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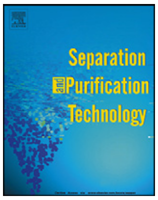

THMs precursor removal by an integrated process of ozonation and biological granular activated carbon for typical Northern China water

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ABSTRACT

The removal of trihalomethanes (THMs) precursor and natural organic matter (NOM) by an integrated process of ozonation and biological granular activated carbon filtration (BGAC) as a deep water treatment process was investigated in pilot-scale tests. A comparison is also made with granular activated carbon filtration (GAC). The characteristics of the THMs precursor and the THMs formation potential (THMFP) were investigated by resin adsorption and ultrafiltration. The results show that the integrated process of ozonation and BGAC (O_3/BGAC) is obviously superior to GAC for the removal of the THMs precursor because a considerable synergetic effect occurs between the ozonation and the BGAC. Although ozonation can limitedly remove dissolved organic carbon (DOC), it can cut down the molecular weight of the NOM, change its polarity, decrease the THMFP, and obviously enhance the efficiency of the BGAC. The BGAC could efficiently remove the hydrophobic base (HoB), hydrophobic neutral (HoN), weakly hydrophobic acid (WHoA), and low molecular weight fraction DOC that was produced in the optimized ozonation process. However, the BGAC stage should be carefully controlled to avoid the leakage of microbes and/or the products of metabolism because it has a high risk for producing THMs in following chlorination process.

1. Introduction

Natural organic matter (NOM) can cause taste, odor, and color problems in potable water, and bacterial regrowth in distribution systems. More importantly, NOM is the precursor for disinfection by-products (DBPs), such as trihalomethanes (THMs) and haloactic acids (HAAs), which are found to be carcinogens [1]. The US Environmental Protection Agency (USEPA) has established more stringent maximum contaminant levels (MCLs) of 80 and 60 μg L^{-1} for THMs and HAAs, respectively, for finished drinking water. To prevent the production of DBPs, NOM must be efficiently removed from raw water before disinfection. However, NOM in micro-polluted raw water is a mixture of humic and synthetic compounds, such as pharmaceutical compounds, detergents, pesticides, polycyclic aromatic hydrocarbons, etc. Some of these compounds are soluble, hardly biodegradable, and irremovable in conventional water treatment processes [2]. Ozonation followed by biological treatment is one of the promising processes to remove them from raw water [3–6].

Some researchers have found that the use of ozonation in the water treatment process results in a decrease in the formation of THMs and HAAs upon subsequent chlorination [7–9]. An increase in the ozone dosages results in a concomitant decrease in the concentrations of THMs and HAAs that formed from subsequent chlorination [10–13]. However, the ozone cannot mineralize organic carbon with a traditional water treatment dose (less than 4 mg L^{-1}); thus, a high removal of the THMs precursor cannot be expected by simple ozonation. Ozone can cleave the unsaturated bonds in aromatic moieties that are found in NOM, which makes the organic molecules smaller, more oxidized, and more biodegradable; thus, refractory NOM transforms to the biodegradable form, i.e., biodegradable dissolved organic carbon (BDOC) [14–18]. BDOC that is produced by ozonation can be removed in subsequent biological treatments. However, Volk et al. [19] and Wricke et al. [20] reported that the maximum BDOC production by ozonation was only around 30% of the total DOC in raw water, even if the ozone dose or reaction time was increased. The ozonation should be set to achieve treatment goals that are based not only on the characteristics of the NOM in the raw water, which optimizes biofiltration, but also on economic benefits [21,22].

The common form of biofiltration is to operate rapid filters in a biologically active mode. BGAC is the most common media in the three primary media types for hybrid biofilters, compared

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Table 1
Water quality characteristics of the water samples.

Sample	DOC (mg L^{-1})	Turbidity (NTU)	pH	Alkalinity (mg L^{-1} as $CaCO_3$)
Raw water	3.80	8.20	8.40	200
Synthetic water	4.48	8.93	7.00	135

with sand and anthracite [23–25]. The superiority of BGAC may be related to its better attachment surface for biofilm bacteria and/or being able to absorb some of the input BDOC or organic materials that are released by microorganisms [6,26,27]. During biofiltration, pollutants that are present in the water are removed in two parallel processes: adsorption on activated carbon and biodegradation. Activated carbon was found to accelerate the decomposition of ozone into highly oxidative species, such as hydroxyl radicals ($HO^\bullet$) [28]. The biodegradation is a result of the presence of microorganisms on the external surface and in macropores of the GAC [6,19]. The microorganisms use organic compounds, both dissolved in water and previously adsorbed onto the carbon, in their metabolic processes, which results in the recovery of the adsorption capacity of the GAC. As a result, the application of ozonation followed by BGAC leads to biologically stable water [6,19,29].

However, there are still some doubts about the mechanisms of the NOM removal and the THMs control by the simultaneous use of ozone and BGAC. This paper studies the performance of a combination of ozonation and BGAC for removal of THMs precursor by investigating the characteristic of the NOM with resin adsorption and ultrafiltration.

2. Materials and methods

2.1. Raw water

Two kinds of water samples were used in this study. Raw water for the pilot-scale test came from the Yellow River, which is a source of water for the Tianjin water treatment plant (Tianjin, China). Synthetic water for the bench-scale test was prepared by adding a certain amount of both kaolin and a commercial humic acid (extracted from Yellow River sediment) to tap water. Table 1 presents the mean raw water and synthetic water quality characteristics.

2.2. Bench-scale tests

The bench-scale ozonation was performed in an airtight contactor. The ozone was generated by an ozonizer OS-IN (Mitsubishi Electric, Japan). The ozone dosage was determined through ozone-demand tests. Ten minutes after the ozone was introduced, the samples were purged with high-pressure pure nitrogen to eliminate residual O_3 and to ensure the contact time. The nitrogen purge time was 10 min. Here the ozone dosage refers to the contact dosage, which is the mean input dosage that is added to the water samples during the contact time.

2.3. Pilot-scale tests

The pilot plant facility has two parallel trains; train one has coagulation, dissolved air flotation (DAF), sand-filter, GAC and disinfection. Train two has coagulation, DAF, sand-filter, mid-ozone, BGAC, and disinfection. The flow rate of each system was controlled at 5 $m^3\,h^{-1}$. The coagulation process was carried out with the following conditions: rapid mixing ($t = 1$ min, $G = 756\ s^{-1}$) and two-stage flocculation (in each stage, $t = 9$ min, $G = 91.5\ s^{-1}$). The surface loading rate of the flotation separation pond was 11 $m^3\,m^{-2}\,h^{-1}$, the recycle ratio was 10%, the saturator pressure was 0.4 MPa, and the residence time was 126 s. The depth of the sand-filter bed was 2.7 m, the filtration rate was 7.86 $m\,h^{-1}$, and the sand with a 400-nm average diameter was used as filter media. Ozonation was carried out in two-stage counter-flow contactors, with a hydraulic retention time of 12 min. The dose of ozone is 1.5–2.0 mg L^{-1}. The ozone was generated by an ozonizer OZAT®CFS-1 (Switzerland). The flow rate of GAC/BGAC filter in both trains is controlled at 1.25 $m^3\,h^{-1}$, the residence time was about 15–20 min, and the filtration rate was 5 $m\,h^{-1}$. Double-layer filter medias were used, granular activated carbons (ZJ15, provided by Shenhua Co., Ningxia, China) and sand (0.5–1.0 mm). The depths of the granular activated carbon and sand-filtration bed are 1.5 m and 0.5 m, respectively. The iodine value of carbon is 1010 ± 20 mg g^{-1}, while the density of the filter media is 0.5 t m^{-3}. GAC combined with ozonation is referred to as the biological granular activated carbon (BGAC) process, or biologically enhanced activated carbon process. The schematic of pilot-scale tests is shown in Fig. 1.

The details of the pilot plant have been reported earlier in the literatures [30,31].

2.4. NOM characteristics

Hollow-fiber modules and ultrafiltration membranes (A/G Technology) with nominal molecular weight cut-offs of 30, 10, 3, and 1 kD (Kilo-Dalton) were used to sequentially fractionate dissolved organic matter (DOM). The membranes were made of cellulose derivatives with a total surface area of 24 cm^2. The applied pressure through the membranes ranged from 250 kPa to 350 kPa. The total organic carbon (TOC) of the effluent from each membrane and the TOC of the raw water were measured to determine the content of each cumulative fraction.

Amberlite XAD-8 and XAD-4 resin were used to fractionate the DOM, which follows the procedures of Thurman and Malcolm [32] and Malcolm and MacCarthy [33]. The water samples were pre-filtered with a 0.45-μm pore size filter membrane to remove the particles; they were then directed to an XAD-8 packed Col-

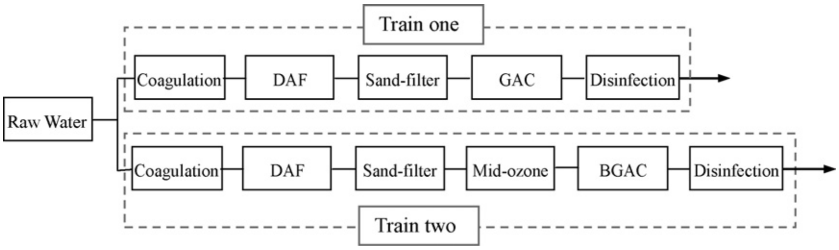

Fig. 1. The schematic of pilot-scale tests.