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# AC/$O_3$-BAC processes for removing refractory and hazardous pollutants in raw water

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**Abstract**

Granular activated carbon (AC)/$O_3$-biological activated carbon (BAC) process was employed to treat raw water and compared to $O_3$-BAC process in its optimum parameters (3 mg/L ozone dosage with 15 min oxidation time and 15 min empty bed contact time in BAC). The results showed that the presence of AC improved ozone utilization and biodegradability of the effluent. For dissolved organic carbon (DOC) removal, AC/$O_3$-BAC was more efficient than $O_3$-BAC and its synergetic effect could be noticed. It was showed that small molecules with molecular weight (MW) < 3 kDa predominated in the raw water accounting for more than 56% DOC, and their amount increased after oxidation, accounting for more than 64% DOC. Except for organic pollutants with MW > 10 kDa, those of other MW range were decomposed better by AC/$O_3$ process than by $O_3$ process alone. GC/MS analysis showed that AC/$O_3$-BAC process was effective in removing phthalate esters (PAEs) and persistent organic pollutants (POPs). PAEs' removal ratio reached more than 93% and reduced with the increase of the length of the alkyl side chains and the alkyl branch chains. POPs-polybromobiphenyls' removal reached more than 94% except for 2,2′,4,5′,6-pentabromophenyl and decreased with the substitutional bromines increase except for 2,2′,5,5′-tetrabromobiphenyl, which could be completely removed.


*Keywords:* Activated carbon; Catalytic ozonation; Biological activated carbon; Dissolved organic compound; Phthalate esters and persistent organic pollutants

## 1. Introduction

Removal of micro-pollutants in raw water is very important for its safe drinking. However, the organic pollutants remained in raw water are mostly refractory and difficult to be further biologically degraded. Conventional treatment process like flocculation-filtration-disinfection is not effective enough to remove them either.

Ozone is a powerful oxidant, and it is well known that ozonation of water would result in considerable organic pollutants' reduction and biodegradability improvement [1–3]. In general, large ozone dosage was needed for organic pollutants' reduction especially for mineralization, which accordingly impedes its large-scale application. On the other hand, the combination of ozonation and activated carbon (AC) (hereafter referred as AC/$O_3$) may offer an interesting potential for implementation at industrial scale, since ozonation may destroy adsorbed molecules and regenerate the adsorption capacity of activated carbon [4–7]. AC can initiate radical-type chain reactions that proceed in solution and accelerate the transformation of ozone into secondary oxidants, such as hydroxyl radical ($^{\bullet}$OH) [8]. It was proved that ozonation of phenols [9], 1,2-dihydroxybenzene [10] and 1,3,6-naphthalene-trisulphonic acid [11] was enhanced in the presence of AC, probably due to catalytic effects provided by active surface groups. AC presents a large surface area where ozone and organic pollutants could be adsorbed and react. The complete mineralization of refractory organic matter in raw waters will also consume a lot of ozone. To increase economical efficiency of ozonation, it was usually combined with biological process for water treatment [12]. Ozonation followed by biological activated carbon (hereafter referred as $O_3$-BAC) is widely used for drinking water treatment [13]. However, AC/$O_3$ followed by BAC (hereafter referred as AC/$O_3$-BAC) process has been not reported.

The objective of this paper was to evaluate the effectiveness of AC/$O_3$-BAC process for removing organic pollutants in raw water, especially phthalate esters (PAEs) and persistent organic pollutants (POPs).

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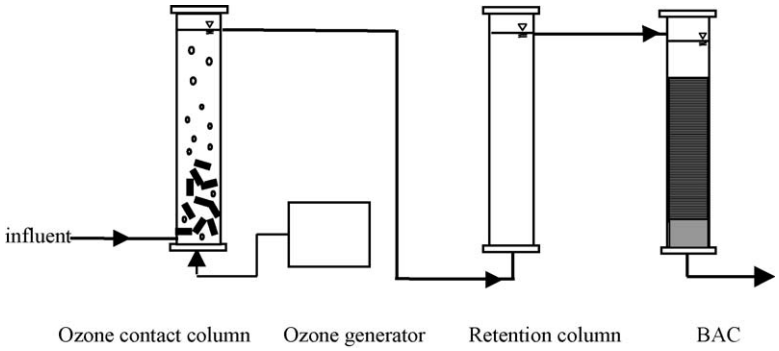


Fig. 1. Schematic diagram of AC/$O_3$-BAC pilot plant.

## 2. Materials and methods

### 2.1. Experimental set-up

Fig. 1 shows the experimental schematic diagram that consists of an ozone contact column, a retention column and a BAC column, all of which had a diameter of 60 mm and a height of 1000 mm except for the oxidation column with a height of 750 mm. There were two sets of parallel experimental set-ups for $O_3$-BAC and AC/$O_3$-BAC, respectively. For AC/$O_3$-BAC, 100 g coal-based granular activated carbon was added in the ozone reactor (fluidized activated beds).

The ozone contact time (empty bed contact time, EBCT) was 15 min. The retention column was used for further reaction and consumption of residual ozone, and its hydraulic retention time (HRT) was 20 min. BAC reactor was generally operated with EBCT of 15 min except specified elsewhere. The ozone gas was continuously bubbled into the water through a porous glass plate. Ozone was produced from pure oxygen using a DHX-SS-001 ozone generator (Harbin Jiujiu Electric Chemical Engineering Ltd.).

### 2.2. Analytical methods

Dissolved organic carbon (DOC) was analyzed with a TOC analyzer (SHIMADZU TOC-5000). $UV_{254}$ was determined with a Shimadzu UV-250 spectrophotometer. Turbidity was analyzed with Lp2000 turbidity-meter (made in Portugal). The ozone concentration in the ozone gas was determined by iodometry method [14]. Biodegradable dissolved organic carbon (BDOC) was determined following the procedure by Servais et al. [15]. It involves sterile filtration of the sample, reinoculation with a natural assemblage of bacteria from the same origin as the sample, and incubation for at least 10 days in the dark at 20 °C. DOC is followed, until a plateau is reached and the difference between initial and final DOC is taken as a measure of BDOC. Ultrafiltration membrane was employed to determine the change of molecular weight (MW). MW distribution was characterized by a series of ultrafiltration membranes with nominal cutoff values of 1, 3 and 10 kDa, and each fraction were collected for DOC determination.

A Hewlett-Packard 5890 GC with a mass detector (MSD) and Chemstation software, were used. The organic pollutants were analyzed by scan mode. The capillary columns were HP-5MS (30 m × 0.25 mm i.d. × 0.25 μm film thickness). The carrier gas was helium. A split-splitless injector in the splitless mode was used and the temperature program was programmed from 60 °C (initial time 3 min) to 120 °C at a rate of 10 °C/min, 120–280 °C at a rate of 5 °C/min and held at 280 °C for 10 min. The injector and mass spectrometer were held at 280 and 280 °C, respectively. The electron impact energy was set at 70 eV.

Before analysis, relevant standards were run to check column performance, peak height and resolution. With each set of samples to be analysed a solvent blank, a standard mixture and a procedural blank were run in sequence to check for contamination, peak identification and quantification. Compounds were identified mainly by their retention times. Selected samples were also analysed by full-scan GC–EI–MS for confirmation.

### 2.3. Water quality of raw water after sand filter

The experiment for advanced purification of raw waters was carried out in Miyun Reservoir of Beijing City. Water quality is shown in Table 1.

## 3. Results and discussion

### 3.1. The optimum parameters in AC/$O_3$-BAC processes

In AC/$O_3$-BAC process, ozone dosage, oxidation time and retention time in BAC unit were three key operation parameters. DOC removal efficiency increased with ozone dosage and oxidation time in both AC/$O_3$ unit and the AC/$O_3$-BAC process. However, DOC removed per unit ozone consumption decreased with ozone dosage. In our study, 3 mg/L ozone dosage with 15 min oxidation time was much more economical. Although DOC removal efficiency increased with EBCT, 15 min EBCT

Table 1
Water quality of raw water

| Parameters | Range |
|---|---|
| $UV_{254}$ ($m^{-1}$) | 4.9–7.4 |
| Turbidity (NTU) | 0.65–0.97 |
| DOC (mg/L) | 4.94–7.27 |
| BDOC/DOC | 0.17–0.19 |
| $NH_4^+$—N (mg/L) | <0.5 |