EFFECTS OF PH AND NATURAL ORGANIC MATTER ON REMOVAL OF
CARBAMAZEPINE AND SULFAMETHOXAZOLE BY NANOFILTRATION AND REVERSE
OSMOSIS MEMBRANES

Miss Katunchalee Phadunghus

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science Program in Environmental Management

(Interdisciplinary Program)

Graduate School

Chulalongkorn University

Academic Year 2013

Copyright of Chulalongkorn University

ผลกระทบจากค่าความเป็นกรด-เบสและสารอินทรีย์ธรรมชาติในการบำบัดสารประกอบยาชนิด
คาร์บามาเซปีนและซัลฟาเมโทซาโซลโดยเยื่อเลือกผ่านนาโนและรีเวอร์สออสโมซีส

นางสาวกตัญชลี ผดุงหัส

Thesis Title	EFFECTS OF PH AND NATURAL ORGANIC MATTER ON REMOVAL OF CARBAMAZEPINE AND SULFAMETHOXAZOLE BY NANOFILTRATION AND REVERSE OSMOSIS MEMBRANES
By	Miss Katunchalee Phadunghus
Field of Study	Environmental Management
Thesis Advisor	Aunnop Wongrueng, Ph.D.
Thesis Co-Advisor	Assistant Professor Patiparn Punyapalakul, Ph.D.

Accepted by the Graduate School, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

....Dean of the Graduate School

(Associate Professor Amon Petsom, Ph.D.)

THESIS COMMITTEE

....Chairman

(Assistant Professor Srilert Chotpantarat, Ph.D.)

....Thesis Advisor

(Aunnop Wongrueng, Ph.D.)

....Thesis Co-Advisor

(Assistant Professor Patiparn Punyapalakul, Ph.D.)

....Examiner

(Associate Professor Pisut Painmanakul, Ph.D.)

....External Examiner

(Assistant Professor Monthon Thanuttamavong, Ph.D.)

กตัญชลี ผดุงหัส : ผลกระทบจากค่าความเป็นกรด-เบสและสารอินทรีย์ธรรมชาติในการบำบัดสารประกอบยาชนิดคาร์บามาเซปีนและซัลฟาเมโทซาโซลโดยเยื่อเลือกผ่านนาโนและรีเวอร์สออสโมซีส. (EFFECTS OF PH AND NATURAL ORGANIC MATTER ON REMOVAL OF CARBAMAZEPINE AND SULFAMETHOXAZOLE BY NANOFILTRATION AND REVERSE OSMOSIS MEMBRANES) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: อ. ดร. อรรณพ วงศ์เรือง, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ. ดร. ปฏิภาณ ปัญญาพลกุล, 111 หน้า.

งานวิจัยนี้มีจุดประสงค์เพื่อศึกษาประสิทธิภาพของเมมเบรนสองชนิด ได้แก่ เมมเบรนนาโน (NF-1) และเมมเบรนรีเวอร์สออสโมซีส (RO-1) ในการกำจัดสารประกอบยาคาร์บามาเซปีน (CBZ) และ ซัลฟาเมโทซาโซล (SMX) โดยผิวของเมมเบรน NF-1 และเมมเบรน RO-1 มีจุดไอโซอิเล็กทริกที่พีเอชเท่ากับ 6 ผลการศึกษาพบว่าเมมเบรน NF-1 สามารถกำจัด CBZ ที่พีเอช 5 6 และ 7 เท่ากับ 93% 93% และ 92% ตามลำดับ และสามารถกำจัด SMX ที่พีเอช 5 6 และ 7 เท่ากับ 87% 91% และ 94% ตามลำดับ เมมเบรน RO-1 สามารถกำจัด CBZ ที่พีเอช 5 6 และ 7 เท่ากับ 93% 94% และ 92% ตามลำดับ และสามารถกำจัด SMX ที่พีเอช 5 6 และ 7 เท่ากับ 94% 97% และ 98% ตามลำดับ จากผลการศึกษาสรุปได้ว่าการกำจัด CBZ โดยเมมเบรนถูกควบคุมด้วยกระบวนการคัดขนาด ในขณะที่การกำจัด SMX โดยเมมเบรนถูกควบคุมด้วยกระบวนการคัดขนาดและแรงผลักทางไฟฟ้าสถิต นอกจากนี้ ประสิทธิภาพการกำจัดสารประกอบยาผสมระหว่าง CBZ และ SMX ด้วยเมมเบรนทั้งสองชนิดมีประสิทธิภาพสูงกว่าการกำจัดสารประกอบยาเดี่ยว อาจเกิดจากการรวมกลุ่มกันของสารประกอบยาทั้งสองชนิดในระหว่างกระบวนการกรองด้วยเมมเบรน ผลการศึกษาการอุดตันของเมมเบรนจากเทนนินและเทนนินผสมแคลเซียมคลอไรด์ต่อการกำจัดสารประกอบยา SMX พบว่า เมมเบรนที่เกิดการอุดตันมีประสิทธิภาพในการกำจัดสารประกอบยา SMX เพิ่มขึ้น ซึ่งอาจเกิดจากการอุดตันที่หน้าผิวของเมมเบรนอย่างหนาแน่น อย่างไรก็ตาม ผลการศึกษาการอุดตันของเมมเบรนโดยใช้น้ำเสียที่ผ่านการบำบัดจากฟาร์มสุกร พบว่า การอุดตันที่หน้าผิวของเมมเบรนไม่มีผลต่อประสิทธิภาพในการกำจัดสารประกอบยาเดี่ยวและสารประกอบยาผสม ซึ่งอาจเกิดจากสารอินทรีย์ในน้ำเสียที่ผ่านการบำบัดจากฟาร์มสุกรมีความเข้มข้นต่ำและไม่ทำให้เกิดการอุดตันของเมมเบรน

สาขาวิชา การจัดการสิ่งแวดล้อม	ลายมือชื่อนิสิต ....
ปีการศึกษา 2556	ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก ....
	ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม ....

5587501320 : MAJOR ENVIRONMENTAL MANAGEMENT
KEYWORDS: SULFAMETHOXAZOLE CARBAMAZEPINE REVERSE OSMOSIS MEMBRANE NANOFILTRATION MEMBRANE PH REJECTION MECHANISM

KATUNCHALEE PHADUNGHUS: EFFECTS OF PH AND NATURAL ORGANIC MATTER ON REMOVAL OF CARBAMAZEPINE AND SULFAMETHOXAZOLE BY NANOFILTRATION AND REVERSE OSMOSIS MEMBRANES. ADVISOR: AUNNOP WONGRUENG, Ph.D., CO-ADVISOR: ASST. PROF. PATIPARN PUNYAPALAKUL, Ph.D., 111 pp.

This study examined the efficiencies of nanofiltration and reverse osmosis membranes on the removals of carbamazepine (CBZ) and sulfamethoxazole (SMX). Reverse osmosis and nanofiltration membranes, namely, NF-1 and RO-1, respectively were investigated. Isoelectric points of NF-1 and RO-1 membranes were observed at pH 6.0. For NF-1 membrane, CBZ rejections at solution pH 5, 6, and 7 were 93%, 93%, and 92%, respectively. SMX rejections at solution pH 5, 6, and 7 were 87%, 91%, and 94%, respectively. For RO-1, CBZ rejections at solution pH 5, 6, and 7 were 93%, 94%, and 92%, respectively. SMX rejections at solution pH 5, 6, and 7 were 94%, 97%, and 98%, respectively. Solution pH had no effect on the CBZ rejection but it affected the SMX rejection. Hence, the removal of CBZ was controlled by size exclusion whereas the removal of SMX was controlled by size exclusion and electrostatic repulsion. Mixed pharmaceuticals showed an increasing in the rejection compared with that of single pharmaceutical. It could be due to a combination of pharmaceuticals during the membrane filtration. Effect of membrane fouling on the selected pharmaceutical removal, i.e. SMX was observed. It was found that when the membranes were fouled by tannic acid in the presence and absence of calcium chloride, tannic acid was accumulated and formed a dense layer on the membrane surface. This dense layer performed as another filtration layer and resulted in an increasing of SMX rejection. In case of membrane fouling by real wastewater from swine farm, the removal efficiencies of the two membranes were not affected. It could be due to the membrane fouling was not severe. The fouled layer was not formed noticeably on the membrane surface. Thus, the aforementioned results were carried out.

Field of Study: Environmental
                 Management

Academic Year: 2013

Student's Signature ....

Advisor's Signature ....

Co-Advisor's Signature ....

ACKNOWLEDGEMENTS

CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS AND SYMBOLS

μm	Micro meter
$^{\circ}C$	Degree Celsius
π	Osmotic pressure
π_B	Osmotic pressure of bulk solution
π_P	Osmotic pressure of permeate water
CBZ	Carbarmazepine
C_B	Concentration on concentrated water
C_M	Concentration on membrane surface
C_P	Concentration in permeate water
cm^2	Square centimeter
DOC	Dissolved solid carbon
EC	Electrical conductivity
HMWC	High Molecular Weight Component
HPLC	High performance liquid chromatography
Ji	Solute flux
Jv	Permeate flux
$(J_v)_{H2O}$	Permeate flux of pure water
k_m	Mass transfer coefficient
k_i	Solute mass transfer coefficient
LMWC	Low Molecular Weight Component
MF	Micro filtration
m^3/day	Cubic meter per day

mg/day	Milligram per day
mg/L	Milligram per Liter
m/s	Meter per seconds
M	Molar
ml	Milli liter
MPa	Mega Pascal
NF	Nanofiltration
nm	Nano meter
NOM	Natural organic matter
R_{int}	Intrinsic rejection rate
R_{obs}	Observed rejection rate
RO	Reverse osmosis
SMX	Sulfamethoxazole
TA	Tannic acid
TMP	Transmembrane pressure
TOC	Total organic carbon
UF	Ultra filtration

CHAPTER 1

INTRODUCTION

1.1 Motivation

Currently, pharmaceutical compounds have been used to treat and prevent illnesses popularly according to their effects, for example antibiotics, anti-inflammatory substances and antihistamines. The abundant quantities of pharmaceuticals were produced and used for both humans and animals. However, some pharmaceutical compounds were discharged into the environment via wastewater treatment plants, expired products, veterinary pharmaceuticals and excretion in which biotransformation occurred in the body (Nghiem et al., 2005). Previous researchers studied the quantity of pharmaceutical compounds which are released via various sources. For example, a water sample from Missouri was found to contain caffeine, ibuprofen and acetaminophen at concentrations of 224, 77.2 and 70 ng/L, respectively (Wang et al., 2011). In surface water, metformin was found ranging from 64-98 µg/L (Schwab et al., 2005). In addition, researchers studied the drug concentrations in soil. The accumulation of ciprofloxacin, sulfamethoxazole and carbamazepine in soil were discovered at levels of 1.4, 4.3 and 5.4 mg/kg, respectively.

Although the amount of pharmaceutical compounds released into the environment were of low concentrations ranging from levels of ng/L to µg/L, scientists found that pollutants due to pharmaceutical compounds had severe impacts on human health for example renal lesions on the kidneys and the environment for example the alterations of the gills in rainbow trout (Schwaiger et

al., 2004) and the adult zebra showed the significantly decreased the embryo production after expose to pharmaceutical (Galus et al., 2013). Long-term risks due to the intake of mixed pharmaceuticals at low levels are uncertain (Kimura et al., 2009).

Two pharmaceuticals, namely, sulfamethoxazole (SMX) and carbamazepine (CBZ) are selected for this study because they exhibit different physicochemical0.273 and 1.2642 properties for example difference in functional group, pKa value and log Kow.

Sulfamethoxazole (SMX) was sulfamide drugs. There are well known commonly used to treat the various systemic infections in human and veterinary medicine since the early 1960s. For the treatment of infection, SMX commonly used combination with trimethoprim or pyrimethamine. Recently, the scientists investigated the concentration of SMX in surface water that could be detected from 30 to 480 ng/L (Heberer et al., 2008) and the municipal sewage treatment plant can be found at 2000 ng/L (Bueno et al., 2007; Roberto et al., 2003).

Carbamazepine (CBZ) was used for treatment of seizure disorders and neuropathic pain. The drug was synthesized in 1960s. CBZ has been found in the surface water (Togola & Budzinski, 2008) and drinking water influent (Roberto et al., 2003). It widespread detection in waste water treatment plants in concentrations up to 3800 ng/L (Celiz et al., 2009).

Their removal from the environment is important for protecting the public health. Several methods (e.g. adsorption, ion exchange, and coagulation-precipitation) have been applied in order to eliminate low levels of pharmaceuticals;

however, there are many challenges with the removal of pharmaceutical compounds at higher levels of efficiency.

The use of the membrane is a new technology and an effective tool applied in the treatment of water because it is able to produce a higher quality of water. There are several types of membranes such as microfiltration, ultrafiltration, nanofiltration, reverse osmosis, and the membrane bioreactor (Yuksel et al., 2013; Zaviska et al., 2013);however, reverse osmosis and nanofiltration membranes are capable of a significant rejection of target compounds at low concentrations, small footprint, and flexible for future explanation (Alzahrani et al., 2013; Mondal& Wickramasinghe, 2008). The wastewater treatment plants, hospital or farm should access this technology because it provides the high rejection rate. The rejection mechanisms of reverse osmosis and nanofiltration involve size exclusion, electrostatic repulsion and diffusion (Nghiem& Hawkes, 2007; Shah et al., 2012; Verliefed et al., 2008).

However, the problem of membrane filtration is membrane fouling. Membrane fouling is generated from the solute or particles accumulate on the surface membrane or into the pore of membrane(Tang et al., 2009) . Natural organic matter (NOM) is one of the foulants present in natural water sources. NOM is released from the living organism for example plants, animals and product waste in the environment. This phenomena affect to the reduction of permeate flux and membrane degradation. However, some researcher found the positive effect of membrane fouling can increase the permeate quality (Nghiem& Hawkes. 2007; Xu et al., 2006).

In this study, researcher would like to enhance the strategy of pharmaceutical removal by membrane filtration. We examined the factors affecting the efficiency of the nanofitration membrane and reverse osmosis membrane for removing two specific types of pharmaceutical compounds, carbamazepine (CBZ) and sulfamethoxazole (SMX). The effects of operating condition and membrane fouling on performance of membranes were carried out.

1.2 Objectives

- To examine the efficiency of nanofiltration and reverse osmosis membranes on the removal of carbamazepine (CBZ) and sulfamethoxazole (SMX).

- To study the effect of pH on the performance of nanofiltration and reverse osmosis membranes.

- To investigate the removal mechanisms of carbamazepine (CBZ) and sulfamethoxazole (SMX) via nanofiltration and reverse osmosis membranes.

1.3 Hypotheses

- Carbamazepine (CBZ) and sulfamethoxazole (SMX) could be removed by nanofiltration and reverse osmosis membranes.

- Water pH affected the removal of carbamazepine (CBZ) and sulfamethoxazole (SMX) by nanofiltration and reverse osmosis membranes

1.4 Scope of the study

- Synthetic contaminated water prepared with carbamazepine (CBZ) and sulfamethoxazole (SMX) and used in this study

- The water pH was in a range of 5-7

- Test cell, C-10T (Nitto Denko, Japan), with an effective filtration area of 60 cm^2 was employed

- The RO membrane (RO-1 membrane) and NF membrane (NF-1 membrane) were tested

- Tannic acid was used as representative of natural organic matters (NOM) in a membrane fouling experiment

1.5 Benefit of this study

- Efficiencies of nanofiltration and reverse osmosis membranes on carbamazepine (CBZ) and sulfamethoxazole (SMX) removals were elucidated

- Effects of some operating conditions, e.g. water pH and membrane fouling on the membrane performances were explored
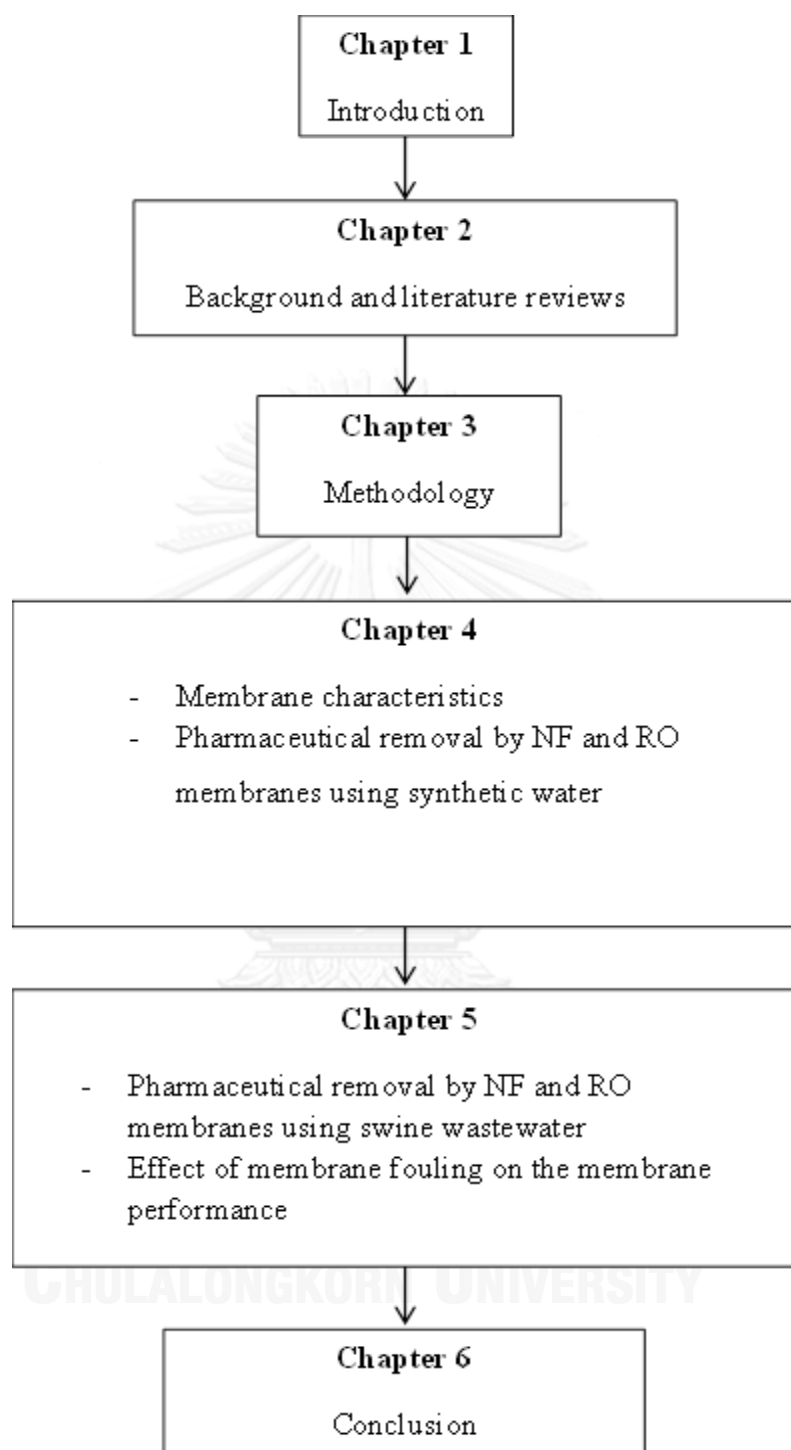
Figure 1.1 Diagram of thesis in each chapter

Flow diagram of this study illustrates in **Figure 1.1**. Chapter 1 presented the motivation, objectives, and hypotheses of this study. Chapter 2 described the existing research results in the field of pharmaceutical compound removal by reverse osmosis membrane and nanofiltration membrane in addition to the background of membrane filtration and pharmaceutical compounds. Chapter 3 explained the experimental methods and materials including chemical reagents and instruments in this study. Chapter 4 reported the membrane characteristics that divided into three parts that were permeate water flux, mass transfer coefficient, and isoelectric point. In addition, the results of carbamazepine (CBZ) and sulfamethoxazole (SMX) removals by nanofiltration and reverse osmosis membranes were carried out. Chapter 5 investigated membrane fouling on the membrane performances. Chapter 6 summarized the results of carbamazepine and sulfamethoxazole removal efficiencies.

CHAPTER 2

BACKGROUND AND LITERATURES REVIEWS

2.1 Pharmaceutical residues

Pharmaceuticals had become the center of health care since the mid-19th century. Pharmaceuticals are chemical products used by enhancing the growth of health of livestock (Enick & Moore, 2007). For humans, their entire lives involved with various drugs in that it had common to take drugs for reducing the risk of disease and increasing the life span. For example, the life span in the U.S. had been increased from the average age of 47 in 1850 to today's 78 years (Dammrich & Bowden, 2005).

The new pharmaceutical industrial sector used many chemicals for developing and producing effective drugs to respond to a pharmaceutical need worldwide that made the pharmaceutical consumption increase (Verlicchi et al., 2012). The pharmaceutical included many substances such as human and veterinary drugs, food additives, cosmetics ingredients, detergents and hormones (Luo et al., 2014). Since the 21st century, scientists realized the emerging micropollutants referring to organic substances at low concentrations (ng/L-ug/L) which was occurring in water (Pasquini et al., 2014; Schwarzenbach et al., 2006).

Figure 2.1 showed the cycle of pharmaceuticals occurring in the environment from medicinal products used in humans and animals. Humans and animals used of pharmaceuticals for treatment seen as a main contaminant source; nevertheless, the emission of drugs took different routes for example expired product, agriculture, hospital effluents, excretion, and wastewater treatment plant. It depends on the pattern that had been established in different countries. A wide

range of pharmaceuticals had been transported to surface water, ground water and drinking water resources (Heberer, 2002).

Pharmaceuticals compound can enter the environment through its effluent however; there are no discharge standards for pharmaceuticals in wastewater treatment plant. Therefore, it is not amazing that the researcher can be detected the pharmaceutical in ground water and drinking water effluent (Roberto et al., 2003).
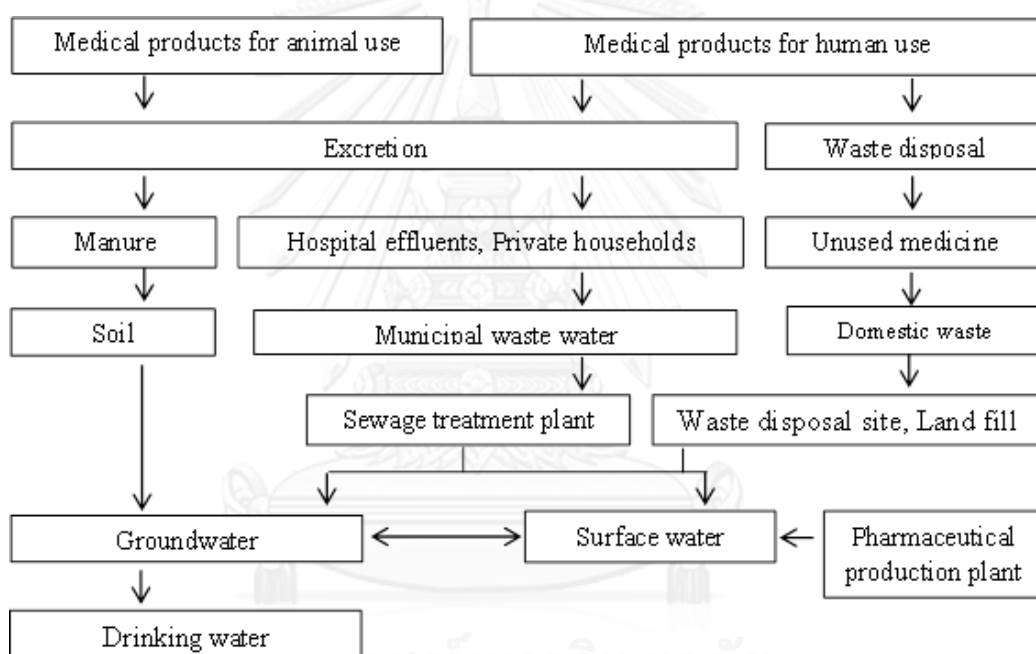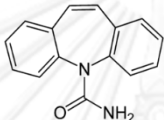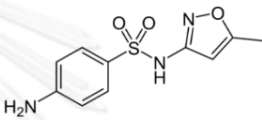
Figure 2.1 The cycle and sources of pharmaceuticals in the environment

Table 2.1 Psysicochemical properties of pharmaceutical compounds

Pharmaceutical	Carbamazepine (CBZ)	Sulfamethoxazole (SMX)
Molecular weight (g/ mol)	236.3	253.3
log K_{ow}	2.45	0.89
K_{oc}	510	72
pKa	pK_{a1} = 13.9	pK_{a1} = 1.6 pK_{a2} = 5.7
Molecular structure		

Carbamazepine   Sulfamethoxazole
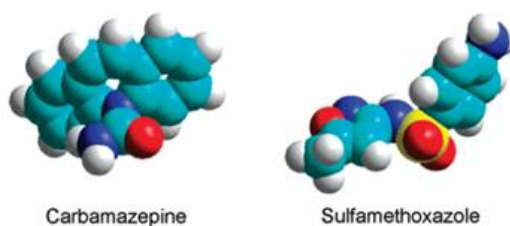
Figure 2.2 The three diamentional model of carbamazepine and

sulfamethoxazole

2.1.1 Sulfamethoxazole

Sulfamethoxazole (SMX) was a derivative form of the sulfanilamide class. Since the 1960s, SMX had been used for preventing urinary tract infections in humans and animals, as well as, killing infectious agents in order to avoid the spread of infection (Chamundeeswari et al., 2014; Travo et al., 2009)

The structure of SMX composed of two aromatic rings linked with the SO_2NH_2 group. This functional group which included electrons from the drawing group could develop a strong charge. When the pH value was more than the drug

pKa, the electrons become ionized rapidly (Mi & Elimelech, 2008). The three dimensional model of sulfamethoxozole molecule which was long and cylindrical in shape with its dipole moment (5.4 D) were show in **Figure 2.2** (Nghiem et al., 2005). The physiochemical properties and molecular structure of SMX were presented in **Table 2.1**.

Various wastes from SMX's production and its use as a human and veterinary antibiotic were released into the environment.

In the atmosphere, SMX appeared in both vapor and particulate phases. In vapor phase, the photochemical-produced hydroxyl radical was the reaction for degraded SMX in air. The half-life for the reaction in the air was estimated at 2 hours. In the particulate phase, in which case SMX had a half-life that might last between 0.2 to 5 days, wet or dry deposition **was the method for its** removal from the atmosphere (Bidleman, 1988).

In the soil, SMX had a high mobility related to the value of the carbon-water partitioning coefficient (K_{oc}) equal to 72. Moreover, the values of pKa_1 and pKa_2 were 1.6 and 5.7, respectively that meant SMX was a present partial anion in the soil. This anion SMX did not adhere more fully to soil which contained a negative complement such as organic carbon and clay as opposed to their neutral complements (Boreen et al., 2004; Doucette, 2000).

In water, SMX was exposed to aquatic organisms at a low level. The average half-life in a field study ranged from 1.5-82 days (Lam et al., 2004). The general way contact occurred with SMX was via the ingestion of food and drinking water. Stackelberg et al. (2004) examined the quantities of SMX in potable water of an

urbanized drinking water treatment plant in the US that was collected over 4 consecutive weeks during November and December. The quantities of SMX were reported at a level of 0.5ug/L. From sewage treatment plant effluents, the concentrations of SMX in France, Greece, Italy and Sweden were reported at 0.07-0.09 ug/L, 0.09 ug/L, non-detected to 0.03 ug/L and 0.02 ug/L, respectively (Andreozzi et al., 2003). The surface water of the Haihe River Basin (China) reported SMX concentrations ranging from non-detected to 940 ng/L (Luo et al., 2011).Hoa et al. (2008) reported that SMX concentrations in an aquaculture-agriculture system in Vietnam ranged from 68.20 ng/L to 326.00 ng/L.

2.1.2 Carbamazepine

Carbamazepine (CBZ) was a widely used antiepileptic drug. It composed of two benzene rings combined with an azepine group that was connected to an amide group (Zhang et al., 2008). Three aromatic rings made the molecule stable; therefore, CBZ was most likely one of the most persistent pharmaceutical compounds in the environment and the structure of CBZ affected the removal from wastewater (Leclercq et al., 2008).The physiochemical properties and molecular structures of CBZ compounds were presented in **Table 2.1**. The three-dimensional models of carbamazepine were shown in **Figure 2.2.** The carbamazepine molecule was bulky in shape and dipole moment (3.6 D) (Nghiem et al., 2005).

The production and use of CBZ as an antiepileptic drug might allocate its released into the environment through many waste streams.

In the air, the release of CBZ into the atmosphere existed in both vapor phase and particulate phase(Bidleman, 1988). In vapor phase, CBZ was aggravated by its reaction with a photochemically-produced hydroxyl radical. It had a half-life approximate to 4 hours. In particulate phase, the structure of CBZ contained a chromophore group which could be absorbed by UV wavelengths of more than 290 nm (Andreozzi et al., 2003). Consequently, CBZ was degraded by a photolysis reaction by sunlight.

If CBZ was released into the soil, the velocity of CBZ was moderate based on an approximate Koc of 510 and log Kow of 2.45 (Dal et al., 1989).

In water, CBZ was moderately persistent, exhibiting a half-life of 63 days as was observed in a field experiment using Epilimnion lake water (Tixer et al., 2003). Many researchers reported the occurrence of CBZ in the environment and waste water treatment plants. The occurrence of CBZ was observed in German sewage treatment plant effluents with a concentration of 6.3 ug/L (Ternes, 2002). The concentration of waste water treatment plant effluents in Switzerland was up to 0.95 ug/L (Tixier et al., 2003). A CBZ concentration had been detected in surface water ranking from 0.02 to 2 ug/L (Ternes, 2002). CBZ concentration in a drinking water treatment plant was found ranging from 8.7–166.5 ng/L(Radjenovic et al., 2008).

2.1.3 The ecotoxicology of SMX and CBZ

The weakness strategies for the removal of pharmaceuticals present serious concerned about the toxicity of drugs to scientists. The presence of pharmaceuticals in the water did not possible to ignore or neglect, although the quantity of these

drugs present in the environment had very low concentration. Very few studies reported information proving the toxicity of drugs to the point of causing chronic effects; thus, risk assessment of pharmaceuticals was still under investigation.

An Accept Daily Intake (ADI) value was established as a method for chemical risk assessment of drugs found in food and drinking water. A common method for accepting the concentration included that no adverse effects are detected which was known as a No-Observed-Adverse-Effect Level (NOAEL) and the lowest concentration at which adverse effects are detected which was referred to as the Lowest-Observed-Adverse-Effect Level (LOAEL)(FAO/WHO, 2009). Additionally, the toxicological studies reported NOAELs value of SMX in rats ranking 350- 512 mg/kg/day (Risk Assessment Forum, 2012). Novartis Pharmaceuticals Canada (1976) showed toxicity studies of CBZ in animals with LOAELs at 3.8 mg/kg/day. While in dogs, NOAELs had been observed between 50 to 100mg/kg/day and LOAELs between 100 and 300 mg/kg/day.

2.1.4 The removal of pharmaceuticals

Most wastewater treatment plants (WWTPs) were not designed for the removal of low organic compounds such as pharmaceuticals. Their main purpose was to eliminate conventional pollutants, for example natural organic matter (NOM), solids and macro-organisms (Claraa et al., 2005). The ability of WWTPs was to eliminate pharmaceuticals up to a biological treatment stage where pharmaceuticals were removed by sorption to suspended solids and biological biodegradation (Nghiem et al., 2005); however, some pharmaceuticals like CBZ were highly persistent and are inert to biological treatment processes (Claraa et al., 2005).

Currently, pharmaceutical removal at a high efficiency was an important consideration. It depended on their physical and chemical characteristics, for example the hydrophobicity and chemical structure. Many researchers had developed advanced wastewater treatment processes, such as photo-chemical, ozonation, adsorption and membrane filtration, which can generally achieve higher removal rates for pharmaceuticals compared with the more conventional processes. The studies done in various literatures reported the removal efficiencies of water treatment processes for pharmaceuticals in drinking-water treatment. Each treatment process showed the measurement method and resulting concentrations.

The chemical ozonation process was one of the most effective treatments for pharmaceutical removal. Ozone (O_3) had proven to be an effective disinfectant and powerful oxidizer (Acero et al., 2001; Xua et al., 2002). Snydera et al., 2007 reported that O_3 was a highly effective oxidant for pharmaceutical removal with a reduction of more than 99%, including the elimination of carbamazepine from drinking water and waste water. However, the major concern of ozonation in wastewater treatment plants was that by treating antibiotics via chlorination, the by-products which resulted from the reaction might be more harmful than the parent compounds themselves (Von et al., 2006).

The adsorption process which involved the accumulation of substances at the interface of two phases could be used to remove pharmaceuticals from both water and wastewater. Powder activated carbon (PAC) and granular activated carbon (GAC) were highly successful in the removal of pharmaceuticals. In which case, removal efficiency was found to depend on the following related functions: hydrophobic compounds, chemical structure, solubility and carbon type (Snyder,

2006; Ternes, 2002; Yoon et al., 2005). Most studies concerning the removal of micropollutants from aqueous solutions by adsorption were carried out by using activated carbon (AC). Yoon et al. (2005) found that the removal percentage was 90% for a very low pollutant concentration (27 ng/L). Nevertheless, the disadvantage of AC adsorption was low selectivity, and the thermal regeneration of AC could produce a toxic compound from the halogen atom present on the molecule of the pollutants.

Membrane filtration was a highly successful technique for the removal of pharmaceuticals from both water and wastewater treatment. Membrane filtration attempts to an interesting alternative technique. They are very adaptable and can be used in many applications that depend on the properties of membranes.

The nanofiltration membrane (NF membrane) proved to be more successful in the removal of pharmaceuticals than using an ultrafiltration membrane (UF membrane) or microfiltration membrane (MF membrane) due to hydrophobicity and size exclusion. The higher molecular weight substances can be removed by size exclusion, especially when using the NF membranes (Khiari, 2007; Y. Yoon, 2006). In addition, the reverse osmosis membrane (RO membrane) was also highly effective, although the quantities of some target compounds were present at low concentrations (Khiari, 2007).

Dolar et al. (2012) studied the removal of anthelmintic drugs, levamisole (LEV), albendazole (ABZ), praziquantel (PZQ), and febantel (FEBA), from water by photolytic reactions with the RO membranes (LFC1, XLE) and NF membranes (NF90, NF270, DK). The results illustrated that LFC1, XLE and NF90 were highly effective in the removal of all anthelmintic drugs (% rejection > 83%). NF270 and DK removed

small compounds (LEV, ABZ) at a less effective rate (% rejection between 22 and 45%); however, NF270 and DK were able to remove large compounds (PZQ, FEBA) at a high efficiency rate (% rejection more than 90%).

Kimura et al. (2009) studied the influence of residual organic macromolecules in wastewater on the removal of six pharmaceuticals including clofibric acid, diclofenac, ketoprofen, mefenamic acid, carbamazepine, and primidone. The results were reported in the case of the RO membrane that there was a significant increase in the removal of pharmaceutical compounds. However, in case of the NF membrane, in comparison between de-ionized pure water spiked with pharmaceutical compounds, removal was limited to 60%, whereas a higher percentage of removal was exhibited by pharmaceutical compounds with organic macromolecules. The occurrences of the membrane becoming fouled with organic compounds produce a positive influence in the process as it actually increased the removal of pharmaceuticals by the membrane.

Dolar et al. (2011) studied the removal of five veterinary pharmaceuticals, sulfamethoxazole, trimethoprim, ciprofloxacin, dexamethasone and febantel from different water matrices, which included milli-Q water, model water, tap water and real pharmaceutical wastewater by using the NF membrane and RO membrane. The results illustrated that the rejection increased with as molecular weight increased. Moreover, natural organic matter (NOM) in model water, tap water and real pharmaceutical wastewater was produced more efficient results using the NF and RO membrane but the flux will be low.

Nghiem et al. (2005) studied the retention mechanism of sulfamethoxazole, carbamazepine and ibuprofen by loose nanofiltration (NF-270) and tight nanofiltration (NF-90) membranes. The main mechanism of pharmaceutical removal in NF-90 was size exclusion while in NF-270 was both size exclusion and electrostatic repulsion. Increasing retention in NF-270 related to a function of pH that could ionized the molecules that was sulfamethoxazole. In neutral form, the retention mechanism of carbamazepine was size exclusion. In addition, the retention mechanism of Ibuprofen adsorbed to the membrane because of its high hydrophobicity.
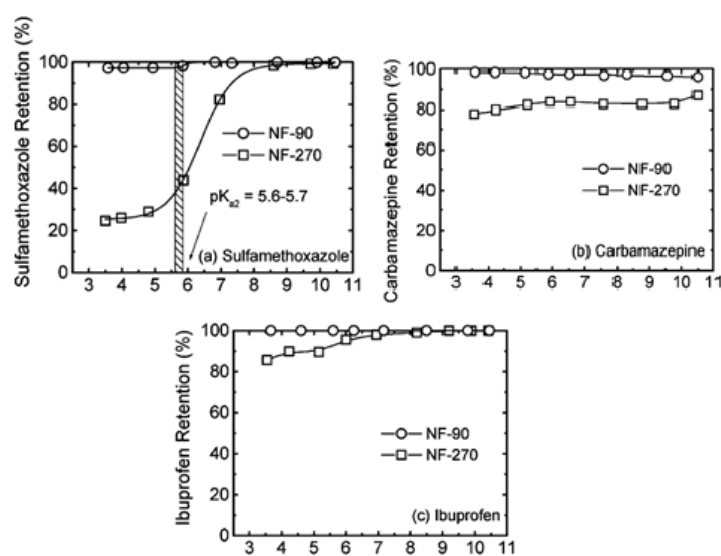
Figure 2.3 %Retention of sulfamethoxazole, carbamazepine and ibuprofen

Ravikumar et al. (2014) studied the effectiveness of NF and RO membrane to remove wastewater solution from pharmaceutical industry. The feed solutions were: (1) non-aerated condensate water (feed A) generated from biological methods that cannot always reduce color and other content. (2) Aerated effluent condensate

water (feed B) generated from activated sludge process. For Feeds A and B, **Figure 2.4** illustrated the % recovery increased from 8% to 60% in NF membrane and 10% to 70% in case of RO membrane. However, the permeate flux decreased because the increasing concentration of feed solution increased the concentration polarization that relate to the transmembrane pressure decrease and reduction of flux.
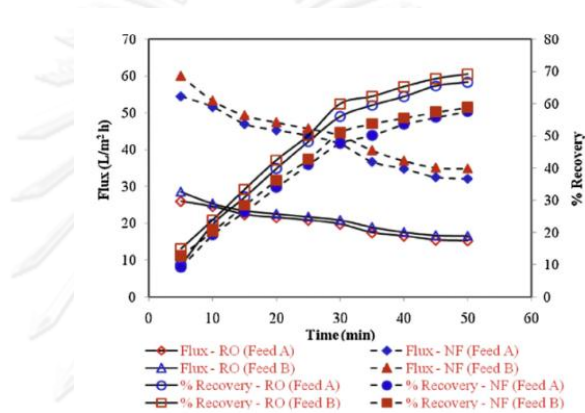
Figure 2.4 Flux and %recovery relate with time for NF and RO membranes process

Vergili (2013) studied three pharmaceuticals (carbamazepine, diclofenac and ibuprofen) that were spiked in water taken from a drinking water. In wastewater, they also found the divalent cation such as calcium ion and magnesium ion. These ions had influenced to reduce the membrane surface charge because Donnan potential was reduced. Hence, the rejections reduced in negative molecules that presented with divalent ions.

2.1.5 Natural organic matter (NOM)

Natural organic matter (NOM) was a group of heterogeneous mixtures with various molecular weights and properties. NOM occurs in natural waters and originates from living and dead plants, animals and microorganisms (Hong & Elimelech, 1997). Basic NOM compounds were humic substances, humic acid, and proteins. NOM can be classified as hydrophilic or hydrophobic. Hydrophilic consists of aliphatic carbon and nitrogenous compounds while hydrophobic was characteristic of having polyaromatic carbon, a phenolic functional group and conjugated double bond moieties in the molecule (Matilainen et al., 2011).
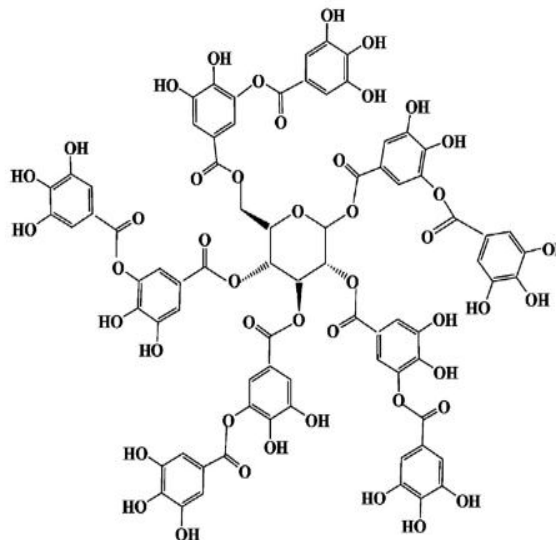
Presently, NOM in water can cause problems with color, taste and odor; moreover, NOM have influence water treatment processes that involve membrane filtration. Yamamura et al. (2007), Gray et al., (2007) and Kimura et al. (2007) had reported that NOM can induce fouling on the surface membrane, which was relative to a reduction in water flux and the percentage of solute from system feed water (% rejection). However, the cleaning of the membrane can restore the flux and % rejection.

2.1.6 Tannic acid (TA)

Tannic acid (TA) which refers to tannin, a type of polyphenol, was one component of NOM that can be dissolved in water. TA was used as an approved additive in various food and beverages. Although TA was harmless to human health in very small amounts, it can cause many problems when found in drinking water and waste water, for example carcinogenic disinfection by-products, the qualities of

water. The properties and chemical structure of TA (Yi et al., 2011) were shown in **Table 2.2**. Due to the properties of TA, it had been possible to induce fouling on the surface membrane, thus, TA was selected as a representative of natural organic matter in this experiment (Cassano et al., 2003; Suthanthararajan et al., 2004).

Table 2.2 The properties and chemical structure of tannic acid

Natural organic matter	Tannic acid (TA)
Molecular formula	$C_{76}H_{52}O_{46}$
Molecular weight (g/ mol)	1700
Water solubility (g/L)	2850
pKa	3.5
Molecular structure	

2.2 Membrane filtration

2.2.1 Classification of membrane filtration

A membrane was a selective barrier that could be used for the removal of some particles or chemicals from a fluid by passing the fluid through the membrane. Membranes were classified according to their general characteristics.

The first classification depended on the pore size of the membrane which could be separated into one of four categories: the microfiltration membrane (MF membrane), ultrafiltration membrane (UF membrane), nanofiltration membrane (NF membrane) and RO membrane (RO membrane). The RO membrane had the highest operating range for the removal of components while the MF membrane had the smallest operating range.

The second classification depended on the structure of the membrane. The membrane could be divided into one of two categories: symmetrical and asymmetrical. A symmetrical membrane showed the same structure of pore size in a cross section which was used as a pre-filter; however, an asymmetrical membrane was composed of different structures in which case, its use depended on its application, for example a thin-film composite membrane was an asymmetric membrane which was bi-layered. The first layer of thin-film composite membrane which was highly porous was coated with monomer or polymer (cellulose acetate, cellulose triacetate, etc.), and the second layer was reacted with a cross-linking agent (cross-linked aromatic polyamide, and aryl-alkyl polyether urea) which was shown in **Figure 2.5**.
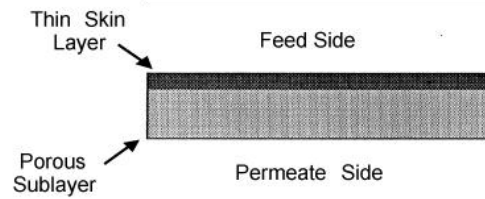
Figure 2.5 **Cross section of thin film composite membrane**

The characteristics of the four membranes were shown in **Table 2.3.** The membrane materials were produced from synthetic polymer that impacted the design and operation of the filtration system. NF and RO membranes were manufactured from cellulose acetate and polyamide materials. They could be used under a wide range of pH and require less pressure to operate for applications. MF and UF membranes were constructed from many materials including ceramic, polysulfone, polyethersulfone or other polymers. They had different properties including pH, surface charge, or strength.

The capabilities of membrane materials were identified by the pore size. The NF, UF and MF membranes were selected for a specific operation depending on their pore size; however, the RO membranes were insignificance in concept of pore size; therefore, the membrane operations fell under the properties of diffusion and molecular interaction.

The operating pressures of a RO membrane (approximately 1.5-150 MPa) and NF membrane (approximately 0.5-3.5 MPa) were characteristically higher than the operating pressures of a UF membrane (approximately 0.1-1MPa) and MF membrane (<0.2 MPa).

Table 2.3 Comparison of characteristic of four membranes(Wagner, 2001)

Characteristic	RO	NF	UF	MF
Structure	Asymmetrical	Asymmetrical	Asymmetrical	Asymmetrical Symmetrical
Pore size (µm)	<0.002	<0.002	0.2-0.02	4-0.02
Rejection	HMWC, LMWC	HMWC, negative ions	Macro molecules	Particles, clay, bacteria
Membrane materials	Cellulose acetate, polyamide	Cellulose acetate, polyamide	Ceramic Polysulfone	ceramic
Pressure (MPa**)**	1.5-15	0.5-3.5	0.1-1	<0.2

2.2.1.1 Nanofiltration membrane

The NF membrane was a thin film composite membrane and chemical group with a negative charge on the surface. The properties allowed it to be operated under a transmembrane pressure of 0.5 to 3.5 MPa. The NF membrane retained substance when the molecular weight was cut off (MWCO) has 200-400 g/mol. The NF membrane could be used for many purposes, for example in the removal of micro pollutants, pharmaceuticals from a wastewater treatment plant and fluoride from ground water. These membranes supplied high flux at low operating pressures and low operating costs when compared with reverse osmosis membranes; thus, due to the many advantages of the NF membrane, it had been reported as a suitable method. The percentage rejection of a NF membrane depended on the size effect, charge, and hydrophobicity effect between the compounds and membrane.

2.2.1.2 Reverse osmosis membrane

The RO membrane had been used increasingly in the treatment processes for hospitals, veterinaries, and pharmaceutical manufacturers. These tend to be processes that used the membrane under pressure to separate the chemical solutions from wastewater. Chemical solutions could not move through a RO membrane if they included materials that tend to be larger in size than the pores of the membrane such as metals, colloid, natural organic matter, bacteria and viruses; thus, chemical solutions had been driven out via the sewer system.

The RO membrane was a thin-film composite membrane. One characteristic property of a RO membrane was that it could remove more than 99% of micropollutants. The RO membrane could be operated under a wide range of pressures. In addition, inorganic solutions tend to be rejected by the RO membrane depending on the size of the ions and the hydrate ions. For an organic solution to be rejected by a RO, depended on whether or not the molecular weight was larger than 100. It meant that the molecular weight was cut off (MWCO) has 100 g/mol.

2.2.2 Osmosis and reverse osmosis phenomenon

Osmosis was a natural phenomenon that involved the separation of the two aqueous solutions of different concentrations by a semi-permeable barrier. Solvent or water passes through this membrane from the side with the lower concentration to the side with the higher concentration. Water flowed continuously until the concentration between the two sides reached a state of equilibrium as a result of osmotic pressure as seen in **Figure 2.6.**
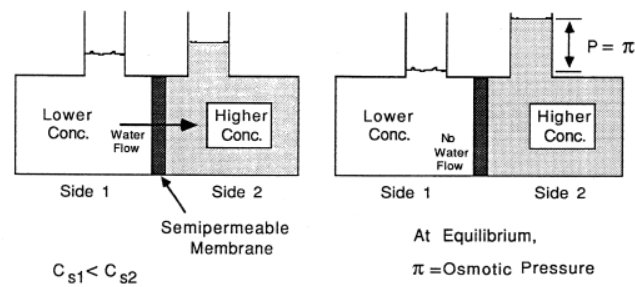
Figure 2.6 Daigram of osmotic pressure

On the other hand, if enough pressure was applied that it reached a level greater than the osmotic pressure, the results showed the flow of water reversed. This insinuates that water flowed from the side with the higher concentration to the side with the lower concentration as was shown in **Figure 2.7.**
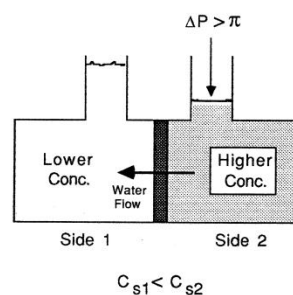
Figure 2.7 Diagram of reverse osmotic pressure

2.2.3 Separation processes design

The two standard separation processes via membranes were dead-end filtration and cross-flow filtration as shown in **Figure 2.8** that modified from Saxena et al., 2009

The dead-end mode was basic form of the filtration. The feed flow was forced perpendicularly to the membrane surface and the filtered matters were build-

up on the surface of the membrane therefore these matters restricted the filtration rate or flux. The dead-end mode technique could be useful for concentrate matter.

In cross-flow mode, the feed solution was filtered flow parallel to the membrane surface and the permeate solution through the membrane owing to pressure difference. The cross-flow mode had a constant turbulent pressure for preventing the accumulation of particles of the membrane process. The reduction of cake on the surface related to keep at stable flux. This mode was wildly applied for filtering liquids with high concentration of filterable matter (Echavarria et al., 2011; Saxena et al., 2009).
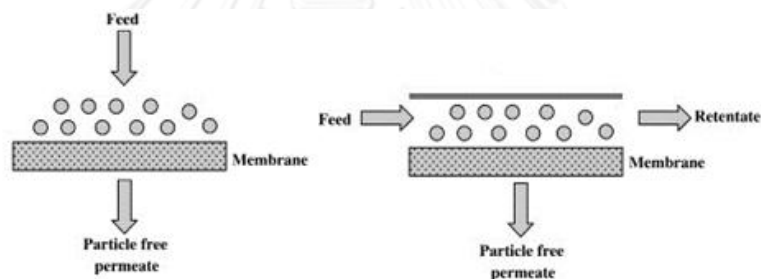
Figure 2.8 Dead end and cross flow filtration mode

2.2.4 Transmembrane pressure and permeability

Transmembrane pressure (TMP) was the pressure that existed between the feed side and the permeate side of the membrane. **Figure 2.9** illustrated a cross section of the cross-flow device. The pressure from the feed side calculated from mean of the pressure between the inlet and outlet sides of the cell test. The formula used to calculate the mean was shown in **Eq. 2.1** below:
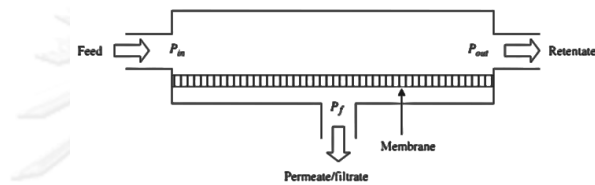
Figure 2.9 Transmembrane pressure in a cross flow device

$$TMP = \frac{(P_{in} + P_{out})}{2} - P_f \qquad (2.1)$$

Where P_{in} and P_{out} = the pressures of the flowing bulk solution at the inlet and outlet of the device, respectively. P_f (the pressure on the filtrate side) was usually negligible.

Hydraulic permeability was the fluid that could move through the pores of the membrane. An important indicator was the volumetric permeate flux (J_V). The formula was shown in **Eq. 2.2**:

$$J_V = \frac{M_p}{\rho_p A} \qquad (2.2)$$

Where M_p was the mass flow rate, A was the membrane surface area and ρ_p was the permeate density.

The volumetric permeate flux (J_V) was related to the TMP. As shown below in the formula in **Eq. 2.3**:

$$J_V = L_p \times TMP \qquad\qquad (2.3)$$

Where L_p was the hydraulic permeability of the membrane. The unit of membrane permeability depended on the unit's permeate flux (ms^{-1}) and the TMP (bar, Pa or Nm^{-2}).

Pure water permeability described the volume of water that passed through a membrane per unit of time. These properties explained the generation of permeate for the membrane and performance of the membrane.

2.2.5 Measurement of solute rejection; concentration polarization

This section explained the method of size exclusion technique that depended on pore size, surface properties of the membrane and the type of the mixture solution. Phenomenon of concentration polarization was shown in **Figure 2.10** (Wongrueng, 2006). The concentration gradient of the feed mixture component dramatically increased in the boundary layer next to the membrane wall because water penetrated through the membrane. Some suspended molecules was remained near the membrane surface, thus, the concentration may be changed in the adjacent environment. The pressure driving force was decreased in this phenomenon.
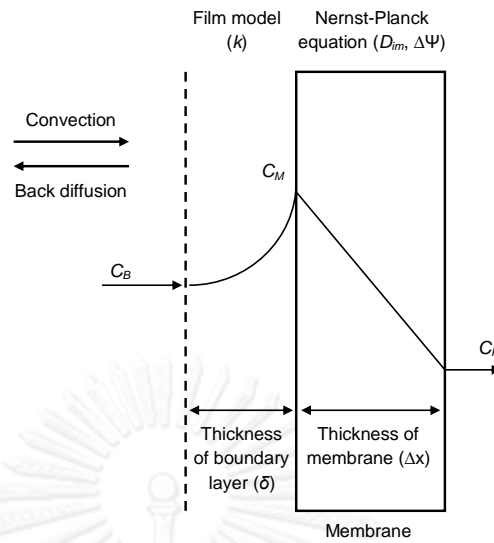
Figure 2.10 The concentration polarization on the boundary layer

The principal of the concentration polarization was flux (J_v). Convection flow near the membrane and back diffusion were given in the following equation:

$$J_S = C_P \cdot J_v = C \cdot J_v - D_i \frac{dc}{dx} \qquad (2.4)$$

Where J_s was the solute flux, J_v was the permeate flux of the solution, C was the solute concentration in the boundary layer, C_p was the solute concentration in the permeate solution, and D_i was the solute diffusion coefficient. Then the **Eq. 2.4** was integrated at the boundary condition ($C_M \longrightarrow C_B$)

$$\frac{(C_M - C_P)}{C_B - C_P} = \exp\left(\frac{J_v \delta}{D_i}\right) \qquad (2.5)$$

Where C_M was the solute concentration at the membrane surface, C_B was the solute concentration in the bulk solution, and δ was the thickness of the boundary layer.

The solute mass transfer coefficient in the solution (k) related to the ratio between the solute diffusion (D_i) and thickness of the boundary layer (δ), which was $k = D_i/\delta$ as shown in **Eq. 2.6**:

$$J_v = k \cdot \ln\left(\frac{C_M - C_P}{C_B - C_P}\right) \tag{2.6}$$

The intrinsic and the apparent solute rejections were defined as follows in **Eq. 2.7** and **Eq. 2.8**

R_a was the observed solute rejection, which was measured by sampling the feed and permeates phases.

$$R_a = 1 - \frac{C_p}{C_b} \tag{2.7}$$

However, R_i was the intrinsic solute rejection, which measures the actual solute concentration at the membrane interface, which was actually not possible to measure.

$$R_i = 1 - \frac{C_p}{C_w} \tag{2.8}$$

Where C_p was the species concentration in the permeate stream, C_w the species concentration at the membrane wall and C_b was the species concentration in the feed stream.

2.2.6 Mass transfer coefficient in solution (k_m)

Mass transfer correlations were valuable tools for predicting the concentration polarization. It's based on the velocity variation method. (Geraldes

and Pinho (2006)) investigated the estimation of the mass transfer coefficient in the solution (km). The theoretical derivation was given as follows:

Permeate flux of pure water was expressed as follows:

$$(J_V)_{H_2O} = K_w \cdot \Delta P \tag{2.9}$$

Where $(J_v)_{H2O}$ was the permeate flux of pure water, k_w was the pure water permeability, and ΔP was the applied pressure.

The permeate flux was decreased when salt was added due to the osmotic pressure across the membrane ($\Delta \pi$).

$$(J_V)_{H_2O} = K_w \cdot (\Delta P - (\pi_M - \pi_P)) \tag{2.10}$$

Where π_M was the osmotic pressure on the membrane surface, π_p was the osmotic pressure in permeate.

From the previous formulas shown in **Eq. 2.9** and **Eq. 2.10**, it could be written as follows:

$$\pi_M - \pi_P = \Delta P \cdot \left[1 - \frac{J_V}{(J_V)_{H_2O}} \right] \tag{2.11}$$

When the osmotic pressure was closely linearly proportional to the salt concentration, the mass transfer coefficient in the solution, k_m, was given by:

$$k_m = \frac{J_V}{\ln\left\{ \frac{\Delta P}{\pi_B - \pi_P} \cdot \left[1 - \frac{J_V}{(J_V)_{H_2O}} \right] \right\}} \tag{2.12}$$

Where π_B = the osmotic pressure in the bulk solution.

CHAPTER 3

METHODOLOGY

3.1 Materials

3.1.1 Test cell

The test cell was used to run the solution in cross-flow filtration system from the Nitto Denko Corporation, Japan. The test cell compose of feed spacer, o-ring, and membrane.
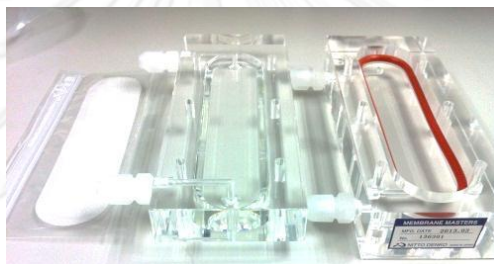
Figure 3.1 Test cell

3.1.2 Feed tank

The feed solution was contained in feed tank that was a beaker 1 L. The temperature was controlled at 30 ± 2 $^\circ$C by using plastic water bath.
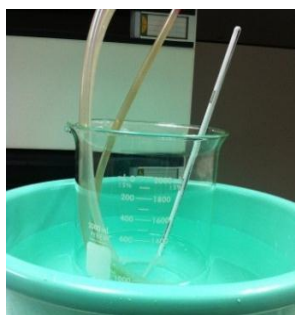
Figure 3.2 Feed tank

3.1.3 Magnetic gear pump

The magnetic gear pump was used to operate the pressure from the Iwaki Company, Japan. The maximum operating pressure was 0.55 MPa and the maximum capacity was 2.0-2.4 liters per minute.

Figure 3.3 Magnetic gear pump

3.1.4 Membrane materials

Reverse osmosis membrane (RO-1) and nanofiltration membrane (NF-1) were purchased from Filmtec, DOW. All membranes were stored in 1% sodium bisulfate acid solution in a cold place at 4°C.

Figure 3.4 RO-1 and NF-1 membranes

3.1.5 Needle value

The needle value was used to adjust pressure in the test cell system

Figure 3.5 Needle value

3.1.6 Pressure gauge

The pressure gauge was set in membrane experiment for detecting the pressure before go through the test cell and the pressure after leave the test cell.

Figure 3.6 Pressure gauge

3.2 Chemical reagents

- Acetonitrile   HPLC   LAB SCAN

- Carbarmazepine   97%   Waico

- Calcium chloride   98%   Univar

- Hydrochloric acid	37%	CARLO ERBA
- Sodium hydroxide	99%	MERCK
- Sodium chloride	99.9%	Univar
- Sulfamethoxazole	98%	Sigma Aldrich
- Tannic acid	70%	Fluka
- Pottassium hydrogen pathalate	99.8%	Univar

3.3 Analytical Instruments

3.3.1 pH meter

The pH of solution was measured by a pH/ISE meter (sensION2 Portable, Hash) with an accuracy of ± 0.01 pH unit. The pH meter was calibrated with a buffer solution at pH levels of 4, 7 and 10, respectively.

Figure 3.7 pH meter

3.3.2 Electrical conductivity meter (EC meter)

The electrical conductivity of the solution was measured by an electrical conductivity meter (CON900, Cond, AMTAST).

Figure 3.8 Electrical conductivity

3.3.3 High performance liquid chromatography (HPLC)

The all samples were prepared by filtrated with membrane Nylon filter 0.45 nm (National Scientific). The analyses of quantity of these pharmaceuticals were carried out by a reverse phase high performance liquid chromatography (HPLC) from Varian Prostar with a C-18 column (ZORBAX Eclipse XDB-C18 2.1 x 100 mm (3.5μm), Agilent, USA). An UV-Vis detector was used to measure the concentrated, feed and permeate water of CBZ and SMZ. The detection of wavelengths of 280 nm was recorded for CBZ and SMX. Temperature was set at 50°C. The elution gradient of mobile phase was conducted using water (A) and acetonitrile (B). The initial elution condition was a mobile phase A 60% v/v reach to 0% v/v within 7 min and phase A gain to 60% v/v within 10 min. A sample injection with a volume of 100μL was used. The flow rate was 1 mL /min.

Figure 3.9 High performance liquid chromatography

3.3.4 Total organic carbon analyzer (TOC analyzer)

The amount of dissolved organic carbon (DOC) in liquid solution was measured by the total organic carbon analyzer. (TOC vcph, Shimadzu, Japan).

Figure 3.10 Total organic carbon analyzer

3.4 Pharmaceutical standards

Researchers selected two pharmaceutical compounds, namely carbamazepine (CBZ) and sulfamethoxazole (SMX). These compounds were represented a range of properties in which the charge on molecules depended on the pH in the solution. SMX was negative charge whereas CBZ was non-charge at neutral pH. SMX and CBZ had similar molecular weight. The different properties of the pharmaceutical compounds were influence membrane rejection.

Sulfamethoxazole (SMX) was a derivative form of the sulfanilamide class. The structure of SMX was composed of two aromatic rings linked with the SO_2NH_2 group. This functional group which included electrons from the drawing group could develop a strong charge. Carbamazepine (CBZ) was a widely used antiepileptic drug. It composed of two benzene rings combined with an azepine group that was connected to an amide group.

Pharmaceutical standards for CBZ and SMX were purchased from Sigma-Aldrich (Saint Louis, MO). These pharmaceutical standards were used at a high purity grade. The stock solutions were prepared in water for both pharmaceuticals. The stock solutions was stored at 4 °C in the dark and used within 4 weeks

3.5 The study area

The study area was in Nakhon Pathom Province, the central part of Thailand. The wastewater from swine farm in Nakhon Pathom Province was selected as the sampling point. The sampling point is shown in **Figure 3.11**. The treated

wastewater sample was collected form swine farm at 20 L with plastic bottles. This side was established by private company to produce the pork for Thai people.

The treatment processes of swine farm consisted of two processes. The first process was separated the manure from wastewater because reduced the contamination of wastewater before flew into the pond. The second process was anaerobic pond. Water from the final pond could bring back to use of watering the trees and releasing to the outside.

Wastewater from swine farm had some organic matter and nutrient that could be deteriorated the water source (Sreesai et al., 2002). In addition, owner farm used the trace organic matter such as pharmaceutical, hormone, and antibiotic to prevent disease in pigs, these treatment processes could not sufficient to remove trace organic matter from wastewater. The trace organic matter might contaminate to the soil and ground water. The swine wastewater characteristics were shown in chapter 5.
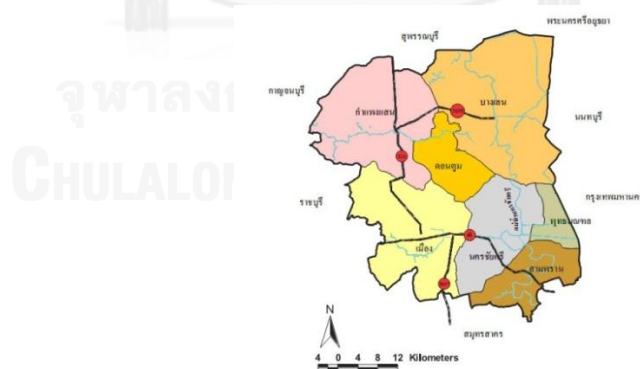
Figure 3.11NakornPathomprovice

3.6 Experimental set up

A laboratory scale membrane filtration system was set up for this study as shown in **Figure3.12**. The equipment in this experiment included a feed tank, a permeate water bottle, a test cell which had a surface area of 60 cm^2, a pressure gauge before go through the test cell in feed line (P_1), a pressure gauge after leave the test cell in the concentrated line (P_2), a needle valve (V), and a pump of the Iwaki company, Japan.
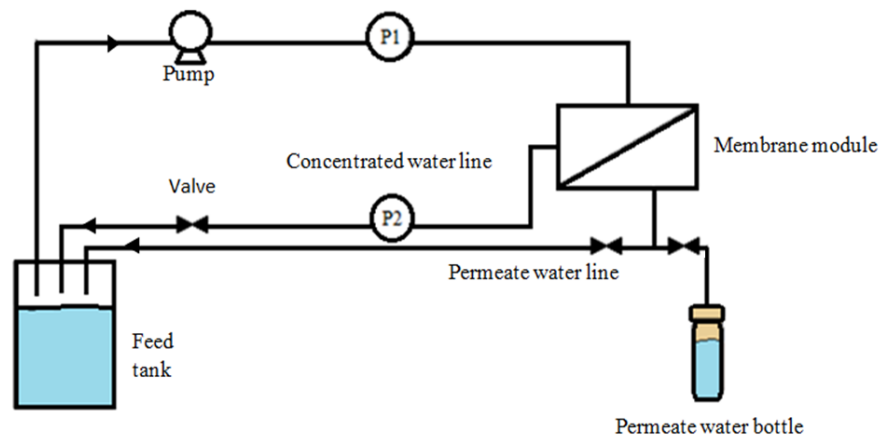
Figure 3.12 Diagram of membrane process

Figure 3.13 explained the schematic framework of the membrane filtration procedure. In the first step, the solution which was contained in the feed tank and was constantly stirred using the magnetic mixer. The solution was pumped through the test cell that supply from the Nitto Denko Corporation, Japan**.** The reverse osmosis membrane and nanofiltration membrane had the surface area of 60 cm^2. It was installed in test cell. In this system, there was pressure gauge for observing the pressure in the system. When the solution in feed tank moved through the membrane, we obtained a solution of low concentration because it filtered through

the RO membrane or NF membrane. In this stage the solution was referred to as the permeate water. In addition, part of the solution flew through only the surface of the membrane and be restored to the tank. This solution was referred to as the concentrated water. This solution was move steadily under a pressure and time that we defined.

Figure 3.13 Experiment set up of the membrane process

3.7 Analysis of membrane characteristics

The physiochemical characterization of the membranes was important information in the membrane filtration process. The important distinctions included pure water permeability, concentration polarization, isoelectric point and solute rejection. Other characterizations were vital in order to determine parameters, such as permeation, pore diameter, barrier thickness membrane elemental composition and surface properties. The separation performance of the membranes could be predicted via these data. Membrane was selected for this study consists of thin polyamide active layer that contain carboxylic and amine functional group. The characteristics of the RO-1 membrane and NF-1 membrane were determined.

3.7.1 Pure water permeability

In all experiment, the RO-1 membrane and NF-1 membrane were immersed in the milli-Q water for 24 hours before using in all experiments.

Milli-Q water was run through the test cell under the following TMP: 0.2, 0.3, and 0.4 MPa for each experiment, respectively. We used 1 L of milli-Q water without a pH adjustment but with at temperature control of 30 ± 2°C. In the feed tank, permeate water and concentrated water were recycled.

The permeate water was collected in a 50 mL cylindrical shape. The timer was set at 2 mins to measure the volume of permeate water. Sampling time was defined as follows: During the initial half hour, the permeate water was collected every ten minutes (10, 20, and 30 min) because there was much fluctuation during this time.

From then on up to fourth hour, the permeate water was observed every 60 minutes (60, 120, 180, and 240 min) to prove the permeate water flux reached completion. We got the volume relate with time, then permeate water flux was calculated

3.7.2 Salt rejection

Salt rejection explained the quantity of salt removed from the feed water by the membrane. High salt rejection showed the membrane has a high performance.

A single salt solution of NaCl was prepared at concentrations of 0.1, 0.05, and 0.01 mol/L, respectively. The solution was run through the test cell under a pressure of 0.4 MPa without change in the pH of the solution.

The RO and NF membrane were immersed in milli-Q water for 24 hours before using and be equilibrated in the test cell. The samples for analysis were put in the test cell for one hour. Then, the samples were collected from the feed line, permeate line and concentrated line for measuring the electrical conductivity and measured water flux.

The EC meter was an instrument for measuring the rejection of salt solution.

3.7.3 Isoelectric point

The RO membrane and NF membrane were immersed in milli-Q water for 24 hours before using. The membrane sheets were cut small in size (4x3 cm). The concentrations of sodium chloride solution (NaCl) were prepared at 0.01 mol/L. The pH solutions were controlled by an adequate addition of hydrochloric acid (HCl) 0.01 mol/L and sodium hydroxide soluition (NaOH) 0.01 mol/L. The pH solutions were adjusted within the range of 2-10.

Membrane sheets were immersed in each bottle that contained the adjusted pH solution. Then, the pH solutions were measured by a pH meter. All bottles were shacked for 200 rpm, 24 hours at room temperature. Afterwards, the pH of the bottles was measured again. The pH values were taken from before and after the experiment and used to plot the graph. Then, the isoelectric point was evaluated.

3.8 Rejection of pharmaceutical compounds in milli-Q water
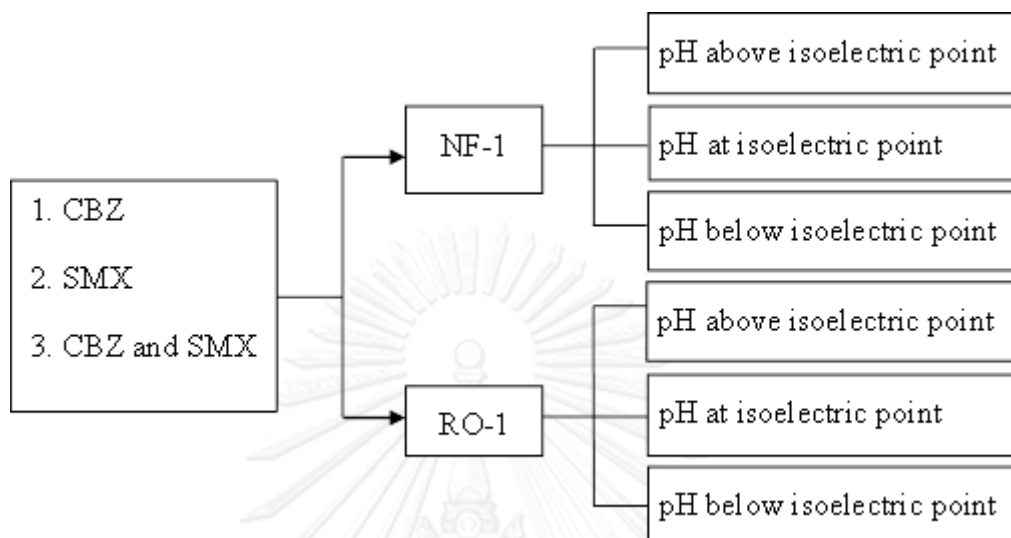
Figure 3.14 Diagram of pharmaceutical removal from milli-Q water

Figure 3.14 illustrated the membrane experiment appliance. We studied the efficiency of the RO membrane and NF membrane in the removal of single pharmaceuticals and mixture between CBZ and SMX pharmaceuticals by spiking the milli-Q water.

A concentration of pharmaceuticals (feed concentration) was prepared at 5 mg/L from stock solution. Then, we adjusted the pH value of the solution into three values that include a pH below the isoelectric point, pH at the isoelectric point and pH above the isoelectric point, respectively (pH at 5, 6 and 7) by using hydrochloric acid (HCl) 0.01 mol/L and sodium hydroxide soluition (NaOH) 0.01 mol/L.

The RO membrane which was set in the test cell was applied first followed by the NF membrane with a controlled pressure of 0.4 MPa and temperature at 30 ±

2 $^{\circ}$C. Before the membrane experiment was operated, we collected the feed water from the feed tank in the feed water bottle. The experiment was performed in recycle mode; thus, the permeate water and concentrated water were returned to the feed tank.

When sampling time achieved a steady state, the permeate water and the concentrated water were collected in the permeated water bottle and concentrated water bottle for determination of concentration by the HPLC measurement and the pH by pH meter, respectively. In addition, the flux solution was determined by measuring the volume of permeate water that timer was set.

3.9 Rejection of pharmaceutical compounds present with NOM and CaCl$_2$
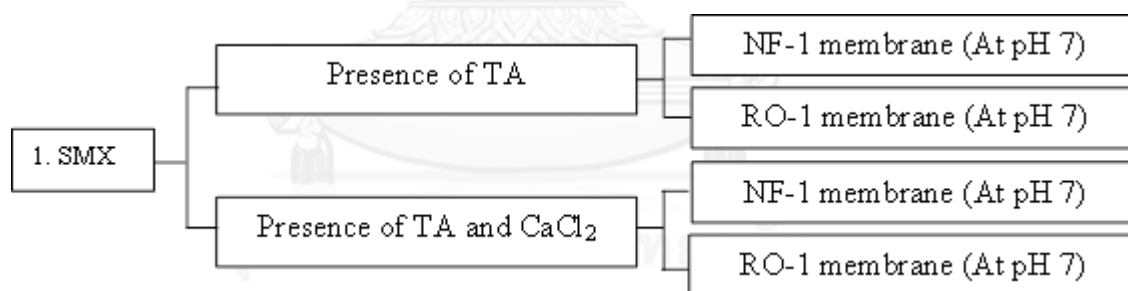
Figure 3.15 Framework of the removal of pharmaceuticals with NOM and CaCl$_2$

In this experiment, we would study the influence of natural organic matter and CaCl$_2$ in order to check the effects of the matrices. **Figure 3.15** shows the framework of this experiment. Section one, SMX was spike in Tannic acid (TA) and the section two, SMX was spike in Tannic acid (TA) and CaCl$_2$.

Tannic acid (TA) was used as a model foulant in the feed solution. TA was hydrophilic compounds that composed of poly phenol. TA form was reported in negatively charged colloid (Mitrouli et al., 2011). TA stock solutions of 500 mg/L were prepared and stored in the dark at 4°C.

The RO membrane and NF membrane were set in the test cell under a TMP of 0.4 MPa. We used 1 L of milli-Q water without a pH adjustment but with a temperature control of 30 ± 2 °C. Water flux was measured via the collection of the permeate water at sampling time from 5 minutes to an hour.

Then, the concentration of SMX at 5 mg/L where organic matter at 10 mg/L and $CaCl_2$ 0.001 M would be used to spike the milli-Q water. Then, we adjusted the pH value to 7. 1 L of feed solution run through the membrane model until the water flux declined 40%.

The concentrated, feed and permeate water was collected for measure the concentration by HPLC, the dissolved organic carbon (DOC) by TOC analyzer, pH and electrical conductivity. The employed membrane was replaced by the new membrane sheet in all experiments.

3.10 Rejection of pharmaceutical compounds in swine wastewater
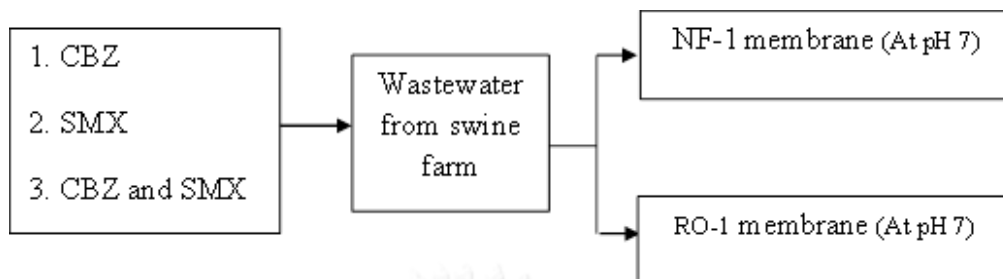
Figure 3.16 Framework of the removal of pharmaceuticals from swine wastewater

We studied the effect of some organic matter in wastewater from swine farm and pH for removing the single pharmaceuticals and mixed pharmaceuticals. **Figure 3.16** presented the framework for the removal of pharmaceuticals spike in wastewater from swine farm.

The natural NOM in wastewater treatment was obtained from swine farm, NakornPhathom provice, Thailand. The concentration of pharmaceuticals (feed concentration) was prepared at 5 mg/L and adjusted the solution volume via swine wastewater. Then, we adjusted the pH value of the solution at a pH level above the isoelectric point (pH 7) by HCl and NaOH. Then, we run the adjusted solution in the RO and NF membranes following the same method as was described in section 3.8.

The feed, concentrate and permeate solution collected in amber glass bottles for measuring the concentration by HPLC measurement. The flux solution, electrical conductivity and pH of all solution were recorded. In addition, the quantity of dissolved organic carbon was analyzed by TOC analyzer. The employed membrane was replaced by the new membrane sheet in all experiments.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Membrane characteristics

4.1.1 Determination of permeate water fluxes and pure water permeability of RO and NF membranes

RO membrane, namely RO-1 membrane and NF membrane, namely NF-1 membrane, were employed in this study.

Permeate water fluxes of RO-1 and NF-1 membranes were evaluated. Milli-Q water was used to operate a membrane filtration at operating pressure ranged from 0.1 to 0.4 MPa, respectively. The data of the permeate water volumes and measuring time under steady state were shown in **Appendix A.** The permeate water fluxes (Jv) can be calculated by using **Eq.4.1**.

$$\text{permeate water fluxes (Jv) } H_2O = \frac{V}{A \times T} \qquad (4.1)$$

Where $(J_v)_{H2O}$ = permeate water fluxes ($m^3/m^2\cdot$day)

V = permeate volume (m^3)

A = surface area of RO-1 and NF-1 membrane sheet (60×10^{-4} m^2)

T = sampling time (day)

The transmembrane pressure (TMP) is a function of the pressure gradient across the test cell (Boyd & Duranceau, 2013). TMP is calculating by using the **Eq. 4.2**.

$$TMP = \left[\left(\frac{P_1 + P_2}{2}\right)\right] - P_3 \tag{4.2}$$

Where P_1 = feed pressure

P_2 = concentrated pressure

P_3 = permeate pressure

Total pressure was the summation of atmospheric pressure and pressure gauge of each line, for example total pressure feed was equal to atmospheric pressure plus the feed pressure gauge. Hence, the atmospheric pressures of three lines could be neglected. In addition, the permeate pressure was negligible because permeate pressure that released to the outside was approximate at zero (Eshed et al., 1998) . The TMP in each experiment was reported in **Table 4.1**.

Table 4.1 Operating transmembrane pressure of RO-1 and NF-1 membranes

Feed pressure (MPa)	Concentrated pressure (MPa)	TMP (MPa)
0.2	0.13	0.165
0.3	0.25	0.275
0.4	0.35	0.375

The results of the permeate water fluxes (Jv) $_{H2O}$ in each the operating TMP of RO-1 and NF-1 membranes were reported in **Table 4.2**

Table 4.2 Permeate water fluxes (m^3/m^2·day) and transmembrane pressure (MPa) of RO-1 and NF-1 membranes

Transmembrane pressure (MPa)	Permeate water fluxes (m^3/m^2·day)	
	RO-1	NF-1
0.165	0.18	0.48
0.275	0.36	0.96
0.375	0.48	1.46

The data illustrated the permeate water fluxes (Jv) of NF-1 and RO-1 membranes in each TMP. It can be indicated that the permeate water fluxes of NF-1 membrane was higher than those obtained from of RO-1 membrane under the same operating TMP.

The phenomenon was explained by the reason of the difference in the pore diameter of NF-1 and RO-1 membranes. Dolar et al., (2011) reported the pore diameter of NF-1 membrane was 1.36-1.92 nm which was classified as nanofiltration membrane type. The pore diameter of RO-1 membrane was approximately 0.6-0.75 nm which was classified as reverse osmosis membrane type. Therefore, the results could be concluded that the quantity of permeate water passing through the membrane with larger pore size were always higher than that of smaller pore size.

The pure water permeability (K$_w$) was defined that the volume of water that passed through a membrane per unit area and unit TMP. K$_w$ was evaluated by plotting graph between permeate water fluxes and TMP via **Eq. 4.3**. The slop of each graph was referred to pure water permeability.

$$(J_v)\, H_2O = K_w \times (\Delta P - \pi) \qquad\qquad (4.3)$$

Where K_w = pure water permeability (m^3/m^2·day·MPa)

    $(J_v)_{H2O}$ = permeate water fluxes (m^3/m^2·day)

    ΔP = transmembrane pressure (MPa)

    π = osmotic pressure (MPa)

Figure 4.1 and **Figure 4.2** illustrated permeate water flux (Jv) $_{H2O}$ at the steady state of each operating TMP of RO-1 and NF-1 membranes, respectively. The linear correlation obtained with high coefficients (R^2) at 0.99 and 0.97 for RO-1 and NF-1 membranes, respectively. The pure water permeabilities were 1.27 and 3.66 (m^3/m^2·day·MPa) for RO-1 and NF-1 membranes, respectively

The results demonstrated that NF-1 membrane exhibited higher permeability than RO-1 membrane. It related to previous studies that NF-1 membrane has large pore size, smoothest and hydrophilic surface (Mondal&Ranil, 2008; Salem et al., 2013)

Furthermore, the permeate water flux was a linear function of operating TMP that followed by **Eq. 4.3**. It was found that the permeate water fluxes at steady state of both membranes increased linearly when the operating TMP increased.
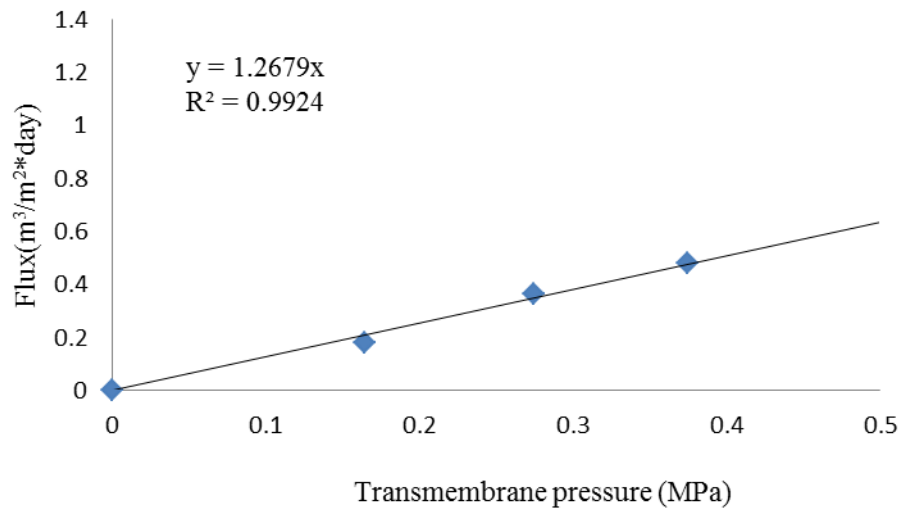
Figure 4.1 The permeate water fluxes at steady state of RO-1 membrane
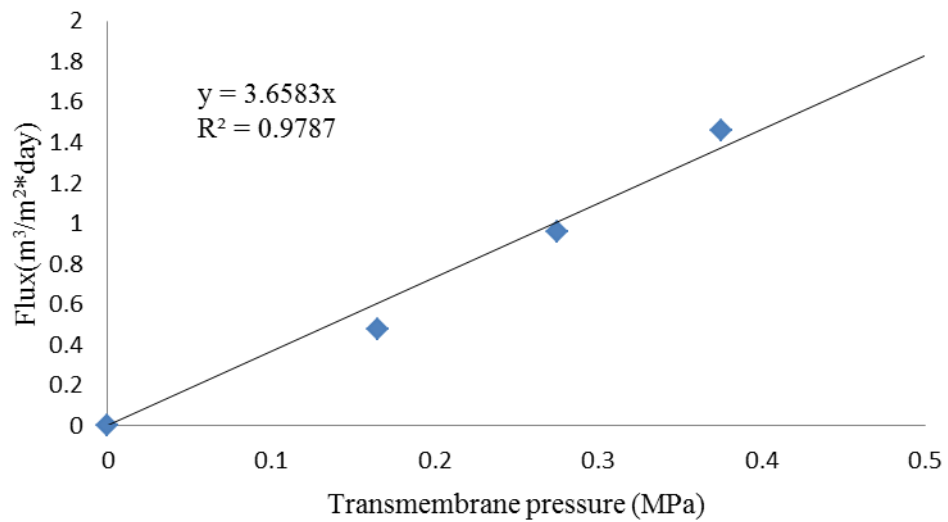
Figure 4.2 The permeate water fluxes at steady state of NF-1 membrane

4.1.2 Determination of the mass transfer coefficient (k_m) and concentration polarization

Mass transfer coefficient was a diffusion rate constant in solution that relate to mass transfer rate, mass transfer area and concentration gradient (Seader & Henle, 2006). Mass transfer coefficient was used to predict the concentration polarization.

The mass transfer coefficient of each membrane was investigated. NaCl solution was used to represent the pharmaceutical solution because NaCl was strong electrolyte that could dissociate completely in solution and NaCl produce one molecule of mono valence ion. NaCl solution was run through RO-1 and NF-1 membranes at operating pressure of 0.4 MPa that produced the highest flux in this study. Then feed solution, concentrate solution and permeate solution were measure by EC meter. The results from EC meter provided the electrical conductivity value (S) then the electrical conductivity was converted to concentration (M) by using calibration curve. The data was provided in **Appendix B**.

Moreover, the concentration of NaCl would be converting to osmotic pressure via Van't Hoff Equation, which can be calculated as follows:

$$\pi = nRT \qquad (4.4)$$

Where   **π**   =   osmotic pressure

n   =   salt concentration

R   =   universal gas constants

T   =   temperature

Table 4.3 shows the three concentrations of NaCl solutions that collect in feed line, concentrate line and permeate line from RO-1 and NF-1 membranes at TMP of 0.375 MPa. Then, the mass transfer coefficient was estimated from **Eq.4.5**.

Table 4.3 The concentration of NaCl and permeate fluxes of RO-1 and NF-1 membranes

Membrane	Concentration (M)			$\pi_B - \pi_P$ (MPa)	Fluxes (Jv) ($m^3/m^2 \cdot$day)	% rejection
	C_F	C_B	C_P			
RO-1	0.094	0.102	0.028	0.186	0.120	73
	0.048	0.053	0.008	0.112	0.216	85
	0.010	0.011	0.001	0.023	0.360	90
NF-1	0.095	0.101	0.062	0.098	0.768	39
	0.048	0.051	0.027	0.059	1.008	47
	0.009	0.010	0.003	0.017	1.296	68

$$k_m = \frac{J_V}{\ln\left\{\frac{\Delta P}{\pi_B - \pi_P}\left[1 - \frac{J_V}{(J_V)_{H_2O}}\right]\right\}}$$ (4.5)

Where
$$A = \ln\left\{\frac{\Delta P}{\pi_B - \pi_P} \cdot \left[1 - \frac{J_V}{(J_V)_{H_2O}}\right]\right\}$$

The mass transfer coefficient for RO-1 and NF-1 membranes were analyzed by plotting graph between the permeate fluxes (Jv) and A $(A = \ln\left\{\dfrac{\Delta P}{\pi_B - \pi_P} \cdot \left[1 - \dfrac{Jv}{(Jv)_{H_2O}}\right]\right\})$.
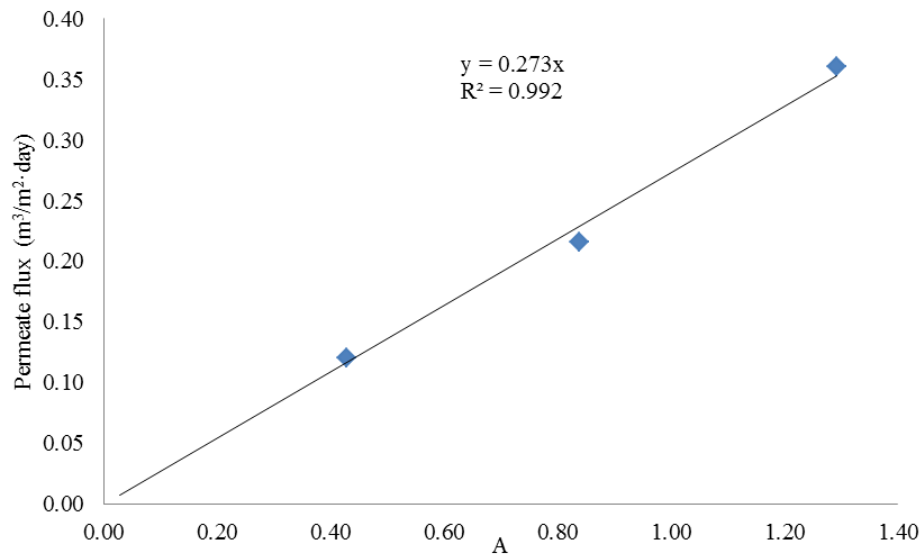
Figure 4.3 The mass transfer coefficient of RO-1 membrane
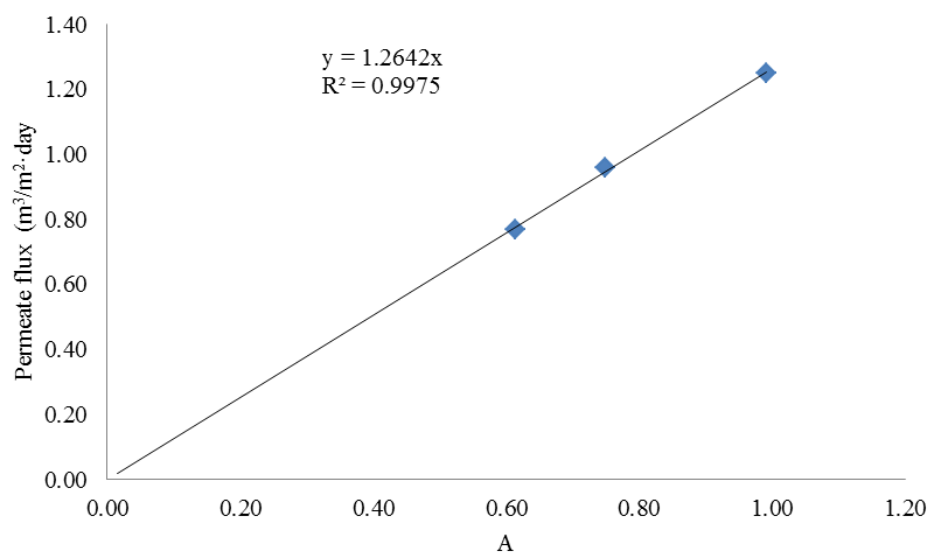
Figure 4.4 The mass transfer coefficient of NF-1 membrane

The mass transfer coefficients of RO-1 and NF-1 membranes were shown in **Figure 4.3** and **Figure 4.4**, respectively. The mass transfer coefficients of RO-1 and NF-1 membranes were 0.273 and 1.2642 $m^3/m^2 \cdot day$, respectively. From the results, it was indicated that NF-1 membrane allowed NaCl passing through itself more than RO-1 membrane.

The effects of concentration of feed water on percent sodium chloride rejection by RO-1 and NF-1 membranes were also investigated as shown in **Table 4.3**. The concentration of sodium chloride was in a range from approximately 0.01 to 0.1 M. The salt rejection was 73-90% and 39-68 % via RO-1 and NF-1 membranes, respectively under the same TMP.

This phenomena could be described as the concentration of salt in permeate line was increased when increasing the concentration in feed solution because the high salt concentration was related to the weakened Donnan potential that present in strong negative charge membrane. The weakening of the Donnan potential lead to the strong negative charge of salt solution increased anion passed through the membrane into to the permeate stream (Childress &Elimelech, 2000; Manttari et al., 2006).

The results indicated the value of the permeate fluxes of salt was declined sharply at the higher concentration of salt because the concentration related to the osmotic pressure from **Eq.4.4.** Moreover, the osmotic pressure was deal with the permeate fluxes from **Eq. 4.3.**

In addition, the mass transfer coefficient (k_m) value in previous section was used to calculate concentration polarization. Concentration polarization was the

phenomena that the solute concentration in the surface area was higher in the bulk solution. Then, the results of concentration polarization of RO-1 and NF-1 membranes were illustrated in **Table 4.4.** In addition, the NaCl concentrations on membrane surface (C_M) of RO-1 and NF-1 membranes were calculated from **Eq.4.6**

$$J_v = k \cdot \ln\left(\frac{C_M - C_P}{C_B - C_P}\right) \qquad (4.6)$$

Table 4.4 The results of concentration polarization of RO-1 and NF-1 membranes

Membrane	Mass transfer coefficient (k_m)	Fluxes (J_v) ($m^3/m^2 \cdot day$)	Concentration (M)		
			C_B	C_P	C_M
RO-1	0.2730	0.120	0.103	0.028	0.148
		0.216	0.053	0.008	0.113
		0.360	0.010	0.001	0.038
NF-1	1.2642	0.768	0.101	0.062	0.13
		1.008	0.051	0.027	0.076
		1.296	0.010	0.003	0.021

The results from **Table 4.4** illustrated that the concentration on the membrane surface was higher than the concentration on the concentrate water in two types of membrane under same TMP. It can be inferred that the concentration gradient of NaCl was increase especially the surface membrane. This phenomenon impacts the performance of membrane process phenomena that arises when the rejected solutes accumulate at the surface of the membrane.

4.1.3 Estimated pH value at isoelectric point of RO-1 and NF-1 membranes

The physical properties of a specific surface membrane were investigated. The titration method was used to determine the isoelectric points of RO-1 and NF-1 membranes (Preocanin & Kallay, 1998).

The relationship between pH value before and after immersing RO-1 and NF-1 membranes into NaCl solution at various pH conditions for 24 hours are shown in **Figure 4.5** and **Figure 4.6**, respectively. An intersection of two lines (i.e., before-before and before-after) was identified as an isoelectric point. The membrane surface charge at this point was became nearly zero (Szoke et al., 2002). It was observed that the isoelectric points of RO-1 and NF-1 membranes were approximately at pH of 6. Other researchers found that many RO and NF membranes have isoelectric point nearly at pH 6. (Tang eat al., 2009)

The charged surface property of RO membrane (RO-1) and NF membrane (NF-1) were studied. From polyamide active layer, it consisting of two functional groups (i.e. carboxylate group (-COOH) and amine group (-NH$_2$)) that can ionize in an aqueous solution. Thus, pH value in solution had affected to surface membrane. In this case, a function of the solution pH had influent for determining the isoelectric point.

At the isoelectric point, the surface charge has a neutral or nearly zero, Hence, it can be investigated that the feed pH value was lower than an isoelectric point, the charge on surface membrane became positive because amine functional group on polyamide- surface layer was protonated, whereas the feed pH value was higher than isoelectric point, the charge on surface membrane became the negative charge due to carboxylate functional group on surface was deprotonated.
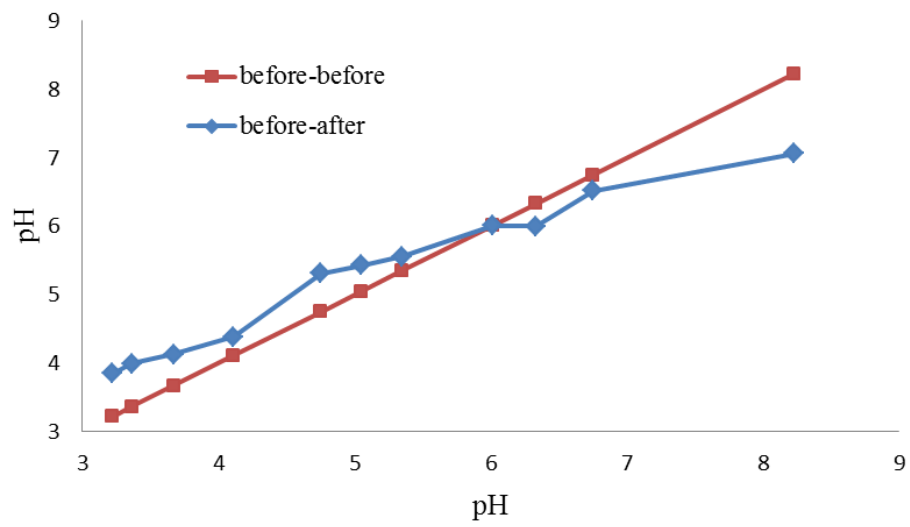
Figure 4.5 An isoelectric point of RO-1 membrane
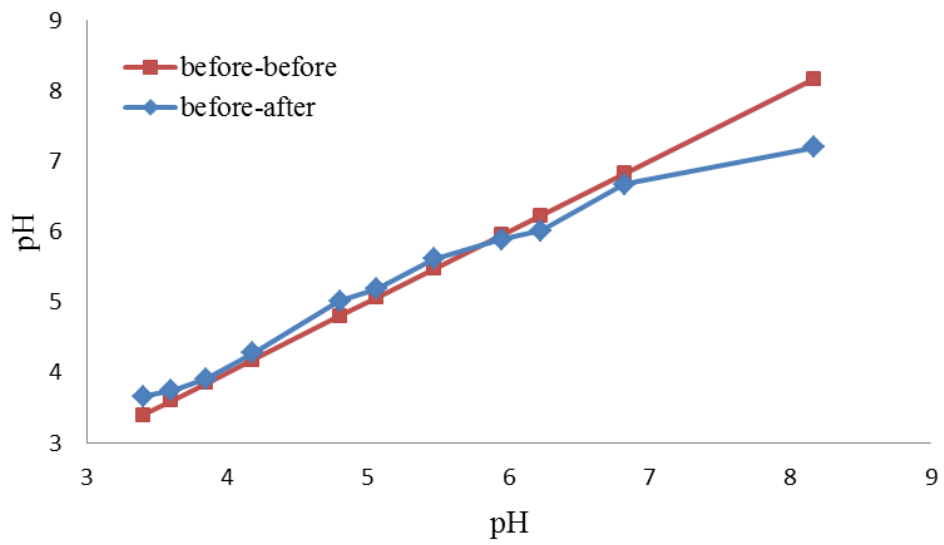
Figure 4.6 An isoelectric point of NF-1 membrane

4.2 Pharmaceuticals removal by RO membrane (RO-1) and NF membrane (NF-1)

4.2.1 Single pharmaceutical spike in milli-Q water

From previous section, the results showed that the isoelectric points of RO-1 and NF-1 membranes were equaled to 6. The single pharmaceuticals, i.e. CBZ and SMX were spiked into milli-Q water and adjusted the pH of CBZ and SMX solutions at pH 5, 6, and 7, respectively.

Each solution was run through the test cell. The samples were collected from concentrate, feed and permeate lines. The concentrations of samples were determined by HPLC instrument and the concentration data were shown in **Appendix C**. **Table 4.5** and **Table 4.6** reported the % rejection of CBZ and SMX under operating TMP 0.375 MPa by RO-1 and NF-1 membranes, respectively.

Table 4.5 % rejection of CBZ and SMX by RO-1 membrane

Pharmaceutical	pH		% Rejection
	Feed	Permeate	
SMX	5.05	4.95	94
	6.14	5.92	97
	7.11	5.59	98
CBZ	5.06	4.56	93
	6.08	5.98	94
	6.93	4.38	92

Table 4.6 % rejection of CBZ and SMX by NF-1 membrane

Pharmaceutical	pH		% Rejection
	Feed	Permeate	
SMX	4.95	5.11	87
	5.92	5.76	91
	7.08	6.65	94
CBZ	5.01	5.51	93
	6.12	5.33	93
	7.10	6.23	92

The pharmaceutical concentration in concentrate, feed, and permeate lines were obtained. The pharmaceutical rejections were calculated. The results of RO-1 membrane are shown in **Table 4.5**. CBZ rejections at the solution pH 5, 6, and 7 were 93%, 94%, and 92%, respectively. SMX rejections at the solution pH 5, 6, and 7 were 94%, 97%, and 98%, respectively.

The results of NF-1 membrane are shown in **Table 4.6**. CBZ rejections at the solution pH 5, 6, and 7 were 93%, 93%, and 92%, respectively. The different analysis of CBZ was analyzed. The test statistic was reported that the three pH value of CBZ rejection was no difference in the statistical significant. In addition, SMX rejections at the solution pH 5, 6, and 7 were 87%, 91%, and 94%, respectively. There were statistically significant differences in SMX rejection of three pH solution.

From the properties of pharmaceuticals, CBZ had pKa_1 equal to 13.9; therefore, CBZ had no effect to charge on CBZ molecule when adjusting the pH in feed solution (CBZ was neutral form). In contrast, SMX had pKa_1 equal to 1.8 and pKa_2 equal to5.6, respectively. It meant that neutral on surface molecule could turn into negatively charged when pH value was higher than pKa_2. The results could be concluded that the rejection of CBZ was relatively pH independent, whereas the rejection of SMZ was relatively pH dependent (Manttari et al., 2006; Nghiem et al., 2006).

It was indicated that CBZ had neutral compound in the pH at 5, 6, and 7; therefore, the removal of CBZ was controlled by size exclusion mechanism and not electrostatic repulsion. **Figure 4.7** illustrates the relationship between %rejection and pH value of two membranes. The rejection of CBZ in RO-1 membrane slightly higher than the rejection of CBZ in NF-1 membrane because of pore sizes of membrane.

In contrast, SMX was transformed from the neutral compound to the negatively charged anion compound, thus upper layer on surface molecule become negatively charge when increasing pH in feed solution. The mechanism for controlling the rejection is both size exclusion and electrostatic repulsion. It was consistent with the finding report by Chang et al., 2012. **Figure 4.8** shows the %rejection of SMX that it was higher % rejection when increasing the pH value because of electrostatic repulsion. In addition, the RO-1 membrane had % rejection more than NF-1 membrane because of size exclusion as well.

In addition the effect of hydrophobicity properties might effect to the RO-1 and NF-1 membrane. Hydrophobicity can be represented by using octanol-water partition coefficient (log Kow). SMX and CBZ were categorized in hydrophilic. The

hydrogen bonds between pharmaceuticals and water molecules might be influenced by water-water bonding because of polar groups therefore the pharmaceutical compounds with water molecule might change the diameter. It was confirm by Braeken et al., 2005. They found that the molecules of xylose increase from 0.69 to 1.21 nm when occur the H bond. Therefore, pharmaceuticals that higher hydrophilic properties had more efficiency for retention in feed solution.

From the membrane experiment, the estimated pH values of the isoelectric points of RO-1 and NF-1 membranes were about 6. The pH value of feed and permeate solution at above isoelectric point, at isoelectric point and at lower isoelectric point which were collected from test cell for RO-1 and NF-1 membranes are shown in **Table 4.5** and **Table 4.6**, respectively.

As the result, the pH in permeate solution is decreased in above an isoelectric point. At the above an isoelectric point, the surface membrane shows the negative ion charge. The H^+ ion in feed solution interacted to negative charge on surface membrane therefore the attractive force was generated. The H^+ ion would move through another side of membrane thus the pH in permeate solution decreased.

The pH in permeate solution is increased at under an isoelectric point. At under an isoelectric point, the surface membrane appears the positive ion charge, H^+ ion in feed solution interacted with positive charge on surface membrane thus the impulsive force was occurred. The H^+ ion cannot pass through another side of membrane therefore, the pH in permeate solution increased.

At an isoelectric point, the pH in permeate as same as in feed solution. the surface membrane is neutral charge, H^+ ion in feed solution and H^+ ion permeate solution are equal in the same side of test cell therefore, the pH in permeate is equal to pH in feed solution.
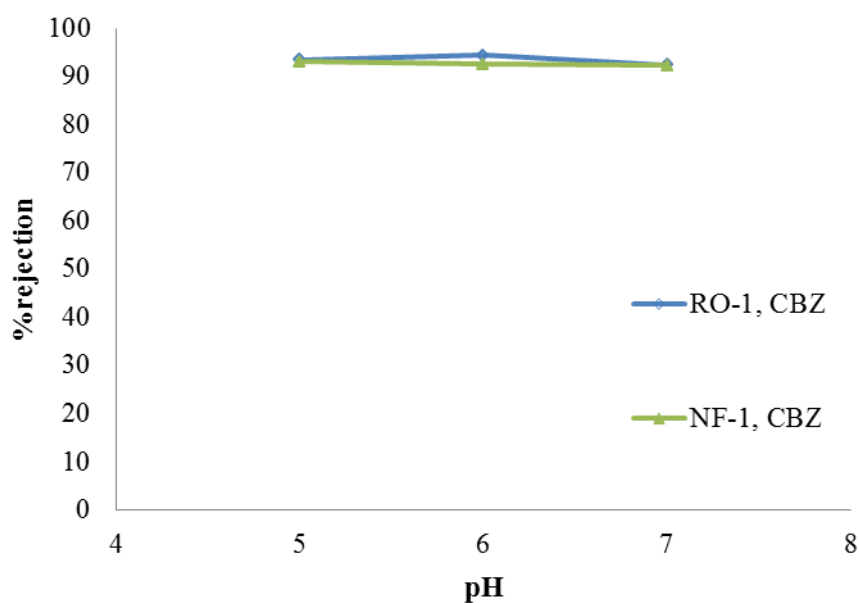
Figure 4.7 Comparison of %rejection CBZ in different pH feed solution by RO-1 and NF-1 membranes
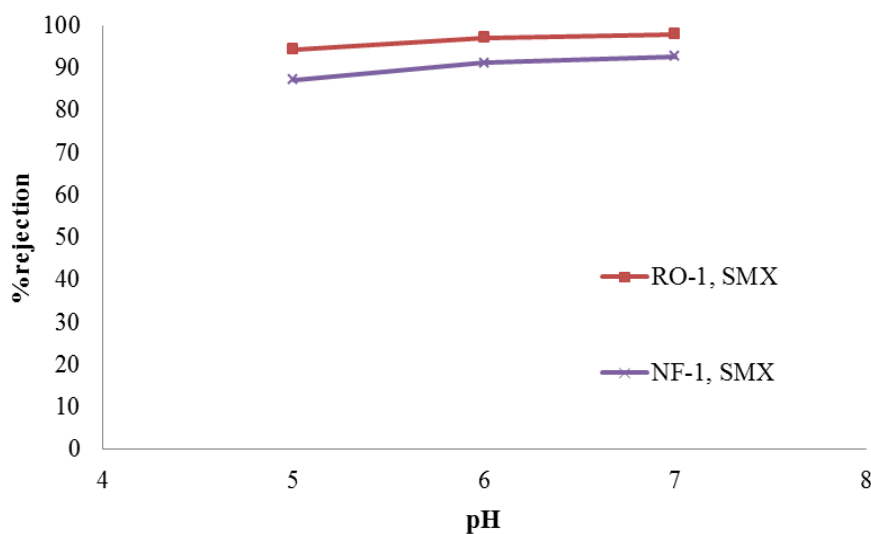
Figure 4.8 Comparison of %rejection SMX in different pH feed solution by RO-1 and NF-1 membranes

4.2.2 Mixture of pharmaceuticals spike in mill-Q water

In this section, an effect of mixed pharmaceuticals of CBZ and SMX spiked into milli-Q water was evaluated. After that, pH values of solutions were adjusted at 5, 6 and 7, respectively. Next, the solutions were run through test cell under operating trasnmembrane pressure of 0.375 MPa.

The concentrations of mixed pharmaceuticals in concentrate, feed and permeate solutions were analyzed by HPLC instrument. The concentration data were illustrated in **Appendix D**.

The pharmaceutical rejections were measured. The data of mixed pharmaceuticals removal at the solution pH 5, 6 and 7 are shown in **Table 4.7**. **Figure 4.9** illustrates the comparison of % rejection in mixed pharmaceutical at different pH solution.

For RO-1 membrane, CBZ rejections in mixed pharmaceuticals at the solution pH 5, 6, and 7 were 98%, 98% and 99%, respectively and those of SMX were nearly constant as 99%. For NF-1, CBZ rejections in mixed pharmaceuticals at the solution pH 5, 6, and 7 were 88%, 91% and 91%, respectively and those of SMX were 82%, 92% and 94%, respectively.

From the results, it was found that the mixture of CBZ and SMX in milli-Q water, the rejection in RO-1 membrane was nearly constant as 99% and NF-1 was near 93%. In addition, mixed pharmaceuticals showed an increasing in the rejection compared to single pharmaceutical. It was due to a combination of all pharmaceuticals in milli-Q water membrane (Dolar et al., 2011). The combination of two pharmaceutical was face to face π stacking interactions between the aromatic rings of two pharmaceutical It was confirm by Kelly et al., 2012, they found π-π complex established by electron- rich and electron-depleted aromatic systems from benzene and hexafluorobenzene. This interaction made the molecule was larger than single molecule and main mechanisms were size exclusion and electrostatic repulsion between solutes and membrane.

The determination of pH value was reported in **Table 4.7**. At above an isoelectric point, the pH in permeate solution is decreased. At under an isoelectric point, the pH in permeate solution is increased and at an isoelectric point, the pH in permeate as same as in feed solution. The reasons for explained this phenomena in mixed pharmaceutical were the same in single pharmaceutical because the membrane structure was the same types. Therefore, the descriptions of pH values of permeate and feed solutions of mixed pharmaceuticals were similar to single pharmaceutical.

Table 4.7 % rejection of mixed pharmaceuticals by RO-1 and NF-1 membranes

Membrane	Mixed pharmaceuticals	pH		% rejection
		Feed	Permeate	
RO-1	CBZ	4.91	4.9	99
	SMX			99
	CBZ	6.15	5.98	98
	SMX			99
	CBZ	7.12	6.41	99
	SMX			99
NF-1	CBZ	4.85	4.96	88
	SMX			82
	CBZ	6.06	5.89	91
	SMX			92
	CBZ	7.2	6.5	91
	SMX			94

Figure 4.9 %rejection of mixed pharmaceuticals in different pH solution in RO-1 and NF-1 membranes

CHAPTER 5

FOULING EFFECTS ON PHARMACUETICALS REMOVAL

5.1 Pharmaceutical spike in Tannic acid and CaCl$_2$ solution

From previous section, the pharmaceutical solution was adjusted to pH above isoelectric point that provided the highest rejection. At solution pH 7, the membrane surface became negatively charged surface that promoted the impulsive force between the membrane surface and substances in the solution. SMX was selected to evaluate the fouling effects. Synthetic wastewater was synthesized by using tannic acid and CaCl$_2$. The rejections of SMX by RO-1 and NF-1 membranes in the presence of natural organic matter (tannic acid) and CaCl$_2$ were evaluated as shown in Table 5.1. The concentration of SMX, tannic acid and CaCl$_2$ was set at 5 mg/L, 10 mg/L and 0.001 M, respectively.

Table 5.1% rejection of SMX spiked into tannic acid and CaCl$_2$ solution

Condition	Fouled membrane		Virgin membrane
	Tannic + CaCl$_2$	Tannic	
RO-1	99	99	98
NF-1	98	99	94

SMX and dissolved organic carbon (DOC) concentrations of feed, concentrate, and permeate were analyzed by HPLC instrument and TOC analyzer, respectively. The data are shown in **Appendix E.** The comparison between RO-1 and NF-1 membrane performances is illustrated in **Figure 5.1.**
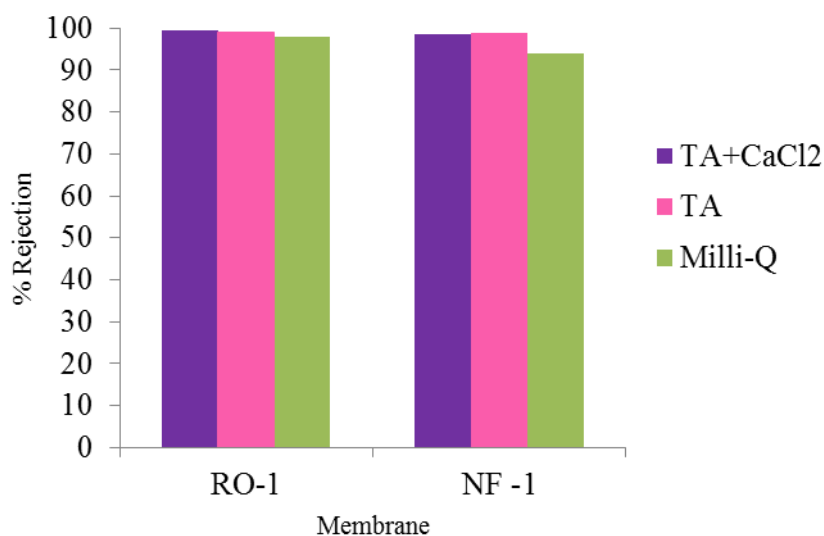
Figure 5.1 SMX rejection by RO-1 and NF-1 membranes

From **Figure 5.1**, it was found that the rejection of SMX in the presence of tannic acid and CaCl$_2$ was higher than those obtained from milli-Q water.

For RO-1 membrane, the percentage rejections of SMX spiked into tannic acid and CaCl$_2$ and sole tannic acid at the solution pH 7 were 99% equally. For NF-1 membrane, the percentage rejections of SMX spiked into tannic acid and CaCl$_2$ and sole tannic acid at the solution pH 7 was 98% and 99%, respectively. The results showed the percentages of pharmaceutical rejections were insignificantly different in comparison between RO-1 and NF-1 membranes.

This phenomenon might be explained by the organic matter fouling on the membrane surface (Verliefde et al., 2009). In this study, Tannic acid was accumulated and formed a dense layer on the membrane surface. The dense fouled layer acted as another filtration layer which resulted in an increasing of SMX rejection.

Other researchers studied the effects of inorganic salt ($CaCl_2$) on pharmaceutical removal. It was found that calcium ion (Ca^{2+}) reduced the Donnan potential length between surface membranes and pharmaceutical. As a result, the rejection of pharmaceutical was decreased (Lee et al., 2005; Li & Elimelech, 2004). In this study, when the membrane was fouled with tannic acid, the presence of $CaCl_2$ did not affect the dense fouled layer. Hence, the increasing of percentage rejections of SMX was obtained. It could be explained that low concentration of calcium ion (less than 6 mg/L) could not affect the pharmaceutical rejection (Dolar et al., 2011).

Figure 5.2 and **Figure 5.3** show the permeate water fluxes of RO-1 and NF-1 membranes during the operating time from 1 minute to 240 minutes. The milli-Q water was pressurized and flew to the test cell during the first 60 minutes. Then, the synthetic wastewater was flown to the test cell. The results showed permeate water flux was dramatically declined due to the membrane fouling when the synthetic wastewater was flown to the test cell. The permeate water flux decline in NF-1 membrane was significantly observed. This could be due to a pore blocking of tannic molecules (Kim et al., 2007). The data of permeate water fluxes were reported in **Appendix E**.

The permeate water fluxes of RO-1 and NF-1 membranes were decreased more rapidly in the presence of calcium comparing to those obtained from a case of sole tannic acid as shown in **Figure 5.4** and **Figure 5.5**, respectively.

The presence of calcium in the synthetic wastewater accelerated the membrane fouling; therefore, the flux declined dramatically, which was consistent with other researches (Lee et al., 2005; Qilin et al., 2007). Fouling mechanism was not attributed to single pharmaceutical. Hoek and Elimelech, 2003 found that membrane

fouled by humic acid and $CaCl_2$ might cause a severe flux decline. The initial rapid fouling was due to pore blocking and then fouling was cake layer formation. Multivalent cations such as calcium performed as a bridging reagent between carboxylic and phenolic functional groups of organic foulants. The bridging reagent made the cross-linked fouling layer (Nghiem et al., 2010).
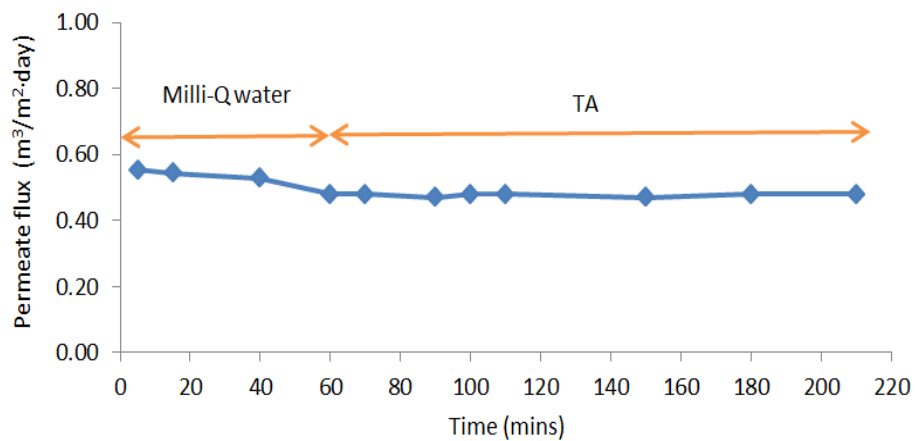
Figure 5.2 Permeate water flux of RO-1 membrane for SMX solution in the presence of tannic acid
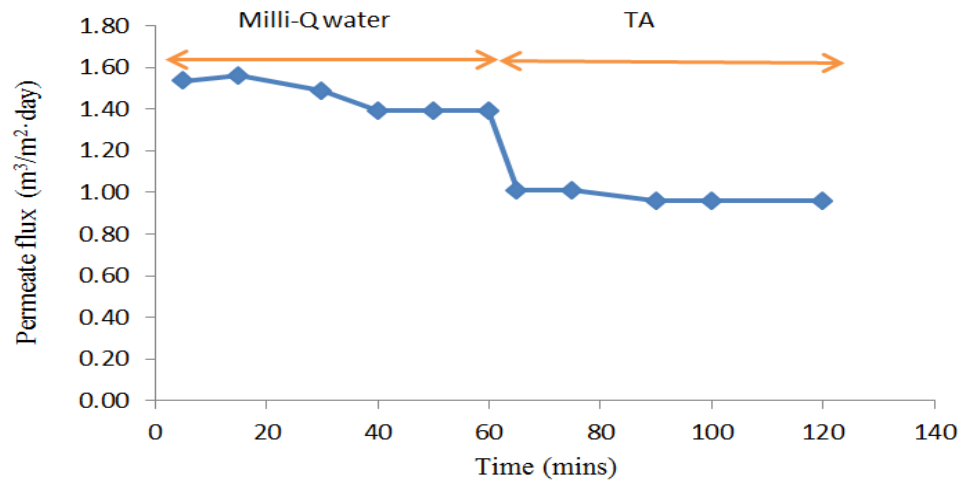
Figure 5.3 Permeate water flux of NF-1 membrane for SMX solution in the presence of tannic acid
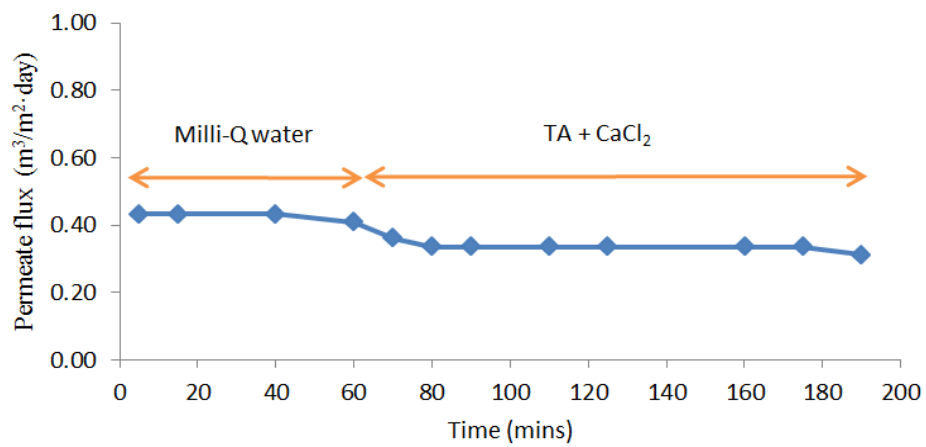
Figure 5.4 Permeate water flux of RO-1 membrane for SMX solution in the presence of tannic acid and $CaCl_2$
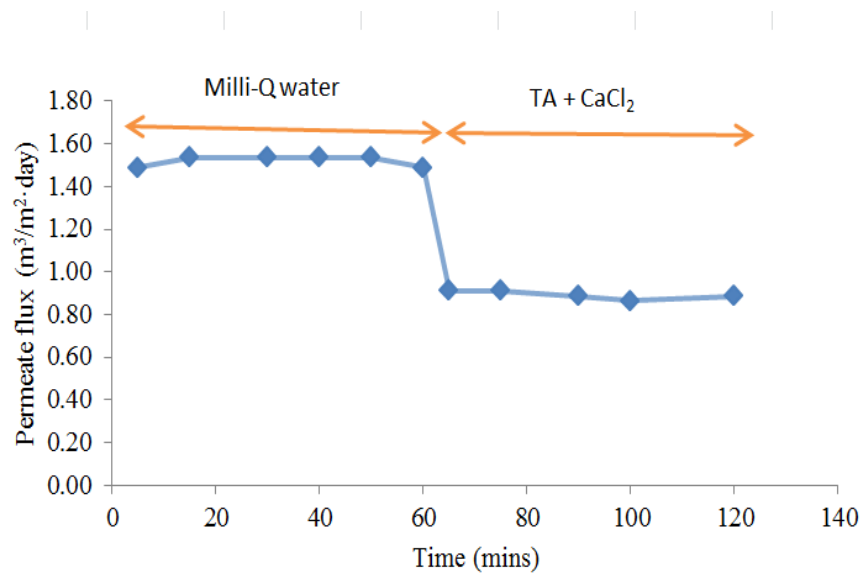
Figure 5.5 Permeate water flux of NF-1 membrane for SMX solution in presence of tannic acid and CaCl$_2$

5.2 Pharmaceutical spike in wastewater from swine farm

Table 5.2 explains the performances of RO-1 and NF-1 membranes on single and mixed pharmaceutical removals in a real wastewater from swine farm. Initial pharmaceutical concentration was 5 mg/L and solution pH was adjusted to 7.

Table 5. 2 %rejection of single and mixed pharmaceuticals by RO-1 and NF-1 membranes

Conditions	Fouled membrane						Virgin membrane	
	Swine wastewater		Tannic + CaCl$_2$		Tannic			
	RO-1	NF-1	RO-1	NF-1	RO-1	NF-1	RO-1	NF-1
SMX	97	94	99	98	99	99	98	94
CBZ	96	77	N.D.	N.D.	N.D.	N.D.	92	92
Mixed CBZ and SMX:								
SMX	98	94	N.D.	N.D.	N.D.	N.D.	99	91
CBZ	98	75	N.D.	N.D.	N.D.	N.D.	99	94

The effect of natural organic matter in swine wastewater on RO-1 and NF-1 membrane performances for pharmaceutical removals was observed. The concentrations pharmaceuticals in feed, concentrate and permeate solutions were analyzed by HPLC instrument and the total organic matters in wastewater from swine farm were analyzed by TOC analyzer. The data are shown in **Appendix F**. Pharmaceutical rejections of RO-1 and NF-1 membranes are reported in **Table 5.2**.

In case of single pharmaceutical, for RO-1 membrane, the percentage CBZ and SMX rejection at the feed pH of neutral pH were 96% and 97%, respectively. For NF-1 membrane, the percentage CBZ and SMX rejection at the feed pH of neutral pH

were 77% and 94%, respectively. **Figure 5.6 and Figure 5.7** show the results of CBZ and SMX rejections by RO-1 and NF-1 membranes using swine farm wastewater, respectively.
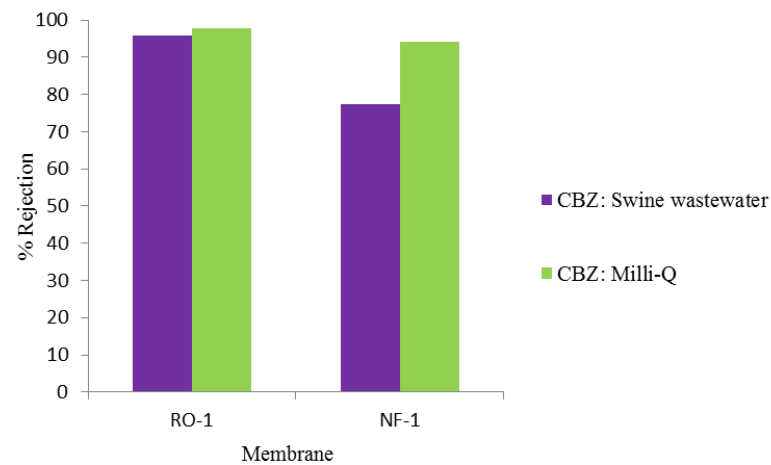
Figure 5.6 CBZ rejections by RO-1 and NF-1 membranes using swine farm wastewater compared with CBZ rejections using milli-Q water at pH 7.
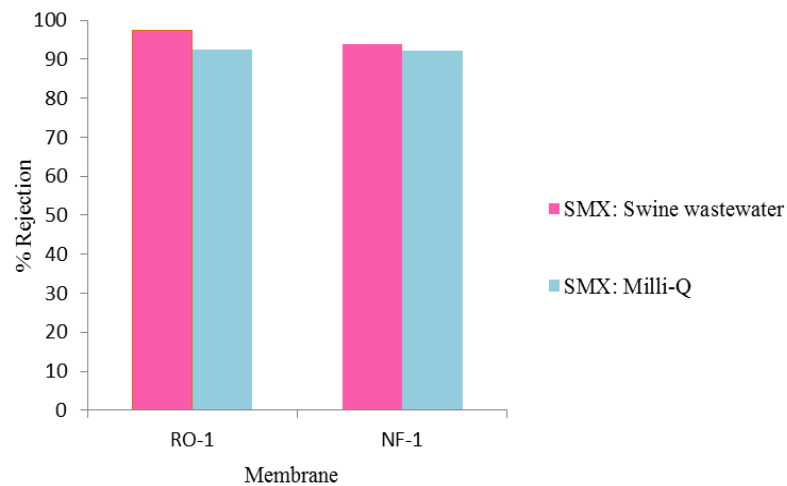
Figure 5.7 SMX rejections by RO-1 and NF-1 membranes using swine farm wastewater compared with SMX rejections using milli-Q water at pH 7.

For mixture of pharmaceuticals, the percentages of both CBZ and SMX rejections by RO-1 membrane were 98%. For NF-1, the percentages of CBZ and SMX rejections by NF-1 membrane were 75% and 94%, respectively, as shown in **Figure 5.8**.

DOC concentration in swine farm wastewater was 0.32 ppm. DOC rejections by RO-1 and NF-1 membranes were between 34-84%. When the membrane was operated with wastewater, membrane fouling could occur and the fouling layer was formed on the membrane surface. It was observed that almost all cases showed the indifference in their rejection efficiencies in comparison between using synthetic water and wastewater from swine farm. It could be stated that the membrane fouling in this case was not severe. The fouled layer was not formed obviously on the membrane surface. As a result, the indifference in their rejection efficiencies was carried out.
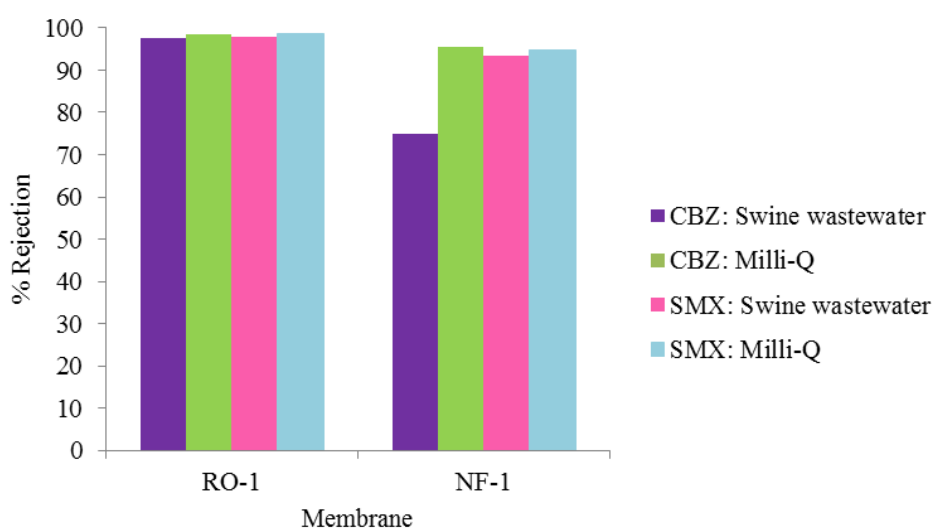
Figure 5.8 Mixed pharmaceutical rejections by RO-1 and NF-1 membranes using swine farm wastewater compared with mixed pharmaceutical rejections using milli-Q water at pH 7
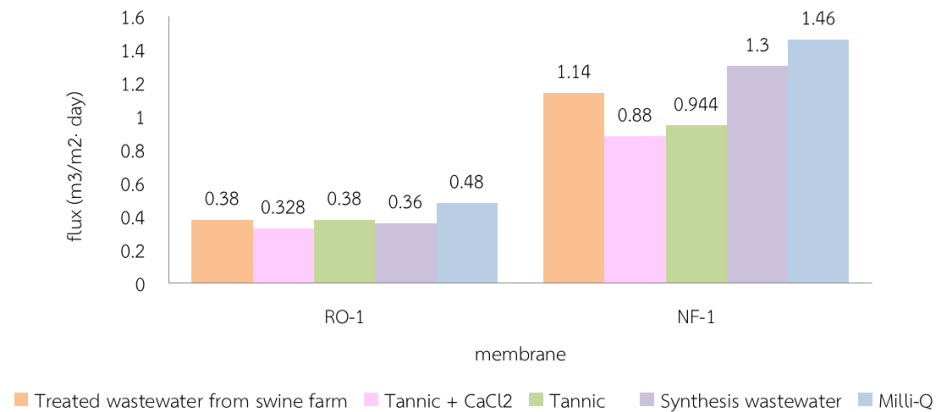
Figure 5.9 Membrane flux in treatment of different water matrices

The flux values for SMX spike in different water matrices are shown in this picture. All membranes showed flux decline when treatment of treated wastewater from swine farm, sole tannic acid and tannic acid and $CaCl_2$ because of fouling effect onto membrane surface. In addition, more severe fouling occurred with larger membrane pores in NF-1 membrane than with smaller ones in RO-1 membrane of membrane properties which is electro static interaction. It was confirm by Norberg et al., 2007, they found that highly negative charge on surface of membrane might be exhibited stable permeate flux because the strong electrostatic repulsion between foulant and membrane when the foulant was the negative charge.

From this result, it can be applied with real situations in wastewater treatment plants by increasing an area of membrane filtration unit for providing high quality of permeate water fluxes. The design of system depended on the volume of daily wastewater discharged. In addition, the concentrated water after the filtration process might collect in a good container for further treatment such as pH neutralization and biotreatment.

CHAPTER 6

CONCLUSION

For RO-1 membrane, the permeate water flux at TMP 0.165, 0.275 and 0.375 MPa were 0.18, 0.36 and 0.48m^3/m^2·day, respectively. For NF-1 membrane, the permeate water flux at TMP 0.165, 0.275 and 0.375 MPa were 0.48, 0.96 and 1.46m^3/m^2·day, respectively. For the result, the permeate water fluxes at steady state of both membranes increased linearly when the operating TMP was enhanced. The permeate water fluxes in NF membrane was higher than the permeate water fluxes in RO membrane because of pore diameters of NF-1 and RO-1 membranes and permeability. pH value at an isoelectric point of RO-1 and NF-1 membranes had approximately at the pH of 6.

The single pharmaceuticals that are CBZ and SMX were spike in milli-Q water and adjusted the pH at pH 5, 6 and 7.The CBZ rejection of all pH is similar values whereas the SMX rejection is increased as pH increased. It could be concluded that the rejection of CBZ was relatively pH independent, whereas the rejection of SMZ was relatively pH dependent. Thus, the removal of CBZ was controlled by size exclusion mechanism. The mechanism for controlling the SMX rejection is both size exclusion and electrostatic repulsion.

For mixed pharmaceutical spike in milli-Q water, the result indicated that mixed pharmaceuticals showed an increasing in the rejection compared to single pharmaceutical. It could be due to a combination of pharmaceuticals between pharmaceutical and the membrane.

The rejection of SMX solution presented with natural organic matter (tannic acid) and CaCl$_2$ was evaluated with RO-1 and NF-1 membranes.

Tannic acid was accumulated and formed a dense layer on the membrane surface. The dense fouled layer acted as another filtration layer which resulted in an increasing of SMX rejection. When the membrane was fouled with tannic acid, the presence of CaCl2 did not affect the dense fouled layer. Hence, the increasing of percentage rejections of SMX was obtained. It could be explained that low concentration of calcium ion (less than 6 mg/L) could not affect the pharmaceutical rejection; however, the permeate fluxes was reduce because fouling on the membrane pores.

The performance of RO-1 and NF-1 membranes on single and mixed pharmaceuticals was spiked in swine wastewater. DOC concentration in swine farm wastewater was 0.32 ppm. The rejection of CBZ and SMX in this case was not severe. The fouled layer was not formed obviously on the membrane surface. As a result, the indifference in their rejection efficiencies was carried out.

REFERENCES

Alzahrani, S., Mohammad, A. W., Hilal, N., Abdullah, P., & Jaafar, O. (2013). Comparative study of NF and RO membranes in the treatment of produced water—Part I: Assessing water quality. *Desalination, 315*, 18-26.

Bidleman, T. F. (1988). Atmospheric Processes: Wet and Dry Deposition of Organic Compounds are Controlled by their Vapor-Particle Partitioning. *Environmental Science and Technology, 22*, 361-367.

Boreen, A. L., Arnold, W. A., & McNeill, K. (2004). Photochemical fate of sulfa drugs in the aquatic environment: sulfa drugs containing five-membered heterocyclic groups. *environmental science & technology, 38*(14), 3933-3940.

Boyd, C. C., & Duranceau, S. J. (2013). Evaluation of ultrafiltration process fouling using a novel transmembrane pressure (TMP) balance approach. *Journal of Membrane Science, 446*, 456-464.

Bueno, M. J. M., Aguera, A., Gomez, M. J., Hernando, M. D., Garcıa-Reyes, J. F., & Fernandez-Alba, A. R. (2007). Application of Liquid Chromatography/Quadrupole-Linear Ion Trap Mass Spectrometry and Time-of-Flight Mass Spectrometry to the Determination of Pharmaceuticals and Related Contaminants in Wastewater. *Analytical Chemistry, 79*, 9372-9384.

Cassano, A., Adzet, J., Molinari, R., Buonomenna, M. G., Roig, J., & Drioli, E. (2003). Membrane treatment by nanofiltration of exhausted vegetable tannin liquors from the leather industry. *Water Res, 37*(10), 2426-2434.

Celiz, M. D., Pérez, S., Barceló, D., & Aga, D. S. (2009). Trace Analysis of Polar Pharmaceuticals in Wastewater by LC–MS–MS: Comparison of Membrane Bioreactor and Activated Sludge Systems Mary. *Journal of Chromatographic Science, 47*, 19-25.

Chang, E. E., Chang, Y. C., Liang, C. H., Huang, C. P., & Chiang, P. C. (2012). Identifying the rejection mechanism for nanofiltration membranes fouled by humic acid and calcium ions exemplified by acetaminophen, sulfamethoxazole, and triclosan. *J Hazard Mater, 221-222*, 19-27.

Claraa, M., Kreuzingera, N., Strenna, B., Gansb, O., & Kroissa, H. (2005). The solids retention time- a suitable design parameter to evaluate the capacity of wastewater treatment plant. *Water Res, 39*(1), 97-106.

Dal, P. A., Donzelli, G., L., R., & A., T. (1989). In vitro model for the evaluation of drug distribution and plasma protein-binding relationships. *International Journal of Pharmaceutics, 50*(2), 97-101.

Dammrich, A., & Bowden, M. E. (2005). A rising drug industry. *Chemical and Engineering News*, 28-42.

Dolar, D., Košutić, K., & Vučić, B. (2011). RO/NF treatment of wastewater from fertilizer factory — removal of fluoride and phosphate. *Desalination, 265*(1-3), 237-241. doi: 10.1016/j.desal.2010.07.057

Dolar, D., Pelko, S., Kosutic, K., & Horvat, A. (2012). Removal of anthelmintic drugs and their photodegradation products from water with RO/NF membranes. *Process Safety and Environmental Protection, 90*, 147-152.

Dolar, D., Vuković, A., Ašperger, D., & Košutić, K. (2011). Effect of water matrices on removal of veterinary pharmaceuticals by nanofiltration and reverse osmosis membranes. *Journal of Environmental Sciences, 23*(8), 1299-1307.

Enick, O. V., & Moore, M. M. (2007). Assessing the assessments: pharmaceuticals in the environment. *Environmental Impact Assessment Review, 27*, 707-729.

Eshed, L., Yaron, S., & Dosoretz, C. G. (2008). Effect of Permeate Drag Force on the Development of a Biofouling Layer in a Pressure-Driven Membrane Separation System. *Appl. Environ. Microbiol., 74*(23), 7338-7347.

Galus, M., Jeyaranjaan, J., Smith, E., Li, H., Metcalfe, C., & Wilson, J. Y. (2013). Chronic effects of exposure to a pharmaceutical mixture and municipal wastewater in zebrafish. *Aquat Toxicol, 132-133*, 212-222. doi: 10.1016/j.aquatox.2012.12.016

Geraldes, V., & Pinho, M. N. D. (2006). Mass transfer coefficient determination method for high-recovery pressure- driven membrane modules. *Desalination, 195*(1-3), 69-77.

Heberer, T. (2002). Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data. *Toxicology Letters, 131*, 5-17.

Heberer, T., Massmann, G., Fanck, B., Taute, T., & Dunnbier, U. (2008). Behaviour and redox sensitivity of antimicrobial residues during bank filtration. *Chemosphere, 73*(4), 451-460. doi: 10.1016/j.chemosphere.2008.06.056

Hoa, P. T. P., Managani, S., Nakada, N., Takada, H., Anh, D. H., Viet, P. H., & Suzuki, S. (2008). Occurrence Rates of Sulfamethoxazole and Erythromycin-Resistant Bacteria and Drug Concentrations in Wastewater of Integrated Aquaculture-Agriculture (VAC) Sites in Northern Vietnam. *Interdisciplinary Studies on Environmental Chemistry*, 355-359.

Hong, S., & Elimelech, M. (1997). Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes. *Membrane Science, 132*(2), 159-181.

Khiari, D. (2007). Endocrine disruptors, pharmaceuticals, and personal care products in drinking water: An overview of AwwaRF research to date. *Awwa Research Foundation*.

Kim, J., Shi, W., Yuan, Y., & Benjamin, M. M. (2007). A serial filtration investigation of membrane fouling by natural organic matter. *Membrane Science, 294*(1-2), 115-126.

Kimura, K., Iwase, T., Kita, S., & Watanabe, Y. (2009). Influence of residual organic macromolecules produced in biological wastewater treatment processes on removal of pharmaceuticals by NF/RO membranes. *Water Res, 43*(15), 3751-3758. doi: 10.1016/j.watres.2009.05.042

Lam, M., Young, C., Brain, R., Johnson, D., Hanson, M., Wilson, C., . . . Mabury, S. (2004). Aquatic persistence of eight pharmaceuticals in a microcosm study. *Environmental Toxicology and Chemistry, 23*(6), 1431-1440.

Leclercq, M., Mathieu, O., Gomez, E., Casellas, C., Fenet, H., & Hillaire-Buys, D. (2008). Presence and fate of carbamazepine, oxcarbazepine, and seven of their metabolites at wastewater treatment plants. *Archives of Environmental Contamination and Toxicology, 56*(3), 408-415.

Luo, Y., Guo, W., Ngo, H. H., Nghiem, L. D., Hai, F. I., Zhang, J., . . . Wang, X. C. (2014). A review on the occurrence of micropollutants in the aquatic environment and

their fate and removal during wastewater treatment. *Sci Total Environ, 473-474*, 619-641. doi: 10.1016/j.scitotenv.2013.12.065

Luo, Y., Xu, L., Rysz, M., Wang, Y., Zhang, H., & Alvarez, P. J. (2011). Occurrence and transport of tetracycline, sulfonamide, quinolone, and macrolide antibiotics in the Haihe River Basin, China. *Environ Sci Technol, 45*(5), 1827-1833. doi: 10.1021/es104009s

Matilainen, A., Gjessing, E. T., Lahtinen, T., Hed, L., Bhatnagar, A., & Sillanpää, M. (2011). An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment. *Chemosphere, 83*(11), 1431-1442. doi: 10.1016/j.chemosphere.2011.01.018

Mi, B., & Elimelech, M. (2008). Chemical and physical aspects of organic fouling of forward osmosis membranes. *Journal of Membrane Science, 320*(1-2), 292-302.

Mitrouli, S. T., Karabelas, A. J., Isaias, N. P., & Al Rammah, A. S. (2011). Application of hydrophilic macromolecules on thin film composite polyamide membranes for performance restoration. *Desalination, 278*(1-3), 105-116. doi: 10.1016/j.desal.2011.05.014

Mondal, S., & Wickramasinghe, S. R. (2008). Produced water treatment by nanofiltration and reverse osmosis membranes. *Journal of Membrane Science, 322*(1), 162-170.

Nghiem, D., & Hawkes, S. (2007). Effects of membrane fouling on the nanofiltration of pharmaceutically active compounds (PhACs): Mechanisms and role of membrane pore size. *Separation and Purification Technology, 57*(1), 176-184. doi: 10.1016/j.seppur.2007.04.002

Nghiem, D., Schafer, I., & Elimelech, M. (2005). Pharmeaceutical Retention Mechanisms by Nanofiltration Membranes. *Environmental Science and Technology, 39*, 7698-7705.

Nghiem, L. D., Coleman, P. J., & Espendiller, C. (2010). Mechanisms underlying the effects of membrane fouling on the nanofiltration of trace organic contaminants. *Desalination, 250*(2), 682-687. doi: 10.1016/j.desal.2009.03.025

Nghiem, L. D., Schafer, A., & Elimelech, M. (2005). Pharmaceutical Retention Mechanisms by Nanofiltration Membranes. *Environmental Science and Technology, 39*, 7698-7705.

Nghiem, L. D., Schäfer, A. I., & Elimelech, M. (2006). Role of electrostatic interactions in the retention of pharmaceutically active contaminants by a loose nanofiltration membrane. *Journal of Membrane Science, 286*(1-2), 52-59.

Novartis Pharmaceuticals Canada, I. (1976). Canadian Product Monograph Tegretol. *Canadian Product Monograph Tegretol*.

Pasquini, L., Munoz, J.-F., Pons, M.-N., Yvon, J., Dauchy, X., France, X., . . . Görner, T. (2014). Occurrence of eight household micropollutants in urban wastewater and their fate in a wastewater treatment plant. Statistical evaluation. *Science of The Total Environment, 481*, 459-468. doi: 10.1016/j.scitotenv.2014.02.075

Preocanin, T., & Kallay, N. (1998). Application of »Mass Titration« to Determination of Surface Charge of Metal Oxides. *CROATICA CHEMICA ACTA, 71*(4), 1117-1125.

Qilin, L., Zhihua, X., & Ingo, P. (2007). Fouling of reverse osmosis membranes by biopolymers in wastewater secondary effluent: Role of membrane surface properties and initial permeate flux. *Membrane Science, 290*(1–2), 173-181.

Radjenović, J., Pérez, S., Petrović, M., & Barceló, D. (2008). Identification and structural characterization of biodegradation products of atenolol and glibenclamide by liquid chromatography coupled to hybrid quadrupole time-of-flight and quadrupole ion trap mass spectrometry. *journal of chromatography a, 1210*(2), 143-153.

Ravikumar, Y. V. L., Kalyani, S., Satyanarayana, S. V., & Sridhar, S. (2014). Processing of pharmaceutical effluent condensate by nanofiltration and reverse osmosis membrane techniques. *Journal of the Taiwan Institute of Chemical Engineers, 45*(1), 50-56. doi: 10.1016/j.jtice.2013.09.021

Risk Assessment Forum. (2012). Benchmark Dose Technical Guidance. *U.S. Environmental Protection Agency, Washington, DC 20460*.

Roberto, A., Marotta, R., & Paxeus, N. (2003). Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment. *Chemosphere, 50*, 1319-1330.

Schifer, A. I., Fane, A. G., & Waite, T. D. (1998). Nanofiltration of natural organic matter: Removal, fouling and the influence of multivalent ions *Desalination, 118*, 109-122.

Schwab, B. W., Hayes, E. P., Fiori, J. M., Mastrocco, F. J., Roden, N. M., Cragin, D., . . . Anderson, P. D. (2005). Human pharmaceuticals in US surface waters: a human health risk assessment. *Regul Toxicol Pharmacol, 42*(3), 296-312.

Schwarzenbach, R. P., Escher, B. I., Fenner, K., Hofstetter, T. B., Johnson, C. A., von Gunten, U., & Wehrli, B. (2006). The challenge of micropollutants in aquatic systems. *Science, 313*(5790), 1072-1077. doi: 10.1126/science.1127291

Seader, J. D., & Henle, E. J. (2006). Separation Process Principles: Chemical and Biochemical Operattion. *New York:John Wiley &Sons 2nd Edition*.

Snydera, S. A., Werta, E. C., & Rexinga, D. J. (2007). Ozone Oxidation of Endocrine Disruptors and Pharmaceuticals in Surface Water and Wastewater. *the International Ozone Association, 28*(6), 445-460.

Sreesai, S., Asawasinsopon, R., & Satitvipawee, P. (2002). Treatment and Reuse of Swine Wastewate. *Thammasat International Journal of Science and Technology, 7*(1), 13-19.

Stackelberg, P. E., Furlong, E. T., Meyer, M. T., Zaugg, S. D., Henderson, A. K., & Reissman, D. B. (2004). Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant. *Sci Total Environ, 329*(1-3), 99-113. doi: 10.1016/j.scitotenv.2004.03.015

Suthanthararajan, R., Ravindranath, E., Chits, K., Umamaheswari, B., Ramesh, T., & Rajamam, S. (2004). Membrane application for recovery and reuse of water from treated tannery wastewater. *Desalination, 164*(2), 151-156.

Szoke, S., Patzay, G., & Weiser, L. (2002). Characteristics of thin film nanofiltration membrane at various pH-values. *Desalination, 151*, 123-129.

Tang, C. Y., Kwon, Y.-N., & Leckie, J. O. (2009). The role of foulant–foulant electrostatic interaction on limiting flux for RO and NF membranes during humic acid fouling—Theoretical basis, experimental evidence, and AFM interaction force measurement. *Journal of Membrane Science, 326*(2), 526-532. doi: 10.1016/j.memsci.2008.10.043

Ternes, T. A. (2002). Removal of pharmaceuticals during drinking water treatment. *environmental science & technology, 36*, 3855–3863.

Tixier, C., Singer, H. P., Oellers, S., & Müller, S. R. (2003). Occurrence and fate of carbamazepine, clofibric acid, diclofenac, ibuprofen, ketoprofen, and naproxen in surface waters. *environmental science & technology, 37*(6), 1061-1068.

Togola, A., & Budzinski, H. (2008). Multi-residue analysis of pharmaceutical compounds in aqueous samples. *J Chromatogr A, 1177*(1), 150-158.

Trovo, A. G., Nogueira, R. F., Aguera, A., Fernandez-Alba, A. R., Sirtori, C., & Malato, S. (2009). Degradation of sulfamethoxazole in water by solar photo-Fenton. Chemical and toxicological evaluation. *Water Res, 43*(16), 3922-3931.

Vergili, I. (2013). Application of nanofiltration for the removal of carbamazepine, diclofenac and ibuprofen from drinking water sources. *J Environ Manage, 127*, 177-187. doi: 10.1016/j.jenvman.2013.04.036

Verlicchi, P., Aukidy, A. M., & Zambello, E. (2012). Occurrence of pharmaceutical compounds in urban wastewater: removal, mass load and environmental risk after a secondary treatment--a review. *Sci Total Environ, 429*, 123-155. doi: 10.1016/j.scitotenv.2012.04.028

von Gunten U., Janex-Habibi M. L., Ternes A.T., & L., W. (2006). Human Pharmaceutical, Hormones and Fragrances: The Challenge of Micropollutants in Urban Water Management. *IWA Publishing London*, 293-322.

Wagner, J. (2001). Membrane Filtration Handbook Practical Tips and Hints. *osmonics*.

Wang, C., Shi, H., Adams, C. D., Gamagedara, S., Stayton, I., Timmons, T., & Ma, Y. (2011). Investigation of pharmaceuticals in Missouri natural and drinking water using high performance liquid chromatography-tandem mass spectrometry. *Water Res, 45*(4), 1818-1828. doi: 10.1016/j.watres.2010.11.043

Wongrueng, A. (2006). Groundwater defluoridation by ultra low pressure reverse osmosis membrane and nano filtration. *M.Sc. Thesis, Environmental Management, Inter-department of Environmental Science, Graduate School, Chulalongkorn University*.

Xu, P., Drewes, E., Kim, U., Bellona, C., & Amy, G. (2006). Effect of membrane fouling on transport of organic contaminants in NF/RO membrane applications. *Journal of Membrane Science, 279*(1-2), 165-175. doi: 10.1016/j.memsci.2005.12.001

Yamamura, H., Chae, S., Kimura, K., & Watanabe, Y. (2007). Transition in fouling mechanism in microfiltration of a surface water. *Water Res, 41*(17), 3812-3822. doi: 10.1016/j.watres.2007.05.060

Yi, Z., Li, X., Xu, X., Luo, B., Luo, J., Wu, W., . . . Tang, Y. (2011). Green, effective chemical route for the synthesis of silver nanoplates in tannic acid aqueous solution. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 392*(1), 131-136. doi: 10.1016/j.colsurfa.2011.09.045

Yoon, Y. (2006). Nanofiltration and ultrafiltration of endocrine disrupting compounds, pharmaceuticals and personal care products. *Membrane Science, 270*, 88-100.

Yoon, Y., Westerhoff, P., & Snyder, S. A. (2005). Adsorption of 3H-Labeled 17-β Estradiol on Powdered Activated Carbon. *Water, Air, and Soil Pollution, 166*(1-4), 343-351.

Zhang, Y., Geissen, S. U., & Gal, C. (2008). Carbamazepine and diclofenac: removal in wastewater treatment plants and occurrence in water bodies. *Chemosphere, 73*(8), 1151-1161. doi: 10.1016/j.chemosphere.2008.07.086

APPENDIX

APPENDIX A

PERMEATE WATER FLUX

Table A. 1 Permeate water flux of RO-1 membrane at TMP 0.165 MPa

Times (mins)	Sampling time (day)	Volume (m^3)	Area (m^2)	Flux (m^3/m^2·day)
10	0.0014	0.0000012	0.006	0.14
20	0.0014	0.0000012	0.006	0.14
30	0.0014	0.0000015	0.006	0.18
40	0.0014	0.0000015	0.006	0.18
60	0.0014	0.0000015	0.006	0.18
100	0.0014	0.0000015	0.006	0.18
120	0.0014	0.0000015	0.006	0.18

Table A. 2 Permeate water flux of RO-1 membrane at TMP 0.275 MPa

Times (mins)	Sampling time (day)	Volume (m^3)	Area (m^2)	Flux (m^3/m^2·day)
10	0.0014	0.000003	0.006	0.36
20	0.0014	0.000003	0.006	0.36
30	0.0014	0.000003	0.006	0.36
40	0.0014	0.0000029	0.006	0.35
60	0.0014	0.0000029	0.006	0.35
100	0.0014	0.0000029	0.006	0.35
120	0.0014	0.0000029	0.006	0.35

Table A. 3 Permeate water flux of RO-1 membrane at TMP 0.375 MPa

Times (mins)	Sampling time (day)	Volume (m^3)	Area (m^2)	Flux (m^3/m^2·day)
10	0.0014	0.0000045	0.006	0.54
20	0.0014	0.000004	0.006	0.48
30	0.0014	0.000004	0.006	0.48
40	0.0014	0.000004	0.006	0.48
60	0.0014	0.000004	0.006	0.48
100	0.0014	0.000004	0.006	0.48
120	0.0014	0.000004	0.006	0.48

Table A. 4 Permeate water fluwxof NF-1 membrane at TMP 0.165 MPa

Times (mins)	Sampling time (day)	Volume (m^3)	Area (m^2)	Flux (m^3/m^2·day)
10	0.0014	0.000004	0.006	0.48
20	0.0014	0.0000037	0.006	0.44
30	0.0014	0.0000037	0.006	0.44
40	0.0014	0.0000039	0.006	0.47
60	0.0014	0.000004	0.006	0.48
90	0.0014	0.000004	0.006	0.48
120	0.0014	0.000004	0.006	0.48

Table A. 5 Permeatewater flux of NF-1 membrane at TMP 0.275 MPa

Time (mins)	sampling time (day)	Volume (m^3)	Area (m^2)	Flux (m^3/m^2·day)
10	0.0014	0.000008	0.006	0.96
20	0.0014	0.0000082	0.006	0.98
30	0.0014	0.0000082	0.006	0.98
40	0.0014	0.0000081	0.006	0.97
60	0.0014	0.000008	0.006	0.96
90	0.0014	0.000008	0.006	0.96
120	0.0014	0.000008	0.006	0.96

Table A. 6 Permeatewater flux of NF-1 membrane at TMP 0.375 MPa

Times (mins)	Sampling time (day)	Volume (m^3)	Area (m^2)	Flux (m^3/m^2·day)
10	0.0014	0.0000118	0.006	1.42
20	0.0014	0.0000118	0.006	1.42
30	0.0014	0.0000118	0.006	1.42
40	0.0014	0.0000118	0.006	1.41
60	0.0014	0.0000112	0.006	1.34
90	0.0014	0.0000116	0.006	1.39
120	0.0014	0.0000120	0.006	1.44

APPENDIX B

THE MASS TRANSFER COEFFCIENT (k_m)

Table B. 1 Calibration curve to convert the concentration unit from electrical conductivity (µs) to Molar

NaCl (M)	Electrical conductivity (µs)
0.002	171.3
0.004	341
0.006	499
0.008	666
0.01	838
0.02	1593
0.04	3160
0.06	4380
0.08	6030
0.1	7330
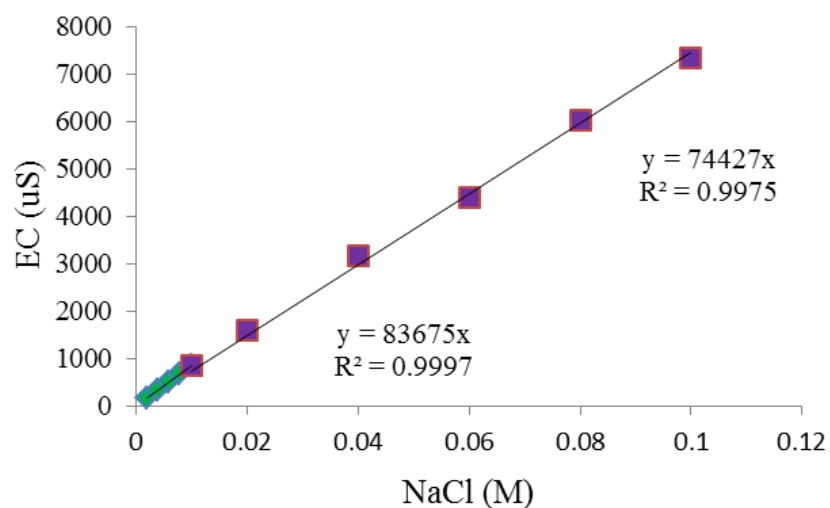
Figure B. 1 Calibrationcurve to convert the concentration unit from electrical conductivity (µs) to Molar

Table B. 2 The calculating data for mass transfer coefficient of RO-1 membrane at TMP 0.375 MPa

Feed		Concentrated solution			Permeate solution			$\Delta \pi$	Flux (m^3/m^2· day)
EC (μS)	(M)	EC (μS)	M	π B (Mpa)	EC (μS)	M	π P (Mpa)	πB - π P (Mpa)	
7020	0.094	7590	0.102	0.25	2360	0.028	16.87	7573.13	0.12
3600	0.048	3970	0.053	0.13	642	0.008	0.65	3969.35	0.22
779	0.010	848	0.011	0.03	85.6	0.001	0.00	848.00	0.36

Table B. 3 The calculating data for mass transfer coefficient of NF-1 membrane at TMP 0.375 MPa

Feed		Concentrate			Permeate			$\Delta \pi$	Flux (m^3/m^2· day)
EC (μS)	M	EC (μS)	M	π B (Mpa)	EC (μS)	M	π P (Mpa)	πB - π P (Mpa)	
7030	0.095	7470	0.101	0.25	5160	0.062	0.15	0.10	0.77
3650	0.048	3830	0.051	0.13	2260	0.027	0.07	0.06	1.01
789	0.009	850	0.010	0.03	275	0.003	0.01	0.02	1.30

Osmotic pressure (π) was calculated by using the equation

$$\pi = nRT$$

Where π = osmotic pressure (MPa)

n= concencentration(mol/L)

R = gas constant (L·MPa/K·mol)

T = temperature (K)

APPENDIX C

REJECTION OF SINGLE PHARMACEUTICAL SPIKE IN MILLI-Q WATER

Table C. 1 Data analysis for membrane experiment of RO-1 membrane of single pharmaceutical filtrated from milli-Q water at TMP 0.375 MPa

Pharmaceutical	pH	Solutions	Area	Concentration (ppm)	Flux (m^3/m^2·day)
CBZ	5.06	feed	1735	4.95	0.31
		concentrate	1810	5.16	
	4.56	permeate	118	0.34	
	6.08	feed	1750	4.99	0.31
		concentrate	1827	5.21	
	5.98	permeate	102	0.29	
	6.93	feed	1530	4.36	0.31
		concentrate	1555	4.44	
	4.38	permeate	118	0.34	
SMX	5.05	feed	946	5.03	0.36
		concentrate	881	4.68	
	4.95	permeate	49.6	0.26	
	6.14	feed	1150	6.11	0.36
		concentrate	1216	6.46	
	5.92	permeate	37.2	0.20	
	7.11	feed	786	4.18	0.36
		concentrate	1155	6.14	
	5.59	permeate	24.23	0.13	

Table C. 2 Data analysis for membrane experiment of NF-1 membrane of single pharmaceutical filtrated from milli-Q water at TMP 0.375 MPa

Pharmaceutical	pH	Solutions	Area	Concentration (ppm)	Flux (m^3/m^2·day)
CBZ	5.01	feed	1785	5.09	1.23
		concentrate	1787	5.10	
	5.51	permeate	124	0.35	
	6.12	feed	1740	4.96	1.23
		concentrate	1620	4.62	
	5.33	permeate	120	0.34	
	7.10	feed	1824	5.20	1.23
		concentrate	1684	4.80	
	6.23	permeate	131	0.37	
SMX	4.95	feed	718	3.82	1.30
		concentrate	818	4.35	
	5.11	permeate	105	0.56	
	5.92	feed	798	4.24	1.30
		concentrate	823	4.38	
	5.76	permeate	73.2	0.39	
	7.08	feed	890	4.73	1.30
		concentrate	1084	5.76	
	6.65	permeate	63.3	0.34	

APPENDIX D

REJECTION OF MIXED PHARMACEUTICALS SPIKE IN MILLI-Q WATER

Table D. 1 Data analysis for membrane experiment of RO-1 membrane of mixed pharmaceuticals filtrated from milli-Q water at TMP 0.375 MPa

Mixed pharmaceuticals	pH	Solution	Area	Concentration (ppm)	Flux ($m^3/m^2 \cdot$ day)
CBZ	4.91	feed	1356	4.82	0.43
		concentrate	1180	4.19	
	4.9	permeate	17.6	0.06	
	6.15	feed	1260	4.48	
		concentrate	1213	4.31	
	5.98	permeate	23	0.08	
	7.12	feed	1254	4.46	
		concentrate	1355	4.82	
	6.41	permeate	20.1	0.07	
SMX	4.91	feed	475	2.53	
		concentrate	475	2.53	
	4.9	permeate	3.65	0.02	
	6.15	feed	419	2.23	
		concentrate	432	2.30	
	5.98	permeate	4.66	0.02	
	7.12	feed	1254	6.67	
		concentrate	1355	7.20	
	6.41	permeate	20.1	0.11	

Table D. 2 Data analysis for membrane experiment of NF-1 membrane of mixed pharmaceutical filtrated from milli-Q water at TMP 0.375 MPa

Mixed pharmaceuticals	pH	Solution	Area	Concentration (ppm)	Flux (m3/m2 ·day)
CBZ	4.95	feed	1189	4.23	1.39
		concentrate	1244	4.42	
	4.96	permeate	74	0.26	
	6.06	feed	1342	4.77	
		concentrate	1354	4.81	
	5.89	permeate	67	0.24	
	7.2	feed	1377	4.89	
		concentrate	1332	4.73	
	6.5	permeate	68	0.24	
SMX	4.95	feed	534	2.84	
		concentrate	674	3.58	
	4.96	permeate	76	0.40	
	6.06	feed	828	4.40	
		concentrate	848	4.51	
	5.89	permeate	62	0.33	
	7.2	feed	814	4.33	
		concentrate	817	4.34	
	6.5	permeate	36	0.19	

APPENDIX E

REJECTION OF SINGLE PHARMACEUTICAL SPIKE IN SYNTHESIS WATER

Table E. 1 Permeate water flux and sampling time of NF-1 membrane of SMX spike in tannic acid and $CaCl_2$ under TMP 0.375 MPa

Time (mins)	Volume (m^3)	Collecting time (mins)	Flux ($m^3/m^2 \cdot day$)
5	0.000031	0.0035	1.488
15	0.000032	0.0035	1.536
30	0.000032	0.0035	1.536
40	0.000032	0.0035	1.536
50	0.000032	0.0035	1.536
60	0.000031	0.0035	1.488
65	0.000019	0.0035	0.912
75	0.000019	0.0035	0.912
90	0.000019	0.0035	0.888
100	0.000018	0.0035	0.864
120	0.000019	0.0035	0.888

Table E. 2 Permeate water flux and sampling time of NF-1 membrane of SMX spike in tannic acid under TMP 0.375 MPa

Time (mins)	Volume (m^3)	Collecting time (mins)	Flux ($m^3/m^2 \cdot day$)
5	0.000032	0.0035	1.536
15	0.000033	0.0035	1.560
30	0.000031	0.0035	1.488
40	0.000029	0.0035	1.392
50	0.000029	0.0035	1.392
60	0.000029	0.0035	1.392
65	0.000021	0.0035	1.008
75	0.000021	0.0035	1.008
90	0.000020	0.0035	0.960
100	0.000020	0.0035	0.960
120	0.000019	0.0035	0.912

Table E. 3 Permeatewater flux and sampling time of RO-1 membrane of SMX spike in tannic acid and CaCl2 under TMP 0.375 MPa

Time (mins)	Volume (m^3)	Collecting time (mins)	Flux ($m^3/m^2 \cdot day$)
5	0.000009	0.0035	0.432
15	0.000009	0.0035	0.432
40	0.000009	0.0035	0.432
60	0.000009	0.0035	0.408
70	0.000008	0.0035	0.360
80	0.000007	0.0035	0.336
90	0.000007	0.0035	0.336
110	0.000007	0.0035	0.336
125	0.000007	0.0035	0.336
160	0.000007	0.0035	0.336
175	0.000007	0.0035	0.336
190	0.000007	0.0035	0.312

Table E. 4 Permeatewater flux and sampling time of RO-1 membrane of SMX
spike in tannic acid under TMP 0.375 MPa

Time (mins)	Volume (m^3)	Collecting time (mins)	Flux (m^3/m^2·day)
5	0.000012	0.0035	0.552
15	0.000011	0.0035	0.542
40	0.000011	0.0035	0.528
60	0.000010	0.0035	0.480
70	0.000010	0.0035	0.480
90	0.000010	0.0035	0.470
100	0.000010	0.0035	0.480
110	0.000010	0.0035	0.480
150	0.000010	0.0035	0.470
180	0.000010	0.0035	0.480
210	0.000010	0.0035	0.480
220	0.000010	0.0035	0.480

Table E. 5 Dataanalysis for membrane experiment of RO-1 and NF-1 membranes
of single pharmaceutical spike in synthesis wastewater at TMP 0.375 MPa

Membrane	Synthesis wastewater	pH	Solutions	Area	Concentration (ppm)
RO-1	tannic + CaCl$_2$	7.03	feed	1024	5.44
			concentrate	1036	5.508
		6.68	permeate	6.87	0.037
	tannic	7.06	feed	993	5.279
			concentrate	1087	5.779
		7.24	permeate	1.19	0.006
NF-1	tannic + CaCl$_2$	7.01	feed	1007	5.354
			concentrate	1025	5.450
		6.76	permeate	15.5	0.082
	tannic	7.09	feed	1018	5.412
			concentrate	1133	6.024
		7.35	permeate	11.3	0.060

Table E. 6 Dataanalysis for membrane experiment of RO-1 and NF-1 of DOC from synthesis wastewater

Membrane	Synthesis wastewater	Solution	Concentration (ppm)	% Rejection
RO-1	tannic + CaCl$_2$	feed	7.643	97
		concentrate	7.013	
		permeate	0.215	
	tannic	feed	8.422	97
		concentrate	9.237	
		permeate	0.265	
NF-1	tannic + CaCl$_2$	feed	7.751	96
		concentrate	6.599	
		permeate	0.231	
	tannic	feed	7.997	97
		concentrate	8.916	
		permeate	0.291	

APPENDIX F

REJECTION OF SINGLE PHARMACEUTICAL SPIKE IN SWINE WASTEWATER

Table F. 1 Concentration of single pharmaceutical spike in wastewater from swine farm filtrated from RO-1 membrane

Swine wastewater	pH	Solutions	Area	Concentration (ppm)	Flux $(m^3/m^2 \cdot day)$
CBZ	7.05	feed	849	3.04	0.408
		concentrate	970	3.47	
	6.76	permeate	41	0.15	
SMX	7.03	feed	1045	4.47	0.384
		concentrate	1065	4.56	
	5.95	permeate	28	0.12	

Table F. 2 Concentration of single pharmaceutical spike in swine wastewater filtrated from NF-1 membrane

Swine wastewater	pH	Solutions	Area	Concentration (ppm)	Flux $(m^3/m^2 \cdot day)$
CBZ	6.98	feed	761	2.72	1.44
		concentrate	930	3.33	
	5.61	permeate	211	0.76	
SMX	7.03	feed	1123	4.81	1.488
		concentrate	1144	4.90	
	6.33	permeate	69.4	0.30	

Table F. 3 Concentration of mixed pharmaceutical spike in swine wastewater filtrated from RO-1 membrane at pH 7

Swine wastewater	pH	Solutions	Area	Concentration (ppm)	Flux $(m^3/m^2 \cdot day)$
CBZ	7.04	feed	1312	4.70	0.41
		concentrate	1322	4.73	
	6.25	permeate	30.7	0.11	
SMX	7.04	feed	1173	5.02	
		concentrate	1132	4.84	
	6.25	permeate	24.8	0.11	

Table F. 4 Concentration of mixed pharmaceutical spike in swine wastewater filtrated from NF-1 membrane

Swine wastewater	pH	Solutions	Area	Concentration (ppm)	Flux $(m^3/m^2 \cdot day)$
CBZ	7.1	feed	939	3.360	1.51
		concentrate	993	3.554	
	6.52	permeate	250	0.895	
SMX	7.1	feed	1078	4.613	
		concentrate	1128	4.827	
	6.52	permeate	73	0.312	

Table F. 5 Dataanalysis of DOC of single pharmaceutical spike in wastewater form swine farm

Membrane	Swine wastewater	Solution	Concentration (ppm)	% Rejection
RO-1	CBZ	feed	0.579	84
		concentrate	0.848	
		permeate	0.139	
	SMX	feed	0.562	78
		concentrate	0.596	
		permeate	0.129	
NF-1	CBZ	feed	0.594	34
		concentrate	0.723	
		permeate	0.478	
	SMX	feed	0.580	76
		concentrate	0.740	
		permeate	0.175	

Table F. 6 Data analysis of DOC of mixed pharmaceutical spike wastewater from swine farm

Membranes	Swine wastewater	Solution	Concentration (ppm)	% Rejection
RO-1	CBZ+SMX	feed	1.350	87
		concentrate	1.318	
		permeate	0.175	
NF-1	CBZ+SMX	feed	1.042	79
		concentrate	1.114	
		permeate	0.239	

VITA

Name   Ms. Katunchalee Phadunghus

Date of Birth   January 28, 1990

Place of Birth   Mae Hong Son, Thailand

Institution Attended Triamudomsuksa Pattanakarn Nonthaburi School

Nonthaburi, Certificate of Mathayomsuksa 6

Chulalongkorn University, Thailand

Faculty of science, majoring in Chemistry

Bacherlor's Degree of Science