Molecular weight distribution variation of assimilable organic carbon during ozonation/BAC process

Shu Shi-hu, Yan Min, Gao Nai-yun and He Wen-Jie

ABSTRACT

Assimilable organic carbon (AOC) was measured combined with molecular weight (MW) distribution during a long time operation of a pilot scale ozonation/BAC (biological activated carbon) process in a water treatment plant in China. The AOC measurement was done on different samples: raw water, water samples after sedimentation, sand filtration, ozonation and BAC filtration. MW distribution variation of AOC during ozonation/BAC process was evaluated. Results showed that AOC was mainly related to the NOM (natural organic matter) with MW $<$ 1 kDa. The fraction of the NOM with MW $<$ 1 kDa corresponds to 53–67% of the dissolved organic carbon (DOC) to all the samples while AOC corresponds to 2.7–5.9% of DOC. So just a small part of the fraction with MW $<$ 1 kDa was AOC. This indicates that ozonation/BAC process removing a large part of DOC will not necessarily result in a great reduction in AOC.

Key words | AOC, MW, NOM, ozonation/BAC process

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INTRODUCTION

Molecular weight (MW) is a valuable tool to characterize complex organic compounds, such as humic substances. Some researchers have shown that MW characterization of the DOC (dissolved organic carbon) provides a means for identifying potential treatment strategies (Chadik & Amy 1987; Amy *et al.* 1988).

Low MW and nonhumic material are difficult to remove by either coagulation or adsorption. Collins *et al.* (1986) found that conventional treatment processes were rather ineffective in removing DOC having a MW of less than 500 Da. In contrast, higher MW proved to be more amenable to removal than lower MW material. Owen *et al.* (1995) and Amy *et al.* (1992) found that chemical coagulation could effectively remove higher molecular material. Water sources with material of medium MW (e.g., 1 to 5 kDa) can also be effectively adsorbed by activated carbon.

Ozonation of drinking water transforms NOM (natural organic matter) into a more biodegradable form. This can cause significant bacterial regrowth in the distribution system if biodegradable organic matter (BOM) is not removed by subsequent treatment steps (Van der Kooij & Hijnen 1984). The concentration of BOM, expressed in terms of assimilable organic carbon (AOC) or biodegradable dissolved organic carbon, increases with increasing ozone dosage (Van der Kooij *et al.* 1982; Servais *et al.* 1989). AOC refers to a fraction of the total organic carbon (TOC) which can be utilized by two specific strains of bacteria, resulting in an increase in biomass concentration that is quantified. AOC typically comprises just a small fraction (0.1–9.0%) of the TOC (Van der Kooij 1990). The inoculum for the AOC bioassay can be composed of a mixture of pure bacterial strains cultivated in laboratory conditions (*Pseudomonas fluorescens* P17 and *Spirillum* NOX). Bacterial growth is monitored in the water samples by colony counts, and the average growth observed during the incubation is converted into AOC units ($\mu g\,L^{-1}$ as acetate-carbon) by using a growth yield of the bacteria from calibration

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curves derived from standard concentrations of organic compounds (acetate or oxalate). A significant correlation exists between the AOC concentration and the density of heterotrophic bacteria in distribution water supplies (Van der Kooij 1990; Block *et al.* 1993). Van der Kooij (1990) showed that heterotrophic bacteria in a non-chlorinated system did not increase when AOC levels were lower than 10 $\mu g\,L^{-1}$. LeChevallier *et al.* (1987), on the other hand, suggested that the regrowth might be limited by AOC levels less than 50–100 $\mu g\,L^{-1}$ in a system maintaining a disinfectant residual.

GAC (granular activated carbon) in actual water treatment processes naturally breeds a bacterial population on its surface, and eventually it functions as biological activated carbon (BAC). With the help of the bioactivity on BAC, the reduction of TOC and other biodegradable organic matter is considered to maintain a longer service time before GAC regeneration. The combination of ozonation and biological treatment with BAC enhances the degradation removal of organic substances, although it only slightly degrades trihalomethane precursors and aldehydes (Cipparone *et al.* 1997).

The purpose of this study was to find out to what extent the biofilm formation potential measured as AOC is related to the various MW fractions of the NOM. This will indicate whether ozonation/BAC process which mainly removes larger organic molecules will give any considerable reduction in the AOC.

MATERIALS AND METHODS

Treatment process

This research was carried out in a water treatment plant in southern China. The source water was obtained from the nearby Yangzi River. Water production is about 200,000 $m^3\,d^{-1}$. Currently, the water treatment works employs conventional treatment processes, including pre-chlorination, coagulation, sedimentation, sand filtration, and disinfection for its water treatment. In this study, only a small part of the water (24 $m^3\,d^{-1}$) after sand filtration (before disinfection) was collected as the influent of the ozonation/BAC process. The pilot scale ozonation/BAC treatment system was installed inside the water treatment works as an advanced treatment process to enhance the water quality. A schematic layout of the pilot system is included as Figure 1.

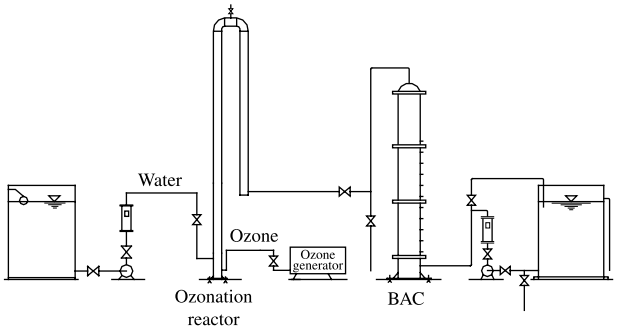

Figure 1 | Ozonation/BAC process flow chart.

The ozone supply to the reactor is provided by ozone generator manufactured by Shun Feng Company in Shanghai. In this study the ozone dosage was 1.5 $mg\,L^{-1}$. The ozonation reactor was 6.0 m high with inner diameter of 160 mm. Contact time of ozonation was about 10 min. The BAC was used to remove the organic matter remaining after ozonation. The BAC filter was 3.0 m high with inner diameter of 300 mm, the column was filled with 2.0 m GAC (1 mm in diameter, 2 ~ 3 mm in length). Raw material of GAC was wood and the manufacturer was a chemical industry company in Nanjing, China. The empty bed contact time of BAC filtration was 8.6 min.

Analytical methods

MW distribution of organic matter was measured using ultrafiltration (UF) membrane. The membrane was the YM series of Amicon produced by Milipore Company in US. The material of the membrane was modified cellulose acetate. After filtrated by 0.45 μm microfiltration membrane to remove particulate matter, the water sample was then applied to a continuous flow system consisting of UF (Amicon® YM-1, YM-3,YM-10, YM-30 series membranes whose MW cut off was 1, 3, 10 and 30 kDa respectively). TOC and UV_{254} of the filtrate was measured then using Phoenix 8,000 TOC Analyzer and UV751GD spectrophotometer respectively. Diameter of the membrane filter was 10 cm. The volume of the membrane filter was 800 ml. There was a churn-dasher driven by magnetic force in the membrane filter. The pressure of the membrane filtration was 0.1×10^6 Pa driven by pure nitrogen.

AOC was analyzed by Liu's method (Liu *et al.* 2002). The water samples were heated at 70°C for 0.5 h within 6 h after sampling to destroy vegetable cells. After cooling,

Pseudomonas fluorescens strain P17 were inoculated into the water samples. The water samples were incubated at 25°C for 2 d and then the cell formation units were counted. Subsequently, the same water sample was heated at 70°C for 0.5 h to kill P17 and then Spirillum NOX strain was incubated. The water samples were then incubated at 25°C for 3 d and the cell formation units were counted. AOC concentration was calculated by comparing the cell formation unit number and yield coefficient. The yield coefficient of P17 and NOX were measured to be 1.4×10^7 CFU mg^{-1} acetate-C and 1.8×10^7 CFU mg^{-1} acetate-C, respectively.

In this study, the AOC measurement was done on different samples: raw water, water samples after sedimentation, sand filtration, ozonation and BAC filtration. AOC was measured with three parallel analyses. The result of each sample was the average value of the three parallel analyses.

RESULTS AND DISCUSSION

MW variation during the treatment process

MW distributions may shift during the treatment processes. Amy *et al.* (1988), and Owen *et al.* (1995) observed that ozonation did not result in NOM destruction, but converted material with higher MW to lower MW. This shift of molecular weight distribution not only changes the properties of NOM but also reduces the THMFP.

MW measurement was done on different samples: raw water, water samples after sedimentation, sand filtration, ozonation and BAC filtration. Prevenient parallel measurements in our lab have shown that the results of MW distribution of organic matter were almost the same under the same conditions. So the MW distribution measurements were done with no replicates. MW variation during the processes can be seen in Tables 1 and 2.

From Tables 1 and 2, it can be seen that organic matter in raw water was mostly in low MW, thereto the ratio of UV_{254} and TOC with MW less than 3 kDa were 50% and 71.5% compared to the whole UV_{254} and TOC. DOC was the result of TOC measurement after water sample was filtrated by 0.45 μm membrane. The fraction with MW $<$ 1 kDa corresponds to 53–67% of the DOC.

Conventional treatment followed by advanced treatment could remove 70% of UV_{254} and 36% of DOC, thereto 45% of UV_{254} and 21% of DOC were removed by conventional treatment and 25% of UV_{254} and 15% of DOC were removed by advanced treatment. Among the removed UV_{254} and DOC, the part which had higher MW ($>$3 kDa) were mostly removed by conventional treatment

Table 1 | UV_{254} in different molecular weight fractions of organic carbon

UV_{254} (cm^{-1})	0.45 μm	0.45 μm ~ 30 kDa	30~10 kDa	10~3 kDa	3 ~ 1 kDa	<1 kDa
Raw water	0.040	0.008	0.007	0.005	0.009	0.011
After sedimentation	0.023	0	0.004	0.001	0.008	0.010
After filtration	0.022	0	0.003	0.002	0.007	0.010
Ozonation	0.013	0	0.002	0	0.003	0.008
BAC filtration	0.012	0	0.001	0.001	0.005	0.005

Table 2 | TOC in different molecular weight fractions of organic carbon

TOC ($mg\,L^{-1}$)	0.45 μm	0.45 μm ~ 30 kDa	30~10 kDa	10~3 kDa	3 ~ 1 kDa	< 1 kDa
Raw water	2.795	0.377	0.213	0.151	0.566	1.488
After sedimentation	2.380	0.173	0.135	0.051	0.560	1.461
After filtration	2.230	0.130	0.117	0.062	0.505	1.416
Ozonation	1.924	0.005	0.070	0.204	0.419	1.226
BAC filtration	1.812	0.002	0.136	0.155	0.301	1.218

Table 3 | Variation of AOC concentration in treatment process

Samples AOC ($\mu g L^{-1}$)	Raw water	Sedimentation	Sand filtration	Ozonation	BAC Filtration	After chlorination
Total	103	116	99	142	92	144
>1 kDa	15	12	10	22	12	22
<1 kDa	88	104	89	120	80	122

and the part which had lower MW (<3 kDa) were mostly removed by advanced treatment.

The reduction in UV_{254} due to ozonation/BAC process was about 50% from 0.022 to 0.012 in Table 1. The reduction of TOC was lower than the reduction of UV_{254}, indicating that mainly the NOM molecules with a relatively high MW cause the UV absorption. Also the structure of the organic compounds affects UV_{254}, e.g. aromatic compounds.

Variation of AOC concentrations in treatment process

Biological stability refers to a condition wherein the treated water quality does not enhance biological regrowth in the distribution system. Maintenance of biological stability requires removing nutrients from the water prior to distribution, especially biodegradable organic matters. Since the concentration of biodegradable organic compounds in drinking water was relatively low and difficult to quantify by chemical analytical methods, AOC was defined as a surrogate parameter for the measurement of potential bio-regrowth and biological stability. In this study, the variation of the AOC concentration is given in Table 3.

Table 3 shows that AOC concentration was only slightly affected by the conventional treatment process (flocculation, sedimentation and sand filtration), probably because the AOC fraction was composed of small MW, non-humic compounds which do not have an impact on coagulation. Hem & Harry (2001) found AOC in NOM with MW $<$ 1 kDa, while the same results were obtained by Volk in 2000 (Volk *et al.* 2000). Therefore, the conventional treatment process mainly removing large molecular organic matters was capable of a small reduction of AOC level (Hem & Harry 2001).

As mentioned earlier, AOC was mainly related to the NOM with MW $<$ 1 kDa. So in this study, MW distribution of AOC was measured only using YM-1 UF membrane which separated MW of AOC into two parts: MW $<$ 1 kDa and MW $>$ 1 kDa. AOC increased sharply by 43.4% after the ozonation process and resulted in biological instability. Ozone can oxidize organic matters to aldehydes, aldoketo acids, carboxylic acids, and other AOC forming matters which cause microbial regrowth (Van der Kooij *et al.* 1989; LeChevallier *et al.* 1992). However, the oxidizing ability was subjected to the characteristics of raw waters. Literatures showed that AOC level was about 2 to 4 times higher after ozonation (Nieminski & Bradford 1991).

BAC filtration showed good effect for AOC removal, reaching 35.2% in this study. This demonstrated that BAC filter was indispensable in counteracting the negative effects caused by ozonation and maintaining biological stability. BAC was very effective at removing AOC because of its high adsorption capacity for small molecular organic matters. Total AOC removal effect of more than 80% was reported. In this experiment, the GAC in the filter had been put in operation for about one year, its adsorption capacity had reduced significantly, because the iodine value was only 68% of virgin GAC. Consequently, AOC reduction in BAC filter was mostly achieved by biological degradation instead of activated carbon adsorption.

As to the MW distribution of AOC in Table 3, the fraction of AOC with MW $>$ 1 kDa was slightly affected by the conventional treatment process. The fraction of AOC with MW $>$ 1 kDa increased from 10 $\mu g L^{-1}$ to 22 $\mu g L^{-1}$ after

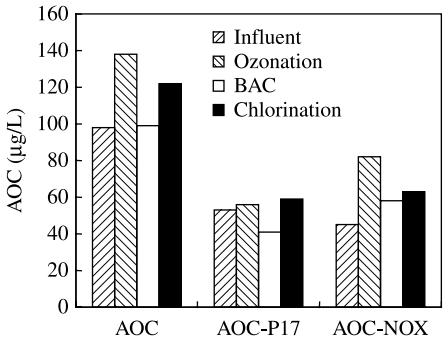

Figure 2 | The AOC concentration in different phases of water treatment.

Table 4 | AOC/TOC ratio in raw water

MW	0.45 μm	0.45 ~ 30 K	30 K ~ 10 K	10 K ~ 3 K	3 K ~ 1 K	<1K
TOC ($mg\,L^{-1}$)	2.795	0.377	0.213	0.151	0.566	1.488
AOC ($\mu g\,L^{-1}$)	103	0	0	0	15	88
AOC in % of TOC	3.7	0	0	0	2.7	5.9

ozonation and then reduced to $12\,\mu g\,L^{-1}$ after BAC filtration. The fraction of AOC with MW $<$ 1 kDa reduced by 50% by conventional treatment process. The fraction of AOC with MW $<$ 1 kDa increased from $89\,\mu g\,L^{-1}$ to $120\,\mu g\,L^{-1}$ after ozonation and then reduced to $80\,\mu g\,L^{-1}$ after BAC filtration. It seems that ozonation/BAC process has nothing to do with AOC of MW $>$ 1 kDa or MW $<$ 1 kDa.

AOC-P17 and AOC-NOX variation of the AOC concentration was given in Figure 2. AOC-P17 means AOC represented by strain P17 ($\mu g\,L^{-1}$), AOC-NOX is AOC represented by strain NOX ($\mu g\,L^{-1}$). AOC-P17 accounts for 54% and AOC-NOX accounts for 46% of total AOC in influent. AOC-P17 accounts for 41% and AOC-NOX accounts for 59% of total AOC in effluent of BAC filtration. After chlorination, AOC-P17 accounts for 48% and AOC-NOX accounts for 52% of total AOC. It indicates that the ozonation/BAC process may change the ratios of organic compounds comprising AOC.

AOC/TOC ratio in raw water

AOC typically comprises just a small fraction (0.1–9.0%) of the TOC. The AOC/TOC ratio indicates how easily assimilable the NOM will be. The AOC/TOC ratios for the MW fractions are shown in Table 4.

The AOC/TOC ratio was 3.7% totally, and 2.7% for the MW fraction 1 ~ 3 kDa, 5.9% for the MW fraction $<$1 kDa. This may indicate a common relationship between the AOC and TOC in raw water, but this has yet to be confirmed experimentally and explained theoretically.

CONCLUSIONS

The AOC reduction was less than 10% from $99\,\mu g\,L^{-1}$ to $92\,\mu g\,L^{-1}$ by the ozonation/BAC process. AOC is mainly related to the smaller organic molecules. The AOC removal by the ozonation/BAC process is low even when both the UV_{254} removal and the TOC removal are high. Results showed that AOC was mainly related to the NOM with MW $<$ 1 kDa. The fraction of the NOM with MW $<$ 1 kDa corresponds to 53–67% of DOC while AOC corresponds to 2.7–5.9% of DOC. So just a small part of the fraction with MW $<$ 1 kDa was AOC. This indicates that the ozonation/BAC process whilst removing a large part of the DOC will not necessarily result in a reduction in the biofilm formation potential.

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