A study on the effects of ozone dosage on dissolved-ozone flotation (DOF) process performance

Xin Jin, Pengkang Jin and Xiaochang Wang

ABSTRACT

Dissolved-ozone flotation (DOF) is a tertiary wastewater treatment process, which combines ozonation and flotation. In this paper, a pilot-scale DOF system fed by secondary effluent from a wastewater treatment plant (WWTP) in China was used to study the effect of ozone dosage on the DOF process performance. The results show that an ozone dosage could affect the DOF performance to a large extent in terms of color and organic matter removal as well as disinfection performance. The optimal color and organic matter removal was achieved at an ozone dosage of 0.8 mg/l. For disinfection, significant improvement in performance could be achieved only when the organic matter removal was optimal. The optimal ozone dosage of at least 1.6 mg/l was put forward, in this case, in order to achieve the optimal color, turbidity, organic matter and disinfection performance.

Key words | dissolved-ozone flotation, ozonation, ozone dosage

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INTRODUCTION

Dissolved-ozone flotation (DOF) is an innovative water treatment process, which combines ozonation and flotation. Consequently, coagulation, separation, decolorization, odor removal and disinfection can occur simultaneously in a DOF reactor (Jin *et al.* 2006; Lee *et al.* 2008; Wilinski & Naumczyk 2012). Because of this, the DOF has become increasingly popular in tertiary wastewater treatment (Jin *et al.* 2006; Lee *et al.* 2007). Compared with the conventional tertiary wastewater treatment process, which comprises coagulation, sedimentation and filtration, the DOF process is superior in decolorization, and odor and organic matter removal. Furthermore, the hydraulic retention time (HRT) of the DOF process is three times shorter than the conventional tertiary wastewater treatment process, which results in much lower space requirements (Jin *et al.* 2006). Moreover, the DOF process is applied in secondary wastewater treatment (Lee *et al.* 2008), drinking water treatment (Lee *et al.* 2009a, b), industrial dyeing wastewater treatment (Kim *et al.* 2011) and livestock wastewater treatment (Lee & Song 2006).

Because of the powerful oxidation potential, ozone has been widely used in water and wastewater treatment (Graham *et al.* 2004; John *et al.* 2005). Usually, ozone is used for various purposes, such as the removal of color (Shu & Chang 2005; Selcuk 2005) and non-biodegradable materials (Saroj *et al.* 2005). The application of ozone facilitates the conventional flotation removal efficiency. Lee *et al.* (2007) reported that ozone enhanced the separation capability of the DOF system, not only by aiding the coagulation of dissolved contaminants, but also by increasing the microbubble volume of the DOF system because ozone has high water solubility. Therefore, the addition of ozone can decrease the dosage of coagulants and enhance the ability of separation. The high oxidation potential of ozone can help improve the color, odor and organic matter removal efficiency in the DOF system (Graham *et al.* 2004; Shu & Chang 2005). Additionally, ozone can serve as a disinfectant in the DOF system to secure discharge safety (Lee *et al.* 2008). Therefore, the dosage of ozone into the DOF system is essential for treatment efficiency, and the effects of different ozone dosages on the removal efficiency of the system still needs investigation. Furthermore, another issue as to whether the ozonation performance for organic matter removal will affect disinfection efficiency needs to be elucidated.

In this paper, a pilot-scale DOF system fed by secondary effluent from the Beishiqiao Wastewater Purification Centre, Xi'an, China was used to evaluate the effect of ozone dosage on the treatment efficiency. The WWTP has a capacity of 200,000 m^3/d with an anaerobic–anoxic–oxic (AAO) process. The effect of ozone dosage on the DOF system treatment efficiency was analyzed. In addition, the

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mechanisms for ozonation in the DOF system were investigated by high performance liquid chromatography (HPLC) and gas chromatography-mass spectrometer (GC-MS). The effect of the ozonation of organic matter on the disinfection performance of the DOF system was also studied.

MATERIAL AND METHODS

Experimental setup

The experimental setup for the DOF system is shown in Figure 1. The major part of the DOF separator is a closed cylindrical compartment with an inner column at the centre, thus, dividing the cylindrical space into a contact zone and a separation zone. On top of the compartment, there is an inversely placed circular cone forming a scum chamber. There are two inlets at the bottom of the separator. One serves as the entrance for the raw water, i.e., the secondary effluent, after coagulant (polyaluminium chloride; PAC) dosing and mixing through the raw water pump and online hydraulic mixer. Another serves as the entrance for the return flow mixed with dispersed ozone. The two flows are well mixed hydraulically as they enter the contact zone at the bottom. Next to the ozone dispersion pump, and following the saturator, gaseous ozone from an ozone generator is dissolved in the water (return flow from the treated water) as micro bubbles. Therefore, a contact reaction of ozone with pollutants and attachment of pollutants onto micro ozone bubbles occurs at the same time in the contact zone. In the separation zone, floating scum accumulates on the top, and treated water is collected through the perforated annular pipe at the bottom. A magnetic valve is installed on the treated water pipe, which is automatically controlled by a time controller so that it can be switched 'open' and 'closed' at pre-set time intervals. As the valve opens, treated water flows out of the DOF separator at a regular rate and the water level decreases in the separator. As the valve closes, the treated water flow is shut down, and the water level begins to rise in the DOF separator. In this way, scum accumulated on the top can be discharged. The effluent of the DOF reactor is further treated by sand filtration. Table 1 shows the standard operational condition of the DOF separator.

Table 1 | Standard operational condition for the DOF separator

Parameters	Value	Parameters	Value
Raw water flow rate	1 m^3/h	Online mixing time	30 s
Air and gaseous ozone flow rate	0.2 m^3/h (at 1 atm)	PAC dosage	80 mg/l
HRT in contact zone	2 min	HRT in the DOF separator	30 min
Stabilized air pressure	0.3 Mpa	Recycle flow rate	0.5 m^3/h
DOF separator height[a]	1.5 m	Diameter	0.65 m
Total volume approx.	0.5 m^3	Surface overflow rate	4.52 m/h

[a]Without sludge chamber.

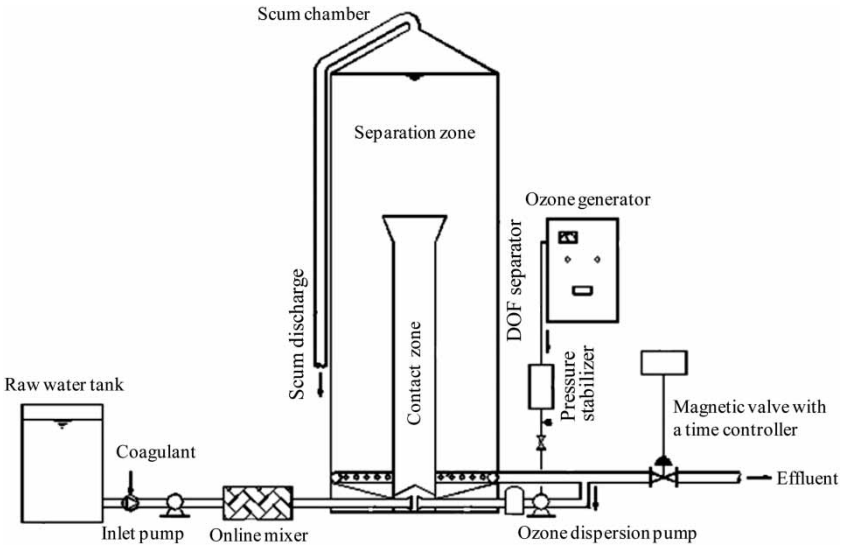

Figure 1 | Experimental setup for dissolved-ozone flotation.

Water quality analysis

Turbidity was measured by the Nephelometric method using an SZD-2 turbidimeter (Shanghai Water Construction & Engineering Co., Ltd, Shanghai, China), whereas color was measured by the platinum–cobalt method using a spectrophotometer (Hitachi 2000, Tokyo, Japan) at 420 nm. Total organic carbon (TOC) and UV_{254} were measured by the catalytic combustion method using a TOC analyzer (Shimadzu TOC-5050, Kyoto, Japan) and a Hitachi 2000 spectrophotometer at 254 nm (cell length 1 cm), respectively. Total bacteria and coliform were analyzed by membrane filter technique, and the results were recorded in terms of colony-forming units.

Molecular weight distribution analysis

HPLC analysis was conducted using an LC-2000 liquid chromatographic analyzer (Shimadzu, Kyoto, Japan) with a W520 gel column and a UV detector at 254 nm. The mobile phase was 150 mM PBS, and the velocity was 0.4 mL/min.

Organic matter structure analysis

Raw and treated water were concentrated with a non-polar column and an anionic-polar column and extracted by a polar organic solvent, methanol and a non-polar organic ethyl acetate, respectively. Extracted samples were detected by Trace2000 GC-MS (Thermo Finnigan, San Jose, CA, USA).

RESULTS AND DISCUSSION

Color removal performance

Figure 2(a) shows the decolorization performance of the DOF process at different ozone dosages. According to Figure 2(a), there was already very good color removal performance from the DOF process before filtration, which could further decrease the effluent color. The color removal efficiency increased with the increasing dosage of ozone within the ozone dosage range of 0–0.8 mg/l. When the ozone dosage was higher than 0.8 mg/l, the color removal efficiency remained constant. The total removal efficiency (after filtration) was above 80%, and it basically remained constant with the increasing ozone dosage. An effluent color of about 10 c.u. was recorded.

The color in water treatment can be divided into two parts. One is the apparent color, which is caused by suspended solids, and the other is the real color, which is caused by unsaturated carbon bonds and aromatic organic matter (Christman & Ghassemi 1966). The conventional tertiary wastewater treatment process can work for the removal of apparent color, but for real color, the removal performance is often poor. The mechanism of decolorization in the DOF process is mainly the result of ozonation, which essentially oxidizes the organic matter to achieve real color removal. In addition, the flotation in the DOF process can remove the apparent color in water. In the DOF process, the ozone gas was dissolved in the recycled treated water and induced into the DOF reactor. Therefore, the ozone can react with the organics more readily, compared with the standard ozonation process. As a result, the ozone dose was relatively small.

Turbidity removal performance

The removal of turbidity in the DOF process is shown in Figure 2(b). The secondary effluent of the wastewater treatment plant contained a certain amount of suspended solids, which caused turbidity in the water. When the inlet turbidity was below 2 NTU, the effluent turbidity of around 1.5 NTU was recorded, which was almost the same as that of the influent. The ozone dosage was increased up to 1.6 mg/l in the experiment conducted in the winter, where higher influent turbidity of around 2.5 NTU was recorded. However, the effluent turbidity of the DOF process was still around 1.5 NTU. The reason for the stable effluent turbidity was that the major part of the flocs could be removed by flotation, but flotation could not remove the very small flocs, which were responsible for the stable residual turbidity of 1.5 NTU. After filtration, the turbidity decreased to less than 1 NTU. The total turbidity removal efficiency was stable without the influence of the ozone dosage. This phenomenon is because the ozone oxidation target in the DOF process was dissolved organic matter other than suspended solids, which were in the form of flocs, in this case.

Organic matter removal performance

Figures 2(c) and 2(d) show the UV_{254} and TOC removal performance, respectively. The meaning of UV_{254} can reflect the amount of organic matter that can absorb UV light at 254 nm, such as unsaturated and aromatic organic matter. It was reported that ozone oxidation could achieve a remarkable removal performance for this part of the organic matter. Figure 2(c) shows that the UV_{254} could be removed even without the addition of ozone, and there was limited enhancement in removal after filtration in each ozone

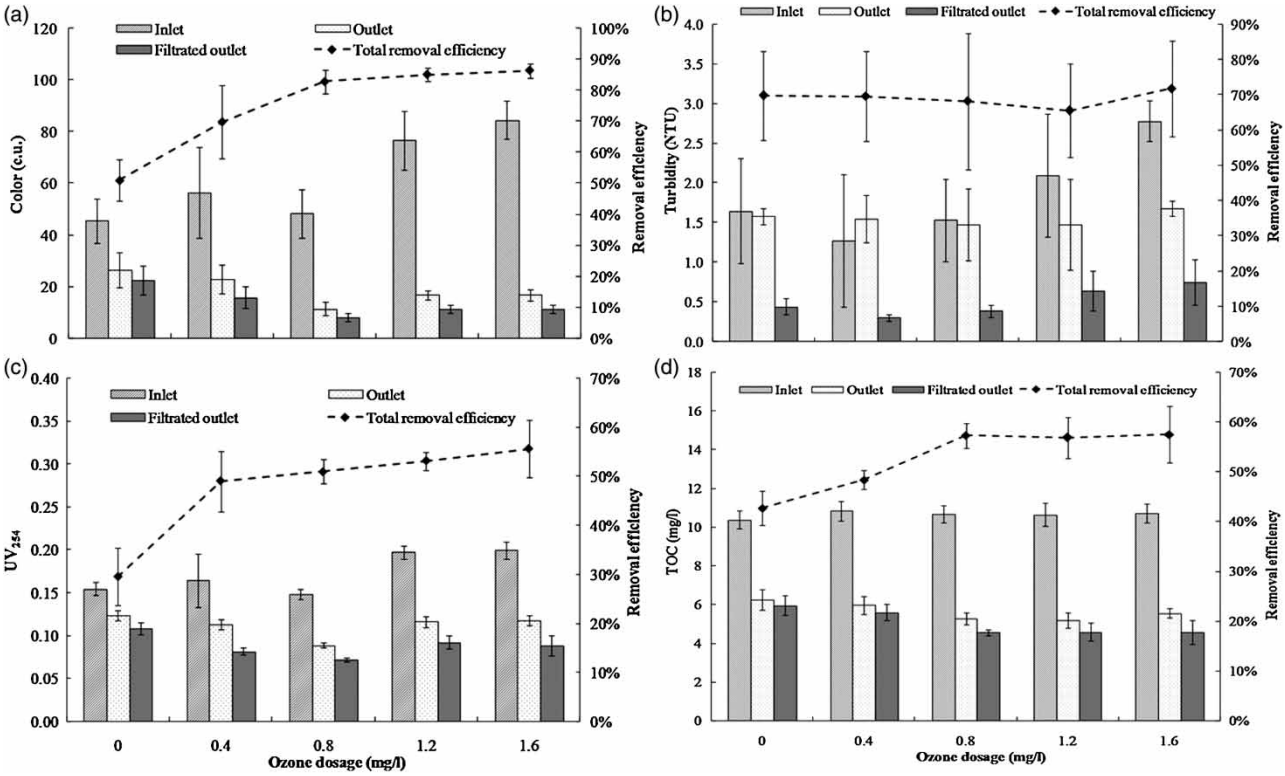

Figure 2 | (a) Color, (b) turbidity, (c) UV_{254}, and (d) TOC removal performance at different ozone dosages.

dosage. The removal efficiency was the worst when there was no ozone addition. When the ozone dosage was 0.4 mg/l, which was the lowest ozone dosage, the UV_{254} removal efficiency increased dramatically. However, the increasing of the removal efficiency was limited with the subsequent increasing ozone dosage, and the removal efficiency remained around 50–60%. It could be expected that ozonation can change the structure of the organic matter, which was mostly unsaturated or aromatic, and formed saturated, small molecular-weight organic matter.

As shown in Figure 2(d), similar to UV_{254} removal, there was TOC removal even without ozone dosage and after filtration there was limited improvement of TOC removal for all ranges of ozone dosage. When the ozone dosage was within 0–0.8 mg/l, the TOC removal efficiency increased with the increasing dosage of ozone. The TOC removal performance was not further influenced by ozone when the dosage exceeded 0.8 mg/l. The removal efficiency remained around 58% with effluent TOC of 5–6 mg/l when the ozone dosage was higher than 0.8 mg/l.

The following assumption, based on the finding above, was made: that the ozone oxidized the organic matter with a simple structure into inorganic carbon, which therefore decreased the TOC. When the ozone dosage exceeded 0.8 mg/l, the ozone reacted with the organic matter with a complex structure with the increasing dosage of ozone. However, because of the complexity of the organic matter, the ozonation could only change their structures without oxidizing them to inorganic carbon, which does not decrease the TOC. This may account for why the TOC did not change significantly when the ozone dosage was higher than 0.8 mg/l. The following organic matter molecular weight and GC/MS analysis at ozone dosage 0.8 mg/l (Figures 3 and 4) can prove this assumption.

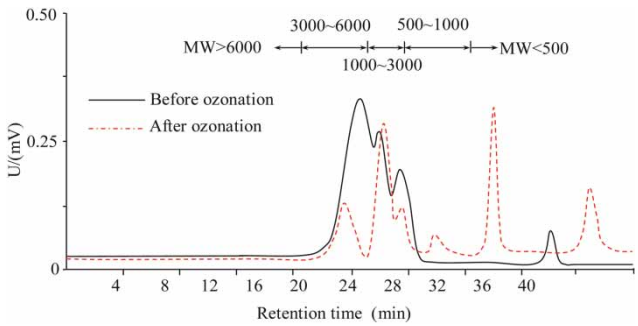

Figure 3 | Molecular weight distribution before and after ozonation.

Organic matter characteristics analysis

As shown in Figure 3, the original molecule weight was mostly distributed within 2,000–6,000 Da and after ozonation at 0.8 mg/l, the distribution mainly ranged from 2,000 to 3,000 Da. The amount of organics that had a molecule weight under 500 Da was improved dramatically. This indicated that macromolecules comprised a high proportion of the raw water, but after ozonation, the proportion of macromolecular organic matter decreased while small molecule weight organics increased, which implied that part of the intermediate material of ozonation was, namely, the increased small molecular-weight organic matter.

As for the structure of the organic matter, Figure 4 shows that, in addition to certain kinds of aliphatic acids, cyclic hydrocarbons were dominant in the raw water. After ozonation, there was an apparent decrease in the amount of cyclic hydrocarbons, while many chain hydrocarbons, aliphatic acids and some newly formed organic matter with carboxyl and hydroxyl functional groups became dominant. The increase of carboxyl and hydroxyl functional groups in the organic matter was beneficial for coagulation. The HPLC and GC-MS analysis, therefore, proved that the organic matter with high-molecular weight changed into low-molecular weight organic matter, and cyclic- or aromatic-structure organic matter transformed into organic matter with more carboxyl and hydroxyl groups.

Disinfection performance

After the tertiary wastewater treatment, the treated water can have several reuse purposes. Whatever the purpose is, the disinfection process is needed to guarantee the safety of the reclaimed water. In the DOF process, there is no need for extra disinfectant addition under certain ozone dosages because the ozone not only serves as an oxidizer but also as a disinfectant. As shown in Figure 5, a better disinfection effect was achieved with the increasing dosage of ozone in general. Figure 5 also shows that the disinfection performance of the DOF process was inadequate when the ozone dosage was less than 0.8 mg/l. At the same time, Figures 2(c) and 2(d) show that there was an increasing rate of organic matter removal at the ozone dosage of less than 0.8 mg/l. When the organic matter removal efficiency reached the highest, at 0.8 mg/l ozone dosage, there was a remarkable enhancement of the disinfection effect. This indicated that the ozone first served as an oxidizer and then as a disinfectant after the oxidation of the organic matter. In other words, it is believed that a favorable disinfection effect can be achieved only if there is adequate ozone to ensure that the optimal organic matter removal can be

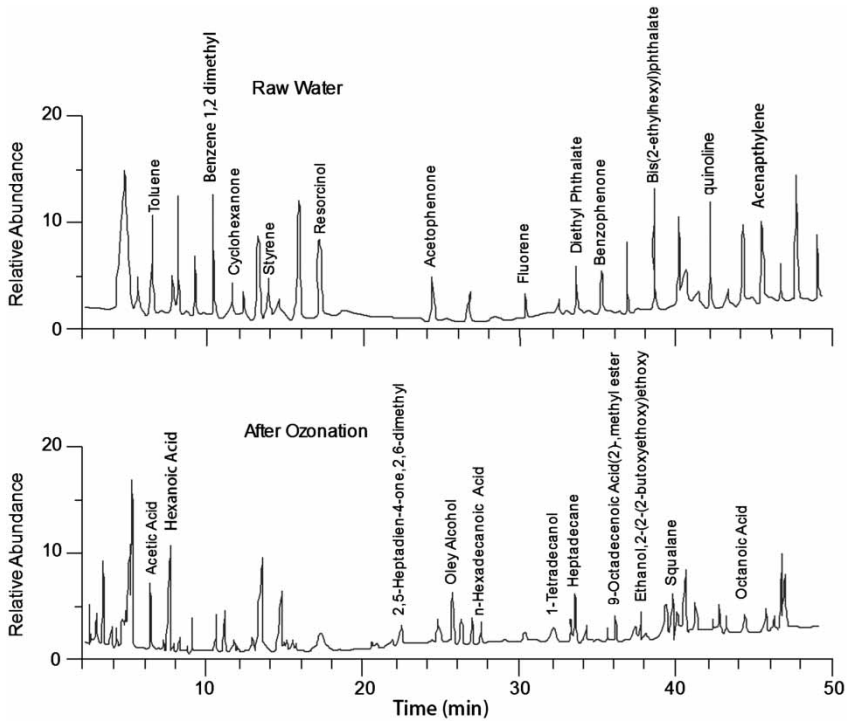

Figure 4 | GC-MS chromatogram of raw water before and after ozonation.

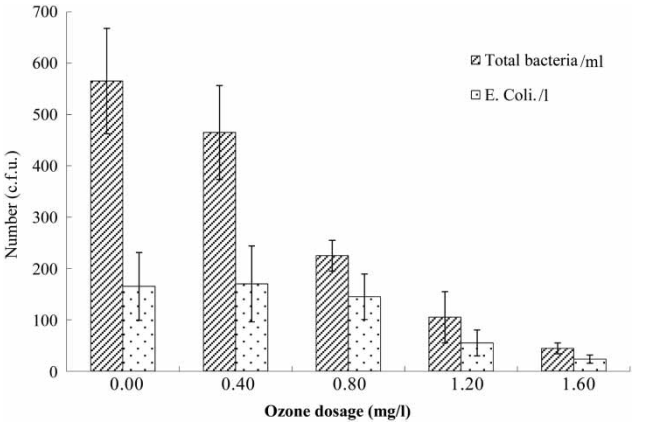

Figure 5 | Disinfection performance at different ozone dosages.

achieved. According to Figure 5, the optimal disinfection performance was obtained when the ozone dosage reached up to the highest level of 1.6 mg/l, which could meet several water reuse requirements in China such as toilet flushing, street flushing, landscaping, car washing and fire fighting.

CONCLUSIONS

The DOF process is a combination of the ozonation and flotation processes. Ozone dosage is of great importance for the DOF process performance. Findings from this study indicate that when the ozone dosage was 0.8 mg/l, the optimal color and organic matter removal could be achieved. Nevertheless, increasing the ozone dosage beyond 0.8 mg/l had little effect on color and organic matter removal. At the optimal organic matter removal, the disinfection performance improved considerably. However, the treated water still did not meet the requirements of certain reuse purposes in China unless the ozone dosage was 1.6 mg/l. Therefore, in order to reuse the treated water in China, the optimal ozone dosage of 1.6 mg/l is recommended for the DOF process. Moreover, the effluent DOF turbidity was mostly stable without the influence of the inlet water turbidity and ozone dosage.

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