



# Application of Submerged Nanofiltration Membrane for Treating Natural Organic Matter from Reservoir Water

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## Abstract

Surface water quality continues to be compromised by expanding residential and industrial activities. Chlorine is widely used in conventional treatment systems due to its low cost and availability; however, its reaction with natural organic matter (NOM) generates disinfection by-products (DBPs), particularly trihalomethanes, which are known as human carcinogens. Despite the increasing interest in nanofiltration (NF) membranes, studies on the application of submerged NF systems for treating real surface water without pretreatment remain limited, especially regarding trihalomethane precursor removal, ion rejection, and permeate stability. Comparative data with conventional treatment systems is also insufficient. This study investigates the performance of a submerged NF membrane relative to a conventional treatment system in a previous study for NOM removal. Water samples were collected every three days from Ang Kaew Reservoir, and the NF system was operated at a constant flux of 11 L/m<sup>2</sup>·h. All samples were analyzed at the Environmental Engineering Laboratory, Chiang Mai University. The NF membrane achieved significant reductions in turbidity (93-98%), electrical conductivity and total dissolved solids (36-65%), UV254 (74-89%), dissolved organic carbon (68-80%), and trihalomethane formation potential (66.54%). In contrast, the conventional system exhibited limited ion removal and, in some cases, increased ion concentrations. These results indicate that submerged NF membranes offer superior ion rejection and effective control of DBP precursors, demonstrating their potential for producing high-quality drinking water from surface water under stable operating conditions.

**Keywords :** disinfection by-products; nanofiltration; natural organic matter; submerged membrane; trihalomethanes

## Introduction

The demand for tap water is continuously increasing. Additionally, water contamination problems are exacerbated by the ongoing expansion and development of urban housing, industrial activities, and surface runoff. Therefore, effective water management is essential to maintaining water quality. In conventional treatment systems, chlorine is commonly used as a disinfectant. However, DBPs are formed when chlorine reacts with NOM present in the water. These DBPs are considered carcinogenic and may pose significant risks to human health. Among the most concerning DBPs are trihalomethanes (THMs) [1]. Potential health risks associated with DBPs include congenital abnormalities, early pregnancy loss, and an increased incidence of bladder cancer. DBPs have been identified in association with the use of the four primary disinfectants—chlorine, chloramines, ozone, and chlorine dioxide—as well as with newer disinfection technologies such as ultraviolet treatment followed by post-chlorination [2, 3]. Sriboonnak et al. [4] reported that the maximum concentration of THMs detected was 189.52  $\mu\text{g/L}$  at the point following sodium hypochlorite disinfection in a conventional water treatment system. The World Health Organization (WHO) sets guideline values for each trihalomethane compound to lower the long-term health risks of drinking water. According to WHO guidelines, the recommended values are 300  $\mu\text{g/L}$  for chloroform (CF), 100  $\mu\text{g/L}$  for bromoform (BF), 100  $\mu\text{g/L}$  for dibromochloromethane (DBCM), and 60  $\mu\text{g/L}$  for bromodichloromethane (BDCM). WHO emphasizes that these values should not be combined into a single “total THMs” limit because each compound has different toxicological characteristics. Instead, WHO recommends assessing cumulative risk by calculating the ratio of the measured concentration of each compound to its respective guideline value and summing these ratios. The total must not exceed 1 for the water to be considered safe for consumption [1].

Previous studies have highlighted that the removal of DBP precursors, such as NOM, is a critical step in minimizing the formation of THMs and haloacetic acids

(HAAs). Techniques including enhanced coagulation, granular activated carbon adsorption, and membrane filtration have been widely investigated for their effectiveness in precursor removal [5, 6]. Alternative disinfection strategies, such as ozone, chloramines, or ultraviolet treatment followed by post-chlorination, can reduce the formation of certain DBPs, yet they may also generate new by-products with potential toxic effects [2]. Although membrane technologies, particularly NF membranes, have demonstrated strong performance in reducing DBP precursors, most studies have been conducted under controlled laboratory conditions or using pressurized NF systems, with limited evidence from submerged NF systems treating real surface water sources [7, 8]. In addition, long-term operational data regarding permeate stability, fouling behavior, cleaning frequency, and ion rejection under variable raw water conditions are scarce. These limitations indicate a clear knowledge gap: there is a need for comprehensive field-based studies to evaluate the effectiveness, reliability, and operational feasibility of submerged NF membranes in minimizing DBP formation in actual surface water treatment scenarios, particularly in regions with variable water quality and limited treatment infrastructure.

NF membranes have a wide range of applications, with wastewater treatment and drinking water production being among their primary uses. NF membranes are versatile and can be employed to treat various water sources, including groundwater, surface water, and wastewater. Additionally, they are often utilized as a pre-treatment step in seawater desalination processes, enhancing overall system efficiency and membrane lifespan [9]. The widespread application of membrane technologies has contributed significantly to the reduction of particulate matter and NOM concentrations in drinking water. The effectiveness of these membrane-based treatments depends on several factors, including membrane type, physicochemical properties, module configuration, operating conditions, and overall system efficiency [10]. Particulate and dissolved pollutants, such as synthetic organics, salts, hardness, pathogenic

bacteria, and DBP precursors, are effectively eliminated by NF membranes. Additionally, in terms of regulating dissolved organic matter (DOM), membrane separation competes with other cutting-edge treatments like granular activated carbon when used in conjunction with the current water treatments. Additionally, membrane separation is competitive in the economy of the future because of the ensuing technological advancements [11]. Sentana *et al.* [12] reported that the amounts of DBPs in natural waters decreased when NF membranes were used. Three commercial NF membranes—models NF270, NF90 (Dow Chemical Inc.), and Desal-HL-51 (GE Water)—have been used to investigate the manufacturing potential of trihalomethane and haloacetic acid (THMFP and HAAFP). The NF90 membrane reduced more than 90% of the possibility of generating DBCM and BDCM. The NF270 and Desal-HL-51 membranes decreased less THMFP. A submerged membrane system is used to separate suspended particles, microbes, and other contaminants. The operation of a submerged membrane system involves submerging the membrane module directly into water. The submerged membrane technology takes far less space than the conventional treatment system. Additionally, this system has outstanding fouling resistance [13]. This study aimed to evaluate the efficiency of a submerged NF membrane, operated without any pretreatment, in reducing THMFP to produce clean water with minimized health risks.

## Materials and Methods

### Experimental protocols

Water samples were collected from Angkaew Reservoir every three days over a two-week experiment period. The samples were subsequently analyzed for physical and chemical characteristics at the Department of Environmental Engineering, Chiang Mai University. The laboratory-scale was operated at a constant permeate flux of approximately 11 L/m<sup>2</sup>.h and maintained at a feed temperature of 20 °C. Daily, 200 mL of permeate was collected and immediately analyzed for water quality parameters. Dissolved organic carbon (DOC) analysis was performed on a weekly

basis, with samples stored under refrigeration until analysis. The THMFP was analyzed once during the experiment. Membrane cleaning was carried out every six days by gently scrubbing the membrane surface with a sponge prior to initiating a new experimental cycle. The specific ultraviolet absorbance (SUVA) was determined to assess the aromaticity of DOM in water samples. SUVA was calculated using the following equations:

$$SUVA = \frac{UV254 (1/cm)}{DOC(mg/L)} \times 100 \quad \text{Equation 1}$$

### Analysis

The electrical conductivity (EC) and total dissolved solids (TDS) were measured using a portable conductivity analyzer (Starter 300C, OHAUS Corporation, USA). Every sample underwent turbidity analysis (Merck, Turbiquant 1100 IR, Sigma-Aldrich Canada Co., or Millipore (Canada) Ltd., Canada). A 0.45-micron nylon membrane filter was used to pre-filter each sample. A TOC analyzer was used to measure the DOC (Multi N/C 3100, Analytikjena, Germany, Standard Method 5310). A UV/VIS spectrophotometer (Lambda365, Perkin Elmer, Perkin Elmer Inc., Boston, MA, USA, Standard Method 5910B) was also used to measure the sample's ultraviolet absorbance at 254 nm (UV254). Chlorination of the raw water and permeate was performed in amber glass bottles at target doses of 10.28 mg/L and 2.85 mg/L, respectively. The chlorinated samples were then stored in the dark for 24 hours. The concentration of free chlorine was determined in accordance with standard methods [14] and maintained in the range of 1-2 mg/L during the experiment to ensure that sufficient residual chlorine remains in the system to completely react with the organic matter. The amount of THMs was determined by adding 5.0 g of sodium sulfate anhydrous to 25 mL of the sample solution in 40 mL amber vials. After that, the mixture was vigorously agitated to create a uniform mix. A 2.5 mL solution of tert-butyl methyl ether (MTBE) was added, and the mixture will be extracted for three minutes. The top layer of MTBE was used for concentration analysis via gas chromatography spectrometry (GC) with an electron capture detector (ECD) system (Agilent 4890D (EPA

551.1)). The GC column uses a VF-X fused silica capillary column (30 m × 0.32 mm × 0.1 micron), and helium was used as a carrier gas. Samples were injected into split mode (5:1) at 200 °C. The oven was programmed from 45 °C to 130 °C at 5 °C/min. The ECD was maintained at 250 °C with nitrogen makeup gas at 45 mL/min. Standard THM solutions in methanol were used for calibration.

### Nanofiltration membrane and module

This study employed the NF270 membrane (DuPont/FilmTec, Midland, MI, USA), with a total effective filtration area of 56 cm<sup>2</sup>. The membrane was operated in a submerged configuration using an outside-in filtration mode. Initially, the pure water flux was determined by filtering deionized water through the submerged NF270 membrane. Subsequently, the collected water samples were analyzed and subjected to the filtration process. The membrane system is installed as shown in **Figure 1**.

## Results and Discussion

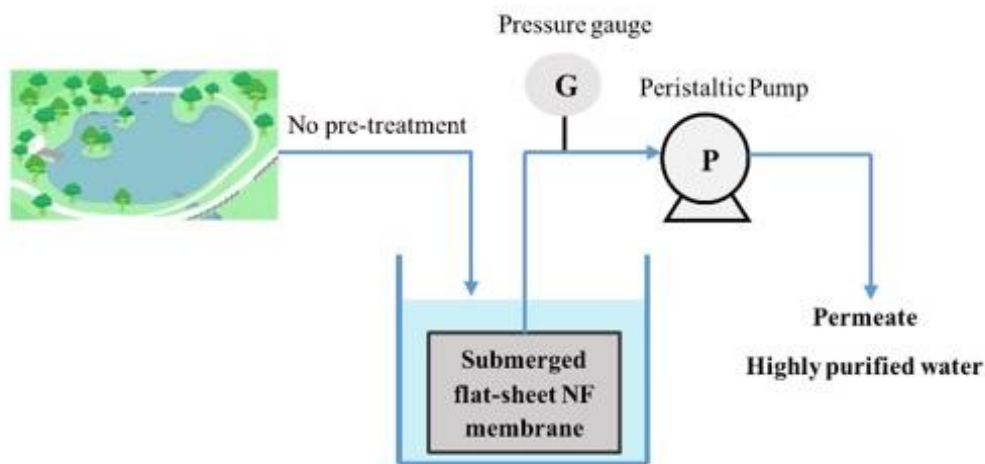
### Membrane Properties

The NF270 membrane (DuPont/Filmtec, USA) is a thin-film polyamide NF membrane that removes solutes via size exclusion and electrostatic interactions [15]. Its active layer contains carboxylic and amine groups and

exhibits characteristic polyamide absorption peaks [16, 17]. NF270 is hydrophilic (contact angle ~27–30°), which enhances water permeability and reduces organic fouling [18, 19]. It remains negatively charged across pH 2–10, lacking an isoelectric point in this range [20].

### Quality of water in reservoir

The pH values of the water samples fell within the neutral range, between 7.5 and 8.5. The raw water quality parameters are summarized in **Table 1**. While the EC and TDS of the raw water were within acceptable limits, its turbidity exceeded the standard threshold. The concentration of DOC was measured at 3.55 mg/L, and the UV254 was 0.0947 cm<sup>-1</sup>. The SUVA index was calculated by dividing the UV254 absorbance value by the DOC concentration and multiplying the result by 100 [21]. The SUVA value below 2 L/(mg·m) typically indicated that the organic matter is predominantly composed of aliphatic hydrocarbons or non-humic substances with low hydrophobicity. In contrast, a SUVA value above 2 L/(mg·m) suggests the presence of hydrophobic and hydrophilic NOM, aromatic hydrocarbons, or aquatic humic substances [22]. The calculated SUVA value for this water source was 2.66 L/(mg·m), indicating that the organic matter present was primarily humic in nature, with a significant proportion of aromatic hydrocarbon structures.



**Figure 1** Experimental setup

**Table 1** Characteristics of a water source

Parameters	Unit	Value	Standard*
pH	s.u.	8.48 ± 0.48	6.5-8.5
EC	μS/cm	141.0 ± 5.30	<500**
TDS	mg/L	70.3 ± 2.54	<600
Turbidity	NTU	11.36 ± 1.62	<4
UV254	cm <sup>-1</sup>	0.0947 ± 0.01	-
DOC	mg/L	3.55 ± 0.22	-

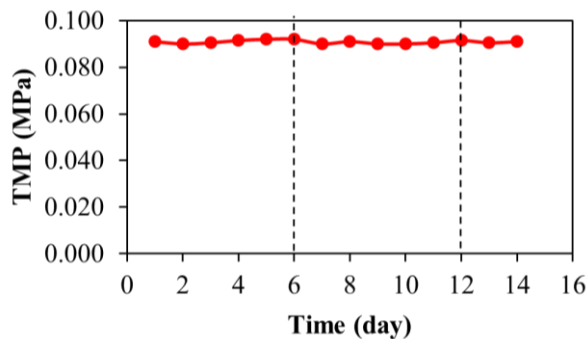
\*Water supply quality standard in Thailand

\*\*Guidelines of Drinking Water Quality, 4<sup>th</sup> ed.; World Health Organization (WHO)

**Operational stability**

Minimal fouling occurred during the experiment when surface water was directly treated using NF at a low permeate flux, resulting in a slight increase in transmembrane pressure (TMP) from 90 to 92 kPa (**Figure 2**). Following membrane cleaning, the TMP exhibited a modest decrease, indicating that the system operated in a relatively stable manner throughout the experiment. The cleaned membrane was subsequently reused for further experiments, confirming that the cleaning procedure effectively restored membrane performance without compromising rejection efficiency.

In the previous study, Fujioka *et al.* [13] indicated that the TMP increased from 35 to 37 kPa. Given that many of Thailand's water sources are characterized by high concentrations of organic matter and turbidity, the relatively high TMP observed in this study is not unexpected. Nonetheless, the TMP increase of approximately 2 kPa observed in both studies suggests that the low and stable permeate flux operation was a key factor contributing to this moderate fouling. Despite variations in the quality of the water sources, the system demonstrated consistent performance throughout the experiment.



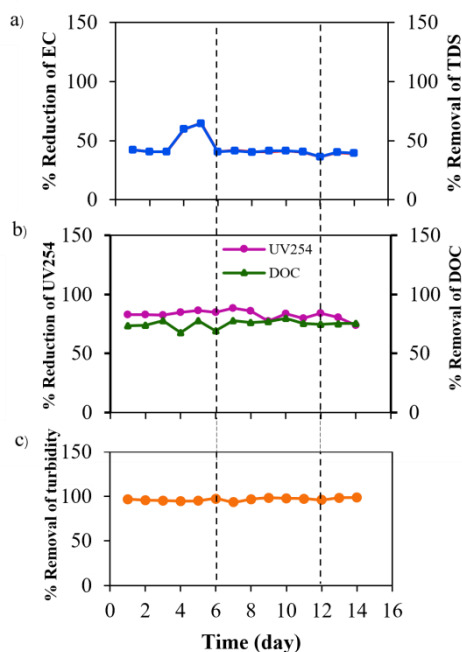
**Figure 2** TMP changes when the reservoir is treated with NF at low permeate flux

The UV254 and DOC results are presented in **Figure 3b**. The submerged NF membrane system demonstrated a high efficacy in rejecting organic compounds, with removal efficiencies ranging from 74% to 89%. This rejection corresponded to organic molecules, such as aromatic hydrocarbons and compounds containing double bonds, as inferred from the characteristics of the raw water. Throughout the operation, the NF membrane was effective in rejecting organic materials with a molecular

weight cut-off (MWCO) between 200 and 1000 Da [24]. Consequently, the accumulation of organic matter in the feed tank increased over time. Furthermore, the permeate quality remained highly consistent, exhibiting a very low UV254 value. This suggests that the NF270 membrane is effective in rejecting small particles, particularly aromatic and double-bonded molecules. The NF270 membrane demonstrated a substantial DOC removal efficiency ranging from 68% to 80%, indicating its ability to reject certain

organic matter dissolved in the water. The DOC value of the resulting permeate was significantly lower, further supporting the conclusion that DOM are effectively rejected by the NF270 membrane. Additionally, the SUVA index decreased from 2.66 to 1.87 L/(mg·m), reflecting a reduction in the concentration of humic substances. Given that humic compounds share characteristics with polyaromatic hydrocarbons in aqueous environments, these results suggest that the NF270 membrane can effectively reject such compounds as well.

The turbidity of the feed water ranged from 9.17 to 13.54 NTU. Throughout the duration of the experiment, the turbidity of the permeate remained consistently low, ranging from 0.20 to 0.76 NTU. The results indicated that the NF270 membrane was highly effective in removing turbidity from surface water, achieving removal efficiencies between 93% and 98% when employed directly, without any pre-treatment (**Figure 3c**). These findings demonstrate that the NF270 membrane is particularly efficient in removing larger particles responsible for turbidity in water sources.



**Figure 3** Membrane efficiency in removing (a) EC and TDS, (b) UV254 and DOC, and (c) turbidity over a period of 14 days

These removal rates are broadly consistent with previous literature, though some differences are evident. For instance, in a nanofiltration study using surface water, the NF270 membrane demonstrated nearly 100% UV254 rejection. Meanwhile, in a study on low-SUVA drinking water [25], Dubowski et al. [26] reported DOC rejection of 86-89% and UV254 reduction of 94-96% for NF270 at various pressures. The higher UV254 and DOC removal in those studies compared to ours may reflect differences in feed composition (e.g., aromaticity, molecular weight distribution of natural organic matter) or operating conditions (such as pressure and recovery). Additionally, while our turbidity removal is very high (93-98%), turbidity is not always reported in the NF270 literature, making direct comparison difficult. Overall, despite some variance, our results confirm that NF270 provides strong removal of organics and particulates and performs reliably in real-water applications, similarly to prior bench- and pilot-scale research.

### THMFP concentrations

THMs comprise four principal compounds: CF, BDCM, DBCM, and BF. The concentrations of total trihalomethanes (TTHMs) detected in this water source are summarized in **Table 2**. Among the DBPs identified, only two THM species—BDCM and CF—were present. The presence of bromide, a key precursor for brominated THMs, is most plausibly attributed to naturally occurring bromine in groundwater. This bromide can migrate upward and mix with surface water, particularly in regions characterized by bromide-rich geological formations or soil strata. [27]. With respect to THMFP, the presence of natural organic matter in water sources plays a critical role in the formation of THMs, as these compounds are produced when organic constituents react with chlorine during the disinfection process. Evaluating THMFP also provides insights into the characteristics of DOM present in the water. Analytical results revealed a TTHMs concentration of 789.73 ppb in the untreated water source. Following treatment with a submerged NF270 membrane, TTHM levels were reduced by 66.54%. Specifically, the

concentrations of CF and BDCM decreased by 51.66% and 84.4%, respectively. Notably, the MWCO of the NF270 membrane exceeds the molecular weights of common THM species (CF = 119.4 g/mol, BDCM = 163.8 g/mol, DBCM = 208.3 g/mol, and BF = 252.7 g/mol), indicating that mechanisms other than size exclusion—such as adsorption or diffusion—may contribute to the observed reductions [28]. Consequently, NF270 removes THMs through the mechanisms of surface adsorption, initial membrane fouling, and gaps between polymer chains [29]. In Thailand, there is currently no explicit national standard for TTHMs in drinking water. Although the Department of Health provides general drinking water quality standards covering various chemical parameters, THMs are not specifically regulated. Some utilities, such as the Metropolitan Waterworks Authority (MWA), refer to the WHO guideline values, using the “sum of ratio” approach to assess compliance and minimize health risks. The overall TTHM ratio for this water source was calculated to be 7.5, which exceeds the recommended safety thresholds. This finding highlights the critical importance of removing NOM from the source water before the chlorination process. By doing so, the formation of THMs during disinfection can be minimized, as NOM plays a key role in the generation of these harmful compounds when chlorine reacts with organic materials in the water.

In the treatment process, the NF270 membrane was used to filter the water, resulting in a permeate with a guideline value (G.V.) of 1.7. While the NF270 membrane effectively reduced the concentration of TTHMs, the G.V. of the treated water remained above the acceptable limit of 1.0. This indicates that, although the treatment significantly lowered the TTHM levels, the water still does not meet the safety standards for direct human consumption. Consequently, further treatment or post-processing would be required to ensure the water is safe for drinking.

### **Comparison between the conventional treatment system and submerged NF system**

Sriboonnak *et al.* [4] indicated that the conventional water treatment systems had an efficiency of removing UV254 and DOC at

74.63% and 58.02%, respectively. The result shows that the efficiency of previous studies is in the same range of removal efficiency as NF, which indicated that NF had higher removal efficiency depending on the water quality. Moreover, Sriboonnak's study showed that the EC in water after conventional treatment increased from 170.0 to 194.7  $\mu\text{S}/\text{cm}$ . The result indicated that the ions in water cannot be eliminated by the conventional treatment system, as shown in **Table 3**. In contrast, the NF system can reject only a small number of ions in the water, even though permeate has a relatively high EC ( $< 88.2 \mu\text{S}/\text{cm}$ ). Furthermore, Sriboonnak's research revealed that the disinfection procedure in the conventional system considerably raised the amount of THMs in the water. NOM and THMFP of water treatment processes were studied by Wong *et al.* (2007) [30]. The results indicated that after water treatment, the MSR plant had a removal efficiency of 44%. On the other hand, the NF system had better efficiency and was successful in lowering THMs by 66.54%. Overall, the findings show that NF is a more successful method than the conventional treatment for removing DOM and ions. Conventional coagulation–sedimentation–filtration (CSF) systems can remove turbidity by 84–95% depending on water quality and operating conditions [31]. However, DOC and UV254 removal are generally lower and more variable. Compared to CSF, NF270 provides more consistent and higher removal of DOC and UV254, and achieves nearly complete turbidity removal, demonstrating its superior ability to improve water quality and control disinfection by-product precursors.

The findings of this submerged NF membrane study consistently demonstrate superior performance in NOM removal and DBP precursor control compared to typical conventional water treatment practices. While conventional systems, typically comprising coagulation-flocculation, sedimentation, and rapid sand filtration, are highly effective in removing suspended solids and turbidity [32, 33], their efficacy in eliminating DOM remains a persistent challenge, particularly for hydrophilic and low molecular weight (LMW)

NOM components [33, 34]. Comparative data from various studies highlights this limitation. Internationally, conventional treatment processes have been reported to achieve total organic carbon (TOC) removal efficiencies averaging around 62.8% [26]. In Thailand, a conventional Water Treatment Plant (WTP) in the southern region showed DOC reductions ranging from 56-56.0% [35]. Even when enhanced coagulation is employed, conventional systems may achieve higher UV254 reductions (up to 89.4% in a South African WTP study [35]) because UV254 primarily measures aromatic/humic substances, which are more readily removed by coagulation than the total DOC [35]. In contrast, the submerged NF270 system used in this research achieved high DOC and UV254 removals ranging from 68-80% and 74-89%, respectively, without the need for chemical pretreatment. The most critical advantage of the NF system is its control over DBP precursors. The limited DOM removal by conventional processes means that the subsequent chlorination step frequently generates high levels of THMs. Studies on chlorinated distribution networks in various Thai

municipalities, such as Chiang Mai and Khon Kaen, have reported total THM concentrations up to 189.52  $\mu\text{g/L}$  [33] and  $\text{CHCl}_3$  concentrations as high as 112  $\mu\text{g/L}$  [36]. This finding confirms the significant risk of THM formation in water treated using conventional methods followed by standard chlorination. Conventional treatment processes, which typically rely on coagulation and chlorination, often leave behind organic materials that can react with chlorine during disinfection, leading to the formation of DBPs such as THMs. The results demonstrate that without adequate removal of these precursors, water treated by conventional methods can pose considerable health risk due to elevated DBP levels. In contrast, the NF270 membrane system achieved a substantial 66.54% reduction in THMFP, offering a strong barrier against the creation of DBPs. This level of performance is comparable to other NF applications, which commonly report THMFP rejections in the range of 70-85% [4]. This confirms the inherent superiority of NF technology over conventional coagulation-based methods for effective DBP precursor control [37].

**Table 2** THMFP in raw water and permeate water

Samples	Species of THMs (ppb)				TTHMs (ppb)
	CF	BDCM	DBCM	BF	
Raw	430.71	359.02	ND <sup>b</sup>	ND <sup>b</sup>	789.73
Permeate	208.19	56.02	ND <sup>b</sup>	ND <sup>b</sup>	264.21
Guideline <sup>a</sup>	300	60	100	100	

<sup>a</sup> Guidelines for Drinking Water Quality, 4th ed.; World Health Organization (WHO)

<sup>b</sup> ND = Not detected, if the concentration was lower than 10 ppb (< 10  $\mu\text{g/L}$ )

**Table 3** Analysis of the differences between conventional treatment systems and the submerged membrane technology

Parameters	Unit	NF270 membrane		Conventional treatment system [4]		Standard*
		Raw	Permeate	Raw	Treated water	
EC	$\mu\text{S/cm}$	138.7	74.1	170.0	194.7	<500**
TDS	$\text{mg/L}$	69.5	37.9	-	-	<600
Turbidity	NTU	10.86	0.32	-	-	<4
UV254	$\text{cm}^{-1}$	0.097	0.0153	0.0800	0.0300	-
DOC	$\text{mg/L}$	3.60	0.79	4.00	2.30	-

Performance data of the conventional system, collected in January 2019

\*Water supply quality standard in Thailand

\*\*Guidelines of Drinking Water Quality, 4<sup>th</sup> ed.; World Health Organization (WHO)



## Conclusions

This membrane system had very high turbidity removal efficiency ( $> 93\%$ ). Even though NF270 membranes also had low efficiency in monovalent ion rejection, causing EC and TDS values to remain high (36-65%). The NF270 membrane is effective in eliminating DOC by 68-80% and can also reduce THMFP by up to 68.48%. In addition, the removal of principal water quality indicators (e.g., UV254) by the NF270 membrane was 74-89%, depending on the water source's quality, which indicates the concentration of humic acid, which has a structure of aromatic rings. When evaluating how well the NF270 membrane system performs in comparison to the conventional treatment system, it was found that conventional treatment methods raise the concentration of certain ions in the water. Consequently, this study demonstrates that, in terms of system performance, when operating steadily, direct surface water treatment using an NF membrane can provide superior water quality. This improvement in water quality not only enhances the safety for consumption but also minimizes the need for additional chemical treatments often required in conventional systems. Therefore, adopting NF membrane technology could significantly benefit communities relying on surface water sources for their drinking water supply. Future studies may conduct further comparative economic studies to determine the cost-effectiveness of using this system to replace the conventional system.

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