

Evolution of Pretreatment Methods for Nanofiltration Membrane Used for Dissolved Organic Matter Removal in Raw Water Supply

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Abstract

Coagulation and microfiltration using polyaluminium chloride (PACl) were investigated as a pretreatment process by nanofiltration to reduce dissolved organic matter in both raw water and treated water at water treatment plants. The dissolved organic matter in the raw water supply may be a precursor of carcinogens produced during the disinfection process. Raw water from pumping stations and treated water from Hat Yai Provincial Waterworks Authority, Songkhla Province, Thailand were used as samples for this study. Fractionation of raw water samples by DAX-8 and XAD-4 resin revealed that they contained hydrophilic, transphilic and hydrophobic groups with hydrophilic the major organic component. PACl coagulation resulted in a higher dissolved organic matter removal than microfiltration techniques. A hybrid coagulation-nanofiltration process was studied. This effectively reduced dissolved organic matter as dissolved organic carbon and UV-254 by 86% and 94% respectively. The hybrid coagulation-nanofiltration process reduced dissolved organic carbons of the hydrophobic group more effectively than the hydrophilic group. Chloroform and bromodichloroform were the two major species of the trihalomethane group produced when raw water reacted with chlorine. The hybrid coagulation-nanofiltration process reduced the trihalomethane formation potential (THMFP) in raw water samples by up to 90%.

Keywords: water supply; coagulation; dissolved organic matter; microfiltration; nanofiltration

1. Introduction

Surface water is the main source of water supply in Thailand. A coagulation process is conventionally used for the removal of contaminants from the raw water before disinfection and distribution. However coagulation does not remove the organic matter, especially dissolved organic matter which serves as a precursor of disinfection by-products (DBPs) when they react with chlorine during the disinfection process. Some of these DBPs such as haloacetic acids (HAAs) and trihalomethanes (THMs) are carcinogenic substances. Natural organic matter, especially dissolved organic matter is released both by nature in ecological systems and also from human activities. Dissolved organic matter is defined as the complex matrix of organic material commonly present in natural water bodies. This can be separated into humic and non-humic fractions. The humic

substances consist of amino acids, sugars, aliphatic acids and a large number of organic molecules (Marhaba *et al.*, 2003), while non-humic substances consist of hydrophilic acids, proteins, amino acids, carbohydrates, carboxylic acids and hydrocarbons (Owen *et al.*, 1993). Trihalomethanes have been identified as potential adverse health agents by the U.S. Environment Protection Agency (USEPA) which proposed the drinking water standard under the DBPs rule with a maximum contaminant level of 0.04 mg/L. Trihalomethanes are usually measured as the summation of four methane derivatives including chloroform (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform (TBM) concentrations. The reaction of organic matter with chlorine can be expressed as follows (Marhaba and Washinton, 1998), Organic matter + free chlorine ---> THMs + HAAs + HANs + cyanogen-halides + other DBPs, where HANs are haloacetonitriles.

The coagulation process not only reduced the suspended solids and turbidity in the water, but also reduced the natural organic matter (USEPA, 2009). However it did not eliminate all the organic molecules in the water, removing mainly the hydrophobic organic group. The hydrophilic organic group still remained in the water after the coagulation process. Hybrid or combined coagulation processes were conducted and reported by other researchers, including adsorption by activated carbon and the use of other coagulant aids and membrane processes that became widely used in water treatment (Kim and Yu, 2005; Inthanuchit, 2009; Suksaroj *et al.*, 2009; Ohno *et al.*, 2010; Choi *et al.*, 2013). Dissolved organic matter was effectively removed during filtration by ultrafiltration and nanofiltration membranes and required relatively low pressure (Yoon *et al.*, 2005; Sari *et al.*, 2013). During the last decade the removal of dissolved organic matter from ground and surface water for drinking water production was increasingly carried out using nanofiltration membranes (Gorenflo *et al.*, 2003). Previous coagulation treatment hybrid processes improved dissolved organic matter removal and decreased the resistance of membranes. To optimise the nanofiltration process and reduce the dissolved organic matter appropriate pretreatment processes were assessed and selected. When flocculation and adsorption were used as pretreatment prior to membrane filtration, membrane fouling was significantly reduced. The dissolved organic matter removal mechanisms not only operated by pore size exclusion, but also utilised other separation mechanisms, including adsorption onto the membrane surface and adsorption onto particles in the cake layer and sieving. These resulted in physical constrictions of the membrane pores due to irreversible fouling (Jacangelo *et al.*, 1997). The U-Tapao Canal is the main canal of the Songkhla Lake basin in southern Thailand. It originates from the Sankarakiri and the Khao Ban Thad Mountain Ranges in Songkhla Province and has a total length of 130 kilometres. It is the main raw water source for water supply serving four districts including Hat Yai. It can be contaminated by dissolved organic matter from the natural degradation of organic substances within the ecological system, by the manufacturing processes of various industries along its length and by agriculture upstream. This paper therefore emphasised the use of coagulation or microfiltration as a pretreatment prior to the nanofiltration membrane process and

investigated possible dissolved organic matter reduction in the raw water supply. Only their dissolved organic removal efficiencies were determined in order to find feasible technique to reduce fouling in nanofiltration membrane. The sampling point was selected at the pumping station of a water treatment plant operated by the Hat Yai Provincial Waterworks Authority, Songkhla Province, Thailand.

2. Materials and Methods

2.1. Raw water

The raw water supply from Pumping Station, Hat Yai Provincial Waterworks Authority (UTM 661975 772906) was sampled during both the rainy and dry seasons of southern Thailand and preserved at 4°C.

2.2. Coagulation-microfiltration process for pretreatment

Two different techniques, the polyaluminium chloride (PACl) and microfiltration process were used as pretreatment prior to the nanofiltration process. They were compared for efficiency of turbidity and dissolved organic matter reduction. The coagulation process used 40 mg/L of PACl and was operated at a pH of 7 (optimal condition) by Jar Test apparatus with 100 rpm rapid mixing for 1 min and then 30 rpm slow mixing for 30 min. The sediment was then left to settle for 1 h before the supernatant was collected for analysis. For the microfiltration process (Model MF2505Mi; membrane material: polysulphone 0.1 µm; Polymem, France), raw water was sucked from the outside to the inside of the membrane at transmembrane pressure of -0.2 bar. The pretreated water was analysed for water quality and dissolved organic matter reduction prior to the nanofiltration process.

2.3. Nanofiltration set-up

The cross flow nanofiltration membrane module used is shown in Fig. 1. The surface area of the membrane was 36.3 cm² (Ø 6.8 cm) and membrane sheets (Model NF2540-90; membrane material: polyamide; membrane surface charge: negative; CSM, Korea) were stored in 1.5% sodium meta-bisulphite (Na₂S₂O₅) to prevent oxidation and moisture loss. Prior to the experiment the membrane sheet was cleaned with deionized water and compacted at operating

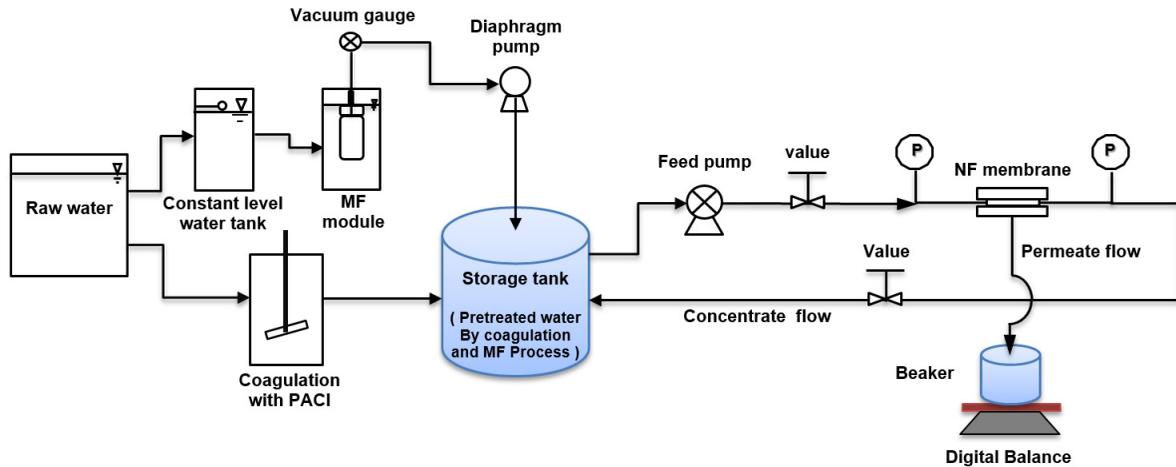


Figure 1. Schematic of experiment apparatus.

conditions. After membrane compaction (indicated by a steady-state permeate flux), the deionised water flux was used to estimate the pure water permeability.

2.4. Analytical methods

The water samples were analysed to determine their pH, turbidity, alkalinity, conductivity, total dissolved solids and dissolved organic matter concentration, following the standard method for examination of water and wastewater (American Public Health Association (APHA), 2012). The trihalomethane formation potential (THMFP) measurements were carried out according to Standard Method 5710B. The residual chlorine was measured according to the procedures outlined in Standard Method 4500-Cl G. Trihalomethanes were extracted with pentane in accordance with Standard Method 6232B (APHA, 1995) and analysed by Agilent Gas Chromatography-6890 with an electron capture detector (ECD) (Agilent technologies Inc., Wilmington, Delaware, USA) and chromatographic column (J & W Science DB-624, DE, USA) with 0.2 mm x 25 m 1.12 m film.

3. Results and Discussion

3.1. Characterisation of raw water

The characteristics of the raw water supply from the pumping station, Hat Yai Provincial Waterworks Authority are shown in Table 1.

The pH of the raw water sources was close to neutral and therefore suitable for coagulation; alkalinity was low for both seasons (< 20 mg CaCO_3/L). To prevent pH drop from alkalinity consumption during the coagulation/flocculation process additional alkalinity was required. The turbidity and dissolved organic carbon values of the raw water were higher during the rainy season than in the dry season. However, turbidity and specific ultraviolet absorption (SUVA) were low. Low turbidity of the water affected the floc formation in the coagulation/flocculation process and the coagulation process was not sufficient to remove dissolved organic matter from the raw water sources. Low SUVA indicated that the raw water contained low levels of aromatic organic groups (Korshin *et al.*, 1997).

Table 1. Characteristics of raw water from pumping station

Parameters	Raw water	
	Rainy season	Dry season
pH	6.57±0.35	6.41±0.05
Alkalinity (mg/L as CaCO_3)	17.5±3.54	12.50±2.12
Conductivity ($\mu\text{s}/\text{cm}$)	54.15±0.21	50.20±1.84
Turbidity (NTU)	29.0±1.84	14.30±1.48
UV-254 (cm^{-1})	0.16±0.01	0.16±0.01
Dissolved organic carbon (DOC, mg/L)	4.24±0.28	3.64±0.04
SUVA (L/mg-m)	3.87±0.41	4.42±0.29

Three organic fractions were investigated to illustrate the dissolved organic carbon mass distribution characteristics in the raw water. Raw water collected during the rainy season contained 37% hydrophobic fraction (HPO), 35% of hydrophilic fraction (HPI) and 28% transphilic fraction (TPI). During the dry season the HPO fraction increased, the TPI fraction decreased and the HPI fraction was unaltered (45%, 20% and 35% respectively). This indicated that the raw water contained a higher proportion of non-humic substances than humic substances. With HPI as the major fraction of the organic groups the water source may be contaminated by wastewater discharged from households or industrial activities. The hydrophobic fraction is primarily made up of humic substances mainly derived from soil, natural water systems and biological processes (American Water Works Association (AWWA), 1993). Musikavong *et al.* (2007) noted that the major dissolved organic matter fraction in raw water derived from river water had organic carbon values in the range 3.8–8.4 mg/L and a hydrophilic fraction over 50%.

3.2. The removal of dissolved organic matter by coagulation-microfiltration process as pretreatment

Fig. 2 illustrates the effectiveness of microfiltration compared to coagulation by 40 mg/L of PACl under optimised conditions as a pretreatment to reduce dissolved organic matter in the water sample.

The results revealed that both microfiltration and PACl processes reduced dissolved organic matter and dissolved organic carbon by 52.9% and 64.3% in the rainy season and 50% and 61.4% in the dry season respectively. Results for UV-254 were 45.6% and 55.4% in the rainy season and 25.5% and 51.6% in the dry season. Dissolved organic carbon removal was therefore higher than UV-254 removal. The result also showed that the PACl process reduced dissolved organic matter in terms of dissolved organic carbon and UV-254 better than the microfiltration process in both seasons. These two pretreatment techniques were more effective for reducing the hydrophobic fraction than the hydrophilic fraction. This was because coagulation preferentially removed high molecular

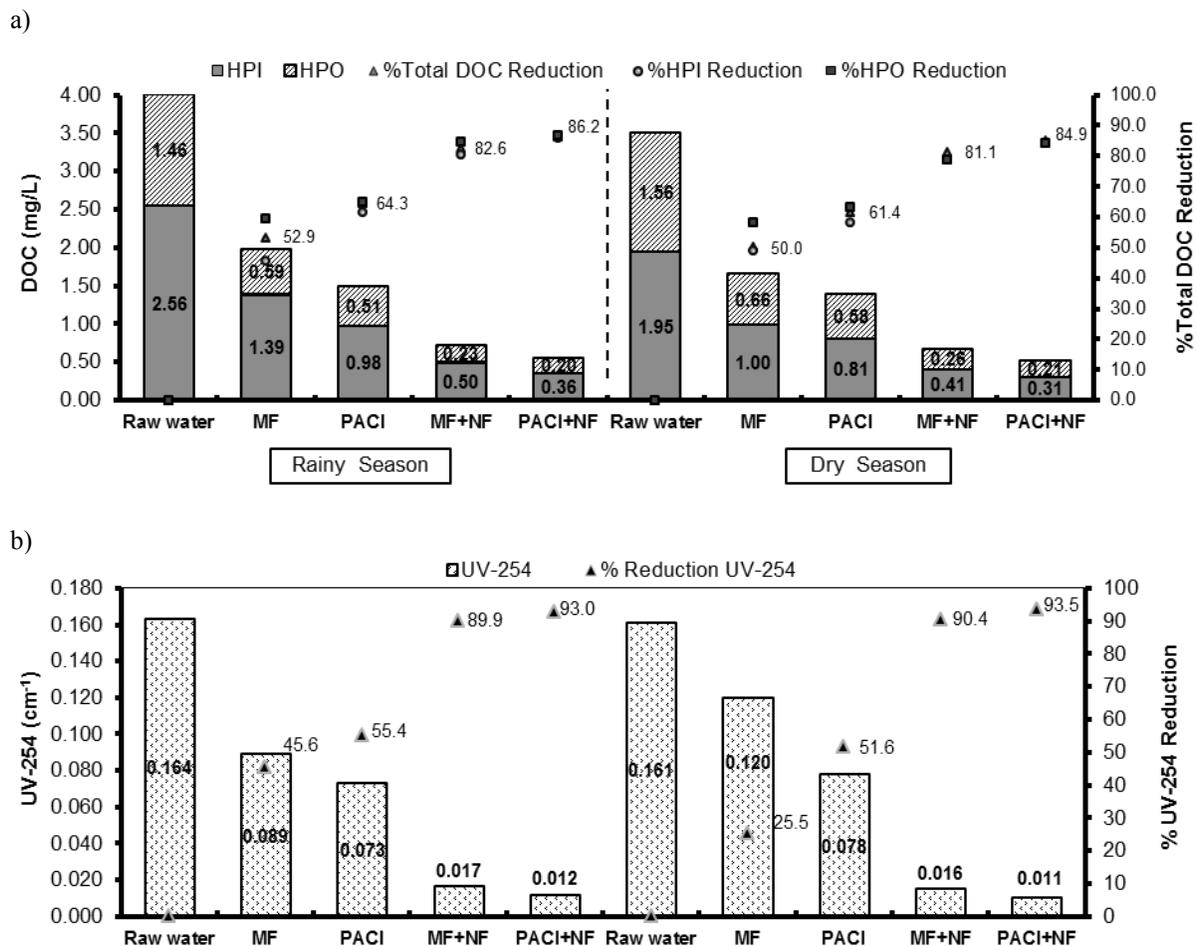


Figure 2. Change in a) dissolved organic carbon and b) UV-254 of raw water and treated water by coagulation-microfiltration process as pre-treatment

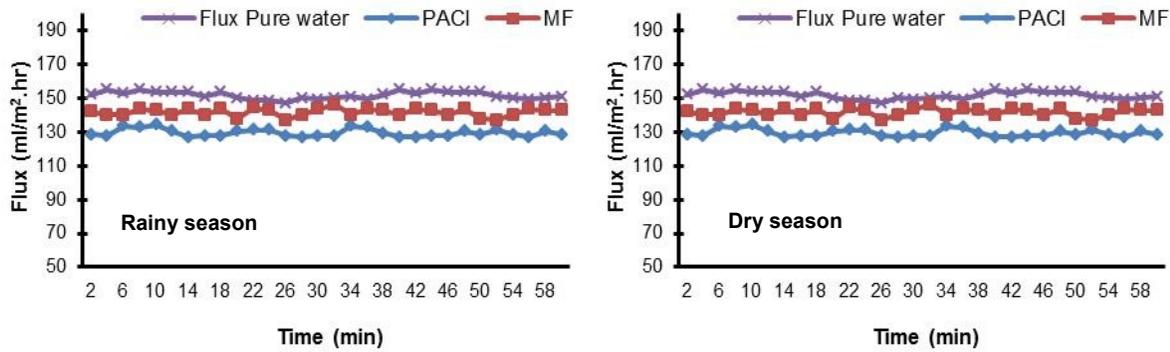


Figure 3. Effect of coagulation and microfiltration on nanofiltration membrane flux decline

weights as the hydrophobic fraction (AWWA, 1993; Sharp *et al.*, 2006). The hydrophobic fraction comprised the humic acid fraction and the fulvic acid fraction for hydrophobic acid treatability coagulation (Bond *et al.*, 2009). The solubility of the hydrophobic substances in raw water reduced because these molecules attached to other anionic organic particles in the raw water (Dentel and Gossett, 1988; Ching *et al.*, 1994). Moreover, the floc formation of PACI favoured the production of non-soluble aluminium complexes with polar molecules and oxygen containing functional groups such as hydroxyl and carboxyl (Licisko, 1993). Therefore, the charge neutralisation destabilised the colloid and caused settling of the metal cations together with the organic anions (Jekel, 1986). In addition, the hybrid PACI with nanofiltration removed the dissolved organic matter as dissolved organic carbon and UV-254 better than nanofiltration; this process showed higher performance in hydrophobic fraction reduction than for the hydrophilic fraction.

3.3. . The role of pretreatment on nanofiltration membrane flux declining and fouling

The effect of coagulation and the microfiltration pretreatment process on nanofiltration flux behaviour was observed (Fig. 3). The measured flux was plotted against time. The nanofiltration membrane flux with 40 mg/L of PACI pretreatment was lower than that pretreated by the microfiltration process. The effect of dissolved organic matter interaction dominated flux decline on the membrane surface. Increasing dissolved organic matter caused accumulation, suggesting increased cake formation on the membrane surface. The cake is mainly a porous and loose structure, representing lower resistance to filtration (Fig. 4).

The coagulated water was filtered by the nanofiltration process and the flocs deposited on the surface of the membrane formed a cake that absorbed the residual dissolved organic matter. The cake was

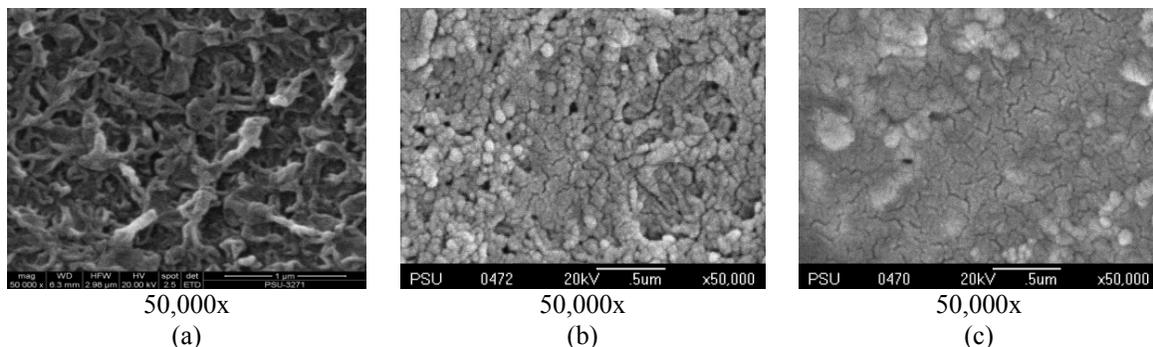


Figure 4. Fouling on surface nanofiltration by SEM analysis; a) New membrane, b) pre-treated by microfiltration and c) pre-treated by PACI

easily removed by backwashing and flushing as it was not stuck to the surface. Microfiltration uses a size sieving mechanism with pore size of 0.1 µm that effectively reduces particles larger than 0.1 µm in water. However, particles smaller than 0.1 µm such as humic substances with particle sizes in the range of 0.0025-0.01 µm were not effectively reduced. The dissolved organic matter substances that remained in the water after the microfiltration process were rejected by the nanofiltration membrane. These substances with small particle size can be plugged or adsorbed into the pores of the nanofiltration membrane as seen in Fig. 4(b). The flocs and uncoagulated dissolved organic matters with sizes smaller to membrane pores may cause pore blocking fouling that is irreversible fouling (Kimura et al., 2008).

3.4. The removal efficiency of trihalomethane formation potential using two different techniques as pretreatment combined with nanofiltration membrane

Trihalomethane formation potential (THMFP) has been commonly used to determine the trihalomethanes (THMs) at the completion of the reaction between dissolved organic matter and the excess amount of chlorine. The THMFP was determined from the summation of Chloroform (CHCl₃), Bromodichloroform (CHCl₂Br), Dibromochloroform (CHClBr₂) and Bromoform (CHBr₃). The results from the evaluation of raw water from the pumping station in both seasons (Table 2) revealed that the total

trihalomethane formation potential in the rainy and dry seasons was 463 µg/L and 350 µg/L respectively. The dominant species of trihalomethanes were chloroform and bromodichloroform. During the rainy season the maximum concentrations of trihalomethanes detected in the chlorinated water samples were 403 µg/L for chloroform and 60 µg/L for bromodichloroform. In the summer dry season the maximum concentrations of trihalomethanes were 286 µg/L for chloroform and 64 µg/L for bromodichloroform. USEPA revised and issued the Disinfectants/Disinfection By-products (D/DBP) rule which reduced the maximum contaminant levels (MCLs) for THMs to 80 µg/L (USEPA, 2009). The World Health Organisation (WHO, 2004) adopted this report as a water quality standard for tap water in Thailand, with maximum acceptable levels for chloroform and bromodichloroform set at 200 µg/L and 60 µg/L.

The trihalomethane formation potential was related more to the hydrophilic fraction than the hydrophobic fraction, whereas the removal efficiency of the hydrophilic fraction was lower than the hydrophobic fraction (Fig. 5). This was due to the smaller molecular size and solubility of the hydrophilic fraction. The raw water from the pumping station contained a high hydrophilic fraction. Appropriate treatment technology and watershed management is important as a large portion of the hydrophilic fraction is produced by human activities. However, the trihalomethane formation potential of water treated by the hybrid nanofiltration process met the international WHO standard and also the local standard of the Metropolitan Waterworks Authority (Thailand).

Table 2. Comparison the ratio of trihalomethane formation potential (THMFP) detected before and after the fractionation in the raw water

Sample	THMFP (%)		
	Unfraction	Chloroform (87%) > Bromodichloroform (13%)	
Pumping station (Rainy season)	HPI	Chloroform (88%) > Bromodichloroform (12%)	THMFP _{HPI} (67%) > THMFP _{HPO} (33%)
	HPO	Chloroform (85%) > Bromodichloroform (15%)	
	Unfraction	Chloroform (82%) > Bromodichloroform (18%)	
Pumping station (Dry season)	HPI	Chloroform (83%) > Bromodichloroform (17%)	THMFP _{HPI} (63%) > THMFP _{HPO} (37%)
	HPO	Chloroform (82%) > Bromodichloroform (18%)	
	Unfraction	Chloroform (82%) > Bromodichloroform (18%)	

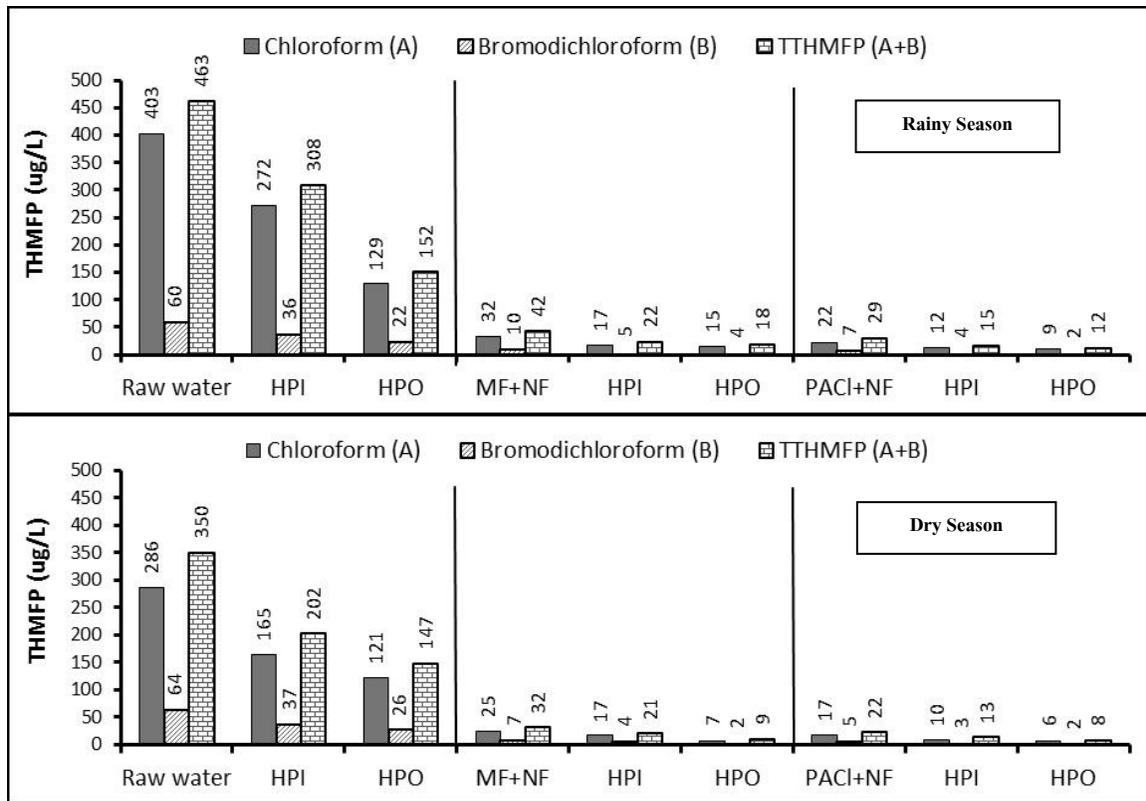


Figure 5. Trihalomethane formation potential removals by Hybrid-nanofiltration process

4. Conclusions

Raw water from the pumping station, Hat Yai Provincial Waterworks Authority had low alkalinity, low turbidity and low SUVA which made it difficult to treat by the coagulation process. Pretreatment with PACI coagulation reduced the dissolved organic matter in terms of dissolved organic carbon and UV-254 more effectively than the microfiltration process in both wet and dry seasons. These two pretreatment techniques were more effective in reducing the hydrophobic fraction than the hydrophilic fraction. The rejection of dissolved organic carbon and UV-254 using the hybrid PACI with the nanofiltration method was 86% and 94% respectively, better than microfiltration with the nanofiltration process at 81% and 91%. Nanofiltration flux decline depended on the pretreatment process and related to the size distribution of the remaining organic substances. Microfiltration with the nanofiltration process yielded higher nanofiltration flux than PACI. Microfiltration or PACI as pretreatment caused different fouling on the nanofiltration membrane. Furthermore, the fouling type on the nanofiltration membrane was affected by the microfiltration membrane pore size used for pretreatment. With microfiltration pore size of 0.1 µm, fouling by pore blocking occurred. A cake

layer formed when PACI was used as a pretreatment. In addition, the trihalomethane formation potential value of the water after treatment by the hybrid nanofiltration process was lower than both the WHO and the Metropolitan Waterworks Authority Thailand standards.

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