Contents lists available at ScienceDirect

## Desalination



# 

# Pilot study of drinking water treatment with GAC, O<sub>3</sub>/BAC and membrane processes in Kinmen Island, Taiwan

### Jong-Sheng Yang<sup>a</sup>, Dong-Xing Yuan<sup>a,\*</sup>, Tzu-Pao Weng<sup>b</sup>

<sup>a</sup> College of Oceanography and Environmental Science, Xiamen University, 3610052, Fujian, China
<sup>b</sup> Kinmen Waterworks, Kinmen County, 893, Taiwan

#### ARTICLE INFO

Article history: Received 25 February 2010 Received in revised form 11 June 2010 Accepted 29 June 2010 Available online 7 August 2010

Keywords: 2-MIB Biological activated carbon Nanofiltration THMFP

#### ABSTRACT

A study on advanced treatment of drinking water was conducted in a pilot scale plant in Tai Lake, Kinmen, Taiwan. The raw water contains a high concentration of disinfection by-product (DBP) precursors and causes serious odor problems. Chlorination of the raw water produced higher haloacetic acid formation potential (HAAFP) than trihalomethane formation potential (THMFP). Therefore, the high concentration of NOMs, which is the major source of DBP precursors, and the removal efficiencies of non-purgeable dissolved organic carbon (NPDOC), UV<sub>254</sub>, THMFP, HAAFP, 2-methylisoborneol (2-MIB), and trans-1, 10-dimethyl-trans-9-decalol (geosmin) were evaluated for both conventional and advanced water treatment processes. 2-MIB and geosmin can be removed efficiently by the GAC and O<sub>3</sub>/BAC process, but bromo-THMs cannot. In addition, the removal efficiency of HAAFP was higher than that of THMFP by the GAC or O<sub>3</sub>/BAC process. The ultrafiltration (UF)-nanofiltration (NF) combined process showed removal efficiencies for NPDOC, UV<sub>254</sub>, THMFP, HAAFP of 88.7%, 94%, 84.3% and 97.5%, respectively. This study found that the GAC or O<sub>3</sub>/BAC process is a promising way to treat odor problems, and the UF–NF membrane process was one of the best available ways to remove NOMs and DBP formation potential.

© 2010 Elsevier B.V. All rights reserved.

#### 1. Introduction

The main sources of drinking water in Kinmen Island are both ground and surface waters, which contribute 49% of the water supply in the west and 51% in the east of the island, respectively. In Kinmen Island, the surface waters are polluted by agricultural activities, domestic wastewater discharges and livestock effluents, which result in eutrophication and cause blooming of algae in the reservoirs. Organic matters in natural water can cause odor, taste, color, and bacterial regrowth problems. Chlorine disinfection is a widely used process for eliminating pathogenic microorganisms in drinking water and preventing water-born diseases. NOMs in raw water react with chlorine to form disinfection by-products (DBPs), which is potentially carcinogenic or mutagenic to animals in laboratory test [1].

The drinking water in Kinmen Island suffers from problems of toxins, metabolite of algae, taste and odor (2-MIB and geosmin), trihalomethanes (THMs) and haloacetic acids (HAAs), which are difficult to remove by conventional treatment processes. In the meantime, the seawater intrusion causes a rising bromide concentration in the groundwater and surface waters. Chlorination of the water with bromide will shift the chlorinated DBPs to brominated DBPs, which increases the total DBPs vield and more easily exceeds the drinking water standard [2]. In order to reduce the production of DBPs, it is better to remove the dissolved organic precursors in the raw water before disinfection. However, the conventional water treatment processes cannot remove the DBPs precursors or the metabolite of algae effectively. The concentration of THMs in drinking water sometimes exceeded 0.1 mg/L in some places in Kinmen Island. Wang et al. [3] indicated that people living in Kinmen Island were threatened with a higher carcinogenic risk of THMs compared with other districts of Taiwan  $(7.77 \times 10^{-5} \text{ and } 7.88 \times 10^{-5} \text{ for male and}$ female, respectively). The water treatment in Kinmen Island is getting more and more stringent and upgrading the conventional to advanced water treatment process is urgent in the near future.

The available technologies recommended for the control of DBPs are NOMs removal or applying suitable disinfectants [4,5]. Enhanced coagulation, granular activated carbon (GAC), ozonation followed by biological activated carbon ( $O_3/BAC$ ), and membrane treatment processes are available to remove NOMs [6–8]. The GAC process can remove organic matters such as dissolved organic carbon (DOC),



Abbreviations: AOC, assimilable organic carbon; BAC, biological granular activated carbon; DBAA, dibromoacetic acid; DBP, disinfection by-product; DCAA, dichloroacetic acid; EBCT, empty bed contact time; EDC, endocrine disrupting compounds; GAC, granular activated carbon; HAA, haloacetic acid; HAAFP, haloacetic acid formation potential; MBAA, monobromoacetic acid; MCAA, monochloroacetic acid; MWCO, molecular weight cutoff; NF, nanofiltration; NOM, natural organic matter; NPDOC, non-purgeable dissolved organic carbon; SUVA, specific ultraviolet absorbance; TCAA, trichloroacetic acid; THM, trihalomethane; THMFP, trihalomethane formation potential; UF, ultrafiltration.

<sup>&</sup>lt;sup>k</sup> Corresponding author. Tel.: + 86 886 592 2184820; fax: + 86 286 592 2183127. *E-mail address:* yuandx@xmu.edu.cn (D.-X. Yuan).

<sup>0011-9164/\$ –</sup> see front matter 0 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.desal.2010.06.069

DBPs, 2-MIB, geosmin, and pesticides. Ozonation can shift a higher molecular weight compound into smaller ones. In this way, the aromatic or hydrophobic organic compounds can be converted to more hydrophilic, biodegradable organic compounds, such as aldehydes, carboxylic acids, ketones and other organic acids [9,10], which can also be further removed in a subsequent biological activated carbon (BAC) process [7,11,12]. Many studies found that NF membranes were effective in removing assimilable organic carbon (AOC), THMs, HAAs, microcystin and endocrine disrupting compounds (EDCs) [13–16]. The UF–NF combined membrane process had better removal efficiency of NOMs compared with other treatment processes, and is found to be the best available way to remove NOMs [13,17]. The main objectives of this paper are to evaluate the removal efficiency of organic matter, THMFP, HAAFP, 2-MIB, geosmin in each treatment unit, and the performance of three advanced treatment processes.

#### 2. Materials and methods

#### 2.1. Pilot plant

The pilot plant for this study was built at the Tai Lake water works in Kinmen Island using the source water from Tai Lake and Ron Lake with a mixing ratio of 1:1. The pilot scale plant conventional treatment process was composed of coagulation, flocculation, dissolved air flotation, sedimentation, and rapid sand filtration. The treatment was divided into three treatment processes, A, B and C. Process A was conventional treatment followed by O<sub>3</sub>/BAC, Process B was Process A followed by UF-NF, and Process C was conventional treatment followed by GAC and UF-NF. Fig. 1 shows the schematic process of the pilot scale plant. The ozone contactor was 2.5 m in height and 0.3 m in inner diameter (ID), which was made of stainless steel. Ozone was produced by an ozone generator, using air as the feed gas. Ozone gas was bubbled into the contactor continuously and used counter flow to increase ozone concentration. The GAC column (height 3 m, ID 0.4 m) was filled with 1.5 m of GAC and 0.3 m silica sand. Filtration velocity was 159 m/day and empty bed contact time (EBCT) was 27.1 min. The BAC column (height 3 m, ID 0.48 m) was filled with 1.33 m of GAC and 0.3 m of silica sand. The filtration velocity was 111 m/day and EBCT was 39.1 min. Both GAC and BAC columns were filled with GAC (Pt. Tanso Putra Asia, Indonesia). The type of UF membrane used was PES-UF made by Koch Membrane Systems (USA). The length and diameter of the module were 1016 mm and 101.6 mm, respectively. The effective surface area of the UF module was 7.5 m<sup>2</sup> and the molecular weight cutoff (MWCO) of the membrane was 10,000. The NF membrane was made of polyamide (Hydranautics, USA). The length and diameter of the module were 1016 and 100.3 mm, respectively. The NF module nominal membrane area was 7.87 m<sup>2</sup>. Table 1 shows the operating parameters of each unit in the pilot plant.

The capacity of the pilot plant was about  $30 \text{ m}^3$ /day. Aluminum sulfate was used as a coagulant with feed concentration about 80-100 mg/L depending on the result of the jar test. Backwashing of both rapid sand filtration and the GAC column were practiced twice a day. UF and NF membranes were cleaned on site every 3 months, or when the operating pressure exceeded the designed value (UF>150 psi and NF>600 psi).

#### 2.2. Analytical methods

Water samples were taken weekly from each of the sample sites from April to September, 2006, and transferred directly to the laboratory. NPDOC,  $UV_{254}$ , THMFP, HAAFP were analyzed weekly, and 2-MIB and geosmin were analyzed once per month.

The dissolved organic matter content of the water was quantified by NPDOC, which was measured by the combustion-infrared method using a total organic carbon analyzer (TOC-5000, Shimadzu, Japan).  $UV_{254}$  was used to obtain a representation of the aromatic characteristic of the organic matter. It was measured at a wavelength of 254 nm (U-1100, Hitachi, Japan).

THMFP was measured by the purge and trap packed-column gas chromatographic method using a GC (3400, Varian, USA) equipped with an electron capture detector (ECD). An adequate amount of sodium hypochlorite (NaOCI) was injected into the sample to ensure that at least 1 mg/L free chlorine residual existed at the end of the 7-



Fig. 1. Schematic diagram of the pilot plant.

Table I
---------

Operating parameters of Tai Lake pilot plant.

Process	Parameter	Design values
Coagulation	Retention time	60 s
	Gradient	$750 \text{ s}^{-1}$
	Rotational speed	200 rpm
Flocculation	Retention time	20 min
	The first stage	$45 \text{ s}^{-1}$
	gradient	
	The first stage	60 rpm
	rotational speed	-
	The second stage	$30 \text{ s}^{-1}$
	gradient	
	The second stage	45 rpm
	rotational speed	•
Dissolved air	Air to solid ratio (A/S)	0.06 mL/mg
flotation (DAF)	Recycle water	$5.3 \text{ m}^3/\text{day}$
	Radius	0.6 m
Sedimentation	Retention time	1.2 h
	Surface loading rate	30 m/day
Rapid sand filtration	Anthracite	1.2 m
*	Sand	0.3 m
	Gravel	0.1 m
	Filtration velocity	$180 \text{ m}^3/(\text{m}^2 \times \text{day})$
GAC	Height	3 m
	Diameter	0.4 m
	Filtration velocity	$159 \text{ m}^{3}/(\text{m}^{2} \times \text{day})$
	Buck density	0.46-0.5 mL/g
	EBCT	27.1 min
Ozone contactor	Ozone dosage	4 mg/L
	Hydraulic retention time	20 min
BAC	Height	3 m
	Diameter	0.48 m
	Filtration velocity	$111 \text{ m}^3/(\text{m}^2 \times \text{day})$
	Buck density	0.46-0.5 mL/g
	EBCT	39.1 min
UF	Flux rate	0.12 m/h
	Maximum feed water	<5
	SDI (15 min)	
	Maximum operation	150 psi
	pressure	· · I ·
NF	Flux rate	0.017 m/h
	Maximum feed water SDI	<5
	(15 min)	
	Maximum operation	600 psi
	pressure	r ·
Clear wells	Retention time	4 h
	Volume (diameter × height)	1.84 m×2 m
	3/	

day (25 °C) incubation period. The five haloacetic acids (HAAs) (monochloroacetic, dichloroacetic, trichloroacetic, monobromoacetic, dibromoacetic acids) were determined with USEPA Standard Method 552.2 by a GC/ECD system (HP 6890, Agilent, USA) using a DB-1701 capillary column.

#### Table 2

Raw water quality of the Tai Lake pilot plant.

Parameter	Measured range	Average
E. coli, CFU/100 mL	10-10,000	522
Total coliform, CFU/100 mL	1500-1,500,000	216,988
Alkalinity, mg/L as CaCO <sub>3</sub>	32-166	79
Odor, TON	26-951	305
TDS, mg/L	182-399	241
THMFP, µg/L	174–571	326
HAAFP, µg/L	164–1036	501
$\mathrm{Br}^-$ , $\mu\mathrm{g}/\mathrm{L}$	42.4–397	108.3
$UV_{254}, m^{-1}$	11.7–19.7	15.1
NPDOC, mg/L	4.6-8.3	6.2
SUVA, $m^{-1}/(mg/L)$	1.53-3.63	2.49
Algae, cells/mL	11,374–165,528	60,007
NH <sub>3</sub> –N, mg/L	0.18-2.0	0.67
Fe, mg/L	0.09-2.68	0.81
2-MIB, ng/L	8.73-67.61	43.3
Geosmin, ng/L	3.87-17.6	7.4
Turbidity, NTU	3.79-152.1	17.43
Colour, PCU	4–503	123.9
pH	6.8-8.4	7.16
conductivity, µS/cm	216-666	355.5
Temperature, °C	18-33	26.54

2-MIB and geosmin were analyzed using the headspace solidphase micro-extraction method coupled with a GC (HP-6890, Agilent, USA) and a mass spectrometer detector (HP-5973, Agilent, USA). The procedure for the analysis of 2-MIB and geosmin was the same as that prescribed by the Standard Methods NIEA W537.50B of Taiwan EPA.

#### 3. Results and discussion

#### 3.1. Raw water characteristics

Table 2 shows the raw water quality parameters of the pilot plant, which is characterized as high NPDOC (>6 mg/L), moderate turbidity, and a high threshold odor number (305 TON). It also contained ammonia-nitrogen (NH<sub>3</sub>–N), probably from domestic, agriculture and livestock wastewaters. The presence of nutrient in the lake water explains the algae bloom, and the concentration of algae was about 60,000 cells/mL. 2-MIB and geosmin were the major odorous compounds with concentrations of 43.3 and 7.4 ng/L, respectively. The taste and odor causing compounds released by algae are one of the major problems in Kinmen Island.

Specific UV absorbance (SUVA) is defined as  $UV_{254}$  divided by NPDOC (i.e.,  $UV_{254}$ /NPDOC), which can be a useful indicator for the characteristics of dissolved organic matter. However, a low SUVA ( $< 2 m^{-1}/(mg/L)$ ) value implied the water contains aromatic carbons to a low extent and was more hydrophilic [18]. Fig. 2



Fig. 2. The variation of SUVA and NH<sub>3</sub>−N in different months. ♦ and □: SUVA and NH<sub>3</sub>.



Fig. 3. The average values of turbidity, UV<sub>254</sub> and NPDOC treated with different units. 🖾 🔲 and 🖾: Turbidity, UV<sub>254</sub> and NPDOC.

shows the trends of SUVA in the raw water, which increased from 1.9 to  $3.3 \text{ m}^{-1}/(\text{mg/L})$  from April to June and then decreased to  $2.5 \text{ m}^{-1}/(\text{mg/L})$  in September. Edzwald and Tobiason [19] indicated that SUVA between 2 and  $4 \text{ m}^{-1}/(\text{mg/L})$  comprised the hydrophilic and hydrophobic NOMs. However, the SUVA below  $2 \text{ m}^{-1}/(\text{mg/L})$  implied the water contained non-humus substance which was relatively lower in both hydrophobic and molecular weight. April to September is the main rainy season in Kinmen Island, contributing 80% of the annual precipitation. Land use in Kinmen Island can be divided into woody vegetation (34%), herbaceous vegetation (45%), lake and river (5%), and nonvegetation (16%) [20]. In the rainy season, many humic substances deposited on the top soil layer were carried into the reservoirs, and resulted in SUVA increasing from April to June. According to the operation department report, the domestic discharge was not all collected to the wastewater treatment plants, because all the pump stations were turned off in a heavy rain or storm, so that the sewage flowed directly into the rivers and reservoirs. On the other hand, the domestic discharge was collected to the wastewater treatment plants only in the dry season and it is the probable reason why the concentration of NH<sub>3</sub>-N increased from April to September. In addition to domestic discharge, the discharges of agricultural activities and livestock effluents were flushed into the reservoirs during the rainy season which resulted in the increase of NH<sub>3</sub>-N concentration.

#### 3.2. Performance evaluation of each treatment process

#### 3.2.1. Rejection of turbidity and organic matters

Fig. 3 shows the water quality after treatment by rapid sand filtration. The turbidity was decreased from 17.4 to 1.3 NTU with removal efficiency of 92%, which meets the drinking water standard.

Treated water flowed through the GAC process in which turbidity was removed almost completely. The NF process should be carefully designed with regard to required pre-treatment to prevent fouling. As the silt density index (SDI) of lake water was much higher than the suggested maximum value of 3, it was clear that removal of colloidal particles and turbidity was necessary prior to membrane filtration. Therefore, this study used water after GAC and BAC processes from the conventional process as feed water for the UF–NF process to avoid fouling. It is thought that an ideal turbidity removal efficiency not only reduces the fouling of particles and backwashing frequency but also increases the lifetime of the following advanced equipment.

During the 6 months of operation, the variation of NPDOC in each treatment process is shown in Fig. 4. Xu [11] and Kim [17] indicated that DOC was difficult to remove by a conventional treatment process which the removal efficiency of DOC was about 30%. In this study, the rejection of NPDOC by the rapid sand filtration process was 33.9%. The concentration of NPDOC in treated water was 4.1 mg/L, which cannot meet the current drinking water management act of Taiwan (TOC<4 mg/L). On the other hand, compared with the rapid sand filtration process, the GAC process could increase the NPDOC removal efficiency about 10% by adsorbing the DOC onto the pore surface of the activated carbons. The O<sub>3</sub>/BAC process enhanced the NPDOC removal efficiency about 30% in comparison with the rapid sand filtration process. Ozonation can produce the two major oxidants ozone and hydroxyl radical, which can react with DOC and break down the molecules into smaller ones. Therefore, the AOC concentrations increase with increasing ozone dosage in the treated water [10]. For examples, organic acids, aldehydes and ketones were biodegraded by microorganisms. Kim et al. [21] indicated that the O<sub>3</sub>/BAC process can increase the elimination efficiency of DOC about 20% by biodegradation. Before the test of this pilot scale study, rapid small-scale column tests (RSSCT) was evaluated the breakthrough time of activated



Fig. 4. The variation of NPDOC concentration in different treatment units. •,  $\Box$ ,  $\triangle$ ,  $\bigcirc$  and •: Raw water, rapid sand filtration, GAC; BAC and UF–NF<sub>B</sub>. UF–NF<sub>B</sub> means UF–NF in process B.



Fig. 5. The treatment of four kinds of THMFP in different units. 🛄, 🖾 and 🗄: CHC1<sub>3</sub>, CHC1<sub>2</sub>Br, CHC1Br<sub>2</sub> and CHBr<sub>3</sub>.

carbon in the laboratory. The bed life of GAC is around 238 days according to the calculation of RSSCT results. Based on the report by Yan et al. [22], the bed life of O<sub>3</sub>/BAC is about 2–3.5 times than that of GAC. Lai et al. [13] pointed out that the UF–NF process reduced the AOC concentration to 4  $\mu$ g acetate-C eq/L, which can avoid microorganism regrowth in the distribution system and ensure the safety of drinking water. In this study, the treated water by the rapid sand filtration, O<sub>3</sub>/BAC and UF–NF membrane process could reduce the NPDOC to 0.7 mg/L with removal efficiency about 88.7% so that it was able to avoid the regrowth of microorganisms.

The removal efficiency of UV<sub>254</sub> was 45.7% by the rapid sand filtration process, 57.6% by the combined GAC process, 81.5% by the combined  $O_3/BAC$  process and 94% by the combined UF–NF membrane process. In comparison to the  $O_3/BAC$  and GAC processes, the removal efficiency of the former was about 24% higher than the latter. Because ozone can oxidize the conjugated or aromatic compounds by cleaving the double bond and transferring the organic compounds to more biodegradable ones, it benefits the following BAC process. In this study, the removal efficiency of UV<sub>254</sub> was higher than NPDOC. It is thought that humic substances were removed easily in comparison with the non-humic portion for the same DOC levels.

#### 3.2.2. Removal of THMFP and HAAFP

The THMFP of four kinds of THMs (chloroform, dichlorobromomethane, dibromochloromethane and bromoform) were investigated in this study. As shown in Fig. 5, the predominant species of THMFP were chloroform formation potential (CHCl<sub>3</sub>FP) and bromodichloromethane formation potential (CHCl<sub>2</sub>BrFP) with concentrations of 210 and 88 µg/L, respectively. As shown in Table 3, the distribution of THMFP concentrations were in the order of CHCl<sub>3</sub>FP>CHCl<sub>2</sub>BrFP>CHClBr<sub>2</sub>FP, and the concentration of bromoform formation potential (CHBr<sub>3</sub>FP) was not available to attribute to the bromide concentration in raw water appearing lower than the formation concentration. After the rapid sand filtration process, the THMFP was 266 µg/L. The effluent of the rapid sand filtration process was treated by the GAC process, and the formation potential of THMFP was 222 µg/L. Similarly, for the water treated by the O<sub>3</sub>/BAC process, the formation potential of

Table 3	
Removal efficiencies of various treatment units	(%).

THMFP was 160 µg/L. According to the testing result, CHClBr<sub>2</sub>FP was not removable by the GAC or O<sub>3</sub>/BAC processes. It is found that bromo-THMs formation potential increased accompanied by the Br<sup>-</sup>/NPDOC ratio increase, because the concentration of DOC decreased after the GAC and BAC processes. Sketchell et al. [23] indicated that the bromo-THMs ratio increase can be attributed to the Br<sup>-</sup>/DOC ratio increase. El-Dib et al. [24] indicated that after the chlorination of organic matters, the CHClBr<sub>2</sub> reaction rate was higher than CHCl<sub>3</sub> and CHCl<sub>2</sub>Br. In the formation process of THMs, CHClBr<sub>2</sub> reached equilibrium faster than the other species. Chang et al. [2] reported that THM species substitution from chloro-THMs to bromo-THMs was associated with bromide, and this will contribute to the substitution rate of HOBr being 25 times higher than HOCl. In this study, the formation potential of bromo-THMs was increased from raw water (35%) to ozonation followed by BAC (55%). After the treatment process, the NPDOC concentration was lower and the number active sites of organic matter were also lower. This probably contributed to the formation of CHClBr<sub>2</sub> which took advantage of reacting with active sites of organic matter more than CHCl<sub>3</sub> and CHCl<sub>2</sub>Br.

The reduction of CHClBr<sub>2</sub>FP concentration was not clear in the rapid sand filtration, GAC and O<sub>3</sub>/BAC processes. Although CHClBr<sub>2</sub>FP concentration increased a little in these three treatment processes, the values were not significantly distinct from each other. The results in this study showed that the GAC and BAC processes were unable to reduce the CHClBr<sub>2</sub>FP effectively. Interestingly, in the rapid sand filtration and GAC process, the formation of CHBr<sub>3</sub>FP did not appear in the treated water, but after the O<sub>3</sub>/BAC process the CHBr<sub>3</sub>FP existed in the treated water. Huang et al. [25] indicated that ozonation of water containing bromide will produce brominated organic compounds such as CHBr<sub>3</sub>, DBAA, 2, 4-DBP, DBAC, DBAN, the formation threshold levels of which were 0.15, 0.25, 0.25, 0.1 and 0.45 mg/L, respectively. Furthermore, ozonation of water containing bromide produces CHBr<sub>3</sub>, too. There was a good linear relationship between bromoform and TOBr ( $R^2 = 0.871$ ), and the four individual DBPs, including bromoform, DBAN, MBAA and DBAA, could only represent 8.0–27.9% of TOBr [26]. von Gunten [27] successfully determined the main pathways for BrO<sub>3</sub><sup>-</sup> (and TOBr) formation during the second phase of an ozonation process.

Treatment process	NPDOC	UV <sub>254</sub>	CHCl <sub>3</sub>	CHCl <sub>2</sub> Br	THMFP	DCAA	TCAA	MBAA	DBAA	HAAFP	2-MIB	Geosmin
Rapid sand filtration	33.9	45.7	23.5	18.9	18.3	37.5	49.5	57.3	41.0	51.9	-	-
GAC	43.6	57.6	37.5	30.5	31.8	51.0	71.9	76.3	48.5	71.6	92.0	83.1
O <sub>3</sub> /BAC	62.9	81.5	66.8	39.8	51.1	68.6	89.4	93.3	61.8	88.6	96.3	100.0
UF-NF <sub>B</sub>	88.7	94.0	86.3	90.3	84.3	77.3	98.5	98.6	95.2	97.5	-	-

-: The item was not analyzed.

UF-NF<sub>B</sub>: B process.



Fig. 6. The treatment of five kinds of HAAFP in different units. 🔲, 🔜, 🖾 and 🔃: MCAA, MBAA, DCAA, TCAA and DBAA.

After the O<sub>3</sub>/BAC process, the water was treated by the UF–NF membrane process, and the formation potentials of CHCl<sub>3</sub>, CHCl<sub>2</sub>Br, CHClBr<sub>2</sub> were 28.7, 8.6, and 6.7  $\mu$ g/L, with removal efficiencies of 86.3%, 90.3% and 75.4%, respectively, and the overall removal efficiency of THMFP was 84.3%. Kim et al. [17] used different advanced treatment processes to treat the water of the Han River and the removal efficiency of THMFP by UF–NF membranes was 85%.

As shown in Figs. 5 and 6, the raw water HAAFP concentration was about 35% higher than the THMFP concentration in the period of this study. HAAFP contained the formation potential of TCAA, DCAA, DBAA and MBAA. Chloro-HAAFP was the predominant species which accounted for about 90% of total HAAFP, and bromo-HAAFP accounted for about 10%. After different treatment processes, bromo-HAAFP species ratio increased from 10% in raw water to 46% in the UF-NF process, and the species of THMFP had a similar trend. The HAAFP removal efficiencies in the rapid sand filtration, GAC, O<sub>3</sub>/BAC and UF-NF processes were 51.9%, 71.6%, 88.6% and 97.5%, respectively. The research was implemented from April to September, the range of temperature was 18 °C to 31 °C and the average water temperature was 26.5 °C. Kim et al. [6] indicated that the reduction of HAA correlated with the activity of microorganisms, and the water temperature increase upgraded the biodegradation of HAA, but biodegradation of THM was low. The degradation of HAA was probably due to the highly favorable conditions for microbial activity. McRae et al. [28] reported that specific type of bacteria (Xanthobacter sp., Sphingomonas sp.) may degrade HAA species such as MCAA, MBAA and TCAA. In the rapid sand filtration process, the removal efficiency of THMFP was about 44% lower than of HAAFP. This result showed the adsorption and biodegradation ability of THM were poorer than HAA. Both THMFP and HAAFP were removed efficiently by UF–NF membranes because of their sieve effect and charge effect.

#### 3.2.3. Elimination of geosmin and 2-MIB

Geosmin and 2-MIB were not removed effectively by the rapid sand filtration process. The rapid sand filtration process followed by GAC and post-ozonation can reduce the geosmin and 2-MIB to below the odor threshold concentrations (geosmin: 4 ng/L; 2-MIB: 9 ng/L) [29]. Therefore, odorant compounds in water need to be removed by further advanced water treatment process. Activated carbon can effectively adsorb geosmin [30] and 2-MIB [31], and the later one is limited to the first 5000–10,000 bed volumes [32]. As shown in Fig. 7 and Table 3, geosmin and 2-MIB were treated by the GAC process; the concentrations were reduced to 1.3 ng/L and 3.5 ng/L with removal efficiencies of 83.1% and 92%, respectively. Geosmin and 2-MIB were treated by the O<sub>3</sub>/BAC process, with removal efficiencies of 100% and 96.3%, respectively. Atasi et al. [12] indicated that after the ozonation process, geosmin was easier to remove than 2-MIB. Ho et al. [33] used different ozone dosages to treat geosmin and 2-MIB, and the results showed a similar trend. This probably can be attributed to the fact that the geosmin has a slightly lower solubility and molecular weight and has a flatter structure.

#### 3.3. Evaluation of performance of treatment processes

Table 4 shows the performance of conventional and three advanced treatment processes in the pilot plant. The reduction of turbidity, THMFP and HAAFP by the conventional treatment process



Fig. 7. The treatment of 2-MIB and geosmin in different units. 🖾 and 🎆: 2-MIB and geosmin.

#### Table 4

Evaluation the performance of conventional and three advanced treatment processes.

Items	Unit	The clean water requirement of Kinmen water works	Conventional	А	В	С
Turbidity	NTU	0.3	1.6	0.3	0.2	0.2
TDS	mg/L	250	-	259	52.4	73.8
THMFP	%	80	18.3	51.1	84.3	-
HAAFP	%	80	51.9	88.6	97.5	96
THM	µg/L	40	-	-	1.14	0.68
HAAs	µg/L	30	-	-	N.A.	N.A.

-: The item was not analyzed.

N.A.: Not available.

did not meet the aim of the pilot scale plant study, so further advanced treatment processes are necessary.

Advanced treatment includes process A, process B and process C. Only turbidity and HAAFP met the requirements for clean water in Process A. Turbidity, TDS, THMFP, HAAFP, THM and HAAs of Processes B and C all met the requirements for clean water. HAAs in Processes B and C were not available. Water quality in Process A was poorer than those in Processes B and C. Process A was unable to reduce the TDS and THMFP effectively. According to the results of this study, the removal efficiency had no difference between process B and C. The UF–NF combined membranes had the best ability for water treatment and this process will be adopted to treat the water of Kinmen Island in the near future.

#### 3.4. Cost analysis of treatment processes

The cost of a 20,000 m<sup>3</sup>/day scale plant was estimated on the base of the results obtained in this study, as shown in Table 5. It was found that construction cost in Process B was the most expensive, and Process A the cheapest. The total capital costs in Processes A, B and C were US\$7,664,833, 17,595,367 and 15,813,867 dollars, respectively. As a result, depreciation of the capital costs of the three processes was based on the straight-line method. Amortization of capital costs in Processes A, B and C were US\$ 383,242,879,768 and 790,693 dollars per year, respectively. In addition, the interest rate in construction

#### Table 5

Comparison of unit cost of product water from three treatment processes.

was set to 6% so the annual construction interest costs in Processes A, B and C were US\$459,890, 1,055,722 and 948,832 dollars, respectively.

Operation costs were mainly electricity and membrane replacement. In process A, electricity cost was 44% of operation costs. In process B, electricity and membrane replacement costs were 28 and 52%, respectively. In process C, electricity and membrane and replacement costs were 21 and 57%, respectively. The estimation of real unit cost of electricity was used. In Kinmen Island, electricity consumption was highly subsidized; general consumers paid US\$0.09 for every kWh of electricity consumed. Without the subsidy, the price of electricity was US\$0.22 per kWh, and the operation cost of electricity will increase 2.4 times. Considering the depreciation of construction costs, 6% interest rate and operation costs, total costs in Processes A, B and C were US\$ 2,574,405, 7,525,581 and 7,059,465, respectively. The unit cost in Processes A, B and C would be US\$0.35, 1.03 and 0.97 per cubic meter, respectively.

The water quality after the advanced treatment processes with UF–NF could meet the drinking water standard, as shown in Table 4. Although there were no significant differences of water quality between Processes B and C, especially turbidity, color, TDS, THMFP, HAAFP, THM and HAA, the cost of Process B (1.03US\$/m<sup>3</sup>) was higher than that of Process C (0.97US\$/m<sup>3</sup>). Therefore, using Process C to build an advanced water treatment plant would be more suitable and economical than the others.

#### 4. Conclusion

This study evaluates the performance of conventional and three advanced water treatment processes for organic matter, odorous compounds and DBPFP.

The conclusions obtained from this study are as follows:

- 1. The raw water of the pilot plant had a high concentration of NPDOC, UV<sub>254</sub>, THMFP, HAAFP, 2-MIB and geosmin. Because the reservoirs were polluted by anthropogenic activities and the algae were blooming, NOM and odor problems were increasing.
- 2. According to the results of this pilot study, in comparison with the conventional treatment process, the GAC and  $O_3/BAC$  process could increase the removal efficiency of NPDOC about 10% and 30%, respectively. The odorant compounds 2-MIB and geosmin were removed easily by GAC and  $O_3/BAC$ .

Component	Items	Process (US \$)			
		A	В	С	
Plant capacity, m <sup>3</sup> /day		20,000	20,000	20,000	
1. Capital costs		7,664,833	17,595,367	15,813,867	
	UF and NF installation	-	6,109,091	6,109,091	
	Granular activated carbon equipment	969,697	969,697	969,697	
	Construction and piping equipment	1,520,212	2,693,273	2,693,273	
	Electricity and instrumentation installation	2,988,212	4,733,818	3,383,636	
	Miscellaneous costs	1,489,909	1,489,909	1,220,545	
	Indirect capital costs	696,803	1,599,579	1,437,624	
2. Depreciation		383,242	879,768	790,693	
(capital costs/20 years)					
3. Interest payment		459,890	1,055,722	948,832	
(6% of capital costs)					
4. Operating costs		1,731,273	5,590,091	5,319,939	
	Membrane replacement	-	3,054,545	3,054,545	
	Granular activated carbon replacement	242,424	242,424	484,848	
	Manpower	175,758	175,758	175,758	
	Electricity	887,879	1,615,152	1,099,333	
	Chemicals	55,303	115,909	115,909	
	Electricity and piping maintenance	74,970	91,364	94,606	
	Sludge disposal	294,939	294,939	294,939	
Annual cost $(2+3+4)$		2,574,405	7,525,581	7,059,465	
Unit cost	US\$/m <sup>3</sup>	0.35	1.03	0.97	

- 3. The raw water of this study contained bromide, which caused the chloro-DBPFPs to shift to the bromo-DBPFPs. The treatment process including conventional, GAC and O<sub>3</sub>/BAC was unable to reduce the CHClBr<sub>2</sub>FP effectively, and ozonation of water containing bromide produced CHBr<sub>3</sub>. Reduction of HAAFP was higher than that of THMFP when it was treated by the GAC or O<sub>3</sub>/BAC processes, because the HAA was more easily adsorbed and biodegraded than THM by the GAC or O<sub>3</sub>/BAC processes.
- 4. The UF–NF membranes were found to produce the highest quality finished water, with 88.7% NPDOC rejection, 94% UV<sub>254</sub> rejection, 84.3% THMFP rejection, 97.5% HAAFP rejection. The UF–NF membranes process could be proposed as one of the best available processes for removing NOM and DBPFP. However, fouling/scaling control is very important to the operation of the NF system.
- 5. According to the water quality and economic evaluation, using Process C to build an advanced water treatment plant is more suitable and economical than the others in the future.

#### Acknowledgements

We express our sincere thanks to the Kinmen Water Works for financial support, and Professors Hsuan-Hsien Yeh and Tsair-Fuh Lin at the National Cheng Kung University of Taiwan for technical support.

#### References

- H. Komulainen, Experimental cancer studies of chlorinated by products, Toxicology 198 (2004) 239–248.
- [2] E.E. Chang, Y.P. Lin, P.C. Chiang, Effects of bromide on the formation of THMs and HAAs, Chemosphere 43 (2001) 1029–1034.
- [3] G.S. Wang, Y.C. Deng, T.F. Lin, Cancer risk assessment from trihalomethanes in drinking water, Sci. Total Environ. 387 (2007) 86–95.
- [4] S. Sorlini, C. Collivignarelli, Trihalomethane formation during chemical oxidation with chlorine, chlorine dioxide and ozone of ten Italian nature waters, Desalination 176 (2005) 103–111.
- [5] C. Guay, M. Rodriguez, J. Serodes, Using ozonation and chloramination to reduce the formation of trihalomethanes and haloacetic acids in drinking water, Desalination 176 (2005) 229–240.
- [6] J.K. Kim, B.S. Kang, DBPs removal in GAC filter-adsorber, Water Res. 42 (2008) 145-152.
- [7] P.C. Chiang, E.E. Chang, C.H. Liang, NOM characteristics and treatabilities of ozonation processes, Chemosphere 46 (2002) 926–936.
- [8] I. Mijatovic, M. Matosic, B.H. Cerneha, D. Bratulic, Removal of natural organic matter by ultrafiltration and nanofiltration for drinking water production, Desalination 169 (2004) 223–230.
- [9] W.J. Huang, G.C. Fang, C.C. Wang, The determination and fate of disinfection byproducts from ozonation of polluted raw water, Sci. Total Environ. 345 (2005) 261–272.
- [10] F. Hammes, E. Salhi, O. Koster, H.P. Kaiser, T. Egli, U. von Gunten, Mechanistic and kinetic evaluation of organic disinfection by-products and assimilable organic carbon (AOC) formation during the ozonation of drinking water, Water Res. 40 (2006) 2275–2286.

- [11] B. Xu, N.Y. Gao, X.F. Sun, S.J. Xia, M.D. Simonnot, C. Causserand, M. Rui, H.H. Wu, Characteristics of organic materials in Huangpu River and treatability with the O<sub>3</sub>-BAC process, Sep. Purif. Technol. 57 (2007) 346–353.
- [12] K.Z. Atasi, T. Chen, J.I. Huddleston, C.C. Young, I.H. Suffet, Factor screening for ozonating the taste- and odor-causing compounds in source water at Detroit, USA, Water Sci. Technol. 40 (6) (1999) 115–122.
- [13] W.L. Lai, H.H. Yeh, I.C. Tseng, T.F. Lin, J.J. Chen, G.T. Wang, Conventional versus advanced treatment for eutrophic source water, J. Am. Water Works Assoc. 94 (12) (2002) 96–108.
- [14] A.D.L. Rubia, M. Rodriguez, V.M. Leon, D. Prats, Removal of natural organic matter and THM formation potential by ultra- and nanofiltration of source water, Water Res. 42 (2008) 714–722.
- [15] M.R. Teixeria, M.J. Rosa, Microcystins removal by nanofiltration membranes, Sep. Purif. Technol. 46 (2005) 192–201.
- [16] Y. Yoon, P. Westerhoff, S.A. Snyder, E.C. Wert, Nanofiltration and ultrafiltration of endocrine disrupting compounds, pharmaceuticals and personal care products, J. Membr. Sci. 270 (2006) 88–100.
- [17] M.H. Kim, M.J. Yu, Characterization of NOM in the Han River and evaluation of treatability using UF–NF membrane, Environ. Res. 97 (2005) 116–123.
- [18] P.C. Singer, Humic substances as precursors for potentially harmful disinfection by-products, Water Sci. Technol. 40 (9) (1999) 25–30.
- [19] J.K. Edzwald, J.E. Tobiason, Enhanced coagulation: US requirements and a broader view, Water Sci. Technol. 40 (9) (1999) 63–70.
- [20] Li, M.Y., An application of satellite imagery for land cover mapping of Kinmen Island. MS thesis, National Taiwan University, Taipei, Taiwan (in Chinese) 2004.
- [21] W.H. Kim, W. Nishijima, E. Shoto, M. Okada, Pilot plant study on ozonation and biological activated carbon process for drinking water treatment, Water Sci. Technol. 35 (8) (1997) 21–28.
- [22] M. Yan, D. Wang, X. Ma, J. Ni, H. Zhang, THMs precursor removal by an integrated process of ozonation and biological granular activated carbon for typical Northern China water, Sep. Purif. Technol. 72 (2010) 263–268.
- [23] J. Sketchell, H.G. Peterson, N. Christofi, Disinfection by-product formation after biologically assisted GAC treatment of water supplies with different bromide and DOC content, Water Res. 29 (12) (1995) 2635–2642.
- [24] M.A. El-Dib, R.K. Ali, THMs formation during chlorination of raw Nile River water, Water Res. 29 (1) (1995) 375–378.
- [25] W.J. Huang, L.Y. Chen, H.S. Peng, Effect of NOM characteristics on brominated organics formation by ozonation, Environ. Int. 29 (2004) 1049–1055.
- [26] X. Zhang, S. Echigo, H. Lei, M.E. Smith, R.A. Minear, J.W. Talley, Effect of temperature and chemical addition on the formation of bromoorganic DBPs during ozonation, Water Res. 39 (2005) 423–435.
- [27] U. von Gunten, Ozonation of drinking water: Part Π. Disinfection and by-product formation in presence of bromide, iodide or chlorine, Water Res. 37 (2003) 1469–1487.
- [28] B.M. McRae, T.M. LaPara, R.M. Hozalski, Biodegradation of haloacetic acids by bacterial enrichment cultures, Chemosphere 55 (2004) 915–925.
- [29] Y.S. Kim, Y.G. Lee, C.S. Gee, E. Choi, Treatment of taste and odor causing substances in drinking water, Water Sci. Technol. 35 (8) (1997) 29–36.
- [30] C. Ng, J.N. Losso, W.E. Marshall, R.M. Rao, Freundlich adsorption isotherms of agricultural by-product-based powdered activated carbons in a Geosmin-water system, Bioresour. Technol. 85 (2002) 131–135.
- [31] P. Pendleton, S.H. Wong, R. Schumann, G. Levai, R. Denoyel, J. Rouquerol, Properties of activated carbon controlling 2-methylisoborneol adsorption, Carbon 35 (8) (1997) 1141–1149.
- [32] J. Cromphout, R. Vanhoucke, Reduction of exploitation costs and improvement of water quality by the implementation of ozonation at the waterworks in Kluizen, Proc. IOA-EA3G-VIVAQUA International Conference on Ozone and Related Oxidants in Advanced Treatment of Water for Human Health and Environmental Protection. Brussels, Belgium, May 15–16, 2008.
- [33] L. Ho, G. Newcombe, J.P. Croue, Influence of the character of NOM on the ozonation of MIB and Geosmin, Water Res. 36 (2002) 511–518.