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Study on full-scale H_2O_2/O_3–UBAC process for removing organic matters in drinking water treatment

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ABSTRACT

Ozone–biological activated carbon process (O_3–BAC) is an advanced drinking water treatment technology that has been widely used. The combined process of O_3/H_2O_2-upflow BAC filter (UBAC)—sand filter has been adopted by a drinking water treatment plant. The paper summarizes the effect of advanced oxidation process (O_3 and O_3/H_2O_2) on the overall combined process in two seasons. The influence of different O_3/H_2O_2dosages on the effluent water quality is investigated and the effectiveness of the combined process is analyzed. The results indicate that O_3 can effectively decompose organic matters in water and increase the biodegradability of dissolved organic carbon. The organic matters removal rate of combined process increases as ozone dosage increases. Biodegradable dissolved organic carbon (BDOC) after ozonation increases by 30, 93, and 101% with increasing ozone dosages from 1.0, 1.5 to 2.0 mg/L. The removal rates of BDOC by the combined process reached 39, 45, and 73%, respectively. H_2O_2/O_3 does not give better effect than O_3 alone. Turbidity removal rate by sand filtration remains stable, which is above 87%. Higher temperature is favorable to microbial degradation by UBAC and sand filter.

Keywords: Drinking water treatment; Ozonation; O_3/H_2O_2; Advanced oxidation process; Biological activated carbon

1. Introduction

Drinking water safety has increasingly become a focus in the world. The effluent water quality with conventional water treatment process in China can no longer meet the requirements of the new Drinking Water Health Standards of China (GB5749-2006) that has been implemented since 1 July 2012. Ozone/biological activated carbon (O_3/BAC) process is one of the most effective of the advanced treatment processes for removing organic contamination from water [1–7]. However, it induces the risk of bromate formation during ozonation of water which contains the bromide [8,9]. In order to meet the new standard, the O_3/BAC process was adopted in a drinking water treatment plant in Shandong, China. Based on the characteristics of raw water from the Yellow River reservoir that contains bromide of about 100 μg/L, the advanced oxidation processes of

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O_3/H_2O_2 was used to control production of bromate with H_2O_2 as catalyst of oxidation in ozone contactor [10]. Meanwhile, the BAC filters were designed and operated in upflow mode (UBAC), expanding the activated carbon layer a little, so that the operating performances were improved in the downflow mode [11]. The integrated process of the waterworks is "Intermediate high-density sedimentation tank + O_3/H_2O_2 + UBAC filtration + Sand filtration." The influence of O_3 and H_2O_2 dosage on organic pollutants removal has been investigated through experiments during full-scale operation.

2. Methods

2.1. Process flow

This facility uses raw water from the Yellow River reservoir. The process has been put into operation since the end of August 2011. The designed processing capacity is 2,00,000 m^3/d. The ozone process contains two three-stage fine-bubble diffuser ozone contactors in parallel operation and each contactor has three chambers for contacting and reaction. The fine bubble diffusers are arranged at the bottom of the chambers to make ozone and water flow in opposite directions. H_2O_2 are added in chambers to catalyze oxidation with ozone. Designed maximum O_3 dose is 3 mg/L and retention time is about 15 min in the ozone contactor. The upflow BAC filter (UBAC) has an overall dimension of 29 m × 55 m × 8.55 m. It is separated into two parts, each part receiving water from one ozone contractor. Each part is divided into six cells with an effective area of 60.48 m^2 per cell. The active carbon filtering layer of UBAC is 3.0 m in thickness and contact time is 15 min. The backwash strength of the scour air is 15 $L/(m^2 s)$. The process flow is shown in Fig. 1.

2.2. Operating conditions

Influent water of the ozone contactor is the effluent water from intermediate high-density sedimentation tank. Tests were conducted in two seasons (November 2011 and May 2012). The water temperature in the two test periods was 7–14 and 20–22℃, respectively. The pH of influent water was 8.0–8.4. In both periods, tests were conducted under six operational conditions of three days each. The ozone dosage ratio in the three chambers of contactor along with the water flow was 3:1:1. The dosing molar ratio of H_2O_2:O_3 was 1.7:1 overall, as well as 1.1:1 in the first-stage chamber. The oxidants dosage is shown in Table 1.

2.3. Analysis item and method

Water quality analysis was referred to the Water and Wastewater Monitoring and Analysis Methods (Fourth Edition, China). Permanganate index (COD_{Mn}) is measured by potassium permanganate method; UV_{254} is measured with UV–visible spectrophotometer (TU-1810); total organic carbon (TOC) is measured with total organic carbon analyzer (TOC-V, Shimadzu); turbidity is measured with a smart scattered light turbidimeter (TSZ-400); biodegradable dissolved organic carbon (BDOC) is measured by biofilm cultivation method. TOC and UV_{254} are monitored after the water samples have been filtered with 0.45 μm microfiltration membrane. Specific ultraviolet absorption (SUVA) = $100UV_{254}/DOC$.

3. Results and discussion

3.1. Influence of oxidants dosage on organic matters removal

In accordance with the six operating conditions, the tests were carried out in November 2011 and May 2012, respectively, to investigate the influence of different O_3 and H_2O_2 dosages at different periods on organics and turbidity removal. The bromide in influent water was about 100 μg/L. The bromate concentration in effluent of the combined process was below

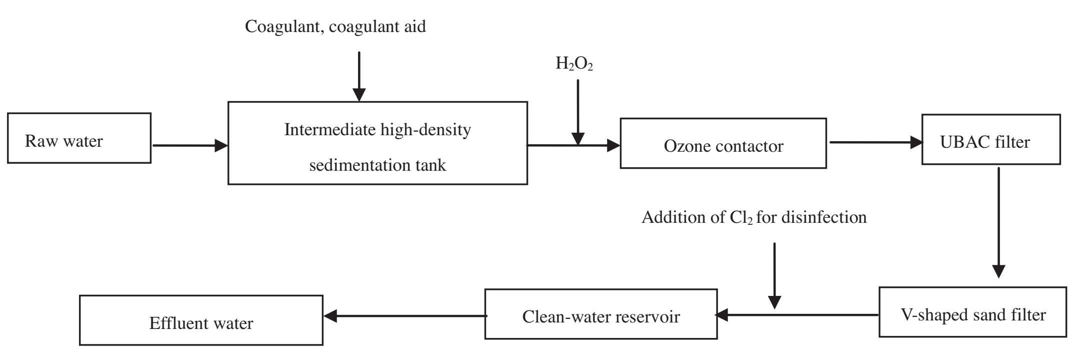

Fig. 1. Process flow of the water treatment plant.

Table 1
Parameters of the six operational conditions

	Tertiary ozone dosage ratio	Ozone dosage (mg/L)	H_2O_2 dosage (mg/L)
Condition 1	3:1:1	1.0	1.2
Condition 2	3:1:1	1.5	1.8
Condition 3	3:1:1	2.0	2.4
Condition 4	3:1:1	1.0	0
Condition 5	3:1:1	1.5	0
Condition 6	3:1:1	2.0	0

8 μg/L in the operation. The tests results are shown in Figs. 2–9. (The ozone removal rate is calculated based on the influent and the effluent of the ozone contactor. The ozone/UBAC removal rate is calculated based on the influent of ozone contactor and effluent of UBAC. The total removal rate is calculated based on the influent of ozone contactor and effluent of sand filter).

Figs. 2 and 3 show the COD_{Mn} removal effect in November and May under different operating conditions. It can be seen from the two figures that COD_{Mn} in influent water of ozone contactor is about 2.0–3.0 mg/L in November and May, and the UBAC removal rate and the total removal rate of COD_{Mn} by processes increase with increase of ozone dosage. The total removal rate does not increase significantly by adding H_2O_2. The BAC removal rate varies greatly. In November, the lowest BAC removal rate of COD_{Mn} is 27.8% and the highest is 40.5%. In May, the lowest BAC removal rate of COD_{Mn} is 19.2% and the highest is 40.6%. It is because of the unstable effluent turbidity of UBAC filter (Fig. 9). Higher temperature favors the metabolism of micro-organisms in the activated carbon filter and sand filter. In May, the biological effect of UBAC and sand filter on dissolved organic matters has become prominent, therefore, the average COD_{Mn} removal rate by UBAC unit combined with sand filter was higher than that in November. The total COD_{Mn} removal effect by the integrated process in May is better than that in November. The lowest total removal rate of COD_{Mn} is 41.6% and the highest is 50.9% in November, while the lowest total removal rate of COD_{Mn} is 52.1% and the highest is 59.1% in May.

Figs. 4 and 5 show that the TOC in influent water was between 2.0 and 2.5 mg/L in the two periods. The removal effects through ozone oxidation are not significant with or without H_2O_2. This may show that the organic compounds in water may be oxidized mainly by breaking up larger molecules, however, complete oxidation to CO_2 is uncommon under the test oxidants dosage. With the increase in ozone dosage, the TOC in effluent water of ozone contactor is higher than influent (Fig. 4). It may be because that the ozone oxidizes the insoluble organic matters into dissolved ones, resulting in increase of TOC in effluent water. As ozone dose increases, the total removal rate of TOC increases. In May, higher water temperature leads to higher microbial activity, so the total average removal rate is 39.0%, higher than that in November of 31.4%. In November, the TOC removal rates under conditions

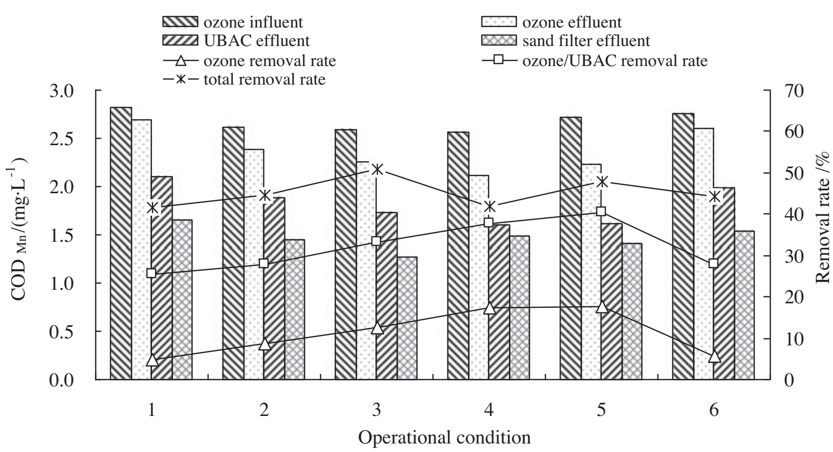

Fig. 2. Effect of operational conditions on COD_{Mn} removal in November.

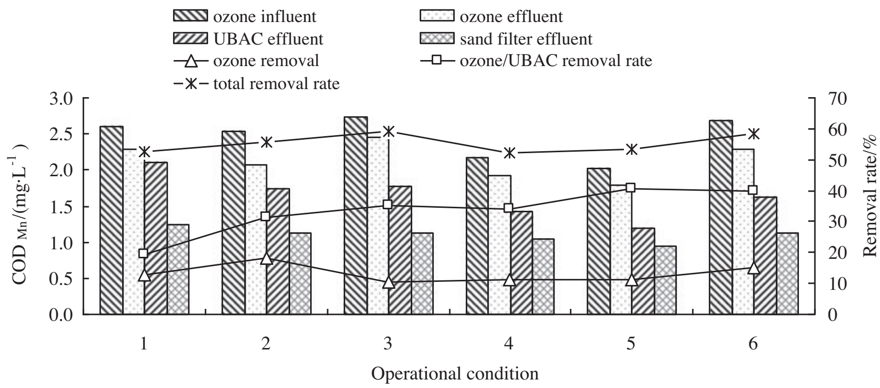

Fig. 3. Effect of operational conditions on COD_{Mn} removal in May.

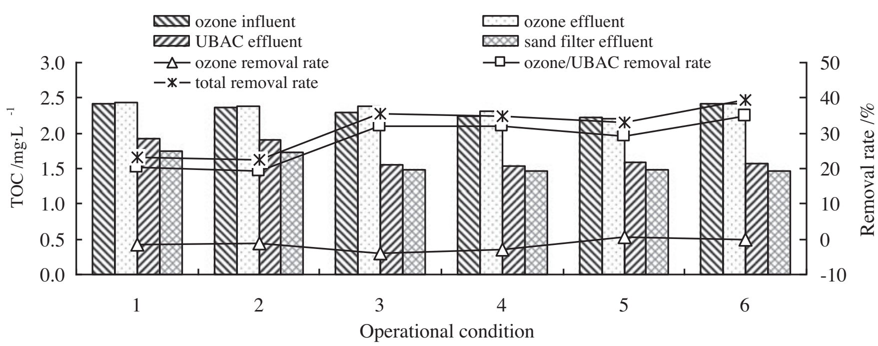

Fig. 4. Effect of operational conditions on TOC removal in November.

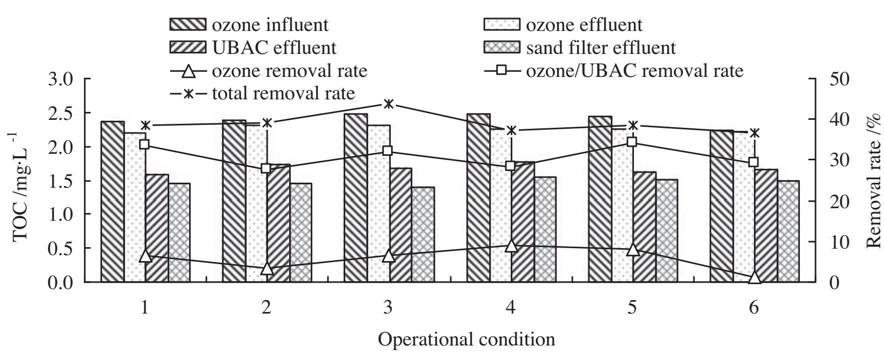

Fig. 5. Effect of operational conditions on TOC removal in May.

1 and 2 are relatively low, and it may be related to the backwashing of UBAC during which the biomass are lost. Ozonation when combines with H_2O_2 can oxidize large organic molecules into small ones, which are favorable for adsorption and degradation by biological activated carbon [12].

UV_{254} refers mainly to the aromatic compounds or unsaturated organic compounds in water [13]. From Figs. 6 and 7, it can be seen that the UV_{254} of influent water was between 0.037 and 0.046 cm^{-1}. UV_{254} removal rate by ozonation with H_2O_2 is not better than that without H_2O_2. Ozone oxidation shows significant effect on UV_{254} removal and UV_{254} in effluent water with ozone lowered significantly, which indicates that ozone can effectively oxidize organic compounds by breaking up carbon–carbon double bonds, and breaking them up into smaller molecules, which improves the absorbability and biodegradability. With the

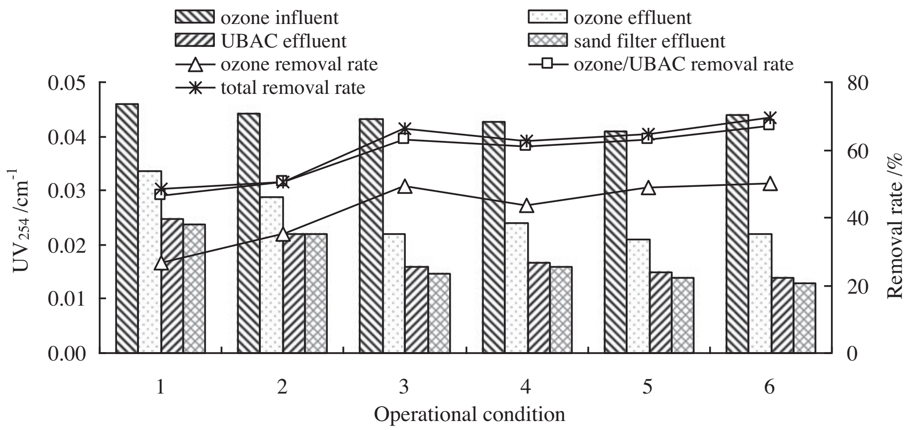

Fig. 6. Effect of operational conditions on UV_{254} removal in November.

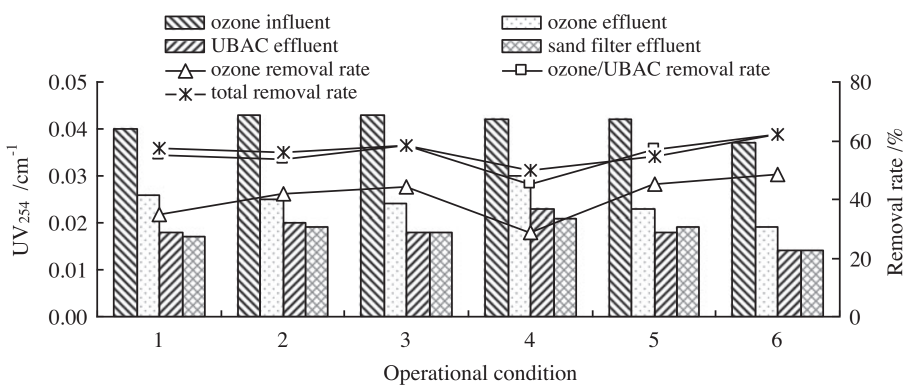

Fig. 7. Effect of operational conditions on UV_{254} removal in May.

increase of ozone dosage, the BAC removal rates and the total removal rates of UV_{254} increase and are close, indicating that UV_{254} removal effect by sand filtration is not obvious. The UV_{254} is mainly reduced by ozone and UBAC unit processes. The average UV_{254} removal rate by integrated process in November is 60.3%, slightly higher than that in May, 56.4%. This may be because UBAC had greater adsorption capacity in November, 2011 than May, 2012. UV_{254} is a substitution parameter of the precursor of chlorinated disinfection by-products (DBPs), O_3/UBAC process can effectively remove DBPs precursors.

From above, it can be seen that organic matters removal effect by the combined process with H_2O_2 is not better than that without H_2O_2. The removal rate of ozonation for COD_{Mn} and UV_{254} is significantly higher than that for TOC. SUVA is reduced significantly by ozonation, about 1.82 in ozone contactor influent and 1.0 in effluent, respectively. This shows that ozone oxidation mainly changes the molecular structure of the organic compounds by decomposing large molecules into small molecules but not mineralization [14]. It is generally known that O_3 combined with H_2O_2 can produce more hydroxyl radicals than ozone alone, however, it may not be more effective than O_3 alone under raw water condition in the test.

Water from the Yellow River reservoir is characterized by high temperature and algae in summer and low temperature and turbidity in winter. Raw water has relatively high turbidity from September to November. From Figs. 8 and 9, it can be seen that the influence of varying O_3 and H_2O_2 dosages on total removal rate of turbidity is small. The total turbidity removal rate by integrated process is high during the two test periods and is mainly contributed by sand filtration. The turbidity removal rates of ozone contactor and UBAC varies in both periods and turbidity of effluent water is sometimes even higher than influent water. This is caused by the activated carbon layer in the UBAC filter being

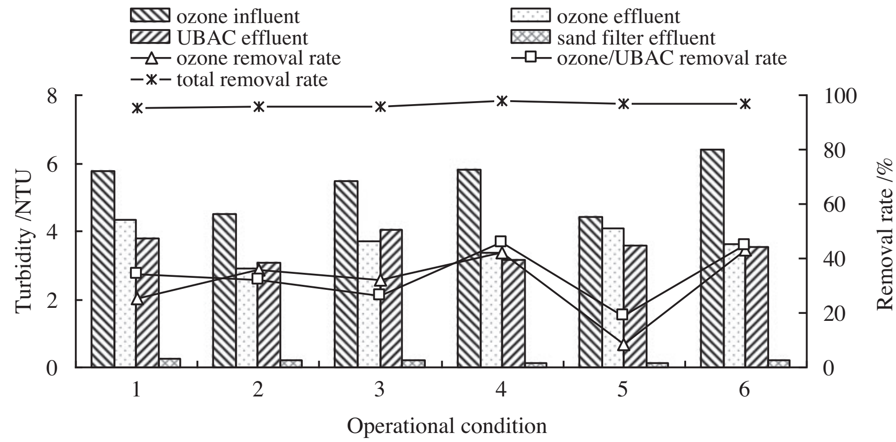

Fig. 8. Effect of operational conditions on turbidity removal in November.

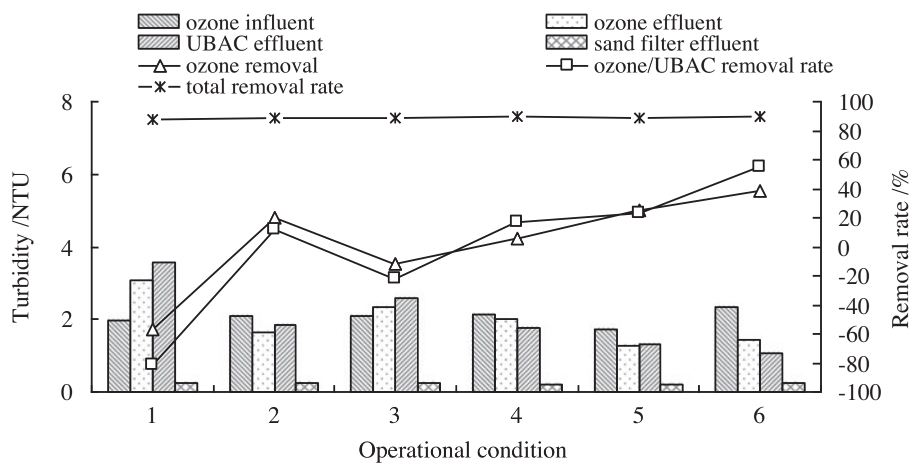

Fig. 9. Effect of operational conditions on turbidity removal in May.

expanded slightly, leading to the particles in the influent, detached biomass and micro-particles in the UBAC layer were occasionally washed out, consequently raising turbidity and COD_{Mn} of effluent water. Turbidity removal rate by sand filtration remains stable, which is above 87%. A postpositive sand filter is vital to the upflow BAC process.

3.2. Effect of O_3 dosage on BDOC

The organic removal efficiency by UBAC is directly related to the amount of BDOC in the influent water. The tests were carried out with ozone dosages of 1.0, 1.5, and 2.0 mg/L. Influence of different O_3 dosages on BDOC in the process has been investigated. The test results obtained are shown in Fig. 10 (the total removal rate is calculated based on the influent of ozone contactor and effluent of sand filter. The UBAC/sand filter removal rate is calculated based on the effluent of ozone contactor and effluent of sand filter. The ozonation increase rate is calculated based on the effluent and the influent of ozone contactor).

BDOC is defined as organic compounds that can be biodegraded to CO_2 or synthesized into cell structure by micro-organisms in water, and is the energy source for microbial growth and reproduction [15]. From Fig. 10, it can be seen that BDOC in influent water ranges from 0.32 to 0.43 mg/L and that in effluent water increases rapidly after ozone oxidization. The organic matter removal rate of combined process increases as ozone dosage increases. BDOC after ozonation increases by 30, 93, and 101% with increasing ozone dosages from 1.0 mg/L, 1.5 mg/L to 2.0 mg/L. The BDOC removal rates of UBAC combined with sand filtration increase with the increase of ozone dosages from 54, 70 to 84%. The results indicate that

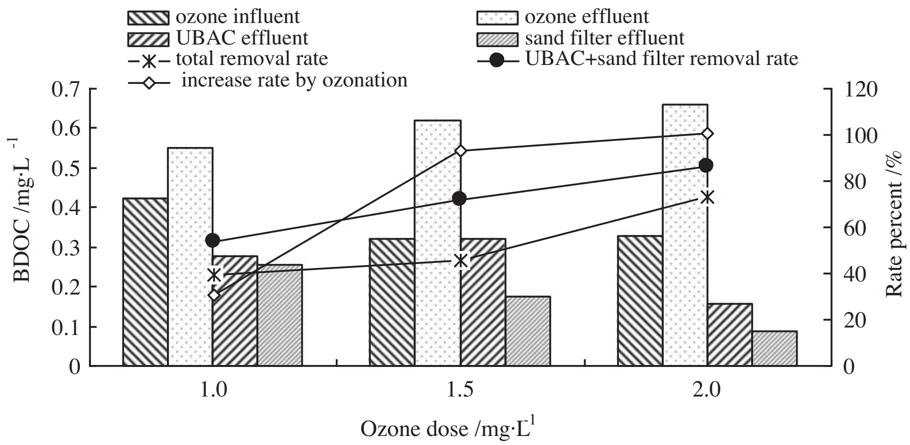

Fig. 10. Effect of different O_3 dosages on BDOC.

ozonation increase the biodegradability of the dissolved organic carbon, and the readily biodegradable portion of BDOC increases with the increase of ozone dosage. UBAC has strong biological action and adsorption effect on small organic molecules which are more absorbable and biodegradable, and hence, it reduces the BDOC greatly. During sand filtration, some of degradable organic matters can be decomposed by micro-organisms attached to sand, so BDOC can be further reduced a little. The removal rates of BDOC via the integrated process are 39, 45, and 73% with the three ozone dosages.

4. Conclusions

(1) COD_{Mn}, TOC, and UV_{254} removal rates via the combined process increases with increase of ozone dosage, but the extent of increase is small. On the whole, applying H_2O_2 does not improve removal effect.
(2) The removal effect of ozone oxidization for COD_{Mn} and UV_{254} is better than that for TOC, indicating that ozone oxidization mainly changes the structure of organic matters by decomposing large organic molecules into small molecules but not mineralization.
(3) COD_{Mn} and TOC removal rates by combined processes are higher in May than that in November. Higher temperature is favorable for biological metabolism in filter.
(4) The turbidity removal rate by UBAC filter has varied greatly while that by sand filtration remains stable above 87%. Postpositive sand filter is vital to the upflow BAC process
(5) With increasing ozone dosages from 1.0, 1.5 to 2.0 mg/L, the amount of BDOC after ozonation increased by 30, 93, and 101% and the removal rates of BDOC by the combined process reached 39, 45, and 73%, respectively. Ozone oxidization can increase BDOC greatly to improve the biodegradation performance of BAC and sand filter.

Acknowledgments

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