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Removal of haloacetic acids by ozone and biologically active carbon

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ABSTRACT: Haloacetic acids are recognized as carcinogens. They are naturally formed on the surface of water or as disinfection by-products of drinking water during the chlorination process. The efficiency of an integrated treatment system combining ozonation and biological activated carbon (BAC) was examined for the removal of five regulated haloacetic acids, namely, chloroacetic, dichloroacetic, trichloroacetic, bromoacetic, and dibromoacetic acid (known collectively as HAA_5), in synthetic water. The effects of ozone dosage, contact time during the ozonation process, and the empty bed contact time (EBCT) of the BAC column were also evaluated. The results demonstrate that the ozonation process is not an effective approach to remove HAA_5 since less than 20% of HAA_5 at the concentration levels found in the water supply system was removed. The majority of HAA_5 in the tested solutions were subsequently removed by the BAC column inoculated with bacteria readily available in surface water. More than 90% of the remaining HAA_5 was eliminated after having been passed through the BAC column with an EBCT of at least 20 minutes. Indigenous microorganism communities inoculated in the BAC column were able to degrade individual HAA_5 species without preference.

KEYWORDS: haloacetic acids, ozone, biologically active carbon, empty bed contact time

INTRODUCTION

Haloacetic acids are probable human carcinogenic compounds[1]. They are also toxic to aquatic organisms[2,3]. Trichloroacetic acid and monochloroacetic acid are also phytotoxic and were used as herbicides until the late 1980s[4]. Haloacetic acids are naturally formed in the atmosphere during the photochemical degradation of chlorinated solvents[5]. In addition, they have been found as disinfection by-products that result from the addition of a chlorine compound, such as hypochlorous acid, hypochlorite, or dichlorine, to water or wastewater for disinfection purposes[6]. Reactions between natural organic matter and chlorine compounds produce haloacetic acids at ppt to ppb ranges in drinking water distribution systems and in ppb to ppm ranges in wastewater[7,8]. The concern over the carcinogenicity of haloacetic acids led the United States Environmental Protection Agency to regulate the allowable concentration of haloacetic acids in drinking water[9] as part of the Disinfectants and Disinfection Byproducts Rule promulgated in 1998. Five haloacetic acids, known as HAA_5, are regulated as a part of the rule. These are monochloroacetic acid (CAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromoacetic acid (BAA), and dibromoacetic acid (DBAA). HAA_5, which is expressed as the sum of the concentrations of these acids, is currently limited there to 60 ppb[10]. The current concentration of HAA_5 in the Bangkok water supply sampled at the chlorination station of the Bangkhen water treatment plant was approximately 50 ppb. Because of their widespread occurrence, toxicity to plants and aquatic organisms, and most importantly their suspected human carcinogenicity, there is a great need to find treatment methods for haloacetic acids.

Ozonation is one of the simplest treatments. No other chemicals aside from ozone are required. The attractive property of ozone is its potent oxidizing power. Under acidic conditions, it has a standard reduction potential of about 2.1 V, almost twice that of oxygen (1.2 V). It readily dissolves in water and can therefore react relatively quickly with soluble organic compounds and oxidize them to smaller or less toxic molecules[11]. Recent studies have shown that ozonation is effective in removing a wide variety of chlorinated organic contaminants[12–14]. Owing to these properties,

ozonation shows promise as a possible treatment for haloacetic acids.

The biodegradation of haloacetic acids is also an alternative treatment for haloacetic acid reduction. A small number of studies reported that haloacetic acids could be naturally removed by aerobic biodegradation processes[15,16]. Several aerobic bacteria are able to degrade haloacetic acids and use them as either co-metabolites[17] or as a sole carbon and energy source[18]. In a water treatment system, biodegradation is typically found associated with the application of granular activated carbon (GAC). After a long running period, GAC usually has a natural bacteria population on its surface, and eventually works as biologically activated carbon (BAC). GAC with a biomass that shows high biological activity is then called BAC[19]. Womba et al[20] reported that BAC reduced the background HAA_5 to below 30 ppb. The primary objective of this study was to investigate the HAA_5 removal efficiency of the integrated ozonation and BAC column treatment system. Effects of ozone dose and contact time during the ozonation process and the impact of the empty bed contact time of the BAC column were also evaluated.

MATERIALS AND METHODS

Sample preparation

The synthetic samples of HAA_5 (i.e., CAA, DCAA, TCAA, MBAA, and DBAA) were used as the feed solutions in the experiments. Samples were prepared using a commercially available HAA_5 standard (Supelco). Three initial HAA_5 concentrations, 60, 90, and 120 ppb, were tested.

Ozone-BAC system

A schematic diagram of the ozone-BAC testing unit used in the experiment is shown in Fig. 1.

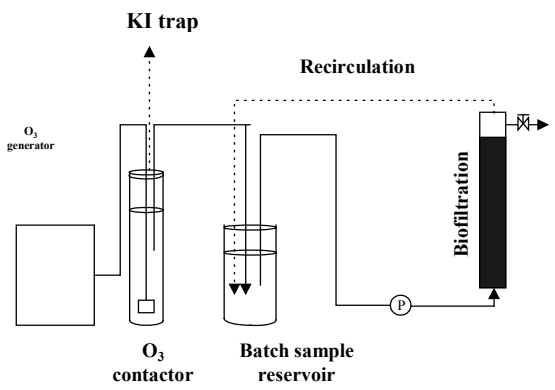

Fig. 1 Schematic diagram of ozone-BAC testing unit.

The ozone-BAC treatment system components were made of stainless steel, glass, and Teflon. The system includes two basic components; an ozone contactor and a biologically active carbon column. Both components were simultaneously used to conduct batch experiments studying HAA_5 removal. HAA_5 sample solutions were first oxidized by ozone and then passed through the BAC column for further degradation.

Ozone contactor

All materials that were in contact with water during the ozonation process were made of glass, PTFE, or stainless steel. The water sample was placed in a 5-litre glass bottle. The water then flowed under the force of gravity into the 5-litre ozone contactor. Ozone was generated from an ozone generator (Sky zone; star 04) that had an ozone generating capacity of 750 mg/h. Ozone was introduced to the contactor using a fritted glass disc at room temperature. The ozone dosages were varied in each experiment by changing the time of ozone production, while all the settings on the ozonation apparatus remained constant for all of the runs. The residual ozone dosage was measured using the indigo trisulphonate method[21]. Off-gas from the ozone contactor was introduced to a potassium iodide solution (KI trap).

Biologically active carbon column

The granular activated carbon (Calgon F200) media was packed into a 3-cm diameter glass column (50 cm in length). An acclimated biofilm was established on the GAC media through the process of seeding using raw water from the Sam Sen raw water distributing canal (Klong Prapa) over a period of 1 year. The column was operated in up-flow mode using a peristaltic pump. Prior to the tests, the establishment of microbial communities in the BAC column was confirmed using the membrane filter technique. A steady colony count indicated the stability of the bacteria community.

Operational conditions

A series of batch experiments were designed to measure HAA_5 removal as a function of ozone dosage, ozonation process contact time, and the empty bed contact time (EBCT) of the BAC column. Three ozone dosages of 0.5, 1.0, and 2.0 mg ozone/mg TOC (mg O_3/mg C) were employed with contact times of 5, 10, and 20 min. The effects of EBCT on BAC performance were investigated at 10, 20, and 30 min. The HAA_5 concentrations were measured from the samples collected at the beginning of each experiment,

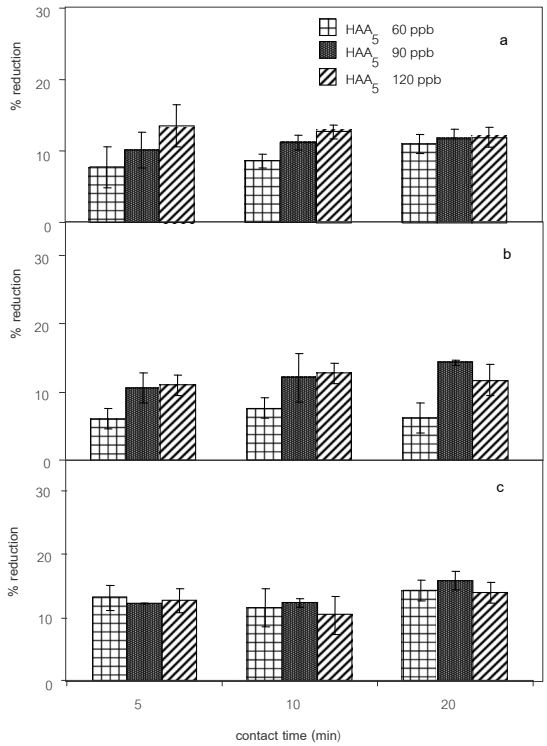

Fig. 2 Efficiency of ozonation process in removing HAA_5 when (a) ozone dose = 0.5 mg O_3/mg C, (b) ozone dose = 1 mg O_3/mg C and (c) ozone dose = 2 mg O_3/mg C.

after the ozone contactor and after the BAC column. All experiments were run in triplicate.

Determination of HAA_5

The HAA_5 amounts were determined using USEPA Method 552.2. Briefly, 20 µl of 2,3-dibromopropionic acid (10 µl/ml) was added to 40 ml of sample as a surrogate for QA/QC. The sample was then adjusted to pH < 0.5 by adding concentrated H_2SO_4 solution. $CuSO_4$ (2 g) were subsequently added to the acidic solution followed by 16 g of Na_2SO_4. The solution was then extracted with 4 ml of methyl-tertiary-butyl ether. Haloacetic acids that had been partitioned into the organic phase were converted to their methyl esters by the addition of 10% H_2SO_4 in methanol and warmed to 50 °C in a water bath. The acidic extract was later neutralized by back extraction with a saturated solution of sodium bicarbonate. The target analytes were identified and measured by gas chromatography using electron capture detection (GC/µECD, Agilent GC6890). A DB-XLB (J&W Scientific) fused silica capillary column (30 m × 0.32 mm i.d. × 0.05 μm film thickness) was used for the separation. The GC oven was programmed to run at 40 °C for 0.5 min, and then from 40–200 °C at a rate of 15 °C/min. After that, the temperature was held constant for 2 min. The injector was set to 250 °C, splitless mode, 30 sec purge activation time, and 50 pg per component. The detector temperature was maintained at 350 °C.

RESULTS AND DISCUSSION

HAA_5 removal by ozonation

Ozonation experiments were carried out with three concentrations of HAA_5: 60, 90, and 120 ppb. Results of the experiments (Fig. 2) indicated that ozonation is ineffective in removing HAA_5 under the test condition (pH ~ 6). As demonstrated in the figure, removal efficiencies in all ozonation experiments ranged from 10–20%. Comparable results were previously observed by Fu et al[22] who reported that only a 10% reduction of CAA was obtained after 1 h ozonation at pH 3.1. An increase in ozone dosage and contact time did not substantially improve the decomposition of HAA_5 by ozone (Fig. 2). Plots between 1/ln (HAA_5/HAA_{50}) and contact time exhibited a linear relationship with R^2 between 0.86–0.99, suggesting that the decomposition of HAA_5 by ozonation follows first-order reaction behaviour. The apparent rate constant of the reaction varied from 0.001 per min to 0.003 per min. The slow reaction rate between the dissolved ozone and HAA_5 could be due to the chemical properties of HAA_5 and the conditions of the experiment. Reactions to ozone can occur via direct and indirect mechanisms[23]. Typically, both direct and indirect mechanisms occur concurrently in a solution. However, depending on the conditions of the reaction, one type of reaction may dominate. Alkaline pH promotes the dissociation of ozone to hydroxyl radicals, and hence the indirect mechanism predominates at high pH[24]. In this study, the pH of the feed HAA_5 solutions was around 6. Under this condition, it was more likely that the majority of HAA_5 had reacted with dissolved ozone via the direct mechanism.

A nucleophilic reaction is the most likely cause of the reaction between HAA_5 and ozone since the HAA_5 compounds contain COO^-, chlorine, and bromide, which are all electron withdrawing groups. The reaction proceeded very slowly because the nucleophilic reaction of ozone is less preferable than other mechanisms[14]. Adam et al[12] noted that the rate of the nucleophilic reaction between dissolved ozone and electron withdrawing groups was exceptionally slow.

The slow reaction rates observed in this study are therefore consistent with previous observations,

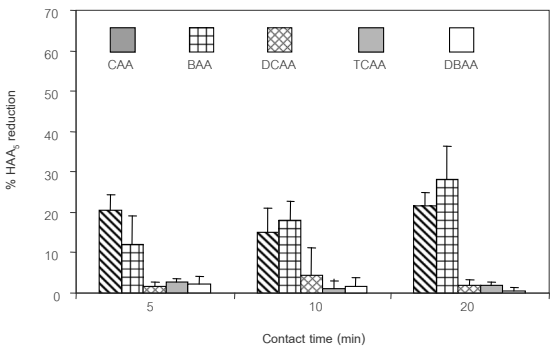

Fig. 3 Removal of individual HAA_5 species by ozonation.

dissolved ozone and haloacetic acids or perhaps other alkyl carboxylic acids. In the past, the attempts to eliminate CAA and oxalic acid during the ozonation process were successful only when a catalyst was used[22,25].

Aside from the slow removal rate, the ozonation of HAA_5 also occurred selectively. It can be seen from Fig. 3 that among the degraded 10–20% of HAA_5, CAA, and BAA were the two HAA_5 species being primarily removed. Other HAA_5 species remain relatively unchanged, particularly TCAA. The low reactivity of ozone towards TCAA, DCAA, and DBAA suggests two possibilities. First, the number of electron withdrawing substituents (i.e. chlorine and bromide) had an effect on the removal of HAA_5 by ozonation. The steric effect is known to lower the rate of nucleophilic reaction[25]. Urbansky[6] noted that two halogen atoms are sufficient to offer stability to the central carbon. Therefore, both di- and trihaloacetic acids do not readily undergo a nucleophilic reaction, especially in the acidic-neutral conditions used in this experiment. The second possibility may be due to a stripping effect since CAA and BAA have lower boiling points.

From these results, it has been demonstrated that ozonation alone is not a good candidate for removing HAA_5 at a pH range that is typically found in a water treatment system. In fact, since the ozonation process had less of an effect on HAA_5 with multiple halogen atoms such as DCAA and TCAA, the ozonation process actually had little effect in minimizing the toxicity of HAA_5.

HAA_5 removal by biologically active carbon (BAC)

The BAC column was installed initially to further improve the treatment efficiency of the ozone contactor. Prior to entering the BAC column, residual ozone in the solution was removed by letting the sample sit for 45 min. The residential time of the ozonated water samples in the BAC column was varied by adjusting the empty bed contact time (EBCT). The efficiency of the BAC column in removing HAA_5 is shown in Fig. 4. In contrast to the ozonation process, BAC is very effective in removing HAA_5. A complete 100% removal of the acids was observed under various experimental conditions. Plots in Fig. 4 also demonstrated that the EBCT of the samples was the most important variable regulating HAA_5 reduction. The longer the solution stayed in the column, the better the HAA_5 removal. In this study, an EBCT of at least 20 min was required to remove 90–100% HAA_5 in the test solutions. The previous study[27] showed that an EBCT of at least 5 min should be used for water above 10 °C.

The removal of HAA_5 via activated carbon adsorption is considered less likely[28]. Before starting the experiment, the BAC column had been continuously fed with raw water for water supply production for one year. It is more likely that the majority or perhaps all of the surface area of the activated carbon had already been exhausted. The direct adsorption of HAA_5 on activated carbon would therefore be limited. Moreover, GAC is typically considered ineffective in adsorbing haloacetic acids because the compounds are hydrophilic and exist in ionized forms at the pH range of potable water. A recent study showed that the removal of BAA by the autoclaved BAC (comparable to virgin GAC) was negligible, whereas the active BAC exhibited 100% removal efficiency[10].

Microorganisms capable of biodegrading multiple haloacetic acids are available in surface water. The microbial decomposition of haloacetic acids such as CAA, BAA, and TCAA at the concentrations found in natural water and in the drinking water distribution system has been reported by McRae et al[7] and Tung et al[29]. In the former report, microorganisms isolated from natural water bodies degraded CAA rapidly at concentrations ranging from 5.7 ppb to 148 ppb. The ^{14}C radiolabelled CAA experiment further revealed that 79% of [^{14}C] CAA was converted to CO_2 and the remaining was incorporated into biomass. Similar results were observed with BAA and TCAA.

Rapid biodegradation of HAA_5 by the BAC column rather suggests that the BAC column alone could eliminate up to 100 ppb of HAA_5 without the assistance of the ozonation process. Concentrations as high as 54–108 ppb of HAA_5 that remained in the feed solution after the ozonation process were subsequently biodegraded by bacteria in the BAC column. Indigenous microorganism communities in surface water inoculated on the BAC column could

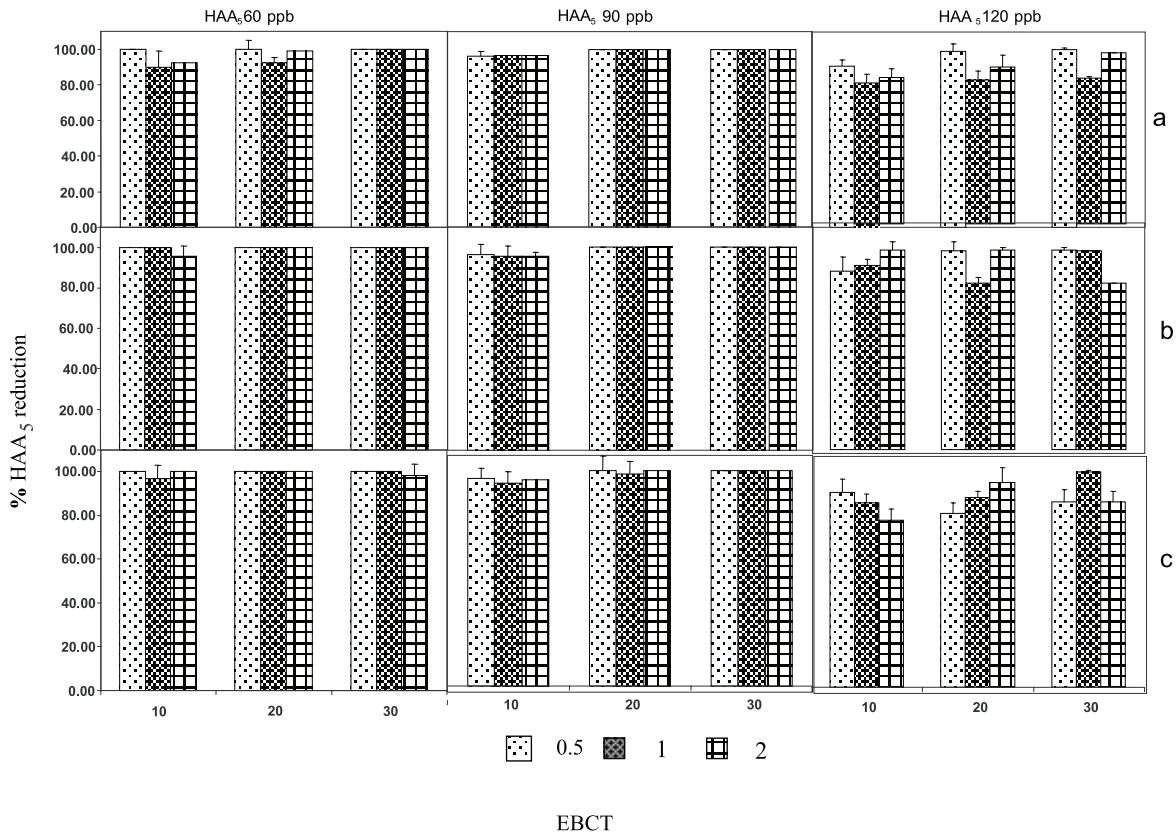

Fig. 4 Efficiency of BAC column in removing HAA_5 after pretreatment with ozone dosages of 0.5, 1, and 2 mg O_3/mg C and (a) ozone contact time of 5 min, (b) ozone contact time of 10 min, and (c) ozone contact time of 20 min.

degrade individual HAA_5 species without preference, supporting the idea that natural HAA_5 biodegradation already exists in the surface water environment.

CONCLUSIONS

The HAA_5 removal efficiency of the ozonation process is low (10–20% reduction), suggesting that ozonation is not an attractive approach for controlling HAA_5. Both ozone dose and contact time had an insignificant effect on the reaction between HAA_5 and dissolved ozone. The use of ozonation as a pretreatment process was therefore deemed to be unnecessary. On the other hand, biofiltration using a BAC column was determined to be a good candidate for controlling HAA_5. The majority of HAA_5 in the tested solutions were removed by the BAC column. The complete removal of HAA_5 could be achieved after having been passed through the BAC column with an EBCT of at least 20 min. Indigenous microorganism communities inoculated in the BAC column were able to degrade individual HAA_5 species without preference.

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REFERENCES

1. U.S. Environmental Protection Agency (1999) EPA guidance manual alternative disinfectants and oxidants. Office of Research and Development, Washington DC.
2. Hanson ML, Sibley PK, Ellis DA, Mabury SA, Muir DCG, Solomon KR (2002) Evaluation of monochloroacetic acid (MCA) degradation and toxicity to *Lemna gibba*, *Myriophyllum spicatum*, and *Myriophyllum sibiricum* in aquatic microcosms. *Aquat Toxicol* **61**, 251–73.
3. Hanson ML, Sibley PK, Mabury, SA, MuirDCG,

Solomon KR (2003) Field level evaluation and risk assessment of the toxicity of dichloroacetic acid to the aquatic macrophytes *Lemna gibba, Myriophyllum spicatum,* and *Myriophyllum sibiricum. Ecotoxicol Environ Saf* **55**, 46–63.

4. Berg M, Müller SR, Mühlemann J, Wiedmer A, Schwarzenbach RP (2000) Concentrations and mass fluxes of chloroacetic acids and trifluoroacetic acid in rain and natural waters in Switzerland. *Environ Sci Technol* **34**, 2675–83.
5. Frank H, Scholl H, Renschen D, Rether B, Laouedj A, Norokorpi Y (1994). Haloacetics acids, phytotoxic secondary air pollutants. *Environ Sci Pollut Res Int* **1**, 4–14.
6. Urbansky ET (2001) The fate of the haloacetates in drinking water-chemical kinetics in aqueous solution. *Chem Rev* **101**, 3233–42.
7. McRae BM, LaPara TM, Hozalski RM (2004) Biodegradation of haloacetic acids by bacterial enrichment cultures. *Chemosphere* **55**, 915–25.
8. Rebhun M, Heller-Grossman L, Manka J (1997) Formation of disinfection by-products during chlorination of secondary effluent and renovated wastewater. *Water Environ Res* **69**, 1154–62.
9. U.S. Environmental Protection Agency (1998) National primary drinking water regulations: Disinfectants and disinfections by-products. *Fed Reg* **63**, 69389–476.
10. Xie YF, Zhou H (2002) Use of BAC for HAA removal. Part 2: Column study. *J Am Water Works Assoc* **94**, 126–34.
11. Gottschalk C, Libra JA, Saupe A (2000) Ozonation of water and wastewater: A practical guide to understanding ozone and its application, Wiley-VCH, Morlenbach, Germany.
12. Adams CD, Cozzens RA, Kim BJ (1997) Effects of ozonation on the biodegradability of substituted phenols. *Water Res* **31**, 2655–63.
13. Dilmeghani M, Zahir KO (2001) Kinetics and mechanism of chlorobenzene degradation in aqueous samples using advanced oxidation processes. *J Environ Qual* **30**, 2062–70.
14. Jung OJ (2001). Destruction of 2-chlorophenol from wastewater and investigation of by-products by ozonation. *Bull Korean Chem Soc* **22**, 850–6.
15. Boethling RS, Alexander M (1979) Effect of concentration of organic chemicals on their biodegradation by natural microbial communities. *Appl Environ Microbiol* **37**, 1211–6.
16. Ellis DA, Hanson ML, Sibley PK, Shahid T, Fineberg NA, Solomon KR, Muir DCG, Mabury SA (2001) The fate and persistence of trifluoroacetic and chloroacetic acids in pond waters. *Chemosphere* **42**, 309–18.
17. Weightman AL, Weightman AJ, Slater JH (1992) Microbial dehalogenation of trichloroacetic acid. *World J Microbiol Biotechnol* **8**, 512–8.
18. Olaniran A (2001) Aerobic dehalogenation potentials of four bacterial species isolated from soil and sewage sludge. *Chemosphere* **45**, 45−50.
19. U.S. Environmental Protection Agency (2001) Controlling disinfection by-products and microbial contaminants in drinking water. Office of Research and Development, Washington DC.
20. Wobma P, Pernitsky D, Bellamy B, Kjartanson K, Sears K (2000) Biological filtration for ozone and chlorine DBP removal. *Ozone Sci Eng* **22**, 393–413.
21. APHA, AWWA and WPCF (1998) Standard methods for the examination of water and wastewater, 17th edn. Washington, D.C.
22. Fu H, Leitner NKV, Legube B (2002) Catalytic ozonation of chlorinated carboxylic acids with Ru/CeO2-TiO2 catalyst in the aqueous system. *New J Chem* **26**, 1662–6.
23. Langlais B, Reckhow DA, Brink DR (1991) Ozone in water treatment application and engineering. AWWA Research Foundation, Lewis Publishers, Chelsea, MI.
24. Wang R, Chen CL, Gratzl JS (2005) Dechlorination of chlorophenols found in pulp bleach plant E-1 effluents by advanced oxidation processes. *Bioresour Technol* **96**, 897–906.
25. Pines DS, Reckhow DA (2002). Effect of dissolved cobalt(II) on the ozonation of oxalic acid. *Environ Sci Technol* **36**, 4046–51.
26. Larson RA, Weber EJ (1994) Reaction mechanisms in environmental organic chemistry. Lewis Publishers, Boca Raton, FL.
27. Wu H, Xie YF (2005) Effects of EBCT and water temperature on HAA removal using BAC. *J Am Water Works Assoc* **97**, 94–101.
28. Tung HH, Unz RF, Xie YF (2006) HAA Removal by GAC Adsorption. *J Am Water Works Assoc* **98**, 107–12.
29. Tung HH, Regan JM, Unz RF Xie YF (2006) Microbial community structure in a drinking water GAC filter. *Water Supply* **6**, 267–71.