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EFFECTIVELY REMOVING HALO-ACETIC ACIDS FROM WATER BY BIO-ACTIVATED CARBON METHOD

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ABSTRACT

This study focused an effective method of bio-activated carbons to treat excess amounts of halo-acetic acids (HAAs) in raw water in a water treatment plant. Experiments were conducted in pilot scale treatment system to evaluate the removal of HAAs in water by bio-activated carbons. HAAs have been thought to be one possible nutrient supporting heterotrophic bacteria regrowth in drinking water. The results showed that pilot scale treatment system reduced over 85% of HAAs under normal conditions. The output water treated by pilot scale treatment system showed increased removal of HAAs and total organic carbon with increased alkalization of bio-activated carbons.

KEYWORDS: Bio-activated carbon method, halo-acetic acids, nutrient control, water treatment.

INTRODUCTION

The main nutrients that influence bacterial activities include organic carbon, nitrogen and phosphorus (Van Der Kooij D, 2003; Mains, C, 2008). Halo-acetic acids (HAAs) are one possible nutrient for heterotrophic bacteria regrowth in drinking water (McRae et al., 2004; Tung et al., 2009a). Excess amounts of HAAs have been identified frequently in the output waters from water treatment plants in southern Taiwan. Excessive amounts of disinfection by-products (DBPs) have 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 relatively large molecular weight and is typically divided into humic acid and fulvic acid (Steven et al. 2011).

After chlorination, NOM of total organic carbon in water sources may form carcinogenic DBPs such as halo-acetic acids (HAAs), which 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 (Warton et al. 2006). Therefore, combining bio-oxidation and filtering methods to remove DBPs may stabilize the quality of drinking water (Lou et al. 2010). Additionally liquid chlorine added to rapid sand filters in water treatment plants for disinfection oxidized and transformed organic macro-molecules into small organic molecules, resulting in increased dissolved organic carbon in treated drinking water (Lou et al., 2012).

Activated carbon, which has a high adsorption capacity, is currently the most widely applied adsorption agent because it is an ideal substance for removal of organic and inorganic pollutants from aqueous solution (Weng et al. 2012, 2013; Lou et al., 2015). The removal mechanisms of biological activated carbon consist of minor adsorption and major biodegradation. During treatment, granular activated carbon (GAC) is packed inside the column to treat HAAs in drinking water. HAAs was removed in manual assembled raw water by using laboratory-scale BACF, and the HAAs removal were 25% and 29% at 4 °C and 50 °C, respectively (Tung et al. 2009b). 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). Activated carbon has been applied in columns packed with two different GACs, PK1-3 and CAgran, to solve this problem (Çigdem et al. 2011). The removal of dissolved organic carbon (DOC) were 81% and 64.5% for PK1-3 and CAgran, respectively, when adsorption was the main mechanism, while they were 45.9% and 37.8% for PK1-3 and CAgran, respectively, when biodegradation was the main mechanism. Because GAC was Previous studies (Lou et al. 2014) have shown that the BACF method removed trihalomethanes in treated drinking water in the proposed pilot under various EBCT. The EBCT model was used to describe this BACF treatment system, a higher EBCT required a large amount of adsorbent and small influent flow rate. During 1 year experiments, the biofilm detachment of microorganisms in BACF treatment system was not found. In this study, a pilot scale of BACF treatment system was used to remove HAAs from treated drinking water under various pH in a water treatment plant. The measured values in output water treated with a BACF treatment system showed the effect of pH on parameters of water quality such as total organic carbon, and HAAs were also evaluated. An attempt to reduce the excess amount of nutrients such as HAAs and total organic carbon entering water distribution systems was made. These findings highlight new procedures and operating parameters of water quality for controlling water pollution by DPBs in water treatment plants.

MATERIALS AND METHODS

Experimental procedure

The raw water sources from the water treatment plant were from lake. The treatment processes in this plant included a raw water regulation basin, a rapid sand filter, post-chlorination disinfection, and a finishing water reservoir. The pilot scale of the BACF treatment system was constructed with the rapid sand filter. From January 2015 to June 2015, water samples were collected from the effluent of a rapid sand filter of water treatment plant in Southern Taiwan and pumped into the BACF treatment system used in this study. The pilot-scale BACF treatment system consisted of a pump and two columns fixed with granular activated carbon (GAC), which was utilized to treat the influent water in a continuous-flow reactor. The BACF treatment system (up-flow of type, column height = 110 cm, column diameter = 21 cm ,GAC bed height = 90 cm, bed volume = 30 L and number of bed = 2; connected in series, inlet flow were between 1.2 - 3 L/min. Effluent samples from BACF treatment system were then analysed for HAAs using gas chromatography (GC) with an electron capture detector. The operation conditions of the BACF treatment system in the water treatment plant were followed with the results of our previous studies (Lou et al., 2014). The conditions of BACF treatment system were including pH ranging from 6 to 10, temperature = 20.4 ± 1.2 °C, and EBCT = 50 minute in this work.

Preparation of BACF system

Preparation of GAC

A bituminous coal GAC manufactured by Calgon Carbon Co. (Tianjin, China) was prewashed using nitric acid with 0.1 M, after which it was washed again using deionized water and dried using natural ventilation. The physical characteristics of the GAC was the same with our previous work (Lou et al., 2014) which including its iodine adsorption capacity, apparent density, and effective grain diameter. The iodine adsorption capacity of the GAC was greater than 900 mg/g.

Enrichment of microorganisms on GAC surface in BACF

During microbial cultivation, the GAC was used as a support and water for microbial cultivation was obtained from the rapid sand filter of the water treatment plant. Specifically, water was poured directly into the BACF treatment system to allow microorganisms to adhere and grow, eventually forming a biofilm on the surface of the GAC. This cultivation period continued for 3 months (ranging from October 2014 to December 2014) prior to starting the experiment to prevent experimental errors caused by the adsorption of activated carbon in BACF treatment system and allow the integrated formation of biofilms on activated carbon. The concentration of total organic carbon (TOC) in the outlet of the BACF treatment system was monitored during the cultivation period.

Measurement of HAAs

HAAs were analysed based on USEPA Method 552.3 (APHA 2003). Briefly, HAAs were extracted using methyl-tert-butyl-ether (MTBE). A surrogate standard (100ppm 2,3-dibromopropionic acid in MTBE, HPLC grade) was then added to each sample to assess method performance. After samples were extracted, they were analysed using a gas chromatograph with electron capture detectors (GC-ECD, Agilent 7890A) and a DB-1701 column (30m×0.32mm 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, after which it was extracted with methyl-tert-butyl ether (MTBE). Sulfuric acid methanol was then added to enable analyses such as HAAs or Dalapon to form methyl esters. The organic solvent layer containing the methyl esters was separated and analysed 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 which HAA_5 accounted about 95 % of the HAA_9, the water temperature was 20 ℃. All average values from the experiments were measured in triplicate (Lou et al., 2014).

RESULTS AND DISCUSSION

Variations of water quality during microorganism cultivation in BACF

Table 1 Summary of water quality of raw water in water treatment plant, influent of BACF, and effluent of BACF during microbial cultivation. From results of Table 1 showed HPC per gram of GAC for microbial count in BACF column were ranging from 1.9×105 to 6.2×105 CFU/g GAC, it indicated micro-organism were successful and stable during cultivation in GAC surface. From results in Table 1, during from October 2014 to December 2014, showed concentrations of TOC of raw water were between 0.96-1.39 mg/L. Plotted the results of Table 1 into Figures 1(a), 1(b), 1(c), and 1(d). Fig.1 is variations of water quality of raw water in a water treatment plant, influent of BACF, and effluent of BACF during microbial cultivation, such as HPC bacterial count, dissolved oxygen, free available residual chlorine, and TOC. In order to monitor the biological activity existed in BACF. From the results of Fig.2 (a) showed HPC bacterial count of first column and second column were 1.2E+05～3.6E+05 CFU/g and 2.5E+05～4.9E+05 CFU/g, the bacterial count of second column was higher than first column. DO of raw water was 7.6～10.52 mg/L, after BACF treatment system the DO increased to 8.01～10.2 mg/L. Finally, the DO of second column of BACF in outflow dropped to 4.02～7.61 mg/L. The concentration of DO sufficient to maintain the desired growth of microorganisms, the results of HPC proved the microorganism stably existed in the columns of BACF.

The Figures 1 (c) and (d) showed that raw water in the water treatment plant have no chlorine, the concentration of TOC was between 0.96～1.39 mg/L, the contain of organic matters were high. After disinfection process, coagulation, sedimentation, rapid sand filtration, the free available chlorine and TOC were 0.01～0.02 mg/L and 0.22～0.32 mg/L. The results showed the organic matters do not have significant change after traditional purification process in this water treatment plant. However, the organic matters were effectively degraded by BACF treatment system, thus the TOC concentration of BACF in outflow is lower than the influent of BACF. Notably, the microorganisms survived in BACF treatment system for treating HAAs and TOC during the free available chlorine in influent was under 1.0 mg/L.

DO refer to the concentration of dissolved oxygen molecules in water; it is an important indicator of water pollution condition. Since all organisms were dependent on oxygen to maintain metabolic process and produce energy for the growth and regeneration of cells, the concentration of DO in water is essential to aquatic organisms. Figure 1 was variation of concentration of DO changed from raw water, influent of BACF, and effluent of BACF. It showed DO changes in BACF treatment system. DO of raw water was ranging from 7.6 to 10.5 mg/L, and DO was 8.0-10.2 mg/L in influent of BACF, then after BACF treatment system DO were decreased to 4.02-7.61 mg/L. Due to the dissolved oxygen concentration was sufficient to maintain the desired growth of microorganisms, therefore it judged presence of microorganisms growth in BACF treatment system. Low free residual chlorine avoided the inhibitory effect of microbial growth in BACF.

Changes of removal of TOC with different pH in BACF

Disinfection byproducts (DBPs) mainly produced from the chemical reaction of organic matters in the raw water during water disinfection process, TOC of drinking water is often used to measure the water quality and humus content basis. Table 2 was average concentrations of influent and effluent of BACF, and removal of BACF operating at varied pH. The results of Table 2 were plotted in Figure 2(a). Figure 2(a) was variation of concentration of TOC changed from raw water, influent of BACF, and effluent of BACF. From results of Figure 3(a), the concentrations of TOC of influent of BACF were 1.40-1.58 mg/L; the TOC in effluent of BACF were 0.27-0.54 mg/L.

Figure 2 (b) was effect of pH on removal of TOC by BACF. Results showed the effect of adjusting different pH on TOC removal by BACF treatment system. When pH was at 6, removal of TOC by BACF was about 62%, changed at pH 7 and 8 the removal of TOC was increased to 78%. Increasing pH to 9 and 10, removal of TOC was increased about 83%. Increased pH could increase the removal of TOC in BACF treatment system. BACF treatment system operated under alkaline conditions leads treatment efficiency of TOC higher than neutral and acidity condition.

Changes of removal of HAAs with different pH in BACF

Halo-acetic acids are one of general DBPs of during drinking water chlorination process; it is also belong to microbial nutrients in water distribution system. Especially the water turbidity and concentration of natural organic matter (NOM) enhance during the rainy season and typhoons, NOM will react with sodium hypochlorite to form halogen acetic acid which will lead to deterioration of water quality and regrowth of microorganisms in the distribution network.

The results of HAAs in Table 2 were plotted with various pH in Figures 3(a) and 3(b). Figure 3(a) was variation of concentration of HAAs changed from raw water, influent of BACF, and effluent of BACF. The results of Figure 3(a) showed the changes of HAAs at various pH of BACF. The concentrations of HAAs in influent of BACF were ranging from 0.306 to 0.396mg/L. After BACF treatment system, the concentration of HAAs in effluent was reduced to 0.030-0.057 mg / L for pass the national drinking water standard.

Figure 3(b) was effect of pH on removal of HAAs by BACF. When pH was at 6 the removal of HAAs was 78%. Compared at pH of 7 in BACF the removal of HAAs about 90%, under pH 8-9 the removal of HAAs by BACF increased to 86%. It indicates high pH condition help the BACF treatment system to remove high amounts of HAAs, but lower pH could has less for the removal of HAAs by BACF treatment system.

CONCLUSIONS

Overall, the results of this study are as follows. The BACF method effectively reduced TOC and HAAs in the proposed pilot in all experiments. Removal of TOC is about 62% at pH 6 comparing with the removal of TOC is 83% at pH10. On the other hand, the removal of HAAs was 78% at pH 6 comparing with the removal of 90% at pH10. The results indicated both HAAs and TOC have positive correlation with pH value. Occasional biofilm in effluent of BACF treatment system was not found during the experiments, it is suggested to connect Ultra-Filtration followed with BACF treatment system for avoiding biofilm detachment in overall design. The extending work could be set in different water treatment unit to further discuss the effectiveness for treating different type of organic high-contamination in raw water by BACF treatment system

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TABLE CAPTIONS

Table 1. Summary of water quality of raw water in water treatment plant, influent of BACF, and effluent of BACF during microbial cultivation.
Table 2. Average concentrations of influent and effluent of BACF, and removal of BACF operating at varied pH.

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

Time	HPC numbers（CFU/gGAC）		DO（mg/L）			Free chlorine（mg/L）			TOC（mg/L）		
	1st column in BACF	2nd column in BACF	Raw water	Influent BACF	Efluent 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

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

	pH	6	7	8	9	10
Influent of BACF	TOC（mg/L）	1.39	1.48	1.57	1.53	1.57
	[a]HAAs（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 of BACF	TOC（mg/L）	0.53	0.36	0.32	0.26	0.27
	[a]HAAs（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

The average concentrations are geometrical mean values of triplicate measurements (the operation conditions: pH = 7.5 ± 0.2, temperature = 20.4 ± 1.2 ℃, EBCT = 50 minute)

[a]Taiwan Environmental Protection Agency set a level 0.06 mg/L (60 μg/L) on HAA_5 level.

Figure Captions

Fig. 1. Variations of water quality of raw water in a water treatment plant, influent of BACF, and effluent of BACF during microbial cultivation.

Fig. 2. Effect of pH on removal of TOC by BACF: the average concentrations are geometrical mean values of triplicate measurements (the operation conditions: temperature= 20.4±1.2 ℃, EBCT= 50 minute).

Fig. 3. Effect of pH on removal of HAAs by BACF: the average concentrations are geometrical mean values of triplicate measurements (the operation conditions: temperature= 20.4±1.2 ℃, EBCT= 50 minute).

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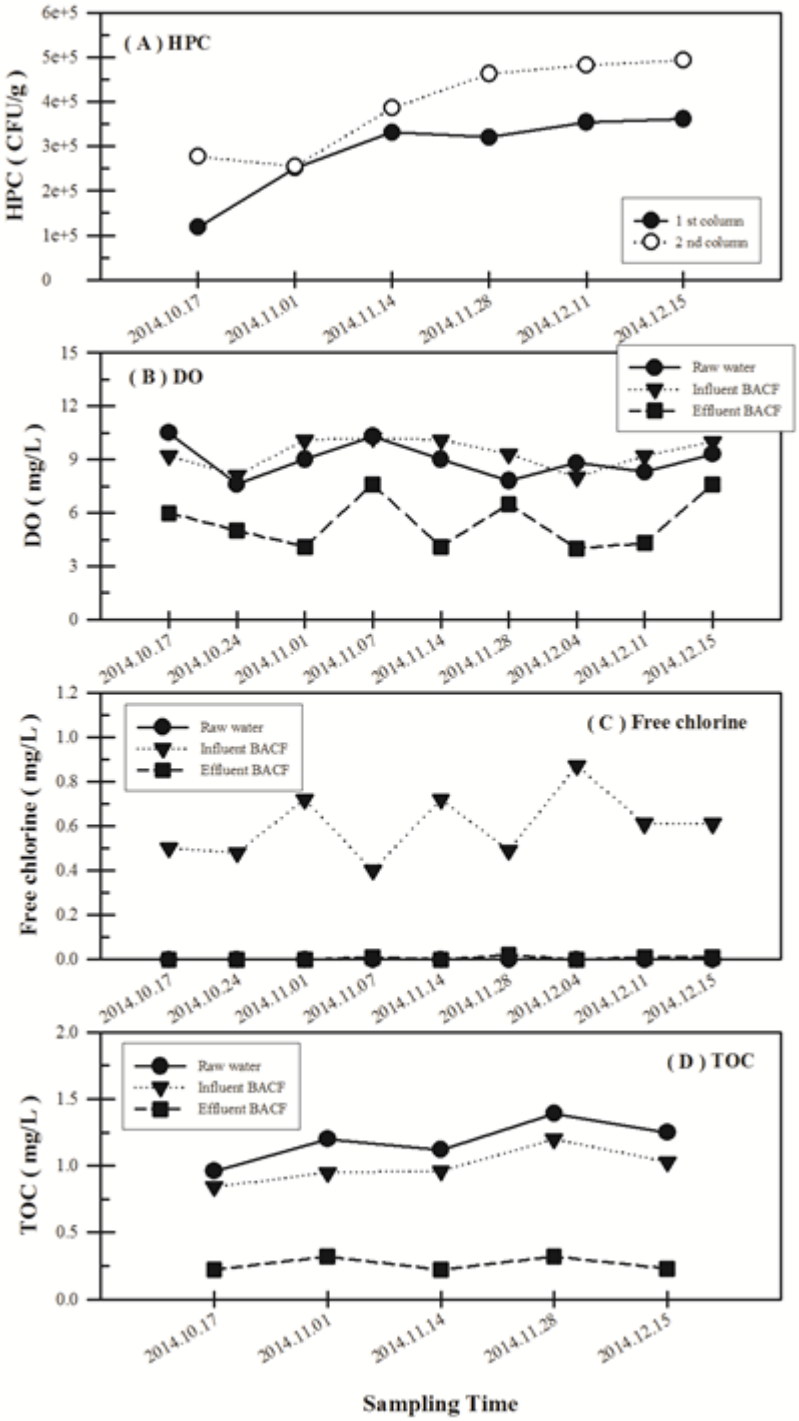

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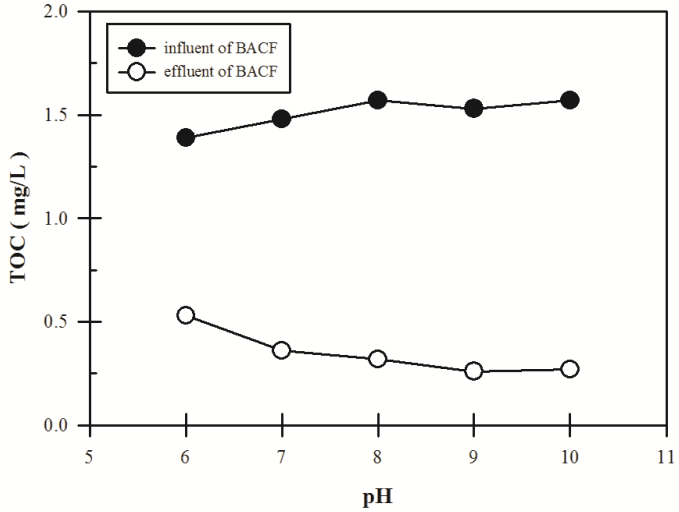
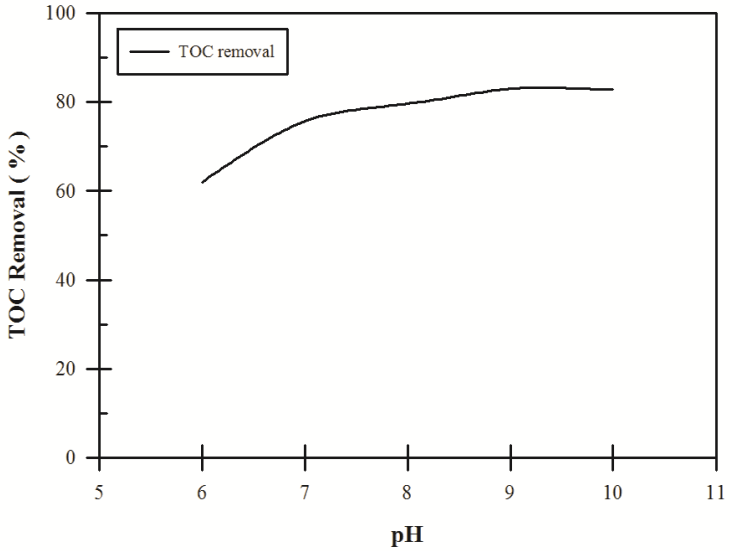


(a) Concentration of TOC at different pH between influent and effluent of BACF



(b) Variation of TOC removal at different pH by BACF

Figure 2. Effect of pH on removal of TOC by BACF: the average concentrations are geometrical mean values of triplicate measurements (the operation conditions: temperature= 20.4±1.2 °C, EBCT= 50 minute).

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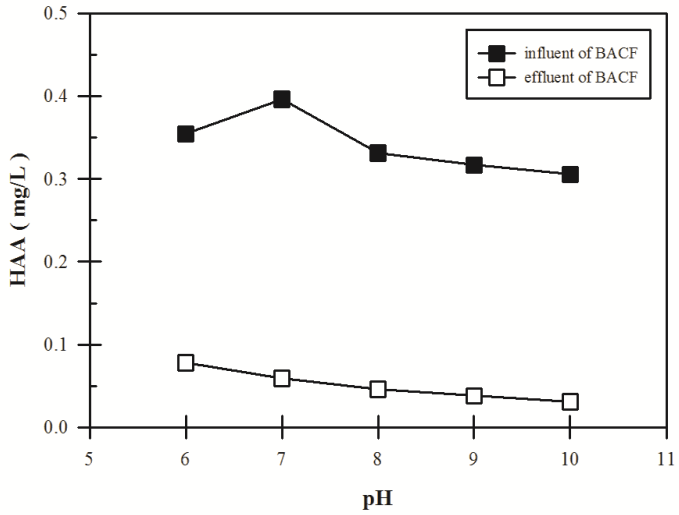
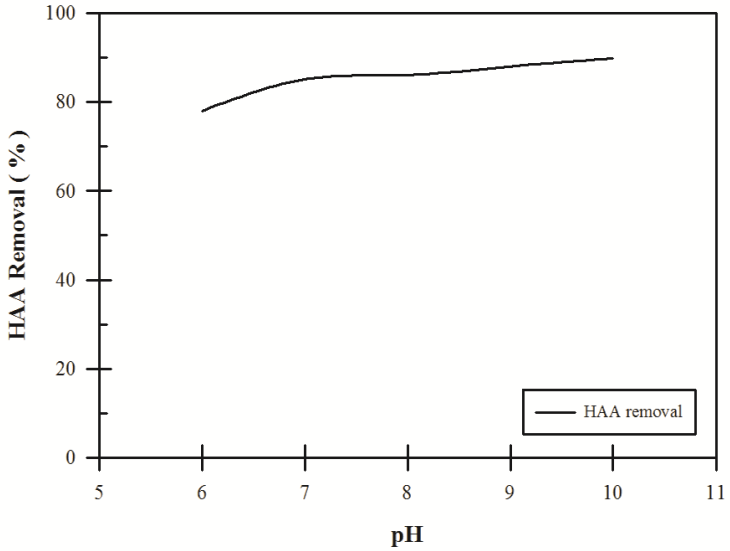


(a) Concentration of HAAs at different pH between influent and effluent of BACF



(b) Variation of HAAs removal at different pH by BACF

[1] **Figure 3. Effect of pH on removal of HAAs by BACF: the average concentrations are geometrical mean values of triplicate measurements (the operation conditions: temperature= 20.4±1.2 °C, EBCT= 50 minute).**