/L oil,100nm membrane

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
5	0-5	2278	1366.8	38.9
10	5-10	1472	883.2	26.3
15	10-15	1034	620.4	24.1
20	15-20	784	470.4	22.5
25	20-25	672	403.2	22.3
30	25-30	627	376.2	21.8
35	30-35	606	363.6	21.4
40	35-40	598	358.8	21.6
45	40-45	593	355.8	21.4
50	45-50	589	353.4	21.1
55	50-55	585	351	21.5
60	50-60	582	349.2	21.9
65	60-65	580	348	21.3
70	65-70	578	346.8	21.2

Permeate flux and oil concentration from restaurant wastewater

first time

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	oil, mg/L
5	0-5	983	589.8	17.3
10	5-10	718	430.8	15.6
15	10-15	525	315	14.6
20	15-20	438	262.8	14.3
25	20-25	364	218.4	13.6
30	25-30	323	193.8	13.4
35	30-35	318	190.8	13.9
40	35-40	315	189	13.4
45	40-45	313	187.8	13.2
50	45-50	310	186	13.2

duplicate

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	oil, mg/L
5	0-5	1032	619.2	16.2
10	5-10	811	486.6	15.8
15	10-15	570	342	15.1
20	15-20	446	267.6	14.3
25	20-25	358	214.8	14.5
30	25-30	315	189	13.6
35	30-35	310	186	13.3
40	35-40	308	184.8	13.3
45	40-45	305	183	13.1
50	45-50	302	181.2	12.8

Permeate flux and TOC concentration under various pH

pH = 3.75

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
1	0-1	332	199.2	3.5
6	5-6	158	94.8	4.5
11	10-11	131	78.6	5.2
16	15-16	117	70.2	10.1
21	20-21	113	67.8	8.7
26	25-26	112	67.2	11.5
31	30-31	110	66	12.1
36	35-36	108	64.8	11.9
41	40-41	106	63.6	11.8
46	45-46	105	63	11.2
51	50-51	105	63	11.4

pH = 5.78

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC,mg/L
1	0-1	275	165	0
6	5-6	174	104.4	14.4
11	10-11	169	101.4	12.9
16	15-16	162	97.2	11.3
21	20-21	159	95.4	10.6
26	25-26	159	95.4	10.8
31	30-31	158	94.8	10.3
36	35-36	157	94.2	9.5
41	40-41	157	94.2	10.1
46	45-46	156	93.6	10.4
51	50-51	156	93.6	10.5

pH = 7.81

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC,mg/L
1	0-1	278	166.8	0
6	5-6	172	103.2	12.6
11	10-11	163	97.8	11.4
16	15-16	156	93.6	11.1
21	20-21	154	92.4	11
26	25-26	152	91.2	10.4
31	30-31	150	90	10.6
36	35-36	149	89.4	10.3
41	40-41	147	88.2	10.1
46	45-46	146	87.6	10.7
51	50-51	146	87.6	11.3

pH = 9.86

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
1	0-1	268	160.8	0
6	5-6	170	102	17.4
11	10-11	156	93.6	14.3
16	15-16	151	90.6	12.2
21	20-21	149	89.4	14.5
26	25-26	147	88.2	15.2
31	30-31	145	87	14.6
36	35-36	143	85.8	15.2
41	40-41	143	85.8	15.6
46	45-46	142	85.2	16.1
51	50-51	142	85.2	15.4

Permeate flux and TOC under various salt concentrations

0 mol/L NaCl

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
1	0-1	275	165	0
6	5-6	174	104.4	14.4
11	10-11	169	101.4	12.9
16	15-16	162	97.2	11.3
21	20-21	159	95.4	10.6
26	25-26	159	95.4	10.8
31	30-31	158	94.8	10.3
36	35-36	157	94.2	9.5
41	40-41	157	94.2	10.1
46	45-46	156	93.6	10.4
51	50-51	156	93.6	10.5

0.001 mol/L NaCl

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
1	0-1	295	177	0
6	5-6	197	118.2	13.7
11	10-11	175	105	12.4
16	15-16	162	97.2	11.6
21	20-21	154	92.4	10.5
26	25-26	151	90.6	11.1
31	30-31	149	89.4	10.2
36	35-36	146	87.6	9.8
41	40-41	146	87.6	11.2
46	45-46	145	87	10.7
51	50-51	144	86.4	10.5

0.005 mol/L NaCl

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
1	0-1	321	192.6	0
6	5-6	185	111	13.4
11	10-11	160	96	13.1
16	15-16	141	84.6	13.2
21	20-21	129	77.4	12.5
26	25-26	125	75	12.3
31	30-31	123	73.8	11.8
36	35-36	120	72	11.5
41	40-41	118	70.8	11.6
46	45-46	117	70.2	10.9
51	50-51	115	69	11.2

0.01 mol/L NaCl

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
1	0-1	345	207	0
6	5-6	174	104.4	14.2
11	10-11	149	89.4	13.7
16	15-16	132	79.2	12.7
21	20-21	125	75	11.4
26	25-26	119	71.4	10.3
31	30-31	113	67.8	10
36	35-36	111	66.6	9.7
41	40-41	110	66	9.8
46	45-46	109	65.4	9.6
51	50-51	108	64.8	9.8

0.05 mol/L NaCl

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
1	0-1	408	244.8	0
6	5-6	166	99.6	11.7
11	10-11	119	71.4	11.9
16	15-16	86	51.6	11.7
21	20-21	77	46.2	11.7
26	25-26	72	43.2	10.7
31	30-31	69	41.4	10.3
36	35-36	66	39.6	9.7
41	40-41	65	39	9.3
46	45-46	64	38.4	8.6
51	50-51	64	38.4	9.1

pH = 3.75, 0.01 mol/L NaCl

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
1	0-1	334	200.4	0
6	5-6	119	71.4	6.2
11	10-11	112	67.2	13.4
16	15-16	106	63.6	11.5
21	20-21	102	61.2	11.1
26	25-26	99	59.4	11.7
31	30-31	97	58.2	11.4
36	35-36	95	57	10.9
41	40-41	94	56.4	11.5
46	45-46	93	55.8	10.6
51	50-51	92	55.2	9.9

pH = 9.86, 0.01 mol/L NaCl

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
1	0-1	315	189	0
6	5-6	157	94.2	10.5
11	10-11	132	79.2	10.2
16	15-16	123	73.8	9.9
21	20-21	114	68.4	9.2
26	25-26	108	64.8	11.8
31	30-31	104	62.4	12.5
36	35-36	102	61.2	11.6
41	40-41	101	60.6	9.9
46	45-46	100	60	10.8
51	50-51	99	59.4	10.4

pH = 9.86, 0.01 mol/L Na₂SO₄

Item	Time, min	Permeate, mL/min	Permeate flux, L/(h m ²)	TOC, mg/L
1	0-1	302	181.2	0
6	5-6	131	78.6	15.6
11	10-11	104	62.4	15.4
16	15-16	96	57.6	14.5
21	20-21	90	54	12.9
26	25-26	86	51.6	12.3
31	30-31	84	50.4	12
36	35-36	84	50.4	13.2
41	40-41	83	49.8	12.7
46	45-46	82	49.2	11.9
51	50-51	82	49.2	12.4

Size and zeta potential under various pH and salt concentrations

Zeta potential under various salt concentration (distilled water), mV

NaCl, mol/L	0.001	0.005	0.01	0.05
1	-33.9	-14.6	-8.1	-7.6
2	-34.8	-14.4	-7.6	-3.6
3	-39.2	-16.6	-7.5	-5.7
4	-40.2	-17.5	-9.4	-3.5
5	-18.6	-5.3	-8.6	-2.8

Size and zeta potential under various pH

pH	3.14	5.98	8.67	9.88
	Size, nm			
1	461.6	478	519.2	486.6
2	469.8	469.2	463	452.3
3	459.4	461.9	403.3	437
4	447.2	459.2	395	443.6
	Zeta potential, mV			
1	-1.2	-22.7	-33.9	-67.4
2	-0.2	-15.3	-30.1	-57.5
3	2.9	-21.1	-22.9	-43
4	-1.9	-17.3	-29.1	-28.5
5	-1.9	-24.1	-29.5	-39.1

Size and zeta potential under various pH (0.001 mol/L NaCl)

pH	3.76	5.89	7.81	9.78
	Size, nm			
1	722.8	549.9	884	606.6
2	709.2	513.5	784.7	628.4
3	622.7	543.6	630	618.3
	Zeta potential, mV			
1	-9.4	-17.6	-24.6	-80.8
2	-11.3	-21.1	-27.1	-74.5
3	-10.6	-17.1	-26.8	-65.1
4	-10.5	-16.9	-26.3	-65.2
5	-11.8	-18.3	-25.1	-79.8

Size and zeta potential under various pH (0.005 mol/L NaCl)

pH	3.75	5.95	7.69	9.83
	Size, nm			
1	525.6	558.5	549.3	518.5
2	529.2	578.9	574.4	559.9
3	532.5	617.4	582.2	583.3
	Zeta potential, mV			
1	-1.7	-11.6	-14.8	-50.1
2	-2.6	-13.7	-15.3	-57.7
3	-1.8	-12.4	-14.6	-66.8
4	-1.9	-12.2	-14.9	-58.6
5	-2.1	-11.6	-15.9	-57.8

Size and zeta potential under various pH (0.01 mol/L NaCl)

pH	3.69	5.96	7.82	9.81
	Size, nm			
1	575.7	793	568.8	572.9
2	623.4	768.8	611.9	629.5
3	642	854.4	618.4	648.4
Duplicate	Size, nm			
1	613	772.7	581.5	535.5
2	648.4	794.9	606.7	588.2
3	656.8	793.8	613.2	613.1
	Zeta potential, mV			
1	-11	-16.2	-17.6	-50.4
2	-17.2	-22.2	-17	-44.2
3	-10.5	-26.3	-14.5	-49.5
4	7.5	-22	-18.6	-43.7
5	-18.1	-13.5	-21.5	-45.4

Size and zeta potential under various pH (0.05 mol/L NaCl)

pH	3.76	5.76	7.76	9.93
	Size, nm			
1	650.9	730.2	559.3	570.2
2	682.5	730.4	565.7	634.3
3	653.3	694	587.9	598.9
Duplicate	Size, nm			
1	667.8	692.6	538.9	537.2
2	683.3	749.5	567.5	555.3
3	651.6	757.8	584.9	558.2
	Zeta potential, mV			
1	-5.8	-10.9	-14.1	-9
2	10.3	8.5	7.4	-23.1
3	1.2	-18.8	6.3	-7.5
4	12	-1.4	6.7	-9.9
5	6.8	8.6	-3.4	-12.6

Part Four: Data from experiment and modeling calculation

50 nm membrane permeate flux (L/m² h)

Time, min	Oil con. mg/L	CFV, m/s	TMP, MPa	Experimental data	Calculated data
5	500	0.21	0.2	363	368.1528
10	500	0.21	0.2	267	270.6268
15	500	0.21	0.2	216	226.0405
20	500	0.21	0.2	189	198.9361
25	500	0.21	0.2	162	180.1712
30	500	0.21	0.2	146.4	166.161
35	500	0.21	0.2	140.4	155.1689
40	500	0.21	0.2	138	146.2366
45	500	0.21	0.2	134.4	138.7856
50	500	0.21	0.2	130.8	132.4427
55	500	0.21	0.2	129	126.955
60	500	0.21	0.2	127.2	122.1439
65	500	0.21	0.2	126	117.8792
70	500	0.21	0.2	125.4	114.0637
5	500	0.42	0.2	375	377.1158
10	500	0.42	0.2	279	277.2154
15	500	0.42	0.2	237	231.5437
20	500	0.42	0.2	198	203.7793
25	500	0.42	0.2	171	184.5576
30	500	0.42	0.2	154.8	170.2063
35	500	0.42	0.2	148.8	158.9466
40	500	0.42	0.2	146.4	149.7969
45	500	0.42	0.2	143.4	142.1645
50	500	0.42	0.2	141	135.6672
55	500	0.42	0.2	139.2	130.0458
60	500	0.42	0.2	138	125.1176
65	500	0.42	0.2	136.8	120.7491
70	500	0.42	0.2	135.6	116.8406
5	500	0.84	0.2	384	389.7913
10	500	0.84	0.2	288	286.5331
15	500	0.84	0.2	244.8	239.3262
20	500	0.84	0.2	202.8	210.6287
25	500	0.84	0.2	177.6	190.761
30	500	0.84	0.2	162	175.9272
35	500	0.84	0.2	157.2	164.2891

40	500	0.84	0.2	154.2	154.8318
45	500	0.84	0.2	151.2	146.9429
50	500	0.84	0.2	148.8	140.2272
55	500	0.84	0.2	146.4	134.4169
60	500	0.84	0.2	145.2	129.323
65	500	0.84	0.2	144	124.8077
70	500	0.84	0.2	143.4	120.7678
5	500	1.68	0.2	396	407.7172
10	500	1.68	0.2	300	299.7104
15	500	1.68	0.2	258	250.3325
20	500	1.68	0.2	219	220.3152
25	500	1.68	0.2	198	199.5338
30	500	1.68	0.2	183	184.0178
35	500	1.68	0.2	174	171.8445
40	500	1.68	0.2	171	161.9523
45	500	1.68	0.2	168	153.7005
50	500	1.68	0.2	166.2	146.676
55	500	1.68	0.2	165	140.5985
60	500	1.68	0.2	163.8	135.2703
65	500	1.68	0.2	163.2	130.5474
70	500	1.68	0.2	162.6	126.3218
5	500	1.68	0.1	181.8	203.832
10	500	1.68	0.1	114	149.8356
15	500	1.68	0.1	96	125.1499
20	500	1.68	0.1	84	110.1432
25	500	1.68	0.1	78	99.75384
30	500	1.68	0.1	75	91.99689
35	500	1.68	0.1	72	85.911
40	500	1.68	0.1	69	80.96557
45	500	1.68	0.1	67.2	76.84023
50	500	1.68	0.1	65.4	73.32842
55	500	1.68	0.1	63.6	70.29007
60	500	1.68	0.1	62.4	67.62633
65	500	1.68	0.1	61.2	65.26517
70	500	1.68	0.1	60.6	63.15264
5	500	1.68	0.15	279	305.748
10	500	1.68	0.15	211.2	224.7534
15	500	1.68	0.15	183	187.7248
20	500	1.68	0.15	153	165.2148
25	500	1.68	0.15	138	149.6308
30	500	1.68	0.15	124.8	137.9953
35	500	1.68	0.15	120	128.8665

40	500	1.68	0.15	117	121.4484
45	500	1.68	0.15	114	115.2603
50	500	1.68	0.15	111.6	109.9926
55	500	1.68	0.15	109.8	105.4351
60	500	1.68	0.15	108.6	101.4395
65	500	1.68	0.15	108	97.89776
70	500	1.68	0.15	108	94.72895
5	500	1.68	0.2	396	407.664
10	500	1.68	0.2	300	299.6712
15	500	1.68	0.2	258	250.2998
20	500	1.68	0.2	219	220.2864
25	500	1.68	0.2	198	199.5077
30	500	1.68	0.2	183	183.9938
35	500	1.68	0.2	174	171.822
40	500	1.68	0.2	171	161.9311
45	500	1.68	0.2	168	153.6805
50	500	1.68	0.2	166.2	146.6568
55	500	1.68	0.2	165	140.5801
60	500	1.68	0.2	163.8	135.2527
65	500	1.68	0.2	163.2	130.5303
70	500	1.68	0.2	162.6	126.3053
5	500	1.68	0.25	528	509.58
10	500	1.68	0.25	390	374.589
15	500	1.68	0.25	318	312.8747
20	500	1.68	0.25	264	275.358
25	500	1.68	0.25	228	249.3846
30	500	1.68	0.25	210	229.9922
35	500	1.68	0.25	201	214.7775
40	500	1.68	0.25	198	202.4139
45	500	1.68	0.25	195	192.1006
50	500	1.68	0.25	192.6	183.321
55	500	1.68	0.25	190.8	175.7252
60	500	1.68	0.25	189	169.0658
65	500	1.68	0.25	187.8	163.1629
70	500	1.68	0.25	187.2	157.8816
5	500	1.68	0.3	642	611.4959
10	500	1.68	0.3	468	449.5068
15	500	1.68	0.3	354	375.4497
20	500	1.68	0.3	294	330.4296
25	500	1.68	0.3	258	299.2615
30	500	1.68	0.3	240	275.9907
35	500	1.68	0.3	222	257.733
40	500	1.68	0.3	219	242.8967
45	500	1.68	0.3	216	230.5207

50	500	1.68	0.3	213.6	219.9853
55	500	1.68	0.3	211.8	210.8702
60	500	1.68	0.3	210	202.879
65	500	1.68	0.3	208.8	195.7955
70	500	1.68	0.3	207	189.4579
5	250	1.68	0.2	415.2	433.0683
10	250	1.68	0.2	316.2	318.3458
15	250	1.68	0.2	270	265.8977
20	250	1.68	0.2	228	234.0139
25	250	1.68	0.2	206.4	211.9404
30	250	1.68	0.2	192	195.4597
35	250	1.68	0.2	184.8	182.5294
40	250	1.68	0.2	178.8	172.0222
45	250	1.68	0.2	175.8	163.2573
50	250	1.68	0.2	172.8	155.796
55	250	1.68	0.2	171	149.3406
60	250	1.68	0.2	169.2	143.6812
65	250	1.68	0.2	168	138.6646
70	250	1.68	0.2	166.8	134.1762
5	500	1.68	0.2	396	407.7172
10	500	1.68	0.2	300	299.7104
15	500	1.68	0.2	258	250.3325
20	500	1.68	0.2	219	220.3152
25	500	1.68	0.2	198	199.5338
30	500	1.68	0.2	183	184.0178
35	500	1.68	0.2	174	171.8445
40	500	1.68	0.2	171	161.9523
45	500	1.68	0.2	168	153.7005
50	500	1.68	0.2	166.2	146.676
55	500	1.68	0.2	165	140.5985
60	500	1.68	0.2	163.8	135.2703
65	500	1.68	0.2	163.2	130.5474
70	500	1.68	0.2	162.6	126.3218
5	1000	1.68	0.2	378	389.7913
10	1000	1.68	0.2	288.6	286.5331
15	1000	1.68	0.2	249	239.3262
20	1000	1.68	0.2	210	210.6287
25	1000	1.68	0.2	189.6	190.761
30	1000	1.68	0.2	175.8	175.9272
35	1000	1.68	0.2	168	164.2891
40	1000	1.68	0.2	164.4	154.8318
45	1000	1.68	0.2	161.4	146.9429
50	1000	1.68	0.2	158.4	140.2272
55	1000	1.68	0.2	156	134.4169

60	1000	1.68	0.2	154.2	129.323
65	1000	1.68	0.2	153	124.8077
70	1000	1.68	0.2	151.8	120.7678
5	1500	1.68	0.2	366.6	381.8499
10	1500	1.68	0.2	276	280.6954
15	1500	1.68	0.2	235.2	234.4503
20	1500	1.68	0.2	208.2	206.3374
25	1500	1.68	0.2	177	186.8745
30	1500	1.68	0.2	163.2	172.3429
35	1500	1.68	0.2	156	160.9419
40	1500	1.68	0.2	151.8	151.6773
45	1500	1.68	0.2	148.8	143.9491
50	1500	1.68	0.2	146.4	137.3702
55	1500	1.68	0.2	144.6	131.6783
60	1500	1.68	0.2	142.8	126.6882
65	1500	1.68	0.2	142.2	122.2649
70	1500	1.68	0.2	141	118.3074
5	2000	1.68	0.2	357.6	377.1158
10	2000	1.68	0.2	265.2	277.2154
15	2000	1.68	0.2	214.8	231.5437
20	2000	1.68	0.2	178.2	203.7793
25	2000	1.68	0.2	158.4	184.5576
30	2000	1.68	0.2	153	170.2063
35	2000	1.68	0.2	150	158.9466
40	2000	1.68	0.2	146.4	149.7969
45	2000	1.68	0.2	142.8	142.1645
50	2000	1.68	0.2	140.4	135.6672
55	2000	1.68	0.2	138	130.0458
60	2000	1.68	0.2	136.2	125.1176
65	2000	1.68	0.2	134.4	120.7491
70	2000	1.68	0.2	133.2	116.8406

50 nm membrane cumulative volume (mL)

Time, min	Oil con. mg/L	CFV, m/s	TMP, MPa	Experimental data	Calculated data
5	500	0.21	0.2	3025	3154.137
10	500	0.21	0.2	5250	5242.617
15	500	0.21	0.2	7050	6989.182
20	500	0.21	0.2	8625	8549.085
25	500	0.21	0.2	9975	9984.562
30	500	0.21	0.2	11195	11328.57
35	500	0.21	0.2	12365	12601.23
40	500	0.21	0.2	13515	13815.99
45	500	0.21	0.2	14635	14982.38
50	500	0.21	0.2	15725	16107.48
55	500	0.21	0.2	16800	17196.72
60	500	0.21	0.2	17860	18254.4
65	500	0.21	0.2	18910	19283.98
70	500	0.21	0.2	19955	20288.31
5	500	0.42	0.2	3125	3232.61
10	500	0.42	0.2	5450	5373.049
15	500	0.42	0.2	7425	7163.067
20	500	0.42	0.2	9075	8761.779
25	500	0.42	0.2	10500	10232.97
30	500	0.42	0.2	11790	11610.42
35	500	0.42	0.2	13030	12914.74
40	500	0.42	0.2	14250	14159.72
45	500	0.42	0.2	15445	15355.13
50	500	0.42	0.2	16620	16508.22
55	500	0.42	0.2	17780	17624.56
60	500	0.42	0.2	18930	18708.56
65	500	0.42	0.2	20070	19763.75
70	500	0.42	0.2	21200	20793.06
5	500	0.84	0.2	3200	3351.552
10	500	0.84	0.2	5600	5570.747
15	500	0.84	0.2	7640	7426.628
20	500	0.84	0.2	9330	9084.164
25	500	0.84	0.2	10810	10609.49
30	500	0.84	0.2	12160	12037.61
35	500	0.84	0.2	13470	13389.93
40	500	0.84	0.2	14755	14680.72
45	500	0.84	0.2	16015	15920.12
50	500	0.84	0.2	17255	17115.63
55	500	0.84	0.2	18475	18273.05
60	500	0.84	0.2	19685	19396.93
65	500	0.84	0.2	20885	20490.95

70	500	0.84	0.2	22080	21558.13
5	500	1.68	0.2	3300	3531.834
10	500	1.68	0.2	5800	5870.402
15	500	1.68	0.2	7950	7826.111
20	500	1.68	0.2	9775	9572.807
25	500	1.68	0.2	11425	11180.18
30	500	1.68	0.2	12950	12685.12
35	500	1.68	0.2	14400	14110.19
40	500	1.68	0.2	15825	15470.41
45	500	1.68	0.2	17225	16776.47
50	500	1.68	0.2	18610	18036.29
55	500	1.68	0.2	19985	19255.97
60	500	1.68	0.2	21350	20440.3
65	500	1.68	0.2	22710	21593.17
70	500	1.68	0.2	24065	22717.76
5	500	1.68	0.1	1515	1765.868
10	500	1.68	0.1	2465	2935.119
15	500	1.68	0.1	3265	3912.947
20	500	1.68	0.1	3965	4786.271
25	500	1.68	0.1	4615	5589.934
30	500	1.68	0.1	5240	6342.386
35	500	1.68	0.1	5840	7054.898
40	500	1.68	0.1	6415	7734.99
45	500	1.68	0.1	6975	8388.002
50	500	1.68	0.1	7520	9017.897
55	500	1.68	0.1	8050	9627.718
60	500	1.68	0.1	8570	10219.87
65	500	1.68	0.1	9080	10796.28
70	500	1.68	0.1	9585	11358.56
5	500	1.68	0.15	2325	2648.802
10	500	1.68	0.15	4085	4402.679
15	500	1.68	0.15	5610	5869.421
20	500	1.68	0.15	6885	7179.406
25	500	1.68	0.15	8035	8384.901
30	500	1.68	0.15	9075	9513.58
35	500	1.68	0.15	10075	10582.35
40	500	1.68	0.15	11050	11602.48
45	500	1.68	0.15	12000	12582
50	500	1.68	0.15	12930	13526.85
55	500	1.68	0.15	13845	14441.58
60	500	1.68	0.15	14750	15329.8
65	500	1.68	0.15	15650	16194.43
70	500	1.68	0.15	16550	17037.84
5	500	1.68	0.2	3300	3531.736

10	500	1.68	0.2	5800	5870.239
15	500	1.68	0.2	7950	7825.894
20	500	1.68	0.2	9775	9572.541
25	500	1.68	0.2	11425	11179.87
30	500	1.68	0.2	12950	12684.77
35	500	1.68	0.2	14400	14109.8
40	500	1.68	0.2	15825	15469.98
45	500	1.68	0.2	17225	16776
50	500	1.68	0.2	18610	18035.79
55	500	1.68	0.2	19985	19255.44
60	500	1.68	0.2	21350	20439.73
65	500	1.68	0.2	22710	21592.57
70	500	1.68	0.2	24065	22717.13
5	500	1.68	0.25	4400	4414.67
10	500	1.68	0.25	7650	7337.799
15	500	1.68	0.25	10300	9782.368
20	500	1.68	0.25	12500	11965.68
25	500	1.68	0.25	14400	13974.83
30	500	1.68	0.25	16150	15855.97
35	500	1.68	0.25	17825	17637.24
40	500	1.68	0.25	19475	19337.47
45	500	1.68	0.25	21100	20970.01
50	500	1.68	0.25	22705	22544.74
55	500	1.68	0.25	24295	24069.29
60	500	1.68	0.25	25870	25549.67
65	500	1.68	0.25	27435	26990.71
70	500	1.68	0.25	28995	28396.41
5	500	1.68	0.3	5350	5297.604
10	500	1.68	0.3	9250	8805.358
15	500	1.68	0.3	12200	11738.84
20	500	1.68	0.3	14650	14358.81
25	500	1.68	0.3	16800	16769.8
30	500	1.68	0.3	18800	19027.16
35	500	1.68	0.3	20650	21164.69
40	500	1.68	0.3	22475	23204.97
45	500	1.68	0.3	24275	25164.01
50	500	1.68	0.3	26055	27053.69
55	500	1.68	0.3	27820	28883.15
60	500	1.68	0.3	29570	30659.6
65	500	1.68	0.3	31310	32388.85
70	500	1.68	0.3	33035	34075.69
5	250	1.68	0.2	3460	3701.128
10	250	1.68	0.2	6095	6151.792
15	250	1.68	0.2	8345	8201.245

20	250	1.68	0.2	10245	10031.67
25	250	1.68	0.2	11965	11716.08
30	250	1.68	0.2	13565	13293.17
35	250	1.68	0.2	15105	14786.54
40	250	1.68	0.2	16595	16211.96
45	250	1.68	0.2	18060	17580.63
50	250	1.68	0.2	19500	18900.84
55	250	1.68	0.2	20925	20178.98
60	250	1.68	0.2	22335	21420.08
65	250	1.68	0.2	23735	22628.21
70	250	1.68	0.2	25125	23806.7
5	500	1.68	0.2	3300	3531.834
10	500	1.68	0.2	5800	5870.402
15	500	1.68	0.2	7950	7826.111
20	500	1.68	0.2	9775	9572.807
25	500	1.68	0.2	11425	11180.18
30	500	1.68	0.2	12950	12685.12
35	500	1.68	0.2	14400	14110.19
40	500	1.68	0.2	15825	15470.41
45	500	1.68	0.2	17225	16776.47
50	500	1.68	0.2	18610	18036.29
55	500	1.68	0.2	19985	19255.97
60	500	1.68	0.2	21350	20440.3
65	500	1.68	0.2	22710	21593.17
70	500	1.68	0.2	24065	22717.76
5	1000	1.68	0.2	3150	3403.533
10	1000	1.68	0.2	5555	5657.148
15	1000	1.68	0.2	7630	7541.812
20	1000	1.68	0.2	9380	9225.056
25	1000	1.68	0.2	10960	10774.04
30	1000	1.68	0.2	12425	12224.31
35	1000	1.68	0.2	13825	13597.61
40	1000	1.68	0.2	15195	14908.42
45	1000	1.68	0.2	16540	16167.03
50	1000	1.68	0.2	17860	17381.09
55	1000	1.68	0.2	19160	18556.46
60	1000	1.68	0.2	20445	19697.77
65	1000	1.68	0.2	21720	20808.75
70	1000	1.68	0.2	22985	21892.49
5	1500	1.68	0.2	3055	3343.413
10	1500	1.68	0.2	5355	5557.22
15	1500	1.68	0.2	7315	7408.594
20	1500	1.68	0.2	9050	9062.104
25	1500	1.68	0.2	10525	10583.72

30	1500	1.68	0.2	11885	12008.38
35	1500	1.68	0.2	13185	13357.42
40	1500	1.68	0.2	14450	14645.07
45	1500	1.68	0.2	15690	15881.46
50	1500	1.68	0.2	16910	17074.07
55	1500	1.68	0.2	18115	18228.68
60	1500	1.68	0.2	19305	19349.83
65	1500	1.68	0.2	20490	20441.19
70	1500	1.68	0.2	21665	21505.78
5	2000	1.68	0.2	2980	3306.299
10	2000	1.68	0.2	5190	5495.532
15	2000	1.68	0.2	6980	7326.354
20	2000	1.68	0.2	8465	8961.51
25	2000	1.68	0.2	9785	10466.24
30	2000	1.68	0.2	11060	11875.08
35	2000	1.68	0.2	12310	13209.14
40	2000	1.68	0.2	13530	14482.5
45	2000	1.68	0.2	14720	15705.16
50	2000	1.68	0.2	15890	16884.54
55	2000	1.68	0.2	17040	18026.33
60	2000	1.68	0.2	18175	19135.03
65	2000	1.68	0.2	19295	20214.28
70	2000	1.68	0.2	20405	21267.05

100 nm membrane permeate flux (L/m² h)

Time, min	Oil con. mg/L	CFV, m/s	TMP, MPa	Experimental data	Calculated data
5	500	0.21	0.2	801	738.296
10	500	0.21	0.2	492	472.462
15	500	0.21	0.2	357	363.885
20	500	0.21	0.2	252	302.346
25	500	0.21	0.2	186	261.875
30	500	0.21	0.2	174	232.863
35	500	0.21	0.2	168	210.857
40	500	0.21	0.2	165	193.482
45	500	0.21	0.2	162	179.349
50	500	0.21	0.2	159.6	167.583
55	500	0.21	0.2	157.8	157.606
60	500	0.21	0.2	156	149.018
65	500	0.21	0.2	154.8	141.531
70	500	0.21	0.2	154.2	134.935
5	500	0.42	0.2	816	749.8538
10	500	0.42	0.2	504	479.8586
15	500	0.42	0.2	369.6	369.5818
20	500	0.42	0.2	261	307.0789
25	500	0.42	0.2	195	265.9745
30	500	0.42	0.2	181.8	236.5087
35	500	0.42	0.2	176.4	214.1576
40	500	0.42	0.2	174	196.5109
45	500	0.42	0.2	171	182.1564
50	500	0.42	0.2	168.6	170.2067
55	500	0.42	0.2	166.2	160.0736
60	500	0.42	0.2	165	151.3505
65	500	0.42	0.2	163.2	143.7464
70	500	0.42	0.2	162	137.0472
5	500	0.84	0.2	822	766.1997
10	500	0.84	0.2	507	490.3189
15	500	0.84	0.2	375	377.6382
20	500	0.84	0.2	270	313.7728
25	500	0.84	0.2	207	271.7724
30	500	0.84	0.2	198	241.6643
35	500	0.84	0.2	192	218.826
40	500	0.84	0.2	189	200.7946
45	500	0.84	0.2	186	186.1272
50	500	0.84	0.2	183.6	173.917
55	500	0.84	0.2	181.8	163.563
60	500	0.84	0.2	180	154.6498
65	500	0.84	0.2	178.8	146.8799

70	500	0.84	0.2	177.6	140.0347
5	500	1.68	0.2	825	789.3163
10	500	1.68	0.2	510	505.1121
15	500	1.68	0.2	379.2	389.0317
20	500	1.68	0.2	285	323.2395
25	500	1.68	0.2	228.6	279.9719
30	500	1.68	0.2	220.8	248.9555
35	500	1.68	0.2	216	225.428
40	500	1.68	0.2	213	206.8527
45	500	1.68	0.2	210	191.7427
50	500	1.68	0.2	207.6	179.1641
55	500	1.68	0.2	205.8	168.4978
60	500	1.68	0.2	204	159.3156
65	500	1.68	0.2	202.8	151.3114
70	500	1.68	0.2	201.6	144.2596
5	500	1.68	0.1	408	458.086
10	500	1.68	0.1	271.2	293.146
15	500	1.68	0.1	217.8	225.777
20	500	1.68	0.1	181.8	187.594
25	500	1.68	0.1	156.6	162.484
30	500	1.68	0.1	142.8	144.483
35	500	1.68	0.1	135	130.829
40	500	1.68	0.1	131.4	120.048
45	500	1.68	0.1	128.4	111.279
50	500	1.68	0.1	125.4	103.979
55	500	1.68	0.1	123.6	97.7889
60	500	1.68	0.1	121.8	92.46
65	500	1.68	0.1	120.6	87.8147
70	500	1.68	0.1	119.4	83.7221
5	500	1.68	0.15	591	629.7646
10	500	1.68	0.15	363	403.0092
15	500	1.68	0.15	270	310.3932
20	500	1.68	0.15	222	257.9002
25	500	1.68	0.15	201	223.3786
30	500	1.68	0.15	187.2	198.6318
35	500	1.68	0.15	180	179.8602
40	500	1.68	0.15	175.2	165.0397
45	500	1.68	0.15	172.2	152.984
50	500	1.68	0.15	169.2	142.9481
55	500	1.68	0.15	166.2	134.4378
60	500	1.68	0.15	164.4	127.1117
65	500	1.68	0.15	163.2	120.7254
70	500	1.68	0.15	162	115.0991
5	500	1.68	0.2	825	824.3799

10	500	1.68	0.2	510	527.5505
15	500	1.68	0.2	379.2	406.3135
20	500	1.68	0.2	285	337.5987
25	500	1.68	0.2	228.6	292.409
30	500	1.68	0.2	220.8	260.0147
35	500	1.68	0.2	216	235.4422
40	500	1.68	0.2	213	216.0416
45	500	1.68	0.2	210	200.2605
50	500	1.68	0.2	207.6	187.1231
55	500	1.68	0.2	205.8	175.9829
60	500	1.68	0.2	204	166.3928
65	500	1.68	0.2	202.8	158.033
70	500	1.68	0.2	201.6	150.668
5	500	1.68	0.25	961.2	940.4366
10	500	1.68	0.25	634.2	601.8195
15	500	1.68	0.25	422.4	463.5146
20	500	1.68	0.25	330.6	385.1261
25	500	1.68	0.25	280.2	333.5745
30	500	1.68	0.25	257.4	296.6198
35	500	1.68	0.25	242.4	268.5879
40	500	1.68	0.25	234	246.4561
45	500	1.68	0.25	231	228.4533
50	500	1.68	0.25	228.6	213.4664
55	500	1.68	0.25	226.8	200.7579
60	500	1.68	0.25	225.6	189.8178
65	500	1.68	0.25	223.8	180.281
70	500	1.68	0.25	222.6	171.8791
5	500	1.68	0.3	1100.4	1085.143
10	500	1.68	0.3	723.6	694.4221
15	500	1.68	0.3	498.6	534.8361
20	500	1.68	0.3	361.8	444.3858
25	500	1.68	0.3	297.6	384.902
30	500	1.68	0.3	270	342.261
35	500	1.68	0.3	255	309.9158
40	500	1.68	0.3	247.2	284.3786
45	500	1.68	0.3	244.2	263.6056
50	500	1.68	0.3	241.8	246.3127
55	500	1.68	0.3	240	231.6487
60	500	1.68	0.3	238.2	219.0252
65	500	1.68	0.3	237	208.0211
70	500	1.68	0.3	235.8	198.3263
5	250	1.68	0.2	841.8	822.008
10	250	1.68	0.2	531	526.033
15	250	1.68	0.2	396	405.145

20	250	1.68	0.2	293.4	336.627
25	250	1.68	0.2	247.2	291.568
30	250	1.68	0.2	231	259.267
35	250	1.68	0.2	222	234.765
40	250	1.68	0.2	217.8	215.42
45	250	1.68	0.2	214.8	199.684
50	250	1.68	0.2	212.4	186.585
55	250	1.68	0.2	210.6	175.477
60	250	1.68	0.2	209.4	165.914
65	250	1.68	0.2	208.2	157.578
70	250	1.68	0.2	207.6	150.234
5	500	1.68	0.2	825	789.3163
10	500	1.68	0.2	510	505.1121
15	500	1.68	0.2	379.2	389.0317
20	500	1.68	0.2	285	323.2395
25	500	1.68	0.2	228.6	279.9719
30	500	1.68	0.2	220.8	248.9555
35	500	1.68	0.2	216	225.428
40	500	1.68	0.2	213	206.8527
45	500	1.68	0.2	210	191.7427
50	500	1.68	0.2	207.6	179.1641
55	500	1.68	0.2	205.8	168.4978
60	500	1.68	0.2	204	159.3156
65	500	1.68	0.2	202.8	151.3114
70	500	1.68	0.2	201.6	144.2596
5	1000	1.68	0.2	814.2	766.1997
10	1000	1.68	0.2	502.8	490.3189
15	1000	1.68	0.2	385.2	377.6382
20	1000	1.68	0.2	292.2	313.7728
25	1000	1.68	0.2	222	271.7724
30	1000	1.68	0.2	214.8	241.6643
35	1000	1.68	0.2	209.4	218.826
40	1000	1.68	0.2	205.8	200.7946
45	1000	1.68	0.2	202.8	186.1272
50	1000	1.68	0.2	199.8	173.917
55	1000	1.68	0.2	197.4	163.563
60	1000	1.68	0.2	195.6	154.6498
65	1000	1.68	0.2	193.8	146.8799
70	1000	1.68	0.2	192.6	140.0347
5	1500	1.68	0.2	792	755.9587
10	1500	1.68	0.2	480	483.7653
15	1500	1.68	0.2	365.4	372.5907
20	1500	1.68	0.2	274.2	309.579

25	1500	1.68	0.2	214.2	268.1399
30	1500	1.68	0.2	204	238.4343
35	1500	1.68	0.2	200.4	215.9011
40	1500	1.68	0.2	195	198.1108
45	1500	1.68	0.2	191.4	183.6394
50	1500	1.68	0.2	188.4	171.5924
55	1500	1.68	0.2	186.6	161.3768
60	1500	1.68	0.2	185.4	152.5827
65	1500	1.68	0.2	184.2	144.9167
70	1500	1.68	0.2	183.6	138.163
5	2000	1.68	0.2	774.6	749.8538
10	2000	1.68	0.2	463.8	479.8586
15	2000	1.68	0.2	351	369.5818
20	2000	1.68	0.2	259.2	307.0789
25	2000	1.68	0.2	224.4	265.9745
30	2000	1.68	0.2	204	236.5087
35	2000	1.68	0.2	195	214.1576
40	2000	1.68	0.2	189	196.5109
45	2000	1.68	0.2	184.2	182.1564
50	2000	1.68	0.2	180.6	170.2067
55	2000	1.68	0.2	177.6	160.0736
60	2000	1.68	0.2	175.2	151.3505
65	2000	1.68	0.2	173.4	143.7464
70	2000	1.68	0.2	172.8	137.0472

100 nm membrane cumulative volume (mL)

Time, min	Oil con. mg/L	CFV, m/s	TMP, MPa	Experimental data	Calculated data
5	500	0.21	0.2	6675	6643.45
10	500	0.21	0.2	10775	9978.96
15	500	0.21	0.2	13750	12622.2
20	500	0.21	0.2	15850	14900
25	500	0.21	0.2	17400	16940.4
30	500	0.21	0.2	18850	18810
35	500	0.21	0.2	20250	20548.8
40	500	0.21	0.2	21625	22183
45	500	0.21	0.2	22975	23730.9
50	500	0.21	0.2	24305	25206.2
55	500	0.21	0.2	25620	26619
60	500	0.21	0.2	26920	27977.3
65	500	0.21	0.2	28210	29287.6
70	500	0.21	0.2	29495	30555.1
5	500	0.42	0.2	6800	6749.412
10	500	0.42	0.2	11000	10138.12
15	500	0.42	0.2	14080	12823.53
20	500	0.42	0.2	16255	15137.62
25	500	0.42	0.2	17880	17210.6
30	500	0.42	0.2	19395	19110.04
35	500	0.42	0.2	20865	20876.54
40	500	0.42	0.2	22315	22536.78
45	500	0.42	0.2	23740	24109.43
50	500	0.42	0.2	25145	25608.21
55	500	0.42	0.2	26530	27043.53
60	500	0.42	0.2	27905	28423.54
65	500	0.42	0.2	29265	29754.74
70	500	0.42	0.2	30615	31042.45
5	500	0.84	0.2	6850	6910.018
10	500	0.84	0.2	11075	10379.36
15	500	0.84	0.2	14200	13128.67
20	500	0.84	0.2	16450	15497.83
25	500	0.84	0.2	18175	17620.13
30	500	0.84	0.2	19825	19564.78
35	500	0.84	0.2	21425	21373.31
40	500	0.84	0.2	23000	23073.05
45	500	0.84	0.2	24550	24683.13
50	500	0.84	0.2	26080	26217.57
55	500	0.84	0.2	27595	27687.05
60	500	0.84	0.2	29095	29099.89
65	500	0.84	0.2	30585	30462.77

70	500	0.84	0.2	32065	31781.13
5	500	1.68	0.2	6875	7153.452
10	500	1.68	0.2	11125	10745.02
15	500	1.68	0.2	14285	13591.19
20	500	1.68	0.2	16660	16043.8
25	500	1.68	0.2	18565	18240.87
30	500	1.68	0.2	20405	20254.03
35	500	1.68	0.2	22205	22126.28
40	500	1.68	0.2	23980	23885.9
45	500	1.68	0.2	25730	25552.69
50	500	1.68	0.2	27460	27141.19
55	500	1.68	0.2	29175	28662.44
60	500	1.68	0.2	30875	30125.06
65	500	1.68	0.2	32565	31535.95
70	500	1.68	0.2	34245	32900.75
5	500	1.68	0.1	3400	4253.39
10	500	1.68	0.1	5660	6388.91
15	500	1.68	0.1	7475	8081.22
20	500	1.68	0.1	8990	9539.53
25	500	1.68	0.1	10295	10845.9
30	500	1.68	0.1	11485	12042.9
35	500	1.68	0.1	12610	13156.1
40	500	1.68	0.1	13705	14202.4
45	500	1.68	0.1	14775	15193.4
50	500	1.68	0.1	15820	16138
55	500	1.68	0.1	16850	17042.5
60	500	1.68	0.1	17865	17912.1
65	500	1.68	0.1	18870	18751
70	500	1.68	0.1	19865	19562.5
5	500	1.68	0.15	4925	5765.057
10	500	1.68	0.15	7950	8659.543
15	500	1.68	0.15	10200	10953.31
20	500	1.68	0.15	12050	12929.9
25	500	1.68	0.15	13725	14700.55
30	500	1.68	0.15	15285	16322.98
35	500	1.68	0.15	16785	17831.84
40	500	1.68	0.15	18245	19249.94
45	500	1.68	0.15	19680	20593.23
50	500	1.68	0.15	21090	21873.43
55	500	1.68	0.15	22475	23099.42
60	500	1.68	0.15	23845	24278.16
65	500	1.68	0.15	25205	25415.22
70	500	1.68	0.15	26555	26515.13
5	500	1.68	0.2	6875	7153.32

10	500	1.68	0.2	11125	10744.82
15	500	1.68	0.2	14285	13590.93
20	500	1.68	0.2	16660	16043.51
25	500	1.68	0.2	18565	18240.54
30	500	1.68	0.2	20405	20253.66
35	500	1.68	0.2	22205	22125.87
40	500	1.68	0.2	23980	23885.45
45	500	1.68	0.2	25730	25552.22
50	500	1.68	0.2	27460	27140.69
55	500	1.68	0.2	29175	28661.91
60	500	1.68	0.2	30875	30124.5
65	500	1.68	0.2	32565	31535.37
70	500	1.68	0.2	34245	32900.14
5	500	1.68	0.25	8010	8456.491
10	500	1.68	0.25	13295	12702.28
15	500	1.68	0.25	16815	16066.89
20	500	1.68	0.25	19570	18966.27
25	500	1.68	0.25	21905	21563.54
30	500	1.68	0.25	24050	23943.41
35	500	1.68	0.25	26070	26156.69
40	500	1.68	0.25	28020	28236.84
45	500	1.68	0.25	29945	30207.25
50	500	1.68	0.25	31850	32085.1
55	500	1.68	0.25	33740	33883.45
60	500	1.68	0.25	35620	35612.49
65	500	1.68	0.25	37485	37280.39
70	500	1.68	0.25	39340	38893.79
5	500	1.68	0.3	9170	9695.632
10	500	1.68	0.3	15200	14563.56
15	500	1.68	0.3	19355	18421.19
20	500	1.68	0.3	22370	21745.42
25	500	1.68	0.3	24850	24723.28
30	500	1.68	0.3	27100	27451.87
35	500	1.68	0.3	29225	29989.47
40	500	1.68	0.3	31285	32374.42
45	500	1.68	0.3	33320	34633.55
50	500	1.68	0.3	35335	36786.57
55	500	1.68	0.3	37335	38848.43
60	500	1.68	0.3	39320	40830.84
65	500	1.68	0.3	41295	42743.13
70	500	1.68	0.3	43260	44592.95
5	250	1.68	0.2	7015	6977.71
10	250	1.68	0.2	11440	10481
15	250	1.68	0.2	14740	13257.3

20	250	1.68	0.2	17185	15649.6
25	250	1.68	0.2	19245	17792.7
30	250	1.68	0.2	21170	19756.4
35	250	1.68	0.2	23020	21582.7
40	250	1.68	0.2	24835	23299.1
45	250	1.68	0.2	26625	24924.9
50	250	1.68	0.2	28395	26474.4
55	250	1.68	0.2	30150	27958.3
60	250	1.68	0.2	31895	29385
65	250	1.68	0.2	33630	30761.2
70	250	1.68	0.2	35360	32092.5
5	500	1.68	0.2	6875	6761.635
10	500	1.68	0.2	11125	10156.48
15	500	1.68	0.2	14285	12846.75
20	500	1.68	0.2	16660	15165.03
25	500	1.68	0.2	18565	17241.76
30	500	1.68	0.2	20405	19144.65
35	500	1.68	0.2	22205	20914.35
40	500	1.68	0.2	23980	22577.59
45	500	1.68	0.2	25730	24153.09
50	500	1.68	0.2	27460	25654.58
55	500	1.68	0.2	29175	27092.5
60	500	1.68	0.2	30875	28475.01
65	500	1.68	0.2	32565	29808.63
70	500	1.68	0.2	34245	31098.67
5	1000	1.68	0.2	6785	6597.881
10	1000	1.68	0.2	10975	9910.506
15	1000	1.68	0.2	14185	12535.63
20	1000	1.68	0.2	16620	14797.76
25	1000	1.68	0.2	18470	16824.2
30	1000	1.68	0.2	20260	18681
35	1000	1.68	0.2	22005	20407.84
40	1000	1.68	0.2	23720	22030.8
45	1000	1.68	0.2	25410	23568.15
50	1000	1.68	0.2	27075	25033.27
55	1000	1.68	0.2	28720	26436.37
60	1000	1.68	0.2	30350	27785.4
65	1000	1.68	0.2	31965	29086.72
70	1000	1.68	0.2	33570	30345.52
5	1500	1.68	0.2	6600	6521.147
10	1500	1.68	0.2	10600	9795.247
15	1500	1.68	0.2	13645	12389.84
20	1500	1.68	0.2	15930	14625.67

25	1500	1.68	0.2	17715	16628.53
30	1500	1.68	0.2	19415	18463.74
35	1500	1.68	0.2	21085	20170.5
40	1500	1.68	0.2	22710	21774.58
45	1500	1.68	0.2	24305	23294.05
50	1500	1.68	0.2	25875	24742.14
55	1500	1.68	0.2	27430	26128.92
60	1500	1.68	0.2	28975	27462.25
65	1500	1.68	0.2	30510	28748.44
70	1500	1.68	0.2	32040	29992.6
5	2000	1.68	0.2	6455	6473.778
10	2000	1.68	0.2	10320	9724.094
15	2000	1.68	0.2	13245	12299.84
20	2000	1.68	0.2	15405	14519.43
25	2000	1.68	0.2	17275	16507.74
30	2000	1.68	0.2	18975	18329.62
35	2000	1.68	0.2	20600	20023.98
40	2000	1.68	0.2	22175	21616.41
45	2000	1.68	0.2	23710	23124.84
50	2000	1.68	0.2	25215	24562.41
55	2000	1.68	0.2	26695	25939.12
60	2000	1.68	0.2	28155	27262.77
65	2000	1.68	0.2	29600	28539.61
70	2000	1.68	0.2	31040	29774.73