REDUCTION OF CHLORIDE IN RAW WATER BY NANOFLTRATION AND REVERSE OSMOSIS

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Abstract. This research is aimed at determining the reduction of chloride in the raw water of a water supply plant using nanofiltration and reverse osmosis. Raw water was prepared by adding NaCl at the concentrations of 300 and 600 mg/L. This work used a PACl at 15 mg/L as the pre-treatment for removing turbidity and DOC. Coagulated water was filtered with GF/C filter as the filtration process for minimizing membrane blockage. At chloride concentrations of 300 and 600 mg/L, the flux values were in the range of 66.7-70.0 and 62.8-65.0 L/m²-h for NF-270 and 17.2-20.6 and 18.3-20.8 L/m²-h for TW-30, respectively. The performance capabilities of NF-270 and TW-30 for reducing chloride were significantly different. NF-270 and TW-30 membranes were able to reduce chloride by 67% and 92% at the added dose of 300 mg/L, respectively. At the added amount of 600 mg/L, NF-270 and TW-30 membranes could reduce chloride by 63% and 85%, respectively. In the case of chloride in raw water at a concentration lower than 600 mg/L, the nanofiltration is suitable for removing chloride in regards to the low operation costs compared with the reverse osmosis. Nanofiltration could reduce chloride to lower concentration levels than the water supply standards of the Provincial Waterworks Authority.

Keywords: Chloride, Nanofiltration, Reverse osmosis, Surface water, Water supply

1. Introduction
Chloride naturally occurs as the major anion found in all-natural waters. It is the most abundant ion in seawater, with a concentration greater than 19,000 mg/L [1]. Salt or sodium chloride (NaCl) intake can lead to the condition known as salt poisoning, salt toxicity, hypernatremia, or water deprivation–sodium ion intoxication. Increased chloride concentrations in some environments have killed off native vegetation and allowed invasive salt-tolerant species to thrive [2]. Chloride is corrosive to steel, thus it may corrode pipes in water treatment and industrial plants. Because it imparts a salty taste to water and is corrosive, elevated chloride levels in drinking water supplies can lead to increased treatment costs. [3,4]. The U.S. Environmental Protection Agency (USEPA) recommends a chronic criterion for aquatic life of a four-day average chloride concentration of 230 mg/L with an occurrence interval of once every three years [5]. The recommended acute criterion is 860 mg/L, which relates to a one-hour average concentration with a recurrence interval of less than once every three years [5]. In Thailand, the water supply standard for chloride concentration of the Provincial Waterworks Authority.
(PWA) for consumption is 250 mg/L, but in areas of the world with water scarcity, drinking water can have considerably greater concentrations of chloride [6]. The main methods of desalination or chloride removal include thermal processes, such as distillation, electrodialysis, and membrane processes, such as reverse osmosis (RO). RO is the finest of all membrane filtration systems, with extremely small pores capable of removing particles as small as 0.1 nm. It is a process in which both dissolved organic matter, salts, and bacteria are removed from water using a different mechanism from distillation, ion exchange or activated carbon processes [7].

Chloride removal from seawater by the reverse osmosis process indicates the efficiency and applicability of RO technology [8,9]. However, due to the fine membrane construction, reverse osmosis not only removes contaminants present in the raw water, it also removes many of the desirable minerals from the raw water. Some researchers have been studying the long-term health effects of drinking demineralized water [10-12]. The NF membrane is a relatively recent technology that was developed mainly for potable water generation. NF delivers coarser filtration than RO, with the ability to remove particles as small as 0.002 to 0.005 µm in diameter. NF can remove harmful contaminants, such as pesticide compounds and organic macromolecules [13]. Nowadays, nanofiltration membranes have been used in the pretreatment of brackish water desalination worldwide due to their remarkable abilities to selectively reject different dissolved salts and provide high water flux at low operating costs and low energy consumption [14].

The U-Tapao Canal is the raw water source that produces the water supply for utility in the area of Songkhla province, Thailand. This canal receives wastewater and treated wastewater from community, agricultural, and industrial activities [15-17]. The Songkhla province area is close to the sea, so during the dry season, the sea level rises above the average level and the freshwater is contaminated by seawater causing chloride content ranges from 50 to 600 mg/l [18]. This research, therefore, focuses on investigating the potential of the NF membrane and RO process to remove chloride from the raw water of the water treatment plant in Songkhla province, Thailand. The challenge is in minimizing the operational costs and energy consumption as well as improving the quality of the water supply.

2. Material and methods

2.1 Materials and chemicals

Raw water samples were collected from the pumping station of the water treatment plant (WTP), Songkhla, Thailand, that is located adjacent to the U-Tapao Canal. The raw water samples were collected in November 2019. All samples were stored below 4ºC until analysis and experiments were conducted. For the study of chloride removal, raw water was prepared by adding NaCl (99.99%) at the concentrations of 300 and 600 mg/L. In regards to membrane technology, this work focused on the mass transfer in the crossflow filtration process using two types of membrane which are NF-270 for nanofiltration membrane and TW-30 for reverse osmosis. All the properties of the membranes according to the manufacturers are shown in Table 1.

| Properties                        | NF-270          | TW-30           |
|-----------------------------------|-----------------|-----------------|
| Manufacturer                      | DOW/Filmtec     | DOW/Filmtec     |
| Water permeability (L m⁻² h⁻¹ bar⁻¹) | 13.5            | 2               |
| Molecular weight cutoff (Daltons)  | 170 to 300      | 100             |
| Contact angle (°)                  | 55.0            | Not available   |
| Zeta potential (mV)               | -19             | -20.6           |

Table 1. Properties of nanofiltration (NF-270) and reverse osmosis (TW-30) membranes in this study
2.2 Methods and analysis

2.2.1 Method

This study used polyaluminium chloride (PACl) at 15 mg/L as the pre-treatment for removing turbidity, suspended solids, and dissolved organic carbon (DOC). PACl was used in the coagulation experiments by the use of a jar-test apparatus (JLT leaching test jar-test - VELP scientific). Samples were placed in the jar-test apparatus and coagulants were injected into each of the samples. The jar-test apparatus was set on a rapid mixing speed of 100 rpm for 1 minute, and then on a slow mixing speed of 60 rpm for 8 minutes, 40 rpm for 8 minutes, and 25 rpm for 5 minutes, respectively.

The pH was controlled in the range of 6.8-7.2 by the addition of sodium hydroxide (NaOH) and sulfuric acid (H2SO4). After a 30-min rest period, the supernatant was measured for its turbidity and color. Coagulated water was filtered through a GF/C filter as the filtration process for minimizing membrane blockage. Then, the chloride was removed from the filtered water by the use of NF-270 and TW-30 membranes, operating at a 4 bar pressure and this was carried out for 8 hours. All experiments were conducted in triplicate.

2.2.2 Analysis

The physical and chemicals properties of the raw water were analysed following standard methods. The pH was directly measured using a HACH pH meter (accuracy of ±0.01pH unit). Alkalinity was determined following the standard method 2320 B (Titration method). Turbidity and color were measured by a turbidity meter (HACH, 2100 N) and a Genesys 10S UV/VIS spectrophotometer (Thermo Electron Corp. Madison, WI, USA). The chloride content was analyzed by the argentometric method following the standard methods for the examination of water and wastewater, APHA, AWWA & WEF, 23rd Edition, 2017[19]. DOC in water samples was determined by a combustion method (Standard Method 5310D) using a total organic carbon analyzer (TOC-V CSN, Shimadzu, Japan) [20].

3. Results and Discussion

3.1 Characteristics of raw water supply

The characteristics of the raw water from the pumping station at the U-Tapao canal in the rainy season are presented in Table 2. The pH value of raw water was close to neutral (6.8 ± 0.2). It can be stated that the pH of the raw water is suitable for coagulation process. Color and DOC values of 39 ± 3 Pt-Co and 3.9 ± 0.1 mg.C/L were determined for this sample. Turbidity is a significant parameter for representing the quality of a raw water supply. In this study, the turbidity was 34 ± 2 NTU. This was higher than 5 NTU and not adequately clear enough to allow for distribution to the public. The conventional process, which commonly consists of coagulation and filtration, is necessary in this case for removing turbidity as pre-treatment for minimizing membrane blockage before using membrane technology. Color, turbidity, and DOC in this work were higher than Provincial Waterworks Authority (PWA) standard [6] and results of other researchers [15,22]. This indicated that the characteristics of raw water in the canal varied according to the time of sampling. In regards to the characteristics of raw water, the water treatment plant must reduce the turbidity and color to be lower than the drinking water standards of 4 NTU and 15 Pt-Co, respectively [16]. Iron, manganese, and chloride content were detected in the raw water at 3.3 ± 0.2, 1.1 ± 0.6, and 19.6 ± 0.8 mg/L, respectively. This study is focused on chloride removal from raw water supply by membrane
technology, therefore, raw water was prepared by adding NaCl at the concentration of 300 and 600 mg/L.

**Table 2. Characterization of raw water**

| Parameters | Units       | Results    |
|------------|-------------|------------|
| pH         | -           | 6.8 ± 0.2  |
| Color      | Pt-Co       | 39 ± 3     |
| Turbidity  | NTU         | 34 ± 2     |
| DOC        | mg C/L      | 3.9 ± 0.1  |
| Alkalinity | mg/L        | 22 ± 0.2   |
| Chloride   | mg/L        | 19 ± 0.8   |
| Iron       | mg/L        | 3.3 ± 0.2  |
| Manganese  | mg/L        | 1.1 ± 0.6  |
| Total Hardness | mg/L as CaCO₃ | 190 ± 5 |

3.2 **Effect of chloride content on the flux of NF-270 and TW-30 membranes**

This study looked at flux as a function of time using DI water as a feed solution of NF-270 and TW-30 membranes at a pressure of 4 bars. The DI water flux of NF-270 and TW-30 membranes were in the range of 69.4 to 73.9 L/m²-h and 29.4 to 33.9 L/m²-h, respectively. Then, the flux values of raw water containing various contents of chloride using NF-270 and TW-30 membranes were tested, and are shown in Figure 1 and 2. DI water (DI), raw water (RW), raw water and chloride at 300 and 600 mg/l (RW+Cl300 and RW+Cl600) were used as the feed solution.

![Figure 1. Flux as a function of time using DI water, raw water, and raw water with added NaCl as a feed solution of NF-270 membrane](image-url)
In the case of NF-270, and raw water containing chloride content at 19, 300, and 600 mg/L, the flux values were in the range of 69.4 to 71.7, 68.3 to 70, and 62.8 to 65 L/m²-h, respectively. When testing using the TW-30 membrane, the flux values were in the range of 25 to 30, 17.2 to 20.5 and 18.3 to 20.8 L/m²-h, respectively. This indicated that the flux value of both systems is directly related to the initial content of chloride. This can be attributed to the raw water containing a high content of chloride which caused clogging. However, the results indicated that the flux value of the nanofiltration system was higher than the reverse osmosis system.

### 3.3 Reduction of chloride and efficiency of NF-270 and TW-30 membranes

Figure 3 shows the chloride content in raw water after using the NF-270 and TW-30 membranes at a pressure of 4 bars for 8 hours. For the NF-270 membrane, and initial concentration of chloride at 19, 300, and 600 mg/L, the chloride content in the raw water was 7.7, 97, and 214 mg/L, respectively. For the TW-30 membrane, and the initial concentration of chloride at 19, 300, and 600 mg/L, the chloride content in raw water was 6.3, 25, and 90 mg/L, respectively.
Figure 3. Reduction of chloride at various initial concentrations using NF-270 and TW-30 membranes

All the results showed that the chloride content in the raw water was lower 250 mg/L after using the NF-270 and TW-30 membranes which is lower than the water supply standard of the Provincial Waterworks Authority, Thailand for consumption [6].

In the comparison of chloride removal efficiency between the NF-270 and TW-30 membranes, the results indicated that the initial chloride concentrations at 300 and 600 mg/L, the chloride removal efficiency of the NF-270 was 67 and 63%, respectively. For TW-30, and the initial chloride concentrations at 300 and 600 mg/L, the chloride removal efficiency was 92 and 84%, respectively. The efficiency of chloride removal of the TW-30 is higher than the NF-270 membrane and the performance capability of TW-30 and NF-270 for reducing chloride was significantly different. Comparing the results obtained from this study and other research (Table 3), it was found that the nanofiltration membrane (NF-270) had the potential to eliminate chloride from water. The flux and efficiency of a nanofiltration membrane depended on the type and pressure in operation.

Table 3. Flux and Efficiency of NF270 membrane at various water sources and conditions

| Source of water | Type of membrane | Initial Chloride Conc. (mg/L) | Flux (LMH) | % Removal | Pressure (bar) | References |
|-----------------|------------------|-----------------------------|------------|-----------|---------------|------------|
| Surface water   | NF270            | 300                         | 71.7       | 66.9      | 4             | This work  |
|                 |                  | 600                         | 70.0       | 62.5      |               |            |
| Synthetic water | NF270            | 1000                        | 113        | 59.1      | 10            | Shin et al., 2020 [23] |
|                 | RO               |                             | 170        | 99.8      |               |            |
| Pure water      | NF270            | 1000                        | 76         | 47.1      | 6             | Chu et al., 2020 [24] |
| Seawater        | NF270            | 5000                        | 50.2       | 2.3-10.9  | 2             | Hilal et al., 2005 [25] |
|                 |                  | 10000                       | 66.5       | 11-29     | 9             |            |
| Seawater        | NF270            | 60000                       | 80         | 19-25     | 5             | Istirokhatun et al., 2018 [26] |
For the application purpose, the Tha Chin River is the main surface water source for water supply plant in Thailand. There are 9 monitoring station and reported that salinity did not change from 2012 to 2014, the while salinity increase significantly between 2015 to 2016.[27] This may affect the growth of some economic plants and the raw water of the water supply plants. Therefore, the results of chloride treatment by using nanomembranes obtained from this research and previous research confirms that the nanofiltration (NF-270) is suitable for removing chloride in the Tha Chin River and other water surface sources of Thailand.

4. Conclusion
This research shows that it is feasible to use nanofiltration membranes (NF-270) as reverse osmosis (TW-30) to reduce the chloride content from a raw water supply and the results can be concluded as follows:

- At chloride concentrations of 300 and 600 mg/L, the flux values were in the range of 66.7-70.0 and 62.8–65.0 L/m²-h for NF-270 and 17.2–20.6 and 18.3-20.8 L/m²-h for TW-30, respectively.
- NF-270 and TW-30 membranes were able to reduce chloride by 68 % and 92 % at the added dose of 300 mg/L, respectively.
- NF-270 and TW-30 membranes were able to reduce chloride by 63 % and 85 %, at the added dose of 300 mg/L, respectively.
- In the case of chloride concentrations lower than 600 mg/L in raw water, nanofiltration is suitable for removing chloride.

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