

CHAPTER II

REMOVAL OF HALOACETIC ACIDS BY NANOFILTRATION



2.1 Introduction

The prime reason for disinfection in water treatment is to control waterborne diseases or to inactivate pathogenic microorganisms (USEPA, 1999). Chlorine is the most widely used disinfectant in the drinking water treatment, because of its effectiveness, low cost and the ease of application (USEPA, 1999). However, it was recently found that chlorination poses potential health risks due to the subsequent generation of carcinogenic compounds called as disinfection byproduct (DBPs). DBPs are formed when water containing organic matters is chlorinated (USEPA, 1998).

Haloacetic acids are one group of DBPs. There are a total of nine haloacetic acid species containing chlorine and bromine: chloro-, dichloro-, and trichloroacetic acid (CAA, DCAA, and TCAA); bromo-, dibromo-, and tribromoacetic acid (BAA, DBAA, and TBAA); and bromochloro-, bromodichloro-, and dibromochloroacetic acid (BCAA, BDCAA, and DBCAA) (USEPA, 1998). Toxicological effects of haloacetic acids are not very well understood, but they are of great concern due to their suspected carcinogenicity as well as developmental, reproductive, and hepatic toxicities (Cowman and Singer, 1996). DCAA and TCAA have been classified according to their carcinogenic potential as group B2 (probable human carcinogen with sufficient evidence from animal studies) and C (possible human carcinogen), respectively (USEPA 1999).

Currently, the total concentration of five haloacetic acids; CAA, DCAA, TCAA, BAA, and DBAA in water supply in the United States has been regulated by the USEPA under the proposed Disinfectants/Disinfection Byproducts (D/DBP) Rule. At present, the rule sets the maximum contaminant level (MCL) for sum of five haloacetic acids (HAA₅) at 60 ppb. It is anticipated that Stage 2 of the D/DBP Rule will lower the MCL to 30 ppb (USEPA, 2001). In Thailand, there is no regulation regarding HAA₅ or other DBPs in drinking water. The existing concentration of HAA₅ in Bangkok water supply, sampling at the chlorination station in Bangkhen

water treatment plant is approximately 50 ppb. This amount exceeds the upcoming MCL of 30 ppb in Stage 2 of the D/DBP rule.

With the approaching of the new USEPA's regulation, the need for new drinking water treatment technologies to control HAA₅ has been intensified. DBPs can be controlled by several means, including removing DBP precursors, modifying the chlorination strategy, changing disinfectants, or removing the DBPs themselves (USEPA, 1999). Membrane filtration particularly nanofiltration (NF) is one of the most effective methods for haloacetic acids and DBP precursor control (Allgeier and Summer, 1995; Koffskey and Lykins, 1999; Chellam, 2000).

NF is a relatively new pressure-driven membrane process. It lies between reverse osmosis (RO) and ultrafiltration (UF) with two distinct features; one is a fractionation capacity for different organic components in aqueous solutions; the other is the Donnan effect to preferentially remove anions of different valency (Rautenbach et al., 1990). Similar to RO membranes, NF membranes are almost non-porous, with sorption and diffusion as transport mechanisms. Most NF membranes contain charged functional groups. Thereby, both pore size and membrane surface charge play an important role in the transport of solute and water molecules across the membrane (Chlidress and Elilelech, 2000). Previous studies have demonstrated that NF is effective in removing several cationic and anionic pollutants, both organic (Jiraratananone et al., 2000; Lee and Lueptow, 2001; Thanuttamavong et al., 2002) and inorganic species (Ratanatamaskul et al., 1996, 1998; Ratanatamaskul and Yamamoto, 1998; Choo et al., 2002; Ahn et al., 1999). Since the technique is readily available with a considerable choices of membranes to select, NF represent one of the promising techniques to control haloacetic acids. In this study, NF was investigated for its performance in removing HAA₅. The objectives of the study are ; *i*) to examine HAA₅ removal efficiencies of three NF membranes, *ii*) to identify the effect of pressure, cross-flow velocity, and HAA₅ concentration on membranes performance, and *iii*) to select a simple mathematic model to explain the relationship between percent HAA₅ removal and operating variables such as pressure, concentration of feed water, or cross-flow velocity.

2.2 Materials and methods

2.2.1 Membrane testing unit

A Schematic diagram of NF testing unit is shown in Figure 2.1. The membrane testing unit consisted of a membrane test cell, booster pump, feed reservoir, pressure gauge, flow meter and regulating valve. The membrane module was a flat-sheet type C-10 T (Nitto Denko Co.) having an effective membrane surface area of 60 cm².

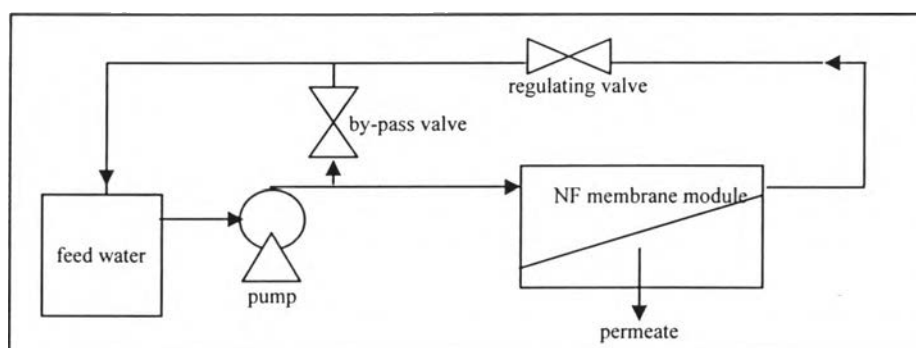


Figure 2.1: Schematic diagram of the nanofiltration experimental set-up.

Three types of flat-sheet NF membranes used in this study were NTR 729HF, NTR 7410 and ES 10 (Nitto Denko Co.). Their main properties are summarized in Table 2.1.

Table 2.1: Characteristics of NF membranes.

Membrane	Materials ^a	Pore size ^a (nm)	MWCO ^a (Da)	Point of zero charge (PZC)
NTR 7410	Sulfonatepolysulfone	4	20,000	3.3 ^b
NTR 729HF	Polyamide/ Polyvinyl alcohol	1	200	5.1 ^b
ES 10	Aromatic polyamide	1	100	3.7 ^c

^a from Ratanatamskul et al. (1996), ^b from Choo et al. (2002), ^c from Tay et al. (2001)

All NF experiments were conducted using the cross-flow bench scale membrane test system. A membrane sheet and a feed channel spacer are mounted between halves of a membrane cell. Prior to the test, the system and membrane sheet were cleaned by running HCl solution (pH 3) at pressure 2 bars for 30 min, following by NaOH solution (pH 10.5) at the same condition.

After cleaning, milli-Q water was filtered at pressure 3 bars and cross-flow velocity 0.7 m/sec. Cleaned water flux was measured after running for 1 to 2 hours to determine the membrane permeability and to check for the steady state. The stable permeate flux will be achieved if the steady state condition is maintained.

2.2.2 Operating conditions

The synthetic sample of HAA₅ (a mixture of CAA, DCAA, TCAA, BAA, and DBAA) was used as a feed solution in this experiment. Three initial HAA₅ concentrations, 60, 90, and 120 ppb, were prepared using HAA₆ standard (GC grade, Supelco). A feed volume of 5 L of synthetic HAA₅ sample was used in each experiment. During the test, both the permeate and retentate were returned to the feed reservoir. Therefore, the composition of feed solution remained constant throughout the run.

A series of batch experiments were designed to measure HAA₅ rejection by three membranes at three feed concentrations. Two operating parameters, pressure and cross-flow velocity were varied in each run. The operating pressure was varied from 1, 3, and 5 bars. Cross-flow velocity was varied from 0.3, 0.5 and 0.7 m/sec. The operating pressure and cross-flow velocity were adjusted and controlled using by-pass and regulating valves. In each experiment, all samples were collected after the system reached the steady state

After each run, the membrane was immediately cleaned. The cleaning process was done in two steps. First a water rinsing was performed followed by a chemical cleaning. Before starting the next run, the permeate flux of milli-Q water was measured. If fouling is taken place, the membrane will be changed.

2.2.3 Analytical method

Concentrations of HAA₅ were determined using USEPA method 552.2, which include liquid-liquid extraction, derivatization and gas chromatography with electron capture detection. Briefly, A 20 µl of 2,3dibromopropionic acid (10 µl/ml) was added in to a 40 mL of sample as a surrogate or QA/QC. Then the sample was adjusted to pH<0.5 by a concentrated H₂SO₄. Two grams of CuSO₄ was subsequently added to the acidic solution followed by Na₂SO₄ 16 g. The solution was then extracted with 4 mL of methyl-tert-butyl ether (MTBE). Haloacetic acids that had been partitioned into the organic phase were converted to their methyl esters by the addition of 10% H₂SO₄ in methanol and warmed to 50 °C in water bath. The acidic extract was later neutralized by back extraction with a saturated solution of sodium bicarbonate. The target analytes were identified and measured by gas chromatography using electron capture detection (GC/ECD) Agilent GC6890. A DB-XLB (J&W Scientific) fused silica capillary column (30 m x 0.32 mm *i.d.* x 0.05 µm film thickness) was used for the separation. The GC oven was temperature-programmed at 40 °C for 0.5 min and then from 40-200 °C at a rate of 15 °C/min, after that the temperature was held constant for 2 min. The injector as operate was kept at 250°C, splitless mode; 30 sec purge activation time, and 50 pg per component. The detector temperature was maintained at 350°C, respectively.

2.3 Results and discussion

HAA₅ removal efficiencies of ES 10, NTR 729HF, and NTR 7410 were evaluated by determining the HAA₅ reduction percentage. The effluent and influent samples from each test condition after a 120-min run were collected and analyzed for HAA₅. The removal percentage was calculated as follows:

$$\% \text{ reduction} = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (1)$$

Where C_p and C_f are concentrations of HAA₅ in the permeate and feed water, respectively. Effects of operating pressure, cross-flow velocity, and concentrations of feed water on the performance of the membranes were discussed as follows.

2.3.1 Effects of operating pressure

Three operating pressures (1, 3, and 5 bars) were applied during the study. The concentration of haloacetic acids in feed water was kept at 60 ppb. HAA₅ removal efficiencies at different pressures are shown in Figure 2.2. From these data, it was observed that the operating pressure provides both negative and positive effects on the performance of tested membranes. An increase in the operating pressure corresponded to the decrease in HAA₅ reduction of ES 10 and NTR 7410, whereas, the effect was opposite with NTR 729HF. Among the three membranes tested, ES 10 exhibited the best HAA₅ removal efficiency at all three operating pressures. For the other two membranes, the performance of NTR 7410 was generally better than that of NTR 729HF at a low pressure range (*i.e.*, 1 and 3 bars). However, at a higher pressure of 5 bars, % HAA₅ reduction of NTR 7410 was comparable to that of NTR 729HF. The superior performance of ES 10 is partly due to the fact that of all three membranes, ES 10 is the tightest one. Its MWCO is approximately 100 Da (Table 2.1). NTR 729HF has a relatively larger pore size, having a MWCO around 200 Da (Table 2.1). NTR 7410, on the other hand, is considered to be a loose membrane. Its MWCO is 20,000 Da (Table 2.1). However, since pH of feed water was around 6, HAA₅ would exist in anion (their pK_a range between 0.51-2.89, Table 2.2). The HAA₅ rejection mechanism of the membranes would not entirely depend on the sieve effect.

Table 2.2: Molecular weights and acid dissociation constants (pK_a) of haloacetic acids (from Wang and Mitra, 2002 and Halaleh et al., 2003)

Name	Abbreviation	MW	pK _a
Monochloroacetic acid	CAA	94.5	2.87
Monobromoacetic acid	BAA	138.9	2.89
Dichloroacetic acid	DCAA	129	1.26
Trichloroacetic acid	TCAA	163.5	0.51
Dibromoacetic acid	DBAA	217.8	1.47

Separation mechanism of NF process could be explained by either sieve or electronic effects or both, depending on property of the feed solution. Sieving

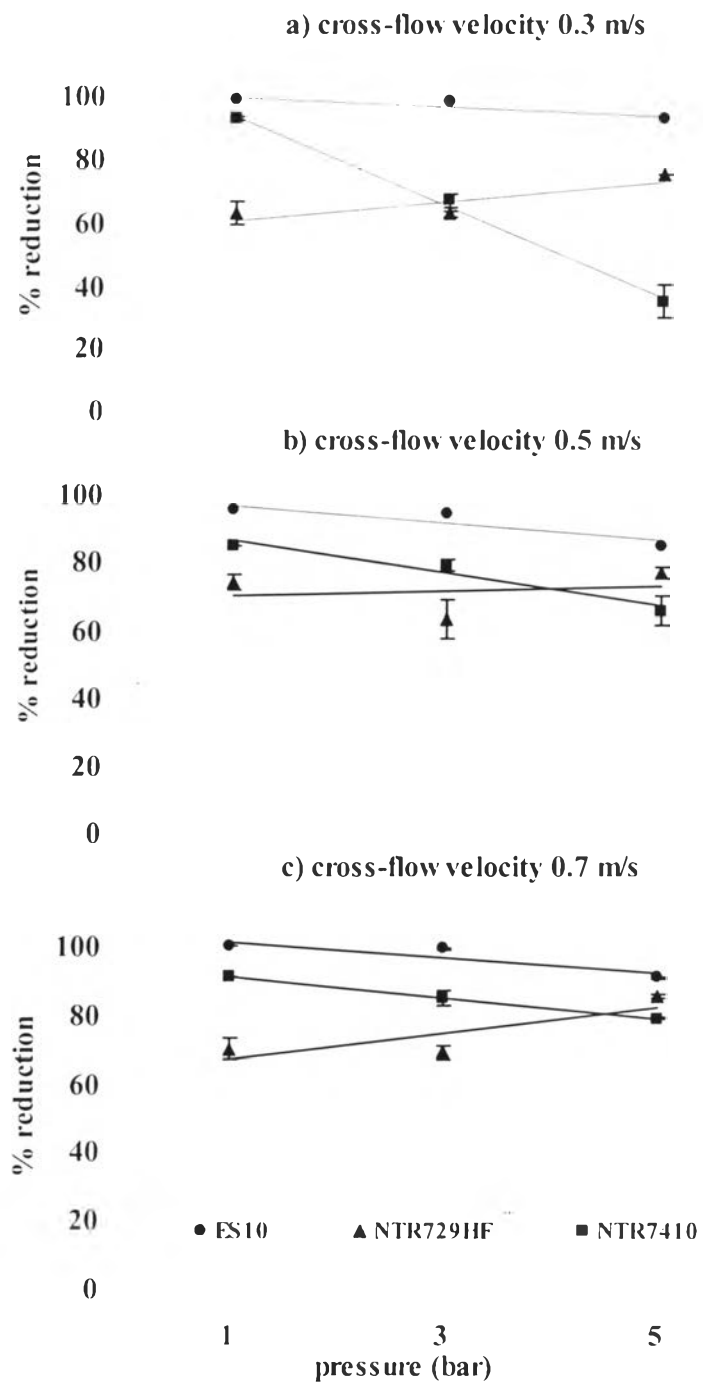


Figure 2.2: Effects of operating pressure on the performance of NF membranes in removing HAA₅ 60 ppb.

mechanism regulates the rejection of an uncharged solute by NF membranes. The extent of the rejection is primarily depends on molecular size of the solute species (Ku et al., 2004). HAA₅ are relatively small species. Their molecular weights range between 94-163 (Table 2.1). Therefore, sieve effect was unlikely the predominant mechanism controlling the rejection of HAA₅ by the three NF membranes, especially the loose membrane NTR 7410. Electrostatic interaction between anions of HAA₅ and membrane surface charge described as Donan exclusion phenomenon (Mehiguene et al., 1999 and Garba et al., 1999) would be a more important driving force.

Due to the composition of membranes and pH of the feed water (pH ~ 6), ES 10, which is made from aromatic amides would have a negatively charged surface due to the deprotonation of carboxylic functional group (normally aromatic thin-film composite membranes are made by the interfacial polymerization reaction of 1,3-benzediamine with trimesoyl chloride, carboxylic functional group would be present on the membrane surface (Childress and Elimelech, 2000). NTR 7410 is made of sulfonated polysulfones (SPES). The SPES membranes have been found more negatively charged than the membrane with carboxylic functional group due to the deprotonation of sulfonate functional group. It is well known that sulfonic acids are so acidic that they are dissociated over nearly the entire pH range. On the other hand, carboxylic functional groups, because of their higher pK_a , are weaker acids (Schaepe and Vandecasteele, 2001). Hence, although its pore size is larger than other two membranes, it is expected that NTR 7410 would have electronegativity at the surface in a certain extent. NTR 729HF is made of polyvinyl alcohol. The membrane had been described as a neutral membrane possibly due to relatively low ionization of hydroxyl functional group of alcohol (Costich and Osterhoudt, 1974; Yoshizuka et al., 1996). According to different surface charge properties of all three membranes, the Donan effect would be more influence in ES 10 and NTR 7410 than in NTR 729HF.

An increase in the operating pressure resulted in the decrease in the performance of ES 10 and NTR 7410. Changes in % HAA₅ reduction of both membranes as a function of operating pressure are related to changes in the permeate flux. With the increasing pressure, permeate flux is increased. As a larger volume of of the solution passing though the membrane, more HAA₅ anions move toward the membrane surface. Higher HAA₅ concentration at the solute-membrane interface enhances the concentration polarization across the membrane resulting in the decrease

in HAA₅ rejection. Relatively small decrease in the performance of ES 10 with the increasing pressure suggests that the sieve effect might participate in some extent. The small pore size of ES 10 would negotiate with the diffusion force enhanced by concentration polarization.

The positive response of NTR 729HF to the increasing pressure would due to the fact that the membrane is considered having a neutral surface. Electrostatic repulsion between HAA₅ and the membrane's surface would be negligible relative those occurred on ES 10 and NTR 7410. However, as the operating pressure increased, more HAA₅ anions would be trapped on the surface of the membrane forming a layer of a negative surface charge. This layer would then repel other anions in the bulk solution. Thus the HAA₅ rejection is improved.

Since the operating pressure has the effect on permeate flux, the model developed by Garba et al. (1999) can be used to predict the effect of pressure on HAA₅ reduction. The model is based the combination of the extended Nerst-Planck equation and the film theory:

$$\ln(1-R) = -\frac{1}{K_{\text{effi}}} J_v + \ln \Phi \quad (2)$$

$$R = 1 - \frac{C_p}{C_f} \quad (3)$$

where J_v is the permeate flux; K_{effi} is the effective transfer coefficient of the ions, and Φ is the ion transmittance. Both K_{effi} and Φ can be estimated by plotting $\ln(1-R)$ versus J_v (Garba et al., 1999; Wu et al., 2004). Data predicted by the model for the experiments running with HAA₅ 60-ppb at cross-flow velocity of 0.7 m/s (the condition providing the highest % reduction) were compared with the experimental results as shown in Figure 2.3. It can be seen that both theoretical and experimental data sets are in a good agreement.

2.3.2 Effect of cross-flow velocity

Cross-flow velocity generally has an effect on the performance of NF membranes. High cross-flow velocity helps increase % rejection because it prevents the accumulation of ions on the surface of a membrane (Ratanatamskul et al., 1996).

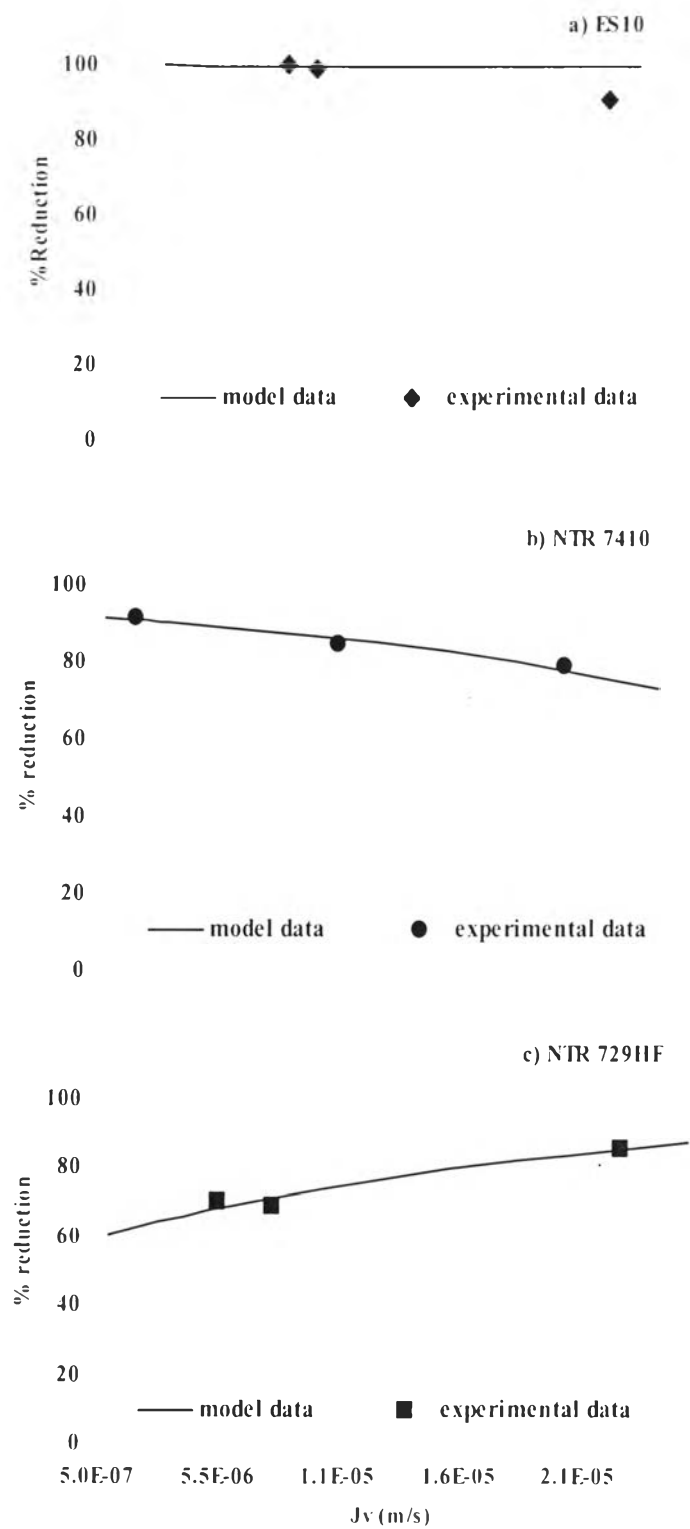


Figure 2.3: Comparison between the data predicted from mathematical model and from NF experiments carried out to remove 60 ppb HAA₅ at the cross-flow velocity of 0.7 m/s

Therefore, it lessens the effect of concentration polarization. However in this study, although % HAA₅ reduction was mostly improved with an increased cross-flow velocity, the extents of the change in % reduction was not pronounced for ES 10, and NTR 729HF. In Figure 2.4, when cross-flow velocity was increased from 0.3 to 0.7 m/s, % reduction of ES10 and NTR 729HF were increased 0-1% and 6.3-10.1%, respectively. The effect of cross-flow velocity, however, was more benefit to the performance of NTR 7410 at the operating pressure of 5 bars. The extent of the effects is substantial. HAA₅ reduction was increased from 35% to 79%. Similar results were reported for the performance of ES 10, NTR 729HF and NTR 7410 by Pholchon (2001). It was mentioned that the negligible effect of cross-flow velocity on the performance of ES10 and NTR 729HF was due to a small pore size of both membranes (~1 nm: Table 2.1). Because of this physical property, sieving mechanism would already mitigate the effect of concentration polarization, even without the benefit from high cross-flow velocity. However, in the NTR 7410 case, a larger pore size of ~ 4 nm would make the sieving effect ineffective. Turbulent flow generated at a high cross-flow velocity would lower the accumulation of HAA₅ anions near the membrane's surface, thus preventing the undesirable effect of the concentration polarization.

2.3.3 Effect of HAA₅ concentrations

Two additional concentrations of HAA₅, 90 and 120 ppb, were tested to simulate the real situation, where the concentration of HAA₅ could exceed 60 ppb. Arora et al. (1997) reported that the concentration of HAA₅ in 16 % of water treatment plants associated with the American Water System would soon exceed 60 ppb. The performance of NF membranes at different feed concentrations was shown in Figure 2.5. As shown in the figure, feed concentration has a negative effect on all three membranes. However, the effect on the performance of ES 10 and NTR 7410 was relatively minor. Both membranes are negatively charged membranes. Electrostatic repulsion (Donan exclusion) that would be enhanced at high feed concentrations would counterbalance a higher diffusive driving force at these two membranes' surface. The extent of the concentration effect on NTR 729HF, on the other hand, was noticeable. With the operating pressure of 5 bars and cross-flow velocity of 0.7 m/s

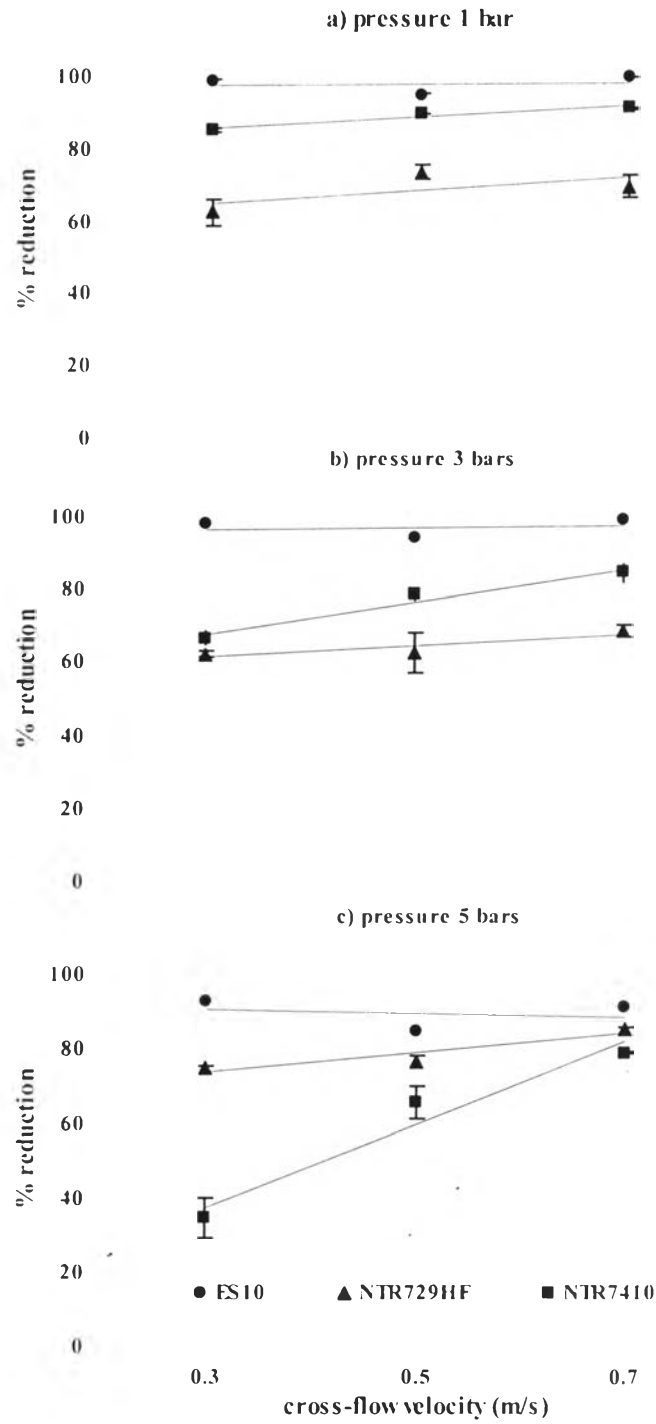


Figure 2.4: Effects of cross-flow velocity on the performance of NF membranes in removing HAA₅ 60 ppb.

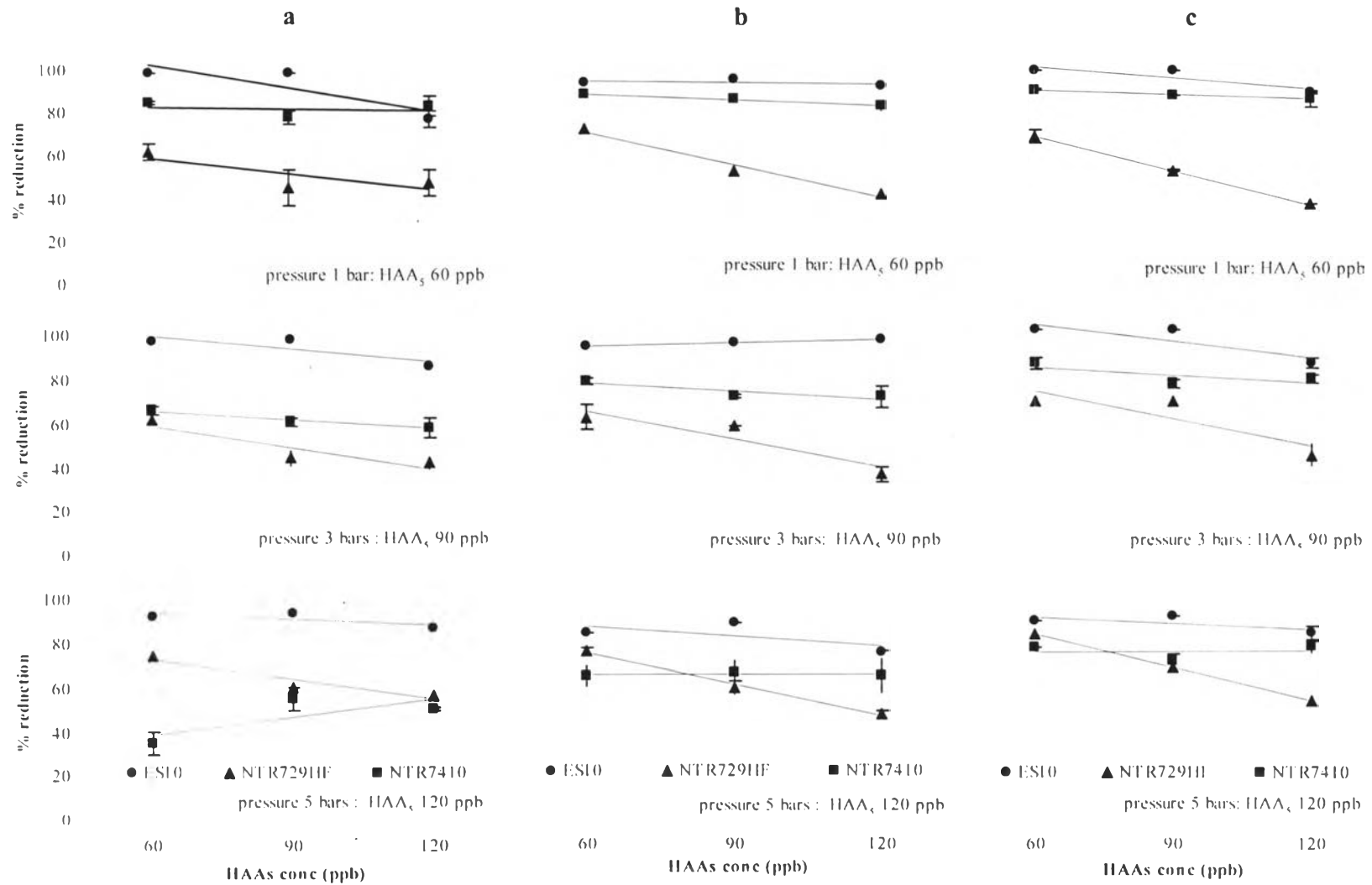


Figure 2.5: Effects of feed concentrations on the performance of NF membranes in removing HAA₅ 60, 90, and 120 ppb: a) cross-flow velocity of 0.3 m/s, b) cross-flow velocity of 0.5 m/s, c) cross-flow velocity of 0.7 m/s,

(the optimum condition), HAA₅ rejection lowered from about 85% to 55% when feed concentration was increased from 60 to 120 ppb. This behavior could be due to the fact that NTR 729 HF is a neutral membrane. With increasing feed concentrations, more HAA₅ anions were accumulated on the membrane surface. The extent of the concentration polarization, would increase and subsequently lead to the higher HAA₅ anions diffusion into the permeate.

In order to predict the effect of feed concentration on % HAA₅ rejection, a model describes the concentration of chemical species in the permeate in terms of the concentration factor was evaluated. The model is described by the following equation (Kilduff and Weber, 1992; Guo et al., 2001; Wu et al., 2004):

$$\ln C_p = \ln(P_c * C_f^0) + (1 - P_c) * \ln (CF) \quad (4)$$

where P_c is the permeate coefficient estimated by a plot between $\ln C_p$ and $\ln CF$. C_f^0 is the initial concentration of the HAA in the feed solution. CF is a volume ratio of initial feed water to retentate and can be calculated from solute and permeate flux data. Results of the model prediction for the performance of NTR 7410 and NTR 729 HF at the optimum conditions (pressure 1 bar, cross-flow velocity 0.7 m/s for NTR 7410 and pressure 5 bars, cross-flow velocity 0.7 m/s for NTR 729 HF) were illustrated in Figure 2.6 (the simulation was not done with ES 10 since % reduction = 100). The predicted data fits relatively well with the experimental data, although the estimates for NTR 729HF are relatively higher than the experimental results.

When considering % reduction of each individual HAA₅, it was observed from Figure 2.7 that % reduction was decreased in the order of CAA, BAA, DBAA, DCAA and TCAA. This pattern is consistent in every test condition. The observation is unexpected. Large HAA₅ species were less retained than their smaller counterparts. It was further noticed that the observed ranking correlates well to the sequence of pK_a values of the anion species (2.87, 2.89, 1.47, 1.26, and 0.51 for CAA, BAA, DBAA, DCAA and TCAA, respectively). The compound with higher pK_a has the better % reduction (Figure 2.8). The case of DBAA, which has the highest molecular weight (Table 2.2) but still be able to transport across the membrane better than other smaller

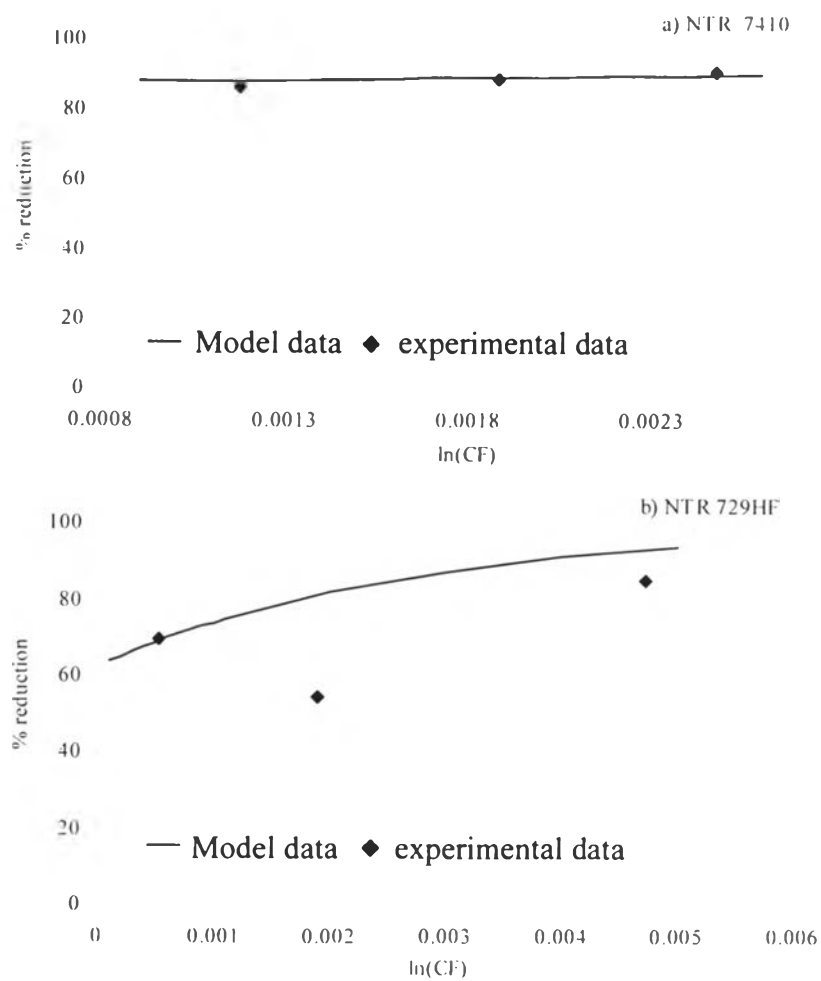


Figure 2.6: Comparison between the data predicted from mathematical model and from NF experiments carried out to remove 60 ppb of HAA₅ at the operating pressure of: a) 1 bar with NTR 7410 and b) 5 bars with NTR 729HF

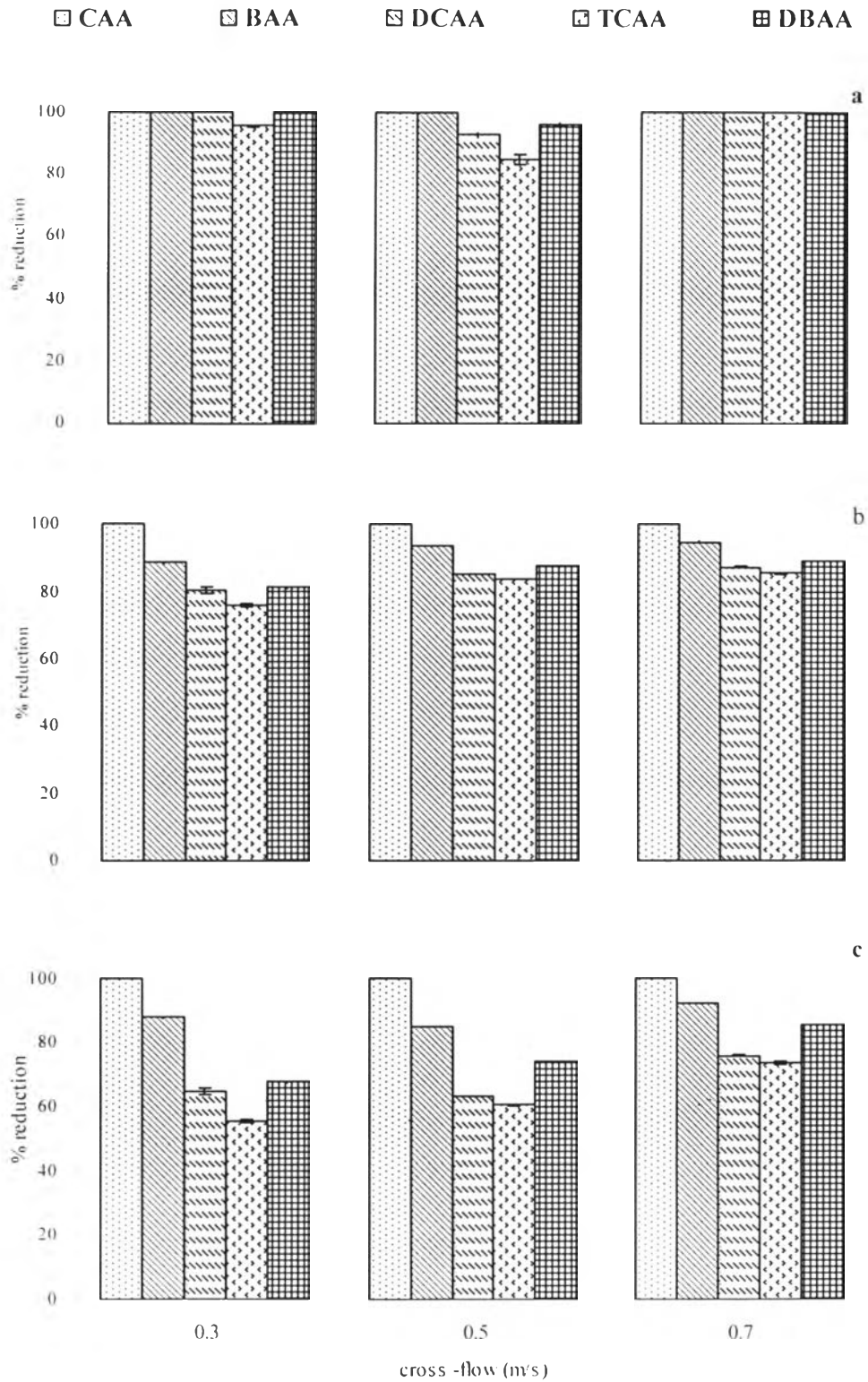


Figure 2.7: Removal of individual HAA species by NF process. Data from: a) ES 10, with HAA₅ 60 ppb, pressure 1 bar, b) NTR 7410 with HAA₅ 60 pp, pressure 1 bar, and c) NTR 729HF with HAA₅ 60 ppb, pressure 5 bars.

molecules, (e.g., DCAA) clearly indicates that steric or sieve effect was not the major mechanism in removing HAA₅ species.

Generally pK_a is an indicator of hydrogen bonding ability; *i.e.*, lower pK_a , better hydrogen bonding ability (Williams et al., 1999). Since haloacetic acids could form hydrogen bond with water molecules, the correlation between pK_a and % reduction observed in the HAA₅ filtration suggests that such interaction also takes part in regulating the filtration process. Upon the hydrogen bond formation, hydrogen atom in water molecule acts as a hydrogen-bond donor, whereas halogen atoms such as chlorine or bromine of haloacetic acids represent hydrogen-bond acceptors ([http://en.wikipedia.org/wiki/Hydrogen bond](http://en.wikipedia.org/wiki/Hydrogen_bond), 2005). Since TCAA, which has three chlorine atoms could be able to form three hydrogen bonds making it more readily soluble than other haloacetic acid species; its removal percentage was observed to be the lowest one. This characteristic would enhance the TCAA movement through the pore of membrane. In a similar manner, higher pK_a values of other HAA₅ species would suggest lower ability for hydrogen bonding with water molecules and reflect their better rejection as observed.

20240408

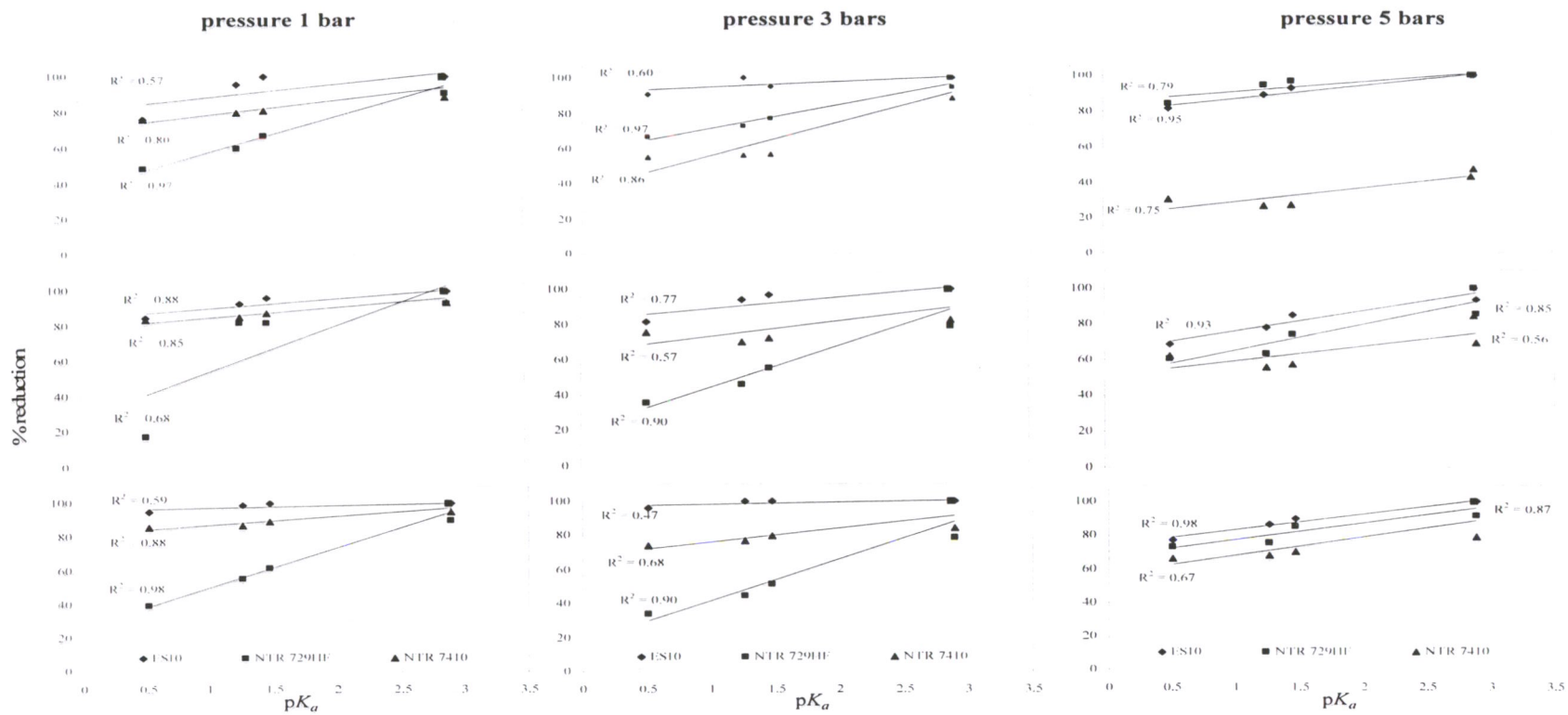


Figure 2.8: Correlation between pK_a and % reduction of individual HAA₅ species

2.4 Conclusions

NF processes showed a good performance in removing HAA₅. ES 10, a dense negatively charged membrane is the most efficient. Neutral surface membrane, such as NTR 729HF, is the least effective. Electrostatic repulsion (Donan exclusion) between HAA₅ anions and negative surface charges of the membrane is the key mechanism regulating the rejection process. Excellent removal efficiency (90-100%) could be obtained even at a low pressure of 1 bar with ES 10 and NTR 7410 membranes. An increase in cross-flow velocity did not have any significant impacts on the performance of membranes with a small pore size, such as ES 10 and NTR 729HF. However, it provided a significant positive impact on the performance of the membrane with larger pore size, such as NTR 7410. The benefit was due to the prevention of the anion accumulation on the surface of the membrane during the high turbulent flow. The event reduces the negative impact of the concentration polarization. In contrast to cross-flow velocity, an increase in HAA₅ concentration has an adverse effect on the performance of all three membranes. Higher amount of HAA₅ concentration enhanced the concentration polarization, strengthening a driving force for the diffusion of HAA anions through the membrane. Among the HAA₅ species, TCAA, the second largest species, was the least retained compound. Lower pKa is then higher water bonding potential. Higher water bonding potential of polar organic carbon might cause less electrostatic repulsion of membrane surface charge.