Comparison of O₃-BAC, UV/O₃-BAC and TiO₂/UV/O₃-BAC processes for removing organic pollutants in secondary effluents

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Abstract

Three processes combining different oxidations and subsequent biological activated carbon (BAC), i.e. O₃-BAC, UV/O₃-BAC and TiO₂/UV/O₃-BAC were employed to treat secondary effluents and compared. The effects of ozone dosage and empty bed contact time (EBCT) in BAC unit on dissolved organic carbon (DOC) removal were investigated. The results showed that the presence of UV and TiO₂ improved ozone utilization and biodegradability of the effluent. DOC removal increased with ozone dosage and EBCT in BAC, however, 3 mg/L ozone dosage with 15 min oxidation time and 15 min EBCT in BAC were more economical and efficient. The synergetic effect between oxidation and BAC is in the order: TiO₂/UV/O₃-BAC > UV/O₃-BAC > O₃-BAC. Among three oxidation processes, organic pollutants with molecular weight (MW) < 10,000 Da were mostly removed by TiO₂/UV/O₃, and those with MW > 10,000 Da were mostly removed by O₃ alone. GC–MS analysis showed dibutyl phthalate, bis(2-ethylhexyl) phthalate, 4-bromo-3-chloroaniline and other phenol derivatives were prevalent organic pollutants found in the secondary effluent. After TiO₂/UV/O₃ treatment, some aromatic compounds including 2,4-dichloro-benzenamine, 4-bromo-3-chloroaniline and 3,5-dimethoxy-acetophenone disappeared and some small molecules were formed, but the kinds and concentration of organic pollutants including phthalate esters were greatly reduced by the subsequent BAC unit.
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Keywords: Secondary effluents; Photocatalysis; Titanium dioxide; Ozonation; Biological activated carbon (BAC); Dissolved organic carbon (DOC)

1. Introduction

Reduction of micro-pollutants in the secondary effluent is very important for its safe reclamation, recycling and reuse. However, the organic pollutants remained in the secondary effluent are mostly refractory and difficult to be further biologically degraded. Conventional treatment processes like flocculation–filtration–disinfection are not effective enough to remove them either.

Advanced oxidation processes (AOPs), on the other hand, have been used to treat many organic pollutants by generating hydroxyl radicals (•OH) as powerful oxidizing species. Among the various AOPs, photocatalytic oxidation has proven effective in degrading refractory pollutants [1–3]. Photochemical treatment processes have been used recently to increase the biodegradability of various recalcitrant pollutants [4–7].

Although AOPs may be a promising method for reducing or mineralizing organic pollutants in wastewater, complete mineralization of refractory organic pollutants in secondary effluents will also consume a lot of oxidant or energy. To increase the efficiency of ozonation, it was usually combined with biological process for water and wastewater treatment [8]. Ozonation followed by biological activated carbon (hereafter referred as O₃-BAC) is widely used for drinking water treatment [9]. However, O₃-BAC process was rarely investigated and used for advanced treatment of secondary effluents. Also to our knowledge, combination of ozone with ultraviolet (UV/O₃) or ozone with ultraviolet in the presence of titanium

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dioxide ($TiO_2/UV/O_3$) followed by BAC process (hereafter referred as UV/O_3-BAC and $TiO_2/UV/O_3$-BAC) has never been reported.

The objective of this paper was to investigate the efficiencies of three combination processes, i.e. O_3-BAC, UV/O_3-BAC and $TiO_2/UV/O_3$-BAC for removing organic pollutants in the secondary effluent.

2. Materials and methods

2.1. Catalysts preparation

The active component of the photocatalysts, namely titanium dioxide, is prepared by a sol–gel method. The procedure was as follows: tetrabutyl titanate, acetyl acetone (inhibitor) and water were added to *n*-propyl alcohol (solvent) orderly to obtain a sol. Carbon black (CB) (Printex L6, made in Degussa, particle diameter: 18 nm) was then added to the sol to increase porosity and the fraction of rutile which can improve the activities of the catalysts [10]. The components of the TiO_2 sol are shown in Table 1. The mixed sol was sonicated for few minutes. The aluminum sheet (720 mm × 185 mm × 0.18 mm) was then submerged in the mixed sol for several minutes before being withdrawn at a constant rate of 2 mm/s. It was dried at room temperature and sintered at 300 °C for 30 min. The coating procedure was repeated several times and the last film coat was sintered at 450 °C for 2 h to obtain CB modified TiO_2 thin films (CB-TiO_2). The photocatalytic activity of the CB-TiO_2 was reported in early literature [10,11].

Table 1
Proportions of the mixed sol

Component	Proportion
Carbon black (mg)	23.5
n-Propyl alcohol (mL)	70
Tetrabutyl titanate (mL)	10
Acetyl acetone (mL)	3.0
Water (mL)	4.0

2.2. Experimental set-up

Fig. 1 shows the experimental schematic diagram that consists of an oxidation contact column, a retention column and
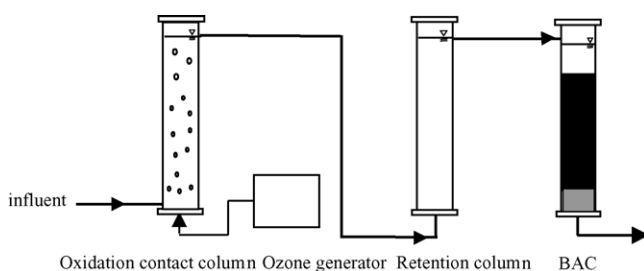

Fig. 1. Schematic diagram of pilot plant.

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. The oxidation reactor is a borosilicate glass column. For $TiO_2/UV/O_3$ process, it consists of the CB-TiO_2 thin films supported on cylindrical Al sheet which is against the interior glass surface, a coaxial UV source (a 15 W low-pressure UV lamp with a characteristic wavelength of 254 nm) surrounded by quartz thimble ($\phi_{out} = 30$ mm). For UV/O_3 process, a coaxial UV source is same as that in the $TiO_2/UV/O_3$-BAC process. There were two sets of parallel experimental set-ups for O_3-BAC, UV/O_3-BAC and $TiO_2/UV/O_3$-BAC.

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 22 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 plate. Ozone was produced from pure oxygen using a DHX-SS-001 ozone generator (Harbin Jiujiu Electric Chemical Engineering Ltd.).

2.3. Analytical methods

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 [12]. BDOC was determined following the procedure by Servais et al. [13]. Ultrafiltration (UF) membrane was employed to determine the change of molecular weight (MW). Molecular weight 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 (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, and the injector and mass spectrometer were held at 280 and 280 °C, respectively. The electron impact energy was set at 70 eV.

2.4. Water quality of secondary effluent after sand filter

The experiment for advanced purification of secondary effluents was carried out at a municipal sewage treatment plant in Beijing city, China. The secondary effluents were pretreated by the sand filtration for suspended solids removal. As shown in Table 2, dissolved organic carbon (DOC) ranged greatly from 7.8 to 14.5 mg/L during experiments,

Table 2
Water quality of secondary effluent after sand filtration

Parameters	Range
UV_{2540} (cm^{-1})	14.6–18.9
Turbidity (NTU)	0.68–1.69
DOC (mg/L)	7.8–14.5
BDOC/DOC	0.21–0.28
NH_4^+–N (mg/L)	14–30
pH	7–7.5

biodegradable organic carbon (BDOC)/DOC was in the range of 0.21–0.28 and pH kept stable at 7–7.5.

3. Results and discussion

3.1. DOC removal comparison of secondary effluent by two BAC parallel filters

Before the run of O_3-BAC, UV/O_3-BAC and TiO_2/UV/O_3-BAC, DOC removal comparison of secondary effluent by two parallel BAC filters alone was conducted. The BAC matured and the treatment efficiency for secondary effluent kept stable after 6 months operation. As shown in Fig. 2, the two parallel BAC filters almost had the same DOC removal efficiency after stable, ranging from 12 to 17% with average of about 14%. The results conformed to the low ratio of BDOC in the secondary effluent shown in Table 1. Because the DOC removal efficiency of two parallel BAC filters was very close, BAC filter itself would not be a factor resulting in different DOC removal among O_3-BAC, UV/O_3-BAC and TiO_2/UV/O_3-BAC.

3.2. The effect of operation parameters on the performance of TiO_2/UV/O_3-BAC

In TiO_2/UV/O_3-BAC process, the ozone dosage and retention time in BAC unit were two key operation parameters. Considering DOC level of the secondary effluent and the treatment cost, three ozone dosages (3–9 mg/L) were tested. TiO_2/UV/O_3-BAC process was firstly run at the ozone dosage
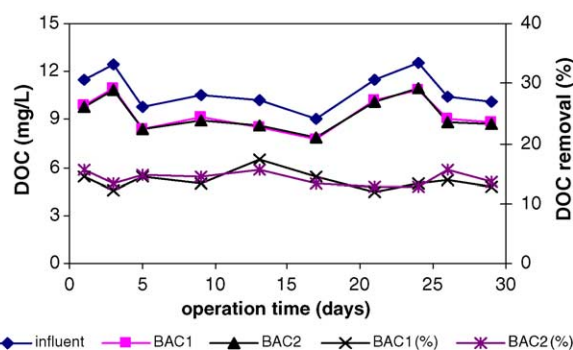

Fig. 2. Comparison of DOC removal by two parallel BAC filters (BAC1-BAC in UV/O_3 or TiO_2/UV/O_3-BAC, BAC2-BAC in O_3-BAC).

of 3 mg/L for about 2 months. And then ozone dosage increased to 6 and 9 mg/L step by step. As shown in Fig. 3, DOC removal efficiency increased with ozone dosage in both TiO_2/UV/O_3 unit and the TiO_2/UV/O_3-BAC process. The total DOC removal efficiency increased from about 52 to 59% in the process when ozone dosage increased from 3 to 9 mg/L. However, DOC removed per unit ozone consumption decreased with ozone dosage. It was 2.11 mg DOC/mg O_3 at 3 mg/L ozone dosage, while it decreased to 0.95 mg DOC/mg O_3 when ozone dosage increased to 9 mg/L. At three ozone dosages (3–9 mg/L), the amount of ozone consumption is 2.38, 4.39 and 6.01 mg/L, respectively. And it indicated that low ozone dosage was much more economically efficient.

Three EBCTs in BAC unit, i.e. 15, 30 and 60 min were investigated while the ozone dosage was kept 3 mg/L. Fig. 4(a) shows that DOC removal efficiency significantly increased with EBCT, they were 52, 59 and 63%, respectively. It reached 63% when EBCT was 60 min, more than 59% at 9 mg/L ozone dosage with 15 min oxidation time and 15 min EBCT in BAC unit shown in Fig. 3. The increase of DOC removal was mostly contributed by the BAC unit, which could be evidently seen in Fig. 4(b). Also it could be seen in Fig. 4(b) that more than 90% of BDOC in the influent of BAC unit was removed when EBCT was 60 min, while it was about 64% as EBCT was 15 min. It indicated that 15 min EBCT was necessary and enough to obtain relatively higher DOC removal efficiency and much more economical.
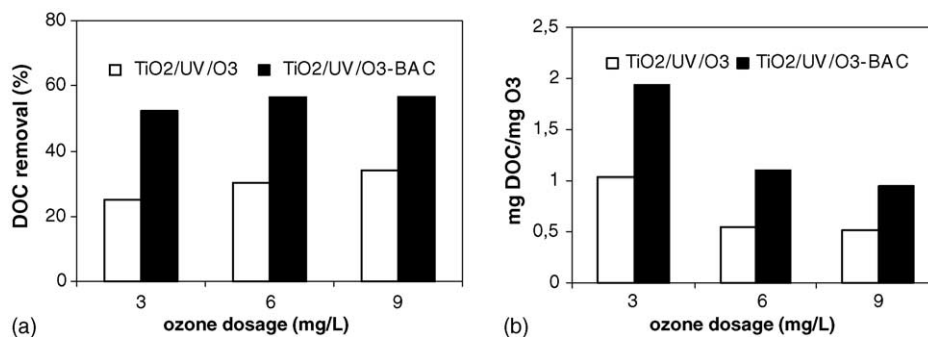

Fig. 3. DOC removal efficiency (a) and DOC removed per unit ozone (b) depending on ozone dosage.
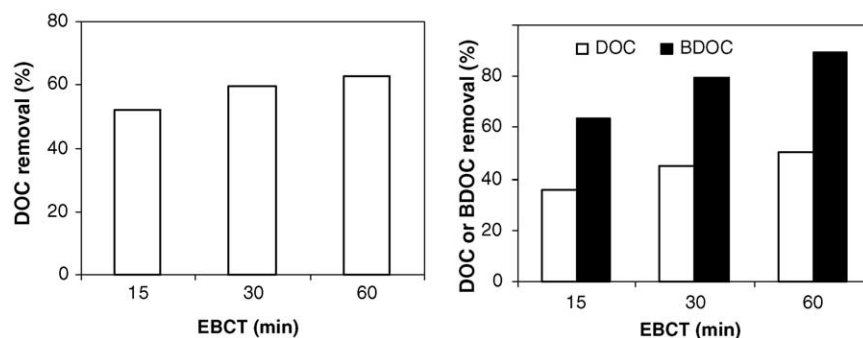
Fig. 4. DOC removal efficiency depending on EBCT in BAC unit (a) by the process, (b) by BAC unit.

3.3. Comparison among $TiO_2/UV/O_3$-BAC, UV/O_3-BAC and O_3-BAC processes at different ozone dosages

Fig. 5 compares DOC removal efficiency by O_3-BAC, UV/O_3-BAC and $TiO_2/UV/O_3$-BAC process at three ozone dosages (3–9 mg/L). It was clearly seen that $TiO_2/UV/O_3$-
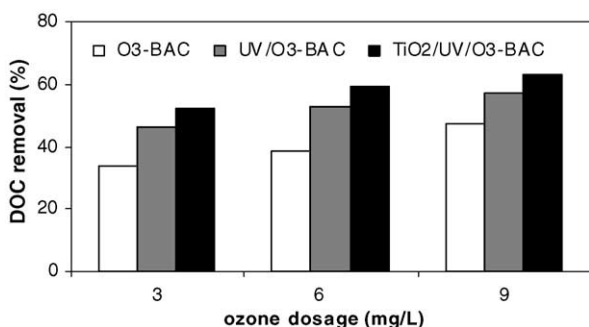

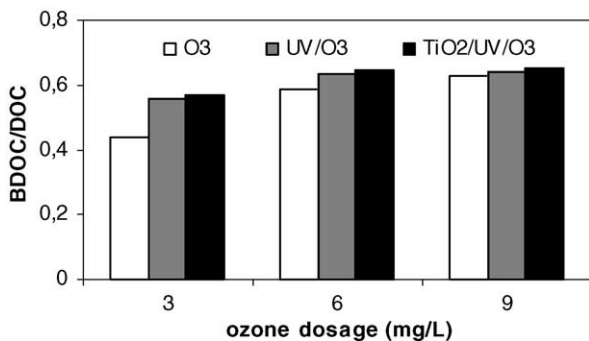Fig. 5. DOC removal efficiency by three processes under three ozone dosages.

Fig. 6. BDOC/DOC of O_3, UV/O_3 and $TiO_2/UV/O_3$ effluents depending on ozone dosage.

Table 3
DOC removal efficiency of three processes at 3 mg/L ozone dosage

Processes	BAC alone (%)	Oxidation alone (%)	Process (%)	Δ (%)
$TiO_2/UV/O_3$-BAC	14	25	52	13
UV/O_3-BAC	14	20	46	12
O_3-BAC	14	12	34	8

Δ: Process − BAC alone − oxidation alone.

BAC process was most efficient and UV/O_3-BAC process was more efficient than O_3-BAC in each ozone dosage investigated. DOC removal efficiency of three processes at 3 mg/L ozone dosage are listed in Table 3. The results showed, the synergetic effect in $TiO_2/UV/O_3$-BAC process was maximal, while UV/O_3-BAC process was more than that in O_3-BAC process.

UV/O_3-BAC process led to a higher reduction of DOC than O_3-BAC process did. In the presence of UV, the higher ozone utilization was obtained in the ozone contact column. At 3 mg/L ozone dosage, 75% of added ozone was consumed in the presence of UV, while it was only 58% without UV. DOC removed per unit ozone consumed (mg DOC/mg O_3) was also higher than in the presence of ozone. It was 0.95 and 0.74 mg DOC/mg O_3 in the presence and absence of UV. The presence of UV could transform ozone into secondary radicals such as hydroxyl radical to initiate a radical-type chain reaction in the aqueous phase, so that the reaction of organic matters with ozone was accelerated [14]. Besides the higher DOC removal in ozonation unit due to higher ozone utilization, the biodegradability of UV/O_3 effluent was also some higher than that of O_3 process as shown in Fig. 6. After ozonation either by O_3 or UV/O_3, the ratio of BDOC/DOC significantly increased. And it increased with ozone dosage in both UV/O_3 and O_3 process, though it increased slowly when ozone dosage was larger than 6 mg/L. At each ozone dosage, BDOC/DOC of UV/O_3 effluent was always higher
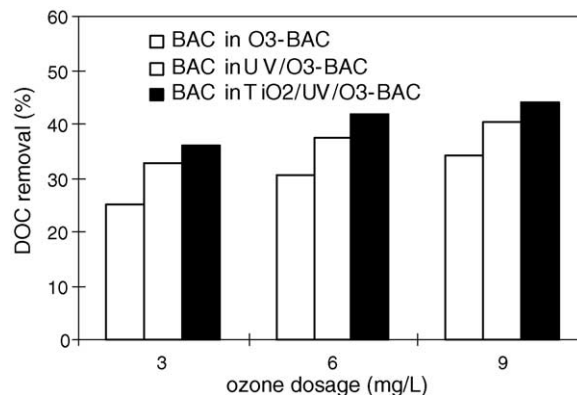

Fig. 7. DOC removed by BAC in three processes depending ozone dosage.

than that of O_3, which accordingly resulted in higher DOC removal by BAC in UV/O_3-BAC process than that by BAC in O_3-BAC process as shown in Fig. 7.

TiO$_2$/UV/O$_3$-BAC process led to a higher reduction of DOC than UV/O$_3$-BAC process did. In the presence of TiO$_2$ thin film catalyst, the higher ozone utilization was obtained in the ozone contact column. At 3 mg/L ozone dosage, 79% of added ozone was consumed in the presence of TiO$_2$ thin film catalyst, while it was only 75% without TiO$_2$ thin film catalyst. DOC removed per unit ozone consumed was also higher than in the presence of UV/O$_3$. It was 1.12 and 0.95 mg DOC/mg O$_3$ in the presence and absence of TiO$_2$ thin film catalyst. When semiconductor is in contact with water, the surface of TiO$_2$ is readily hydroxylated. Under near-UV illumination, electron-hole pairs are formed in the semiconductor, the oxidation potential of hydroxylated TiO$_2$ must lie above the position of the semiconductor valence band, the oxidation of surface-bound OH$^-$ and H$_2$O by TiO$_2$ valence band holes to form $^\bullet$OH is thermodynamically possible and

expected [15]. Besides the higher DOC removal in oxidation unit due to higher ozone utilization, the biodegradability of TiO$_2$/UV/O$_3$ effluent was also some higher than that of UV/O$_3$ process as shown in Fig. 6, which resulted in higher DOC removal by BAC in TiO$_2$/UV/O$_3$-BAC process than that by BAC in UV/O$_3$-BAC process as shown in Fig. 7.

3.4. The effect of O_3, UV/O_3 and TiO$_2$/UV/O_3 processes on molecular weight distribution

As well known ozone generally reacts with macromolecules quickly and would decompose them into low molecules. The MW distribution of raw water and oxidized water with addition of 3 mg/L ozone is presented in Table 4. It was showed that small molecules with MW < 1000 Da predominated in the raw water and oxidized water, accounting for more than 50% DOC. It was interesting that only the fraction with molecule weight of 1000–3000 Da increased after ozonation either by O$_3$, UV/O$_3$ or TiO$_2$/UV/O$_3$. Of course,
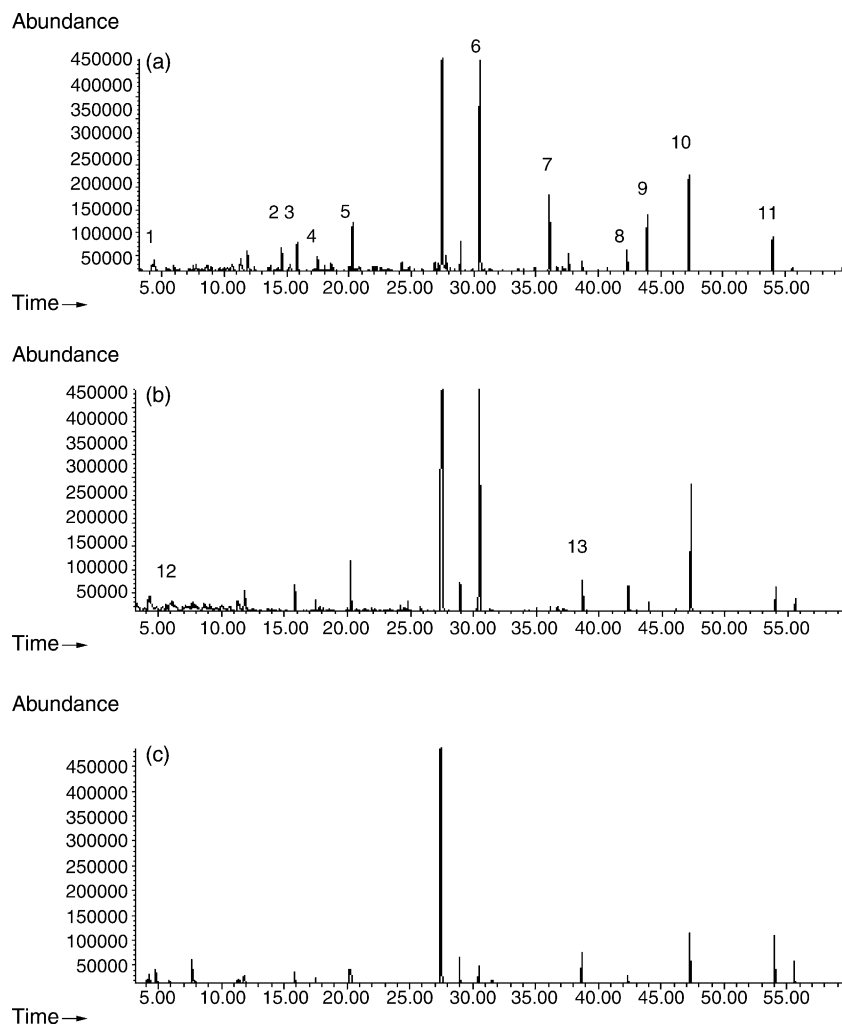

Fig. 8. Total ion GC–MS chromatogram of (a) secondary effluent, (b) TiO$_2$/UV/O$_3$ effluent and (c) TiO$_2$/UV/O$_3$-BAC effluent. (1) phenol, (2) dimethyl phthalate, (3) butylated hydroxyanisole, (4) 2,6-bis(1,1-dimethylethyl)-phenol, (5) tributyl phosphate, (6) dibutyl phthalate, (7) 4-bromo-3-chloroaniline, (8) 9-octadecenamide, (9) 2-propanone-ethylhydrazone, (10) bis(2-ethylhexyl)phthalate, (11) squalene, (12) 1,3-cyclohexanediamine, (13) *tert*-butyldimethylsilanol.

Table 4
MW characteristics of untreated and oxidized water

MW range	DOC concentration (mg/L)					DOC weight ratio (%)		
	Influent	$TiO_2/UV/O_3$	UV/O_3	O_3	Influent	$TiO_2/UV/O_3$	UV/O_3	O_3
<1,000	5.536	4.416	4.57	4.775	54	53	53	52
1,000–3,000	1.62	2.138	2.272	2.500	16	25	26	27
3,000–10,000	1.646	0.939	0.957	1.144	16	11	11	12
>10,000	1.498	0.901	0.904	0.842	14	11	10	9

the accumulation of this fraction was the results of decomposition of fractions with higher molecule weight and further decomposition got slow by oxidation process. $TiO_2/UV/O_3$ was most efficient in removing molecules with MW smaller than 10,000 Da; O_3 alone was most efficient in removing molecules with MW more than 10,000 Da. Though ozone in the water also reacted quickly with large molecules as in O_3 process, the addition of UV decreased the ozone amount for directly reacting with large molecules. As a result, less amount of large molecules like MW > 10,000 Da was decomposed by UV/O_3 and $TiO_2/UV/O_3$.

3.5. GC–MS analysis of $TiO_2/UV/O_3$-BAC process

Endocrine disruptors like estrogen, phthalate esters, nonylphenol, etc. were often identified in the secondary effluent of municipal sewage treatment plant [16–18], which brought up potential risks to the ecosystem and humans. In this study, phthalate esters and other chemicals in water were analyzed by GC–MS before and after $TiO_2/UV/O_3$-BAC treatment, the results in the previous optimal experimental conditions (3 mg/L ozone dose with 15 min oxidation, 15 min EBCT in BAC unit) are shown in Fig. 8(a–c). Fig. 8(a) shows that dibutyl phthalate, bis(2-ethylhexyl) phthalate, 4-bromo-3-chloroaniline, 2-propanone-ethylhydrazone and phenol derivatives are prevalent organic compounds found in the secondary effluent. Besides, 2,4-dichloro-benzenamine, 3,5-dimethoxyacetophenone, diethyl phthalate and butylated hydroxytoluene were also found. Fig. 8 (b) shows that some aromatic compounds including 3,5-dimethoxy-acetophenone, 4-bromo-3-chloroaniline and 2,4-dichloro-benzenamine disappeared after $TiO_2/UV/O_3$ treatment. However, phenol is not reduced by $TiO_2/UV/O_3$ process, conversely increased by 18%. During the photocatalytic degradation of halogenated aromatic hydrocarbon, phenol derivatives, •OH attacks, for example, C–Cl, C–Br, etc., and resulted

Table 5
Removal of phthalate esters and halogenated hydrocarbons by $TiO_2/UV/O_3$-BAC process

Organic pollutants	Influent (μg/L)	Effluent (μg/L)	Removal (%)
Diethyl phthalate	2.8	Not detected	100
Dibutyl phthalate	54.3	2.9	95
Bis(2-ethylhexyl) phthalate	13.5	2.4	82
2,4-Dichloro-benzenamine	2.3	Not detected	100
4-Bromo-3-chloroaniline	9.7	Not detected	100

Table 6
Removal of micro-pollutants by $TiO_2/UV/O_3$-BAC process

Organic pollutants	Removal (%)	
	$TiO_2/UV/O_3$	$TiO_2/UV/O_3$-BAC
Phenol	−18	82
1,3-Cyclohexanediamine	Oxidation product	95
^{1}H-Pyrrole-2,5-dione	100	100
1,3,5,7-Cyclooctatetraene	100	100
2,2,4-Trimethyl-3-pentanoic acid	25	100
2-Methyl-2-ethyl propanoic acid	21	90
2,4-Dichloro-benzenamine	100	100
Butylated hydroxyanisole	100	100
3,5-Dimethoxy-acetophenone	100	100
Butylated hydroxytoluene	44	95
2,6-Bis(1,1-dimethylethyl) phenol	70	100
Diethyl phthalate	40	100
Tributyl phosphate	22	92
Dibutyl phthalate	28	95
4-Bromo-3-chloroaniline	100	100
7,8-Dimethyl-Benz[c]acridine	100	100
3-Thiophenecarboxylic acid	100	100
tert-Butyldimethylsilanol	Oxidation product	100
9-Octadecenamide	−9	69
2-Propanone-ethylhydrazone	92	100
bis(2-Ethylhexyl) phthalate	32	82
Squalene	52	−11

in the formation of the phenol and corresponding phenol [19,20]. In addition, some small molecules were generated, for example, 1,3-cyclohexanediamine, 9-octadecenamide, *tert*-butyldimethylsilanol and phenol, which are easily biodegradable. After further biological treatment by BAC, the kinds and concentration of organic compounds were greatly reduced except for the increase of squalene, which might be a component of cells that released during cell lysis, diffuse through the cell membrane, or excreted for some purpose. The removal of phthalate esters, halogenated aromatic hydrocarbons and other micro-pollutants is listed in Tables 5 and 6, which showed that $TiO_2/UV/O_3$-BAC process was very effective to degrade phthalate esters, halogenated aromatic hydrocarbons and other pollutants.

4. Conclusions

Three combination processes that integrated AOPs with BAC were investigated to treat the secondary effluents.

TiO$_2$/UV/O$_3$-BAC process was the most efficient for DOC reduction compared with UV/O$_3$-BAC and O$_3$-BAC, and its DOC removal rate reached 52% when the ozone dosage was 3 mg/L and EBCT in BAC unit was 15 min. Though the biodegradability of the secondary effluent was greatly improved by all three oxidation processes and increased with ozone dosage, it was most improved by TiO$_2$/UV/O$_3$. As a result, the synergetic effect between oxidation process and biological treatment occurred most significantly in the TiO$_2$/UV/O$_3$-BAC process. A series of ultrafiltration membranes were used to determine the influence of oxidation on the molecular weight (MW) distribution of organic pollutants in the secondary effluent. It was showed that organic matters with MW < 10,000 Da were most removed by TiO$_2$/UV/O$_3$ and those with MW > 10,000 Da were most removed by O$_3$ alone. GC–MS analysis showed that dibutyl phthalate, bis(2-ethylhexyl) phthalate, 4-bromo-3-chloroaniline and phenol derivatives were prevalent organic pollutants found in the secondary effluent. After TiO$_2$/UV/O$_3$ treatment, some aromatic compounds including 4-bromo-3-chloroaniline, 2,4-dichloro-benzenamine and 3,5-dimethoxy-acetophenone disappeared and some small molecules, for example, 1,3-cyclohexanediamine, 9-octadecenamide, *tert*-butyldimethylsilanol and phenol which are easily biodegradable, were formed, but the kinds and concentration of organic matters including phthalate esters were greatly reduced by the subsequent BAC unit.

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