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**ORGANIC FOULING**  
**DURING REVERSE OSMOSIS (RO) PROCESS**

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*Zou Yang*

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## ABSTRACT

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Reverse osmosis (RO) membrane processes have been used in seawater desalination for over couples of decades. In recent years, new applications of RO membrane processes for reclamation of treated effluent have become popular due to its good performance in rejecting contaminants of very small size. A major obstacle for RO membrane processes is membrane fouling caused by natural organic matter (NOM). A review of literature revealed that the characteristics of NOM and solution chemistry play important roles on RO membranes performance. Operation parameters, such as operating pressure, are also reported to greatly influence the rate and extent of membrane fouling. In this study, a lab-scale RO membrane system was set up to systematically investigate the roles of operating pressure and NOM hydrophobicity on membrane performance. In addition, the effects of pH, ionic strength and divalent cations ( $\text{Ca}^{2+}$ ) on the fouling potential of fractionated NOM components were also studied.

Secondary effluent was used as feed water to evaluate the influence of operating pressure on the performances of three RO membranes. It was observed that each membrane had a threshold operating pressure, below which the membrane fouling can be effectively controlled. Results of hydraulic cleaning showed that although under high operating pressure the normalized permeate flux after 24-hr running decreased to

a great extent (>40% decline), it could almost be completely restored to the initial value. This indicated that short-period membrane fouling is reversible, and backwash commonly adopted in industry is a necessary and effective method for fouling control. To have a more clear insight of NOM fouling, synthetic NOM solutions were used in the second stage of research. A commercial humic acid, the representative of NOM, was treated by a hydrophobic resin (DAX-8) to be fractionated into its hydrophobic and hydrophilic components, respectively. Fouling experiments with the resulting two fractions were conducted under different solution chemistries. 24-hr operation results showed that the hydrophilic NOM had a higher fouling potential (28.65% normalized permeate flux decline) than that of hydrophobic fraction (22.94% decline). When pH value was decreased from 7 to 4, fouling potentials of both hydrophobic and hydrophilic fractions increased to a great extent (approximately 38% normalized permeate flux decline for each fraction). Calcium ions exhibited a contrary influence on the performances of fractionated NOM. With  $10^{-3}$ M calcium ions added, normalized permeate flux of hydrophobic NOM decreased from 77.06% to 70.75%. In contrast, normalized permeate flux of hydrophilic NOM increased from 72.35% to 81.90%.

**Keywords:**

*Reverse osmosis (RO) membrane; natural organic matter (NOM); membrane fouling; solution chemistry; hydrophobicity.*



## NOMENCLATURE

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AWWA	American Water Works Association
AWM	Average Molecular Weight
DBPs	Disinfection By-products
DI	Deionized
DOC	Dissolved Organic Carbon
HA	Humic Acid
HPLC	High Performance Liquid Chromatography
HSs	Humic Substances
IC	Ion Chromatography
MF	Microfiltration
MWCO	Molecular Weight Cutoff
NF	Nanofiltration
NOM	Natural Organic Matter
NUS	National University of Singapore
ppm	Parts Per Million
RO	Reverse Osmosis
SEM	Scanning Electron Microscopy
SOC	Synthetic Organic Compounds
SUVA	Specific Ultraviolet Absorbance
TDS	Total Dissolved Solid
TOC	Total Organic Carbon
UV <sub>254</sub>	Ultraviolet Absorbance at 254 nm
UF	Ultrafiltration

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## **INTRODUCTION**

### **1.1 Background**

Since the development of synthetic asymmetric membranes in 1960s, interest in membrane processes for water and wastewater treatment has grown steadily, and membrane technologies in water related area are now the object of substantial research, development, commercial activity, and full-scale application. The membrane market has grown rapidly, from \$363 million in 1987 to more than \$4.5 billion in 2002 (Malika, 2002).

This relatively recent global increase in the use of membranes in environmental engineering applications can be attributed to at least three factors: (1) increased demand for water requiring exploitation of water resources of lower quality than those relied upon previously; (2) increased regulatory pressure to provide better treatment for both potable and waste waters; and (3) market forces surrounding the development and commercialization of the membrane technologies as well as the water and wastewater industries themselves (AWWA, 1992).

The importance of water scarcity around world can be illustrated by the fact that, while approximately 97 percent of the earth's water is contained in the oceans, the high salt content of 35,000 mg/L makes this vast resource virtually useless for beneficial application without treatment. There are only approximately  $5 \times 10^{15}$  m<sup>3</sup> of fresh waters in rivers, lakes and shallow aquifers that meet the typical daily needs of 6,000 million people in the world (Taylor *et al.*, 1987). However, fresh water and rainfall are unevenly distributed over the landmasses, and thus many areas of the world today are subject to serious and recurring droughts. In many arid regions, groundwater resources contain high salt concentrations due to natural processes. In addition, owing to lack of planning and irresponsible practices of humankind activities, available fresh water supplies have been seriously polluted and will be continually polluted. Therefore, additional water quality-based scarcities have been created.

Membrane processes can play a key role in reducing water scarcity. They may be used to treat wastewaters before the discharge to surface water, to recover materials used in industry before they enter waste streams, and, of course, to treat waters for potable use. In this last regard, membrane may enable us to utilize water resources such as the ocean that were previously inaccessible due to technical or economic considerations. These capabilities of membranes have been significant in driving their use in water and wastewater treatment, particularly in areas with water supplier shortage (Strathman, 1989).

### **1.1.1 Membrane Operation**

Membrane operation is defined as an operation where a feed stream is divided into two streams: a permeate containing material that can pass through the membrane and a retentate containing the nonpermeable species. It can be used to concentrate or to purify a solution or a suspension (solvent-solute or particle separation) and to fraction a mixture (solute-solute separation) (Aptel *et al.*, 1991).

Among the separation technologies, membrane offers following basic advantages:

- Separation takes place at ambient temperature without phase change, which offers an energetic advantage compared to distillation. This explains, for example, the success of reverse osmosis in water desalination.
- Separation takes place without accumulation of products inside the membrane. Membranes are then well adapted to run continuously without a regeneration cycle as in ion-exchange resin operation or without an elution cycle as in chromatography.
- Separation does not need the addition of chemical additives. This gives advantages for the quality of the product and leads to less pollutant wastes and explains the success of pervaporation for the fractionation of azeotropic mixtures and ultrafiltration for water clarification.

When driving force is a pressure difference across the membrane, membrane can be divided into four major types, which are reverse osmosis (RO) membrane, nanofiltration (NF) membrane, ultrafiltration (UF) membrane and microfiltration (MF)



membrane. The major differences used to classify these four membrane types are membrane pore size and the operating pressure. Figure 1.1 gives the basic information of these membrane operations used in water treatment.

Size $\mu\text{m}$	Ionic Range	Molecular Range	Macromolecular Range	Microparticle Range	Macroparticle Range		
	0.001	0.01	0.1	1.0	10	100	1,000
Approximate Molecular Weight	100 200	1,000 10,000 20,000	100,000 500,000				
Relative Size of Various Materials in Water	Metal ions Aqueous salts	Viruses	Humic acids	Clays Asestos fibers	Bacteria Algae Cysts Silt	Sands	
Separation Process	Reverse Osmosis	Nanofiltration	Ultrafiltration	Microfiltration	Conventional filtration processes		

**Fig. 1.1 Selected membrane operations in water treatment (Osmonics Inc.)**

Among all those available membrane technologies, RO membrane is one of the most popular membranes used in desalination of seawater and brackish water. Since RO technology can offer a versatile approach to meeting multiple water quality objectives, such as the control of organic, inorganic and microbial contaminants, it has also been frequently used in secondary effluent treatment in anticipation of increasingly stringent water regulation (Bersillon, 1989). By now, the major application of RO membrane has accounted for about 50% of total membrane sales (Wiesner, 1999).

### **1.1.2 Membrane Fouling**

With the increased application of membrane operations, however, membrane fouling that is indicated by permeate flux decline or increased operating pressure is always being regarded as a major obstacle for the efficient use of membrane systems. It is reported that aquatic organic matters and dissolved salts are the major targeted solutes for RO membranes in reclaimed water treatment. Unlike colloid particles, which only have physical contact with membranes, organic matters usually have a much stronger chemical interaction with membranes that makes them tend to be adsorbed to the membrane surface (Amy *et al.*, 1999; Bersillon, 1989; Crozes *et al.*, 1997; Jucker *et al.*, 1994). The adsorption of organic matters over time onto the membrane surfaces results in an increased membrane resistance that is difficult to reverse. Therefore, organic matters have been reported as a major fouling agent to RO membranes and organic fouling is often regarded as a controlling factor in determining membrane performance (Kaiya *et al.*, 1996; Moody *et al.*, 1983).

The knowledge of exact mechanisms of organic fouling is still limited because there are so many factors involving in the reaction between the membrane and organic matters. Some well-accepted factors that affect the rate and extent of irreversible organic fouling include membrane physical and chemical properties (hydrophobicity, water permeability, charge), bulk organic properties (the organic matters concentration, humic/non-humic organic fraction, molecular mass distribution), solution conditions ( $\text{Ca}^{2+}$  concentration, pH, and ionic strength) and filtration process conditions (the

organic matters concentration at the membrane interface, controlled by flux rate and mass transfer in the fluid boundary layer) (Cho *et al.*, 2000). In cases where electrostatic interactions or conformational changes at the membrane surface are important, membrane fouling is controlled by reactions at the adsorption surfaces. That is, chemical properties of organic matters and membrane surface play important roles (Hansen *et al.*, 1959; Baret, 1968).

Aquatic natural organic matters (NOMs) represent a wide range of complex compounds, among which humic substances that are formed from the chemical and biological degradation of plants and animal residues account for one major type, about 50% of the total organic carbon (TOC) (Fan *et al.*, 2001). It was proposed that the most likely structure of dissolved humic acids is stretched long-chain molecules that may be slightly cross linked. However, this structure could change with various pH values, salt content, NOM concentration of the bulk solution, and the presence of divalent cations to a great extent (Fan *et al.*, 2001). This means NOM fouling could be markedly influenced by solution chemistry.

In practical RO processes for drinking water treatment, acidification is a commonly used disinfection method for controlling most bacterial contaminants (Samir *et al.*, 2000). In some cases, feed waters may be acidified to avoid precipitation of scale as well. It is also known that majority of ions can be retained by RO membrane.

Therefore, to investigate the influence of pH, ionic strength and the presence of divalent ions on NOM fouling during RO processes is of realistic importance.

Apart from solution chemical conditions (pH, ionic strength, nature of humic acid and the presence of divalent cations), hydrodynamic operating conditions can also have a significant influence on NOM fouling, especially for cross flow filtration pattern. The previous researches reported either empirically or academically that for low-pressure membranes there should be a certain threshold of operating pressure, below which organic fouling can be prevented efficiently (Braghetta, 1995; Crozes *et al.*, 1997; Hong *et al.*, 1997; Winters, 1997). However, there is a dramatic increase of trans-membrane pressure in RO membrane processes, which are often used to treat seawater and municipal water. Thus the influence of operating pressure on NOM fouling may be different and is worthy of a further evaluation.

## **1.2 Objectives and Scopes**

The overall objective of this study was to conduct a quantitative evaluation of organic fouling on RO membrane under different chemical and hydrodynamic situations. Separate studies were carried out with emphasis on these two scopes:

### **A. Organic Characteristics and Solution Chemistry on NOM Fouling**

As mentioned above, solution chemistries, namely solution pH, ionic strength and divalent cations, play important roles on NOM fouling. However, while there have

been many findings on the influence of solution chemistry on the rate and extent of fouling in membrane processes when treating NOM as a whole, previous researches did not focused on their effects on the individual hydrophobic and hydrophilic NOM fractions. In fact, organic hydrophobicity was also found to play an important role in membrane fouling. Therefore, the first and major objective in this study was to systematically investigate the different effects of pH, ionic strength and the presence of calcium ions on the fouling tendencies of hydrophobic and hydrophilic NOM components.

The model NOM used here was fractionated commercial humic acids on the basis of hydrophobicity and acidity. The performance of membranes and its associated fouling mechanisms were examined from the measurement of flux decline over time during filtration of solutions containing fractionated NOM.

## **B. RO Fouling Behavior with Real Water**

The second aim of this research involved the study of RO membrane performance in a simulated industrial real water treatment process, and its relative foulants analysis. The effect of operating pressure on membrane fouling was also investigated. The real water sample was a secondary effluent after MF collected from a local wastewater treatment plant.

## **LITERATURE REVIEW**

### **2.1 Reverse Osmosis (RO) Process**

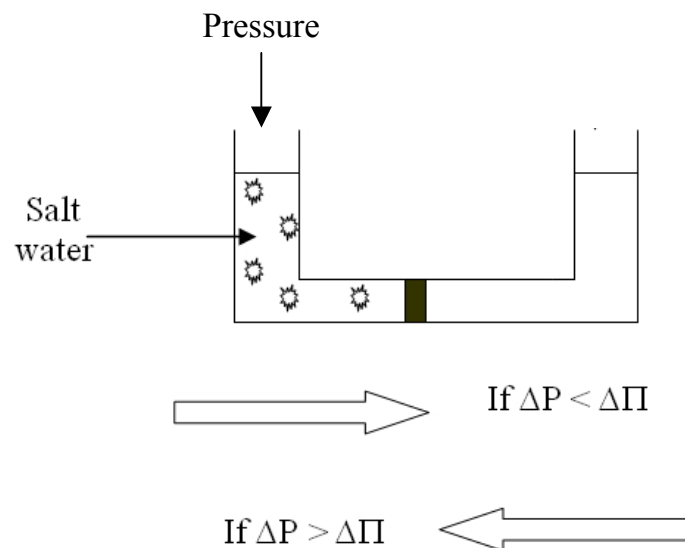
#### **2.1.1 Description of RO Process**

Osmosis is the phenomenon of water flow through a semi permeable membrane that blocks the transport of salts or other solutes. When two water (or other solvent) volumes are separated by a semi permeable membrane, water will flow from the side of low solute concentration to the side of high solute concentration. The flow may be stopped, or even reversed by applying external pressure on the side of higher concentration. In such a case the phenomenon is called reverse osmosis (RO). It is applied to water purification and desalination, waste material treatment, and many other chemical and biochemical laboratory and industrial processes.

RO process is a pressure-driven membrane process that is used to separate relatively pure water from solution containing salts, dissolved organic molecules, and colloids. The difference between RO and nanofiltration (NF) or even ultrafiltration (UF) lies in the size of the solute. RO is capable of rejecting contaminants or particles with

diameters as small as  $0.0001\mu\text{m}$ , whereas nanofiltration can reject contaminants no smaller than  $0.001\mu\text{m}$ .

Figure 2.1 shows a schematic drawing of a membrane separating pure water from a salt solution. The membrane is permeable to the solvent but not to the solute. In order to allow water to pass through the membrane, the applied pressure is higher than the osmotic pressure. Water flows from dilute solution to the concentrated solution if the applied pressure is lower than the osmotic pressure. When the applied pressure is higher than the osmotic pressure, the water flows from the concentrated solution to the dilute solution. The pressures used in RO range from 20 to 100 bar, which are much higher than those used in ultrafiltration process.



**Fig. 2.1 Principle of reverse osmosis process**

According to Van't Hoff, the osmotic pressure,  $\Delta\Pi$  is given by

$$\Delta\Pi = BcRT \quad (2.1)$$

where  $B$  = dissociation number

$c$  = molar solute concentration

$R$  = molar gas constant

$T$  = absolute temperature

There are various theories or mechanisms developed to describe membrane transport.

In general, the permeate water flux is proportional to the net driving pressure, whereas the solute flux is proportional to the concentration gradient. According to the Solution-diffusion model (sorption-diffusion model),

$$v = \frac{\Delta p - \Delta\Pi}{R_m} \quad (2.2)$$

$$J_s = B\Delta C \quad (2.3)$$

where  $v$  = permeate flux,  $L/m^2.s$

$\Delta p$  = driving pressure, psi

$R_m$  = membrane resistance,  $psi \cdot m^2.s/L$

$J_s$  = solute flux,  $L/m^2.s$

$\Delta C$  = concentration gradient,  $mg/L$



Salt rejection is a more commonly used parameter than solute flux.

$$R_{rej} = 1 - \frac{C_{permeate}}{C_{feed}} \quad (2.4)$$

where  $R_{rej}$  = rejection

$C_{permeate}$  = concentration of permeate, mg/L

$C_{feed}$  = concentration of feed, mg/L

It has been known that RO separation process takes place at ambient temperature without any phase change. Therefore, in the context of desalination, RO process is clearly preferred than the conventional distillation method since distillation required considerably more energy in changing the water from liquid to gaseous phase.

RO process is intrinsically a physical separation process and thus there is no need of chemicals addition. This means a large saving on operational costs, especially in large treatment plants. In today, membrane modules available in the market are generally compact and have a small footprint. For instance, the spiral wound module provides a high membrane surface to volume ratio, which allows greater flow rate of influent. The feed-channel spacers placed between membranes could promote turbulent flow, a feature that reduces fouling and lengthens membrane lifespan.

Owing to the high rejection for almost all aquatic contaminants, RO process can remove and reduce the potential of contamination in potable water supplies. There is simply no other treatment process that can produce the same water quality from a highly saline or organic groundwater source as economically as RO. Since high quality effluent could be recovered from RO process, the use of RO in water reclamation has become an attractive alternative.

### **2.1.2 Targeted Contaminants of RO Process**

The major issues in current water treatment have involved both water supply and quality. Reverse osmosis process has increased the raw water supply by making possible the use of brackish waters for potable water supply. RO can also increase water quality to a great extent.

Significant quality issues include disinfection by-products (DBPs), disinfection, bacteria regrowth, synthetic organic compounds (SOCs) and corrosion. RO could be described as diffusion-controlled process in which mass transfer of ions through the membrane is controlled by diffusion. Consequently, RO process can efficiently remove salts, hardness, pathogens, turbidity, (DBPs) precursors, synthetic organic compounds (SOCs), pesticides, and almost all contaminants in potable water known today (Taylor *et al.*, 1987).

The efficiency of RO process in rejection of dissolved solids or salts makes it becomes the most commonly utilized membrane process for drinking water production in the world today. There are more than 100 water treatment plants in the United States that are using RO to produce drinking water from brackish water; and several major facilities using RO for desalination of seawater have been founded in the Middle East (Strohwalde *et al.*, 1992).

DBPs are a major type of targeted contaminants that can be controlled by reverse osmosis. DBPs are formed when the natural organic matter (NOM) in drinking water reacts with chlorine or other chemical oxidizing agents used for disinfection. Not all of the NOMs are assumed to be DBP precursors, but RO can effectively control DBPs by rejecting the NOMs or DBP precursors (Tan *et al.*, 1991).

RO membranes that have molecular weight cutoffs (MWCO) of 500 or less have been found to reject more than 90 percent of the NOMs from feed waters. The removal of NOM not only reduces DBP formation but also decreases chlorine demand in the distribution system. Consequently, the minimum disinfectant residual concentrations required by regulation are more easily maintained with these systems. The increased removal of NOM would minimize the bacteriological food source and very likely reduce biological activity and bacteria regrowth in the distribution system.

## **2.2 RO Membrane Fouling**

Although membrane technologies have many advantages compared with other conventional water treatments, as mentioned in the first chapter, membrane fouling is the most prevalent problem faced in the use of RO systems. When feed water passes through the membrane, the solute or any targeted constituents that are rejected would accumulate on the membrane surface. This phenomenon is called membrane fouling. In principle, membrane fouling reduces the net driving force or increases the net resistance of the RO system, thus reducing the amount of permeate flux with time.

The direct consequences of membrane fouling are the reduced capacity of the permeate production, or the need of high driving force to maintain a required rate of permeate production. In some cases, the quality of permeate could also deteriorate due to membrane fouling. The membrane foulants could be removed through membrane cleaning, at least, to certain level. However, the cost of down time and membrane cleaning should be carefully considered since it could be a significant part of the total cost of membrane process. Alternatively, pre-treatment could be employed to reduce the rate of membrane fouling.

### **2.2.1 Types of Membrane Fouling**

In general, there is a great variety of possible foulants in water and wastewater treatment applications of membranes, which include organic solutes (adsorption),

inorganic ionic soluble materials (scaling), and particulates (cake formation). The four major kinds of fouling commonly observed in membrane processes are as follows:

**Colloidal fouling.** Particulates are a major class of foulants in all kinds of membrane processes. Under the drag force of permeate flux, particulates can be held onto the membrane surface. The accumulation of the particulates on membrane surface forms a cake layer. Such phenomenon is also known as colloidal fouling. Algae, bacteria, and certain organic matters also fall into the size range of particle and colloids; however, they are different from inert particles such as silts and clays. To distinguish the different fouling phenomena, particles and colloids here are referred to biologically inert particles.

**Inorganic fouling.** Inorganic fouling or scaling is caused by the accumulation of inorganic precipitates such as metal hydroxides, and “scales” on membrane surface. Precipitates are formed when the concentration of chemical species exceeded their saturation concentrations. Slightly soluble inorganic salts could reach saturation when part of the water pass through the membrane. Feed water containing inorganic salts, in particular those of calcium and/or barium that may be sparingly soluble in water, would tend to deposit on the surface of the membrane. Scaling is a major concern for RO and NF as these processes usually has a high rejection for inorganic species.

**Biofouling.** Microbial fouling is a result of formation of biofilm on membrane surfaces. Microorganisms in membrane systems tend to adhere to surfaces and produce extracellular polymeric substances (EPS) to form a viscous, slimy, hydrated gel layer called biofilm, which participates in the separation process as a secondary membrane. This accumulation and growth of microorganisms on membrane surface cause biofouling. Although the initial attachment of microorganisms on membranes might obey some physical laws, biofouling is essentially a biological phenomenon. The overall hydraulic resistance of the membrane could increase due to the formation of biofilm.

**Organic fouling.** Organic fouling is profound in membrane filtration with source water containing relatively high concentration of natural organic matters (NOMs). Surface water (lake, river) typically contains higher NOM than ground water, with exceptions. Organic constituents in the feed water can accumulate on membrane through adsorption because the organic matter usually has a high affinity for the organic polymeric membrane materials. The NOMs in feed water are relatively complex and vary from different locations and seasons. This makes the phenomenon of organic fouling rather complicated, and thus the knowledge of its exact mechanisms is still limited.

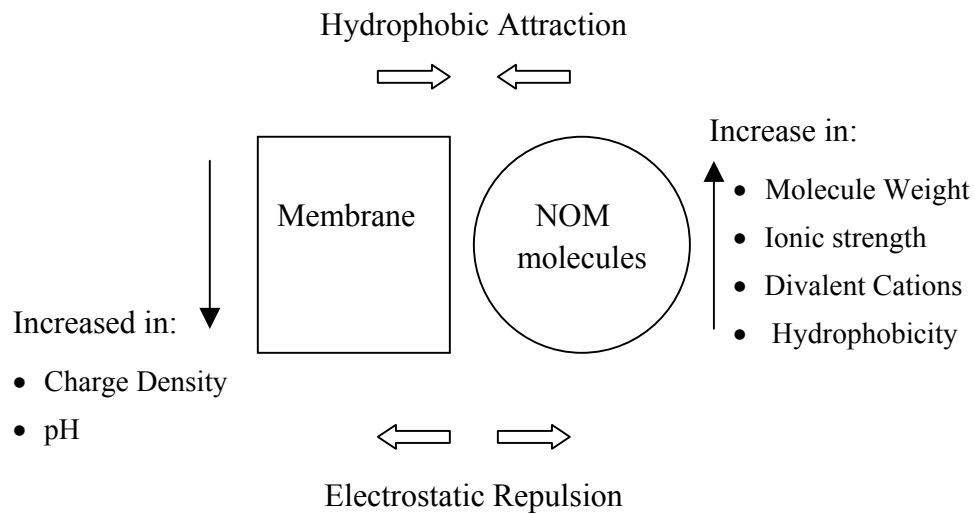
RO membrane has been reported as an effective method for desalination of brackish water and secondary effluent treatment due to its very compact or even non-porous

structure; and the general targeted solutes of RO membrane are dissolved salts and small-sized organic matters. Unlike other foulants, such as colloids, organic matter has an inherent affinity to the polymeric membrane, which makes it relatively easy to adsorb onto the membrane surface. Therefore, NOM has been reported as a major fouling agent to RO membranes, and this kind of fouling would be the area of focus in our research.

### **2.2.2 Mechanisms of Organic Fouling**

Membrane fouling is a complicated phenomenon and typically resulted from poorly understood multiple causes. In spite of its complexity, electrostatic and hydrophobic /hydrophilic interactions that involve both the membrane and fouling materials are recognized to have significant influence, especially for membrane fouling dominated by natural organic matter (NOM). Electrostatic repulsion occurs among functional groups of membranes, fouling materials, and water primarily through dissociation, which strongly depend on the pH, ionic strength, and concentrations of multivalent cations in the solution.

The core issue is hydrophobic and electrostatic interactions between the membrane and fouling materials, as well as among fouling materials themselves. For membrane fouling dominated by the adsorption of NOM, the fouling and cleaning could be illustrated by a simple conceptual model as shown in Figure 2.2.



**Fig. 2.2 Conceptual model of membrane fouling and cleaning**

NOM macromolecules that are retained by membrane will accumulate on and near the membrane surface where they are subjected to hydrophobic attraction and electrostatic repulsion (Fu *et al.*, 1994). The balance between hydrophobic attraction and electrostatic repulsion essentially determines if a membrane is being fouled or being cleaned. As molecular weight and mass/charge ratio of solutes, ionic strength, and the concentration of divalent cations increases, hydrophobic attraction tends to increase, so does the potential of membrane fouling. On the other hand, increases in charge density and polarity of solutes, as well as pH, will increase electrostatic repulsion between the membrane and solutes, and thus results in the reduction in adhesion between the membrane and fouling materials.



This model is simplistic in the sense that it only focuses on two major interactions – electrostatic repulsion and hydrophobic attraction between the membrane and fouling materials. Other possible interactions such as hydrogen bonds and dipolar moment are not being considered. In addition, the model does not address the hydrodynamics aspect of mass transport, which would be discussed later in the report. Nevertheless, the model provides a conceptual framework on understanding the chemical aspects for membrane fouling, which is the focus of this paper.

### **2.2.3 Membrane Cleaning**

Effective membrane cleaning is often just as important as pretreatment for efficient operation of RO membrane system (Potts *et al.*, 1981). The frequency and type of cleaning depends on the quality of the feed stream. Apart from pure hydraulic cleaning, typical cleaning solutions contain a variety of chemicals such as sodium dodecyl sulfate, phosphate and sodium hydroxide. Metal chelators, often known as sequestering agents, are also included in cleaning solutions to enhance cleaning efficiency (Wilbert, 1993). It should be noted that selection of cleaning agent based on membrane material, as well as cleaning conditions, such as temperature, pH range, frequency and duration, have significant effects on cleaning efficiency.

### **2.3 Natural Organic Matter (NOM)**

NOM represents a wide range of complex compounds and its exact composition is relatively unknown. The limited knowledge shows that dissolved NOM is a mixture of ill-defined aliphatic and aromatic compounds with mainly carboxylic and phenolic functional groups (Dalvi *et al.*, 2000; Liu *et al.*, 1999).

NOM plays a significant biochemical and geochemical role in aquatic ecosystems. There is increasing interest in incorporating its chemical properties into predictive models of equilibrium and kinetic processes. Many studies also have shown the importance of NOM in controlling the speciation and toxicity of trace metals in aquatic environments (Cabaniss *et al.*, 1988; Malcolm, 1985).

NOM can be broadly divided into humic and non-humic fractions. The humic fraction is considered most important in terms of chemical properties and implications for water treatment. The humic content of a water can be described by its specific ultraviolet absorbance (SUVA). SUVA is defined as ultraviolet absorbance at 254 nm ( $UV_{254}$ ) divided by the dissolved organic carbon (DOC) concentration. Typically, SUVA at  $<3$  L/mg.m indicates largely non-humic (non-hydrophobic) material, whereas SUVA in the range of 4.5 L/mg.m represents mainly humic materials (Karsner *et al.*, 1999).

### **2.3.1 Humic/ Non-humic Substances**

Humic substances (HSs), which are described as heterogeneous polyfunctional polymers, are formed through the breakdown of plant and animal tissues by chemical and biological processes (Liu *et al.*, 1999). Generally, HSs are more hydrophobic in character and comprises mainly humic and fulvic acids. They contain both aromatic and aliphatic components with primarily carboxylic and phenolic functional groups, in which carboxylic functional groups account for 60-90% of all functional groups (Aiken *et al.*, 1985). HSs are reported as refractory anionic macromolecules of low to moderate molecular weight.

HSs account for over 50% of the dissolved organic carbon (DOC), and are mainly responsible for the color in natural waters (Thurman *et al.*, 1981). Although HSs are reactive components for interactions with many inorganic and organic pollutants, and may decrease toxicities of these pollutants, they are themselves precursors of numerous chlorination by-products that are carcinogenic. HSs are still among the least understood and characterized components in the environment due to their complex polymeric properties.

The non-humic substances of NOM are composed of transphilic acids, proteins, amino acids and carbohydrates, and are responsible for 20-40% of the DOC in natural waters. The non-humic fractions are less hydrophobic than the humic fractions (Aiken *et al.*, 1992; Owen *et al.*, 1995).

### **2.3.2 NOM Fractionation**

In general, there are two major limitations in the determination and testing of organic materials dissolved in various type of water. These are (i) the lack of practical isolation procedures that separate these organic materials from the water and inorganic salt matrix in which they are dissolved; and (ii) the lack of meaningful fractionation procedures to isolate similar groups of compounds for testing and analyses.

Conventional solvent-extraction procedures used in organic analysis of drinking water have isolated, on the average 10% of the dissolved organics solutes. Thus solvent extraction is considered to be ineffective in obtaining quantitative isolation of dissolved organic carbon in natural waters and most wastewaters. Adsorption techniques using various synthetic resins and granular activated carbon are much more efficient in removing organic solutes from water (Malcolm *et al.*, 1992).

However, low solute recoveries from the sorbent, especially from granular activated carbon, have limited the use of adsorption techniques to analysis of certain types of organic solutes. Evaporative techniques are limited to non-volatile solutes, and there is no separation of organic solutes from inorganic solutes. There is no single technique that can achieve quantitative isolation of all organic solutes from water, but it should be aimed to correctly combine various techniques into a comprehensive analytical procedure that can result in the quantitative isolation of most organic solutes from the water samples.

The first comprehensive isolation and fractionation procedure for determining organic solutes in various river waters was developed by Sirotkina and the co-workers (1970). It sequentially used (i) freeze concentration, (ii) adsorption upon and desorption from ion-exchange celluloses, and (iii) Sephadex-gel filtration. The utility of this procedure was more applicable to macromolecular polyelectrolytes found in natural waters than to low molecular weight contaminants found in many wastewaters.

### **2.3.3 Resin Fractionation of NOM**

An analytical procedure called DOC fractional analysis developed by Leenheer *et al.* (1981) has been described as an effective method for fractionating NOM. Using advanced dual-resins (XAD-8 and ion-exchanged resin) method, organic solutes can be quantitatively classified into six fractions, namely, hydrophobic-bases, -acids, -neutrals fractions and hydrophilic-bases, -acids, -neutrals based upon their adsorption upon non-ionic and ion-exchange resin adsorbents. These groups of organic matter have different characteristics of hydrophobicity, size, shape and charge density.

Some of the apparent advantages from this fractionation procedures are (i) higher recovery as compared to solvent extraction techniques, (ii) suitability for scale-up to large volume samples so that milligram to gram-sized quantities of organic solutes in each fraction can be obtained, (iii) an interpretable and reproducible fractionation so that the constitution of each fraction can be obtained, (iv) separation of organic solutes from inorganic salts of the sample, (v) low levels of contaminants introduced by

reagents and resin adsorbents, and (vi) suitable applications to a variety of waters ranging from concentrated wastewaters to dilute natural waters.

## **2.4 Factors Affecting NOM Fouling**

Previous researches have revealed that humic substances, mainly humic acids, constitute the predominant portion of NOM. Generally, humic acids account for over 50% of solution TOC (Fan *et al.*, 2001; Thurman *et al.*, 1981), and in some cases the ratio can be as high as 80-90% (Jucker *et al.*, 1994). Therefore, humic acids have been identified as a major fouling agent in the application of membrane technology for water and wastewater treatment. A complete investigation of humic acids-membrane interaction can lead to a better understanding of NOM fouling.

Considerable studies have shown that RO membrane fouling by humic acid is affected by many factors, including the characteristics of NOM and membranes, feedwater chemistry, and the hydrodynamic and operating parameters (e.g., pressure, feedwater velocity) (Cho *et al.*, 2000).

### **2.4.1 Chemical Aspects**

As mentioned above, electrostatic interaction between the NOM, membrane and dissolved divalent ions in the feed water is one of the significant factors during NOM fouling. There is a natural electrostatic repulsion between negatively charged NOM

and negatively charged membranes. It is reported that NOM fouling becomes more severe at lower pH and higher ionic strength of feed waters as a result of charge neutralization, electric double layer compression, and NOM complexation with dissolved divalent ions (Fane *et al.*, 1998; Braghetta *et al.*, 1998).

#### **2.4.1.1 Effect of Ionic Strength**

Ionic strength has been found to play an important role on NOM fouling. Considerable researches have reported that NOM fouling becomes more severe as the ionic strength of feed solution increases (Cho *et al.*, 2000; Jones *et al.*, 2000; Liu *et al.*, 1999; Nazzal *et al.*, 1994). This phenomenon could be explained by an increase in the hydraulic resistance of the fouling layer that is caused by an increase in ionic strength.

The hydraulic resistance of the NOM fouling layer is determined mainly by its thickness and compactness. Generally, humic acids and polymeric membranes are negatively charged at the neutral circumstance. At high ionic strength, the charges of the membrane surface and humic macromolecules are significantly reduced, due to double layer compression and charge screening. This leads to a drop in electrostatic repulsion between the membrane surface and NOM. As a result, the deposition of NOM onto membrane surface is greatly enhanced. Furthermore, due to reduced inter-chain electrostatic repulsion at high ionic strength, humic macromolecules become coiled and spherical in shape (Ghosh *et al.*, 1980). Consequently, a more compact

fouling layer is formed. The resulting fouling layer provides a significant hydraulic resistance to water flow, causing a significant reduction in permeate flux.

On the other hand, at low ionic strength, strong electrostatic repulsion between membrane surface and NOM hinders NOM deposition. A much looser fouling layer is formed since humic macromolecules have a flat linear configuration at low ionic strength. The long range of double layer repulsion at low ionic strength also prevents the formation of closely packed NOM fouling layer. Thus, the decline in flux is not as significant as it is at high ionic strength.

#### **2.4.1.2 Effect of Solution pH**

Solution pH is another important factor in determining the NOM fouling. Neutral feed water (pH  $\approx$  7) is preferred for membrane filtration processes since NOM fouling increases as pH decreases. A more significant decline in product water flux due to NOM fouling is always observed when solution pH is decreased from 7 to 3 (Jones *et al.*, 2000; Liu *et al.*, 1999; Hong *et al.*, 1997). This permeate flux decline could be attributed to charge reduction of both the humic macromolecules and the membrane at low pH.

A polymeric membrane acquires surface charge when brought into contact with an aqueous medium. Generally, the membrane surface charge is presented as a function of pH. With solution pH increasing, the surface charge of the membrane is positive in the



low pH range, after passing through an isoelectric point, becomes negative in the higher pH range. This means membrane surface charge becomes less negative with decreasing pH. For most polymeric membranes, the isoelectric point is around pH 3 to pH 5.

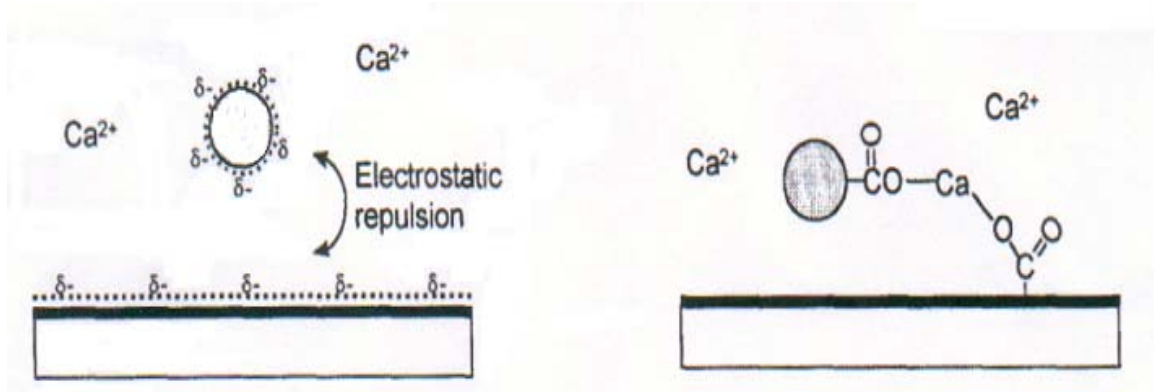
On the other hand, at a decreasing pH, more carboxylic groups of NOM become protonated, thus also resulting in a reduction of negative charge of humic macromolecules. From these two points, the electrostatic repulsion between the membrane surface and NOM, as well as between the NOM in solution and deposited NOM, is reduced at low pH. As a result, the deposition rate of NOM on the membrane surface increases.

Apart from that, NOM has a smaller macromolecular configuration at pH 4, due to the reduced electrostatic repulsion between neighboring functional groups. Hence, a denser fouling layer is achieved at the membrane surface.

#### **2.4.1.3 Effect of Divalent Ions (Calcium)**

Unlike monovalent ions such as  $\text{Na}^+$ , divalent ions bind specifically through complex formation with the acidic functional groups (predominantly carboxylic) of NOM. As a result, in the presence of calcium ions, the charge of the NOM is reduced significantly not only due to effective charge screening but also due to complex formation, which

leads to a more serious NOM fouling. Mechanism of NOM adsorption onto membrane surface in the addition of calcium ions is shown in Figure 2.3 (Yoon *et al.*, 1998).



**Fig. 2.3 Mechanisms of NOM adsorption with calcium ions (Yoon *et al.*, 1998)**

Reduced interchain electrostatic repulsion of NOM macromolecules due to calcium complexation also results in the formation of small, coiled humic macromolecules, and thus a more compact and denser fouling layer is formed.

#### **2.4.1.4 Effect of NOM Hydrophobicity**

Hydrophobicity of organic matters was also found to play an important role in NOM fouling. In a study on NF fouling using conventionally treated effluent as feed water, it was found that the NOM components fouled membrane in the order of humic substances, proteins, polysaccharides and amino sugars (Speth *et al.*, 1996).

Lin *et al.* (2000) studied the effects of the characteristics of the fractionated humic acid on the performance of a negatively charged hydrophobic UF membrane. It was

observed that the hydrophilic fraction induced the worse flux decline despite little rejection of DOC. However, Nilson and DiGiano (1996) reported that hydrophobic NOM should be responsible for nearly all permeate flux decline in the NF experiments when using a relatively hydrophilic membrane. These studies suggested the importance of hydrophobic interactions in the fouling of low molecular weight cut-off (MWCO) membranes.

#### **2.4.2 Hydrodynamic Aspects**

Hydrodynamic operating conditions have significant influence on NOM fouling, especially for crossflow reverse osmosis filtration pattern. RO is a pressure-driven process, in which water is forced to permeate the membrane by the application of pressure. When transmembrane pressure is applied, organic macromolecules are transported to the membrane and accumulate near the membrane surface. The permeate flux rate is generally proportional to the applied pressure until the accumulation of solutes in the concentration polarization layer reaches a threshold concentration that limits further increases in flux (Porter, 1972). After that, an immobile fouling layer is formed and an additional resistance to water flow is created.

Hong and his co-workers investigated the influence of hydrodynamic conditions on membrane fouling, and reported that more serious NOM fouling occurred with higher initial permeate fluxes, which indicates higher applied pressures (Hong *et al.*, 1997). This phenomenon is attributed to the increased accumulation rate of NOM

macromolecules on membrane surface due to a higher applied pressure. At a given solution composition and cross flow, higher convective transport of NOM toward the membrane at higher initial fluxes inevitable results in a greater deposition of rejected NOM.

However, it was also found that at any given chemical condition, a critical permeate flux exists below which the fouling rate is very low. Crozes (1997) also confirmed empirically from over 36 pilot studies that there was a certain threshold operating pressure for UF membrane, below which organic fouling can be effectively prevented. Hong (1997) attributed this observation to the interplay between permeation drag resulting from the convective flow toward the membrane and electrostatic double layer repulsion. When hydrodynamic force acting on the transported NOM macromolecules can overcome the electrostatic repulsion between the NOM and the membrane thus resulting in NOM deposition.

## **MATERIALS & METHODOLOGY**

Reverse osmosis filtration tests were conducted using synthetic humic acids solutions and one type of RO membrane to investigate the effects of organic hydrophobicity, pH and ionic strength of feed water, as well as the addition of calcium ions on NOM fouling. To study the influence of operation pressure, secondary effluent after MF and three types of membranes were adapted during RO operations. The amount and rate of membrane fouling depend on properties of the feed water, humic acids, membranes and the operational conditions imposed by test apparatus. The laboratory analyses of these properties as well as the experimental setup and methods of tests are described below.

### **3.1 RO Membrane Test**

#### **3.1.1 Membrane Test Units**

The lab-scale crossflow RO membrane test unit consisted of membrane cells, main pump, booster pump, feed tank, temperature controller, and data acquisition system.

Figure 3.1 shows a schematic description of the RO operation setup.

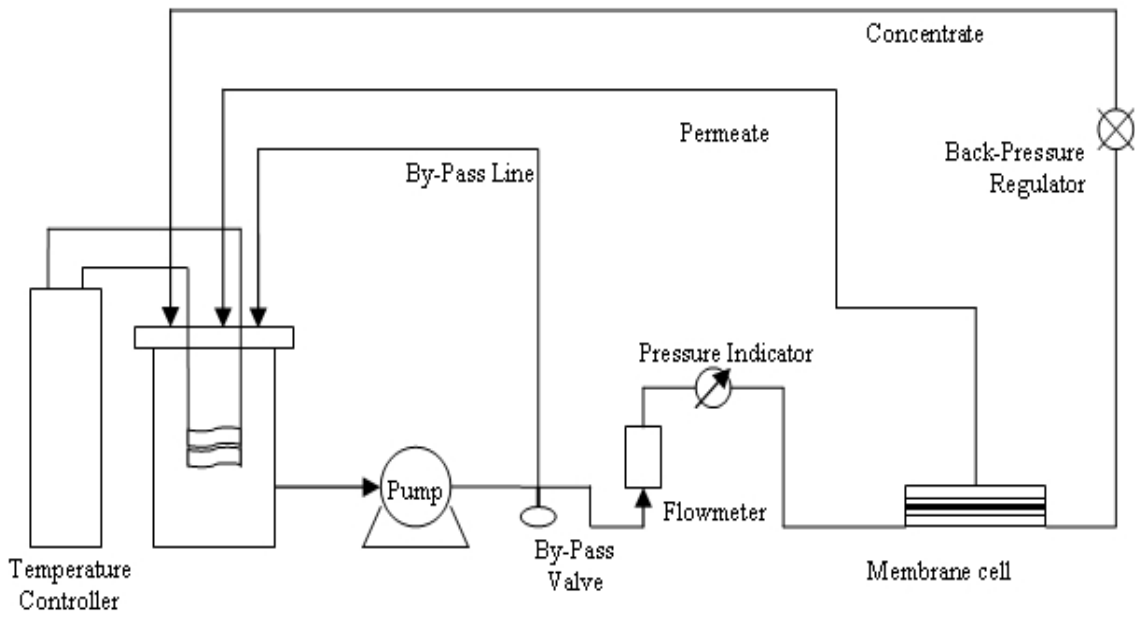


Fig. 3.1 Schematic description of the crossflow RO membrane test unit

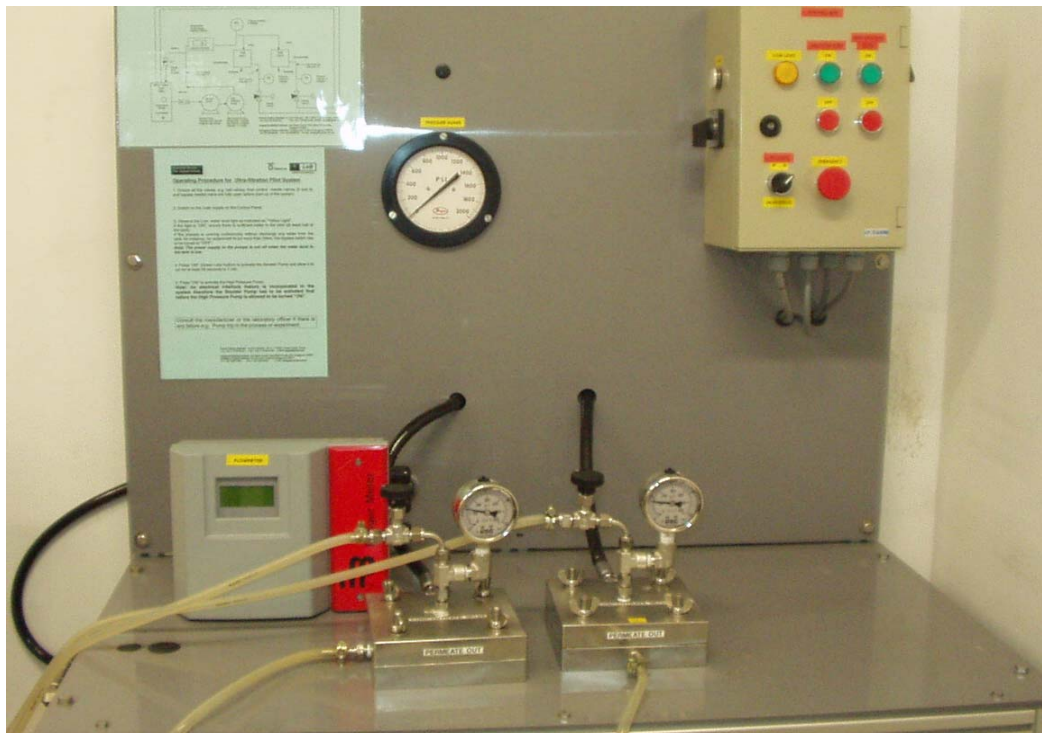


Plate 3.1 Crossflow membrane cell units

The key portion of this RO system was composed of two high-pressure membrane cells (SS 316, Osmonics, USA). These plate-and-frame membrane cells were configured in parallel type. Each cell contained a flat membrane sheet, placed in a square channel with an area of 81 cm<sup>2</sup> and 0.7 cm high. The actual laboratory test cells set-up arrangements is shown as Plates 3.1. The product water was collected from the bottom of membrane cells, while the brine was recirculated back to the feed tank.

In this unit, the test solution was held in a 30 liters reservoir (Fiber glass) and fed into the membrane cells by a high-pressure pump (C-110E, ALTO DENSIN, Denmark) (plate 3.2), capable of providing a maximum pressure of 500 psi and a maximum flow of 0.12 m<sup>3</sup>/h. In addition, a booster pump (CRN1-25, Grundfos, Denmark) (plate 3.3) was used to maintain a steady feed flow to main pump.



**Plate 3.2 High-pressure pump**



**Plate 3.3 Booster pump**

Since operating conditions also play an important role in membrane fouling, throughout all experiments, the desired transmembrane pressure was maintained at a constant value by adjusting a back-pressure regulator (USG, USA). The crossflow velocity in the membrane cells was controlled through bypassing a portion of the test solution using a bypass valve. The crossflow velocity was kept at around 3.54cm/s. At this condition, the Reynolds number of the flow was approximate 391, which belongs to laminar.

In order to minimize the influence of operation temperature on the permeate flux, temperature controller (Plate 3.4) was used to keep solution temperature at  $30 \pm 1^\circ\text{C}$  during all filtration processes in this research. The cooling process was fulfilled by cooling a portion of feed water back from the bypass.



**Plate 3.4 Temperature controller**

Pressure, crossflow and temperature were measured by an installed pressure gauge (Dwyer Instrutments, USA), magnetic flowmeter (Badger Meter Europa, German) and thermometer, respectively. Permeate flux was manual measured with stopwatch and mass balance.



### 3.1.2 RO Membranes

Three thin-film composite hydrophobic membranes, namely AG, CG and AK, supplied by Osmonics (USA) were selected as the model RO membranes in this study. According to the manufacturer, the membranes were made out of cross-linking polyamides and cellulose acetate. The MWCOs were between 70-100kDa. The specific descriptions of membranes are summarized in Table 3.1. All these membranes were provided as a dry, rolled flat sheet with size of 305×305 mm, and were stored as received at room temperature.

**Table 3.1 Descriptions of three RO membranes\***

Model	Polymer	Salt rejection (%)	25°C pH Range	Typical flux/pressure (GDF/psi)
AG	PA	99.5	4-11	26/225
CG	CA	92	2-8	30/420
AK	PA	99	4-11	16/225

\* Data are from the manufacturer

### 3.1.3 Preparation of Test

For each filtration test, a new membrane specimen was soaked into deionized (DI) water and left overnight (approximately 16 hour) before test to rinse away water-soluble surface coatings. After that, two 12×12 mm membrane samples were cut from the prepared membrane sheet. Using a template, the necessary holes were cut into the samples.

The membranes were then rinsed with DI water again and put into a beaker containing the electrolyte solution to be tested. After the membranes were rinsed in the solution for approximately 20 min, the membranes (along with the formers and spacers) were assembled into the measuring cell and ready for filtration tests. It should be noted that a fresh membrane was used for each run throughout the whole study.

The membrane cell was first flushed with DI water for approximately 3 min and then with the test solution for long enough to displace the entire DI water in the system. The test solution was later recirculated through the cell. The desired pH of the test solution was adjusted with hydrochloric acid (HCl) (MERCK, USA) and sodium hydroxide (NaOH) (Scharlau Chemie, Spain), and the solution was recirculated for 10 min before the first pH measurement was made. In most fouling experiments, the total ionic strength of the feed solution was fixed at TDS  $\approx 750$ mg/l by adjusting the NaCl (Scharlau Chemie, Spain) concentration.

#### **3.1.4 RO Filtration Protocol**

The protocol developed for NOM fouling experiments is summarized in Table 3.2. The membrane was first stabilized and equilibrated in the membrane test unit with NOM-free solution and under desired transmembrane pressure and feed water velocity for 24 hours. This step is necessary to achieve stable water, and to produce reproducible results during the fouling tests.

**Table 3.2 Experimental protocols for NOM fouling tests**

Step	Time (h)	Description
1	0 - 24	Stabilization and equilibration with DI water under desired operation conditions.
2	24 - 30~32	Adjustment and equilibration of solution pH and ionic strength; Baseline performance test.
3	32 - 60	Addition of humic acid; Fouling experiment.

pH and ionic strength of this NOM-free solution were subsequently adjusted to desired values by adding concentrated HCl, NaOH and NaCl. This equilibrium process lasted for another 6-8 hours until a stable initial permeate flux was achieved again. Following that, the performance of the membrane was characterized in terms of permeate flux. These performance data served as a baseline for the subsequent fouling experiments.

Lastly, fouling process was initiated by adding a concentrated stock solution of humic acid into feed solution to achieve the desired humic concentration (7 mg/l). Changes in membrane performance were assessed throughout the fouling test by continuous measurements of permeate flux.

For real water tests, the first equilibrium step was same as that of the NOM fouling test protocol. After stabilization, however, the DI water was discharged and real water was pumped into the membrane cells instead. Due to the sudden change of feed solution

properties, the measurement of permeate flux should be commenced after one hour from solution being introduced to eliminate the influence of concentration polarization and osmosis pressure.

However, permeate flux have been reported to increase with a higher temperature. In cases where membranes are operated under changed temperatures, it is suggested to correct permeate flux to a reference temperature (e.g.25°C) for purpose of comparison. Expressions have been successfully developed for correcting permeate flux of RO membranes over a limited range of temperatures. In all cases, these corrections for permeate flux apply within the tolerant temperature ranges of membranes. Using a reference temperature of 25°C, the following expression for the temperature correction factor was corrected to within approximately 3 percent:

$$J_{25} = \frac{J_T}{1.03^{(T-25)}} \quad (3.1)$$

where  $J_T$  = permeate flux measured at an arbitrary temperature T

$J_{25}$  = permeate flux at a reference temperature of 25°C

## **3.2 Feed Waters**

### **3.2.1 NOM Solutions**

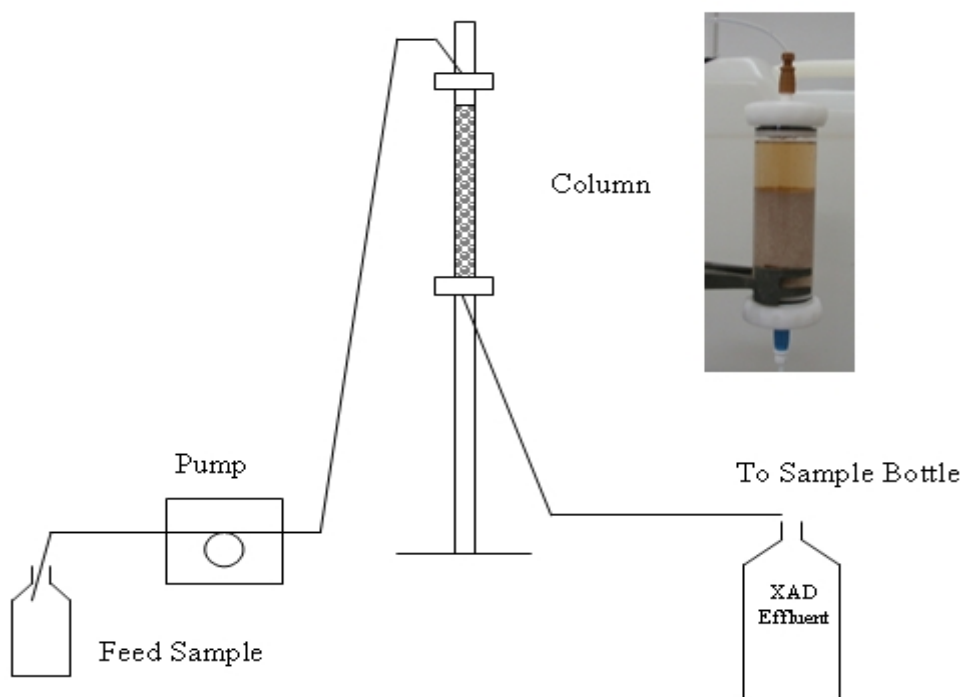
A commercial humic acid, which was purchased from Aldrich Chemicals (Milwaukee, Wisconsin, USA), was chosen as the model NOM in this study. The humic acid was received in a powder form. The detailed preparation process of humic acid solution is described as follow:

A few diluted solutions (150mg/l) were prepared by dissolving the humic acid into DI water. In order to remove particulate materials, humic stock solution was first placed into six 80ml polypropylene centrifuge tubes and centrifuged at 150,000rpm for 15 minutes. Following the centrifugation, the precipitate was discarded and the pH of suspension was adjusted to approximate 2 and reintroduced to centrifuge tubes. This cleaning procedure was repeated three times, after which the suspension was subjected to a 0.45 $\mu$ m membrane filter paper (Gelman Sciences, Michigan, USA). The resulting permeate was diluted to about 1800 mg/L TOC and raised its pH to around 8 through the addition of NaOH. Finally, the prepared stock solution was kept under refrigeration (4°C) before the resin fractionation procedure.

A series of resin adsorbents, namely XAD-8 hydrophobic resin, AG-MP-50 cation-exchange resin and IRA-96 anion-exchange resin, were used to isolate complex mixtures of organic solutes and to fractionate these solutes into six compound classes based upon their hydrophobicity and acidity (Leenheer, 1981).

### 3.2.1.1 Preparation of Resins

**XAD-8 resin.** The XAD-8 hydrophobic resin (0.24-0.32mm size, 160 m<sup>2</sup>/g mean surface area, 0.023µm mean pore diameter, Supelite) was used for fractionation of humic acid according to its hydrophobicity. Before packing into a 35mm chromatography column (Omnifit), XAD-8 resin was initially washed with methanol and DI water. The XAD-8 resin column should be rinsed with 0.1M NaOH, 0.1M HCl and distilled water one more time just before application of the sample. Figure 3.2 shows the resin fractionation setup and the real image of resin column.



**Fig. 3.2 Setup for humic acid fractionation**

**AG-MP-50 resin.** The AG-MP-50 cation-exchange resin (Bio-Red Laboratories) is a strong acid, sulfonated, polystyrene macro porous resin. As a hydrogen-form resin, it was purified by Soxhlet extraction with methanol for 24 h before use. After that, AG-MP-50 resin was cleaned by distilled water and packed into column to be used. Pump 2M NaOH through the column until breakthrough of ammonia was observed. Hydrogen-saturated resin was prepared by pumping four bed volumes of 2M HCl through the resin and rinse with distilled water until the specific conductance of the effluent was less than 10 $\mu$ m ho. Lastly, AG-MP-50 cation-exchange resin was stored in methanol.

**IRA-96 resin.** IRA-96 anion-exchange resin (Amberlite) is a weak base, macroporous, phenol-formaldehyde condensation product, which is an industrial-grade preparation in the form of flakes up to 1mm in diameter (Leenheer, 1981). IRA-96 resin was prepared by sieving out the large flakes with a 1.4-mm sieve. Fines were removed by slurring in distill water and decanting. The resin was then soxhlet extracted with acetone for 24 h. After that, the resin was slurried with distilled water and packed in the column to be used.

1M HCl was continuously pumped through the column until the DOC of the effluent was 1 mg/L or less. The resin initially has a high DOC bleed with 1M HCl, and the resin bed expanded 30% during conversion from the free-base form to the hydrochloride form. Therefore, when the column was packed with free-base-form resin,

enough column head space was provided to allow resin expansion (Leenheer, 1981). Following HCl rinse, 2M NaOH was pumped through the column until the specific conductance of the effluent was less than 10  $\mu\text{mho}$ . The IRA-96 anion-exchange resin was stored in distilled water and was reused after repeating the 2M NaOH and distilled water rinses.

### 3.2.1.2 Resin Fractionation Procedure

The humic acid fractionation procedure by the series of resins is presented in a flowchart, as shown in Figure 3.3.

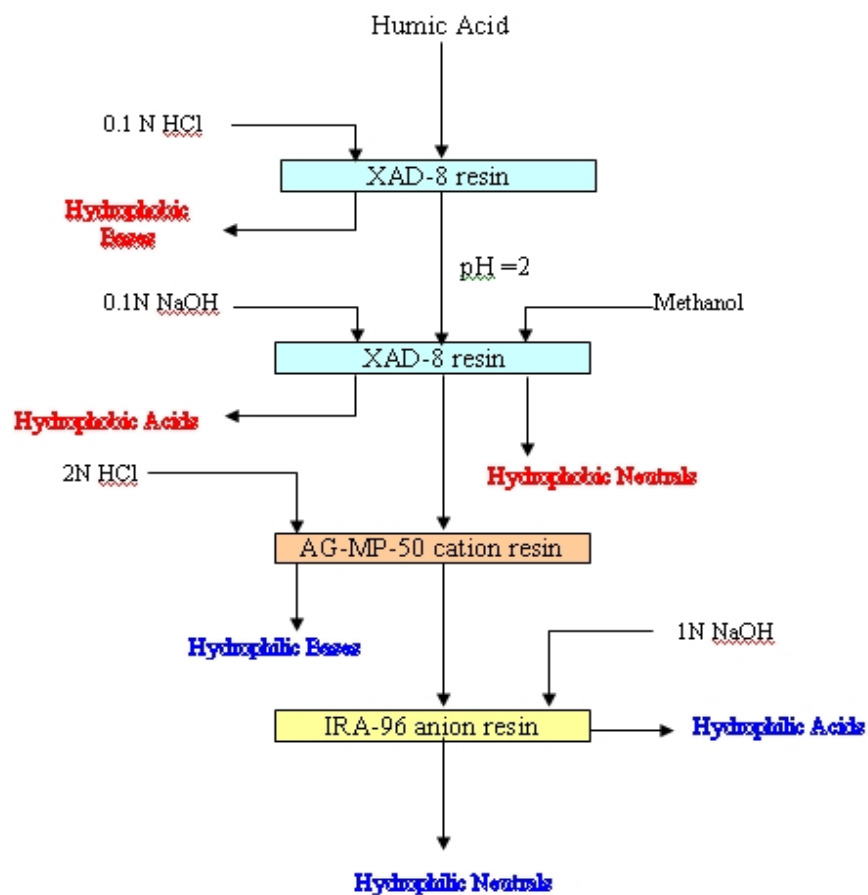


Fig. 3.3 Humic acid fractionation flowchart



The stock humic solution was first pumped by a pump (7553-75, Cole-Parmer Instrument Company, USA) into the XAD-column for its adsorption of hydrophobic bases. The flow rate was adjusted to around 10-20 ml/min (less than 30 bed volumes/h) according to manufacturer. The effluent was acidified to pH 2 and reintroduced into the resin for collection of the hydrophilic fraction. When XAD-8 resin was subsequently eluted with 500ml of 0.1M HCl, 1000ml of 0.1M NaOH and 50ml of methanol, hydrophobic bases, hydrophobic acids and hydrophobic neutrals were collected, respectively.

A corresponding isolation of hydrophilic fraction on the basis of acidity was achieved by being passed through the AG-MP-50 cation-exchange resin and the IRA-96 anion-exchange resin in sequence. The final effluent was hydrophilic neutral. Hydrophilic bases were eluted out by introducing 50 ml of 2M HCl into the adsorbed AG-MP-50 cation-exchange resin, while hydrophilic acids were collected by pumping 50 ml of 1M NaOH into the adsorbed IRA-96 anion-exchange resin.

After this series of resins two major components of humic acid solution, namely hydrophobic and hydrophilic NOM, and six sub-components, which are hydrophobic acids, hydrophobic neutrals, hydrophobic bases, and hydrophilic acids, hydrophilic neutrals, hydrophilic bases, were obtained respectively. The humic contents were calculated on the basis of the dissolved organic carbon (DOC) values before and after each resin. It should be noted that the fractionation procedure resulted in a substantial

increase in the ionic strength of both the hydrophobic and hydrophilic fractions due to the use of HCl, NaOH and NaCl to adjust pH of solution.

### **3.2.2 Real Water**

The real feed water used in this study was secondary effluent collected from a local wastewater treatment plant. The water was collected and transported to the laboratory within 3 hours and stored at 0-4°C before use. It was noted that the collected secondary effluent has been filtered by MF with pore size of 0.2µm in site. Therefore, no further pre-treatment for this feed water was needed. Table 3.3 summarizes the characteristics of the secondary effluent after MF treatment.

**Table 3.3 Characterization of MF (0.2µm) effluent**

TOC	TDS	NTU	pH	Na <sup>+</sup> (ppm)	Ca <sup>2+</sup> (ppm)
7.563	497	0.24	7.56	116.34	31.1

### 3.3 Fouling Run Description

#### 3.3.1 NOM Fouling Runs

The different fractions of humic acids (hydrophobic and hydrophilic), diluted with DI water to about 7 mg/L, were used as the feed water for the NOM fouling experiments. All these solutions were supplemented with HCl, NaOH and NaCl to achieve the required pH and TDS. In cases where a calcium source was needed, calcium chloride ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) (MERCK) was used. AG membrane was used as the model RO membrane throughout all NOM fouling experiments. The experimental conditions for all eight runs are summarized in Table 3.4.

**Table 3.4 Experimental conditions for NOM fouling runs**

	Hydrophobic NOM		Hydrophilic NOM
1	Pressure = 250 psi Influent Flowrate = $1.5 \pm 0.5$ L/min DOC $\approx$ 7 mg/L pH $\approx$ 7 TDS $\approx$ 250 mg/L	2	Pressure = 250 psi Influent Flowrate = $1.5 \pm 0.5$ L/min DOC $\approx$ 7 mg/L pH $\approx$ 7 TDS $\approx$ 250 mg/L
3	Pressure = 250 psi Influent Flowrate = $1.5 \pm 0.5$ L/min DOC $\approx$ 7 mg/L pH $\approx$ 7 TDS $\approx$ 750 mg/L	4	Pressure = 250 psi Influent Flowrate = $1.5 \pm 0.5$ L/min DOC $\approx$ 7 mg/L pH $\approx$ 7 TDS $\approx$ 750 mg/L
5	Pressure = 250 psi Influent Flowrate = $1.5 \pm 0.5$ L/min DOC $\approx$ 7 mg/L pH $\approx$ 7 $\text{Ca}^{2+} = 10^{-3}$ M TDS $\approx$ 750 mg/L	6	Pressure = 250 psi Influent Flowrate = $1.5 \pm 0.5$ L/min DOC $\approx$ 7 mg/L pH $\approx$ 7 $\text{Ca}^{2+} = 10^{-3}$ M TDS $\approx$ 750 mg/L
7	Pressure = 250 psi Influent Flowrate = $1.5 \pm 0.5$ L/min DOC $\approx$ 7 mg/L pH $\approx$ 4 TDS $\approx$ 750 mg/L	8	Pressure = 250 psi Influent Flowrate = $1.5 \pm 0.5$ L/min DOC $\approx$ 7 mg/L pH $\approx$ 4 TDS $\approx$ 750 mg/L

### **3.3.2 Real Water Runs**

To investigate the effect of operation pressure on membrane fouling, three RO membranes (AG, CG and AK), and three operation pressures (250 psi, 350 psi and 450 psi) were used. The solution pH was kept around 7 for each run.  $10^{-2}$  M NaCl was added to the secondary effluent as a back electrolyte. Crossflow and solution temperature were maintained at  $3.54 \times 10^{-2}$  m/s and  $30 \pm 1^\circ\text{C}$  throughout all the tests.

## **3.4 Analytical Methods**

### **3.4.1 TOC Measurement**

TOC (total organic carbon), represents the organic, carbonaceous material in water, is not, under most circumstances, a key parameter in the design of RO membrane systems. It may, however, be the predominated contaminant to be removed by RO system, or to contribute to organic or bacterial fouling of the membrane.

Samples were filtered through  $0.45\mu\text{m}$  pore size filter papers (GN-6 Grid 47 mm,  $0.45\mu\text{m}$ , Gelman Science, USA) for TOC test. O. I. Analytical 1010 Total Organic Carbon Analyzer was used to analyze TOC using computer software package WinTOC<sup>®</sup> Model 1010 for Windows (O. I. Analytical, USA.). It uses the US Environmental Protection Agency approved persulfate oxidation method for analysis of samples containing 2ppb to 10,000ppm of organic carbon.

### **3.4.2 TDS Measurement**

Total dissolved solid (TDS) is a measure of the total weight of impurities found in water. Although it is a general parameter, it does permit a quick, rough estimate of the performance of RO membrane. The HANNA online TDS controller, HI983318 and HI983329, were adopted in the system to observe the permeate quality MF and RO, respectively.

### **3.4.3 Ion Chromatography (IC) Measurement**

The Dionex Ion chromatography DX 500 system was used to test the concentration of interested ions in the water sample. It consisted of a CD 20 Conductivity Detector, a GP 50 Gradient Pump, and LC 20 Chromatography Enclosure.

During the analysis, a water sample was injected into a stream of carbonate-bicarbonate eluent and passed through a series of ion exchangers. The ions of interests were separated on the basis of their relative affinities for a low capacity anion/cation exchanger (guard and separator columns). The separated ions were directed through a hollow fiber cation exchanger membrane (fiber suppressor) or micro-membrane suppressor bathed in regenerant solution. In the suppressor the separated ions were converted to their highly conductive acid forms and the carbonate-bicarbonate eluent was converted to weakly conductive carbonic acid. They were identified on the basis

of retention time as compared to standards. Quantity was determined by measurement of peak area or peak height.

#### **3.4.4 Turbidity and pH Measurement**

Analysis of physical-chemical parameters, such as pH and turbidity were performed according to Standard Methods (APHA, 1995). Turbidity is a measure of the extent to which light is scattered by particulates in the water. A TU 1100 turbidity meter was used to determine the turbidity of water samples.

The pH, or the measure of the concentration of hydrogen ions in the water, determines the percentage of inorganic carbon that is in the form of carbon dioxide, bicarbonate, or carbonate. It determines the extent to which carbon dioxide will appear in the permeate water, or whether calcium carbonated is likely to precipitate. A Horiba F-24 pH meter was used to determine the solution pH value immediately after sampling.

#### **3.4.5 Specific Absorbance (SUVA)**

The ratio  $UVA_{254} / DOC$  is define as the specific absorbance (SUVA) of solution, and provides an index of the humic content of the NOM. An UV-visible spectrophotometer (UV-160A, Shimadzu) was used to measure water sample absorbance at 254nm ( $UVA_{254}$ ). An O. I. Analytical 1010 Total Organic Carbon Analyzer was used to measure dissolved organic carbon (DOC) in water sample.

### **3.4.6 Average Molecular Weight (AMW)**

Average molecular weight (AMW) of the NOM components was measured by using a high-pressure, size-exclusion chromatograph (HPLC, Shimadzu) with a Waters Protein-Park 125 column calibrated with polystyrene sulfonates. Before the injection of water sample, it was first filtrated by a 0.2 $\mu$ m pore size filter paper (Whatman, England).

## **RESULTS & DISCUSSIONS**

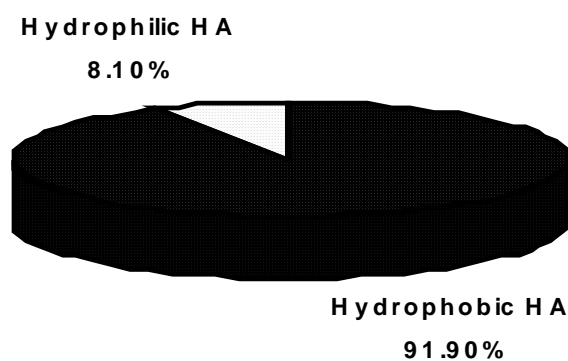
In this study, a crossflow reverse osmosis filtration system was employed to investigate the RO membrane performances with different feed waters, as well as under different solution chemistry and hydrodynamic operation conditions. The entire study was mainly divided into two phases. Phase one focused on NOM fouling research, including studies on the effect of NOM hydrophobicity on RO membrane performance, and the effects of solution pH, ionic strength and calcium ions on the fouling potential of different NOM components. Phase two mainly studied the influence of operation pressure on RO membrane fouling.

### **4.1 NOM Fouling Research**

#### **4.1.1 Aldrich Humic Acid (HA) Composition**

From the resin separation procedure, the composition of fractionated hydrophobic and hydrophilic components of Aldrich humic acid (HA) are presented in Figure 4.1.





**Fig. 4.1 Organic composition of Aldrich HA**

It could be seen that hydrophobic organics (91.90%) was the predominant portion of total TOC in Aldrich HA while hydrophilic organics only accounted for 8.10% of the sample TOC. This result was consistent with the hydrophobicity composition of Aldrich HA reported by Lin, in which the hydrophobic fraction was also found to be the major portion (86.0%) of the TOC recovered (Lin *et al.*, 1998).

However, the fact is that the actual constitution of NOM in natural environment is very complicated, and hydrophobicity components of aquatic humic substances vary markedly with water sources and other environmental factors (Malcolm *et al.*, 1986). Fan *et al.* (2001) reported that the hydrophobic components accounted for the majority of DOC (70.0%) in Maroondah water (Australia); however, with other two water samples collected respectively from Moorabool and Mt. Zero surface waters (Australia), almost an equal DOC percentage for the hydrophobic and hydrophilic component was presented for each water sample.

Nilson *et al.* (1996) and Collins *et al.* (1986) also made similar observations in some natural water samples. According to their findings, the hydrophobic and hydrophilic fractions had almost an equal recovery of DOC in certain natural waters; while for comparison, the hydrophilic portion accounted for 65% of sample DOC in another natural water sample.

The above observations show that commercial HA may not represent the exact humic substances constitution in natural environment. Therefore, when using commercial HA as the model NOM, all the experimental results should be analyzed together with its specific composition.

#### **4.1.1.1 Characteristics of Aldrich HA**

The characteristics of the fractionated hydrophobic and hydrophilic Aldrich HA are summarized in Table 4.1.

**Table 4.1 Characteristics of humic fractions**

HA fractions	DOC (mg/l)	UVA <sub>254</sub> (cm <sup>-1</sup> )	SUVA* (l/m-mg)	AWM (Da)
Hydrophobic HA	519	2.5	0.482	12,350
Hydrophilic HA	150	0.296	0.197	31,187

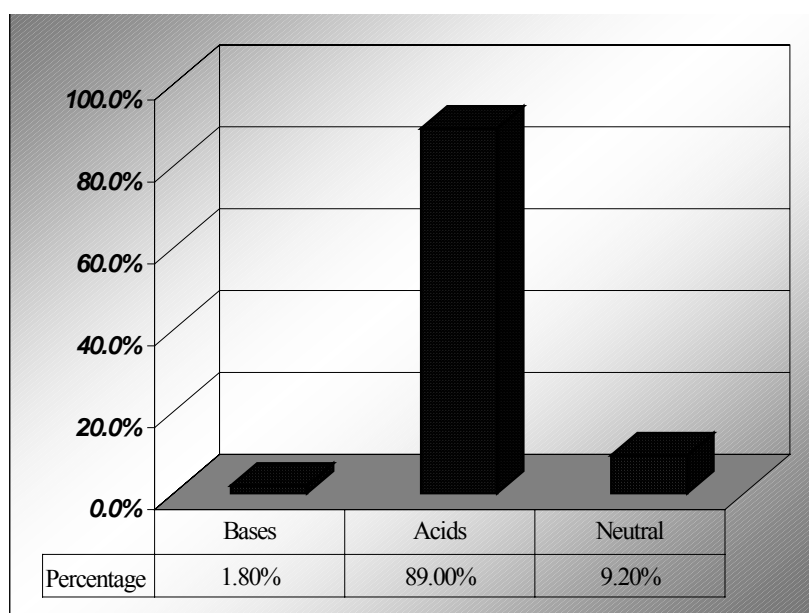
\* SUVA is a ratio of UVA<sub>254</sub> to DOC

From Table 4.1, it can be seen that the specific UV absorbance (SUVA), an index of aromaticity or hydrophobicity, for the hydrophobic fraction was 0.482 as compared to 0.197 for the hydrophilic fraction. This difference in SUVA values suggested that the hydrophobic organics were relatively more aromatic in nature.

The average molecular weight (AMW) of the hydrophilic fraction (31,187) was about 2.5 times the AMW of the hydrophobic fraction (12,350). This indicated that the hydrophilic molecules of humic acid had much larger size than that of the hydrophobic humic acid.

#### **4.1.2 Characteristics of Hydrophobic HA**

Based on DOC recovered from the XAD resins, the amount of acids, bases and neutrals in the hydrophobic HA fraction could be accounted for, as shown in Fig. 4.2.



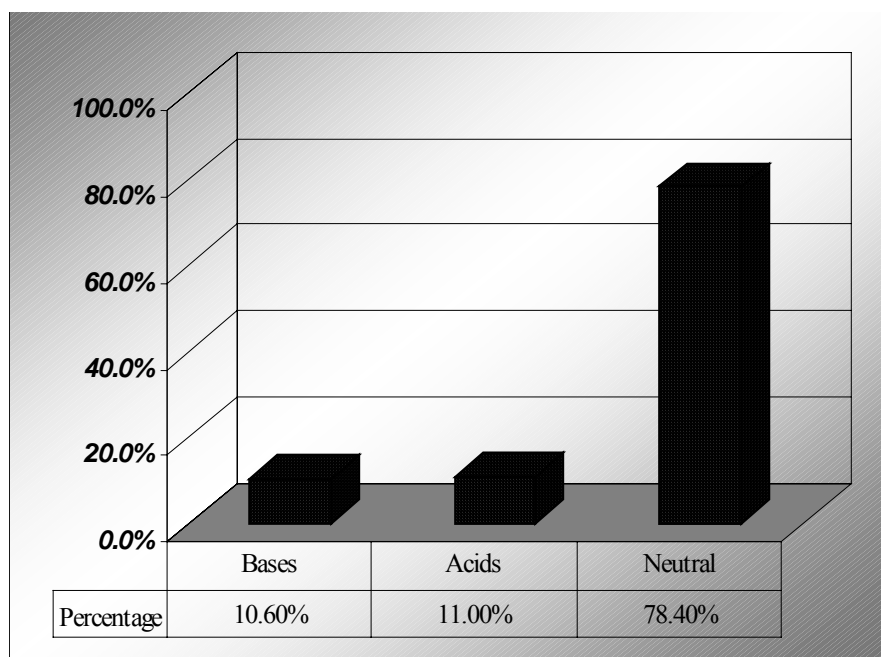
**Fig. 4.2 Characteristics of hydrophobic HA components**

From Fig. 4.2, it is found that the majority of the hydrophobic Aldrich HA components were hydrophobic acids fraction. The amount of hydrophobic acids accounted for about 89.0% of the whole hydrophobic components, while the other two fractions, namely bases and neutrals were only responsible for the rest 11.0% DOC of the hydrophobic HA.

When taking the high DOC ratio (91.90%) of the hydrophobic components in Aldrich HA (Fig. 4.1) into consideration, hydrophobic acids fraction should account for 81.80% of total DOC in Aldrich HA. This high DOC percentage indicated that the overwhelming components of Aldrich HA were hydrophobic acids. This observation is relatively consistent with the findings of Lin *et al.* (1999). Since humic acids fraction was always simply regarded as the hydrophobic components of natural water samples (Cho *et al.*, 1999; Nilson *et al.*, 1996), this result might confirm the reliability of this simplification.

#### **4.1.3 Characteristics of Hydrophilic HA**

Using the method of organic carbon isolation by AG-MP-50 cation-exchange resin and IRA-96 anion-exchange resin, the hydrophilic fractions could also be fractionated into 3 sub-fractions: hydrophilic acids, hydrophilic bases and hydrophilic neutrals. Based on the DOC reduction after AG-MP-50 resin and IRA-96 resin, the quantity of organic carbon in each sub-fraction could be deduced. Figure 4.3 presents the composition of sub-fractions in the hydrophilic HA components.



**Fig. 4.3 Characteristics of hydrophilic HA components**

Fig. 4.3 shows clearly that the majority of hydrophilic organic carbon (78.40%) was from the hydrophilic neutrals fraction, which was different from the hydrophobic HA components. Combined with the respective AWM value of each fraction, 31187 for the hydrophilic HA components and 12350 for the hydrophobic HA components, it can be concluded that the hydrophilic HA used in this study was a relatively larger-size and neutral-based NOM, while the hydrophobic HA was a small-size and acid-based NOM.

#### 4.1.4 Effect of NOM Hydrophobicity on NOM Fouling

NOM fouling tests with the hydrophobic/hydrophilic HA as feed solutions were conducted under similar operation conditions. Same AG membranes from Osmonics were chosen as the model RO membranes. Figure 4.4 presents the normalized permeate fluxes, the ratio of the permeate flux to the initial flux,  $J/J_0$ , for both the hydrophobic and hydrophilic HA fractions. The disrupted fouling curve of the hydrophobic HA (from 12 ~20h) was caused by the discontinuous work during night since the permeate flux must be manually measured. It is also the reason for other similar fouling curves presented later.

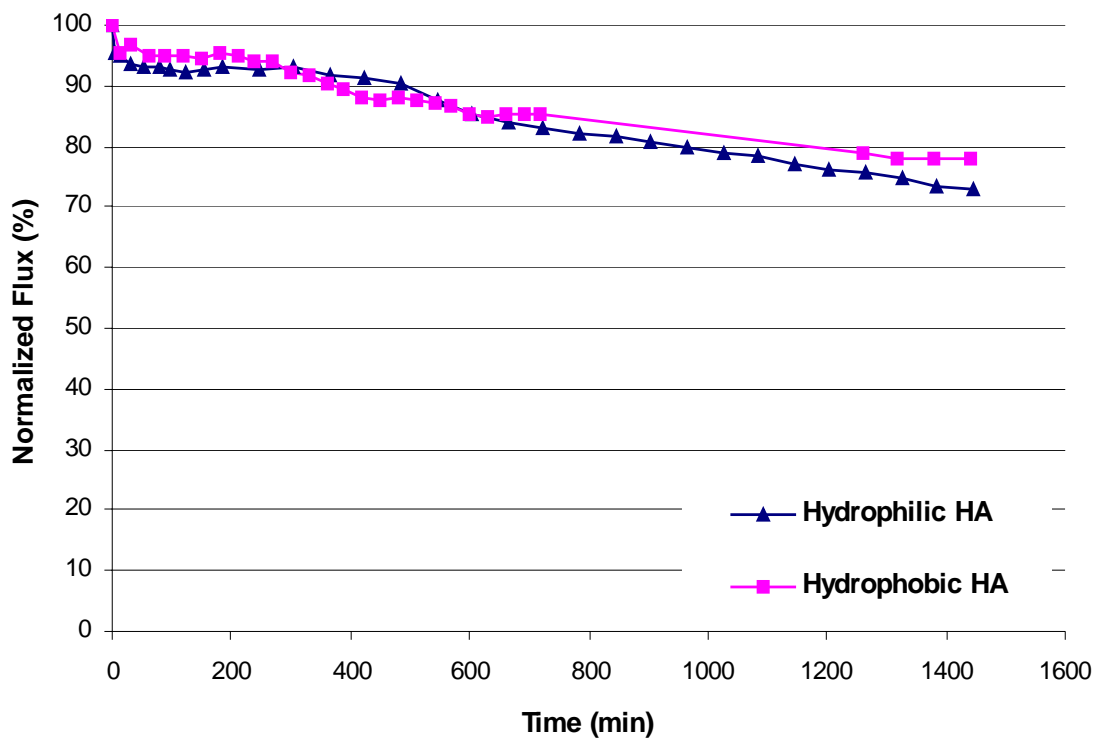


Fig. 4.4 Normalized flux of fractionated HA components;

TOC = 7 mg/l, pH = 7, TDS = 250 mg/l

The bulk concentrations of two fractionated HA components were diluted to an approximately fixed TOC of 7mg/l in both cases, as well as those presented in later parts. The transmembrane pressure was kept at 250 psi during all the filtration processes. The initial water permeate flux ( $J_0$ ) for all membrane tests including those mentioned later were quite similar, with  $J_0$  ranging from 0.287 to 0.302 ml/s. From the manufacturer, it is known that the AG membrane is a hydrophobic RO membrane, which is negatively charged in neutral solutions.

From Fig. 4.4, it could be seen that although the hydrophilic HA produced a higher permeate flux in a certain phase of operation (approximately first 6 ~ 9h), a more severe NOM fouling was created by it than that of the hydrophilic HA during most of the operation time. The hydrophilic HA represented a worse permeate flux decline as only 73.10% of the original flux remained after 24-hour operation, while the hydrophobic HA displayed 77.80% of the initial permeate flux after the same period.

This observation is somehow out of our expectation since according to hydrophobic interactions between the membrane surface and NOM, the hydrophobic HA components should induce a serious NOM fouling to the hydrophobic AG membrane. Considerable researches have proven that hydrophobic interactions are influential factors on permeate flux decline (Cho *et al.*, 2000; Fan *et al.*, 2001; Nilson *et al.*, 1996; Yamagiwa *et al.*, 1993). Therefore, the general consensus is that the hydrophobic

NOM should tend to adsorb more favorably onto the hydrophobic membrane surface than the hydrophilic NOM.

Nilson *et al.* (1996) reported that a hydrophilic NOM solution (effluent of XAD-8) exhibited little permeate flux decline, while a hydrophobic solution (XAD-8 isolate) was responsible for predominant organic fouling in a NF unit. Fan *et al.* (2001) also suggested that NOM with higher hydrophobicity fractionated from natural water resulted in a greater permeate flux decline to a hydrophobic microfiltration (MF) membrane. A hydrophobic PSf membrane with a hydrophobic nonionic surfactant was also used to demonstrate more flux decline than a relatively hydrophilic membrane with the same surfactant (Yamagiwa *et al.*, 1993).

The main reason for this conflicting result might be attributed to electrostatic interactions, another key factor of foulant-adsorption mechanisms, between the NOM particles and membrane surface. As discussed in chapter 2, NOM macromolecules that are larger than the membrane pores will accumulate on and near the membrane surface where they are subjected to hydrophobic and electrostatic interactions (Fu *et al.*, 1994). The balance between hydrophobic attraction and electrostatic repulsion essentially determines if the NOM macromolecules could deposit on the membrane. Therefore, NOM fouling might be simplified as the outcome of interplay between hydrophobic and electrostatic interactions.



According to composition analysis of the individual hydrophobic and hydrophilic Aldrich HA (Figs. 4.2 and 4.3), the model NOM used here, the hydrophobic HA fraction is composed mainly of hydrophobic acids (89.0%) with aromatic structure; while for the latter, the majority component is neutral organics (78.40%) with aliphatic structure.

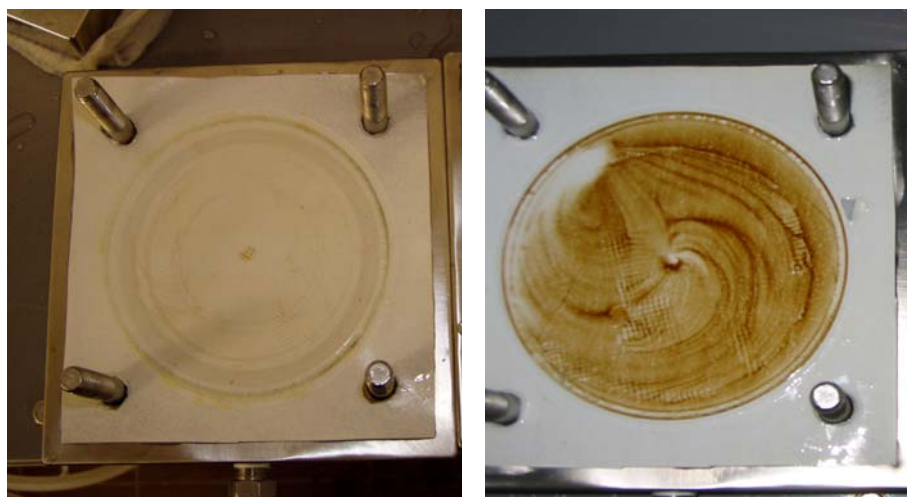
It is known that under the neutral operation condition ( $\text{pH} \approx 7$ ), the hydrophobic acids typically carry a negative charge due to deprotonated carboxylic and phenolic functional groups. Cho *et al.* (2000) also suggested that there was a strong synergy between the aromaticity and charge density of the solutes, which indicated that the hydrophobic acids had a relatively higher negative charge density than neutrals and bases. Therefore, the hydrophobic HA composed mainly of hydrophobic acids should possess a higher charge density than that of the hydrophilic NOM.

Since AG membrane surface is also negatively charged in pH 7 solution, compared with the hydrophilic HA fraction that carries less negative charges, a higher tendency of electrostatic repulsion is thus occurred between the membrane surface and hydrophobic HA, which makes it easier to be rejected by membrane.

Apart from the forces of charge repulsion between the hydrophobic HA foulants and the membrane, another possible reason is intermolecular forces. It has been known that intermolecular forces such as van der Waals interaction also play important roles in the NOM adsorption during membrane filtration. Generally, due to van der Waals force, there is a higher tendency of attraction/adhesion between the solutes with a larger AMW and membrane surface molecules. As the hydrophilic HA fraction has 2.5 times the AMW of that of the hydrophobic HA fraction, the hydrophilic HA is easier to be retained on the membrane surface, thus presenting a higher fouling potential.

Cho *et al.* (2000) hypothesized that the larger-sized neutral and/or basic NOM components should account for the major foulants to a negatively charged, hydrophobic UF membrane. According to our observation, in the cases when the RO membrane is hydrophobic and negatively charged, this assumption is also agreeable.

Combined all the discussions above, it is thus suggested that the predominant mechanisms of NOM fouling during RO process might be electrostatic repulsion and intermolecular forces between NOM foulants and membrane molecules rather than hydrophobic interactions.



**Hydrophilic HA foulants**

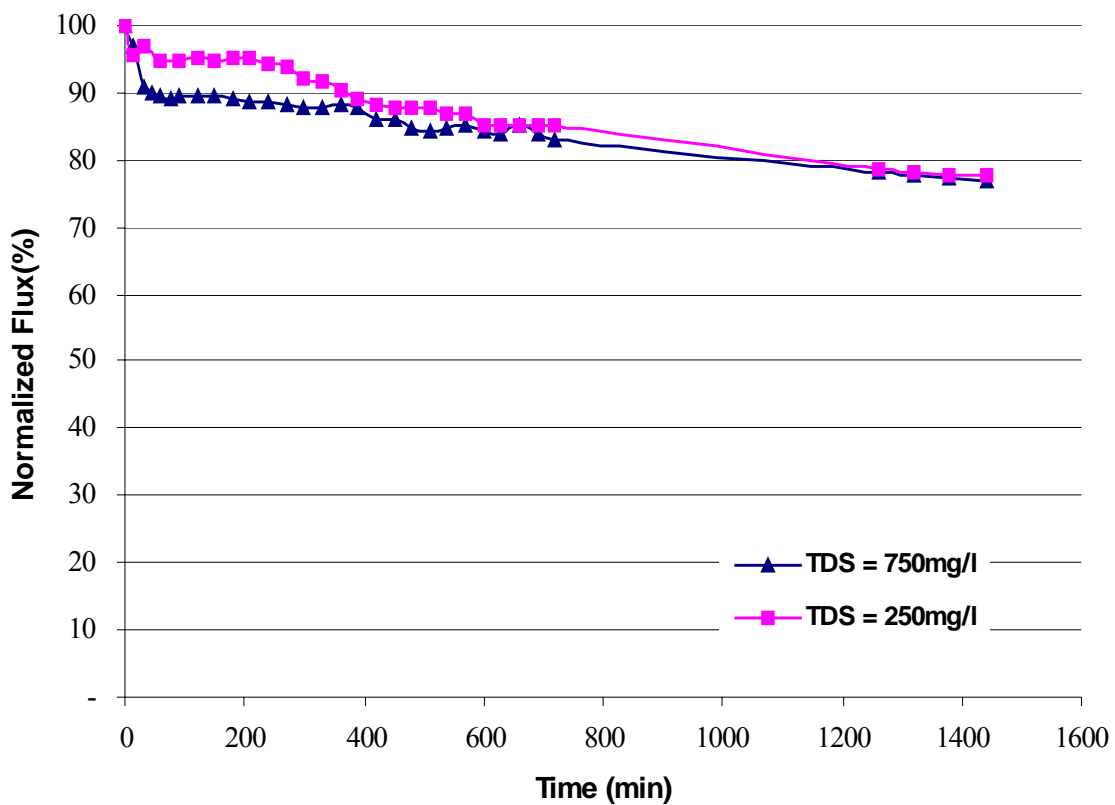
**Hydrophobic HA foulants**

**Plate 4.1 Membrane fouled with hydrophilic/hydrophobic HA**

Plate 4.1 shows the real images of fouled AG membranes by the hydrophilic HA and the hydrophobic HA, respectively. It should be noted that although the hydrophobic HA induced a lighter NOM fouling, it seemed that the amount of accumulated hydrophobic HA foulants were much greater than those of the hydrophilic HA presented in the picture. Actually, this misunderstanding is from the fact that hydrophobic component are mainly responsible for the color in NOM (Thurman *et al.*, 1981), which makes the hydrophobic HA foulants visible.

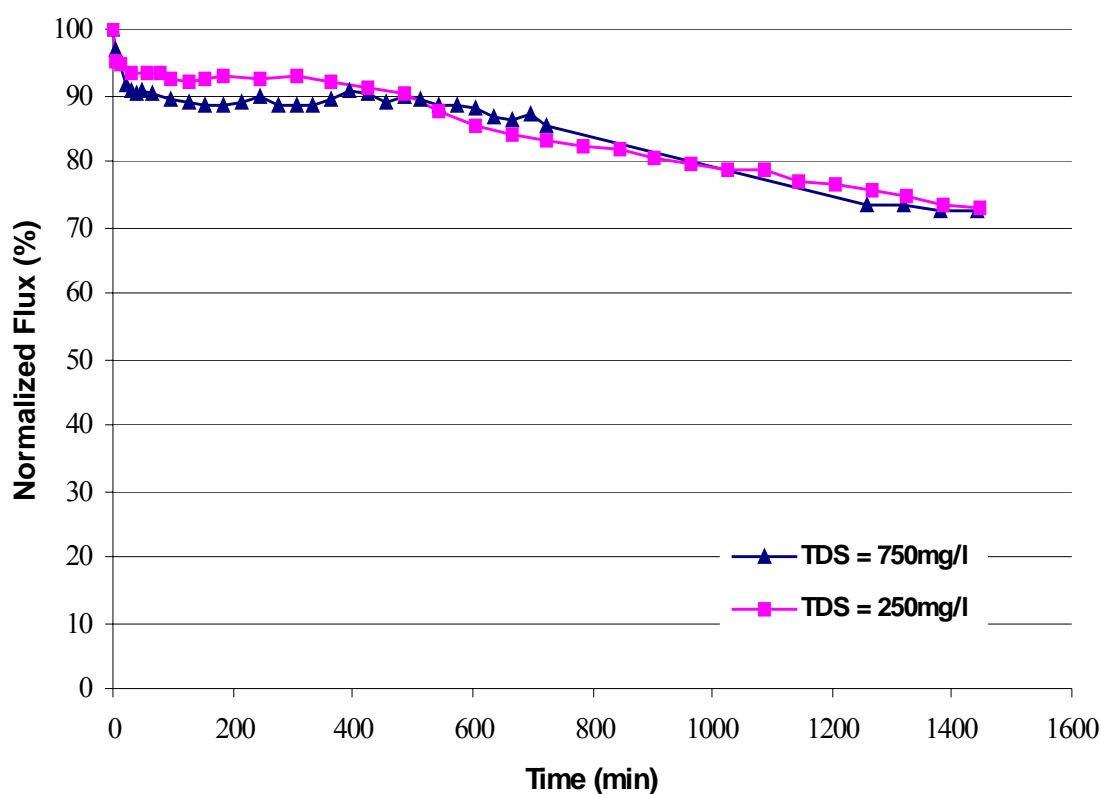
#### 4.1.5 Effect of Ionic Strength on Fractionated HA Fouling

The investigation was now directed to the influence of solution chemistry on the fouling potentials of the fractionated HA components. Under similar operation conditions, the normalized permeate fluxes with changed solution ionic strength, TDS from 250mg/l to 750mg/l, for the individual hydrophobic and hydrophilic HA fractions are presented in Figs. 4.5 and 4.6, respectively.



**Fig. 4.5 Effect of ionic strength on hydrophobic HA components;**

**TOC = 7 mg/l, pH = 7**



**Fig. 4.6 Effect of ionic strength on hydrophilic HA components;**

**TOC = 7 mg/l, pH = 7**

Compared the four fouling curves shown in Figs. 4.5 and 4.6, it could be seen that, at the initial stage of operation (approximate first 7h), there was a substantial decline of permeate flux with increased ionic strength (TDS from 250 mg/l to 750 mg/l) for each HA fraction. Moreover, a more significant influence of ionic strength on the fouling potential was observed for the hydrophobic HA components at this period. This behavior could be attributed to charge reduction of both the membrane and NOM molecules at higher ionic strength.

When the primary mechanism of NOM fouling is electrostatic interactions between charged functional groups, just like the fouling process discussed here, it could be expected that a significant changes of charge density of the NOM macromolecules and membrane functional groups should have a significant influence on NOM foulants-membrane adsorption.

Generally, effect of ionic strength on NOM fouling is primarily attributed to the repulsive charges screening and double layer compression. At higher ionic strength, with salts added into NOM solutions, the charge densities of both NOM molecules and membrane surface are reduced, leading to a decrease in electrostatic repulsion between the both sides. Consequently, NOM deposition onto membrane surface is greatly enhanced, which in turn results in a serious organic fouling (Hong *et al.*, 1997; Jones, *et al.*, 2000; Nazzal *et al.*, 1994).

Furthermore, Ghosh *et al.* (1980) suggested that at high ionic strength, due to reduced inter-chain electrostatic repulsion between the NOM macromolecules, the most likely structure of organic particles was changed from stretched and cross-link to spherical and coiled. This shape shift, as a result, leads to a more compact NOM fouling layer formed. Therefore, a greater permeate flux decline would be expected with increased solution ionic strength.

The more obvious influence of ionic strength on the hydrophobic HA fraction should attribute to its extremely high acidity contents, which represents a much higher charge density. On the contrary, the hydrophilic HA fraction carries a relatively lower charge density due to its high neutral components. In cases where charge interaction is predominant, therefore, the hydrophobic HA should be expected to suffer more from increased ionic strength and experience a more severe flux decline, just like what presented at the initial stages in Figs. 4.5 and 4.6.

However, although there were obvious declines of permeate flux for both fractional HA components during first 7 hours, fouling curves in Figs. 4.5 and 4.6 show that there was little or even no decline of the normalized permeate fluxes occurred at the end of 24-hour running, 77.80% to 77.06% for the hydrophobic HA fraction and 73.10% to 72.35% for the hydrophilic HA fraction.

We infer the possible reason for such conflicting observation to the limited increment of solution ionic strength in our study. This ionic strength increase might not be great enough to introduce an obvious long-term flux decline. According to previous researches, it has been shown that at most cases the normalized permeate flux was significantly affected when ionic strength was increased by ten to hundred times (Cho *et al.*, 2000; Hong *et al.*, 1997; Liu *et al.*, 1999; Fan *et al.*, 2001; Nazzal *et al.*, 1994), while the TDS in this study was only increased by three times.

Based on above observations, it could be concluded that although it has been reported that the increased solution ionic strength could affect the rate and extent of NOM fouling markedly, without enough increment, however, the long-term (such as 24h) influence might be very limited.

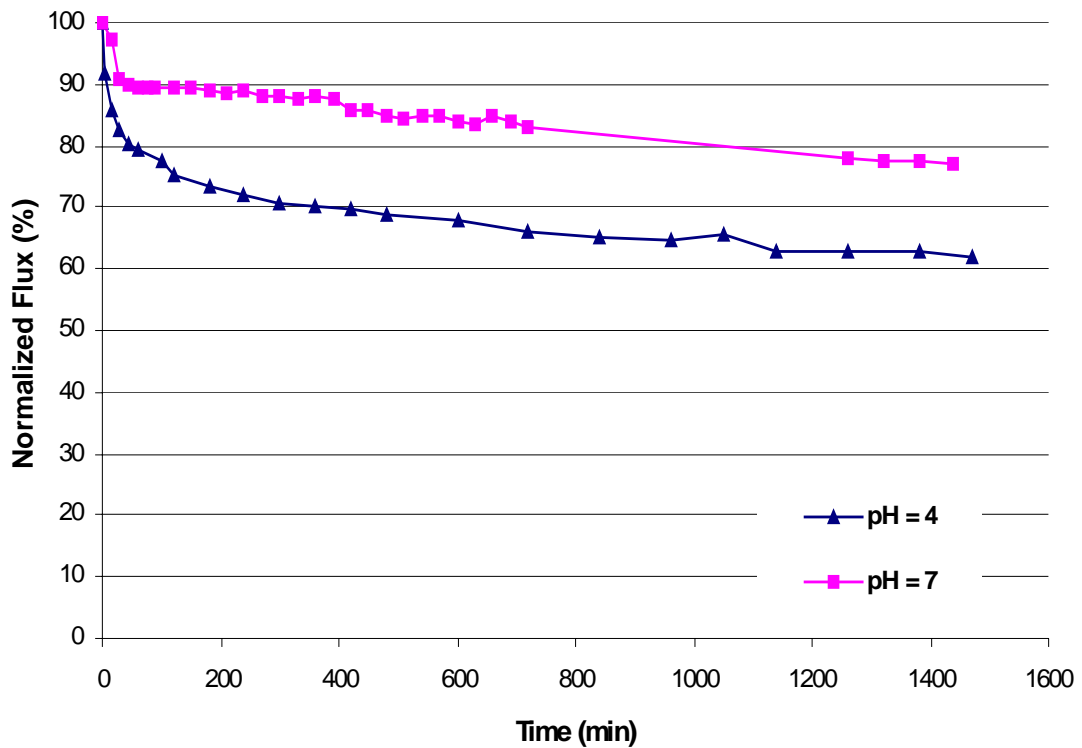
According to our experimental protocol (section 3.2.4), before the HA fractions addition, the DI water should be stabilized a long enough time under desired operation conditions to eliminate the fluctuant flux caused by sudden change of solution pH and ionic strength. However, as mentioned in section 3.3.1.2, due to the use of HCl, NaOH and NaCl to adjust solution pH during the resin fractionation procedure, either the hydrophobic HA or the hydrophilic HA fraction carried a substantial ionic strength. Therefore, with the addition of fractional HA fractions into the DI water, a sudden but limited increase of solution ionic strength was inevitable during all fouling experiments conducted in this research.

It is very important to note the influence of this ionic strength increase on fouling behavior since it could not be avoided in the next stage of experiments for investigating the effects of pH and calcium ions. According to the observation outlined in last paragraph, this sudden ionic strength change might influence the fouling rate, but its limited increase value could not affect much to our 24-hour flux value. Therefore, we believe that the influence of ionic strength in fractional HA solutions on all the fouling results presented later could be neglected.



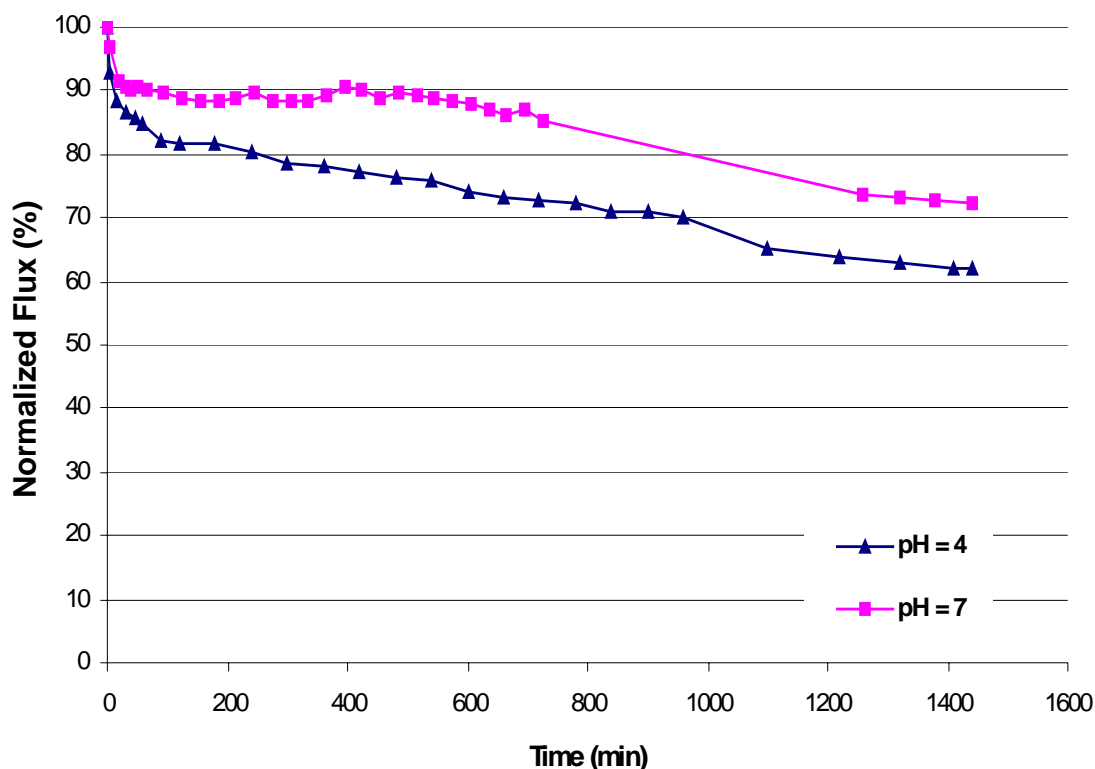
#### 4.1.6 Effect of pH on Fractionated HA Fouling

The effect of pH change on normalized permeate flux was evaluated with both the hydrophobic and hydrophilic HA components, as shown in Figures 4.7 and 4.8. These two fouling runs were conducted under similar operation conditions.



**Fig. 4.7 Effect of pH on hydrophobic HA components;**

**TOC = 7 mg/l, TDS = 750 mg/l**



**Fig. 4.8 Effect of pH on hydrophilic NOM components;**

**TOC = 7 mg/l, TDS = 750 mg/l**

It could be clearly seen that with solution pH decreased from 7 to 4, significant drops of permeate flux were observed for both fractional HA components during the whole fouling process. At the end of 24-hour operation, normalized permeate flux decreased from 77.06% to 62.04% for the hydrophobic NOM, and 72.35% to 61.95% for the hydrophilic NOM, respectively. This observation consisted with what was expected since previous researches have suggested that the sign and density of membrane surface charge, as well as the charge density of organic particles, vary as a function of pH (Jones *et al.*, 2000; Nazzal *et al.*, 1994; Bhave, 1991).

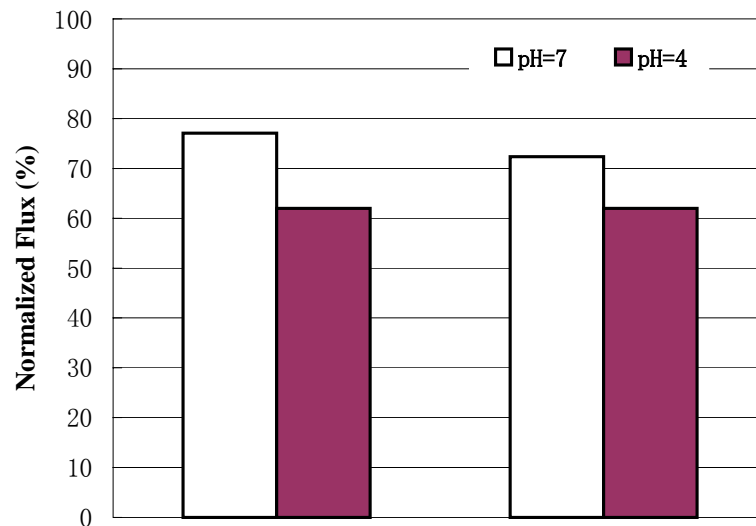
Thin-film composite polyamide (PA) membranes are usually synthesized by the interfacial polymerization of aromatic amine with acyl chloride (Petersen, 1993; Glater *et al.*, 1994), and the zeta potential for PA membranes transits from positive to negative at a certain solution pH (Childress *et al.*, 1996; Cho *et al.*, 2000; Jones *et al.*, 2000). Ozaki *et al.* (2002) reported that a RO membrane of PA was negatively charged when solution pH was above 5; on the contrary, after the pH decreased below 5, a positive charge density would be presented. Cañas *et al.* (2001) made a similar observation that the isoelectric points of polyamide-thin-film composite RO membranes were between pH 4 and 5.

In addition, more carboxylic groups of NOM are protonated with decreasing pH, thus resulting in a reduction in charge of the NOM molecules (Hong *et al.*, 1997). Therefore, it could be expected that at pH 4, the approximate isoelectric point of AG membrane, electrostatic repulsion between the membrane surface and NOM particles could be reduced to a great extent. As a result, the deposited organic particles on the membrane surface increased significantly.

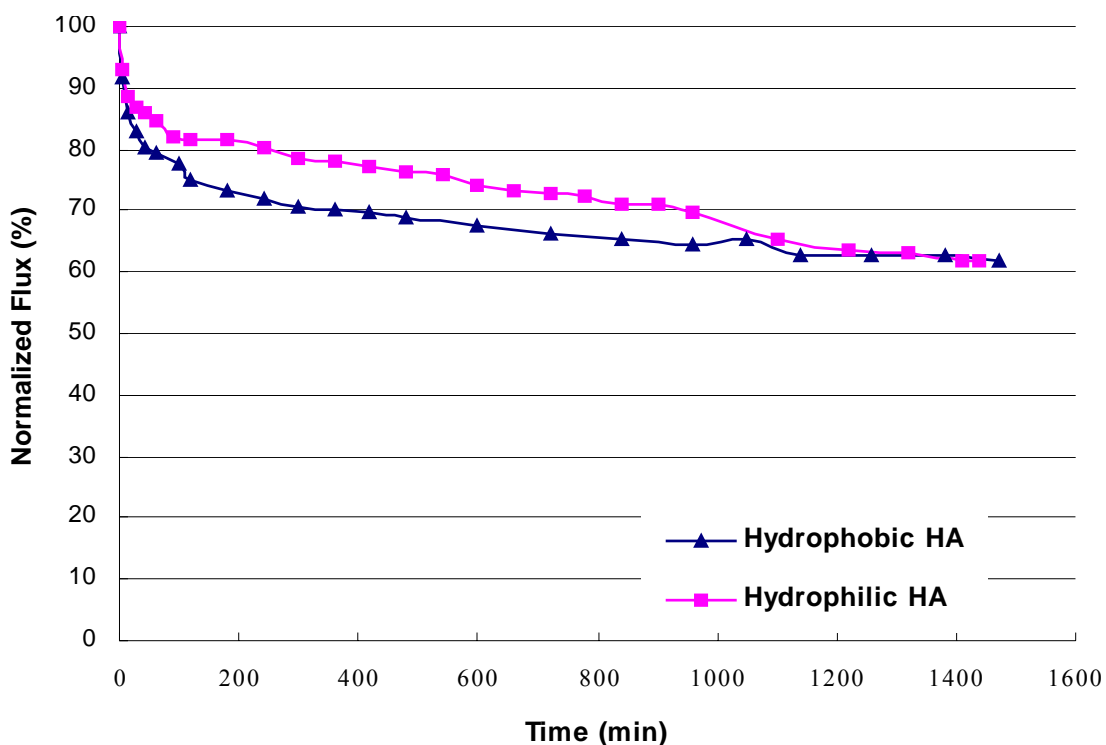
Moreover, due to reduced electrostatic repulsion between neighboring functional groups, a more compact organic macromolecular configuration could be expected and thus leading to a denser NOM fouling layer on the membrane surface.

From these two points, a more serious NOM fouling should be induced when solution pH changed from neutral to acid, which in turn led to a more obvious permeate flux decline from the beginning of fouling test, as observed in Figs. 4.7 and 4.8.

It should be noted that at pH 4, both of the hydrophobic and hydrophilic HA factions represent an almost equal permeate flux decline of 62% from its original flux after 24-hour operation. When compared with the fouling behaviors at neutral condition, 77.80% flux decline for the hydrophobic HA faction and 73.10% flux decline for the hydrophilic HA faction, it is likely suggested that pH has a greater influence on the hydrophobic HA components that has a higher charge density in neutral situations, as Fig. 4.9 demonstrated.



**Fig. 4.9 Effect of pH on normalized permeate flux declines of fractionated HA components**



**Fig. 4.10 Effect of pH on fractionated NOM components;  
pH = 4; TOC = 7 mg/l, TDS = 750 mg/l**

To obtain a better understanding of the influence of pH on respective hydrophobic/hydrophilic HA components, Fig. 4.10 compares the normalized permeate fluxes as a function of time at pH = 4 for both fractions.

It can be clearly seen that although the extent of flux decline of either the hydrophobic or hydrophilic fraction was largely similar after the long-term running, the fouling rate of the hydrophobic HA components was higher than that of the hydrophilic HA components during most operation period especially at the first 12 hours. This might indicate that with a higher charge density, the hydrophobic fraction was affected more

promptly and markedly by the change of charges resulted from a pH drop. Also hydrophobic interaction is suggested to play an increased role on NOM adsorption on the membrane surface with the minimized electrostatic repulsion between the NOM macromolecules and membrane functional groups.

#### 4.1.7 Effect of Calcium on Hydrophobic HA Fouling

The normalized permeate flux with the addition of calcium ( $10^{-3}$  M  $\text{Ca}^{2+}$ , 750mg/l total ionic strength) for the hydrophobic HA fractions are represented in Fig. 4.11.

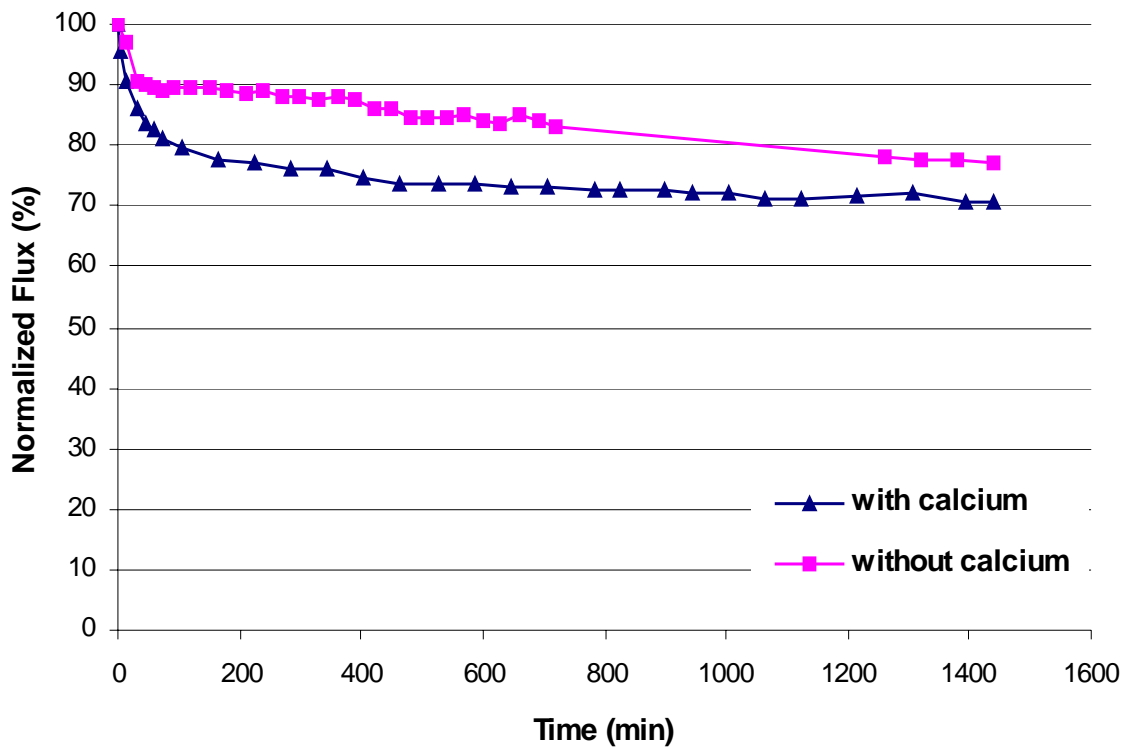


Fig. 4.11 Effect of calcium on hydrophobic HA components;

TOC = 7 mg/l, pH = 7, TDS = 750 mg/l

Results show that for the hydrophobic HA fraction, a more significant normalized permeate flux decline could be experienced during the whole fouling run, and a substantial flux decrease from 77.06% to 70.75% was observed after 24-hour operation with calcium addition. This increased fouling potential experienced by the hydrophobic HA fraction was in agreement with previous researches (Childress, 1996; Hong *et al.*, 1997; Cho *et al.*, 2000). They reported that product water flux decreased dramatically in the presence of calcium.

The influential role of calcium ions in NOM fouling is attributed to its complexation with organic macromolecules. Unlike monovalent cations,  $\text{Ca}^{2+}$  ions bind specifically through complex formation with the acidic functional groups of NOM (Hering *et al.*, 1992). Thus, in the presence of calcium, the charge of the NOM would be reduced significantly not only due to effective charge screening but also due to the complex formation.

Calcium may also adsorb to the negatively charged membrane surface and thereby reduce the charge density of the membrane surface, making decreased electrostatic repulsion between the membrane and the organic molecules. Jucker *et al.* (1994) suggested that calcium acted as a bridge between the negatively charged membrane surface and the organic molecules. Therefore, an increased deposition rate of NOM on the membrane surface could be expected to present.

Based on above discussion, it is easily concluded that a more severe NOM fouling should be experienced in the presence of calcium ions, just like the performance of the hydrophobic HA fraction presented.

#### 4.1.8 Effect of Calcium on Hydrophilic HA Fouling

The normalized permeate flux with the addition of calcium ions ( $10^{-3}$  M  $\text{Ca}^{2+}$ , 750mg/l total ionic strength) for the hydrophilic HA fractions are represented in Figure 4.12.

The operation condition was the same as that of the hydrophobic HA fouling run.

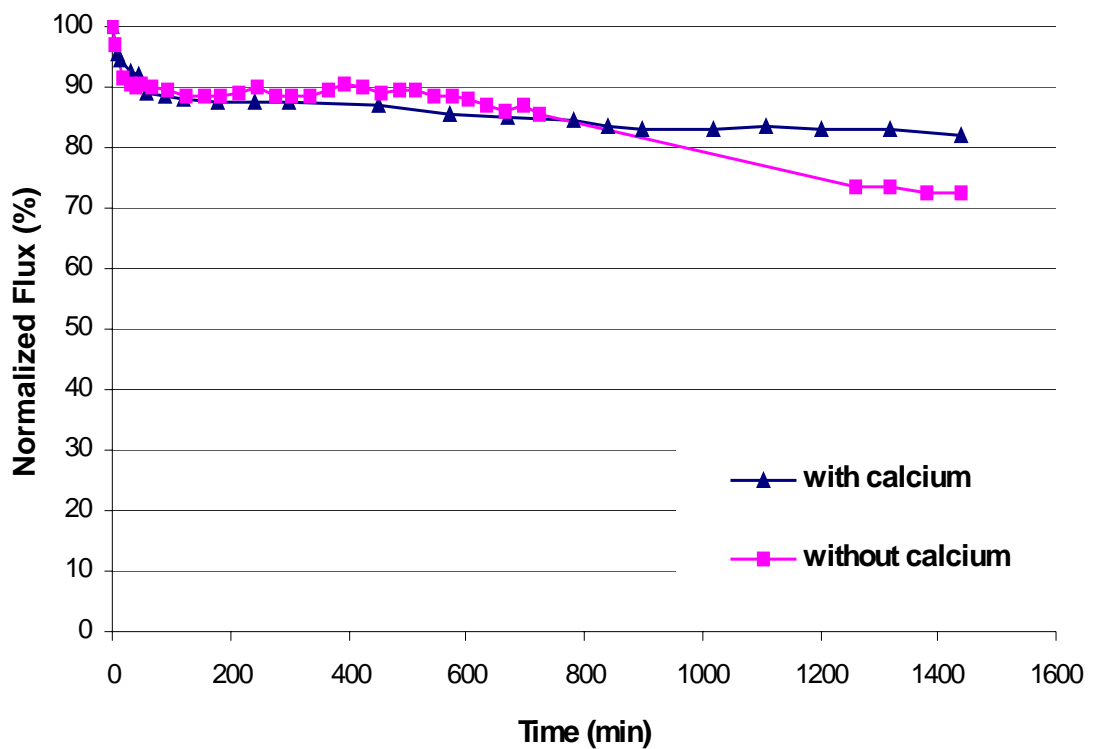


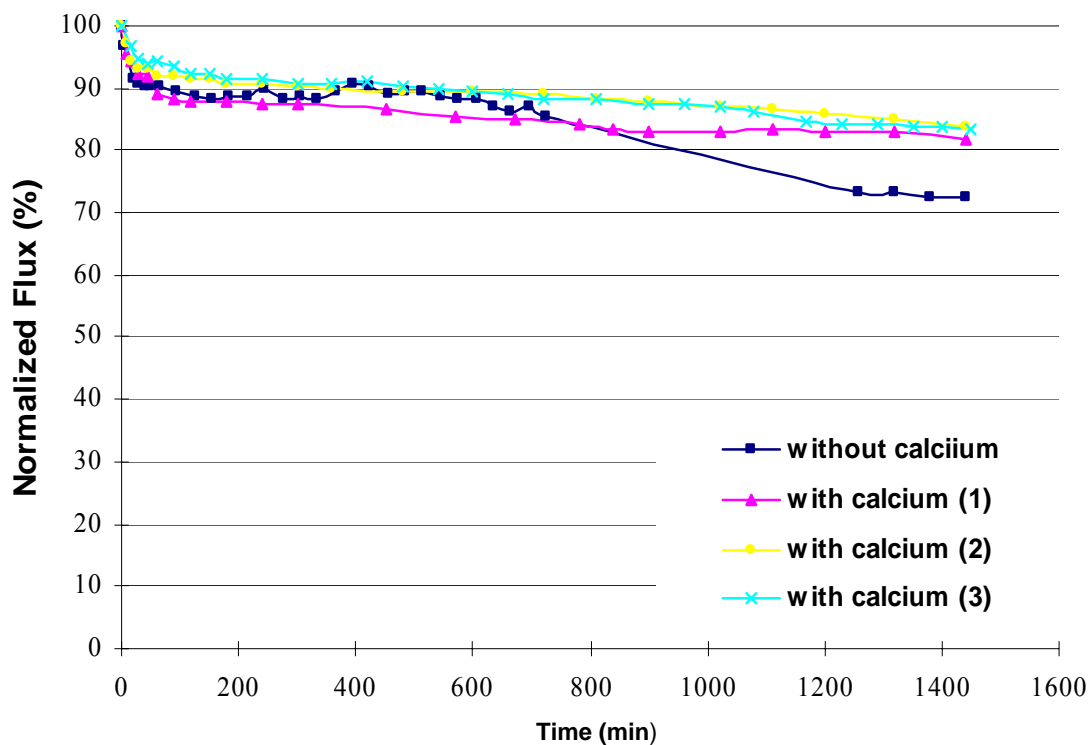
Fig. 4.12 Effect of calcium on hydrophilic HA components;

TOC = 7mg/l, pH= 7, TDS = 750mg/l



Compared with Figs. 4.11 and 4.12, a totally contrary fouling tendency in the presence of calcium was observed for the hydrophilic/hydrophobic HA fractions. Different from the substantial permeate flux decline revealed in the hydrophobic HA test, for hydrophilic HA fraction, there was no obvious change of normalized permeate flux in the first half operation period, and most important observation was that a remarkable permeate flux increase was presented at the end of 24-hour fouling run (from 72.35% to 81.90%) with the addition of calcium ions.

This observation of permeate flux increase was beyond our expectation and also contradicts to all published reports (Hering *et al.*, 1992; Jucker *et al.*, 1994; Childress, 1996; Hong *et al.*, 1997; Cho *et al.*, 2000). In case that the result might be shifted by some operational factors, filtration processes with same operation parameters and same calcium ions concentration were repeated for 3 times in order to test the reliability of this contradictory result. The hydrophilic HA fouling data of these three tests are presented in Fig. 4.13. It could be seen that in the presence of same amount of calcium ions, similar NOM fouling behaviors were observed.



**Fig. 4.13 Effect of calcium on hydrophilic HA components (for verification);**

**TOC = 7 mg/l, pH = 7, TDS = 750 mg/l**

The possible reason for this conflicting finding might be attributed to the chemical properties of both the fractionated HA components and AG membrane used in this study.

As addressed previously, calcium ions could form bridging between the negatively charged membrane molecules and NOM molecules, and between the neighboring acidic functional groups in NOM. According to characteristics analysis of the fractional HA components discussed in sections 4.1.2 and 4.1.3, it is known that hydrophobic acids accounted for the predominant components of the hydrophobic HA

components. Therefore, the presence of calcium could exert a greater influence on this HA fraction, and a more significant NOM fouling could be expected, as shown in Fig. 4.11. For comparison, hydrophilic HA fraction only contained 11.00% acidic components, and the majority is neutral content. Since the large proportion of hydrophilic neutral could not participate in the intramolecular calcium-bridging mechanisms, it is expected that the influence of calcium ions on hydrophilic HA should not be obvious, just like the fouling behavior in the first operation phase (Fig. 4.12).

In addition, we hypothesize that there is an inherent affinity between molecules with similar properties, which means calcium is more readily to form bridging between two similar functional groups rather than between two functional groups with different properties. As mentioned above, AG membrane surface was hydrophobic and carried abundant aromatic functional groups, which were the same major components of the hydrophobic HA. Therefore, it is possible that calcium binding was easier to be formed between the aromatic functional groups in both the membrane and the hydrophobic HA. Consequently, abundant hydrophobic HA particles could adsorb onto the membrane surface.

On the other hand, the predominant component of hydrophilic HA is aliphatic functional groups, which is different from that of the hydrophobic membrane. Therefore, the hydrophilic parts of HA are directed towards the solution, and more

intramolecular calcium-NOM complexes should be expected to form within the hydrophilic HA functional groups rather than between the hydrophobic membrane molecules and the hydrophilic HA molecules. As a result, larger hydrophilic HA particles were formed. This hypothesis could be proven by the substantial increase of hydrophilic HA AMW from HPLC test. Compared with 31,187, AMW value of the hydrophilic HA fraction before calcium addition, a larger AMW (32,746) was measured in the presence of 0.01M CaCl<sub>2</sub>.

To larger particles in solution, a greater hydraulic drag force would be created and therefore less hydrophilic HA molecules could be brought to the membrane surface. Furthermore, for those deposited HA particles, based on the Kozeny equation, a cake of a given thickness composed of larger particles will produce less resistance than that composed of smaller particles (Nazzal *et al.*, 1994). Jucker and Clark (1994) also suggested that small molecules fluoresced more than large molecules and large molecules absorb more light than small molecules. From these points, a looser hydrophilic HA fouling layer would be expected to form on the hydrophobic membrane surface, and a decreased long-term fouling potential should be presented in the addition of calcium, as shown in Fig. 4.12.

It should be noted that there are no previous reports on this contradictory fouling tendency of the hydrophilic HA with the addition of calcium. This could be due to the insignificant TOC percentage of hydrophilic components in most commercial humic

acids. For instance, the hydrophilic HA faction was only responsible for 8.1% of the total DOC in Aldrich HA. Therefore, when taking humic acid as a whole to investigate the NOM fouling, the contrary fouling tendency of the hydrophilic components could be shielded.

This contradictory effect of calcium ions on the respective hydrophobic and hydrophilic HA is very interesting and its exact mechanism is worthy of a more detailed investigation. It has been reported that calcium ions could accelerate the NOM fouling in membrane processes, and thus some pretreatments have been employed to reduce water hardness in order to ease this type of membrane fouling. However, if this observation is the real fact and can be applied to any divalent ions (mainly  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) and any ions concentration, the presence of hardness should be beneficial to the feed waters that contain major organic matters in the hydrophilic components.

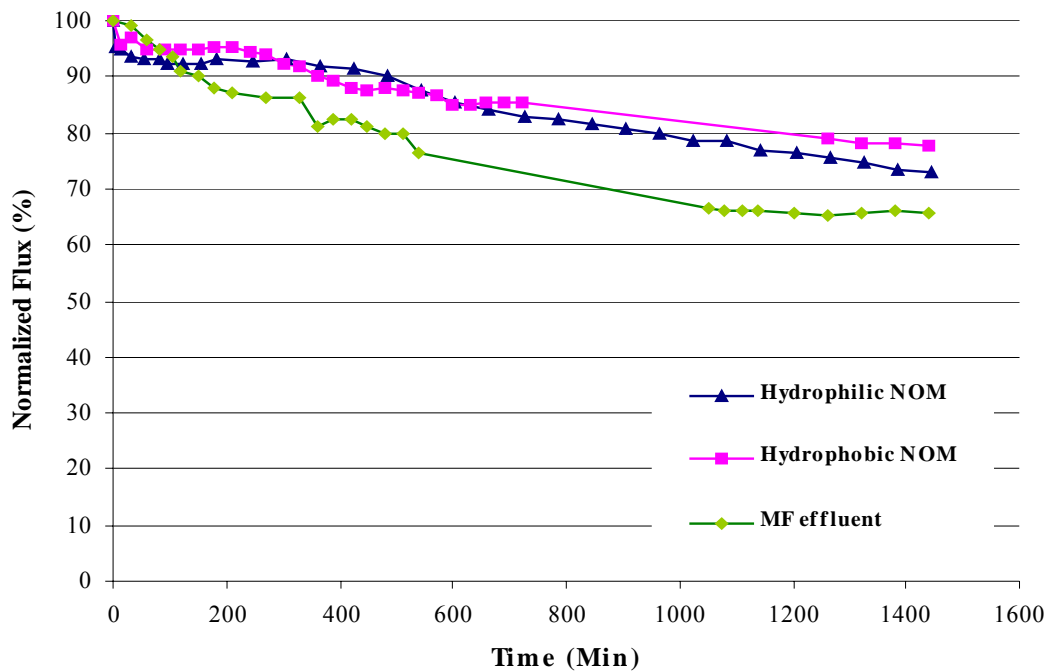
## **4.2 RO Process in Real Water Treatment**

Reverse osmosis operation has been regarded as a promising technology in the reuse of reclaimed water, especially in Singapore that has not enough natural water sources. However, with the presence of numerous possible fouling agents in real waters, far more than NOM, real membrane fouling process is much more complex. Therefore, in this part of investigation, RO filtration processes using the real water (secondary effluent after MF) collected at site were conducted and membrane foulants were analyzed. Furthermore, since the hydrodynamics of membrane modules have been reported to be an important factor on the mass transfer, separation, and fouling behavior of crossflow membrane systems, the effect of operation pressure on the RO membrane performance in real water treatment was systematically examined.

### **4.2.1 Fouling Behavior of AG Membrane**

In order to compare the different membrane performances in treating real water and synthetic NOM solution, AG membrane, the same type of membrane used throughout the first research stage, was selected as the membrane model in this RO fouling run as well. The feed solution was real water samples (secondary effluent after 0.2 $\mu$ m MF) without any further pretreatment in lab. A 24-hour RO filtration process with no backwash was conducted under a neutral condition. An approximately constant operation pressure of 250 psi and crossflow velocity of 0.035 m/s, which were same as those in NOM fouling test, were maintained throughout the test.

Figure 4.14 shows the normalized permeate flux decline caused by this MF effluent as a function of time. For comparison, NOM fouling curves under similar operation conditions (with reference to section 4.1.3) are also plotted in this figure.



**Fig. 4.14 Fouling behaviors of AG membrane with different feed solutions**

From Fig. 4.14, it could be clearly seen that compared to other two synthetic NOM solutions, real water caused a more serious membrane fouling throughout the operation time, and especially a more steady and faster flux decline at the initial stage. There was only 65.80% flux remained after 24-hour operation in real water fouling run. Since hydrodynamic operating condition and feed water property are reported as two influential factors involving in membrane fouling, solution chemistries and operating parameters in these three RO processes are summarized in Table 4.2.

**Table 4.2 Comparison of solution chemistries and operation conditions**

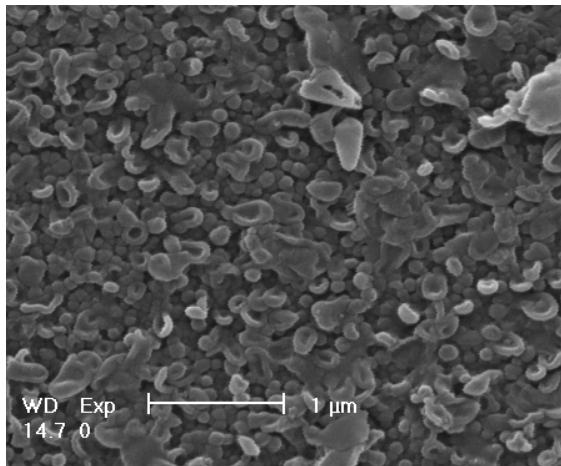
	TDS (ppm)	TOC (ppm)	Pressure (psi)	Crossflow velocity (m/s)	Temperature (°C)	pH
Real water test	497	7.563	250	0.035	30 ± 1	≈ 7
NOM tests	≈ 250	≈ 7	250	0.035	30 ± 1	≈ 7

Comparing the data listed in above table, just a distinguished difference of solution TDS is observed (497ppm in real water while 250ppm in NOM solutions). However, according to the observation made from previous discussions on how ionic strength affects NOM fouling during RO process (section 4.1.5), it is suggested that no such big difference of fouling extent could be resulted from a double increase of solution ionic strength. Therefore, this observation confirms that more foulants rather than NOM should be responsible for membrane fouling occurred in real water.

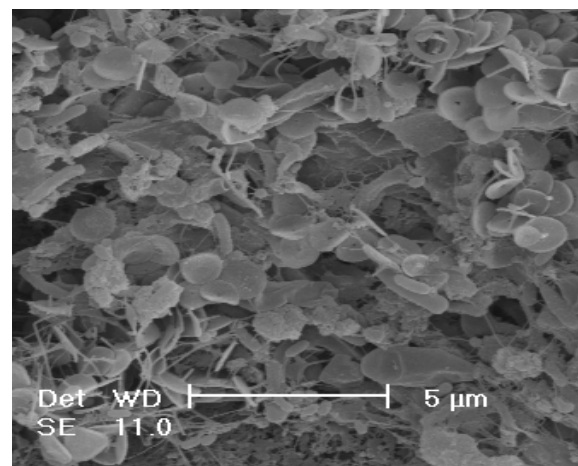
#### **4.2.1.1 Membrane Foulants Analysis**

In order to obtain a better understanding on these RO membrane foulants, scanning electron microscopy (SEM) test was employed. Plates 4.2 is the SEM image of the clean AG membrane. Plates 4.3 and 4.4 show the different sections of the fouled membrane, which indicate the various fouling materials on the membrane surface.

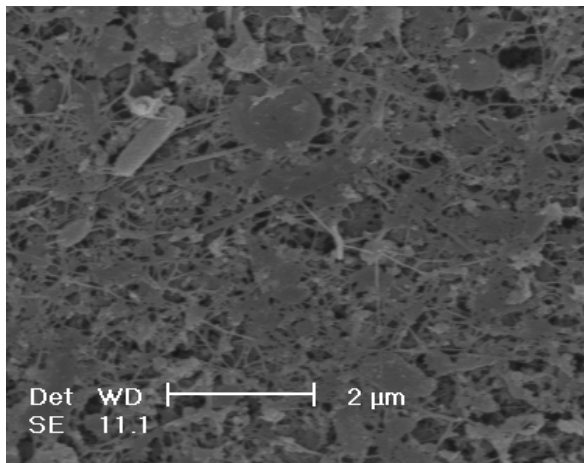




**Plate 4.2 Clean membrane**



**Plate 4.3 Fouled membrane section (1)**



**Plate 4.4 Fouled membrane section (2)**

It can be found that after the 24-hour operation, AG membrane surface was fully covered by abundant mushroom-like particles with size of around 1 μm (Plate 4.3) and cross line matters (Plate 4.4). It is very hard to identify these foulants and stat the exact material groups that they belong to only on the basis of these SEM pictures. However, according to their shapes and sizes, and with reference to relative researches (Crozes *et*

*al.*, 1993; Mallevalle *et al.*, 1989), we believe that the mushroom-like particles belong to clay (Kaolinite) and those cross line matters are some kinds of bacteria.

Generally, SEM test can only provide an ambiguous concept of such foulants, and from above SEM pictures, the presence of NOM usually with size less than 1 $\mu$ m could not be distinguished. However, organic matter has been reported as one of the major membrane fouling agents in water treatment, especially to those feed waters with abundant organic contents (Kaiya *et al.*, 1996; Moody *et al.*, 1983), therefore, a further quantitative analysis of NOM presented in the membrane foulants was carried out.

At first, two fouled membranes were gently removed from the cell and placed into a 1L basic (0.1M NaOH) solution for about 3 hours, in which deposited organic matters were dissolved. After complete removal of organic matters from the membrane surface, the resulting solution was subjected to TOC measurement. The deposited NOM mass was calculated by multiplying solution volume (1L) and its TOC value (1.81ppm from TOC test), which was 1.81mg. According to TOC value of feed water (7.563ppm, Table 3.3) and the feed volume (30L), the total NOM amount of feed water can also be obtained through the same calculation, which was approximate 227mg. Compared these two data, it can be seen that the deposited NOM only accounted for a minor percentage of total NOM in feed water, and NOM should not be responsible for the serious flux decline observed in Fig. 4.14.

This finding contradicted to what reported by Kaiya *et al.* (1996), which indicated that the decline in membrane permeability was mainly caused by organic matter. This contradiction was likely attributed to differences in experimental conditions such as the quality of the raw water, treatment conditions and membrane materials. Furthermore, it should be noted that there was no backwash during our 24-hour operation, and this might be the major reason because the particles with larger size, such as clay and bacteria, have accumulated onto the membrane surface at the initial operation stage, which hindered the adsorption of NOM.

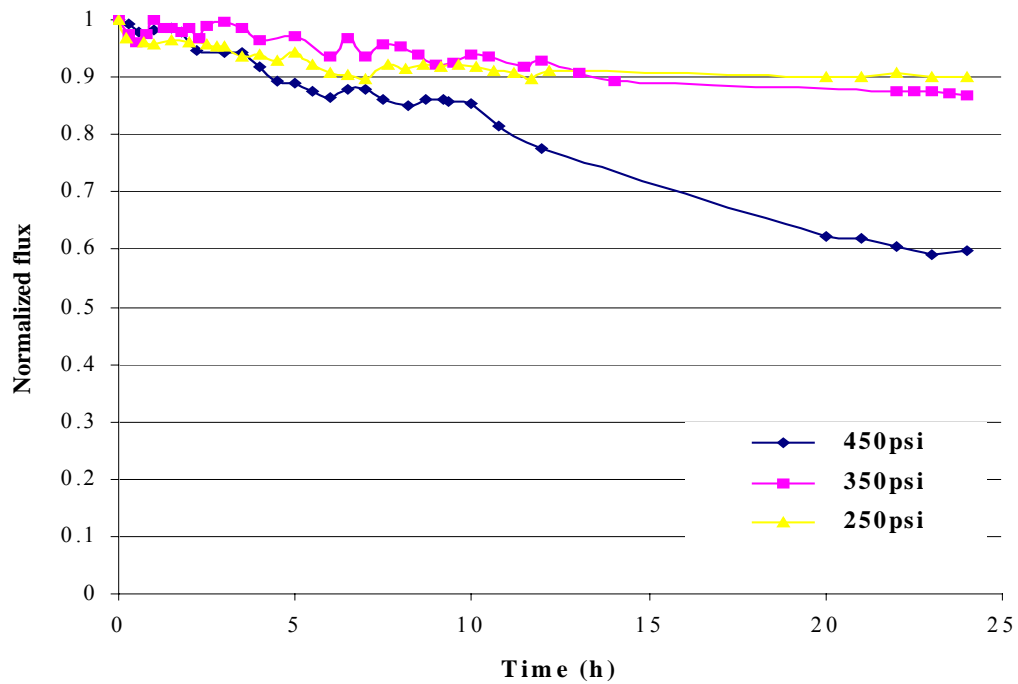
A similar RO operation with same real water sample was repeated under the same operation condition. The only difference was an additional backwash at the end of 24-hour fouling run. A very similar membrane performance could be observed and an almost same flux loss (66.50%) was presented at the end of operation. However, after the membranes were backwashed for a total period of 5 min, flux was almost 100 percent recovered. This additional experiment shows that the severe membrane fouling presented in Fig. 4.14 belongs to hydraulically reversible fouling, which is different from irreversible fouling mainly caused by organic adsorption. Moreover, this result suggests that periodical hydraulic cleaning is necessary and might be good enough for a satisfactory performance of whole RO systems in industrial applications.

#### **4.2.2 Effect of Operating Pressure on Membrane Performance**

In typical crossflow membrane modules, the flow field is composed of a convective flow perpendicular to the membrane (permeate flow) and a shear flow parallel to the membrane surface (crossflow) (Song *et al.*, 1995). Particles are transported to the membrane surface by the permeate flow and swept away by the crossflow. Therefore, these two flows are regarded as the influential hydrodynamic factors to membrane fouling.

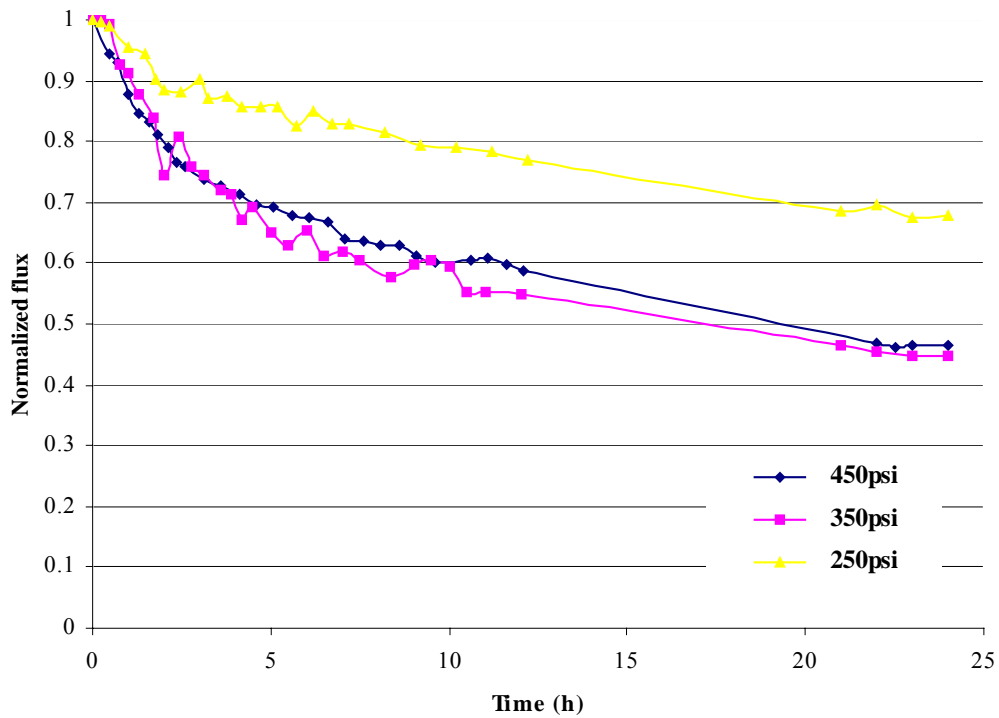
While the influences of crossflow and permeate flow on NF membrane fouling caused by synthetic NOM solutions have been systematically explored (Braghetta, 1995; Hong *et al.*, 1997), the effect of permeate flow on RO membrane fouling caused by real water is our main research interests. According to the solution-diffusion model, permeate flux is directly proportional to applied pressure (Eq. 2.2). Therefore, in this section, the effect of operation pressure on membrane fouling has been investigated with two RO membranes.

The results of CG and AK membrane performances under three different operation pressures are presented in Figs. 4.15 and 4.16, respectively. All these six fouling runs were conducted with a same water sample, which is the secondary effluent after MF collected on site, and under similar operation conditions including crossflow velocity (0.035 m/s) and temperature ( $30 \pm 1^\circ\text{C}$ ).



**Fig. 4.15 Effect of operation pressure on CG membrane performance;  
Typical flux/pressure of CG = 30/420 (GDF/psi)**

From Fig. 4.15, it is found that for CG membrane, only slight permeate flux declines (both around 10% flux loss at the end of 24-hour operation) could be noticed at applied pressures of 250 psi and 350 psi. However, when applied pressure was increased to 450 psi, close to the pressure recommended by the manufacturer (420 psi), a steady permeate flux decline was noted throughout the operation process, and only 59.90% of initial permeate flux left after the 24-hour operation.



**Fig. 4.16 Effect of operation pressure on AK membrane performance;  
Typical flux/pressure of AK = 16/225 (GDF/psi)**

For the case of AK membrane, product water flux was observed to decline steadily at all three applied pressures studied (Figure 4.16). Moreover, compared to the typical pressure (250psi) recommended by the manufacturer, more substantial flux losses could be found at operating pressures of 350 psi and 450 psi.

Although these two membranes showed different fouling behaviors with the variation of applied pressure, a general fouling tendency, that is a more dramatic decline in product water flux with increased operating pressure, could be observed regardless of membrane type.

This observation could be attributed to the enhanced deposition of particles on the membrane surface at a higher applied pressure (Song *et al.*, 1995). When operating pressure increased, a higher permeate flux would be produced which in turn brings more particles towards the membrane surface. Therefore, at a constant crossflow velocity, representing a fixed shear force to sweep the accumulated particles away from the membrane surface, more dissolved particles would accumulate near or onto membrane surface and result in a higher concentration polarization and fouling when the membrane system is operated on elevated pressure.

From the fouling curves, especially which presented in Fig. 4.15, it could be seen that there was a certain pressure value below which membrane fouling could be effectively controlled. This phenomenon has been reported with different membrane types applied either in theoretical researches or industrial applications (Seidel *et al.*, 2002; Hong *et al.*, 1997; Winters, 1997).

It has been known that particles fouling is controlled by an interplay between the permeate drag force and other counter forces caused by crossflow, colloidal interaction and electrostatic repulsion (Cohen *et al.*, 1986; Bacchin *et al.*, 1996; Hong *et al.*, 1997). Permeation drag induced by permeate flow refers to the hydrodynamic force that acts perpendicular to the membrane surface and carries dissolved particles to the membrane surface. The permeation drag is opposed by those counter forces, which prevent the dissolved particles from attaching to the membrane surface.

When applied pressure is high enough to create a high permeate rate, resulting permeation drag can be strong enough to overcome the influences from other interactions and, as a result, the deposition of particles on the membrane surface is inevitable. At a low operation pressure, however, permeate drag might be smaller than the counter forces, leading to less membrane fouling. Therefore, applied pressure controls the particle deposition rate, namely the rate of membrane fouling.

The existence of critical pressure is a very useful phenomenon in practice application since membrane fouling can be effectively controlled through decreasing operating pressure to lower than its critical pressure. However, the main problem hindering the application of critical pressure theory is how to decide its exact value. From Figs. 4.15 and 4.16, it can be clearly seen that the critical pressure is different for these two membrane types. In addition, as particle deposition rate is controlled by both permeate drag and other counter interactions such as crossflow velocity and electrostatic repulsion, the value of critical pressure would also be varied with different feed waters and different operating conditions. Therefore, the efficient application of critical pressure concept still needs further intensive investigation.



## **SUMMARY, CONCLUSIONS & RECOMMENDATIONS**

### **5.1 Summary**

In this project, a reverse osmosis operation system was set up to study the membrane fouling behaviours with two different feed waters, which were synthetic NOM solutions and secondary effluent after MF treatment. The whole study was thus divided into two parts.

In the first phase of this study, the effects of NOM characteristics and solution chemistries (pH, ionic strength and calcium ions) on RO membrane fouling were systematically investigated with the NOM solutions. In the second phase, membrane foulants in real water were quantitatively analysed, and the effect of operating pressure on membrane performance was also studied.

## **5.2 Conclusions**

### **NOM Fouling Test**

1. Unlike most organic matters composition presented in natural aquatic system, the hydrophobic fraction accounted for the majority of TOC in the commercial humic acid (HA) product. The hydrophobic HA components largely consisted of highly aromatic organic acids and thereby had a higher negative charge density. The predominant components of the hydrophilic HA were organic neutrals which were believed to be long-chain aliphatic carbons, and carried less negative charges.
  
2. The rate and extent of RO membrane fouling was found greatly influenced by the chemical composition of NOM in feed water. RO filtration tests based on NOM hydrophobicity revealed that when filtered by a hydrophobic membrane, the hydrophilic HA presented a greater fouling potential than the hydrophobic HA fraction. The low-aromatic hydrophilic neutrals were identified as the main determinant of permeate flux decline. These observations, along with the characteristics of fractionated organics, suggested that NOM fouling during RO process was controlled by electrostatic repulsion and intermolecular forces between the charged membrane functional groups and organic molecules, rather than by NOM-membrane hydrophobicity interaction.

3. Solution pH had significant influence on NOM fouling since more substantial product water declines were observed when pH was decreased from 7 to 4 for both fractionated HA components. However, limited increment of ionic strength only accelerated the initial fouling rate but hardly affected the long-term fouling extent.

With higher charge density, the fouling rate and extent of hydrophobic HA components were affected more significantly than those of the hydrophilic HA components. It was also suggested that during the process with solution pH decreased to around isoelectronic point of membranes, hydrophobic interaction between the membrane surface and organic molecules had a greater influence on NOM fouling.

4. For a hydrophobic RO membrane, the presence of calcium increased the fouling potential of hydrophobic HA components. In contrast, it decreased the fouling potential of hydrophilic HA fraction. This was likely due to the specific calcium-complex formed between the functional groups with similar property. Calcium ions preferentially formed NOM-bridging between the hydrophilic molecules than between the hydrophilic molecules and hydrophobic membrane surface. Therefore, with larger hydrophilic organic particles formed, a looser fouling layer was presented on membrane surface and consequently the higher permeate flux was produced. This finding (contradicted to observations

reported in literatures) could be attributed to the low TOC percentage of hydrophilic components presented in commercial HA products (8.10% the total TOC of HA).

### **Real Water Test**

1. Clay and bacteria presented in real water were verified as the main fouling materials during the 24-hour RO filtration study, and the membrane fouling caused by these foulants belonged to reversible fouling. Therefore, periodical hydraulic cleaning could be adequate for a satisfactory performance of whole RO systems in industrial application.
2. Operating pressure controlled the rate of membrane fouling to some extent. It was found that there was a specific critical pressure for different membranes, below which a decline in product water did not occur. This phenomenon was resulted from interplay between permeation drag force and other counter forces.

### **5.3 Recommendations for Future Studies**

1. The contradictory observation of calcium ions on the respective hydrophobic and hydrophilic HA components is very interesting, and the exact mechanism of this phenomenon is worthy of further investigation. The observed phenomenon might have economic implication to industrial applications.
2. The results obtained in this study were derived from a commercial humic acid instead of using NOM separated from natural waters. In view of this, further study using NOM directly extracted from natural waters should be conducted.

## REFERENCES

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Aiken G. R., Mcknight D. M., Thorn K. A. and Thurman E. M. *Isolation of hydrophilic organic acids from water using nonionic macroporous resins*. *Org. Geochem.*, 18(4), pp.567-573. 1992.

Aiken G. R., Mcknight D. M., Wershaw R. L. and MacCarthy P. *Humic substances in soil, sediment, and water*. Wiley, New York. 1985.

Amy G. and Cho J. *Interactions between natural organic matter (NOM) and membranes: Rejection and fouling*. *Water Sci. Tech.*, 40(9), pp.131-139. 1999.

Aptel P. and Rovel J. M. *Separation by membranes*, In Degremont (ed.). *Water treatment handbook*. Lavoisier, Paris. 1991.

AWWA membrane technology research committee. *Committee report: membrane processes in potable water treatment*. *J.AWWA*, 84(1), pp.59-67. 1992.

Baret J. F. Kinetics of adsorption from a solution. *Role of the diffusion and of the adsorption-desorption antagonism*. *J. Phys. Chem.*, 72, pp.2755-2758. 1968.

Beckett R., Jue Z. and Giddings J. C. *Determination of molecular weight distributions of fulvic and humic acids using flow field-flow fractionation*. *Environ. Sci. Tech.*, 21, pp.289-295. 1987.

Bersillon J. L. *Fouling analysis and control*. In: Cecille L. and Toussaint J.C. (eds). *Future industrial prospects of membrane processes*. Elsevier Science, Amsterdam. 1989.

Bhave R. R. *Inorganic membranes: synthesis, characteristics and applications*. Van Nostrand Reinhold, New York. 1991.

Braghetta A. *The influence of solution chemistry operating conditions on nanofiltration of charged and uncharged organic macromolecules*. Ph.D. Dissertation, University of North Carolina. 1995.

Braghetta A., Digiano F. A. and William P. B. *NOM accumulation at NF membrane surface: Impact of chemistry and shear*. J. Envir. Eng., 123(11), pp.1087-1097. 1998.

Cabaniss S. E. and Shuman M. S. *Copper binding by dissolved organic matter II. Variation in type and source of organic matter*. *Geochimica et Cosmochimica Acta.*, 52(1), pp.195-200. January 1988.

Cañas A., Ariza M. J. and Benavente J. *Characterization of active and porous sublayers of a composite reverse osmosis membrane by impedance spectroscopy, streaming and membrane potentials, salts diffusion and X-ray photoelectron spectroscopy measurements*. J. Mem. Sci., 183, pp.135-146. 2001

Childress A. E. and Elimelech M. *Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes*. J. Mem. Sci., 119, pp. 253-268. 1996.

Cho J., Amy G. and Pellegrino J. *Membrane filtration of natural organic matter: factors and mechanisms affecting rejection and flux decline with charged ultrafiltration (UF) membrane*. J. Mem. Sci., 164, pp.89-110. 2000.

Cohen R. D. and Probstein R. F. *Colloidal fouling of reverse osmosis membranes*. J. Colloid Interf. Sci., 114, pp.194-207. 1986.

- Collins M. R., Amy G. L. and Steelink C. *Molecular weight distribution, carboxylic acidity, and humic substances content of aquatic organic matter: implication for removal during water treatment*. *Envir.. Sci. Tech.*, 20, pp.1024-1032. 1986.
- Crozes G., Anselme C. and Mallevialle J. *Effect of adsorption of organic matter on fouling of ultrafiltration membrans*. *J. Mem. Sci.*, 84, pp.61-77. 1993.
- Crozes G. F., Jacangelo J. G., Anselme C. and Lainé J. M. *Impact of ultrafiltration operating on membrane irreversible fouling*. *J. Mem. Sci.*, 124, pp.63-76. 1997.
- Crozes G. F., Jacangelo J. G. and Anselme C. *Impact of ultrafiltration operating conditions on membrane irreversible fouling*. *J. Mem. Sci.*, 124, pp.63-76. 1997.
- Dalvi A. G. I., Al-Rasheed R. and Javeed M. A., *Studies on organic foulants in the seawater feed of reverse osmosis plants of SWCC*. *Desalination*, 132, pp.217-232. 2000.
- Fan L. H., Harris J. L., Roddick F. A. and Booker N. A. *Influence of the characteristics of natural organic matter on the fouling of microfiltration membranes*. *Water Rs.*, 35(18), pp.4455-4463. 2001.
- Fane A. G., Schäfer A. I. and Waite T. D. *Nanofiltration of natural organic matter: Removal, fouling and the influence of multivalent ions*. *Desalination*, 118, pp.109-122. 1998.
- Ghosh K. and Schnitzer M, *Macromolecular structures of humic substances*. *Soil Sci.*, 129, pp.266-276. 1980.
- Glater J., Hong S. and Elimelech M. *The search for a chlorine resistant reverse osmosis membrane*. *Desalination*, 95, pp.325- 345. 1994.



Fu P., Ruiz H., Thompson K. and Spangenberg C. *Selecting membranes for removing NOM and DBP precursors*. J. AWWA, 86(12), pp.55-72. 1994.

Hansen R. S. and Wallace T. C. *The kinetics of adsorption of organic acids at the water-air interface*. J. Phys. Chem., 63, pp.1085. 1959.

Hayes M. H. B., MacCarthy P., Malcolm R. L. and Swift R.S. (eds). Chapter 24, *Humic substances II. In search of structure*. Chichester: Wiley. 1989.

Hering J. G. and Morel F. M. M. *Principles and applications of aquatic chemistry*. Wiley, New York. 1992.

Hong S. and Elimelech M. *Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes*. J. Mem. Sci., 132, pp.159-181. 1997.

Jones K. L. and O'Melia C. R. *Protein and humic acid adsorption onto hydrophilic membrane surfaces: effects of pH and ionic strength*. J. Mem. Sci., 165, pp.31-46. 2000.

Jucker C. and Clark M. M. *Adsorption of aquatic humic substances on hydrophobic ultrafiltration membranes*. J. Mem. Sci., 97, pp.53-66. 1994.

Kaiya Y., Itoh Y., Fujita K. and Takizawa S. *Study on fouling materials in the membrane treatment process for potable water*. Desalination, 106, pp.71-77. 1996.

Krasner S. W., Chowdhury Z. K., Edwards M. A. and Bell K. A. *Use of SUVA in developing revised TOC removal requirements*. Membrane Technology Conference, AMMA, Long Beach, California. 1999.

Leenheer J. A. *Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters*. *Envir. Sci. Tech.*, 15(5), pp.578-587. 1981.

Liu C. and Huang P. M. *Atomic force microscopy of pH, Ionic strength and Cadmium effects on surface feature of humic acid*. In: Ghabbour E. A. and Davies G. (eds). *Understanding humic substances*. Cambridge: Royal Society of Chemistry, pp.87-100. 1999.

Lin C. F., Lin T. Y. and Hao O. J. *Effects of humic substance characteristics on UF performance*. *Water Res.*, 4, pp.1097-1106. 2000.

Malcolm R. L. *The geochemistry of stream fulvic and humic acids*. In: Aiken G. R., Mcknight D. M., Wershaw R. L. and MacCarthy P. (eds). *Humic substances in soil, sediment, and water: geochemistry, isolation, and characterization*. New York, NY: Wiley, pp.181-209. 1985.

Malcolm R. L. and MacCarthy P. *Limitations in the use of commercial humic acids in water and soil research*. *Environ. Sci. Technol.*, 20, pp.904-911. 1986.

Malcolm R. L. and MacCarthy P. *Quantitative evaluation of XAD-8 and XAD-4 resins used in tandem for removing organic solutes from water*. *Envir. Int.*, 18, pp.597-607. 1992.

Mallevalle J., Anselme C. and Marsigny O. *Effects of humic substances on membrane processes*. In: Suffet I. H., MacCarthy P. (eds). *Aquatic humic substances: Influence on fate and treatment of pollutants*. ACS, Washington, pp.749-767. 1989.

Moody C. D. and Kaakinen J. W. *YUMA desalting test facility: foulant component study*. Desalination, 47, pp.239-253. 1983.

Nazzal F. F. and Wiesner M. R. *pH and ionic strength effects on the performance of ceramic membranes in water filtration*. J. Mem. Sci., 93, pp.91-103. 1994.

Nilson J. A. and DiGiano F. A. *Influence of NOM composition on nanofiltration*. J. Am. Water Works. Assoc., 88, pp.53-66. 1996.

Owen D. M., Amy G. L., Chowdhury Z. K., Paode R., McCoy G. and Viscosil K. *NOM characterization and treatability*. J. AWWA, 87(1), pp.46-63. 1995.

Ozaki H. Sharma K. and Saktaywin W. *Performance of an ultra-low-pressure reverse osmosis membrane (ULPROM) for separating heavy metal: effects of interference parameters*. Desalination, 144, pp.287-294. 2002.

Petersen R. J. *Composite reverse osmosis and nanofiltration membranes: Review*. J. Mem. Sci., 83, pp.81-150. 1993.

Potts D. E., Ahlert R. C. and Wang S. S. *A critical review of fouling of reverse osmosis membranes*. Desalination, 36, pp.235-264. 1981

Samir E. M. and Azza H. *Technical management of RO system*. Conference on membranes in drinking and industrial water production, Vol 1, pp329-344. 2000

Seidel A. and Elimelech M. *Coupling between chemical and physical interactions in natural organic matter (NOM) fouling of nanofiltration membranes: implications for fouling control*. J. Mem. Sci., 203, pp.245-255. 2002.

Sirotkina Y. I., Nesmeyanov A. N., Leshchova I. F., Ustynyuk Y. A., Bolesova I. N., Isayeva L. S. and Volkenau N. A. *Nuclear magnetic resonance spectra of arenecyclopentadienyliron compounds*. J. Organometallic Chem., 22(3), pp.689-696. 1970.

Song L. and Elimelech M. *Particle deposition onto permeable surface in laminar flow*. J. Colloid Interf. Sci., 173, pp.165-180. 1995.

Song L. and Elimelech M. *Theory of concentration polarization in crossflow filtration*. J. Chem. Soc. Faraday Trans., 91, pp.3389-3398. 1995.

Speth T. F., Summers R. S. and Gusses A. M. *Evaluating of membrane foulants from conventionally treated drinking waters*, Natural Organic Matter Workshop, Poitiers, France, pp.44. 1996.

Strathman H. *Economic evaluation of membrane technology*. In: L. Cecill and Toussaint J. C. (eds). *Future industrial prospects of membrane processes*. Elsevier Science Publishers Ltd., Amstercam. 1989.

Strohwald N. K. H. and Jacobs E. P. *An investigation into UF system in the pretreatment of sea water for RO desalination*. Wat. Sci. Techno., 25(10), pp.69-78, 1992.

Tan L. and Amy G. L. *Comparing ozonation and membrane separating for color removal and disinfection by-product control*. J. AWWA, 83, pp.74-79. 1991.

Taylor J. S., Thompson D. M. and Carswell J. K. *Applying membrane processes to groundwater sources for trihalomethane precursor control*. J. AWWA, 79(8), pp.72-82. 1987.

Thurman E. M. and Malcolm R. L. *Preparative isolation of aquatic humic substances*. Environ. Sci. Tech., 15, pp.463-466. 1981.

Tombacz E. and Rice J. A. *Change of colloidal state in aqueous system of humic acid*. In: Ghabbour E. A. and Davies G. (eds). *Understanding humic substances, advanced methods, properties and applications*. Cambridge: Royal Society of Chemistry, pp.69-78. 1999.

Malika R. *Membrane market growth to be explored at 20<sup>th</sup> annual*. Membrane/ Separations Technology Planning Conference. August 2002.

Wilbert M. C. *The desalting and water treatment membrane manual: A guide to membranes for municipal water treatment*. U. S. Department of the Interior Bureau of Reclamation. 1993.

Winters H. *Twenty years experience in seawater reverse osmosis and how chemicals in pretreatment affect fouling of membranes*. Desalination, pp.93-96, 1997

Yamagiwa K., Kobayashi H., Ohkawa A. and Onodera M. *Membrane fouling in ultrafiltration of hydrophobic nonionic surfactant*. J. Chem. Eng., 26(1), pp.13-18. 1993.

Yoon S. H., Lee C. H., Kim K. J. and Fane A.G. *Effect of calcium ion on the fouling of nanofilter by humic acid in drinking water production*. Water Res., 32(7), pp.2180-2186. 1998.