REVERSE OSMOSIS AND NANOFILTRATION MEMBRANE REJECTION OF ENDOCRINE DISRUPTING CHEMICALS

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ABSTRACT

Removal of endocrine disrupting chemicals (EDCs) in the water reclamation process has been a major concern to the potable water industry. Membrane technology has emerged as a suitable system in water reuse processes, but yet trace EDC rejection using this technology is still not completely understood. Adsorption, physical sieving and electro-repulsion have been reported to influence estrone rejection by hydrophobic polyamide membranes.

In this study, the effects of competition among EDCs on their rejection, pH, ionic strength, adsorption, and 24-hour operation were investigated using two types of membrane materials (cellulous acetate and polyamide). A synthetic feed water was used to evaluate factors influencing EDC rejection by reverse osmosis (RO) and nanofiltration (NF) membranes. Rejection of EDCs was investigated at a permeate flux of 0.007 $m^3/(h \cdot m^2)$ in a bench scale study.

The RO process was observed to be more effective at trace EDC removal, compared with the NF membrane. Physical sieving and adsorption were the likely cause of high estrone rejection by NF and RO membranes. Estrone was used as a representative of EDCs. Adsorption would have been helpful in the short term for estrone rejection. Adsorption and physical sieving could be attributed to the early stages of the 24-hour operation while physical sieving would have been the dominant mechanism over the 24-hour operation. Membrane adsorption of EDCs

was affected by competition among the EDCs in a mixture. This resulted in a decreased rejection of any one EDC in the mixture.

Electro-repulsion can not contribute to a higher estrone rejection by NF and RO membranes. The selected membranes and estrone are negatively charged under the high pH condition. Electro-repulsion between the negatively charged membrane and negatively charged estrone can be expected. This would have contributed to the relatively high rejection of estrone by cellulose acetate ST-28 and SP-28 membranes in contrast to removal of estrone by the polyamide AG membrane. The reduced rejection by the polyamide membrane was attributed to membrane surface modification under the high pH condition. The membrane surface was defined in terms of its surface morphology, roughness analysis, and zeta potential.

Key words:
Membranes, endocrine disrupting chemicals, estrone, rejection, nanofiltration, reverse osmosis.

ACKNOWLEDGEMENTS

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NOMENCLATURE

AFM	-	Atomic Force Microscopy
RO	-	Reverse Osmosis
NF	-	Nanofiltration
GC/MS	-	Gas Chromatography Coupled with Mass Spectrometry
HPLC	-	High-performance Liquid Chromatography
LC/MS/MS	-	Liquid Chromatography with Mass Spectrometry
EDCs	-	Endocrine Disrupting Chemicals
ppb	-	Parts Per Billion

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CHAPTER 1 INTRODUCTION

1.1 Background

To purify and reclaim water from wastewater, typically about 160 compounds need be removed [1]. After their removal, the water can be regarded as clean and potable. However, some researchers have recently reported the existence of endocrine-disrupting chemicals (EDCs) in the treated wastewater could potentially have an adverse impact on health, indicated by the proliferation of breast cancer MCF-7 cells and intersex roaches with oocytes in the testes [2]. An endocrine-disrupting chemical (EDC) is defined as "an exogenous substance that causes adverse health effects in an intact organism, or its progeny, consequent to the changes in endocrine function" [3]. The EDCs include hormones, alkylphenol polyethoxylates, prescription/non-prescription drugs, pesticides, disinfectants, and metals [4]. The key EDCs are natural estrone, natural estradiol and synthetic ethinyl estradiol [5].

Methods for removing EDCs have received great attention. However, due to the relatively low concentrations of the EDCs in water, it is a challenge to eliminate them effectively in the recycling procedure. Johnson [6] has reported that the mean estrogen removal in industrial sludge treatment works can be up to: 87 % estradiol, 61 % estrone, 85 % ethinyl estradiol, and 95 % estriol, where estrone and ethinyl estradiol are persistent in sewage effluent and the

concentrations of estrone and estradiol in the effluent are 15 ~ 220 ng/l and 4 ~ 88 ng/l, respectively.

In industry, reverse osmosis (RO) and Nanofiltration (NF) have been widely used to remove contaminants in water. They can remove pollutants with very low concentrations effectively. Kiso et al. [7, 8] have examined the rejection properties of alkyl phthalates, a group of the EDCs, by NF membranes. Physical sieving and adsorption mainly influenced the rejection of alky phthalates during the membrane separation process. Schäfer and her co-workers [9-13] reported that microfiltration (MF), NF and RO could exhibit short-term high adsorption of estrone, up to 97 % rejection. However, when the surface concentration on the membrane reached an equilibrium value, the adsorption of estrone by a MF membrane will come to zero, but rejection by NF and RO are still observable probably due to the physical sieving and charge effect on membranes. Although a number of studies have reported on the mechanisms affecting EDC rejection, these have neither been extensively studied nor well understood.

In this project, NF and RO membranes were investigated to determine the factors influencing EDC rejection, Measurements of EDCs in aqueous samples were made using LC/MS/MS.

1.2 Objectives

The overall objective of this project was to investigate the factors influencing EDC rejection from a synthetic feed water using NF and RO membranes. Two RO (AG & ST-28) and one NF (SP-28) membrane are selected in this study. To achieve the objective, the following were the sub-objectives:

1) To compare the rejections of three EDCs (estrone, 17β-estradiol & 17α-ethinyl estradiol) by NF and RO membranes, in relation to properties of the EDCs, such as their dissociation coefficient (pKa) & Octanol-water partition coefficient *(log P)*;

2) To explore the effects of various physical and chemical parameters on EDC rejection, including adsorption, competition among EDCs on their rejections, ionic strength, pH and 24-hour operation.

1.3 Scope

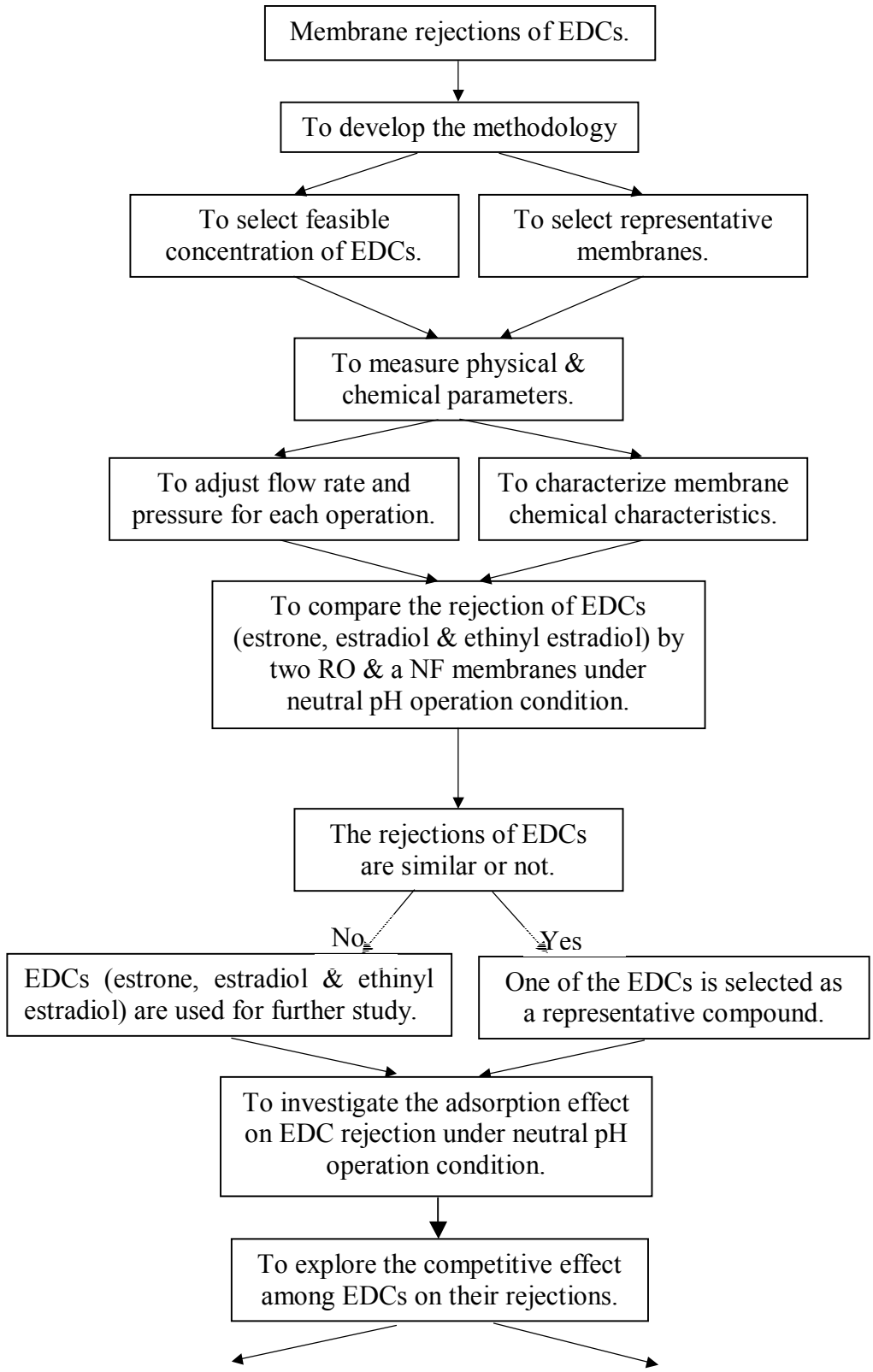
The project was a bench-scale study for 2-hour and 24-hour operation and. It was separated into three phases:

- Phase I - Start-up: To develop the LC/MS/MS methods for determining EDC concentration;

- Phase II - Tests: To determine the physical and chemical characteristics of each membrane (membrane surface morphology by Atomic Force Microscopy, hydrophobicity of membrane by contact angle measurement, membrane zeta potential by Electro Kinetic Analyzer);

- Phase III - Membrane operation: To investigate the factors that will affect the rejection of EDCs during the membrane separation process, which includes rejection comparison, competitive effect among EDCs, and ionic strength, pH, adsorption, and longer term (24-hour) operation effects on the rejection of EDCs.

Figure 1.1 shows the investigative flow of the project.


Membrane rejections of EDCs.
To develop the methodology
To select feasible concentration of EDCs.
To select representative membranes.
To measure physical & chemical parameters.
To adjust flow rate and pressure for each operation.
To characterize membrane chemical characteristics.
To compare the rejection of EDCs (estrone, estradiol & ethinyl estradiol) by two RO & a NF membranes under neutral pH operation condition.
The rejections of EDCs are similar or not.
No
Yes
EDCs (estrone, estradiol & ethinyl estradiol) are used for further study.
One of the EDCs is selected as a representative compound.
To investigate the adsorption effect on EDC rejection under neutral pH operation condition.
To explore the competitive effect among EDCs on their rejections.

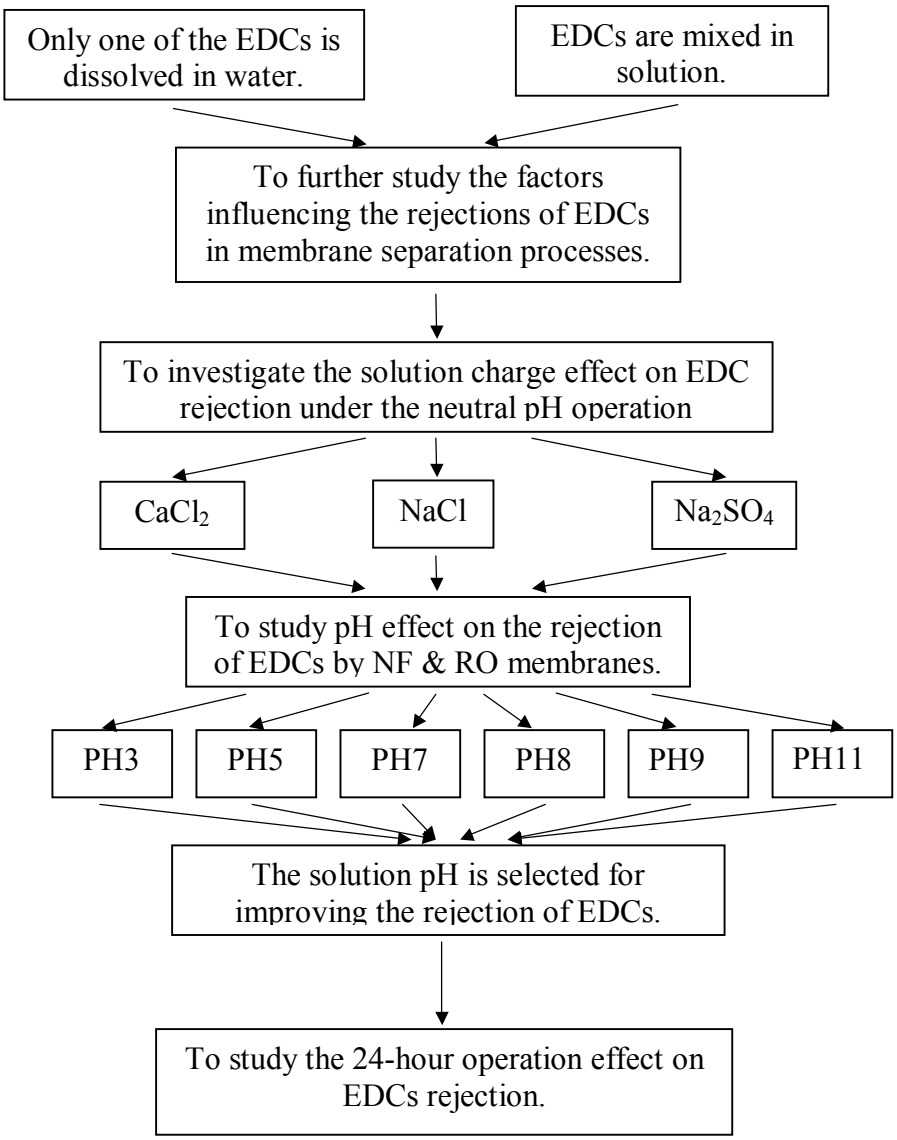


Figure 1.1 Work Flow Chart

CHAPTER 2 LITERATURE REVIEW

2.1 Endocrine Disrupting Chemicals (EDCs)

Chemicals interacting with the endocrine system in an adverse way are termed endocrine disrupting chemicals (EDCs) or endocrine disrupters. It was defined by the U.S. EPA and the IPCS that "*an endocrine disrupter is an exogenous substance that causes adverse health effects in an intact organism, or its progeny, consequent to changes in endocrine function.*"

EDCs mainly include:

- Pesticides (insecticides such as o, p'-DDT, endosulfan, dieldrin, methoxychlor, kepone, dicofol, toxaphene, chlordane; herbicides such as alachlor, atrazine and nitrofen; fungicides such as benomyl, mancozeb and tributyl tin; nematocides such as aldicarb and dibromochloropropane)
- Products associated with plastics (bisphenol A, phthalates)
- Pharmaceuticals (drug estrogens - birth control pills, DES, cimetidine)
- Ordinary household products (breakdown products of detergents and associated surfactants, including nonylphenol and octylphenol)
- Industrial chemicals (polychlorinated biphenyls or PCBs, dioxin and benzo(a)pyrene)
- Heavy metals (arsenic, lead, mercury, and cadmium).

2.2 Sources of Key EDCs

The key EDCs are estrogens or female steroid sex hormones based on a cholesterol skeleton. They are produced naturally in vertebrates in the gonads and adrenal cortex of both sexes. Estrogens are present in both sexes but estrogens dominate in the females while androgens (male sex hormones) dominate in the male. The major sources of estrogens are metabolites and estrogen therapy.

Firstly, the key hormones are metabolized mainly in the liver. Estradiol is both metabolized reversibly and irreversibly. In the reversible metabolism, Estradiol is transformed to estrone and estrone sulphate. These circulate in the blood stream and act as estradiol reservoirs. In the irreversible metabolism, estradiol is transformed to cathecol estrogens or estriol. The metabolites are finally conjugated with sulphate and glucuronides and excreted in the urine. A minor amount of the estrogens are excreted via faeces as un-conjugated metabolites.

Secondly, estrogen therapy may be given to menopause, contraceptive women or those who have had their uterus and ovaries removed. These therapies include drugs containing estrogens (estrone, 17β-estradiol and 17α-ethinyl estradiol). The total excretion of estrogens including metabolites and from estrogen therapy taken by in Denmark 2001 is shown in Table 2.1 [14].

Table 2.1 Total Estimated Excretion of Estrogens in Denmark 2001 [14]

EDC	Total Amount of Excretion (g/d)
Estrone	68.6
Estradiol	35.7
Ethinyl estradiol	3.2

2.3 Fate of Estrogens in Municipal Sewage Treatment Plants

Sewage effluent has been reused indirectly in many industries for a considerable time. However, the release of EDCs into the aquatic environment has raised concerns over water quality. The sewage treatment works (STW), which is commonly used to remove the bulk of the organic compounds, cannot break down all the compounds completely. Field data suggests that the STW can only remove 85 % of estrone, 17β-estradiol and 17α-ethinyl estradiol [15]. However, even the relatively low doses of their residues may cause effects on reproductive organs and even cancers [16, 17].

Vitellogenin induction in male or juvenile fish has become a useful biomarker for identifying estrogenic contamination of aquatic environment [19]. The Vitellogenin is a complex precursor protein for the production of yolk in all oviparous vertebrates. In fish, vitellogenin is normally found in the blood of

maturing female, whereas the levels in male juvenile fish are very low. Many EDCs (alkyphenonlic compounds, phyto-estrogens, synthetic estrogens and certain pesticides) are the inducers of the vitellogenin synthesis in both males and females [18].

Many studies have shown the relationship between the induction of vitellogenin synthesis in male fish and existence of estrogens in sewage effluents by vitellogenin bioassay [5, 20]. Fawell et al. [20] studied steroidal compounds, suspected of estrogenic activity in the region of Severn Trent Water, by using a combination of vitellogenin assay to integrate exposure over time, and advanced chemical analysis. Estrogenic activity, as measured in the rainbow trout vitellogenin assay, was detected at the Tame/Trent confluence, although this activity was relatively weak.

Desbrow [5] developed a fractionation system, combined with a vitellogenin assay for detecting estrogenic activity, to isolate and identify the major estrogenic chemicals in seven STW effluents, receiving primarily domestic effluent, discharging into British rivers. In his study, three sterols were isolated from the estrogenic fractions of sewage extracts. These were the natural hormone 17β-estradiol and estrone, and the synthetic hormone 17α-ethinyl estradiol. The data obtained from the experiment suggested that the observed induction of vitellogenin synthesis in male fish placed downstream of effluent discharges from STWs is due to the natural and synthetic hormones. STW effluents throughout the

U.K. have been shown to be estrogenic, inducing vitellogenin synthesis in caged and wild fish downstream of the effluent discharge. Rodgers-Gray [2] explored the vitellogenic response of male fish to long-term fluctuation in the concentrations of the estrogenic components of STW effluent. The concentration of estrogenic components in the effluent fluctuated temporally over 8 months. The vitellogenic response was both time and dose dependent.

2.4 Rejection of Estrogens by Membranes

Since the estrogenic activity could give rise to health issues, there is interest on how to remove the EDCs effectively. Membrane technology is commonly used to remove contaminants in water and wastewater treatment, even where the contaminant concentrations are very low.

A membrane, as a selective barrier between two different solutions, is a thin film of porous material, between which some forms of mass exchange can exist but not bulk mixing. A number of chemicals can be separated from water and wastewater. The membrane process, acting as a mass transfer process, can occur under a variety of driving forces. These can be concentration, pressure, temperature or electrical potential. Some membrane processes and their driving forces are summarized in Table 2.2. The driving forces ΔP, ΔC, ΔE *and* ΔT are pressure difference, concentration difference electric potential difference, and temperature difference through the membrane, respectively.

Table 2.2 Some Membrane Processes and Their Driving Forces

Membrane Process	Driving Forces
Ultrafiltration (UF)	ΔP
Microfiltration (MF)	ΔP
Nanofiltration (NF)	ΔP
Reverse Osmosis (RO)	ΔP
Pervaporation	ΔP
Osmosis	ΔC
Dialysis	ΔC
Electrodialysis	ΔE
Thermo-osmosis	ΔT
Membrane Distillation	ΔT

Among these membrane processes, pressure-driven processes are the most common and include microfiltration (MF), ultrafiltraton (UF), nanofiltration (NF), and reverse osmosis (RO). Table 2.3 shows the characteristics of pressure-driven processes and their applications.

Table 2.3 Pressure-driven Membrane Processes

Process	Operating Pressure	Pore Size	Material Retained
MF	~ 10 psi	0.1 μm -1.0 μm	Particulate removal
UF	~ 10 – 100 psi	0.001μm - 0.1μm	Microorganism and all types of particles
NF	~ 10 – 100 psi	1.0nm - 10nm	Multivalent salts, organics
RO	~ 100 – 800 psi	<1.0 nm	Salts and low-molecular-weight solutes

2.4.1 MF Membranes

Cross flow microfiltration is a chemical-free separation process for suspensions of particles in the size range of 0.1 ~ 1.0 μm. Microfiltration membranes are asymmetric and porous, and can be made from polymers or ceramics. One of the main industrial applications is the sterilization and clarification of beverages and pharmaceuticals in the food and pharmaceutical industries. The dominant problem using microfiltration membranes is the flux decline due to fouling and concentration polarization [21, 22].

Chang et al. conducted a study, which included evaluation of the adsorption of the trace natural estrogen estrone by hydrophobic microfiltration hollow fiber

membranes [9]. However, in his study, Chang et al. reported that breakthrough could occur after the membrane reached its adsorptive capacity.

Chang et al. assessed the partitioning of estrone and aqueous phase at equilibrium, the concept of membrane rejection of estrone as a result of adsorption, adsorption kinetics, and the potential application of membrane adsorption through batch adsorption and dead-end filtration studies using solutions containing trace estrone. He also reported that adsorption could result in significant accumulation of estrone on MF membrane surfaces, as the hydrophobicity of estrone is very high ($log\ P = 3.43$). The partitioning of estrone between membranes and aqueous phase could be characterized by the Freundlich equation. He found that when the membrane surface concentration of estrone reached equilibrium, corresponding to the estrone concentration in feed water, the rejection by microfiltration membrane would become very low as no further adsorption occurred.

2.4.2 UF Membranes

Ultrafiltration (UF) is an offshoot of reverse osmosis and really came into use only in 1960s. After a hollow fiber module was pioneered by Du Pont in the late 1960s for use in desalination, the units of UF were developed. Brehant and Kim [23 and 24] have already studied the separation properties of UF membranes. It was found UF provided the best pretreatment for RO resulting in increased

productivity, stable total dissolved solids (TDS) rejection, and efficient flux recovery by physical cleaning and reduction in chemical cleaning duration.

In addition, Schäfer also studied the adsorption of estrone on natural particles with the low-pressure ultrafiltration (UF) [10]. The adsorption of estrone on natural particles can enhance the possibility of estrone removal by UF membranes and thus is critical for estrone removal in water and wastewater treatment. In the practical application of this finding, actived sludge during ultrafiltration can adsorb estrone and thus enhance the rejection of the hormone.

2.4.3 NF & RO Membranes

The international Union of Pure and Applied Chemistry (IUPAC) defined reverse osmosis (RO) as a "pressure-driven process in which applied transmembrane pressure causes selective movement of solvent against its osmotic pressure difference" (1996). RO processes have been widely used for separating solutes in many fields, since its first commercial application in 1975, when Dow Chemical, Du Pont and Fluid Systems developed large-scale modules for the Office of Water Research and Technology, USA, for application in the water and wastewater, and food industries [25].

Another most important advance in membrane technology is the nanofiltration (NF) membranes process. This has been developed and widely used for removal of salts in wastewater treatment, and the separation of salts and small molecules in

a number of industries, e.g. recycle of dye bath waste water in textile industry and cheese whey deashing in dyes industry. According to IUPAC, nanofiltration is defined as a "pressure-driven membrane-based separation process in which particles and dissolved molecules larger than about 2 nm are rejected". NF membranes have properties which are between those for ultrafiltration (UF) and RO membranes. The solute separation mechanisms of NF membranes have been studied by Bowen and Peeters [26, 27]. Donnan exclusion can influence the NF membrane retention.

NF and RO membranes are similar in some aspects. They can be affected by the charge of the particles being rejected. Thus, particles with larger charges are more likely to be rejected than others. However, NF is not as fine a filtration process as RO. The NF membrane's pores are typically much larger than the RO membrane pores. Therefore, NF is not effective at the removal of small molecular weight organics, such as methanol.

NF and RO membranes, as selective barriers to the transport of matter, have the potential to remove EDCs from water and wastewater. Some studies have been done to investigate the rejection properties of EDCs, like aromatic pesticides and alkyl phthalates, by NF and RO membranes [7, 8, 11 - 13].

Nghiem and Schäfer investigated the rejection of estrone by NF and RO membranes [11 - 13]. Adsorption and physical sieving are the main mechanisms for the rejection of estrone by NF/RO membranes. Estrone may be adsorbed onto

NF/RO membranes, which could result in an initially high rejection. However, for large pore-size membranes, breakthrough could be observed when the membrane adsorptive sites are saturated and further adsorption came to zero, while small pore-size membranes could show a high potential in the removal of the trace contaminant estrone, since estrone could not pass through the membrane pores even if adsorption could not occur at the membrane surface. Breakthrough phenomenon will occur after a long period of nanofiltration in a lab-scale system [10].

2.5 Removal Mechanism and Affecting Parameters

Several mechanisms of water and solute transport through NF/RO membranes were discussed in the literature [7 - 13]. Although many researchers have studied the rejection properties of pollutants by NF/RO membranes, mechanisms of separation and physicochemical criteria for organic rejection are still not complete. Here are several mechanisms and effects of organic rejection by low-pressure membrane processes, proposed by previous researchers as summarized below.

- Physical sieving, steric hindrance or size exclusion;
- Adsorption on the membrane surface or internal structure;
- pH effect;
- Concentration of solution;
- Characteristics of membranes.

The mechanisms that play dominant roles in estrogenic removal depend on the properties of estrogens being filtered, the characteristics of the membranes (pore size, charge, membrane structure and membrane material), and chemistry of the solution being filtered.

2.5.1 Sieving and Adsorption

Physical sieving is one of the most important organics rejection mechanisms in membrane processes. Sieving is based on the difference between the solute and solvent molecular size. It assumes the membrane's pore size is larger than the solvent's molecular size but smaller than that of solute's molecular size. As a result, the solute can be rejected at the membrane-solution interface, while solvent (e.g. water) penetrates the membrane. However, even when the pore size of membrane is larger than the molecular size of the solute, rejection of pollutants still occurs. This meant that there are some other mechanisms involved in the rejection of the solutes.

While physical sieving does play an important role, it is difficult to isolate it from other effects. In Mohammad's study, he used polyamide membranes with molecular weight cut off (MWCO) ranging from 200 to 2000 Daltons to investigate the significance of steric and charge effects [28]. The rejection performance of membranes was found to be influenced by a combination of steric hindrance and charge effects. However, the pattern of rejection was quite varied

and inconsistent, making it difficult to assess the relative contribution of steric hindrance and membrane charge effects.

Adsorption of pollutants on membranes is of concern, as it is one of the major rejection mechanisms but it may also result in pollutants leakage or bulk release when desorption occurs [13, 29, 30]. Adsorption onto a polyamide membrane is possibly due to hydrogen bonding [13], as shown in Figure 2.1.

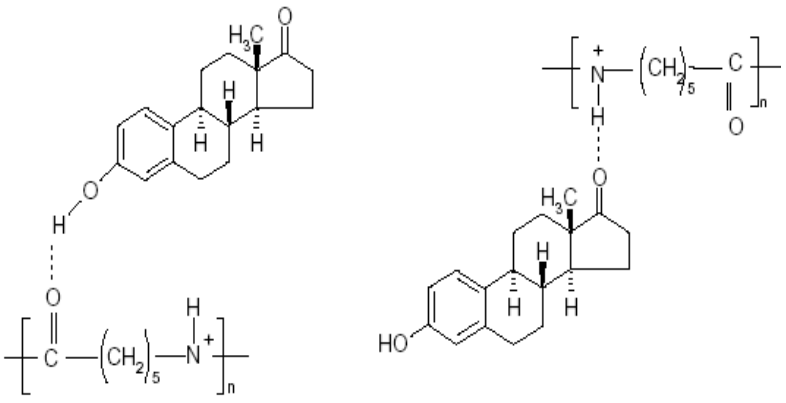


Figure 2.1 Possible H-bonding Between an Organic Molecule and the Membrane Polymer [13]

Kiso et al. reported that NF membranes could reject pesticides and alkyl phthalates effectively [7, 8]. They elucidated that the rejections of these organics were controlled by both steric hindrance (sieving) and adsorption effect, and these were affected by molecular width and hydrophobicity (*log P*), respectively. The rejection rate of all organics studied in his research can reach 97 % or more.

In another study, Schäfer et al. also investigated the adsorption of estrone by NF and RO membranes. Adsorption is the main mechanism of rejecting estrone from water and a breakthrough would occur when equilibrium has been reached between the membrane and estrone. Higher estrone adsorption in the hydrophobic membrane filtration process even with a large pore size membrane can occur. [13].

The dominating effect of continuous adsorption of hormones on RO membrane polymer during the membrane fouling was observed by Ng et al. [31]. Colloidal layer developed on the membrane may limit back diffusion of organic solute from the membrane surface to the bulk solution. Hormones concentration in the feed decreased continuously and approached to equilibrium even though most of the colloidal particles had deposited on the membrane, which may be attributed to the diffusion of hormones through the skin (active) layer of the RO membrane.

2.5.2 pH Effect

Another important effect between solute and membrane is the pH. Figure 2.2 shows the zeta potentials of some NF/RO membranes under different pH values by Elimelech et al. [32 - 36]. It was found that when the pH value was higher than 4.0, all the measured NF/RO membranes were negatively charged. The change of pH value could influence the distribution of ions at the membrane-solution interface: co-ions of charged molecules with charged membrane (i.e., ions of same charge as the membrane) will be electro-repulsed by the charged

membrane, while counter-ions (i.e., ions with the opposite charge) may be attracted by the charged membrane.

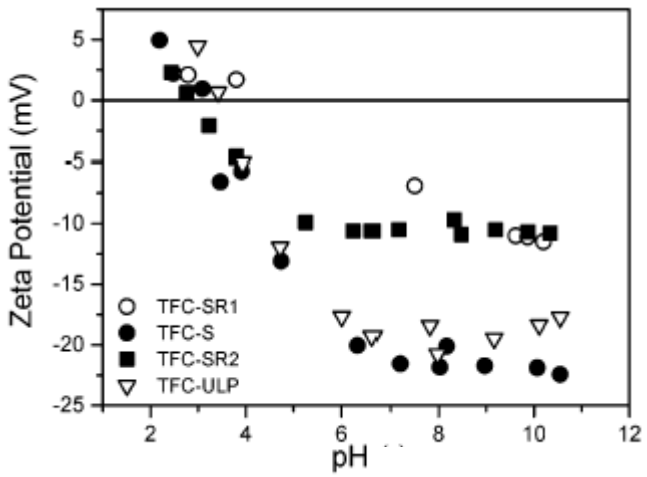


Figure 2.2 NF & RO Membrane Zeta Potentials Measured at Different pH in Background Solution (10 mM NaCl, 0.5 mM $CaCl_2$, and 1 mM $NaHCO_3$; TFC-SR1, TFC-S, TFC-SR2 and TFC-ULP are thin film polyamide membranes on polysulfone support) [13].

Schäfer et al. reported that adsorption of estrone on membranes would be affected by pH value. When the pH value increased, the adsorption of estrone would decrease due to the electro-repulsion between a negatively charged membrane and negatively charged estrone. In addition, the rejection of estrone by NF/RO membranes was strongly influenced by pH above the pKa value of estrone (10.4). Figure 2.3 shows that the rejection of estrone would sharply decrease as pH increased above 10.4. [13].

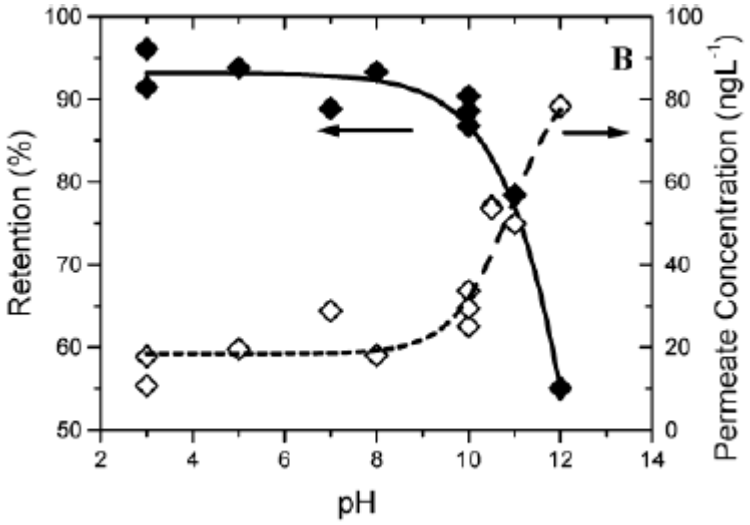


Figure 2.3 Effect of pH on Rejection of Estrone by TFC-SR2 Polyamide Membrane (1 mM $NaHCO_3$, 20 mM NaCl, pH varies from 3 to 12) [13].

2.5.3 Ionic Strength

Rejection is a complex interaction of steric hindrance, electrostatic repulsion, and solution effects between the membrane and solute. The presence of ionic strength in solution greatly affects membrane rejection of pollutants. The solution ionic strength may partially screen the charge associated with functional groups and thus reduce the apparent size of the pollutant's molecules. At the same time, it may shield the electrostatic potential generated by the membrane surface function groups and thus reduce electrostatic repulsive effects.

Zander elucidated the ionic strength effect on solute rejection and productivity [37]. In all cases, the presence of divalent cations decreased the rejection of both conductivity causing and organic matter. The lowest ionic strength solutions

showed the greatest total organic carbon (TOC) and conductivity rejection. Divalent cations increased the rate of decline in specific flux significantly over monovalent cations for the membranes investigated.

Schäfer et al. [13] also studied the effect of ionic strength on the rejection of estrone by NF and RO membranes. Ionic strength did not have a big impact on the rejection of estrone, as shown in Figure 2.4 and Figure 2.5. She suggested the ionic strength may have little or no effect on the rejection of estrone by membranes, which was probably due to the low concentration of estrone in water.

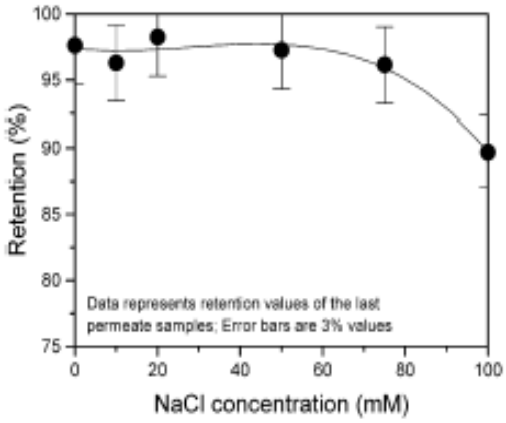


Figure 2.4 Effect of NaCl Concentration on Estrone Rejection (NaCl varies from 0 mM to 100 mM) [13].

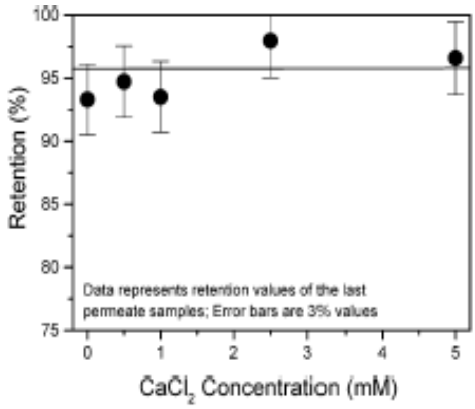


Figure 2.5 Effect of $CaCl_2$ Concentration on Estrone Rejection ($CaCl_2$ varies from 0 mM to 5 mM) [13].

2.5.4 Concentration of Solution

Van De Bruggen et al. [38] found that pesticide rejection by NF membranes was independent of the feed concentration (100 ~ 500 μg/l). They also mentioned that although the NF process was not expected to be influenced by the concentration of the pesticide, the interactions with the water matrix could be changed by the relative concentration of pesticide and matrix components. A similar result was also obtained by Schäfer when investigating concentration effects on estrone rejection [13].

2.5.5 Characteristics of Membrane

Characteristics of a membrane include pore size distribution, membrane material and membrane surface charge.

KoŠutić et al. investigated the removal of organic pollutants by NF and RO membranes of characterized porosity [39, 40]. It was found that the rejection of non-ionized organic solutes by the small pore size RO membranes were dominantly affected by membrane porosity parameters e.g. pore size distribution (PSD), as shown in Figure 2.6. While the rejections of non-ionized organic pollutants by large pore size membranes were dominantly affected by the physicochemical interactions among membrane surface, non-ionic solute and solvent molecules, e.g. adsorption effect.

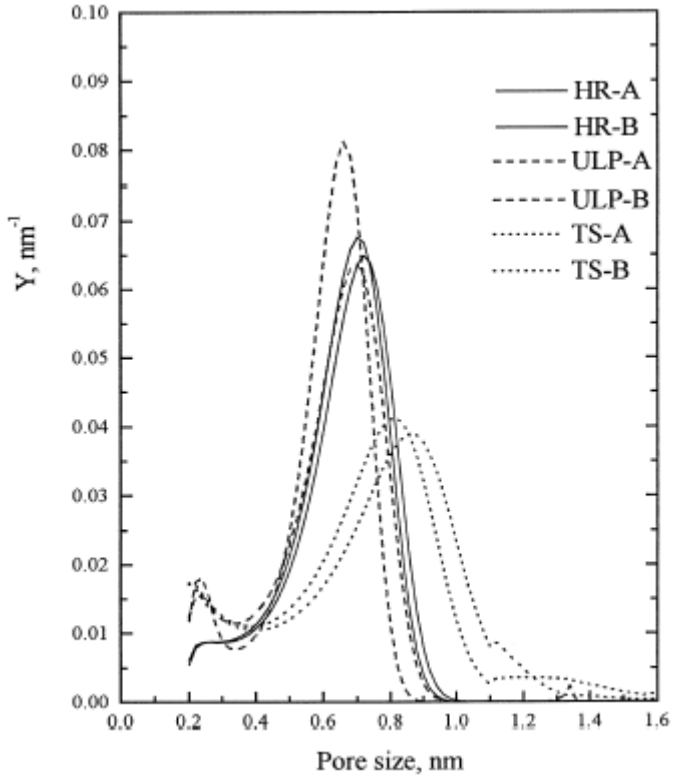


Figure 2.6 Pore Size Distribution of NF & RO Membrane Samples at the pressure of 6.8 bar (HR-A, HR-B, ULP-A and ULP-B are RO membranes; TS-A and TS-NB are NF membranes; Y is the defined pore size distribution) [39].

2.6 Diffusive Versus Convective Transport Model

Depending on the pore size to molecule size ratio, the transport of trace organics across the membrane active layer can be described as diffusive and/or convective. A modified diffusion model by Jones and O'Melia [41] is proposed to assess the ratio of diffusive to convective transport of trace contaminant estrone across the membrane [12].

The solute flux to the membrane surface is:

$$J = \left[1 - \frac{\Gamma_{(t)}}{\Gamma_e}\right] C_0 \left(\frac{D_{(sw)}}{\pi t}\right)^{1/2} \quad (1)$$

where C_0 is the bulk concentration of the solute, t is the time, $D_{(sw)}$ is the diffusion coefficient of the solute in water, Γ_e is the amount of trace organic which can be adsorbed on the membrane at equilibrium for a given concentration, $\Gamma_{(t)}$ is the amount of trace organic adsorbed on the membrane surface at time t.

The change in the mass adsorbed on membrane with time:

$$J = \frac{d\Gamma}{dt} \quad (2)$$

The flux of trace organic through the thin film interface at the membrane surface is equal to the change in the mass adsorbed with time. Therefore, Eq. (1) and (2) can be solved to yield:

$$\ln\left(1 - \frac{\Gamma_{(t)}}{\Gamma_e}\right) = \frac{-2C_0\theta}{\Gamma_e}\left(\frac{D_{(sw)}}{\pi}\right)^{1/2} t^{1/2} \quad (3)$$

θ is the extent to which adsorption can occur inside the pores of the membranes. According to their revised model, the low values of θ indicated that

the diffusion process of trace organics in the membrane material was usually much slower than the convective transport of water so that estrone rejection by that membrane is high, as is confirmed by his experimental results. When the values of θ are relatively high, estrone could penetrate into the pores of those membranes and transport of estrone across the membrane would then largely depend on convection.

2.7 Analytical Methods for the Determination of Estrogens

A variety of analytical procedures for identifying the estrogenic chemicals present in different research programs have been reported since the first method was described by Johnson et al. to measure estrogens in STW [42, 43]. However, the determination of EDCs is a very difficult analytical task, due to the very low detection limits required and the complexity of the wastewater matrix. Therefore, in general, complicated, time-consuming extraction and purification processes, usually based on the application of solid-phase extraction (SPE), are performed before a final determination, e.g. by immunoassay, high-performance liquid chromatography (HPLC), or, gas chromatography coupled with mass spectrometry (GC/MS). The procedure used for identification and quantification of estrogens in sewage effluents was summarized in Figure 2.7 [42, 43].

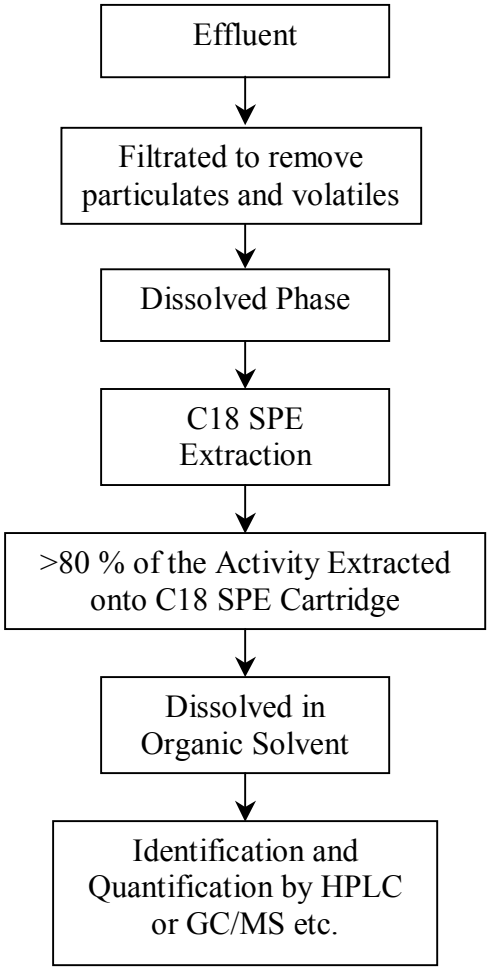


Figure 2.7 The Procedure Used for Identification and Quantification of Estrogens in Sewage Effluent.

2.7.1 Biological Technique

Biological techniques, e.g. immunoassay, are among the most sensitive analytical methods, but are limited by the availability of the specific antisera and are subject to cross-reactivity [44, 45]. Therefore, they have rarely been used for the analysis of estrogens in wastewater and water.

Snyder et al. investigated the analysis of estrogens by bioassay and achieved a better sensitivity, in the pg/l range. They used radioimmunoassay (RIA) for the determination of estradiol and ethynyl estradiol with the detection limit of 107 pg/l and 53 pg/l, respectively [45].

2.7.2 Gas Chromatography Coupled with Mass Spectrometry (GC/MS or GC/MS/MS)

GC/MS or GC/MS/MS is the technique used for the determination of estrogens in wastewater extracts. The detection limits achieved with different methods by GC/MS were in the range of 0.5 ~ 74 ng/l [5, 26].

However, GC/MS or GC/MS/MS analysis is time-consuming and could be a source of inaccuracy due to the derivatization required before each analysis [5]. An advantage of GC/MS in the analysis of estrogens is the availability of extensive libraries of mass spectra useful for identification of unknown peaks in estrogenically active fractions.

2.7.3 High-performance Liquid Chromatography (HPLC)

Most authors detected the estrogens with LC and MS detection, except for Snyder et al. [44] and López de Alda et al. [46]. Liquid chromatography coupled with mass spectrometry (LC/MS), unlike GC/MS, is not limited by such factors as non-volatility and high molecular weight, and enables the determination of both

conjugated and unconjugated estrogens without the need for derivation. In addition, the sensitivity of LC/MS is superior to GC/MS.

Electrospray (ESI) and atmospheric-pressure chemical ionization (APCI) are the LC/MS interfaces currently most widely used in the environmental analysis of organic pollutants. The use of triple-quadropole mass spectrometers in LC/MS/MS [26] has substantially increased the selectivity and sensitivity of the determination, resulting in limits of detection far better than those achieved by use of single-quadruple HPLC-MS.

2.8 Summary of Reviews

In this chapter, the development of membrane processes for removal of pollutants from both water and wastewater by membrane process has been reviewed. In these publications, high rejection of estrone, which is one compound of the trace EDCs in water, has been achieved with NF and RO processes. Adsorption of estrone on the membrane was found to be one of the important factors in the removal of the EDC.

However, most research reported was based on estrone removal with polyamide membranes. The key EDCs include estrone, 17β-estradiol and 17α-ethinyl estradiol. Although these have similar molecular structures, they have different hydrophobicities. Little is known of the rejections of 17β-estradiol and

17α-ethinyl estradiol. Competition among hydrophobic EDCs for adsorption onto membranes is expected to influence the EDC rejection by NF and RO membranes. The competitive effect among EDCs on their rejections will be investigated in this project. In addition, although polyamide and cellulose acetate membranes are both the most common materials used in NF and RO membrane separation processes, only a few formal utilizations of cellulose acetate to EDC rejection has been reported over the years. Compared with the polyamide membrane, the cellulose acetate membrane is a very low protein binding membrane with a constant surface charge under basic pH, and has a more stable performance in the filtration of pollutants. To further study the rejection of estrone as well as 17β-estradiol and 17α-ethinyl estradiol, two types of cellulose acetate membranes (ST-28 and SP-28 membranes) are used in this project. The results obtained by the cellulose acetate membrane are compared with those by a polyamide membrane (AG).

CHAPTER 3 MATERIALS AND METHODS

This chapter will present the preparation of equipment, reagent, samples and glassware, which is required for performing the experiments and analyzing the results.

3.1 Solution Chemistry and Chemicals

All the chemicals are analytical grade. Carbonate buffer are chosen as a natural matrix. The background electrolyte consists of 1 mM $NaHCO_3$ (Scharlau Chemie, Spain) and 20 mM NaCl (Scharlau Chemie, Spain), which provide buffering to pH 8 ± 0.2. pH is adjusted by 1M HCl (MERCK, USA) and 1M NaOH (Scharlau Chemie, Spain). $CaCl_2$ and Na_2SO_4 (Scharlau Chemie, Spain) are added as required in the investigation of ionic strength effect section.

Estrone, 17β-estradiol and 17α-ethinyl estradiol were purchased from Sigma-Aldrich Pte Ltd, Singapore. The EDCs were stored with a concentration of 200 mg/l in methanol solution. The stock solution was stored in the dark with a temperature below 4 °C.

As reviewed in Chapter 2, concentration effect is not critical to organic rejection by membranes. 5μg/l was selected as a feasible initial concentration of EDC in water. The 5 μg/l feed solutions were prepared by adding 375 ml of 200

mg/l EDC solution into Milli Q water for every 75 μg required. The Milli Q water is distilled water purified by a Millipore Q system to a water conductivity of 16 ~ 18 Ω.

3.2 Characteristics of EDCs

According to their octanol-water partition coefficient (log *P*), three key EDCs (estrone, 17β-estradiol and 17α-ethinyl estradiol) are selected in this project, which are quite similar in their molecular structure, as are shown in Figure 3.1. The chemical characteristics of each molecule are summarized in Table 3.1. They have similar pKa value but different log P, which is a representative of molecule hydrophobicity.

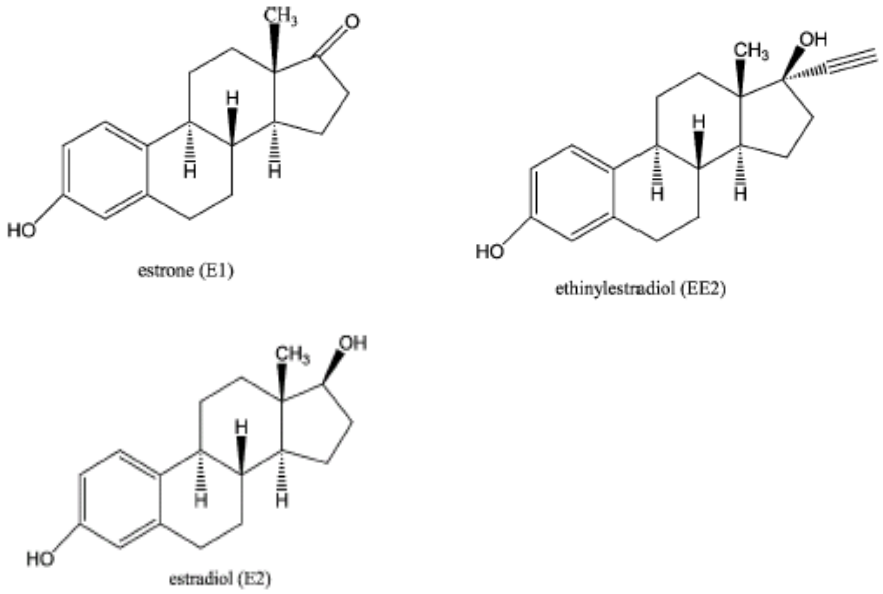


Figure 3.1 Structures of EDCs [49]

Table 3.1 Characteristics of Key EDCs

Solute	Molecular weight (g/mol)	pKa	Solubility in water (mg/l at 20C) [13]	*Log P* [13, 47, 49]
Estrone	270.36	10.4 [10]	13	3.43
17β-estradiol	272.36	10.4 [10]	13	3.94
17α-ethinyl estradiol	296.39	10.2 [33]	4.8	4.15

3.3 Membranes and Experimental Setup

3.3.1 Membranes

Based on their membrane materials, rejection rates and typical flux, a commercial flat-sheet NF membrane and two commercial flat-sheet RO membranes (see Table 3.2) were selected for this study. All membranes were pre-cut with a length of 14.0 cm and width of 14.0 cm before being stored in the Milli Q water. Before use, the membranes were soaked in a beaker of Milli Q water for 10 hours to remove the preservative solution. The efficient membrane physical surface area is 81.1 cm^2.

Table 3.2 Descriptions of NF & RO Membrane Operating Characteristics

Class	Polymer	Rej-Size %	25 ˚C pH Range	Maximum Temperature (°C)	Typical Flux / psi GFD@PSI
RO (AG)	Polyamide	99.5 (200 psi net, 1,000 mg/L NaCl feed)	Optimum 6.5 - 7.5; operating 4-11	50	26 / 225
RO (ST-28)	Cellulose triacetate/ diacetate blend	97 (400 psi net, 1,000 mg/L NaCl feed)	Optimum 6 - 7; operating 2 - 8	30	23.5 / 420
NF (SP-28)	Cellulose triacetate/ diacetate blend	92 (230 psi net, 2,000 mg/l Na_2SO_4 feed)	Optimum 6 - 7; operating 2 - 8	30	28 / 220

1. Rejection is based on membrane performance after 24 hours without fouling or boundary layer effects;
2. 1 GFD ≈ 1.67 L/hr-m^2; 100 psi ≈ 6.90 kPa;
3. The membrane characteristics presented in the table are provided by Osmonics, USA.

For this project, two different membrane materials (with physical area 81 cm^2) were used: polyamide and cellulous acetate.

The membranes were divided into two main categories: NF and RO. Figure 3.2 gives the basic information of these membrane operations used in water treatment. Polyamide and cellulose acetate membranes are commonly used in NF and RO processes. Cellulous acetate membranes have been widely used since a long time ago. Compared with the surface of a polyamide membrane, the surface of a cellulose acetate membrane is smoother, is more sensitive to pH, higher pressure requirements and has a small surface charge. However, because of the

relatively small charged surface and tolerance to free chlorine [43], cellulose acetate membranes will usually have a more stable performance than polyamide membranes in applications, especially for the feed water with a high fouling potential, such as with municipal effluent and surface water supplies. The chemical structures of polyamide and cellulose acetate are shown in Figure 3.3.

To get a comparable flux, the operating pressures were adjusted to a transmembrane pressure of 80 and 100 psi for the two RO membranes (AG and ST-28 membrane, respectively), and 60 psi for the NF membrane (SP-28 membrane). To control the pressures, flow valves were used to make the adjustments.

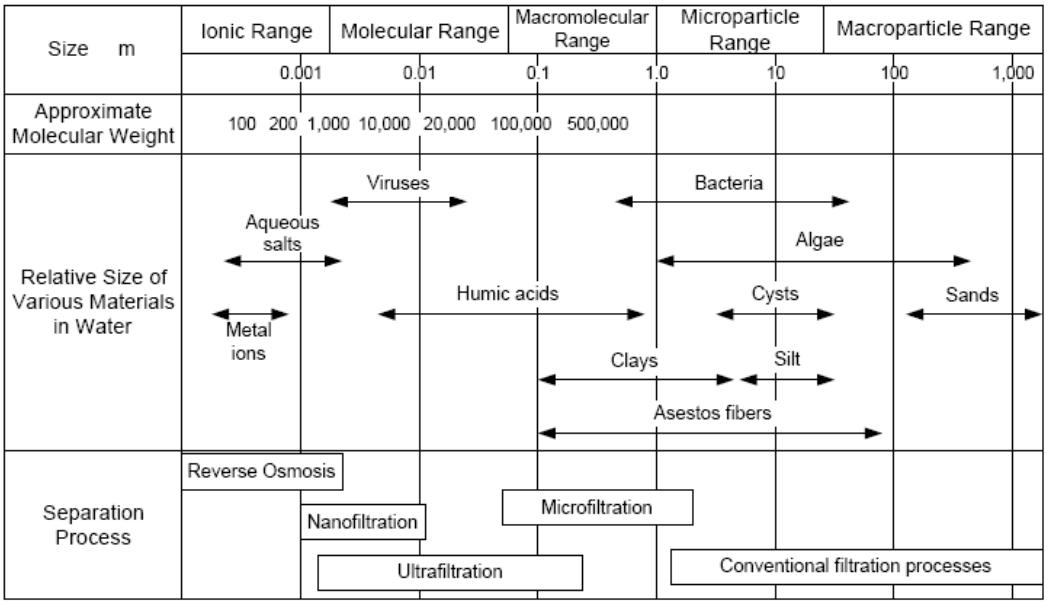


Figure 3.2 Membrane Operations in Water Treatment (Osmonics Inc.)

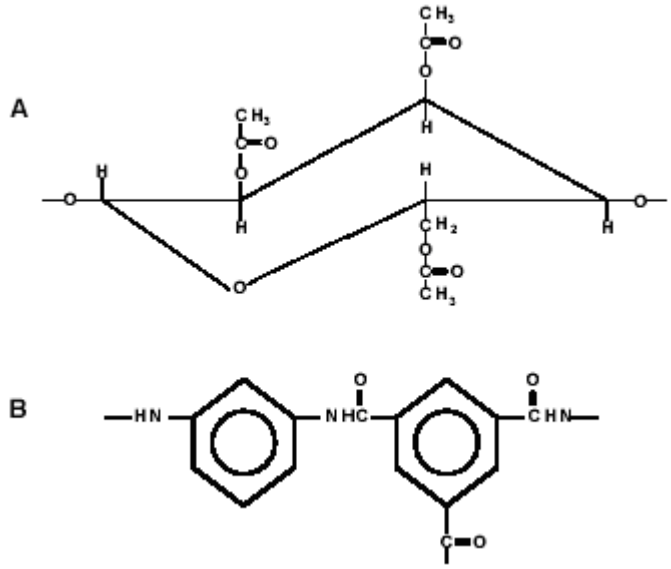


Figure 3.3 Chemical Structures of (A) Cellulose triacetate and (B) Polyamide Membrane Materials [46]

3.3.2 Membrane Cell

The equipment in this project is a laboratory scale cross-flow membrane filtration unit. It consists of a cell holder with a pressure gauge, a cell body top, a piece of permeate carrier, a piece of feed spacer and a cell body bottom with concentrate pressure gauge. It can be operated up to 200 psi. Figure 3.4 shows two square polypropylene test cell units.

3.4 Membrane Cell Units

3.3.3 Experimental Setup

The bench-scale setup included a low pressure test cell unit from Osmonics, USA, which consisted of two square polypropylene test cell units with the flat sheet membranes embedded in between. Samples were collected from three sampling points (Point 1 - Feed, Point 2 - Permeate, Point 3 - Concentrate) as is shown in Figure 3.5.

A membrane is placed over the feed spacer by four alignment pins to hold it in position. The feed stream is pumped from the feed tank and the pressure can be adjusted by a bypass valve. Each solution ran through the experimental setup (see Figure 3.6) at a permeate flow rate of 1.0 ± 0.2 ml/min. The feed solution was

maintained at room temperature of 26 ± 2 ^{o}C. To rinse away the residual preservative chemicals on membrane surface, the equipment ran continuously for 2 hours at 60 psi with Milli Q water before the test solution was filled into the tank. In the meanwhile, the system was checked out for leaks.

The Solution, spiking 5 μg/l EDCs in Milli Q water, was then filtrated by each of the three membranes. Before the experiment, the membrane filtration unit would be operated with Milli Q water for 30 mins. 1mM $NaHCO_3$ and 20 mM NaCl would be used as the background solution. 15 L of bulk solution would be processed through membrane filtration unit. Permeate samples would be collected at different internals for analysis. 30 ml permeate samples were collected by an auto-sampler. Feed samples were also collected for analysis. Each sample was concentrated by solid phase extraction (SPE) before measured. The concentrated EDC solutions of each aqueous sample were measured by LC/MS/MS. Each sample was measured for three times. Three times for each experiment were also required.

The operation mode will be repeatedly operated at the following conditions to find out the effect of the solution parameters on the operations.

- The rejections of estrone, 17β-estradiol and 17α-ethinyl estradiol were compared under the neutral pH conditions.
- Adsorption of EDCs onto the membranes was investigated under the neutral pH condition for 24 hours.

- Competitive effect was investigated under the acidic, neutral and basic pH.
- Charge effect was studied with the addition of $CaCl_2$, NaCl and Na_2SO_4 (from more positive to more negative charge in the solution).
- pH effect on rejection of representative compound by different membranes was investigated at pH 3, 5, 7, 9 and 11, respectively.
- EDC rejection for 24 hours under neutral pH condition was to investigate the factors influencing the EDC rejection over the longer duration. Samples were collected at internals for analysis.

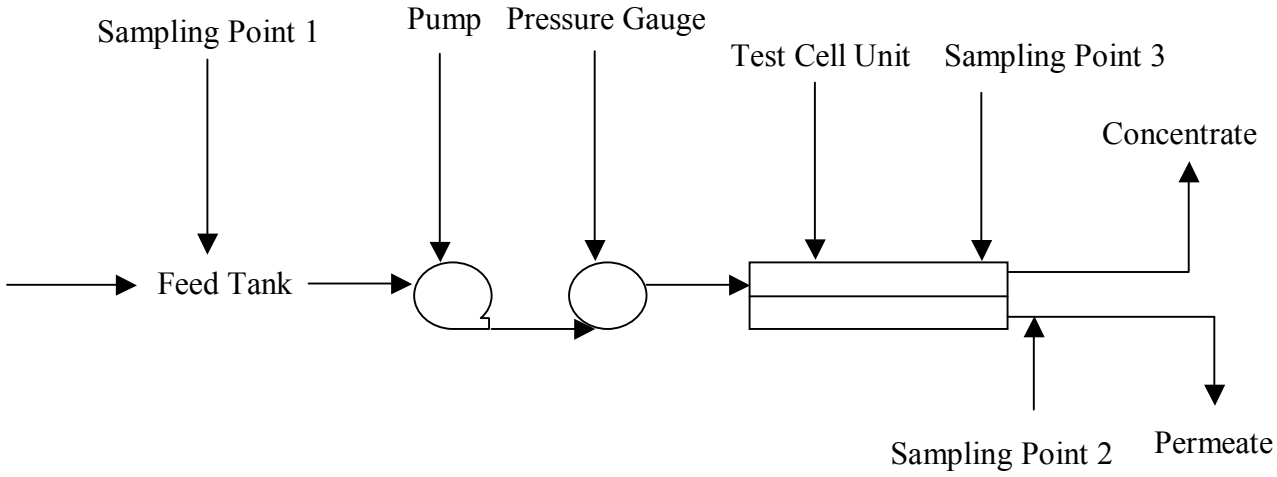


Figure 3.5 Schematic Diagram of Bench Scale Setup.

The rejection *R* can be calculated by,

$$R = \left(1 - \frac{C_p}{C_0}\right) \times 100\,\%$$

where C_p and C_0 are the concentrations for the permeate and bulk solution, respectively.

Figure 3.6 Membrane System with an Auto-sampler.

3.3.4 Adsorption Setup

500 ml 5 μg/l estrone, with one piece of membrane (2.7 cm× 5 cm) was prepared in each standard flask. Fresh membrane would be used for each experiment. 1 mM $NaHCO_3$ and 20 mM NaCl would be used as the background solution, and the pH of the bulk solution was adjusted to the neutral pH. Each experiment would be carried in three replicate. The setup is shown in Figure 3.7. The standard flasks were vibrated by an auto-shaker for 24 hours. Samples would be collected after 0.5 *h*, 1 *h*, 2 *h*, 4 *h*, 8 *h*, 12 *h*, 16 *h*, 20 *h* and 24 *h* for analysis.

Figure 3.7 Set-up for Adsorption Test

3.4 Reproducibility of Results

Each experiment was replicated three times, on different days and in different analytical batches. The differences in the EDC rejections between runs have a variation of ± 2 %, except for the AG membrane by AFM analysis. The relatively larger difference for the AG membrane roughness analysis was observed due to the inconsistent morphology of polyamide AG membrane surface.

3.5 Preparation of Glassware

All glassware are treated so as to be carbon free to avoid contamination. The glassware are soaked in 10 % HCl for 12 hours, rinsed thoroughly with Milli Q water, dried in the oven at 100 ºC before wrapping them with aluminum foil and placing them in the oven at 550 ºC for 6 hours.

3.6 Measurement of Physical and Chemical Parameters

3.6.1 pH and Temperature

pH and temperature of the samples were monitored to ensure that there was a relative uniformity. The pH meter (Horiba F-22) was used to determine the pH. The temperature of the samples was determined using a thermometer.

3.6.2 Analysis of EDCs

In this project, LC/MS/MS (Perkin-Elmer Sciex API-2000 tandem triple quadropole), equipped with an electrospay interface, was used for measuring EDC concentration of all aqueous samples [47].

3.6.2.1 Solid Phase Extraction

Apparatus, Visiprep™ Solid Phase Extraction Vacuum Manifolds coupled with C 18-M cartridge, is shown in Figure 3.8. Analytes were extracted from aqueous samples by solid-phase extraction cartridges Strata C18-M (pore size 143 Å, average particle diameter 58 μm). The steps are summarized below:

Step 1. Conditioning the cartridges:

Each aqueous sample of 30 ml was adjusted by acetic acid to pH 3 ± 0.3. Before the analytes were extracted, the cartridge was conditioned sequentially with 10 ml of acetronitrile, 5 ml of methanol, and 10 ml of Milli Q water. The flow rate was maintained at 10 ml/min by controlling the vacuum gauge at -5 inch Hg.

Step 2. Extracting samples:

The acidified liquids subsequently passed through the cartridge by clean transfer lines (Telfon®) with the aid of a vacuum pump.

Step 3. Eluting the compounds and evaporating the samples:

The cartridge was rinsed with 5ml of acetronitrile. After 5 minutes, the residue of analytes is extracted from the cartridge by passing through another 5mL of acetronitrile, at a flow rate of about 10 ml/min. The final eluate is collected in a brown glass vial (2 cm in length, 1.4 cm i.d.). After collecting the last drops of this solvent mixture, the solvent in the vial is dried under a gentle stream of nitrogen at 150 ml/min and 4 bar (4,000 kPa), as is shown in Figure 3.9. After drying, 250 μl of methanol is added to the vial, and the final extract is injected into the LC column. The recovery is around 75 %. The concentration factors manage to reach 120.

Figure 3.8 Solid Phase Extraction Setup.

Figure 3.9 Drying Setup With Nitrogen Tank.

3.6.2.2 Optimization of the Method

The LC/MS/MS with an electrospay interface was operated in negative ion-mode. Phase A was water, and phase B was methanol. The initial composition of the mobile phase is 30 % A and 70% B. The flow rate of the mobile phase is 0.2 ml/min. High purity nitrogen gas is used as the nebulizer, drying curtain and collision gas. The settings for the curtain gas is 40 psi. For all the analytes, the declustering potential is 30 *V*. Multiple reaction monitoring (MRM) mode is chosen for quantification. The ion spay voltage is – 4.5 kV and the probe

temperature is 450 ^{o}C. All the source and instrument parameters for monitoring EDCs are optimized by standard solutions by a syringe pump. After observing the collision-induced dissociation (CID) spectra obtained by full-scan production experiments, the following MRM pairs were chosen: estrone: 269.2/145.0; 269.2/143.0. 17β-estradiol: 271.2/183.0; 271.2/145.0; 271.2/143.0. 17α-ethinyl estradiol: 295.1/159; 295.1/145.

Analytes are quantified by the external standard quantification procedure. Standard solutions are prepared, 200 *ppb*, 100 *ppb*, 50 *ppb*, 20 *ppb*, 10 *ppb*, 5 *ppb*, 3 *ppb*. For every analyte, the peak area versus injected amount chart is obtained by measurement of the resulting peak area at any injected amount. The response of the system was linearly related to injected amounts of the analytes up to 300 ~ 400 *ng*.

3.6.3 Atomic Force Microscopy (AFM) Analysis

The purpose of performing an AFM analysis on the membrane is to investigate the membrane surface morphology.

AFM used a micro-fabricated cantilever with a small tip probed systematically the surface of each sample to generate a topographical image. The technique allowed the surface study of materials down to the nanometer scale. Little

previous preparation of samples was needed. It can be used to provide membrane surface morphology with a 3-D view image [48].

Fresh membrane was used for each test. Membranes for high pH treatment were soaked in Milli Q water at pH 11 for 2 hours. The pH was adjusted using sodium hydroxide (NaOH). Three small pieces were cut from each kind of membrane (AG, ST-28 and SP-28). Before analyzing, all the membrane specimens were treated with high pH solution for 2 hours, drying for 2 hours and degassing using nitrogen in the sequence at room temperature. The high pH treated and the corresponding clean membrane surfaces were analyzed by AFM.

3.6.4 Membrane Hydrophobicity

The contact angle measurement can be used to determine the relative surface hydrophobicities of membranes. An air bubble was introduced into a liquid reservoir beneath a submerged sample. The angle formed at contact between the hydrated sample surface and air bubble was calculated from the bubble's height and diameter at the interface, and is reported as contact angle in degrees: the greater the contact angle, the greater the hydrophobicity of the polymer surface. A hydrophilic membrane would cause the bubble to spread over the membrane surface since water is excluded from the bubble-membrane interface.

The contact angle among a water droplet, the membrane surface and air was measured using a goniometer, (Contact Angle Analysis OCA 20 supplied by LMS

Technologies PTE. LTD.), by the sessile drop method. The medium used was Milli Q water.

3.6.5 Membrane Zeta Potential Measurement

Zeta potential is the potential at the plane of shear between the surface and solution where motion occurs between them. The streaming potential technique is the most suitable for membrane surfaces.

Using an Electro Kinetic Analyzer, the zeta potential was determined by measuring both the streaming potential and specific electrical conductivity of the electrolyte solution (1L 1mM KCl) based on the Fairbrother/Mastin equation. The membrane zeta potential provides a measure of the electrical charge of the membrane surface.

3.6.6 Adsorption Amount of Estrone Measurement

The adsorption of estrone by the membranes was determined by mass balance calculation. The mass balance in the adsorption process is defined as:

$$C_0 V_0 = A\Gamma + V_s \sum_{1}^{m} C_{si} + C_e V_e$$

where A is the membrane area (cm^2), Γ is the amount of estrone adsorbed per surface area ($\mu g/cm^2$) and m is the number of collected samples. $C_{0,}$ C_{si} *and* C_e are the initial, the i^{th} collected sample's and equilibrium concentration, respectively. $V_{0,}$ V_{si} *and* V_e are the initial, the i^{th} collected sample's and equibrium volume, respectively.

CHAPTER 4 RESULTS AND DISCUSSION

Presented in the first phase of this chapter are the results and discussion in relation to the membrane characteristics selected for study.

EDC rejections by NF and RO membranes will be compared under neutral pH condition. This will be followed by investigating factors influencing the EDC rejection by NF and RO membranes, including competitive effect, adsorption, ionic strength, pH, and 24-hour operation effects on the EDC rejection.

4.1 Membrane Characteristics

Two RO (AG and ST-28) and a NF (SP-28) membrane from Osmonics (USA) were selected for study. Their characteristics in terms of the membrane materials, typical flux and rejection size are summarized in Table 3.1. Membrane characteristics in terms of surface morphology, surface charge and hydrophobicity will influence EDC rejection during the membrane operation process. These characteristics were investigated by AFM surface analysis, membrane zeta potential measurement and membrane contact angle measurement.

4.1.1 Membrane Surface Morphology and Roughness

Investigation of membrane surface morphology could provide an understanding of how membrane surface characteristics influence EDC rejection by polyamide and cellulous acetate membranes. Atomic Force Microscopy (AFM) was used in this project to scan the membrane surface. It allows study of the surface down to the nanometer scale and provides a 3-D image of the former.

Three clean membranes investigated in this project were treated by NaOH (at pH 10.86). Surfaces of the three high-pH treated and the corresponding three clean membranes (AG, ST-28 and SP-28) were analyzed by AFM and 3-D view images of the six membrane surface morphologies are shown in Figure 4.1. The corresponding roughness values of their surfaces were given in Figure 4.2. Table 4.1 shows their membrane surface area ratios, which are calculated by Nanoscope software for AFM analysis.

On comparing Figure 4.1 (a), (b) and (c), it may be noted cellulose acetate (ST-28 and SP-28) membranes have relatively smoother surfaces whereas the polyamide (AG) membrane had a more irregular surface. This surface variation was attributed to the nature of the membrane materials. With a rougher surface, it could be easier for pollutants to accumulate on the polyamide membrane surface as compared to the smoother cellulose acetate membrane surface. Therefore, the

AG membrane is expected to adsorb more EDCs among these three membranes, if surface roughness was the only determinant.

Little difference was observed between the ST-28 and SP-28 membrane surface morphology (See Figure 4.1 (b) and (c)). This suggested that surface morphology would not be the primary determinant in pollutant rejection. These two membranes, however, could have different pore sizes. This difference in pore size distribution can be suggested by their solute rejections. SP-28 exhibited poorer sodium rejection (92 %), compared with ST-28 membrane (97 %) (Table 3.1). This suggested the ST-28 membrane, which is a RO membrane, had smaller pores than the SP-28 membrane.

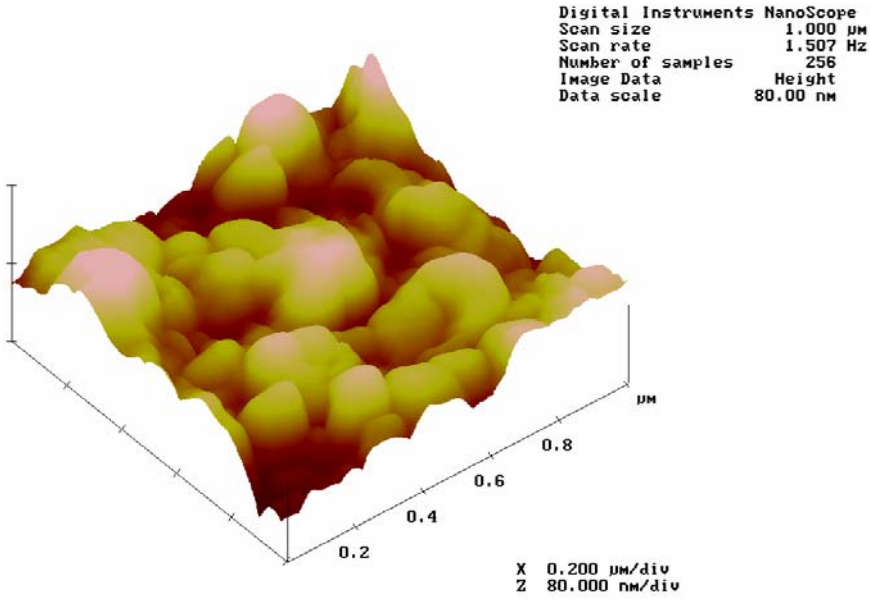
On comparing the micrographs of Figure 4.1 (a) and (d), variation between surfaces of clean AG membrane and high pH treated (pH 10.86) AG membrane was noted. Roughness of high-pH treated AG membrane was increased as well, as seen in Figure 4.2. The rougher surface of the high-pH treated AG membrane can be attributed to the high pH condition.

Many researchers have reported polyamide membranes have wider pH tolerance, compared with cellulose acetate membranes to enable a certain ease in RO system design [51]. The manufacturer also reported that polyamide membranes were wide pH tolerance under pH 2 ~ 11.

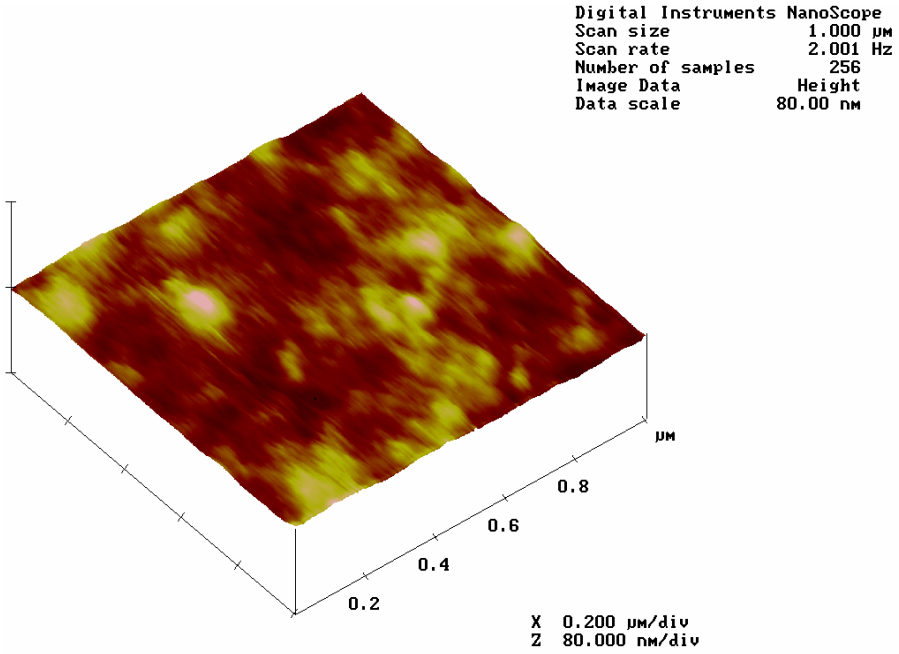
The results indicated that characteristics of AG polyamide membrane were modified under the strong basic pH. Since the membrane material is sensitive of pH, EDC rejection could then also be sensitive to pH if this membrane was used.

At high pH values (8 ~ 10), it has been reported the uncharged solute rejection decreased, which was attributed to an increase in pore size of a membrane to minimize the electrostatic repulsion between the acidic functional groups within the membrane [57, 59]. This indicated that polyamide membrane itself could have the ability to minimize changes affected by surroundings. It assumed that under strong basic pH, the negatively charged acidic functional groups of membrane surface could enlarge the membrane surface to minimize the electro-repulsion between co-ionic functional groups within the membrane.

It was seen that there was only a small difference between the clean cellulose acetate (ST-28 and SP-28) and high-pH treated cellulose acetate membrane surface morphology. This was indicative of the cellulose acetate membrane's relative stability to high pH, at least over a short of period of exposure.

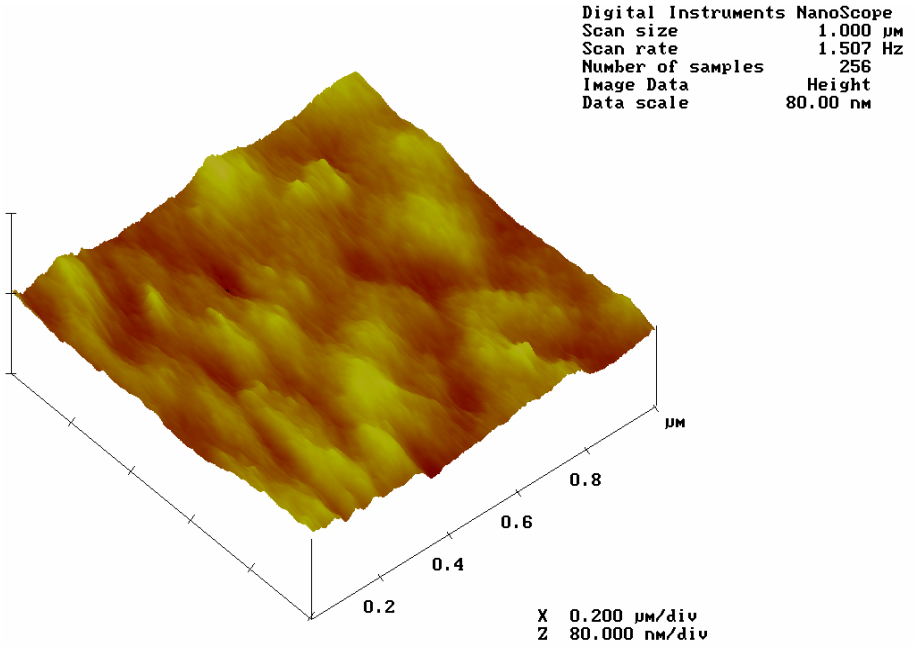


(a) Surface Image for Clean AG Membrane.

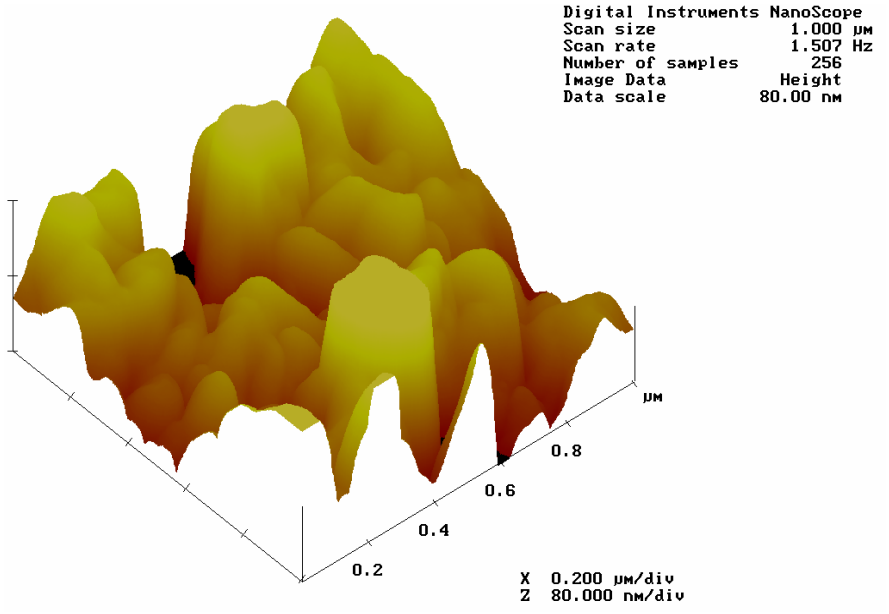


(b) Surface Image for Clean ST-28 Membrane.

Figure 4.1 Membrane Surface Analyses.

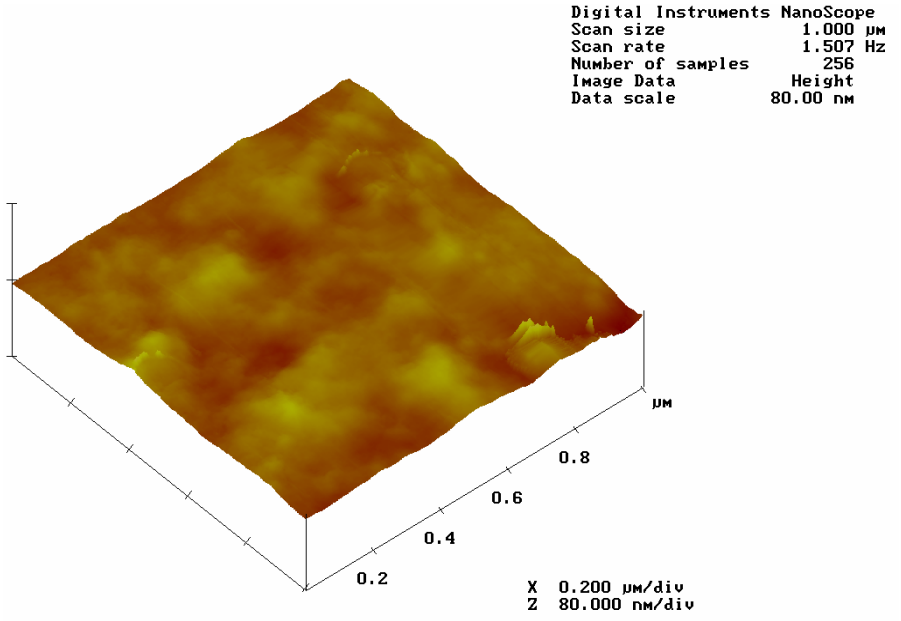


(c) Surface Image for Clean SP-28 Membrane.

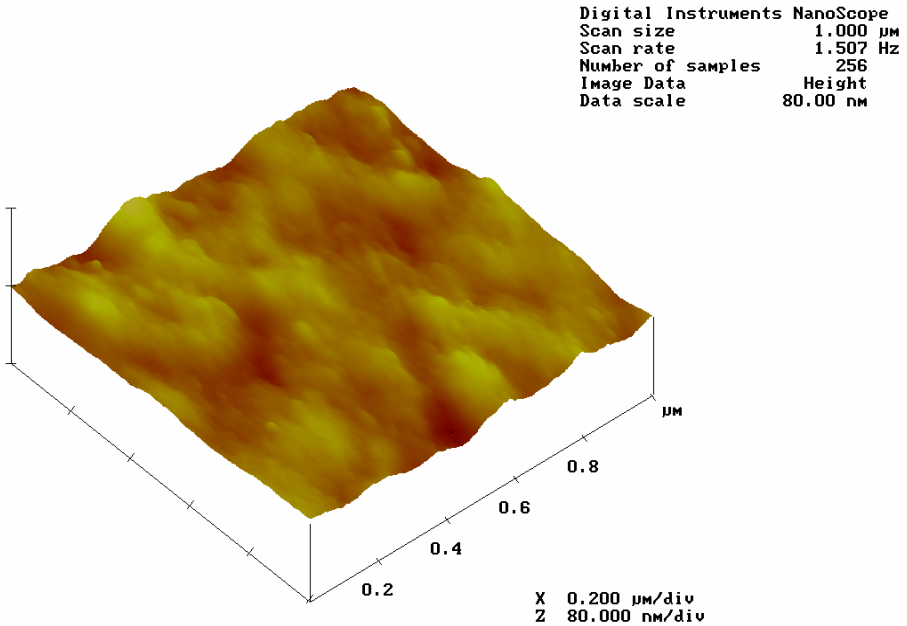


(d) Surface Image for High pH Treated AG Membrane.

Figure 4.1 Membrane Surface Analyses.

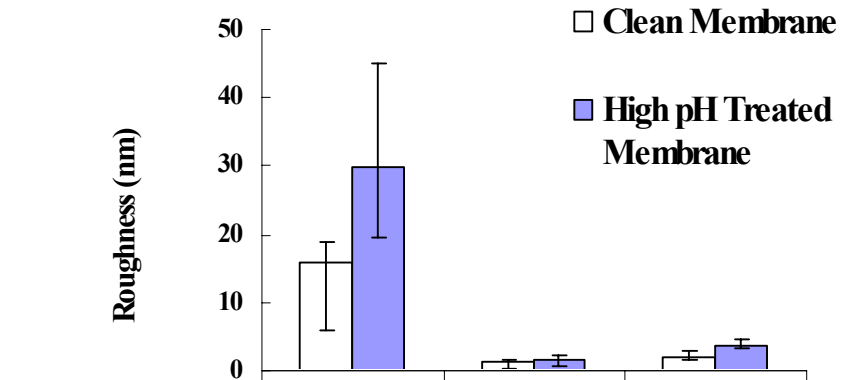


(e) Surface Image for High pH Treated ST-28 Membrane.



(f) Surface Image for High pH Treated SP-28 Membrane.

Figure 4.1 Membrane Surface Analyses.



	AG	ST-28	SP-28
Clean Membrane	16.00	1.31	2.14
High pH Treated Membrane	29.76	1.66	3.79

Figure 4.2 Surface Roughness of Membranes.

Table 4.1 Membrane Surface Areas

Membrane	Physical Surface Area (μm^2)	Actual Surface Area (μm^2)	Surface Area Ratio
AG	1.00	1.127±0.050	1.127±0.050
ST-28	1.00	1.005±0.004	1.005±0.004
SP-28	1.00	1.010±0.010	1.010±0.010

4.1.2 Membrane Hydrophobicity

Contact angle provides information of membrane hydrophobicity. It uses the sessile drop technique with Milli Q water as its reference liquid. The contact angles of the three membranes are measured by a goniometer and summarized in Figure 4.3.

The contact angles of SP-28 (60.2 °) and ST-28 (58 °) membrane were 10.1 º ~ 12.3 º higher than that of the AG membrane (47.9 °). Contact angle increases as hydrophobicity of membranes increases. Hydrophobicity of materials was termed having little tendancy to adsorb water but high potential to adsorb hydrophobic compounds. Hydrophobicity can be one of the determinants for the adsorptive amount of EDCs on membranes.

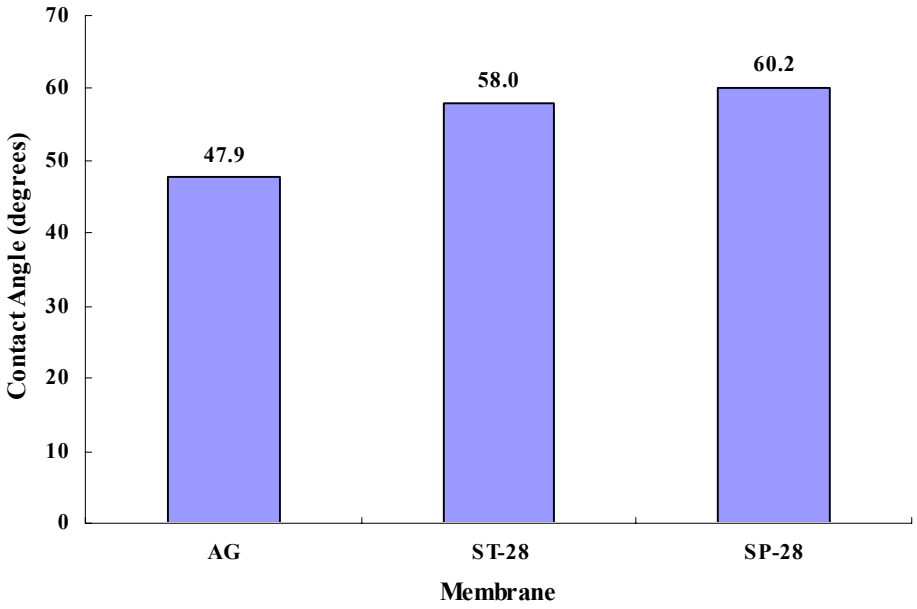


Figure 4.3 Membrane Contact Angles.

4.1.3 Membrane Zeta Potential

Membrane zeta potential provides the information of a membrane surface electrical charge. The zeta potentials were measured under pH range 2 ~ 11 by an electro kinetic analyzer. The results are shown in Figure 4.4, which are fitted with quadratic regression, due to experimental fluctuation of points.

It can be seen from the figure that all the membranes had a negative charge from pH 2 to pH 11. Although the zeta potential of AG membrane at pH 11 was not covered, but the pattern of the AG membrane surface zeta potential trend within pH range 2 ~ 11 can be predicted in Figure 4.4.

No positive charge of membrane was presented within the pH range 2 ~ 11. It could be because the isoelectric point of membrane was out of the pH range. Isoelectric point was the pH of a solution at which the net charge on membrane surface is zero. The isoelectric points of all membranes are below pH 2.

AG membrane surface zeta potential within pH range exhibited large variation in Figure 4.4. It indicated the charge and resulting zeta potential of the membrane is pH dependent. Membrane functional groups can protonate or deprotonate over the pH range. The negative charge on the membrane surface is usually caused by sulfonic or carboxylic acid groups that are deprotonated at neutral pH [52, 53].

It was noted the AG membrane zeta potential became more negative as pH increased while under acidic conditions, but began to decrease when pH was 7 and above. The increasingly negative potential was attributed to the presence of a carboxylic functional group in the structure of polyamide (See Figure 3.3), which will be deprotonated. While the decreasing negative potential under the basic pH implied the negative charge on the membrane surface would be decreased with pH increase under the basic pH. The unexpected decreasing negative charge can be indicative of AG polyamide membrane surface modification. The membrane modification under strong basic pH was also suggested by the membrane roughness analysis. This pattern of AG polyamide membrane zeta potential is relatively consistent with that of the polyamide membrane surface zeta potential of Schäfer et al. [13]. It might confirm the reliability of this simplification.

However, the ST-28 and SP-28 membrane became increasingly negatively charged as pH increased from the acidic to basic range until leveling off became evident above pH 9. The relatively small change in the negative charge above pH 9 suggested that the electro-repulsion force between negative charged membrane and negative charged EDCs would be relatively stable under the high pH condition.

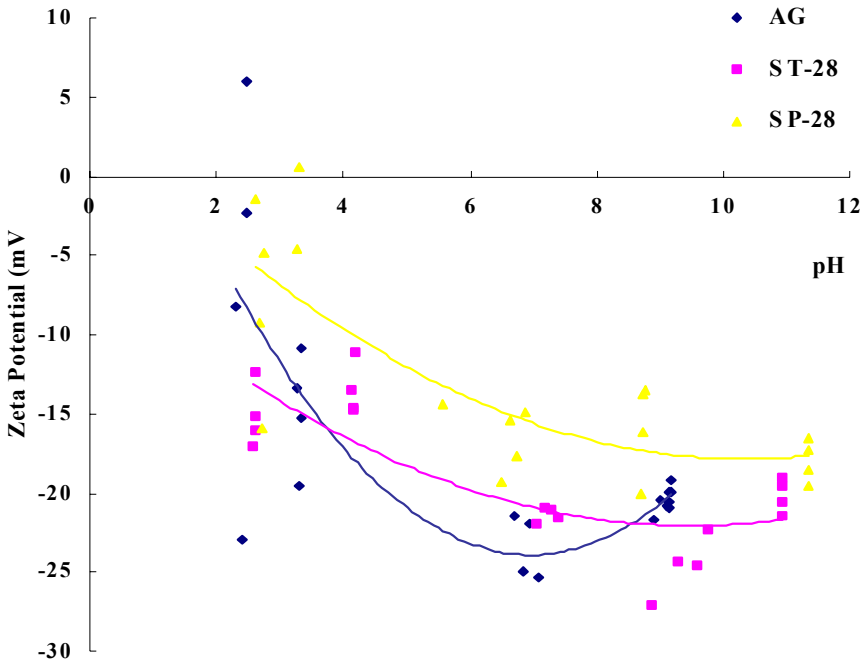


Figure 4.4 Membrane Zeta Potentials at Different pH (Background Solution of 1 mM KCl).

4.2 EDC Rejection

Three EDCs were selected with similar molecular structure but different hydrophobicity, including estrone, 17β-estradiol and 17α-ethinyl estradiol. The EDC rejections were compared under neutral pH operation condition and shown in Figure 4.5.

It was noted that the membranes exhibited very high EDC rejections (98.33 % ~ 89.88 %) under the neutral pH condition by RO (AG, ST-28) and NF (SP-28) membranes, which was attributed to the hydrophobicity of membranes and EDCs. It was seen in Table 3.2 that estrone, 17β-estradiol and 17α-ethinyl estradiol were all highly hydrophobic compounds, as the larger *log P* is, the higher the hydrophobicity of the pollutants. As discussed in section 4.1.2, the selected membranes (AG, ST-28 and SP-28) were all highly hydrophobic. The highly hydrophobic EDCs and hydrophobic membrane surface indicated EDCs could be strongly adsorbed onto a membrane surface and thus retained by membranes.

Only a small difference was observed in Figure 4.5 among the rejections of the three EDCs. Although the EDCs have different hydrophobicities, the relatively similar EDC rejection indicated that the adsorption on the membranes surface might not been saturated for trace organics during the short-term operation. The hydrophobicity difference among EDCs was not critical to the trace EDC rejection by NF and RO membranes.

From the Figure 4.5, it can also be seen the RO (AG and ST-28) membranes exhibited better EDC rejection (91.85 % ~ 98.33 %) than the NF (SP-28) membrane. It can be explained by their sodium rejections [See Table 3.1]. The sodium rejection by SP-28 membrane is 92 %, lower than the other two membranes (97 %). The higher EDCs rejections by RO membranes could be attributed by the smaller pore size of RO membranes.

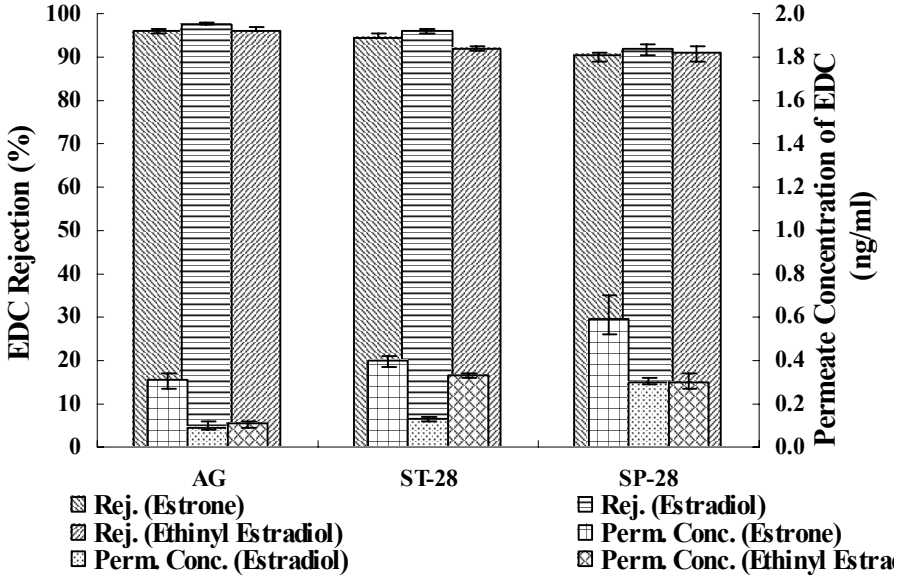


Figure 4.5 EDC Rejection (Estrone, 17β-estradiol and 17α-ethinyl estradiol) by NF and RO Membranes under Neutral pH Condition.

4.3 Effect of Adsorption on Estrone Rejection

As discussed above, estrone, 17β-estradiol and 17α-ethinyl estradiol exhibited largely similar rejections. Estrone would be selected as a representative EDC for the further study.

Estrone and the selected membranes were all highly hydrophobic. Adsorption effect could be one of the factors influencing the rejection of estrone by membranes. The adsorption of estrone onto membranes was investigated and the results are shown in Figure 4.6.

In the Figure 4.6, the residual concentration of estrone in solution following contact with the AG membrane was the lowest, followed by SP-28 and ST-28 membranes. It indicated adsorption amount of estrone onto AG membrane were the highest, followed by ST-28 and SP-28. The main reason for this result was that membrane adsorption of estrone was both determined by the membrane hydrophobicity and roughness. ST-28 and SP-28 membranes have higher hydrophobicity than the AG membrane, which was indicative of higher adsorption potential of pollutants. However, The AG membrane had the highest surface roughness, compared with the ST-28 and SP-28 membranes (See Figure 4.2). The AG membrane could have more surface area for adsorption of estrone.

Adsorptive amount of estrone per centimeter square on each membrane within 24 hours was calculated by mass balance and shown in Figure 4.7. Both sides of

membranes were counted for areas in contact with estrone. The sequence of the adsorptive amount of estrone per centimeter square on membranes was: SP-28 > AG > ST-28, which was different from the results in Figure 4.7. It can be explained that the hydrophobicity of SP-28 is the largest among membranes, which contributed to the highest adsorption of estrone while AG membrane surface area in contact with estrone is the largest among membranes and contributes to a relatively higher adsorption amount of estrone.

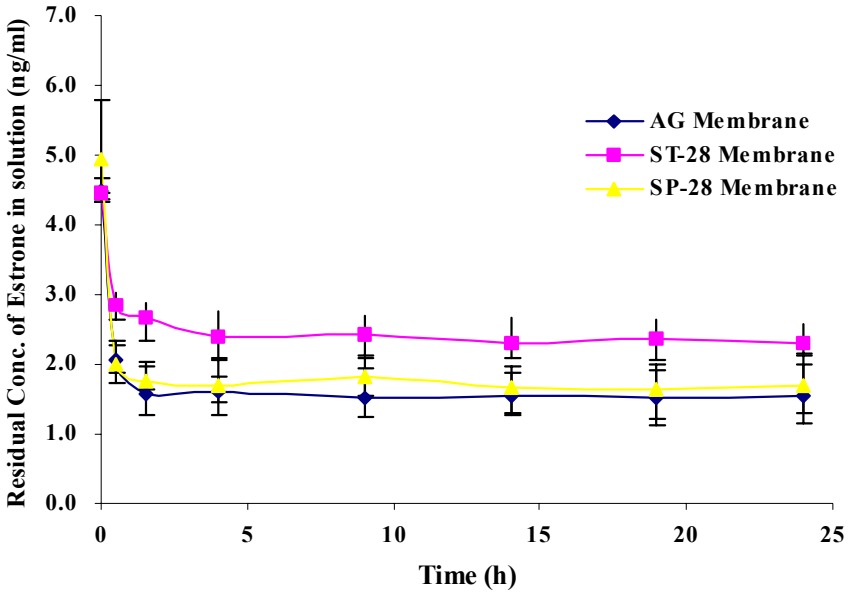


Figure 4.6 Adsorption of Estrone on NF & RO Membranes.

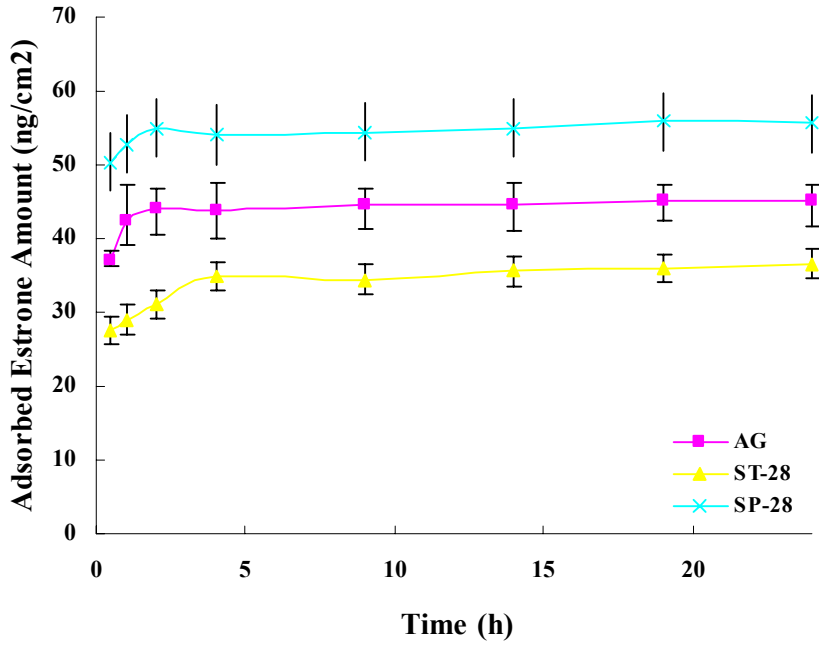


Figure 4.7 Estrone Adsorption onto the Membranes.

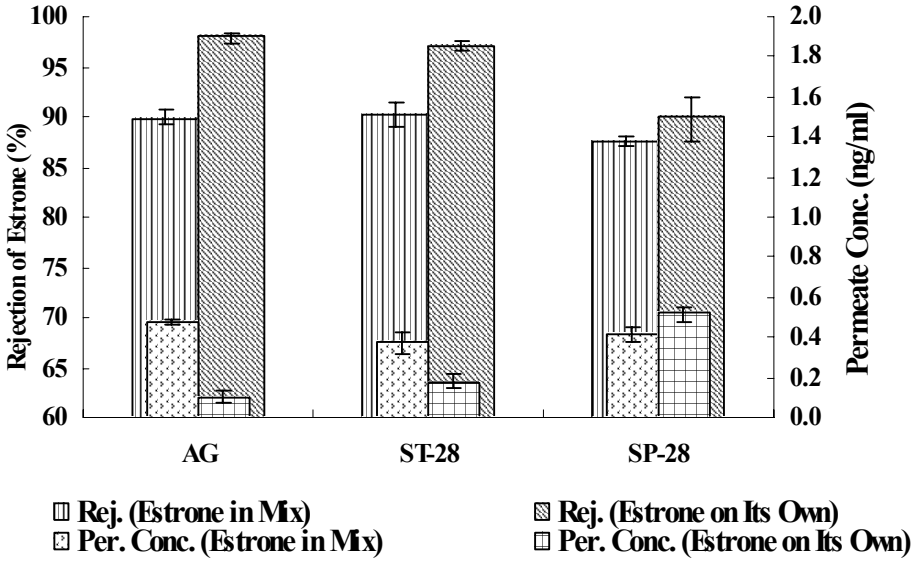
4.4 Competitive Effect on the EDC Rejection

As discussed in section 4.3, all membranes selected will reach their adsorption equillibrium within 24 hours. Competitive effect among EDCs on their rejections was investigated.

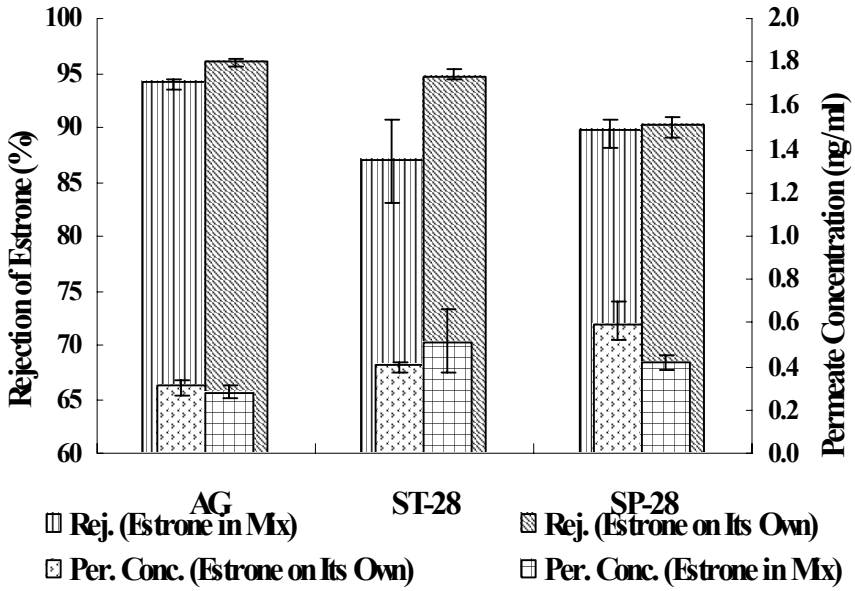
Estrone, 17β-estradiol and 17α-ethinyl estradiol were mixed in Milli Q water. 1 mM $NaHCO_3$ and 20 mM NaCl were used as the background electrolytes. The rejection of estrone on its own in solution and estrone in a mixture of estrone, 17β-estradiol and 17α-ethinyl estradiol were compared at pH 3, 7 and 11 in Figure 4.8.

It was seen from the Figure 4.8 that the rejection of estrone in the mixture was poorer than that of estrone on its own. This drop could be because the adsorptive amount on the membrane surface were very limited. Therefore, the adsorption mechanism can not now as readily remove estrone when it was in a mixture of hydrophobic compounds.

Under strong basic pH, less difference was observed between estrone rejection in the mixture and on its own. It indicated that the competitive effect among EDCs under basic pH could be neglibile. The reson could be explained that electro-repulsion between negatively charged membrane and negatively charged EDC was formed under the strong basic pH (pH 11), which would reduce the affinity between EDC and membrane.

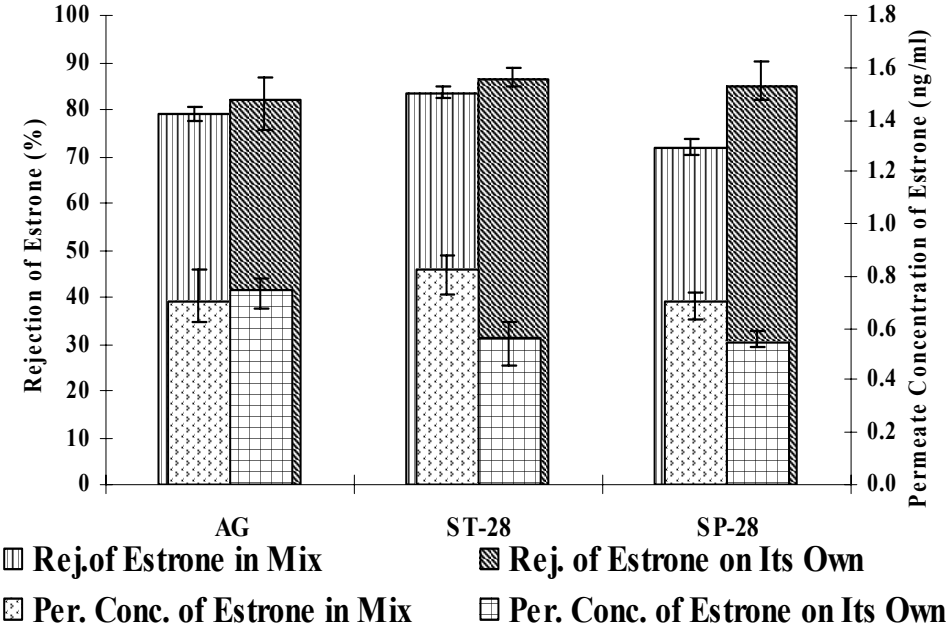


(a) Competitive Effect at pH 3.



(b) Competitive Effect at pH 7.

Figure 4.8 Competitive Effect Among EDCs on Their Rejection.



(c) Competitive Effect at pH 11.

Figure 4.8 Competitive Effect Among EDCs on Their Rejection.

4.5 Effect of Ionic Strength on Estrone Rejection

The ionic strength effect on estrone rejection was investigated in this section with the addition of 5 mM $CaCl_2$, NaCl and Na_2SO_4 in solution, respectively. The charge of three electrolytes was from more positive to more negative in the order of Ca^{2+}, Na^+/ Cl^- and SO_4^{2-}.

Similar rejections of estrone were observed in Figure 4.9. It indicated that there was little impact by the ionic strength on the membrane's rejection of estrone under the neutral pH operation condition.

However, Schäfer reported a very small ionic strength effect on estrone rejection [13]. She explained the molecular structure of estrone was asymmetric with polar bond (carboxylic group) present. The oxygen end of the molecule is slightly negative charged, while the other end of the molecule is slightly positive charged. The presence of counter-ions in the solution may partially screen the charge associated with these functional groups and the electrostatic potential generated by membrane surface functional groups and thus reduce the electrostatic repulsive effects. The electro-repulsion between membrane and estrone was expected to keep estrone away from the membrane. [13].

Yoon et al. also reported a presence of counter ions (Ca^{2+}, K^{+}) would decrease the rejection of perchorate (ClO_4^{-}) as electro-repulsion between negatively charged perchorate and negatively charged membrane was decreased by the counter ions [55, 56].

The reason for this result is that estrone is not charged under neutral pH condition. Electro-repulsion between negatively charged membrane and negatively charged estrone functional group was very minor under such condition. Adsorption effect will still dominate the high EDC rejection under the neutral pH condition. Therefore, the estrone's non-ionic nature would contribute to the little impact of ionic strength on the high rejection of estrone by NF and RO membranes. It can be concluded that ionic strength effect is not critical to estrone rejection by NF and RO membranes under neutral pH condition.

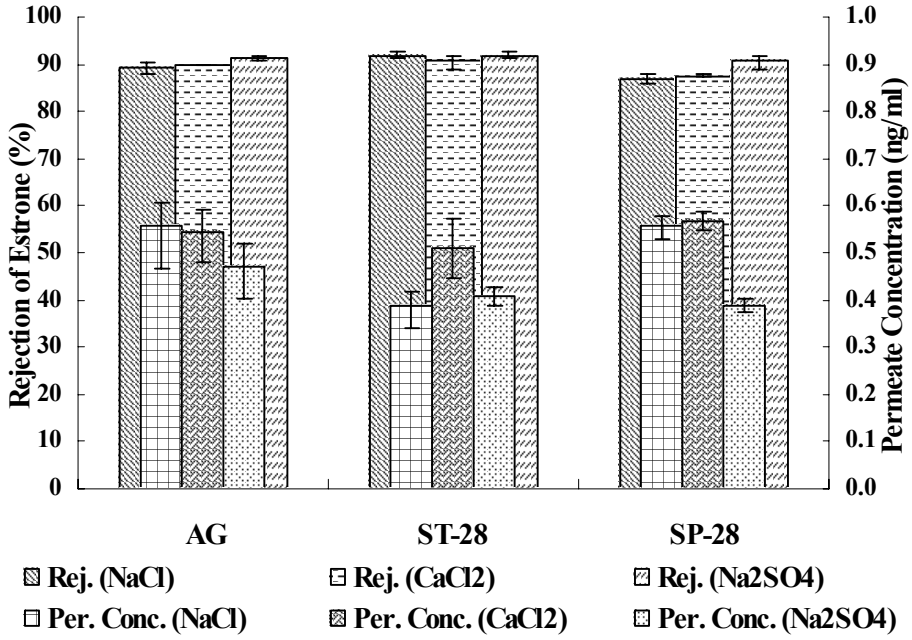


Figure 4.9 Ionic Strength Effect on Estrone Rejection.

4.6 Effect of pH on Estrone Rejection

Cellulose acetate (ST-28 and SP-28) and polyamide (AG) membrane were selected in this study. Estrone rejections by these two types of membrane materials were compared under experimental condition. The experiments were performed at pH 3, 5, 7, 9 and 11 for a time period of 2 hours at a temperature of 26 ± 1 ºC. The selection of 2-hour operation was for purpose of stabilization, and membrane rejection comparision with previous results in the literature. The estrone concentration in the permeate and feed water were obtained and the results were plotted to illustrate the effect of pH on the rejection of estrone by AG, ST-28 and SP-28 membrane as shown in Figure 4.10.

With pH increase, estrone rejection by the AG membrane decreased sharply (from 99.76 % to 82.85 %), while the estrone rejection only decreased slightly for ST-28 and SP-28 membrane (98.37 % to 91.41 %, and 90.76 % to 85.57 %, respectively). The decrease rejection was attributed not by adsorption, physical sieving, but by electro-repulsion between the negatively charged membrane and negatively charged estrone.

However, Hu et al. found low MW acids had higher rejections by NF and RO membranes than larger neutral organics due to electrostatic repulsion [54]. Yoon et al. reported ClO_4^- rejection was increased as pH increased [55, 56]. Berg et al. also observed charged organics were rejected at higher levels than non-charged organics of the same size [57].

The results may be explained that the AG membrane surface characteristics (membrane surface morphology, roughness and zeta potential) were modified at pH 10.86. When negative charge of AG membrane decreased at high pH (shown in Figure 4.4), the electro-repulsion was reduced correspondingly, and this may be one of the reasons for the decreased estrone rejection under strong basic pH.

Although electro-repulsion may help the pollutant rejection, the repulsion force between membrane and pollutant may not be sufficient to prevent the estrone molecule through the membrane. Bellona et al. observed low electrostatic repulsion between a weak negatively charged membrane and negatively charged

organic compound could result in a poor rejection, when molecular weight of organic compound was smaller than molecular weight cut-off [58].

As discussed in section 4.1, the AG membrane surface roughness increased at pH 10.86. Large membrane roughness may enhance adsorption of estrone onto the membrane. An increasing roughness may contribute to an increasing surface area. However, the electro-repulsion between negatively charged membrane and negatively charged estrone will largely reduce the adsorption of estrone onto the membrane.

Another reason for the sharply decreased estrone rejection could be that the membrane pore size might increase under the strong basic pH. Braghetta and Berg reported at high pH values (8 ~ 10), the rejection of uncharged solutes decreased. This phenomenon may be the result of an increase in pore size of a membrane caused by the electrostatic repulsion between the acidic functional groups within the membrane [57, 59]. Yoon et al. and Freger et al. also reported at low ionic strength when membrane zeta potential is more negative, pore radii can increase in size to minimize electrostatic repulsion between the negative functional groups [60, 61].

The rejection of estrone by ST-28 and SP-28 membranes was relatively stable under the pH conditions investigated. The stable characteristics (zeta potential, membrane morphology and membrane roughness) of both membranes contributed to the stable rejection performance. The morphology and roughness of ST-28 and

SP-28 had minor variation. The negative charge of ST-28 and SP-28 increased as pH increased but plateaued after pH 7. The electro-repulsion could contribute to the rejection of estrone by ST-28 and SP-28 at high pH, if the repulsion force is sufficient to keep estrone away from membrane.

As discussed above, it can be concluded that acidic and neutral pH conditions are recommended for estrone rejection and that electro-repulsion contributing to a high rejection depends on strong membrane surface charge.

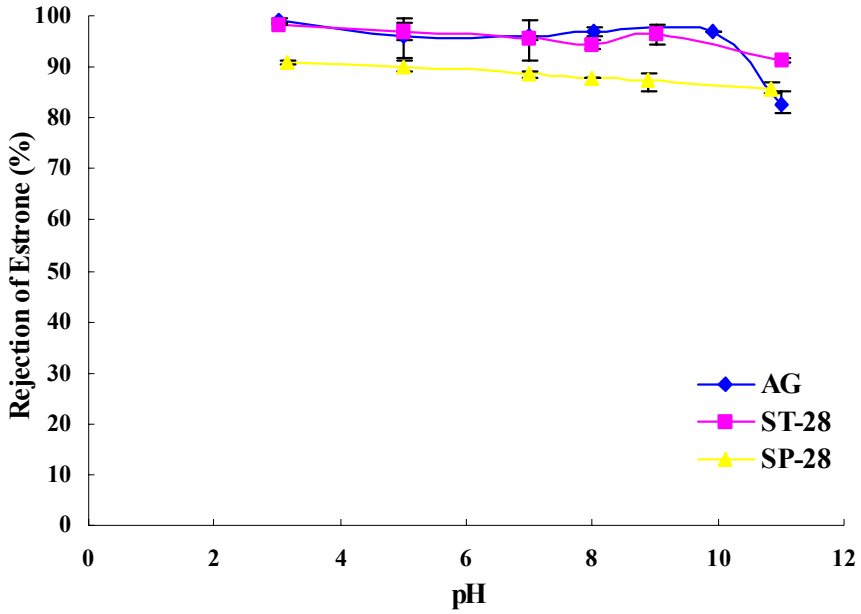


Figure 4.10 pH Effect on Rejection of Estrone by NF & RO Membranes.

4.7 Effect of 24-hour Operation on Estrone Rejection

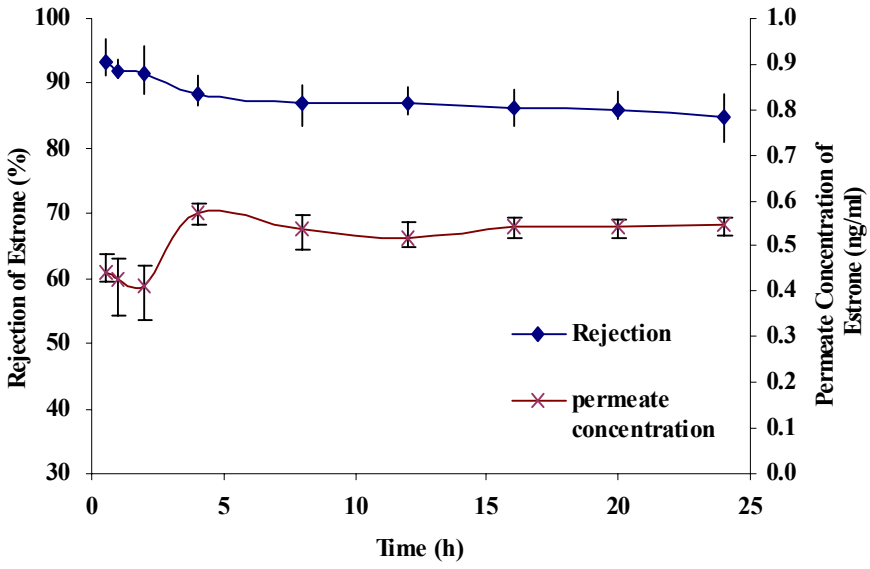
Estrone rejections by NF and RO membranes were investigated for 24-hour filtration under the neutral pH operation condition. The results were shown in Figure 4.11, which was fitted with logarithmic regression due to experimental fluctuation.

Decreasing estrone rejection with time was observed for all three membranes in Figure 4.11. Estrone is a highly hydrophobic compound with a branched and sterically complex molecular structure. Adsorption and then physical sieving would be the major cause of estrone rejection over the 24-hour. When the membrane surface reached its adsorption equilibrium, further adsorption effect would be negligible. Other factors, such as physical sieving would become important for estrone rejection.

Estrone rejection by NF and RO membranes decreased until it reached equilibrium. Percentages differences between initial and equilibrium values were summarized in Table 4.2. The percentage difference by SP-28 membrane was the highest, followed by AG and ST-28 membranes. The highest percentage difference indicated that adsorption of estrone on SP-28 membrane had been an important part of estrone rejection, which was attributed to its largest pore size.

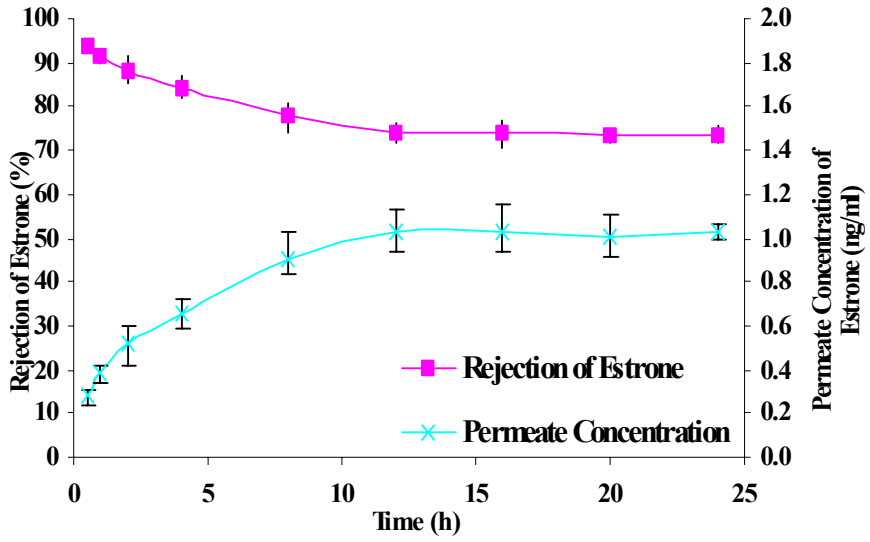
Adsorption amount of estrone by NF and RO membranes in the 24-hour operation process were summarized in Figure 4.12. It was observed that the adsorption curves of ST-28 and SP-28 membranes were quite similar, which was attributed to their membrane material, cellulose acetate. The results presented agreed the hydrophobicity sequence of membranes: SP-28 > ST-28.

The total adsorption amount of estrone per centimeter square by SP-28 membrane was the highest than that by the other two membranes. It was attributed to its highest membrane hydrophobicity, which was also agreeable with the results in section 4.3 - adsorption effect on estrone rejection by membranes.

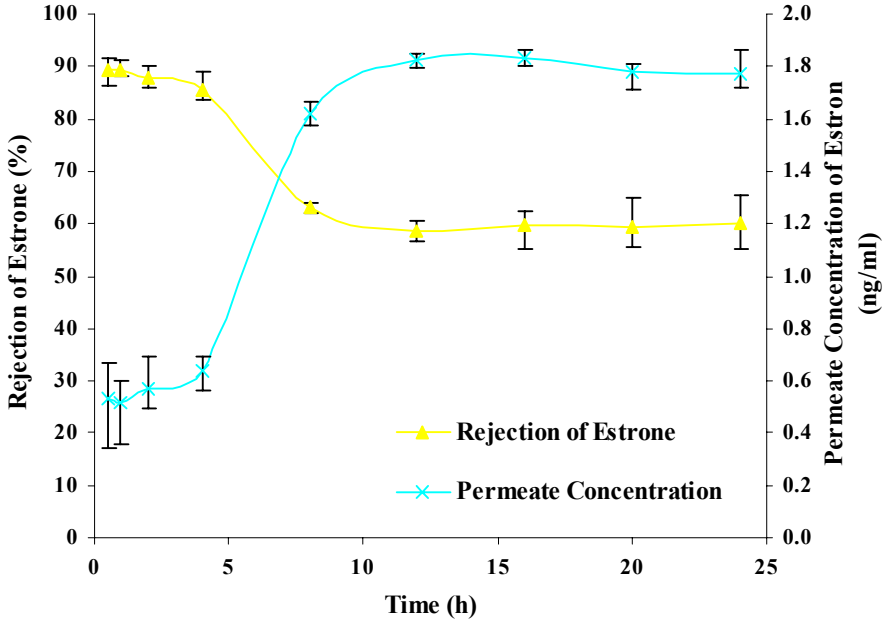


(a) Estrone Rejection by AG membrane.

Figure 4.11 24-hour Operation Effect on Estrone Rejection.



(b) Estrone Rejection by ST-28 Membrane.



(c) Estrone Rejection by SP-28 Membrane.

Figure 4.11 24-hour Operation Effect on Estrone Rejection.

Table 4.2 Estrone Rejection Decrease by NF & RO Membranes

Membrane	The percentage difference between initial and equilibrium values (%)
AG	6.57
ST-28	20.87
SP-28	34.67

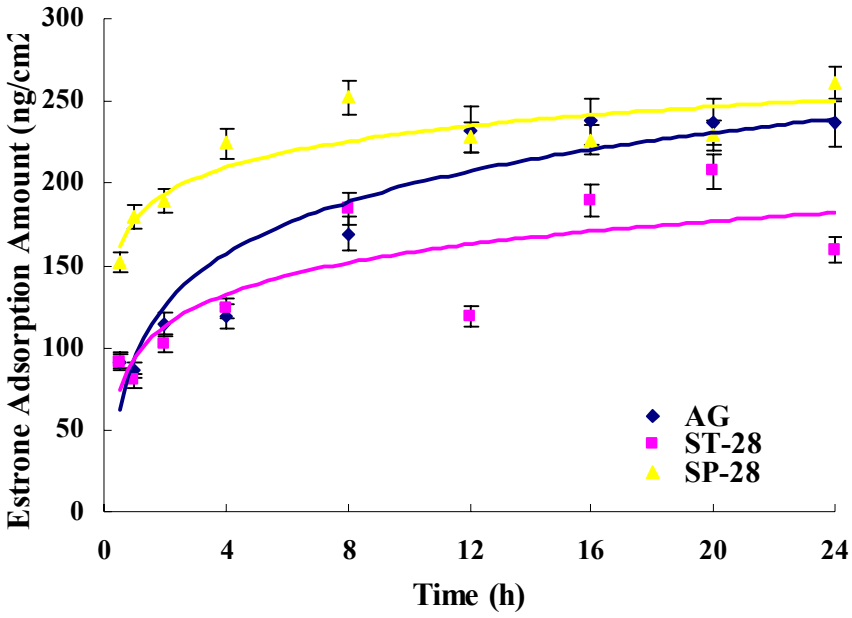


Figure 4.12 Adsorption of Estrone on NF & RO Membranes (Measured in the 24-hour Operation Effect Study).

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the results presented and discussion herein, the following conclusions are drawn:

1. Adsorption and physical sieving are instrumental to maintain high rejection of hydrophobic EDCs during the NF and RO membrane separation. The results showed that adsorption contributed to the initial high estrone rejection by NF and RO membranes while physical sieving would continue to contribute to the estrone rejection during the later stage of study. Electro-repulsion does not contribute significantly to the rejection of estrone. Ionic strength effect on trace EDC rejection can be negligible under neutral pH .

2. RO membranes (AG and ST-28 membranes) were found to be more effective at the EDC rejection after 24-hour operation with rejections ranging from 73 % ~ 85 %. Physical sieving was a significant factor in determining RO removal of EDCs.

3. Acidic and neutral pH were more suitable for estrone rejection than the basic pH, although electro-repulsion between the negatively charged membrane and negatively charged EDC under the strong basic pH was expected to help. The unexpected drop in estrone rejection at high pH could be due to membrane surface modification at high pH, which can be observed in the membrane surface morphology and membrane roughness analysis by AFM, and the membrane zeta potentials.

4. The AG polyamide membrane was the most efficient for removal of estrone under the neutral pH condition, both for short term and longer term (24-hour) operation.

5.2 Recommendations

The following recommendations for the further studies are made:

Pore size distribution of the membrane could not be determined directly using the AFM analysis. Therefore, it is suggested that other methods like fractional rejection of polyethylene glycols (FR-PEG), bubble point method, liquid displacement and solute probe technique can be used to measure its distribution for better understanding of physical sieving effect on EDC rejection.

The EDC rejection in the wastewater can be compared with rejection of estrone in a synthetic feed water. The variation of the rejection may provide

information on the factors influencing EDCs rejections during the membrane separation.

Natural organic matter (NOM) could be one of the factors influencing EDC rejection by membranes. A comparison between EDC rejection with NOM and without NOM can be investigated to understand the contribution of NOM to EDC rejection by membranes.

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