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High removal of haloacetic acids from treated drinking water using bio-activated carbon method

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ABSTRACT

This study focused on an effective method of using bio-activated carbon to treat excess amounts of haloacetic acids (HAAs) in treated drinking water from a water treatment plant. Experiments were conducted in a pilot-scale treatment system to evaluate the removal of HAAs in drinking water using a biological activated carbon filter (BACF). HAAs have been thought to be one possible nutrient that supports heterotrophic bacteria's regrowth in drinking water. Under neutral conditions, the results showed that the pilot-scale treatment system reduced approximately 80% of HAAs. At increased alkalization conditions, the output water treated by the pilot-scale treatment system by the BACF showed an increased removal of HAAs. In addition, the concentration of assimilable organic carbon (AOC) primarily indicates micro-organisms' growth in the water supply network. The amount of AOC in water is reduced after BACF treatment. The empirical equation for the HAAs concentrations that can reduce pathogenic contamination in the treated water was established by examining other nutrients (e.g. dissolved organic carbon), with ultraviolet absorbance at 254 nm wavelength (UV_{254}), and ammonia (nitrogen) concentration. These findings may be useful in designing advanced processes for conventional water treatment plants or for managing water treatment and distribution systems that provide high-quality drinking water.

Keywords: Haloacetic acids; Carcinogen; Assimilable organic carbon; Nutrient control; Water treatment

1. Introduction

The main nutrients that influence bacterial activities include organic carbon, nitrogen, and phosphorus [1,2]. Haloacetic acids (HAAs) are one possible nutrient for heterotrophic bacteria's regrowth in drinking water [3,4]. Excess amounts of HAAs have been frequently identified in the output waters from water treatment plants in Southern Taiwan. Excessive amounts of disinfectant byproducts (DBPs) have also been identified in the output water from water treatment plants in Southern Taiwan. Natural water contains copious amounts of natural organic matter (NOM), but the properties and types differ according to region, time of year, season, and local anthropogenic activities. The primary source of NOM in uncontaminated water sources is humus, which has a

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relatively large molecular weight and is typically divided into humic acid and fulvic acid [5].

After chlorination, the NOM of total organic carbon (TOC) in water sources may form carcinogenic DBPs, such as haloacetic acids (HAAs). These can substantially influence the quality of water from treatment plants, and may result in excess amounts of DBPs and microbial regrowth in water supply networks [6]. Therefore, combining bio-oxidation and filtering methods to remove DBPs may help stabilize the quality of drinking water [7]. Liquid chlorine is also added to the rapid sand filters in water treatment plants for disinfection and to oxidize and transform organic macromolecules into small organic molecules. This process results in decreased dissolved organic carbon (DOC) in treated drinking water [8].

Activated carbon, which has a high adsorption capacity, is currently the most widely applied adsorption agent because it is an ideal substance for removing organic and inorganic pollutants from aqueous solution [9–11]. The removal mechanisms of biological activated carbon consist of minor adsorption and major biodegradation. During treatment, granular activated carbon (GAC) is packed inside a column to treat HAAs in drinking water. In prior work, HAAs were removed from synthetic raw water using a laboratory-scale biological activated carbon filter (BACF). The removal amount was 25 and 29% at 4 and 50°C, respectively [12]. The major operating factors associated with HAAs removal include temperature, type and dose of disinfecting agents, dissolved oxygen levels, and empty bed contact time (EBCT). Two types of GACs (PK1-3 and CAgran) have been packed into columns to solve the excess amounts of DOC in secondary effluent in a wastewater treatment plant [13]. When adsorption was the main mechanism, the removal of DOC was 81 and 64.5% for PK1-3 and CAgran, respectively. In contrast, when biodegradation was the main mechanism, the removal was 45.9 and 37.8% for PK1-3 and CAgran, respectively.

Therefore, combining bio-oxidation and filtering methods to remove assimilable organic carbon (AOC) may stabilize the quality of drinking water [8]. Bacteria may regrow using trace amounts of organics that remain in treated drinking water as substrates. AOC, in particular, has been used as an indicator during water distribution. AOC is determined by a method that uses two bacterial species and is sensitive to trace amounts of organics [14,15]. In Taiwan [16], it has been reported that the concentration of AOC in treated drinking water should be controlled under 50 μg C/L when the concentration of residual chlorine in the distribution system ranges from 0.2 to 1.0 mg/L.

In this study, a pilot-scale BACF treatment system was used to remove HAAs from treated drinking water that was taken from a water treatment plant at various pH levels. The measured values of water quality parameters (such as HAAs) in the output water from the BACF treatment system were evaluated and showed the effect of pH levels. This work attempts to reduce excess amount of nutrients (such as HAAs) when entering water distribution systems. Only some HAAs can be biodegraded. These findings highlight new procedures and operating parameters for controlling water quality and pollution by HAAs in water treatment plants.

2. Materials and methods

2.1. Experimental procedure

The raw water sources for the water treatment plant were from the Agoden lake. The treatment processes in this plant included a raw water equalization pond, a rapid sand filter, post-chlorination disinfection, and a finishing water reservoir. A pilot scale of the BACF treatment system was constructed with the rapid sand filter. In this study, from January 2015 to July 2015, water samples were collected from the effluent of a rapid sand filter at a water treatment plant in Southern Taiwan and pumped into the BACF treatment system. The pilot-scale BACF treatment system consisted of a pump and two columns fixed with GAC, which was utilized to treat the influent water in a continuous-flow reactor. The BACF treatment system had the following characteristics: up-flow type column, with height = 110 cm, diameter = 21 cm, GAC bed height = 90 cm, bed volume = 30 L, and number of bed = 2. The beds were connected in series, and the inlet flow was between 1.2 and 3 L/min. The effluent samples from the BACF treatment system were then analyzed for HAAs using gas chromatography (GC) with an electron capture detector. The operating conditions of the BACF treatment system in the water treatment plant were similar to the conditions of BACF treatment system. In this work, the pH level ranged from 6 to 10, the temperature = 20.0 ± 2.0°C, and the EBCT = 50 min.

2.2. Preparation of the BACF system

Bituminous coal GAC used in this work was manufactured by Calgon Carbon Co. (Tianjin, China). It was prewashed using 0.1 M nitric acid and was washed again using deionized water. It was dried using natural ventilation. The physical characteristics of the GAC, including iodine adsorption capacity,

apparent density, and effective grain diameter, were the same as described in previous work [16]. The iodine adsorption capacity of the GAC was greater than 900 mg/g.

2.3. Enrichment of the micro-organisms on the GAC surface in the BACF

During microbial cultivation, the GAC was used as a support. Water was used for microbial cultivation and was obtained from the rapid sand filter of the water treatment plant. Specifically, the water was poured directly into the BACF treatment system to allow micro-organisms adhere and grow. This eventually formed a biofilm on the surface of the GAC. This cultivation period continued for at least 3 months (from October 2014 to December 2014) prior to starting the experiments of HAAs by BACF treatment. This was to reduce the effect caused by the adsorption of activated carbon in the BACF treatment system and allow major biodegradation by the integrated formation of biofilms on the activated carbon. During the cultivation period, the HPC bacteria and concentration of the TOC at the outlet of the BACF treatment system were monitored for the formation of the biofilm on the surface of the GAC.

HPC bacteria were enumerated by the pour plating procedure with R2A agar (Nippon Pharmaceuticals Co., Ltd, Tokyo) after 7 d of incubation at 20˚C [17]. Measurements of HPC bacteria on the GAC surface were taken by supersonic instruments and then by the pour plating procedure with R2A agar after 7 d of incubation at 20˚C. The average values of HPC at all times were the geometrical mean values of duplicate measurements, and the standard deviation was less than 5%.

2.4. Measurement of HAAs

HAAs were analyzed using USEPA Method 552.3 [18]. In brief, HAAs were extracted using methyl-tert-butyl-ether (MTBE). A surrogate standard (100 ppm 2,3-dibromopropionic acid in MTBE, HPLC grade) was then added to each sample to assess the individual method performance. After the samples were extracted, they were analyzed using a gas chromatograph with electron capture detectors (GC-ECD, Agilent 7890A) and a DB-1701 column (30 m × 0.32 mm ID; film thickness, 0.25 m). The HAAs content was determined as described by NIEA W538.51B. The water sample was first acidified to pH 0.5, and extracted with MTBE. Sulfuric acid methanol was then added to form methyl esters and enable the analyses for HAAs or Dalapon. The organic solvent layer containing the methyl esters was separated and analyzed by GC/ECD. The five brominated and chlorine-containing HAA5 are monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA). In the HAA5 and at a water temperature of 20˚C, HAA9 accounted for approximately 95%. All the average values from the experiments were measured in triplicate [16].

2.5. Measurement of the AOC

The determination of the AOC concentration was performed using the original bioassay method [18]. This bioassay procedure involves the use of *Pseudomonas fluorescens* P17 (ATCC 49642) and *Spirillum species* NOX (ATCC 49643). Prior to the AOC analysis, the samples of the non-treated and treated water were sterilized at 70˚C for 40 min. The resulting samples were then cooled to room temperature and incubated with P17 and NOX at 25˚C for 8 d. The culture medium was Lab-Lemco Nutrient Agar (LLA). Next, the number of cell units formed was counted on days 1, 3, 5, 7, and 8. The concentration of AOC was estimated as the maximum number of organisms multiplied by the standard carbon yield. The unit of measurement was μg acetate C/L. All samples were measured in triplicate.

Another ideal method to measure the concentration of AOC over three days was developed using an AOC bioassay. A liquid chromatograph, coupled with organic carbon detection (LC-OCD, Dionex DX-500), was used [19,20].

2.6. Statistical analysis

Statistical methods were applied to the current study in organizing, analyzing, and evaluating data, which were used to facilitate predictions. The SPSS 17.0 statistical package was used in this work. Regression analysis is a statistical method commonly used to make predictions and evaluations. The influence of one or more independent variable(s) on the dependent variables is examined. Data with one or more independent variables are described and predicted or estimated based on a given dependent variable. Regression analyses are categorized into simple and multiple regressions. Several water quality parameters were used to conduct a multivariable analysis on the AOC to identify the coefficient of determination (R^2), and the predicted equation.

3. Results and discussion

3.1. Variations in the water quality during micro-organism cultivation in the BACF

Table 1 is a summary of the raw water quality from the water treatment plant, and the influent and effluent of BACF during microbial cultivation. The results show that HPC per gram of GAC (for microbial count in the BACF column) ranged from 1.9 × 105 to 6.2 × 105 CFU/g GAC. This indicates that the micro-organisms were successful and stable during cultivation on the GAC surface. The results also show that from October 2014 to December 2014, the concentration of TOC in the raw water was between 0.96 and 1.39 mg/L. The results monitored the biological activity existing in the BACF. The results in Table 1 show the HPC bacterial count of the first and second columns to be 1.2E+05–3.6E+05 CFU/g and 2.5E+05–4.9E+05 CFU/g, respectively. The bacterial count of the second column was higher than the first. The DO level of raw water was 7.6–10.52 mg/L. After the BACF treatment system, the DO level increased to 8.01–10.2 mg/L. Finally, the DO of the second column in the outflow dropped to 4.02–7.61 mg/L. The concentration of the DO was sufficient to maintain the desired growth of the micro-organisms. The results of the HPC proved that the existence of the micro-organism in the BACF columns was stable.

The raw water, prior to the equalization pond in the water treatment plant, had no chlorine added. The concentration of TOC was between 0.96 and 1.39 mg/L, and contained high amounts of organic matter. After the pre-disinfection process, coagulation, sedimentation, and rapid sand filtration, free chlorine, and TOC were 0.01–0.02 mg/L and 0.22–0.32 mg/L, respectively. The results showed that the organic matter did not change significantly after the traditional purification process in this water treatment plant. However, the organic matter was effectively degraded by the BACF treatment system. Therefore, the TOC concentration at the outflow of the BACF is lower than the influent. Notably, the micro-organisms survived in the BACF treatment system because treating HAAs and TOC, with free chlorine in the influent, was under 1.0 mg/L.

DO refers to the concentration of dissolved oxygen molecules in water. It is an important indicator of water pollution conditions. All organisms are dependent on oxygen to maintain metabolic processes and produce energy for the growth and regeneration of cells. Therefore, the concentration of DO in water is essential to aquatic organisms. The concentration of DO changed from the raw water to the influent and effluent of the BACF. This shows that the DO concentration changes in the BACF treatment system. The DO content of the raw water ranged from 7.6 to 10.5 mg/L. The DO content in the influent of the BACF was 8.0–10.2 mg/L. After the BACF treatment system, the DO decreased to 4.02–7.61 mg/L. The DO concentration was sufficient to maintain the desired growth of the micro-organisms. Therefore, the presence of micro-organism growth in the BACF treatment system was judged by the DO concentration. Low free residual chlorine avoided the inhibitory effect of microbial growth in BACF.

Table 1
Summary of raw water quality from the water treatment plant, and the influent and effluent of BACF during microbial cultivation

	HPC numbers (CFU/g GAC)		DO (mg/L)			Free chlorine (mg/L)			TOC (mg/L)		
Time	1st column in BACF	2nd column in BACF	Raw water	Influent BACF	Effluent BACF	Raw water	Influent BACF	Effluent BACF	Raw water	Influent BACF	Effluent BACF
2014.10.17	1.2E+05	2.8E+05	10.5	9.2	6.0	ND	0.5	ND	0.96	0.84	0.22
2014.10.24	–	–	7.6	8.1	5.0	ND	0.48	ND	–	–	–
2014.11.01	2.5E+05	2.5E+05	9.0	10.1	4.1	ND	0.72	ND	1.20	0.95	0.32
2014.11.07	–	–	10.3	10.2	7.6	ND	0.4	0.01	–	–	–
2014.11.14	3.3E+05	3.9E+05	9.0	10.1	4.1	ND	0.72	ND	1.12	0.96	0.22
2014.11.28	3.2E+05	4.6E+05	7.8	9.3	6.5	ND	0.49	0.02	1.39	1.20	0.32
2014.12.04	–	–	8.8	8.0	4.0	ND	0.87	ND	–	–	–
2014.12.11	3.5E+05	4.8E+05	8.3	9.2	4.3	ND	0.61	0.01	–	–	–
2014.12.15	3.6E+05	4.9E+05	9.3	10	7.6	ND	0.61	0.01	1.25	1.03	0.23

3.2. Changes of HAAs with different pH levels in the BACF

Haloacetic acids are used as a general DBP during the chlorination process of drinking water. It also belongs to the microbial nutrients in the water distribution system. The water turbidity and concentration of NOM are especially enhanced during rainy seasons and typhoons. The NOM reacts with sodium hypochlorite to form halogen acetic acid. This leads to deterioration of water quality, and regrowth of microorganisms in the distribution network.

The results of the HAAs in Table 2 were plotted against various pH levels (Fig. 1(a) and (b)). Fig. 1(a) shows the variation in HAAs concentration, which changed between the raw water and the influent and effluent of the BACF. The results in Fig. 1(a) show the changes of HAAs at various pH of BACF. The concentration of HAAs in the influent of BACF ranged from 0.306 to 0.396 mg/L. After the BACF treatment system, the concentration of HAAs in the effluent was reduced to 0.030–0.057 mg/L, which passes the national drinking water standard.

Fig. 1(b) shows the effect of pH on the removal of HAAs by BACF. When the pH was at 6, the removal of HAAs was 78%. In contrast, at pH 7, the removal of the HAAs was approximately 90%. At pH 8–9, the removal of HAAs increased to 86%. This indicates that higher pH conditions help the BACF treatment system to reduce high amounts of HAAs. At pH 10, HAAs hydrolysis may have occurred because of the alkaline conditions. The adsorption of HAAs by the BACF was probably the major process, with biodegradation as the minor process.

3.3. Removal of the HAA at neutral pH

Fig. 2 shows the changes in the HAA5 concentration with respect to time in a continuous-flow model in the pilot plant. The EBCT ranged from 30 to 50 min. The results of the various EBCTs on HAA5 removal from the water indicate an average HAA5 concentration of 46 ± 5.2 μg/L in the water. After the BACF treatment, the average HAA5 removal rates were about 80, 81, and 83% after 30, 40, and 50 min of EBCT, respectively. Therefore, the BACF is a good selection for reducing HAA5 concentrations from treated drinking water. The most effective EBCT time was 50 min. However, effective HAA5 removal can be achieved after 30 min of EBCT and is, therefore, recommended for cost savings. The water quality standard of HAA5 (30 μg/L) was set by the Taiwan Water Corporation and was adopted as an assessment standard in this study. In the near future, the Environmental Protection Administration of Taiwan is expected to establish an upper limit for HAA5 in its drinking water quality standards.

The EBCT model was used in this BACF system. The EBCT model can be expressed using Eq. (1):

$$\mathrm{EBCT} = \frac{V}{Q} \tag{1}$$

Here, V is the bed volume (m^3) and Q is the volumetric rate (m^3/min). Therefore, the BACF value in this study was expressed in minutes (min). Higher EBCTs required a larger amount of adsorbent and a smaller influent flow rate.

Table 2
Average concentrations of influent and effluent of BACF, and the removal of BACF operating at varied pH levels

BACF	pH	6	7	8	9	10
Influent	TOC (mg/L)	1.39	1.48	1.57	1.53	1.57
	HAAs[a] (mg/L)	0.354	0.396	0.331	0.317	0.306
	DO (mg/L)	8.8	8.9	8.6	8.8	8.8
	Free residual chlorine (mg/L)	0.72	0.58	0.57	0.64	0.52
Effluent	TOC (mg/L)	0.53	0.36	0.32	0.26	0.27
	HAAs[a] (mg/L)	0.078	0.059	0.046	0.038	0.031
	DO (mg/L)	6.6	6.3	6.0	6.1	6.2
	Free residual chlorine (mg/L)	ND	0.01	ND	ND	0.01
TOC removal (%)		62	76	80	83	83
HAAs removal (%)		78	85	86	88	90

Notes: The average concentrations are geometrical mean values of triplicate measurements (the operation conditions: pH 7.5 ± 0.2, temperature = 20.4 ± 1.2°C, and EBCT = 50 min).

[a]Taiwan Environmental Protection Agency set a level 0.06 mg/L (60 μg/L) on HAA5 level.

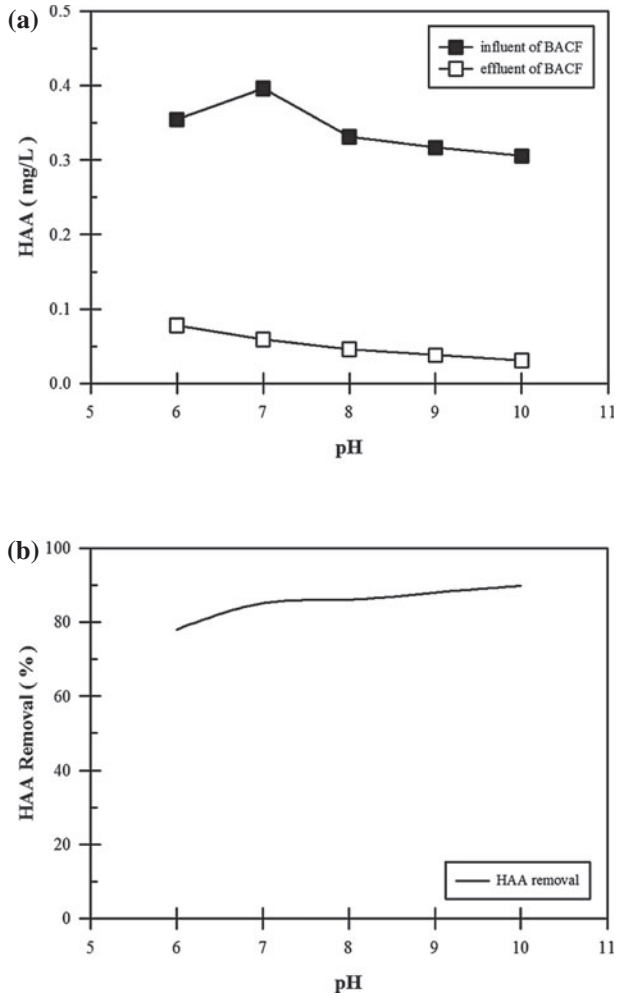

Fig. 1. Effect of pH on the removal of HAAs by BACF: the average concentrations are geometrical mean values of triplicate measurements (the operation conditions: temperature = 20.4˚C, EBCT = 50 min). (a) Concentration of HAAs at different pH between influent and effluent of BACF and (b) variation of HAAs removal at different pH by BACF.

Table 3 presents the analytical results for the HAA5 in the influent and effluent waters. The concentrations of the HAA5 in the effluent, after the BACF system, decreased as the retention time increased. Recent research [21] has demonstrated that the hydrophilic fraction of water is a precursor to the HAA5. In this study, DCAA, MBAA, and DBAA were the three major HAA5 species that were identified in the treated drinking water. These three species represent approximately 76.8% of the HAA5 in the effluent water. From a toxicological point of view, the DCAA species is the most important HAA5. The results presented in Table 3 show that TCAA is not easily removed by biological filtration methods. This finding is consistent with many other reported studies [3].

Table 4 compares the removal of HAA at different operating conditions for various water sources using the BACF or a biological activated carbon (BAC) combined with the advanced oxidation process (AOP). All drinking water samples that used these biological methods exhibited a removal amount ranging from 60 to 90% on HAA5. In addition, the removal of the different species of the HAA showed that the TCAA was not easily removed by the biological filter. The UV–H_2O_2-based AOP was used to treat raw water surface water. Relative to the untreated raw water, the combined AOP-BAC treatment showed a reduced efficiency of 43, 52, and 59%, for DBPs, TOC, and UV_{254}, respectively [22]. The sequential Fe^0-BAC process to treat artificial drinking water containing HAA reported [23] the removal efficiencies for TCAA and total HAAs were 77 and 59%, respectively. TCAA was significantly removed by reduction in the Fe^0 column. Prior work [24] reported that the advanced O_3/BAC process removed approximately 94% haloacetic acids formation potential (HAAFP) in the lake water at a pilot plant. The main sources of the lake water were both the ground and the surface.

Biodegradation is a potentially important removal process for HAAs and HAA. The degraders were successfully enriched from the biofilm (BAC) and distribution system. [25] Other carbon sources are likely to be present in the distribution systems (including mixtures of HAA and other organic compounds), which could result in a decrease in the HAA degradation rates. Thus, the effects of temperature, pH, and chlorine residue may need to be considered. The application [26] of temperature stress (4 and 50˚C) and a chloramine shock to BAC operating at 20˚C resulted in the removal of HAA degradation, which indicates that biodegradation is the major process of HAA removal. Batch culture tests, with six HAAs, revealed that all HAAs degraded under aerobic and anoxic conditions, except TCAA, which failed to degrade under anoxic conditions.

Currently, the best available technologies for HAAs control include enhanced coagulation/softening, GAC adsorption, and bio-activated carbon method for precursor removal and the use of alternative disinfectants [27]. A biologically activate carbon (BAC) filter [28] was continuously operated on site for the treatment of HAAs in an outdoor swimming pool at EBCT of 5.8 min. Results showed the removal of HAAs from the pool water with a nominal efficiency of 57.7% by BAC while the chlorine residual was 1.71 ± 0.90 mg/L. THMs and TOC were not removed and thus were not considered as indicators of the effectiveness of BAC filtration.

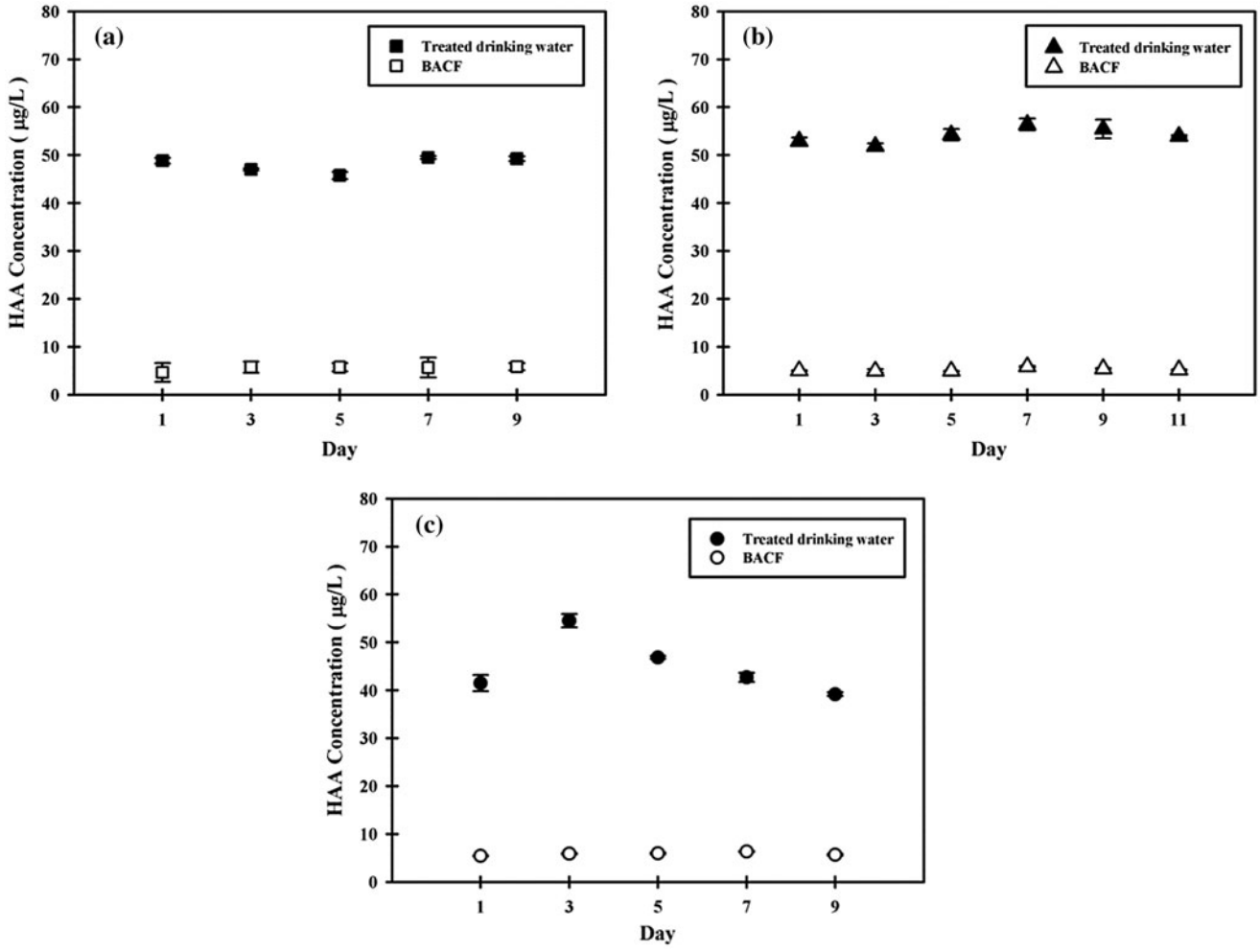

Fig. 2. Changes in concentration of haloacetic acids with respect to time by BACF at neutral conditions: (a) EBCT 30 min, (b) EBCT 40 min, and (c) EBCT 50 min. Error bars indicate the standard deviation from triplicate measurements.

Additional bio-molecular by biofilm detachment is suspected to be DBP precursors. The treatment of BACF may release extra bio-molecular. The release of extracellular polymeric substances by attached microorganisms is a very complicated process, which is affected by many factors [29]. A better understanding of the factors affecting the biosynthesis for extracellular polymers and its role will help in the eradication of attached bacteria from the surface. An ideal method to measure the rate of biofilm detachment has been developed under a dynamic in shear stress, which was monitored using Focused Beam Reflectance Measurements (FBRM, LASENTEC) and mass fractionation [30].

3.4. Correlation analysis of HAA with the water conditions

A reduction of HAA5 concentration in the samples, which were collected for the water quality tests, was observed after conducting the BACF. This reduction indicated the removal of HAA5. To examine their relationships with the HAA5, the qualities of the input water (in the water treatment plant), BACF, and the output water were selected for the correlation analyses.

The SPSS 17.0 statistical package was used to derive multiple regression equations and to identify the HAA5 from the BACF. The highest coefficient of determination (R^2) for the empirical linear regression equations was determined.

The empirical equation for the HAAs concentrations in the water was established by examining the major water parameters that were related to the HAA reactions, including DOC, UV_{254}, and ammonia nitrogen (NH_3-N).

A multivariable empirical equation of HAA5 is shown in Eq. (2):

Table 3
Results of mean concentration changes in the five species of HAA5 at various EBCTs by the BACF system

Species of HAA_5	EBCTs (min)	Influent (μg/L)	Effluent (μg/L)
MCAA	30	3.07	0.09
DCAA		8.16	0.29
TCAA		5.87	3.91
MBAA		20.93	4.42
DBAA		8.55	0.09
MCAA	40	4.64	0.35
DCAA		7.48	0.53
TCAA		7.40	4.64
MBAA		17.38	2.79
DBAA		4.56	0.17
MCAA	50	4.61	0.55
DCAA		7.91	0.71
TCAA		6.19	3.39
MBAA		18.48	1.64
DBAA		7.99	0.09

Table 4
Comparisons for removing HAA using the BACF and BAC-advanced oxidation processes

Treatment process	Parameters	Removal of HAA	Refs.
BAC	Feed water: surface water EBCT 8.2 min	DCAAFP: 29% TCAAFP: 46%	[22]
UV/H_2O_2—BAC	UV: 500–3,000 mJ/cm^2 H_2O_2: 10–20 mg/L BAC: EBCT 8.2 min	TOC: 52% UV_{254}: 59%	[22]
UV/H_2O_2—BAC	UV: 500 mJ/cm^2	DCAAFP: 37% TCAAFP: 50%	
UV/H_2O_2—BAC	UV: 550 mJ/cm^2	DCAAFP: 3% TCAAFP: 42%	
UV/H_2O_2—BAC	UV: 1,300 mJ/cm^2	DCAAFP: 40% TCAAFP: 71%	
UV/H_2O_2—BAC	UV: 3,000 mJ/cm^2	DCAAFP: 63% TCAAFP: 85%	
Zero valent Fe—BAC	Feed water: artificial water Operation time: 14 d EBCT: 2.5–30 min Biomass: 10^8 cell/g Column: length 30 cm × diameter 3 cm EBCT: 10 min EBCT: 30 min	 Total HAAs: 100% Total HAAs: 100%	[23]
O_3—BAC	Feed water: effluent of rapid sand filter of a conventional WTP Ozone dosage: 4 mg/L Hydraulic retention time for ozone contactor: 20 min BAC: length 3 m × diameter 0.48 m EBCT: 39.1 min	DCAAFP: 69% TCAAFP: 89% MBAAFP: 93% DBAAFP: 62% Total HAAFP: 89%	[24]

(*Continued*)

Table 4 (*Continued*)

Treatment process	Parameters	Removal of HAA	Refs.
BACF	Feed water: effluent of rapid sand filter of a conventional WTP EBCT: 10–60 min for total HAA_5 EBCT: 30–50 min for five species of HAA_5 Temperature = 22.0 ± 2℃ pH 7.8–8.5 Free residual chlorine < 0.01 mg/L TOC < 1.0 mg/L NH_3-N < 0.5 mg/L BACF is designed before post-chlorination	HAA_5: 68–88% MCAA: 96% DCAA: 92% TCAA: 40–55% MBAA: 78–82% DBAA: 98%	This study
BAC	Water source: river water HPC: 3×10^{11} CFU/g GAC (wet weight)	HAA_5: >75%	[25]
BAC	Water source: synthetic water and finished water obtained from WTP BAC: 50-mL glass burettes column EBCT: 10 min Free chlorine concentration in influents: 1.2–2.0 mg/L Synthetic influents HAA_6: 100 μg/L Temperature: 4, 20, and 50℃	DCAA: 98% (Temp. 20℃) DCAA: 25% (Temp. 4℃) DCAA: 29% (Temp. 50℃) MCAA: 93% (EBCT: 20 h) DCAA: 60% (EBCT: 20 h) TCAA: 15% (EBCT: 20 h)	[26]
BAC	Water source: surface water; the WTP uses rapid mixing, flocculation, and clarification GAC/sand filtration and post-chlorine BAC columns: 50-ml glass burettes (1.05 cm ID, height 46 cm, and flow rates at 2.0–8.0 mL/min) Feed water: raw water in the plant EBCT: 5, 10, 15, and 20 min	MCAA: 50%(10℃, EBCT: 6–8 min) DCAA: 50% (10℃, EBCT: 6–8 min) TCAA: 50% (10℃, EBCT: 17.3 min)	[27]
BAC	Water source: swimming pool BAC columns: PVC (10.16 cm ID, cross-sectional area of 81 cm^2, and a depth of 0.9 m) Feed water: ozonized water from a WTP EBCT: 4.5, 4.7, 5.1, and 6.4 min	HAA: 57.7% (EBCT:5.8 min, chlorine residual :1.71 ± 0.9 mg/L	[28]

$$\mathrm{HAA}\ (\mu g/L) = 5.84 - 8.04 \times [\mathrm{DOC}\ (mg/L)] + 34.27 \times [\mathrm{UV_{254}}\ (1/m)] + 40.93 \times [\mathrm{NH_3\text{-}N}\ (mg/L)] \quad (2)$$

Influent of BACF is limited: Temp. = 20–24℃, pH 7.2–8.5, free residual chlorine < 0.01 mg/L, TOC < 1.0 mg/L, NH_3-N < 0.5 mg/L, and the BACF was designed before post-chlorination.

3.5. Verification of the empirical equation of HAA

The empirical equation was verified using the analyzed value. Fig. 3, which shows a high coefficient of determination ($R^2 = 0.82$), shows a good comparison between the calculated and measured values of HAA_5 after treatment with the BF system.

Based on these verification results, the DOC is the primary factor that affects the formation and removal of the HAA. The secondary factors are NH_3-N and UV_{254}.

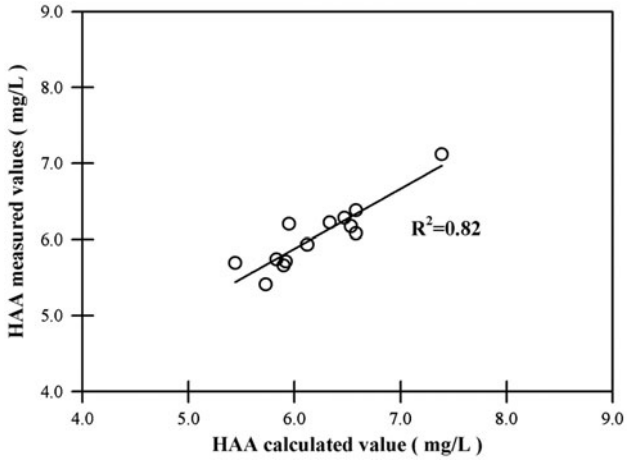

Fig. 3. Comparison between verified HAA5 values using Eq. (1) and the measured values in the effluent of BACF system. Errors were less than 5%.

3.6. Treatment of AOC

Fig. 4 shows changes in the concentration of AOC with respect to time in a continuous-flow model of the pilot-scale plant from 30 to 50 min. The results indicate that the average AOC value in the treated drinking water (after BACF treatment) is between 22 and 38 μg acetate C/L. The AOC value decreases significantly, suggesting effective removal. The AOC removal rate reached approximately 40% to as high as 65%. The initial average value of AOC in treated drinking water was 59 ± 8 μg acetate C/L.

The rate of AOC removal increased with an increase in the EBCT. The removal effect is significant and steady with an EBCT of 50 min. The results suggest that BACF considerably reduces the concentration of AOC while using biodegradation with an EBCT for at least 30 min.

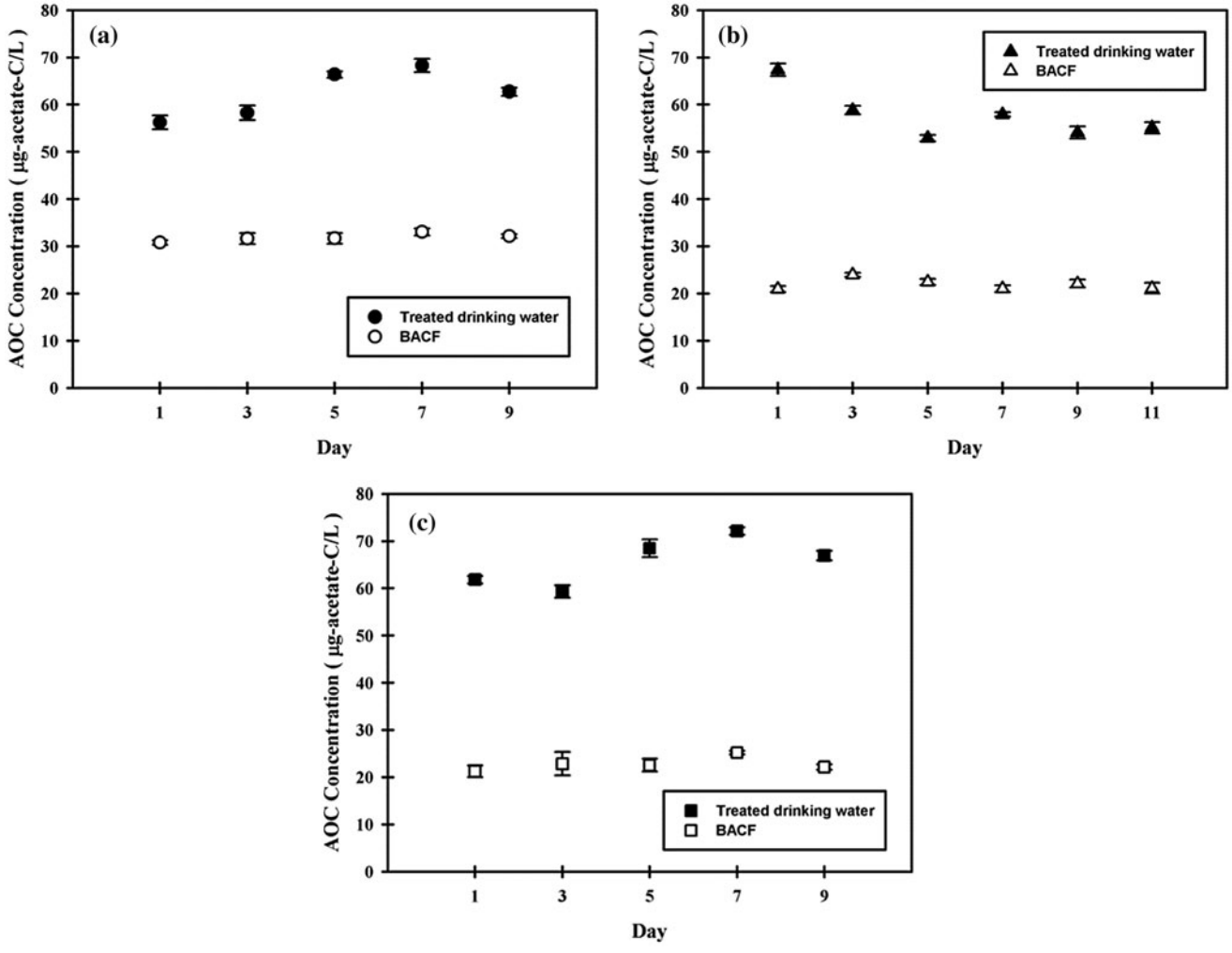

Fig. 4. Changes in concentration of AOC with respect to time by BACF under neutral conditions: (a) EBCT 30 min, (b) EBCT 40 min, and (c) EBCT 50 min. Influent conditions: temperature = 24.0 ± 2.0°C, pH 7.2 ± 0.1, and free residual chlorine = 0.6 ± 0.09 mg/L. The average concentrations at all times are geometrical mean values of triplicate measurements, and the standard deviation was less than 5% for all data points.

4. Conclusions

The overall results of this study are as follows. In all experiments, the BACF method effectively reduced HAAs in the proposed pilot plant. The removal of HAAs ranged from 78 to 83% around neutral and is most suitable. Occasional biofilm in the effluent of the BACF treatment system was found by measuring HPC bacteria in the effluent during the experiments. The BACF system reduced the concentrations of the total HAAs and the five HAA species in the water. In this investigation, DCAA, MBAA, and DBAA were the three main HAA5 species that were present in the treated drinking water. Combined, these three species represent approximately 80% of the HAA5 in the finished water after the BACF. The verification of the empirical HAA equation for the outlet in the BF system indicates a linear relationship with high correlation coefficients. The BACF method reduced the AOC values in the proposed pilot mode in the experiments, and prevented an excess amount of AOC in the water distribution system of the treated drinking water. The selected EBCT of the BACF system for treated drinking water was approximately 50 min, which is relatively effective at removing AOC pollutants from treated drinking water in the conventional water treatment plants.

In addition, bio-molecules are suspected to be DBP precursors. The treatment by BACF may release extra bio-molecules. Future studies should be conducted to investigate the DBP concentration after chlorination, which should be monitored in greater detail with and without BACF.

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