Ozone–biological activated carbon integrated treatment for removal of precursors of halogenated nitrogenous disinfection by-products

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1. Introduction

Recently, research efforts have been made to study the formation of halogenated nitrogenous disinfection by-products (N-DBPs), including haloacetamides (HAcAms), halonitromethanes (HNMs) and haloacetonitriles (HANs), with the purpose of acquiring knowledge to control their formation during chlorination (Lee et al., 2007; Yang et al., 2007; Krasner, 2009; Chu et al., 2010a). The formation mechanisms of these N-DBPs appear to be too complicated, so that it is difficult to effectively prevent their formation by controlling disinfection operational conditions (e.g. disinfectants dosages, contact time, and pH) in practice. Consequently, using either advanced post-treatment technologies or addition of pre-treatment to existing water treatment plants (WTPs) for removal of the precursors of the emerging N-DBPs prior to disinfection becomes a significant strategy to prevent their production.

Precursors of the halogenated N-DBPs in source waters are a mixture of autochthonous and allochthonous compounds, such as microorganism-associated (e.g. algae and bacteria) products, wastewater effluent organic matters, amino acids and proteinaceous compounds (Reckhow et al., 2001; Westerhoff and Mash, 2002; Joo and Mitch, 2007; Chu et al., 2010b). Many of these compounds are characterized by low molecular weight, low hydrophobicity, and poor removal efficiencies in conventional WTPs using coagulation–sedimentation–filtration (Dotson and Westerhoff, 2009; Chu et al., 2011a), which results in the formation of halogenated N-DBPs in the WTP effluent when using chlorine and/or chloramine as a disinfectant (Krasner, 2009; Chu et al., 2011b).

Ozonation integrated with biological activated carbon (O3–BAC) has been increasingly used into WTPs to improve the removal of dissolved organic matters (DOMs) and ammonia prior to disinfection. The O3–BAC process can significantly reduce the precursors of regulated DBPs such as trihalomethanes (THMs) and haloacetic acids (HAA5s) (Karnik et al., 2005; Xu et al., 2007; Yan et al., 2010). However, it is uncertain whether an O3–BAC process also removes the precursors of halogenated N-DBPs.

Specifically, it is unclear to what extent the O3–BAC process removes organic nitrogen (DON), regarded as a key indicator of the presence of precursors of N-DBPs. The goal of this study was to assess the formation potentials (FPs) of several selected halogenated N-DBPs (HAcAms, HNMs and HANs) and regulated DBPs (THMs), as well as the removal efficiencies of their precursors, by
an O3–BAC process subsequent to a conventional surface water treatment train (coagulation–sedimentation–filtration).

2. Materials and methods

2.1. Site description and materials

All the raw water was collected through an intake in the Meiliang Bay of Lake Taihu, the third-largest lake in China. The lake is a major potable water source in Eastern China, supplying Shanghai City, Jiangsu Province, and Zhejiang Province. Over the past years, the water quality of the lake has been significantly degraded as a result of nutrient enrichment and industrial pollution (Yang et al., 2008; Zhang et al., 2010). As such, several local WTPs have added the O3–BAC process to the existing treatment facilities. The quality of the raw water used in this study (November and December, 2008) is shown in Supplementary material (SM), Table SM-1.

In this study, two HAcAms (dichloroacetamide, DCACAm and trichloroacetamide, TCAcAm), four HANs (dichloroacetanitride, DCAN, trichloroacetanitride, TCAN, bromochloroacetanitride, BCAN and dibromoacetanitride, DBAN) and trichloronitromethane (TCNM) were measured. In addition, four THMs were determined and compared with the N-DBPs. The details of the DBP standards and other reagents have been reported earlier in the literature (Chu et al., 2011a,b).

2.2. Pilot-plant process flow

The pilot plant was located within a WTP of Wuxi City near Lake Taihu. A flowchart of the pilot plant is shown in Fig. 1; the pilot was composed of coagulation, sedimentation, sand filtration, ozonation and BAC filtration. The pilot plant operated at a design flow of 1 m³ h⁻¹.

2.2.1. Conventional processes (coagulation–sedimentation–filtration)

Coagulation was performed in a three-stage flocculation chamber (1.2 m [L] × 0.4 m [W] × 0.5 m [L]). The average velocity gradients in the three consecutive stages were set as 45, 24 and 11 s⁻¹, respectively. Sedimentation was carried out in an inclined sedimentation tank (1.5 m [L] × 0.7 m [W] × 1.4 m [H]). Filtration was achieved at a filtration rate of 7 m h⁻¹ in a filter column with a diameter of 0.3 m and a 0.9 m bed depth. The filter medium was quartz sand with a grain diameter of 0.7–1.0 mm. More details regarding the pilot plant is available elsewhere (Chu et al., 2011a).

2.2.2. Advanced process (O3–BAC)

Ozonation was carried out in an ozone contact chamber (4.5 m in height, and 0.4 m in diameter) operated in concurrent flow mode. Ozone was generated from air using an ozone generator (HMY-F, Huangming, China) and continuously entered the water in the form of small bubbles through a porous titanium plate. Dissolved ozone dosage was 1.5–2.0 mg L⁻¹, and the contact time was 30 min. Subsequent to ozonation, the water was fed into a granular activated carbon (GAC) filter (4.0 m in height, and 0.3 m in diameter) to perform the BAC process. The empty bed contact time and filtration rate of the BAC column were maintained at 15 min and 7.0 m h⁻¹, respectively. The bed depth, effective size, uniformity coefficient, iodine value, methylene blue value, and density of the filled GAC were 1.6 m, 0.55–0.75 mm, <1.9, 1000 mg g⁻¹, 266 mg g⁻¹ and 450 g L⁻¹, respectively. The BAC performance with and without pre-ozonation was compared.

2.3. Analytical methods

Once collected from several sampling locations shown in Fig. 1, water samples were immediately stored in either 5 L glass bottles or 40 mL glass vials, then transported to the laboratory at Tongji University, and finally stored in a refrigerator at 4 °C until use. The most water quality parameters were measured on the day of sample collection. The DBPFP tests were conducted with 48 h of sample collection and involved chlorination for a further 24 h.

UV₂₅₄ and UV₂₇₁ were determined by a UV/Vis double beam spectrophotometer (Unico4802, USA). Three-dimensional fluorescence excitation–emission matrix (EEM) spectra were obtained by measurement of the emission (Em) and excitation (Ex) from 200 to 600 nm, at 5-nm intervals. The detailed information regarding EEM analysis and measurement of solution pH, temperature, dissolved oxygen, turbidity, dissolved organic carbon (DOC), dissolved inorganic nitrogen and DON was available elsewhere (Chu et al., 2011a,b).

THMs, HANs (DCAN, TCAN, BCAN and DBAN) and HNM (TCNM) were analyzed using a purge & trap sample concentrator (eclipse 4660, OI, USA) prior to GC/MS (Shimadzu-QP2010, Japan), based on USEPA method 524.2 (USEPA, 1992). HAcAms were measured using liquid–liquid extraction and the GC/MS analysis mentioned above. The detailed procedures of the DBP analyses are available elsewhere (Chu et al., 2010b, 2011a). The DBPFP test using free chlorine followed the approach developed by Kraser et al. (2007) and described in detail in previous publications (Chu et al., 2011a). The detection limits for chloroform (CF), DCAN, TCAN, BCAN and DBAN were analyzed using a purge & trap sample concentrator (eclipse 4660, OI, USA) prior to GC/MS (Shimadzu-QP2010, Japan), based on USEPA method 524.2 (USEPA, 1992). HAcAms were measured using liquid–liquid extraction and the GC/MS analysis mentioned above. The detailed procedures of the DBP analyses are available elsewhere (Chu et al., 2010b, 2011a). The DBPFP test using free chlorine followed the approach developed by Kraser et al. (2007) and described in detail in previous publications (Chu et al., 2011a). The detection limits for chloroform (CF), DCAN, TCAN, BCAN and DBAN were listed in Table SM-2.

3. Results and discussion

3.1. Turbidity, DOC, and UV₂₅₄

As shown in Fig. 2a, the mean overall removal rates of turbidity, DOC, and UV₂₅₄ reached 98%, 57%, and 31%, respectively, by the conventional water treatment (coagulation-sedimentation-filtration) and increased to 99%, 72%, and 53%, respectively, after the O₃–BAC treatment. The turbidity, DOC, and UV₂₅₄ in the effluent from the combined treatment decreased to <0.4 NTU, 2.0 mg L⁻¹, and 0.05 cm⁻¹, respectively. This finding demonstrated that addition of the O₃–BAC treatment to an existing conventional water treatment indeed improves the quality of the effluent, particularly in terms of improved reduction of organic matter.

3.2. Inorganic and organic nitrogen (DIN and DON)

As shown in Fig. 2b, the introduction of the O₃–BAC process significantly enhanced the removal of NH₃-N from 16% to 93%, in agreement with other studies (Karnik et al., 2005; Chiang et al., 2009;
Yan et al., 2010; Yapsakli et al., 2010). Meanwhile, the average overall removal rate of NO\textsubscript{3} was increased from 86% to 100%, but the removal of NO\textsubscript{2} was decreased from 54% to 45%, after the O\textsubscript{3}–BAC treatment. The increase in NO\textsubscript{2} caused by the O\textsubscript{3}–BAC process was probably because part of NO\textsubscript{3} was oxidized to NO\textsubscript{2} by ozone. It is well known that biological nitrification is a two-step process occurring in the BAC process (Yapsakli et al., 2010). Although O\textsubscript{3}–BAC increased the concentration of NO\textsubscript{3}, NO\textsubscript{2} was not a concern in this study because its level was <2.0 mg N L\textsuperscript{-1}, which is still below the maximum contaminant level (10 mg N L\textsuperscript{-1}) of the Chinese National Standards of Drinking Water Quality and USEPA National Primary Drinking Water Regulations.

The average removal percentages of the effluent DON in the conventional treatment process and by the further O\textsubscript{3}–BAC treatment were 35% and 74%, respectively. Of the 39% removal achieved by the O\textsubscript{3}–BAC alone, 11% and 28% of DON were removed by the ozonation and BAC processes, respectively. The BAC removal of DON with and without ozonation was also compared (Fig. SM-1). With and without pre-ozonation, 21% and 28% of DON, respectively, were removed by the BAC process, indicating that ozonation followed by BAC improves the DON removal. This is likely because ozonation transforms large N-containing organic molecules to smaller ones, increases their biodegradability.

3.3. CF and DCAN

Since the bromide concentration in the lake water was low (<10 µg L\textsuperscript{-1}, Table SM-1), CF and DCAN typically accounted for the sum of DBPs (i.e. there were few brominated analogues). In addition, the TCAN and TCAcAm levels in most of the water samples were below their respective detection limits. Therefore, our attention was primarily taken to chlorinated DBPs (CF, DCAN, DCAcAm, and TCNM) rather than brominated DBPs in this study.

From Fig. 3, the removal of the FPs for CF and DCAN both gradually increased with the progress of treatment steps in the pilot WTP. Overall, the conventional treatment removed 53% and 50% of the precursors of CF and DCAN, respectively, while the O\textsubscript{3}–BAC combined process further improved the removal of CFFP and DCANFP to 85% and 80%, respectively. This observation was in agreement with previous findings that ozonation and BAC substantially reduces the formation of CF, regardless of the quality of raw water (Karnik et al., 2005; Chiang et al., 2009; Yan et al., 2010).

Additionally, the conventional process (coagulation–sedimentation–filtration) and advanced treatment process (O\textsubscript{3}–BAC) both had higher removal for the FPs of CF and DCAN than those of TCNM and DCAcAm. As a potential explanation, it is known that dissolved humic materials, the primary fraction of the total organic matter in freshwaters (Lee et al., 1993), are the major precursors of CF and DCAN (Rook, 1974; Reckhow et al., 2001) but have little potential to transform to TCNM and DCAcAm (Chu et al., 2010b; Hu et al., 2010). Also, hydrophilic low-molecular weight (MW) organic matter trends to form more TCNM and DCAcAm, and they are more poorly removed than high-MW humic materials (Xu et al., 2007; Chu et al., 2011a).

3.4. TCNM

The TCNM removal efficiency was –188% after ozonation (i.e. ozone increased the formation of TCNM), but was +50% after BAC (Fig. 3). After ozonation, 46% of DON had been removed relative to the raw water (Fig. 2), but TCNMFP increased from 2.7 to 7.4 µg L\textsuperscript{-1}. This was probably because the ozone-induced oxidation increased the content of highly reactive specific organic compounds with high HNMFP (Hu et al., 2010), even though the overall DON was reduced.

The performance of the BAC process in terms of controlling TCNM formation either with or without pre-ozonation was also examined (Fig. SM-2). The TCNMFP removal efficiency accomplished by BAC without ozonation pre-treatment was only 38%, less than 50% achieved by the combined O\textsubscript{3}–BAC. Thus, although ozone increases the TCNMFP, it also enhances the biodegradability of the organics responsible for HNMFP to facilitate their removal in the following BAC treatment.

Fig. 2. Removal of different water quality parameters (a: turbidity, DOC, and UV\textsubscript{254}; b: DON and DIN) in different sampling locations (from Fig.1, sampling 1–5 represented the water samples collected from the raw water; after coagulation–sedimentation, filtration, O\textsubscript{3} and BAC processes, respectively). The presented data in the figure are averages of three observations. And their relative standard deviations (n = 3) are below 6%.

Fig. 3. Removal of the FPs of CF, DCAN, TCNM and DCAcAm in different stages of the water treatment process (from Fig.1, sampling 1–5 represented the water samples collected from raw water; after coagulation–sedimentation, filtration, O\textsubscript{3} and BAC processes, respectively). The presented data in the figure are averages of three observations. And their relative standard deviations (n = 3) are below 10%.
3.5. DCAcAm

Fig. 3 also provided the important information in removal of DCAcAm. The subsequent BAC process significantly improves the removal of the precursors of DCAcAm (60% removal). UV/Vis (Fig. SM-3) and EEM (Fig. 4) spectra were used to characterize the NOM. As seen in Fig. SM-3, at any particular wavelength within the range of 220–300 nm, the UV absorbance of the effluent from the BAC column was significantly lower than that of raw, filtered, and ozonated waters, indicating that BAC is an effective process to remove a range of organic compounds over a broad characteristic UV absorbance range.

The fluorescence index (FI) can be calculated as the ratio of fluorescence intensities at emission 450 and 500 nm, at excitation 370 in the EEM data. Higher and lower FI values reflect organic contents of an autochthonous (microbial) origin and an allochthonous (terrestrial) origin, respectively (McKnight et al., 2001; Chu et al., 2011a). From Fig. 4, the FI value after BAC significantly increased from 1.7 to 8.7, probably because the allochthonous organics were metabolized to autochthonous organics as a result of microbial activities in BAC. According to the fluorescence regional integration (FRI) method developed by Chen et al. (2003), the EEM spectra was operationally summarized into five regions (Fig. SM-4). As shown, the NOM of the raw water (Fig. 4a), filtered water (Fig. 4b) and ozonated water (Fig. 4c) all had two intense peaks in the soluble microbial products (SMPs) (λ<sub>ex</sub> > 250 nm, λ<sub>em</sub> < 380 nm) and aromatic proteins (APs)-like regions (λ<sub>ex</sub> < 250 nm, λ<sub>em</sub> < 380 nm), and the fluorescence intensities of two peaks in the raw (SMP: 988.6 mV and AP: 988.2 mV), filtered (SMP: 985.0 mV and AP: 983.7 mV) and ozonated water (SMP: 982.5 mV and AP: 981.8 mV) were similar. Thus, the conventional treatment process and ozonation were ineffective at removing the SMP-like and AP-like substances.

It should be noted that the FI and FRI methods both provide only a qualitative and/or semi-quantitative analysis of the data, but they cannot separate the complex measured signal into its individual underlying fluorescent phenomena with specific excitation. In order to further understand the characteristics of DBP precursors with the EEM spectra, and ascertain the performance of conventional and advanced treatment processes on removal of the DOMs with different characteristics, an improved EEM analysis model will be adopted in the future experiments. For example, parallel factor analysis is a valuable tool for characterizing and quantifying changes in DOM fluorescence, and enabling the tracing of different fractions in the natural environment (Jørgensen et al., 2011).

3.6. UV<sub>272</sub> and TOX

Korshin et al. (1997) reported that a decrease in UV absorbance at 272 nm caused by the chlorination of DOM correlates linearly with the amount of total organic halogen (TOX) formed, under a wide range of water quality conditions and reaction times. In the
present study, therefore, the decrease of UV272 (ΔUV272) before and after the DBPF test was assessed and the removal efficiencies (ΔUV272) in different stages of the treatment process were used to suggest the removal of TOXFP. Removal of TOX (ΔUV272) by the conventional process (coagulation–sedimentation–filtration), ozonation, and BAC filtration was 44%, 45% and 72%, respectively. This suggests that the BAC process has potential to control halo- nated DBPs generally, including unidentified DBPs.

Acknowledgements

The authors gratefully acknowledge financial support from the National Natural Science Foundation of China (51108327), Research and Development Project of Ministry of Housing and Urban-Rural Development (No. 2009-k7-4), International Science & Technology Cooperation Program of China (2010DFA91800), State Key Laboratory of Pollution Control and Resource Reuse Foundation (PCRRY11015) and Postdoctoral Science Foundation of China (20110490073). We also thank the Wuxi Water Company, Tsinghua University, Southeast University and Hohai University for their cooperation. We acknowledge Stuart W. Krasner (Metropol- itan Water District of Southern California, USA) and Paul Westerhoff (Arizona State University) for their ongoing assistance in our N-DBP study. We also sincerely appreciate the revision suggestions from editor and reviewer of Chemosphere which improved this manuscript substantially.

Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2011.11.070.

References