Study on the surface modification of membrane for water filtration and its performance of chlorine resistance

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Nagasaki University, Graduate School of Engineering

Moe Ma Ma Tin

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長崎大学
NAGASAKI UNIVERSITY

Academic Supervisor:

Professor Shuji Tanabe

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CHAPTER 1

Introduction

1.1. Background

Membrane technology is increasingly becoming popular for the advanced treatment of municipal wastewater. This is mainly because of growing concerns about water quality and pollution trends in relation to more complex global challenges such as rapid urbanization and increasing fresh water demand in the domestic and industrial sectors. To deal with these challenges, several methods have been developed to treat the wastewater and reuse it. In the past few decades, wastewater treatment and reuse has gained interest, and so has advanced wastewater treatment technologies. Among these new technologies, membrane-assisted ones offer consistently high quality treatment of effluent. However, one drawback of this technology is the fouling of the membrane. Such fouling often results in reduced system performance; especially in terms of permeate flux. The decrease in permeate flux and the increase in pressure drop due to fouling can adversely impact the membrane filtration efficiency. Therefore, many research efforts have been dedicated to the development of chlorine-resistant membranes [1]. However, these membranes are susceptible to membrane fouling due to the deposition and adhesion of organic and microbial foulants on membrane surface [2]. To control membrane fouling, the feed water often has to be pretreated using chlorine oxidants to avoid the growth and propagation of microorganisms. Chlorine disinfectant is commonly used in water desalination to reduce biofouling. However, the aromatic polyamide (PA) active layer in reverse osmosis (RO) and Nanofiltration (NF) thin film composite membranes are very sensitive to such chlorine treatment. According to the manufacture, the free chlorine resistance for commercial PA-TFC membrane is 0.1 mg /L. Partial failure of the dechlorination process can result in the deterioration of PA membranes, making the whole membrane useless. Therefore, the development of advances membranes with higher thermal and chemical resistance as well as anti- fouling properties is critically required for water purification.

1.2. Reverse Osmosis and Nanofiltration Membrane

The RO process, which uses polymeric membranes to achieve selective mass transport, has become the simplest and most efficient technique to desalt the seawater and brackish water. An industrially useful RO membrane must exhibit several characteristics such as high water flux, high salt rejection, mechanical stability, tolerance to temperature variation, residual to fouling, and low cost. Commercial available RO membrane for desalination is the (TFC) aromatic PA membrane. Since it appeared around 1980, the TFC have dominated the water desalination market because they show both high flux and very high salt rejection. A typical membrane exhibits a NaCl rejection of 99.5% and a flux of 1.2 m^3/m^2 day for a feed solution of 35mg/L NaCl at 800 psi. A typical base layer of a woven or a nonwoven fabric is over coated with a layer of an anisotropic microporous polymer (usually polysulfone). The surface of the microporous support is coated with an ultrathin layer of a crosslinked aromatic PA. The porous support provides mechanical strength; whereas the thin PA top- layer performs the separation. Still aromatic polyamide have several disadvantages including: Low resistance to fouling: Membrane fouling (scaling, slit, biofouling, organic fouling etc) is the main cause of permeate flux decline and loss of water quality. Limited oxidation tolerance due to the existence of secondary amides and electron–rich aromatic rings [3]. Chlorine is commonly used to kill bacteria in water. However, membrane selectivity is rapidly and permanently lost once exposed to feed water containing more than a few ppb levels of chlorine or hypochlorite disinfectants, which means that additional pre-treatment steps to remove chlorine must be taken before feed water is exposed to polyamide TFC membranes. Commonly, NF membranes are negatively charged so that they can effectively reject multivalent anions such as sulfate and phosphate. The rejection to monovalent ions such as sodium chloride varies from 20% to 80% depending on the feed concentration and the material and manufacture of the membranes. The operation pressure for NF is considerably lower than the one for RO, which reduces the operating cost significantly. With the advantage of high fluxes, low operating pressure, high rejection to divalent ions and low retention of monovalent ions, low investment and operating cost, the NF process has been widely applied in the softening of drinking water [4], the removal of heavy metals from wastewater and the concentration of the natural compound [5]. Industrial applications of nanofiltration are quite common in the food and dairy sector, in chemical processing, in the pulp and paper industry, although the chief application continues to be in the treatment of flesh, process and wastewater. Membrane materials for NF include polyethersulfone and polyamides. These materials, however, quickly lose their stability in contact with organic solvents. They are also subject to scaling and fouling and have low stability at high temperature and extremes pH condition [6,7]. Recently, a chlorine-resistant NF membrane has been developed to deliver a membrane system with a high performance in fouling control. Nevertheless, due to lack of actual applications using these membranes; their performance has not yet been understood. Therefore, the motivation for this dissertation was to evaluate the performance of the new produced NF chlorine resistant membrane and develop a proper cleaning protocol using chlorine-based oxidant to optimize operating conditions.

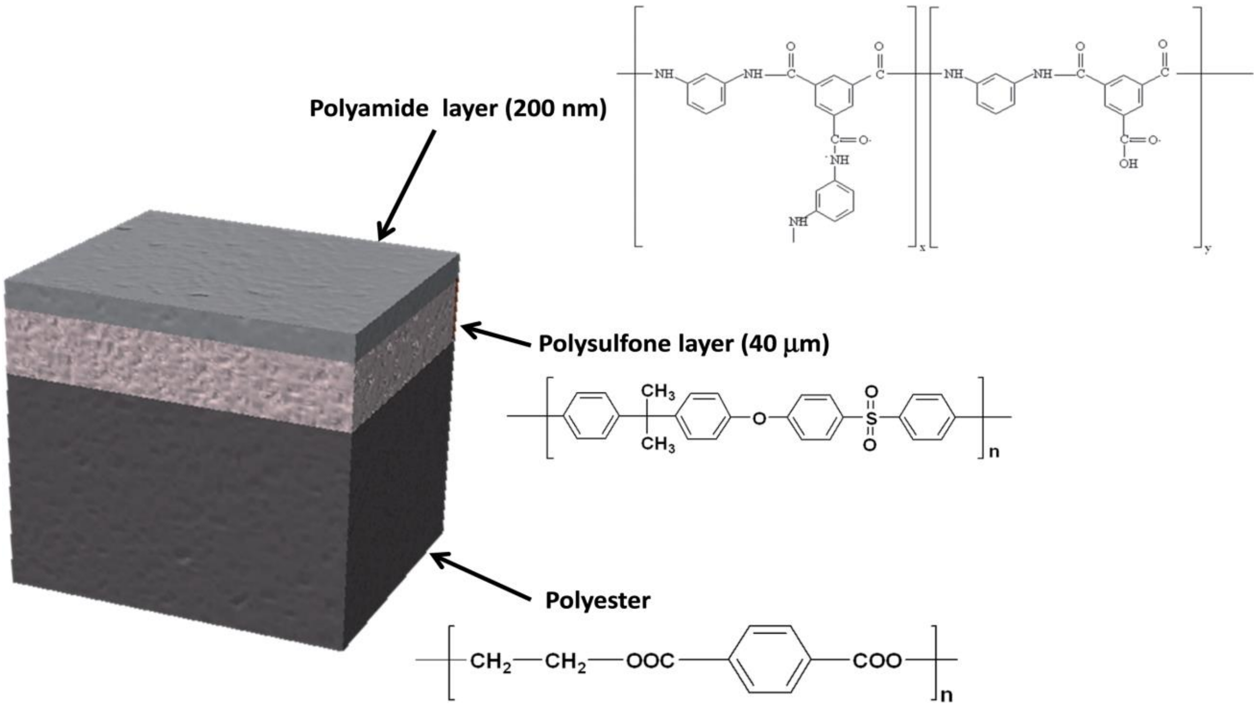

Fig. 1. 1 Schematics of the TFC membrane structure and its composition [8].

1.2.1. Related Works on Surface Modification of Membrane

In surface functionalization, functional groups can be introduced to the membrane surface by plasma treatment or classical organic reactions like sulfonation. For example, by oxygen plasma treatment, aromatic PA RO membranes showed improve hydrophilicity and permeability due to the formation of carboxyl groups [9]. Both water flux and salt rejection were thus increased. However, most membrane materials such as polysulfone, polyethersulfone, polypropylene and polyvinylidenefluoride (PVDF) are hydrophobic. Although these membranes have excellent thermal, chemical and mechanical stabilities, they are easily susceptible to fouling ,i.e., nonspecific adsorption of solutes on the membrane surface and pores resulting in severe flux decline [10]. A common strategy is to graft a layer of hydrophilic polymer on the membrane. Hydrophilic surfaces have proven to be less susceptible for fouling [11] and chlorination [12]. For example, hydrophilic polyethylene glycol (PEG) chains have often been grafted on commercial polyamide membranes for fouling improvement [13]. Other grafting monomers include acrylic acid (AA) N-vinyl pyrrolidone, N,N-Dimethylaminoethyl methacrylate (DMAEMA) [14] and 2 –acrylamido-2-methyl-1-propanesulfonic acid (AMPS) [15]. In grafting, hydrophilic species are covalently bonded to the membrane surface. Membrane properties are therefore permanently change and long term stability of the membranes may be decreased. In coating, however, the chemistry of the initial membranes is retained and a new layer of hydrophilic film bearing the antifouling property is coated on top of the membrane surface via hydrophobic interactions hydrogen bonding, van der Waals attractions, and electrostatic interactions [16]. Two applied techniques have been frequently applied, namely dip coating and dynamic coating. In dip coating, the membrane is dipped into coating solution and the polymer material is then adsorbed on the membrane surface [17]. Dynamic coating can be carried out in dead-end or cross-flow modes. The membranes are loaded in a filtration cell with the surface facing the coating solution. Then, the coating solution is circulated under pressure resulting in the in-situ formation of a layer of polymer film on the membrane surface [16]. To increase the chemical, thermal and mechanical stability of PVA, cross-linking was often conducted by reacting with aldehydes, anhydrides or diisocyanates [18]. Such coatings can be multilayer or monolayer and show high resistance to common organic foulants like proteins and humic substances. If the fouling still occurs, membrane cleaning can be easily applied to regenerate the membrane [19].

1.3 **Research Objective**

Specific objectives in pursuit of this goal are:

1. To investigate the fouling behavior antifouling performance of ESPA2 and CR10 membranes with model organic foulants.
2. To evaluate the effectiveness of epoxy resin as a coating polymer for improving chlorine resistance of RO membranes and the physical effects of the coatings on membrane properties
3. To determine the performance of the new chlorine resistance NF membrane for fouling control that will achieve optimum flux recovery when applied in the wastewater
4. To study the performance of membranes in detrimental ion (calcium, sodium) rejection and to monitor fouling on membranes with their subsequent chemical cleaning
5. To elucidate the correlation between the membrane surface properties affected by chlorination
6. To recover the flux of fouled NF membranes by a chemical cleaning process

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CHAPTER 2

Literature Review

2.1 Overview

During the past few years, demand for freshwater increases rapidly because of rise in population growth and industrial development. To deal with water scarcity, several methods have been developed to treat the waste water and reuse it. As a rising technology, membrane separation technologies have been widely used, which replaced some of the conventional techniques because it does not require phase change and are energy-saving. The membrane separations are becoming an increasingly important tool for separation and concentration of materials. Although there is considerable interest in the use of membrane technology, its efficient operation is hindered by two major factors, namely, concentration polarization and fouling. In search for solution for the problem led to the development of some chlorine-resistant membranes.

2.2 Membrane Separation Characteristics

Membrane separation is characterized by simultaneous reaction of species and product flow through the semipermeable membrane. Membrane performance is based on its high selectivity and flux; good mechanical, chemical and thermal stability of membrane materials, defect – free production, minimal fouling during operation, and good compatibility with the operating environment [1].

2.2.1 Membrane separation basics

A membrane is defined as a permselective barrier between two homogeneous phases. Membrane processes are continuous study- state operations consisting of three streams: feed, product (permeate) and reject (retentate). No one membrane process is suitable for every fluid stream owing to the nature of feed and product requirements as well as the nature of the membrane process and the membrane designed for that process (Table 2.1 and Figure 2.1). Even for the same membrane process, the performance varies depending on the type of feed.

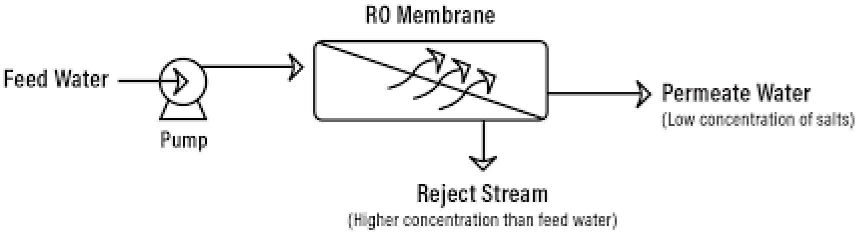

Fig.2.1 Membrane – separation processes [1].

Table 2.1 Classification of water reclamation membrane process.

Process	**Pore size**	**Driving force**	**Transport mechanism**
Microfiltration(MF)	0.05-10 µm	Pressure, 1-2 bar	Sieving
Ultrafiltration(UF)	0.001-0.05 µm	Pressure, 2-5 bar	Sieving
Nanofiltration(NF)	< 0.6 nm	Pressure,15-100 bar	Donnan exclusion / sorption-capillary flow
Reverse Osmosis(RO)	~0.6nm	Pressure, 15-100 bar	Preferential-sorption capillary flow

For example, in the case of RO, the membrane allows the passage of water but rejects almost all the ions and salts resulting in a concentrated salt on the feed side of the membrane, and virtually ion – free product on the other side of the membrane. Thus, the most permeable component (water) gets enriched in the permeate stream while the least permeable component gets enriched in the retentate (salt) stream.

2.3 Membrane Selectivity

Membrane separation is governed by the chemical and physical nature of the membrane material. Separation occurs because of differences in size and shape, chemical properties, or electrical charge of the substances to be separated; for example, microporous membranes control separation by size and discrimination. Rejection coefficient, R, is a reliable indicator of the separation ability of a membrane process [3]:

$$\text{Rejection } (\%),\ R{=}\left(\frac{\text{feed/bulk solute concentration}-\text{product solute concentration}}{\text{feed/bulk solute concentration}}\right)\times \mathbf{100}$$

2.4 Reverse Osmosis

RO is a process for removing solutes such as dissolved ions from a solution using a semipermeable membrane under hydraulic pressure. When a semipermeable membrane is used a barrier to separate water from a concentrated solution of ions, the water moves through the membrane to the concentrated solution due to osmosis to even out the water concentration or equilibrate. Water continue to flow until sufficient osmostic pressure builds up on the concentrated solution side to prevent further flow of water up the concentration gradient. When pressure greater than the osmotic pressure is applied, the flow is reversed. The process is called “reverse osmosis” and results in a concentrated salt solution on the feed side of the membrane and a near pure solution on the other side of the membrane; in effect, water gets squeezed out and flows out through the membrane under pressure. The effective water flow through the membrane at constant temperature is defined by the following equation.

$$J_w = A\,(\Delta P\text{-}\Delta\pi) \tag{2.1}$$

Where J_w is the membrane water flux, A the membrane permeability coefficient for water, ΔP the hydraulic pressure differential across the membrane and $\Delta\pi$ the osmotic pressure differential across the membrane. In practice, the membrane is permeable to some low molecular weight solutes (rejection is always less than 100%). Hence, the real osmotic pressure is $\sigma\Delta\pi$ where σ is the reflection coefficient. Osmotic pressure depends on solute concentration, solution temperature and the type of ions present. For dilute solutions (applicable to membrane case), the osmotic pressure is approximately using the van't Hoff relationship [4]:

$$\Pi = \gamma_i c_i RT \tag{2.2}$$

Where Π is the osmotic pressure, γ_i the number of ions formed when the solute dissociate (e.g., γ_i is 2 for NaCl and, γ_i is 3 for $BaCl_2$), c_i the molar concentration of the solute, R the gas constant and T the absolute temperature. Thus, $\gamma_i c_i$ is the total concentration of ions in kmol/m^3). The solute (salt) flux through the membrane is given by the following equation:

$$J_s = B\,(\Delta C_s) \tag{2.3}$$

Where J_s is the solute flux, B the solute permeability coefficient and ΔC_s the solute concentration difference across the membrane. The value of B is in the range of $5\ (10^{-3})$-$1(10^{-4})$ m^3/m^2 h for RO membrane with NaCl as the solute. While the water flux increases linearly with pressure difference (equation 2.1), the solute flux is independent of pressure and is a function of the concentration difference (equation 2.3). Hence, when the membrane is operating near the osmotic pressure of the feed, the salt passage is not diluted by the product water. During normal operation, when the permeate water flux drops, it follows that the permeate salt concentration will increase. Homogeneous asymmetric cellulose acetates and polyamides made by the phase inversion process and cross- linked TFC polyamides have been the workhorse of RO plants for more than 30 years [5]. A typical spectrum of TFC membranes for various applications is given in Table 2.1. The choice of membrane and membrane element is usually determined by the composition of feed water (e.g, fouling potential) and product water quality. Membranes are synthesized with rejection tailored to the type of application; for example, in the case of SWRO membrane rejection is typically >99.6%, whereas in the case of BWRO, membrane rejection id typically <99%. RO membrane rejection efficiency varied depending on the solute [6].

- Multivalent ions (Ca^{2+}, Mg^{2+}) have a higher rejection than monovalent ions (Na^+).
- Undissociated or poorly dissociated substances have lower rejection (e.g., silica)
- Acids and bases are rejected to a lower extent than their salt.
- Rejection of weak acids and bases is highly pH dependent; when ionized, the rejection is high, and low when non- ionized (e.g., boric acid)
- Co-ions affect the rejection of a particular ion (Na^+ has a higher rejection as Na_2SO_4 than as NaCl).
- Undissociated low molecular weight organic acids are poorly rejected while their salts are well rejected.
- Trace quantities of univalent ions are generally poorly rejected.
- The average rejection of nitrate is significantly less than that of other monovalent ions.
- Negative rejection is sometimes observed for phenol and benzene with CA membranes.
- Rejection of neutral organic solutes generally increases with the molecular weight or diameter of the solute (e.g., caprolactam rejection) is higher than ethanol. Organic components with MW> 100Da are rejected almost completely [7].

Table 2.2 Typical TFC membranes for various applications.

Membrane Type	**Remarks**
Seawater RO membrane[1]	Seawater conversion to industrial water and drinking water purify high TDS brackish water(>10,000 ppm)
Brackish water RO membrane[2]	Production of high – purity water, concentration of food and heavy metal recovery from well water, river water, lake water, or industrial waste water
Low pressure RO membrane[3]	Low pressure brackish water membrane Ideal for small drinking water systems due to low energy consumption
Fouling – resistance RO membrane[4]	Improved fouling – resistance characteristics possibly (not revealed) due to a hydrophilic character and a net negative charge. Applicable where fouling tendency is high
Household RO membrane[5]	For removing solutes larger than 10^{-4} µm, carcinogens such as THM, heavy metal ions, bacteria and germs in household water
NF membrane[6]	Water softening; >98% rejection of divalent ions Removal or concentration of dyes, paints and food liquids

Test Condition:

1. 55 bar g; 32.000ppm NaCl; 25°C; 6.5- 7.0 pH; 10% recovery.
2. 15.5 bar g; 2000 ppm NaCl; 25°C; 6.5-7.0 pH ; 15% recovery
3. 10 bar g; 2000 ppm NaCl; 25°C; 6.5-7.0 pH; 15% recovery
4. 15.5 bar g; 2000 ppm NaCl; 25°C; 6.5-7.0 pH; 15% recovery
5. 4 bar g; 250ppm NaCl; 25°C; 6.5-7.0 pH ; 15% recovery
6. 15.5 bar g; 2000 ppm $MgSO_4$; 25°C; 6.5-7.0 pH ; 15% recovery

Source: CSM membrane catalogue.

2.5 **Disinfection**

Disinfection of RO/NF feed water is required to prevent biofouling of the membranes. However, the disinfected water must be treated with reducing agents if the membrane polymer, (e.g. PA) is damage by oxidants. Disinfection is the selective destruction of pathogenic organisms (bacteria and viruses. Recently, micro constituents such as endocrine disrupting compounds as well as pharmaceutical and personal care products have also come under review. Disinfection is not the same as sterilization, which implies the destruction of all organisms. Disinfection treatment methods commonly used include (a) chlorination ozonation chemical means, (b) photochemical means, e.g. ultraviolet disinfection and (c) physical means such as membrane filtration. Parasites such as *Giardia lamblia* and *Cryptosporidium parvum* are resistant to conventional forms of disinfection such as chlorination, but are removed by other methods such as ozone, ultraviolet irradiation, and membrane filtration [8]. The disinfectant action of chlorine results from its strong oxidizing action on bacterial cell's chemical structure that destroys the enzymatic processes required for life. The effectiveness of chlorine disinfection is a function of the product of contact time and chlorine residual. Chlorine gas is soluble in water (7160 mg/L at 20 °C and 1 bar), and hydrolyses rapidly to form hypochlorous acid or as the hypochlorite of sodium and calcium;

$$Cl_2 + H_2O \longrightarrow HOCl + H^+ + Cl^- \tag{2.3}$$

$$NaOCl + H_2O \longrightarrow HOCl + NaOH^- \tag{2.4}$$

$$Ca(OCl)_2 + H2O \longrightarrow 2\ HOCl + Ca(OH)_2 \tag{2.5}$$

Hypochlorous acid (HOCl) dissociates in water to hydrogen ions and hypochlorite ions (OCl^-). The sum of Cl_2, NaOCl, $Ca(OCl)_2$, HOCl and OCl^- is referred to as "free available chlorine". The power of free chlorine residual decreases with increasing pH. Hypochlorous acid concentration at 20 °C is 90% at pH 7, 50% at pH 7.6 and 10% at pH 8.6. Almost the reverse is true for hypochlorite ions. Hence, automatic monitoring of residual chlorine and automatic feedback of injection rate is necessary to prevent over-dosage or inadequate disinfection.

Minimum chlorine residuals for bactericidal disinfection after 60 min of contact vary between 1 ppm at pH 6.0 and 1.8 ppm at pH 8.0. A hypochlorous residual of 0.5-1 ppm is effective within 30 min. A membrane is viewed to be chlorine resistant if exposure to a biocidal concentration of chlorine (<1 mg/L) does not cause membrane damage in several years [9].

2.6 **Membrane Fouling on RO/NF membrane**

One of the most important issues affecting the development of membrane filtration has been fouling. To device effective cleaning strategies a thorough understanding of membrane fouling and its cause is required. Fouling of NF membrane is typically caused by inorganic and organic materials present in water that adhere to the surface and pores of the membrane and results in deterioration of performance (reduced membrane flux) with a consequent increase in production cost due to increased energy demand, chemical cleaning, reduction in membrane life expectancy and additional labour for maintenance. Membrane foulants can be both inorganic and organic components. Fouling strongly depends on the feed water quality, especially the nature of the foulants and ionic composition of the feed water[10]. The main reasons for membrane fouling are:

- Organic molecules adsorption (e.g. organic fouling, proteins, humic substances)
- Particulate deposition (e.g. colloidal fouling, clay, iron, and alumina silicate)
- Microbial adhesion (e.g. biofouling, bacteria)

General guidelines to minimize fouling are given in Table 2.3. As the SDI value increases, the potential for fouling increases. Iron and manganese are included as suspended solids since under most operation conditions, iron and manganese that are soluble in RO feed water oxidise (soluble ferrous iron, Fe^{2+} => insoluble ferric iron, Fe^{3+}) and deposite on the surface of the membranes. Furthermore, oxidation of the metal can catalyse the oxidation of the membrane leading to membrane failure. The levels of iron, manganese and nickle in feed water must be less than 0.1 mg/L.

Table 2.3 Feed water requirements to minimize fouling [11].

Parameter	Value
SDI_{15}	< 4 or 5
Turbidity	< 1[a] NTU
Iron[b]	< 0.05 mg/L
Manganese	< 0.05 mg/L
Hydrogen sulphide	< 0.1 mg/L
Organics (TOC)	< 10 mg / L

[a] Some membrane manufacturers recommend that turbidity be < 0.2NTU

[b] At pH >7.0 and 5-10 mg/L dissolved oxygen; at lower pH and lower oxygen level, slightly higher iron levels can be tolerated.

As the SDI value increases, the potential for fouling increases. Most manufacturers require that the feed water SDI_{15} (the SDI determined by a 15-min tests) be less than five, while some require an SDI_{15} less than four. Hydrogen sulphide is considered as a suspended solid because it is readily oxidized to form colloidal sulphur; it reacts instantaneously with chlorine to precipitate sulphur at the pH of typical feed water sources. Various techniques can be used to reduce the loading of suspended solids, organics and microbes in feed water. These include physical processes such as media filtration, cartridge microfiltration and chemical treatments. Chemical addition enhances the filter- ability of the solids such as the addition of coagulants. Foulants and their control strategies are addressed in Table 2.4. Since any traces of solids and organics get removed in the first membrane modules in RO and NF systems, these materials typically foul the first stage of an RO/NF system [12].

Table 2.4 Treatment methods for controlling fouling [12].

Foulant	**Fouling control**
General	Hydrodynamics/shear, operation below critical flux, chemical cleaning
Inorganic (Scaling)	Operate below solubility limit, pre- treatment, reduce pH to4-6 (acid addition), low recovery, additives(anti- scalants).Some metals can be oxidized with oxygen
Organics	Pre-treatment using biological processes, activated carbon, ion exchange, ozone, enhanced coagulation
Colloids (<0.5 µm)	Pre- treatment using coagulation and filtration, MF, UF
Biological solids	Pre-treatment using disinfection (e.g. chlorination/dechlorination), filtration, coagulation, MF,UF

Once deposited on the membranes, foulants attract additional solids there by accelerating any fouling problem that might already exist. In addition to solids, microbes, and organics, soluble heavy metals (such as iron) can foul RO membranes when oxidized within the membrane modules. Oxidation can occur in any stage of an RO system when the p H and dissolved oxygen concentration are suitable. Microbes, if left untreated, can reproduce and spread, thereby fouling the entire RO system.

2.6.1 Organic Fouling in nanofiltration membrane

In general, NF membrane are used in water treatment as alternative processes for the removal of natural organic matter (NOM) that cause contamination, taints and color and are vehicles for other materials that bind to these substances [13]. Organic fouling could cause either reversible or irreversible flux decline. The reversible flux decline, due to NOM fouling, can be restored partially or fully by chemical cleaning. Whereas the irreversible flux decline cannot be restored at all even by rigorous chemical cleaning is applied to remove NOM [14]. Membrane fouling in the presence of NOM can be influenced by membrane characteristics [14], including surface structure as well as surface chemical properties, chemistry of feed solution including ionic strength [14], pH[15]; the concentration of monovalent ions and divalent ions [16]. These factors either increase or decrease the fouling rate have been summarized in Table 2.4. As it can be seen that the chemical (Ionic strength, NOM fraction, etc.) and physical parameters, such as pressure, velocity and permeate flux, play a major role in NOM fouling at NF membrane surface. Humic substances in aquatic environments are considered to be the major fraction of NOM, are refractory anionic macromolecules of low to moderate molecular weight. Humic substance contains both aromatic as well as aliphatic components with primarily carboxylic (carboxylic functional groups account for 60-90% of all functional groups) and phenolic functional groups) [17]. As a result, humic substances generally are negatively charged in the pH range of natural waters [18].

Table 2.5. Natural organic matter fouling factors [19].

	Value	NOM Fouling rate	Cause
Ionic concentration	Increased	Increased	Electrostatic repulsion
pH	High pH	Increased	Hydrophobic forces
	Low pH	Increased	Electrostatic repulsion
Divalent cations	Presence	Increased	Electrostatic repulsion and bridging between NOM and membrane surfac
NOM fraction	Hydrophobic	Increased	Hydrophobicity
	Hydrophilic	Decreased	
Molecular or membrane charge	High charge	Increased	Electrostatic repulsion
CP	High	Increased	
Surface morphology	Higher	Increased	Valley blocking
Permeate flux (High Recovery)	Higher	Increased	Hydrophobicity
Pressure	Higher	Increased	Compaction

2.7 Fouling Minimization

Two strategies are usually employed to minimize the effect of fouling. The first group includes minimizing of fouling by using adequate feed pretreatment, membrane treatment and membrane modification. The second group involves membrane remediation by chemical cleaning, which is carried out to restore membrane fluxes. Conventional coagulation filtration pretreatment was designed to remove most of the potential foulant materials from the pretreated feed by prefiltration and more rarely by sedimentation. The degree of the pretreatment, however, is dependent on the raw water quality, particularly its content of organic and inorganic suspended matter. Coagulant and coagulant aids can be added in a pretreatment to increase separation efficiency. When water is treated with coagulant, the fouling usually decrease after prefiltration. Another approach is to avoid scale formation by the addition of scale inhibitors. It is obvious that scaling intensity depends upon the chemical composition of feed water; therefore water with a high scaling potential requires treatment using scale [20]. The chemical species, such as lime and soda or caustic soda are added to hard water in order to remove or reduce the hardness ions. The application of microfiltration (MF) as well as ultrafiltration (UF) as NF prefilters has emerged in the last decade as an efficient method in pretreating surface water. Attempts have been made to modify membrane surfaces in order to make them less vulnerable to fouling [21]. In some cases, the surface roughness increases membrane fouling by increasing the rate of attachment onto the membrane surface and hence the membrane with a rough surface is more prone to fouling than membrane with a smoother surfaces [22]. Colloidal interactions are also important in fouling and charged components tend to cause fouling because of electrostatic attractions between charged components and the membrane. Development of membranes with lower surface charge or surface charge similar to that of the foulant, with hydrophilic character may help solve this specific problem. The effect of the particle concentration on the ultrasonic control of the membrane fouling was investigated by Chen et al [23,24]. The basic principle of operation is that ultrasound removes particles from the surface by causing particle movement in or near membrane.

2.8 Fouling Study Protocols

It is a typical protocol used in fouling studies. For a constant flux operation a protocol would measure the variation of Transmembrane pressure in a similar protocol, where Transmembrane pressure increases with fouling. According to Huiting et al [25] variable system parameters need to be normalized in order to compare system performance and correctly evaluate fouling. Those varying parameters are pressure, temperature and feed water quality. The normalized parameters are

- Normalized water flow or productivity (expressed as mass transfer coefficient (MTC)
- Normalized pressure drop (NPD)
- Normalized salt passage (NSP)

Feed water analysis can give some indication of likelihood of fouling. Some indices have been widely used to determine fouling potential of feed water such as silt density index (SDI) and the modified fouling index (MFI). Also feed water analysis plays an important role in the determination of fouling potential.

2.9 Membrane Cleaning

The decline in membrane performance can be corrected by cleaning the membrane. Cleaning can be defined as “a process where material is relieved of a substance, which is not an integral part of the material” [25]. Physical cleaning methods include for example: hydrodynamic forward or reverse flushing, permeate back pressure, air spurge and automatic sponge ball cleaning. These methods depend on a mechanical treatment to dislodge and remove foulants from the membrane surface. The physio-chemical cleaning methods use mechanical cleaning meth An ideal cleaning process should not only be effective against several foulants, but gentle to the membranes so as to maintain and restore their characteristics. The optimal choice of the cleaning agent is a function of membrane material as well as foulants. The chemical reaction between the chemical agents and the foulant takes place either by changing the morphology of the foulant or by altering the surface chemistry of fouling layer in order to remove the foulants from the membrane surfaces [26]. Although, there are a number of cleaning techniques such as physical or chemical or combination of both, only the chemical cleaning methods are widely used by NF and RO industries for membrane cleaning and regeneration [27]. A large number of chemical cleaning agents are commercially available, and the commonly used ones fall into six categories: alkalis, acids, metal chelating agents, surfactants, oxidation agents and enzymes [28,29]. In general, these cleaning agents do improve the membrane flux to certain extent. Combination of these chemical agents has also been tried in order to improve the flux restoration. Even though, many of these cleaning agents can restore the flux over 100% (enhanced flux), they can also impair the selectivity of the membrane thereby reducing the product water quality. NF membranes are extremely vulnerable to natural organic material (NOM) fouling, especially in the presence of divalent cations [30]. The choice of the preferred cleaning agent depends on feed characteristics. For example, acid cleaning is suitable for the removal of precipitated salts, such as $CaCO_3$, while alkaline cleaning is used to remove adsorbed organics [31]. Chlorine and hydrogen peroxide are most common oxidants used for membrane cleaning. The oxidation of organic polymers generates more oxygen-containing functional groups such as carboxyl and phenolic groups which increase hydrophilicity. Therefore, oxidation reduces the adhesion of fouling materials to membranes. Quite often, oxidants are mixed with caustic to form a cleaning “cocktail”. There are four reasons to mix oxidants, specifically chlorine with caustic:

- To enhance cleaning efficiency, the mixture provides a synergy for NOM dominated fouling because fouling layer tends to have more open structure at caustic conditions due to the change in configuration. This synergy provides more access to chlorine to reach inner layer of fouling materials, facilitates the mass transfer and reactions between chlorine and fouling materials, and enhances the cleaning efficiency.
- To control excess oxidation to membrane and other module components
- Both caustic and oxidants are needed for efficient membrane cleaning. Mixing them allows the cleaning to be conducted in one step
- Reduce the health hazards of cleaning operation.

The success of chemical cleaning methods depend on many factors such as nature of the foulant, type of cleaning agents, temperature, pH, concentration of the cleaning chemicals, contact time between the chemical solution and the membrane and operation conditions such as cross-flow velocity and pressure. These factors play very important role in flux recovery and therefore need thorough investigation in order to establish the optimum cleaning system. Conventional assessment of cleaning by flux measurement has been used in the last decades in order to optimize and evaluate the cleaning procedures. In membrane process industries, membrane cleaning is one of the most important concerns from both economical and scientific points of view. Though cleaning is important to recover membrane performance, an inappropriate selection of cleaning agents may result into unsatisfactory cleaning or irreparable membrane. The choice of the optimal cleaning agent or mix composition depends on the feed characteristics. For example, acid cleaning is suitable for the removal of precipitated salts, such as $CaCO_3$, while alkaline cleaning is used to remove adsorbed organics [32]. NaOCl is widely recognized as a very efficient membrane cleaning agent, particularly for Biofouling and fouling by organic matter, its use is problematic in that many polymeric formulations are susceptible to attack by chlorine. Membrane degradation by NaOCl is highly dependent on the conditions of pH [33], where pH values above the dissociation constant for hypochlorous acid (pH 7.5) is particularly aggressive even for polysulfone membranes [34]. Sohrabi et al [35] reported that change in contact angle of membrane surface before and after chemical cleaning is a good indicator for monitoring of cleaning efficiency.

2.10 Chlorine effect on RO membrane

Amide nitrogen and aromatic rings of the polyamide RO membrane are the sites that are sensitive to free chlorine and can be easily attacked by it. Chlorine mainly attacks the polyamide layer in four routes as shown in **Fig.2.4.**

(1) The hydrogen of amide group can be substituted by chlorine atom when polyamide is attacked by active chlorine species such as hypochlorous acid, leading to the formation of N-chlorination

(2) Direct ring chlorination mechanism in which the aromatic ring of m-phenylene diamine (MPD) can be directly replaced by chlorine atom when they are attacked by active (electrophilic) chlorine species and the substitution mainly occurs at a the para position

(3) Indirect ring chlorination in that a rapid N- chlorination first occur, then the chlorine migrates to the ring by intramolecular rearrangement called Orton rearrangement and

(4) Hydrolysis of amide group, which is promoted by chlorine, leading to the formation of amido and carboxylic groups.

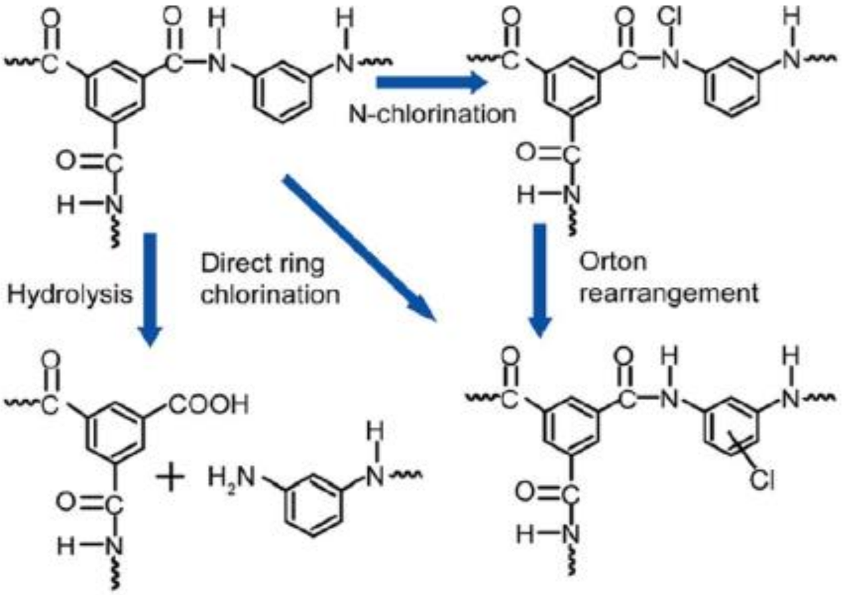

Fig.2.2. Four approaches for the attack of polyamide by active chlorine species

Furthermore, the hydrolysis of C-N bond can be facilitated by chlorination because the polarization of the amide group due to the chlorine substitution at the nitrogen makes the carbon more susceptible to nucleophilic attack by hydroxide [36]. The formation of N-chlorination and ring- chlorination reactions disrupt the intermolecular hydrogen bonds and destroy the symmetry of polyamide network, resulting in conformational changes of the polymer chains, and thus causes the failure of the polyamide RO membrane resulting in decreased salt rejection and increased water flux after chlorination [37]. Therefore, chlorine can affect the polyamide TFC RO membranes both on the structures and the separation properties. The ability of membranes to withstand exposure to chlorine or chlorine-induced oxidants is an important membrane property because chlorine is widely added to water as a disinfectant and bactericide. A membrane is viewed to be chlorine resistant if exposure to a biocidal concentration of chlorine (<1 mg/L) does not cause membrane damage in several years. NF membranes have attracted much attention because NF is more suitable for producing drinking water without remineralization. For the development of chlorine-resistant nanofiltration membranes, a thin-film-composite membrane was prepared by the interfacial polymerization of N-phenylethylenediamine and 1,3,5-benzenetricarbonyl trichloride on a microporous polysulfone support substrate [38]. This type of membrane is called TFC. The polymerization on the substrate surface was confirmed by Fourier transform infrared measurements, and membrane surface properties such as the roughness and ζ potential were characterized. Another procedure is the modification of a reverse-osmosis (RO) membrane. A polyamide RO membrane and a cellulose acetate RO membrane can be modified for the use of NF. NF membranes can also be prepared from ultra- filtration membranes with different polymers. It was showed that the rejections of NaCl and isopropyl alcohol of this membrane were 95 and 50%, respectively. The membrane showed much higher chlorine resistance than a commercial polyamide membrane when the membranes were immersed in an aqueous NaOCl solution [38]. Polyamide-based thin film composite (TFC) membranes are widely used for reverse osmosis (RO) and nanofiltration (NF) applications because of their high water fluxes and solute rejections [23,39]. However, the amide bonds (-CO-NH-) can be attacked by chlorine, which is commonly used in the form of sodium hypochlorite as a disinfectant to control biofouling or as a membrane cleaning agent [25,40]. Severe chlorine attack will deteriorate the separation performance (e.g., a decline in salt rejection) and degrade the membrane chemically under certain circumstances. The degradation of polyamide membranes normally occurs due to N-chlorination of the amide nitrogen and ring chlorination [41,42]. The N-chlorination involves the substitution of hydrogen to chlorine on amide nitrogen to form N-chloroamide. Subjected to further intermolecular Orton rearrangement, the N-bonded chlorine atom can be eliminated to yield molecular chlorine, which will then attack the aromatic ring via electrophilic substitution, resulting in indirect ring chlorination. Composite polyamide nanofiltration membranes comprising of an inner sub layer of polyethylenimine (PEI)/trimesoyl chloride (TMC) cross links and an outer sub layer of piperazine (PIP)/TMC cross links fabricated via layer-by-layer sequential interfacial polymerization shows an improvement of the chlorine resistance by the outer sub layer [43]. And the membrane properties (e.g., surface charge, permeation flux and salt rejection) can be tailored by controlling the PIP and PEI concentrations used in the membrane fabrication [44]. The effects of the chlorination conditions, including pH and concentration of the chlorine solution and exposure time, on the nanofiltration performance of the membranes shows that the chlorination intensity is customarily measured in the literature by the product of the chlorine concentration (ppm) and the exposure time (h), expressed in the unit of (ppm-h). It is often used as a standalone parameter to characterize chlorine resistance of membranes, especially for comparisons of chlorine resistances of different membranes treated at different chlorination conditions. It was elucidated that the joint effects of chlorine concentration and exposure duration on membrane chlorination cannot be represented by the chlorination intensity (ppm-h), a single composite parameter based on a multiplication of the two. In a research work that looked into the effects of chlorine exposure on nanofiltration performance of the multilayered polyamide membranes with positive surface charges; these membranes showed a high isoelectric point [44] and high rejection to divalent cationic salt $MgCl_2$ at pH 6.8 [43]. However, several studies [21,22,45,46] have shown that chlorine treatment will decrease the isoelectric point, that is, the membrane surfaces become more negatively charged when chlorinated. This is consistent with physical reasoning that N-chlorination does not form $–NH_2^+$/$-NH_3^+$ groups on the membrane surface due to the formation of N-Cl bonds, but more $-COO^-$ groups will be formed due to deprotonation of –COOH. Negatively charged membrane surfaces favor the rejection of multivalent anionic solutes (i.e., $MgSO_4$ and Na_2SO_4) and this may explain the different behavior of the membranes to reject different solutes.

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CHAPTER 3

Membrane fouling, chemical cleaning and separation performance assessment of a chlorine-resistant nanofiltration membrane for water recycling applications

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3.1 Introduction

Water purification using nanofiltration (NF) membrane has been widely applied for drinking water, wastewater, and industrial wastewater treatment applications over the past decades [1, 2]. NF membrane, which is classified between ultrafiltration and reverse osmosis (RO) membranes, is capable of rejecting multivalent ions and dissolved organic molecules including many trace organic chemicals [3-7]. Most commercially available NF membranes comprise of a composite polyamide (PA) ultrathin skin layer on top of a microporous polysulfone supporting layer. In response to worsening water scarcity, rapid population growth, industrialization and worsening droughts due to climate change, water purification using NF membranes has attracted increasing interests for water reuse.

A major challenge to all membrane-based water treatment systems is membrane fouling. Membrane fouling is inevitable and is caused by the deposition of impurities (foulants) on the membrane surface, resulting in a drop in permeability and changes in separation performance [8-10]. To date, most water recycling systems using high pressure membranes (i.e. NF and RO) have deployed a pretreatment with MF or ultrafiltration (UF) as a pretreatment step for fouling mitigation [11]. The additional pretreatment processes increase capital and operating costs in water reuse, thus, the elimination of these pretreatment processes could provide an advantage on reducing the water recycling cost and make water reuse more feasible.

Without pretreatment, NF filtration operation is likely to face accelerated membrane fouling but can be counteracted by frequent and effective chemical cleaning. In conventional NF operation, chemical cleaning is periodically conducted by filling up the feed side of the membrane with solutions containing caustic (e.g. NaOH) or acidic (e.g. HCl) chemicals and recirculating the solutions [12]. The downside of frequent chemical cleanings is the disruption to the continuous operation of the membrane skid, because typical chemical cleaning requires a cleaning period of up to 8 h [13]. In addition to these conventional chemicals, membrane cleaning with a chlorine-containing solution (e.g. hypochlorite) has attracted attention in recent years due to its inexpensive and affordable supplies of sodium hypochlorite and its high ability in fouling mitigation [14, 15]. Major mechanisms of hypochlorite cleaning are to disinfect the membrane and to oxidize the functional groups of organic foulants to ketone, aldehyde and carboxylic groups. The presence of these functional groups increases the hydrophilicity and charges of their parent compounds, reducing the adhesion and attraction of fouling substances to the membranes [16]. In fact, many MF- or UF-based water reclamation systems are equipped with cleaning facilities with a hypochlorite solution [17]. However, hypochlorite cleaning cannot be applied to conventional NF and RO membranes that are widely used in water recycling, because their PA active skin layer is readily degraded by chlorine [18-20].

The problem of the chlorine contact with PA-based NF membranes is the degradation of amide bonds (-CO-NH-) of the membrane structure [21]. The extended contact with chlorine ultimately causes the deterioration in separation performance [22-24]. To avoid the degradation issue, significant research work has devoted to the development of chlorine-resistant PA membranes [25-29]. For example, Shintani et al. [30] developed a chlorine-resistant PA NF membrane and reported that the immersion of the NF membrane in a sodium hypochlorite solution (200 ppm) over 70 days did not change the separation performance. However, no previous studies have demonstrated the effectiveness of hypochlorite cleaning in fouling mitigation of a chlorine-resistant membrane for direct filtration of secondary treated wastewater.

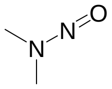
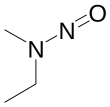
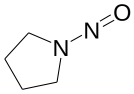
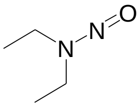
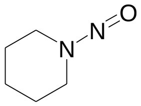
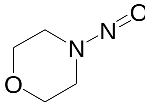
This study aimed to assess the effectiveness of hypochlorite cleaning for fouling mitigation of a prototype chlorine-resistant NF membrane. The chlorine resistance and separation performance of the prototype NF membrane were also compared to commercial NF and RO membranes. Separation performance of the NF membrane was evaluated using inorganic salts and uncharged trace organic contaminants (i.e., *N*-nitrosamines) of significant concern in water recycling applications. A secondary treated effluent was used to simulate the elimination of pretreatment in NF filtration. Solutions containing a model foulant (sodium alginate, humic acids or bovine serum albumin) were also used to identify organic substances in wastewater that are persistent against hypochlorite cleaning.

3.2 Materials and methods

3.2.1 *Chemicals*

Analytical grade NaCl, $NaHCO_3$ and $CaCl_2$ were purchased from Wako Pure Chemical Industries (Tokyo, Japan) and used as background electrolyte. Analytical grade sodium hypochlorite solution (10% available chlorine) was purchased from Sigma-Aldrich (St Louis, MO, USA). Six analytical grade *N*-nitrosamines were purchased from Ultra scientific (Kingstown, RI, USA). They include *N*-nitrosodimethylamine (NDMA), *N*-nitrosomethylethylamine (NMEA), *N*-nitrosopyrrolidine (NYPR), *N*-nitrosodiethylamine (NDEA), *N*-nitrosopiperidine (NPIP) and *N*-nitrosomorpholine. (NMOR) **(Table 3. 1)**. A stock solution was prepared at 1.0 mg/mL of each *N*-nitrosamine in pure methanol. Analytical grade luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) was supplied from Wako Pure Chemical Industries (Tokyo, Japan). Three model foulants used here include sodium alginate (SA), bovine serum albumin (BSA), humic acids (HA). Sodium alginate and humic acid were supplied by Sigma-Aldrich (St Louis, MO, USA). BSA was purchased from Wako Pure Chemical Industries (Tokyo, Japan). Secondary treated effluent was collected after activated sludge treatment but prior to post chlorination at a municipal wastewater treatment plant in Japan. This study used the collected secondary treated effluent without any pretreatment to promote membrane fouling during filtration experiments.

Table 3.1. Selected *N*-nitrosamine physicochemical properties.

Compound	NDMA	NMEA	NPYR	NDEA	NPIP	NMOR
Structure						
Molecular formula	$C_2H_6N_2O$	$C_3H_8N_2O$	$C_4H_8N_2O$	$C_4H_{10}N_2O$	$C_5H_{10}N_2O$	$C_4H_8N_2O_2$
Molecular weight [g/mol]	74.05	88.06	100.06	102.08	114.08	116.06
Low *D* at pH 8[a]	0.04	0.40	0.44	0.52	0.44	-0.18

[a] Chemicalize (http://www.chemicalize.org).

3.2.2 Membrane and Filtration System

Prototype chlorine-resistant NF membrane was supplied as flat sheet samples by Nitto Denko (Osaka, Japan). Two other commercial flat sheet membranes – namely DK NF membrane (GE, USA) and ESPA2 RO membrane (Hydranautics, USA) – were also used. The DK NF and ESPA2 membranes have been widely used for water recycling applications [31, 32]. A bench-scale cross-flow filtration system was used **(Fig.3.1)**. The system comprised of a stainless-steel membrane cell with an effective surface diameter of 2.2 cm, an effective surface area of 3.80 cm^2, a channel height of 0.44 cm, a pressure gauge, a 2 L feed tank and a high-pressure pump (KP-12, FLOM, Tokyo, Japan). Feed solution in the feed tank was stirred throughout each experiment. Feed solution temperature was controlled at 20.0 ± 0.1 ^{o}C by a temperature control unit (CCA-1112, Tokyo Rikakikai, Tokyo, Japan) which was equipped with a stainless steel heat exchange coil. Permeate flow was monitored using a digital balance (FX-300i, A&D, Tokyo, Japan) that was connected to a computer for data logging.

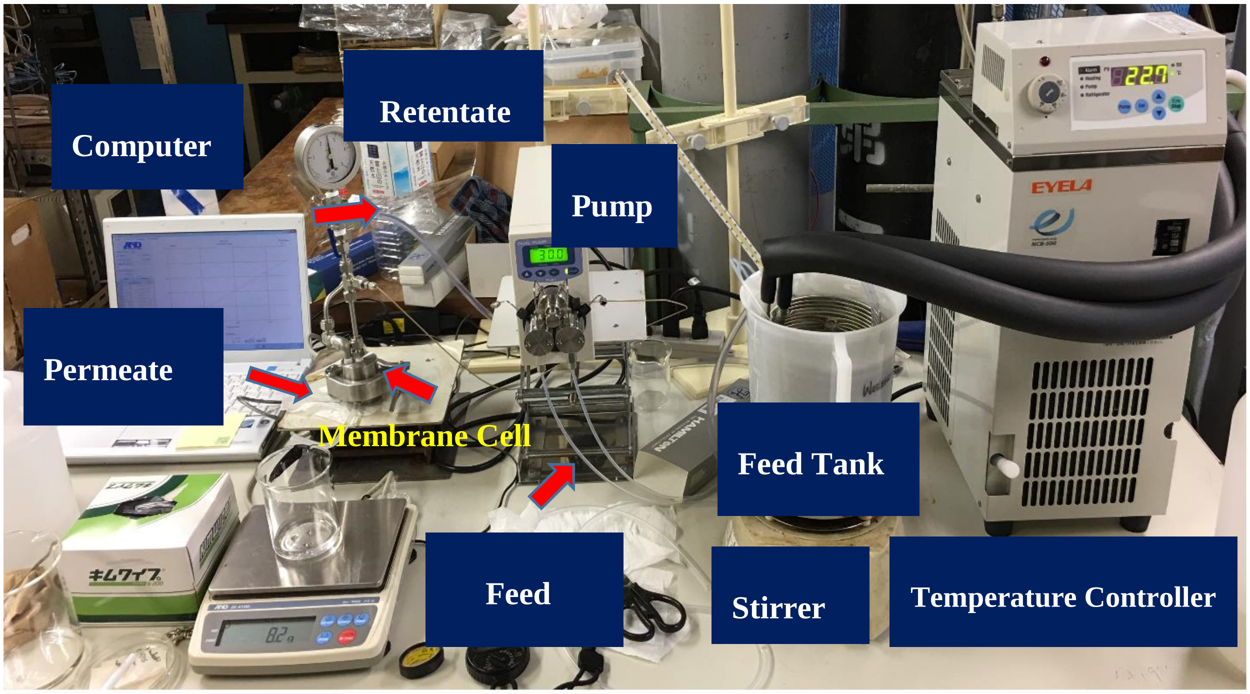


Fig. 3.1 Bench-scale cross flow NF filtration experimental set up.

3.2.3 Experimental Protocols

3.2.3.1 Chlorine Exposure

Prior to the chlorine exposure experiments, membrane coupons were gently rinsed and soaked in Milli-Q water overnight. To simulate a long-term exposure of the membrane to chlorine, NaOCl solutions were prepared in pure water to obtain a concentration of either 1,000 ppm (as NaOCl at pH 11.0) or 100,000 ppm (as NaOCl at pH 11.0). Each membrane sample was immersed in a 50 mL NaOCl solution in a Pyrex glass beaker covered with aluminum foils and placed in a water bath at 20.0 ± 0.1 ^oC for a specified duration. As soon as the chlorine exposure experiments ended, the membranes were rinsed with a copious amount of deionized water and were stored in the dark at 4 ^oC. Permeability of each membranes was evaluated at the permeate flux of 20 L/m^2h Milli-Q water. Conductivity rejection of the membranes was evaluated using a 20 mM NaCl solution at the permeate flux of 20 L/m^2h. Throughout the tests, a cross-flow velocity of the feed solution was maintained at 0.52 cm/s. Feed and permeate samples were collected after at least 1 h operation for conductivity evaluation. Conductivity rejection was determined by measuring conductivity of the feed and permeate solutions.

3.2.3.2 Seperation Performance

Separation performance of the three selected membranes was evaluated by measuring the rejection of cations (Na^+ and Ca^{2+}) and uncharged organic solutes (*N*-nitrosamines). The membrane sample was first compacted by operating system with Milli-Q water at 1 MPa for 1 h. Background electrolytes were then added at a concentration of 20 mM NaCl, 1 mM $NaHCO_3$, 1 mM $CaCl_2$ in Milli-Q water. *N*-nitrosamines were also spiked into the feed at a high concentration of 1,000 ng/L for each *N*-nitrosamine to ensure measurable concentrations in the permeate, while a previous study [33] reported that *N*-nitrosamine concentration does not influence their separation by polyamide RO membrane. pH of the feed solution, which may be found at 6.5-7.5 at water recycling plants [34] but plays a negligible impact on *N*-nitrosamine rejection [33], was adjusted at 8. The filtration system was operated at a constant flux of 20 L/m^2h, and a cross-flow velocity of the feed solution was maintained at 0.52 cm/s. The concentrate and permeate were recirculated into the feed tank to avoid any increase in the concentrations of chemicals in the feed. After at least 1 h of filtration, feed and permeate samples were collected in amber vials.

3.2.3.3 Hypochlorite cleaning

The effectiveness of hypochlorite cleaning on fouling mitigation was evaluated with the prototype chlorine-resistant NF membrane using three filtration cycles of fouling and cleaning **(Fig.3.2)**. The membrane sample was first compacted using Milli-Q water at 1 MPa for 1 h **(Fig.3.2a)**. The Milli-Q water was then replaced with an NF-treated wastewater for the measurement of permeate flux in treated wastewater without the effects of foulants. The NF-treated wastewater was prepared by filtering the secondary treated effluent by an NF membrane (ESNA1-LF2, Hydranautics, USA), which has a capacity of removing foulants but has a negligible capacity of removing ions. With the wastewater treated with the ESNA1-LF2 NF membrane, permeability of the membrane was measured at 1 MPa **(Fig.3.2b)**. Thereafter, the NF-treated wastewater was replaced with the secondary treated effluent for fouling development. The filtration system was operated at a constant feed pressure of 1.0 MPa for 10 h **(Fig.3.2c)**. Feed cross-flow velocity and feed temperature in the feed tank were maintained at 0.52 cm/s and 20.0 ± 0.1 °C, respectively. After 10 h filtration, membrane cleaning was performed with a NaOCl solution (2,000 ppm as NaOCl and pH 11.0) **(Fig.3.2d)**. Cleaning started with flushing the membrane with Milli-Q water. Hypochlorite cleaning comprised of three steps: (1) recirculation with the NaOCl solution at a cross-flow velocity of 0.52 cm/s for 15 min, (2) settling for 30 min and (3) another recirculation with the chlorine solution at a cross-flow velocity of 0.52 cm/s for 15 min. These cleaning steps were performed without providing a pressure on the membrane cell. After the filtration system was thoroughly rinsed with Milli-Q water, two more filtration cycles comprising of (b) permeability measurement, (c) fouling development and (d) chlorine cleaning were conducted and only permeability measurement was performed in the 4th filtration cycle **(Fig.3.2)**. Same experimental procedure described above was applied to the evaluation of chlorine-based chemical cleaning for model foulants (HA, SA and BSA). The model foulant solutions contained background electrolytes (20 mM NaCl, 1 mM $NaHCO_3$, 1 mM $CaCl_2$) and 100 mg/L of one of the model foulants in Milli-Q water.

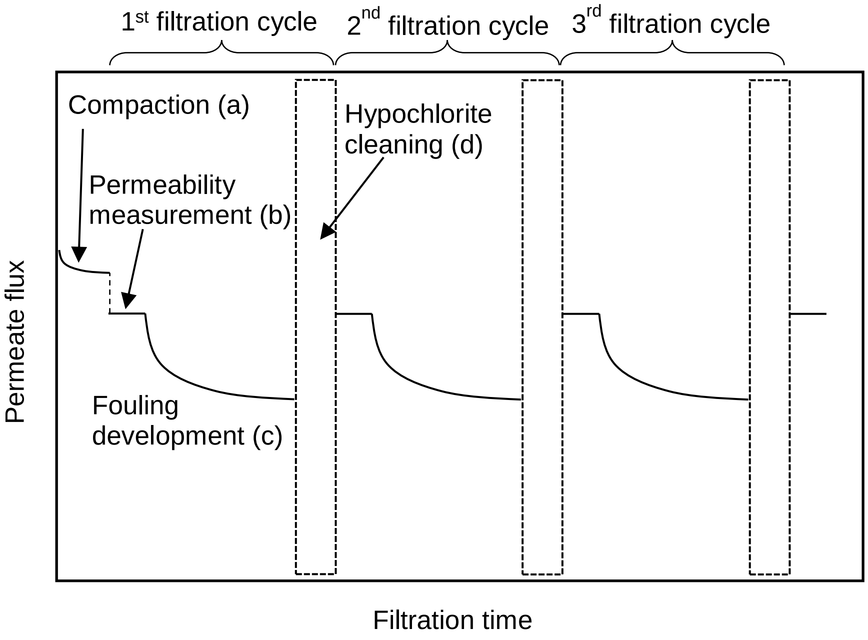


Fig. 3.2 – Conceptual diagram of the NF filtration cycles.

3.2.4 Analytical techniques

High performance liquid chromatography photochemical reaction chemiluminescence (HPLC-PR-CL) was used to determine *N*-nitrosamine concentrations in solution. The volume of the injection sample was in the range of 200 µL. This analytical technique has been described in details elsewhere [35, 36]. Concentrations of Na^+ and Ca^{2+} ions were determined using an ion chromatography-conductivity detection system equipped with IC Pak C M/D column (Waters, MA, USA). Solution pH and conductivity were measured by a pH meter (Navi F-53, Horiba, Kyoto, Japan) and a conductivity meter (LAQUAact ES-71, Horiba, Kyoto, Japan), respectively.Organics in the secondary treated effluent were characterised by a liquid chromatography-organic carbon detection (LC-OCD) system (DOC-LABOR, Karlsruhe, Germany) [37, 38]. The analysis was performed at 1.1 mL/min flow rate with a mobile phase of phosphate buffer, 2.5 g/L KH_2PO_4 and 1.5g/L $Na_2HPO_4 \cdot 2H_2O$. Samples were pre-treated with a 0.45 µm filter, and a volume of 1.0 mL of sample was injected.

3.3 **Results and discussion**

3.3.1 Chlorine exposure

Stability in the performance of the prototype NF membrane against chlorine exposure was evaluated and compared to that of the other two commercial membranes. When prototype NF membrane was exposed to a 1,000 ppm NaOCl solution for up to 50 h (= 5×10^4 ppm-h), the permeability remained constant at 2.9 L/m^2hbar **(Fig.3.3a)**. In addition, the prototype membrane revealed a stable rejection of 48.0% for up to 5×10^4 ppm-h **(Fig.3.3b)**. The results suggested that the prototype NF membrane can be used without any discernible damage on separation performance for chlorine exposure of up to 5×10^4 ppm-h. The exposure of prototype NF membrane to NaOCl solution was further extended to 73 h with a very high concentration of NaOCl solution (100,000 ppm as NaOCl) to accelerate membrane degradation. The cumulative chlorine exposure of 7.3×10^6 ppm-h equates to 1,825 day (= 5 year) operation, when the membrane is assumed to undergo hypochlorite cleaning with a 2,000 ppm NaOCl solution for 1 h twice a day. As a result, permeability of the prototype NF membrane increased from 2.9 to 4.9 L/m^2hbar and conductivity rejection (i.e., salt rejection) decreased from 48.0

to 42.0%. The results indicate a small but nevertheless discernible degradation of the prototype NF membrane after an extended period of chlorine exposure (equivalent to 7.3×10^6 ppm-h). Despite of the slight change in separation performance the results here demonstrated that the prototype NF membrane can be considered as a chlorine-resistant NF membrane.

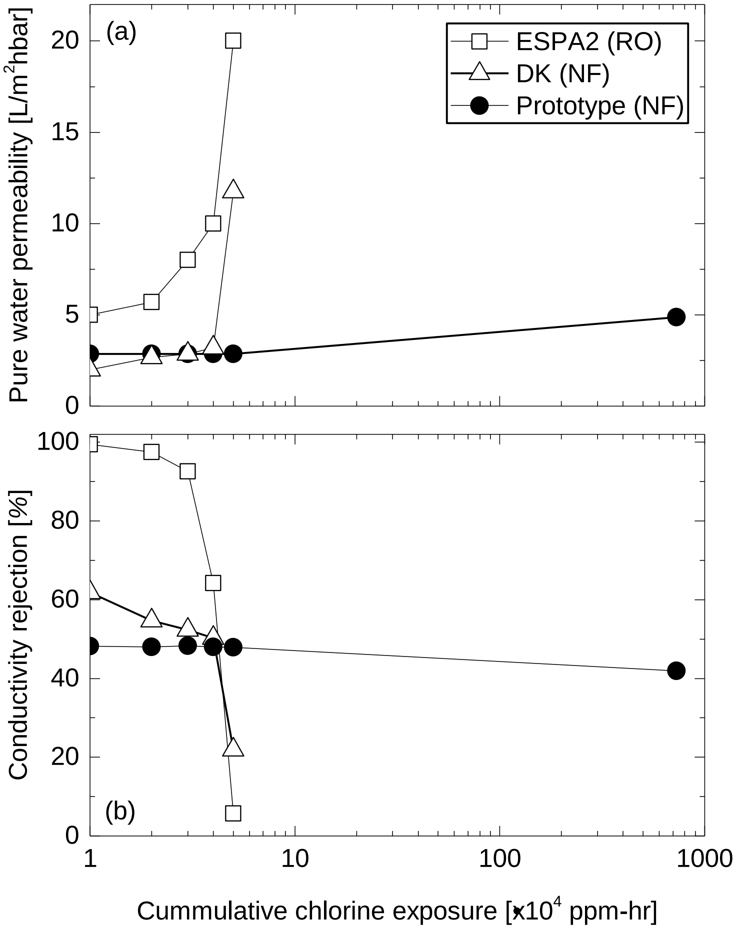


Fig. 3.3 – Changes in (a) permeability and (b) conductivity rejection as a function of chlorine exposure. Chlorine exposure was performed at a NaOCl concentration of 1,000 ppm (at up to 5×10^4 ppm-h) or 100,000 ppm (at 7.3×10^6 ppm-h) at pH 11.0. Pure water permeability was measured at the permeate flux of 20 L/m^2h. Conductivity rejection was measured at a NaCl concentration of 20 mM, permeate flux of 20 L/m^2h and feed temperature of 20 ^{o}C.

In contrast, the permeability of the other commercial membranes increased over time and revealed a sharp increase after 40 h exposure (= 4×10^4 ppm-h), which caused an increase in permeability over four times – from 5.0 to 20.0 L/m^{2}hbar for ESPA2 RO membrane and from 2.0 to 11.8 L/m^{2}hbar for DK NF membrane **(Fig.3.3a)**. Likewise, the considerable change was also observed for conductivity rejection. Conductivity rejection by the ESPA2 RO membrane remained at >90% until chlorine exposure of 3×10^4 ppm-h, thereafter it dropped down to 5.7% at 5×10^4 ppm-h **(Fig.3.3b)**. The DK NF membrane revealed a similar but less deterioration in conductivity rejection from 61.8 to 21.9 % from 0 to 5×10^4 ppm-h. The considerable increase in the permeability of the commercial membranes after chlorine exposure is the indication of the degraded membrane by chlorine attack [23].

3.3.2 Seperation Performance

The separation performance of low molecular weight chemicals by the three selected membranes was evaluated using inorganic chemicals (Na^+ and Ca^{2+}) and six uncharged organic chemicals (*N*-nitrosamines). The prototype and DK NF membranes revealed similar but low rejections of *N*-nitrosamines all below 60%, which were by far lower than those by ESPA2 RO membrane (50–94%) **(Fig.3.4)**. The low separation of the NF membranes were comparable to other commercial NF membranes (e.g. NF270 and NF90, Dow/Filmtec) that were reported in a previous study [39]. In contrast, the rejections of sodium ions and calcium ions by the prototype NF membrane were relatively high (45% and 62%, respectively) **(Fig.3.4)**. This was also observed for DK NF membrane (35% for sodium ions and 75% for calcium ions, respectively). Because sodium and calcium ions are strongly hydrated at the tested pH, their hydrated ion size can lead to the enhanced rejections. In addition, the rejection of charged ions can also be enhanced by the electrostatic interactions that occur between the ions and membrane [40]. The separation performance of the prototype NF membrane was greater than that of DK NF membrane for sodium ions, but vice versa for calcium ions.

A previous study [6] has also observed variable rejections depending on ionic constituent among NF membranes, while the cause still remains unclear and this could be scope for future study. The results here indicate that the prototype chlorine-resistant NF membrane is comparable to commercial NF membranes in terms of the separation performance for Na^+ and Ca^{2+} ions and low molecular weight organics.

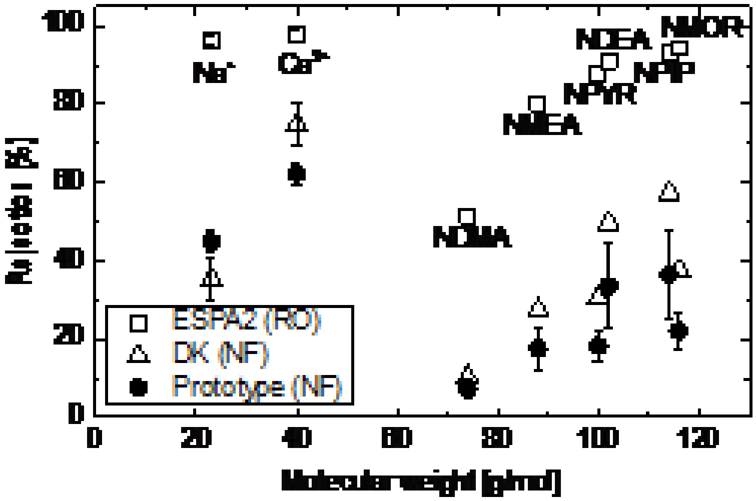


Fig. 3.4 – Separation performance of the three selected membranes (20 mM NaCl, 1 mM $NaHCO_3$, 1 mM $CaCl_2$, 1 μg/L of each *N*-nitrosamine, permeate flux = 20 L/m^2h, feed temperature = 20 ^oC and feed pH = 8). Values reported here are the average and ranges of duplicate samples.

3.3.3 Membrane Chemical Cleaning

3.3.3.1 Secondary treated effluent

The effectiveness of hypochlorite cleaning on fouling mitigation of the prototype chlorine-resistant NF membrane was evaluated using a secondary treated effluent. The direct filtration of the secondary treated effluent resulted in a progressive decrease in the permeability of the prototype NF membrane by 25% over 10 h of filtration at the first filtration cycle **(Fig. 3.5)**. Hypochlorite cleaning using a 1,000 ppm NaOCl solution (pH 11.0) did not sufficiently remove foulants, leading to only 89% of the initial permeability at the beginning of the 2nd filtration cycle. In contrast, hypochlorite cleaning using a 2,000 ppm NaOCl solution (pH 11.0) recovered the permeability to 99 %. The degree of membrane fouling was less significant during the 2nd (from 11 to 22 h) and 3rd (from 23 to 34 h) filtration cycle – 21 and 22% decrease in permeability, respectively. After hypochlorite cleaning of the 2nd and 3rd filtration cycles, the permeability was restored to 99 %. The cause of changes in flux reduction after multiple filtration cycles remains, but it is likely to be caused by changes in membrane property after exposing to hypochlorite cleaning solutions. The results here indicate that hypochlorite cleaning using a 2,000 ppm NaOCl solution (pH 11.0) for 1 h was sufficient to clean the prototype NF membrane fouled with the secondary treated effluent.

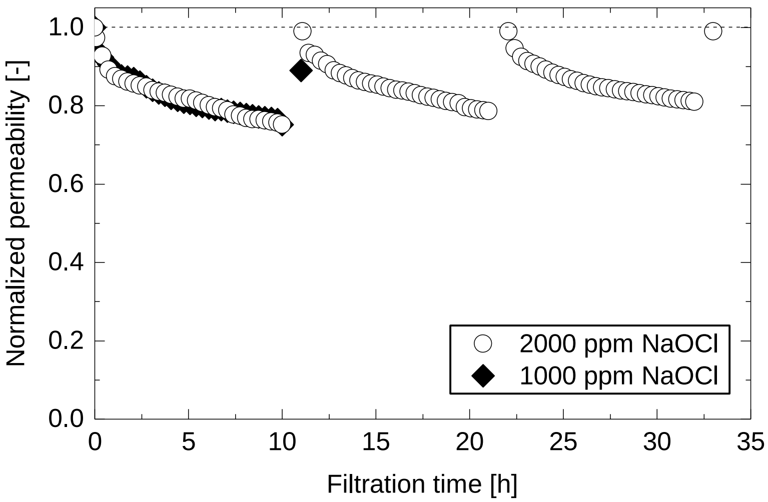


Fig. 3.5 – Effects of fouling on the prototype NF membrane using the secondary treated effluent and NaOCl cleaning (2,000 and 1,000 ppm). Filtration was performed at 1.0 MPa feed pressure and 20 ^{o}C feed temperature for 10 h. The initial permeate flux was 31 L/m^{2}h. Each chemical cleaning was performed at 20±0.1 ^{o}C for 1 h.

The secondary treated effluent contained a variety of dissolved organic constituents as characterised by LC-OCD **(Fig.3.6)**. The distribution of these organic contents was biopolymers (14%), humic substances (44%), building blocks (15%) and low molecular weight (LMW) neutrals (18%). Fraction of biopolymers (>20,000 Da) represents polysaccharides and proteins in the secondary treated effluent, and fraction of humics (approximately 1000 Da) represents humic acid-like substances [38, 41]. Corresponding model substances of these large fractions include sodium alginate (i.e. polysaccharide), BSA (i.e. protein) and humic acids, and they were used as model foulants in the next section. It should be noted that no appropriate model foulants were found for dissolved organics with smaller fractions such as building blocks (300–500 Da) and LMW neutrals (<350 Da).

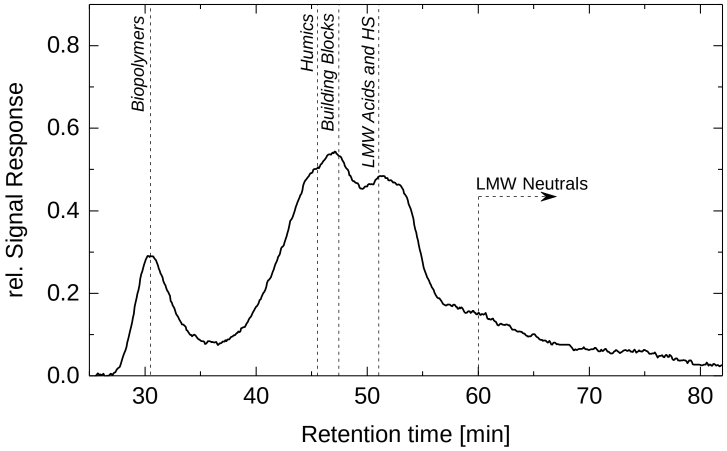


Fig. 3.6 – LC-OCD chromatogram of the secondary treated effluent.

3.3.3.2 Model foulant solutions

To achieve a sustainable NF process using hypochlorite cleaning, potential foulants in treated wastewater that are persistent to the prototype chlorine-resistant NF membrane were investigated by filtering a solution containing one of the model foulants (sodium alginate, BSA or humic acid) and performing hypochlorite cleaning (2,000 ppm as NaOCl and pH = 11.4) for 1 h. Sodium alginate and BSA represent biopolymers (polysaccharide and protein, respectively) in treated wastewater. Humic acids represent humic-like substances in treated wastewater. The substance that most reduced permeability was sodium alginate, causing a 50% reduction in permeability **(Fig.3.6)**. However, the permeability was well restored to 98% after hypochlorite cleaning. Likewise, the permeability of the prototype NF membrane fouled with BSA was also sufficiently restored with hypochlorite cleaning, while filtration with the BSA solution caused less membrane fouling through 10 h filtration. The results suggest that hypochlorite cleaning is effective for the removal of biopolymers. The model foulant most persistent in this study was humic acid **(Fig.3.6)**. Membrane fouling with humic acid solution caused a 29% reduction in permeability and the permeability was recovered only slightly to 78% by hypochlorite cleaning. The effective removal of biopolymers can be due to the enhanced cleavage of polysaccharides and proteins into sugars and amides by hydrolysis after oxidation of these substances with hypochlorite [42]. In contrast, humic substances could be strong complexes with calcium ions, which provide limited permeability recovery [43, 44].

The results indicate that the cleaning protocol used in this study may not be sufficient for the treated wastewater with abundant humic-like substances.

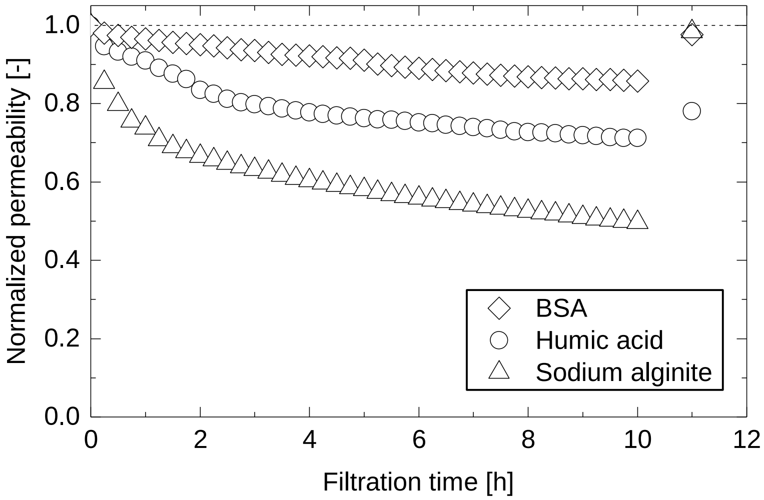


Fig. 3.7 – Effects of fouling on the prototype chlorine-resistant NF membrane using the model foulant solutions (20 mM NaCl, 1 mM $NaHCO_3$, 1 mM $CaCl_2$, 100 mg/L model foulant and pH = 8.0) and NaOCl cleaning. Filtration was performed at 1.0 MPa feed pressure and 20°C feed temperature. The initial permeate flux was 33 L/m^{2}h. Each chemical cleaning was performed with a 2,000 ppm NaOCl solution (pH = 11.4) at 20 °C for 1 h.

3.3.4 Conclusions

This study assessed the effects of hypochlorite cleaning on fouling mitigation of a prototype chlorine-resistant NF membrane for direct filtration of a secondary treated effluent. The exposure of the chlorine-resistant NF membrane to a 1,000 ppm NaOCl solution revealed that the permeability and separation performance remained stable for up to the cumulative chlorine exposure of 5×10^4 ppm-hr. The separation performance of the prototype NF membrane for Na^+ and Ca^{2+} ions and *N*-nitrosamines was comparable to a commercial NF membrane. Filtration of the secondary treated effluent by prototype NF membrane resulted in a gradual decrease in permeability down to 75%, while hypochlorite cleaning with a 2,000 ppm NaOCl solution (pH =11.0) for 1 h restored the permeability. The recovery in permeability was demonstrated up to three cycles, indicating that hypochlorite cleaning can be an effective cleaning strategy to the direct filtration of secondary treated effluent. Further investigations using model foulants revealed that humic substances were persistent to the prototype NF membrane and hypochlorite cleaning protocol used in this study was not sufficient. To make water recycling systems using a chlorine-resistant NF membrane and hypochlorite cleaning feasible, optimization techniques of cleaning protocols such as NaOCl concentrations, pH and temperature are required. In addition, the concentrations of chlorine disinfection by-products formed through reactions between organics on the membrane and residual chlorine need to be evaluated if the membrane cleaning solution is eventually discharged to the water environment.

3.4 Acknowledgements

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CHAPTER 4

Effect of epoxy resin on membrane surface modification for improvement of chlorine resistance

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4.1 Introduction

High performance RO membranes are the fully aromatic polyamide and are typically made out of a thin polyamide layer (<200 nm) deposited on top of a polysulfone porous layer (about 50 microns) on top of a non-woven fabric support sheet [1]. These three layer configuration gives the desired properties such as high rejection, high filtration rate, and good mechanical strength. Nevertheless, it has still limited by two major drawbacks of surface fouling: Colloidal particulates, bacteria infestation (biofouling) and limited chlorine stability. Maximum limit of free chlorine stability for commercial polyamide thin film composite membrane is 0.1 mg /L [2,3]. RO pretreatment and treatment processes typically use chlorine disinfection of the membrane in order to control microorganisms or as a membrane cleaning agent [3–5]. The degradation of polyamide membranes normally occurs due to N-chlorination of the amide nitrogen and ring chlorination [3,6]. The N-chlorination involves the substitution of hydrogen to chlorine on amide nitrogen to form N-chloroamide. Subjected to further intermolecular Orton rearrangement, the N-bonded chlorine atom can be eliminated to yield molecular chlorine, which will then attack the aromatic ring via electrophilic substitution, resulting in indirect ring chlorination [7].

Partial failure of the dechlorination process can result in the deterioration of PA membranes, making the whole membrane useless. A number of methods have been reported to increase chlorine stability. Based on the degradation mechanisms of PATFC membranes, the effective approaches include elimination of chlorine-sensitive sites in membrane and coating a protective layer on the membrane surface, and modification of polymer structure which can retard or prevent the hydrogen on the amide nitrogen (C=O –N-H) from being attacked by free chlorine [6]. For example, N position hydrogen atom by attempt to substitute with (-CH_3) or phenyl group (-C_6H_5) in the amide group [9]. For example, Meihong Liu et al. grafted polyvinylalcohol (PVA) onto the surface of PATFC membrane through surface grafting polymerization and demonstrated that the graft membrane showed improved chlorine stability and anti-fouling properties [10]. Moreover, the surface modification, such as grafting with high chlorine resistance polymers hexafluoroalcohol-containing polyamide layer (HFAPA) [11] and the P(MDBAC –r-am-r-HEMA) [12], was an fascinating way to improve the chlorine resistances of polyamide membrane. Choi et al [13] has been developed a coated graphene oxide (GO) multilayers on the PATFC membrane surface via layer by layer to enhance oxidative compound stability. From the above information, it can be clearly seen that surface modification with proper monomer is possible and easiest way to improve chlorine stability in commercial manufacturing situation. The objective of this study was to explore novel facile, long-lasting and economically favorable surface modification methods for the enhancement of the chlorine resistance of PA TFC membrane and to compare the chlorine stability properties with new chlorine resistance membrane CR 10. Therefore, in this study water based epoxy resin was used as a chlorine protective layer on the surface of membrane because epoxy polymers have been widely used in protective coating and adhesive due to its strong adhesion, high chemical resistance, and good processing characteristics [14]. In addition, it has superior quality such as good wetting properties and low shrinkage during cure. However, there is no report on applying epoxy resin as a barrier material on polyamide thin film composite membrane. The chemistry of GPTMS has a hydrophilic epoxy group and flexible carbon chain. GPTMS was hope to use more hydrophilic property on membrane surface. It is used to improve not only the adhesion of double-component epoxy sealing agent but also grafting agent to surface modification [15]. The figure below shows the idealized chemical structure of a typical epoxy. The enhanced chlorine stability can be firstly attributed to the covalent attached of neutral hydrophilic PAA molecules at the sites of the end amino groups and amide linkages (-CONH-) onto the membrane surface. Furthermore, the PAA molecules on the membrane surface combine with epoxy coating solution via hydrogen bond, which can reduce the chlorination sites in aromatic polyamide chains [16]. The reaction protocol was shown in **Fig.4.1.**

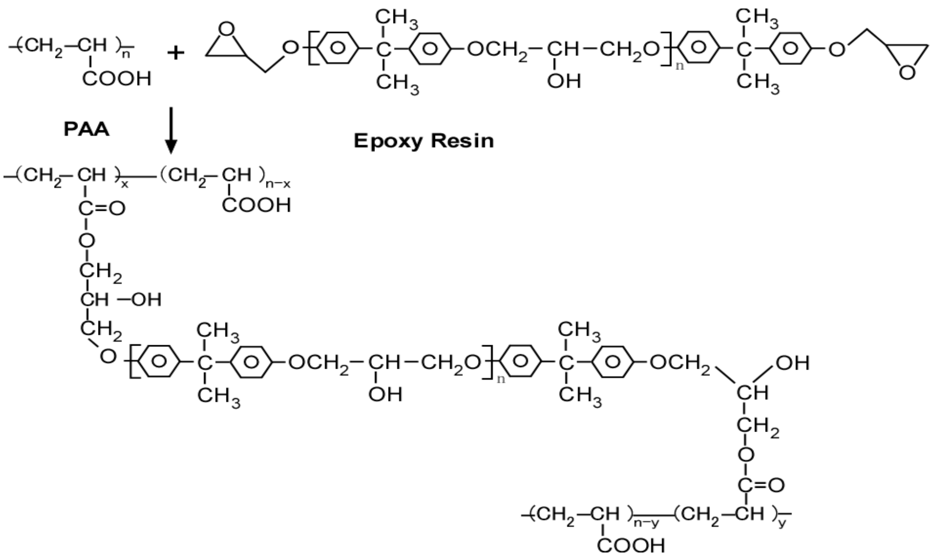

Fig. 4.1 Schematic diagram of the crosslinking reaction between PAA and epoxy resin on the surface of polyamide membrane.

Further, attenuated total reflectance mode Fourier transform infrared spectroscopy (ATR-FTIR) measurements were performed to confirm the successful coating of the epoxy resin onto the membrane surface. Changes in the membrane surface properties, elemental composition and chemical binding information were characterized using scanning electron microscopy energy dispersive spectroscopy (SEM-EDS), fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy, respectively. In addition, exposures of the membranes to free chlorine solutions of different concentrations were carried out to evaluate membrane chlorine stability. Antifouling properties of the coated membrane were demonstrated using BSA as a model foulant.

4.2 Experimental

4.2.1 Materials and Chemicals

The low- pressure RO membrane ESPA2 (Hydranautics, USA) was used in this study. This membrane was received as flat sheet sample and stored wet in Milli Q water at 4° C. Analytical grade sodium hypochlorite solution (10% available chlorine) was purchased from Sigma-Aldrich (St Louis, MO, USA. Bovine serum albumin (BSA, molecular weight 67 kDa), was purchased from Wako Pure Chemical Industries (Tokyo, Japan). Commercially available Industrial grade (Konishi chemical IND CO., LTD, two Components Epoxy Resin Adhesive ‘Bond Quick 5’epoxy resin was applied for coating material. Absolute ethanol (≥ 99.8%, Sigma -Aldrich) was use as a solvent for epoxy resin. Polyacrylic Acid (PAA), average molecular weight = 20,000 g/mol, was purchased from Wako Pure Chemical Industries (Tokyo, Japan) and it was as a hydrophilic protective layer on top of the membrane surface. Other reagents such as sodium chloride (NaCl) (Wako, Japan) and 3-Glycidyloxypropyl-trimethoxysilane (TCI, Japan) were used as received.

4.2.2 Cross flow membrane filtration system

Permeation properties, in terms of permeability and rejection were measured using a bench-scale cross-flow filtration set up as described in our previous work [17], which consists of a stainless-steel membrane cell with an effective surface diameter of 2.2 cm, an effective surface area of 3.80 cm^2. 2L feed tank equipped with stirrer, a temperature controller and a high-pressure pump (KP-12, FLOM, Tokyo, Japan) were used in this study. Permeate flow was monitored using a digital balance (FX-300i, A&D, Tokyo, Japan) that was connected to a personal computer. The entire filtration test was conducted at 20.0 ± 0.1 ^oC by temperature controller under the circulation mode to maintain the feed solution constant. The test for rejection were done using concentration of 20mM NaOCL solution.

Membrane surface modification ***(2 wt/v%***

Prior to membrane modification, the base flat –sheet membrane coupons were soaked in Milli Q water (18 mΩ) and was stored at 4°C. The membranes were immersed in an aqueous solution containing 0.5% (w/v) of polyacrylic acid for 30 min. After a residence time of 30min the excess solution was drained off from the membrane surface, and the coated membrane was air dried in the room temperature until no liquid remain and then dried in the hot air oven of a preset temperature of 45°C for 15 min. The membrane were treated with the solution containing epoxy resin volume percentage (0.001 to 0.05) wt/v% and GPTMS (0.001% wt/v). After reaction for 30 min, the modified membranes were cured at 45°C for another 15 min. Finally, the resulted membrane coupon was soaked in Milli Q water until they were test separation performance.

4.2.3 Sodium hypochlorite exposure

The sodium hypochlorite (NaOCl) used in this study was of analytical grade solution (10% available chlorine) was purchased from Sigma-Aldrich (St Louis, MO, USA). Membrane exposure to NaOCl was simulated by immersing the membrane samples in a container containing 1000mg/L were used to induce an accelerated chlorine exposure effect. The pH of chlorine solution was adjusted by 0.1 M NaOH solution. In the chlorine exposure tests, membrane samples were exposed to 1000-ppm solution at pH 11 for 10, 30, 40, 50 h, to accelerate laboratory degradation process. Samples were contained 50ml NaClO solution and covered with aluminium foil (to prevent the chlorine from sunlight degradation). The chlorination intensity is customarily measured in the literature by the product of the chlorine concentration (ppm) and the exposure time (h), expressed in the unit of (ppm-h) [18]. It is often used as a standard parameter to characterize chlorine resistance of membranes; especially for comparisons of chlorine resistances of different membranes treated at different chlorination conditions. The total chlorine exposures of the chlorinated membranes were 10,000, 20, 000, 30, 000, 40,000 and 50,000ppm-hr, respectively. The Pristine membrane and chlorinated pristine membrane with these concentrations were represented as P_0, P_{10}, P_{20}, P_{30}, P_{40} and P_{50}, respectively. In addition, coated membrane and chlorinated coated membrane were designated as C_0, C_{10}, C_{20}, C_{30}, C_{40} and C_{50}, individually. The conductivity meter (Horiba-LAQUAct ES-71, UK) was used for salt rejection in membrane performance test. Solute rejection (R) was represented as $R = (1 - \frac{C_p}{C_f}) \times 100\%$, where C_p and C_f are the salt concentration of the permeate and feed solution, respectively.

4.2.4 Membrane antifouling property evaluation

Bovine serum albumin (BSA) was selected a model foulant to evaluate the antifouling property of the membrane because protein are ubiquitous in secondary treated effluent. 100mg/L BSA was completely dissolved in the background electrolyte solution that contained 1m M $NaHCO_3$, and 1m M $CaCl_2$ at an ionic strength of 20mM (adjust with NaCl).

4.3 Membrane characterization

4.3.1 Fourier Transform Infrared Spectroscopy Analysis (ATR-FTIR)

FTIR measurement was performed with an IR affinity (Nicolet ThermoNicolet Nexus 670 NT FTIR, Shimadzu, Kyoto, Japan). The air-dried membrane samples were pressed ATR accessory (diamond crystal) and the measured spectrum was collected between 700 cm^{-1} and 4000 cm^{-1}. The acquisition conditions are as follow; 20 scans, 2cm^{-1} resolution. Background spectrum was recorded for each sample.

4.3.2 X- Ray Photoelectron Spectroscopy (XPS)

For all scans, a spot size of 250 µm x 1000 µm was used. High-resolution scans were obtained by averaging 100 scans for Cl 2p peak from 0 -1000 eV with a resolution of 1 eV. Elements of interest are mainly Chlorine, Carbon, Nitrogen and Oxygen on the membrane surface.

4.3.3 Scanning electron microscopy with energy dispersive spectroscopy

Surface microscopy was observed with a field emission scanning electron microscope (JEOL, JSM- 7500 FAM, Japan), working at a low accelerating voltage of 5kV. Working distance is 7.7 mm. Before imaging, the membranes were sputter coated with a uniform layer of approximately 10 nm gold using applied voltage 1.2 kV, 1.2 mA for 30 s. Moreover, Scanning electron microscopy (SEM) analysis was conducted using a JEOL EDS system (JEOL, Japan), which was equipped with an integrated energy dispersive spectrometer (EDS). EDS analysis of all membrane samples was taken at 50k times magnification, apply voltage of 15 kV.

4.4 **Results and Discussion**

4.4.1 Effect of hypochlorite exposure on the virgin and coated membrane

Figure 4.2 shows changes in performances (water flux and salt rejection) by the virgin and coated membrane. Modified membrane performed in this work results in a significantly decrease of water flux from 41.2 to 38.23 L/m^{2}h and slightly increased in salt rejection (99.42 to 99.67%) compare to the virgin membrane. This is possibly due to the organic binder

(GPTMS), where it has three methoxy groups for hydrolysis and one epoxy group for curing. .The decreased flux is possible to be due to the membrane rigid caused by the coated polymer while the improved salt rejection is due to the sealing of the defective pores by the coated polymer which excluded the convective transport of salt ion [19]. The chlorine resistance nanofiltration membranes (CR 10) has a stable rejection (48%) and it can be used for five years without any damage on chlorine exposure that is described in our previous study [17].

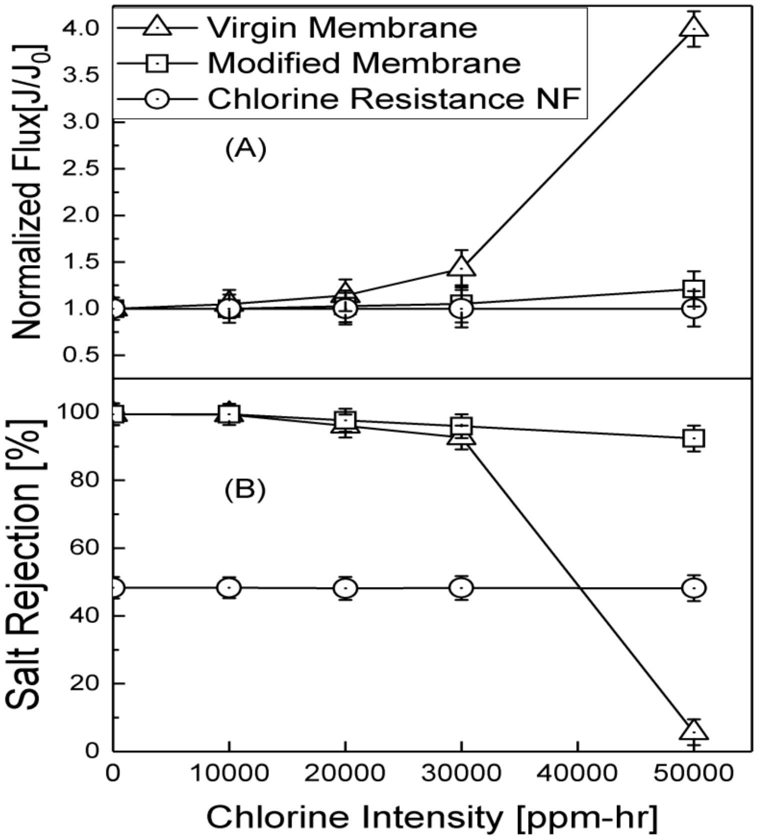

Fig. 4.2 Variation in separation performance of pristine and coated membranes: (a) normalized flux (b) conductivity rejection, tested with 20 mM NaCl aqueous solution, permeate flux of 20 L/m^{2}h and feed temperature of 20° C.

The rejection of the pristine membrane samples deteriorated a lot after chlorination which salt rejection was obviously dropped from 99.62% to 5% [17]. Nevertheless, for epoxy coating membranes, the decrease in rejection was less obvious than that of virgin membrane. In that case, the salt rejections decreased from 99.62% to 92.4%. In contrast, after the chlorination 50,000 ppm-hr as shown in **Fig .4.2** (a) the normalized water flux of the virgin membrane over quadruple while the coated membrane was slighter higher than original membrane even after exposure to 50,000 ppm hr hypochlorite solution. It was seen that epoxy coated membranes presented an ameliorative chlorine resistance while the virgin membranes apparently suffered severe chlorine attack the aromatic ring via electrophilic substitution. This reaction is called Orton –rearrangement [3].

4.5 **Membrane surface characterization of the modified membranes**

4.5.1 Scanning Electron microscopy with energy dispertive spectroscopy

The surface morphology of pristine membranes and the epoxy resin modified membranes were shown in Fig.4.3 (A, B, C, D). Even the chlorinated modified membrane samples, the ridge and valley structure can still be seen under same magnification with virgin membrane. This characteristic is the typical morphology for the polyamide thin film composite membrane by interfacial polymerization.

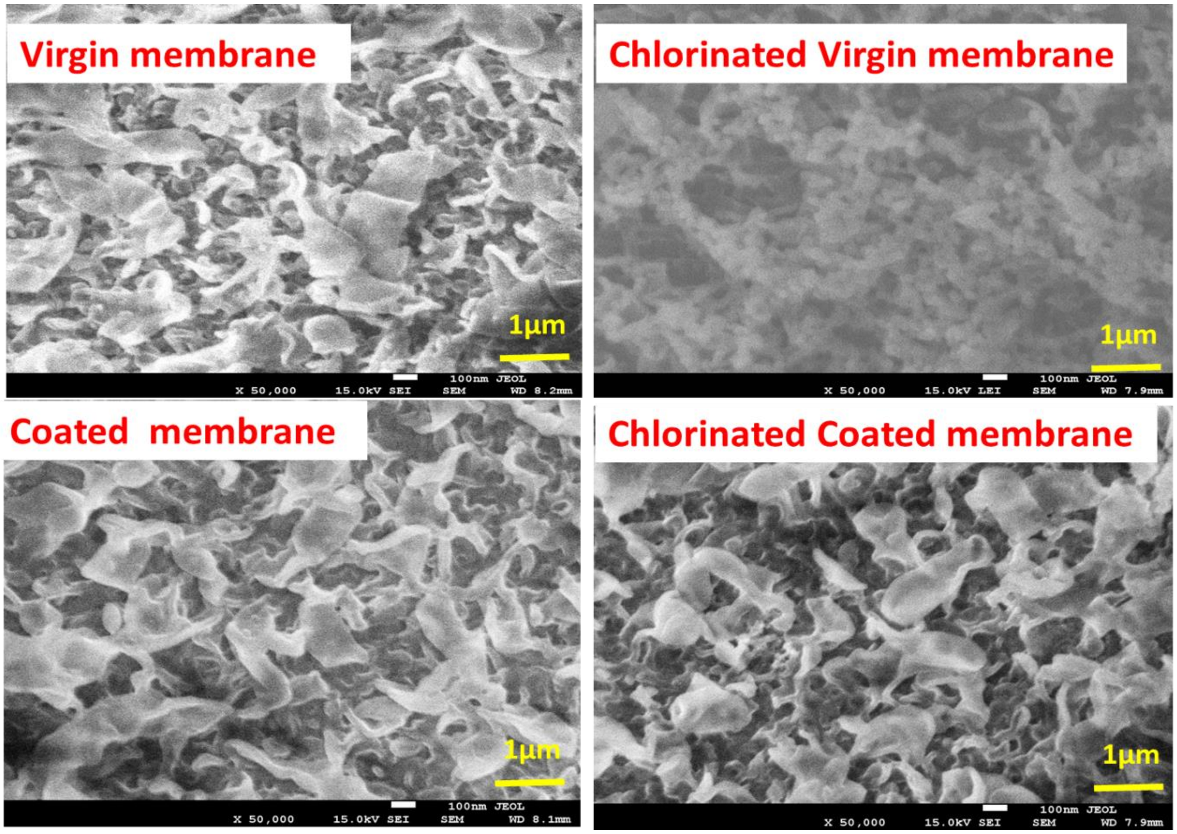

Fig. 4.3 SEM images of the chlorinated coated and uncoated membrane at 50 k (A) virgin membrane, (B) chlorinated virgin membrane, (C) coated membrane chlorinated and (D) coated membrane.

The elements deposited on the membrane surface was obtained from SEM with additional energy dispersive spectrometer (EDS) analysis. After being treated to a hypochlorite solution, effect of chlorine exposure on the surface morphology were examined by SEM-EDX. It was noted that chlorine was detected in all sample including the virgin membrane as a result of sodium chloride rejection performance test. Furthermore, a small amount of Si was found in modified membrane because of glycidoxypropyltrimethoxysilane exist in coated solution. On the EDX analysis of these samples (spectra 1 and 2), traces of the oxidants (chlorine) can clearly be seen by atomic composition. Specifically, the level of Cl in modified chlorinated membrane is significantly smaller than virgin chlorinated membrane (Fig.4.4A and B).

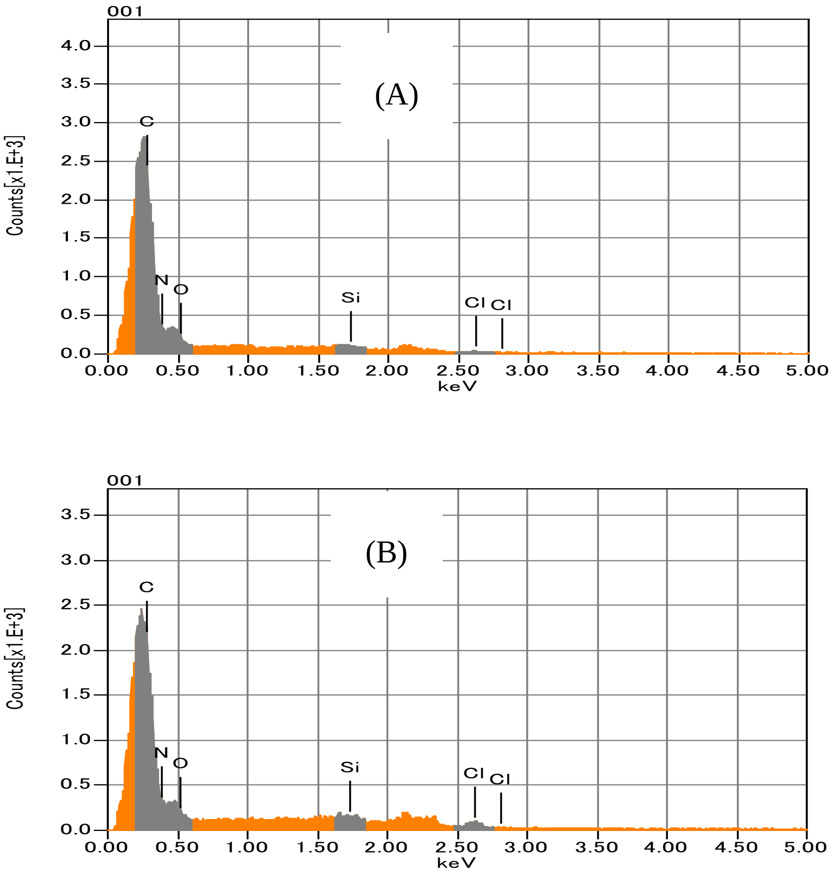

Fig. 4. 4 EDS data of the chlorinated coated ESPA2 membrane (A), chlorinated virgin ESPA2 membrane (B).

Table 4.1. EDX quantitative analysis of virgin and coated membranes before and after chlorine treatment

Membrane	**Cl Treatment**	**Elemental Content (mass%)**		
		C	O	Cl
Virgin	Before	80.7	18.4	0.8
	After	77.5	18.0	4.6
Coated	Before	82.2	11.2	0.8
	After	77.8	19.3	1.6

4.5.2 XPS elemental analysis on membrane surface

The atomic percentages of nitrogen, carbon, oxygen and chlorine on the surface of virgin and modified membranes are shown in Table 4.2. Elemental compositions were computed based on O (1s), N (1s), and C (1s) and Cl (2p) peaks, which are centered around 530 eV, 399.4 eV, 281.8 eV and 200eV, respectively. The XPS wide scan of coated membrane and pristine membrane are displayed in **Fig. 4.5**. It was apparent that low chlorine composition existed in the modified chlorinated membranes but a distinct Cl absorption peak appeared in the virgin chlorinated membranes. The chlorine content of the chlorinated virgin membranes reached to 6.04 %, compared to only 1.61% in the modified chlorinated membranes. Totally, 73.34% of the chlorine uptake was reduced after the surface coating with epoxy resin. The membrane showed an increased atomic percent of oxygen after epoxy resin coating, indicating that the epoxy coating layer was successfully formed on the membrane surface. The epoxy resin do not have N compound but polyamide has (C-O=N-H). From the result of elemental analysis, the decrease of N content means that epoxy resin layer shields polyamide layer. The atomic ratio of Cl/N decreased by quadruple after the PA membrane surface modified with epoxy resin. The high O/N ratio (>2.0) for coated membranes suggest that there might be additional O sources adding on the membrane surface. Such XPS elemental analysis reported that a coating layer rich in O might be present on top of the polyamide layer for these coated membranes. This information is reported previous studies [20]. After modification, the content of C and O increased significantly from 73.99% to 75.22% and from 14.65% to 17.22%, respectively. However, the content of N declined from 10.01% to 6.77%. Since epoxy resin contained no N and had a higher C and O content than the original membrane, the increase in C and O contents and decreases in N content after modification were reasonable and proved that epoxy was modified successfully to membrane surface. The use of neutral hydrophilic polymer polyvinyl alcohol (PVA) as a coating material has been reported [21].

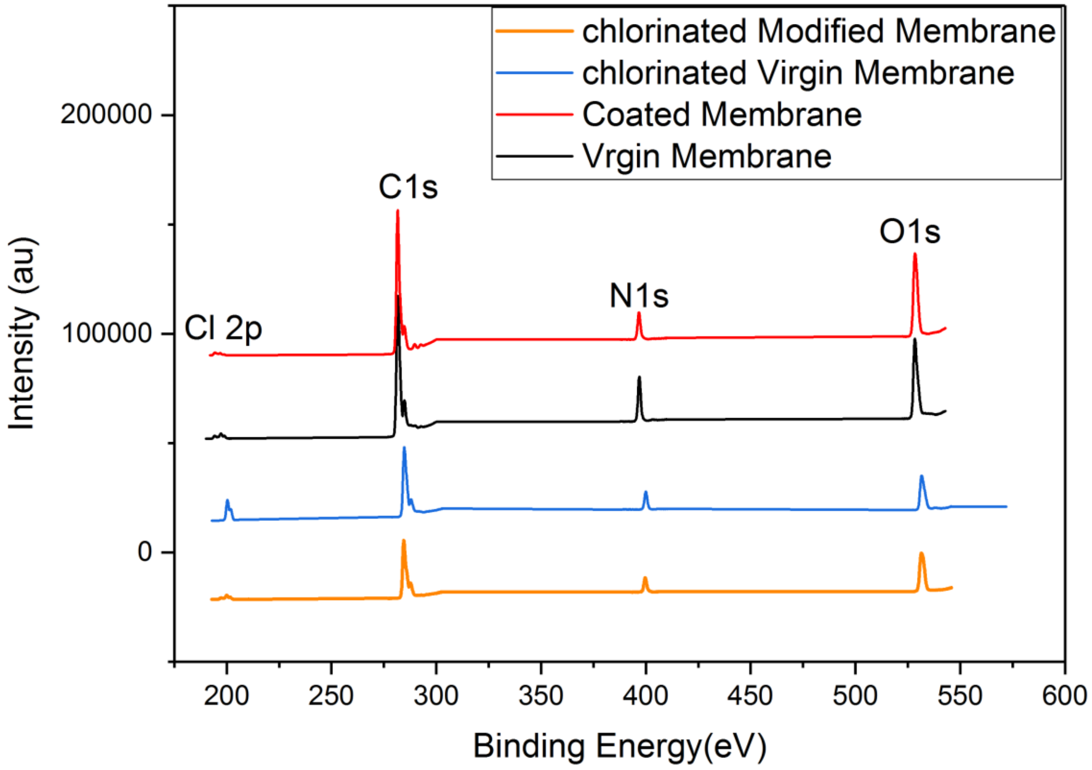

Fig. 4.5 XPS element analysis of virgin membrane, coated membrane, chlorinated virgin membrane and chlorinated modified membrane

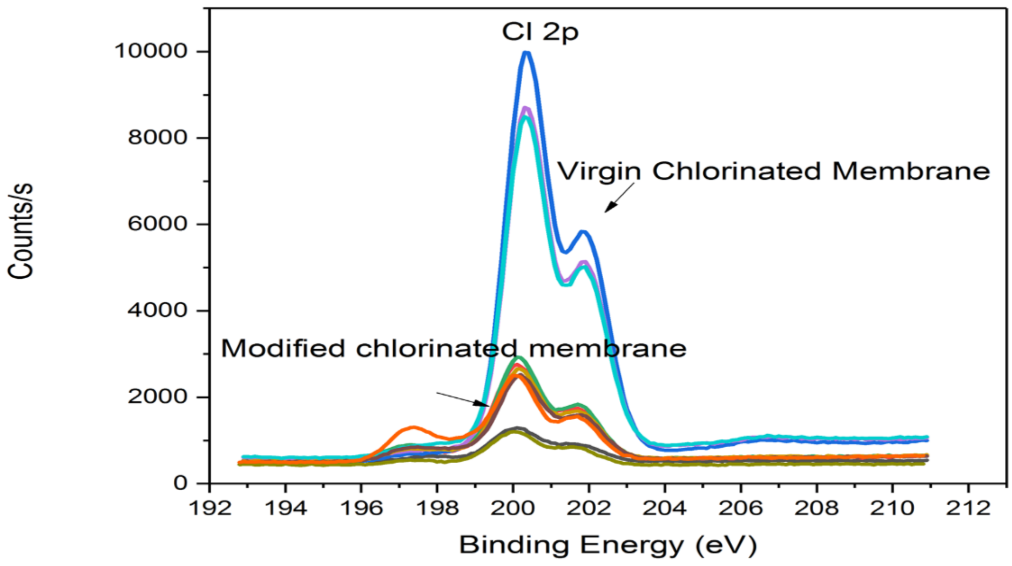

Fig. 4.6. Cl2p spectrums of chlorinated virgin membrane and chlorinated modified membrane

4.5.3 Fourier transform infrared spectroscopy

As for the spectra of virgin membrane , the absorption at 1541 cm^{-1} is mainly contributed by N-H bending motion (amide II) and the absorption 1667 cm^{-1}, is contributed by C=O stretch (amide I). The absorption at 1608 cm^{-1} is associated with the hydrogen-bonded carbonyl of the amide. These absorptions are characteristic of the PA layer of reverse osmosis membrane. As for the spectra of the chlorinated virgin membranes, for the absorption at 1541 cm^{-1} and 1608 cm^{-1}, indicated that the replacement of hydrogen of the amide nitrogen with chlorine due to the electrophilic substitution in N- chlorination. Consequently, the chlorination of amide band 1541 cm^{-1} and 1608 cm^{-1} (amide II and III) is shifted to lower wavelength and the band intensity decreased. The most noticeable changes of the spectra caused by chlorination were the disappearance of the peaks at amide II was completely disappeared due to the destruction of hydrogen bonds of C=O and N-H groups in virgin chlorinated membrane.

By contrast, the change on these absorptions for coated chlorinated membrane due to chlorination is minimal, which suggests that the hydrogen bond between polymer chains are not seriously damaged under this condition (pH 11). It can be seen from Fig. 4.7 that virgin and coated membrane had very similar peaks at low wave numbers (650-2000 cm^{-1}). Major differences, however, were found between coated and uncoated membranes at high wave numbers around 3000 cm^{-1}. It is seen that after coating with epoxy solution, the two news peak at 2920 cm^{-1} and 2850 cm^{-1} might be assigned to stretching of aliphatic C-H stretching, consistent with a coating material abundant in aliphatic carbons [22]. As earlier studies [23] the small peaks around 3000cm^{-1} correspond to C-H vibration. For uncoated membrane, peaks around 3100-3000 cm^{-1} can be assigned to aromatic =C-H stretching. For coated membranes, peaks around 3330 cm^{-1} can be assigned to O-H stretching [22]. Moreover, it is evident that the peak intensity at about 3500cm^{-1} corresponding to the O-H stretching of the secondary hydroxyl in epoxy resin. It can be explained as the introduction of resin after the ring opening

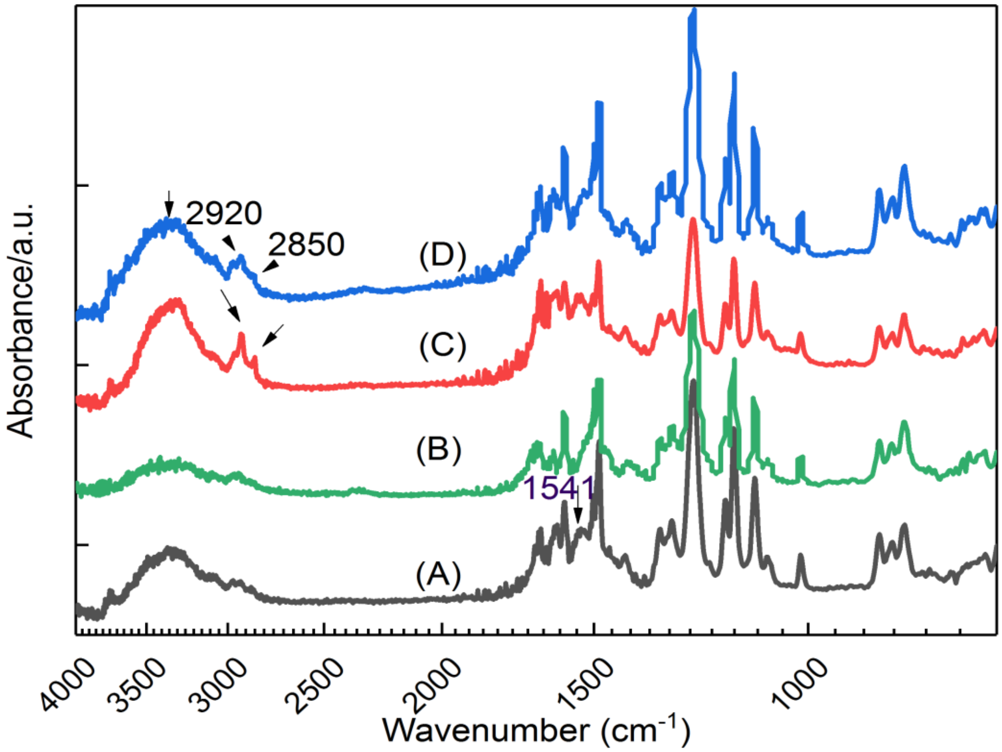

Fig. 4.7. ATR-FTIR spectra of (A) virgin, (B) chlorinated virgin, (C) coated, and (D) chlorinated coated membranes.

4.5.4 Membrane antifouling performance evaluation

A significantly decline of the normalized flux were observed both of the membranes during the first hour filtration. Then, it can be seen that the filtration gap between coated and pristine membrane significantly start to widen. After 10 hr fouling test, the normalized flux of the virgin membrane was reduced to nearly 10%, while that of the coated membrane was around 4% in the same condition as shown in Fig.4.8.

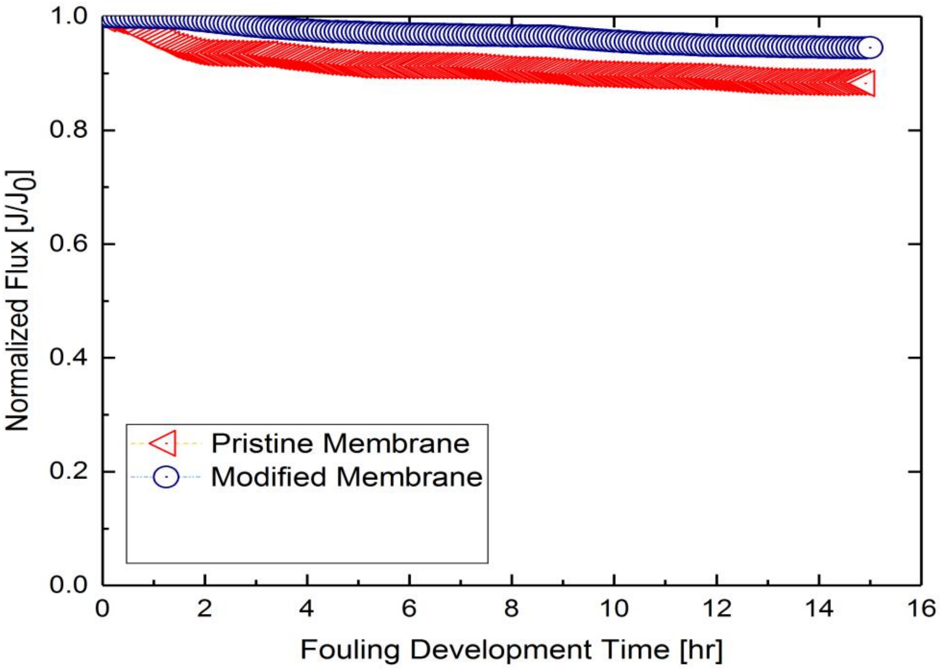

Fig .4.8. Variation in normalized flux between Pristine and Coated membrane using the BSA model foulant solution. Test condition: (20 mM NaCl, 1 mM $NaHCO_3$, 1 mM $CaCl_2$, 100 mg/L model foulant and pH = 8.0). Filtration was performed at 1.0 MPa feed pressure and 20°C feed temperature. Each chemical cleaning was performed with a 2,000 ppm NaOCl solution (pH = 11.4) at 20 °C for 1 h.

4.6 Conclusions

The effect of epoxy resin coating on RO polyamide were investigated based on chlorine stability. Each result supported the successful incorporation of an epoxy coating layer on the membrane surface. Surface morphology of virgin, coated membrane and chlorinated coated membrane showed a typically ridge and valley surface structure by SEM measurement. It is clearly shown that the epoxy resin coated membrane kept its initial morphology after chlorination 50.000 ppm-hr. XPS and SEM-EDS analysis revealed that the presence of high concentration of chlorine within the uncoated membrane polymer matrix after being exposed to hypochlorite. In addition, the chlorine exposure test using a NaOCl solution (50.000 ppm-hr) showed that the modified surface membranes were much less susceptible to chlorine attack and had enhanced chlorine stability. Over the whole testing period, both the salt rejection and water flux vary slightly and lie within the scopes of 99.6% to 92.5% and 41.2 to 45 L/m^{2}h, respectively, indicating that the coated membrane possesses good durability and long- term performance stability than the virgin membrane.

4.7 Acknowledgements

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CHAPTER 5

Conclusions

5.1 Organic Fouling and Chemical Cleaning

This study examined the effects of hypochlorite cleaning in fouling mitigation of a chlorine-resistant CR10 NF membrane using a secondary treated effluent. The exposure of the chlorine-resistant NF membrane to a 1,000 ppm NaOCl solution revealed that the permeability and separation performance remained stable for up to the cumulative chlorine exposure of 5×10^4 ppm-hr. The separation performance of the CR10 NF membrane for Na^+ ions, Ca^{2+} ions and *N*-nitrosamines (45% and 62%, respectively) was comparable to a commercial NF membrane (DK NF). Filtration of the secondary treated effluent by CR10 NF membrane resulted in a gradual decrease in permeability down to 75%, while hypochlorite cleaning with a 2,000 ppm NaOCl solution (pH = 11.0) for 1 h restored the permeability. The recovery in permeability was demonstrated up to three cycles, indicating that hypochlorite cleaning can be effective to the direct filtration of secondary treated effluent. Further investigations using model foulants suggested that humic substances are persistent to CR10 NF membrane even after hypochlorite cleaning. To make water-recycling systems using the chlorine-resistant NF membrane feasible, optimization techniques of cleaning protocols such as NaOCl concentrations, pH and temperature are required.

The presence of various foulant types in wastewater effluents adds to the complexity in understanding the fouling mechanisms of RO membranes because of the physical and chemical interactions among the various foulants. Moreover, Membrane surface chemistry is another vital factors as it affects the attractive and repulsive interactions between membrane and foulants that are contributed to fouling. Therefore, extensive research work should be carried out to evaluate the effectiveness of the available chemical agents, including the commercially available cleaning agents, and to develop more technically and economically feasible cleaning procedures. The important of membrane cleaning should certainly be recognized and addressed, and more time and effort should be devoted to understand fouling mechanisms and to develop more feasible, cost- effective cleaning, and restoration procedures for each type of fouling.

5.2 Surface Modification of reverse osmosis membrane

Membrane degradations by fouling and free chlorine oxidation are the major obstacles for aromatic polyamide to realized high performance over a long period of operation. In this work, epoxy modified reverse osmosis membrane was devised as a new type RO membrane to solve both the problems at the same time. In the research of study on chlorine resistance performance improvement in reverse osmosis membrane, two membrane has been selected and compared based on the chlorine stability at pH=11. Heat treatment of the polyamide RO membrane ESPA2 reduced the pure water permeability but improved the separation efficiency and fouling resistance. Hence, the concentration of coating solution has been optimized, manufactured and the characteristic of optimized of coating layer is confirmed by the various spectroscopy analysis. The method is efficient as the resulted membranes show much better wettability, chlorine and fouling resistances than the virgin membranes. The surface analysis indicates that the surface coating has significantly varied the physicochemical properties of the membrane surface. A chlorine-resistant coating layer was formed using a multi-functional epoxy compound, epoxy resin hydrogen bond. The higher concentration of the coating solution used in the modification process, the more epoxy molecules were incorporated into the aromatic polyamide, causing the more obvious decrease in membrane separation performance.(i.e., low water permeability, low salt rejection). To avoid excessive water flux loss, concentration of epoxy glue and glycidylsilane was need to optimize. Despite the loss of water permeability resulting from the formation of the coating within the polyamide thin film composite membrane, the use of epoxy as anti-chlorine resistance was significantly improved. The various analytical instrument confirms the characteristic of optimized membrane. The stability of chlorine resistance properties was tested by 1000ppm NaOCl solution. Typical reverse osmosis membrane structure are captured by SEM without severe deteriorating membrane surface even after 50,000 ppm-hr concentration. Detailed discussion about the effect of epoxy coating in performing chlorine resistance of coated membrane is also presented. The development membranes revealed excellent stability pH range in acid and alkali phase, even under prolonged exposure (up to 50,000 ppm-hr). In surface modified experiments, all of these results show drastically enhanced chlorine resistance of the surface modified RO membrane. In depth analysis to confirm the chemistry was need to carried out Transmission

Electron Microscopy. Wetting and hydrophilicity of the membrane coating material play a crucible on controlling fouling resistance and release of adsorbed foulants. Studies have shown that the membrane hydrophilicity can hinder fouling by protein. In the separation performance test, permeability of the coated membrane was slightly reduced from 41.2 to 38.2 L/ (m^2 h) and the salt rejection of coated membrane 99.6% was higher than the virgin membrane 99.4%. This is probably because the epoxy coating layer increased the resistance to water transport through the modified membrane. In the statically accelerating chlorination, the two-step modified membrane exhibited ameliorative chlorine resistance both in the acidic and alkali aging conditions. The resultant chemical composition changes of membrane surface was examined by XPS to confirm the successful coating of the polymer. Moreover, it was found that contact angles were reduced from 62% of untreated to 57% of treated membranes, indicating enhanced hydrophilicity and the coating generally smoothed RO membrane surface. Since the improvement of surface hydrophilicity, the decrease of roughness and the ridge and valley like topology are all advantageous to enhancing antifouling properties.

In antifouling experiment test, the filtration tests of protein solution revealed that the longer-term flux of modified membranes maintained at a constant level without decline, compared to the untreated membranes that flux declined rapidly. At the end of 600 minutes of filtration, a 15% reduction of the initial flux was observed for the untreated membranes whilst the modified membranes did not show any trend of decline. Anti-fouling properties of the membranes under consideration were improved with the epoxy treatment.

Although epoxy treatment improved chlorine resistance and antifouling properties, the impact of coating on the long-term performance and life-time of membranes is still unknown. Further research should be proceed that the stability of modifiers should be verified in actual application because it may be easily deteriorated in long-term operation due to the loss of modifiers. The acid, alkaline or other cleaning environments may cause the degradation of modifiers, which should be also considered in practical application. Generally, the chemically covalent linkage between membrane and modifiers is superior to physical combination and has better practical utility. However, special equipments or chemical reagents are usually needed in chemical modification method. These will increase the production cost or cause environmental pollution. Few studies should be focused on the stability of surface modifiers in cleaning operation because the cleaning step is a necessary process in RO membrane use.

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LIST OF FIGURES

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1. *****Moe Ma Ma Tin, Anioke George, Osamu Nakagoe, Shuji Tanabe, Hitoshi Kodamatani, Long D.Nghiem, Takahiro Fujioka; Membrane fouling , chemical cleaning and separation performance assessment of a chlorine – resistance nanofiltration membrane for water recycling applications, *Journal of separation and purification Technology.,189,* pp.170-175(2017.12) (Chapter 3)
2. *****Moe Ma Ma Tin, Hiroto Murakami, Osamu Nagagoe, Hideaki Sano, Guobin Zheng, Shuji Tanabe; Enhancement of chlorine resistance on RO membrane by surface modification with epoxy glue, *Chemistry Letters* (Submitted) (Chapter 4)