

TiO₂/UV/O₃-BAC processes for removing refractory and hazardous pollutants in raw water

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Abstract

TiO₂/UV/O₃-BAC (biological activated carbon) process was employed to treat raw water and compared to UV/O₃-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 TiO₂ improved ozone utilization and biodegradability of the effluent. For the dissolved organic carbon (DOC) removal, TiO₂/UV/O₃-BAC was more efficient than UV/O₃-BAC and its synergetic effect is more than that in UV/O₃-BAC process. It was showed that small molecules with MW < 3000 Da predominated in the raw water accounting for more than 56% DOC, they were increased after oxidation, accounting for more than 64% DOC. GC/MS analysis showed that TiO₂/UV/O₃-BAC process was effective in removing phthalate esters (PAEs) and persistent organic pollutants (POPs). PAEs' removal ratio reached more than 94% and reduced with the increase of the length of the alkyl side chains and the alkyl branch chains. TiO₂/UV/O₃-BAC process was also very effective in removing POPs. Polybromobiphenyls' removal rate reached more than 89% and decreased with the increase of substitutional bromines except for 2,2',5,5'-tetrabromobiphenyl, which can be completely removed.
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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. On the other hand, photocatalytic oxidation has been 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].

Photocatalytic oxidation may be a promising method for reducing or mineralizing organic pollutants in water, but complete mineralization of refractory organic pollutants in water 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, combination of ozone with ultraviolet in the presence of titanium dioxide (TiO₂/UV/O₃) followed by BAC process (hereafter referred as TiO₂/UV/O₃-BAC) has never been reported.

The purpose of this research was to evaluate the effectiveness of TiO₂/UV/O₃-BAC process for removing organic pollutants in raw water, especially phthalate esters (PAEs) and persistent organic pollutants (POPs).

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 TiO₂ sol are shown

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Table 1
Proportions of the mixed sol

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

in Table 1. The mixed sol was sonicated for a 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 TiO₂ thin films (CB-TiO₂). Photocatalytic activity of CB-TiO₂ was reported in early literature [10,11].

2.2. Experimental set-up

Fig. 1 shows the experimental schematic diagram that consists of an oxidation 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. The oxidation reactor is a borosilicate glass column. For TiO₂/UV/O₃ process, it consists of the CB-TiO₂ thin films supported on cylindrical Al sheet (the 720 mm × 185 mm × 0.18 mm aluminum sheet was made a cylinder) 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 ($\Phi_{\text{out}} = 30$ mm). For UV/O₃ process, a coaxial UV source is same as that in the TiO₂/UV/O₃-BAC process. There were two sets of parallel experimental set-ups for O₃-BAC, UV/O₃-BAC and TiO₂/UV/O₃-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

Dissolved organic carbon (DOC) was analyzed with a TOC analyzer (SHIMADZU TOC-5000). UV₂₅₄ 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]. Biodegradable dissolved organic carbon (BDOC) was determined following the procedure by Servais et al. [13]. 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 (UF) 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, 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 raw water

The experiment for advanced purification of raw water was carried out in Miyun Reservoir of Beijing City. Water quality is shown in Table 2.

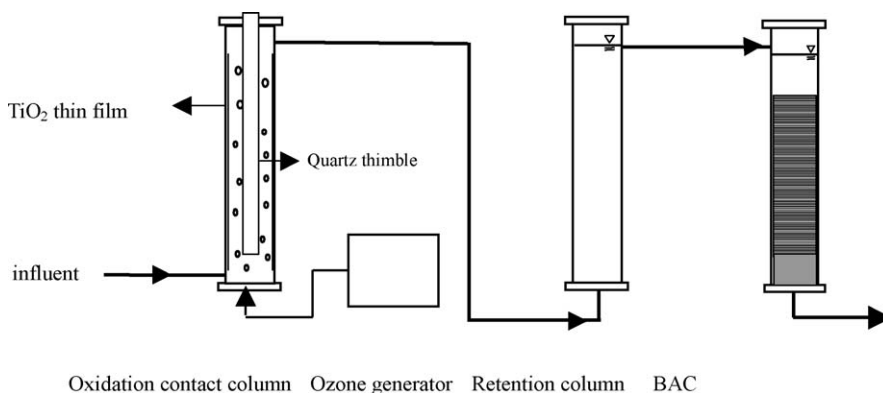


Fig. 1. Schematic diagram of pilot plant.

Table 2
Water quality of raw water

Parameters	Range
UV ₂₅₄	4.9–7.4 m ⁻¹
Turbidity	0.65–0.97 NTU
DOC	4.94–7.27 mg/L
BDOC/DOC	0.17–0.19
NH ₄ ⁺ –N	<0.5 mg/L

3. Results and discussion

3.1. The optimum parameters in TiO₂/UV/O₃-BAC processes

In TiO₂/UV/O₃-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 TiO₂/UV/O₃ unit and the TiO₂/UV/O₃-BAC process. However, DOC removed per unit ozone consumption decreased with the increase of 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 was necessary and enough to obtain relatively higher BDOC removal efficiency in the subsequent BAC and much more economical.

3.2. Comparison between TiO₂/UV/O₃-BAC and UV/O₃-BAC processes

Before the run of TiO₂/UV/O₃-BAC and UV/O₃-BAC, DOC removal comparison by two BAC filters alone was conducted. The BAC matured and the treatment efficiency kept stable after 6 months operation. Their DOC average removal was about 11.6%. After the treatment efficiency of two processes reached the steady state, DOC removal comparison by two processes was listed in Fig. 2. It was clearly seen that TiO₂/UV/O₃-BAC process was more efficient than UV/O₃-BAC process.

The DOC removal efficiency in two processes was listed in Table 3. The results showed the synergetic effect in TiO₂/UV/O₃-BAC process was more than that in UV/O₃-BAC process.

TiO₂/UV/O₃-BAC process led to a higher reduction of DOC than UV/O₃-BAC process did. In the presence of TiO₂ thin film

Table 3
DOC removal efficiency of two processes

Processes	BAC alone (%)	Oxidation alone (%)	The whole process (%)	Δ (%)
TiO ₂ /UV/O ₃ -BAC	11.6	16.7	46.5	18.2
UV/O ₃ -BAC	11.6	13.4	41.6	15.6

Δ = The whole process – BAC alone – oxidation alone.

catalyst, the higher ozone utilization was obtained in the ozone contact column. At 3 mg/L ozone dosage, 61% of added ozone was averagely consumed in the presence of TiO₂ thin film catalyst, while it was only averagely 56% without TiO₂ thin film catalyst. DOC removed per unit ozone consumed was also higher than in the presence of UV/O₃. It was 0.55 and 0.48 mg DOC/mg O₃ in the presence and absence of TiO₂ thin film catalyst. When semiconductor is in contact with water, the surface of TiO₂ is readily hydroxylated. Under UV illumination, electron–hole pairs are formed in the semiconductor, the oxidation potential of hydroxylated TiO₂ must lie above the position of the semiconductor valence band, the oxidation of surface-bound OH⁻ and H₂O by TiO₂ valence band holes to form •OH is thermodynamically possible and expected [14]. Besides the higher DOC removal in oxidation unit due to higher ozone utilization, the biodegradability of TiO₂/UV/O₃ effluent (0.504) was also some higher than that of UV/O₃ process (0.472), which resulted in higher DOC removal by the subsequent BAC in TiO₂/UV/O₃-BAC process than that by subsequent BAC in UV/O₃-BAC process as shown in Table 4.

3.3. The effect of UV/O₃ and TiO₂/UV/O₃ 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 was presented in Table 5. It was showed that small molecules with MW < 3000 Da predominated in the raw water, accounting for more than 56% DOC, they were increased after oxidation, accounting for more than 64% DOC. It was interesting that only the fraction with molecule weight of 1000–3000 Da increased after oxidation either by UV/O₃ or TiO₂/UV/O₃. TiO₂/UV/O₃ was more efficient than UV/O₃ in removing every MW range.

3.4. TiO₂/UV/O₃-BAC process for removing PAEs and POPs

Phthalate esters (PAEs) are a class of chemical compounds primarily used as plasticizers and additive in special paints and

Table 4
Influent BDOC values and its removal values in subsequent BAC unit

Process	BDOC (mg/L)	BDOC removal values (mg/L)
BAC alone	1.05	0.71
UV/O ₃ -BAC	2.34	1.76
TiO ₂ /UV/O ₃ -BAC	2.46	1.90

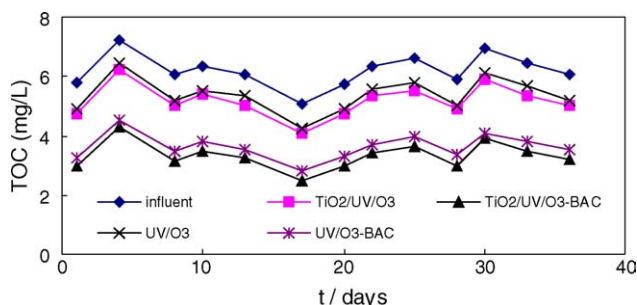


Fig. 2. comparison of the effluent DOC between two processes.

Table 5
MW characteristics of untreated and oxidized water

MW range	DOC concentration (mg/L)			Influent	DOC weight ratio (%)	
	Influent	TiO ₂ /UV/O ₃	UV/O ₃		TiO ₂ /UV/O ₃	UV/O ₃
<1000	2.649	2.200	2.314	44.2	43.7	44.2
1000–3000	0.734	1.023	1.072	12.2	20.4	20.5
3000–10000	1.084	0.914	0.946	18.1	18.2	18.1
>10000	1.526	0.890	0.902	25.5	17.7	17.2

adhesives [15]. As a consequence, they are released into the natural environment during manufacture, use, disposal and leaching from plastic materials. They are found to accumulate in the environment and to be toxic to a variety of aquatic organisms, which are at the base natural food chain in both marine and fresh environments [16]. Their toxic properties are even more important considering their high bioaccumulation rate (range from 100 to 3000) in different organisms [17]. The United States Environmental Protection Agency (USEPA) and its counterparts in several other countries have classified the most commonly occurring PAEs as priority pollutants and endocrine disrupting compounds. PAE concentrations have been reported in the range of 0.1–300 µg/l for surface marine waters and freshwater sites, and 0.1 ng/g–100 µg/g for river sediments [18,19].

Polybrominated biphenyls (PBBs) are persistent, lipophilic substances that have structural conformity similar to that of polychlorinated biphenyls (PCBs) and share many of the same biological and toxicological properties, but are even more resistant to degradation [20]. PBBs have been detected in the marine food chain in the Baltic Sea, the North Sea and in the North Atlantic Ocean [21]. PBBs have been detected in a human population in Michigan due to an accident where food products were contaminated [22]. PBBs have also been detected in two sediment samples from the River Calder and one from the River Ribble in the UK [23]. But PBBs are still manufactured for use as flame-retardants in electronic equipment, plastics, building materials, and carpets around the world. Their production scale and use are increasing, and their emission is diffuse and difficult to control [24]. For example, in the Netherlands, the annual consumption has recently been up to 250 tonnes per year [25]. Reported effects of PBBs have been cancer, neu-rotoxicity and immunotoxicity [22,25,26].

In this study, the raw water in Beijing Miyun reservoir is better, no PAEs and POPs are detected. Some PAEs and POPs were added to raw water and thoroughly mixed to known starting concentrations. The added PAEs were dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP) and di(2-ethylhexyl) phthalate (DEHP), respectively. The added POPs are hexachlorobenzene (HCB), 4-bromobiphenyl (PBB003), 2,6-dibromobiphenyl (PBB10), 2,2',6-tribromobiphenyl (PBB18), 2,2',5,5'-tetrabromobiphenyl (PBB52) and 2,2',4,5',6-penta-bromophenyl (PBB103), respectively.

PAEs in water were analyzed by GC/MS before and after treatment. The removal of PAEs was listed in Table 6, which showed that TiO₂/UV/O₃-BAC process was effective in removing PAEs. Their removal ratios are more than 94%, but removal of PAEs reduced with the increase of the length of the alkyl

Table 6
Removal of phthalate esters TiO₂/UV/O₃-BAC process

PAEs	Influent (µg/L)	Affluent (µg/L)	Removal (%)
DMP	593.2	0.027	99.99
DEP	753.9	0.039	99.99
DBP	106.8	1.49	98.6
DEHP	23.0	1.16	94.9

side chains and the alkyl branch chains. The short-chain PAEs, such as DMP and DEP, were degraded at higher rate than the long-chain PAEs, such as, DBP and DEHP. In the degradation process of PAEs, the nature of the identified by-products gives evidence for a major attack on the aliphatic chain, which is a general enough finding in the previous works [15]. The increase of the length of the alkyl side chains and the alkyl branch chains may inhibit interaction with oxidative species produced in the aqueous phase.

POPs in water were also analyzed by GC/MS before and after TiO₂/UV/O₃-BAC treatment. The removal of POPs was listed in Table 7. The results showed that TiO₂/UV/O₃-BAC process was very effective in removing POPs. PBBs' removal rate reached more than 89% and decreased with the substitutional bromines increase except for PBB52. The lower brominated congeners show greater levels of disappearance than those with more brominated did. Since PBBs have structural conformity similar to that of PCBs, hydroxylation is an important initial step in the PBB degradation pathways because lower brominated congeners may be more susceptible to advanced oxidation processes (AOPs) destruction because of the greater number of sites available for hydroxylation. Alternatively, the lower solubility of more highly brominated congeners may inhibit interaction with oxidative species produced in the aqueous phase. In either case, the negative correlation between the extent of congener disappearance and bromination may have important practical implications for PBB destruction by AOPs.

Table 7
POPs removal in TiO₂/UV/O₃-BAC process

POPs	Influent (ng/L)	Affluent (ng/L)	Removal (%)
HCB	220.9	12.4	94.4
PBB003	165.4	5.3	96.8
PBB10	90.1	5.2	94.2
PBB18	55.9	3.7	93.4
PBB52	185.7	No	100
PBB103	150.5	16.1	89.3

4. Conclusions

TiO₂/UV/O₃-BAC process was employed to treat raw water. Its optimum parameters are 3 mg/L ozone dosage with 15 min oxidation time and 15 min EBCT in BAC. The results showed that the presence of TiO₂ improved ozone utilization and biodegradability of the effluent, compared to UV/O₃-BAC process. As a result, TiO₂/UV/O₃-BAC was more efficient than UV/O₃-BAC in DOC removal and its synergetic effect between oxidation process and biological treatment occurred more significantly. A series of ultrafiltration membranes were used to determine the influence of oxidation on the molecular weight (MW) distribution of organic pollutants in the raw water. It was showed that small molecules with MW < 3000 Da predominated in the raw water accounting for more than 56% DOC, it was increased after oxidation, accounting for more than 64% DOC. TiO₂/UV/O₃ was more efficient than UV/O₃ in removing DOC with any MW range.

GC/MS analysis showed that TiO₂/UV/O₃-BAC process was effective in removing PAEs and POPs. PAEs' removal ratio reached more than 94% and reduced with the increase of the length of the alkyl side chains and the alkyl branch chains. POPs-polybromobiphenyls' removal rate reached more than 89% and decreased with the substitutional bromines increase except for 2,2',5,5'-tetrabromobiphenyl, which can be completely removed.

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