Membrane Fouling and Its Control in Drinking Water Membrane Filtration Process

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ABSTRACT

Treatment of surface water in the presence of natural organic matters (NOM) becomes a challenging issue to meet stringent rules of Safe Drinking Water Act (SDWA). Ultrafiltration (UF) membrane is emerging as an efficient technology for the purpose of potable water production. However, membrane fouling, ageing and chemical cleaning affect its performance and properties.

The effects of ageing and chemical cleaning on performance and properties of the membrane were studied using UF membrane from full scale drinking water membrane filtration plant and simulated chemical cleaning sequences in laboratory. Organic and inorganic foulants, and membrane properties such as tensile strength, membrane morphology and surface functional groups were characterized using various analytical tools. The results from simulated chemical cleaning experiments were consistent with those from a full-scale plant, in terms of the effects of chemical cleaning on membrane properties. The results show that membrane ageing deteriorated the tensile strength and membrane integrity, and led to accumulation of foulants. Hypochlorite cleaning resulted in a decrease in membrane tensile strength, while citric acid cleaning had limited effect on membrane tensile strength. The decrease in membrane tensile strength correlated to a decrease in intensity of functional groups measured by FTIR. The results suggest that hypochlorite concentration and cleaning time should be minimized to reduce their impacts on membrane properties.

Additionally, membrane cleaning strategies (cleaning agents' concentration, cleaning time, pH, backwash frequency, and production time) currently used in Bare Point Water Treatment Plant were studied using a ZW-1000 pilot scale plant. The membrane performance in terms of permeability recovery was assessed using the recorded data; and organic and inorganic foulants were analyzed using Total Organic Carbon analyser (TOC) and Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). In sodium hypochlorite (NaClO) cleaning, lower concentrations combined with longer soak time achieved higher permeability recovery, with TOC results indicating that the major foulants responsible for permeability decrease were organic. Similarly, the results of citric acid cleaning suggest that lower pH was more effective in permeability recovery.

Furthermore, the effect of production cycle or backwash frequency on the membrane performance was also studied to optimize water recovery; the results revealed that the membrane performances, fouling rate in terms of rate of change of TMP, recovery (%), and organic fouling depended on permeate cycle length or back wash frequency. This research concludes with the hypothesis that membrane fouling and ageing deteriorate membrane performance, whereas chemical cleaning agent (NaClO) enhances membrane performance and properties, respectively.

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List of Nomenclature

AFM	Atomic force microscopy
AMW	Atomic molecular weight
BPA	Bisphenol A
C	Concentration
CA	Cellulose acetate
CIP	Cleaning in place
CLSM	Confocal laser microscopy
CRM	Confocal Raman microscopy
Da	Dalton
DBP	Disinfectant by product
DO	Direct observation
DW	Distilled Water
EDTA	Ethylenedineaminetetraacetate
EPS	Extracellular polymeric substance
FISH	Fluorescence in situ hybridization
Fp	Permeate flow
FTIR	Fourier Transform infrared spectroscopy
GAC	Granular activated carbon
HA	Humic acid
HIOP	Heated iron oxide particles
HPI	Hydrophilic
HPO	Hydrophobic
HP-SEC	High performance-size exclusion chromatography
HS	Humic Substances
ICP-AES	Inductivelu coupled plasma- Atomic emission spectroscopy
J	Permeate flux
LC-OCD	Liquid chromatography-Organic carbon detection

LMH	Liter.m^{-}2.hr $^{-1}$
Lp	Membrane permeability
MF	Microfilter
MPa	Megha Pascal
MW	Molecualr weight
MWCO	Molecular weight cut off
η	Water viscosity
NF	Nano filter
NMR	Nuclear magnetic Resonance
NOM	Natural organic matters
NTU	Nephelometric Turbidity Units
PAC	Powder activated carbon
PAC	Permeability after cleaning
PAN	Polyacrylnitrile
PBC	Permeability before cleaning
PCR-DGGE	Polymerase chain reaction denaturing gradient scanning electron microscopy
PE	Polyether
PES	Polyether sulfone
Pf	Final permeability
Pi	Initial permeability
PLC	Programmable logic controller
PS	Polysulfone
PVC	Polyvinyl chloride
PVDF	Polyvinylidenedifluoride
R	Mmembrane resistanced
RC	Regenerated cellulose
RO	Reverse Osmosis
S	Membrane Surface area
SDS	Sodium Dodecyl sulphate

SEM-EDX	Scanning electron microscope- electron diffraction X-ray
SMP	Soluble microbial product
SUVA	Specific ultra violet adsorption
t	Time
T	Temperature in Kelvin
TDS	Total dissolve substances
THM	Trihalomethane
THMFP	Trihalomethane formation potential
TMP	Trans-membrane pressure
TMPf	Final transmembrane pressure
TMPi	Initial transmembrane pressure
TOC	Total Organic Carbon
UF	Ultra filter
UMFI	Unified membrane fouling index
UN	United nation
UV/VIS	Ultrvoilet/visible spectroscopy
ΔP	Trans membrane pressure

CHAPTER 1: INTRODUCTION

1.1 Background

Today, the production of drinking water has become a global concern for many local, national and international authorities. Resources such water are very scarce within the biosphere. The total volume of water on Earth is approximately 1.4×10^9 km^3. However, only 4.2×10^6 km^3 or 0.3 % of total volume of water is considered as fresh water and actually useable for living beings (Koltuniewicz and Drioli, 2008). The fresh water resources are unevenly distributed, as is the world population. Experts are considering that severe water scarcities are caused by inclination of population, poverty, water contamination, water use pattern, hydrological cycles etc., resulting in two-thirds of the world population under the condition of absolute water scarcity by 2025 (UN, 2006). The United Nation reports indicate that there is a significant impact on global economy and health due to contamination of drinking water. Water-related diseases (such as diarrhoea, cholera, malaria, dengue fever, gastrointestinal disease etc.) are transported to communities due to inadequate treatment and contaminated drinking water, which cause almost a million deaths every year. This especially affects children under age five (UN-Water, 2007).

Multidisciplinary approaches, such as preventative measures and awareness to all decision-makers, suppliers, and users about water-borne diseases, sources of contamination, development of national and local level policies will help to establish efficient scientific and technical knowledge for water treatment. Clean technology concept, which is believed to have social impact, including economy, employment, health, safety, and environment, was introduced in the 1980s; various approaches were recommended especially in water treatment field. As an example conventional water treatment method relies on the use of physical and chemical process for contaminants removal: This method commits many challenging issues such as financial burden, environmentally unfriendly, and low water quality, which direct experts to search for alternative technologies, such as membrane filtration technology, the most effective separation process capable of separating microscopic contaminants including viruses, organic and inorganic matters up to molecular and elemental level (Kiso *et al.*, 2001; Fiksdal and Leiknes, 2006; Koltuniewicz and Drioli, 2008; Gao *et al.*2011;). Moreover, compared to conventional water treatment processes, UF process has several advantages as shown in the Table1.1. However, the membrane technology also has several challenging issues regarding its performance due to fouling during its application in drinking water treatment.

Table 1-1: Comparison between conventional water treatment methods and membrane filtration methods

Conventional Water Treatment Method	Membrane Filtration Method
• It involve coagulation/flocculation, sedimentation, filtration (PAC/GAC/sand) and disinfection processes	• The drinking water quality achieve easily and superior
• Disinfectants such as chlorine have been using which has chance to form disinfectants by products(DBPs) such as trihalomethanes	• It is used to control disinfectants by product as a result it has less chance to form DBPs.
• Expensive to deal with hardness due to large sedimentation tank and more sludge production, which need extra space to manage.	• It can deal with hardness and need much less space compare to conventional methods.
• Required large volume of water to backwash sand filter	• It has a wide range of removal of pathogens, organic and inorganic substances.
• Due to use of chemicals in various stages, it is environmentally unfriendly	• Less chemical is required compared to conventional methods and it is environmentally friendly.
• Difficult to remove metals.	• Low operating and capital cost

Membrane fouling is a process of building up of different foulants like inorganic substances, organic matters, colloid particulate, and microorganism on the surface or inside the membrane matrix. This causes degradation of membrane life span, and limits membrane performance. Therefore, it is important to remove those foulants from the membrane. Many researchers studied various membrane cleaning methods to enhance the membrane performance (Hong and Elimelech, 1997; Ang *et al.*, 2006; Yamamura *et al.*, 2007; Zondervan and Roffel, 2007; Porcelli and Judd, 2010; Puspitasari *et al.,* 2010; and Tian *et al.*, 2010). Physical methods, for examples backwashing, air scouring (Al-Amoudi and Lovitt, 2007), chemical methods, for examples acids, bases, oxidants, adsorbents (Fritzmann *et al.*, 2007), and biochemical methods, such as enzymes, have been used to remove foulants from the membrane surface or inside membrane matrix. However, due to the lack of complete knowledge of interaction between foulants and membrane materials, foulants and foulants, foulants and cleaning solution, membrane and cleaning solution (Gao *et al.* 2011), fouling still remains a challenging issue. It is believed that foulants bear some responsibility in reduction of membrane performance, permeate flux decline, transmembrane pressure (TMP) increase, and shortened life span, resulting in a rise in operation and management costs (Her *et al.*, 2007).

To control fouling, cleaning-in-place is regularly performed with chemical agents such as sodium hypochlorite and citric acid, to recover the membrane permeability. Cleaning strategy is generally dependent upon the feed water quality, membrane materials, and operating conditions. Meanwhile, the potential effect of chemicals on polymeric membrane ageing has drawn attention, and several studies have reported membrane ageing caused by chemical agents, particularly sodium hypochlorite; for example, polysulfone (PS) polymer membrane chain breakage occurred due to the exposure of NaClO, altering mechanical properties (Causserand *et al.*,2008, and Rouaix *et al.*, 2006). Furthermore, polyethersulfone (PES) membrane showed unchanging characteristics after a long-term treatment with alkali, acid and alkaline cleaning solution, except alkaline chlorine oxidant which broke C-S bond in PES and formed Cl-S bond (Begoin *et al.*, 2006). Moreover, it was reported that both mechanical strength and absorbance intensity of O-C-O bond decreased continuously when free chlorine concentration increased (Arkhangelsky *et al.*, 2007). It was also observed that membrane chemical groups and mechanical properties worsened after extended exposure of PVDF membrane to accelerated sodium hypochlorite concentration indicating that NaClO could cause membrane ageing (Puspitasari *et al.* 2010). Based on these findings, it appeared that chemical agents such as NaClO could cause membrane ageing by degrading mechanical strength and altering functional properties. Most studies regarding degradation and chemical cleaning effect are conducted at lab scales; however, there is a lack of studies at full and pilot plant scales.

In this study, membranes from a full scale and pilot scale water treatment plant were analyzed. Change in membrane properties, such as tensile strength and membrane surface functional group degradation, due to daily operation were examined to observe membrane ageing effect. Fiber morphology, FTIR and tensile strength studied to examine membrane ageing effect. Membrane fouling from CIP strategy in full scale was examined by measuring the organic and inorganic matters remaining on the membranes. At the same time, a simulation study at a lab scale was engaged to characterize the effects of membrane cleaning agents on membrane properties, i.e. mechanical property and surface chemistry, by separating its effect from mechanical stress of daily operation.

During the pilot plant scale study, the membrane cleaning agent's effectiveness was examined in terms of membrane permeability at various concentrations and pHs. Furthermore, pilot plant recovery was studied at various permeate cycles and membrane morphology, membrane foulants, such as organic and inorganic matters were also examined.

1.2 Objectives:

Membrane performance has been deteriorated and recovered by various means during its application, thereby building a competitive, knowledge-based water treatment system that is sustainable under growing global market. The general objective of this research was to evaluate the performance of ultrafiltration membranes made by polyvinylidiene fluoride (PVDF) for drinking water treatment and reuse.. The following specific objectives were designed:

- To observe the ageing effect via evaluating mechanical stress and membrane degradation.
- To Perform a simulated study at a lab scale in order to evaluate the effect of cleaning agents on a mechanical property and surface chemistry by separating from mechanical stress of daily operation.
- To characterize the nature of organic and inorganic foulants on membrane surface.
- To develop the cleaning strategies (cleaning agents concentration, cleaning time, pH, back pulse frequency and production cycles) currently used in Bare Point Membrane Filtration Water Treatment Plant.

CHAPTER 2: LITERATURE REVIEW

2.1 Membrane Filtration

Membrane filters are nonporous, porous, water-permeable, polymeric films (Lozier et al, 2008). They are flat sheets or hollow fibres like structure, which allow water to seep through, but block impurities that are larger than the pores. Figure 2-1 illustrates a single hollow fibre outside-in filter. As shown in the figure, it has a hollow cylindrical shape. Several fibres are bundled together forming a filter membrane module (Figure 2-2). In the filter module, one end of the fiber is blocked allowing water to flow through just one end. Suction is applied at the open end to facilitate water to flow through the filter using pressure. These types of filter are also termed as pressure-driven filters. The ability of the filter to block contaminants from reaching the permeate depends on the pore size of the membrane used. Sometimes contaminants can bond to the surface of the filter membrane, thus blocking them from reaching the permeate.

Depending on pore size, charge of retained particle or molecule, separation mechanism, morphology, geometry, and pressure exerted, pressure driven membrane filtration process is classified as micro-filtration (MF), ultra-filtration (UF), nano-filtration (NF) and Reverse Osmosis (RO) (Bruggen, 2003; Cui and Mularidhara, 2010; Lozier *et al.* 2008). The properties of various pressure driven membrane filtration systems are given in Table 2-1. Figure 2-1 shows the working principle of a hollow fiber membrane filtration process. As shown in the figure, the membrane fiber is outside - in working principle i.e. feed water is in contact with outside surface and permeate will flow from inside the fiber. Whereas, another type of hollow fibers has exactly opposite mechanism i.e. inside-out. Numbers of these fibers are attached horizontally between two vertical plastic headers to construct a membrane module, leaving top and bottom open to create a vertical flow upwards through the fibers as shown in Figure 2-2.

Table 2-1: Overview of pressure driven membrane processes and their characteristics (Bruggen *et al.*, 2003).

	Microfiltration	Ultrafiltration	Nano filtration	Reverse Osmosis
Permeability(L/M^2.h.bar)	>1000	10-1000	15-30	0.05-1.5
Pressure(bar)	0.1-2	0.1-5	3-20	5-120
Pore Size(nm)	100-10000	2-100	0.5-2	<0.5
Rejection				
Monovalent ions	-	-/+	+	+
Multivalent ions	-	-	-/+	+
Small organic Compounds				
Macromolecules	-	+	+	+
Particles	+	+	+	+
Separation Mechanism	Sieving	Sieving	Sieving Charge effects	Solution Diffusion
Applications	Clarification; pre-treatment; Removal of bacteria	Removal of Macromolecules; Bacteria, viruses	Removal of (multivalent) ions, relatively small organics	Ultrapure water; desalination.

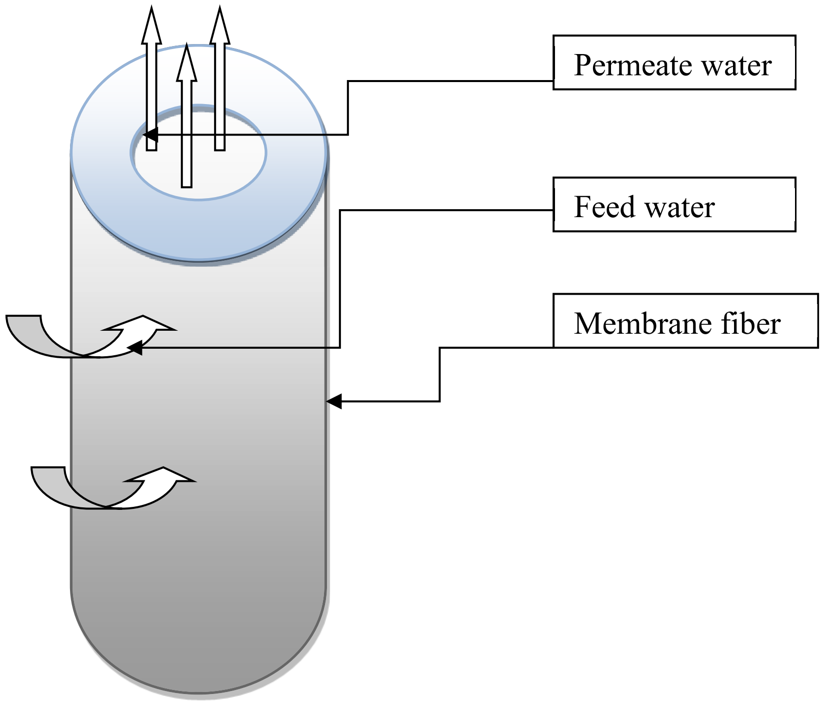


Figure 2-1: Single Hollow fiber membrane with working principle

Figure 2-2: Membrane module used in this project (Bare point Water Treatment Plant- pilot plant)

2.2 Membrane Materials:

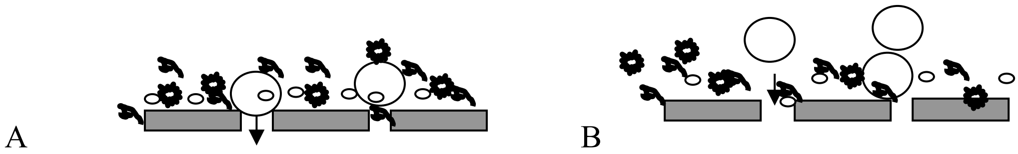
Membranes are manufactured from different materials such as organic polymers and inorganic materials. Inorganic membranes such as alumina, zirconia, titania etc. are also used. However, these inorganic membranes are more expensive and commonly brittle (Bruggen *et al.*, 2003). Most commercial membranes are made of hydrophobic and hydrophilic organic polymer such as polyvinyldene fluoride (PVDF), polyacrylnitrile (PAN), polyether sulfone (PES), polysulfone (PS), and poly vinyl chloride (PVC). These materials have good chemical and thermal resistance and can work in a wide range of pH. These materials vary in their chemical and mechanical properties like mechanical strength, burst pressure, oxidant tolerance and operating pH range (Lozier *et al.*, 2008; Cui and Mularidhara, 2010). It is very important to be familiar with the properties of each type of filter to ensure that the selected material is compatible with feed water quality, operating conditions, and chemicals used.

Table 2-2: Summarizes physical and mechanical properties of commonly used membranes.

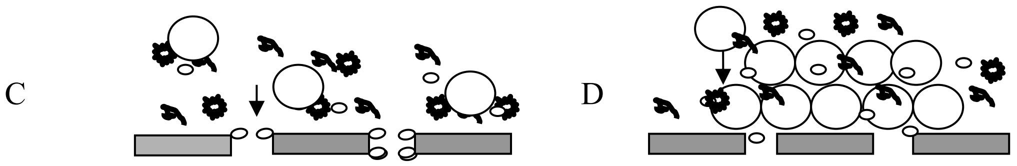
Membrane Materials			
PVDF	PES	CA	PP
Hydrophobic	Stable at high temp	Cheap, wide range of pore sizes	Hydrophobic
Tolerate a wide range of pH 0 -12	Wide pH range 1-13	Narrow pH range (4-8)	Chemical resistance high
High resistance hydrocarbon, oxidizing environment, temperature	It has high resistance for chlorine for short time.	Narrow operating temperature recommend below 30^0C	Tolerate moderately high temperature

2.3 Membrane fouling:

Membrane fouling is the accumulation of substances on the membrane surface and/or within the membrane pores, which results in deterioration of membrane performance. Major Foulants in natural water are colloidal and suspended particles, organic matter, sparingly soluble salts (e.g. calcium sulphate), and biological growth (Hong and Elimelech, 1997; Vrouwenvelder *et al.*, 2003). Membrane performance is affected by various interactions between feed water composition and membrane properties, dissolved organic carbon composition, divalent cations, and mono-valent cations. (Hong and Elimelech, 1997; Lin *et al.*, 2001; Mozia *et al.*, 2005; Chuang *et al.*, 2009). The fouling potential of an individual membrane can be quantified by a unified membrane fouling index (UMFI). Huang *et al.*, 2008, revised the mathematical model of UMFI based upon the Hermia model. The schematic diagrams of mode of fouling are given as below-



(Complete pore blocking) (Intermediate pore blocking)



(Standard pore blocking) (Cake layer formation)

Figure 2-3 : Schematic diagrams of four modes of membrane fouling

2.3.1 Organic Matters

Natural organic matter (NOM) is the primary foulant in natural water. Several investigation demonstrated the role of NOM fouling on/in membrane for natural water (Fan *et al.*, 2001; Schafer *et al.*, 2002; Gray *et al.*, 2007). The major fraction of NOM consists of humic substances. It has been shown that a fraction of humic substances are of large apparent molecular weight (AMW: 6.5 -33.6 kDa) which cause a rapid flux decline (Lin *et al.*, 2000). Small AMW fractions (having carboxylic and phenolic functional groups) also have effect on a flux decline. It also revealed that UF membrane could remove a significant amount of trihalomethane (THM) from large AMW fractions. However, a hydrophilic fraction causes very sharp decrease in flux (Lin *et al.*, 2001). In addition, the use of powdered activated carbon (PAC) for pre-treatment of hydrophilic and hydrophobic humic acid for PAC-UF system causes more membrane fouling (Lin *et al.*, 2000). The pH of natural water ranges from 6.6-8.5. Within this range, humic substances are negatively charged (Hong and Elimelech, 1997). Table 2-3 is the summary of study on fouling by humic acids on different membrane.

Table 2-3: Summary of studies on NOM and various analytical methods used by various researcher

Membrane	Study	Analytical methods	Reference
UF	Humic substance characteristics	TOC, UV/VIS, Resin(DAX-8), GFC	Lin *et al.*, 2000
UF	Humic substance functional group	TOC, FTIR, Resin(weak base)	Lin *et al.*, 2001
MF	Characteristics of NOM	TOC, SUVA, UVA, UV/Vis	Fan *et al.*, 2001
UF	Charge effect in fractionation of NOM	TOC, UV/Vis, HP-SEC, LC-OCD.	Schafer *et al.*, 2002
UF	Effect of NOM characteristics	TOC, UV, SUVA, Resin, NMR, LC-DOC.	Gray *et al.*, 2007.

Schafer *et al.* (2002) studied the effect of fouling on the rejection of the membrane for filtration of natural water. They concluded that primarily fouling was caused by colloids, coagulant flocs, organic-calcium flocs, and aggregates. The NF membrane rejected divalent ions more effectively than mono-valent ions. It can be explained by Donna exclusion mechanism of charged porous membrane. The NOM removal process was explained by two different mechanisms, size exclusion and electrostatic repulsion. The equilibrium between charged membrane and the bulk solution is characterized by electric potential, the Donna potential (Bruggen, *et al.*, 2003). The rejection of NOM by NF varies with pH, showing a better result at pH 8 than at pH 4. At low pH, humic substances have a smaller macromolecular configuration due to reduced inter chain electrostatic repulsion and pass easily through the membrane pores. The surface charge of NF membrane is also significantly affected by divalent cations. This was reported that due to the decrease in the negativity of zeta potential with increasing divalent cation concentration. However, they also concluded that different divalent cations might have a similar effect on NOM fouling. Hydrophobic nature is also important for the adsorption of humic acids and more favourable at a low pH. At a low pH, membrane surface charge is slightly negative and humic macromolecules are more hydrophobic. The negative charge variation on the membrane surface may be due to the carboxylic acidity (Her *et al.*, 2000). At a low pH, the negative charge comes from the large fraction of functional groups and at high pH, most of the carboxylic group deprotonated and gave negative charge to the membrane surface (Elimelech *et al.*, 1997). The membrane performance is affected by the fraction for example hydrophobic and hydrophilic of humic substances present in the feed water (Lin *et al.*, 2000; 2001; Fan *et al.*, 2001). However, studies on the feed water with and without pre-treatment by PAC-UF system, iron-oxide, fraction and unfractionated humic substance showed conflicting results for flux decline. The conflicting result due to the commercial humic acids may not represent humic substance in the natural environment, and humic substance components could vary with season and environmental source (Lin *et al.*, 2000). The measurement of these phenomenon rely on hydrophilic and hydrophobic nature of particles, operation conditions such as pH, pressure, temperature, ionic strength, concentration and composition of membranes (Her et al, 2000; Kimura *et al.*, 2006). Flux declining and elevating in transmembrane pressure (TMP) are indications of membrane fouling. This brings the financial burden as well as decreases in water quality. Membrane fouling depends upon the natural organic matter (NOM) characteristics and its interaction with membranes (Lee *et al.*, 2005).

2.3.2 Inorganic substances

Besides NOM, inorganic particles were also found to be as significant as foulants. Generally, researchers believe that inorganic fouling occurs by scale formation on the membrane surface. This activity happens due to the increase in concentration and beyond their solubility limits, and can overcome this problem by operating membrane filtration system under critical solubility limits (Al-Amoudi, 2010). The situation in which ionic product of slightly soluble salt exceeds its equilibrium solubility product, then scaling fouling and precipitation fouling will occur (Schafer, 2001). The configuration of deposits of inorganic salts such as Calcium carbonate, calcium sulphate, and calcium phosphate is generally termed as scaling. On the study, scaling causes the physical damage on the membrane surface (NF) and becomes hard to recover membrane performance due to difficulties in removing scaling and irreversible membrane pore blocking (Schafer *et al.*, 2002).

Thanuttamavong et al. (2002) investigated that membrane fouling is an important key for the application of a long-term operation and rejection characteristics of the membrane. During their study, the transmembrane pressure was controlled at a low range of 0.15 MPa and the temperature was normalized to 25^0C. Since membranes, in general, have charge surface, rejection characteristics of membrane depends upon the molecular size and molecular charge of interested pollutants. The performance of NF membrane combine with MF membrane and NF alone was investigated and found that the rejection of all components remain stable during the long-term operation pre-treatment with MF. The rejection of organic and inorganic component studied and found that the fouling layers did not affect the rejection mechanism. Size exclusion mechanism can explain the rejection of organics matters by NF membranes. Furthermore, inorganic matters such as divalent ions examples $Ca^{2+,}$ Mg^{2+}, and $SO_4{}^{2-}$ rejected more compare to mono-valent ions such as Na^+, K$^+$, Cl$^-$, NO^{3-} and HCO^{3-}. These rejection activities can be explained by charge effect of the NF membranes. The effective charge density also played important role on the rejection of ionic solute and establish different interaction between ionic species to the membrane materials. The ionic species of larger molar volume such as nitrate, corresponding to larger surface area would have a lower surface charge density compared to the smaller molar volume ionic species such as chloride ion. The rejection mechanism of chloride ion was similar for fresh and fouled NF membrane whereas, for nitrate ion a negative rejection was observed for fouled membrane and a positive rejection for fresh membrane (Thanuttamavong *et al.*, 2002)

Table 2-4: Summary of various studies on organic and inorganic foulants.

Membrane Types	Pore size (µm)	Materials	Feed water Source	DOC(mg/L)	pH	Foulants	References
NF(Six type)	NA	Aromatic Polyamide Poly vinyl alcohol, Sulfonated poly sulfones	Tama River water	NA	7.2-7.5	Organic/Inorganic	Thanuttamavong *et al,* (2002)
UF cross flow		Polysulfone (Hydrophobic)	Lake Austin+ Missouri River water			Organic/Inorganic	Kweon *et al* (2004)
MF(2 type)	0.1	Polyethylene/PVDF	Chitose River water, JP	1.4		NOM/Inorganic	Lee N *et al.*, 2004
UF	100000 Da	Polyacrylonitrile(PAN)		1.4		NOM/Inorganic	Lee N *et al.*, 2004
MF Flat sheet	0.22	PVDF(Hydrophilic)	Myoonga Reservoir/Woronora Dam	11.7/2.2	7.8/6.7	HA/ Inroganics	Fabris et al (2007)
UF	NA	Thin film polysulfone	Surface water reservoir, Ubon Ratchathani's University, Thailand	10	7	Organic/Inorganic	Jarusutthirak *et al*, 2007
UF	100 kDa	PES	HA ,IHSS, polysaccharide alginate, Kaolinite	0.02,0.2,and 2 (HA), 0.02-0.2 and (alginate), 10 and 100 (kaolinite)		Organic/Inorganic	Jermann *et al* , 2008
MF hollow fibre	0.1	PVDF	Chitoos River water, JP			Organic/Inorganic	Chae *et al* (2009)
MF hollow fibre	0.1	PVDF	Han River water, Korea	1.53		Organic/Inorganic	Moon *et al* (2009)
UF Hollow fiber	0.01	Poly vinyl Chloride	Songhua River water	7.22	7.74	Organic/Inorganic	Tian *et al* (2010)

2.3.3 Biofouling:

Biofouling is another type of membrane fouling. It is concerned with the deposition, growth, metabolism of bacteria cells and formation of colonies on the membrane surface, and this phenomenon raised significant issues in the membrane filtration during water treatment process (Gao *et al.* 2011; Pang *et al.*, 2005; Wang *et al.*, 2005). However, this fouling is more problematic for wastewater treatment process than drinking water treatment. In drinking water treatment due to the frequent application of chlorine to clean membrane, microorganisms may have died before fouling the membrane (Gao *et al.*, 2011). Several researchers argued that biofouling begins with the deposition of single cell then multiply and form a cake layer. Importantly, SMP (soluble microbial products) and EPS (extracellular polymeric substances) secreted by microorganisms play vital roles in forming cake layer on the membrane surface (Liao *et al.* 2004). Furthermore, biofouling can also cause irreversible damage to membrane reliability, shorten membrane life, increased operational and maintenance costs as a result it reduces efficiency. The extent of bio-film depends upon the chemical properties of membrane surface, its roughness, pore size distribution and shape (Hilal et al, 2004).

2.3.4 Membrane fouling mechanism

Declination of flux and elevation of the TMP during the water treatment process are the indication of membrane fouling. The main types of fouling are categorized as inorganic fouling caused by dissolved inorganic materials ($CaSO_4$, $CaCO_3$, $MgSO_4$); organic fouling (humic substances), biofouling (attachment of microbial), and particulate and colloidal fouling (suspended particles) (Vrouwenvelder *et al.*, 2003). Adsorption (Howe *et al.*, 2002; Kweon *et al.*, 2004) pore blocking (Lee *et al.*, 2004) and cake layer formation (Lee et al, 2005) are reported to be the main membrane fouling mechanisms. In macro solute or particle adsorption fouling, the foulants are adhesive due to hydrophobic interaction, hydrogen bonding, van der Waals attraction and extracellular macromolecular interaction (Hong and Elimelech, 1997; Ang *et al.*, 2006). This is an irreversible fouling mechanism (Yamamura *et al.*, 2007) resulting from intermolecular interactions between the contaminant particles and the membrane. Another fouling phenomenon, cake layer formation, is reversible and results from the deposition of macro solute or particles such as cells, cell debris and other rejected particles on the membrane surface. To enhance membrane performance, it is necessary to remove above mentioned contaminants.

Reversible and irreversible fouling are considered as the main mechanisms of the membrane fouling. Reversible fouling occurs at the surface of membranes forming cake layers and can remove easily by physical means such as backwashing, air scouring (Ma *et al.* 2000). Cake formation is simple process of depositing of contaminants on membrane surface and create extra layer on the membrane surface and resist permeate flow-causing declination of flux. Pore blockage increases membrane resistance and happens by adsorbing particulate inside the membrane matrix. Level of these processes depend upon the composition of feed waters (humic substances, minerals, microorganism), operating conditions (pH, pressure, temperature, ionic strength, concentration), and the nature of membrane substances (hydrophobic , hydrophilic), and materials used to make membranes like PVDF, PES, PP, PVC,PAN etc.

Membrane fouling is composite physicochemical activities and several mechanisms involved at the same time, for example, a protein containing solution contacts with the membrane, then the phenomenon starts with the aggregates depositing on membrane surface and thereby blocking its pores together with disulphide linkage, van der Waal forces, electrostatics interaction, hydrophobic interactions and hydrogen bonding (Ma *et al.*, 2001). Various researches demonstrated that macro solute or particle adsorption is established by the intermolecular interaction among the particles and membranes even if no filtration process occurs and is usually an irreversible process. During water treatment process, irreversible fouling occurs due to a hydrophobic interaction, hydrogen bonding, van der Waals attraction forces and extracellular macromolecular interaction (Ma *et al.* 2000). Similarly, filtration induced macro solute or particle deposition generally reversible fouling, where the accumulation of cells debris, cells and other rejected particles on membrane surface were found, and fouling occurs additional external layer and weakly depends upon chemistry of the membranes' surface (Taniguchi *et al.* 2003). Fouling occurs during ultrafiltration membrane process due to NOM and it has a greater role in the irreversible fouling (Li *et al*., 2011)

2.4 Factors Affecting Membrane Fouling:

2.4.1 Membrane materials and properties:

Membrane technology is virtually capable of removing all substances bigger than the pore size. However, some membranes such as UF and MF are widely used to remove particulates and pathogens. The achievements of removal of soluble materials in the surface water depend upon the membrane materials (Jung *et al.*, 2006). Jung *et al.*, 2006 studied the effect of various membrane materials on membrane fouling. They used hydrophobic and hydrophilic membranes provided by Millipore. In their study, they found that the permeate flux declination rate for hydrophobic membrane was significantly greater than that for a hydrophilic membrane. Yamato *et al.*, 2006 also studied membrane fouling using different membrane materials, such as PVDF and PE, in municipal waste water. The results revealed that the rate of fouling on PE membrane was faster than that of PVDF. At the same time, irreversible fouling was the dominant portion on PE, while reversible foulants were on PVDF (Yamato *et al.*, 2006). Similarly, the fouling affinity performed by Zhang *et al.*, 2008, between EPS and three polymeric ultrafiltration membranes demonstrated that the affinity of three membranes was as given of the order: PAN < PVDF< PES. They suggested that PAN membrane had less fouling affinity than other PVDF and PES membranes. Membrane properties such as pore size, zeta-potential also accounted for membrane fouling. Comparatively, larger pore size of membrane are more favourable for irreversible fouling due to the deposition of the low to medium MW components of NOM in the inner parts of the membrane during the constant pressure and flux operation modes (Lee *et al.*, 2008). It was also revealed that inorganic membrane such as aluminium, zirconium and titanium oxide are higher hydraulic, chemical and thermal resistance and are probable substitute for high temperature water treatment. However, those inorganic membranes are not suitable option due to their high costs (Meng, *et al.*, 2009).

2.4.2 Membrane Module Design:

Membrane module design is another important factor that can cause alternations of the hydrodynamic conditions and affect membrane fouling. Commonly, hollow fibers and flat sheet membrane modules have been extensively used in the water treatment process. A packing density is a central parameter of membrane module design. Several researches have demonstrated that smaller packing density than critical value reduced build-up of foulants on membrane surface between the fibers; furthermore, membrane module length and distance between membrane fibers alter the number of collision of flocs, then disturb the accumulation of foulants on membrane surface (Liao *et al.*, 2004).

2.4.3 NOM:

Commonly, membranes are employed in water treatment as an alternative technology to reduce NOM. Humic substance is considered as a major portion of NOM in the surface water containing both aromatic and aliphatic components with carboxylic and phenolic functional group (Schafer, 2001). Since NOM contain carboxylic and phenolic functional group, humic substances demonstrated as negatively charged components in the pH range of natural waters. NOM fouling depends upon the ionic strength of solution, pH of the solution, concentration of divalent ions (Ca^{2+}) (Hong and Elimelech, 1997, Ang *et al.* 2006). In addition to this, various organic fractions such a hydrophobic, hydrophilic, trans-hydrophilic and neutral have variable molecular weights, sizes and charge densities.

Therefore, the interaction between membrane materials and these substances are normal. The hydrophilic fraction of natural water contains colloids and macromolecules, such as protein and polysaccharides were the causes of fouling in a low-pressure membrane. This was also supported by the presence of high amount of DOC (Li *et al.*, 2005). The presence of organic matter in the source water can be reversible or irreversible fouling, which can be removed partially or almost completely by physical and chemical cleaning (Al-Amoudi et al 2007). There are a number of factors affecting the membrane fouling in existence of NOM in feed water, such as NOM properties together with molecular weight, polarity, hydrophobicity (Schafer *et al.*, 2001, 2004; Bruggen *et al.*, 2002; Bellona *et al.*, 2004).

2.4.4 Hydrophobic/Hydrophilic nature:

Surface water commonly contains humic substances. Natural humic substances consist of hydrophobic, hydrophilic and neutral fractions. Membrane fouling by natural water generally contains NOM associated with hydrophobic acid, hydrophobic neutral and bases. Hydrophobic and hydrophilic fractions demonstrate high trihalomethane formation potential (THMFP) (Lin *et al.*, 2000; 2001). UF membranes are effective in reducing turbidity, particulates, organics, and bacteria; however, they are not effective in removing humic substances. Hydrophilic components demonstrated more flux declines and the use of PAC for pre-treatment of natural water facilitates membrane fouling (Lin *et al.*, 2000). The functional group of the humic substances also have an effect on the membrane fouling in term of flux decline. The carboxyl fraction shows more flux decreases, however permeate still contains THM. The pre-treatment of PAC for carboxylic and phenolic fractions assist in membrane fouling, but THMFP has been decreased significantly (Lin *et al.*, 2001). Hydrophilic membranes for examples cellulose acetate(CA) and polysulfone ether(PE) showed better performance for the feed water containing more hydrophobic fraction than higher than hydrophilic fraction (Lin *et al.* 2001, Yamamura *et al.* 2007). They demonstrated that hydrophilic compound such as carbohydrate was a dominant component causing physically irreversible fouling despite the type of membrane. In the same study, it was found that physically irreversible fouling of small molecules such as humic substances (hydrophobic in nature) were adsorbed on the surface or in the membrane matrix by hydrophobic interaction and worked as glue for carbohydrate and assisted in confining them on or in the membranes. PVDF membrane is more hydrophobic than PE and adsorbs humic substances more quickly than PE membrane. Carbohydrate and humic substance are produced in feed water as an excretory product of microorganisms.

Table 2-5: Table represent the study by various researchers on hydrophobicity of NOM

Membrane materials	Source water	Study on	References
PS UF	Aldrich HS+ Sodium salt	Effect of hydrophobic and hydrophilic HS	Lin *et al.*, 2000
PS UF	Aldrich HS + sodium salt	Effect of functional groups of HS	Lin *et al.*, 2001
PVDF MF	Maroondah, Moorabool and Mt zero water	Effect of NOM characteristic on the fouling.	Fan *et al.*, 2001
PP , PVDF(HPO, HPI)	Lake Eppalock , Moorabool river	Fouling mechanism of each fraction of NOM.	Gray *et al*, 2007

2.4.5 Ionic strength:

Ionic strength plays a vital role in membrane fouling process. Hong and Elimilech (1997) studied various ionic concentrations and found that fouling become more serious by increasing the ionic concentration. As the ionic strength increases, the level of negatively charged molecules decreases due to a high amount of Na+, resulting in the adsorption of soluble substances on membrane (Hong and Elimilech,1997). The presence of organic macromolecules in solutions can change the effect of solution chemistry on electric repulsion. As a result, at a high ionic strength and low pH, the declination of membrane permeability was reported in absence of organic macromolecules whereas both membrane permeate flux and solute rejection reduced significantly in the presence of organic macromolecules in solutions (Lin *et al.*, 2000). Thereby, organic fouling is found to be most severe under a low pH, high ionic concentration and the presence of multivalent cations such as calcium ions (Nghiem et al 2008). Researchers pointed out that reasons for these activities were: at low pH and high ionic strength, the reduction of electrostatic charges occur; as a result organic matter rejection decreases and then the layer of organic matter pile up on the membrane surface. The effect of ionic strength on the flux containing phenolic compound is less noticeable compared to the carboxylic compound. As ionic strength increases, the concentration of positive ions increases and negatively charged molecules is reduced, resulting in adsorption of contaminant molecules onto the membrane surface, which then causes a flux decline (Lin *et al.*, 2001).

Table 2-6: Various study on effect of ionic strength on membrane fouling.

Membrane Materials	Effect studied	Ionic strength	Reference
Aromatic polyamideTFCS	Permeate flux, TDS rejection	0.001M(NaCl)	Hong *et al.*,1997
PS	Flux decline, HS rejection	0.01 M(NaCl)	Kulovaara *et al.*, 1999
PES	Flux decline, HS rejection	0.001M(NaCl)	Yuan and Zydney., 2000
RC	Static and dynamic adsorption, Flux decline	0.001; 0.2M(NaCl)	Jones and O'Melia, 2001
PS	Flux decline, DOC removal	5g/L,10%, Nacl	Lin *et al.*, 2001
Semi aromatic Polyamide-NF	Interaction force, Flux variation	0.1; 0.01 M(NaCl)	Li and Elimelech, 2004
CA	Flux decline, HS rejection	0.001; 0.01M(NaCl)	Costa and de Pinho, 2005
PAN	Membrane Resistance	0.034; 0.17 M(NaCl)	Mousa 2007

2.4.6 pH:

The effect of pH on NOM fouling has been analyzed by various researchers (Hong and Elimelech, 1997; Lin *et al.*, 2001; Shim *et al.*, 2002). Water flux was observed declining at pHs 4 and 8, and foulants layer was found to be denser at the lower pH as electrostatic repulsion between the membrane surface and NOM was reduced (Hong and Elimelech, 1997). More carboxylic group ($RCOO^-$) at a higher pH (11) of NOM become protonated carboxylic group (RCOOH) at lower pH 4 causing a reduction in charge of humic substances (Lin et al, 2001). Calcite precipitation process was found to be favourable at a high pH and high calcium concentration resulting organic molecules adsorbed on the calcite surface. This leads to the deposition of calcium and the adsorption of organic molecules on the calcite surface with an increase in the pH and elevated membrane fouling (Schafer, 2001). It was also revealed that inorganic scalants were responsible for flux declination. Jarusutthirak *et al.* (2007) performed a model study and reported that divalent cations such as Ca^{2+} and Mg^{2+} formed various scales with combination of polyanions i.e. CO_3^{2-}, SO_4^{2-} and PO_4^{3-}, and the amount of precipitation was increased with increasing pH of the solution up to a certain range of pH. At the same time, they also revealed that calcium species had a higher flux declination compared to magnesium species (Jarusutthirak *et al.*, 2007).

Table 2-7: Represent the study of effect of pH on different membrane materials and flux.

Membrane material	Effect studied	pH	Feed Concentration	Reference
Aromatic polyamideTFCS	Permeate flux, TDS rejection	4 and 8	Suwannee river, Peat and Aldrich humic acid.	Hong *et al.*,1997
PS	Flux decline, HS rejection	4.5, 5.5, 6.5	Natural water, Nordic HA	Kulovaara *et al.*, 1999
PES	Flux decline, HS rejection	3, 7	Aldrich	Yuan and Zydney., 2000
RC	Static and dynamic adsorption, Flux decline	4.7,10	IHSS	Jones and O'Melia, 2001
Semi aromatic Polyamide-NF	Interaction force, Flux variation	4.8, 11	Suwannee river humic acid	Li and Elimelech, 2004
CA	Flux decline, HS rejection			Costa and de Pinho, 2005

2.4.7 Divalent cations:

Divalent cations, such as calcium, interact with humic acid and form metal-humic complexes. This complex formation changes the properties of the NOM and, therefore increases membrane fouling. The amount of complex formation depends on the chemical properties of NOM. The addition of calcium is to enhance the binding capacity with the carboxylic groups of alginate and the formation of bridge between adjacent alginate molecules, which resulted in the cross-linked fouling layer on the membrane surface (Ang *et al.* 2006). The characteristics of water are important to understand fouling. Divalent cations (Ca^{+2}) were found significantly high in white river and Scottsdale. This high amount of cations binds with negative charged functional groups and cause a flux decline (Li *et al.*, 2005). The concentration of calcium ions in the feed solution considerably enhanced the humic acid fouling and membrane fouling appreciably affects the separation of BPA (Nighiem *et al.*, 2008). Also, calcium scale was found responsible for the higher flux decline compare to magnesium (Jarusutthirak *et al.*, 2007). It was also noticed that the fouling layer disturbed the solute–membrane interaction when both solute and foulant layers are hydrophobic and has an effect on separation process (Nighiem *et al.*, 2008).

2.4.8 Operating condition

Wang *et al.* (2008) investigated the effect of several operational parameters such as raw water concentration, permeability, cross-flow velocity, backwash interval, and backwash pressure and backwash mode on ultra-filtration membrane treatment. The experiment was carried out using Kraft pulp liquor diluted with well water in different concentration in terms of UV254. The UF hollow fibre made by cellulose acetate (CA) of molecular cut-off of 150kDa (Toray Company Japan). The temperature of permeated water was 20±1.5 ^{0} C. The outcomes of this study were that a high concentration of organic matter caused rapid TMP increases and the efficiency of process can be lost. After certain levels of the concentration of organic matter (UV 254 = 0.35) an irreversible fouling can result. It was suggested that raw water should be pre-treated to reduce the concentration of organic matters. Hence, the operating conditions play a critical role in keeping stable TMP and permeability for a long term.

2.4.9 Temperature:

Temperature is also another factor that can alter the fouling rate on/in the membrane by changing properties of the membrane (pore size), shear stress close to membrane surface, diffusivity, solubility, adsorption (Drews A., 2010) of the constituents and viscosity of the feed water. According to the Darcy's law (Equation 1), the permeate flux is inversely proportional to the value of water viscosity.

$$J = {}^{\Delta P}/_{\mu R} \text{ ---------------------------(1)}$$

Where, J= permeate flux ($m^3m^{-2}s^{-1}$), ΔP= TMP (Pa), μ=viscosity of water(Pa.s), R = Resistance(m^{-1}).

At a low temperature, membrane shrinks and the pore size decreases. Therefore, more pressure is required for maintaining constant membrane performance, and a more compact layer of the foulants is formed on the membrane surface. However, the fouling rate can be reduced by using a constant operating mode when temperature is lower than 5^0 C (Guo *et al.*, 2009). Temperature also affects the scale formation on the membrane surface. Calcium carbonate particles were detected on the NF membrane surface and the solubility product of calcium carbonates and calcium sulphate decreased with increasing temperature (Her *et al.*, 2000). Seasonal variation also affects the rate of reversible and irreversible fouling. It was studied by Miyoshi *et al.* 2009 that reversible fouling was major during low temperature period, whereas irreversible foulants were found more significant during a high temperature period.

2.4.10 Hydrodynamic Condition:

Hydrodynamic conditions are vital for membrane fouling. Accumulations of foulants depend upon the hydrodynamic condition. Generally, both air and liquid are employed for maintaining a hydrodynamic condition and the efficiency of removing foulants depend on the air/liquid velocity during backwashing. Several researchers employed aeration to create shear stress expecting scouring in the membrane surface and reducing membrane fouling. In a low pressure membrane system, backwashing is completely computerized, and it starts when TMP reaches a certain fixed value. Typically, backwashing is implemented 20 to 120 min of permeate cycles for few seconds to 5 minutes. Bubble sizes and their flow rates also have a significant effect on the membrane fouling. Fan *et al.* (2005) studied the effect of bubble sizes on membrane fouling using two different sizes of nozzles i.e. 05 and 0.1 mm to produce bubbles with different magnitudes. It was found that smaller bubble remarkably enhanced the fouling control. However, Prieske *et al.* (2008) concluded that bigger bubbles were efficient to scour membrane surface due to higher circulation velocities.

2.5 Foulants characterization:

MF and UF membrane are widely accepted as potential technology for the filtration of drinking water. These processes are capable of removing particles, colloidal species, colour, and bacteria from surface water (Huang *et al.*, 2007). These technologies have grown to be a multibillion-dollar industry and are still growing. The treatment of water using membranes is relatively new and this process demonstrates effectiveness for purification of surface water. Due to its capability of removing even smallest viruses, purified water can be achieved in many stages as an alternative process for a conventional treatment plant. In practice, the activities of membrane vary over time and continue to decline in performance with time. Such a decline in performance results from membrane fouling. Membrane fouling has a great impact on energy consumption because of flux decline and hence elevates the cost of water treatment. To reduce the cost and increase the efficiency and life span of the membranes, it is very important to control fouling. For this purpose, the characterization of foulants is necessary. The characterization of foulants based on the analysis of easily measurable process parameters such as membrane permeability is important. Since fouling is a complex process, it is very difficult to understand. Until this day there are a number of studies that have been done regarding the characterization of fouling. Table 2-8 is the representative summary of some studies carried out for characterization of membrane fouling.

Table 2-8: Summary of various membrane, materials, and foulants found in the study.

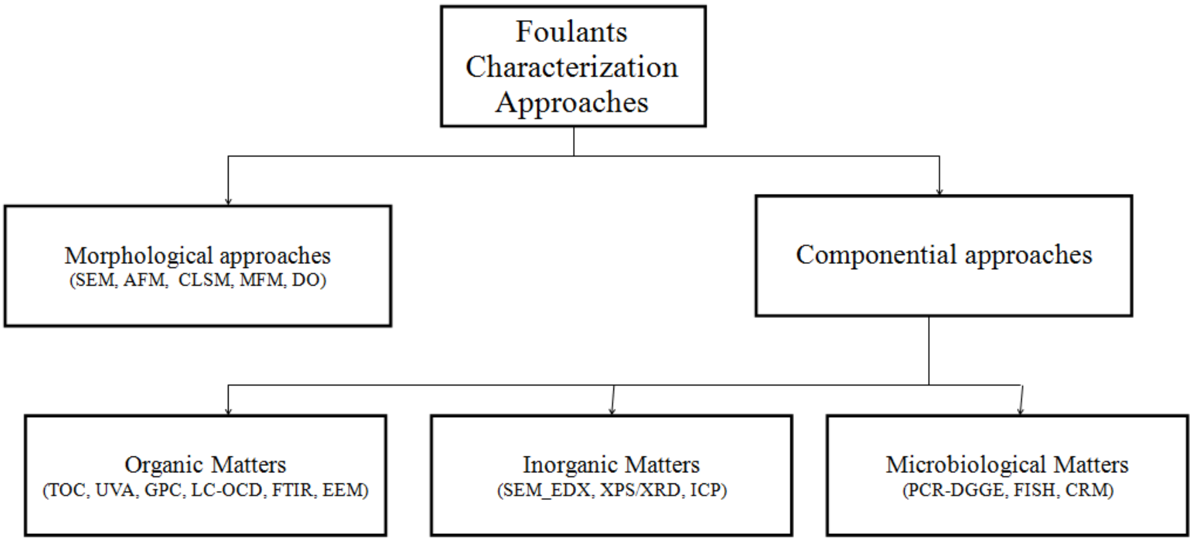
Membrane	Materials	Foulants	Reference
NF	Polyamide TFCS	Organic /inorganic	Hong et al 1997
MF	PVDF-1HPO/PVDF-2HPi, PES-2(0.1µm)	Organic/inorganic	Gary et al 2007
UF3/MF1	PVDF/PES	Organic	Huang et al 2007
MF	Mixed cellulose ester (0.22µm)	Organic(Polysaccharides)	Hughes et al 2007
NF	Polysulfone(0.01µm)	Organics particulate	Jacquemet et al 2005
UF	PE/PVDF/PAN	Organics (remaining particulate)	Mosqueda and Huck 2006
UF	(0.01µm/100000Da)	Organic(Carbohydrate)	Remize et al 2010
MF2/UF1	PVC	HPo/HPi Humic/protein like substance.	Yamamura et al 2007

Membrane fouling is a universal phenomenon with membrane process used in water treatment. This term is usually used to describe the loss of membrane permeability due to accumulation of materials on the membrane surface during the filtration process, causing drop in efficiency of membrane, and finally increasing the cost of operation. The mechanism and cause of fouling are still not completely understood. However, many studies reveal that Natural Organic Matters (NOM), membrane materials, operating conditions and characteristics of feed water potentially affect fouling during surface water treatment. Many researchers have tried to characterize the foulants. Mosqueda-Jimenez *et al.* (2008) found that most of the fouling materials were organic in nature with a high number of microorganisms. Huang et al. (2007) studied the effect of NOM source and hydrodynamic condition on fouling of low pressure membranes and found that, fouling potential for each water source is generally specific to the type of membrane used. Using hollow fibre membranes, carbohydrates were leading foulants despite the types of membranes used. However, PVDF and PE are predominantly used for water treatment due to their high chlorine, heat and chemical resistance. PVDF is more hydrophobic than PE and PVDF adsorbs humic substance more rapidly than PE (Yamamura *et al.* 2007). Hence, studies suggested that deeper characterization of both NOM and membrane is important to understand the fouling mechanism of low-pressure membranes.

2.5.1 Various techniques for foulants characterization:

Foulants characterization is very important in order to select cleaning strategies. Numbers of approaches have been employed to characterize the foulants on the membrane surface or in the membrane pores. Various techniques mentioned in several published articles are summarized in Figure 2-4. Morphological examination is a very strong analytical method due to its capacity to deliver spatial images by straight examining or indirect scanning of membrane surface, and it also explains significantly the membrane fouling mechanism such as surface coverage and pores blockage (Lee *et al.*, 2005, Meng *et al.*, 2010). Morphological examination can be done by using a number of techniques, such as scanning electron microscope (SEM). These techniques were extensively used to analyse membrane surface and were able to characterize the origin of foulants e.g. colloidal foulants (Boss *et al.*, 2007), inorganic foulants (Shih *et al.*, 2005), organic foulants (Zhang *et al.*, 2003), biofouling (Herzberg *et al.*, 2007). However, the wide application of such techniques is limited due to requirement of pre-treatment of samples such gold coating and dehydration (Meng *et al.*, 2010).

Atomic force microscopy (AFM) is another strong analytical tool. Due to its capacity to produce 3-d images, this technique is widely used to obtain more information of the membrane surface fouled by various material. Furthermore this techniques is applicable in order to elucidate the pore size and density (Mosqueda-Jiminez and Huck, 2006), interaction force such as Vander Waal forces, chemical bonding, electrostatic force and the key feature for popularity of AFM is that it capture images in air or in liquid without any pre-treatment of samples (Bowen *et al.*, 2002, Meng *et al.*, 2010).



SEM- Scanning electron microscopy; AFM- Atomic force microscopy; CLSM- Confocal laser scanning microscopy; MFM- Multi-photon fluorescence microscopy; DO- Direct observation; TOC- Total organic compounds; UVA- ultra violet adsorption, GPC- Gel permeation chromatography, LC-OCD- Liquid chromatography with organic carbon detection, FTIR- Fourier transform infrared spectroscopy; EDX- Energy diffusive X-ray; XPS- X-ray photoelectron spectroscopy; XRD- X-ray diffraction, ICP- Inductively couple plasma; PCR_DGGE- Polymerase chain reaction denaturing gradient scanning electron microscopy; FISH- Fluorescence In situ Hybridization; CRM- Confocal Raman microscopy.

Figure 2-4: Schematic representation chart of foulants characterization.

Total organic carbon analyser (TOC) is an analytical tool used for quantitative analysis of total organic carbon (TOC), total inorganic carbon (TIC) and total carbon (TC). The principle of the analyser is based on the oxidation of organic compounds to transform in to carbon dioxide (CO_2) via a UV radiation and an oxidizing agent for example ammonium persulfate. The inorganic carbon concentration is determined by measuring CO_2, HCO_3^-, and CO_3^{-2} concentration and total carbon (TC) is calculated once oxidation of organic compounds. Then, the total organic carbon is determined as TOC = TC - TIC (GE Analytical Instrument, 2010). Dissolved organic carbon (DOC) in source water is a basic and important parameter in the field of filtration process in water treatment. TOC analyser has been used by several researchers to determine the dissolved organic carbon (DOC) in the source water.

Table 2-9: Various membrane type, source water, and DOC and foulants types with references.

Membrane Types	Water source	DOC (mg/L)	Foulants Types	References
MF hollow fibre	Spring water	1.2	N/A	Lipp and Baldauf (2002)
UF hollow fibre	Spring water	0.6	N/A	Lipp and Baldauf (2002)
UF flat cushion	After underground passage	0.9-1.5		Lipp and Baldauf (2002)
UF Hollow fiber	Songhua River water	7.22	Organic/Inorganic	Tian *et al.*(2010)
UF Flat cushion	Model Solution(HA+Phenol)	4.5	HA	Mozia *et al.* (2005)
MF Flat sheet	MyoongaReservoir/ Woronora Dam	11.7/2.2	Ha, Inorganics	Fabris *et al.* (2007)
MF hollow fibre	Han River water, Korea	1.53	Organic/Inorganic	Moon *et al* (2009)
UF	Marne River	2.7	NOM	Lee *et al.* 2004
UF	Cazau lake	4.99	NOM	"
MF	La Bultiere Reservoir	6.86	NOM	"
MF	Yaffinic river	8.42	NOM	"
UF	Tomhannock Reservoir, NY	3	NOM	Taniguchi *et al.*, 2003

UV Absorbance (UVA_{254}) is an analytical tool. This has been using to characterize organic matters in water. The UV light generally produced via applying a high voltage through a gas mixture. As the UV light transmit from the source , it interacts with material and absorbs on a different level, depending upon the substance composition. UV absorbance quantifies the decrease in the amount of incident light when it passes through the water sample. UV absorbance at 254nm (A254) is a commonly used parameter to characterize the organic substances and DBP formation potential of water (Linden and Malley, 2006). Specific ultra-violet absorption (SUVA) has been widely used as an indicator of humic substance. Low SUVA value indicate non-humic (hydrophilic fraction) substance originated from polysaccharides like substances and protein and high SUVA value indicate the present of humic substance with aromatic characters (Her *et al.*, 2007, Lee *et al.* 2004, Zularisam *et al.*, 2007)

Attenuated total reflection Fourier transform Infra-Red (ATR/FTIR) is another analytical tool used for the determination of functional groups in the organic matters. It can cover the whole frequency range, typically 5000-400 cm^{-1}, and have several advantages over other spectrometric method, such as it can scan the whole spectrum within a few seconds, high resolutions, useful for small samples, and can easily subtract the spectrum of pure substance from the mixture to disclose spectrum of other components (Williams and Fleming, 1995). This technique is useful to characterize organic matter providing the individual characteristic absorption spectra of humic substance such as 3000-3400 cm^{-1} for hydroxyl, 2900 cm^{-1} for aliphatic carbon, 1725 cm^{-1} for carboxylic acids, 1600-1660 cm^{-1} for carboxylate, carbonyl or amide (Howe *et al.*, 2002). ATR-FTIR is a smart technique for studying of protein due to its non-invasive surface-sensitive technique. Protein and polysaccharide like substance are reported as major foulants, which was reported by analysing FTIR spectra in which spectral peaks were observed at 1652 cm^{-1}(C=O), at 1550 cm^{-1} (C-N) and at 1048 cm^{-1} for C-O bond from alcohol (Her *et al.*, 2007). Furthermore, it can be used to characterize the surface of membrane. Belfer *et al.* studied PES modified membrane surface and reported new absorption band in the aliphatic stretching region 2991-2875 cm^{-1}(Belfer *et al.*, 2000). However, there are several problems associated with this analysis due to the incomplete dehydration of samples such interference the spectra due to water molecule, which is observed near to 3400-1cm of OH stretching band (Belfer *et al.*, 2000). Therefore to overcome such problem, sample should be dehydrated (Meng *et al.*, 2010).

2.6 Fouling Control:

As described above, membrane fouling is the main problem and responsible for the reduction in membrane performance as well as the increase in the operating cost. Until today, many techniques have been employed to control fouling on the membranes, such as periodic backwashing, operating under critical flux, changing cross flow velocity and scouring with air bubble (Lee *et al.*, 2001, Zhang *et al.*, 2003). However, these techniques cannot fully remove the foulants, such as irreversible fouling. This can only be reduced by using chemical cleaning (Zhang *et al.*, 2011; Kimura *et al.* 2006). Some techniques employed to control fouling are briefly discussed below.

2.6.1 Pre-treatment process:

Pre-treatment such as coagulation combined with low-pressure membranes is the most effective and popular process for the removal of contaminants such as dissolved organic substances (Moon *et al.*, 2009). This process helps to reduce membrane fouling and enhances membrane performance (Fabris et al. 2007; Moon et al. 2009; Li *et al.* 2010; Humbert *et al.* 2010). It is clear that NOM concentration in feed water is the main component of foulants (Hong and Elimelech, 1997; Lin *et al.* 2000; Fan *et al.* 2001; Gary *et al.* 2007). NOM can be reduced by using pre-treatment processes and many studies suggested that reducing divalent cations in feed water also helps to alleviate fouling. Li *et al.* (2010) demonstrated the effectiveness of coagulation process on reducing fouling which depended on the dosage and found the alleviation of fouling with alum dosage in series of 1 to 4 mg/L. However, a high alum dosage (8 mg/L) could have a negative effect on membrane performance. These pre-treatment processes are commonly used in water treatment systems due to the enhancement in the removal of aquatic contaminants, such as micro-pollutants as well as disinfectants by-products (DBP) and decline in membrane fouling (Haung et al 2009; Li *et al.,* 2010). Adsorbent particles such as powder activated carbon (PAC), heated iron oxide particles (HIOP) and SiO_2 show significant benefits in the removal of NOM and reduction of fouling. However, effect of those substances highly depend on the structure of cake layer and its interaction with both NOM and membrane surface (Zhang *et al.*, 2003).

2.6.2 Surface modification:

Membrane surface modification is another way to control the membrane fouling. The membrane fouling is affected by the tendency of membrane materials to adsorb contaminants of the feed water more easily than other solutions. Several methods such as photo initiated graft polymerization, interfacial polymerization, chemical and low-temperature plasma (Kilduff *et al.*, 2000; Hilal *et al.*, 2003, 2004) are used for membrane surface modification with a significant reduction in fouling. The surface modification of membranes is an attractive approach for changing surface properties of the membrane without altering its pore structures in a selective way. Photo-induced grafting has many features, such as mild reaction conditions, selectivity to absorb UV light without affecting the bulk polymer, permanent change of membrane surface with an easy control of chemistry, and includes low cost of operation (Ma *et al.*, 2000). Surface modification with back pulsing is an effective method to reduce fouling at a low concentration. Photo-induced graft polymerisation method can easily achieve desired characteristics like hydrophobicity and ionic charges. Studies showed that due to the deposition, the flux with and without combination of back pulsing were less dependent on the surface chemistry. The effectiveness of surface modification to reduce membrane fouling with back pulsing was observed with increasing *E. coli* concentration (Ma *et al.*, 2000).

2.6.3 Chemical Cleaning:

Irreversible or reversible foulants can be removed from the membrane surface or inside the membrane matrix by physical methods for example backwashing, air scouring, and chemical agents treatment for example acids, bases, oxidants, adsorbents and biochemical enzymes. Many researchers studied various membrane cleaning methods to enhance the membrane performance (Ang *et al.*, 2006; Yamamura *et al.*, 2007; Zondervan and Roffel, 2007; Porcelli and Judd, 2010; Puspitasari *et al.*, 2010; Tian *et al.*, 2010). However, due to the lack of complete knowledge of interaction between contaminants and membrane materials, undesired materials remain on/in the membranes and reduce membrane performance as well as its life span. Various types of cleaning substances are commercially obtainable. Due to their availability, cost and their efficiency in removing foulants on /in the membranes surfaces reagents, such as sodium hydroxide, hydrochloric acid, nitric acid, citric acid, EDTA, SDS, sodium hypochlorite (Lee *et al.*, 2001; Liikanen *et al.*, 2002; Zondervan and Roffel, 2007) are generally used. The cleaning efficiency of various chemical agents depends upon the membrane materials such as PAN, PVDF, PVC (Kimura et al, 2004; 2006), operating conditions, and source water composition (Ang et al, 2006).

Liikanen *et al.* (2002) studied the cleaning efficiency of several cleaning agents on NF membrane. In his study, chemical cleaning solutions such as Citric acid, NaOH, HCl, Oxalic acid, Na_4EDTA, $Na_2S_2O_4$ were used. During the cleaning experiment, they compared acidic cleaning and alkaline cleaning efficiencies. Alkaline cleaning was found better compared to acidic cleaning. The alkaline chelating agent Na_4EDTA with NaOH was more effective than NaOH alone, which showed better membrane permeability probably by making complexes with the membrane materials. This made the membrane more open and permeable. NOM complexes were the main foulants and suggested that alkaline chelating cleaning agents were more effective, but acidic cleaning was regularly needed to remove inorganic precipitants (Liikanen et al, 2002).

Kimura *et al.* (2004) performed the analysis of irreversible fouling caused by the surface water. Low-pressure hydrophobic UF membrane made by polysulfone of MWCO 75,000 Da was employed for the filtration process. The number of cleaning agents such as NaOH (pH 12), NaClO, EDTA, HCl (pH 2) and oxalic acid (pH 2) were used to desorb the foulants. Analytical methods such as adsorptive fractionation method, fluorescence excitation emission matrix (EEM) and FTIR were employed to characterize the organic fraction that caused the irreversible fouling. The obtained SUVA values give an indication of the fraction of organic matter. Lower SUVA value demonstrated a relatively hydrophilic fraction and protein and/or polysaccharides were responsible for irreversible membrane fouling (Kimura *et al.*,2004).

The similar fraction of NOM (hydrophilic likely protein/or polysaccharides) were responsible for fouling (Kimura et al, 2006). During their study, five different types of MF/UF were made by polyacrylonitrile (PAN), polyvinylidenefluoride (PVDF) membranes, and four different types of organic matter from different origin were collected. They found that the fouling on PVDF membrane was significant than on PAN membranes. The characterization of the NOM was carried out using TOC analyser, SUVA, hydrophilic/hydrophobic fractionation and EEM. However, these techniques are inadequate for the forecast of the level of irreversible fouling. They also reported that hydrophilic fraction of NOM was accountable for the fouling, despite the membrane type and organic matter. On the other hand, different membrane materials have different fouling compositions. The cleaning efficiency of agents differ with respect to the condition applied during the process such as types of cleaning agents, cleaning solution pH, dose, time, cross-flow velocity and solution temperature (Ang *et al.*, 2006). Therefore, it is important to run fouling experiments and cleaning experiments at the same conditions with respect to feed solution chemistry and operating conditions. The chemical reactions of cleaning reagents with deposited foulants and mass transfer phenomenon are important in membrane cleaning. Elevation of temperature from 20^0 to 40^0 C enhanced the cleaning efficiency significantly due to alteration of mass transfer of the foulants from the fouling layer to the bulk solution (Ang *et al.* 2006).

Sodium hypochlorite is generally used to clean membrane due to its several benefit such as effectiveness, easily available, cheap, and it also produces free chlorine in the water. Chlorination generally implied for the drinking water disinfection. It is capable of killing microbes for broad categories such as bacteria, viruses and protozoa. The disinfection efficacy of chlorine depends upon microbial characteristics, specific species, strain etc. (Havelaar, A. H. & Melse, J. M., 2003). The doses of chlorine required to disinfect water are shown as in Table 2-10. However, a high amount of sodium hypochlorite is responsible for membrane degradation and ageing; and become weak due to change in physical properties such as tensile strength, and young module. (Arkhangelsky *et al.*, 2007; Puspitasarei,*et al.*, 2010). Table 2-11 is a summary of dedicated studies to clean membrane using various chemical reagents.

Table 2-10: Dose of chlorine used to remove various microbial (World Health Organization, 2008)

Microbial Types	Chlorine Dose and condition
Bacteria	0.08 mg. min/L at 1-2°C at pH 7
	3.33 mg. min/L at 1-2^{0}C at pH 8.5
Viruses	12 mg. min/L at 0-5^{0}C
	8mg.min/L at 10^{0}C at pH 7-7.5
Protozoa	*Giardia:* 230 mg. min/L at 0.5 0C
	100 mg. min/L at 10 0C
	41 mg. min/L at 25 0C all at pH 7-7.5
	Cryptosporidium not killed.

Table 2-11: Summary of cleaning studies on various membrane filtration materials by different researchers

Membrane	Cleaning agents	Reference
NF(Aromatic polyamide)	NaOH(0.1M); Na2 EDTA (10e-3M)	Hong and Elimelech,1997
UF(PES)	NaOH (0.1M); Citric Acid (0.1M); SDS (0.001M)	Lee *et al.*, 2001.
NF(Spiral wound)	NaOH (0.06%); Citric Acid (1.6%); HCl (0.3%); Oxalic Acid (0.1%); Na_4EDTA (0.2%)	Liikanen *et al.*, 2002
UF(PS-HPO)	NaOH(0.01M); NaClO (500mg/L); HCl (0.3%); Oxalic Acid(pH2); EDTA (20mM)	Kimura *et al.*, 2004
RO	NaOH(pH11); SDS(2M); Na2EDTA(0.5mM)	Ang *et al.*, 2006
MF(PE+PVDF); UF(PAN)	NaOH(pH12); NaClO (700mg/L); HCl (pH12); EDTA (20mM)	Yamamura *et al.*, 2007
UF	NaOH (1-2%); HCl (1-3%); H_2SO_4 (pH2-4); Citric Acid (0.6- 7.5 g/L); H_2O_2 (0.5-1.5%)	Porcelli and Judd, 2010
Flat Sheet(PVDF)	NaClO (1%)	Puspitasari *et al.*, 2010
Hollow Fiber(PVC)	NaOH(1%); Citric Acid(2%); Ethanol	Tian *et al.*, 2010
UF (PVC)	NaOH (500mg/L); NaClO (100mg/L); HCl (500mg/L); EDTA (150mg/L)	Zhang *et al.*, 2011
MF (PVDF)	NaOH (0.3%, pH12), NaClO (0.1-0.3%), Citric Acid (1-2%), Oxalic acid (1%)	Moon *et al.*, 2009

2.6.4 Hydrodynamic Conditions:

Several researchers revealed that hydrodynamic conditions play an important role in controlling fouling. In recent years, studies were focused on controlling of fouling using various rates of aeration and backwashing. Water backwashing, gas backwashing, cross flushing were also studied for their effectiveness to reduce membrane fouling and reported that the permeate volumes after filtration were approximately doubled with backpulsing compared with no backpulsing. Furthermore, the result demonstrated that the recovered flux of a membrane fouled with backpulsing after long backwashing was less than that of without backpulsing, which indicated that internal fouling was major fouling mechanism, and combination with surface modification showed promising results on reducing both adhesive and non-adhesive fouling (Ma et al, 2001). The fouling could be reduced by using various sizes of air bubbles and it was reported that fouling control was remarkably enhanced by using smaller nozzle with smaller bubbles (Fane *et al*, 2005). A contradictory result was suggested that larger bubbles were found more efficient than smaller bubbles due to the induction of a slower circulation velocity by smaller bubbles (Prieske *et al.*,2008). It also revealed that airflow rate and increment on fouling reduction were proportional to a certain value and after that value no further raise was found (Ndinisa et al, 2006). Furthermore, the cleaning efficiency of chemical agents influenced by the cross flow velocity. It was reported that, a higher cross-flow velocity with combination of longer cleaning time had a higher cleaning efficiency. However, this efficiency was negligible for a high ionic strength cleaning (Lee et al, 2001). Lee *et al.* (2001) concluded that, increasing cross-flow velocity and cleaning time enhanced the cleaning effectiveness. Yet, this effect was negligible for a high ionic strength cleaning (Lee *et al.*, 2001). In addition to this, a study performed by Ang et. al., 2006 on different cross flow velocities with different concentrations of cleaning agents (EDTA) showed various cleaning efficiency. Although the cross flow velocity resulted in an increased in the shear rate, the extent of rate of mass transfer is dependent upon the cross velocity rate as well as the chemical concentration (Ang *et al.*, 2006). The system configuration together with hydrodynamic conditions also affect the membrane fouling. A study performed by Berube and Lei (2006) investigated the contribution of single-phase (water only) and dual-phase (with air sparging) cross-flow using single and multi fibers membrane modules on permeate flux. The outcome of their study was that the dual-phase cross flow was more efficient on enhancing membrane flux than single-phase. Moreover, multi fibers membrane module for dual-phase cross-flow system was able to enhance permeate flux by mechanically peeling off foulants from membrane surface due to a physical contact between the membrane fibers (Berube and Lei, 2006).

Table 2-12: Summary of various studies on hydrodynamic conditions

Membrane filter	foulants	scale	Hydrodynamic conditions	Reference
UF(PES)	NOM	Bench	(8.6 , 17.2) m/s	Lee *et al.*, 2001
MF(PP)	Organic		Back pulsing (0.05-0.3)s	Ma *et al.*, 2001
Hollow fibers			Gas flow(0.0001-1)l/min, gas bubbles	Fane *et al.*, 2005
Hollow Fibers PVDF		Bench	Bulk cross flow(0, 0.2, 0.3, 0.4)m/s	Berube & Lei, 2006
Flat sheet MF	Organic	Lab	Air flow (2, 4, 6, 8) l/min	Ndiniso et al, 2006
TFC RO	Organic	Lab	(10.7, 21.4, 42.8)cm/s	Ang *et al.*,2006
Flat sheet			(0.6, 3.45) m^3/h	Prieska *et al.*, 2008

2.7 Future Direction:

Analytical methods such as specific ultra-violet adsorption (SUVA), XAD fractionation and excitation-emission matrix (EEM) represent common properties of organic matter, which are insufficient analysing the fouling properties (Kimura *et al.*, 2006). Therefore, further research is necessary to develop analytical techniques that can be able to explain the specific property of organic matters. Furthermore, no single analytical techniques is complete to diagnose foulants on the membrane surface, more in-depth analysis is necessary to obtain characteristics of foulants.

The mechanisms of fouling of various foulants on different types of membranes materials are different. Generally, the removal rates of UF membrane are higher than the MF membrane due to their smaller pore size. However, the aluminium concentration on UF membrane made by PAN is higher than MF membrane made by PE and PVDF, which necessitates further studies for demonstrating the mechanism.

Biofouling is another type of fouling and is harder to control by reducing the numbers of microorganisms. This activity initiates the irreversible linkage of one or more bacteria forming bio-film on the membrane surface. An effective method to control the growth of microorganisms is accomplished by injecting continuous and high concentration of chlorine. However, due to the stricter regulation of discharge of chlorine into the surface water, this method is not always appropriate. Therefore, a suitable efficient method is necessary to produce antimicrobial membrane surface by modifying commercially available membranes

The rate of membrane fouling is found different in different foulants and membrane materials (Yamamura *et al.*, 2007; Yamato *et al.*, 2006). It was demonstrated that the foulants characteristics play important role in membrane fouling. However, still it is not clear what the role of various membrane materials is on the rate of membrane fouling. Hence, it is necessary to clarify the role of various membrane materials on the rate of membrane fouling.

Research must be based on an in-depth understanding of principles of low-pressure membrane filtration and should able to distinguish differences between available membrane filtration to present novel insights into the method of membrane fouling. Research is needed to differentiate membrane fouling of each membrane filtration and compare their findings.

It is also necessary to identify the particular foulants and know about its reaction with contaminants and membrane surface. For a broad use, assessment must be done incorporating the performance of low-pressure membranes with impurities removal, and the control of foulants through modification of membrane. It seems that fundamental analysis is still needed on the interaction of natural organic matters with inorganic precipitation, co-precipitation of inorganic and natural organics, and precipitation of calcium-organic complexes. In addition, the process conditions should be optimized to obtain the best performance.

Previous studies suggested that attachment between NOM, inorganic particles, other contaminants and membrane is the primary reason for irreversible membrane fouling, which should be identified as the priority in the research, design and operation of membrane systems.

Temperature causes various physical and chemical changes to water and the membrane. Viscosity, solubility of organic and inorganic substances, the growth of microorganisms vary with water temperature. Surface morphology and pore size of membranes could also change with temperature. These affect the efficiency of membrane filtration process. Thus, study of the effect of temperature on membrane performance and fouling potential, and membrane surface and its physical properties are all important.

CHAPTER 3: MATERIALS AND METHODS

3.1 Chemicals and Membrane

Sodium hypochlorite solution 12% w/w free available chlorine, Citric acid (50%, w/w) supplied by FloChem Ltd, and phosphoric acid 75% w/w supplied by Univar Canada Ltd were used in this research. Unless stated otherwise, the water used in the experiments was distilled water (DW). The membranes studied in this project were UF hollow fiber membrane and were made from polyvinylidene fluoride (PVDF). Membrane modules from different years were used (used in a full scale plant) and membrane fibers were harvested for various analyses, while virgin membranes were harvested from a new membrane module.

3.2 Pilot plant treatment system:

This study was performed in a pilot scale plant at Bare Point water treatment plant in the City of Thunder Bay, Ontario. The particular system named ZeeWeed®1000 was obtained from GE Water and Process Technologies, Ontario, Canada. A photograph of the typical equipment was used in a pilot set-up is shown in Figure 3-1.

Figure 3-1:Typical ZeeWeed®1000 ultrafiltration pilot system

The pilot plant, a scale down version of a full scale treatment plant, consists of single module Polyvinylidene fluoride (PVDF) ultrafiltration membrane fibers connected to a permeate collection header, which is operated under a negative pressure at constant flux mode. The characteristics of the membrane module are given in Table 3-1 and the operational parameters and conditions of the plant are given in Table 3-2. The process flow sheet of the plant is given in Figure 3-2.

Table 3-1: ZeeWeed®1000 Membrane module characteristics as provided in the manual

Size of module used in study	0.691m×0.683m×0.104 m (L×H×W)[a,b]
Configuration	Outside-in hollow fiber
Nominal membrane area	46.45 m^2
Nominal membrane pore size	0.02 µm
Membrane material	PVDF (Polyvinylidene Fluoride)
Membrane surface properties	Hydrophilic
Typical operating TMP	-0.068 to -0.896 bar (-1 to -13 psi)
Maximum operating temperature	35^0C (95^0F)

Note: (a) Four years old membrane module from a full scale water treatment plant for sodium hypochlorite optimization experiment. (b)Two years old membrane module for rest of other experiments.

Table 3-2: Pilot plant operational parameters and conditions.

Parameter	**Value**
Production cycle time	20 min[a]/120 min[b]
Permeate flow rate	0.6 L/s
Pre backwash aeration duration	15 sec
Back wash duration	15 sec
Back pulse flow rate	0.95 L/sec
Clean type	Soak
Chemical type	Sodium hypochlorite, citric acid
Clean water back wash duration	15 sec
Sub-level 1 aeration time	15 sec
Sub- level 2 aeration time	15 sec
Soak duration	180 minutes
Membrane total area	46.45 m^2

Note: (a) Sodium hypochlorite optimization. (b) Citric Acid at pH 2.2 and 3.0

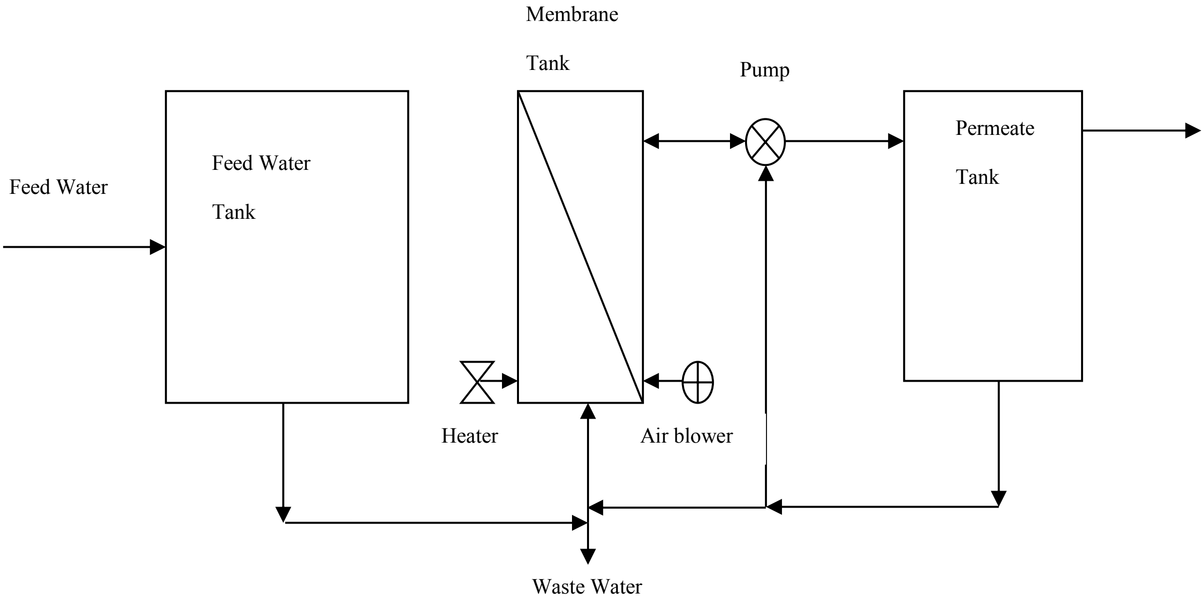


Figure 3-2: Simple schematic representation of ZeeWeed$^{®}$1000 pilot process

The pilot plant was operated in a constant flux/variable TMP and batch (tank-drain) mode in which, multi-step processes were involved, such as fresh feed water being continuously maintained at a constant level. Dead-end infiltration of feed water enclosed the membrane within the membrane tank. The programmable logic controller (PLC) controlled the pilot plant furnished with many pumps, transmitters, pressure gauges, turbidity meters, flow meters, chemical feed systems, water sample taps, and automatic operation valves among other parameter gauges. Data was logged on 5 second intervals to enable data analysis and performance assessment. A touch screen user system was allowed for the outline of operating parameters and pilot plant status observation. The feed water was supplied directly from the pumping station of the full scale plant to the feed tank of the pilot plant. The feed water level was continuously maintained by the use of an automatic valve. Generally, the pilot plant operation cycle sequence involved forward filtration, back wash, aeration, and maintenance cleaning modes. The permeate cycle can be set according to the experimental design. After the permeation cycle, aeration began from the bottom of the tank to scour the membrane fibers during backwash (reversal of permeate flow) for 15 seconds. The aim of the backwash is to wipe out deposition within the pores and on the membrane surface by forced flow. The aeration then continued until the tank was completely drained. The membrane tank was re-filled and permeation started again. Permeation was continued until the system reached a TMP range of particular value according to the experimental design.

Feed water from the Lake Superior was supplied via a pump directly from the full scale pumping station. The characteristics of feed water are presented as in Table 3-3.

Table 3-3: Feed water characteristics

Parameters	Values
Conductivity(μS/cm)	101.8 - 106.7
Turbidity (NTU)	1.13 – 7.37
pH	7.32 - 8.34
Al(mg/L)	0.16-0.47
Ca(mg/L)	11.33-14.34
Fe (mg/L)	0.0001-0.044
K(mg/L)	0.5246-0.6456
Mg(mg/L)	2.422-3.073
Na(mg/L)	1.971- 2.282
Si(mg/L)	1.102-1.301
TOC(mg/L)	1.37-1.98

From various literature reviews, sodium hypochlorite has been developed as an efficient chemical cleaning agent. However, degradation in membranes' physical properties (tensile strength) and modification of chemical properties (functional group) have been reported due to the higher concentration of sodium hypochlorite. Therefore, cleaning efficiency of various concentrations of sodium hypochlorite at different soak times was evaluated in term of **dose.** Dose is expressed as a product of concentration (C) and the soak time (t), **(concentration(C) × soak time (t))** in unit of mg.hr/L (Gitis *et al.* 2006;

Arkhagelsky *et al.* 2007 ; Lozier *et al.* 2008). This dose concept is also applied to disinfect water (WHO, 2008). Based on these concepts, different sodium hypochlorite (NaClO) concentrations and soak times were selected and cleaning efficiency of various NaClO concentrations and soak times evaluated. Each NaClO clean was conducted when TMP value reached 70±3 kPa. Membrane fibers are harvested before and after each cleaning of sodium hypochlorite for analysis of organic, inorganic (metals) foulants, and surface morphology analysis. Due to problems with permeate collection socket from (14/11/2011 to 18/11/2011), membrane fibers were not harvested for that time span.

This study was performed under ambient condition. Due to unavailability of the heating system in the pilot plant, feed water temperature could not be controlled. Therefore, permeability was corrected at 20^0C to account for temperature variation. According to Zenon (2006), the formula used to calculate permeability at 20^0C is provided in Equation (2):

$$\textit{Permeability at } 20^0C = \textit{Permeability at } T^0C \times (1.025)^{(20-T)} \text{ ------------ } (2)$$

3.3 Membrane Characterization

3.3.1 Permeability, SEM, Tensile strength and ATR-FTIR

Membrane permeability data post CIP from three years of operation was obtained from the plant's operational database. The membrane permeability is defined as follows:

$$Lp = \frac{Jw}{\Delta P} = \frac{F_p}{S \times \Delta P} \qquad \text{---------------------------}(3)$$

Where, Lp is membrane permeability (L. m^{-2}. h^{-1}.bar^{-1}), Jw is the flux (L.m^{-2}.h^{-1}). The unit of flux some time also expressed as LMH, ΔP is the trans-membrane pressure driving force (bar), F_p is permeate flow rate (L/hr.), and S is effective membrane surface area (m^2). The results have been corrected to 20 °C according the equation from membrane supplier.

The surface morphology of membrane samples were studied by using Scanning Electron Microscope (SEM), Hitachi SU70 Analytical FE-SEM with Oxford Aztec SDD Premium EDX detector (124ev) and Gatan MiniCL Imaging system. Membrane fibers were cut into small pieces of about 2 cm long and freeze dried to remove the moisture from the membrane and then kept into a small air tight glass sample vial and stored in a desiccator to avoid absorbing moisture on /in the membranes until they were coated by gold.

The mechanical property of the hollow fiber membranes was evaluated by measuring tensile strength. Tests were conducted with a Dual-Range Force Sensor (A.U. Physics Enterprises, MI, USA) with a setting range of ±10 N under room temperature (~23 ℃).The sample hollow fiber was first cut into a 10 cm length and knotted onto the hook of the sensor. The initial gauge length was around 5cm and the hand pulling speed was approximately 0.5cm/sec. The tensile strength at break of the hollow fiber membranes were recorded by a Data-Collection Software (Logger Pro 3, Vernier Software & Technology). Each sample was repeated at least three times and the average value was reported.

The One-Way Analysis of Variance (ANOVA) was performed to determine the statistical significance of the experiment results by the help of Microsoft excel (2010). Significance differences were considered at a 95% confidence interval ($p< 0.05$).

The surface chemical compositions of hollow fiber membranes were characterized by attenuated total reflection (ATR)-Fourier transform infrared (FTIR) spectroscopy. FTIR-ATR measurements were conducted by a TENSOR Series FTIR Spectrometers (Bruker Tensor 37, Bruker Optic GmbH, Germany) instrument equipped with an ATR sampling accessory (PIKE MIRacle™, PIKE Technologies, WI, USA). Each spectrum was performed 32 scans at a resolution of 4 cm^{-1} with subtracting the appropriate background. Hollow fiber samples were air dried overnight before scanning by the ATR-FTIR instrument. Each sample was scanned five times and the average value was reported.

3.4 Foulants Analysis:

a) Organic Foulants

(I) DOC analysis:

Membrane samples of different ages were selected namely- virgin, 2 years, and 3 years old to measure the organics attached on the membrane surface. The samples were then cut to a fiber of 10 cm in length. A duplicate was also prepared using the same method. The Skalar method 311-000 (Skalar Analytical B.V.) was applied to detect the amount of organics attached on the membrane surface. In brief, the dissolved organic carbon (DOC) was extracted from the membrane samples by using 25 mL of 0.2 M H_2SO_4. The extracted DOC was then measured using a segmented flow analyzer with persulfate-UV-colorimetric method.

(II) TOC analysis:

Total organic carbon was analyzed using Sievers 5310 C Laboratory and portable Total Organic Carbon Analyzers provided by GE Power and Water, Water and Process Technologies, USA.

TOC analyzer was verified using self-made standard glucose solution. The Dextrose Anhydrous Powder supplied by Avantor performance Materials Inc., USA, was used. The plot between Measured TOC values versus theoretical TOC values is shown in Figure 3-3.

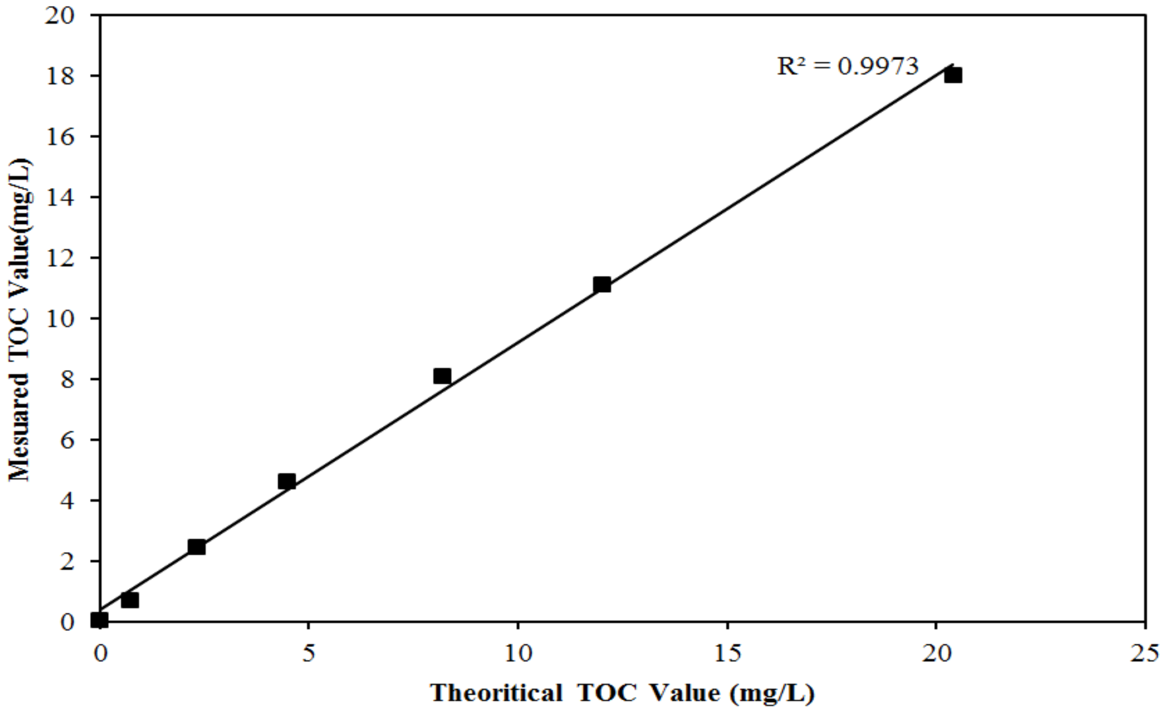


Figure 3-3: Theoretical TOC value and measured TOC value.

TOC from the membrane surface was extracted by sonication method. This method has been used in various studies (Lozier *et al.*, 2008). However, the sonication time varied from one to another in different studies. Therefore, the maximum sonication time was selected according to the experiment performed below. A single membrane fiber was taken and its length was measured. The fiber was then cut into small pieces approximately 5 cm long and immersed into a 300 ml of sodium hydroxide (NaOH) solution of pH 10.00 ±0.05 into a beaker before starting sonication. Sonication was started and about 30 ml sample was taken at a certain interval of sonication. Then, TOC was analyzed for each sample.

Two experiments were performed and extract sample was taken at various time interval as shown in Figure 8 and its TOC was measured. The plot between organic extract from the membrane surface and sonication time is as shown in Figure 3-4. According to Figure 8, the extract amount was increased with an increase in sonication time. From the result of experiment 1, it was noticed that TOC extract was increased with increasing sonication time. No distinct peak was obtained during 180 minutes. It was suspected that the membrane fiber was degraded and contributed to the TOC amount due to longer time interval of sampling. Therefore, second experiment was repeated with another fiber by reducing sampling time interval up to 90 minutes sonication time. The extract TOC amount versus sonication time was plotted; the curve was obtained as in Figure 3-4 experiment 2. The curve of experiment 2 clearly showed two distinct peaks, it was suspected that the first peak was due to the contribution of organic foulants on/in the membrane and second peak at 50 minutes time frame was due to membrane degradation, resulting in higher TOC values. Therefore, the first peak at 30 minutes was selected for sonication time to all membrane samples during TOC analysis in this study.

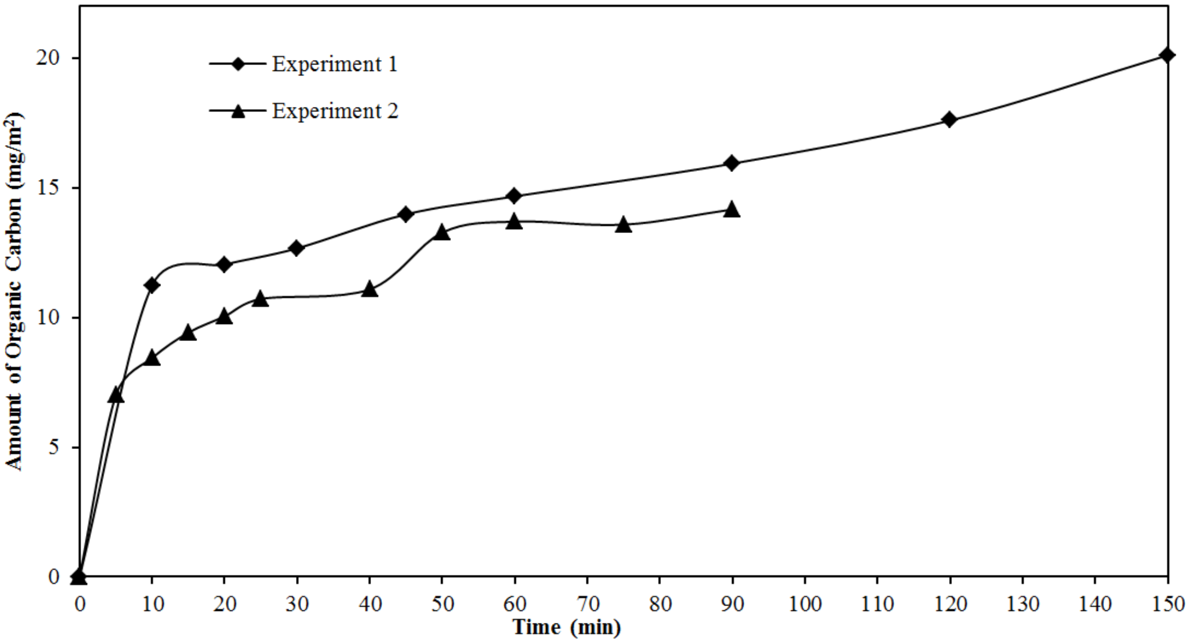


Figure 3-4: Sonication time and amount of organic carbon extracted from membrane surface.

b) Inorganic Foulants

Inorganic foulants (mainly metal ions) were analyzed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), Varian Vista Pro CCD Simultaneous ICP-OES, CETAC ASX-510 Auto Sampler, situated at the Lakehead University Instrumentation Laboratory. Membrane fiber length was measured and cut into small pieces of length approximately 0.5cm in a ceramic crucible and burned into a muffle furnace at 550^0C for two hours. Then samples were taken out from furnace and cooled down to room temperature. Residue in the crucible was digested adding 0.5 ml of concentrated hydrochloric acid (HCl) and diluted to make 10 ml solution. The diluted acidic digested solution was further filtered by filter paper before it was measured by ICP-AES instrument. The blank sample (i.e., without hollow fiber) was also prepared by the same procedure and analyzed by ICP-AES instrument.

3.5 Simulated Chemical Cleaning Study

In membrane water treatment plants, chemical clean-in-place (CIP) is routinely performed to recover membrane flux. In order to characterize the effect of CIP chemicals on membrane properties, a simulation study was employed in a lab scale. A typical CIP strategy for organic and inorganic fouling removal was chosen for the simulation study. The study simulated a 6 hours CIP using a sodium hypochlorite solution containing 500 mg/L free available chlorine each month and a 5 hours CIP using a 200 mg/L citric acid every two months for a total simulated exposure of 36 months (3 years). Membranes were harvested from a new membrane module and were cut into 10 cm lengths. Four treatment series were created; the membranes were immersed in (1) tap water for 216 hours, (2) sodium hypochlorite for 216 hours, (3) citric acid for 90 hours and (4) sodium hypochlorite for 216 hours and citric acid for 90 hours solutions simulating the exposure time to chemicals of the simulated CIP strategy. Membranes after an equivalent exposure to an annual CIP schedule were characterized by tensile strength and ATR-FTIR technique to examine the change of membrane properties.

CHAPTER 4: RESULT AND DISCUSSION

4.1. Effect of Membrane Age and Chemical Cleaning on Membrane Properties and Performance.

4.1.1 Membrane performance

The membrane permeability over three years of operation is shown in Figure 4-1. Two regions of permeability variation were observed as follows: (1) during the first year's and followed 8 months of operation, the permeability decreased gradually first and could be restored properly by thorough chemical cleaning; (2) in the latest 12 months of operation, the permeability dropped gradually initially and no significant permeability decline occurred, while the permeability did not recover even by thorough chemical cleaning. The initial membrane permeability was approximately 184.5 $L.m^{-2}.h^{-1}.bar^{-1}$ and decreased to 120.5 $L.m^{-2}.h^{-1}.bar^{-1}$ over two and half years of operation, a permeability loss of approximately 35%. The permeability decrease with extended operating time is a general phenomenon (Hofman *et al.*, 1998, Choi *et al.*, 2005). Although the chemical cleaning has recovered some of permeability caused by reversible fouling, irreversible fouling has been occurring after long term operation (Weber and Knauf, 1998).

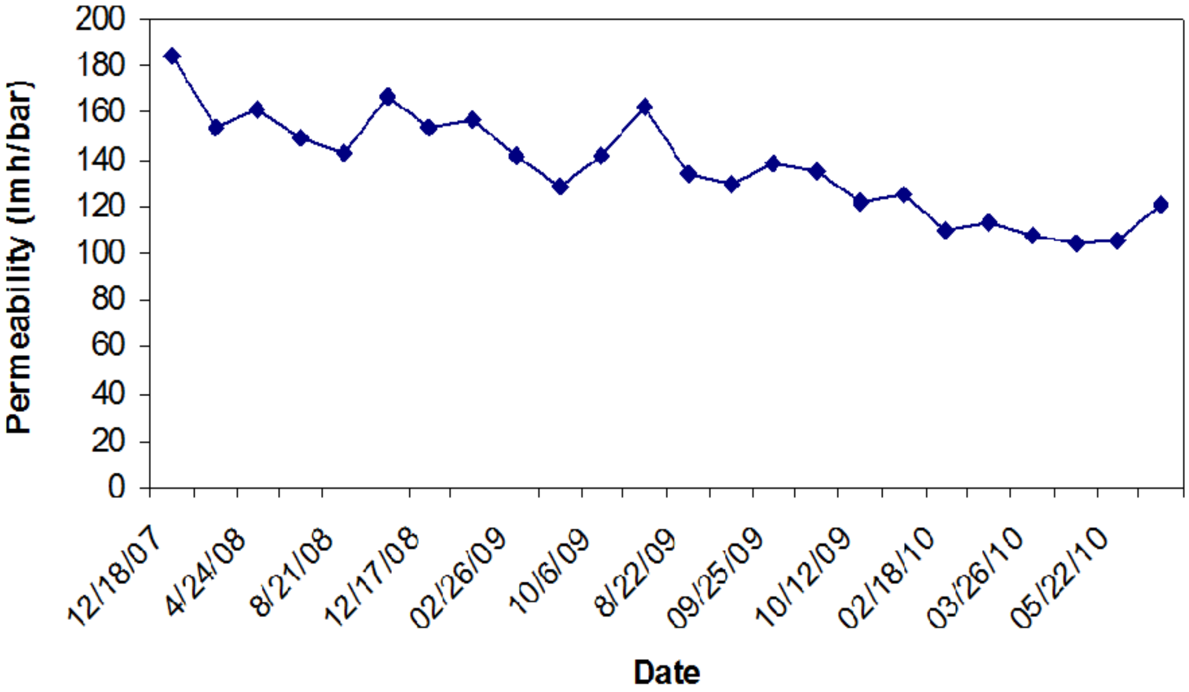
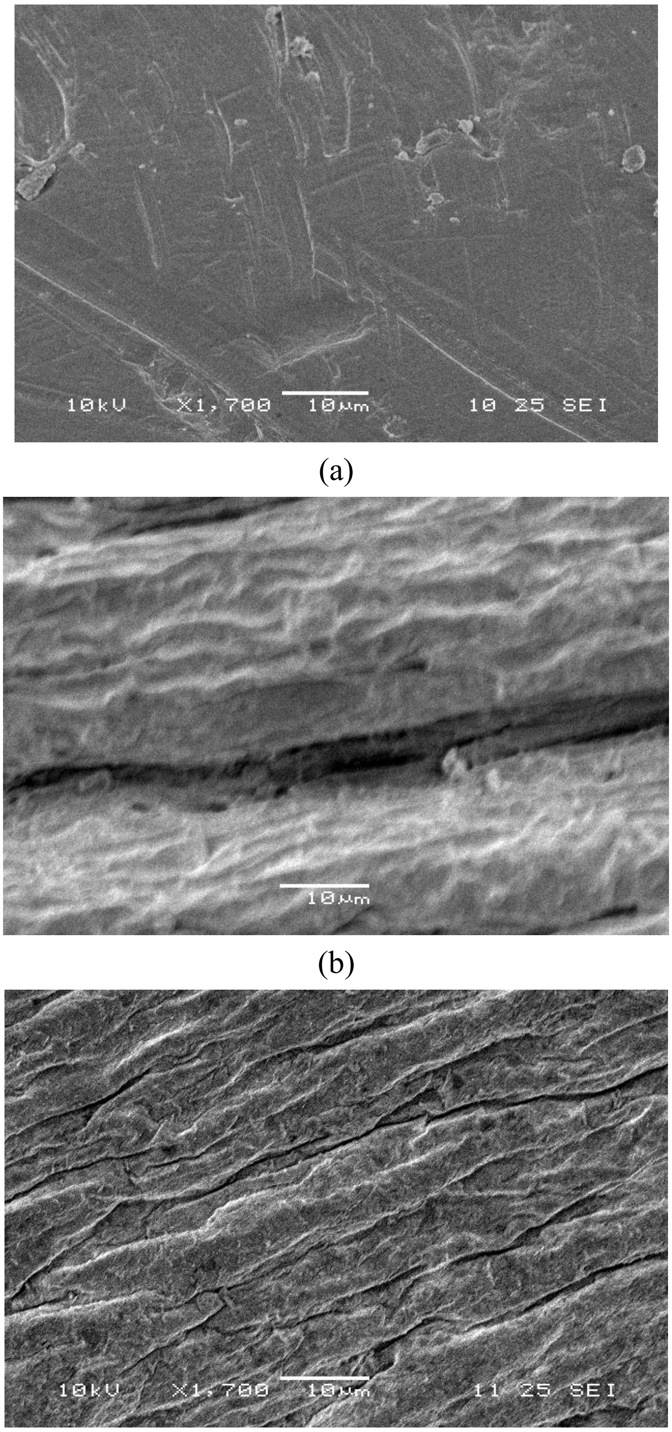


Figure 4-1: Permeability change with age of membrane

4.1.2 Membrane Properties

a) Morphology

SEM photographs of virgin and fouled membranes of various ages (Figures 4-2: a, b and c) revealed a significant difference in their surfaces. As shown in Figure 4-2, the virgin membrane surface was very smooth. However, with a longer operational time, the fiber's surface degrades and appears to become rough as shown in Figure 4-2 c. The degradation could be caused by various factors, such as chemical cleaning and the mechanical stress of daily operation. The surface of the fiber in operation for 2 years appears to have a surface roughness between the virgin and the 3 years old membrane.



(a)

(b)

(c)

Figure 4-2: SEM photograph of different years' membrane at 1700× magnification: (a) virgin, (b) 2 years and (c) 3 years

b) Tensile strength

Tensile strength is typically used to evaluate the mechanical property of a membrane. The impact of fouling on the mechanical properties is still largely debated though it could be deduced that the mechanical properties of a membrane would change due to backwashing and cleaning which is done in order to remove fouling from the surface of a membrane. Due to these operations, the used membrane may lose its mechanical strength and become more brittle, reducing the life of the membrane or affecting the polymer chain, which may have an impact on the pore size such as change in pore size (Nghiem and Schafer, 2006). The tensile strength of different accumulated operating times (expressed in years) of hollow fiber membranes are shown in Figure 4-3.

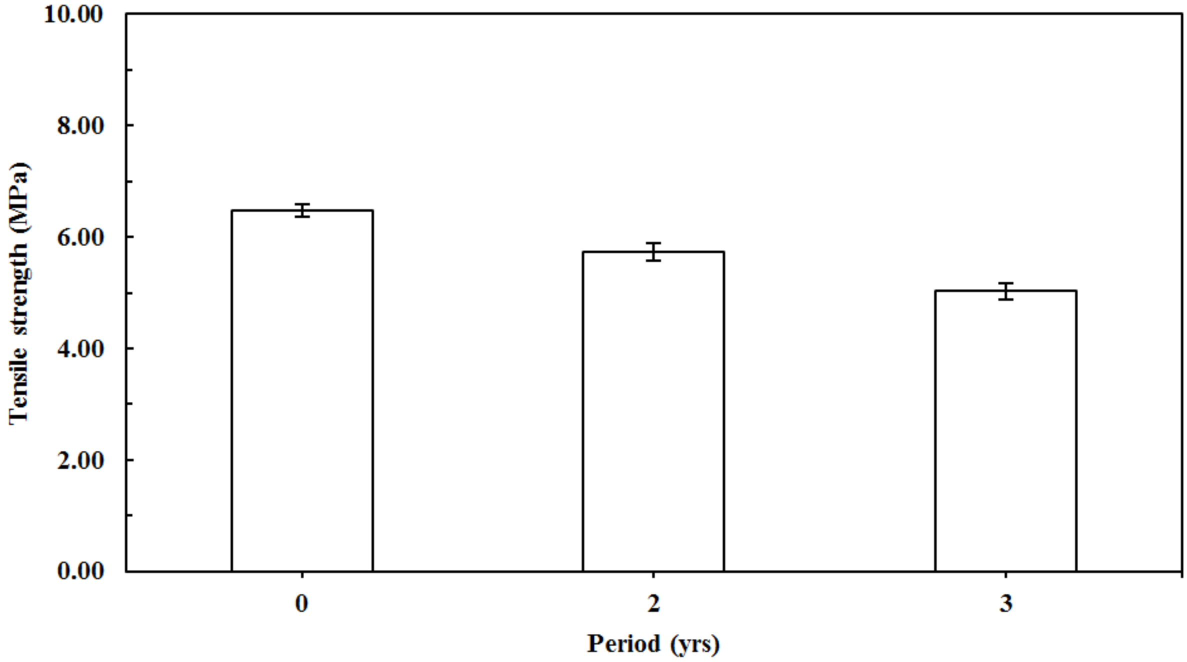


Figure 4-3: Tensile strength of different years' membrane from the full-scale plant

As shown in Figure 4-3, the tensile strength of the PVDF membrane decreases with operational time (ANOVA, $p<0.05$). This suggests that the mechanical property of membrane deteriorated with increasing operating time, which was likely due to the daily operation (suction and backwash) and chemical cleaning. This trend is in agreement with the literature (Nghiem and Schafer, 2006).

c) ATR-FTIR spectroscopy

ATR-FTIR is a convenient and effective approach to characterize the membrane surface chemistry by the determination of molecular structure and organization of membranes (Zavastin *et al.*, 2010). ATR-FTIR spectroscopy was conducted on the virgin, 2 yrs. and 3 yrs. membrane fibers in order to detect the chemical property of membrane surface. The results are shown in Figure 4-4 and the respective peaks at various wavelengths are shown in Table 4-1.

Compared with the spectrum of the original one, no other new peaks appearing or disappearing in the spectra of used membranes was observed. It is clear that the intensity of the peaks of original membrane is much higher than that of used membrane. Moreover, it can also be found that the relative intensity of all the representative peaks changed simultaneously. These are consistent with the investigation conducted by Wang *et al.* (2010) indicating that a partial scission of the PVDF functional group polymer occurred.

Table 4-1: Identification of the main peaks from FTIR spectrum.

Peak value (cm^{-1})	Type of vibration	References
841	CH_2 rocking	Puspasari *et al.*, 2010
1070	CH_2 wagging	Puspasari *et al.*, 2010
881, 1177, 1404	CH out of plane deformation	Wang *et al.*, 2010
1234, 1275	PVDF fingerprint	Boccaccio *et al.*, 2002 Boributh *et al.*, 2009.
1753	Carbonyl peak	Puspasari *et al.*, 2010

The identification of the main chemical groups detected in Figure 4-4, some of them being spectrum specifically characterizing PVDF material. Peak at 841 cm^{-1} represents CH_2 rocking and peak at 1070 cm^{-1} result from CH_2 wagging (Puspitasari *et al.*, 2010). The peaks of 881, 1177 and 1404cm^{-1} exhibit CH out of plane deformation vibrations (Wang *et al.* 2010). The absorption peaks at 1234 (Boccaccio *et al.*, 2002) and 1275 cm^{-1} (Boributh *et al.*,

2009) are the typical characteristic of PVDF. Peak at 1753 cm^{-1} characterizes the carbonyl group (C=O), which could generate from as additive, i.e. polyvinylpyrrolidone (PVP) has been found to increase membrane hydrophilicity (Puspitasari *et al.*, 2010).

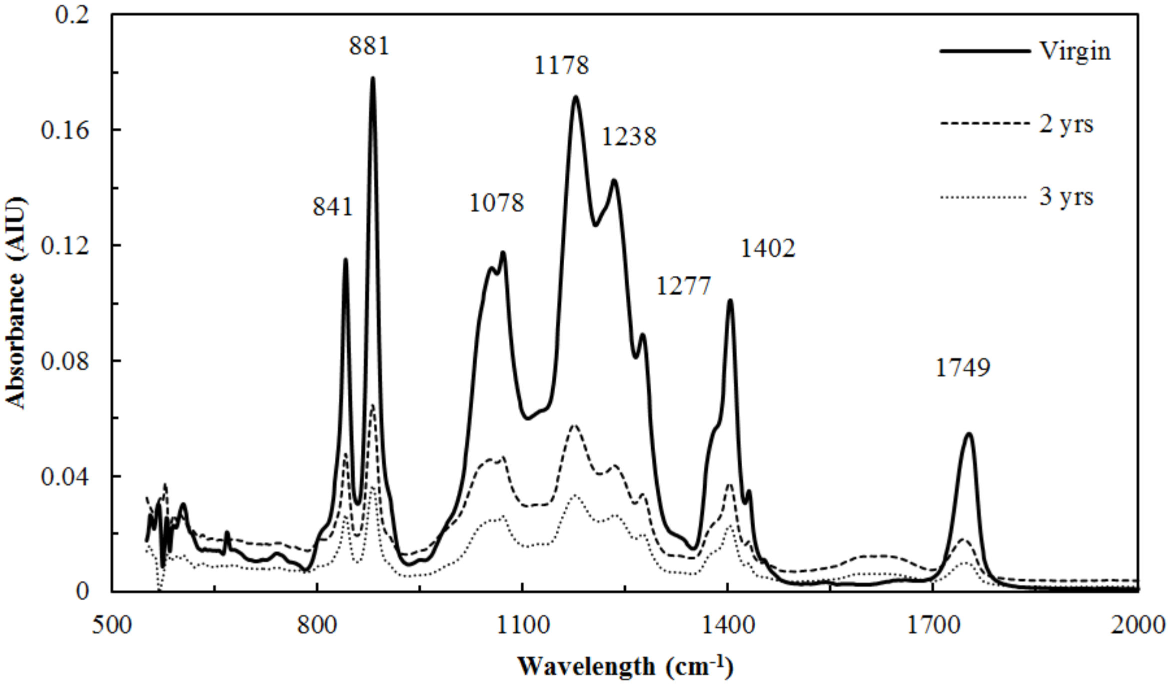


Figure 4-4: FTIR spectra of virgin and used membranes from water treatment plant

4.1.3 Foulants Analysis

4.1.3.1 Organic matter

The results of dissolved organic carbon remained on the virgin, 2 and 3 years old membrane are shown in Table 4-2. As seen in Table 4-2, there is a definite increase in the concentration of organic matter on the surface of the membrane with respect to membrane age. It is also noted that unlike 2 and 3 yrs. membrane, the virgin membrane was washed twice. This was done to ensure that the additives which are typically added to preserve the membrane prior to use do not interfere with the results. This wash was justified since the 2 and 3 years membrane have been in use for a sufficient time and hence, the organic coating would have dissipated.

Table 4-2: Organic matters remained on the membrane

Membrane age (yrs.)	0* (Virgin)	2	3
Dissolved Organic Carbon/Membrane area (g/m^2)	ND	0.140±0.004	0.212±0.005

*After two washes with 0.2% H_2SO_4

ND refers non-detectable

4.1.3.2 Inorganic matter

The major inorganic matters attached on different years' membrane are shown in Figure 4-5. It is evident from Figure 4-5 that virgin membrane was quite clean as very low concentration of inorganic matter was detected. However, a number of inorganic elements were found on 2 and 3 years' membranes. It is also interesting to note that all of five major inorganics detected on used membranes were multivalent metal ions possibly due to their high binding capacity than that of monovalent metal ions. The results clearly show that not all of the inorganic foulants could be effectively removed by chemical cleaning.

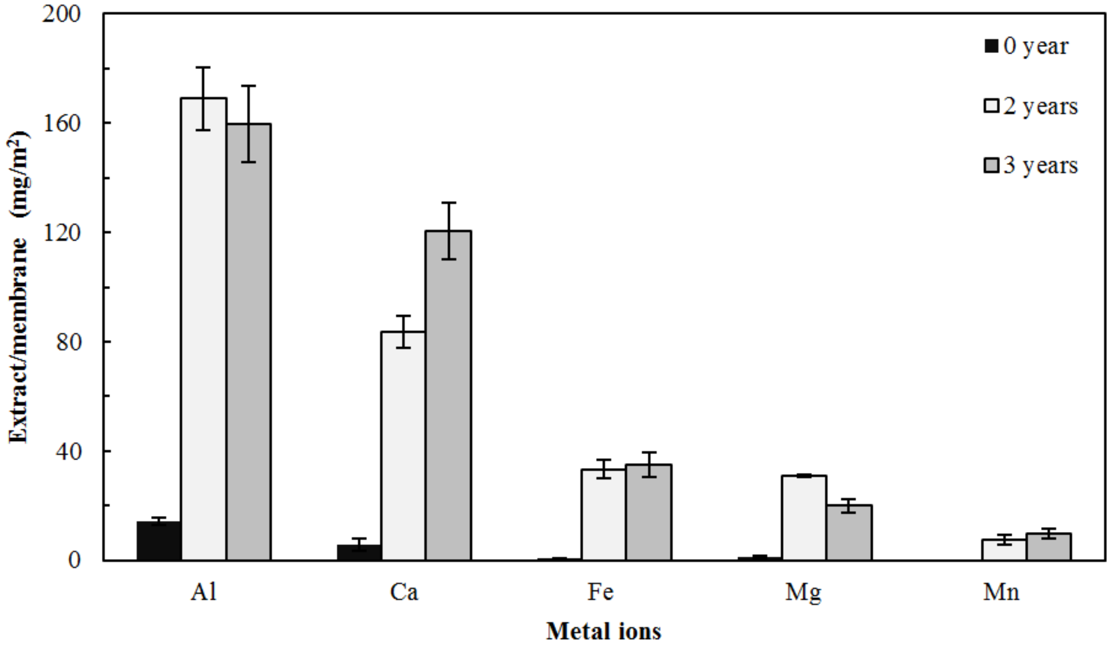


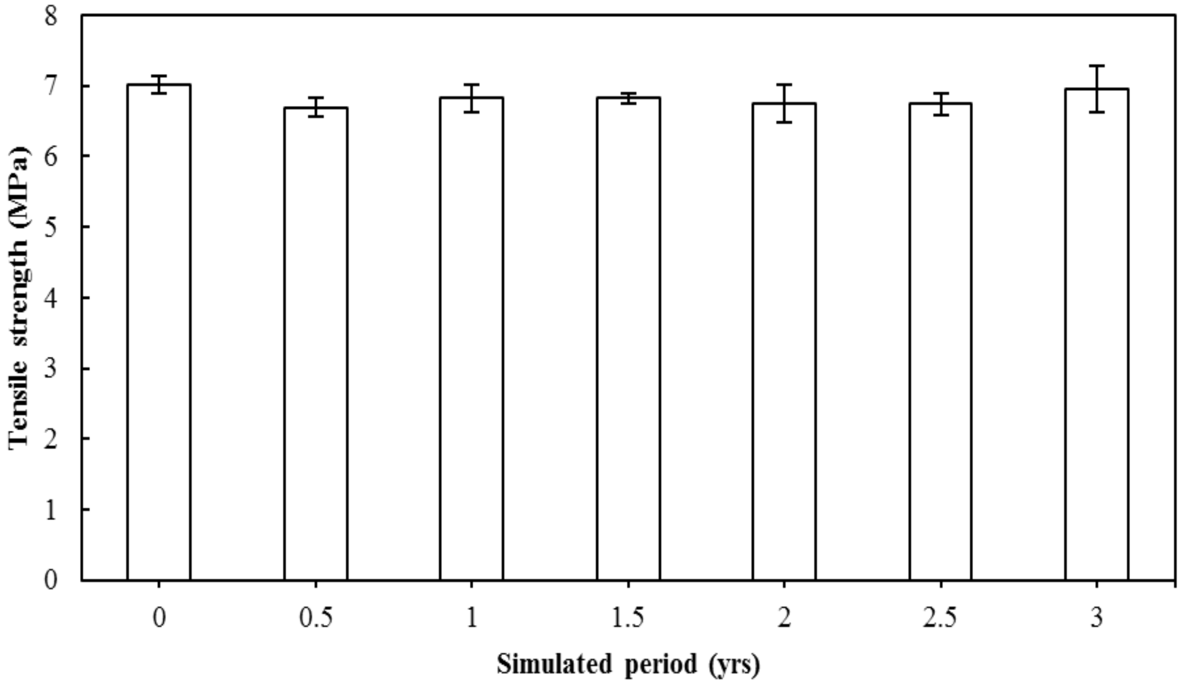
Figure 4-5: Metal ions detected on different years' membrane.

4.1.4 Simulated Chemical Cleaning Study

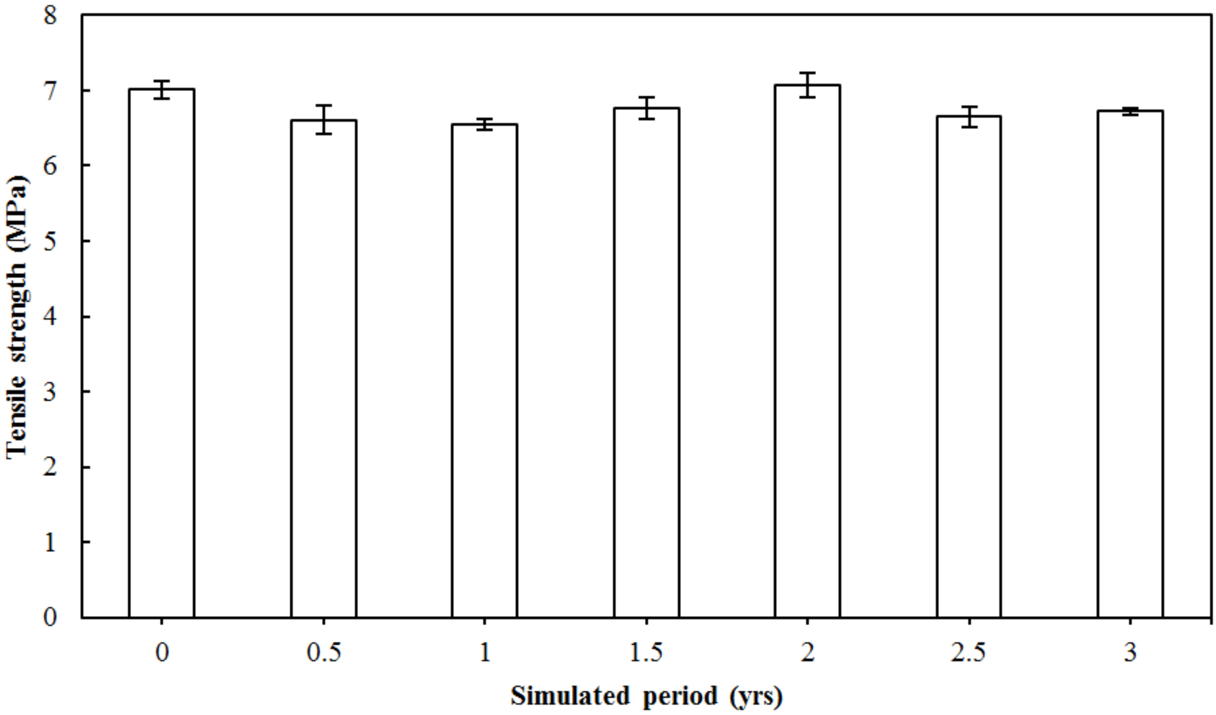
4.1.4.1 Tensile strength

Figure 4-6 presents the tensile strength under different chemical treatments. As shown in Figure 4-6a, it is clear that the tensile strength did not change significantly (ANOVA, $p>0.05$) when membranes only immersed in tap. However, ANOVA results ($p<0.05$) for citric acid (Figure 4-6b), sodium hypochlorite(Figure 4-6c) and sodium hypochlorite/citric acid (Figure 4-6d) treatments showed a significant change in tensile strength. The tensile strength results for citric acid treatment showed a significant change but did not follow any conclusive trend. However, sodium hypochlorite treatment negatively impacted the tensile strength and decreased with extending time of exposure.

In the series of sodium hypochlorite treatments, where the hypo exposure time increased from 0 (virgin) to 216 hours, the membrane's tensile strength decreased from 7.01 to 5.48 MPa (Figure 4-6c). In a series of sodium hypochlorite/citric acid treatments, the tensile strength also decreased from 7.01 to 5.7 MPa (Figure 4-6d) where the exposure time of sodium hypochlorite and citric acid increased from 0 (virgin) to 216 and 0 to 90 hours, respectively. As shown in Figures 4-6c & 4-6d, the mechanical properties of membranes degraded gradually with increasing chemical exposure time and the final degradations were around 22% and 19%, respectively, when the membranes were treated by sodium hypochlorite and sodium hypochlorite/citric acid. The results are similar sufficiently to suggest that the addition of citric acid had no negative impact even combined with sodium hypochlorite.

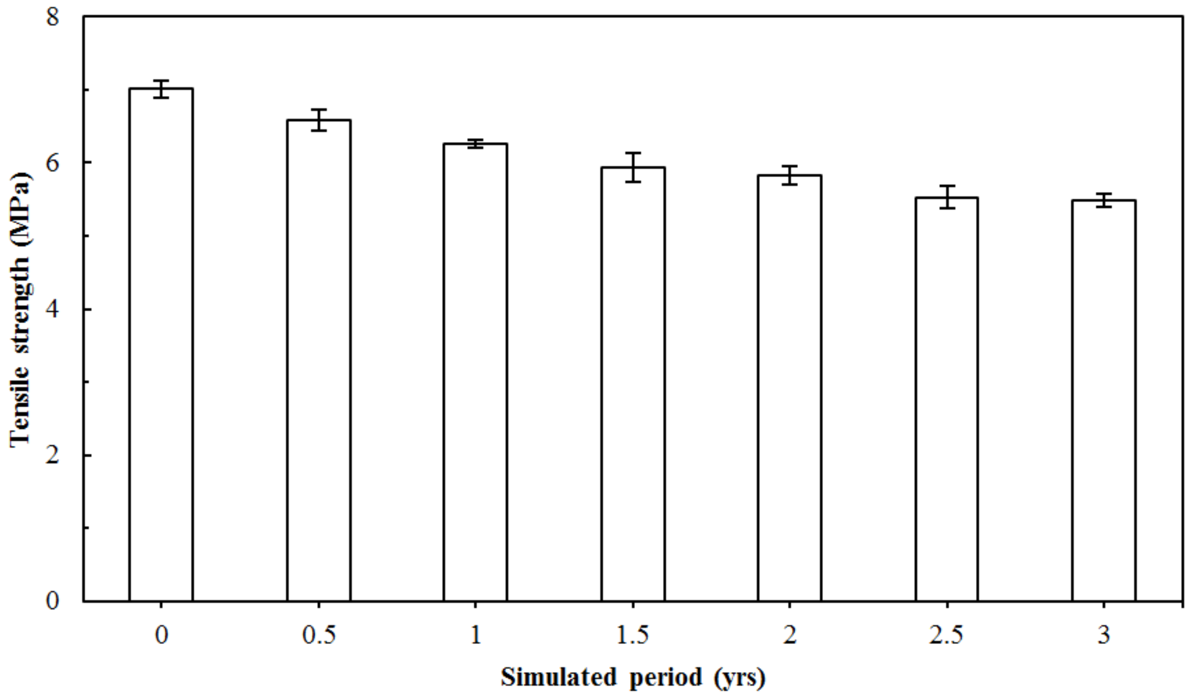


(a)

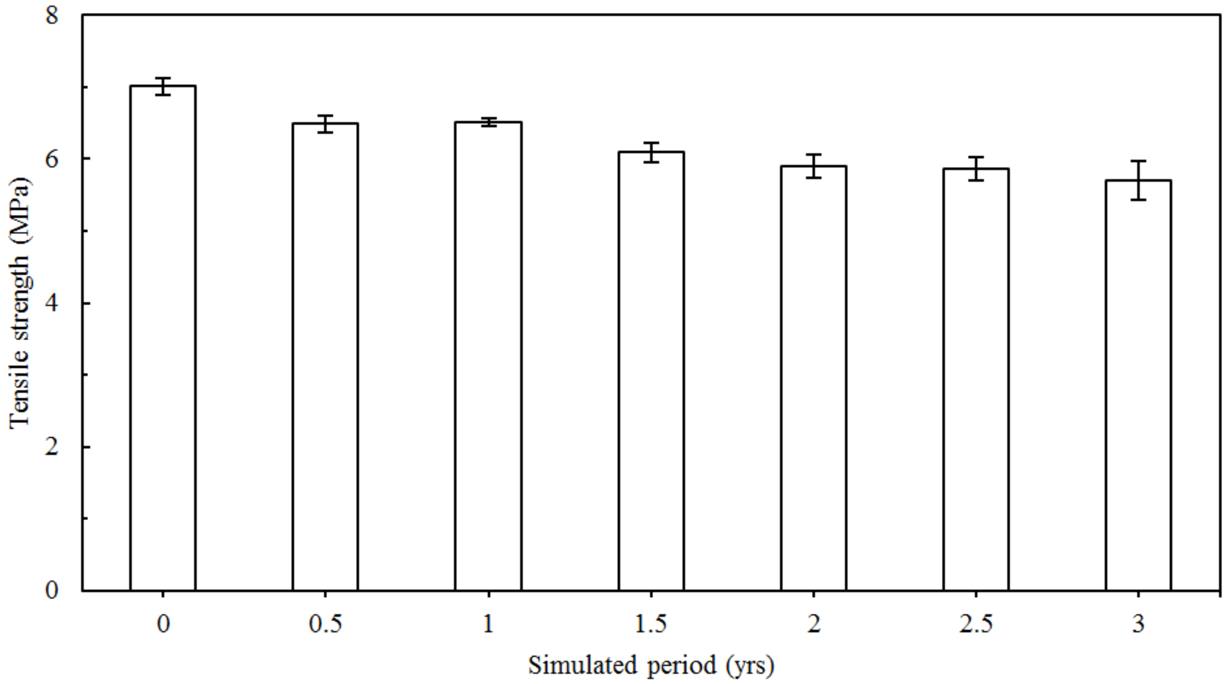


(b)

Figure 4-6: Tensile strength at break of different chemical treatment: (a) Tap water, (b) Sodium hypochlorite



(c)

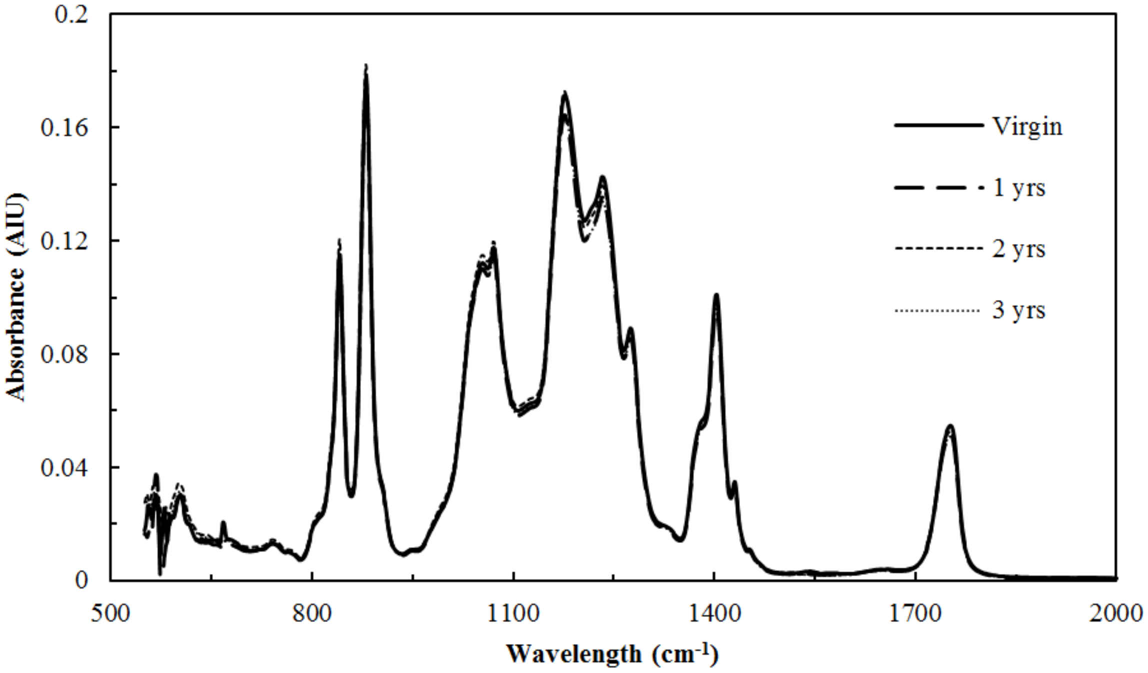


(d)

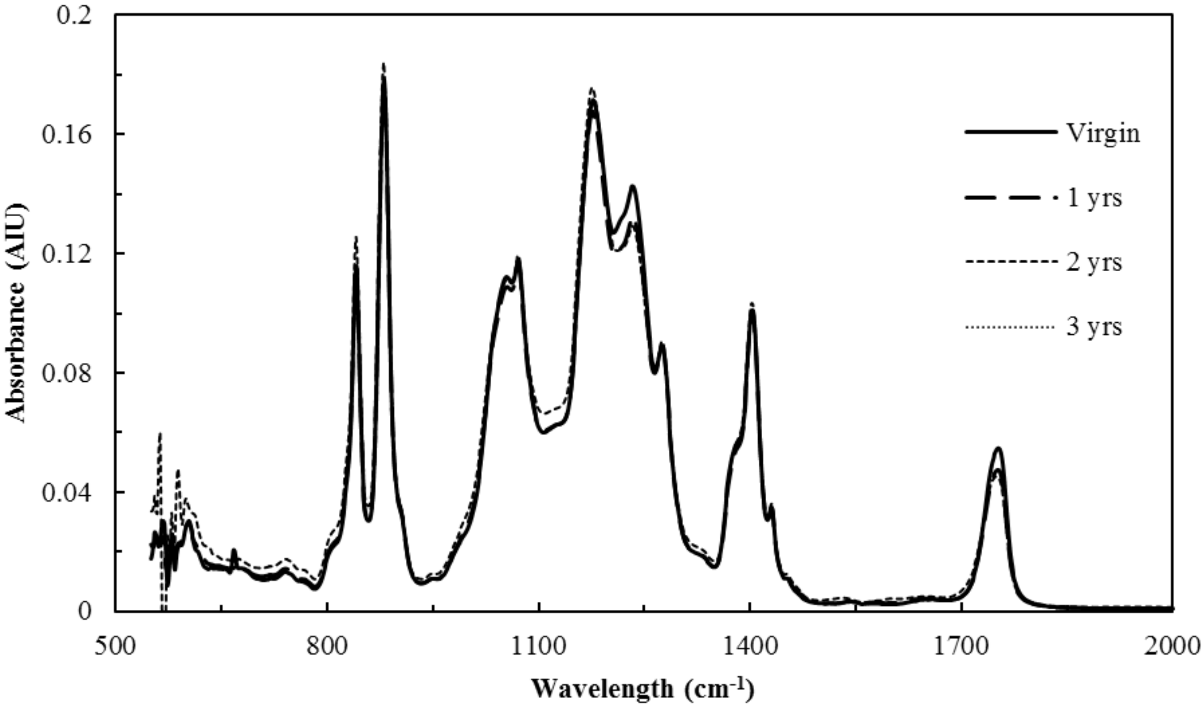
Figure 4-6: Tensile strength at break of different chemical treatment: (c) Citric acid and (d) Sodium hypochlorite/Citric acid treatment

4.1.4.2 ATR-FTIR spectroscopy

The FTIR spectra of different chemical treatments are shown in Figure 4-7. It is a common phenomenon that both the peak height and peak numbers were not changed while the membranes were only immersed in tap water (Figure 4-7a). As observed above, the citric acid did not attack the membrane as the FTIR spectra did not significantly change (Figure 4-15b). The sodium hypochlorite, as with the tensile strength, had an adverse effect on membrane surface chemistry. As shown in Figures 4-7c & 4-7d, when the membrane was treated by sodium hypochlorite or sodium hypochlorite/citric acid, the chemical properties of membrane surface deteriorated continuously as the absorbance of function groups (i.e., the height of peaks) decrease gradually with the increase of immersed time in the sodium hypochlorite cleaning solution. It is also found that the intensity of all the representative peaks decreased simultaneously which is consistent with the tendency of the membranes from full scale plant. Comparing with Figures 4-7b, 4-7c and 4-7d, it also verifies that sodium hypochlorite had remarkable impact on membrane surface chemical property while citric acid had insignificant effect. Chemical cleaning using sodium hypochlorite played the dominant role in the deterioration of membrane properties.

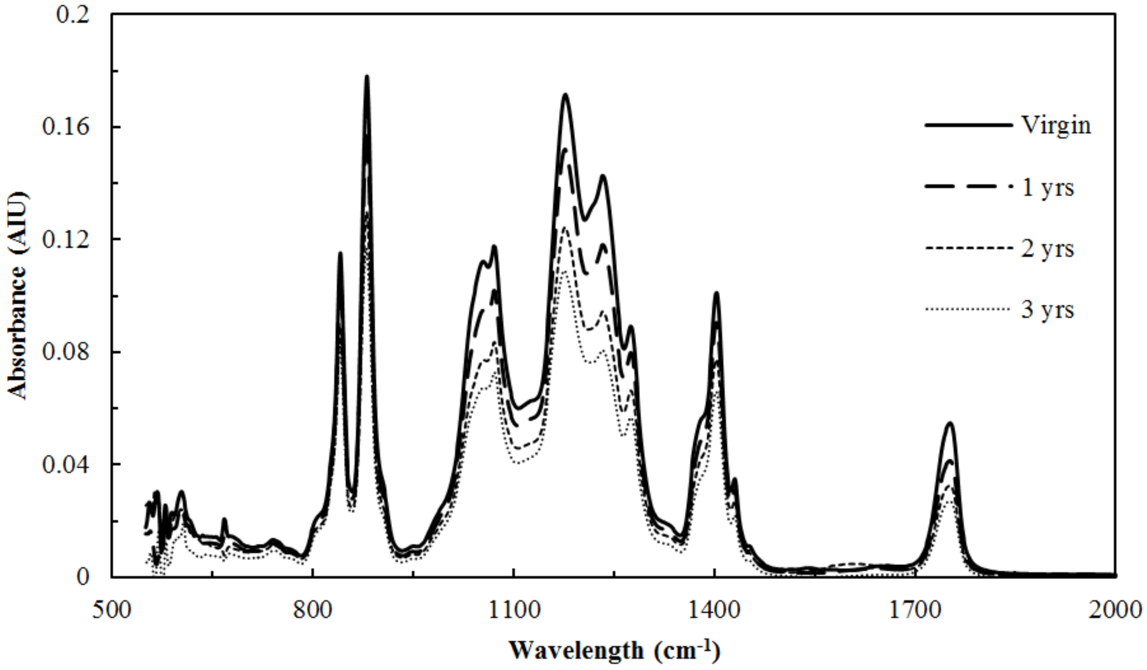


(a)

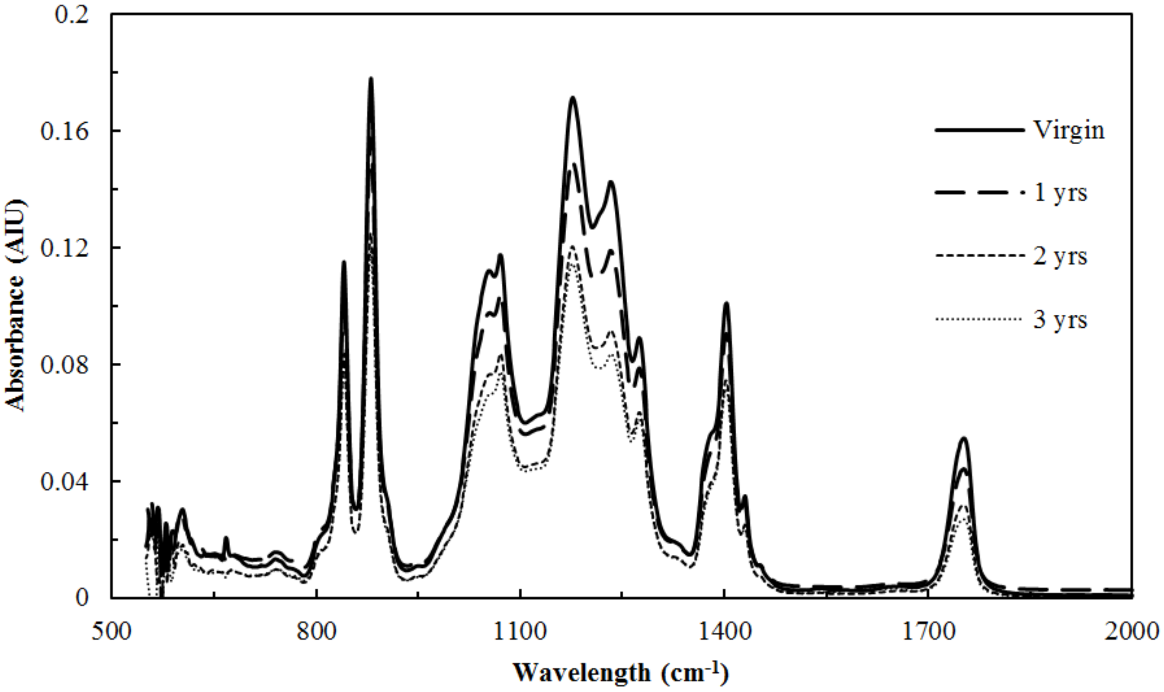


(b)

Figure 4-7: FTIR spectrum of different chemical treatment: (a) Tap water, (b) Sodium hypochlorite



(c)



(d)

Figure 4-7: FTIR spectrum of different chemical treatment: (c) Citric acid and (d) Sodium hypochlorite/Citric acid treatment

4.1.2 Discussion

The chemical cleaning of UF polymer membranes has been approved as an effective method to recover membrane flux and is widely accepted by membrane treatment plants (Arkhangelsky *et al.*, 2007). The chemicals can loosen and dissolve the foulants (Madaeni and Mansourpanah, 2004); however, they may attack the membrane and deteriorate the membrane properties (Zondervan *et al.* 2007; Yadav and Morison, 2009). Thus, both full scale and simulated chemical cleaning studies were conducted in this study to evaluate the direct effects of the current membrane cleaning procedures on membranes properties.

The results of Table 4-2 and Figure 4-5 show some organic and inorganic foulants still remain on the membrane surface or in the membrane pores despite repeated CIPs of the membrane. These foulants could be contributing to a gradual decrease of membrane flux (Fig. 9). As shown in Figures 4-2, 4-3, and 4-4, the membrane ageing could cause more roughness of membrane surface and partly break the polymeric chains of PVDF membranes; consequently, the mechanical properties became weak.

Comparing Figure 4-3 with Figure 4-6d, the tensile strength of membranes at water treatment plant after 2 and 3 years' operating time (5.73 and 5.02 MPa) were lower than the results of simulated chemical cleaning study (5.9 and 5.7 MPa). These results reveal that the degradation of mechanical properties of the ageing' membranes was due to both the mechanical fatigue stressors of daily operation and periodical chemical cleanings. With the comparison of Figures 4-4 and 4-7d, it is observed that the deterioration of surface chemistry of the hollow fiber membranes appears to be greater in the membranes from the plant compared to the simulated chemical cleaning study membranes.

The results of Figure 4-6d and 4-7d are consistent with the findings from full-scale plant membrane samples (Figures 4-3 and 4-4). Comparing the results of Figures 4-3 and 4-4, the smaller decrease in membrane tensile strength and peak intensity of FTIR measurements from the simulated chemical cleaning experiments suggest that both chemical cleaning and mechanical stress of daily operation contributed to the deterioration of membrane properties (tensile strength and functional group intensity) and chemical cleaning played the dominant role.

4.2. Effect of Chemical Cleaning on Membrane Performance and fouling

The purpose of this study was to optimize the chemical cleaning strategies (sodium hypochlorite and Citric acid) currently used at Bare Point Membrane Filtration Plant to reduce the chemical usage and minimize the impact of sodium hypochlorite and citric acid on membrane properties during chemical cleaning.

4.2.1. Sodium hypochlorite Cleaning

UF polymer membrane has emerged as a popular technology due to its low cost and high pathogen removal ability with least energy consumption. Several researches and our previous study (chapter 4.1) also demonstrated that chemical cleaning agents such as sodium hypochlorite (NaClO) deteriorates membrane properties like ultimate tensile strength, elongation and elasticity (Arkhangelsky et al 2007). There is also ageing effects by the modification of membrane surface resulting in increased hydrophobicity (Puspitasari *et al.*, 2010) and enlargement of pores (Arkhangelsky et al 2007). Due to these reasons, this study focused on reducing the concentration of NaClO solution with the combination of soak time during membrane chemical cleaning. In this study the effectiveness of various concentrations of sodium hypochlorite with combination of relevant soak time (e.g. different doses) has been evaluated in terms of change in permeability as given below:

$$\textbf{Change in permeability} = (P_{AC} - P_{BC}) \qquad (4)$$

Note: P_{AC}= Permeability after clean; P_{BC} = Permeability before clean)

At the same time, in order to evaluate the change in permeability of backwash and permeate water, membrane module was soaked into a permeate water without adding any sodium hypochlorite solution for approximately 21 hours (control experiment). This made sure that any relevant changes in permeability without adding NaClO can be recorded and taken into account during experimentation.

4.2.1.1. Membrane performance

The plot between change in permeability and soak time under different NaClO concentrations is shown in Figure 4-8. The experiment was performed as explained in the previous chapter 3.1 at different average doses of NaClO (417 mg.hr/L, 608 mg.hr/L, and 828 mg.hr/L) by adjusting soak time of membrane into different concentrations of sodium hypochlorite (100, 200, 300 and 500 mg/L). There were some variations in the actual dose of the NaClO as compared to the targeted doses. Reasons for the variations were due to slight change in volume of permeate water filled into the membrane tank from the permeate tank, which was accomplished automatically during cleaning process.

Figure 4-8 demonstrated that the change in permeability of the membrane increased with an increase in soak time under different NaClO concentrations. However, the change in permeability in 200 mg/L NaClO soaked for 4 hours and 300 mg/L NaClO soaked for 2.7 hours decreased as compared to same concentration of NaClO (200 and 300 mg/L) soaked for 3 and 2 hours, respectively. These exceptions suggest 3 and 2 hours soak time were favourable for 200 and 300 mg/L NaClO concentration.

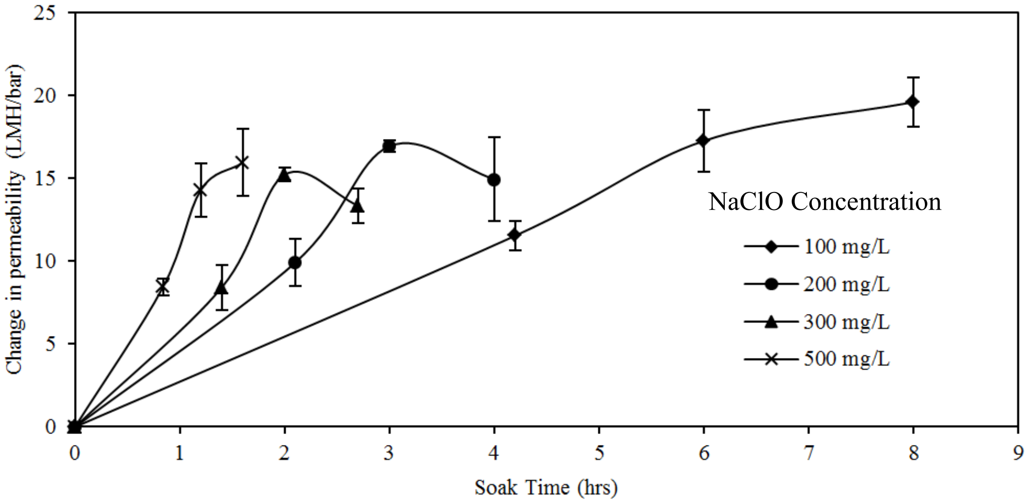


Figure 4-8: Change in permeability and soak time under different NaClO concentrations

Similarly, the plot between change in permeability and NaClO dose under different NaClO concentrations is given in Figure 4-9. It revealed that the combination of a lower NaClO concentration and a longer soak time achieve a larger permeability recovery at the same NaClO dose. Considering the negative impact of NaClO on membrane properties, it is suggested to use a lower NaClO concentration and longer soak time for higher permeability recovery.

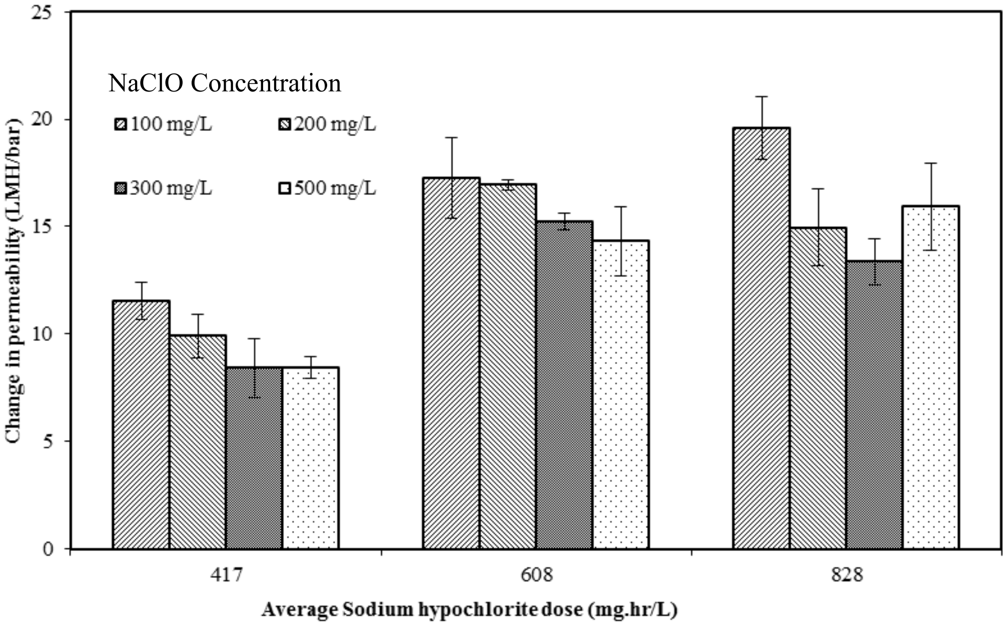


Figure 4-9 : Change in permeability and NaClO doses at various sodium hypochlorite concentrations.

4.2.1.2. Foulants Analysis

a) Organic Foulants:

The plot between soak time and TOC removal efficiency under different NaClO concentrations is shown in Figure 4-10. The results show that TOC removal efficiency increased with an increase in soak time.

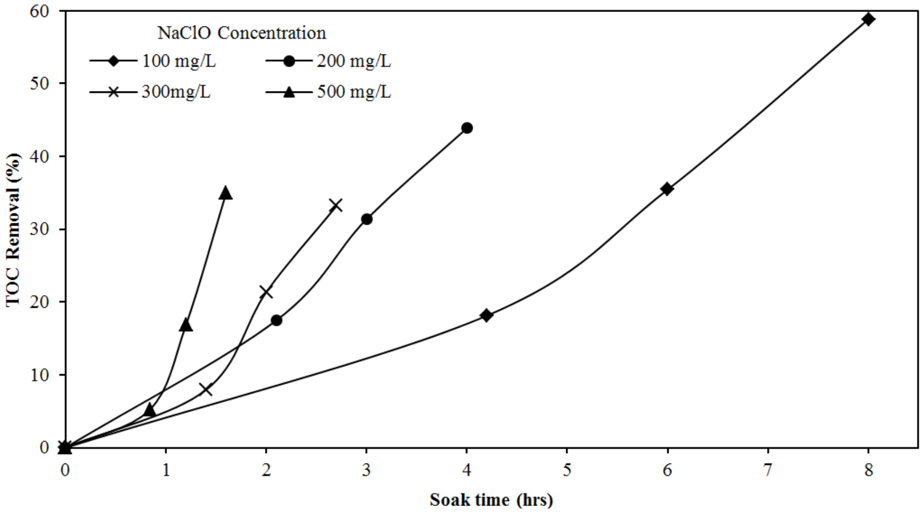


Figure 4-10: TOC removal (%) versus soak time plot at various sodium hypochlorite concentration.

Figure 4-11 is the plot between the removal efficiency of TOC and NaClO doses at different NaClO concentrations. The results demonstrated that the removal efficiency of TOC increased with an increase in the NaClO dose. By comparing the removal efficiency of TOC under different NaClO concentrations, it was found that the combination of a lower concentration with a longer soak time was more efficient for TOC removal at the same NaClO dose (Figure 4-10). This is consistent with the observation of permeability recovery as discussed above.

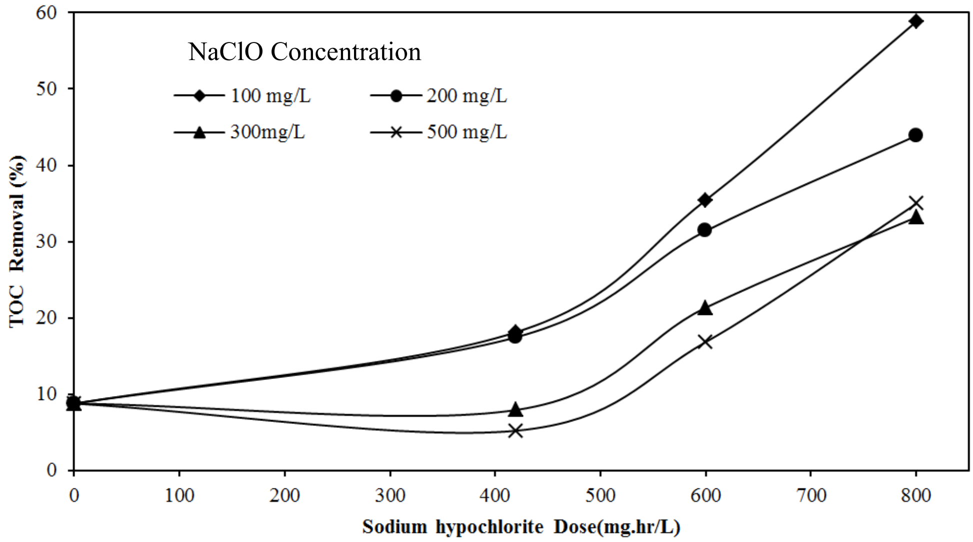


Figure 4-11: TOC removal (%) versus sodium hypochlorite dose at various NaClO concentration.

Figure 4-12 is the plot between TOC removal efficiency and change in permeability due to the exposure of various concentrations of NaClO. This plot clearly indicated that the change in permeability was dependent upon the TOC removal efficiency. Therefore, it is suggested that organic matters are the major foulants, which were responsible for degradation of membrane performance.

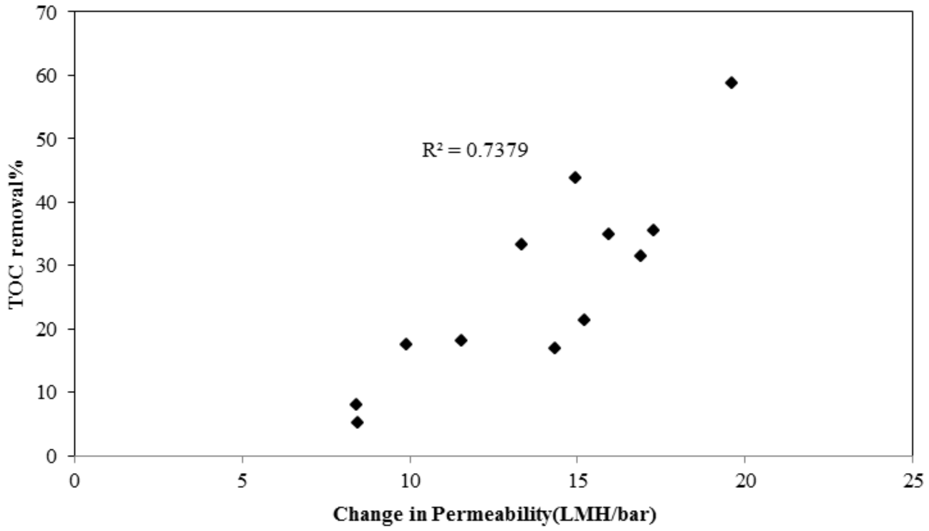
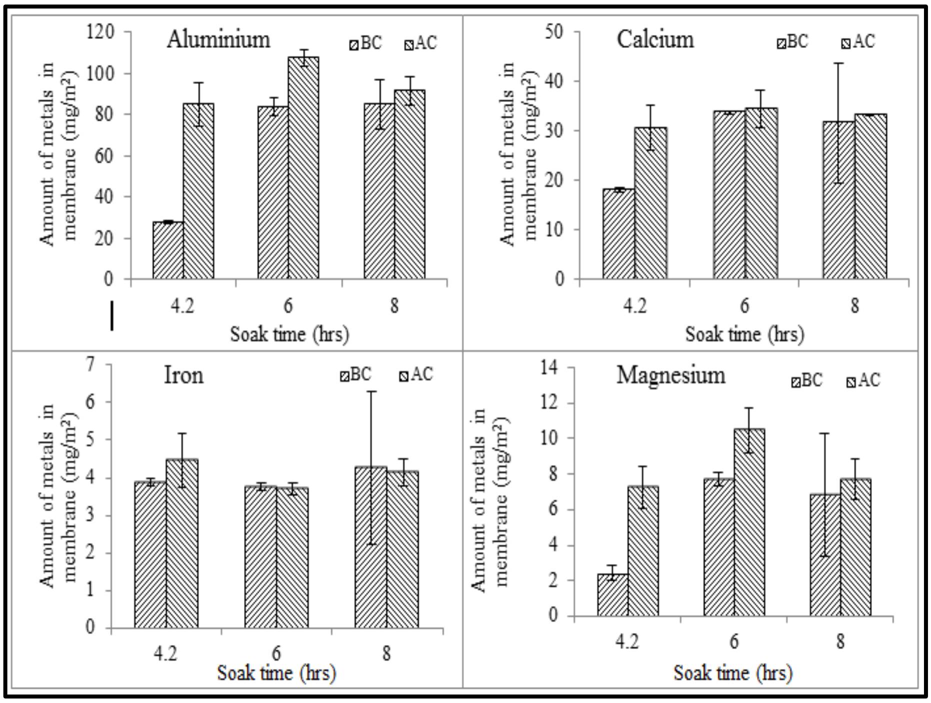


Figure 4-12: TOC removal (%) and change in permeability

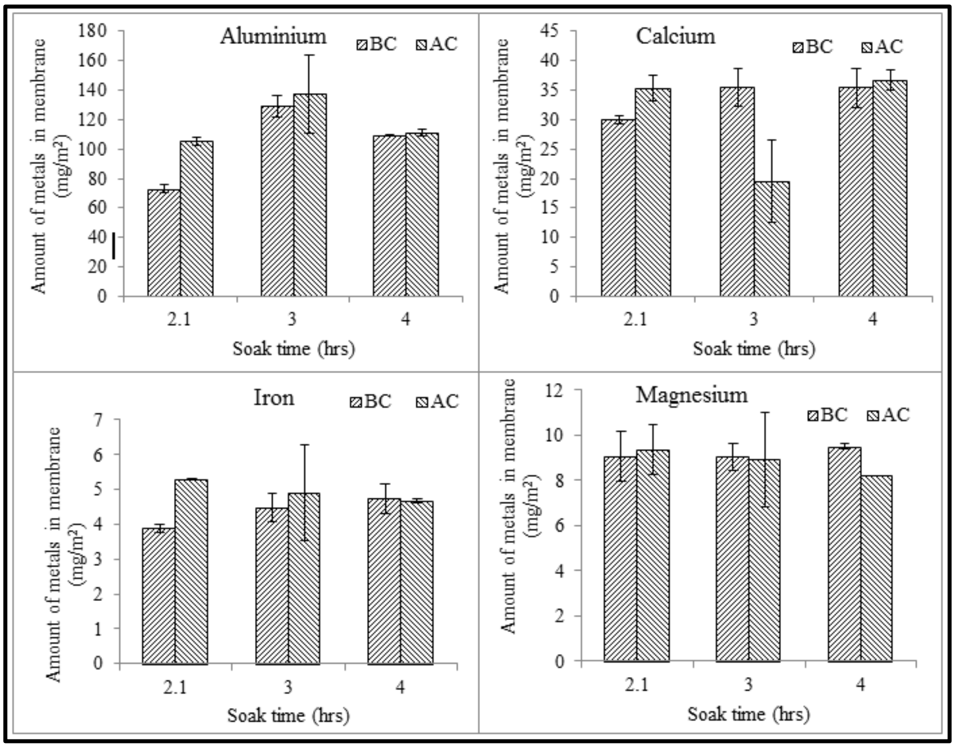
b) Inorganic foulants

Many researchers reported that inorganic salts in the feed water are responsible for inorganic scaling. It is also known that UF membrane is unable to filter metals as well as small organic molecules in feed water. Therefore, the study of metals ions was performed on the membrane fibers harvested from membrane module before and after NaClO treatment. Two membrane fibers were taken from each sample and ICP- AES analysis was performed. The plot of the amount of main multivalent metals ions concentrations in membrane vs. various soak time is shown in Figure 4-13. The result suggested that the major multivalent metal ions were Al, Ca, Fe, and Mg existed in the membrane. Aluminium and calcium were among the dominant elements found, (27.6-129.1)mg/m^2 and (18- 35.5) mg/m^2, respectively.

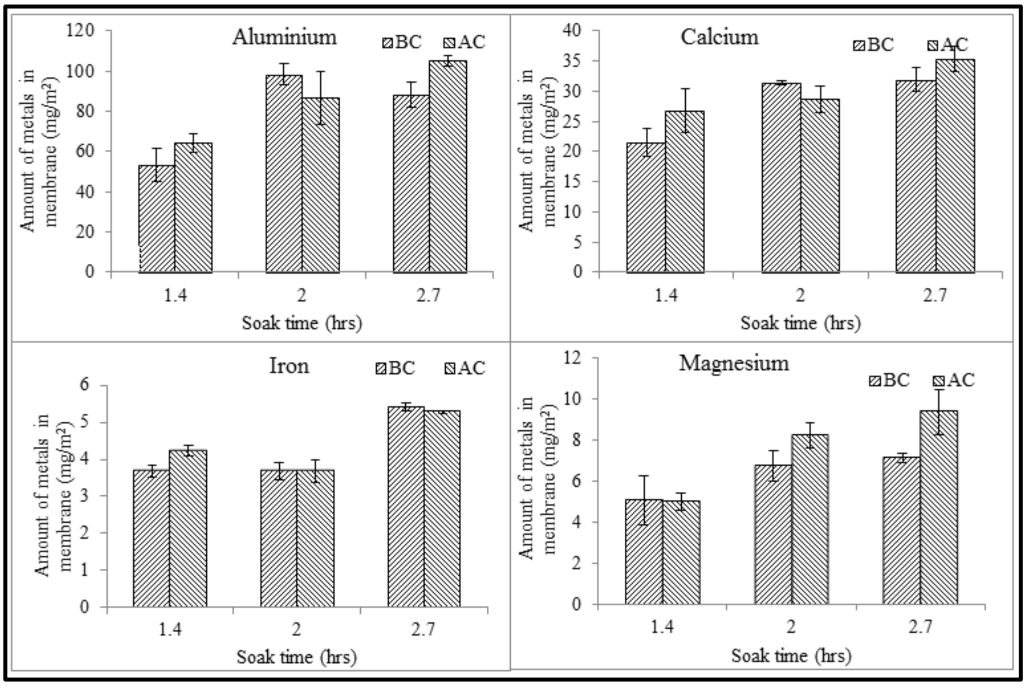
Figure 4-13 (A, B, C, and D) represents the amount of major metal ions present in the membrane before and after NaClO treatment at a given NaClO concentration at different soak times. From the result, it was noted that the amount of metals ions after sodium hypochlorite treatment increased in most cases. However, the accumulation of metals on/in membrane did not show any conclusive relationship with concentration and soak time. The increase in metal concentration after NaClO treatment could be explained by the fact that NaClO treatment raised the pH of the solution and always found approximately high pH (9.3 - 10.5) and would result in metals precipitation on membrane surface and pores.


Aluminium
BC
AC
Amount of metals in membrane (mg/m²)
0
20
40
60
80
100
120
4.2
6
8
Soak time (hrs)
Calcium
BC
AC
Amount of metals in membrane (mg/m²)
0
10
20
30
40
50
4.2
6
8
Soak time (hrs)
Iron
BC
AC
Amount of metals in membrane (mg/m²)
0
1
2
3
4
5
6
7
4.2
6
8
Soak time (hrs)
Magnesium
BC
AC
Amount of metals in membrane (mg/m²)
0
2
4
6
8
10
12
14
4.2
6
8
Soak time (hrs)

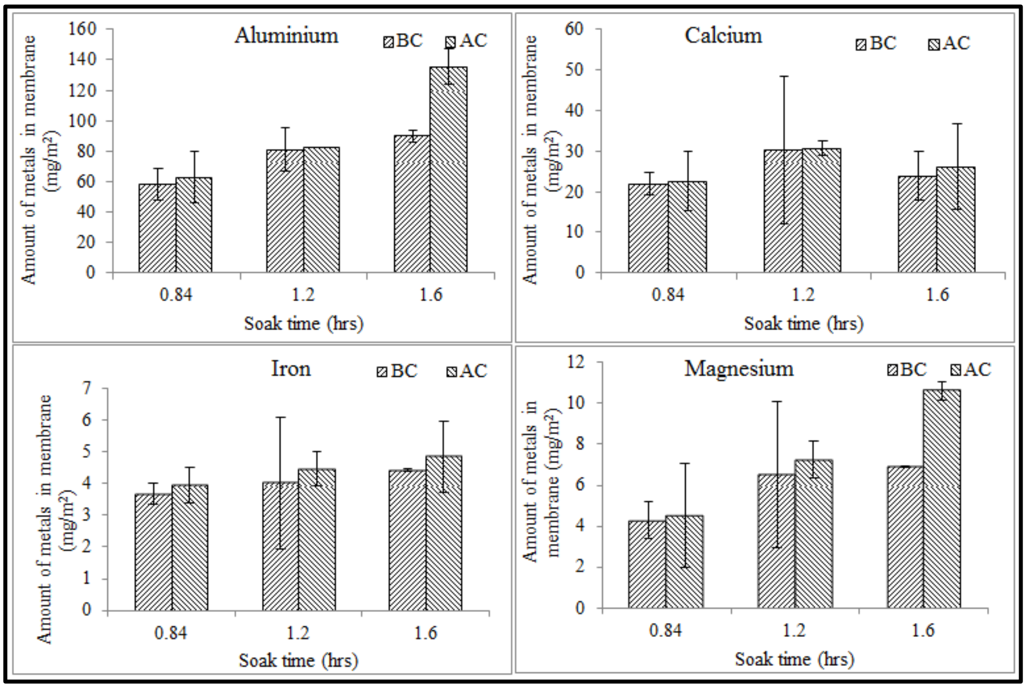
(A)


Aluminium
BC
AC
Amount of metals in membrane (mg/m²)
0
20
40
60
80
100
120
140
160
180
2.1
3
4
Soak time (hrs)
Calcium
BC
AC
Amount of metals in membrane (mg/m²)
0
5
10
15
20
25
30
35
40
45
2.1
3
4
Soak time (hrs)
Iron
BC
AC
Amount of metals in membrane (mg/m²)
0
1
2
3
4
5
6
7
2.1
3
4
Soak time (hrs)
Magnesium
BC
AC
Amount of metals in membrane (mg/m²)
0
2
4
6
8
10
12
2.1
3
4
Soak time (hrs)

(B)



(C)



(D)

Figure 4-13 : Major metal ion concentrations in membrane before (BC) and after (AC) NaClO treatment (A) 100 mg/L, (B) 200 mg/L, (C) 300 mg/L, and (D) 500 mg/L.

4.2.1.3. Discussion:

The permeability of the membrane increased change in exposure of membrane to hypochlorite. Longer exposure to NaClO resulted in a greater water permeability as shown in Figure 4-8. This could be mainly due to the TOC removal by NaClO oxidation. NaClO treatment was previously used to modify hydrophobic polymer membranes; the modified membranes had a large amount of water flux due to increase in pore size of the membrane (Qin and Wong, 2002; Wolff and Zydney, 2004). There is a most favourable exposure time for hypochlorite to achieve hydrophilic membrane with superior flux (Qin and Wong, 2002).

However, a longer contact time with NaClO would decrease ultimate tensile strength and ultimate elongation elasticity modulus of UF membranes. As NaClO is an oxidant, various end groups such as aldehyde (CHO), Carboxyl (COOH), and ketone (C=O) could be oxidized by exposure to hypochlorite solution. This could be the reason of gradual degradation in the mechanical properties of the membranes. The sodium hypochlorite cleaning had a relatively good recovery of water permeability, due to the oxidation and removal of organic fouling layer. This could also be due to an increase in pore size in the membrane surface, resulting in partial peeling off from the membrane layer (Wolff and Zydney, 2004).

As evident from Figure 4-12, an increase in the TOC removal efficiency correlated well with an increase in the change in permeability. In general, an increase in soak time for each concentration of NaClO solution resulted in incremental removal of TOC. Several researchers reported that organic fouling was the major issue that contributed to membrane fouling during UF treatment for surface water containing NOM (Schafer *et al.*, 2001; Gitis *et al.* 2006; Zularisam *et al.* 2007). As NaClO was used during this study, the pH remained between 9.3-10.5. As a result, the membrane crust was negatively charged. It was also reported that long-time exposure to bleach significantly increased the zeta potential of the membrane surface, although the elemental composition of the membrane surface were identical (Wolf and Zydney, 2004). Hence, a longer exposure to NaClO caused an increase in negative charges, both on membrane and NOM, resulting in an increase in electrostatic repulsion. Simultaneously, hydrophobic and size exclusion interaction between membrane and NOM constituents resulted in an increase in TOC removal when increasing soak time.

The result of the metals analysis, as shown in Figure 4-13, displays that almost every NaClO treatment increased the amount of metals ions in/on the membrane. This is likely due to the fact that sodium hypochlorite treatment increases the pH (9.3-10.5). In high pH, membrane surface have net negative charges, residual NOM in/on membrane and smaller organic matters from permeate also have negative charges (Song *et al.*, 2004; Gitis *et al.*, 2006). Therefore, it assumed that, an electrostatic attraction between two opposite charges assisted metal ions for the accumulation on the membrane surface.

It was noted that the TOC removal and permeability change have linear relationship with R^2= 0.7853. This relation revealed that as TOC removal efficiency increases, the change in permeability also increases. This indicates that organic foulants played an important role in determining membrane permeability.

In summary of the series of the above results and discussion, NaClO seems to effectively remove organic matters and restore membrane permeability. It was also revealed that treatment of NaClO resulted in an increase of metals on/in the membrane. However, the real cause of the increase of metals on membrane fibers remained unclear and needed further investigation to determine whether the metal ions in NaClO solution or in feed water is responsible for the increase. Organic matters were main components of the foulants and responsible for membrane permeability reduction. Previous studies indicated that inorganic fouling is also responsible for the reduction of flux and the increase in TMP due to scaling and precipitation on the membrane surface. There are various parameters and conditions which need to be maintained to form scale and precipitation during membrane filtration process, such as salt concentration, temperature, pH, larger ionic product than equilibrium solubility product, operating conditions (Schafer, 2001; Al-Amoudi and Lovitt, 2007), and cleaning frequency. Therefore, the metals ions did not get the chance to form scale. Without forming scale, the presence of dissolved metal ions is not solely responsible for reduction of membrane performance, and inorganic fouling by precipitation shows negligible effect on membrane fouling (Kweon and Lawler, 2004). Above all, metal ions in dissolved form could not be removed effectively (Chae et al, 2009). Therefore, it was observed that NaClO treatment increased metals ions in/on the membrane without affecting membrane performance.

4.2.2 Citric Acid Cleaning

4.2.2.1. Membrane performance

The cleaning efficiency of citric acid at pH 2.2 and 3.0 was studied by varying citric acid concentrations (200, 400, 600, and 800 mg/L). Each set of concentration was studied at both pH levels. To maintain uniformity at beginning of each cleaning experiment, a similar TMP value (60±3 kPa) was maintained by monitoring the related computer screen attached to the pilot plant. Cleaning was performed with a combination of various processes such as back wash, sodium hypochlorite and citric acid. The plot between citric acid concentrations and average change in permeability is presented in Figure 4-14. From the results, the change in permeability, before clean and after clean at different citric acid concentrations, was not significant except for 800 mg/L citric acid for both pH values. The cleaning efficiency of individual component (backwash, sodium hypochlorite, and citric acid) was also evaluated. The permeability change in the experiment using only the backwash process was found to be 38.0±5.0 L m^{-2} h^{-1} bar^{-1}. Similarly, the effectiveness of NaClO in term of permeability change was 15.0 L m^{-2} h^{-1} bar^{-1}. Furthermore, the effectiveness of each component of cleaning process was evaluated in percentage, comparing maximum permeability difference among the experiments. Maximum permeability change during the process was 65.5 L m^{-2} h^{-1} bar^{-1} [at cleaning condition Backwash + NaClO (200 mg/L) +Citric Acid (600 mg/L) + pH 2.2]. The percentage of permeability change due to backwash was 58%, which underscored the importance of backwash in permeability recovery. Similarly, the percentage of permeability change due to sodium hypochlorite alone is 22.9%. For various citric acid concentrations (200, 400, 600, and 800 mg/L) at pH 2.2, the percentage of permeability change were found to be 14.5%, 16.03%, 20%, and 5.3% respectively. Similarly, the percentage change in permeability for different concentrations (200, 400, 600 and 800 mg/L) of citric acid at pH 3.0 were found to be 6.9%, 7.6%, 6.1% and 0%, respectively. The results suggest that a lower pH (2.2) was effective in permeability recovery compared to a higher pH (3.0), which signifies the importance of pH in permeability recovery.

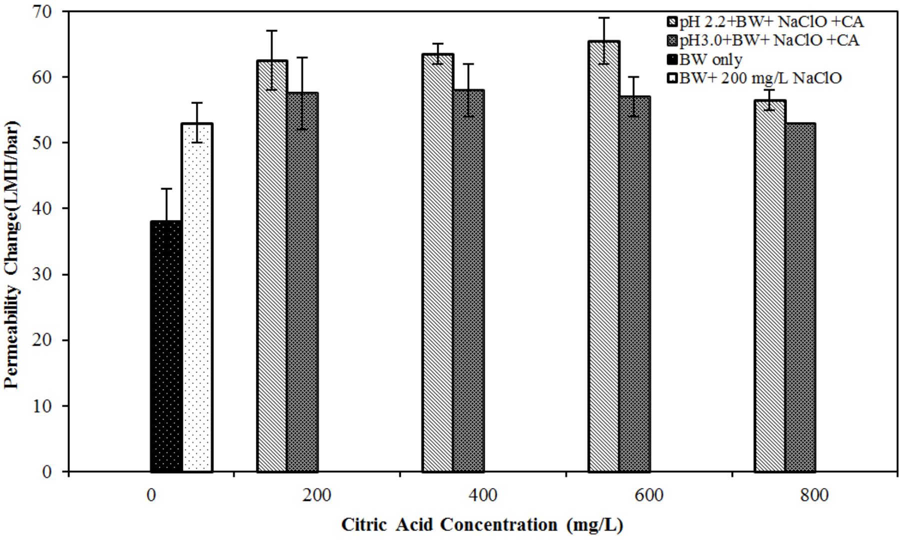


Figure 4-14: Permeability change versus citric acid concentration under various conditions

4.2.2.2. Foulants analysis

a) Inorganic Foulants:

Several studies revealed that divalent cations such as Ca^{2+} exhibited greater flux decline compared to monovalent cations (Elimelech, 1997; Jarusutthirak *et al.*, 2007). Therefore, focus was given for multivalent cations such as Al^{3+}, Ca^{2+}, Fe^{2+}, and Mg^{2+}. The results obtained from the ICP-AES analysis of metal ions are presented in Figures 4-15 and 4-16. Metal ion quantities in the membrane can be evaluated and compared before chemical cleaning, after NaClO cleaning, and after cleaning with various concentrations of citric acid at pH 2.2 and 3.0. The result revealed that there were certain multivalent metal ions (Al^{3+}, Ca^{2+}, Fe^{2+} and Mg^{2+}) present in a significant amount in the membrane. For each experiment, a further increase in the amount of metal ions was found after sodium hypochlorite treatment, which is consistent with the finding of our previous study presented in section 4.2.1.2. The results indicated that Aluminium was the most abundant multivalent metal present in the membrane and the concentration ranged from 76.6±7.3 to 145.2±1.7 mg/m^2. Calcium, Magnesium, and Iron were among other metal ions substantially present in the membrane. The amount ranged 21.3±0.5-37.1±0.9 mg/m^2 for Calcium, 5.7±0.1-9.3±1.2mg/m^2 for Magnesium, and 3.5±0.1- 4.8±0.1 for Iron. The metal ions in membrane were not substantially removed by various concentrations of citric acid at pH 2.2 and 3.0. However, the result revealed that there was some reduction in the amount of metals after citric acid treatment at pH 2.2 and 3.0 as compared to the amount after sodium hypochlorite treatment.

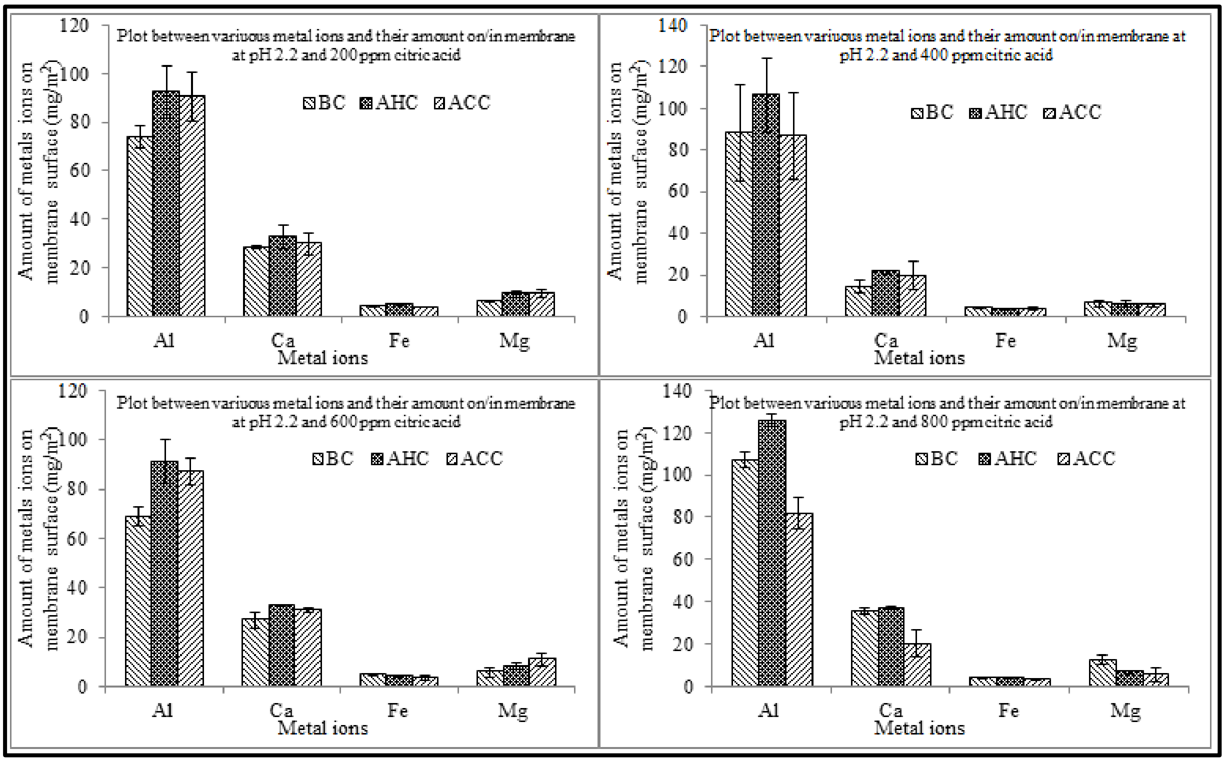


Figure 4-15: Metal ions concentration in membrane fibers during citric acid treatment at pH 2.2

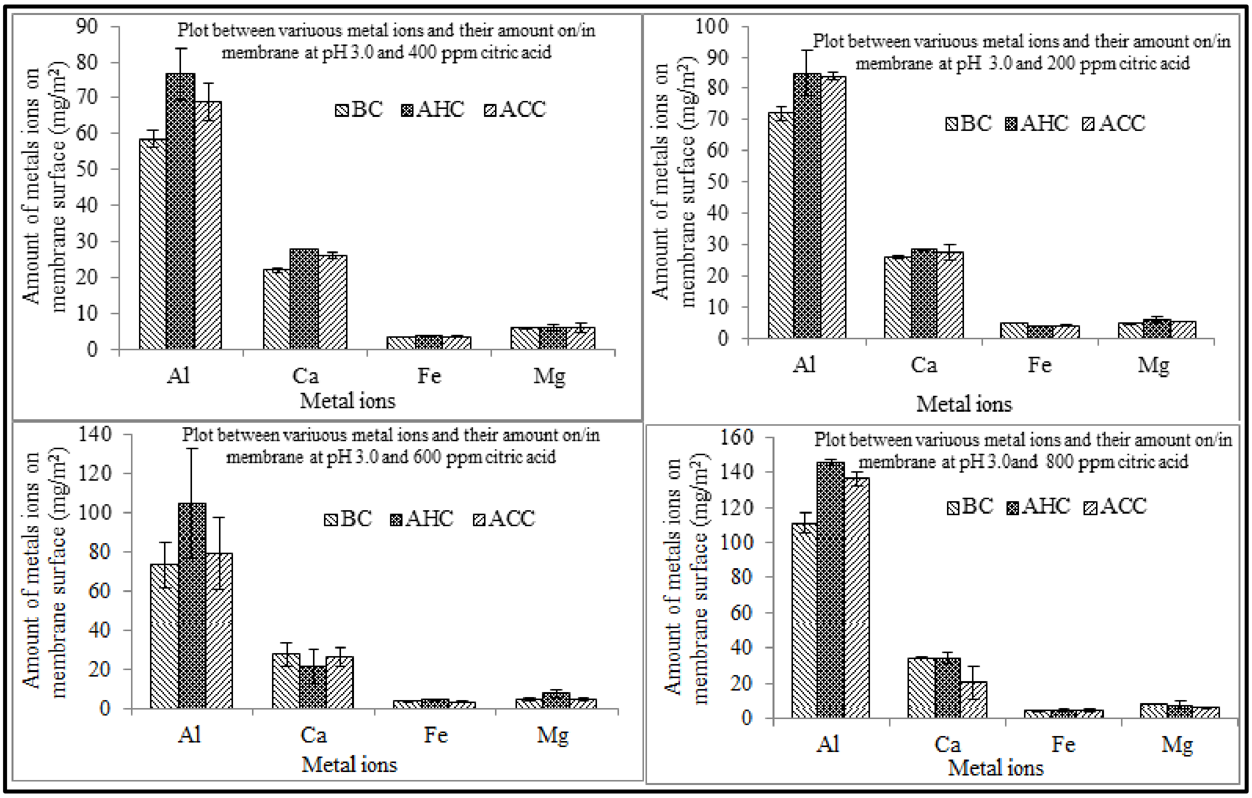


Figure 4-16: Metal ions concentration in membrane fibers during citric acid treatment at pH 3.0

(Note: BC= Before chemical cleaning; AHC= After sodium hypochlorite cleaning; ACC= After citric acid cleaning.)

4.2.2.3 Discussion:

The results of membrane performance at various cleaning conditions (backwash, backwash + NaClO, and backwash + NaClO + citric acid (pH 2.2 and 3.0), as shown in Figure 4-14, revealed that there was no noticeable increase in membrane performance, in terms of permeability, at various citric acid concentrations with similar pH values. However, the membrane performance decreased at the highest citric acid concentration. Hence, the concentration of citric acid does not appear to be a significant factor in explaining the results of Figure 4-14. On the other hand, pH was more important in permeability recovery. This might be due to the fact that metal ions have a higher solubility at lower pH and citric acid as a chelating agent is only effective in removing certain types of metal ions (such as Fe) (Liu *et al.*, 2001).

The membrane permeability recovery for back wash was 58%. This value is dramatically higher than other components. This clearly indicates that major foulants is external form and in the form of cake layer. As earlier studies revealed, backwash is one of the crucial factors that affect UF membrane performance (Chellam *et al.*, 1998; Decarolis *et al.*, 2001). Backwashing by air and water is an effective method for eliminating foulants from the membrane filtration system (Decarolis *et al.*, 2001). During backwashing, reversal of water flow and air bubbling resulted in an increase in the shear stress of membrane and removed the foulants from the pore and peeled off the cake layer on the membrane surface (Decarolis *et al.*, 2001). Precipitation of metal ions (iron, calcium, manganese) was often detected and was suspected to be the cause of membrane fouling. The mentioned elements are also present in surface water in dissolved form. They cannot be removed by UF, and chemical-enhanced backwash seems to effectively reduce concentration of metal ions (Decarolis *et al.*, 2001). However, the use of chlorine during backwash process may boost manganese and carbonates precipitation. The use of air during backwash may increase carbonate precipitation due to CO_2 stripping. This case is more serious for outside-in membrane configuration (Laine *et al.*, 2003).

The membrane permeability increased further after backwash + NaClO treatment. The value of change in permeability due to combined effect of backwash and NaClO was 53.0±3.0 L m^{-2} h^{-1} bar^{-1}, which meant that 22.9% permeability recovery was due to NaClO treatment. This result is in agreement with study of Chae *et al.*, 2009, who suggested that most of the foulants are organic matters. It was also revealed that citric acid treatment further increased the membrane permeability. However, it is not as effective as NaClO. The permeability recovery was up to 16.03% for citric acid concentration of 600 mg/L at pH 2.2. As shown in Figures 4-15 and 4-16, the removal of metal ions was not significant as expected. Citric acid treatment did not seem to effectively remove metals from the membrane. In some cases, there was an increase in amount of metal ions that remained on the membrane after chemical cleaning.

The citric acid treatment targeted to remove metals in membrane yielded variable results. The reason could be one among several factors {i.e. permeate water used to soak with citric acid also contained metals ions, membrane fouling was not uniform on the membrane surface, harvested fibers (5-10) a small sampling compared to thousands of membrane fibers tangled in a single membrane module}. Furthermore, the existence of metals ions in feed and permeate water would mainly be in dissolved form (Chae *et al.*, 2009). UF membrane is not able to remove metals, therefore metals were present in permeate as well as inside the lumen of the membrane. These are likely the causes for fluctuation on amount of metals in/on membrane during this study. Further enhancement of membrane permeability and removal of metals could be achieved by using milliQ water during the backwash and cleaning process. Therefore, further investigation is required to predict responsible factors to recover membrane permeability and chemically enhanced backwashing (specifically the use of citric acid, which may be beneficial for removing metals).

Compared to the cleaning efficiency of various methods such as physical method and chemical methods, physical method was more effective than the chemical methods. Among the various chemical methods, NaClO was found more effective, which was also indicated by Chae *et al.*, (2009).

4.3. Effect of various permeate cycles on membrane performance

The results reported in above sections indicate that backwash is an important factor in permeability recovery. Thus, an optimal permeate cycle can be found to achieve the minimum frequency of backwash, and then a maximum water recovery can be achieved, which has a significant economic impact. This study was focused on evaluating the membrane performance in terms of TMP and permeability, as well as, TOC values, rate of change in TMP, recovery at various permeate cycles (different permeation times). Two sets of experiments (Set I- 19/03/2012 to 19/04/2012 and Set II- 24/04/2012 to 31/05/2012) were performed at various permeate cycles, keeping constant flux mode by controlling permeate flow rate (typically 0.6L/s) over 48 hours of operation. The main parameters used for evaluating membrane performance were normalized permeability and TMP. With a constant flow rate, the data recorded in the computer system for TMP and permeability were downloaded and extracted every four hours. During this study, membrane fouling was observed with an increased rate of TMP (kPa/hr.), which was evaluated from the slope of TMP curves. The equations for TMP increase and permeability decrease are given by equations (5) and (6). Water recovery was also evaluated for each production cycle according to formula in the operation manual, given by equation (7). The permeate cycle in this study was defined as the continuous filtration time between two backwashing events. Sometimes a production cycle was also used to express permeate cycle. Therefore, permeate cycle of 10 minutes would result in six backwashing events in one hour. Membrane samples were harvested before starting operation and after 48 hours of operation. After completion of 48 hours operation, membrane module was cleaned with NaClO (200 mg/L), followed by 200 mg/L citric acid at pH 2.2 adjusted by adding phosphoric acid. The membrane module was soaked for 3 hours in each chemical solution in the membrane tank.

For each of the sets, the increase in TMP percentage (%) was calculated according to the formula:

$$\text{TMP increase(\%)} = \frac{(\text{TMP}f - \text{TMP}i)}{\text{TMP}i} \times 100 \qquad (5)$$

Where, TMP_i= Initial TMP; TMP_f= Final TMP

Similarly, permeability decreased (%) was calculated according to the formula below:

$$\text{Permeability decrease (\%)} = \frac{(\text{P}i - \text{P}f)}{\text{P}i} \times 100 \qquad (6)$$

Where, P_i = Initial permeability; P_f = Final permeability.

4.3.1. Membrane performance

Figures 4- 17 (A) and (B) represent the TMP profiles for set-I and set-II study over 48 hours of pilot plant operation. Similarly, Figures4-18 (A) and (B) denote permeability profiles for set-I and set-II study over 48 hours of pilot plant operation. TMP increased and permeability decreased over 48 hours of operating time. From the TMP and permeability profiles, it was noted that an increase in permeate cycle length (a decrease in backwash frequency) resulted in an increase in TMP and a decrease in permeability. Those observations indicated that the changes in TMP and permeability are dependent on the permeate cycle length or backwash frequency.

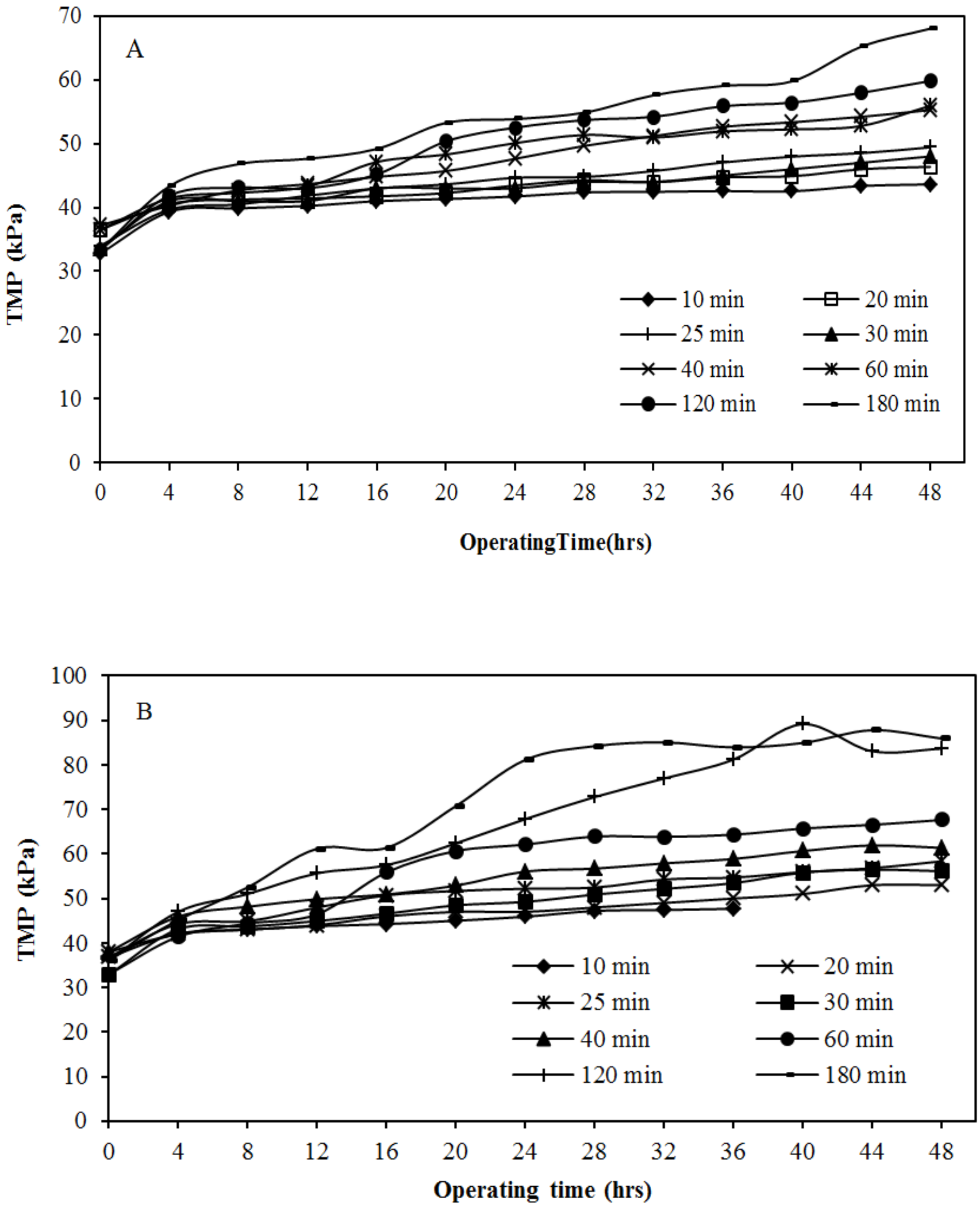


Figure 4-17: TMP profile for different permeate cycles over 48 hours operation time. (A)-(set-I) and (B)- (set-II)

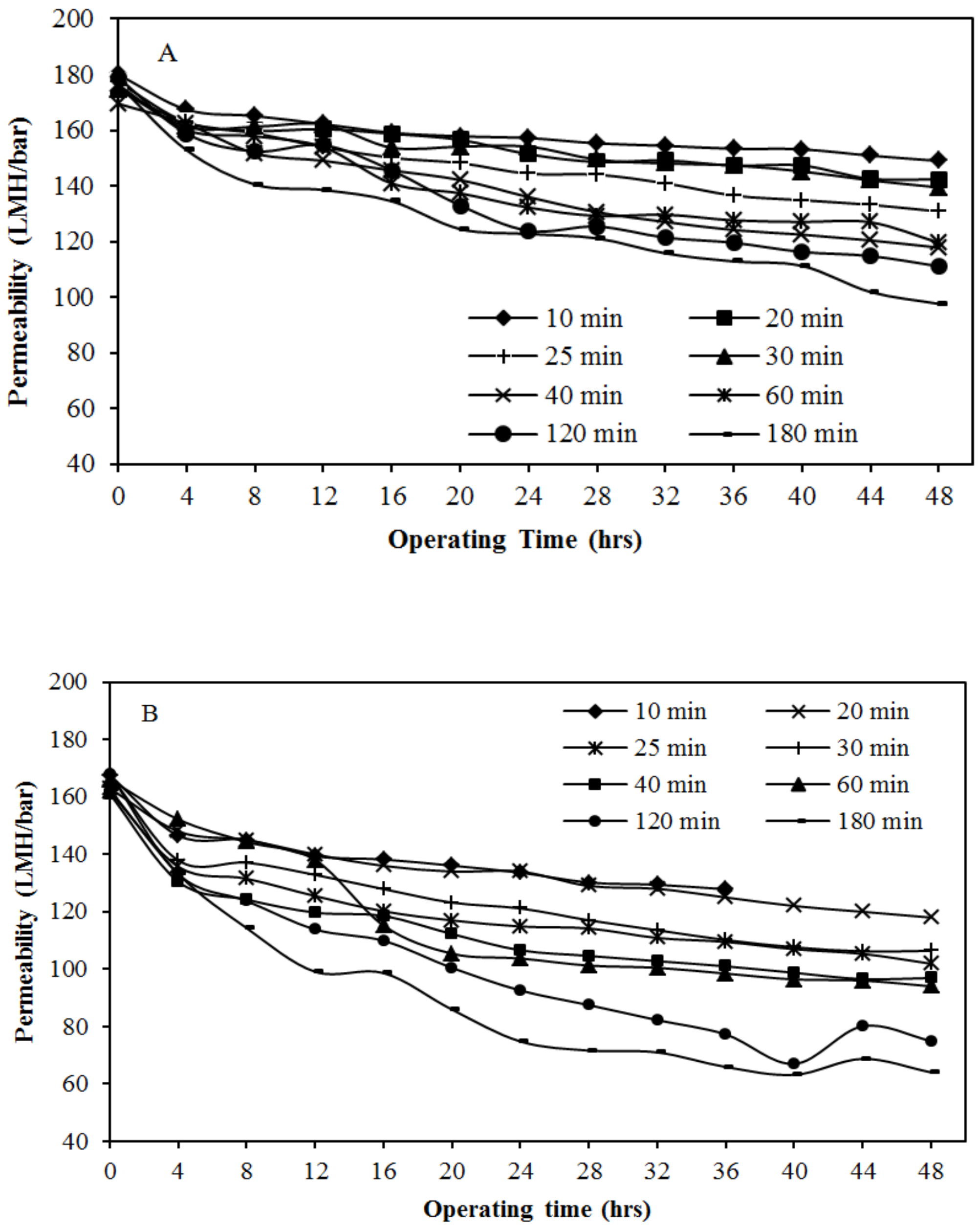


Figure 4-18: Permeability profile at different permeate cycles over 48 hrs. operation time. (A) - (Set-I) and (B) - (set-II)

Table 4-3 and 4-4 show the TMP increase (%) and permeability decrease (%) at various permeate cycles ranged from 10 – 180 minutes for set-I and set-II studies, respectively. According to the results for set-I, the permeability decrease (%) (ranged from 17% - 45%) and TMP increase (%) (ranged from 33% - 104 %) increased with the increasing permeate cycle length (decreasing backwash frequency). Though, similar trends were also observed during set-II study, the values of TMP increase (%) and permeability decrease (%) were substantially different with set-I study. These results revealed that decreasing permeate cycles or increasing backwash frequency noticeably reduced fouling.

Table 4-3: Summary of TMP increased (%) and Permeability decrease (%) at various permeate cycles (Set-I)

Permeate cycle time(min)	10	20	25	30	40	60	120	180
TMP increase (%)	33	27	45	43	49	53	80	104
Permeability decrease (%)	17	18	26	20	30	32	38	45

Table4-4: Summary of TMP increased (%) and permeability decrease (%) at various permeate cycles (Set-II)

Permeate cycle time(min)	10	20	25	30	40	60	120	180
TMP increase (%)	33	39	58	71	62	105	132	138
Permeability decrease (%)	24	28	37	37	40	43	55	61

4.3.2. Foulants analysis

a) Organic analysis:

Figures 4-19 and 4-20 represent the extracted TOC amount at different permeate cycles. For each set of experiment, membrane fibers were harvested from the membrane module and analyzed for organic foulants using TOC analyser, as explained in chapter 3. Two membrane fibers for each permeate cycle were analyzed. The values in Figure 4-19(A) and 4-20(A) are the average extracted TOC amount from membrane surface. Figure 4-19(B) and 4-20(B) shows the plot between different amounts of TOC extracted from the membrane surface (before operation and after 48 hours operation and permeate cycles). Similarly, Figure 4-19(C) and 4-20(C) represents the TOC amount on/in the membrane after 48 hours operation. These results demonstrated that TOC amount on/in membrane surface increased with an increase in permeate cycle time. Although extracted TOC amount on the membrane surface after 48 hours operation was small, those values increased with increasing permeate cycle length. There is one exception for 25 minutes production cycle (set-II), TOC amount during that production cycle was observed slightly lower compared to others. The reason could be sampling error. The data for 60 minute permeate cycle (set-II) is not included due to a problem that occurred at the pilot plant and therefore membrane fibers couldn’t be harvested.

R^2 values achieved from both set of experiments as shown in Figures 4-19(b), 4-19(c), 4-20(b) and 4-20(c). From those figures, extracted TOC amount is positively correlated with permeate cycles. This suggests that organic foulants were the major foulants and responsible for the deterioration of membrane performance.

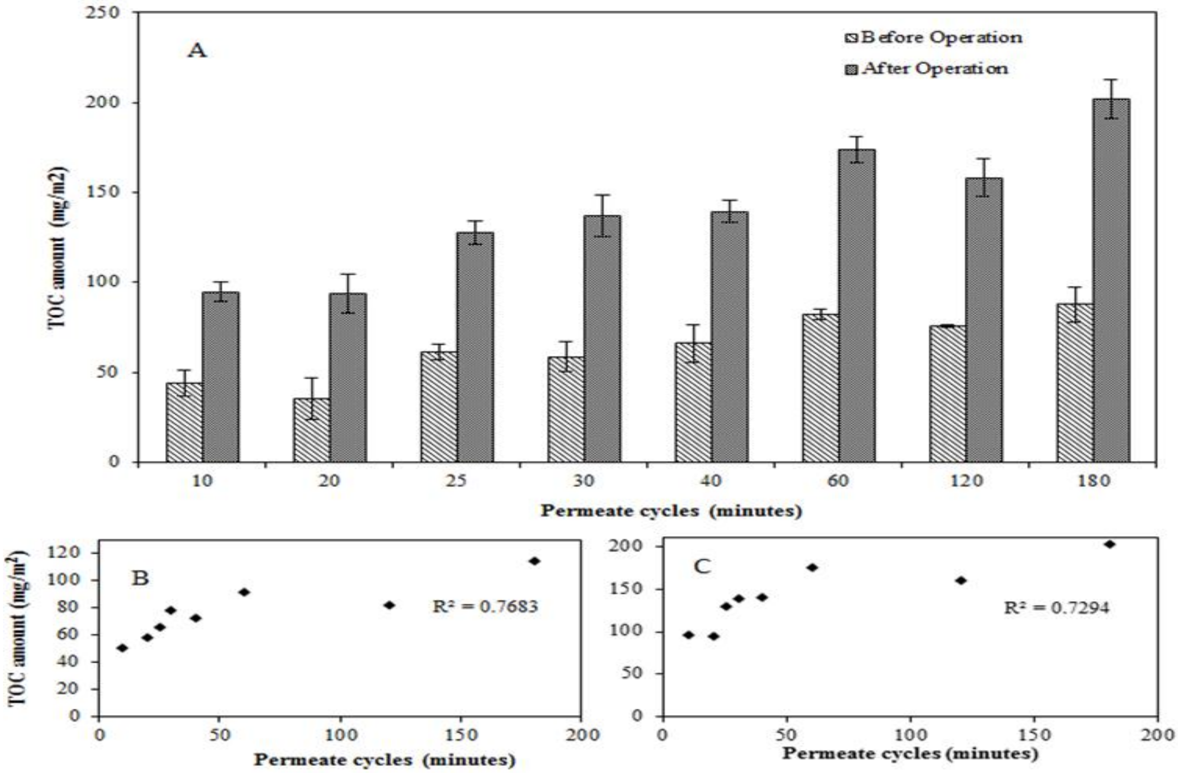


Figure 4-19: (A) TOC extracted from membrane surface, (B) Difference in TOC amount, and (C) TOC amount on the membrane surface after 48 hours operation at various permeate cycles (Set –I).

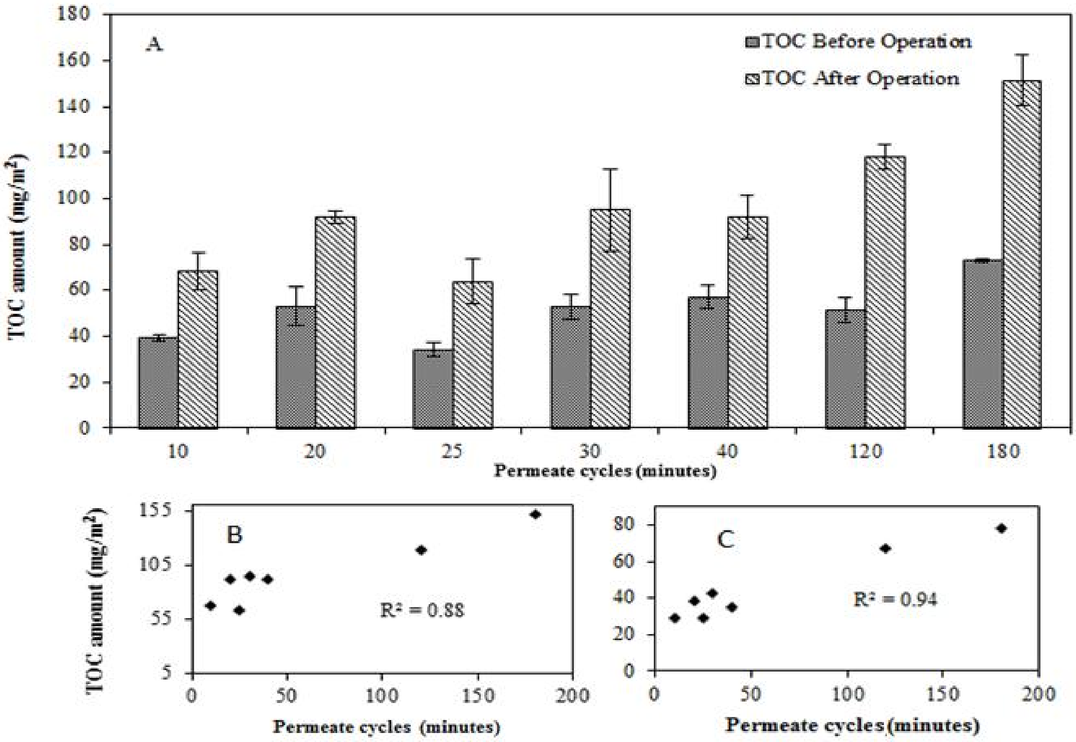
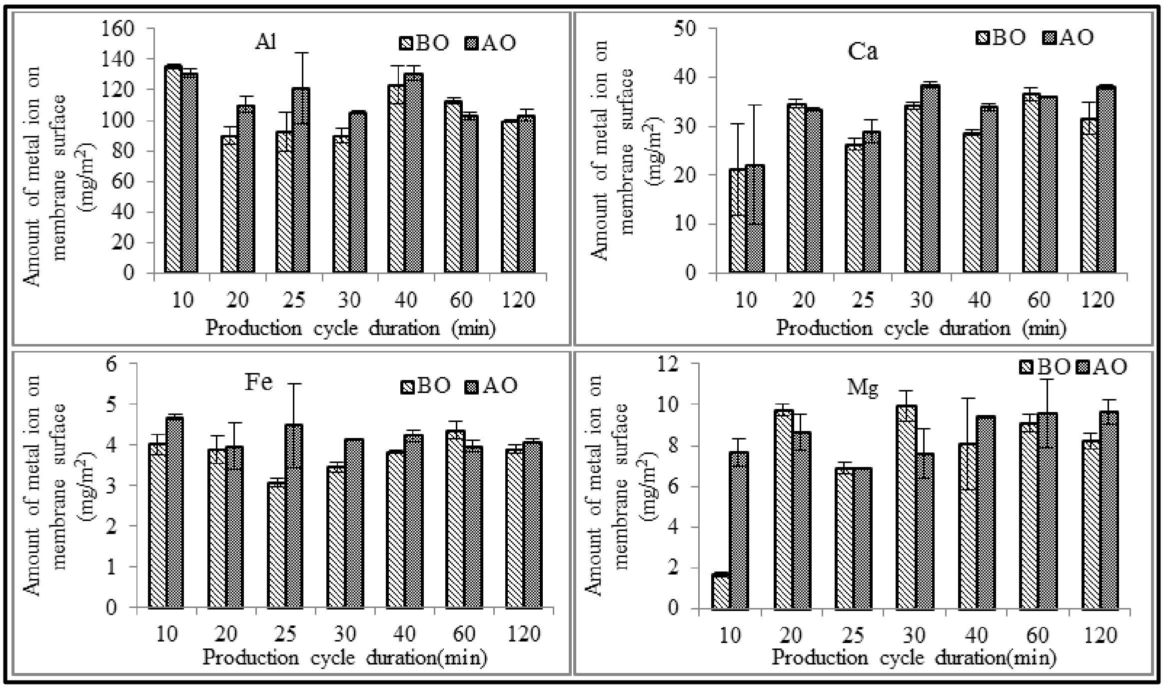


Figure 4-20: (A) TOC extracted from membrane surface, (B) Difference in TOC amount, and (C) TOC amount on the membrane surface after 48 hours operation, cycles (set-II).

b) Inorganic Analysis:

Membrane fibers harvested before and after 48 hours operations for each permeate cycle were analyzed using ICP-AES, as explained chapter 3. Two membrane fibers were used from each sample to prepare duplicates. Figure 4-21 represents the amount of metal ions in the membrane surface before and after 48 hours operation at various permeates cycles. Several studies revealed that divalent cations such as Ca^{2+} exhibited greater flux decline compared to monovalent cations (Jarusutthirak *et al.*, 2007). Therefore, the data reported here only accounted for multivalent metal ions such as Al^{3+}, Ca^{2+}, Mg^{2+}, and Fe^{2+}. The amount of metal ions in the membrane increased after 48 hours operation. However, the amount of metal ions after 48 hours operation didn't show any correlation with permeates cycles. As showed in previous experiments, more aluminium (i.e. up to 135.2±1.2 mg/m^2) than any other metals was found. Calcium was the second (38.5±0.5 mg/m^2), followed by magnesium (9.7±0.3 mg/m^2), and Iron (4.7 ± 0.1 mg/m^2).



(Note: BO: Before Operation, and AO: After Operation)

Figure 4-21: Amount of major multivalent metals ions present in membrane

4.3.3 Recovery:

Permeate cycle length or backwash frequency is often regarded as two important parameters for low pressure membrane filtration of water treatment processes. Permeate cycles are generally used for recovery of membrane filtration. A typical value of recovery is in the range of 90% to 98%. Backwash is effective if backwash pressure is higher than double the operating pressure (Schafer, 2001). Therefore, it would be economically advantageous if backwash frequency is reduced by limiting energy cost during the backwash process. The permeate cycles used during this study ranged from 10 – 180 minutes. Recovery in each permeate cycle is calculated as given in standard operating procedure of the ZeeWeed®1000 pilot plants. The equation used to calculate the recovery % is given below:

$$\text{Recovery (\%)} = \frac{(Total\ permeate\ volume\ )}{(Total\ \ Feed\ water\ volume)} \times 100$$

$$= \frac{(Total\ permeate\ volume)}{(Total\ permeate\ volume + Total\ water\ volume\ of\ membrane\ tank)} \times 100 \qquad (7)$$

The result from Figure 4-22 indicates that an increase in permeate cycle time or a reduction in backwash frequency lead to an increase in the water recovery of the membrane filtration process. Similar trend was reported by Chelan *et al.* (1998). The lowest recovery was 86.1% for the 10 minutes permeate cycle. The highest recovery (%) was found to be 99.1% for the permeate cycle time of 180 minutes.

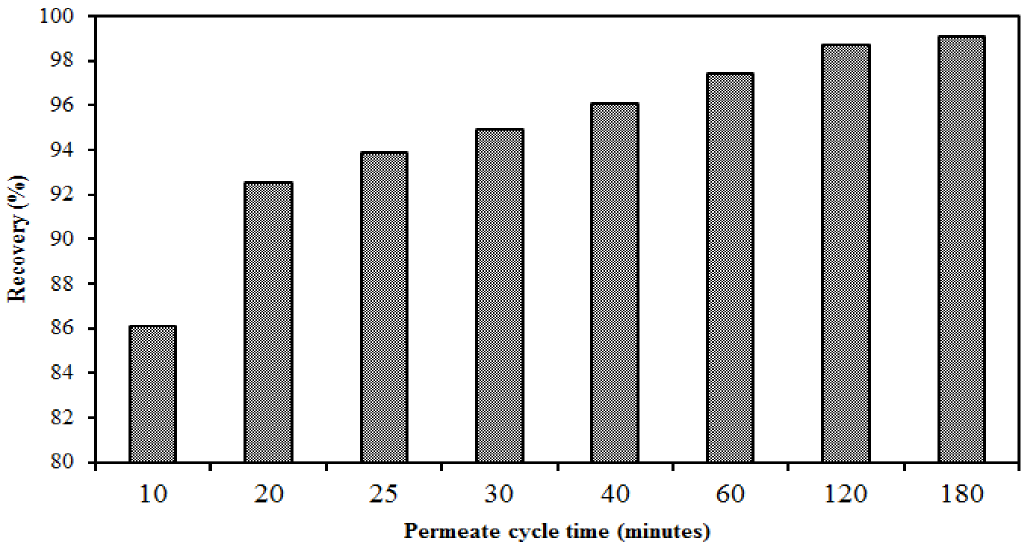


Figure 4-22: Achieved recovery (%) at various permeate cycles.

4.3.4 Rate of change of TMP:

Figure 4-23 presents the plot between fouling rate in term of rate of change of TMP and water recovery obtained at various production cycles for set-I and set-II studies. Up to a certain range of recovery (%), the fouling rate did not have a substantial rise. After that recovery (%), the fouling rate significantly increased. It is clear that the rate of change of TMP increased in an exponential manner (R^2=0.9706, and 0.9494), with elevated recovery (%).

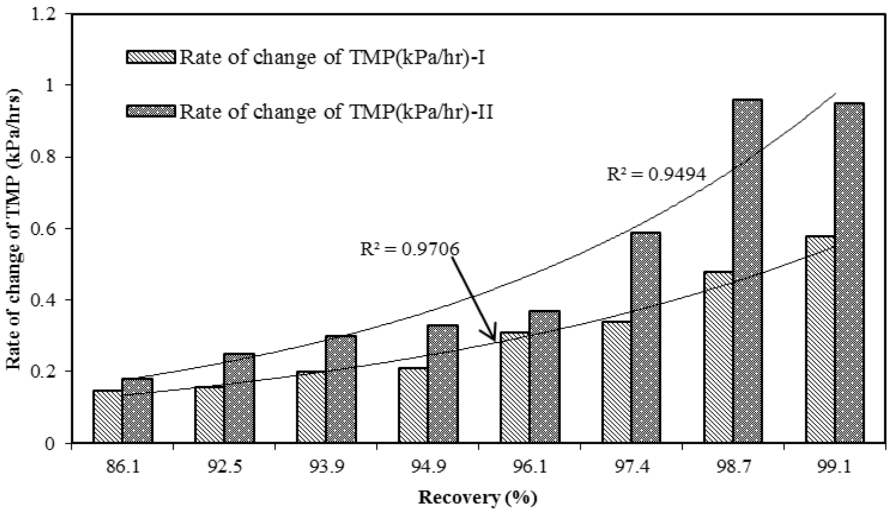


Figure 4-23: Plot between rate of increase of TMP and recovery (%).

4.3.3. Discussion:

Currently, UF membrane technology is increasingly applied in the water treatment field. Backwash is widely used to hydraulically clean the UF membranes by moving back the water flow after certain filtration period. The fraction of fouling that can be removed by the process of backwash is defined as reversible fouling. At the same time, the fouling that cannot be removed by backwash is defined as irreversible fouling. The permeate cycle time or backwash frequency are important parameters to control fouling during membrane filtration process. As shown in Figures 4-17 and 4-18, the extent of the increase in TMP and the decrease in permeability was dependent upon them. A shorter permeate cycle time or higher backwash frequency resulted in a slower declination of membrane performance by alleviating foulants accumulation and cake layer formation, and a longer permeate cycle or lower backwash frequency led to increased membrane fouling, which is consistent with the results observed by Decarolis *et al.*, (2001). Many studies reported that membrane fouling mechanism of NOM on the membrane surface may be due to various processes such as adsorption-deposition on the membrane surface, adsorption-deposition in the pores, and cake formation (Ma *et al.*, 2001; Kweon *et al.*, 2004; Lee et al, 2005). It was proposed that at the beginning of the filtration process, adsorption and deposition occurred in the pores. This was supported by the rapid decrease in the membrane permeability at the beginning of the profile as shown in Figure 4-18. It was also proposed that there was less chance of cake formation on the membrane surface due to shorter permeate cycles. As shown in Figure 4-23, a lower rate of change of TMP was observed when the permeate cycle length was shorter than 30 minutes. The declination of membrane permeability up to this range of permeate cycle was caused mainly by the irreversible fouling. For longer permeate cycles, adsorption-deposition in the pores occur, followed by pore blocking and thicker cake layer formation on the membrane surface. Both irreversible and reversible fouling became major mechanisms during the extended permeate cycle, resulting in higher declination of membrane permeability.

The amounts of TOC during the various permeate cycles after 48 hours operation and difference amount of TOC on/in the membrane surface before and after 48 hours operation of pilot plant are linear with the permeate cycle time (Figure 4-19 and 4-20). An increase in the permeate cycle time or a decrease in the backwash frequency increases the amount of TOC on/in the membrane, indicating that organic matters are the major components of foulants on/in the membrane surface. For shorter permeate cycles, fresh and loosely attached foulants can be easily removed by backwashing. For longer production cycles, thicker and compact organic matters were difficult to remove by backwashing because they become firmly attached to the membrane surface as well as adsorbed into the membrane pores.

According to the ICP-AES result, certain multivalent metals such as Al, Ca, Fe, and Mg were in substantial amounts in the membranes. However, the amount of metals did not follow any conclusive pattern with respect to permeate cycles. The enhancement of membrane permeability is dependent upon the backwash method. Li *et al.* (2009) demonstrated that the backwashing of UF membrane with demineralized water was more efficient than backwashing with UF permeate and the presence of metal ions, especially calcium, was shown to be more responsible for reducing membrane permeability. This is likely due to charge-screen effect, electrical double layer, and calcium complexation (bridging effect between membrane and NOM molecules) (Li *et al.*, 2009). Therefore, above mentioned effects also contributed to the declination of membrane performance.

Comparing the results from two sets of experiments, although similar trends were achieved in both set of studies, the membrane performance in terms of permeability and TMP varied from one to the other (Table 4-3 and 4-4). The membrane performance declined more severely during set-II study as compared to set-I study. Furthermore, the fouling rates in terms of the rate of change of TMP increased with an increase in water recovery or the permeate cycles; however, the fouling rate for set-II was higher than that for set-I (Figure 4-23). In both set of studies, the operating conditions such as permeate flow rate, backwashing duration, cleaning conditions, and starting TMP were similar except seasonal variations and feed water characteristics that may play an important role for the variation of membrane performance.

Both sets of studies were performed from 21/03/2012 to 02/06/2012. The feed water characteristics, such as turbidity, conductivity, pH, and temperature were recorded on different dates. The turbidity, conductivity and temperature values were slightly lower during set-I study compared to set-II study. However, the pH values were slightly higher during set-I study, and the study time frame for set-II was more vulnerable to climate changes compared to the time frame for set-I. For example, snow melting, precipitation; spring turnover, etc. could have been governing factors for the variation of membrane performance.

Several studies indicated that an increase in temperature enhanced the membrane performance due to the decrease in water viscosity (Her *et al.* 2000; Guo *et al.* 2009). A study performed by Guo *et al.* (2000) demonstrated that the TMP decrease was not noticeable when the temperature decreased from 13^0C to 5^0C, and a substantial TMP increase was observed when temperature decreased from 5^0C to 0^0C (Guo *et al.*, 2009). The temperature during this study was varying from 5.6^0C to 9.9^0C. Based on the above facts, temperature may not be the major contributor for the degradation of membrane performance. However, temperature could disturb both equilibrium situation and reaction rate of precipitation and the equilibrium constant of inorganic salt, such as calcium carbonate and calcium sulphate which declines with temperature rise. Hence pH of the solution also declines, which can create favourable condition to precipitate $CaCO_3$, $CaSO_4$ and co-precipitation of organic matters (Her *et al.*, 2000). Kweon *et al.* (2004) observed that the dramatic membrane fouling behaviour was observed by natural particles than other synthetic inorganic particles. An increase in turbidity during set-II study could be an increase in natural particles in the feed water and contributed to the membrane fouling process. The above mentioned explanations are some of the suspected factors responsible for more membrane fouling during set-II experiment. However, a detailed study is needed to confirm specific factors responsible for the degradation of membrane performance and fouling.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions:

The objectives of this study were to evaluate the ageing effect on membrane used in a full scale plant and to develop cleaning strategies (chemical concentration and soak time) to improve the cleaning efficiency and extend membrane lifespan by using pilot scale plant testing at Bare Point water treatment plant. Based on the results presented in chapter 4, the following conclusions can be inferred:

1. Sodium hypochlorite exposure contributes to membrane ageing, while citric acid exposure has a limited effect on membrane ageing.
2. Membrane fouling increases with an increase in operating time. Inorganic foulants mainly include Al, Ca, Mg, and Fe ions.
3. Cleaning chemical exposure does not account for all of the increase in membrane ageing. The mechanical stressors of trans-membrane pressure (TMP), backwash, and aeration agitation may have some positive correlations to membrane ageing. However, chemical cleaning plays the dominant role in membrane mechanical strength deterioration (i.e., ageing).
4. The cleaning efficiency of sodium hypochlorite at various concentration and different soak times showed that the combination of lower concentration (100 mg/L) and longer soak time (8 hours) showed higher permeability recovery within experimented concentration limit. an optimal NaClO cleaning at 100mg/L and 8 hours soak time is suggested.
5. Organic foulants were the major foulants and responsible for the declination of membrane permeability. Inorganic foulants such as Al, Ca, Fe, and Mg have negligible effects on membrane performance. At the same time, sodium hypochlorite

was effective for organic foulants removal. On the other hand, its application increased the metal ions on membranes.

6. Among the efficiency of various cleaning processes, physical cleaning process was more efficient in cleaning the membrane. For example, backwash with air sparging showed a superior method compared to chemical cleaning.
7. There were not substantial differences in permeability recoveries of different concentrations of citric acid treatment within the limit in this study. PH value was shown to be more important than concentration of citric acid. A lower pH value (2.2) showed a higher permeability recovery than a higher pH (3.0). An optimal citric acid cleaning at 200pm and pH 2.2 is suggested.
8. Backwash frequency is an important operating parameter used to recover stable membrane performance and control membrane fouling. Lower permeate cycle or more backwash frequency was able to achieve stable permeability over the operating time by substantially reducing fouling rate.
9. Increasing permeate cycle or decreasing backwash frequency resulted in an increase in feed water recovery, up to a certain period of permeate cycle. This achievement of recovery remained almost stable after certain permeate cycle time, emulating a logarithmic relationship.

5.2 Recommendations:

1. Membrane fouling is importantly dependent upon the characteristics of feed water and it influenced the whole water treatment process. Therefore, it is very important to explore general correlations between fouling potential and feed water characteristics (TOC, SUVA, particle counts, turbidity, pH, temperature, inorganic ions concentrations, organic fractionation, and molecular distribution.)

2. Characteristics of back washing water also influenced the cleaning efficiency of the whole cleaning process. UF membrane is unable to filter metals and small organic molecules, resulting in a significant amount of metals and organics in UF permeate. Therefore, it would be beneficial to explore the membrane performance using demineralized water and chemical enhancement backwashing.

3. The temperature of the feed water affects the properties of membrane and fouling potential of various organic and inorganic constituents. Therefore, it would be beneficial to install a temperature control instrument in the pilot plant for further study.

4. The backwash cleaning demonstrated an effective method for controlling fouling; therefore further research is needed to optimize the cleaning efficiency of backwash process. This includes backwash duration, backwash frequency, air sparging time, and chemically enhanced backwash.

5. From the results of the current study, soak time, chemical strength, cleaning circumstances, back wash frequency, and back wash procedure affect the membrane performance. Therefore, further study needs to explore the effect of varying cleaning parameters on membrane life and operational cost. The seasonal changes in membrane fouling and performance are recommended for further studies.

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APPENDICES: A

Table A1: Sodium hypochlorite concentration, dose and corresponding soak time.

Sodium hypochlorite			
Concentration(mg/L)	Dose (mg.hr/L)		
	420	600	800
	Soak time (hrs.)		
100	4.2	6.0	8.0
200	2.1	3.0	4.0
300	1.4	2.0	2.7
500	0.84	1.2	1.6

Table A2: TOC analyser verification experiment

Experiment	Glucose Conc.(mg/L)	Theoretical TOC value (mg/L)	Measure TOC value (mg/L)	Exact TOC (mg/L)
Blank	0.00	0.00	0.09	0.09
1	1.80	0.72	0.81	0.72
2	5.80	2.32	2.55	2.46
3	11.20	4.48	4.74	4.65
4	20.50	8.20	8.20	8.11
5	30.00	12.00	11.20	11.11
6	51.00	20.40	18.10	18.01

Table A3: TOC extract measured at various time intervals during experiment 1.

Membrane length(m)	0.480											
Area m^2	0.011304											
		Time(min)										
		Blank	5	10	15	20	25	40	50	60	75	90
Volume of NaOH(pH 9.98) Solution		298	300	270	240	210	180	150	120	90	60	30
TOC(ppb)			562	622	668	702	744	772	842	882	867	978
Exact Conc(ppb)			264	324	370	404	446	474	544	584	569	680
Amount of Organic Carbon(mg)			0.08	0.10	0.11	0.11	0.12	0.13	0.15	0.15	0.15	0.16
Organic carbon Extract(mg/m^2)			7.0	8.4	9.4	10.0	10.7	11.1	13.3	13.7	13.6	14.2

Table A4: TOC extract measured at various time intervals during experiment 2.

Membrane length (m)	0.48									
Area (m^2)	0.011304									
		Time (min)								
		Blank	10	20	30	45	60	90	120	150
Volume of NaOH (pH 9.98) Solution			300	270	240	210	180	150	120	90
TOC(ppb)		273	685	718	747	815	858	950	1103	1410
Exact Concentration (ppb)			412	445	474	542	585	677	830	1137
Amount of Organic Carbon(mg)			0.12	0.13	0.14	0.15	0.16	0.18	0.19	0.22
Organic carbon Extract(mg/m^2)			11	12	13	14	15	16	18	20

Table A5: Simulated study results of tensile strength of membrane fibers during various chemical treatment.

Time(year)	Tap Water		Citric Acid		NaClO		NaClO + Citric Acid	
	Average tensile strength(Mpa)	Error (Mpa)	Average tensile strength(Mpa)	Error (Mpa)	Average tensile strength(Mpa)	Error (Mpa)	Average tensile strength(Mpa)	Error (Mpa)
0.0	7.01	0.12	7.01	0.12	7.01	0.12	7.01	0.12
0.5	6.69	0.13	6.61	0.19	6.58	0.14	6.49	0.12
1.0	6.82	0.19	6.55	0.07	6.26	0.06	6.51	0.05
1.5	6.82	0.07	6.76	0.14	5.94	0.20	6.09	0.14
2.0	6.75	0.27	7.07	0.17	5.83	0.12	5.90	0.16
2.5	6.74	0.15	6.65	0.14	5.53	0.15	5.87	0.16
3.0	6.95	0.33	6.72	0.04	5.48	0.09	5.70	0.27

Table A6: Permeability recorded at different NaClO concentration at various soak time.

Soak time (hrs.)	Sodium hypochlorite				Permeability (LMH/Bar)			
	Concentration (mg/L)	Average Conc. (mg/L)	Dose (mg.hr/L)	Average dose (mg.hr/L)	Before clean	After clean	Change	Average Change
21.00	0.00	0.00	0.00		86	93	7	7
4.20	102.50	105.00	430.50	441.00	81	91	11	11.5
4.20	107.50		451.50		81	93	12	
2.10	195.00	196.25	409.50	412.13	80	91	11	9.9
2.10	197.50		414.75		78	87	9	
1.40	285.00	286.25	399.00	400.75	82	89	7	8.4
1.40	287.50		402.50		83	93	10	
0.84	485.00	495.00	407.40	415.80	85	94	9	8.4
0.84	505.00		424.20		85	92	8	
6.00	107.50	107.50	645.00	645.00	85	104	19	17.3
6.00	107.50		645.00		80	96	15	
3.00	192.50	198.75	577.50	596.25	74	91	17	16.9
3.00	205.00		615.00		76	92	17	
2.00	297.50	300.00	595.00	600.00	88	103	15	15.2
2.00	302.50		605.00		84	100	16	
1.20	470.00	492.50	564.00	591.00	85	101	16	14.3
1.20	515.00		618.00		85	98	13	
8.00	110.00	106.25	880.00	850.00	85	107	21	19.6
8.00	102.50		820.00		81	99	18	
4.00	207.50	208.75	830.00	835.00	81	95	13	14.9
4.00	210.00		840.00		76	93	17	
2.70	310.00	310.00	837.00	837.00	85	100	14	13.4
2.70	310.00		837.00		79	92	12	
1.60	480.00	492.50	768.00	788.00	87	101	14	15.9
1.60	505.00		808.00		85	103	18	

Table A7: Summary of permeability change during NaClO treatment.

NaClO Conc (mg/L)	**Soak time (hrs.)**	**NaClO Dose (mg.hr/L)**	**Average Change in permeability (LMH/bar)**	**Standard Deviation**	**Error**
0	21.00	0	6.58	0	0
100	4.20	420	11.54	1.3	0.9
200	2.10	420	9.91	1.4	1.0
300	1.40	420	8.42	1.9	1.4
500	0.84	420	8.45	0.7	0.5
100	6.00	600	17.26	2.6	1.9
200	3.00	600	16.94	0.4	0.2
300	2.00	600	15.22	0.6	0.4
500	1.20	600	14.30	2.3	1.6
100	8.00	800	19.60	2.1	1.5
200	4.00	800	14.95	2.5	1.8
300	2.70	800	13.36	1.5	1.0
500	1.60	800	15.94	2.9	2.0

Table A8: Summary table for soak time, permeability change at various concentration of sodium hypochlorite

Soak time (hrs.)	Actual NaClO Dose (mg.hr/L)	Average Change in permeability (LMH/bar)	Error
100 mg/L Sodium Hypochlorite			
0.0	0.0	0.0	0.0
4.2	441.0	11.5	0.9
6.0	645.0	17.3	1.9
8.0	850.0	19.6	1.5
200 mg/L Sodium Hypochlorite			
0.0	0.0	0.0	0.0
2.1	412.1	9.9	1.0
3.0	596.3	16.9	0.2
4.0	835.0	15.0	1.8
300 mg/L Sodium Hypochlorite			
0.0	0.0	0.0	0.0
1.4	400.8	8.4	1.4
2.0	600.0	15.2	0.4
2.7	837.0	13.4	1.0
500 mg/L Sodium Hypochlorite			
0.0	0.0	0.0	0.0
0.84	415.8	8.5	0.5
1.20	591.0	14.3	1.6
1.60	788.0	15.9	2.0

Table A9: Summary table of change in permeability at various NaClO cleaning conditions

NaClO Concentration (mg/L)	Soak time (hrs.)	Exact NaClO Dose (mg.hr/L)	Average Change in permeability (LMH/bar)	Error
		420 mg.hr/L		
0	21	0	6.58	0
100	4.2	441	11.54	0.9
200	2.1	412	9.91	1.0
300	1.4	401	8.42	1.4
500	0.84	415	8.45	0.5
		600 mg.hr/L		
0	21	0	6.58	0.0
100	6	645	17.26	1.9
200	3	596	16.94	0.2
300	2	600	15.22	0.4
500	1.2	591	14.30	1.6
		800 mg.hr/L		
0	21	0	6.58	0.0
100	8	850	19.60	1.5
200	4	835	14.95	1.8
300	2.7	837	13.36	1.0
500	1.6	788	15.94	2.0

Table A10: Summary of TOC result during sodium hypochlorite clean

Conc of NaOCl (mg/L)	Soak time(hrs)	Dose(mg.hr/L)	TOC Before Hypo Clean(mg/m2)	Error	TOC After Hypo Clean(mg/m2)	Error	TOC Difference(mg/m2)	Error	Removal %
500	0.84	420	78.46	2.4	73.64	0.1	4.82	2.5	6.14
500	1.2	600	138.91	3.7	115.5	6.3	23.41	2.6	16.85
300	1.4	420	112.1	3.1	103.2	4.6	8.8	7.6	7.94
500	1.6	800	96.72	1.8	62.94	6.0	33.77	4.1	34.93
300	2	600	113.8	1.9	89.46	3.9	24.34	5.8	21.39
200	2.1	420	107.03	3.4	88.33	12.0	18.69	15.8	17.47
300	2.7	800	122.6	3.2	81.9	7.9	40.7	11.1	33.20
200	3	600	130.9	14.9	89.8	11.3	41.1	3.5	31.40
200	4	800	96.39	3.1	54.11	0.8	42.28	3.9	43.86
100	4.2	420	127.84	7.9	104.76	2.2	23.08	5.7	18.05
100	6	600	78.68	2.6	50.77	4.1	27.89	6.7	35.47
100	8	800	117.06	0.9	48.2	2.3	68.85	3.2	58.82
0	21	0	88.83	1.6	80.99	2.7	7.84	4.2	8.83

Table A11 : Summary of multivalent metal ions in/on membrane during sodium hypochlorite treatment

Conc. of NaClO (mg/L)	Soak time (hrs.)	Al				Ca				Fe				Mg			
		BC	Error	AC	Error	BC	Error	AC	Error	BC	Error	AC	Error	BC	Error	AC	Error
100	4.2	27.6	0.8	84.6	10.4	18.0	0.5	30.5	4.5	3.9	0.1	4.5	0.7	2.4	0.5	7.3	1.2
300	1.4	53.4	8.3	64.1	4.3	21.5	2.4	26.8	3.6	3.7	0.2	4.2	0.1	5.1	1.2	5.0	0.4
500	0.84	58.3	10.2	62.8	17.0	22.0	2.8	22.6	7.4	3.7	0.3	4.0	0.6	4.3	0.9	4.5	2.5
300	2.7	88.2	6.2	105.1	2.5	31.8	2.0	35.3	2.1	5.4	0.1	5.3	0.0	7.1	0.2	9.4	1.1
300	2	98.1	5.3	86.7	13.0	31.4	0.4	28.6	2.2	3.7	0.2	3.7	0.3	6.8	0.7	8.2	0.6
500	1.6	90.2	3.9	135.6	11.4	23.9	5.9	26.1	10.6	4.4	0.0	4.9	1.1	6.9	0.0	10.6	0.5
500	1.2	81.0	14.4	82.3	0.2	30.4	18.2	30.7	1.8	4.0	2.1	4.5	0.5	6.5	3.6	7.2	0.9
100	6	83.4	4.4	107.2	4.2	33.8	0.3	34.4	3.9	3.8	0.1	3.7	0.1	7.7	0.4	10.5	1.3
100	8	84.9	12.0	91.1	6.9	31.6	12.2	33.1	0.2	4.3	2.0	4.1	0.4	6.9	3.5	7.7	1.2
0	21	76.2	3.1	86.1	7.3	27.9	13.6	34.0	4.9	4.9	2.5	3.6	0.3	7.3	3.3	8.3	0.5
200	2.1	72.8	2.8	105.1	2.5	30.0	0.6	35.3	2.1	3.9	0.1	5.3	0.0	9.1	1.1	9.4	1.1
200	3	129.1	7.4	137.3	26.4	35.5	3.3	19.5	6.9	4.5	0.4	4.9	1.4	9.1	0.6	8.9	2.1
200	4	109.1	0.5	111.3	2.1	35.4	3.3	36.6	1.7	4.7	0.4	4.7	0.1	9.5	0.1	8.2	0.0

Note: BC= Before Sodium hypochlorite clean, AC: After sodium hypochlorite clean.

Table A12: Summary table of result of citric cleaning

pH	Concentration of NaClO (mg/L)	Concentration of Citric Acid (mg/L)	Average Permeability change (LMH/bar)	Error	Permeability change%	Remarks
	0	0	38.0	5.0	58	Backwash only
	200	0	53.0	3.0	22.9	Backwash + NaClO
2.24	200	200	62.5	4.5	14.5	Backwash+NaClO +Citric Acid
		400	63.5	1.5	16.03	
		600	65.5	3.5	20	
		800	56.5	1.5	5.3	
3.00	200	200	57.5	5.5	6.9	Backwash + NaClO +Citric Acid
		400	58.0	4.0	7.6	
		600	57.0	3.0	6.1	
		800	53.0	0	0	

Table A13: Amount of various multivalent metals ion in/on membrane at different cleaning conditions

pH	Citric Acid Conc(mg/L)	Cleaning condition	Amount of various metals (mg/m^2)							
			Al	Error	Ca	Error	Fe	Error	Mg	Error
2.22	200	BC	73.8	4.6	28.5	0.4	4.1	0.2	6.1	0.2
		AHC	92.3	10.7	32.7	5.0	4.8	0.1	9.3	1.2
		ACC	90.4	9.9	29.9	4.8	3.8	0.0	9.4	1.8
2.26	400	BC	87.8	23.0	14.4	3.2	4.1	0.5	6.2	1.6
		AHC	106.2	17.9	21.3	0.5	3.5	0.1	6.1	1.4
		ACC	86.4	20.8	19.4	6.7	3.7	0.5	5.5	0.8
2.24	600	BC	68.6	12.4	26.8	3.3	4.6	0.5	5.9	0.5
		AHC	91.2	1.5	32.6	1.1	3.9	0.1	8.3	0.3
		ACC	87.0	4.2	30.9	0.1	3.5	0.0	10.8	0.8
2.26	800	BC	107.0	3.5	35.5	1.6	4.0	0.2	12.4	2.2
		AHC	125.7	2.7	37.1	0.9	3.8	0.2	6.9	0.8
		ACC	81.7	7.7	20.1	6.4	3.5	0.3	5.7	3.5
2.98	200	BC	71.9	2.4	26.0	0.5	4.8	0.1	4.6	0.1
		AHC	84.9	7.3	28.2	0.1	4.0	0.0	5.7	0.9
		ACC	83.9	1.2	27.6	2.6	3.9	0.3	5.3	0.1
2.99	400	BC	58.5	2.4	21.8	0.5	3.3	0.1	5.7	0.1
		AHC	76.6	7.3	27.9	0.1	3.5	0.0	6.0	0.9
		ACC	68.8	5.4	26.0	0.9	3.3	0.2	6.0	1.3
3.06	600	BC	73.3	11.5	27.5	5.8	3.5	0.5	4.8	1.1
		AHC	104.5	27.8	21.4	8.7	4.4	0.6	7.7	1.8
		ACC	78.9	18.5	26.4	5.0	3.4	0.4	4.9	0.9
3.04	800	BC	111.0	5.5	34.3	0.2	4.2	0.2	8.3	0.0
		AHC	145.2	1.7	34.1	3.1	4.5	1.0	7.4	2.1
		ACC	136.0	3.8	20.2	9.4	4.6	0.9	6.0	0.4

Note: BC: Before Cleaning; AHC: After NaClO Cleaning; ACC: After Citric Acid Cleaning.

Table A14: Summary table for TMP and Permeability at different cleaning conditions.

TMP (kPa)			Permeability (LMH/bar)			Temperature ^0C	Concentration of Citric Acid (mg/L)	pH	Concentration of NaClO (mg/L)	Remarks
Before clean	After clean	Change	Before clean	After clean	Change					
59	36	23	79	128	49	7.3	200	2.29	200	
58	36	22	80	130	50	7.2	400	2.26	200	
61	36	25	77	128	51	6.7	600	2.24	200	
59	37	22	80	128	48	6.3	200	2.98	200	
58	37	21	80	124	44	6.1	400	2.99	200	
59	38	21	80	121	41	6.3	0	9.36	200	BW+NaClO
57	38	19	82	125	43	6.1	600	3.06	200	
57	36	21	82	128	46	6.1	400	2.26	200	
60	43	17	77	108	31	7.0	0	8.05	0	Back wash
62	41	21	76	113	37	4.9	400	2.97	200	
58	40	18	80	120	40	4.3	200	2.24	200	
60	39	21	78	120	42	5.1	600	2.16	200	
61	42	19	76	110	34	4.6	0	10.02	200	BW+NaClO
58	45	13	80	102	23	4.8	0	8.03	0	Back wash
60	40	20	77	115	38	4.8	600	3.01	200	
57	41	16	81	117	36	4.6	200	3.00	200	
58	40	18	80	118	37	4.9	800	3.04	200	
60	40	20	78	118	40	4.6	800	2.26	200	
58	40	18	80	116	36	5.0	800	2.97	200	
60	40	20	78	115	38	4.7	800	2.28	200	

Table A15: TMP recorded at various permeate cycles over 48 hours operation (set-I)

TMP recorded at various operating time(hrs.)	**TMP(kPa) recorded at various permeate cycles(hrs.)**							
	10	20	25	30	40	60	120	180
0	33	36	34	34	37	36	33	33
4	39	41	40	41	40	41	42	43
8	40	41	40	41	43	42	43	47
12	40	41	42	41	44	43	43	48
16	41	42	43	43	45	47	45	49
20	41	42	44	43	46	48	50	53
24	42	43	45	43	48	50	53	54
28	42	44	45	44	50	51	54	55
32	42	44	46	44	51	51	54	58
36	43	45	47	45	53	52	56	59
40	43	45	48	46	53	52	56	60
44	43	46	49	47	54	53	58	65
48	44	46	49	48	55	56	60	68
TMP increased%	33	27	45	43	49	53	80	104

Table A16: Permeability recorded for various permeate cycles over 48 hours operation (Set-I)

Operating time(hrs.)	Temperature Corrected Permeability (LMH/bar) at various permeate cycles(min)							
	10	20	25	30	40	60	120	180
0	180	175	177	175	170	176	179	176
4	167	163	163	161	162	160	159	153
8	165	160	159	161	152	158	152	140
12	162	160	154	162	149	154	155	139
16	159	159	150	154	146	141	146	134
20	158	157	148	154	142	137	133	124
24	157	151	144	154	136	132	124	123
28	155	149	144	149	131	129	125	121
32	154	149	141	148	127	130	121	116
36	153	147	137	147	124	128	120	113
40	153	147	135	145	122	127	116	111
44	151	143	133	142	120	127	115	102
48	149	142	131	139	118	120	111	98
Permeability decrease%	17	18	26	20	30	32	38	45

Table A17: Amount of TOC extracted from membrane surface(Set-I)

Permeate cycle (minutes)	Average TOC(mg/m^2)				
	Before Operation	Error	After Operation	Error	Difference in TOC(mg/m2)
10	44.1	7.1	94.6	5.4	50.5
20	35.2	11.4	93.8	11.1	58.6
25	61.4	4.5	127.7	6.5	66.3
30	58.7	8.1	137.1	11.3	78.4
40	66.2	10.6	139.4	6.1	73.2
60	82.2	2.6	173.9	7.2	91.7
120	75.4	0.8	158.1	10.4	82.7
180	87.7	9.5	202.2	10.7	114.5

Table A18: Summary of the result of ICP-AES analysis for multivalent metals in membrane fibers(Set-I)

Metal ions (mg/m^2)	Al		Ca		Fe		Mg	
Production cycle time(min)	BO	Error	BO	Error	BO	Error	BO	Error
10	135.2	1.2	21.2	9.2	4.0	0.2	1.7	0.1
20	89.9	5.5	34.6	0.9	3.9	0.3	9.7	0.3
25	92.5	12.7	26.3	1.1	3.1	0.1	6.9	0.3
30	90.0	5.1	34.2	0.7	3.5	0.1	9.9	0.8
40	123.3	12.1	28.8	0.5	3.8	0.0	8.1	2.2
60	112.6	1.9	36.7	1.3	4.4	0.2	9.1	0.4
120	99.7	0.8	31.7	3.4	3.9	0.1	8.2	0.4
	AO	Error	AO	Error	AO	Error	AO	Error
10	130.9	2.7	22.2	12.1	4.7	0.1	7.6	0.7
20	110.1	5.3	33.5	0.4	4.0	0.6	8.6	0.9
25	120.8	23.4	29.0	2.4	4.5	1.0	6.9	0.0
30	105.3	1.1	38.5	0.5	4.1	0.0	7.6	1.2
40	130.8	5.0	34.0	0.8	4.2	0.2	9.4	0.1
60	102.6	2.3	36.0	0.2	4.0	0.1	9.6	1.7
120	103.1	3.7	38.2	0.4	4.1	0.1	9.6	0.6

Table A19: TMP recorded at various permeate cycles over 48 hours operation (set-II)

TMP(kPa) recorded at various permeate cycles(minutes) during 48 hours operation								
Operating Time (hrs.)	10	20	25	30	40	60	120	180
0	37	38	37	33	38	33	36	36
4	42	42	44	43	46	41	47	45
8	43	43	45	44	48	44	51	52
12	44	44	48	45	50	46	56	61
16	44	46	51	47	51	56	57	61
20	45	47	52	48	53	61	62	71
24	46	47	52	49	56	62	68	81
28	47	48	52	51	57	64	73	84
32	47	49	54	52	58	64	77	85
36	48	50	55	53	59	64	81	84
40		51	56	56	61	66	89	85
44		53	57	56	62	67	83	88
48		53	58	56	61	68	84	86
TMP increased%	33	39	58	71	62	105	132	138

Table A20: Permeability recorded for various permeate cycles over 48 hours operation (Set-II).

Operation time (hrs.)	Temperature Corrected Permeability (LMH/bar) at various permeate cycles(minutes)							
	10	20	25	30	40	60	120	180
0	168	163	162	168	161	176	168	163
4	147	148	136	138	131	152	133	133
8	145	145	132	137	124	144	124	114
12	139	140	125	133	120	138	114	99
16	138	136	120	128	119	115	110	99
20	136	134	117	123	112	105	100	86
24	134	134	115	121	107	104	93	75
28	130	129	114	117	105	101	87	72
32	129	128	111	114	103	100	82	71
36	128	125	109	110	101	98	77	66
40		122	107	108	99	96	67	63
44		120	105	106	97	96	80	69
48		118	102	106	97	94	75	64
Permeability decrease%	24	28	37	37	40	43	55	61

Table A21 : Amount of TOC extracted from membrane surface (set-II)

Permeate cycle Time (min)	Average TOC(mg/m^2)				
	TOC Before Operation	Error	TOC After Operation	Error	Difference in TOC(mg/m2)
10	39.3	1.4	68.1	8.1	28.8
20	53.1	6.8	91.8	2.6	38.7
25	34.4	3.0	63.9	9.7	29.6
30	52.8	5.4	95.1	18.1	42.3
40	57.0	5.0	91.8	9.6	34.8
120	51.5	5.5	118.5	5.4	67.0
180	73.04	0.5	151.6	11.2	78.5

Table A22: Rate of increase of TMP and recovery % at various permeates cycle.

Production cycle(min)	Rate of change of TMP(kPa/hr.) (set-I)	Rate of change of TMP(kPa/hr.) (set-II)	Recovery%
10	0.15	0.18	86.1
20	0.16	0.25	92.5
25	0.2	0.3	93.9
30	0.21	0.33	94.9
40	0.31	0.37	96.1
60	0.34	0.59	97.4
120	0.48	0.96	98.7
180	0.58	0.95	99.1

Table A23: Feed water characteristics on various dates.

Feed Water characteristics				
Date	Turbidity (NTU)	Conductivity (µS/cm)	Temperature (^{0}C)	pH
21/03/2012	1.74	101.7	5.6	8.06
24/03/2012	1.43	98.2	6.5	8.06
28/03/2012	1.67	99.0	6.2	8.09
31/03/2012	2.10	99.7	6.1	8.14
05/04/2012	1.52	99.2	5.8	8.09
08/04/2012	1.63	100.6	6.2	8.11
16/04/2012	1.13	101.2	6.3	8.09
19/04/2012	1.82	101.7	6.3	8.14
24/04/2012	2.13	102.7	6.6	7.96
02/05/2012	2.43	102.3	7.6	7.70
18/05/2012	2.63	103.6	9.4	7.61
21/05/2012	2.26	101.2	9.7	7.41
29/05/2012	3.01	104.5	9.9	7.32
31/05/2012	3.21	102.1	9.9	7.36

APPENDICES: B

One Way Analysis of variances (ANOVA) results of simulated study of Tensile strength of membrane fibers.

Table 1B: Summary results of Tap Water Treatment.

Anova: Single actor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
0 year	3	21.37	7.12	0.00
0.5 year	3	20.06	6.69	0.05
1 year	3	20.45	6.82	0.02
1.5 year	3	20.45	6.82	0.04
2 year	3	20.24	6.75	0.21
2.5 year	3	20.21	6.74	0.07
3 year	3	20.84	6.95	0.32

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.41	6.00	0.07	0.67	0.68	2.85
Within Groups	1.42	14.00	0.10			
Total	1.83	20.00				

Table 2B: Summary results of Citric Acid treatment.

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
0 year	3	21.37	7.12	0.00
0.5 year	3	19.82	6.61	0.11
1 year	3	19.64	6.55	0.02
1.5 year	3	20.28	6.76	0.06
2 year	3	21.20	7.07	0.08
2.5 year	3	19.96	6.65	0.06
3 year	3	20.17	6.72	0.01

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.91	6.00	0.15	3.19	0.03	2.85
Within Groups	0.67	14.00	0.05			
Total	1.58	20.00				

Table 3B: Summary results of sodium hypochlorite treatment.

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
0 year	3	21.37	7.12	0.00
0.5 year	3	19.75	6.58	0.06
1 year	3	18.79	6.26	0.01
1.5 year	3	17.83	5.94	0.13
2 year	3	17.48	5.83	0.04
2.5 year	3	16.60	5.53	0.07
3 year	3	16.45	5.48	0.02

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	6.32	6.00	1.05	22.06	2.21E-06	2.85
Within Groups	0.67	14.00	0.05			
Total	6.99	20.00				

Table 4B: Summary results of sodium hypochlorite/citric acid treatment.

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
0 year	3	21.37	7.12	0.00
0.5 year	3	19.46	6.49	0.04
1 year	3	19.54	6.51	0.01
1.5 year	3	18.25	6.08	0.06
2 year	3	17.69	5.90	0.08
2.5 year	3	17.62	5.87	0.08
3 year	3	17.10	5.70	0.21

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	4.45	6.00	0.74	10.65	1.55E-04	2.85
Within Groups	0.98	14.00	0.07			
Total	5.43	20.00				