

GROUNDWATER DEFLUORIDATION BY A CO-PROCESS OF DOLOMITE ADSORPTION  
AND NANOFILTRATION

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งานวิจัยนี้ศึกษาการกำจัดสารฟลูออไรด์โดยใช้กระบวนการร่วมของการดูดซับด้วยโดโลไมท์และการกรองด้วยเยื่อกรองชนิดนาโน โดยใช้โดโลไมท์ขนาดเส้นผ่าศูนย์กลาง 0.42 มิลลิเมตร เป็นตัวดูดซับและใช้เยื่อกรองนาโน-1 สำหรับกระบวนการกรอง นอกจากนี้ยังมีการศึกษาคุณสมบัติของโดโลไมท์และเยื่อกรองนาโน-1 ซึ่งได้แก่ จุดไอโซอิเล็กทริก พื้นที่ผิวจำเพาะ องค์ประกอบแร่และสารเคมี ลักษณะพื้นผิว จลนพลศาสตร์การดูดซับ การซึมผ่านของน้ำบริสุทธิ์ และคอนเซนเตรชันโพลาริเซชัน ผลจากการศึกษาคุณสมบัติของโดโลไมท์พบว่า จุดไอโซอิเล็กทริกของโดโลไมท์อยู่ที่ค่าพีเอช 8.5 พื้นที่ผิวจำเพาะของโดโลไมท์มีค่า 1.17 ตารางเมตรต่อกรัม และปริมาตรรูพรุนเฉลี่ยเท่ากับ 105.7 อังสตรอม องค์ประกอบแร่หลักของโดโลไมท์ได้แก่ แร่ โดโลไมท์ แคลไซต์ และควอตซ์ ส่วนองค์ประกอบหลักทางเคมีพบว่ามีส่วนประกอบ แคลเซียมออกไซด์ 72.19 เปอร์เซ็นต์ และแมกนีเซียมออกไซด์ 22.61 เปอร์เซ็นต์ การดูดซับโดโลไมท์เข้าสู่สมดุลใช้เวลาสัมผัส 12 ชั่วโมง แบบจำลองจลนพลศาสตร์ที่เหมาะสมได้แก่ แบบจำลองของจลนพลศาสตร์อันดับสองแบบเทียม ซึ่งมีค่าคงที่การดูดซับเท่ากับ 21.07 กรัมต่อมิลลิโมลาร์ต่อนาโน และผลการศึกษาคุณสมบัติของเยื่อกรองนาโน-1 พบว่า จุดไอโซอิเล็กทริกของเยื่อกรองนาโน-1 อยู่ที่ค่าพีเอช 6 ค่าการซึมผ่านของน้ำบริสุทธิ์มีค่า 3.66 ลูกบาศก์เมตรต่อตารางเมตรต่อวินาทีต่อเมกะปาสคาล ค่าสัมประสิทธิ์การเคลื่อนย้ายสารฟลูออไรด์เท่ากับ 1.539 ลูกบาศก์เมตรต่อตารางเมตรต่อวินาที การทดลองนี้เก็บตัวอย่างน้ำใต้ดินจากโรงผลิตน้ำประจวบจวนประจวบคีรีขันธ์ใน จังหวัดลำพูน ประเทศไทย ซึ่งมีค่าความเข้มข้นของสารฟลูออไรด์อยู่ระหว่าง 12.14-15.38 มิลลิกรัมต่อลิตร ประสิทธิภาพของการกรองด้วยเยื่อกรองนาโน-1 เพียงอย่างเดียวพบว่า เยื่อกรองนาโน-1 สามารถบำบัดสารฟลูออไรด์ในน้ำใต้ดินภายใต้ค่าพีเอช 7 เท่ากับ 91 เปอร์เซ็นต์ และประสิทธิภาพของการกรองด้วยเยื่อกรองนาโน-1 เพียงอย่างเดียวพบว่า เยื่อกรองนาโน-1 สามารถบำบัดสารฟลูออไรด์ในน้ำใต้ดินภายใต้ค่าพีเอช 7 เท่ากับ 99 เปอร์เซ็นต์ ส่วนกระบวนการร่วมโดยการปรับค่าพีเอชของน้ำใต้ดินให้มีค่าเท่ากับ 7 หลังจากการดูดซับด้วยโดโลไมท์ ก่อนที่จะนำไปกรองผ่านเยื่อกรองนาโน-1 สามารถบำบัดฟลูออไรด์ได้ 78 เปอร์เซ็นต์ โดยโดโลไมท์สามารถบำบัดสารฟลูออไรด์ในน้ำใต้ดินได้ 9 เปอร์เซ็นต์ ซึ่งสามารถอธิบายผลการทดลองนี้ว่าอาจเป็นผลมาจากการปล่อยไอออนและแร่ต่างๆออกมาจากโดโลไมท์ระหว่างกระบวนการดูดซับทำให้เกิดค่าความแรงไอออนในน้ำสูงและมีความเป็นไปได้จากการดูดซับของเยื่อกรองระหว่างกระบวนการกรองซึ่งส่งผลให้กระบวนการร่วมมีค่าการบำบัดฟลูออไรด์น้อยกว่าการบำบัดด้วยเยื่อกรองนาโน-1 เพียงอย่างเดียว จากผลการวิจัยดังกล่าว ถึงแม้ว่าประสิทธิภาพของกระบวนการร่วมระหว่างการดูดซับด้วยโดโลไมท์และการกรองด้วยเยื่อกรองชนิดนาโน-1 จะสามารถบำบัดสารฟลูออไรด์ได้น้อยกว่าการบำบัดด้วยเยื่อกรองนาโน-1 เพียงอย่างเดียว แต่งานวิจัยนี้สามารถใช้เป็นแนวทางในการปรับปรุงคุณภาพของตัวดูดซับเพื่อให้มีประสิทธิภาพสูงขึ้นในการบำบัดสารฟลูออไรด์ในน้ำใต้ดินเพื่อนำมาประยุกต์ใช้ร่วมกับกระบวนการกรองด้วยเยื่อกรองนาโนในอนาคตต่อไป

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ปีการศึกษา 2556

ลายมือชื่อนิสิต .....

ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก .....

# # 5587565520 : MAJOR ENVIRONMENTAL MANAGEMENT

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Co-process of dolomite adsorption and nanofiltration (NF) membrane for a removal of fluoride was investigated. Dolomite with a diameter of 0.42 mm was used as adsorbent and NF-1 membrane was used for filtration. Dolomite sorbent and NF-1 membrane properties were characterized i.e. point of zero charge, specific surface area, mineral and chemical composition, surface morphology, adsorption kinetic, pure water permeability, and concentration polarization. Point of zero charge (PZC) of dolomite was observed at pH 8.5. Specific surface area was  $1.17 \text{ m}^2/\text{g}$ . Average pore size was  $105.7 \text{ \AA}$ . Dolomite, calcite, and quartz were major components of dolomite rock. Main chemical compositions included calcium oxide (CaO) 72.19% and magnesium oxides (MgO) 22.61%. Equilibrium contact time of dolomite adsorption was 12 hr. The suitable kinetic model was pseudo-second order kinetic, which had the rate constant of  $21.07 \text{ g}/\text{mM min}$ . An isoelectric point of NF-1 membrane was found at pH 6.0. Pure water permeability of NF-1 membrane was  $3.66 \text{ m}^3/\text{m}^2 \times \text{day} \times \text{MPa}$ . The mass transfer coefficient of fluoride was  $1.539 \text{ m}^3/\text{m}^2 \times \text{day}$ . Groundwater containing high fluoride concentration (12.14-15.38 mg/L) from Pra Too Khong bottle drinking water plant, Lamphun Province, Thailand was collected. Fluoride could be removed under feed groundwater pH 7 by 91% and 99 % via a sole NF-1 and RO-1 membrane, respectively. The co-process with an adjustment of defluoridated groundwater pH after dolomite adsorption to pH 7 prior to NF-1 membrane filtration showed 78% of fluoride rejection (9% fluoride rejection via dolomite adsorption). This explains that many ions and minerals released from dolomite during adsorption process. It caused high ionic strength in the water together with possibility of membrane fouling during membrane filtration process. As the result, the co-process presented lower fluoride rejection. Although the efficiency of the co-process dolomite adsorption and nanofiltration (NF) membrane presented lower fluoride rejection than using sole NF-1 membrane, this study can be applied to improve the quality of adsorbent to enhance the efficiency for fluoride removal in groundwater combine with NF membrane in future.

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## LIST OF ABBREVIATIONS

$C_B$	Concentration on concentrated water
$C_{Gel}$	Concentration on gel layer surface
$C_M$	Concentration on membrane surface
$C_p$	Concentration in permeate water
Da	Dalton
EC	Electro conductivity
$F$	Concentration polarization level
IC	Ion Chromatography
$J_i$	Solute flux
$J_v$	Permeate flux
$(J_v)_{H_2O}$	Permeate flux of pure water
$k$	Mass transfer coefficient
$k_w$	Pure water permeability
$k_i$	Solute mass transfer coefficient
MF	Microfiltration
NF	Nanofiltration
PZC	Point of zero charge
$\Delta P$	Transmembrane pressure
$\pi$	Osmotic pressure

$\pi_B$	Osmotic pressure of bulk solution
$\pi_P$	Osmotic pressure of permeate water
RO	Reverse osmosis
TMP	Transmembrane pressure
TFC	Thin-film composite
TDS	Total Dissolved Solids
UF	Ultrafiltration





# CHAPTER 1

## INTRODUCTION

### 1.1 Motivation

Many countries have been faced with a fluorosis problem due to high fluoride concentrations in groundwater such as India, Sri Lanka, Pakistan, China and parts of East Africa (Deshmukh et al., 2009). Exposing high fluoride levels in water in human, which is used for cooking and drinking, fluorosis might be cause a greater loss of the surface enamel than is normal. In Chiang Mai and Lumphun provinces, Thailand, the population was received the high amount of fluoride in groundwater (McGrady et al., 2012). Fluoride enriched in groundwater of Chiang Mai Basin was observed in aquifers of alluvial plains, with the highest concentration level reaching 16.1 mg/L (Matsui, 2007). The World Health Organization defines the maximum limit of fluoride concentration in drinking water at 1.5 mg/L (WHO, 2004). The Ministry of Industry in Thailand set the standard of fluoride concentration in drinking water at 0.7 mg/L (Ministry of Industry of Thailand).

An adsorption technology relates to the passage of water through an absorbent where polluted compounds are removed by ion exchange or surface chemical reaction. Adsorption is a physical-chemical treatment and high removal effective. Adsorption technology works without any addition of excessive chemicals which is different from the use of precipitation-coagulation technologies. Thus, it requires smaller footprints and the absence of sludge generation in the process (Ayoob & Gupta, 2006). Moreover, the technology of adsorption depends on the effectiveness, operation cost and reusing of the adsorbent. Researchers studied

about low-cost and naturally occurring materials such as dolomite (Sasaki et al., 2012). Dolomite is a low cost adsorbent that containing of magnesium carbonate and calcium compound. The property of Dolomite is like to limestone that known as magnesium limestone in the industry. Several researchers used dolomite to treat many heavy metal ions such as  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  from water (Kocaoba, 2007). Furthermore, calcined dolomite could be applied to remove phosphate ( $\text{PO}_4^{3-}$ ) from solutions that adsorption of phosphate occurs through physical interaction (Karaca et al., 2006) .

In addition, membrane technologies such as reverse osmosis (RO) and nanofiltration (NF) membranes had also determined for fluoride removal from contaminates groundwater. Even if NF and RO processes are similar, NF is manipulated at lower pressures and could produce same permeate flux at lower pressure (Tahaikt et al., 2007).

Thus, adsorption technologies by using dolomite as an adsorbent and the nanofiltration membrane could be combined to use in the defluoridation of groundwater. Combining process of two technologies might be as alternative to remove fluoride from groundwater.

## 1.2 Objectives

- To study charges on surface of dolomite, nanofiltration membrane, and reverse osmosis membrane.
- To evaluate the performances of dolomite, nanofiltration membrane, and reverse osmosis membranes on fluoride removal efficiencies.

- To elucidate an efficiency of a co-process of dolomite adsorption and nanofiltration membrane compared with a sole nanofiltration membrane on fluoride removal.

### 1.3 Hypothesis

- Dolomite can be applied to remove fluoride ion from groundwater.
- Dolomite adsorption and membrane filtration efficiencies are strongly influenced by water pH.
- A co-process of dolomite adsorption and nanofiltration membrane can remove fluoride with a high efficiency comparable to reverse osmosis membrane filtration.

### 1.4 Scope of study

- Synthetic water and groundwater were investigated.
- NF membrane (NF-1) and RO membrane (RO-1) were examined.
- Test cell, C-10T (Nitto Denko, Japan), with an effective filtration area of 60 cm<sup>2</sup> was employed.
- Dolomite was utilized as an adsorbent.
- The pH of water was in a range of 5-7.

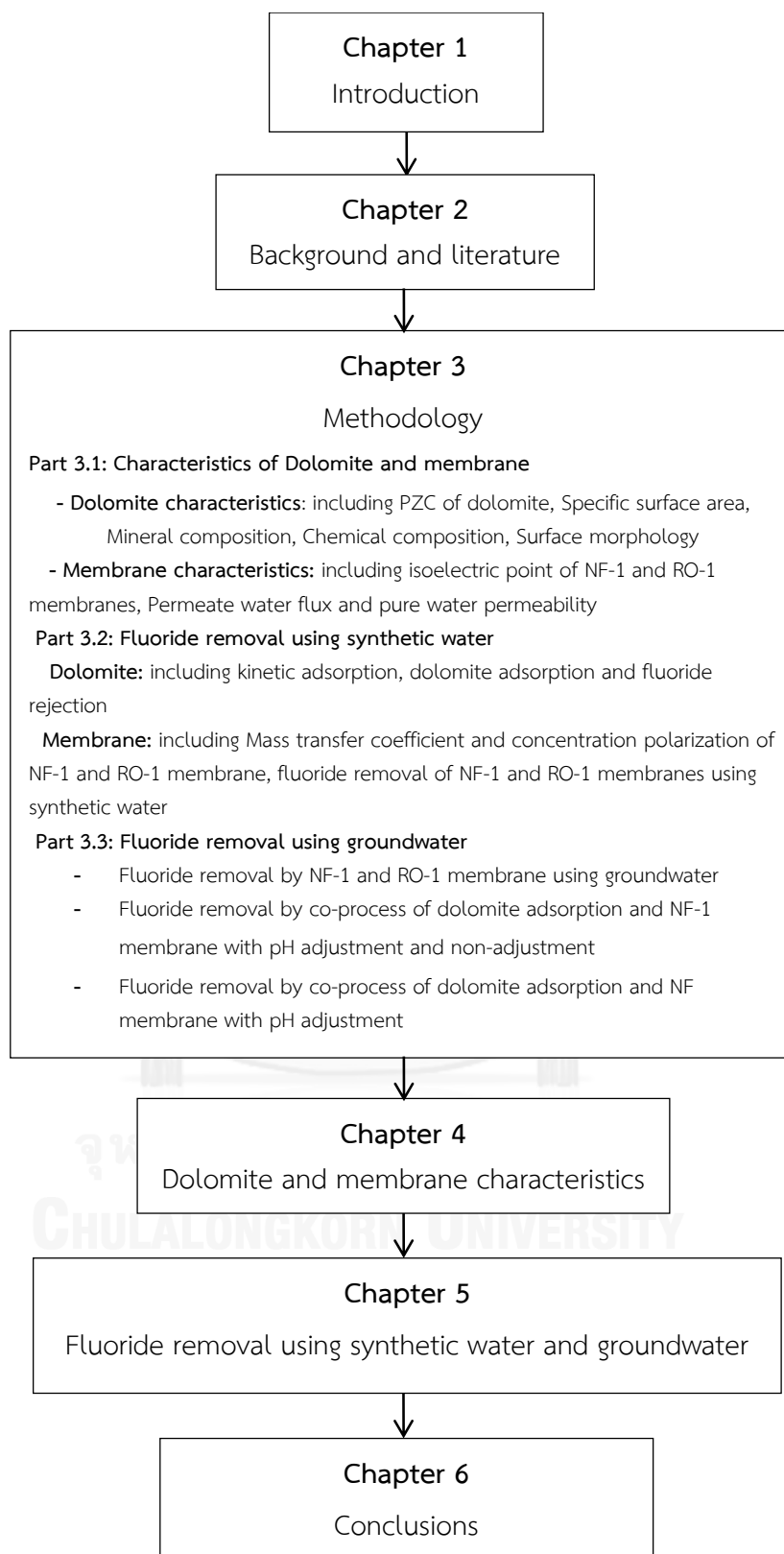
### 1.5 Benefit of study

- Knowing the performances of dolomite, nanofiltration and reverse osmosis membranes for defluoridation of synthetic water and groundwater that have high fluoride concentration than drinking water standard.

- Results of this study would be useful for developing a co-process between adsorption and membrane technology to remove fluoride for Thailand in the future.

- Results of this study would be useful for reducing the operating cost by using dolomite adsorption combine with nanofiltration membrane instead of reverse osmosis membrane.

The structure of thesis is shows in show as **Figure 1.1**.



**Figure 1.1** Structure of this thesis

Structure of this thesis demonstrates in **Figure 1.1**. Chapter 1 presents the motivation, objectives, and hypotheses of this study. Chapter 2 described the background of fluoride compound in groundwater, health impact of fluoride, adsorption, and membrane filtration. Not only the research of fluoride removal by nanofiltration and reverse osmosis membranes were described in this chapter but also, the research in the field of fluoride removal by dolomite adsorption also described in this part. Chapter 3 explains the methods of experiments and materials including chemical reagents and analytical instruments used in this study. Chapter 4 reports the dolomite and membrane characteristics. Characterization of dolomite can be divided into 5 parts that were an isoelectric point, specific surface area, mineral composition, chemical composition, and surface morphology. The membrane characteristics were divided into 3 parts that were permeate water flux, pure water permeability and isoelectric point. Chapter 5 reports fluoride removal using synthetic water and groundwater and also investigated mass transfer coefficient, concentration polarization and fluoride rejection. Chapter 6 concludes the removal performance of dolomite adsorption together with NF membrane filtration.

## CHAPTER 2

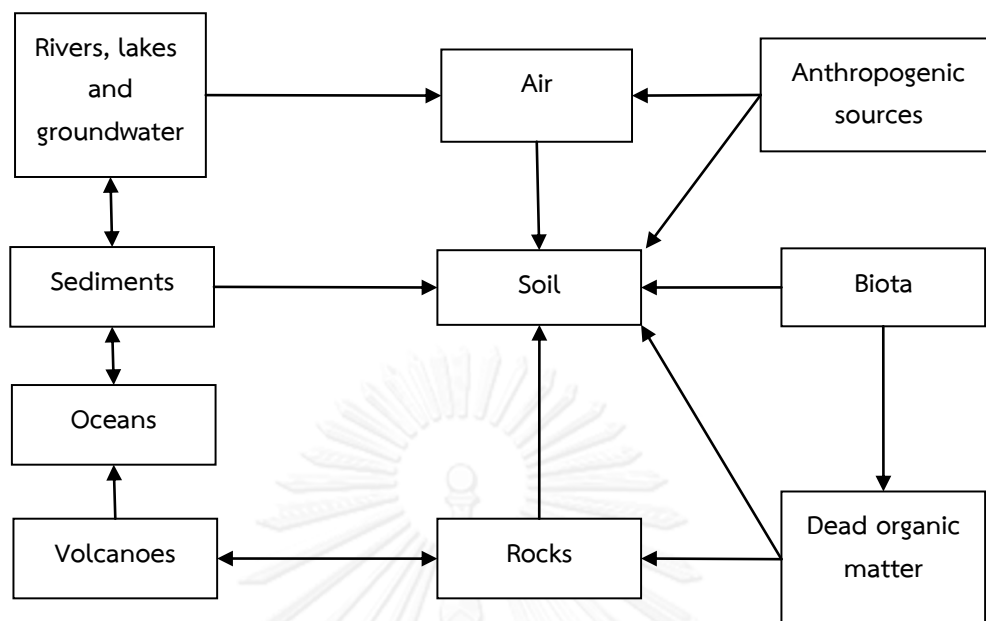
### BACKGROUND AND LITERATURE REVIEW

#### 2.1 Fluoride

##### 2.1.1 Background

In nature, fluoride occurs as an element in minerals, natural water system and geochemical. It enters food chains through drinking water and eating of plants. Fluoride has ability to form complexes with various cations of minerals, which containing fluoride has a low solubility. Fluoride is one of the most reactive and it is lightest member of the halogen group. However, fluoride is also the most electronegative of all elements (Hem, 1989). This implied that it is a strong influenced to become negatively charged, and when find in a solution in form a fluoride ion ( $F^-$ ).

**Figure 2.1** shows the cycle of fluoride in environment. Fluoride in the atmosphere is affected by vaporization, formation of wet aerosol, hydrolysis and dry deposition (Environment Canada, 1994). The International Program on Chemical Safety (IPCS, 2002) reported that atmospheric fluoride could be sent out from both anthropogenic and natural sources. They might be in particulate and gaseous forms. The transformations of fluorides in water are affected by water hardness, pH and the express of ion-exchange materials such as clays (Environment Canada, 1994). In the area of high acidity and alkalinity, fluoride could leach from fluoride, which contained the minerals into surface water and groundwater (Cuker & Shilts, 1979).



**Figure 2.1** Cycling of fluoride in environment

Adapted from: (Wongrueng, 2006)

### 2.1.2 Fluoride characteristics

Fluoride is an inorganic anion of fluorine with the chemical formula  $F^-$ . Fluoride is the main component of fluorite and contributes a distinctive bitter taste, but no odor to fluoride salts. Fluoride is classified as a weak base. Its salts are important chemical reagents and industrial chemicals. Fluoride ions occur on earth in several minerals, particularly fluorite, but are only present in trace quantities in water (IPCS, 2002).



### 2.1.3 Fluoride in groundwater

In 1937, the excessive fluoride problem in groundwater was discovered in the state of Andhra Pradesh, India. The 62 million, which consist of 6 million children, suffer from skeletal fluorosis and dental fluorosis owing to the consumption of high fluoride groundwater (Susheela, 1999). Fluoride concentration in natural groundwater usually less than 10 mg/L but up to 1,600 mg/L in brines (Todd, 1980). The concentration of fluoride in natural water was found varying from a small to as high as 2800 mg/L in environments such as the Soda Lakes in the East African Rift System. The total intake fluoride concentration of 14 mg/day, there is a clear excess risk of skeletal adverse effects and there is suggestive evidence of an increased risk of effects on the skeleton at total fluoride intakes above about 6 mg/day (Li, 2001).

The main factor, which influence the concentration of fluoride in natural groundwater include; the type of rock traversing of mineral by groundwater, solubility of fluoride in an aquifer matrix, geological condition, contact time with fluoride-bearing materials, and the chemical composition of traversing water (Apambire et al., 1997). In Quebec of Canada, the population more than 20% has been used groundwater as the main supply of drinking water. There have been many places of the world, which had high fluoride concentration including large parts of Africa, the Middle East, Southern Asia and China. The exceeding amount of fluoride, is considered as international health problem (Gessner et al., 1994). Groundwater in some areas of the world consists of fluoride concentrations higher than 10 mg/L. In natural water, the concentration of fluoride was indicated from the reaction between the minerals containing in the local geology and in the water. Thus, groundwater in expose with fluoride-containing minerals consisted of higher quantity of fluoride than

seawater or surface water (Takeda, 2008). The excessive fluoride problem in Thailand was found fluoride enriched in groundwater in the Chiang Mai Basin was observed in highest concentration level reaching 16.1 mg/L (Maisui et al., 2006). The population in Chiang Mai and Lumphun province, Thailand was exposed to high levels of fluoride in groundwater (McGrady et al., 2012). Fluoride was discovered significantly levels in various of minerals such as mica, fluorspar, rock phosphate, cryolite, apatite and others (Murray, 1986). Furthermore, fluoride was highly reactive, which never competition in its element gaseous state except in some industrial processes. The fluoride occurs as fluorite or fluorspar, sellaite, Villianmite, cryolite, Bastnaesite and fluorapatite. The minerals containing fluoride are given in **Table 2.1**.

**Table 2.1** The mineral composition of fluoride

Mineral	Chemical formula	%fluorine
Sellaite	MgF <sub>2</sub>	61 %
villianmite	NaF	55 %
Fluorite (Fluorspar)	CaF <sub>2</sub>	49 %
Cryolite	Na <sub>3</sub> AlF <sub>6</sub>	45 %
Bastnaesite	(Ce,La)(CO <sub>3</sub> )F	9 %
Fluorapatite	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>3</sub> F	4 %

Adapted from: (Nagendra Rao, 2003)

#### 2.1.4 Health impact of fluoride

Fluoride in humans is indicated as hydrofluoric acid that was absorbed via skin in animals and humans. The adsorption of fluoride is dispersed through the body via blood that about 99% deposited in bones and teeth (Watanabe et al., 1975). A low concentration of fluoride is necessary for the formation of caries-strong dental

enamel and for the process of mineralisation in hard tissues. Excessive amounts of fluoride concentrations was found in groundwater of more than 20 countries, which composing of India in 19 states were facing problems with fluorosis (Meenakshi & Maheshwari, 2006). Major effect of fluoride exposure on human health includes dental fluorosis and skeletal fluorosis. These are disease which caused by the ingestion of high concentrations of fluoride through water and food. Fluoride expose with water moved on accumulating in bones up to the age of 55 years. Moreover, high concentrations of fluoride can disturb with the metabolism of lipid proteins, carbohydrates, vitamins, enzymes and minerals. In addition, the ingestion of water containing 1 mg of fluoride per liter over a long term led to dental fluorosis.

#### 2.1.4.1 Dental fluorosis

Dental fluorosis transforms the white color on surface of the teeth and turn to brown color of the teeth is shown in **Figure 2.2**. Dental fluorosis is an indicator for the health effects on human organs. Because it is easier to investigate than others symptoms of fluoride consumption, determination by dentists is easily to diagnose fluorosis among fluoride-burden areas that people living. Fluoride can destroy on enamel-forming cells of teeth that result to mineralization disorder and the porosity of sub-surface enamel is increased (Takeda, 2008).



**Figure 2.2** Advance level of dental fluorosis

Source: (Tomoko & Takizawa, 2008)

#### 2.1.4.2 Skeletal fluorosis

Skeletal fluorosis relates with the high ingestion of fluoride. Skeletal fluorosis was a chronic metabolic bone and joint disease by ingest of large amount of fluoride via water. When, the body attained water that contained more than 3-6 mg/L of fluoride could cause skeletal fluorosis. The effects of young and old were same. When the mother consumed water and food that contain high fluoride concentration during pregnancy, fluoride could also damage the fetus due to calcification of blood vessels (Nagendra Rao, 2003).

The body of human and animal bones are contained of hydroxylapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) that hydroxyl groups can be replaced by fluoride to produce fluoroapatite ( $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ ). This cause bones became brittle and their tensile strength could be reduced. Human bones was redeposited and resorbed during one of lifetime and high fluoride interfere the homeostasis of bone mineral metabolism (Fordyce et al., 2007). Skeletal fluorosis, which was observed in Lamphun Province, Thailand is shown in **Figure 2.3**.



**Figure 2.3** Skeletal fluorosis in Lamphun Province, Thailand area

Source: (Y. Matsui, 2007)

#### 2.1.4.3 Other health effects of fluoride

Additionally, consumption of excessive fluoride lead to several illnesses aside from dental and skeletal fluorosis such as gastro intestinal problems, neurological, head-ache, muscular and allergic manifestations and the carries of teeth is destroyed at an early age. The relation between concentration of fluoride and the biological effects are concluded in **Table 2.2**.

**Table 2.2** Concentration of fluoride and biological effects

Concentration of Fluoride. ppm*	Medium	Effect
0.002	Air	Injury to vegetation
1	Water	Dental caries reduction
2 or more	Water	Mottled enamel
8	Water	10% osteosclerosis
50	Food and water	Thyroid changes
100	Food and water	Growth retardation
120	Food and water	Kidney changes
*In water-medium. ppm can be taken as equivalent to mg/L		

Adapted from: (Nagendra Rao, 2003)

## 2.2 Adsorption

### 2.2.1 Background

Adsorption is a phenomenon which occurs when a liquid solute or gas adsorbate accumulate on the surface of a solid or a liquid (adsorbent) and formed atomic film of the adsorbate on the surface of the adsorbent. The adsorption process occurs in three steps: macrotransport, microtransport, and sorption, while desorption is the reverse process. Macrotransport relate with the movement of adsorbate such as organic matter through the water to liquid or solid interface by diffusion and advection. Microtransport relates with the diffusion of the organic material the macropore (>25 nm) system of the solid adsorbent to the adsorption sites in the micropore (<1 nm) and the solid adsorbent. The adsorption process was utilized widely for improve cleaning of treated wastewater discharge, consisting toxicity reduction, which caused to intensive investigation and applied the process of adsorption on various absorbent (Metcalf & Eddy, 2003).

The adsorption process occurs in four more or less steps: (1) bulk solution transport, (2) film diffusion transport, (3) pore transport, and (4) adsorption (or sorption). First, bulk solution transport relate to the transport of the organic material to be adsorbed pass the bulk liquid to the boundary layers of fixed film of liquid around the adsorbent. Second, film diffusion transport relate to the transport by diffusion of the organic material through the liquid film and enters into the pores of the adsorbent. Third, pore transport relate to the transport of the material to be adsorbed through the pores by co-process of molecular diffusion through the pore liquid. The last step, adsorption relate to the attachment of the material to be adsorbed to adsorbent at a suitable adsorption site. Adsorption can occur on the outer surface of the adsorbent and in the macropores (>25 nm), mesopores (>1 nm, < 25nm), micropores (<1 nm) and submicropores, while the surface area of the macropores and mesopores is small when compare with the surface area of the micropores and submicropores (Metcalf & Eddy, 2003).

### 2.2.2 Kinetic model

Different kinetic model, such as first-order, second-order, pseudo-first order and pseudo-second order equation are applied to describe the rate constant of reaction.

The first-order equation (House, 2007) as shown in **Eq. (2-1)**.

$$\ln q = -kt + \ln q_0 \quad (2-1)$$

Where  $q_0$  and  $q$  are amounts of fluoride adsorbed (mM/g of dolomite) at initial time and time  $t$ ,  $k$  is rate constant of adsorption ( $\text{min}^{-1}$ ) and  $t$  is time (min).

The second-order equation (Ho, 2006) as shown in **Eq. (2-2)**.

$$\frac{1}{q} = k_2 t + \frac{1}{q_0} \quad (2-2)$$

Where  $q_0$  and  $q$  are amount of fluoride adsorbed (mM/g of dolomite) at initial time and time  $t$ ,  $k_2$  is rate constant of adsorption (g/mM min),  $t$  is time (min).

The pseudo-first order equation (Tseng, Wu, & Juang, 2010) as shown in **Eq. (2-3)**.

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (2-3)$$

Where  $q$  and  $q_e$  are amount of fluoride adsorbed (mM/g of dolomite) at time  $t$  and equilibrium,  $k_1$  is the rate constant of adsorption ( $\text{min}^{-1}$ ) and  $t$  is time (min).

**Eq. (2-3)** is called the Lagergren's first-order (LFO) equation (Tseng et al., 2010). Generally,  $k_1$  is obtained by plotting  $\ln(q_e - q)$  vs.  $t$ . For expressing adsorption characteristics, **Eq. (2-3)** is rewritten as shown in **Eq. (2-4)**.

$$\ln\left(1 - \frac{q}{q_e}\right) = -k_1 t \quad (2-4)$$

The pseudo-second order equation (Ho, 2006) as shown in **Eq. (2-5)**.

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2-5)$$

Where  $q$  and  $q_e$  are amount of fluoride adsorbed (mM/g of dolomite) at time  $t$  and equilibrium,  $k_2$  is rate constant of adsorption (g/mM min) and  $t$  is time (min).

### 2.2.3 Dolomite sorbent

Dolomite is a low cost adsorbent that consisting of magnesium and calcium carbonate compound. The dolomite is applied both for the mineral dolomite



calcium magnesium carbonate ( $\text{CaMgCO}_3$ ), and for the dolomite rock, which consist of the mineral dolomite. The properties of dolomite are similar to that of limestone and it is known in the industry as magnesium limestone. The dolomite group in general is  $\text{AB}(\text{CO}_3)_2$ , which A can be placed by barium or strontium, calcium and B could be placed by magnesium, iron, zinc or manganese. The group of dolomite structure is occurred from the calcite group structure. The group of calcite structure was layered with metal ion layers and carbonate layers (Duffy, Walker, & Allen, 2006). The picture of a dolomite rock is shown in **Figure 2.4**.



**Figure 2.4** Dolomite rock

Dolomite is a complex mineral, due to it can form as a hydrothermal metamorphic phase or form as a primary precipitate, a diagenetic replacement phase. Every phase require the permeability, which is a mechanism to help liquid flow and a sufficient supply of magnesium. At first time, Dolomite material might form at the surface or in the subsurface and it might generate or lose porosity many times. Dolomite can be replaced by later more stable phases with such replacements

repeated many times during metamorphism (Pehlivan et al., 2009). In Thailand, dolomite was found in many Province including Phare, Kanchanaburi, Chonburi, Chanthaburi, Suratthani and Nakhon Si Thammarat, Province (Department of mineral resource, 2007).

Dolomite is interesting material due to its used as an adsorbent in several studies determining its lot of applications for water treatment because of its performance can absorb the toxic substances. The sorption of cations onto dolomite occurred mainly through a physical adsorption mechanism but can be also occurred by ion exchange or surface precipitation between the calcium and magnesium ions within the dolomite and metal cations in aqueous solutions (Stefanial et al., 2000).

Many researchers used dolomite as an adsorbent in several studies. The possibility of using raw and calcinated dolomite under a CO<sub>2</sub> atmosphere for phosphate removal in laboratory experiments was explored. It could be concluded that adsorption of phosphate occurred through physical interactions, and the dolomite sample had a heteroporous structure (Karaca et al., 2006). The research of dolomite adsorption was carried out for removal of acidic gaseous pollutants. The results indicated the dolomite sorbent was potentially cost (Duffy et al., 2006). The kinetics of a reactive dye adsorption onto dolomite sorbents was studied. The experiment data showed the conformance with an adsorption process, with the removal rate dependent on both external mass transfer and intra-particle diffusion (Walker et al., 2003). The kinetic and thermodynamic are studied on adsorption of fluoride by dolomite. The result indicated that dolomite could be used potentially to decrease the amount of fluoride in water containing excessive amounts. The percentage removal of fluoride depend on the particle size of the adsorbent

(Karthikiyan et al., 2002). The sorption of fluoride on partially calcined dolomite was studied. The result showed that partially calcined dolomite might be a potential sorbent for defluorination of water (Sasaki et al., 2013).

## 2.3 Membrane filtration

### 2.3.1 Background

Membrane filtration has many advantages such as high performance, convenient operation, easy equipment and low energy consumption. Thus, membrane filtration is become one of the most important separation methods and has been utilized to purify contaminated water by passing water through a membrane as a filter material. Membrane is a selective barrier, which can permit the components move through it and retain other components of the mixture (Cheryan, 1998). The membrane can be separated into four categories, i.e., reverse osmosis (RO) membrane, ultrafiltration (UF) membrane, nanofiltration (NF) membrane and microfiltration (MF) membrane by using differential pressure on both side of each membrane and the pore size of each membrane (Metcalf & Eddy, 2003). The characteristics of membrane are shown in **Table 2.3**.

**Table 2.3** Characteristics of each membrane

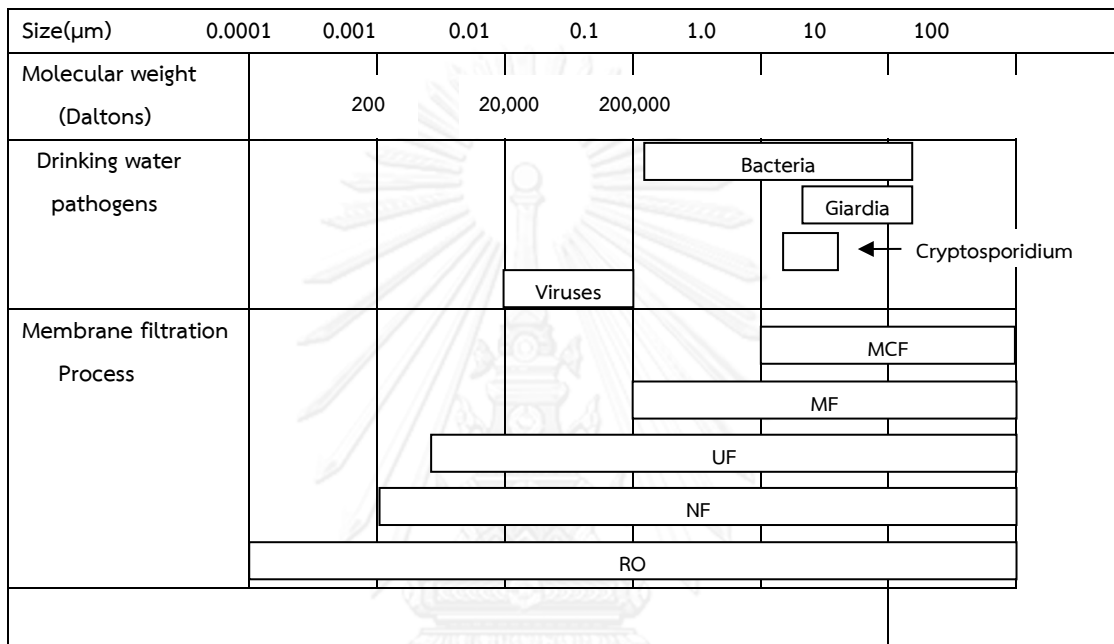
Characteristic	RO	NF	UF	MF
Structure	Asymmetrical	Asymmetrical	Asymmetrical	Asymmetrical Symmetrical
Pore size ( $\mu\text{m}$ )	<0.002	<0.002	0.2-0.02	4-0.02
Rejection	HMWC, LMWC	HMWC, negative ions	Macro molecules	Particles, clay, bacteria
Membrane materials	Cellulose acetate, polyamide	Cellulose acetate,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

Adapted from: (Wagner, 2001)

MF and UF membrane are used for remove large particle, macro-molecular compounds, or colloids. While NF and RO membrane are applied for remove the components that are ions or micro-molecular compounds. MF can apply to remove suspended particles by a sieving mechanism depend on the membrane pore size (4-0.02 mm). UF is classified the pore size in the range of 0.2-0.02 mm. NF is identified as a pressure-driven membrane separation process that operated the principle of reverse osmosis to remove dissolved contaminants from water. NF membrane has a pore size about 0.001 mm. RO is the pressure-driven membrane separation process that used the principle of reverse osmosis to remove dissolved contaminants from water same as NF.

The mechanism of RO membrane is to manipulate the reverse of the general osmosis process such as passing of water through a semipermeable membrane from a solution of lower concentration to a solution of higher concentration. It against the

concentration gradient, which occur by utilizing pressure greater than the osmotic pressure to the more concentrated solution (EPA, 2005). Comparisons of filtration application of all membranes are shown in **Figure 2.5**.



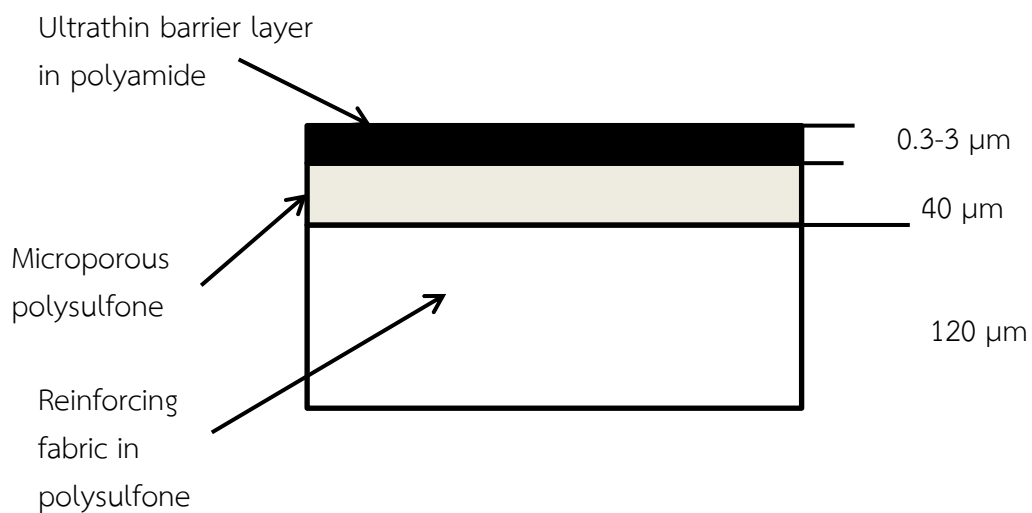
**Figure 2.5** Comparison of membrane filtration applications in drinking water

Adapted from: (EPA, 2005)

### 2.3.2 Thin-film composite membrane

Thin-film composite (TFC) membranes are generally used in nanofiltration (NF), reverse osmosis (RO) and other membrane that base on separation processes for various countries of applications such as water desalination and reuse, treatment of industrial wastewater. A thin-film composite membrane is classified as a bi-layer film pattern by a two-step process. In regularly, membrane contain of a thick, nonselective layer pattern, porous in first step, which is over-coated with an ultra-

thin barrier layer on top surface in the second step. The two layers are not same from one another in chemical composition. Each part of layer is utilized for its particular function such as the ultra-thin barrier layer can be usable for the require combination of solute rejection and solvent flux, whereas the porous support layer can be utilized for optimum strength and compression resistance combine with minimum resistance to permeate flow. Various compositions of chemical can be formed into ultra-thin barrier layers, including both linear and cross-linked polymers (Petersen, 1993). The diagram of thin composite membrane is shown in **Figure 2.6**.



**Figure 2.6** Diagram of thin composite membrane

Source: (Pontié et al., 2006)

### 2.3.3 Nanofiltration (NF) membrane

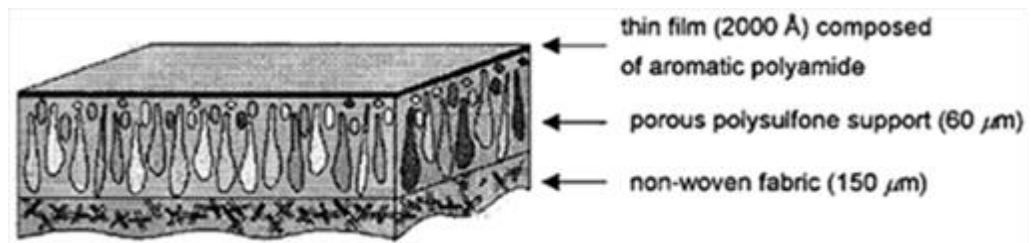
Most of NF membranes are thin-film composite membranes. NF membrane is defined as a process with characteristics between the ultrafiltration (UF) membrane and reverse-osmosis (RO) membrane. NF membrane is applied for removing

mechanisms relate with both electrical Donnan effects and steric (sieving) effects. The performance of prediction process efficiency of NF membrane removing can be useful for the designing of processes. Such predictions used available physical property data of process stream and a membrane. The structural parameter that involve for NF membranes such as membrane thickness, the pore radius and the electrical parameters, i.e. volumetric charge density or surface charge density (Bowen & Mohammad, 1998).

NF membrane can remove various components included fluoride completely and also reported as a suitable for groundwater treatment. It has many advantages such as high flux, high rejection of multivalent anion salts and an organic molecular above 300, low operation pressure, easy operation and good quality product. Moreover NF has the applicability to reduce the ionic strength of the solution and can remove organics, particulate contaminants and hardness in water (Wang et al., 2005). Due to these advantages, the application of NF worldwide has been increased.

#### 2.3.4 Reverse osmosis (RO) membrane

Most of reverse osmosis membranes are characterized as thin film composite membrane as same as nanofiltration membrane (NF) as illustrated in **Figure 2.7**. The charge of thin layer consists of negatively charged sulfone or carboxyl group. Reverse osmosis is process that separate the chemical solution from contaminated water via membrane under pressure. If the samples have bigger particular size more than reverse osmosis membrane, the samples cannot move through.



**Figure 2.7** Schematic of the thin-film composite (TFC) reverse osmosis (RO) membrane and the chemical structure of the aromatic polyamide thin-film layer

Source: (Kwak et al., 2001)

Reverse osmosis (RO) membrane is described as the NF membrane but is better than commercial NF membrane in flux production and ions rejection. RO membrane was applied under the operating transmembrane pressure in the range of 0.2-0.9 MPa. In addition, RO membrane could be provided a specific flux of more than  $60 \text{ L/m}^2\text{-h} \times \text{MPa}$ . This specific flux was about 2 times of the current generations of composite reverse osmosis membrane. If normal osmosis takes place, solution moved from the side that lower concentration to the side that higher concentration. Water would be flow continuously until the concentration between two sides was equilibrium. On the other hand, reverse osmosis would be occurred when the water moved through the membrane against the concentration gradient, from lower concentration to higher concentration (Ozaki, 2000).

### 2.3.5 Fluoride removal by NF and RO membrane

Many researchers used NF and RO to achieve for remove fluoride in water. In 1999, certain areas in Finland had a problem of high fluoride and aluminium in groundwater because of soil properties. Therefore, the city of Laitila constructed a membrane filtration plant, which had two trains, one with reverse osmosis (RO) and



the other with nanofiltration (NF) combine together for control fluoride and aluminium concentration in drinking water (Kettunen, 2000). In addition, NF and RO membrane was utilized to remove hardness, nitrates, iron, strontium, fluoride and TDS (Pervov et al., 2000).

The feasibility of applying reverse osmosis (RO) membrane separation to reduce fluoride load to less than 1 Kg/d was studied. The results indicated that the rejection of fluoride ion was essentially higher than 98%. Considering that the RO membrane was fully regenerated after each set of experiment (Ndiayeet et al., 2005).

Fluoride removal in groundwater by using a nanofiltration pilot plant by using two modules (90 and 400 Da) was studied. The results indicated the fluorides were rejected by NF 90 membrane. The fluoride amount of the product water was lower than the standards of initial fluoride content. This study confirmed the efficiency of the nanofiltration in the fluoride reduction (Tahaikt et al., 2007).

Removal of fluoride and phosphate form fertilizer factory by using a RO and NF membrane for treatment of wastewater was studied. The results indicated that the rejections of fluoride with RO membrane were higher than 80% for model waters and higher than 96% for real wastewater, and with NF membrane higher than 40% (Dolar et al., 2011).

### 2.3.6 Membrane characterization

Membrane characterization is an important property of membrane research due to the design of membrane processes and systems depends on reliable data relating to membrane properties. The membrane is characterized through the utilization of adjustable parameters such as the effective membrane thickness, average pore size, and electrical parameters such as the volumetric charge density or the surface charge density. The important characterization in this study is water flux rates, salt rejection. The other characterization for determining parameters such as surface properties, surface morphology and surface functional groups.

### 2.3.7 Membrane transport theory

Transportation processes through a membrane can be described by utilizing many mathematical models. Generally, when solutes in solution are separated by using a membrane, several forces such as different pressures, different temperatures as a difference result in a water flux or flow that through the membrane.

#### 2.3.7.1 Irreversible thermodynamic model

The irreversible thermodynamic model is studied the membrane separation process that stayed in equilibrium or closely equilibrium. This model is used to explain the transportation of solute through a membrane (Dickson, 1988).

The equations for water flux based on membrane area ( $J_v$ ) were provided by Kedem and Katchalsky as cited in (Slezak & Bryll, 2004). And the solute flux based on membrane area ( $J_s$ ) in **Eq. (2-6)** and **Eq. (2-7)**, respectively.

$$J_v = L_p(\Delta p - \sigma\Delta\pi) \quad (2-6)$$

$$J_i = \omega\Delta\pi + (1 - \sigma)C_i J_v \quad (2-7)$$

Where  $L_p$  is pure water permeability,  $\sigma$  is reflection coefficient,  $\omega$  is solute permeability, and  $C_i$  is logarithmic mean solute concentration. From the van't Hoff equation,  $\Delta\pi = RT\Delta C_i$

### 2.3.7.2 Diffusive flow model

Normally, when the component in solution is separated by membrane through diffusion mechanism, various parameters are related including the driving forces of temperature, pressure, electrical potential and concentration. The flux of water ( $J_v$ ) through the membrane can be expressed as:

$$J_v = k_w(\Delta P - \Delta\pi) \quad (2-8)$$

Where  $k_w$  is pure water permeability,  $\Delta P$  is transmembrane pressure,  $\Delta\pi$  is osmotic pressure and the solute flux ( $J_i$ ) through the membrane, it can be expressed as:

$$J_i = k_i(C_M - C_p) \quad (2-9)$$

Where  $k_i$  is solute mass transfer coefficient,  $C_M$  is concentration of membrane surface,  $C_p$  is concentration of permeate.

### 2.3.7.3 Charge membrane models

Charged membrane model is used to predict ionic solute separation. Furthermore, charged membrane is characterized as membranes which contain

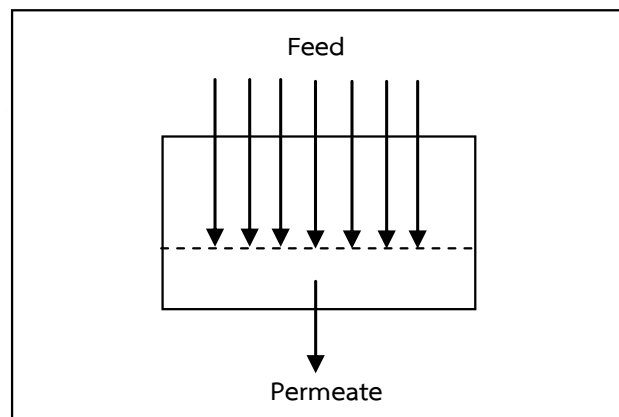
charged chemical groups. This model explained electrostatic effects in order to explain the solute separation. Large number of membrane at membrane surface express in form negative charged. The counter-ion of solution that express against charge to attach membrane charges (regularly sulfonic groups or carboxylic groups) and express in membrane at higher concentration than that of co-ion. These results of electrostatic attraction and repulsion effected between the fixed membrane charge and ionic species in the solution create a Donnan Potential. This Donnan potential protected the diffusive exchange of counter-ion and co-ion between the solution membrane phases. If a pressure driving force is utilized to force the solution through the charged membrane, the effect of Donnan potential is to repel the co-ion from the membrane due to electro-neutrality need to maintain in the solution phase, the counter-ion also rejected (Williams, 2003). Donnan equilibrium models is explained the distribution coefficient between the solution phase of salt and a negative charged membrane (Bhattacharyya & Cheng, 1986). This model not only predicts the rejection of solute is a function of effective charge density but also can be predicted solute concentration in external solution and valence of solute.

### 2.3.8 System design

The system design for membrane filtration can be classified into 2 types: dead-end operation and cross-flow operation. All the feed is driven through the membrane, which implies that the concentration of rejected components in the feed increase and therefore the quality of the permeate decrease with time (Thanuttamavong, 2002).

### 2.3.8.1 Dead-end filtration

For dead-end filtration, all of the water that enters through the membrane surface is moved through the membrane. Some elements attach on membrane surface while water flow through. The dead-end operation is shown in **Figure 2.8**.

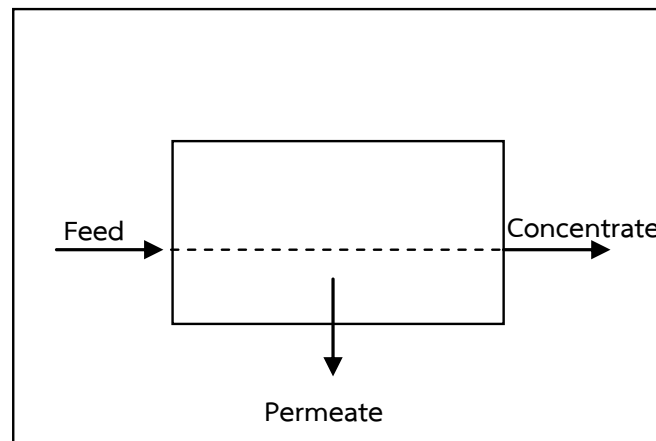


**Figure 2.8** Dead-end operation

Adapted from: (Thanuttamavong, 2002)

### 2.3.8.2 Cross-flow filtration

In many cases of filtration system, a cross-flow operation is preferred because of the lower fouling phenomena than in dead-end operation. In the cross-flow operation, the feed of solution flowed parallel to the membrane surface with the inlet feed stream moved into the membrane module at a certain composition. The feed stream of module is classified into 2 parts: a permeate stream and a concentrate stream. **Figure 2.9** shows the cross-flow operation.



**Figure 2.9** Cross-flow methods

Adapted from: (Wongrueng, 2006)

The important problems in membrane processes in water treatment are fouling and concentration polarization. Fouling is a contamination of the membrane as a result to decreasing flux or increasing transmembrane pressure. The fouling of membrane need to maintenance a permeate water flux processes or clean a membrane. Concentration polarization is the accumulation of retained solute on the surface membrane. Thus, fouling and concentration polarization should be considered when the membrane process is utilized for water treatment.

### 2.3.9 Concentration polarization

Concentration polarization is explained as an undesirable phenomenon which caused by the accumulation of retained solutes on surface of membrane and relate with surface properties, pore sizes and types of mixture solution. Formation of gel layer occurs on membrane surface when the concentration of solute exceeds its saturation and elevates solute concentration on membrane surface that cause the refection rate decrease. When concentration polarization occurs, there is a differential solute concentration between the membrane surface and the bulk of the

feed stream. The osmotic pressure in the polarized layer due to the high local solute concentration lowers the transmembrane pressure therefore decreasing flux (Wongrueng, 2006).

Figure 2.10 shows model describes the transport phenomena in the concentration polarization boundary layer on the feed side adjacent to the membrane.

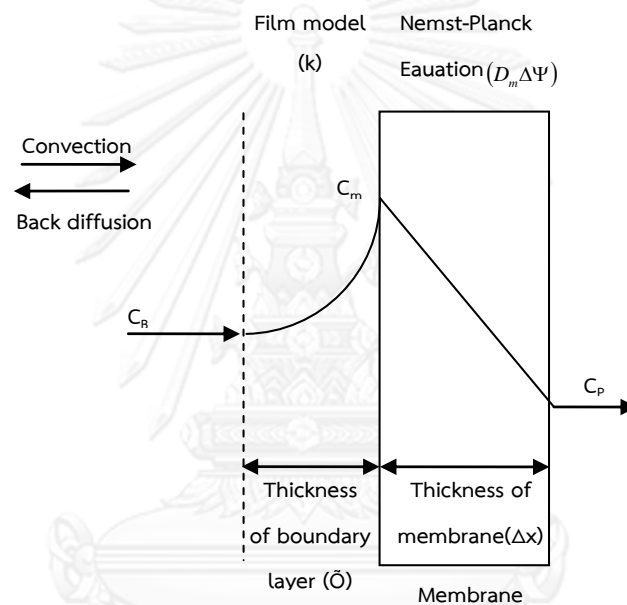


Figure 2.10 Concentration polarization phenomena on the boundary layer

Adapted from: (Wongrueng, 2006)

The model of the concentration polarization relate with the model of the coupled convective-diffusion encounter in a boundary layer. The solution method utilizes the boundary layer approximations relate with the solution of the coupled velocity and concentration fields in a concentrated boundary layer closely the membrane surface. Solution of the governing differential equations requires the

incorporation of an appropriate model for the transport of permeate through the membrane as a boundary condition.

From the thin film model, the equations that use to describe the solute concentration on the membrane surface are given by;

$$(J_v)_{solute} = k \ln \left( \frac{C_M - C_P}{C_B - C_P} \right) \quad (2-10)$$

Where  $k$  ( $D / \delta$ ) is mass transfer coefficient,  $D$  is solute diffusion coefficient,  $\delta$  is thickness of boundary layer,  $(J_v)$  solute is permeate flux of solute solution,  $C_M$  is solute concentration at membrane surface,  $C_P$  is solute concentration in permeate solution, and  $C_B$  is solute concentration in bulk solution.

The mass transfer coefficient can be used for predicting the concentration polarization which base on velocity variation method. The mass transfer coefficient ( $k$ ) in solution was determined by (Geraldes & Pinho, 2006). The theoretical derivation is given as follows:

Permeate flux of pure water is expressed by follows:

$$(J_v)_{H_2O} = k_w \times \Delta P \quad (2-11)$$

Where  $(J_v)_{H_2O}$  is the permeate flux of pure water,  $K_w$  is the pure water permeability, and  $\Delta P$  is the applied pressure.

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

$$(J_v)_{H_2O} = (K \cdot (\Delta P - (\pi_M - \pi_p))) \quad (2-12)$$



Where  $\pi_M$  is the osmotic pressure on the membrane surface,  $\pi_p$  is the osmotic pressure in permeate.

From the previous data shown in Eq. (2-11) and Eq. (2-12), it could be written as follows:

$$\pi_M - \pi_p = \Delta P \cdot \left[ 1 - \frac{J_v}{(J_v)_{H_2O}} \right] \quad (2-12)$$

When the osmotic pressure is closely linearly proportional to the salt concentration, the mass transfer coefficient in the solution,  $k$ , is given by:

$$k = \frac{(J_v)_{solute}}{\ln \left\{ \frac{\Delta P}{\pi_B - \pi_p} \cdot \left[ 1 - \frac{(J_v)_{solute}}{(J_v)_{H_2O}} \right] \right\}} \quad (2-13)$$

Where  $(J_v)_{H_2O}$  is permeate flux of pure water,  $\Delta P$  is transmembrane pressure,  $\pi_B$  is osmotic pressure of bulk solution, and  $\pi_p$  is osmotic pressure of permeate solution.

Transmembrane pressure ( $\Delta P$ ) is the change in the pressure of the water as it passes through the membrane is calculated by;

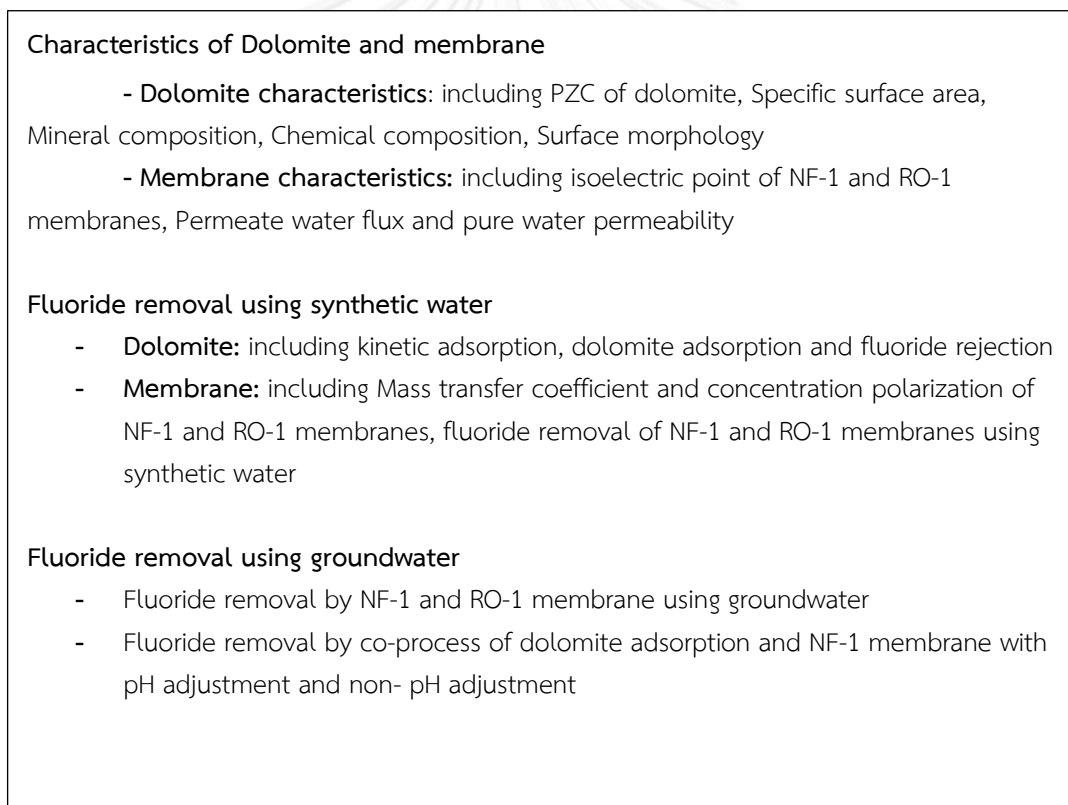
$$\Delta P = \frac{(P_{in} + P_{out})}{2} - P_f \quad (2-14)$$

Where  $P_{in}$  is pressure of bulk solution at the inlet side,  $P_{out}$  is the pressure of bulk solution at outlet side;  $P_f$  is pressure on the filtrate side.

## CHAPTER 3

### METHODOLOGY

The conceptual framework of experiment in this work includes the characteristics of dolomite and membrane, which was characterized in various parameters. Moreover, the fluoride removal using synthetic water and groundwater were investigated for fluoride rejection in this study. The conceptual framework of methodology is shown in **Figure 3.1**



**Figure 3.1** The conceptual framework of methodology

#### 3.1 Characteristics of dolomite and membrane

This study was conducted by using dolomite rock as adsorbent and sodium fluoride (NaF) as adsorbate.

- **Adsorbent**

Dolomite rock was collected from the P.C. Nisith mine at Suratthani Province, Thailand. Before using in experiments, the dolomite rock was crushed into small sizes by a disc mills machine and put through a sieve of different size, utilized a different size of standard mesh sieves between 0.420-0.074 mm to investigated dolomite properties. The 0.42 mm. size of dolomite sorbent was selected in this experiment. Then, it was washed in pure water and dried at room temperature. The raw dolomite from P.C. Nisith mine at Suratthani Province, Thailand before experiment was presented in **Figure 3.2**.



**Figure 3.2** Dolomite rock

- **Water sample**

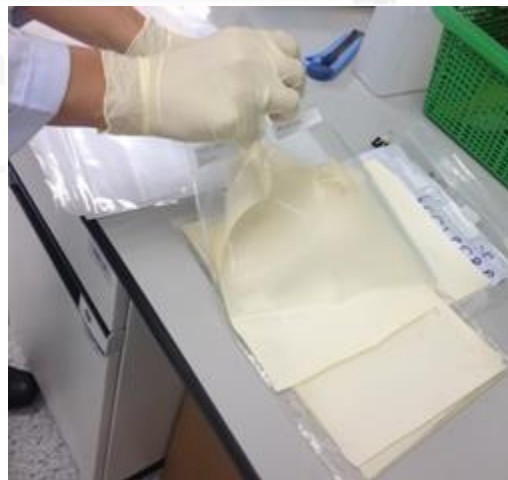
Water samples for this experiment include synthetic water, in addition to groundwater taken from an area in Lumphun Province, Thailand which was previously defined as having a very high fluoride concentration. The source of ground water from Pra Too Khong Bottled Drinking Water Plant in Lumphun Province, Thailand is shown in **Figure 3.3**.



**Figure 3.3** Groundwater sample source from Bottled Drinking Water Plant in Lumphun Province, Thailand

- **Preparation of the membrane experiment**

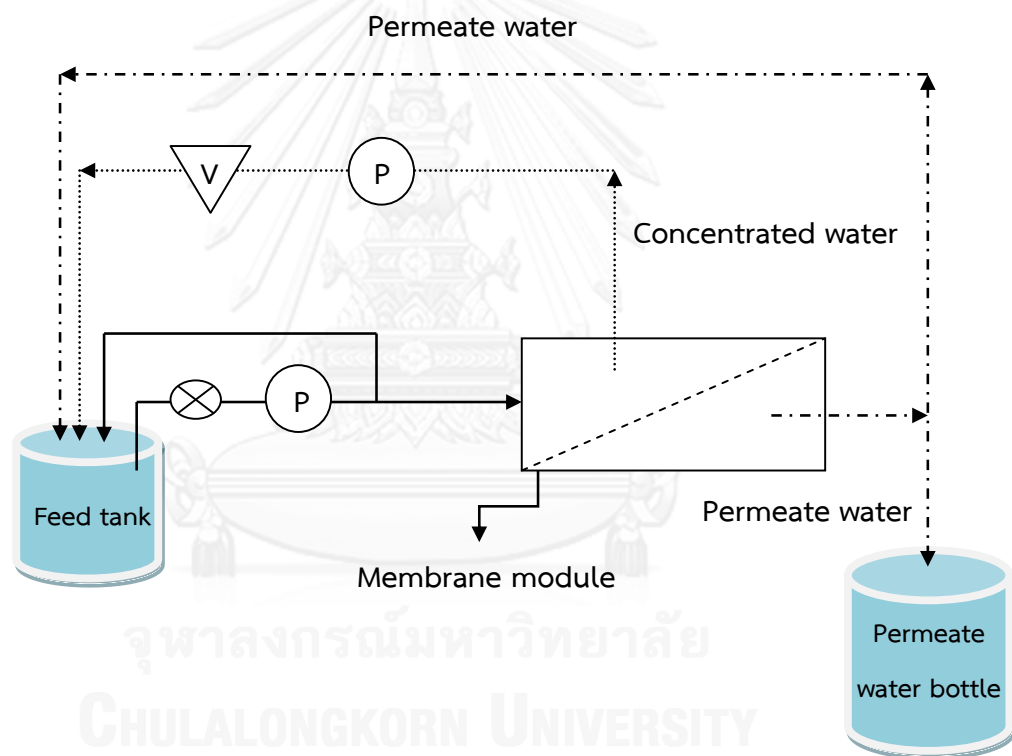
The RO membrane (RO-1) and NF membrane (NF-1) were characteristically thin-film composite membranes were cut, and then both of membrane were immersed in milli-q water prior to using in the experiment as shown in **Figure 3.4**.



**Figure 3.4** NF-1 and RO-1 membranes were immersed in pure water before experiment

- Membrane experimental set-up

This experiment was set-up as a cross-flow operation. The equipment was necessary for this experiment included a feed tank with a 2 L capacity, a permeate bottle, a module membrane from the Nitto Denko Corporation in Japan, which provides a surface area of 60 cm<sup>2</sup>, 1 needle valve (V), 2 pressure indicators (P) (1 for the feed line and 1 for the concentrated line) and a pump from the Iwaki Company in Japan. The operating membrane process was set up in **Figure 3.5**.



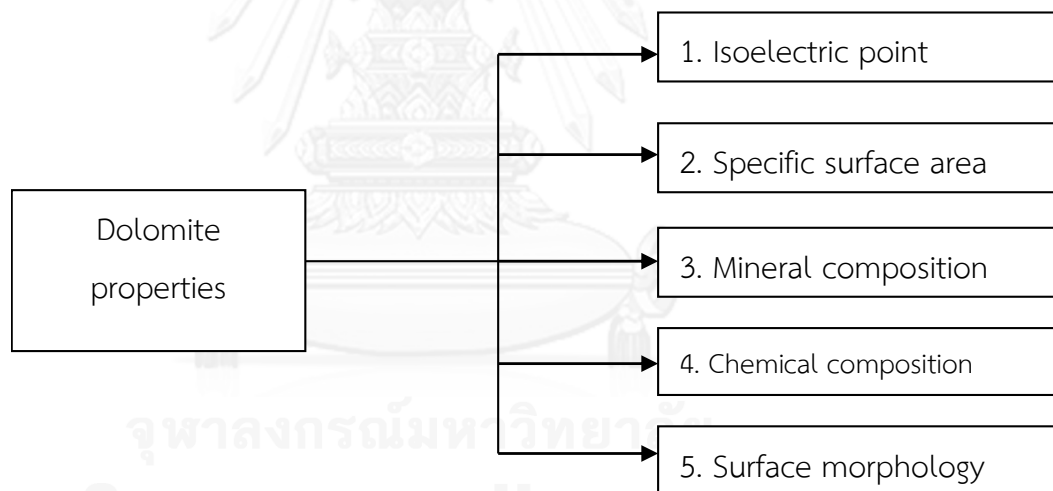
**Figure 3.5** Experimental set up in the membrane process

**Figure 3.5** demonstrated the membrane filtration process. In the first step, the solution in the feed tank was pumped through the membrane module. The pressure in the feed line was adjusted via the flow gate and pressure gate. After the solution moved through the membrane, the concentration decreased due to the

filtration by the NF-1 and RO-1 membranes. This line was referred to as the permeate water. Furthermore, some of solution flowed on the surface of the membrane and restored to the feed tank. This line was referred to as the concentrated water. The flow rate of the solution, time and pressure depend on the operation.

### 3.1.1 Dolomite characteristics

Characterization of dolomite is shown in **Figure 3.6** including an isoelectric point, specific surface area, mineral composition, chemical composition and surface morphology.



**Figure 3.6** Characterization of dolomite properties

#### 3.1.1.1 Point of zero charge (PZC) of dolomite

- Before the experiment, the dolomite sorbent was washed in pure water, 2-3 times. Then, the dolomite sample was dried in an oven for 12 hours.

- NaCl solution 0.01 mol/L was prepared. HCl and NaOH 0.01 mol/L was used to adjust the pH solution within a range of 2-12.

- 1 g of dolomite sorbent was immersed in each volumetric bottle that contains the adjusted pH (2-12) solution. The pH value of each solution was measured by a pH meter. Then, all volumetric bottles were shaken for 12 hours on rotary shaker, at 200 rpm at room temperature. Afterwards, the pH of each bottle was measured again. PZC of dolomite was determined by plotting graph between pH before shake dolomite and pH after shake dolomite on rotary shaker.

#### **3.1.1.2 Specific surface area**

The specific surface area and pore size of dolomite was analyzed by using a nitrogen adsorption isotherm (BET).

#### **3.1.1.3 Mineral composition**

A mineral composition of dolomite was determined by X-ray diffraction analysis (XRD).

#### **3.1.1.4 Chemical composition**

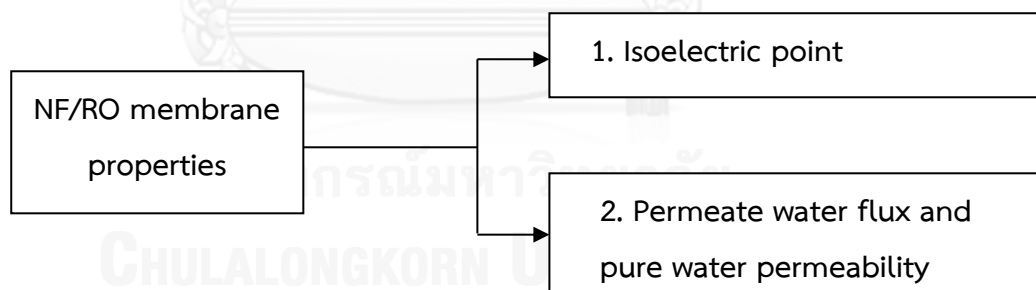
The chemical compositions of dolomite sample were investigated by X-Ray Fluorescence Spectrometer (XRF).

### 3.1.1.5 Surface morphology

Surface morphology of dolomite was detected by the scanning electron microscopy (SEM).

### 3.1.2 Membrane characteristics

Membrane characterization is a very important part of membrane research because the design of membrane processes and systems depends on reliable data relating to membrane properties. The membrane is characterized through the utilization of adjustable parameters such as the effective membrane thickness, average pore size, and electrical parameters such as the volumetric charge density or the surface charge density. The important properties in this study are isoelectric point, Permeate water flux and pure water permeability. **Figure 3.7** demonstrates the experiment in order to characterize membrane properties.



**Figure 3.7** Characterization of NF and RO membranes

#### 3.1.2.1 Isoelectric point of NF-1 and RO-1 membranes

This property explains the pH value that balances the electric charges of molecules to neutral which can identify the range of the pH for the run solution



which passes through each kind of membrane. The isoelectric point was determined by the following procedure:

- Before the experiment, the NF-1 and RO-1 membranes were immersed in the pure water for 24 hours. The membrane sheets were cut small in size (4x3 cm).

- NaCl solution 0.01 mol/L was prepared. HCl and NaOH 0.01 mol/L was used to adjust the pH solution in the range of 2-10.

- The sheets of the membranes were immersed in each volumetric bottle that contains the adjusted pH (2-10) solution. The pH value of each solution was measured by a pH meter. Then, all volumetric bottles were shaken for 24 hours, at 100 rpm at room temperature. Afterwards, the pH of each bottle was measured again.

- The pH values from before and after shake on rotary shaker were taken to plot the graph and the isoelectric point was determined.

### **3.1.2.2 Permeate water flux and pure water permeability of NF-1 and RO-1 membranes**

Pure water permeability explains the volume of water that passes through a membrane per unit of time. The property of this pure water permeability describes the generation of permeate for the membrane and uses to compare the initial efficiency of the membrane. Pure water permeability was measured by the following procedure:

- Before the experiment, the NF-1 and RO-1 membranes were immersed in the pure water for 24 hours.

- One liter of pure water was used to run through the membrane module under various transmembrane pressures of 0.2, 0.3, and 0.4 MPa without pH adjustments and under a controlled temperature of 28°C to 30 °C. In the feed tank, permeate water and concentrated water were recycled.

- The permeate water was collected in a 50 ml measuring cylinder. Sampling time was recorded. The details were listed in the next step.

- The permeate water was collected every ten minutes (10, 20, and 30 minutes) for the initial half hour, because during this period of time the membrane was not compressed and there was much fluctuation.

- After the initial half hour, the permeate water was determined in intervals of 60 minutes (60, 120, 180, and 240 minutes) up until the fourth hour, to confirm the steady state of water flux.

## **3.2 Fluoride removal using synthetic water**

### **3.2.1 Kinetic adsorption experiment of dolomite**

The groundwater from Pra Too Khong Bottled Drinking Water Plant in Lumphun province, Thailand was used in batch adsorption experiments. Before the experiment, the pH of groundwater was adjusted to pH 7 by adding 0.01 M NaOH or 0.01 M HCl solutions. The experiment was carried out in a 100 ml Erlenmeyer flask containing 5 g of dolomite sorbent in 50 ml of groundwater at room temperature. Then, it was shaken at 200 rpm on a rotary shaker.

The kinetic experiment was determined according to the time intervals: 10, 30 min and 1, 3, 6, 12, and 24 hr. At each time interval, 2 ml of groundwater was

collected and filtered through a nylon syringe filter with pore size of 0.45  $\mu\text{m}$ . The concentration of fluoride was analyzed by ion chromatography (IC).

### 3.2.2 Dolomite adsorption experiment

1000 ml of groundwater from Pra Too Khong Bottled Drinking Water Plant in Lumphun province, Thailand was poured into an Erlenmeyer flask that is larger than the measured amount allowing for a margin of 2 liters. The water sample was adjusted to a neutral pH by the addition of a 0.01 M NaOH or 0.01 M HCl solution. Then, the groundwater was poured from the larger Erlenmeyer flask to one measuring 1000 ml, and 100g of dolomite sorbent was added to create a ratio of 1:10 of the groundwater. With the groundwater at room temperature, it was put on a rotary shaker at 200 rpm, which shown in **Figure 3.8** until equilibrium was reached. After the shaking phase was completed, the groundwater was filtered through 70 mm. glass microfiber filters (GF/F) and collected in a 10 ml flask to measure the concentration of fluoride ion ( $\text{F}^-$ ) by ion chromatography (IC). The residual groundwater sample was collected for filtration through the membrane experiment, and the steps were repeated.



**Figure 3.8** Dolomite sorbent was shaken on rotary shaker at 200 rpm

### 3.2.3 Mass transfer coefficient and concentration polarization of NF-1 and RO-1 membranes

Mass transfer coefficient explains diffusion rate constant in solution that relate to mass transfer rate, mass transfer area and concentration gradient. Concentration polarization is explained as an undesirable phenomenon which is caused by the accumulation of retained solutes on the surface of the membrane. Mass transfer coefficient and concentration polarization was measured by the following procedure:

- The feed solution was prepared by using the pure water spike with varied sodium fluoride (NaF) concentrations of 0.01, 0.05 and 0.1 M.
- 1 L of feed solution in the feed tank was put through the membrane under a pressure of 0.4 MPa without adjusting the pH in the solution. The conductivity and pH of the feed solution was measured.
- The sample was put in the membrane for one hour and collected from permeate line and concentrated line for measuring the conductivity and water flux.

### 3.2.4 Fluoride rejection of NF-1 and RO-1 membranes using synthetic water

The rejection of fluoride was investigated to determine the performance of fluoride removal from water. Fluoride rejection was measured by the following procedure:

- Synthetic water was prepared from the pure water spike with sodium fluoride (NaF) at 10 mg/l. Then the prepared solution was adjusted in three pH values: the pH below the isoelectric point, pH at the isoelectric point and pH above the isoelectric point.

- The synthetic water was put through the NF-1 membrane prior and follows by the RO-1 membrane without any pH adjustment, under a controlled pressure of 0.40 MPa. The membrane module was run while the concentrated water and permeate water were restored in the feed tank.

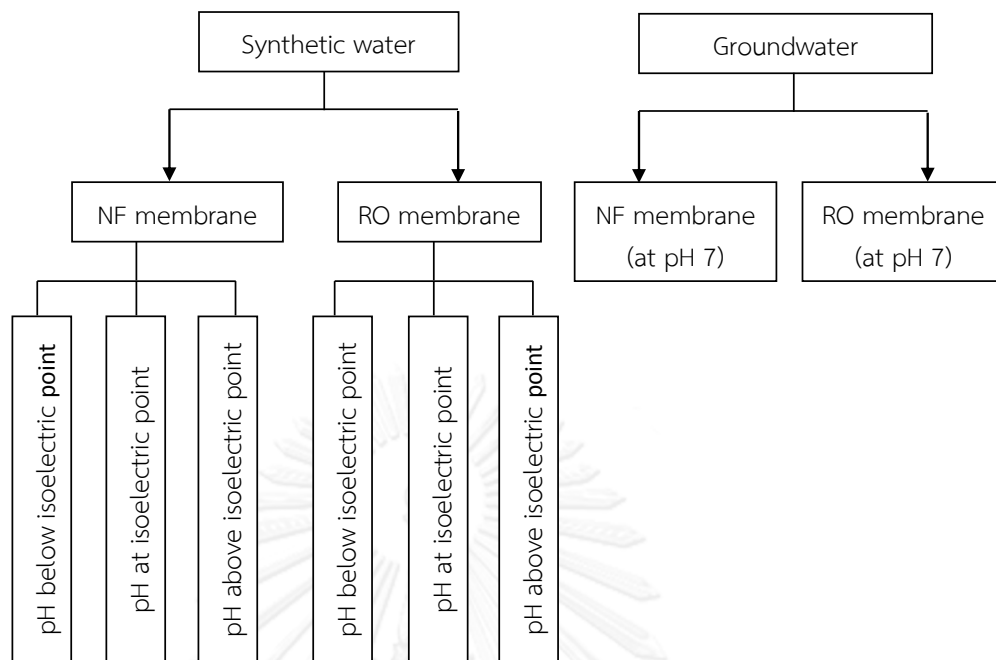
- When the sample time reached the steady state, the permeate water and concentrated water were collected in the permeate bottle and concentrated bottle, respectively, for the determination of the pH and fluoride concentration.

### **3.3 Fluoride removal using groundwater**

#### **3.3.1 Fluoride rejection of NF-1 and RO-1 membranes using groundwater**

1000 ml of groundwater from Pra Too Khong Bottled Drinking Water Plant in Lumphun province, Thailand was adjusted to pH 7. Then, put through the NF-1 and RO-1 membranes. When the sample time reached the steady state, the permeate water and concentrated water were collected in the permeate bottle and concentrated bottle, respectively, for the determination of the pH and fluoride concentration.

The procedure of membrane experiment for study the performance of the NF-1 and RO-1 membrane on fluoride removal in synthetic water and groundwater was shown in **Figure 3.9**.

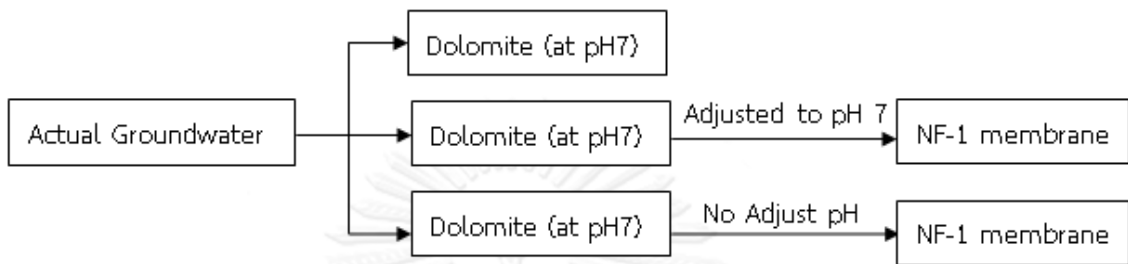


**Figure 3.9** Membrane experiment procedure for study the performance of the NF-1 and RO-1 membrane on fluoride removal in synthetic water and groundwater

### 3.3.2 Fluoride removal by co-process of dolomite adsorption and NF-1 membrane with pH adjustment and non-pH adjustment

After completing the dolomite adsorption experiment, the pH in the filtrated groundwater sample was adjusted one experiment to neutral again by adding 0.01 M NaOH or 0.01 M HCl solution and without any pH adjustment for one experiment. Then, the water sample was poured into a larger flask allowing for a margin of 2 liters more than the measured liquid and run through the membrane module. When the sample time reached a steady state, the permeate water and the concentrated water were collected in permeate bottle and concentrated bottle, respectively, and the pH and concentration of fluoride ion ( $F^-$ ) was analyzed by a pH meter and ion chromatography (IC), respectively. Fluoride rejection of dolomite adsorption without combining it with membrane filtration experiment was compared with adsorption

experiment combined with membrane filtration experiment in case of adjust pH before run and none of pH adjustment. The experiment procedure was shown in Figure 3.10.



**Figure 3.10** Fluoride removal by co-process of dolomite adsorption and NF-1 membrane procedure with pH adjustment and non-adjustment

### 3.4 Analytical Method

#### 3.4.1 Specific surface area of dolomite

The specific surface area of dolomite sample was investigated by Surface Area Analyzer (Quantachrome, Autosorb-1).

#### 3.4.2 Mineral composition of dolomite

The Mineral composition was investigated by X-Ray Diffraction meter (XRD) Model D8 Advance: Bruker AXS, Germany.

#### 3.4.3 Chemical composition of dolomite

The chemical compositions of dolomite sample were investigated by X-Ray Fluorescence Spectrometer (XRF): Bruker AXS, Germany, Model: S4 Pioneer Wavelength dispersive X-Ray Fluorescence (WDXRF) Spectrometry.

#### 3.4.4 Surface morphology of dolomite

The Surface morphology was measured by Scanning Electron Microscope (SEM).

#### 3.4.5 Fluoride ion

The concentration of fluoride was measured by Ion chromatography(IC) ISC-2500 automated IC system (Dionex, Ireland).

#### 3.4.6 Electrical conductivity

Electrical conductivity was measured by Electrical conductivity meter (CON900, Cond, AMTAST).

#### 3.4.7 pH

pH was measured by a pH/ISE meter (sensION2 Portable, Hash).



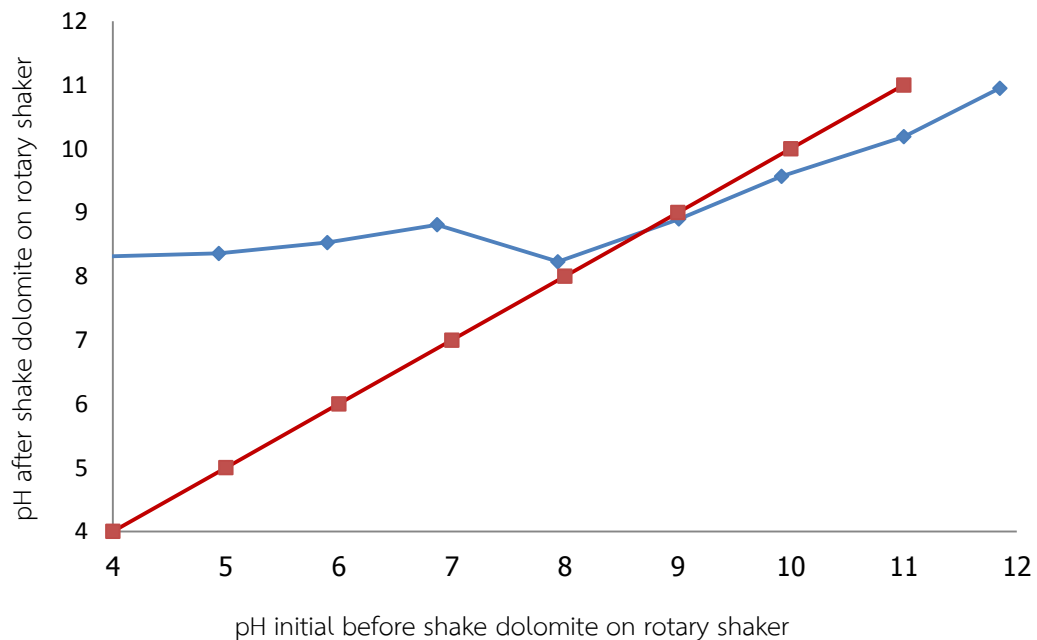
## CHAPTER 4

### DOLOMITE AND MEMBRANE CHARACTERISTICS

#### 4.1 Dolomite characteristics

##### 4.1.1 Point of zero charge (PZC) of dolomite

A point of zero charge (PZC) of dolomite was found at pH 8.5 as shown in **Figure 4.1**, which was closed to the results of (Pokrovsky et al., 1999). It meant at solution pH 8.5, dolomite surface was neutral or nearly zero charged. At solution pH below PZC of dolomite ( $\text{pH} < 8.5$ ), dolomite surface was positively charged due to  $[\text{MgOH}^+] + [\text{CaOH}^+] > [\text{HCO}_3^-]$ . When pH of solution was above PZC of dolomite ( $\text{pH} > 8.5$ ),  $[\text{MgOH}^+] + [\text{CaOH}^+] < [\text{HCO}_3^-]$ , the dolomite surface was negatively charged (Gence & Ozbay, 2006).



**Figure 4.1** PZC of dolomite

In this study, dolomite was used to adsorb fluoride ion which is a negative charge ion. Adsorption process could occur at solution pH lower than pH at PZC because the charge on dolomite surface was positively charged.

#### 4.1.2 Specific surface area

Specific surface area is a property of solids which is the total surface area of a material per unit of mass. It is important for chemical reaction. Although the same material that has the same volume and weight, the surface activity and adsorption volume are altered according to the specific area. Thus, it is important to measure the specific area to evaluate the activity and adsorption capacity of materials.

The specific area, average pore diameter, and total pore volume of adsorbent were determined using BET technique, which was important analysis technique for the measurement of the specific surface area of a material (Brunauer et al., 1983). The specific surface area was investigated by Surface Area Analyzer (Quantachrome, Autosorb-1) and the result of specific surface area and total pore volume of dolomite sorbent are shown in the **Table 4.1**.

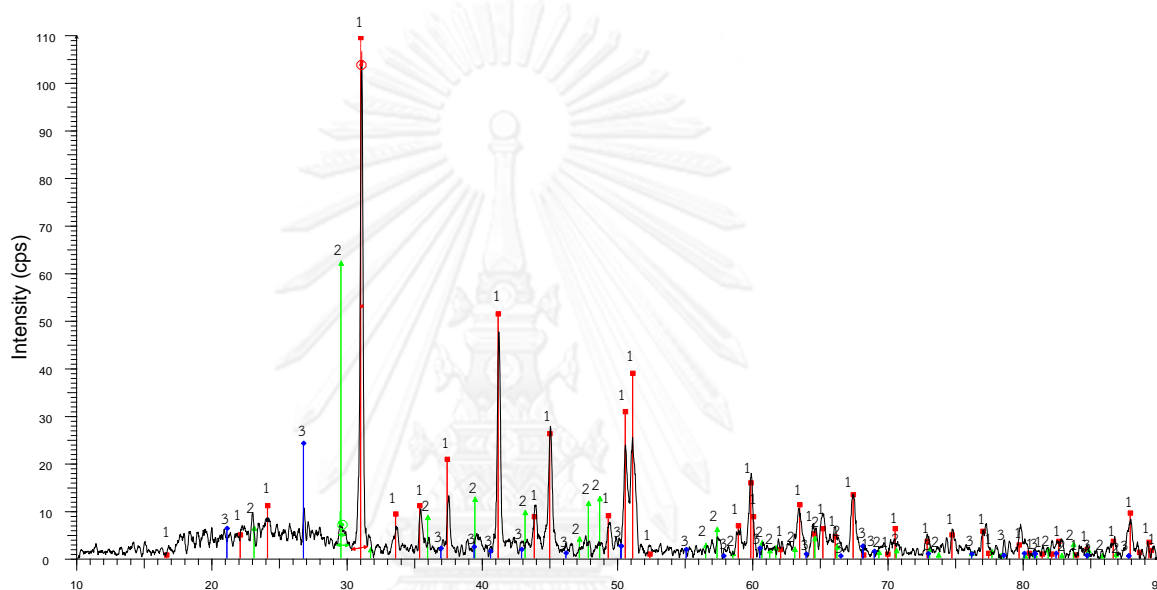
**Table 4.1** Specific surface area and total pore volume of dolomite sorbent

Sample	Mutipoint BET (m <sup>2</sup> /g)	Total pore volume ( cc/g)	Average pore diameter (Å)
dolomite sorbent	1.17	0.0031	105.7

### 4.1.3 Mineral composition

The mineral composition of dolomite samples were investigated by X-ray diffraction (XRD) analysis and the results found that dolomite sorbent was consisted of calcite and dolomite. Moreover, it contained some quartz as illustrated in **Figure**

### 4.2.



**Figure 4.2** X-ray diffraction patterns of dolomite. Number indicate identified phases:  
(1) Dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), (2) Calcite ( $\text{CaCO}_3$ ), (3) Quartz ( $\text{SiO}_2$ )

From **Figure 4.2**, it shows peaks of three mains of mineral including Dolomite  $\text{CaMg}(\text{CO}_3)_2$ , Calcite ( $\text{CaCO}_3$ ) and Quartz ( $\text{SiO}_2$ ). The areas under peak of graph were calculated to find the percentage of each mineral. It was found that the percentage of dolomite; calcite and quartz mineral were 89.09%, 6.85% and 4.06%, respectively.

#### 4.1.4 Chemical composition

Chemical composition refers to the identities, and relative numbers of the elements that make from any particular compound. A chemical compound may consist of two or more chemical elements and is a pure chemical substance.

The chemical compositions of dolomite sample were investigated by X-Ray Fluorescence Spectrometer (XRF): Bruker AXS, Germany analysis (Range 0.2 – 20 Å) (60 – 0.6 keV), Total resolution 3 – 100 eV, Typical measurement time 2 – 10 s per element), and the chemical compositions of dolomite sorbent are shown in **Table 4.2**. CaO, MgO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, and Na<sub>2</sub>O were 72.19%, 22.61%, 2.35%, 1.31%, 0.771%, 0.295%, 0.063%, 0.051%, 0.058%, respectively.

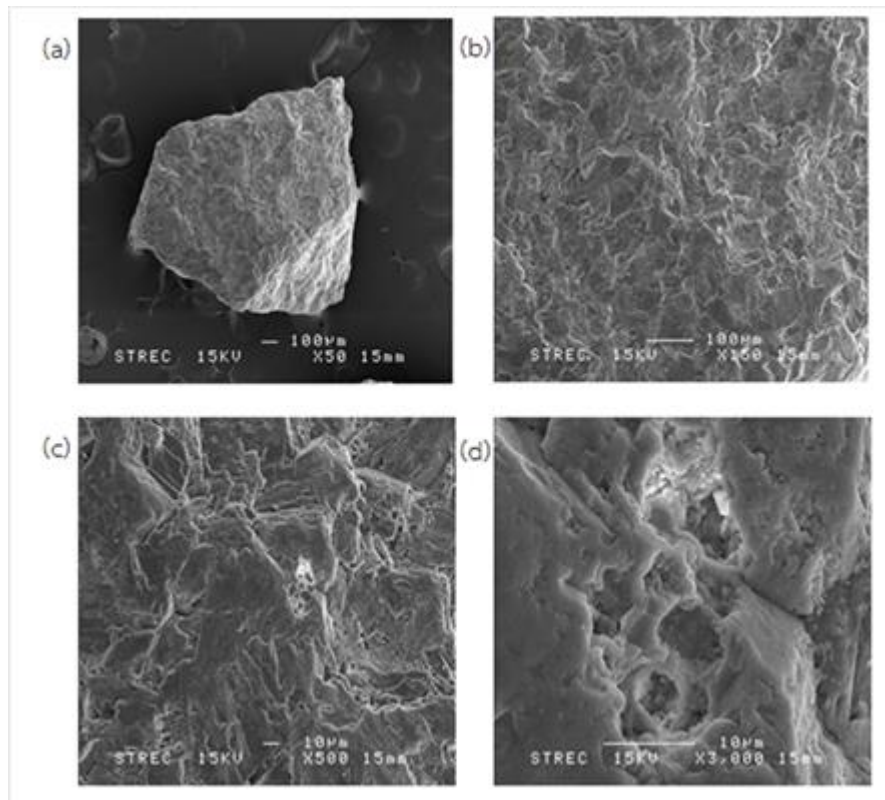
**Table 4.2** The chemical compositions of dolomite sorbent

Compound	Percent composition (%)
CaO	72.19
MgO	22.61
SiO <sub>2</sub>	2.35
Al <sub>2</sub> O <sub>3</sub>	1.31
Fe <sub>2</sub> O <sub>3</sub>	0.771
K <sub>2</sub> O	0.295
TiO <sub>2</sub>	0.063
P <sub>2</sub> O <sub>5</sub>	0.051
Na <sub>2</sub> O	0.058

#### 4.1.5 Surface morphology

Surface morphology is the study of the form or shape of material. This study, the structure of dolomite surface was investigated by SEM analysis. **Figure 4.3** shows

the SEM images of dolomite sorbents in each magnifying power ((a)  $\times 50$ , (b)  $\times 150$ , (c)  $\times 500$  and (d)  $\times 3000$ ), which found smooth surface with porous structure.



**Figure 4.3** SEM images of dolomite sorbents in each magnifying power ((a)  $\times 50$ , (b)  $\times 150$ , (c)  $\times 500$  and (d)  $\times 3000$ )

## 4.2 Membrane characteristics

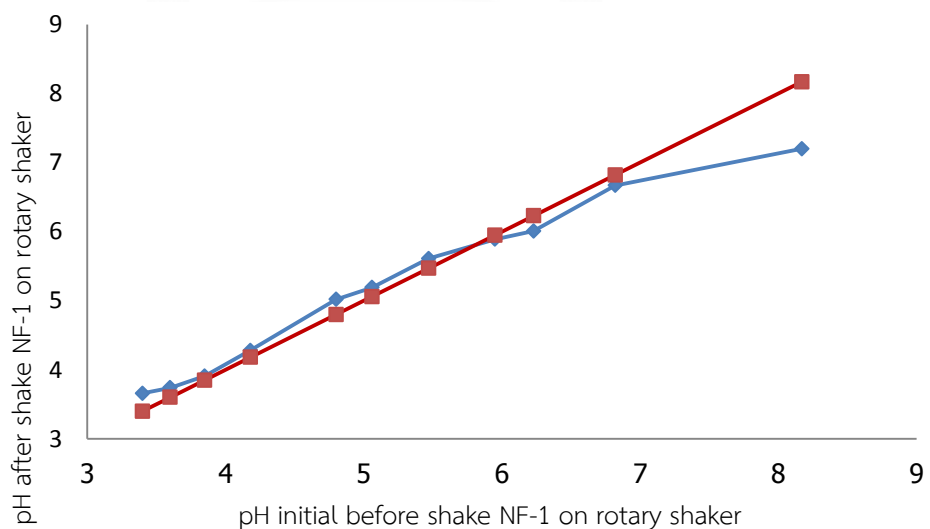
### 4.2.1 Isoelectric point of NF-1 and RO-1 membranes

The characterization of isoelectric point of membrane is very useful tools to help in the prediction of filtration properties. Separation mechanism of charged membrane depended on not only the “sieve effect” but also the “charge effect” (Tsuru et al., 1991). As a result, the charge of membrane was affected by pH. Thus,

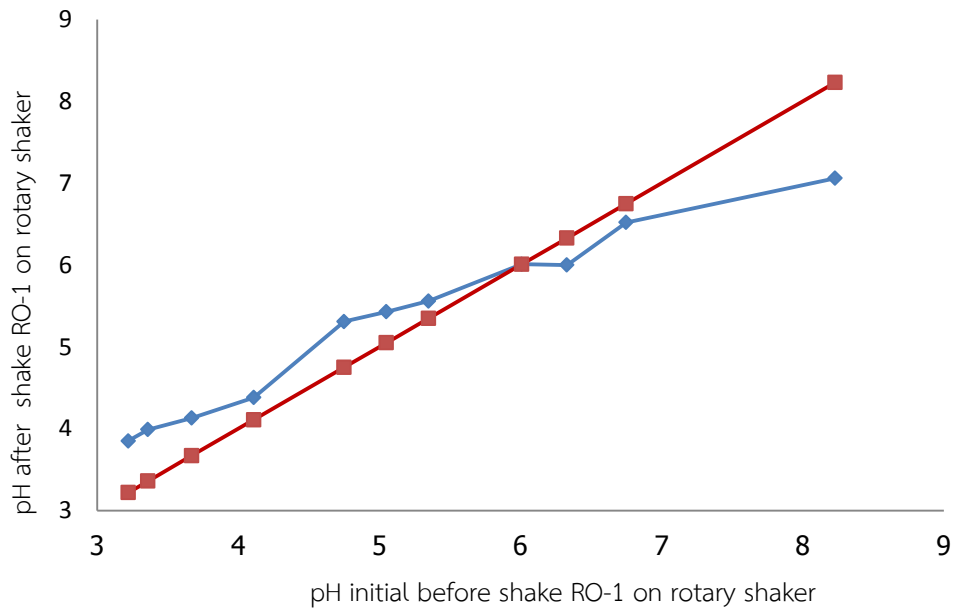
we should estimate an isoelectric point of membrane to find out the optimum efficiency of fluoride rejection through membrane filtration.

RO and NF membranes consist of a polyamide (PA) active layer that is characterized by two functional groups (i.e. carboxylic group (-COOH) and amine group (-NH<sub>2</sub>)). The carboxyl group (-COOH) in medium solution dissociates and becomes negatively charged (COO<sup>-</sup>). Unlike the carboxyl groups, the protonated amino groups (NH<sub>3</sub><sup>+</sup>) are only positively charged in an acidic pH medium (Bauman et al., 2013).

In **Figures 4.4** and **4.5**, pH 6 was defined as isoelectric points of NF-1 and RO-1 membranes, which was a neutral or nearly zero for surface charge. Thus, when the feed pH was higher than the isoelectric point, the surface charge became negatively charged because proton from carboxylic group on surface membrane was deprotonated to the solution, while the feed pH was lower than the isoelectric point, the charge on surface membrane became positively charged due to protons from the solution was protonated to amine group on surface layer.



**Figure 4.4** An isoelectric point of NF-1 membrane



**Figure 4.5** An isoelectric point of RO-1 membrane

#### 4.2.2 Permeate water fluxes of NF-1 and RO-1 membranes

Pure water was used to test NF-1 and RO-1 membranes at the operating pressure of 0.2, 0.3, and 0.4 MPa, respectively. The data of the permeate water volume and measuring time during membrane operation were shown in **Appendix A**.

The permeate water flux was calculated by **Eq. (4-1)** as follows;

$$J_v = \frac{V}{A \times T} \quad (4-1)$$

Where  $J_v$  = permeate water flux ( $\text{m}^3/\text{m}^2 \times \text{day}$ )

$V$  = permeate volume ( $\text{m}^3$ )

$A$  = surface area of NF-1 and RO-1 ( $60 \times 10^{-4} \text{ m}^2$ )

$T$  = sampling time (day)

**Table 4.3** Permeate water fluxes of NF-1 and RO-1 membranes

Transmembrane pressure (MPa)	Permeate water flux ( $\text{m}^3/\text{m}^2 \times \text{day}$ )	
	NF-1	RO-1
0.165	0.48	0.18
0.275	0.96	0.36
0.375	1.46	0.48

From **Table 4.3** shows the permeate water fluxes of NF-1 and RO-1 membranes. It was observed that when the operating transmembrane was increased, the permeate water flux was increased dramatically. The permeate water fluxes of NF-1 membrane at the operating transmembrane 0.165, 0.275, and 0.375 MPa were 0.48, 0.96, and 1.46  $\text{m}^3/\text{m}^2 \times \text{day}$ , respectively. The permeate water fluxes of RO-1 membrane at the operating transmembrane 0.165, 0.275, and 0.375 MPa were 0.18, 0.36, and 0.48  $\text{m}^3/\text{m}^2 \times \text{day}$ , respectively. The highest operating transmembrane pressure (0.375MPa) provided the highest permeate flux. It was due to the pressure directly effect to the permeability of water for moving through the membrane surface. The permeate water flux of NF-1 membrane was higher than that of RO-1 membrane. This was due to a different pore size of the membrane. A larger pore size provided a higher permeate water flux. Pore size of NF-1 membrane was 0.84 nm (Nghiem & Hawkes, 2007). RO-1 membrane's pore was observed in between 0.22 and 0.44 nm (Kosutic K, 2002).



#### 4.2.3 Pure water permeability of NF-1 and RO-1 membranes

The pure water permeability is defined as the volume of water that pass through a membrane per unit time, per unit area and per unit of transmembrane pressure.  $k_w$  was calculated by plotting graph between permeate water flux and transmembrane pressure via **Eq. (4-2)**. The slope of each graph referred to pure water permeability.

$$J_v = k_w \times (\Delta P - \pi) \quad (4-2)$$

Where  $k_w$  = pure water permeability ( $\text{m}^3/\text{m}^2 \times \text{day} \times \text{MPa}$ )

$J_v$  = permeate water flux ( $\text{m}^3/\text{m}^2 \times \text{day}$ )

$\Delta P$  = transmembrane pressure (MPa)

$\pi$  = osmotic pressure (MPa)

**Figure 4.6** and **Figure 4.7** demonstrate permeate water flux ( $J_v$ ) at the steady state of each operating transmembrane pressure of NF-1 and RO-1 membranes, respectively. The slopes between permeate water flux and transmembrane pressure were 3.66 and 1.27  $\text{m}^3/\text{m}^2 \times \text{day} \times \text{MPa}$  for NF-1 and RO-1 membranes, respectively. The result illustrated that NF-1 membrane gave higher water permeability than RO-1 membrane. The result could support the higher permeate water flux of NF-1 membrane comparing with that of RO-1 membrane.

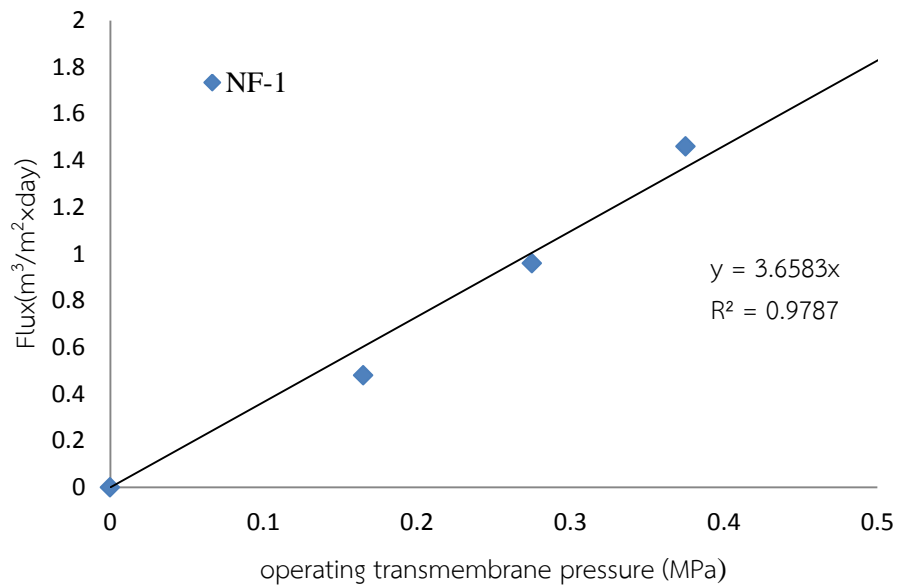


Figure 4.6 The permeate water flux at steady state of NF-1 membrane

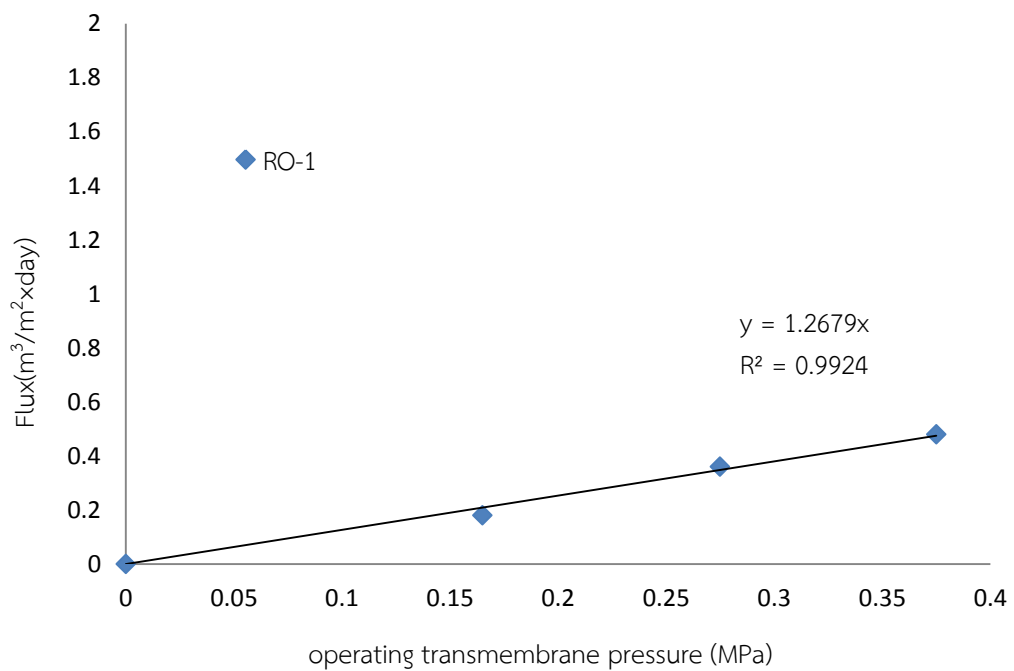


Figure 4.7 The permeate water flux at steady state of RO-1 membrane

## CHAPTER 5

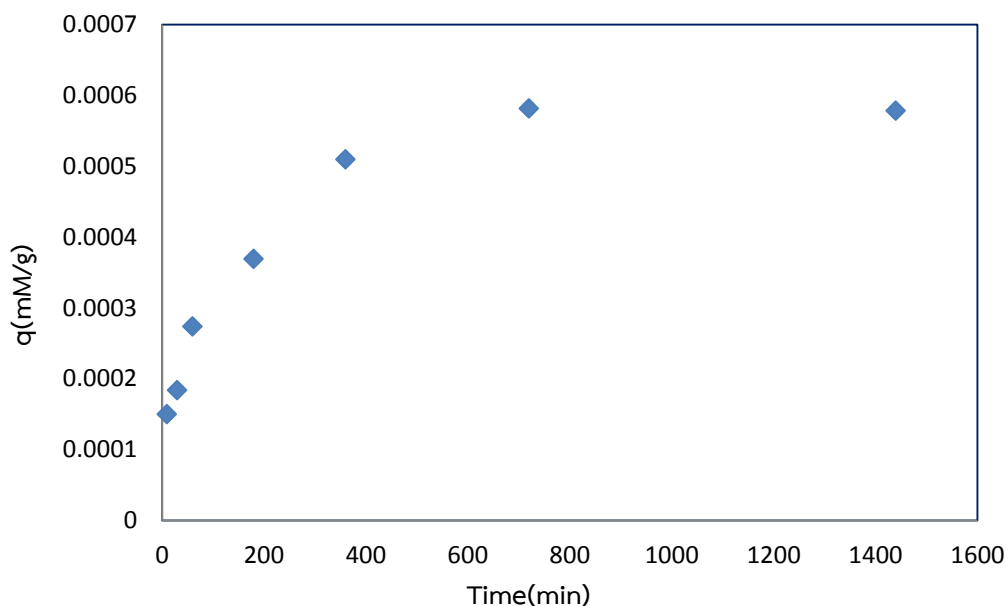
### FLUORIDE REMOVAL USING SYNTHETIC WATER AND GROUNDWATER

#### 5.1 Kinetic adsorption of dolomite

A kinetic adsorption experiment was investigated to obtain the time for equilibrium of fluoride adsorption by dolomite sorbent.

When cation of dolomite ( $Mg^{2+}$ ,  $Ca^{2+}$ ) and anion ( $CO_3^{2-}$ ) diffused into aqueous solution, it caused the hydrolysis and proton reaction to generate  $HCO_3^-$  and  $MOH^+$  in dissolution process. After dolomite surface reacted with water molecules, it caused to produce  $HCO_3^-$  and  $MOH^+$  and the surface charge of dolomite occurred from unequal composition of  $HCO_3^-$  and  $MOH^+$ . At pH below PZC of dolomite ( $pH < 8.5$ ), dolomite surface was positively charged due to  $[MgOH^+] + [CaOH^+] > [HCO_3^-]$ . While pH above PZC of dolomite ( $pH > 8.5$ ),  $[MgOH^+] + [CaOH^+] < [HCO_3^-]$ , thus, dolomite surface was negatively charged (Gence & Ozbay, 2006).

Consequently, kinetic adsorption of fluoride by dolomite was carried out at solution pH 7, which the electrostatic interaction between the dolomite surface and fluoride ion was preferred. **Figure 5.1** illustrates the kinetic adsorption of fluoride by using dolomite sorbent at solution pH 7.



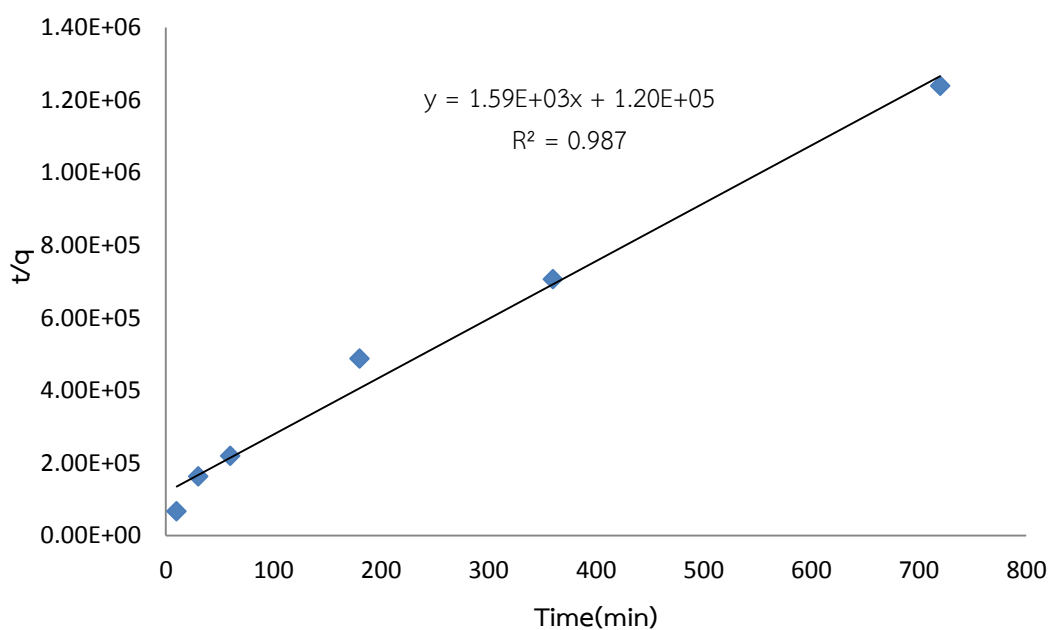
**Figure 5.1** Kinetic adsorption of fluoride by using dolomite sorbent at pH 7 of solution

Dolomite adsorbed fluoride rapidly in the first hour. Then, the adsorption was gradually slow until reaching the equilibrium time at 12 hr. At the equilibrium time, dolomite could adsorb fluoride by 8%. The data were provided in **Appendix D**.

## 5.2 Kinetic models of dolomite

In order to investigate the rate constant of adsorption of fluoride on dolomite, the data obtained from experiments were fitted to four kinetic models. The constant (K) values of first-order, second-order and pseudo-first order were calculated from slope of each regression line. The constant (K) of pseudo-second order kinetic model was calculated from square of slope divide by intercept of regression line. In this study, the coefficient of determination,  $R^2$  was used to test the

best-fitting of the kinetic model. The correlation coefficients for the linear graph of pseudo-second order are higher than other models. Thus, it could be concluded that the pseudo-second order kinetic model was the kinetically controlled the reaction rate of the fluoride adsorption by dolomite as shown in **Figure 5.2**.



**Figure 5.2** Representative plot for linear equation of pseudo-second order kinetic model

**Figure 5.2** shows the correlation coefficients ( $R^2$ ) for the linear graph of pseudo-second order, which was 0.987. The pseudo-second order rate constant of fluoride adsorption on dolomite was calculated (Ho, 2006).

$$k = \text{slope}^2 / \text{intercept} \quad (5-1)$$

From **Eq. (5-1)**, the pseudo-second order rate constant of fluoride adsorption on dolomite was 21.0675 g/mM min.

### 5.3 Mass transfer coefficient of NF-1 and RO-1 membranes

The mass transfer coefficient was a diffusion rate constant that related to the mass transfer rate, mass transfer area, and concentration gradient as driving force (Seader & Henley, 1998). The mass transfer coefficient could lead to the well-known phenomena of concentration polarization.

The mass transfer coefficients of NF-1 and RO-1 membranes were investigated. NaF solution was used. NaF solution was run through NF-1 and RO-1 membranes at the operating transmembrane pressure 0.4 MPa that produced the highest flux in this study. Then, feed solution, concentrate solution and permeate solution were measured by electrical conductivity meter (EC). The results from EC meter provided the conductivity value (S) and then it was converted to concentration (M) by using calibration curve of sodium fluoride. The data was provided in **Appendix B**.

The concentration of sodium fluoride (NaF) would be converted to osmotic pressure via Van't Hoff Equation, which can be calculated as follows **Eq. (5-2)**.

$$\pi = nRT \quad (5-2)$$

Where n = salt concentration (mol/L)

R = universal gas constants ( $J \times K^{-1} \times mol^{-1}$ )

T= temperature (K)

**Table 5.1** Concentration of NaF and permeate fluxes of NF-1 and RO-1 membranes

membrane	Concentration (M)			$\pi_B - \pi_P$ (Mpa)	flux (Jv) (m <sup>3</sup> /m <sup>2</sup> ×day)	% rejection
	Feed (C <sub>F</sub> )	Concentrate (C <sub>B</sub> )	Permeate (C <sub>P</sub> )			
NF-1	0.103	0.104	0.044	0.147	0.576	56.9
	0.052	0.053	0.011	0.105	0.768	80.0
	0.008	0.009	0.001	0.020	1.296	87.8
RO-1	0.103	0.105	0.027	0.194	0.112	74.4
	0.050	0.053	0.005	0.119	0.216	90.5
	0.008	0.009	0.001	0.020	0.432	91.0

**Tables 5.1** illustrate the concentrations of sodium fluoride (NaF) and permeate fluxes of NF-1 and RO-1 membrane. Each sample was collected from feed line, concentrate line and permeate line at transmembrane pressure at 0.375MPa. It showed the relationship between NaF concentrations, permeate fluxes and salt rejection. The salt rejection was 56-88% and 74-91% in NF-1 and RO-1 membranes, respectively. From the results, the higher of salt concentration provided the higher in the osmotic pressure and the lower in the permeate flux. The salt concentration in permeate line was increased when increasing the concentration of NaF solution in feed water. The rejection of NaF decreased when increasing of feed concentration of solution due to the combination of steric and Donnan effects (Koyuncu & Topacik, 2003). The donan effect became less effective with increasing salt concentration and

the electrostatic interactions between the membrane and NaF promoted the rejection with the negatively charge membrane. Hence, NaF removal decreased with increasing salt concentration (Koyuncu, 2002).

Then, the mass transfer coefficient was estimated from Eq. (5-3).

$$k = \frac{(J_V)_{solute}}{\ln \left\{ \frac{\Delta P}{\pi_B - \pi_P} \cdot \left[ 1 - \frac{(J_V)_{solute}}{(J_V)_{H_2O}} \right] \right\}} \quad (5-3)$$

The mass transfer coefficient of NF-1 and RO-1 were obtained by plotting

between  $(J_V)_{solute}$  and  $A = \ln \left\{ \frac{\Delta p}{\pi_B - \pi_P} \times \left[ 1 - \frac{J_V}{(J_V)_{H_2O}} \right] \right\}$ .

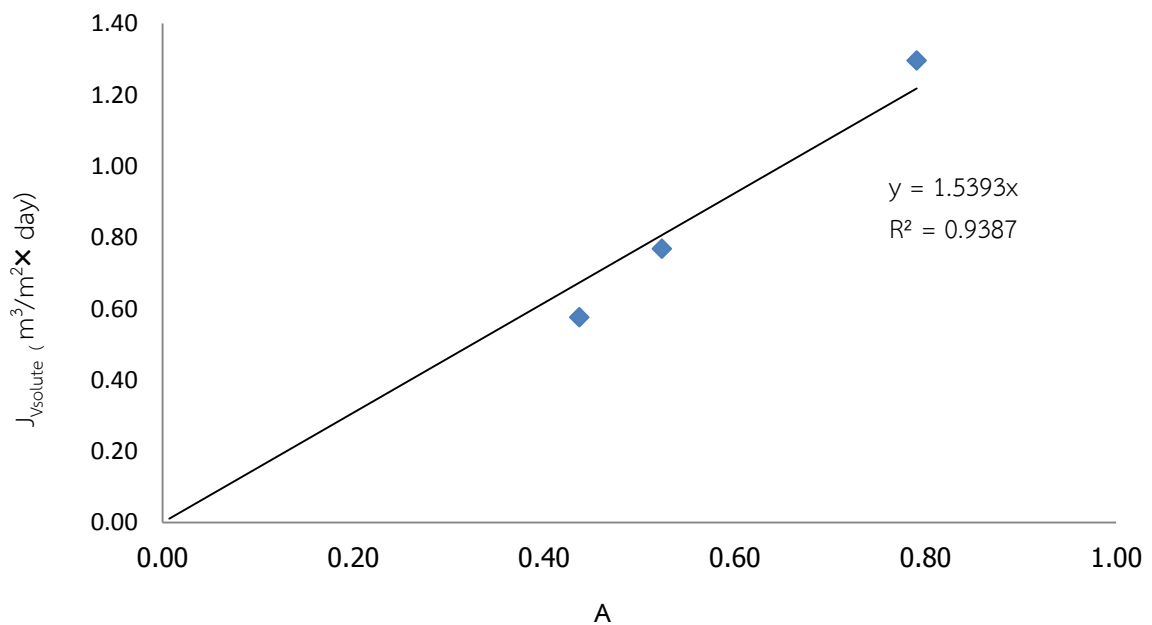
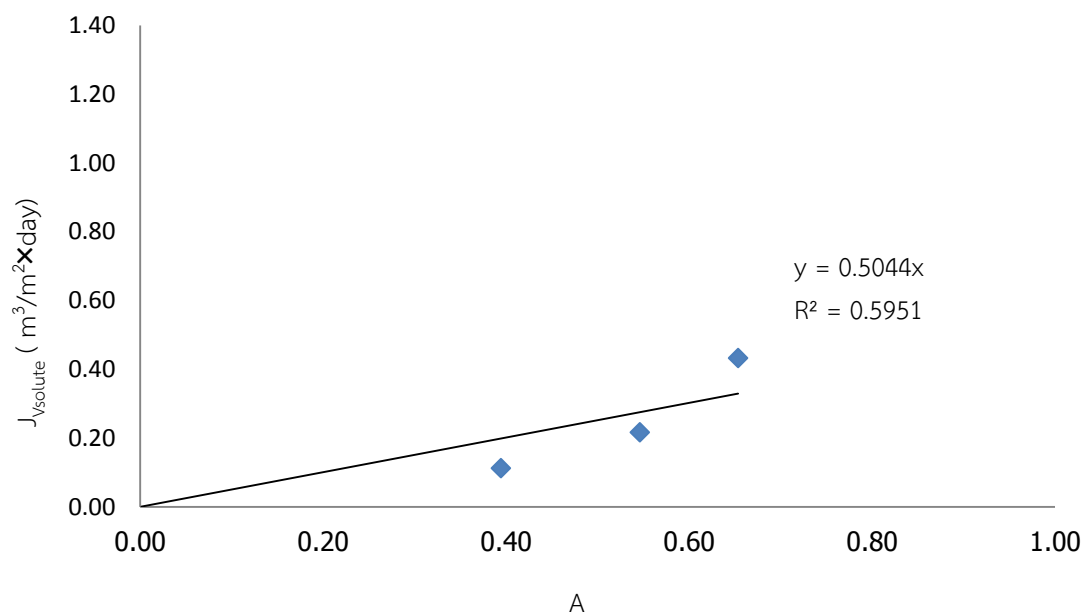


Figure 5.3 Mass transfer coefficient of NF-1 membrane





**Figure 5.4** Mass transfer coefficient of RO-1 membrane

The mass transfer coefficients of NF-1 and RO-1 membranes are shown in **Figure 5.3** and **Figure 5.4**, respectively. The mass transfer coefficients of NF-1 and RO-1 membranes were 1.539 and 0.504  $\text{m}^3/\text{m}^2\cdot\text{day}$ , respectively. From the results, it was concluded that NaF could pass through NF-1 membrane more than RO-1 membrane.

#### 5.4 Concentration polarization of NF-1 and RO-1 membranes

The concentration polarization of NF and RO membranes were studied. The feed solution was varied the fluoride concentration at 0.01, 0.05 and 0.1 M by dissolving NaF in pure water. From previous results of mass transfer coefficient ( $k$ ) was used to calculate concentration polarization. The results of concentration polarization level ( $f = C_M/C_B$ ) of NF-1 and RO-1 were estimated in **Table 5.2**.

The NaF concentration on membrane surface ( $C_M$ ) was calculated from Eq. (5-4).

$$J_V = k \cdot \ln\left(\frac{C_M - C_P}{C_B - C_P}\right) \quad (5-4)$$

**Table 5.2** The results of concentration polarization of NF-1 and RO-1 membranes

membrane	Mass transfer coefficient (k)	Flux( $J_V$ ) ( $m^3/m^2 \times day$ )	Feed solution	Concentrate water ( $C_B$ ) M	Permeate water ( $C_P$ ) M	membrane surface ( $C_M$ ) M	$f(C_M/C_B)$
NF-1	1.539	0.576	0.103	0.103	0.045	0.184	1.786
		0.768	0.052	0.052	0.011	0.144	2.769
		1.296	0.008	0.009	0.001	0.057	6.333
RO-1	0.054	0.112	0.105	0.105	0.027	0.157	1.495
		0.216	0.05	0.053	0.005	0.134	2.528
		0.432	0.008	0.008	0.001	0.057	7.125

From the results in **Table 5.2**, it was found that the NaF concentration on the membrane surface ( $C_M$ ) was higher than NaF concentration in feed solution in both membranes (NF-1 and RO-1). It could be indicated that the concentration gradient of NaF was increased particularly at the surface membrane. Thus, excessive concentration polarization could cause some salts to concentrate at the membrane surface to its solubility limit, leading to precipitation of this NaF salt at the membrane surface.

### 5.5 Fluoride removal by NF-1 and RO-1 membranes using synthetic water

From characterization of membrane in previous section, the results showed that an isoelectric point of NF-1 and RO-1 membranes were observed at pH 6. This

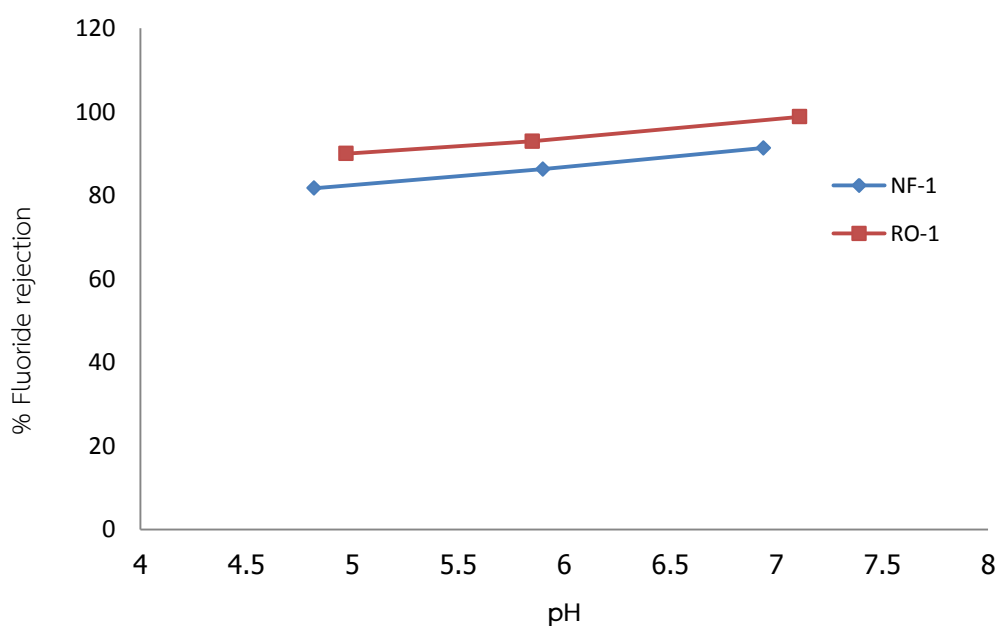
experiment varied synthetic water pH including pH at isoelectric point, pH below isoelectric point, and pH above isoelectric point to study the effect of solution pH on fluoride rejection. Sodium fluoride (NaF) was spiked into pure water and synthetic water pH was adjusted to 5, 6, and 7. Then, the synthetic water was run through the membrane module. The water samples were collected from feed, concentrate, and permeate line. Concentrations of fluoride in the water sample were measured by an ion chromatography. The permeate water flux at steady state was calculated with the same Eq. (4-1) and the data of fluoride rejection was provide in Appendix C .The rejection of fluoride and permeate water flux by using synthetic water are shown in Table 5.3.

**Table 5.3** Percentage of fluoride rejection and permeate water flux by using synthetic water

	NF-1	RO-1
%rejection of fluoride at feed pH of 5	82	90
%rejection of fluoride at feed pH of 6	86	92
%rejection of fluoride at feed pH of 7	91	99
permeate water flux at steady state ( $\text{m}^3/\text{m}^2 \times \text{day}$ ) under TMP 0.4 MPa	1.18	0.4

The results are shown in Table 5.3. For NF-1 membrane, fluoride rejections increased with an increasing of synthetic water pH. Fluoride rejections at the synthetic water pH 5, 6, and 7 were 82%, 86%, and 91%, respectively. For RO-1 membrane, fluoride rejections at the solution pH 5, 6, and 7 were 90%, 92%, and 99%, respectively. These results were due to an electrostatic force between the

charged membrane surface and ions (Qin et al., 2004). At synthetic water pH 6, the membrane showed a neutral charged membrane surface. A rejection of fluoride could be controlled solely by a diffusion mechanism. At the synthetic water pH 5, the membrane surface was positively charged. Thus, an electrostatic interaction between the membrane surface and fluoride ion was observed and resulted in a high fluoride ion on the membrane surface. Consequently, a large amount of fluoride could pass through the membrane and a decreasing in fluoride rejection was found. In contrast with the synthetic water pH 7, the membrane surface showed negatively charged membrane surface. Hence, an electrostatic repulsion between the membrane surface and fluoride ion occurred and resulted in a small amount of fluoride ion on the membrane surface. This led to an increasing in fluoride rejection. **Figure 5.5** illustrates the fluoride rejections by NF-1 and RO-1 membranes at different synthetic water pH, respectively.



**Figure 5.5** Fluoride rejections by NF-1 and RO-1 membrane using synthetic water

## 5.6 Fluoride removal by NF-1 and RO-1 membranes using groundwater

Groundwater from Pra Too Khong drinking water plant, Lamphun Province, Thailand was collected. The pH of the groundwater was 8.08. Electrical conductivity was 153.2  $\mu\text{S}/\text{cm}$ . The concentration of fluoride was in a range of 12.14-15.38 mg/L. It was extremely higher than the standard of fluoride in drinking water. Then, the groundwater was filtrated by NF-1 and RO-1 membranes to remove the excessive concentration of fluoride. This experiment operated at groundwater pH 7.

The results are shown in **Table 5.4**. For NF-1 membrane, fluoride rejection was 91%. For RO-1 membrane, fluoride rejection was 99%. Both obtained results were similar to those obtained from the case of using synthetic water. It could be stated that fluoride rejection was influenced by feed water pH. It could be explained differences in water characteristics between synthetic water and groundwater did not affect fluoride rejection of the membranes in this study.

Furthermore, It was found that the permeate water fluxes at steady state using synthesis water in previous experiment was higher than those achieved when using groundwater for both NF-1 and RO-1 membranes. It might be due to higher ionic strength in groundwater that resulted in lower permeate water flux.

**Table 5.4** Percentage of fluoride rejection under operating transmembrane pressure 0.38 MPa and permeate water flux in groundwater

	NF-1	RO-1
%rejection of fluoride at groundwater pH 7	91	99
permeate water flux at steady state (m <sup>3</sup> /m <sup>2</sup> ×day) under TMP 0.4 MPa	0.93	0.27

### 5.7 Fluoride removal by co-process of dolomite adsorption and NF-1 membrane with pH adjustment and non-pH adjustment

Groundwater was adjusted to pH 7, which the electrostatic interaction between the dolomite surface and fluoride ion was preferred. The adsorption process was done for 12 hr. After that, defluoridated water by dolomite adsorption was further filtrated via NF-1 membrane with and without pH adjustment. The results are shown in **Table 5.5**

**Table 5.5** Fluoride rejections by the co-process of dolomite adsorption and NF-1 membrane filtration with pH adjustment and non-pH adjustment

pH operation	Applied process	Fluoride rejection (%)
adjust pH before run NF-1	Dolomite	9
	Dolomite + NF-1 membrane	78
no adjust pH before run NF-1	Dolomite	9
	Dolomite + NF-1 membrane	71

From the **Table 5.5** shows the percentage of fluoride rejection on dolomite was 9% that lower the fluoride rejection comparing with rice husk was 50% at pH 2,

which decreases up to 15% as the pH of the solution increases (Deshmukh et al., 2009) observed the similar results using citrus limonum (lemon) leaf, which the optimal value of pH 2 was observed where the adsorbent showed the maximum defluoridation capacity of 70% of 2 mg/L of fluoride ion (Tomar et al., 2014). In this study, the percentage of fluoride rejection was low. This may be at high pH values, the reduction in adsorption contain large amount of  $\text{OH}^-$  ions causing increase hindrance to diffusion of fluoride ion. Thus, at high pH the adsorption could be reduces. So, enhancing the efficiency of fluoride adsorption on dolomite might be occurred at low pH due to the large amount of  $\text{H}^+$  altered neutralizes the negative charge  $\text{OH}^-$  ion on adsorbed surface to positive charge lead to increasing of fluoride adsorption.

For the co-process with an adjustment of defluoridated groundwater pH (pH 7) after dolomite adsorption prior to NF-1 membrane filtration, fluoride was rejected by 78%. While the co-process without an adjustment of defluoridated groundwater pH after dolomite adsorption prior to NF-1 membrane filtration provided fluoride rejection of 71%. Adjustment of the defluoridated groundwater pH offered higher fluoride rejection. This results might be pH value after defluoridated groundwater by dolomite adsorption effect to the increasing the ionic strength in solution leading to change the pH value of concentration which not suitable to operate through NF-1 membrane. Moreover, this experiment without the buffer of solution might be leads to changing of pH in solution all time. In condition without adjustment of pH might be decrease pH value lower than isoelectric point of NF-1 membrane which, depend on charge on surface membrane. Due to the NF-1 membrane surface consists of two layer i.e. polysulfone and polyamide, which was layer that used to water treatment

including of amine group ( $\text{NH}_2$ ) and carboxylic group ( $\text{COOH}$ ). The pH in case without pH adjustment might be lower than pH 7 that lower under isoelectric point of NF-1 membrane leading to High amount of  $\text{H}^+$  in solution was protonate to amine group to surface charge of NF-1 membrane. Thus, the surface charge of NF-1 membrane become the positive charge and anion of fluoride could be passed in the permeate water leading to reduction of fluoride rejection. However, this pH adjustment was to control and prevent membrane fouling. Without pH adjustment, the membrane fouling could occur and reduce membrane efficiency. Basic water pH could enhance precipitation of some carbonate species, e.g. calcium carbonate on the membrane surface. As a result, the pH adjustment was desired.

**Table 5.6** Comparison percentage of fluoride removal in each method

Sole RO-1	sole RO-1	Dolomite adsorption	Co-process of dolomite adsorption and NF-1 membrane
99%	91%	9%	78%

From **Table 5.6** When compared between using of the sole RO-1 gave the 99% for fluoride removal For NF-1 membrane and the co-process, fluoride rejection by the sole NF-1 membrane gave 91% that higher efficiency of fluoride removal than co-process. It might be explained that defluoridated groundwater pH after dolomite adsorption might contain many ions and minerals that released from dolomite itself. This caused significant increasing of ionic strength in the defluoridated groundwater after dolomite adsorption. High ionic strength in the water together with the membrane fouling, the co-process presented lower fluoride rejection.



## CHAPTER 6

### CONCLUSIONS AND RECOMMENDATIONS

#### 6.1 Conclusions

From the results of this study, the following conclusions can be drawn:

1. PZC of dolomite was found at pH 8.5. The pH of water sample should be lower than 8.5, hence a positively charged surface was marked. As a result, the electrostatic interaction between the dolomite surface and fluoride ion was preferred.

2. The equilibrium time of batch experiment of dolomite adsorption was reached at 12 hr. At the equilibrium time, dolomite could adsorb fluoride by 8%. The pseudo-second order kinetic model was the kinetically controlled the reaction rate of the fluoride adsorption by dolomite. The percentage of fluoride removal from groundwater via dolomite was equal to 9%.

3. Isoelectric points of NF-1 and RO-1 membranes were determined at 6. Thus, the pH of water sample should be higher than 6.0 because a negative surface charge was favored. Therefore, the electrostatic repulsion between the membrane surface and fluoride ion was preferred.

4. NF-1 membrane showed a higher permeate water flux and pure water permeability under the same operating transmembrane pressure compared with RO-1 membrane. It was due to a larger pore size of NF-1 membrane.

5. It was found that fluoride rejections of NF-1 and RO-1 membranes increased with an increasing in synthetic water pH. The results show pH effect on the fluoride rejection by NF-1 and RO-1 membrane.

6. The co-process of dolomite adsorption together with NF membrane using groundwater in case of pH adjustment to 7 before feeding through membrane module and without pH adjustment provided 78% and 71% of fluoride rejection, respectively. Thus, the co-process of dolomite adsorption together with NF membrane filtration without pH adjustment to 7 before feeding through membrane module was preferred due to a strong electrostatic repulsion between the membrane surface and fluoride ion.

7. Fluoride rejection of groundwater by sole NF-1 membrane at pH 7 was 91% and Fluoride rejection of co-process was 78%. The co-process of fluoride rejection by the sole NF-1 membrane gave higher efficiency. It might be explained that defluoridated groundwater pH after dolomite adsorption might contain many ions and minerals that released from dolomite itself. This caused significant increasing of ionic strength in the defluoridated groundwater after dolomite adsorption. High ionic strength in the water together with the membrane fouling, the co-process presented lower fluoride rejection. Although the efficiency of the co-process dolomite adsorption and nanofiltration (NF) membrane presented lower fluoride rejection than using sole NF-1 membrane, this study can be applied to improve the quality of adsorbent to enhance the efficiency for fluoride removal in groundwater combine with NF membrane in future.

## 6.2 Recommendations for future researches

Based on the results of this study, the recommendation for future studies can be proposed.

1. In this study, the dolomite sorbent was selected only one size for experiment to investigate the performance of fluoride adsorption. Thus, the size of dolomite should be varied in future work to study the effect of particle size of dolomite sorbent on adsorption.

2. In this study, the efficiency of dolomite on fluoride adsorption less than first expectation. It may be interaction between ions, which contain in groundwater. Hence, the competitive ion for fluoride adsorption should be study in future research.

3. The structure of dolomite should be modifying before adsorption experiment and compare the performance in each method of purification (i.e. immerse in acid or heat by incinerator).

4. The proportion between fluoride solution and dolomite sorbent may not suitable for effective adsorption. So, the amount of dolomite sorbent should be increased in future experiment.

5. The influence of other factors of rejection on the membrane, such as temperature, contact time, individual ion and combine ion should be investigated in future work.

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APPENDICES

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Appendix A

Permeate water flux

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**Table A-1** Permeate water flux of NF-1 membrane at TMP 0.165 Mpa

times (mins)	sampling time (day)	volume(m <sup>3</sup> )	area ( m <sup>2</sup> )	flux(m <sup>3</sup> /m <sup>2</sup> ×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
50	0.0014	0.000004	0.006	0.48
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-2** Permeate water flux of NF-1 membrane at TMP 0.275 MPa

time (mins)	Sampling time (day)	volume(m <sup>3</sup> )	area ( m <sup>2</sup> )	flux (m <sup>3</sup> /m <sup>2</sup> ×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
50	0.0014	0.000008	0.006	0.96
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-3** Permeate water flux of NF-1 membrane at TMP 0.375 MPa

times (mins)	sampling time (day)	volume(m <sup>3</sup> )	area ( m <sup>2</sup> )	flux(m <sup>3</sup> /m <sup>2</sup> ×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
50	0.0014	0.0000120	0.006	1.44
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

**Table A-4** Permeate water flux of RO-1membrane at TMP 0.165 MPa

times (mins)	Sampling time (day)	volume(m <sup>3</sup> )	area ( m <sup>2</sup> )	flux(m <sup>3</sup> /m <sup>2</sup> × 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-5** Permeate water flux of RO-1membrane at TMP 0.275 MPa

times (mins)	sampling time (day)	volume(m <sup>3</sup> )	area ( m <sup>2</sup> )	flux(m <sup>3</sup> /m <sup>2</sup> ×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-6** Permeate water flux of RO-1membrane at TMP 0.375 MPa

times (mins)	sampling time (day)	volume(m <sup>3</sup> )	area ( m <sup>2</sup> )	flux(m <sup>3</sup> /m <sup>2</sup> ×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-7** Permeate water flux of NF-1 and RO-1 membranes at pH 5, 6 and 7 in synthetic water at TMP 0.375 MPa

conditions	sampling time (day)	volume(m <sup>3</sup> )	area ( m <sup>2</sup> )	flux(m <sup>3</sup> /m <sup>2</sup> ×day)
NF-1 at pH 5	0.0035	0.000025	0.006	1.18
NF-1 at pH 6	0.0035	0.000025	0.006	1.2
NF-1 at pH 7	0.00345	0.000025	0.006	1.18
RO-1 at pH 5	0.0104	0.000025	0.006	0.4
RO-1 at pH 6	0.0104	0.000024	0.006	0.384
RO-1 at pH 7	0.0104	0.000025	0.006	0.392

**Table A-8** Permeate water flux of NF-1 and RO-1 membranes at pH 7 in groundwater from Pra Too Khong, Lamphun province Thailand at TMP 0.375 MPa

conditions	sampling time (day)	volume(m <sup>3</sup> )	area ( m <sup>2</sup> )	flux(m <sup>3</sup> /m <sup>2</sup> ×day)
NF-1 at pH 7	0.0055	0.00003	0.006	0.93
RO-1 at pH 7	0.0188	0.00003	0.006	0.27



## Appendix B

The mass transfer coefficient ( $k$ )

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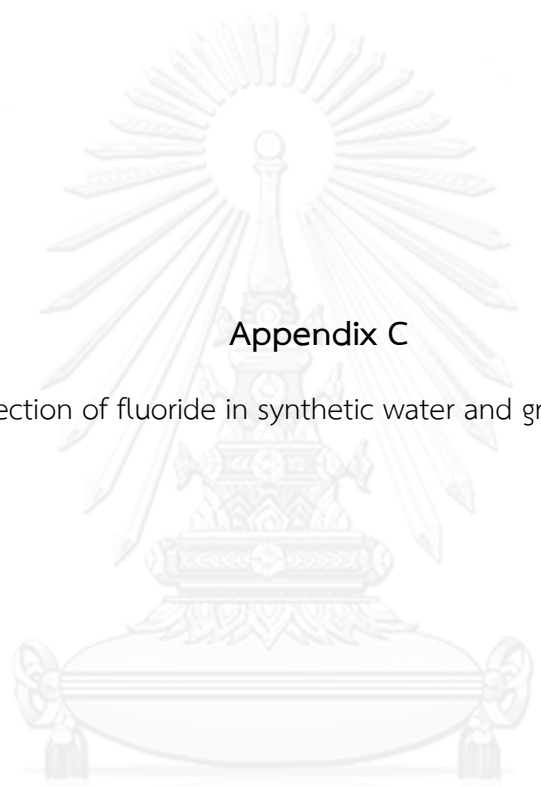


**Table B-1** Calibration curve to convert the concentration unit from electroconductivity ( $\mu\text{s}$ ) to Molar

NaF (M)	Electroconductivity ( $\mu\text{s}$ )
0.004	284
0.006	409
0.008	539
0.01	679
0.02	1244
0.04	2510
0.06	3740
0.08	4900
0.1	6030
0.12	6910
0.14	7910

**Table B-2** The calculating data mass transfer coefficient of NF-1 membrane at transmembrane pressure 0.375 MPa

Feed solution		Concentrated solution			Permeate solution			$\Delta \pi$	Flux ( $\text{m}^3/\text{m}^2$ $\times \text{day}$ )
EC ( $\mu\text{s}$ )	(M)	EC ( $\mu\text{s}$ )	M	$\pi_B$ (Mpa)	EC ( $\mu\text{s}$ )	M	$\pi_P$ (Mpa)	$\pi_B - \pi_P$ (Mpa)	
6030	0.103	6070	0.104	0.258	2750	0.045	0.111	0.147	0.576
3160	0.052	3210	0.053	0.132	827	0.011	0.026	0.105	0.768
711	0.008	745	0.009	0.023	90.3	0.001	0.003	0.02	1.296



Appendix C

Rejection of fluoride in synthetic water and groundwater

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**Table c-1** Data analysis of fluoride rejection on NF-1 and RO-1 membranes, pH solution and concentration of fluoride in synthetic water at TMP 0.375 MPa were measured by IC

Conditions	solutions	pH	Fluoride concentration (mg/l)	% Rejection of fluoride
NF-1 (pH 5)	feed	4.82	9.1577	81.73
	permeate	5.56	1.8435	
	concentrate	5.31	10.0887	
NF-1 (pH 6)	feed	5.90	10.8560	86.3
	permeate	6.18	1.5442	
	concentrate	6.26	11.2718	
NF-1 (pH 7)	feed	6.94	10.3587	91.36
	permeate	5.2	0.9727	
	concentrate	5.47	11.2567	
RO-1 (pH 5)	feed	4.97	10.3187	90.00
	permeate	5.89	1.1441	
	concentrate	5.74	11.4435	
RO-1 (pH 6)	feed	5.85	10.0664	92.95
	permeate	5.94	0.8065	
	concentrate	6.05	11.4367	
RO-1 (pH 7)	feed	7.11	11.2828	98.84
	permeate	4.68	0.1362	
	concentrate	5.09	11.7337	

**Table c-2** Data analysis of fluoride rejection on NF-1 and RO-1 membranes, pH solution and concentration of fluoride in groundwater water Groundwater from Pra Too Khong, Lamphun province Thailand at TMP 0.375 MPa by IC

Conditions	solutions	pH	Fluoride concentration (mg/L)	% Rejection of fluoride
NF-1 (pH 7)	feed	7.02	15.3363	80.69
	permeate	5.49	3.0175	
	concentrate	5.36	15.6282	
RO-1 (pH 7)	feed	7.15	15.0062	89.69
	permeate	4.92	1.5743	
	concentrate	5.11	15.2745	



Appendix D

Kinetic adsorption experiment data

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**Table D-1** Data of fluoride concentration under pH 7, which adsorbed by dolomite sorbent

Time (min)	Initial F <sup>-</sup> Concentration (C <sub>0</sub> ) (mg/L)	F <sup>-</sup> Concentration at time t (C) (mg/L)	Amount of F <sup>-</sup> adsorbed on dolomite (q) (mM/g of dolomite)
10	15.6282	15.3433	0.000149947
30	15.6282	15.2793	0.000183632
60	15.6282	15.1084	0.000273579
180	15.6282	14.9269	0.000369105
360	15.6282	14.66	0.000509579
720	15.6282	14.5238	0.000581263
1440	15.6282	14.5294	0.000578316

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