CHAPTER IV
COMPARING NANOFILTRATION AND OZONE – BIOLOGICAL ACTIVATED CARBON FOR HALOACETIC ACID REMOVAL

4.1 Introduction

With an increasing number of populations, the demand for portable water is invariably escalated. Although several water treatment processes have been developed to improve the quality of water supply, chlorination remains a popular disinfection method (USEPA, 1999). Despite its several advantages over other disinfection techniques, the downside of chlorination process is the formation of a large variety of disinfection by-products (DBPs). Among them, trihalomethanes (THMs) and haloacetic acids are found in the highest concentrations and with the greatest frequency in water after the chlorination process (Barth and Fair, 1992). Both THMs and haloacetic acids are potentially harmful. Dichloroacetic acid (DCAA), for example, is a suspected human carcinogen.

One recently proposed rule by the U.S. Environmental Protection Agency (USEPA) regarding the control of DBPs is the Disinfectants/Disinfection By-Products (D/DBP) Rule. The rule is driven by the concern to protect the public from long-term exposure to DBPs. One of the most important elements of the D/DBP rule is the enforcement of the maximum contaminant level (MCL) for five haloacetic acids (HAA_5, *i.e.,* chloro-, dichloro-, and trichloroacetic acids (CAA, DCAA, and TCAA); bromo-, dibromoacetic acids (BAA, and DBAA)) at 60 ppb (USEPA, 1998). The impending Stage 2 of the D/DBP rule (effective in 2005) will lower the existing MCL for HAA_5 to 30 ppb (www.awwarf.org, 2005).

While the majority of DBP control strategies focus on DBP precursor removal, the insight on the effectiveness of the existing treatment technologies in direct removing HAA_5 is limited. Ozonation coupled with the biological activated carbon (BAC) treatment is one of the prompting technologies widely used in many water treatment facilities (Nigel and Graham, 1999). It combines the potent oxidizing power of ozone and biodegradability of bacteria available in the water environment. Ozonation provides a benefit to BAC by decreasing the average molecular size and weight of organic compounds in water, allowing indigenous bacteria growing on

activated carbon to easier biodegrade them. A small number of reports showed that haloacetic acids could be degraded by aerobic bacteria (Weightman et al., 1992; Olaniran, 2001). Therefore, BAC represents the readily available technique that might directly lower HAA_5. The combination of the ozonation process should increases the possibility for biodegradation of HAA_5.

Nanofiltration (NF) is another treatment process receiving a considerable attention due to its applicability to drinking water system (USEPA 2001). NF is a fairly recent development in membrane technology. The performance of NF falls between those of the reverse osmosis (RO) and ultrafiltration (UF). NF combines the performance attributes of RO and the operational assets of UF. The transport mechanisms across NF membranes involve sieving, convection, and diffusion that could be explained by mathematical models for homogeneous surface diffusion, film theory, and several salt flux models (Taylor et al. 1989). In addition, since most NF membranes are made of composite materials carrying either a positive or negative charge, the membranes are also able to reject charges and ionized species, such as haloacetic acids. The primary objective of this study was to evaluate the effects of NF process and ozone oxidation coupled with BAC on the removal of HAA_5. Additionally, the study also included the determination of variables affecting the performance of NF membranes, ozonation and BAC column (*i.e.,* pressure, cross-flow velocity, and concentrations of HAA_5 for NF, dose and contact time for ozonation, and empty bed contact time for BAC).

4.2 Materials and method

4.2.1 Sample preparation

Synthetic samples of HAA_5 (CAA, DCAA, TCAA, MBAA, and DBAA) were used as feed solution in this experiment. Samples were prepared using a commercially available HAA_6 standard (Supelco). Three initial HAA_5 concentrations, 60, 90, and 120 ppb were tested.

4.2.2 NF testing unit

A Schematic diagram of NF testing unit is shown in Figure 4.1. 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 cm^2.

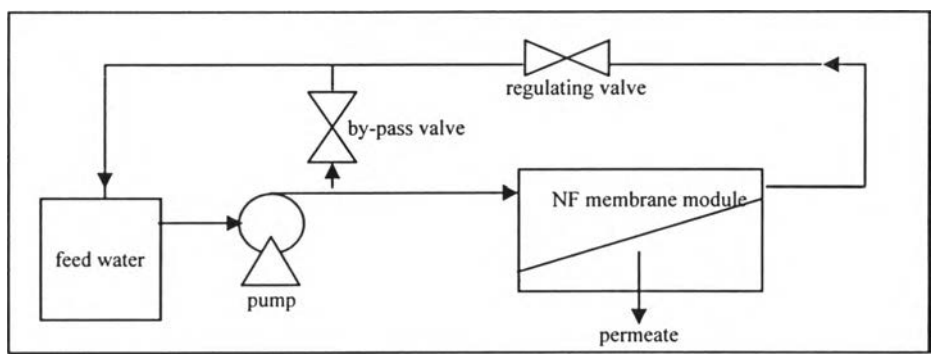

Figure 4.1: Schematic diagram of the nanofiltration experimental set-up.

Three types of flat-sheet NF membranes used in this study were NTR 729HF, NTR 7410 and ES 10 (Nitto Denko Co.). 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 testing, 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 hrs 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.

A series of batch experiments were designed to measure HAA_5 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.

4.2.3 Ozone-BAC system

A Schematic diagram of the ozone-BAC testing unit is shown in Figure 4.2.

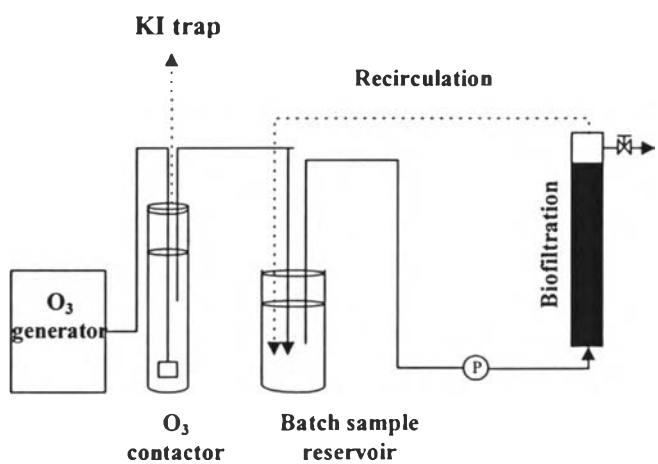

Figure 4.2: A Schematic diagram of ozone-BAC testing unit

The Ozone-BAC treatment system components were made of stainless steel, glass, and Teflon. The system includes two basic components: ozone contactor and biological activated carbon column. The system was used to conduct batch experiments studying the HAA_5 removal by ozone and BAC processes.

Water sample was placed in a 5-L glass bottle and flowed to a 5-L ozone contactor by gravity. Ozone was generated from an ozone generator (Sky zone; star 04) that has an ozone generating capacity of 750 mg/hr. Ozone was introduced to the contactor by fritted glass disc at room temperature. The ozone dosage was varied in each experiment by adjusting the ozone production period, while all settings on the ozonation apparatus remain the same for all runs. The residual ozone dosage was measured using the indigo trisulfonate method (Standard Methods, 1998). Off-gas from the ozone contactor was introduced to a potassium iodine solution (KI trap).

The granular activated carbon (GAC) media was packed into a glass column (50 cm high and ϕ 3 cm). An acclimated biofilm was established on the GAC media (Calgon F200) by seeding with raw water from Sam Sen raw water distributing canal (Klong Prapa) over a period of 1 year. The filter was operated in an upflow mode by a peristaltic pump. Prior to the tests, the establishment of microbial communities in the BAC column was confirmed using the membrane filter technique. A steady colony count indicates the stability of the bacteria.

A series of batch experiments were designed to measure HAA_5 removal as a function of ozone dosage, contact time of the ozonation process, and empty bed contact time (EBCT) of the BAC column. Three ozone doses, 0.5, 1.0, and 2.0 mg ozone/mg TOC were experimented with contact times varied from 5, 10, and 20 min. The effect of EBCT on BAC performance was investigated at 10, 20, and 30 min. HAA_5 concentration was measured from samples collected at the beginning of each experiment, after ozone contactor and after the BAC column. Additional samples (500 mL each) were also taken after the ozonation process and BAC column for assimilated organic carbon (AOC) bioassay.

4.2.4 Analysis of HAA_5

The amounts of HAA_5 were determined using USEPA method 552.2. 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 H_2SO_4. Two grams of $CuSO_4$ was subsequently added to the acidic solution followed by Na_2SO_4 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% H_2SO_4 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 analysts 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, and operated in a splitless mode, 30 sec purge activation time, and 50 pg per component. The detector temperature was maintained at 350°C.

4.3 Results and discussion

4.3.1 Nanofiltration

Results from NF experiments are illustrated in Figure 4.3. Data in the figure correspond to the performance of three selected NF membranes ES 10, NTR 7410, and NTR 729HF. The experiments were carried out with 60-ppb HAA_5, operating pressure of 1 bar and cross-flow velocity of 0.3 m/s. The results show that ES 10 performed better than NTR 7410 and NTR 729HF in retaining HAA_5. The membrane removed more than 95% of HAA_5 in the feed solution.

A superior performance of ES 10 is partly due to its small pore size. Among three selected membranes, ES 10 is the tightest one. Its molecular weight cut-off (MWCO), approximately 100 Da and NTR 729HF and NTR 7410 have a relatively larger pore size, having a MWCO around 200 Da, 20,000 Da, respectively (Polchan, 2001). However, the separation mechanism of HAA_5 by the nanofiltration process could not be explained by sieve effect alone. Sieving mechanism regulates the rejection of an uncharged solute by nanofiltration (Ku et al., 2004). HAA_5 are relatively small species. Their molecular weights range 94 to 163. Therefore, sieve effect was unlikely a predominant mechanism controlling the rejection of HAA_5 by the three membranes, especially with the loose membrane NTR 7410.

At the pH range of feed solutions (~6.0), HAA_5 would present in anion forms during the filtration process (pK_a range between 0.51-2.89). Electrostatic interaction between anions of HAA_5 and membrane surface charge described as Donan exclusion phenomenon (Mehiguene et al., 1999 and Garba et al., 1999) would be more important influence. ES 10 which is made from aromatic amides has a negative charge 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). It also possesses a negative charge surface. NTR 729HF is made of polyvinyl alcohol. The membrane had been described as neutral membrane possibly due to relatively low ionization of hydroxyl functional group of alcohol (Costich and Osterhoudt, 1974; Yoshizuka et al., 1996). With the combination of Donan and sieve effects, the performance of ES 10 would be enhanced greater than those of NTR 7410 and NTR 729 HF.

The performance of ES 10 was apparently decreased with higher operating pressure but remain relatively unaffected by the increasing cross-flow velocity as shown in Figure 4.4. The effect of operating pressure is related to the solute flux passing through the membrane. With increasing pressure, the flux increased, and as a consequence, the larger amount of HAA_5 anions was transported from the bulk solution toward the membrane surface. Such event enhances the concentration polarization resulting in the decrease in HAA_5 rejection. The same situation would also occur when the observed HAA_5 rejection decreased with increased HAA_5 concentrations (Figure 4.5).

It was noticed that the membrane preferentially rejected individual HAA_5 species. In contrast to what would be expected, low MW haloacetic acids were rejected by the membrane more than their high MW counterparts. The removal efficiency decreased in the order of CAA, BAA, DBAA, DCAA and TCAA. This sequence is consistent in every test condition and well correspond to the order of HAA_5' pK_a values (2.87, 2.89, 1.47, 1.26, and 0.51 for CAA, BAA, DBAA, DCAA and TCAA, respectively; Figure 4.6)

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 HAA_5 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, 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 HAA_5 species

would suggest lower ability for hydrogen bonding with water molecules and reflect their better rejection as observed.

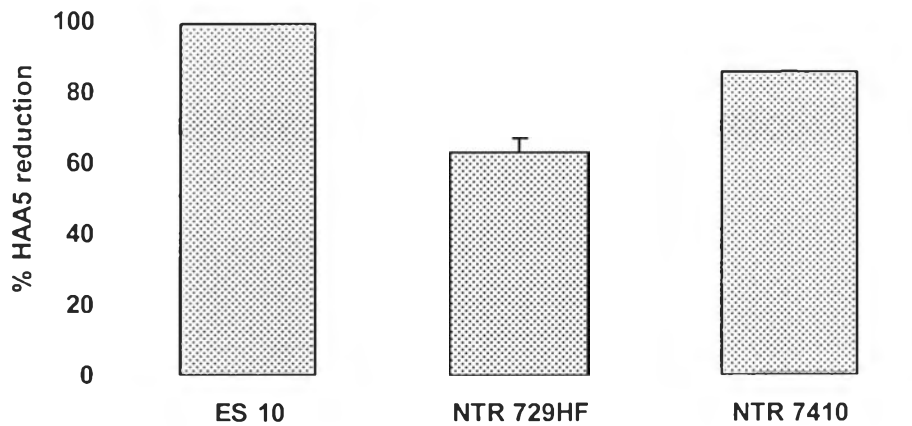

Figure 4.3: HAA $_5$ removal efficiency of NF membranes.

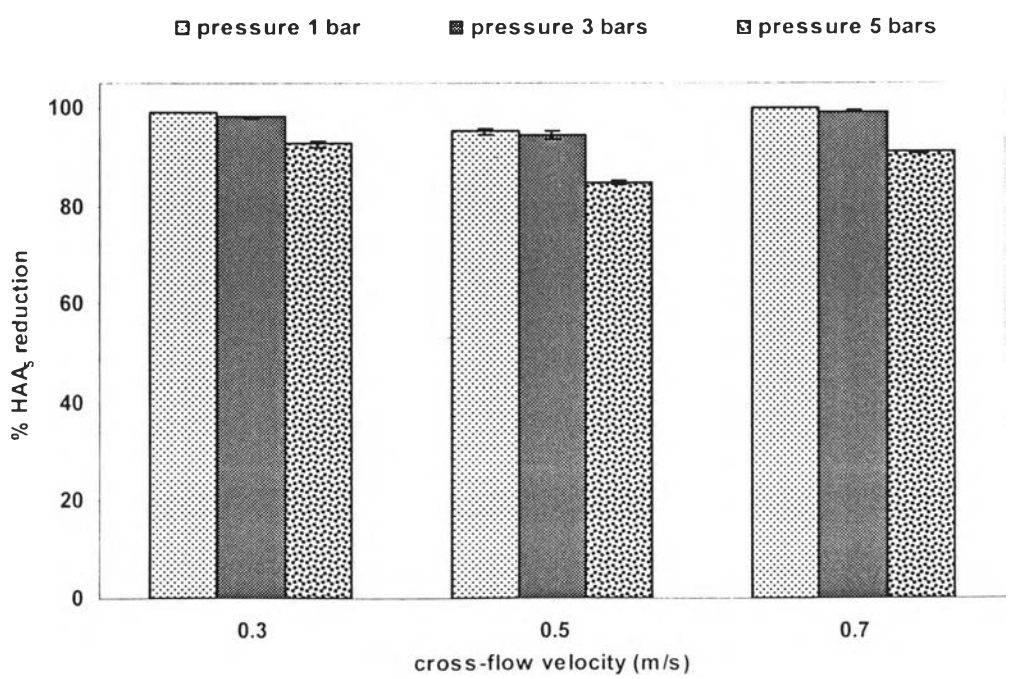

Figure 4.4: Effect of operating pressure and cross-flow velocity on the performance of ES 10

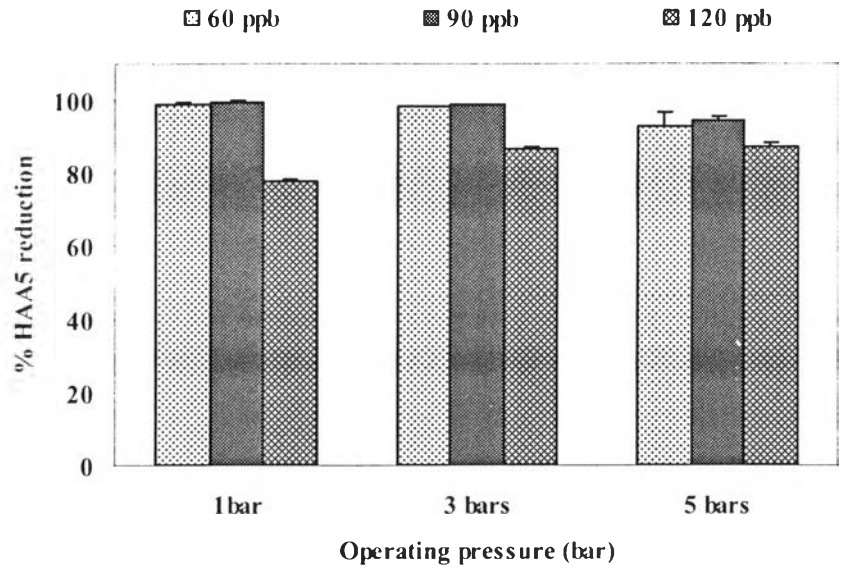

Figure 4.5: Effect of feed concentration on the performance of ES 10

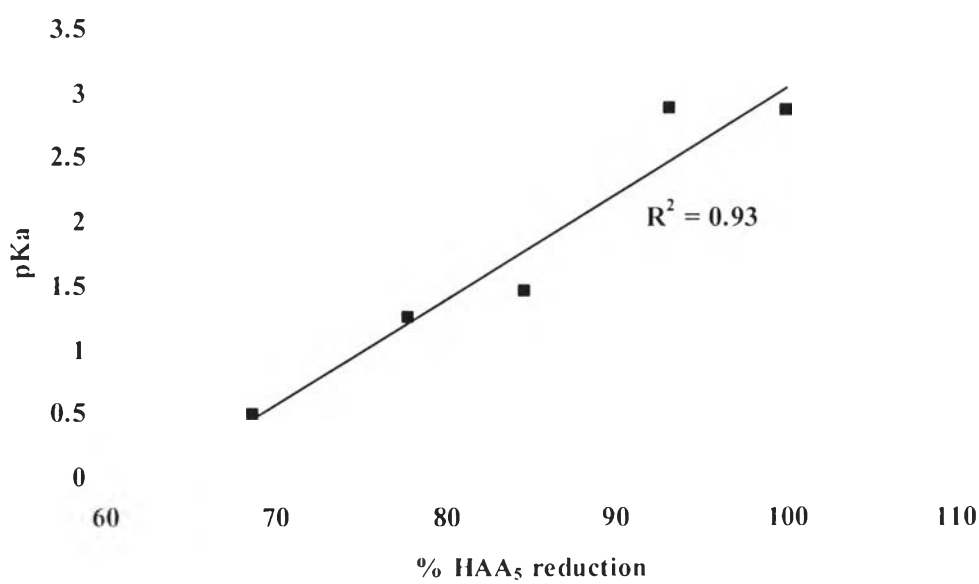

Figure 4.6: Correlation between p*Ka* and % removal of individual HAA species by ES 10 membrane.

4.3.2 Ozone-BAC

Ozonation experiments were also carried out with three HAA_5 concentrations, 60, 90, and 120 ppb. Results of the experiment shown in Figure 4.7 indicate that ozonation is not effective in removing HAA_5 under the testing condition (pH ~6). The removal efficiencies in all ozonation experiments range between 10-20%. The decomposition of HAA_5 by ozonation process follows the first-order behavior with the apparent rate constant of the reaction varies from 0.001 min^{-1} to 0.003 min^{-1} (Figure 4.8) The first-order simulation suggests that the apparent reaction rate of the ozonation of HAA_5 is not dependent on the concentration of dissolved ozone under the experiment conditions.

Ozone can either react with organic compounds directly or disintegrates into hydroxyl radicals that further oxidize the organic species reaction. Since pH of the experiment was around 6, the formation of hydroxyl (OH) radical from dissolved ozone was less likely. Dissociation of ozone to OH radical is preferred at a basic pH (Wang et al., 2005). Chlorine and carboxylic functional, both are electron withdrawing substituents in HAA_5 molecules, should direct the reaction between dissolved ozone and HAA_5 toward the nucleophilic reaction (Adam et al., 1997).

Ozonation of HAA_5 occurred selectively with individual HAA_5 species. Figure 4.9 showed that CAA and BAA are two primary HAA_5 species that were removed during the ozonation process. Other HAA_5 species remained relatively intact. Low reactivity of ozone toward TCAA, DCAA, and DBAA indicates that number of electron withdrawing substituent (i.e., chlorine and bromide) have the impact on the removal of HAA_5 by ozonation. Urbansky (2001) noted that two halogen atoms are sufficient to offer stability to the center carbon. Therefore, both di- and trihaloacetic acids do not readily undergo a nucleophilic reaction, especially in nonbasic solution such as the condition in this experiment.

HAA_5 reduction was drastically improved after the ozonated HAA_5 solution passing through BAC column that was inoculated with common bacteria in raw water. A complete removal of HAA_5 was observed in nearly all experimental conditions. The EBCT of 20 min or more was sufficient to remove 85-100% of HAA_5 in test solutions.

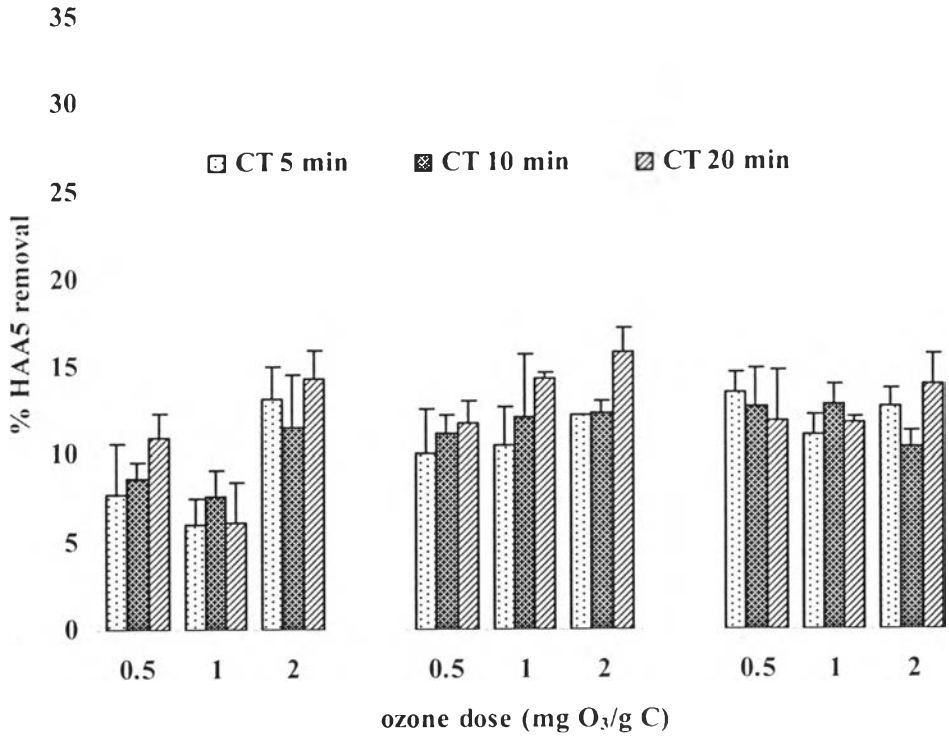

Figure 4.7: HAA_5 removal efficiency of the ozonation process.

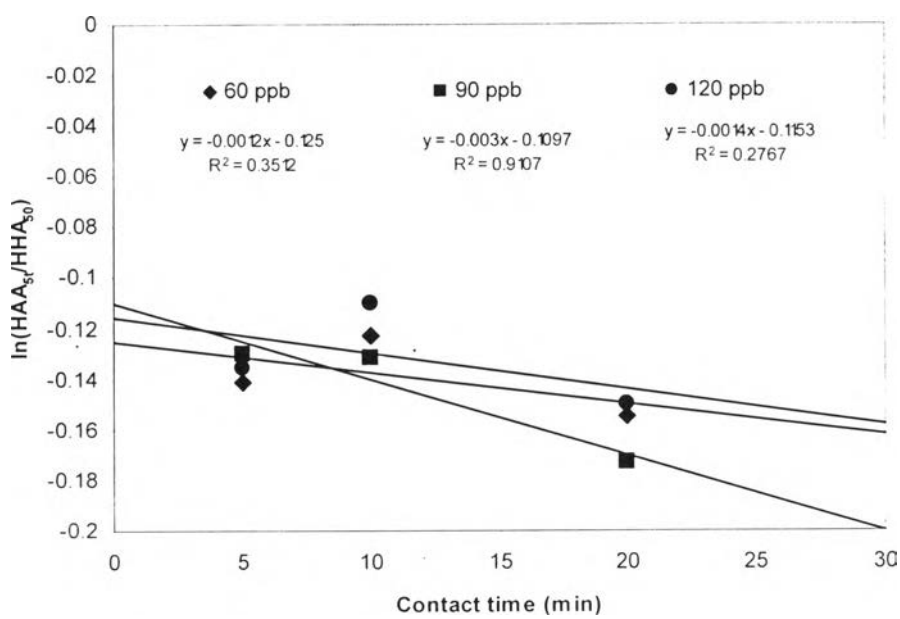

Figure 4.8 The first-order conversion of HAA_5 during ozonation.

The adsorption of HAA_5 on BAC is considered less likely. The BAC column had been fed with raw water for one year before running the HAA_5 experiment. The majority or perhaps all surface area of activated carbon should already been occupied by bacteria. Recent study showed that the BAA removal by the autoclaved BAC was negligible compared to a 100% removal efficiency of the original BAC (Xie and Zhou, 2002).

4.3.3 Comparing NF and Ozone-BAC

4.3.3.1 Performance

In the NF experiments, ES 10 provided the best performance among the three membranes selected. Its optimum condition was found at the operating pressure of 1 bar, and cross-flow velocity of 0.7 m/s. For ozone-BAC, according to the obtaining results of BAC experiments, the optimum condition was set at the ozone does of 0.5 mg ozone/mg carbon, contact time of 5 min, and EBCT of 20 min. Comparison of NF and ozone-BAC in removing HAA_5 was done based on data at these two optimum conditions. Figure 4.10 shows that the performance of NF is comparable to that of ozone-BAC in removing HAA_5 at the concentrations of 60 and 90 ppb. Both methods were able to almost completely eliminate HAA_5 (99-100% reduction) in the feed water. At the higher concentration of 120 ppb, however, the performance of ozone-BAC is better. The efficiency of ozone-BAC remained steady but that of NF lowered to approximately 77%.

4.3.3.2 Post-treatment product

The fundamental difference between NF and ozone-BAC must be recognized. NF physically removes HAA_5 intact, whereas ozone-BAC transforms HAA_5 into more benign product, such as CO_2. Although, both NF and ozone-BAC are equally effective in removing HAA_5 at concentrations of 60, and 90 ppb, NF does not actually eliminate HAA_5. The retentate remains concentrated with HAA_5. Further treatment of the acids is obviously necessary. This aspect is not a problem for ozone-BAC system since HAA_5 are mineralized to CO_2 and incorporated into biomass.

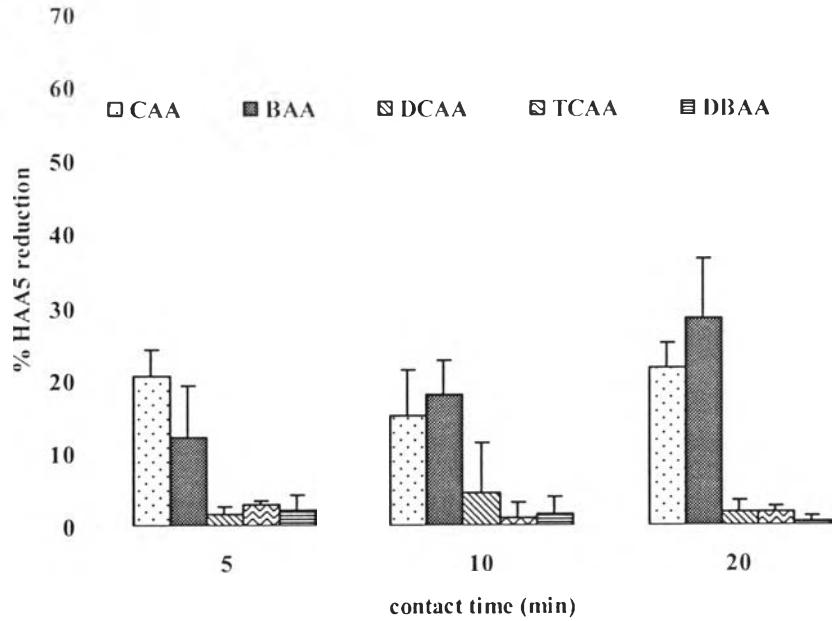

Figure 4.9: Removal of individual HAA species by ozonation.

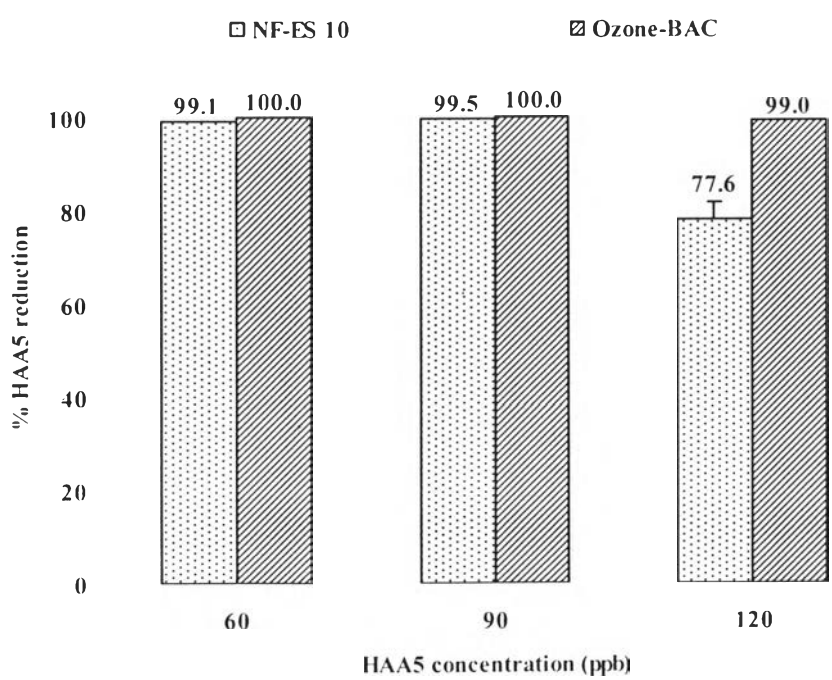

Figure 4.10: Comparison between the performances of NF using ES 10 membrane and ozone-BAC method.

NF, however, has one advantage over ozone-BAC. If used after chlorination, residue chlorine might not significantly affect the performance of the NF membrane, although it might shorten the membrane lifetime. Ozone-BAC, on the contrary, is sensitive to residue chlorine. Native bacteria growing on BAC would not be able to remain fully active in chlorinated water. Singer et al., (1999) reported that the extent of haloacetic acids removal by BAC depends upon residue chorine concentration. Moreover, residue chlorine adsorbed on activated carbon would make the carbon more brittle (Lykins et al., 1988). Another shortcoming of ozone–BAC is that the finished water might contaminate with bacteria in the BAC column. These aspects are trade-offs of both treatment methods.

4.3.3.3 Cost

Cost estimation for NF and ozone-BAC is based on the expense for electricity used for operating and maintaining the NF and ozone-BAC systems. In the NF system, electrical supply is needed for a DC booster pump (48 V), and a DC adapter (output 48V, 1A). For ozone-BAC system, power supply was required for an ozone generator (20 W) and a peristaltic pump (100VA.). Assuming pump efficiency at 80 %, and cost for electricity at 3 baht / unit, the estimated cost for NF and Ozone-BAC showed that the expense for the operation of the ozone-BAC system is higher than the NF system. Details of the calculation are as follows.

For NF system 48 V * 1 A = 48 W/sec

= (48/1000)/ (1/3600)

= 172.8 kW/hr (≈ 173 kW/hr)

Assuming: a) the pump efficiency 80 %

= 173*0.8 ≈ 138 kW/hr.

b) electricity fee is estimated to be 3 Baht / unit

estimated cost for NF = [(138 kW/hr*2 hr/batch)/Q)]* 3 Baht /unit

where Q = permeate volume at optimum condition of ES 10 in 2 hr.

= [(138 kW/hr*2hr/batch)/7.2 m^3]*3 Baht /unit

= 115 Baht /unit

For Ozone-BAC system

Ozone generator = 20 W/sec

= (20/1000)/ (1/3600) = 72 kW/hr.

Peristaltic pump = 100 W/sec

= (100/1000)/ (1/3600) =360 kW/hr.

Total = 72+360 = 432 kW/hr

Assuming: a) the pump efficiency 80 %

= 432*0.8 ≈ 345 kW/hr.

b) electricity fee is estimated to be 3 Baht /unit

estimated cost for ozone-BAC = [(345 kW/hr *2 hr/batch)/Q]* 3 Baht /unit

where Q = volume of effluent from biofilter at optimum EBCT(20 min.) in 2 hrs.

= [(345 kW/hr*2 hr/batch)/15.6m^3]*3 Baht /unit

= 132.7 Baht/unit

4.4 Conclusions

NF using ES 10 membrane and the ozone-BAC system are comparable in removing HAA_5 at concentrations of 60 and 90 ppb (95-100% removal). Ozone-BAC, however, is more superior at the higher feed concentration of 120 ppb. The performance of the NF membrane was regulated by the operating pressure and concentration of HAA_5 in feed water. Better HAA_5 removal was attained at low operating pressure and low feed concentration. Unlike NF, the performance of ozone-BAC system was uninterrupted by the HAA_5 concentrations. The EBCT of the BAC column was the primary controlling parameter of the system since the pretreatment using ozonation process is considered unnecessary. Less than 20 % of the initial HAA_5 was removed by the reaction with ozone. The majority of HAA_5 (80-90%) was biodegraded in the BAC column. Due to a superior performance of BAC, it is expected that BAC column could be used alone to control HAA_5 without any prior treatment.