Chapter 1

Introduction

1.1 Basic Characterization of Oil-in-Water Emulsion

The food processing industry seeks effective technologies to remove fats, oils and greases from food processing wastewater at acceptable costs. The baking, dairy, oil extraction (e.g., olive, soybean, cotton seed oil), fish processing, meat and poultry industries, as well as manufacturers of oil-containing foods (e.g., margarine and salad dressing) face the problem of reducing the oil contaminant load to downstream wastewater systems. Recovering valuable byproducts, such as proteins and milk fat in the dairy industry, while reducing the biochemical oxygen demand (BOD) and total suspended solids charges from the publicly owned treatment works makes systems that can remove fats, oils and greases increasingly economical [PATTERSON 1985].

Oil and grease is a common pollutant in a wide range of industries. Stable oil-water emulsions are generated in diverse industrial technologies, as shown in Table 1.1. Industries such as steel, aluminum, food, textile, leather, petrochemical and metal finishing are some that report high levels of oil and grease in their effluents. For instance, in metal working industry oil-water emulsion is often used as coolant and lubricant to increase the useful life of tool and die. In the past time the used emulsion was often discharged to either sanitary sewers or public waterways without previous treatment, causing environmental pollution and loss of oil.

Oil and grease in wastewater can exist in several forms: free, dispersed or emulsified. The differences are based primarily on size. In an oil-water mixture, free oil is characterized with droplet sizes greater than 150 μ m in size, dispersed oil has a size range of 20-150 μ m and emulsified oil has droplets typically less than 20 μ m. As one of oil-water mixtures, stable oily emulsion is a dispersed system in which the phases are immiscible or partially miscible liquids. The globules of the dispersed liquid are generally between 0.1 μ m and 10 μ m in diameter, and so are larger than the particles found in sols. If an emulsion is prepared by homogenizing two pure liquid components, phase separation will be rapid, especially if the concentration of the dispersed phase is at all high. To prepare reasonably stable emulsions a third component – an emulsifying agent (or emulsifier) – must be present. The materials which are most effective as emulsifying (and foaming) agents can be broadly

classified as: (1) surface-active materials; (2) naturally occurring materials; (3) finely divided solids. The functions of the emulsifying agent are to facilitate emulsification and promote emulsion stability. The emulsifying agent forms an adsorbed film around the dispersed droplets which helps to prevent flocculation and coalescence.

Table	1.1	Oil	and	grease	concentrations	in	effluents	of	selected	industries
[CHER	YAI	N 19	98]							

Industrial source	Oil and grease concentration (mg/l)
Food processing Food processing (fish)	3 800 13 700
Can production (forming)	200 000
Wool scouring	12 200
Tanning waste, hide curing	40 200
Metal finishing	6 000
Petroleum refinery	3 200
Steel-rolling coolant	48 700
Aluminum rolling	50 000

In nearly all emulsions one of the phases is aqueous and the other is (in the widest sense of the term) oil. If the oil is the dispersed phase, the emulsion is termed an oil-in-water (O/W) emulsion; if the aqueous medium is the dispersed phase, the emulsion is termed a water-in-oil (W/O) emulsion. The type of emulsion which tends to form depends on the balance between the hydrophilic and lipophilic properties of the emulsifier-alkali-metal soaps favour the formation of O/W emulsions because they are more hydrophilic than lipophilic, whereas the reverse holds for heavy-metal soaps.

The amphiphilic nature of many emulsifying agents (particularly non-ionic surfactants) can be expressed in terms of an empirical scale of so-called HLB (hydrophile-lipophile balance) numbers. The latest hydrophilic surfactants are assigned the lowest HLB values. A number of different formulae have been established for calculating HLB numbers from composition data and they can also be determined experimentally, e.g. from cloud-point measurements [SHAW 1991]. For mixed emulsifiers, approximate algebraic additivity holds. Figure 1.1 shows the structure of a stable oil-in-water emulsion.



Figure 1.1 Schematic diagram of stable oil-in-water emulsion

The application of oil-in-water emulsion is numerous. Among the industries where oil-in-water emulsion is encountered are petroleum, cosmetic, pharmaceutical, agriculture, food, polymer, textile, paper, prints, polish and leather [MARK 1990, HAGG 1998, NABI and MEIRELES 2000]. The used emulsion was often discharged to either sanitary sewers or public waterways without treatment in the past time. It resulted in environmental pollution and loss of oil [LAHIERE and GOODBOY 1993, NAZZAL and WIESNER 1996, BENNETT 1973, 1983, HILL 1983]. Therefore, it is of great significance to study the separation behavior of oil-in-water emulsion to environmental protection.

1.2 Separation Methods for Oil-in-Water Emulsion

1.2.1 Conventional treatment methods

Conventional approaches to treating oily wastewaters have included gravity and skimming, dissolved air flotation, de-emulsification, coagulation and flocculation [NOEMAN 1982]. Gravity separation followed by skimming is effective in removing free oil from wastewater. Oil-water separators such as the API separator and its variations have found widespread acceptance as an effective, low cost, primary treatment step. These, however, are not effective in removing smaller oil droplets and emulsions. Oil that adheres to the surface of solid particles can be effectively removed by sedimentation in a primary clarifier.

Dissolved air flotation (DAF) uses air to increase the buoyancy of smaller oil droplets and enhance separation. Emulsified oil in the DAF influent is removed by de-emulsification with chemicals, thermal energy or both, DAF units typically employ chemicals to promote coagulation and increase floc size to facilitate separation. Emulsified oil in wastewater is usually pretreated chemically to destabilize the emulsion followed by gravity separation [DICK 1982]. The wastewater is heated to reduce viscosity, accentuate density differences and weaken the interfacial films stabilizing the oil phase. This is followed by acidification and addition of cationic polymer/alum to neutralize negative charge on oil droplets, followed by raising the pH to the alkaline region to induce floc formation of the inorganic salt. The resulting floc with the adsorbed oil is then separated, followed by sludge thickening and sludge dewatering. In some cases, the sludge may be further processed. Frequently, a high molecular weight flocculant such as acrylate-acrylamide copolymers may be used to enhance oil removal and reduce floc carry over. Improvements in chemical treatment are frequently centered on selection of the appropriate blend of chemicals, and process optimization to lower costs of operation.

Physical methods for breaking emulsions include heating, centrifugation, precoat filtration, fiber beds, ultrafiltration and reverse osmosis, and electrochemical methods. Centrifugation is normally applied to oily sludges though it might be employed for small volumes of dilute oil waste in special cases. Precoat filtration and coalescers have also been successfully employed for breaking oil emulsions. Typically, precoat filtration and coalescers are used for separating particles in the 20 – 100 μ m size range. Electrocoagulation and electroflotation are some of the other technologies that utilize both chemical and physical emulsion separation mechanisms in the presence of an electric field.

Gravity separation is the most common primary treatment of oily wastewater. If the resulting effluent does not meet required discharged limits, secondary treatment steps are used to lower the levels of dissolved, emulsified and dispersed oils. Breaking of emulsions with chemicals, followed by DAF or sedimentation, is then used to remove additional oil.

Chemical emulsion breaking is effective if properly applied, but it suffers from several shortcomings [CHERYAN and RAJAGOPALAN 1998]:

1. The process is highly susceptible to changes in influent quality.

2. It requires customization at every site to determine the type and quantity of chemicals required.

3. It requires close control and skilled operators to achieve optimal operation.

- 4. It produces large volumes of sludge.
- 5. The equipment has a large footprint.

- 6. The operating costs can be high, depending on the application.
- 7. There could be corrosion problems due to acidification of the influent.
- 8. Mechanical problems may arise due to clogging of chemical feeding lines.
- 9. Dissolved solids content in the effluent increases.

10. It is more suitable for large volumes, e. $g_{.} > 1.0 \times 10^{6}$ liters per day; it is difficult to operate and maintain in smaller facilities with fewer resources.

Thermal treatment (evaporation and incineration) is more universal and perhaps more suitable for many types of oily emulsions. Its drawbacks are high-energy costs and loss of entrained oils in the vapors from the evaporators, making it necessary to treat the condensate.

Coalescers and precoat filtration are more effective in reducing high levels of oil and grease in the appropriate particle size range. Problems can be encountered in coalescers due to gradual adsorption of material on the coalescing media. This leads to its poisoning and loss of effectiveness. The extra volume of sludge produced is a problem with precoat filtration and electrocoagulation.

1.2.2 Membrane technology

Membrane processes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are increasingly being applied for treating oily wastewater [BHAVE and FLEMING 1988, CHEN et al. 1991, DAIMINGER et al. 1995]. Of the three broad categories of oily wastes - free-floating oil, unstable oil/water emulsions, and highly stable oil/water emulsion -- membranes are most useful with stable emulsions, particularly water-soluble oily wastes. Free oil, on the other hand, can be readily removed by mechanical separation devices which use gravitational force as the driving force. Unstable oil/water emulsion can be mechanically or chemically broken and then separated by gravity. Pretreatment to remove large particles and free oil is needed, especially if thin-channel membrane equipment is used. The membrane unit is usually operated in a semibatch recycle. The wastewater feed is added to the process tank at the same rate as clean permeate is withdrawn, thus keeping a constant level in the tank. The retentate containing the oil and grease is recycled to the process tank. When the oils and grease and other suspended matter reach a certain predetermined concentration in the tank, the feed is stopped and the retentate allowed to concentrate. Usually, this results in a final concentrate volume that is only 3-5% of the initial volume of oily wastewater fed to the process tank. The system is then usually cleaned.

Membranes have several advantages, among them:

1. The technology is more widely applicable across a wide range of industries.

2. The membrane is a positive barrier to rejected components. Thus, the quality of the treated water (the permeate) is more uniform regardless of influent variations. These variations may decrease flux, but generally does not affect quality of its output.

3. No extraneous chemicals are needed, making subsequent oil recovery easier.

4. Membranes can be used in-process to allow recycling of selected waste streams within a plant.

5. Concentrates up to 40-70% oil and solids can be obtained by UF or MF. Since most oily wastes contain 0.1-1% oil, this means the volume of waste that has to be subsequently hauled away or treated is reduced to 1/40-1/200 the initial feed volume.

6. Membrane equipment has a smaller foot print.

- 7. Energy costs are lower compared to thermal treatments.
- 8. The plant can be highly automated and does not require highly skilled operators.

For example, flux that can be obtained with Koch's tubular modules is about 50 l/m²h at 25 °C and 3.5 bar, with emulsified oil at 1-2% feed concentration and 60% retentate concentration [CHERYAN and RAJAGOPALAN 1998]. Synthetic oils tend to foul the membrane less and have high flux. Natural fats and oils exhibit low flux and foul the membrane more. The chemical nature of the membrane can have a major effect on the flux. For instance, free oils can coat hydrophobic membranes resulting in poor flux (emulsified oil is usually not as much of a problem, unless it is concentrated to such a high level that the emulsion breaks, releasing free oils). Hydrophilic membranes preferentially attract water rather than the oil, resulting in much higher water flux. Hydrophobic membrane can be used, but usually in a tubular configuration that allows a high degree of turbulence (cross-flow velocity) to be maintained to minimize oil wetting of the membrane.

Membranes with pore sizes equivalent to 50 000-200 000 molecular weight cut off (MWCO) should result in permeates with less than 10-100 ppm of oil, unless high concentrations of a soluble surfactant or polar solvent are present. MF membranes with pore sizes of 0.1 μ m have also been used, especially if it is necessary to recover surfactants in the permeate. If the salt content of the oily wastewater is too high for direct reuse of the permeate in the plant, it can be treated by RO or NF.

Membrane processes have some limitations:

1. Scale-up is almost linear above a certain size. Thus capital costs for very large effluent volumes can be high.

2. Polymeric membranes suffer from fouling and degradation during use. Thus they may have to be replaced frequently (generally every two years [CHERYAN and RAJAGOPALAN 1998], which can increase operating costs significantly).

In spite of the above disadvantages, membrane processing of oily wastewaters, sometimes in conjunction with other methods for treating the residuals, is a commercial success with more than 3 000 polymeric UF/MF installations and over 75 inorganic/ceramic units worldwide. Membranes are gaining wider acceptance for two reasons: it consistently produces effluents of acceptable discharge quality and it is perceived to be a simple process from an operational viewpoint.

1.3 Objectives of This Thesis

Industrial wastewater treatment, pollution prevention, and resource recovery applications frequently require separation of emulsified oils. Membrane filtration technologies are playing a more prominent role in accomplishing these separations. Ultrafiltration is an effective and economical method to treat emulsified oily wastewater from the industry. Ultrafiltration is also a physical treatment process to remove contaminants from an oily wastewater and permit sewer discharge, and can be used to comply with strict environmental laws as well as provide a first step towards water recycling and oil recovery.

The basis for selecting membranes and membrane operating conditions for removing water from oily water supplies and wastewater streams remains largely empirical, which includes molecular weight cut off (MWCO), pore size and distribution, transmembrane pressure, temperature, flow velocity, cleaning of membrane and others to achieve adequate rejection of emulsified oil and chemical oxygen demand (COD) in the permeated water while maintaining permeate flux.

Therefore, the objectives of this investigation are the establishment of operation conditions and selection of membrane parameters to minimize concentration polarization and membrane fouling, the achievement of adequate rejections of COD and oil, and the development of a suitable pilot scale-up procedure involving membrane module arrangements, operation parameters and membrane nature to obtain the high water recovery essential in oil-in-water emulsion treatment.

The concentration polarization and membrane fouling is a serious problem in membrane filtration. It is well known that many models for cross-flow membrane filtration have been reported in the literatures. These models, especially film theory and the resistance-in-series model, have been modified for ultrafiltration of oil-in-water emulsion by many authors, as stated in the following section of literature survey. However, there is no generally accepted, simple and practical comprehensive model. The reasons may be ascribed to the membrane variety and composition complexity of oil-in-water emulsion etc. In actual ultrafiltration process, the theoretical results were not in good agreement with the experimental values.

The second goal of this research is to introduce a calculation method of gel concentration at the membrane surface and to develop a new numerical model which can describe the flux decline behavior due to membrane fouling during cross-flow UF of oil-in-water emulsions. The theoretical analysis and calculation have to be verified by many experimental results.

1.4 Outline

A review of the literature available will be presented in Chapter 2. Current technology and novel developments of ultrafiltration characteristics and membrane technology, especially in the application of separation of oil-in-water emulsion, will be explained more extensively in this chapter.

Chapter 3 will be devoted to the description of experimental procedures, including experimental apparatus, membranes and methods either in laboratory or pilot field.

In Chapter 4 the influence of membrane type and operation condition on the flux were investigated in laboratory and pilot scales. The recovery of permeability of ultrafiltration membrane was subsequently studied. Then the next section is dedicated to the characterization of gel concentration at the membrane surface.

In the last section of Chapter 4 the theoretical results of the membrane fouling model will be compared with experimental results under various operation conditions.

Conclusions and research potentials will be given in Chapter 5.

Chapter 2

Literature Survey

The ultrafiltration membrane process is quite recent and presents undeniable advantages: it needs no chemical reagent, the ultrafiltered water shows no oil content, the ultrafiltration plants are quite compact and are fully automated [LOEB and SOURIRAJAN 1964]. Therefore the research and development on the ultrafiltration behavior of oil-in-water emulsion have been investigated worldwide. Many studies have reported the application of ultrafiltration to the treatment of oil-in-water emulsions [ANDERSON and SAW 1987, DAL-CIN et al. 1998, VIADERO et al. 2000, LIN and LAN 1998].

However, two kinds of limitations are commonly encountered in this process: (1) Concentration polarization due to the accumulation of oil droplets on the membrane surface. This over-concentration leads to the formation of a viscous oily gel layer containing 30 to 40% of oil and which causes a strong decrease in the flux [LEE et al. 1984]; (2) Membrane fouling due to an inlet of oil drops into some pores or to the adsorption of either oil or surfactants or co-surfactants or of some other organic matter on the membrane surface. This long term phenomenon causes a progressive decrease of the flux over time and can induce a loss of separation efficiency in the fouled areas.

Therefore, the major hurdles to be overcome in the development of a practical industry unit are concentration polarization and membrane fouling. Almost the current researches of ultrafiltration in oil-in-water emulsion have been focused on the problems mentioned above, in order to improve the permeate flux. They contain: (1) the mechanisms of concentration polarization and membrane fouling [LEE et al. 1984, VAN DEN BERG and **SMOLDERS** 1989. NAKAO et al. 1986. FERNANDEZ-SEMPERE and RUIZ-BEVIA 1996, GEKAS and HALLSTROM 1987]. (2) preventing or reducing methods of concentration polarization and membrane fouling [AGASHICHEV 1999, KARODE 2000, HAMZA et al. 1997, LIPP 1988, MA et al. 2000]. (3) membrane material (including novel membrane material and its surface modification etc) [HYUN and KIN 1997, GANCARZ 2000, HOWELL et al. 1994, CASTRO et al. 1996, PEINEMANN and NUNES 1994, LINDAU and JONSSON 1999]. (4) optimizing the basic operation parameters (transmembrane pressure, cross-flow velocity, feed concentration, temperature) [CROZES et al. 1997, LOPEZ et al. 1995, LINDAU 1998, MORES and DAVIS

9

2000]. (5) pretreatment of chemical adjunction salt in the feed solution [TECKENTRUP 1995] and additional force fields (using an external DC electric field) [CORNELISSEN 1997, HUOTARI et al. 1999] or ultrasonic treatment [CHAI et al. 1998, 1999]. (6) membrane cleaning procedure and novel hybrid process combining with biotechnology, gravity, air-flotation and other treatment methods [TROUVE 1994, CANNING and TONELLI 1995, LINDAU and JONSSON 1992].

2.1 Mechanism of Concentration Polarization and

Membrane Fouling

Ultrafiltration (UF) has a great potential for removing particles, microorganisms, and colloidal material from potable water supplies and wastewater streams. A major obstacle to these applications is that the permeate flux decline due to concentration polarization and fouling. During ultrafiltration of colloidal suspensions, particles within the feed and recycled flow stream are convectively driven to the membrane surface where they accumulate and tend to form a cake or gel layer. This particle build-up near the membrane surface is known as concentration polarization, and results in increasing hydraulic resistance to permeate flow; therefore the permeate flux declines in function of time.

It is believed that there are two essential mechanisms for membrane fouling in cross-flow UF, namely, pore blocking which is responsible for the initial sharp drop from the flux of pure water filtration, and cake formation which is the reason of long-term gradual flux decline [SONG 1998]. Both pore blocking and cake formation may be affected by many factors. The necessary condition for pore blocking and cake formation (or the fundamental cause of membrane fouling) is the non-equilibrium operation of UF, where the applied pressure is much higher than the critical pressure that can be absorbed by the concentration polarization layer. In such operation, the membrane pores will be quickly blocked and a cake layer will form to absorb the excessive pressure.

It was investigated that the transition from concentration polarization to cake formation for the membrane filtration of colloidal silica by imposing flux and observing the system response [CHEN et al. 1997]. It appears that once J_{crit} is exceeded, the colloids in the polarized layer form a consolidated cake structure that is slow to depolarize and which reduces the flux. These results are ascribed to formation of a stagnant, highly concentrated layer near the membrane surface due to consolidation and aggregation of solute resulting from very rapid flux increases.

NIKOLOVA et al. [1998] explained the mechanism of flux decline: in absence of flow through the membrane, some macromolecules are adsorbed on the membrane surface. Thus the initial total resistance is higher than that the membrane exerts during the filtration of pure water. The higher the feed concentration, the higher the initial adsorbed layer resistance. During the ultrafiltration process, gradually a concentration polarization layer is developed, causing increased osmotic pressure and increased adsorption resistance. The later plays the decisive role in the flux decline.

Some results on the fouling mechanism have been reported for UF membranes used for the removal of lubricating and cutting oils used in the metal industry. BHATTACHARYYA et al. [1979] observed internal and external fouling during UF of a lubricating oil-nonionic detergent-water solution through noncellulosic, tubular membranes. They noted that membrane fouling and cleaning requirements depend on the type of oily water systems and membranes. LEE et al. [1984] studied concentration polarization and fouling during UF of a soluble oil-surfactant-water emulsion through a polymeric membrane in a stirred filtration cell. They found that fouling was due to adsorption of oil on the membrane structure, which modified the critical surface tension and the wettability, as well as the effective pore diameter, resulting in reduced membrane permeability. LIPP et al. [1988] studied the UF behaviour of soluble oil-in-water emulsions through a batch cell containing various polymeric and cellulosic membranes. They stated that fouling followed a gel-polarized, film-model behavior, with the oil droplets coalescing into the surface-fouling oil film. In addition, MUELLER et al. [1997] reported that the UF performance of cutting oil with polysulfone membranes was studied. It is presented that the results of changing various operating variables, including the increase in flux observed at higher cross-flow velocities due to washing away of the polarized layer. They also proposed a model for the prediction of the permeate flux which incorporates droplet coalescence and shear rate.

POPE et al. [1996] reported measurements of the thickness of the concentration polarization layers formed during cross-flow membrane filtration of an oil-water emulsion. The formation and development of the oil polarization layers was visualized non-invasively using NMR (nuclear magnetic resonance) chemical shift selective micro-imaging. A series of images was acquired during the transient state of the filtration, (i.e. while the polarization layer was forming and the flux of filtrate was changing), prior to the establishment of steady state conditions. An estimate of the specific resistance of the concentration polarization layers was then obtained by determining the average oil layer thickness and concentration at a given time from the resulting images and measuring the corresponding (length averaged) flux of filtrate gravimetrically. After the establishment of steady state conditions, the dependence of the steady state filtrate flux on cross-flow Reynolds number was found to be consistent with Brownian diffusion being the main mechanism controlling the build-up of the oil polarization layers, at least under a special range of operating conditions.

2.2 Mathematical Models of Permeate Flux

The capital and operational costs of membrane systems are directly dependent on membrane permeate flux. Therefore, the permeate flux and the factors affecting it are central considerations in determining membrane process performance and cost.

Many different models have been proposed to predict flux decline during UF and MF [LEE et al. 1984, VAN DEN BERG and SMOLDERS 1989, CHEN et al. 1997, KOLTUNIEWICZ et al. 1995, ARNOT et al. 2000, CAKL et al. 2000]. Among them there are two basic models: one is the gel layer model [TANSEL et al. 2000, LEE and CLARK 1998, BLATT et al. 1970] in which the extra hydraulic resistance of a gel layer in addition to the membrane resistance reduces the flux, and the other is the osmotic pressure model [FANE 1986, SOURIRAJAN and MATSUURA 1988] in which the applied pressure is reduced by the osmotic pressure and the decreased driving force causes the flux decline. When a suspension or emulsion contains molecules which are too large to enter the membrane pores, then a sieving mechanism is dominant and a cake layer of rejected molecules forms on the membrane surface. The cake layer provides an additional resistance to filtration, so the permeate flux declines in function of time. The cake layer and membrane may be considered as two kinds of resistance in series, and the permeate flux is then described by Darcy's law provided neglecting the effect of diffusion:

$$J = \frac{\Delta P}{\eta \ (R_m + R_c)} \tag{1.1}$$

where J = permeate flux, $\Delta P =$ transmembrane pressure, $\eta =$ viscosity of the permeate, $R_m =$ membrane resistance, and $R_c =$ cake resistance. The cake filtration theory has been successful in describing flux decline during dead-end MF/UF of particulate suspensions. Many experimental results demonstrate the well-known relationship drawn from cake filtration theory, $V \propto t^{1/2}$ (V = total volume of permeate, t = filtration time). The theory for the transient cake build-up and the associated flux decline for conventional dead-end filtration may also apply for the initial cake build-up in cross-flow filtration, prior to the action of the tangential flow which

causes the cake growth to be restrained [DAVIS 1992]. Macromolecules and/or colloidal molecules experience diffusion is not considered in this model.

The concentration polarization model based on the film theory was developed to describe the back diffusion phenomenon during filtration of macromolecules. In this model, the rejection of molecules gives rise to a thin fouling layer on the membrane surface, overlaid by a concentration polarization layer in which molecules diffuse away from the membrane surface. At steady state, convection of molecules towards the membrane surface is balanced by diffusion away from the membrane [PORTER 1972]. If the solute retention is assumed to be equal to one, i. e. all molecules are assumed to be rejected by the membrane, then the steady-state permeate flux can be obtained by integrating the one-dimensional convective-diffusion equation across the concentration polarization layer:

$$J = \frac{D}{\delta} \ln \frac{C_w}{C_b} = K \ln \frac{C_w}{C_b}$$
(1.2)

where D = diffusion coefficient, $\delta =$ thickness of concentration boundary layer, $C_w =$ rejected molecules volume fraction at the wall, $C_b =$ rejected molecules volume fraction in the bulk solution, and K = mass transfer coefficient = D/δ . This model introduces two important parameters – the mass transfer coefficient (K) and the rejected molecules volume fraction at the wall (C_w) – which should be determined either theoretically or experimentally.

Two distinctive models have been developed: one is the lateral migration model and the other is the shear-induced hydrodynamic diffusion model. According to the lateral migration model proposed by GREE and BELFORT [1980], the permeate flux declines until the permeation velocity equals the lift velocity evaluated at the surface of cake layer. However, during membrane filtration the diffusion is another important mass transport mechanism, and this was not considered in GREEN and BELFORT's model. It was proposed to modify the concentration polarization model by replacing the Brownian diffusion coefficient with the shear–induced hydrodynamic diffusion coefficient [ZYDNEY and COLTON 1985]. In addition, it was developed a more comprehensive model based on the shear–induced hydrodynamic diffusion phenomenon [DAVIS and LEIGHTON 1987, ROMERO and DAVIS 1988]. They deliberately incorporated two-dimensional characteristics of cross-flow filtration into the one-dimensional convective-diffusion equation by defining the shear-induced hydrodynamic diffusion into the one-dimensional convective-diffusion equation by defining the shear-induced hydrodynamic diffusion the one-dimensional convective-diffusion equation by defining the shear-induced hydrodynamic diffusion into the one-dimensional convective-diffusion equation by defining the shear-induced hydrodynamic diffusion into the one-dimensional convective-diffusion equation by defining the shear-induced hydrodynamic diffusion coefficient.

As an alternative to back-transport of molecules away from the membrane by mechanisms such as shear-induced diffusion and inertial lift, it is possible that the molecules are carried to the membrane surface by permeate flow and then roll or slide along the membrane surface due to the tangential flow. The rejected molecules are assumed to form a flowing cake layer. Convective-flow mathematical models describe the simultaneous deposition of molecules into the cake layer and the flow of this layer towards the filter exit [LEONARD and VASSILIEFF 1984, DAVIS and BIRDSELL 1987]. The fully developed laminar flow equations were solved for the velocity profiles in the bulk suspension and in the cake layer, and the thickness and the permeate flux at a steady state cake can be determined. In general, the cake layer thickness increases and the permeate flux decreases with increasing distance from the filter entrance. This surface transport model predicts that the steady state permeate flux increases with shear rate and radius of rejected molecules.

Recently, many attempts have been made to fully describe two-dimensional mass transport mechanisms involved in cross-flow filtration [LEE and CLARK 1998]. The most popular one is the continuum approach. The particle movement during cross-flow filtration is governed by the two-dimensional convective-diffusion equation. Many different authors have tried to solve the differential equation numerically in order to obtain the concentration profiles inside the membrane channel; most of these efforts were limited to the steady-state case. Although the concentration profiles can explain the trends in flux decline, they can not be directly used to predict the flux decline. Therefore, it is necessary to develop a comprehensive model which can predict the flux decline during cross-flow filtration.

2.3 Flux Enhancement Methods

Flux decline in membrane filtration is a result of the increase of the membrane resistance because of the development of those additional resistances, such as concentration polarization and fouling resistances. The successful operation of membrane plant requires careful management of polarization and fouling of the membrane. Their avoidances are probably not possible, but their impacts can be limited by a variety of techniques. The choice of membrane, module, process configuration and pretreatment are all important to varying extents, if a high degree of separation is to be achieved without productivity being lessened unacceptably by fouling and polarization. In addition to improve filtration rates, avoidance of fouling makes easier to clean the membranes. This may limit the need for a severe cleaning regime and can prolong the service lifetime of polymeric membranes.

2.3.1 Pretreatment

Permeate flux can be enhanced by pretreating the feed. This technique is commonly used either to remove particles that may cause clogging in the module or to prevent particles or macromolecules from reaching and depositing on the membrane surface, or to reduce the total contaminant load in downstream membrane modules. The use of innovative pretreatment can significantly extend the UF volumes that can be economically treated.

Pretreatment can involve either physical or chemical processes. Physical processes usually include prefiltration or centrifugation to remove suspended solids which may plug the module or blind the membrane. Chemical processes include feed pH adjustment so that molecular or colloidal foulants will be far from their isoelectric point, thereby reduce the tendency to form a gel layer. It may involve precipitation, coagulation or flocculation or the use of proprietary chemicals such as anti-scalants or disinfectants.

BELKACEM et al. [1995] reported their dedication on the application of membrane technology for wastewater treatment of metal working fluids and more precisely of oily emulsion stabilized by anionic surfactants. The permeate fluxes have been considerably increased by the adjunction of a reactive salt (CaCl₂) at a very low concentration in the feed solution. After this treatment, the ultrafiltration membrane behaves as efficient surface coalescer. This treatment and procedure reduces the polarization layer resistance giving an increased permeate flux which is nearly constant and independent of the concentration ratio.

WEHLE et al. [1988] used a method to break emulsion in pretreatment of feed. They invented an apparatus for treating an oil/water emulsion having a reaction vessel and an emulsion-breaker vessel, from which emulsion breaker can be delivered into the reaction vessel. A sensor device being provided for the determination of transmitted light and scattered light as a measure of turbidity of the oil-in-water emulsion in the reaction vessel. The addition of emulsion breaker can be controlled according to measurement results obtained by the sensor apparatus. Furthermore, the invention also relates to a process for treating an oil/water emulsion, in which the water emulsion is first divided, with addition of an emulsion breaker and vortexing, into flocks which can be separated off on the one hand residual dispersion, on the other hand the flocks are separated off from the residual dispersion, contaminated residual water arising in the process being subjected to a membrane filtration.

2.3.2 Operation conditions

Optimizing the operation conditions may involve maintaining a high cross-flow velocity, limiting transmembrane pressure, temperature, periodical hydraulic and/or mechanical cleaning, choice of cleaning chemicals and frequency of cleaning etc.

Concentration polarization and cake formation in commercial membrane module is controlled either by increased shear at the membrane surface or the use of turbulence inducers. Increased shear is obtained by pumping the feed at higher flow-rates or by using thin flow channels above the membrane surface. The performance of membrane processes can be improved when unsteady fluid instabilities are superimposed on cross-flow. Whereas steady flows often require high cross-flow velocities in the turbulent regime, unsteady flows can be effective in both the laminar and the turbulent regimes. These fluid instabilities have been used to disturb foulants, and rough channels have been used to induce fluid mixing at the membrane-solution interface [CHUNG et al. 1993].

The high feed/retentate velocities used in UF modules require a high pressure, but a low transmembrane pressure is needed to prevent compaction of deposits on the membrane. In addition, high pressure may cause other problem in UF of oil-in-water emulsion, because there are some surfactants in emulsion. Sweet reported that the surfactants present in water/oil/surfactant emulsions can be selectively separated from the emulsions by practicing an ultrafiltration process under specific conditions of pressure and ultrafiltration membrane pore size [SWEET 1990]. It has been discovered that increasing the applied pressure results in an increase in the permeability of the surfactant without a commensurate increase in the permeability of the water or oil.

MISRA et al. [1999] studied model metalworking fluids, characterized by phase separation of functional components at elevated temperatures. Results of membrane filtration experiments with three oils of different chemical nature confirm the feasibility of specific removal of finely dispersed contaminant oils without the simultaneous loss of active components from adequately formulated fluids. Prerequisites are that membrane materials and pore sizes be suitably chosen and that operating temperatures be kept below the cloud point of the least soluble component. The most suitable filter was a hydrophilic regenerated cellulose membrane with a MWCO of 100 000 Dalton. It was also found that intrinsically water-soluble boundary lubricants of the polyglycol ether type are retained by membranes. This is of considerable practical importance since it offers the possibility of designing

water-soluble boundary lubrication and extreme pressure additives which are activated by the presence of an inversely soluble component above its cloud point.

LOPEZ et al. [1995] emphasized the importance of the temperature in cross-flow UF of hydrocarbon emulsions. The flux performance depends on the droplet size distribution which depends strongly on the temperature. The flux has a maximum at 25°C but the internal clogging limits the membrane regeneration by counter-washing. At 18°C, the fouling results essentially from the accumulation of oil against the wall of the membrane.

The high feed/retentate velocities reduce cake formation and polarization in ultrafiltration. The pressure drop on the feed side is therefore fairly high, while the permeate channel is often at, or near to, atmospheric pressure. The transmembrane pressure at the feed end of the filter is therefore greater than at the retentate discharge end, causing more cake formation (the extent of compaction depends on the properties of the feed) at the feed end. This leads to a rapid drop in flux and high rejection of solutes. It is common practice to pump filtrate back through the membrane into the feed channel to give a periodic backwash to lift deposited material off the membrane surface. SRIJAROONRAT et al. [1999] studied the backflushing effect in UF treatment of unstable secondary oil/water emulsion. It was found that the ceramic membrane (α -alumina or zirconium) could be used successfully to treat oily wastewater. The concentration polarization and fouling can be controlled by periodic backflushing with ceramic membrane, and the flux was found to increase. Rapid backwashing (also known as back-pulsing or back-shocking) is sometimes more effective. Back-pulses are of short duration (about 0.1 second or shorter) and can be particularly useful with colloidal suspensions and with streams requiring protein transmissions through the membrane [CHERYAN 1998].

Besides the periodic hydraulic cleaning and mechanical cleaning, chemical cleaning is also used to enhance flux and reduce fouling. Cleaning solutions are usually circulated with a pressure somewhat lower than that used during filtration to prevent deeper penetration of the foulants into the membrane. There is no *a priori* rule which can be applied to predict which cleaning technique might be most successful in any particular application. KIM et al. [1993] investigated the relationships between membrane fouling and cleaning in terms of flow conditions, transmembrane pressure, pH, membrane properties and cleaning agents using a stirred batch-cell and aqueous albumin solution. In addition, BELKACEM et al. [1995] introduced also the application of specific micellar cleaning solutions to fouled membranes to renew their initial water permeability and their initial hydrophilic properties.

2.3.3 Process design

The process design may include additional force fields (for example electric and/or ultrasonic), choice of membrane material and modification of membrane surface, use of turbulence promoters, pulsed/reversed flow and rotating/vibrating membranes etc.

The application of an electric field to improve the efficiency of pressure driven filtration processes has been practiced for a long time. [HUOTARI et al. 1999a, 1999b] reported the effect of an electric field in the filtration of an oil emulsion. Limiting fluxes for low flow rate increased significantly under the conditions studied, from 75 l/m^2h without an electric field to more than 350 l/m^2h using an electric field. The limiting flux increase was affected by the electrophoretic mobility of the oil droplets and the applied electric field strength. The critical electric field strength was determined, and experimentally obtained values were corresponded with calculated values. Permeate quality was also improved to some extent and a membrane with a large pore size could be used when using the electric field.

The passage of ultrasound waves through a suspension can cause many phenomena, including particle dispersion, viscosity reduction, changes in particle surface properties and cavitation [KOST and LANGER 1988]. CHAI et al. [1998] reported that an ultrasound cleaning technique was applied to remove fouling of ultrafiltration and microfiltration membranes, as peptone solution was permeated by cross-flow filtration. The ultrasound employed had a frequency of 45 kHz and an output power of 2.73 W cm⁻². For each polymeric membrane made of polysulfone, polyacrylonitrile and polyvinylidene fluoride, cleaning experiments were carried out with three kinds of methods using sonication, water cleaning and water cleaning under sonication. It was found that water cleaning under sonication was an effective method for the recovery of permeate flux. The ultrasound effect on the cleaning of fouled membranes was also examined at different filtration temperatures using various peptone concentrations. It is suggested that the cleaning of fouled membranes by ultrasound association with water cleaning is an effective new method.

The membrane material influences the separation behaviour to a greater degree in case of ultrafiltration, largely through the tendency of some materials to adsorb solutes more readily than others do. Appropriate choice of membrane material and modification of membrane surface can lead to looser binding of the solutes to the membrane surfaces, which can have the effect of lessening and membrane-solute interaction (such as molecule or particle penetration into the surface pores). This leads to a reduction in membrane permeability, and it may also make the solute easier to

remove during cleaning. In addition, modification of membrane surfaces to increase hydrophilicity is also selectable in UF of oil-in-water emulsion. HAMZA et al. [1997] has developed a membrane with low surface energy to reduce fouling in UF-applications, and reports successful results from experiments with a surface modified polyethersulfone (PES) ultrafiltration membrane. The surface was modified with various amounts of macromolecules as additives, and it was found that a modified PES-membrane had higher flux when treating oil-in-water emulsion, than the control membrane (unmodified).

It is also noticed the difference in permeate flux by Nakatsuka and Miyano where a hydrophilic cellulose acetate (CA) membrane was compared with a hydrophobic PES membrane [NAKATSUKA et al. 1996]. The flux through the CA membrane was found to be much higher than that of the PES-membrane, a phenomenon which was explained by the difference in membrane fouling due to adsorption of substances in raw water on and in the pores of the membranes. In order to maintain the high and stable flux on the CA-membrane the operating back-washing pressure would be more than twice higher than the filtration pressure. Efficient removal of organic compounds from raw water was accomplished by the CA-membranes.

It was invented a kind of membrane which had a non-porous hydrophilic separation layer which made of a polymer (I) with at least one polyether segment. In the swollen state the membrane contains at least 10 wt.% water, and the polyether segment contains 2-4 C divalent ether units [PEINEMANN and NUNES 1994]. Polymer (I) is polyamide-polyether block copolymer with of formula а units $HO-(CO-PA-CO-PE-O)_m-H$ (with PA = polyamide segment; PE = polyether segment; m = positive integer), or an epichlorohydrin-ethylene oxide copolymer of formula. This UF membrane has a very low tendency to fouling; absorption of hydrophobic materials (fats, oils, proteins) is also very low. Its applications include water treatment, recovery of electrophoretic paint form effluent, purification of oil/water emulsions, milk processing etc.

HOWELL et al. [1994] discovered that the hydrophilicity of hydrophilic polymers in the form of heat-cross linked coatings on porous membranes, is increased by exposure to an oxygen plasma, preferably for about 60 seconds. The plasma is generated at an oxygen gas pressure of about 1.5 Torrs in a chamber subjected to radio frequency electromagnetic radiation with a power of 25-100 Watts. Such highly hydrophilic membranes have increased efficiency and durability when used as ultrafiltration membranes for separating hydrophobic and hydrophilic materials, such as smoke-air and oil-water mixtures. BELLHOUSE [1994] has described designs of tubular membranes in which are placed concentric screw thread inserts. The inserts have a clearance with the tubular membranes to permit substantial leakage flow in the resulting annular gap. The helical screw thread is semi-circular in shape to pass along the helical path. A corkscrew vortex is superimposed on the helical flow. This causes radial mixing in the flow field. The screw thread vortex generators in a tubular membrane reduce hold-up in the feed channel, increase feed velocities and wall shear rates, and produce secondary flows or instabilities. In spite of reported fluxes being 50% to 300% higher than in a conventional cross-flow filter, the use of inserts in the feed channel is not commonly practiced commercially.

Oscillations and unsteady flows can be obtained by introducing pulsations into the feed or filtrate channels. It can enhance shear at the membrane surface to decrease concentration polarization. It was found flux improvements of up to 300% when using periodically spaced, doughnut-shaped baffles in ultrafiltration tubes together with pulsed flows, with an oscillation frequency up to 2.5 Hz [FINNIGAN and HOWELL 1989].

A high shear stress can be developed at the membrane surface by rotating the surface at high speed, rather than pumping feed across the surface at a high cross-flow velocity [WRONSKI 1989]. This rotating membrane – high-shear (dynamic) filtration is achieved in dynamic membrane filters, which have a rotating disc or cylinder element. The magnitude of the shear stress can be varied independently of the over-pressure of the slurry in the filter by varying the rotational speed of the rotating elements.

A "hybrid" process, actually a dual membrane process, may be the solution for water treatment rather than one single type of membrane process. A process of this type is presently in the early stage of commercialization by a US company [SCOTT 1995]. Their hybrid process is claimed to have significant advantages for the treatment of wastewater streams containing oily substances, halogenated organics or organic solvent. The first stage uses a cellulosic hollow fiber membrane and the permeate then passes to a separate NF or RO system. In some applications, the second stage permeate is further treated by activated carbon to remove trace organic elements. For the most difficult waste streams containing appreciable quantities of soluble hydrocarbons a four-stage process is advised comprising pretreatment prior to hollow fiber membrane separation, a further nanofiltration or reverse osmosis membrane stage, and final treatment with activated carbon to remove any remaining low molecular weight dissolved organics.

Chapter 3

Materials and Methods

3.1 Laboratory and Pilot-scale Apparatuses

The experiments were carried out on a laboratory scale ultrafiltration apparatus using cross-flow flat-sheet modules. The experiments were performed with two kinds of experimental set-up: the first one (ND-2) was used to evaluate the effects of operation conditions and the other one (TZA 944 Test Rig) the membrane nature and feed concentration.

The flow diagram of the first experimental set-up is shown in Figure 3.1, this is a ND-2 membrane apparatus designed and built in Nanjing University of Chemical Technology, China. The membrane area of the laboratory cross-flow module was 35 cm². The TZA 944 Test Rig with two units ready for operation was manufactured in Amafilter Membrantechnik GmbH, Germany. Its working principle was similar with that of ND-2, only the membrane surface of each unit was 44 cm².

In the ND-2 set-up, the oil-in-water emulsion was stored in the tank (1) and pumped to the ultrafiltration cell (6) using a pump (2). This volumetric pump ensured a constant flow rate and thus constant velocity at the inlet of the ultrafiltration cell. The flow rate was monitored by the electromagnetic flowermeter (3). The concentrate was recycled in the tank. The pressure at the outlet of the module could be adjusted with a discharge valve (4). Two pressure transducers (5) measured the pressure at the inlet and outlet of the module in the concentrate compartment. To maintain a constant temperature, a thermostat (9) was placed in the tank. The evaluation of permeate mass versus time was measured by a balance (8). The voltage output of the balance was sent to a personal computer (7) that converted the signal into a flow rate and stored in disk files.

Chapter 3. Materials and Methods



1: Feed tank; 2: Pump; 3: Flowmeter; 4: Discharge valve; 5: Manometer; 6: Membrane module; 7: Computer; 8: Balance; 9: Thermostat

Figure 3.1 ND-2 UF experimental set-up

A schematic diagram of the batch pilot-scale MA-CO ultrafiltration unit operated in this study is shown in Figure 3.2. The unit equipped with industrial size spiral-wound ultrafiltration membrane modules placed in a stainless steel housing, feed and permeate tanks, feed sanitary centrifugal pump, recycle and permeate flow-meters etc. Three modules of industrial size spiral-wound ultrafiltration membrane can be used simultaneously, or individually. Pressure data were from pressure transducers located at the membrane inlet and outlet. The recycled retentate and the permeate flow rates were measured by variable section flowmeters.

Chapter 3. Materials and Methods



Figure 3.2 Schematic diagram of pilot-scale unit

3.2 Investigated Membranes

The experimental UF membranes in laboratory scale were produced in different companies included Mavibran FS and FF from Magyar Viscosa Corporation, Hungary; Celfa CMF DY and DS from Celfa Company, Switzerland; Filmtec FS, RC and ETNA from Dow Chemicals Membrane Group, Denmark and TS 6V 205 from Hoechst Company, Germany. Tables 3.1 and 3.2 show the physical and filtration properties of the membranes used. The membranes were chosen so that they would have different materials and cut-off values.

Membrane	Material ¹⁾	MWCO	Water Flux ²⁾	Max. Temp.
		[kD]	[l/m² h]	[°C]
TS 6V-205	PES	100	800	60
FP 055 A	PVDF	60-80	1 000	60
FS 202-09	PES	20	700	60

 Table 3.1
 Properties of UF membranes in ND-2 set-up

1: PES: polyethersulfone; PVDF: polyvinylidene fluoride.

2: Feed pressure 3 bar and temperature at 20°C.

 Table 3.2
 Properties of UF membranes applied in UTZ 944 membrane unit

Membrane	Manahanana	Mataria11)	MWCO	Water Flux ²⁾	Max. Temp.
Trademark	Memorane	Wraterial '	[kD]	[l/m² h]	[°C]
Mavibran	FS 102-05	PES	10	550	60
Mavibran	FS 202-09	PES	20	700	60
Mavibran	FF 20-K5	PVDF	20	500	60
Mavibran	FF 502-04	PVDF	60	1 000	60
Celfa	CMF-DY-010	PAN	10	250	45
Celfa	CMF-DY-040	PAN	40	700	45
Celfa	CMF-DS-040	PES	40	400	95
Celfa	CMF-DS-100	PES	100	800	95
Dow	FS 50PP	PVDF	50	300-700	60
Dow	FS 40PP	PVDF	100	300-800	60
Dow	RC 70PP	Cellulose ³⁾	10	150-250	60
Dow	ETNA 20A	Coating ⁴⁾	20	250-450	60

1: PES: polyethersulfone; PVDF: polyvinylidene fluoride; PAN: polyacrylonitrile.

- 2: Feed pressure 3 bar and temperature at 20°C.
- 3: Regenerated cellulose.
- 4: Coated, hydrophilic.

Generally, fresh pieces of membrane were used with TZA 944 Test Rig test. For the experiments with ND-2 set-up, membranes were reused after each experiment, following an elaborate cleaning procedure. After each experiment, the emulsified oil/water solution was removed from the feed tank and pipelines. Then fresh tap water was placed into the feed tank and circulated through the membrane in 30 minutes. After water circulation detergent solution, micellar solution with sodium dodecyl

sulfate, n-pentanol and water were prepared in the feed tank and recycled through the membrane for 30 min. At the end of cleaning, tap water was fed into the feed tank, and the residual cleaning agent of the membrane was purged into the tank. Finally, distilled water was circulated through the membrane for 60 min, and permeate flux of pure water was determined. The cleaning procedure was repeated until the permeate flux of the cleaned membrane was similar to that of the virgin membrane (96-99%).

The pilot-scale unit was operated with three industrial spiral-wound membrane modules, denoted as TS-102, TS-202 and TS 502 manufactured by Zoltek Magyar Viscosa Corporation. TS-102, TS-202 and TS 502 membranes had a MWCO of 6-8, 15-20 and 55-65 kD, respectively. Both TS-102 and TS-202 membranes were constructed of PES (polyethersulfone). TS 502 membrane was made of PVDF (polyvinylidene fluoride) material. Each membranes had a transfer area of 5 m^2 , and their characteristics are given in Table 3.3.

Membrane type	Membrane area	MWCO	Min. PWF*	Max. Pressure	Temperature	pH-ran ge
	[111]		[1/111 11]	[Uai]		
FS 10 (PES,TS-102)	5	6-8	1 000	8	60	1-13
FS 20 (PES,TS-202)	5	15-20	1 200	6	60	1-13
FF50 (PVDF,TS-502)	5	55-65	1 300	6	60	1-13

 Table 3.3
 Properties of industrial spiral wound modules used in the pilot scale

* pure water flux.

Before each experiments the standardization was measured with pure distilled water to give a reference (recycle flow rate: 3 000 l/h; feed pressure: 4 bar; temperature: 20° C; time: 1 hour). The permeate volume was measured in function of time.

3.3 Characteristics of the Applied Emulsions

For the laboratory experiments, the stable oil-in-water emulsion, HW-1, was obtained from Anhui Petrochemical Company, and was used without further purification. It contains engine oil, surfactants and deionized water. Two different concentrations of the oil-in-water emulsion were prepared in batches of 10 liters. Oil-in-water emulsions with oil concentration of 0.5 and 5 vol. % were used as feed solutions to the cross-flow filtration cell to foul the membranes. The flow rate of the feed oil-in-water emulsion, operating pressure and temperature were fixed at 200 l/h, 3 bar and 40 °C, respectively, for the duration of the experiments unless stated otherwise. The permeate flux (l/m²h) of the membrane was measured by voluming the permeate conversed from the weight by the computer automatically. The emulsions produced were quite stable with respect to coalescence. Viscosity (η) of feed oil-in-water emulsion at 20°C was: $\eta = 1.381 \times 10^{-3}$ N s/m² at 5% feed concentration; $\eta = 1.139 \times 10^{-3}$ N s/m² at 0.5% feed concentration. The viscosity of deionized water was 1.005 × 10⁻³ N s/m² at 20°C.

For the pilot-scale operation, the stable oil-in-water emulsion (c.a. 300 liters) was provided by Zoltek Magyar Viscosa Corporation and prepared by dispersing the engine oil with emulsifier in deionized water. The oil concentration in the feed emulsion was 0.5 vol. %. The emulsion produced was quite stable with respect to coalescence. The viscosity of feed emulsion at 20°C was $\eta = 1.147 \times 10^{-3} \text{ N s/m}^2$. Tests were carried out at fixed temperature and transmembrane pressure. The experimental conditions were as follows: feed flow rate was 5 000 l/h, feed pressure 3 bar, temperature 40°C unless stated otherwise. The experimental selection criteria were established to facilitate performance of the pilot study in a number of different ways. The transmembrane pressure and temperature operation criterion was set to reduce the risk of membrane integrity problems or irreversible fouling.

3.4 Methods of Measurements, Analysis and Elaboration

Transmembrane pressure was measured by manometer in the apparatus. The temperature of feed emulsion was monitored by thermocouple meter and controlled by heat exchanger automatically. The permeate flux was determined by volume from the permeate output.

The methods of COD and oil concentration measurements were carried out according to Standard Method for the Examination of Water and Wastewater. The COD values (mg/l) were measured using the Hungarian National Standard MSZ 260/16-82 and National Standard of China GB 11914-89 in the individual experiments respectively. The title of both measurement methods was Potassium Dichromate Method. Its principle is based on the amount of standard potassium dichromate solution consumed to oxidized the reduction matter in the sample water in the presence of strong acid.

The excessive potassium dichromate was measured with the help of titration of standard ammonium ferrous sulphate solution. The calculation equation was shown as follows:

$$COD_{Cr}(O_2, mg/l) = \frac{8 \times c(V_1 - V_0)}{V_W} \times 10^3$$

where c -- concentration of standard ammonium ferrous sulphate solution, mol/l;

- V_1 -- volume of standard ammonium ferrous sulphate solution used to titer sample water, ml;
- V_0 -- volume of standard ammonium ferrous sulphate solution used to titer pure water, ml;
- V_W -- volume of sample water, ml
- 8 -- molar weight of half oxygen (g/mol)

The oil concentrations (mg/l) were determined according to the Hungarian National Standard MSZ 260/22-74 and National Standard of China GB 12153-89 using Determination of Mineral Oil – Ultraviolet Spectrophotometry respectively. Its measurement principle is based on spectrophotometric analysis, because hydrocarbon has its specific absorption peaks in the ultraviolet range. Different concentrations of oily solution have various transmitting light performances. Thus a standard spectrophotometric calibrations curve can be plotted according to the transmitting light ability under different concentration of standard oily solution. The oil concentrations in the feed and permeate solutions were analyzed using UV spectrophotometer type SPECTROMOM 195 in Viscosa and UV spectrophotometer type SHIMADZU UV260 in China respectively. The calculation equation can be seen as follows:

$$Oil \ concentration (mg/l) = \frac{m \times 1000}{V_W}$$

where *m* -- oil concentration based on the standard spectrophotometric calibrations curve, mg;

 V_W -- volume of sample water, ml.

The oil rejection coefficient (*R*) is defined as [TANSEL et al. 2001]:

$$R = \left(1 - \frac{C_P}{C_R}\right) \times 100\% \tag{3.1}$$

where *R* -- oil rejection coefficient, %;

 C_P -- the observed oil component concentration in permeate, mg/l;

 C_R -- the observed oil component concentration in retentate, mg/l.

The topography of membrane surface and compositions of fouling substances were analyzed with the help of Hitachi S-570 SEM and MAGNA-750 FT-IR with OMNIC data analysis system, respectively. The details can be seen in Chapter 4.2.

3.5 Methods of Mathematical Modelling and Data

Acquisition

All of the pressures (inlet, outlet and permeate) were measured using pressure gauges. The permeate and retentate flows were measured using the flowmeters equipped with conversion modules. The temperature was also recorded, using an electronic temperature probe connected to a thermistor. The flow and pressure transducers generated voltage signals that could be read and recorded by a computerized data acquisition system.

The pressure, temperature and permeate flux were continuously logged onto a Legend computer by an instrumentation and analysis program called LEASQ-Memb. These operation parameters were recorded in time. This program was configured in such a way as to control the operation of the ultrafiltration system as designed originally. During the filtration runs, the computer calibrated and stored its input in a specified file. The stored data was later analyzed using Microsoft Excel 97 and then graphed using Origin 4.0 and Sigmaplot 5.0.

Chapter 4

Results and Discussion

According to the experiments the processing of oil-in-water emulsions with conventional ultrafiltration membranes leads to concentration polarization, rapid membrane fouling and flux decline, and is generally uneconomic because of those problems. Therefore, the major hurdles to overcome in the development of practical industrial units are concentration polarization and membrane fouling. The factors which affect the concentration polarization and membrane fouling include the following three broad categories [THOMAS et al. 2000]:

Membrane type: the membrane material, pore size and distribution, and module configuration;

Operating conditions: factors such as pressure, temperature, cross-flow velocity and turbulence;

Solution characteristics: the nature of both solvent and solute, concentration and nature of the bulk fluid.

Although there have been many models to predict the effects of concentration polarization and membrane fouling presented by lots of researchers, among these results some are too complicated to have their values in practical application, and some introduce many boundary conditions.

This chapter discusses firstly the effects of different types of membrane (material, pore size and distribution, molecular weight cut off), feed oil concentration, transmembrane pressure, temperature in feed and other factors which influence the permeate flux, oil rejection and chemical oxygen demand (COD) in permeate. Then pilot-scale ultrafiltration experimental results are studied and compared with previous ones in a laboratory scale. The recovery performance of ultrafiltration membrane using different cleaning procedures is also compared and discussed. Finally, according to the above experimental results a model for estimating the gel concentration at the membrane surface and a mathematical model for membrane fouling were presented and identified. In case of our published results the sources are systematically mentioned in this chapter.

4.1 Influence of Membrane Nature and Operation Parameters on Filtration Characteristics

4.1.1 Effect of membrane nature

4.1.1.1 Effect of membrane material

The interfacial property of membrane material and porous structure on the asymmetrical membrane surfaces are two important factors that influence the membrane separation [HU et al. 1996a]. The difficulty with emulsion is that after longer working the oil is accumulated at the membrane surface and may form a continuous layer which is usually named concentration polarization. The controlling mechanism for oil-in-water emulsion separation by UF is gel polarization [HU et al. 1996b].

The UF membrane studies have been focusing on the selection of membrane proper material and the preparation of membrane. The different membrane materials have different critical surface tensions and wettabilities. The preparation of membrane determines the MWCO, pore size and its distribution and so on.

Permeate flux is an important parameter to characterize membrane separation efficiency [WU et al. 1999]. With the development of polymer material science and technology, many kinds of polymer membranes have been invented or improved in order to increase permeate flux [ZAIDI et al. 1992]. In the present study, the effects of different membrane materials on the average permeate flux are shown in Table 4.1.1. It can be found that the permeate flux of hydrophilic membrane (Celfa PAN) with the same nominal MWCO is much higher than that of hydrophobic membrane (Celfa PES) either at feed concentration of 0.5% or at 5%.

For an actual rejection and feed oil concentrations the decline in membrane permeate flux over a time period (minutes to days) is often accompanied by an increase in oil rejection, is attributable to a variety of mechanisms known as fouling. Fouling can be expressed in terms of the resistance to permeate flux observed at each stage of operation relative to the resistance of the clean membrane. PAN with hydrophilic group (–CN) has high permeate flux and high mechanical strength, as it was published [HU et al. 1996b]. With the same nominal MWCO, 40 KD, the permeate flux of PAN (CMF-DY-040) is much higher than that of hydrophobic PES (CMF-DS-040) either at feed concentration of 0.5% or at 5%, as shown in Figure 4.1.1



Figure 4.1.1 Permeate flux as a function of time as two different membrane materials with the same MWCO (40 kD) at feed oil concentration 0.5%

Effect of membrane material on oil rejection and COD are shown in Tables 4.1.2 and 4.1.3. The rejection coefficients of Celfa and Dow membranes are more than 99%; the rejection coefficients of Mavibran membranes are about 98-99%. At higher oil concentration, Celfa's COD values are about 1 000 mg/l, Dow 2 000 mg/l; Mavibran 1 000--2 000 mg/l. At lower oil concentration the average COD values of Celfa membranes are less than 150 mg/l, the COD values of Mavibran and Dow membranes are about 200 mg/l. These results show that at higher feed concentration the examined membranes have higher rejection than that at lower feed concentration. Meanwhile Celfa CMF membranes have always higher rejection and lower COD, compared with other membranes. The permeate containing less than 10 ppm oil could be used as cleaning water or discharged to public sewers [HU et al. 1996a].

Membrane	Membrane	Material	MWCO	Permeate flux ^{a)}	Permeate flux ^{b)}
Trademark			[kD]	$[l/m^2h]$	$[l/m^2h]$
Mavibran	FS 102-05	PES	10	153.2	112.4
Mavibran	FS 202-09	PES	20	243.7	107.1
Mavibran	FF 20-K5	PVDF	20	229.8	74.0
Mavibran	FF 502-04	PVDF	60	246.4	123.2
Celfa	CMF-DY-010	PAN	10	177.9	81.5
Celfa	CMF-DY-040	PAN	40	300.8	91.7
Celfa	CMF-DS-040	PES	40	138.2	55.6
Celfa	CMF-DS-100	PES	100	296.4	81.3
Dow	FS 50PP	PVDF	50	105.7	72.9
Dow	FS 40PP	PVDF	100	185.1	88.2
Dow	RC 70PP	Cellulose	10	161.6	76.1
Dow	ETNA 20A	Coating	20	157.7	70.7

 Table 4.1.1
 Effects of different membranes on permeate flux [HU et al. 1996b]

a): Feed oil concentration 0.5%; b): Feed oil concentration 5%.

Table 4.1.2	Oil rejection of differen	t membranes [HU et al. 1990	5b]
-------------	---------------------------	---------------	----------------	-----

Membrane	Membrane	Material	MWCO	Oil rejection	Oil rejection
Trademark			[kD]	$R, [\%]^{a)}$	$R, [\%]^{b)}$
Mavibran	FS 102-05	PES	10	99.90	99.99
Mavibran	FS 202-09	PES	20	98.65	99.97
Mavibran	FF 20-K5	PVDF	20	98.65	99.96
Mavibran	FF 502-04	PVDF	60	99.99	99.12
Celfa	CMF-DY-010	PAN	10	99.95	99.99
Celfa	CMF-DY-040	PAN	40	99.28	99.99
Celfa	CMF-DS-040	PES	40	99.88	99.99
Celfa	CMF-DS-100	PES	100	99.97	99.99
Dow	FS 50PP	PVDF	50	99.71	99.83
Dow	FS 40PP	PVDF	100	99.40	99.94
Dow	RC 70PP	Cellulose	10	99.97	99.99
Dow	ETNA 20A	Coating	20	99.95	99.83

a): Feed oil concentration 0.5%; b): Feed oil concentration 5%.

Membrane	Membrane	Material	MWCO	Oil concn.	Oil concn.	COD	COD
Trademark			[kD]	$[mg/l]^{a)}$	$[mg/l]^{b)}$	$\left[mg/l \right]^{a)}$	$\left[mg/l \right]^{b)}$
Mavibran	FS 102-05	PES	10	10	0.0	140	860
Mavibran	FS 202-09	PES	20	52	50	220	1 850
Mavibran	FF 20-K5	PVDF	20	52	60	220	2 300
Mavibran	FF 502-04	PVDF	60	1.5	11	170	1 200
Celfa	CMF-DY-010	PAN	10	5.5	0.0	120	1 100
Celfa	CMF-DY-040	PAN	40	46	5	155	1 000
Celfa	CMF-DS-100	PES	40	2.0	0.0	140	730
Celfa	CMF-DS-040	PES	100	13.3	7.0	135	560
Dow	FS 50PP	PVDF	50	14.5	83.8	190	1 600
Dow	FS 40PP	PVDF	100	29.8	29.5	240	1 500
Dow	RC 70PP	Cellulose	10	5.0	16	250	1 950
Dow	ETNA 20A	Coating	20	9.0	36	210	2 1 5 0

 Table 4.1.3
 Oil concentration and COD in permeate [HU et al. 1996b]

a): Feed oil concentration 0.5%; b): Feed oil concentration 5%.

4.1.1.2 Effects of MWCO and pore size of membrane

Flux reduction due to membrane fouling has to be distinguished from that concentration polarization by its irreversibility. Oil accumulation at the membrane undergoes physicochemical interactions with the membrane and with itself and is thus rendered immune to the mediating effects of diffusive mass transfer or particle back-transport. Figures 4.1.2, 4.1.3 and 4.1.4 summarized the effects of MWCO of PES membrane on permeate flux, COD in the permeated water and rejection coefficient, respectively. These results indicated that the permeate fluxes with a feed concentration of 0.5% are higher than that with a feed concentration of 5%. The higher the oil concentration in feed emulsion, the greater the accumulation of oil drops on the membrane surface. That causes the lower permeate flux and higher COD. The COD and oil rejections of PES membrane with MWCO of 20 kD can not attain the expected results, especially for 0.5% emulsion, although the permeate flux is rather high. For the PES membrane with 100 kD, its separation efficiency for 0.5% emulsion is obviously much better than that of other membranes with lower MWCO. The PES membrane with 10 kD and small pore size gets a satisfied results, especially for 5% emulsion.



Figure 4.1.2 Permeate flux on PES membranes with different MWCO



Figure 4.1.3 Effect of MWCO of PES membrane on COD in permeate



Figure 4.1.4 Oil rejection of PES membranes with different MWCO

Table 4.1.4 shows the permeate flux, COD and oil concentration in permeate of CMF-UF membranes with different MWCO at variable feed oil concentrations.

 Table 4.1.4
 Separation behaviours of CMF-membranes with different MWCO

Manahanana	Flux ^{a)}	Flux ^{b)}	COD ^{a)} *	COD ^{b)} *	Oil ^{a)} **	Oil ^{b)} **
Memorane	[l/m² h]	[l/m² h]	[mg/l]	[mg/l]	[mg/l]	[mg/l]
DY-040	300.8	91.7	155	1000	46	5
DY-010	177.9	81.5	120	1100	5.5	0
DS-040	138.2	55.6	135	560	13.3	7
DS-100	296.4	81.3	140	730	2	0

a): Feed oil concentration 0.5%; b): Feed oil concentration 5%;

COD*: COD in permeate; Oil**: Oil concentration in permeate.

At lower feed oil concentration MWCO is a dominative factor. For PAN membrane CMF-DY-040 with 40 kD and medium pore size, the oil concentration in permeate water from 0.5% emulsion can not attain the direct dischargable standard. CMF-DY-010 (PAN) with 10 kD and small pore size can remove water from 0.5 and 5% emulsions, although the permeability is lower. CMF-DS-100 (PES) with 100 kD

and big pore size is superior to CMF-DS-040 with medium pore size (PES) in permeate flux, COD and oil rejection for 0.5% and 5% emulsions. In addition, the low feed oil concentration may lead to low COD. Rejected oil accumulates near the membrane will tend to mitigate increased retention of emulsified oil with reduced membrane pore size: as oil accumulates near the membrane, the membrane may eventually become oil-wet, causing some drops to coalesce into the oil-wet layer and pass directly through membrane pores. In this case, the concentration of oil in the membrane permeate may be enriched relative to the feed concentration [HU et al. 1995, VATAI et al. 1997, MARCHESE et al. 2000].

4.1.2 Effect of feed oil concentration

In actual oily waste water treatment processes oil concentration in emulsion often changes because of different input situations. Generally the higher the feed oil concentration in emulsion is, the lower permeate flux is produced. Table 4.1.1 also testifies that at lower feed concentration, the permeate flux is higher. The feed concentration has a strong influence on the size of oil droplet and its distribution [LIPP et al. 1988]. Therefore the feed oil concentration has a direct influence on adsorption of oil (fouling). Fouling is mainly due to adsorption of oil on the membrane structure, which modifies the critical surface tension and the wettability, as well as the effective pore diameter, resulting in reduced membrane permeability [LEE et al. 1984]. The high oil concentration in feed increases the oil adsorption and causes easily great resistance for permeating water. The different membranes have different critical surface tension and wettability.

Figures 4.1.2, 4.1.3 and 4.1.4 compare the effect of feed oil concentration on permeate flux. As for Mavibran membranes, only the permeate flux of FS 102-05 membrane changes slightly with a variation in the feed oil concentration. The others change obviously, and the permeate flux decreases with the operating time. It expresses that the permeate capacity of Mavibran products is influenced easily by concentration polarization and fouling. As for CMF and Dow membranes the curves of permeate flux via time are smooth, especially for Celfa DY-010 and Celfa DS-040, on the contrary to Celfa DY-040 and Celfa DS-100. The permeability of Dow FS 50PP is less affected by feed oil concentration.

Investigating the effects of feed oil concentration on COD and oil rejection it was found out that the oil rejections at both feed concentrations are very high (over 98.5%), as shown in Tables 4.1.2 & 4.1.3. The separation efficiency is obvious. In addition, a lower feed oil concentration may lead to lower COD. For the emulsion
with oil concentration of 5% the permeate ultrafiltered by Celfa membranes can be discharged directly (oil concentration in permeate is less than 10 mg/l). In cases of Mavibran and Dow membranes the permeated water must be treated further and then can be discharged directly, except of Mavibran FS 102-05. For the emulsion with oil concentration of 0.5%, the permeate can discharge directly as using Mavibran FS 102-05, FF 502-04, Celfa CMF-DY-010, CMF-DS-100, Dow ETNA 20A and RC 70PP. The permeate treated by other membranes can not attain the standard of direct discharge.

4.1.3 Effect of transmembrane pressure

Transmembrane pressure has a significant effect on the permeate flux during membrane operation. The operating pressure for UF is usually about 0.1-0.7 MPa. In this study, the experiments were run at an emulsion concentration of 0.5 and 5 vol.% and influent feed velocity of 0.9 m/s unless stated elsewhere. Experiments were performed at initial transmembrane pressures of 1, 2, 3, 4, 5 and 6 bar to evaluate the effect of transmembrane pressure. The effects of operating pressure for the selected membranes on permeate flux at two feed concentrations are shown in Figures 4.1.5, 4.1.6 and 4.1.7.

Taking Figures 4.1.5, 4.1.6 and 4.1.7 together, some common phenomena for the tested membranes can be observed:

(1) At a lower emulsion concentration three kinds of UF membrane have higher abilities to permeate water. At each experimental temperature the flux increased approximately with an increase in the operating pressure, especially in case of the PES membrane. It shows that the effect of concentration polarization or gel layer is not obvious.

(2) At a higher emulsion concentration the effect of the operating pressure on the flux becomes complicated. At a lower pressure, the permeate flux is directly proportional to the transmembrane pressure. When the operation pressure is over a critical value, the flux is not influenced by the operating pressure and reaches a plateau. This kind of variation tendency is the same on each membrane. It is estimated that the membrane fouling and concentration polarization become more serious with increasing the operating pressure at higher emulsion concentration.

(3) The critical pressure for different membrane is variable, which depends on the capillary pressure. When transmembrane pressure is over the capillary pressure, oil can easily pass and deposit in the membrane pores thus decreasing membrane pore

size and increasing membrane fouling [WILLIAMS and WAKEMAN 2000]. At higher operating pressure the effect of membrane fouling is more important than the effect of pressure. The critical pressures for FS 202-09 and FP 055A membranes are about 2 bar, whereas it is about 3 bar for TS 6V membrane.

(4) The fouling resistance of FVDF (FP 055A) membrane is lower than that of PES membrane (FS 202-09 and TS 6V-205) at lower feed concentration (see Figures 4.1.5 (a), 4.1.6 (a) and 4.1.7 (a)), in which the flux is almost not influenced by higher transmembrane pressure for PES membrane.

(5) The effect of pressure on the flux is controlled by the temperature for PES membranes (FS and TS 6V). At different temperatures the extent of pressure influence is different.



Figure 4.1.5 (a) Permeate flux as a function of transmembrane pressure for FP 055A at feed oil concentration of 0.5%



Figure 4.1.5 (b) Permeate flux as a function of transmembrane pressure for FP 055A at feed oil concentration of 5%



Figure 4.1.6 (a) Permeate flux as a function of transmembrane pressure for FS 202-09 membrane at feed oil concentration of 0.5%



Figure 4.1.6 (b) Permeate flux as a function of transmembrane pressure for FS 202-09 membrane at feed oil concentration of 5%



Figure 4.1.7 Permeate flux as a function of transmembrane pressure for TS 6V-205 membrane at feed oil concentration of 0.5%



Figure 4.1.7 Permeate flux as a function of transmembrane pressure for TS 6V-205 membrane at feed oil concentration of 5%

As well known, the transmembrane pressure is applied to overcome the membrane resistance and the pressure drop of the fluid on the membrane surface [WANG 1984]. The effect of transmembrane pressure depends on the membrane property and the behaviors of the boundary layer. It should be paid more attention to air bubble in permeate as treating an emulsion under a higher operating pressure. Because there are some surfactants in the feed emulsion, the air bubble can pass through the membrane and enter into permeate under a higher operating pressure. The air bubble may influence greatly the mass transfer coefficient and may lead to variation of permeate flux. The further study on the effect of air bubble is necessary for ultrafiltration of oily emulsion.

The experimental results of COD and oil concentration in permeate under their critical pressures at 40° C are presented in Table 4.1.5. It shows that the three investigated membranes have satisfactory results at low feed concentration (0.5 %): the permeate from both membranes of FS 202-09 and TS 6V-205 can achieve the level to discharge according to the National Standard of China (the oil concentration in permeate is <10 mg/l, COD <100 mg/l). At high feed concentration (5 %) their COD values increase, whereas their oil concentrations are lower.

When the pressure increased to 4 bar, the COD values and oil concentrations in the permeate were increased more rapidly, as shown in Table 4.1.6. Therefore these membranes are not suitable to treat the selected emulsion with a high feed concentration at high transmembrane pressure. This is because the membrane fouling (loss of permeability) can be negligible at lower operating pressure, the membrane fouling, however, becomes more important as the pressure is over a critical pressure. The reason of this phenomenon seems to be that concentration polarization gives a higher probability for the oil drops to contact the membrane pores, and at some pores the operating pressure exceeds the capillary pressure so that the oil drops can be deformed and enter the membrane structure [LEE et al. 1984, SEIFERT and STEINER 1996].

 Table 4.1.5
 Oil concentration and COD in permeate

Membrane	COD	COD	Oil concentration	Oil concentration
	$[mg/l]^{a)}$	$[mg/l]^{b)}$	$[mg/l]^{a)}$	$[mg/l]^{b)}$
TS 6V-205 (3 bar)	62	124	2.0	5.0
FP 055 A (2 bar)	158	140	19	8.0
FS 202-09 (2 bar)	80	160	7.0	9.0

a): Feed oil concentration 0.5%; b): Feed oil concentration 5%.

 Table 4.1.6
 Oil concentration and COD in permeate at 4 bar

Membrane	COD ^{a)}	COD ^{b)}	Oil concentration ^{a)}	Oil concentration ^{b)}
	[mg/l]	[mg/l]	[mg/l]	[mg/l]
TS 6V-205	290	1,870	26	54
FP 055 A	435	2,560	65	78
FS 202-09	376	2,950	42	126

a): Feed oil concentration 0.5%; b): Feed oil concentration 5%.

4.1.4 Effect of operating temperature

In general, the permeate flux increased with an increase in the temperature. The higher temperature may lead to an enhancement of the activity of water molecules and a decline of the emulsion viscosity, therefore the permeate flux increases. The

increase of the temperature from 20 to 60° C caused 20-100 % increase in the permeate flux (Figure 4.1.8). The temperature coefficients are about $0.0047/1^{\circ}$ C and $0.008/1^{\circ}$ C at the feed emulsion concentrations of 0.5% and 5%, respectively (It means that the permeate flux increased subsequently by about 0.47% and 0.8% respectively, as the temperature increased 1°C). Too high temperature may, however, lead to the damage of the membrane, to an increase in the resistance of the permeation and a decrease in the flux.



Figure 4.1.8 (a) Permeate flux as a function of temperature for different membrane at pressure 3 bar and feed oil concentration of 0.5%



Figure 4.1.8 (b) Permeate flux as a function of temperature for different membrane at pressure 3 bar and feed oil concentration of 5%

Comparing the experimental data in Figure 4.1.8 (a) and (b) it is found that the tested membranes have similar permeate flux of water at a higher feed emulsion concentration. At a lower emulsion concentration PVDF membrane has a super-ability in the permeate flux of water. Thus, FP 055A membrane is especially suitable to treat oil-in-water with lower concentration. In addition, FES membrane (FS 202-09 and TS 6V 205) may have a stronger ability to resist concentration polarization than PVDF (FP 055A), because there is a greater difference for FP 055A in the permeating flux as the emulsion concentration is different.

The selection of the operation temperature is based on the physicochemical property and bio-stability of the fluid. Membrane should be operated below the permitted temperature of the membrane and the treated fluid. Because higher temperature can reduce the viscosity of the fluid and increase the efficiency of mass transfer, an increase in the feed temperature can improve the permeate flux. The relation of temperature and diffusion coefficient can be described as follows [SHAO 2000]:

$$\eta D/T = \text{constant}$$
 (4.1.1)

The higher the temperature (*T*) and the lower the viscosity (η), the greater is the diffusion coefficient (*D*). On the other hand, however, too high temperature may make the membrane deformed and compressed, and decreases the flux, as mentioned before. From the experimental results, it can be found that the effect of temperature is more obvious at higher feed concentration than at lower one.

4.1.5 Effect of cross flow velocity

Cross-flow velocity is an important operation parameter for UF. High flow velocity is used to reduce cake formation and/or concentration polarization. The convection to and diffusion away from the membrane surface determine the rate of build-up of fouling. The rate of convection to the membrane is a function of the permeate flux, and the diffusion away is linked to the degree of turbulence. An increase in the cross-flow velocity will directly increase the degree of physical scouring at the surface and improve back-transport into the bulk solution.

Velocities of 0.5, 0.9 and 1.5 m/s were investigated with the operating conditions of 3 bar transmembrane pressure and 5 % emulsion concentration. The operating velocities range, correspond to Reynolds numbers of 3 500, 6 300 and 10 500 is found in the turbulence region. The effect of influent velocities on flux is shown in Figure 4.1.9. It can be suggested that the higher the cross-flow velocities applied to the membrane surface, the higher the flux volume observed. This can be explained by the high flow rate which generates high shear rates at the membrane surface. However, the increment of flux becomes smaller with an increase in the flow velocity. It shows that increasing the cross-flow velocity does not always lead to an improvement in the permeate flux as the state of dispersion of the oil droplets and the size distribution also affects the flux. At the same time, there is an economical limit of the increase of cross-flow velocity. The selection of flow velocity depends on the membrane module and feed concentration [WILLIAMS and WAKEMAN 2000].



Figure 4.1.9 Permeate flux of FP 055A membrane as a function of cross-flow velocity at feed concentration of 5%

4.2 Scale up: Evaluation of Pilot Scale Membrane Modules

When assessing the application of membranes to a separation problem, pilot work is usually required. For a new plant a strategy for fouling management may include the design of a pretreatment system for the feed, careful selection of the membrane module and its housing, system design and the specification of operating conditions and cleaning procedures. For an installed plant the options for fouling abatement become more limited, and are focused on the physical and chemical methods, either in pretreatment, design or operation etc [MARCHESE et al. 2000].

It was reported that the oil concentration in the permeate water by UF would generally be less than 10 to 50 ppm according to the experimental results [HU et al. 1996a]. The permeated water containing less than 10 ppm oil can be used as cleaning water or discharged to public sewers. The laboratory results, however, are not sometimes consistent with those of practical production scale. It is necessary to study the experimental results in a pilot unit scale. This investigation deals with the separation behaviour of oil-in-water emulsion by UF membrane in an industrial unit.

4.2.1 Influences of membrane nature

Compared the results in Figures 4.2.1 and 4.2.2 it can be found that the permeate flux of TS-202 with a higher MWCO is much higher than that of TS-102, although both of the membrane material are PES. On the other hand, the PVDF membrane is more suitable for treating oil-in-water emulsion than PES membrane due to high permeate flux, as shown in Figure 4.2.3.



Figure 4.2.1 Permeate flux as a function of transmembrane pressure for TS-102 membrane in pilot scale unit at feed oil concentration 0.5% and temperature 40°C



Figure 4.2.2 Permeate flux as a function of transmembrane pressure for TS-202 membrane in pilot scale unit at feed oil concentration 0.5% and temperature 40° C



Figure 4.2.3 Comparison of flux with time for different membranes in a pilot scale at feed pressure 3 bar, temperature 40° C and 100 l/min recirculation flow rate

 Table 4.2.1
 Comparison of laboratory and pilot plant experiments

Membrane	Туре	Flux [l/m ² h]	Oil* [mg/l]	COD* [mg/l]	Oil rejection [%]	COD rejection [%]
FS 10 (PES,TS-102)	Lab.	153.2	10	140	99.9	98.9
	Pilot	77.7	21.4	599.5	99.6	95.2
FS 20 (PES,TS-202)	Lab.	243.7	52	220	98.6	98.2
	Pilot	128.2	15.2	545	99.7	95.6
FF50 (PVDF,TS-502)	Lab.	246.4	1.5	170	99.9	98.6
	Pilot	196.2	16.5	299	99.7	97.0

*: in the permeate

The pilot scale conditions were as follows: feed pressure: 3 bar, feed temperature: 40° C. Feed emulsion with oil concentration 0.5 vol. %.

Table 4.2.1 presents the results on laboratory and pilot equipment. The change of permeate flux in function of time in pilot was similar to that in laboratory scale. The permeate flux of the same membrane in laboratory was higher than that in pilot scale because of the difference in the hydrodynamics of the two modules. The oil rejection was about 99% both in laboratory and in pilot. The COD rejection both in laboratory and in pilot scale were over 95%.

According to these results the UF membranes measured could be used successfully in practical production to treat oil-in-water emulsion.

4.2.2 Influence of pressure on wettability

For the oil drop to move through the pore, surface tension effects associated with the advancing (in the pore) and lagging (on the membrane surface) oil-wet interfaces must be overcome [TANSEL et al. 2001]. Thus a tighter membrane should require higher transmembrane pressures to initiate oil drop movement through membrane pores if all other factors are equal. According to Figures 4.2.1 and 4.2.2 it was shown that the flux increased with the transmembrane pressure, using TS-102 and TS-202 membranes. The permeate flux is almost proportional to the transmembrane pressure because of lower feed concentration. This tendency was approximately consistent with the laboratory results discussed in the section 4.1.3. In particular, higher transmembrane pressures will tend to increase permeate flux and the flow of oil drops to the membrane pressures can increase oil passage by forcing drops through membrane pores, as well as increasing the flux of drops to the membrane surface. It can be further explained that the pressure *P* required to force the oil flow through a membrane pore of diameter D_m is given by the following equation [LIPP et al. 1988]:

$$P = \frac{4\gamma\cos\theta}{D_m} \tag{4.2.1}$$

where γ = interfacial tension between the oil and the solvated surface, θ = the contact angle. Oil droplets collected upon the pores will tend to coalesce and spread over the surface of the membrane, causing fouling. Each membrane has a specific pore size distribution. Clearly, when the oil front reaches a pore which satisfies the equation above, oil break-through will result. It follows that for the same membrane the oil rejection will decrease with increasing pressure. Conversely for the same pressure the greater the pore size, the lower will be the oil rejection coefficient.

4.2.3 Influence of flow velocity

The flow velocity influences directly the separation behaviour. It has been verified experimentally that a higher cross-flow velocity (or higher mass transfer coefficient) will result in a higher rejection coefficient, according to the concentration polarization theory, for oil-in-water emulsion in an UF system [LOEB and SOURIRAJAN 1964]. Thus the higher oil rejection in this case was probably due to the higher cross-flow velocity used. However, the higher flow velocity leads not only to a higher pressure drop and consumption of energy, but also a decline in the separation performance [SHAO 2000]. If the flow velocity is slow, it is easy to result in concentration polarization, which affects the permeability. Figures 4.2.1 and 4.2.2 illustrate also the effect of flow velocity (Q = 50, 100, 150, 200, 250 l/min) determined over the 1-5 bar range of transmembrane pressure for TS-102 and TS-202 in a pilot scale. It is found that the highest flux is not caused by the highest flow velocity either in FS-102 or FS-202. The selection of flow velocity depends on the feed concentration, membrane module and others.

4.2.4 Permeate flux change in time

Under a given transmembrane pressure, the more the number of oil droplets of appropriate size is near the membrane surface, the greater the passage of oil is across the membrane. Oil drop accumulation at the membrane surface will be enhanced as concentration polarization becomes more important. In Figure 4.2.3 the effect of permeate flux was determined in function of time for different membranes in a pilot scale. It shows that the permeate flux decreases with time and tends to form a relative by stable value. This is because the concentration polarization and fouling reach a dynamic equilibrium.

4.3 Analysis of Membrane Fouling of UF Membrane for Oil-in-Water Emulsion

4.3.1 Membrane cleaning procedure

Flux decline due to concentration polarization and fouling is a serious problem in membrane filtration. An improvement of the filtration efficiency and a decrease of membrane fouling have been investigated by many membrane researchers. There are different methods to decrease fouling, such as backwash, vibration filtration, ultrasound wave, chemical cleaning etc. It is well known that cleaning of membrane is one of the effective ways to restore filtration ability. Fouled membranes are commonly rejuvenated by using cleaning-in-place (CIP) procedures. CIP involves shorter downtimes than cleaning-out-of-place (COP), and many membrane suppliers will recommend CIP protocols for their membranes. These may, or may not, involve external chemicals. For example, the techniques that may be employed include a periodic reversal in flow direction to prevent particulates from clogging the module inlet; periodic backflushing of the membrane by reverse flow of permeate (this can be effective for removing surface foulants from the membrane); and periodic reductions in feed pressure while maintaining a high cross-flow (this can help to control gel layer growth) [SHAO 2000, MULLER 1991, JONSSON and JOHANSEN 1989, SWART and JACOBS 1996, LI et al. 1998, MAHDI and SKOLD 1990, FANE and FELL 1987, HLAVACEK 1999]. Large-diameter tubular membranes can be cleaned mechanically using sponge balls [WILLIAMS and WAKEMAN 2000].

However, selection of membrane cleaning process depends on the characterization of membrane fouling, although proprietary cleaning solutions are available. The general information about types of cleaning solutions is given in Table 4.3.1. The choice of cleaning solution is determined not only by the foulant type, but also by the compatibility of the membrane with the solution at the cleaning temperature. Many cleaning solutions have a temporary adverse effect on membrane rejection, in addition to the sought-after effect of increased flux of permeate. An inferior rejection can be attributable to membrane swelling during contact with the cleaning solution; swelling of polysulfone membranes has been reported when using Ultrasil-10 cleaning solution [MULLER 1991]. It is remarkable that it was introduced the application of specific micellar cleaning solutions (microemulsion) for fouled membranes to restore their initial water permeability and their initial hydrophilic properties [BELKACEM et al. 1995]. The microemulsions can be used to effectively clean the membranes which

have been fouled with oily macroemulsions. As these solutions contain antifoam and anticorrosion products and a bactericide they are well suited to the industrial constraints. In addition, in some cases, for low macroemulsion concentrations, they can also have a preventive anti-fouling action.

Table 4.3.1 Examples of cleaning solutions and their applications [WILLIAMSand WAKEMAN 2000]

Type of cleaning solution	Effective against typical foulants
Mineral acids, sodium hexametaphosphate,	Salt precipitates, mineral scalants
polyacrylates, ethylenediaminetetra-acetic	
acid (EDTA)	
Sodium hydroxide-based cleaner, with or	Solubilising fats, proteins
without hypochlorite	
Enzyme cleaners based on proteases,	Used in specific instances at a neutral
amylases and glucanases	pH

It is reported that the relationships between membrane fouling and cleaning have been investigated in terms of flow conditions, transmembrane pressure, pH, membrane properties and cleaning agents using a stirred batch-cell and aqueous albumin solution [KIM et al. 1993]. Fouling was less at the pH extremes than at the isoelectric point for both retentive and partially permeable membranes. Membranes with partial permeability showed a greater tendency to foul and were less responsive to cleaning.

One of the objectives of this study concerns the analysis of membrane fouling of ultrafiltration membrane used for oil-in-water emulsion. The second aim is to evaluate the recovery permeability of membrane by various cleaning solutions to remove fouling. This is because oil-in-water emulsion is used in various industrial aspects: chemical, food, metal working etc. There are lots of surfactants, which are the substances occurring fouling. Different surfactant has variable wettability to ultrafiltration membrane.

4.3.1.1 Membrane cleaning experiments

The experimental apparatus for evaluation of recovery of membrane permeability was described in Figure 3.1. Three UF membranes, TS 6V-205, FS-202-09 and FP 055A were selected to evaluate their surface fouling and recovery of flux, were provided by Hoechst Company, Germany and Magyar Viscosa Corporation, Hungary, respectively. Their basic properties are shown in Table 4.3.2.

After the permeate flux reached a plateau in function of time, filtration was continued for another 30 min. Then a PWF (pure water flux) was performed on the fouled membrane to evaluate the degree of membrane fouling. The membrane was then cleaned by different cleaning solution, and another PWF was subsequently performed to determine the degree of restoration of permeate flux.

Membrane	Material ¹⁾	MWCO	Water Flux ²⁾	Max. Temp.
		[kD]	[l/m² h]	[°C]
TS 6V-205	PES	100	800	60
FP 055 A	PVDF	60-80	1 000	60
FS 202-09	PES	20	700	60

 Table 4.3.2
 Properties of UF membranes in ND-2 set-up

1: PES: polyethersulfone; PVDF: polyvinylidene fluoride;

2: Feed pressure 3 bar and temperature at 20°C.

The membrane cleaning procedure was as follows: After each experiment, the emulsified oil-in-water solution was removed from the feed tank and pipelines. Then fresh tap water was placed into the feed tank and circulated through the membrane. The membrane was physically cleaned for a total of 30 min by the retentate and permeate, which were recycled into the feed tank. At the conclusion of physical washing, the cleaning solution was prepared in the feed tank and recycled through the membrane. At the end of cleaning, tap water was fed into the feed tank, and the residual cleaning agent of the membrane was purged into the tank. Finally, distillate water was circulated through the membrane, and permeate flux was determined.

In this study two kinds of cleaning solutions were selected. One includes a micellar solution with a mixture of 1.9 wt.% sodium dodecyl sulfate, 3.7 wt.% n-pentanol and 94.4 wt.% water. Cleaning time was 30 minutes using this kind of detergent solution,

then it was followed by rinsing and operating with distilled water and by measuring the permeate flux under the pressure 3 bar at 20 $^{\circ}$ C.

Another cleaning solution includes 2% hydrochloric acid (HCl) aqueous solution, Aviation Gasoline 80 (Exxon Oil Company) and 2% sodium hydroxide (NaOH) aqueous solution respectively. After cleaned by the above physical method, the fouled membrane was immersed and filtrated orderly in three steps: firstly with 2% HCl aqueous solution in 10 min, then aviation gasoline in 10 min, and then with 2% NaOH aqueous solution in 10 minutes. Each cleaning step needs a 10 min filtration with deionized water. Finally the permeate flux was measured under the pressure of 3 bar at 20°C.

4.3.1.2 Analysis methods

The cleaning efficiency (ϕ) and recovery (ϕ) in Table 4.3.3 are defined by the following expressions [SHAO 2000]:

$$\varphi = \frac{J_a - J_b}{J_o - J_b} \times 100\%$$
(4.3.1)

and
$$\phi = \frac{J_a}{J_o} \times 100\%$$
(4.3.2)

where J_a is permeability after cleaning, J_b is permeability before cleaning, J_o is the original permeability of unused membrane.

The topography of membrane surface and compositions of fouling substances were analyzed with the help of Hitachi S-570 Scanning Electron Microscopy (SEM) and MAGNA-750 Fourier Transform Infrared (FT-IR) with OMNIC data analysis system, respectively. The membrane samples were frozen in liquid nitrogen and broken, and then dried and coated by a thin gold film before observing by SEM. The fouling matter powder can be obtained by scratching with a knife on the fouled membrane surface, and mixed deformed together with KBr. Finally the sample was sent to analyze by FT-IR.

4.3.2 Surface topography of fouled membrane

The pretreatment and cleaning of the membrane depend on the membrane form and the characterization of membrane fouling. The best way to identify the membrane fouling is to analyze the pollution substance by-dissecting the membrane units fouled [BELFER et al. 2000]. Usually, the fouling substance can be classified into inorganic, organic and bio-substance. In the actually used oil-in-water emulsion, inorganic substances were the chips from the machined metal surface and sands from the grinding wheel. The organic fouling matters are from the surfactants and engine oil. At the same time, the emulsions consist with surfactants and engine oil which are easy to be attacked by microbes and lead to the emulsion corruption, and lots of microbes are propagated in the fluids, especially in summer.

In order to investigate the composition and topography of the foulants on the membrane surface, infrared (IR) spectrum analyses were carried out by MAGNA-750 FT-IR spectrometer. Figures 4.3.1, 4.3.2 and 4.3.3 show the FT-IR spectra of substances on the different membrane surfaces before and after ultrafiltration, and their subtraction spectrum. Upon comparing the IR spectra above, it was found that the peaks at the 2954 cm⁻¹, 2854 cm-1 and 1464 cm⁻¹ are corresponding with alkyl adsorption bands which are the typical peaks of hydrocarbon. The amount of this kind of oily substance is higher obviously according to the peaks' magnitude. In addition to the oily matter, it was found that some impurities were remained on the membrane surface based on the IR spectra in the figures above.

At the same time in order to identify the analysis results from IR, scanning electron microscopy of the membrane surface after the oil-in-water emulsion runs was taken, as shown in Figures 4.3.4. On the membrane surface there are lots of white spots which were oil drops adsorbed on the membrane surface. The most foulants are oil droplets and surfactants under the present experimental conditions.



Figure 4.3.1 FT-IR spectra of membrane surface of FP 055A FP 055A-1 is unused membrane, FP 055A -2 is fouled membrane, the rest is the subtraction spectrum



Figure 4.3.2 FT-IR spectra of membrane surface of FS 202-09 FS 202-09-1 is unused membrane, FS 202-09-3 is fouled membrane, the rest is the subtraction spectrum





Figure 4.3.3 FT-IR spectra of membrane surface of TS 6V TS 6V-1 is unused membrane, TS 6V-2 is fouled membrane, the rest is the subtraction spectrum



Figure 4.3.4 Photomicrographs of fouled membrane surfaces by SEM (a) FP 055A; (b) FS 202-09; (c) TS 6V 205

From the facts discussed above, the formation of a gel of oil droplet and surfactants on the membrane surface can be explained as follows: because of concentration polarization, an accumulation of emulsified drops appears near the membrane surface. In this concentration boundary layer, the oil drop concentration is raised so that the collisions between oil drops become more frequent. At certain collisions, the drops are present in a situation where the interactions between them are strong enough for them to form aggregates. With an increase in the concentration, the aggregates become more numerous and large. After a certain time, a dynamic equilibrium can be reached with a certain number of aggregates per unit volume, and this state may be called a gel.

4.3.3 Evaluation of recovery of permeability by chemical

cleaning

In ultrafiltration of oil-in-water emulsion the most important foulant is the oil, as discussed above, and it is expected that if the oil adsorbed on the membrane surface can be removed perfectly by cleaning, the wettability of the membrane attains its original value and complete recovery of permeate rate can be obtained. It is reported that the micellar solution was efficient for removing the oil adsorbed on the membrane surface [LEE et al. 1984]. The oil adsorbed on the membrane structure could form a microemulsion with a micellar solution consisting of a surfactant and an alcohol in water, it could be removed completely and the permeability could be recovered.

FP 055A membrane fouled, whose pure water permeability is $324 \text{ l/m}^2\text{h}$ as an unused membrane, was immersed and cleaned by the two solutions mentioned above, respectively. After washing them with distilled water, it was observed that the white spots found on used membrane disappeared. The efficiencies of cleaning solutions and the recovery of permeability for membrane cleaning were presented in Table 4.3.3.

Washing liquid	Permeate flux	Efficiency	Recovery	
	Before cleaning,	After cleaning,	<i>φ</i> , [%]	<i>ø</i> , [%]
	J_b	J_a		
Micellar solution	284	312	70.0	96.3
Acid-gasoline-alkali	286	315	76.3	97.2

Table 4.3.3	Relation of	washing lie	quid and	permeate	flux o	of FP	055A

*The permeate flux of unused membrane with pure water is $324 \text{ l/m}^2 \text{ h}$.

It seems evident that the role of micellar solutions in membrane cleaning is to make a microemulsion with the oil adsorbed on the membrane structure, thereby removing it completely. The removal of oil drops on the membrane surface can be identified by SEM, as shown in Figure 4.3.5. The results show that using either micellar solution or acid-gasoline-alkali step-cleaning process it can be achieved a recovery of the fouled membrane. However, using micellar solution is more favorable than applying acid-gasoline-alkali step-cleaning process because of the complexity and economy of the cleaning procedure.



Figure 4.3.5 SEM photograph of membrane after cleaning by micellar solution (a) FP 055A; (b) FS 202-09; (c) TS 6V 205

4.4 Characterization of Gel Concentration

There are two significant problems which are always found during the membrane operation: (1) concentration polarization, which is the build-up of a concentrated layer on the membrane surface. The permeate resistance of water increases greatly, and the permeate flux declines; (2) membrane fouling, which results from the adsorption of solute in the membrane structure and mainly causes changes in surface chemistry. These effects lead to a decrease in the separation efficiency.

Many literatures have introduced and enucleated the concentration polarization and the UF model of gel layer [ORLICH and SCHOMAECKER 1999, BARTHELMES and BUGGISCH 1999, WETTERAU et al. 1996, PERKINS et al. 1999, SONG 1998, BACCHIN et al. 1996, PRADANOS et al. 1995, SETHI and WIESNER 1997, BOUCHARD et al. 1994]. Two typical models are widely accepted, hydraulic resistance model and osmotic pressure model [BERG and SMOLDERS 1989]. The coefficient of mass transfer at the membrane surface has been studied according to Reynolds number and Schmidt number. However the relationship between models of the concentration polarization and gel layer has been less referred. This research introduces the calculation expression of gel concentration on the basis of understanding concentration polarization and gel layer for the ultrafiltration separation of oil-in-water emulsion.

4.4.1 Concentration polarization and gel concentration

During ultrafiltration of pure water, the permeate flux is directly proportional to the transmembrane pressure, it can been expressed as:

$$J_w^0 = \frac{\Delta P}{\eta_o R_m} \tag{4.4.1}$$

where J_w^o is the permeate flux of pure water (l/m²h); ΔP is transmembrane pressure (bar); R_m the intrinsic resistance of the clean membrane (1/m); η_0 is water viscosity (N s/m²).

The permeate flux is directly proportional to the operating pressure only if the concentration and pressure are below a certain limit. However, its membrane resistance is greater than that of pure water.

During ultrafiltration the solutes are carried and accumulated at the membrane surface, and formed a concentration difference between the membrane surface and bulk solution. It results that the solutes diffuse into the bulk solution backward till a balance situation of concentration is attained (see Figure 4.4.1).



Figure 4.4.1 Concentration profile in the boundary layer of UF

The following is the differential equation of mass transfer for steady state ultrafiltration:

$$J_{w}\frac{dC}{dx} - D\frac{d^{2}C}{dx^{2}} = 0$$
(4.4.2)

where *D* is the diffusion coefficient of solute (m^2/s) . By integrating equation (4.4.2) it can give the following equation:

$$J_w C - D\frac{dC}{dx} = C_1 \tag{4.4.3}$$

where J_wC is the solute flux on to membrane; $D\frac{dC}{dx}$ is the solute diffusion flux in the backward direction. The difference is equal to the solute permeate flux, which is a constant at a stable situation. Hence, the integral constant C_1 can been replaced with J_s . Then,

$$J_s = J_w C - D \frac{dC}{dx} \tag{4.4.4}$$

where J_s is the solute permeate flux, which is equal to $J_w C_f$; C_f is the solute concentration in the permeate (vol%). According to the boundary conditions: x = 0, $C = C_b$; $x = \delta$, $C = C_m$. By integrating equation (4.4.4) we can obtain the following equation:

$$J_w = \frac{D}{\delta} \ln \frac{C_m - C_f}{C_b - C_f}$$
(4.4.5)

where C_b is the solute concentration in the bulk solution of feed (vol.%); C_m is the solute concentration at the membrane surface (vol.%); δ is the thickness of the boundary layer (polarization layer) (m).

If the retention of ultrafiltration membrane is perfect, there is no any solute in the permeate, C_f can be ignored. Thus equation (4.4.5) can be simplified as:

$$J_w = K \ln \frac{C_m}{C_b} \tag{4.4.6}$$

where $K = \frac{D}{\delta}$, mass transfer coefficient.

Although equation (4.4.6) does not present the relation between the pressure and other factors, an increasing pressure can improve permeate flux of water, and the solute concentration at the membrane surface also increases. The concentration polarization becomes more severe, which causes the flux of the solute diffusion backward to be increased. As an UF process becomes steady state at a certain pressure, the logarithm functional relation between J_w and C_m fulfils equation (4.4.6).

In addition, the thickness of boundary layer in equation (4.4.6), δ , depends on the hydrodynamic conditions, such as, the flow velocity is parallel to the membrane surface. The diffusion coefficient *D* is related with the solute property and feed

temperature. If the treated object is a macromolecular solution, the solute concentration at the membrane surface, C_m , increased greatly because of the smaller D, and the backward-diffusion flux of solute is lower as well. It causes an increase in the ratio of C_m/C_b . If C_m is increased to yield the gel layer under a certain pressure, the pressure at that moment is called critical pressure. The solute concentration at the membrane surface is named of gel concentration (C_g). Therefore equation (4.4.6) can be changed into:

$$J_w = \frac{D}{\delta} \ln \frac{C_g}{C_f}$$
(4.4.7)

For a selected solute, the gel concentration can be regarded as a stable value under certain conditions. The gel concentration is related with the solubility of the solute in water. Thus, J_w can also be considered as a determined value. If the transmembrane pressure increases continually, the backward-diffusion flux of the solute can not be enhanced. In a short time the permeate flux may be increased, but the pressure increased is balanced by the gel layer resistance quickly with increasing the thickness of the gel layer. Thus, the permeate flux of water returns to the previous level.

According to equation (4.4.7) the following conclusions can be seen: (1) When the gel layer is formed the permeate flux of water does not increase with the pressure. (2) The permeate flux decreases linearly with the logarithm relation of the solute concentration, C_b . (3) The permeate flux still depends on the hydrodynamic conditions which defined the thickness of the boundary layer.

In a word, the relation of J_w and ΔP can be summarized, as shown in Figure 4.4.2 for the UF process and macromolecular solution. The relation between J_w and ΔP can be considered within three regions:

- The first is a direct line, which stands for a direct proportional relation like in equation (4.4.1).
- The second region shows that the J_w is a functional relation with ΔP , and the relation of J_w and C_m can be expressed by equation (4.4.6).
- The third region is nearly a parallel line, which shows that the J_w has no relationship with ΔP , C_m is equal to C_g . J_w can be calculated based on equation (4.4.7).



Figure 4.4.2 Relationship between permeate flux and transmembrane pressure

On the other hand, there is a polarization layer resistance besides the membrane resistance if the polarization layer can not be ignored. According to the additivity of resistance, the permeate flux can be expressed as:

$$J_{w} = \frac{\Delta P}{\eta (R_{m} + R_{p})} \tag{4.4.8}$$

where R_p is the resistance of polarization layer (1/m); η is the permeate viscosity (N s/m²)

As the gel layer is formed, the resistance of ultrafiltration includes still the resistance of gel layer (acts as main action). The permeate flux is governed by the so-called general filtration equation given as:

$$J_w = \frac{\Delta P}{\eta (R_m + R_p + R_g)} \tag{4.4.9}$$

where R_g is the resistance of gel layer (1/m).

From equation (4.4.9), it can be seen:

(1) Because $R_g \gg R_p$, R_p can be ignored. Thus equation (4.4.9) can be simplified as:

$$J_w = \frac{\Delta P}{\eta (R_m + R_g)} \tag{4.4.10}$$

(2) If the pressure is variable, an increase in the pressure can enhance the permeate flux in a shorter time and forces more solute to the membrane surface, the thickness of gel layer and the resistance of gel layer increases. Thus it seems that $R_g \propto \Delta P$ at that time, equation (4.4.10) can be modified as:

$$J_{w} = \frac{\Delta P}{\eta (R_{m} + \alpha \cdot \Delta P)}$$
(4.4.11)

The equation above also shows the relation of J_w and ΔP .

(3) Comparing equation (4.4.11) with equation (4.4.6), it can be seen that equation (4.4.11) can not reflect the influences of flow velocity of bulk solution and feed oil concentration. Moreover equation (4.4.6) can not show directly the effects of the pressure and resistance. However there is a common fact between the equations above, which shows the relations of $J_w - \Delta P$ and $J_w - C_m$ under the concentration polarization and gel layer respectively. Substituting equation (4.4.6) into equation (4.4.11) and rearranging it the results is:

$$\frac{\Delta P}{\eta(R_m + \alpha \Delta P)} = K \ln \frac{C_m}{C_b}$$

Subsequently the following equation can be attained

$$C_m = C_b \exp \frac{1}{K} \left(\frac{\Delta P}{\eta (R_m + \alpha \, \Delta P)} \right) \tag{4.4.12}$$

With respect to the equation above, it can calculate approximately the solute concentration within concentration polarization region under different pressures and gel concentration under critical pressure at the membrane surface, respectively.

4.4.2 Calculations of membrane resistance and gel layer

resistance

The relationship between the permeate flux and transmembrane pressure was discussed in the section 4.1.3 in this thesis. An increase in the transmembrane pressure can improve the permeate flux. At lower emulsion concentration (0.5 vol. %), the concentration polarization is not obvious, the permeate flux is almost increased linearly with the transmembrane pressure. At higher emulsion concentration (5 vol. %) the effect of pressure on the permeate flux depends on the magnitude of pressure. Under a lower pressure the flux is also increased with pressure. The flux, however, is controlled by the gel layer at higher pressure (not by the pressure). Thus the membrane has a critical flux at higher feed concentration. Figure 4.4.3 was selected to show the permeate flux as a function of operating pressure for FP 055A membrane at 30° C under different emulsion concentrations.

Equation (4.4.11) can be expressed as:

$$\frac{\Delta P}{J_w} = \eta R_m + \eta \alpha \,\Delta P \tag{4.4.13}$$

A plot of $\Delta P/J_w$ vs. ΔP at feed concentration of 0.5% is shown in Figure 4.4.4. The intercept of the line with Y-axes, $\eta R_m = 0.0059$ bar m²h/l. Thus, R_m can be attained as long as the viscosity of permeate at 30°C. The permeate viscosity (η) can be regarded approximately to 0.801×10⁻³ N s/m² at 30°C. $R_m = 0.0059/\eta = 2.65 \times 10^{12} \text{ m}^{-1}$.

The slope of the line, $\eta \alpha = 0.0026 \text{ m}^2\text{h/l}$. For the emulsion with feed concentration of 0.5%, $\eta R_g = 0.0026 \Delta P$ bar m²h/l. Then, R_g is also attained: $R_g = 0.0026 \Delta P/\eta = 1.17 \Delta P \times 10^7 \text{ m/N}$.



Figure 4.4.3 Modeling of permeate flux and transmembrane pressure for FP 055A membrane at different concentration emulsion

Therefore, the relation of flux and transmembrane pressure can be expressed as the following equation:

$$J_{w} = \frac{\Delta P}{0.0059 + 0.0026\Delta P}$$
(4.4.14)

Using the same methods, another plot of $\Delta P/J_w$ with ΔP at feed concentration of 5% is shown in Figure 4.4.5, in which $\eta R_m = 0.0075$ bar m²h/l, $\eta \alpha = 0.0069$ m²h/l. Thus, for the emulsion with feed concentration of 5% at 30°C, the permeate viscosity (η) can be regarded approximately to 0.801×10^{-3} N s/m².

Because $\eta R_m = 0.0075$ bar m²h/l, thus, $R_m = 3.37 \times 10^{12}$ m⁻¹. At the same time $\eta R_g = 0.0069 \Delta P$ bar m²h/l. Then, $R_g = 0.0069 \Delta P / \eta = 3.10 \Delta P \times 10^7$ m/N.

Here, the deviation of membrane resistance with different feed oil concentration might be resulted from the estimation of permeate viscosity at 30°C, errors from making diagram and experiment.

Therefore, the next equation can be obtained:

$$J_{w} = \frac{\Delta P}{0.0075 + 0.0069\Delta P}$$
(4.4.15)

Both equations of (4.4.14) and (4.4.15) show the expressions of J_w - ΔP for FP 055A membrane under different feed concentrations, respectively. In Figure 4.4.3, the square symbols are the experimental values; the dash line is the calculated results at feed concentration of 5 vol. %. The cycle symbols are the experimental values; the real line is the calculated results at feed concentration of 0.5 vol. %. From these results, it can be seen that the experimental and calculated values are in a good agreement. The equation (4.4.13) can be used to express the relation of $J_w - \Delta P$ for oil-in-water emulsion.



Figure 4.4.4 A diagram of $\Delta P/J_w - \Delta P$ at oil concentration of 0.5%



Figure 4.4.5 A diagram of $\Delta P/J_w - \Delta P$ at oil concentration of 5%



Figure 4.4.6 A diagram of $R_g - \Delta P$ for FP 055A membrane

Figure 4.4.6 plotted R_g vs transmembrane pressure for FP 055A membrane under different emulsion concentrations. It shows that the effect of transmembrane pressure on R_g under a lower concentration is weaker than that under a higher concentration.

4.4.3 Modelling of oil concentration at the membrane surface

According to data in Figure 4.4.3, the critical flux $J_{critl} = 276 \text{ l/m}^2\text{h}$ as $C_{bl} = 0.5$ vol. % at a steady state; the critical flux $J_{crit2} = 120 \text{ l/m}^2\text{h}$ as $C_{b2} = 5$ vol. %. Since the cross-flow velocity was constant throughout, it can be assumed that the mass transfer coefficient (*K*) was also constant under different feed concentrations and therefore the plot appears linear for the theory to hold true. According to equation (4.4.6)

$$J_{crit1} - J_{crit2} = K \ln \frac{C_{b2}}{C_{b1}} = K \ln \frac{5}{0.5} = 276 - 120 = 156$$
 l/m²h

Therefore K = 67.75 m/h. Substituting K into equation (4.4.6), the relationship between the critical flux and the gel concentration can be expressed as:

$$J_{crit1} = 67.75 \ln \frac{C_g}{0.5} \tag{4.4.16}$$

Thus, C_g can be solved as about 29.4 vol. %. The variation of flux with the concentration at membrane surface can be expressed as:

$$J_{w} = 67.75 \ln \frac{C_{m}}{0.5} \qquad \text{for the feed concentration of } 0.5 \text{ vol. \%} \qquad (4.4.17)$$

$$J_w = 67.75 \ln \frac{C_m}{5}$$
 for the feed concentration of 5 vol. % (4.4.18)

According to equation (4.4.12) the oil concentration, C_m , at the membrane surface can be expressed by the following equation:

$$C_m = 0.5 \bullet \exp \frac{1}{67.75} \left(\frac{\Delta P}{0.0059 + 0.0026 \Delta P} \right)$$
(4.4.19)

or

$$C_m = 5 \bullet \exp \frac{1}{67.75} \left(\frac{\Delta P}{0.0075 + 0.0069 \Delta P} \right)$$
(4.4.20)

Substituting different operating pressure into equation (4.4.19) or equation (4.4.20) above, the oil concentration, C_m , at the membrane surface can be calculated approximately. Figure 4.4.7 showed that the oil concentration at the membrane surface varied with the transmembrane pressure. As the operating pressure increases, C_m approaches C_g (about 30 vol.%).



Figure 4.4.7 Oil concentration at the membrane surface (C_m) in function of transmembrane pressure (ΔP) for FP 055A membrane treated 5% feed oil concentration emulsion by calculation
4.5 Modelling of UF Membrane Fouling

Membrane separation, developed obviously in the last more than 30 years, is one of the alternative treatments for separating secondary emulsions. Both microfiltration and ultrafiltration have been used for concentrating emulsions, as they are highly efficient for removing oil, do not require chemical additives and are more economical than conventional separation techniques [WEHLE et al. 1988]. However, the flux in all membranes declined monotonically with time. Such behaviour appears to be common to all membrane processes and is usually attributed to membrane fouling [MICHEALS 1980]. For some application systems membrane fouling is more serious in reducing the flux than the concentration polarization. In this case, the flux decline is irreversible. Even it may lead to the membrane separation difficult to continue. It is estimated that about \$500 million loss because of membrane fouling every year [CHERYAN 1998]. It has been focusing on membrane fouling research worldwide. Many methods have been used to reduce the influence of membrane fouling, such as improving flow conditions at the membrane surface, addition of secondary phase in the bulk feed and development of membrane materials etc [BIAN et al. 2000, PANPANIT and VISVANATHAN 2001, FAIBISH and COHEN 2001].

Up till now, however, the mechanism of fouling is yet not fully understood. A model or well defined procedure for quantitative description of the fouling dynamics, which can bee used well by the engineers in process design and operation of cross-flow filtration, is still unavailable. In the case of oil fouling, it is likely to be a surface tension effect since, for a well solvated membrane surface, the interfacial tension with oil droplets will be large [LOEB and SOURIRAJAN 1964]. Surface chemistry, solute-solute or solute-membrane interaction and wettability are the keys to understanding these phenomena, which can be explained in terms of the interfacial tension between oil and water, the contact angle of the oil drop [LEE et al. 1984]. In order to reduce membrane fouling effect it is necessary to study the mechanism and model of membrane fouling for ultrafiltration separation of oil-in-water emulsion.

4.5.1 Fundamentals of Ultrafiltration Membrane Fouling

When solutes are present, there is a permeate flux decline due to membrane fouling. A decrease in flux is a rather complex phenomenon involving adsorption of macromolecules to the membrane surface and involving pore blocking, concentration polarization, and formation of a gel-like cake layer within membrane pores. Several

models have been used to describe solute fouling, among them hydraulic resistance, osmotic pressure, gel polarization, and film models [MARCHESE et al. 2000].

The early works on membrane fouling theories include the development of the pore blocking and cake formation models [SONG 1998]. Flux decline in membrane filtration is a result of the increase of the membrane resistance and the development of another resistance layer, which can be elucidated in terms of pore blockage and cake formation, respectively. The pore blocking increases the membrane resistance while the cake formation creates an additional layer of resistance to the permeate flow. In this sense, pore blocking and cake formation can be considered as two essential mechanisms for membrane fouling. Other factors, such as solute adsorption, particle deposition within the membrane pores, and characteristics change of the cake layer, can affect membrane fouling through enhancement or modification of either or both of these two essential mechanisms. The development of a concentration polarization layer can also add another layer of resistance. However, the effect of the concentration polarization layer can be considered by modifying the applied pressure.

Membrane fouling is actually a process to achieve the equilibrium state from the non-equilibrium state, rather than a process to deteriorate from the normal operation. While the cake thickness remains constant in the non-equilibrium region grows with time. The filtration operation attains steady state when the equilibrium region has expanded to the end of the filter. At steady state, the flux will not change because the thickness of the cake layer in the entire filter channel does not change in function of time.

Using membrane filtration for oil-in-water emulsion under high pressure, the membrane becomes fouled and wetted by the oil phase, leading to a change in the critical surface tension, contact angle and pore size of the membrane. Generally, the capillary pressure of oil droplets has a negative value and prevents the oil droplet from entering the membrane pore against the operating pressure. Depending on the deformability of the oil drops, the operating transmembrane pressure should not be more than this capillary pressure otherwise the oil droplets will pass through a small pore and contaminate the permeate. They can also adsorb and plug the membrane pore, leading to membrane fouling.

In general, the model for membrane fouling can be classified the following two aspects: one is the empirical model in a form of exponential decay function for permeate flux in ultrafiltration [SHI et al. 2001], it can be expressed as follows.

$$J_w = J_0 e^{-bt} (4.5.1)$$

or

$$J_w = A + Be^{-bt} \tag{4.5.2}$$

where J_w is the permeate flux; J_0 the initial permeate flux; A, B and b are constants; t is ultrafiltration time. This kind of model can be in good agreement with the experimental results. However, this kind of model including less influence factors is limited by some specified conditions and is not of multi-purpose characteristics. At the same time, it is obscure for the physical meaning of each parameter included in this model. The another kind of model describes the membrane fouling based on membrane structure and feed properties [FANE 1986, SONG 1998]. For example, one of simple expressions in the literature can be described in the following form:

$$J_{w} = e^{\beta t} \frac{\Delta P}{R_{m}} + (1 - e^{\beta t}) \frac{(\Delta P - \Delta P_{c})}{R_{bm}} \times (1 + \frac{2r_{c}(\Delta P - \Delta P_{c})}{R_{bm}^{2}} \frac{C_{b}}{C_{g}} t)^{-0.5}$$
(4.5.3)

where ΔP is transmembrane pressure; ΔP_c is the critical pressure for cake formation, which can be determined by the particle radius, Boltzman constant, temperature, and the critical filtration number; β is the blocking coefficient; R_{bm} is the resistance of the blocked membrane; r_c is the specific resistance of the cake layer; R_m is intrinsic membrane resistance; C_g is gel concentration at the membrane surface. Although the parameters included in this model have their defined physical meanings and the model is quite consistent with the experimental results, the expression of this kind model is complex, because it contains too many parameters needed to be determined. So this model is not convenient in actual engineering applications.

In principle, as for the determined membrane and application system, the relation between the permeate flux and time can be described as shown in equation (4.5.2). When the UF time is long enough, the variation of flux with time is decreased and tends to a stable value. Generally it is more suitable to characterize the membrane-fouling phenomenon using exponential decay function as fouling model, and it is testified that the exponent of flow velocity is between 0.3 to 0.8 by comparing the experimental data when the flux as a function of flow velocity is expressed [HUOTARI et al. 1999]. WITMER [1974] in his ultrafiltration studies with sewage effluents, found J_w to be proportional to flow velocity to the 0.5 power. At the same time, it is found that the exponent of feed concentration is also between -0.05 to -0.6 under a stable flow velocity on the basis on the experimental results [BHATTACHARYYA et al. 1975, CHEN 1999].

The permeate flux is related not only with the ultrafiltration object and operation conditions, but also with membrane material and its structure. The flux is directly proportional to the transmembrane pressure applied on the membrane as the treated object is diluted unlimitedly [CHEN 1999]. The initial permeate flux is characterized as:

$$J_0 = A_1 + B \frac{\Delta P}{\eta_o R_m} \tag{4.5.4}$$

where η_o is the solvent viscosity; A_I , and B are constants for the specified ultrafiltration membrane and application system.

According to the analyses mentioned above, the effects of feed concentration and flow velocity should be considered in the new model. Both empirical constants of m and n are used to characterize the influences of feed concentration and flow velocity. The permeate flux can be expressed as the following equation:

$$J_w = A \frac{U^m}{C_b^n} + B \frac{\Delta P}{\eta_o R_m} e^{-bt}$$
(4.5.5)

where both U and C_b are the flow velocity and concentration of bulk solution respectively; A, B and b are constants for the specified ultrafiltration membrane and application system. If the influence of gel layer is not negligible, such as higher concentration solution, the gel resistance must be considered besides the intrinsic membrane resistance. At the same time, if the separating object is an aqueous solution, the water viscosity (η_o) is replaced with the viscosity of permeate (η). Therefore, the exponential equation for the membrane fouling can be improved as follows:

$$J_{w} = A \frac{U^{m}}{C_{b}^{n}} + B \frac{\Delta P}{\eta(R_{m} + R_{g})} e^{-bt} = A \frac{U^{m}}{C_{b}^{n}} + B \frac{\Delta P}{\eta(R_{m} + \alpha \Delta P)} e^{-bt}$$
(4.5.6)

in which R_g is gel layer resistance; α is constant.

In treating actual ultrafiltration process, firstly taking simply both empirical constants of m and n as primary estimating values, then using stepwise and multiple linear regression analysis to modify the A, B and b until the derivation can be acceptable.

4.5.2 Experimental investigation of membrane fouling

The experimental apparatus and ultrafiltration membrane properties are described in Chapter 3. The FP 055A ultrafiltration membrane was selected as example to characterize the model of membrane fouling in this study. The experimental solution was oil-in-water emulsion with feed concentration (C_b) of 5 vol. %. The viscosity of emulsion was 1.381×10^{-3} N s/m² at 20 °C. The permeate water viscosity can be known approximately as 1.005×10^{-3} N s/m² at 20 °C. The variation of permeate flux in function of time was shown in Figure 4.5.1 under different pressure with a flow velocity of 0.9 m/s at 20 °C.

The experimental pressure and temperature profiles for ultrafiltration behaviors of emulsified oily water were investigated in Chapter 4.1. The intrinsic membrane resistance (R_m) can be calculated on the basis of the model described in Chapter 4.4. According to the relation between pressure and flux (equation 4.4.11) a plot of the $\Delta P/J_w - \Delta P$ can be attained, as shown in Figure 4.5.2. The intercept of the line with Y-axes is equal to 0.0052 bar m²h/l. Therefore (ηR_m) = 0.0052 bar m²h/l. The slope of the line is 0.0078. Thus, (ηR_g) = 0.0078 ΔP bar m²h/l. The average percent deviation, defined as

$$\Sigma \frac{100 \left| J_{w \exp} - J_{w cal} \right|}{J_{w \exp}} / \text{Number of points}$$

where $J_{w exp}$ is the experimental value of permeate flux, $J_{w cal}$ is calculated value of permeate flux

4.5.3 Model validity investigations

On the basis of equation (4.5.6) and the experimental data used in Figure 4.5.1 four sets of experimental data are analyzed using linear-regression with the help of specified calculation program listed in Appendix.

As taking both empirical constants of *m* and *n* as 0.5, a series values of *A*, *B* and *b* were calculated, respectively. Taking their mean values as their primary respectively, an iterative algorithm was employed for the four sets of data. A set of optimal *A*, *B* and *b* was chosen. A = 171.42, B = 0.37, b = 0.62. Under the present experimental conditions, an exponential equation for the fouling model of FP 055A membrane was established:

$$J_{w} = 171.42 \left(\frac{U}{C_{b}}\right)^{0.5} + 0.37 \frac{\Delta P}{0.0052 + 0.0078 \Delta P} e^{-0.62 t}$$
(4.5.7)

Equation (4.5.7) is the fouling model of FP 055A membrane during treating oil-in-water emulsion. The Figures 4.5.3, 4.5.4 and 4.5.5 compare the experimental results with the calculated values by equation (4.5.7) under various experimental conditions. It is found the calculated values are consistent with the experimental results, although the average percent deviation is less than 16%.

This type of model should have a wider application because it is based on the membrane properties and application system, and the effects of the operation parameters.



Figure 4.5.1 Permeate flux as a function of time for FP 055A under different transmembrane pressures



Figure 4.5.2 Relation between $\Delta P/Jw$ and ΔP for FP 055A membrane to ultrafiltrate emulsion with a concentration of 5% at 0.9 m/s and 20°C



Figure 4.5.3 Comparison of experimental and calculated results for FP 055A membrane under different flow velocities, feed concentration 5%; transmembrane pressure 3 bar; temperature 20° C



Figure 4.5.4 Comparison of experimental and calculated results for FP 055A membrane under different feed concentrations, pressure 3 bar; flow velocity 0.9 m/s, temperature 20° C



Figure 4.5.5 Comparison of experimental and calculated results for FP 055A membrane under different pressures, feed concentration 5%; flow velocity 0.9 m/s; temperature 20° C

In equation (4.5.6), all parameters have their clear physical meaning and correspond to transmembrane pressure, flow velocity, temperature, membrane material and structure, feed concentration and operation time etc. It reflects not only the effects of membrane fouling caused by the membrane nature on the flux, but also the operation parameters. For the ultrafiltration of oil-in-water emulsion, each coefficient of the exponential equation of membrane fouling can be determined, as shown in equation mentioned above.

As an example for FP 055A membrane equation (4.5.7) was used to study the variation of flux with time under different pressure, feed concentration and cross-flow velocity. The calculated values based on the exponential equation above were compared with the experimental results under the present experimental conditions, as shown in Figures 4.5.3, 4.5.4 and 4.5.5 respectively. The mean relative errors of the permeate flux with time between the calculated results and actual measurement values are less than 16% under various operating conditions. A possible explanation for the yielding errors is that the calculation of gel resistance is an approximation only in equation (4.5.7). The effects of oil droplet size, porosity of layer and specific resistance of the gel layer and other affect factors have not be introduced and considered in this model. In fact, ΔP and R_m remain constant during filtration. The flux declines because the value of R_g increases due to gel layer formation on the membrane surface [LEE et al. 1998]. The value of R_g is very difficult to attain accurately because it depends strongly on particle size, properties of cake, shear rate and other factors. The another possible reason for the deviations may be the hypothesis of laminar flow conditions. If the flow is not laminar, the permeate flux is not directly proportional to the flow velocity with an exponent of -0.5. Based on the principle of simplicity and applicability, however, it is no doubt that this model in this present study can be acceptable in the ultrafiltration process, especially for lower flow velocity and stable cake layer.

This new model involves four operation parameters related with the process: feed concentration, flow velocity, transmembrane pressure and viscosity, in addition it is necessary to introduce the resistance coefficients, which are related to membrane material and feed. Therefore, for the selected membrane and application system this equation can be used to predict flux and estimate the operation parameters in a wider application ranges than other exponential equations introduced in the literature.

4.6 New Scientific Results

1. It was found that the chemical nature of membrane influences the separation performance. From hydrophilic property towards hydrophobic characteristic the investigated membranes can be arranged as follows: Cellulose > PAN > PES > PVDF. The permeate flux at 0.5 vol.% feed oil concentration reached higher values on hydrophilic than on hydrophobic membranes. The next table shows that PAN membrane with hydrophilic group (–CN) has high permeate flux. With the same nominal MWCO, the permeate fluxes of PAN membrane (DY-040 and DY-010) are higher than those of hydrophobic PES membranes (DS-040 and FS102-05) at feed oil concentration of 0.5%. This is probably an effect of the expected superior oil-repelling nature of the former membranes. Similar behaviour was observed comparing PES (DS-100) and PVDF (FS-40PP) membranes with 100 kD of MWCO.

Membrane	Material	MWCO [kD]	Average permeate flux at feed concentration of 0.5%, [l/m ² h]
DY-040	PAN	40	300.8
DS-040	PES	40	138.2
DY-010	PAN	10	177.9
FS102-05	PES	10	153.2
DS-100	PES	100	296.4
FS 40PP	PVDF	100	185.1

2. The effects of MWCO on flux depends on feed oil concentration. Comparing membranes of the same material but with different MWCO it can be established that high MWCO may lead to high flux at lower feed oil concentration; while its influence becomes weaker at high feed oil concentration. PES membranes have the same tendency at low feed concentration. At high feed concentration the flux of PES decreased with increasing MWCO, because the flux of PES membrane was easy to be influenced by gel layer. The higher the MWCO of PES is, the more serious the gelling tendency is.

Membrane	Material	MWCO [kD]	Flux, [l/m² h] ^{a)}	Flux, [l/m ² h] ^{b)}
DY-010	PAN	10	177.9	81.5
DY-040	PAN	40	300.8	91.7
DS-040	PES	40	138.2	55.6
DS-100	PES	100	296.4	81.3

Feed oil concentration 0.5 vol. %; b) Feed oil concentration 5 vol. %

3. Complete separation of oil from emulsion was not attained if the pure water flux of the hydrophilic membrane exceeded a critical value, because this low viscosity compound was easily sheared into small droplets which might pass the membrane freely. The permeate flux was better in case of PAN membrane with a higher pure

Membrane M	Matarial	MWCO	Pure water flux,	Flux	COD*	OIL**
wiemorane wiateriai		[kD]	$[l/m^2h]$	[l/m² h]	[mg/l]	[mg/l]
DY-010	PAN	10	250	177.9	120	5.5
DY-040	PAN	40	700	300.8	155	46
DS-040	PES	40	400	138.2	135	13.3
DS-100	PES	100	800	296.4	140	2

water flux at low feed oil concentration, however, its oil concentration and COD in permeate were higher.

Feed oil concentration: 0.5 vol. %; pressure: 3 bar; temperature: 40°C

COD* means the COD in permeate; OIL** means the oil concentration in permeate

4. The effect of transmembrane pressure was based on the variation of membrane resistance which was related to the concentration polarization and gel polarization. At lower emulsion concentration (0.5 vol.%), the permeate flux increased almost linearly with the transmembrane pressure. At higher emulsion concentration (5.0 vol.%) the effect of pressure on the permeate flux depended on the magnitude of pressure. As the transmembrane pressure is over a critical value, the flux is controlled by gel layer. The critical transmembrane pressure was about 2 bar for FS 202-09 and FP 055A, about 3 bar for TS 6V membrane with the experimental set up of ND-2.

5. The effect of pressure on the flux is still controlled by the temperature. At different temperatures the extent of pressure-effect is different. The flux increases with temperature at either lower or higher feed concentration because of the enhancement of diffusion coefficient. This kind of synergic effect for pressure and temperature on the permeate flux (l/m^2h) can be identified by the results of FP 055A at feed concentration of 5 vol.%:

Flux,	Transmembrane pressure, [bar]					
Temp.	1	2	3	4	5	6
30	85.8	90	103	103	119	130
50	94.2	98.6	106.1	111.4	133	144
60	102.8	107.2	114.5	120	141.5	148.6

6. The scale up experiments substantially proved that using the same membrane there is no significant difference in the oil rejection and COD rejection either in laboratory or in pilot scale. However the permeate flux of pilot was lower than that of laboratory, which is believed to be caused by the different membrane modules (the spiral wound module was used in pilot and plate and frame module with flat sheet membranes was used in laboratory scale).

Chapter 4.6. New Scientific Results

Membrane	Туре	Permeate flux [1/m ² h]	Oil rejection	COD rejection
FS 10 (PES, TS-102)	Lab.	153.2	99.9	98.9
	Pilot	77.7	99.6	95.2
FS 20 (PES, TS-202)	Lab.	243.7	98.6	98.2
	Pilot	128.2	99.7	95.6
FF 50 (PVDF, TS-502)	Lab.	246.4	99.9	98.6
	Pilot	196.2	99.7	97.0

* Feed emulsion concentration 0.5 vol. %

7. Using Infrared (IR) and Scanning Electron Microscopy (SEM) techniques for the investigation of membrane surface it was found that there are lots of oil drops adsorbed on the membrane surface after the oil-in-water emulsion runs were taken. The most foulants were oil droplets and surfactants under the present experimental conditions. The cleaning procedure, using micellar solution, removed the oil droplets from the surface.

8. With respect to the mass transfer theory and resistance-in-series equation of ultrafiltration, a calculation model for oil concentration in boundary layer was expressed by the following equation:

$$K \ln \frac{C_m}{C_b} = \frac{\Delta P}{\eta(R_m + R_g)} = \frac{\Delta P}{\eta(R_m + \alpha \Delta P)}$$

where *K* is the coefficient of mass transfer, (m h⁻¹); C_m , (vol.%) and C_b , (vol.%) are the oil concentrations at the membrane surface and in the bulk emulsion of feed respectively; η is the permeate viscosity, (N s m⁻²); ΔP is transmembrane pressure, (bar); R_m is the intrinsic membrane resistance, (m⁻¹) and R_g , (m⁻¹) is the gel-layer resistance; α is constant, (m⁻¹ bar⁻¹).

After rearranging the above equation, the oil concentration at the membrane surface (C_m) can be attained, as follows:

$$C_m = C_b \exp \frac{1}{K} \left(\frac{\Delta P}{\eta (R_m + \alpha \Delta P)} \right)$$

On the basis of the above equation the oil concentration can be calculated approximately within the concentration polarization region at different pressures and the gel concentration (C_g) on the membrane surface at critical pressure. As the operating pressure increases, C_m approaches to C_g . The C_g (vol.%) was about 30 vol.% in the present experimental conditions:

Chapter 4.6. New Scientific Results

<i>C_m</i> , [vol.%]	Transmembrane pressure, [bar]						
C_b , [vol.%]	1	2	3	4	5	6	
0.5	2.84	7.14	12.67	18.71	24.82	30.75	
5.0	13.94	19.99	24.04	26.88	28.98	30.58	

Validity of the equation: feed temperature 20-60°C, transmembrane pressure 1-6 bar. The average percent deviation is less than 0.5%.

9. An empirical model in a form of exponential decay function was introduced to model UF membrane fouling:

$$J_{w} = A \frac{U^{m}}{C_{b}^{n}} + B \frac{\Delta P}{\eta(R_{m} + R_{g})} e^{-bt} = A \frac{U^{m}}{C_{b}^{n}} + B \frac{\Delta P}{\eta(R_{m} + \alpha \Delta P)} e^{-bt}$$

Where J_w is permeate flux, $(1 \text{ m}^{-2}\text{h}^{-1})$; R_m is the intrinsic membrane resistance (m^{-1}) and R_g is the gel-layer resistance, (m^{-1}) ; η is the viscosity of permeate, (N s m^{-2}) ; ΔP is transmembrane pressure, (bar); U is the cross-flow velocity, (m s^{-1}) ; and C_b is concentration of bulk emulsion, (vol.%); t is time, (hour); A, B and b are constants for the specified ultrafiltration membrane and application system. Both constants of m and n varies between 0.3-0.8 and 0.05-0.6, respectively.

For FP 055A membrane the model of membrane fouling had the next form:

$$J_w = 171.42 \left(\frac{U}{C_b}\right)^{0.5} + 0.37 \frac{\Delta P}{0.0052 + 0.0078 \Delta P} e^{-0.62t}$$

Validity of the equation: flow velocity 0.5-1.5 m/s; transmembrane pressure difference 1-6 bar; temperature 20-60°C; feed emulsion concentration 0.5-5 vol.%. The average percent deviation is less than 16%.

Chapter 5

Conclusions and Propositions

In this chapter conclusions of the present work and recommendations for further research are given.

5.1 Conclusions

1. Using ultrafiltration process is a feasible way to remove water from oil-in-water emulsion. The permeate flux, oil rejection and COD in permeate of ultrafiltration performance of oil-in-water emulsion depend on the membrane nature (material, nominal molecular weight cut-off and pore size), membrane module, feed emulsion components and operation conditions (feed oil concentration, transmembrane pressure, flow velocity and feed temperature).

2. The polymeric UF membranes are successful and efficient for treating oily wastewater. The permeate flux was better in case of PAN and PES membranes with big pore size at low feed oil concentration, and the membranes mentioned above had the best oil and COD rejection. With the same nominal MWCO the permeate flux of hydrophilic membranes is much higher than that of hydrophobic membranes either at feed concentration of 0.5 vol. % or at 5 vol. %. The high feed concentration may result in lowering the permeate flux and grow COD value. The feed concentration has slight effect on oil concentration in permeate.

3. An increase in the transmembrane pressure, flow velocity and temperature can improve the permeate flux. At lower emulsion concentration (0.5 vol. %), the gel polarization is not obvious, the permeate flux is almost increased linearly with the transmembrane pressure. At higher emulsion concentration (5 vol. %) the effect of pressure on the permeate flux depends on the magnitude of pressure. Below at a critical pressure the flux is also increased with pressure. The flux, however, is controlled by the gel layer at higher pressure, not by pressure. Almost each tested membrane has a critical flux at higher feed concentration. In addition, increasing flow velocity enhances the flux to certain extent due to the development of shear rate at the membrane surface. However there is an economical limit of the increase of cross-flow

velocity. The flux increases with temperature because of the enhancement of diffusion coefficient.

4. By analyzing the surface of membrane fouled by Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FT-IR) it is found that membrane fouling is mainly due to the adsorption of oil on to the membrane structure which modifies the wettability of the membrane and the effective pore diameter. Complete membrane regeneration may be almost performed with a micellar solution of the sodium dodecyl sulfate - n-pentanol - water system or using acid-gasoline-alkali step-cleaning process.

5. As using an industrial spiral wound modules to remove water from oil-in-water emulsion in a pilot scale apparatus, it was found that the results are consistent with those in laboratory well. Using spiral wound module of membrane its permeate flux is a bit lower than that of flat-sheet membrane module.

6. The gel concentration can be calculated approximately under critical transmembrane pressure at the membrane surface by the following new equation.

$$C_{m} = C_{b} \exp \frac{1}{K} \left(\frac{\Delta P}{\eta(R_{m} + \alpha \Delta P)} \right)$$

7. The new model of membrane fouling, which is based on the membrane properties and the influence factors in the application system, as follows.

$$J_{w} = A \frac{U^{m}}{C_{b}^{n}} + B \frac{\Delta P}{\eta(R_{m} + \alpha \Delta P)} e^{-bt}$$

Further investigation of this model is under consideration.

5.2 Proposals

By studied the separation of oily emulsion by ultrafiltration membrane, the candidate believes that the following aspects should be focused and further studied as the future research topics.

1. Because it is unavoidable for the complexity and variety of composition in actual oil-in-water emulsion, there is always a tendency to produce air bubble. The effect of

air bubble on the mass transfer coefficient, formation of gel-layer is still a very plain research content. The formation mechanism of air bubble during ultrafiltration of oil-in-water emulsion should be paid more attention. The ultrafiltration behaviours of oil-in-water emulsion in presence of air bubble should be further investigated.

2. In an actual oil-in-water emulsion used, there are other particles and compounds, such as scraps, sand particles from the grinding wheel and microbes because of deterioration of emulsion, their effects on ultrafiltration behaviours are complex, the pure oil-in-water emulsion can not reflect the actual results at all. Further studies, therefore, should use more realistic conditions, particularly in the presence of suspended solids and other macromolecular species.

3. Particular attention should still be paid to the studying of new high performance coupled- and facilitated-transport membranes, and suitable carriers should be sought from among the voluminous literature of inorganic and biological chelation or other type of complexing agents.

4. It should be stressed that the study of reducing concentration polarization and membrane fouling. Especially, application of electric fields, ultrasonic fields or combined electric and ultrasonic fields in membrane transport fundamentals would likely bear fruit.

Finally, any program aimed at exploiting membrane technology should remain responsive to future breakthroughs. The worldwide activity in membranes is now so broad-ranging and intense that unplanned advances that will alter current thinking and economics seem a virtual certainty over the next several years.

Summary

Oil-in-water emulsion is widely used in the food, mechanical, petroleum, cosmetics, pharmaceutical, agriculture, polymer and leather industries. In the past time the used emulsion was often discharged to either public sewers or rivers without treatment. It resulted in environmental pollution and loss of oil. Therefore the separation of oil-in-water emulsion has a great importance either for **environmental purposes** or for **recovery** and **reuse** of the separated components.

The purpose of the thesis is the establishment of operation conditions and selection of membrane parameters to minimize concentration polarization and membrane fouling, the achievement of adequate rejections of COD and oil in laboratory and pilot scale units. At the same time, the second goal of the thesis is to introduce a calculation method of gel concentration and to develop a model which can describe the flux decline behavior due to membrane fouling during cross-flow UF of oil-in-water emulsions.

Twelve kinds of membrane with different intrinsic nature (material, nominal molecular weight cut-off and pore size) were investigated under different operation parameters (feed oil concentration, transmembrane pressure, flow velocity and feed temperature) in laboratory scale and pilot scale ultrafiltration apparatuses. The permeate flux, COD, oil concentration and membrane surface were analyzed.

The experimental results showed that:

Ultrafiltration process is a feasible way to remove water from oil-in-water emulsion. The permeate flux, oil rejection and COD in permeate of ultrafiltration performance of oil-in-water emulsion depend on the **membrane nature** (material, nominal molecular weight cut-off and pore size), membrane module, feed emulsion components and **operation conditions** (feed oil concentration, transmembrane pressure, flow velocity and feed temperature).

The **hydrophilic towards hydrophobic property** of the investigated membranes strongly influenced permeate flux in this order: Cellulose > PAN > PES > PVDF. The influence of MWCO on flux depends on feed oil concentration. At lower feed oil concentration the flux increases with MWCO, while at higher feed oil concentration the growth can be negligible.

An increase in the **transmembrane pressure**, flow velocity and temperature can improve the permeate flux. At lower emulsion concentration (0.5 vol. %), the gel

polarization is not obvious, the permeate flux is almost increased linearly with the transmembrane pressure. At higher emulsion concentration (5 vol. %) the effect of pressure on the permeate flux depends on the magnitude of pressure. As the transmembrane pressure is over a critical value, the flux is controlled only by gel layer. The critical pressure of investigated membranes was about 2-3 bar. In addition, increasing flow velocity and temperature enhance the flux to certain extent due to the development of shear rate at the membrane surface and the enhancement of diffusion coefficient.

With respect to **Scanning Electrical Microscopy and Infrared results** the most foulants on the fouled membrane surface are oil droplets and surfactants in case of industrial oil-in-water emulsion. The membrane fouling is mainly due to the adsorption of oil on to the membrane structure which modifies the wettability of the membrane and the effective pore diameter. Complete membrane regeneration may be almost performed with a micellar solution of the sodium dodecyl sulfate – n-pentanol – water system.

The scale up experiments proved that there is no significant difference in the oil rejection and COD rejection either in laboratory or in pilot scale. Using industrial spiral wound module of membrane its permeate flux is a bit lower than that of flat-sheet membrane module, which is believed to be caused by the difference in hydrodynamics.

According to experimental data two kinds of mathematical models describing the gel concentration and membrane fouling in the ultrafiltration of oil-in-water emulsion were analyzed and discussed subsequently. The gel concentration at the membrane surface is defined by the critical pressure. A form of exponent equation used for describing membrane fouling was also developed. With the help of this model it can be studied the effects of operation parameters (transmembrane pressure, feed concentration, temperature, flow velocity, viscosity) and membrane properties (intrinsic membrane resistance and gel resistance) on membrane fouling. The theoretical calculation values attained by two equations above were consistent with the experimental evidence.

Finally I have proposed **further studies** including the effect of bubbles on the mass transfer coefficient and formation of gel layer, and the two or three-phase UF performance because of the presence of solid particles and components in the industrial oil-in-water emulsions

Összefoglalás

Az olaj-a-vízben emulziókat széles körben alkalmazzák: a gépiparban, a petrolkémiai-, a kozmetikai iparban, a gyógyszergyártásban, a mezőgazdaságban, az élelmiszeriparban, a műanyag-, textil-, papír- és nyomdaiparban, a fényező- és bőriparban. Régebben a használt emulziót kezelés nélkül a csatornába, vagy folyókba engedték. Ez a környezet szennyezését és olajveszteséget eredményezett. Ezért az olaj-víz emulzió szétválasztása nagy jelentőségű a környezet védelme és a szétválasztott komponensek visszanyerése és újrahasznosítása szempontjából.

Munkám célja az üzemeltetési körülmények és a membrán-paraméterek megállapítása a koncentráció–polarizáció és a membrán-eltömődés minimalizálása során, a KOI és az olaj megfelelő visszatartásnak biztosítása laboratóriumi és félüzemi méretű berendezésben. Ezzel egyidőben másik cél, a gélkoncentráció számolására alkalmas módszer bevezetése és a membrán-eltömődés miatti fluxus-csökkenés leírására alkalmas modell felállítása az olaj-víz emulziók keresztáramú ultraszűrésénél.

Tizenkét különböző tulajdonságú (anyagú, névleges vágási értékű és pórusméretű) membránt vizsgáltam különböző üzemeltetési paraméterek (olaj-koncentráció, transzmembrán nyomás, áramlási sebesség és hőmérséklet) mellett, laboratóriumi és félüzemi méretű ultraszűrő berendezésen.

A kísérleti eredmények a következőket mutatták:

Az ultraszűrési eljárás alkalmas a víz eltávolítására olaj-a-vízben emulzióból. Az olaj-víz emulzió ultraszűrésekor keletkező pemeátum fluxusa, az olaj-visszatartás és a kémiai oxigén igény (KOI) függ a membrán természetétől (anyagától, névleges vágási értékétől és pórusméretétől), a membránmodul típusától, a betáplált emulzió komponenseitől és az üzemeltetési körülményektől (kiindulási olaj-koncentráció, transzmembrán nyomás, áramlási sebesség és hőmérséklet).

A vizsgált membránok **hidrofil-hidrofób jellege** erősen befolyásolja a fluxust a következő sorrendben: cellulóz > PAN > PES > PVDF. A vágási érték (MWCO) hatása a fluxusra függ a betáplálás olajtartalmától. Alacsony olaj-koncentrációnál a fluxus nő a vágási értékkel, míg magasabb olaj-tartalomnál a növekedés elhanyagolható.

A **transzmembrán nyomás**, az **áramlási sebesség** és a **hőmérséklet** növelésével a permeátum fluxusa növelhető. Alacsony emulzió-koncentrációknál (0,5 térfogat %)

a gél-polarizáció nem jelentős, a fluxus közel lineárisan nő a transzmembrán nyomással. Nagyobb emulzió-koncentrációnál (5 térfogat %) a nyomásnak a fluxusra gyakorolt hatása függ a nyomás nagyságától. Ha a transzmembrán nyomás nagyobb a kritikus értéknél, a fluxust csak a gélréteg határozza meg. A vizsgált membrán kritikus nyomása kb. 2-3 bar. Az áramlási sebesség és a hőmérséklet növelése egy bizonyos értékig növeli a fluxust.

A membrán-felszín deformálódási fokán és a diffúziós tényező növekedésén keresztül összehasonlítva a **Pásztázó elektron-mikroszkópos és az Infravörös eredményeket** ipari olaj-víz emulzió esetén, a membrán eltömődését az olajcseppek és a felületaktív anyagok okozzák. A membrán eltömődését a membrán szerkezetében adszorbeálódott olaj okozza, mely módosítja a membrán nedvesedését és a tényleges pórusátmérőt. Teljes membrán-regenerálás nátrium-dodecil-szulfát–n-pentanol–víz rendszerrel valósítható meg.

A méretnövelési kísérletek bebizonyították, hogy nincs szignifikáns különbség az olaj- és a KOI visszatartásban a laboratóriumi és a félüzemi berendezés esetében. Ipari spirálcsöves membránmodult használva, a permeátum fluxusa egy kicsit alacsonyabb, mint a lap-membrán modul esetében, aminek a hidrodinamikai különbség lehet az oka.

Az olaj-víz emulzió ultraszűrésének kísérleti eredményei alapján а gélkoncentráció és a membrán eltömődésének leírására kétféle matematikai modellt vizsgáltam. A membrán felületén kialakuló gélréteg koncentrációját a kritikus nyomás határozza meg. Exponenciális egyenletet állítottam fel a membrán eltömődésének leírására, melynek segítségével az üzemeltetési paraméterek (transzmembrán nyomás, betáplálási koncentráció, hőmérséklet, áramlási sebesség, viszkozítás) és a membrán tulajdonságok (belső membrán-ellenállás és gél-ellenállás) hatása tanulmányozható az eltömődésre. A két egyenlettel számolt értékek jól közelítik a mért eredményeket.

Végül **további vizsgálatokat** tervezek a buborékok hatásának tanulmányozására az anyagátadási együtthatóra, a gél-réteg képződésére, valamint az ipari olaj-víz emulziókban jelenlévő szilárd részecskék miatt kettő, vagy háromfázisú ultraszűrés megvalósítására.

Appendix 1

References

AGASHICHEV S. P. (1999): Modeling concentration polarization phenomena for shell-side flow in ultrafiltration process, *Sep. Sci. Tech.*, **34** (2), 243-261.

ANDERSON G. K. and SAW C. B. (1987): Oil/water separation with surface modified membrane, *Environ. Tech. Lett.*, **8**, 121-132.

ARNOT T. C., FIELD R. W. and KOLTUNIEWICZ A. B. (2000): Cross-flow and dead-end microfiltration of oily-water emulsions: Part II - Mechanisms and modeling of flux decline, *J. Membr. Sci.*, **169** (1), 1-15.

BACCHIN P., AIMAR P. and SANCHEZ V. (1996): Influence of surface interaction on transfer during colloid ultrafiltration, *J. Membr. Sci.*, **115** (1), 49-63.

BARTHELMES G. and BUGGISCH H. (1999): A model for the Influence of boundary layers on the rheology of agglomerating suspensions, *Chem. Eng. Tech.*, **22** (10), 831-835.

BELFER S., FAINCHTAIN R., PURINSON Y. and KEDEM O. (2000): Surface characterization by FTIR-ATR spectroscopy of polyethersulfone membranes-unmodified, modified and protein fouled, *J. Membr. Sci.*, **172** (1-2), 113-124

BELKACEM M., MATAMOROS H., CABASSUD C., AURELLE Y. and COTTERET J. (1995): New results in metal working wastewater treatment using membrane technology, *J. Membr. Sci.*, **106** (3), 195-205.

BELLHOUSE B. J. (1997): *Membrane filters*, US Patent 5,628,909.

BENNETT E. O. (1973): The disposal of metal cutting fluids, *Lubrication Eng.*, **29** (7), 300-307.

BENNETT E. O. (1983): Water based cutting fluids and human health, *Tribology International*, **18** (3), 133-136.

BHATTACHARYYA D., GARRISON K. A. JUMAWAN A. B. and GRIEVES R. B. (1975): Membrane ultrafiltration of a nonionic surfactant and inorganic salts from

complex aqueous suspensions: design for water reuse, *AIChE Journal*, **21**(6), 1057-1065.

BHATTACHARYYA D., JUMAWAN A. B. and GRIEVES R. B. (1979): Ultrafiltration characteristics of oil-detergent-water systems: membrane fouling mechanisms, *Sep. Sci. Tech.*, **14**, 529-549.

BHAVE R. R. and FLEMING H. L. (1988): Removal of oily contaminants in wastewater with microporous alumina membranes, *AIChE Symp. Ser.* 84 (261), 19-27.

BIAN R., YAMAMOTO K. and WATANABE Y. (2000): The effect of shear rate on controlling the concentration polarization and membrane fouling, *Desalination*, **131**(1-3), 225-236.

BLATT W. F., DRAVID A., MICHAELS A. S. and NELSON L. (1970): Solute Polarization and Cake Formation in Membrane Ultrafiltration: Causes, Consequences, and Control Techniques, in J. E. FLINN (Ed.): Membrane Science and Technology, Plenum Press, New York.

BOUCHARD C. R., CARREAU P. J., MATSUURA T. and SOURIRAJAN S. (1994): Modeling of ultrafiltration: predictions of concentration polarization effects, *J. Membr. Sci.*, **97** (0), 215-229.

CAKL J., BAUER I., DOLECEK P. and MIKULASEK P. (2000): Effects of backflushing conditions on permeate flux in membrane crossflow microfiltration of oil emulsion, *Desalination*, **127** (2), 189-198.

CANNING R. P. and TONELLI F. A. (1995): *Membrane bioreactor system for treating synthetic metal-working fluids and oil-based products*, US Patent 5,401,400.

CASTRO R. P., COHEN Y. and MONBOUQUETTE H. G. (1996): Silica-supported polyvinylpyrrolidone filtration membranes, *J. Membr. Sci.*, **115** (2), 179-190.

CHAI X., KOBAYASHI T. and FUJI N. (1999): Ultrasound-associated cleaning of polymeric membranes for water treatment, *Sep. Purif. Tech.*, **15**, 139-146.

CHAI X., KOBAYASHI T. and FUJI N. (1998): Ultrasound effect on cross-flow filtration of polyacrylonitrile ultrafiltration membranes *J. Membr. Sci.*, **148** (1), 129-135.

CHEN H. (1999): Membrane fouling model, *Tech. Water Treat.*, **25** (3), 144-147. (in Chinese)

CHEN S., FLYNM J. T., COOK R. G. and CASADAY A. L. (1991): Remove of oil grease and suspended solids from produced water with ceramic crossflow microfiltration, *SPE Production Eng*.

CHEN V., FANE A. G., MADAENI S. and WENTEN I. G. (1997): Particle deposition during membrane filtration of colloids: transition between concentration polarization and cake formation, *J. Membr. Sci.*, **125** (1), 109-122.

CHERYAN M. and RAJAGOPALAN N. (1998): Membrane processing of oily streams. Wastewater treatment and waste reduction, *J. Membr. Sci.*, **151** (1), 13-28.

CHERYAN M. (1998): Ultrafiltration and Microfiltration Handbook, Technomic, Lancaster, PA.

CHUNG K. Y., BREWSTER M. A. and BELFORT G. (1993): Dean vortices with wall flux in a curved channel membrane system. 4. Effect of vortices on permeation fluxes of suspensions in microporous membranes, *J. Membr. Sci.*, **81** (1/2), 139-150.

CORNELISSEN E. (1997): Membrane fouling in waste water filtration, *Thesis*, Enschede, The Netherlands.

CROZES G. F., JACANGELO J. G., ANSELME C. and LAINE J. M. (1997): Impact of ultrafiltration operating conditions on membrane irreversible fouling, *J. Membr. Sci.*, **124** (1), 63-76.

DAIMINGER U., NITSCH W., PLUCINSKI P. and HOFFMANN S. (1995): Novel techniques for oil/water separation, *J. Membr. Sci.*, **99** (2), 197-203.

DAL-CIN M. M., LICK C. N., KUMAR A. and LEALESS S. (1998): Dispersed phase back transport during ultrafiltration of cutting oil emulsions with a spinning membrane disc geometry, *J. Memb. Sci.*, **141** (2), 165-181.

DAVIS R. H. and BIRDSELL S. A. (1987): Hydrodynamic model and experiments for crossflow microfiltration, *Chem. Eng. Commun.*, **49**, 217-234.

DAVIS R. H. and LEIGHTON D. T. (1987): Shear-induced transport of a particle layer along a porous wall, *Chem. Eng. Sci.*, **42** (2), 275-281.

DAVIS R. H. (1992): Modeling of fouling crossflow microfiltration membranes, *Sep. Purif. Methods*, **21**, 75-126.

DICK R. M. (1982): Ultrafiltration for oily waste water treatment. *Lubrication Eng.*, **38** (4), 219-222.

FAIBISH R. S. and COHEN Y. (2001): Fouling-resistant ceramic-supported polymer membranes for ultrafiltration of oil-in-water microemulsions, *J. Membr. Sci.*, **185**(2), 129-143.

FANE A. G. and FELL C. J. D. (1987): A review of fouling and fouling control in ultrafiltration, *Desalination*, **62**, 117-136.

FANE A. G. (1986): *Ultrafiltration: Factors Influencing Flux and Rejection*, Progress in Filtration and Separation, Vol. IV, in R. J. WAKEMAN (Ed.), Elsevier.

FERNANDEZ-SEMPERE J. and RUIZ-BEVIA F. (1996): The study of concentration polzrization in ultrafiltration processes, *Lat. Am. Appl. Res.*, **26** (3/4), 157-166.

FINNIGAN S. M. and HOWELL J. A. (1989): The effect of pulsatile flow on ultrafiltration fluxes in a baffled tubular membrane system, *Trans. IChemE.*, **67**, 278.

GANCARZ I., POZNIAK G. and BRYJAK M. (2000): Modification of polysulfone membranes - 3. Effect of nitrogen plasma, *Euro. Polym. J.*, **36** (8), 1563-1569.

GEKAS V. and HALLSTROM B. (1987): Mass transfer in the membrane concentration polarization layer under turbulent cross flow I. Critical literature review and adaptation of existing Sherwood correlations to membrane operations, *J. Membr. Sci.*, **30**, 153-170.

GREEN G. and BELFORT G. (1980),: Fouling of ultrafiltration membranes: lateral migration and the particle trajectory model, *Desalination*, **35**, 129-147.

HÄGG M. B. (1998): Membrane in chemical processing, *Sep. Purif. Methods*, **27** (1), 51-168.

HAMZA A., PHAM V. A., MATSUURA T. and SANTERRE J. P. (1997): Development of membranes with low surface energy to reduce the fouling in ultrafiltration applications, *J. Membr. Sci.*, **131** (1-2), 217-227.

HILL E. C. (1983): Microbial aspects of health hazards from water based metal working fluids, *Tribology International*, **18** (3), 136-140.

HLAVACEK M. (1999): Break-up of oil-in-water emulsions induced by permeation through a microfiltration membrane, *J. Membr. Sci.*, **102**, 1-7.

HOWELL B. F., VENKATACHALAM R. S. and WEHRLE J. P. (1994): *Process for producing hydrophilic polymer membranes*, US Patent 5,356,936.

HU X., BEKASSY-MOLNAR E., VATAI Gy, MEISZEL L. and OLAH J. (1998): The study of oil/water separation in emulsion by ultrafiltration membranes, *Chem. Technik*, **50**(3), 119-123.

HU X., BEKASSY-MOLNAR E., VATAI Gy. and MEISZEL L. (1996a): Oil-water emulsion separation by ultrafiltration, 12th International Congress of Chemical and Process Engineering, Praha, Czech Republic, P3.56

HU X., BEKASSY-MOLNAR E., VATAI Gy., MEISZEL L. and OLAH J. (1996b): Removal of water from oil-water emulsion by ultrafiltration membrane, *Hungarian J. Ind. Chem.*, **24**, 241-246.

HU X., VATAI Gy. and BEKASSY-MOLNAR E. (1995): Development and application of ultrafiltration membrane in the separation of oil-water emulsion, *Proceedings of the Annual Meeting on Technical Chemistry* '95, Veszprém, Hungary, 80 p.

HUOTARI H. M., HUISMAN I. H. and TRAGARDH G. (1999a): Electrically enhanced crossflow membrane filtration of oily waste waters using the membrane as a cathode, *J. Membr. Sci.*, **156**, 49-60.

HUOTARI H. M., TRAGARDH G. and HUISMAN I. H. (1999b): Crossflow membrane filtration enhanced by an external DC electric field: A review. *Trans IChemE. Part A*, **77**, 461-468.

HYUN S. H. and KIN G. T. (1997): Synthesis of ceramic microfiltration membranes for oil-water separation, *Sep. Sci. Tech.*, **32** (18), 2927-2943.

JONSSON G. and JOHANSEN P. L. (1989): *Selectivity of Ultrafiltration Membranes*, in Indo-ECC Membrane Workshop, Department of Science & Technology, New Delhi, India.

KARODE S. K. (2000): A method for prediction of the gel concentration in macromolecular ultrafiltration, *J. Membr. Sci.*, **171** (1), 131-139.

KIM K. Y., SUN P., CHEN V., WILEY D. E. and FANE A. G. (1993): The cleaning of ultrafiltration membranes fouled by protein, *J. Membr. Sci.*, **80**, 241-249.

KOLTUNIEWICZ A. B., FIELD R. W. and ARNOT T. C. (1995): Cross-flow and dead-end microfiltration of oily-water emulsion. Part I: Experimental study and analysis of flux decline, *J. Membr. Sci.*, **102**, 193-207.

KOST J. and LANGER R. S. (1988): Ultrasound enhancement of membrane permeability, US Patent 4,780,212.

LAHIERE R. J. and GOODBOY K. P. (1993): Ceramic membrane treatment of petrochemical wastewater, *Environ. Prog.*, **12**, 86-89.

LEE S., AURELLE Y. and ROQUES H. (1984): Concentration polarization, membrane fouling and cleaning in ultrafiltration of soluble oil, *J. Membr. Sci.*, **19**, 23-38.

LEE Y. and CLARK M. M. (1998): Modeling of flux decline during crossflow ultrafiltration of colloidal suspensions, *J. Membr. Sci.*, **149** (2), 181-202.

LEONARD E. F. and VASSILIEFF C. S. (1984): The deposition of rejected matter in membrane separation processes, *Chem. Eng. Commun.*, **30**, 209-217.

LI H., FANE A. G. and COSTER H. G. L., et al. (1998): Particle deposition on the membrane surface near the critical flux. *Preprints of International Conference on Membrane Science and Technology (ICMST'98)*, Beijing, China, June, 392-393.

LIN S. H. and LAN W. J. (1998): Waste oil/water emulsion treatment by membrane processes, *J. Hazardous Materials*, **59** (2-3), 189-199.

LINDAU J. and JONSSON A. S. (1999): Adsorptive fouling of modified and unmodified commercial polymeric ultrafiltration membranes, *J. Membr. Sci.*, **160** (1), 65-76.

LINDAU J. and JONSSON A. S. (1992): Cleaning of ultrafiltration membranes after treatment of oily wastewater, *J. Membr. Sci.*, **87**, 71-78.

LINDAU J., JONSSON A. S. and BOTTINO A. (1998): Flux reduction of ultrafiltration membranes with different cut-off due to adsorption of a low-molecular-weight hydrophobic solute-correlation between flux decline and pore size, *J. Membr. Sci.*, **149** (1), 11-20.

LIPP P., LEE C. H., FANE A. G. and FELL C. J. D. (1988): A fundamental study of the ultrafiltration of oil-water emulsions, *J. Membr. Sci.*, **36**, 161-177.

LOEB S. and SOURIRAJAN S. (1964): *High flow porous membranes for separating water from saline solution*, US Patent 3,133,132.

LOPEZ R. V., ELMALEH S. and GHAFFOR N. (1995): Cross-flow ultra-filtration of hydrocarbon emulsion, *J. Membr. Sci.*, **102**, 55-64.

MA H., BOWMAN C. N. and DAVIS R. H. (2000): Membrane fouling reduction by backpulsing and surface modification, *J. Membr. Sci.*, **173** (2), 191-200.

MAHDI S. M. and SKOLD R. O. (1991): Experimental study of membrane filtration for the recycling of synthetic water-based metal working fluids, *Tribology International*, **24**, 389-395.

MAHDI S. M. and SKOLD R. O. (1990): Ultrafiltration for the recycling of a model water-based metalworking fluid: process design considerations, *Lubrication Eng.*, **47** (7), 686-690.

MARCHESE J., OCHOA N. A., PAGLIERO C. and ALMANDOZ A. (2000): Pilot-scale ultrafiltration of an emulsified oil wastewater, *Environ. Sci. Tech.*, **34**, 2990-2996.

MARK C. P. (1990): Handbook of Industrial Membrane Technology, Park Ridge, NJ.

MICHEALS A. S. (1980): In Ultrafiltration Membranes and Application, A. R. Cooper (Ed.), Plenum Press, N. Y.

MISRA S. K. and SKOLD R. O. (1999): Membrane filtration studies of inversely soluble model metalworking fluids, *Sep. Sci. Tech.*, **34** (1), 53-67.

MORES W. D. and DAVIS R. H. (2000): Theoretical and experimental flux maximization by optimization of backpulsing, *J. Membr. Sci.*, **165** (2), 225-236.

MUELLER J., YANWEI C. and DAVIS R. H. (1997): Crossflow microfiltration of oily water, J. Membr. Sci., 129 (2), 221-235.

MULLER M. (1991): *Basic Principles of Membranes Technology*, Kluwer Academic Publishers, The Netherlands.

NABI N. and MEIRELES M. (2000): Ultrafiltration of an olive oil emulsion stabilized by an anionic surfactant, *J. Membr. Sci.*, **166** (2), 177-188.

NAKAO S. I., WIJMANS J. G. and SMOLDERS C. A. (1986): Resistance to the permeate flux in unstirred ultrafiltration of dissolved macromolecular solutions, *J. Membr. Sci.*, **26**, 165-178.

NAKATSUKA S., NAKATE I. and MIYANO T. (1996): Drinking water treatment by using ultrafiltration hollow fiber membranes, *Desalination*, **106** (1-3), 55-61.

NAZZAL F. F. and WIESNER M. R. (1996): Microfiltration of oil-in-water emulsion, *Water Environ. Research*, **68** (7), 1187-1191.

NIKOLOVA J. D. and ISLAM M. A. (1998): Contribution of adsorbed layer resistance to the flux-decline in an ultrafiltration process, *J. Membr. Sci.*, **146** (1), 105-111.

NOEMAN N. L. (1982): *Recent Development in Separation science*, Vol. VII, CRC Press.

ORLICH B. and SCHOMAECKER R. (1999): Ultrafiltration of water/oil microemulsion in biocatalysis, *Chem.-Ing.-Tech.*, **71** (1/2), 156-159.

PANPANIT S. and VISVANATHAN C. (2001): The role of bentonite addition in UF flux enhancement mechanisms for oil/water emulsion, *J. Membr. Sci.*, **184**(1), 59-68.

PATTERSON J. W. (1985): *Industrial Wastewater Treatment Technology*, 2nd ed., Butterworths, Stoneham, MA.

PEINEMANN K. and NUNES S. P. (1994): Ultrafiltration membrane with low tendency to fouling - has a non-porous, hydrophilic separation layer consisting of a polyamide-polyether block copolymer, Ger. Patent DE 4,237,604.

PERKINS T. W., SAKSENA S. and VAN REIS R. (1999): A dynamic film model for ultrafiltration, *J. Membr. Sci.*, **158** (1-2), 243-256.

POPE J. M., YAO S. and FANE A. G. (1996): Quantitative measurements of the concentration polarisation layer thickness in membrane filtration of oil - water emulsions using NMR micro-imaging, *J. Membr. Sci.*, **118** (2), 247-257.

PORTER M. C. (1972): Concentration polarization with membrane ultrafiltration, *Ind. Chem. Prod. Res. Dev.*, **11** (3), 234-248.

PRADANOS P., DE ABAJO J., DE LA CAMPA J. G. and HERNANDEZ A. (1995): A comparative analysis of flux limit models for ultrafiltration membranes, *J. Membr. Sci.*, **108** (1-2), 129-142.

ROMERO C. A. and DAVIS R. H. (1988): Global model of crossflow microfiltration based on hydrodynamic particle diffusion, *J. Membr. Sci.*, **39**, 157-185.

Scott K.: Handbook of Industrial Membranes, Elsevier, Oxford, (1995), p.626.

SEIFERT R. and STEINER R. (1996): Operating behavior of capillary and tubular modules in the ultrafiltration of lubricating coolant emulsions and compressor condensates, *Chem.-Ing.-Tech.*, **68** (4), 428-438.

SETHI S. and WIESNER M. R. (1997): Modeling of transient permeate flux in cross-flow membrane filtration incorporating multiple particle transport mechanisms, *J. Membr. Sci.*, **136** (1-2), 191-205.

SHAO G. (2000): *Water Treatment Technology by Membrane*, Metallurgy Industry Press, Beijing. (in Chinese)

SHAW D. J. (1991): Introduction to Colloid and Surface Chemistry, Fourth edition, Butterworth - Heinemann Ltd, Great Britain.

SHI J., YUAN Q. and GAO C. (2001): *Handbook of Membrane Technology*, Press of Chemistry Industry, Beijing. (in Chinese)

SKOLD R. O. (1990): Field testing of a model water-based metalworking fluid designed for continuous recycling using ultrafiltration, *Lubrication Engineering*, **47** (7), 653-659.

SONG L. (1998): A new model for the calculation of the limiting flux in ultrafiltration, *J. Membr. Sci.*, **144** (1-2), 173-185.

SONG L. (1998): Flux decline in crossflow microfiltration and ultrafiltration: mechanisms and modeling of membrane fouling, *J. Membr. Sci.*, **139** (2), 183-200.

SOURIRAJAN S. and MATSUURA T. (1988): *Reverse Osmosis/Ultrafiltration Process Principles*, Ottawa, Canada, 904

SRIJAROONRAT P., JULIEN E. and AURELLE Y. (1999): Unstable secondary oil/water emulsion treatment using ultrafiltration: fouling control by backflushing, *J. Membr. Sci.*, **159** (1-2), 11-20.

SWART M. P. and JACOBS E. P. (1996): Characterisation techniques for organic foulants adsorbed onto flat-sheet UF membranes used in abattoir effluent, *J. Membr. Sci.*, **119** (1), 1-8.

SWEET J. R. (1990): Pressure induced surfactant recovery during ultrafiltration of water-oil emulsions, US Patent 4,892,660.

TANSEL B., BAO W. Y. and TANSEL I. N. (2000): Characterization of fouling kinetics in ultrafiltration systems by resistances in series model, *Desalination*, **129** (1), 7-14.

TANSEL B., REGULA J. and SHALEWITZ R. (2001): Evaluation of Ultrafiltration Process Performance for Treatment of Petroleum Contaminated Waters, *Water Air & Soil Pollution*, **126**(3/4), 291-305.

TECKENTRUP A. D. (1995): *Emulsion separation process*, Ger. Patent DE 4,411,691.

THOMAS H., JUDD S. and MURRER J. (2000): Fouling characteristics of membrane filtration in membrane bioreactors, *Membr. Tech.*, **122**, 10-13.

TROUVE E., URBAIN V. and MANEM J. (1994): Treatment of municipal wastewater by membrane bioreactor: Results of a semi-industrial pilot-scale study, *Water Sci. Tech.*, **30**, 151-157.

VAN DEN BERG G. B. and SMOLDERS C. A. (1989): The boundary-layer resistance model for unstirred ultrafiltration, A new approach, *J. Membr. Sci.*, **40**, 149-1172.

VATAI Gy., BEKASSY-MOLNAR E. and HU X. (1997): Ultrafiltration for separation of oil-water emulsions, *Olaj, Szappan Kozmetika*, **46** (6), 228-230.

VIADERO R. C. JR., MASCIOLA D. A., REED B. E. and VAUGHAN R. L. JR. (2000): Two-phase limiting flux in high-shear rotary ultrafiltration of oil-in-water emulsions, *J. Membr. Sci.*, **175** (1), 85-96.

WANG N. (1984): The relationship between models of concentration polarization and gel layer in ultrafiltration, *Tech. Water Treat.* **10** (6), 51-58. (in Chinese)

WEHLE V., WERLE H. and SPEI B. (1988): *Apparatus and process for treating an oil/water emulsion*, Ger. Patent DE 3,712,106.

WETTERAU G. E., CLARK M. M. and ANSELME C. (1996): A dynamic model for predicting fouling effects during the ultrafiltration of a groundwater, *J. Membr. Sci.*, **109** (2), 185-204.

WILLIAMS C. and WAKEMAN R. (2000): Membrane fouling and alternative techniques for its alleviation, *Membr. Tech.*, **124**, 4-10

WITMER F. E. (1974): The use of semipermeable membranes to filter and renovate sewage effluents, Presented at First World Filtration Congress, Paris, France.

WRONSKI S., MOLGA E. and RUDNIAK L. (1989): Dynamic filtration in biotechnology, *Bioprocess Eng.*, **4**, 99.

WU D., HOWELL J. A. and FIELD R. W. (1999): Critical flux measurement for model colloids, *J. Membr. Sci.*, **152** (1), 89-98.

ZAIDI A., SIMMS K., KOK S. and NELSON R. (1992): *Recent Advances in the Application of Membrane Technology for the Removal of Oil and Suspended Solids from Produced Water*, in J. P. RAY and F. R. ENGELHART (Eds.), Produced Water, Plenum Press, New York.

ZYDNEY A. L. and COLTON C. K. (1985): A concentration polarization model for the filtrate flux in cross-flow microfiltration of particulate suspensions, *Chem. Eng. Commun.*, **47**, 1-21.

Appendix 2

Calculation Program for the Model of Membrane Fouling

```
DIMENSION X(6), Y(6), YY(6), Q(3), Z(3)
   DIMENSION S(3,3),T(3,3),INTER(3,2),TT(3,3)
   OPEN(60,FILE='LEASQ.IN')
   OPEN(70,FILE='LEASQ.OUT')
   OPEN(80,FILE='LEASQ1.OUT')
   DO 11 I=1,6
11 READ(60,*)X(I),Y(I)
   READ(60,*)a,b,c
   DO 88 L=1,30
   DO 22 I=1.6
22
     YY(I) = a * EXP(b * X(I)) + c
     DO 33 I=1,3
   Q(I)=0.
   DO 33 J=1,3
     S(I,J)=0.
33
     T(I,J)=0.
   DO 44 I=1,6
   S(1,1)=S(1,1)+EXP(b*X(I))**2
   S(1,2)=S(1,2)+a*X(I)*EXP(b*X(I))**2
   S(1,3)=S(1,3)+EXP(b*X(I))
   S(2,1)=S(2,1)+a*X(I)*EXP(b*X(I))**2
   S(2,2)=S(2,2)+(a*X(I)*EXP(b*X(I)))**2
   S(2,3)=S(2,3)+a*X(I)*EXP(b*X(I))
   S(3,1)=S(3,1)+EXP(b*X(I))
   S(3,2)=S(3,2)+a*X(I)*EXP(b*X(I))
   S(3,3)=6.
44
     CONTINUE
   WRITE(80,9)((S(I,J),J=1,3),I=1,3)
9
     FORMAT(1X,F17.2,2X,F17.2,2X,F17.2)
   WRITE(80,10)
     10
     DO 55 I=1,6
```

```
Q(1)=Q(1)+(Y(I)-YY(I))*EXP(b*X(I))
   Q(2)=Q(2)+(Y(I)-YY(I))*a*X(I)*EXP(b*X(I))
   Q(3)=Q(3)+(Y(I)-YY(I))
     CONTINUE
55
   CALL MATINV(3,S,T,INTER)
   DO 666 I=1,3
   DO 666 J=1,3
   TT(I,J)=0.
   DO 666 K=1,3
666 TT(I,J)=TT(I,J)+S(I,K)*T(K,J)
   WRITE(80,9)((T(I,J),J=1,3),I=1,3)
   WRITE(80,10)
   WRITE(80,9)((TT(I,J),J=1,3),I=1,3)
   WRITE(80,3)
   DO 66 I=1,3
   Z(I)=0.
   DO 66 J=1,3
   Z(I)=Z(I)+T(I,J)*Q(J)
66
     CONTINUE
   deta=Z(1)
   detb=Z(2)
   detc=Z(3)
   WRITE(70,6)L
6
      FORMAT(1X,'L=',I3)
   ERROR=0.
   ERROR=ERROR+SQRT(deta**2+detb**2+detc**2)
   WRITE(70,1)ERROR
      FORMAT(1X,'ERROR=',F12.5)
1
   WRITE(70,4)deta,detb,detc
      FORMAT(1X,'deta=',F12.5,2X,'detb=',F12.5,2X,'detc=',F12.5)
4
     a=a+deta
   b=b+detb
   c=c+detc
      WRITE(70,3)
3
      FORMAT(1X,'-----')
   WRITE(70,2)a,b,c
2
      FORMAT(1X,'a=',F12.5,6X,'b=',F12.5,6X,'c=',F12.5)
88
     CONTINUE
```

END

```
SUBROUTINE MATINV(N,A,B,INTER)
C N: THE DIMENSION OF MATRIX TO BE INVERTED
C A(N,N): THE MATRIX TO BE INVERTED
C B(N,N): THE MATRIX WHICH THE RESULTS ARE STORED TO
C INTER(N,2): WORK MATRIX
   DIMENSION A(N,N),B(N,N),INTER(N,2)
C ***
                                                     ***
      COPY A(N,N) INTO B(N,N) TO SAVE THE ORIGINAL
   DO 2 I=1,N
   DO 2 J=1,N
2
       B(I,J)=A(I,J)
C ***
      SEACH FOR LARGEST PIVOT ELEMENT
                                           ***
   DO 10 K=1,N
   JJ=K
   IF(K.EQ.N) GOTO 4
   KP1=K+1
   BIG=ABS(B(K,K))
   DO 3 I=KP1,N
   AB=ABS(B(I,K))
   IF(BIG.GE.AB) GOTO 3
   BIG=AB
   JJ=I
3
  CONTINUE
C ***
       STORE NUMBER OF ROWS INTERCHANGED. IF JJ=K,
C THERE IS NO INTERCHANGE &
                              ***
С
       INTER(K,1)=INTER(K,2)
4
  INTER(K,1)=K
   INTER(K,2)=JJ
   IF(JJ.EO.K) GOTO 6
C *** ROW INTERCHANGE
                           ***
   DO 5 J=1,N
   TEMP=B(JJ,J)
   B(JJ,J)=B(K,J)
       B(K,J)=TEMP
5
C *** CALCULATE NEW ELEMENTS OF PIVOT ROW EXCEPT PIVOT
ELEMENT ***
6
       DO 7 J=1,N
   IF(J.EQ.K) GOTO 7
   B(K,J)=B(K,J)/B(K,K)
7
  CONTINUE
C *** CALCULATE NEW ELEMENT REPLACING PIVOT ELEMENT ***
   B(K,K)=1./B(K,K)
```

```
C *** CALCULATE NEW ELEMENT NOT IN PIVOT ROW OF PIVOT
COLUMN ***
   DO 9 I=1,N
   IF(I.EQ.K) GOTO 9
   DO 8 J=1,N
   IF(J.EQ.K) GOTO 8
   B(I,J)=B(I,J)-B(K,J)*B(I,K)
8
       CONTINUE
9
   CONTINUE
       ***
С
            CALCULATE REPLACEMENT ELEMENTS FOR PIVOT
С
            COLUMN EXCEPT FOR PIVOT ELEMENT
                                                *****
   DO 10 I=1,N
   IF(I.EQ.K) GOTO 10
   B(I,K)=-B(I,K)*B(K,K)
10 CONTINUE
С
       ***
            REARRANGE COLUMNS OF FINAL MATRIX
                                                   ***
   DO 12 L=1,N
   K=N-L+1
   KROW=INTER(K,1)
   IROW=INTER(K,2)
   IF(KROW .EQ. IROW) GOTO 12
       DO 11 I=1,N
   TEMP=B(I,IROW)
   B(I,IROW)=B(I,KROW)
   B(I,KROW)=TEMP
11
       CONTINUE
12
       CONTINUE
       RETURN
   END
```

Acknowledgements

I would like to express my sincere gratitude to Prof. Dr. E. Békássy-Molnár and Prof. Dr. Gy. Vatai for their constant supervisions and stimulating discussions, and for their critically reviewing this dissertation. It is the enormous support and encouragement from Prof. Dr. E. Békássy-Molnár that I have been inspiring continuously to complete my doctoral study and research.

I express my gratitude to Dr. Béla Szabó, Director of Chemitechnik-Pharma Corporation of Budapest, for the scholarship and financial support of doctoral activity. I thank the financial support of the Foundation for Exchange Scholars between Hungary and China.

I appreciate the help from Mr. J. Mora, Mr. A. Koris, Ms. E. Márki and other colleagues in the Department of Food Engineering, Szent István University, Hungary.

Particular acknowledgment is also made to Dr. L. Meiszel in Zoltek Magyar Viscosa Corporation, Hungary for his generous support for my part of experimental work in this field. I am also very much indebted to Mrs. Horvath for her skillful experimental assistance, Mrs. Wendl, Mrs. Lakatos and Mr. Szavjolov for sample analysis in Zoltek Magyar Viscosa Corporation, Hungary.

In addition, I am deeply grateful for the numerous helpful discussions with Prof. Dr. X. L. Wang, and Mr. H. Feng in the ultrafiltration separation test and analyses of COD and oil concentration at Institute of Membrane Technology, Nanjing University of Chemical Technology, China. Fruitful discussion with Mr. S. C. Peng, assistance in SEM and FT-IR analyses from Mr. F. Li and Mr. K. L. Hu, and help in calculation programs from Mr. B. Yang at Hefei University of Technology are also acknowledged.

Finally, I would like to express my sincere thanks to the experimental membranes' supply of the following companies: Membrane Laboratory of Magyar Viscosa Corporation, Hungary for Mavibran membranes, Dow Chemicals Membrane Group for the Dow membranes, CM Celfa Company for the Celfa membranes, and Hoechst Corporation for the TS membranes.
Biography

Basic Information:

Surname:	Hu
First Name:	Xianguo
Sex:	Male
Nationality:	Chinese
Date of Birth:	November 4 th 1963
Birthplace:	Anhui, People's Republic of China
Permanent Address:	Institute of Tribology, Hefei University of Technology, 193 Tunxi Road, 230009 Hefei, P. R. China

Education:

M Eng: Hefei University of Technology, P. R. China (1988).

B Eng: Hefei University of Technology, P. R. China (1985).

Short Term Positions:

11.200105.2002	Studying at the Szent István University, Hungary
04.199605.1997	Studying at the Technical University of Berlin, Germany
05 199509 1995	Studying at the Szent István University, Hungary.
04 199404 1995	Studying at the Technical University of Budapest, Hungary.

Professional Memberships:

Member of Society of Tribologists and Lubrication Engineers (STLE), USA.

Member of American Chemical Society (ACS), USA.

Member of Academic Committee of Faculty of Mechanical & Automobile Engineering, Hefei University of Technology.

Professional Experience:

12.1998Present	Research Professor at the Institute of Tribology, HFUT
12.199311.1998	Associate Research Professor at the Institute of Tribology, HFUT
07.199111.1993	Assistant Research Professor at the Institute of Tribology, HFUT
06.198806.1991	Practice Researcher at the Institute of Tribology, HFUT

Publications related to the Dissertation:

X. Hu, E. Békássy-Molnár, Gy. Vatai, L. Meiszel and J. Oláh: Removal of water from oil-water emulsion by ultrafiltration membrane, *Hungarian Journal of Industrial Chemistry*, 24 (1996), 241-246.

X. Hu, E. Békássy-Molnár, Gy Vatai, L. Meiszel and J. Oláh: The study of oil/water separation in emulsion by ultrafiltration membranes, *Chemische Technik*, **50**(3) (1998), 119-123.

Gy. Vatai, E. Békássy-Molnár and X. Hu: Ultrafiltration for separation of oil-water emulsions, *Olaj, Szappan, Kozmetika*, 46(6) (1997), 228-230.

X. Hu, Gy. Vatai and E. Békássy-Molnár: Development and application of ultrafiltration membrane in the separation of oil-water emulsion, *Proceedings of the Annual Meeting on Technical Chemistry*'95, Veszprém, Hungary, (1995), 80.

X. Hu, E. Békássy-Molnár, L. Meiszel, J. Oláh and Gy. Vatai: Separation of oil-water emulsion on UF in laboratory and pilot scale, 7th National Congress on Membrane *Technology*, Nyergesújfalu, Hungary, (1995).

X. Hu, E. Békássy-Molnár, Gy. Vatai and L. Meiszel: Oil-water emulsion separation by ultrafiltration, *12th International Congress of Chemical and Process Engineering*, Praha, Czech Republic, (1996), P 3.56.

E. Békássy-Molnár, L. Meiszel, J. Oláh Gy. Vatai and **X. Hu**: Investigation of ultrafiltration characteristics of oil-emulsions on laboratory and pilot scale units, 7th *World Filtration Congress*, Budapest, Hungary, (1996), X42.

X. Hu and L. Jiang: Preparation and characterization of oil-containing POM/PU blends, *Journal of Synthetic Lubrication*, **15**(1) (1998), 19-29.

X. Hu: Friction and wear behaviours of toughened polyoxymethylene blend under water lubrication, *Polymer-Plastics Technology & Engineering*, **39**(1) (2000), 137-150.

X. Hu: Study of friction and wear performance of zinc dialkyldithiophosphate in the presence of trace ketone, *Tribology Letters*, **12** (2002), 67-74.

X. Hu, E. Békássy-Molnár and Gy. Vatai: Characterization of gel concentration in ultrafiltration of oil-in-water emulsion, *Hungarian Journal of Industrial Chemistry*, 30 (1) (2002), (in press)

X. Hu, E. Békássy-Molnár and Gy. Vatai: Study of ultrafiltration behaviour of emulsified metalworking fluids, *Desalination*, 14 (2002), (to be published)

X. Hu, E. Békássy-Molnár and Gy. Vatai: Modeling of membrane fouling during crossflow ultrafiltration of oily wastewater, *Hungarian Annual Meeting on Technical Chemistry'02*, Veszprém, Hungary, (2002)

X. Hu, E. Békássy-Molnár and Gy. Vatai: Evaluation of oil concentration on the membrane surface in ultrafiltration of oil-in-water emulsion, *Hungarian Annual Meeting on Technical Chemistry'02*, Veszprém, Hungary, (2002)