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Identifying oxidation intermediates formed during ozone–UV of fulvic acid

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ABSTRACT

The purpose of this study was to determine the different classes and yields of oxidation intermediates, compared ozone (O_3), ultraviolet (UV) irradiation and the combined O_3–UV advanced oxidation process, as well as investigated on the effects of irradiation time, UV intensity, O_3 dosage on the removal of fulvic acid (FA), which is regarded as the main disinfection by-products (DBPs) precursor. Based on that, the knowledge gap of DBPs generated was made up. The results showed that by UV irradiation and O_3 oxidation, FA broke down into smaller molecules which were more hydrophilic, namely formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, glyoxal, methylglyoxal, formic, fumaric, benzoic, protocatechuic and 3-hydroxybenzoic acids. Meanwhile, unsaturated conjugated double bonds in the structure of FA were destroyed, which lead to UV_{254} decrease. Due to the synergistic effect of O_3–UV, dissolved organic carbon and UV_{254} significantly decreased and remained stable after the reaction of 10 min, indicating that O_3–UV system had a stronger potential of mineralization and lower selectivity. Besides, the kinds and concentration levels of the intermediates were obviously reduced with increase in light intensity. Furthermore, in O_3–UV system with high O_3 dosage, fumaric and benzoic acid concentration gradually decreased, which were relatively inert to O_3. Due to the fact that the high concentration level of •OH radical that could mineralize some organics which could not be mineralized by O_3.

Keywords: UV; Ozone; Ozone–UV; Fulvic acid; DBPs

1. Introduction

Natural organic matter (NOM) exists in all surface, groundwater and soil water. NOM is composed by a series of compounds, ranging from aliphatic to aromatic, also having all sorts of chemical compositions and molecular sizes. The content of NOM in water varies with climate and the hydrological situation, as well as other environmental factors [1]. NOM is divided into hydrophobic and hydrophilic components. Hydrophobic NOM is rich in aromatic carbon, conjugated double bonds and phenolic structures. The largest component is usually hydrophobic acids, which constitutes approximately 50% of the total organic carbon (TOC) in water [2]. Hydrophobic acids can be expressed as humic substances containing humic acid (HA) and fulvic acid (FA). However, hydrophilic NOM contains more aliphatic carbon and nitrogenous compounds.

Currently, chlorine, chloramine, chlorine dioxide and ozone (O_3) are the most common disinfectants, and each of them generates its own unique disinfection by-products (DBPs) [3]. DBPs have been attracted much attention in drinking water treatment plants (DWTPs) during the past decades. More than 700 DBPs have been corroborated, among which trihalomethanes (THMs) and haloacetic acids (HAAs) are the most common and the highest concentrations in drinking waters worldwide [3]. NOM is regarded as the main DBPs precursor in general, particularly for the hydrophobic NOM with high aromatic carbon content, but hydrophilic or low molar mass NOM also has an important influence on DBPs formation [4,5]. To avoid DBPs formation, two methods are generally applied in DWTPs. One is a non-chlorine

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disinfection process applied as primary disinfectant and chlorine addition as secondary disinfectant. The other is the reducing NOM content in the raw waters before disinfection using physical or chemical processes [6]. Ozonation followed by biological filtration is the most common treatment means applied to remove NOM. Recalcitrant organic compounds are decomposed to smaller molecules which are more hydrophilic and biodegradable through the direct reaction with O_3 and/or indirect reaction with hydroxyl radical (•OH) which is generated from O_3 decomposition. Although ozonation followed by biological filtration has the ability to remove NOM, this process has high variation in removal efficiency ranging from 10% to 75% [7–9]. This variation attributes to different reaction selectivity between O_3 with organics.

In addition, advanced oxidation processes (AOPs) are an alternative technology, which can be used to reduce DBPs formation [6,10]. Ozonation is one of the AOPs, which involves •OH formation and •OH as a highly reactive and non-selective oxidant to destroy compounds that cannot be oxidized by conventional oxidants. Through the combined catalyst-oxidant, to generate more •OH, such as ozone–ultraviolet (O_3–UV), hydrogen peroxide–ultraviolet (H_2O_2–UV) and ozone–hydrogen peroxide (O_3–H_2O_2) [11]. Among these AOPs, O_3–UV generates the highest yield of •OH per oxidants [11]. Besides, UV disinfection is regarded as a low-cost and easy-to-operate system in DWTPs [12]. However, O_3 and UV cannot maintain throughout distribution system, they cannot guarantee the biological safety of tap water. Thus, chlorine addition carries out secondary disinfectant before water leaving the factory. Moreover, many researchers have found that UV can change dissolved organic matter (DOM) structure and increase biodegradability [13–15]. Under strong oxidation conditions, higher molecular weight compounds are decomposed into smaller and more biodegradable carbonyl compounds, such as aldehydes and carboxylic acids. Such changes in the chemical properties and structures of NOM lead to not only TOC concentrations declining but also DBPs precursor changing, and then influencing DBPs formation from subsequent chlorination [16–18].

There is incomplete information about NOM oxidation intermediates. The main identified oxidation intermediates are formic, acetic and oxalic acids as well as several ketoacids [19]. As far as aromatic acids, they are rarely identified in water as well as their influence on DBPs, owing to lack of proper analytical methods. Aromatic acids should be transformed into low polar and stable derivates apply to gas chromatograph (GC) detection. In order to avoid the complicated derivatization procedure, our team employed solid phase extraction-ultra-high performance liquid chromatography (SPE-UPLC) to detect aromatic acids. Moreover, our previous studies showed that carbonyl compounds were widespread in raw water and the each process unit of DWTPs using O_3 disinfectant. FA is an appropriate model for predicting and evaluating oxidation intermediates. On the one hand, FA is ubiquitous presence in the terrestrial environment. On the other hand, FA was detected in the treated water by sand filtration in DWTPs [20]. Most model compounds studies are for the purpose of DBPs formation. Few studies have examined oxidation intermediates formation.

Therefore, the objective of this study involved, namely: (1) applied SPE-UPLC method to determine the different classes and yields of oxidation intermediates, (2) compared O_3, UV and O_3–UV for FA removal and (3) investigated on the effects of irradiation time, UV intensity and O_3 dosage of O_3–UV process on the mineralization of FA, as well as DBPs formation following chlorination.

2. Materials and methods

2.1. Materials

FA was standard chemical, which was obtained from Sigma-Aldrich (Shanghai, China). Its molecular formula is $C_{14}H_{12}O_8$ and molecular weight is 308.24. The analytical standard containing 15 carbonyl compounds (formaldehyde, acetaldehyde, propanal, butanal, pentanal, hexanal, cyclohexanone, crotonaldehyde, heptanal, octanal, benzaldehyde, nonanal, decanal, glyoxal and methylglyoxal) and the derivatization agent *O*-(2,3,4,5,6-pentafluoro-benzyl) hydroxylamine were purchased from AccuStandard (New Haven, USA). High performance liquid chromatography grade *n*-hexane Anpel (Shanghai, China) was used as a solvent for the liquid–liquid extraction. Organic free water was provided by the Synergy UV-Ultrapure Water System (Millipore, Molsheim, France).

Standards of the carboxylic acids (>95% purity), formic, oxalic, fumaric, protocatechuic, 3-hydroxybenzoic, benzoic acid, chloroform and standard of HAAs were purchased from J&K (Beijing, China). Stock solutions of the individual acids (10 g/L) were prepared in purified water. All these solutions were stored at 4°C.

Potassium dihydrogen phosphate, hydrochloric acid, sodium hydroxide, sodium hypochlorite and orthophosphoric acid were analytical reagent and supplied by Shanghai (Shanghai, China). LiChrolut EN (particle size 40–120 μm) was purchased from Merck (Darmstadt, Germany). Silica-reverse phase sorbent with octadecyl functional groups (Supelclean ENVI-18) was supplied from Supelco (Bellefonte, PA, USA).

2.2. Experimental procedures

A schematic of the experimental program was shown in Fig. 1. Stock solution of FA was prepared by dissolving 1 g FA in 1,000 mL purified water mixing for 24 h. Working solution at 20 mg/L concentration was obtained by water dilution.

All ozonation of FA experiments were operated on 500 mL SIMAX bottles fitted with a magnetic stirring bar. O_3 was generated from pure oxygen (≥99.2% purity) by COM-AD-01 O_3 generator (4 g/h, ANSEROS, Germany) and transferred immediately into the ultrapure water using a diffuser placed at the bottom of the reactor. The O_3 concentration of the stock solution (20 mg/L) was determined using the direct UV absorbance method at 258 nm with a molar absorptivity of 2,950 M^{-1} cm^{-1} [21]. The ozonation reactions were terminated by sodium nitrite (J&K, Beijing, China).

The UV lamps (emitting light at a wavelength of 254 nm, 5 W, 10 W and 15 W; Philips, Poland) were used to deliver UV dose to the sample. The UV lamp was inserted into a hollow quartz pipe located at the center of the reactor. The solution was stirred with a magnet during irradiation. The O_3 and O_3–UV samples were stored at 4°C for not >24 h before the chlorination experiments. The experimental matrix encompassed

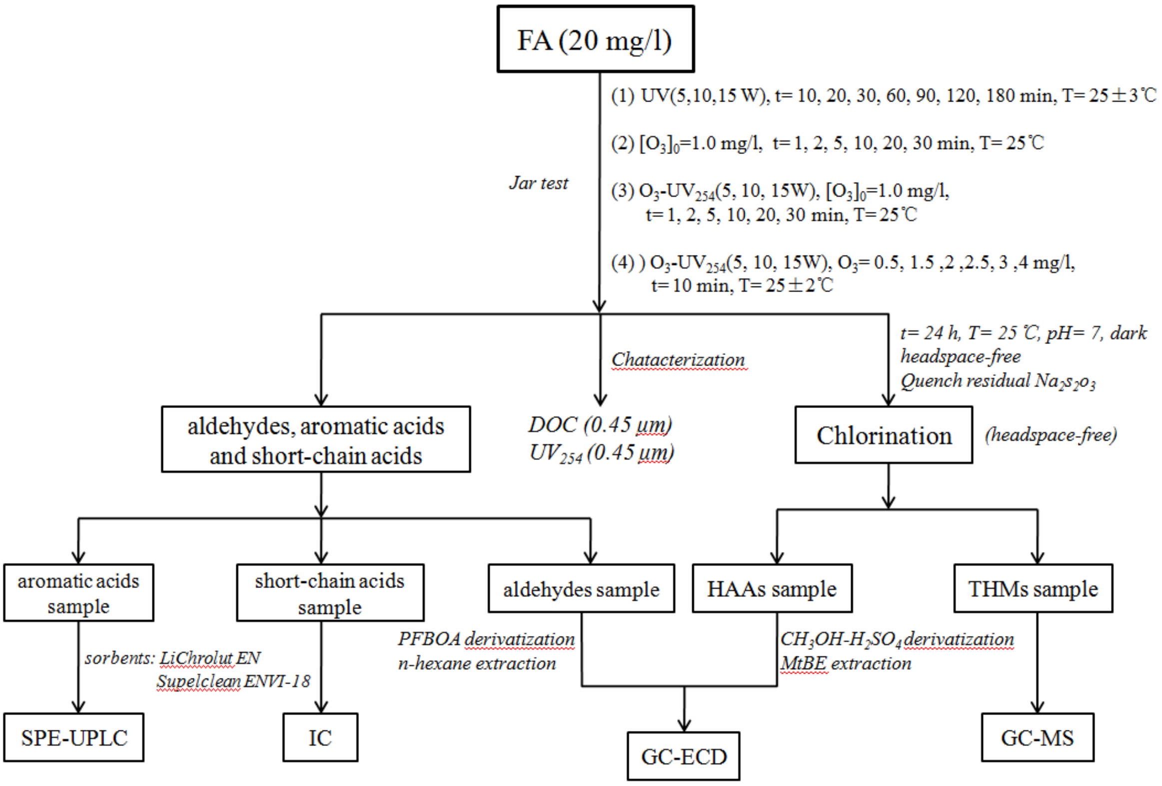

Fig. 1. The experimental schematic.

the following ranges of conditions: (1) UV alone, UV intensity: 5 W, 10 W and 15 W, irradiation time: 10, 20, 30, 60, 90, 120 and 180 min; (2) O_3 alone, $[O_3]_0$ = 1.0 mg/L, contact time: 1, 2, 5, 10, 20 and 30 min; (3) O_3–UV_{254}, UV intensity: 5 W, 10 W and 15 W, irradiation time: 1, 2, 5, 10, 20 and 30 min, $[O_3]_0$ = 1.0 mg/L and (4) O_3–UV_{254}, UV intensity: 5 W, 10 W and 15 W, $[O_3]_0$ = 0.5–4 mg/L, irradiation time: 10 min.

All samples were filtered with a 0.45 μm membrane to remove particles. Dissolved organic carbon (DOC) concentration and UV absorbance at 254 nm (UV_{254}) were analyzed.

Chlorination was conducted on ozonated samples using 100 mL chlorine-free bottles. Cl_2 doses were chosen to ensure that a substantial Cl_2 residual was present after incubation for 24 h so that formation reactions would not be chlorine limited. After being dosed with chlorine, samples were stored headspace-free at pH of 7, 25°C ± 1°C in the dark for 24 h. Sodium thiosulfate was used to quench the residual chlorine.

2.3. Analytical methods

DOC concentrations were measured using a TOC analyzer (OI, Aurora1030) according to Standard Method 5310 [21]. UV_{254} was measured by a UV–visible spectrophotometer (Shimadzu, UV-1800).

The EPA 556 method and the EPA 552.2 method were individually used to the analysis of aldehydes and HAAs in water samples (EPA, 1998 and EPA, 2003). Aldehydes and HAAs were analyzed by 7890B gas chromatograph fitted with electron capture detector (Agilent Technologies, Palo Alto, USA). The DB-5MS capillary column (30 m × 0.25 mm inner diameter × 0.25 μm film thickness; Agilent Technologies, Bellefonte, PA, USA) was applied for the separation. The carrier gas was He (1 mL/min) and the detector make-up gas was N_2 (30 mL/min). The aldehydes temperature program was: 50°C hold for 1 min, program at 4°C/min up to 220°C, program at 20°C/min up to 250°C and hold at 250°C for 10 min. The HAAs temperature program was: 35°C hold for 10 min, program at 2°C/min up to 40°C, program at 5°C/min up to 75°C and hold at 75°C for 15 min, program at 40°C/min up to 100°C and hold at 100°C for 15 min and program at 40°C/min up to 135°C.

According to the purge and trap gas chromatographic method, chloroform was measured using 4660-7890B-5077A gas chromatograph (Agilent Technologies, Palo Alto, USA) equipped with mass spectrometer. The operating conditions were: magnetic mass analyzer scanned from 35 to 200 m/z, 70 eV electron energy, ion source 250°C; carrier gas: He (1 mL/min), temperature program: 30°C hold for 10 min, program at 7°C/min up to 72°C and hold at 72°C for 1 min and program at 40°C/min up to 220°C and hold at 220°C for 1 min.

The three aromatic organic acids and one aliphatic carboxylic acid (fumaric, protocatechuic, 3-hydroxybenzoic and benzoic acids) were analyzed by SPE-UPLC [22]. The SPE system (Anpel, Shanghai, China) was assembled from a GAST pump (MI, USA). The sorbent column was conditioned with 1 mL acetonitrile–methanol (1:1) and 1 mL purified water. Chromatographic analyses were carried on a Waters H-class ultra-high performance liquid chromatography (Waters, USA). The column was an ACQUITY UPLC

BEH C$_{18}$ (2.1 × 50 mm I.D., particle size 1.7 μm, Waters, USA). A PHS-2C pH meter (Shanghai, China) was used to adjust the pH value. In brief, 100 mL standard solution or water sample with concentrations aromatic acids at pH ~1.3 (adjusted with 5 M HCl) was passed through the sorbent column at 2–3 mL/min. The sorbent column was filled with 80 mg of the mixture LiChrolut EN/Supelclean ENVI-18 (1:1) sorbents. Later, target analytes were eluted by 1 mL methanol and collected in a 2 mL amber glass GC vial.

The short-chain carboxylic acids were analyzed by ICS-2100 Ion chromatography (IC, Thermo Scientific, USA) equipped with a Dionex IonPac AS-19 capillary column (0.4 mm × 250 mm) and a Dionex IonPac AS-19 guard column (0.4 mm × 50 mm). The mobile phase was produced by a Dionex RFIC-EG eluent generator at flow of 10 μL/min with following concentrations: 0–10 min 10 mM KOH, 10–42 min linear ramp to 52 mM KOH, 42–45 min linear ramp to 70 mM KOH and 45–50 min 10 mM KOH.

2.4. Quality control

Calibration curves prepared for each compound were linear ($R^2 > 0.980$). The method of aldehydes detection limits varied from 0.2 to 4.0 μg/L. The method of eight carboxylic acids detection limits varied from 0.8 to 5.0 μg/L. The recovery rates of each compound were >80%. Experiments were carried out in duplicate. Relative standard deviation of the two measurements was generally below 15%. The SPSS software (IBM SPSS, version 17) was used for statistical analysis of data.

3. Results and discussion

3.1. UV irradiation alone

Experiments including UV irradiation (5 W, 10 W and 15 W) high concentration of FA aqueous solution (20 mg/L) were carried out to determine the effect on DOC and UV$_{254}$. The changes of DOC and UV$_{254}$ at different UV irradiation time and light intensity were shown in Fig. 2.

Under high concentration FA solution, DOC had a certain increase and UV$_{254}$ had a slight decline, due to UV light irradiation. Besides, DOC increase and UV$_{254}$ reduction along with irradiation time and light intensity, respectively. The result of DOC increase could be attributed to UV irradiation made FA break down into smaller molecules which were more hydrophilic, and the water solubility of FA improved [23,24].

UV$_{254}$ was an important parameter for characterization of compounds with aromatic structure and unsaturated conjugated double bonds. Humic substances strongly absorbed UV radiation. Due to the long time and high intensity of UV irradiation, contributing to the destruction of unsaturated conjugated double bonds in the structure of FA, which lead to UV$_{254}$ a slight decrease. The olefinic structure of the DOM is probably more readily degraded by photolysis than aromatic structure, since aromatic structure generally has a high chemical stability [25].

Humic substances are decomposed to lower molecular size during UV irradiation [25–27]. The photochemical reactions taking place in FA solution are not only complicated but also contribute to generating many low-molecular-weight compounds at the same time during UV irradiation. The formation of intermediates by UV at different irradiation time and light intensity was displayed in Figs. 3(a)–(f). Formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, glyoxal, methylglyoxal, formic, fumaric and benzoic acid were predominant oxidation intermediates, with formaldehyde and formic acid exhibiting the highest concentration (Figs. 3(a)–(f)). The yields of aldehydes and carboxylic acids increased steadily with UV irradiation time. Furthermore, propionaldehyde and butyraldehyde generated after UV irradiation 90 min later. With the light intensity increased, the generation of carbonyl compounds improved, especially for carboxylic acids. It should be pointed out that fumaric and benzoic acids were the major degradation products. This result is in accordance with Corin et al. [25]. Moreover, with the exception of irradiation time and light intensity, the production of aldehydes and carboxylic acids were associated with temperature. With the increase of irradiation time, the solution temperature increased, and FA decomposition was accelerated, thus the yields of aldehydes and carboxylic acids were enhanced. These aldehydes and carboxylic acids constituted a major part of newly formed assimilable organic carbon (AOC).

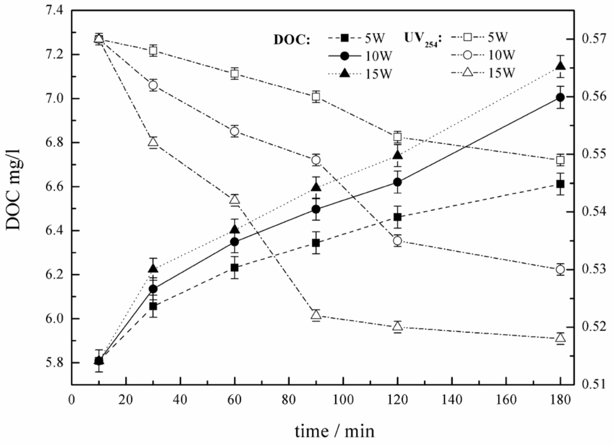

Fig. 2. The changes of DOC, UV$_{254}$ at different irradiation time and UV light intensity (initial FA = 20 mg/L).

3.2. O$_3$ alone

The changes of DOC, UV$_{254}$, and the generation of oxidation intermediates at different O$_3$ (1.0 mg/L) contact time were shown in Figs. 4 and 5(a) and (b), respectively. DOC and UV$_{254}$ gradually decreased with contact time. Although O$_3$ is a strong oxidizer with selectivity, it cannot mineralize organics in a certain time [28].

The oxidation intermediates yields in FA ozonation with O$_3$ contact time ranging from 0 to 30 min. The low-molecular-weight aldehydes, carboxylic acids and aromatic acids were detected, including formaldehyde, glyoxal, methylglyoxal, formic, fumaric, protocatechuic, benzoic and 3-hydroxybenzoic acids. This result was consistent with previous studies, where O$_3$ react with NOM, resulting in monocarboxylic, dicarboxylic and aromatic acids generation [29,30]. In addition, this discovery was in accordance with our pervious findings that aldehydes and carboxylic acids

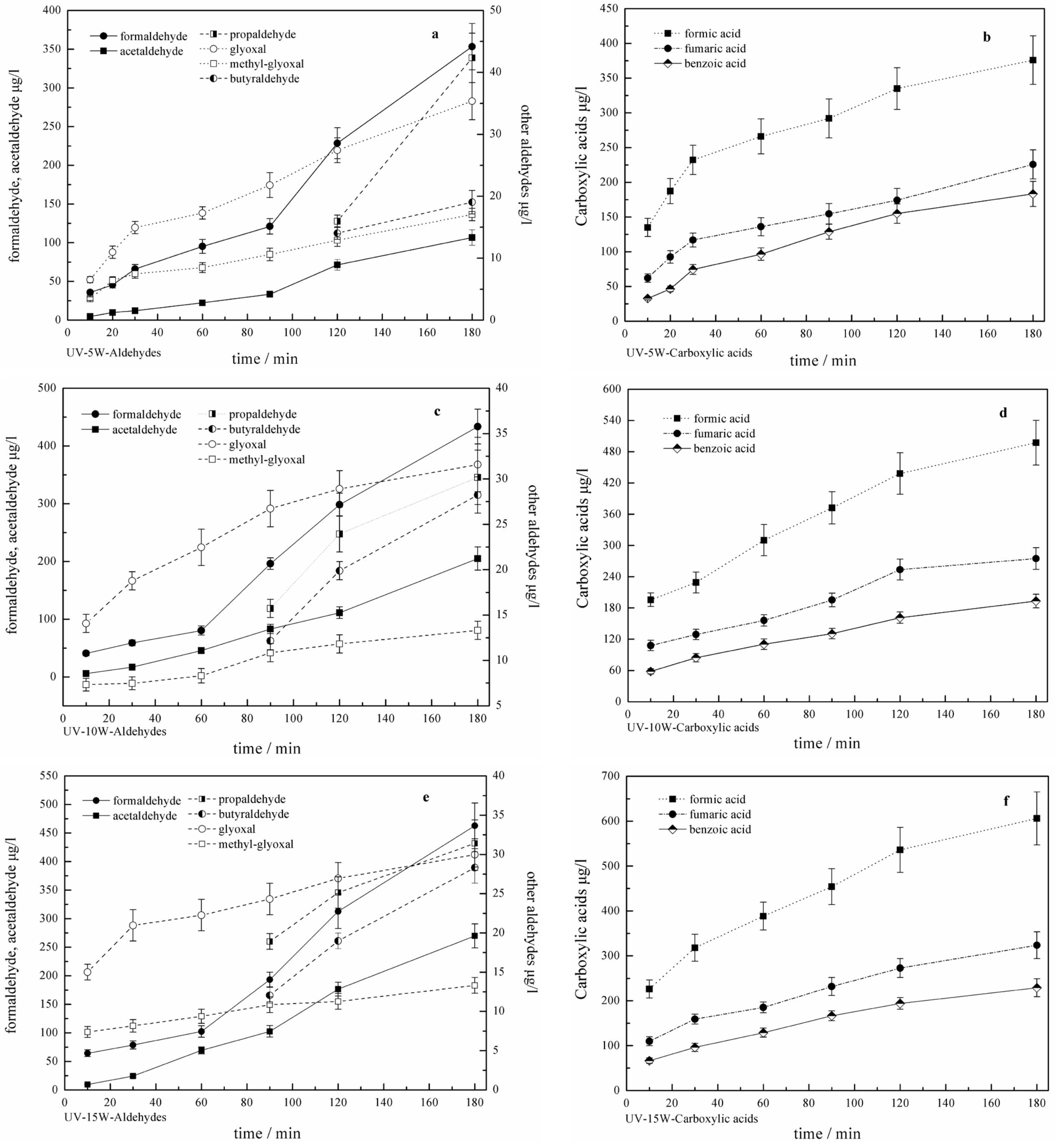

Fig. 3. Oxidation intermediates formation by UV at different irradiation time and light intensity (initial FA = 20 mg/L). (a) UV-5W-Aldehydes; (b) UV-5W-Carboxylic acids; (c) UV-10W-Aldehydes; (d) UV-10W-Carboxylic acids; (e) UV-15W-Aldehydes and (f) UV-15W-Carboxylic acids.

were ubiquitous in raw water of Taihu Lake as well as the each process unit of DWTPs.

The yields of aldehydes and carboxylic acids increased steadily along with time, except for hydroxybenzoic acid (protocatechuic and 3-hydroxybenzoic acids). First, aldehydes are easily oxidized to corresponding carboxylic acids or other organic acids by O_3 or •OH radical [15,31]. Second, ozonation cleaves unsaturated bonds, opens aromatic rings, and removes or oxidizes alkyl groups to aldehydes and carboxylic acids. Lastly, aldehydes oxidation rates were typically lower than their formation, as well as short-chain carboxylic acids were relatively inert to O_3, so they would be accumulated in O_3 treated water.

It should be noted that protocatechuic and 3-hydroxybenzoic acids initially formed around 65 and 10 μg/L, respectively. Subsequently, the levels of their concentration declined rapidly. This was possible because that O_3 is a strong oxidizer with selectivity. Previous studies suggested that O_3 direct oxidation was effective for degradation of organic compounds bearing active groups, such as –OH, $–NH_2$ and double bond [32,33]. The existence of active groups was beneficial for O_3 to electrophilic attacking aromatic ring. Some hydroxybenzoic acids initially formed when O_3 reacted with NOM, and then decreased over time, indicating that they were further oxidized [34]. Besides, our pervious finding that the order of the reactivity of O_3 with aromatic acids was protocatechuic acid > 3-hydroxybenzoic acid > benzoic acid > phthalic acid.

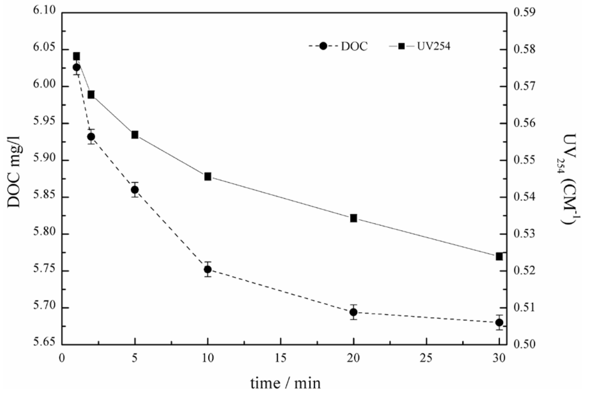

Fig. 4. The changes of DOC, UV_{254} at different O_3 contact time ($[O_3]_0$ = 1.0 mg/L, initial FA = 20 mg/L).

3.3. O_3–UV

3.3.1. Different O_3 contact time

Compared with UV irradiation and O_3 oxidation, DOC significantly decreased due to the synergistic effect of O_3–UV. The higher light intensity, the faster degradation rate. DOC remained stable, after the reaction of 10 min (Fig. 6(a)). For O_3–UV system, there was no need to react >10 min. It should be pointed out that UV_{254} immediately dropped down to 0.521 cm^{-1} and stabilized at 0.516 cm^{-1} thereafter (not shown in Fig. 6(a)). Besides, DOC and UV_{254} gradually decline with O_3 dosage, indicating that O_3–UV system had a stronger potential of mineralization and lower selectivity [6].

The processes of O_3 decomposition and •OH radical generation from O_3–UV system can be divided into two stages.

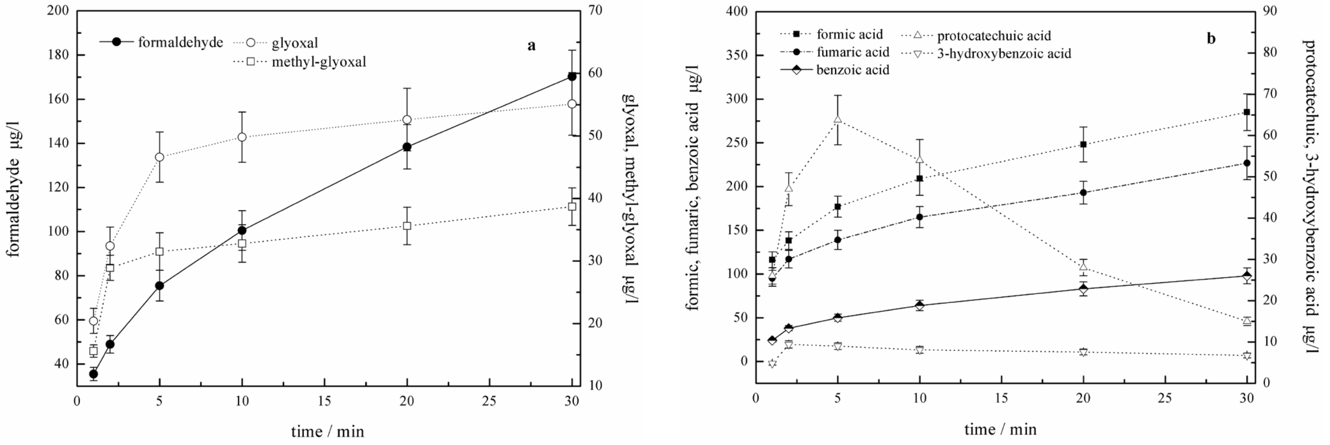

Fig. 5 Oxidation intermediates formation disinfected by O_3 alone at different contact time ($[O_3]_0$ = 1.0 mg/L, initial FA = 20 mg/L). (a) Aldehydes and (b) carboxylic acids.

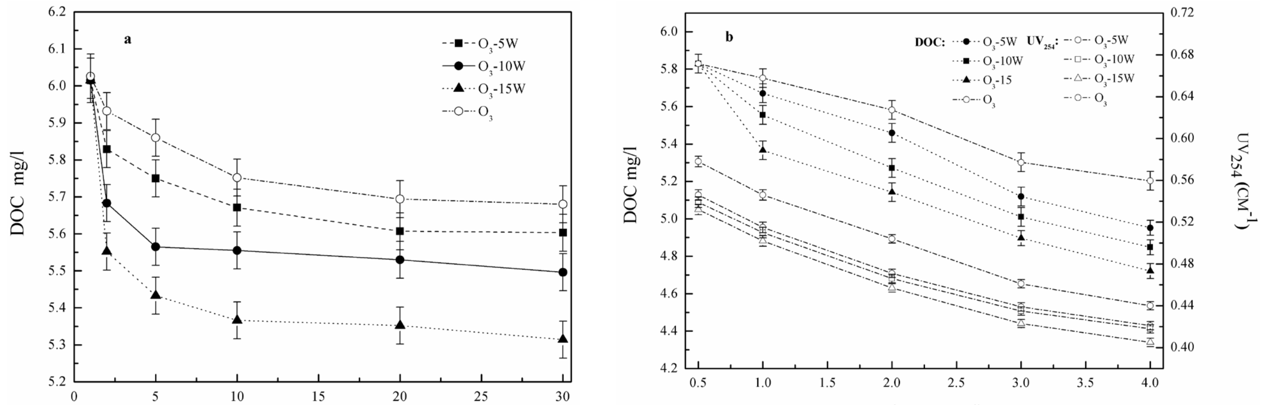

Fig. 6. The changes of DOC, UV_{254} with light intensity increasing at different O_3 contact time and O_3 dosage. (a) Initial FA = 20 mg/L, $[O_3]_0$ = 1.0 mg/L, *t* = 1, 2, 5, 10, 20 and 30 min; (b) $[O_3]_0$ = 0.5–4.0 mg/L, *t* = 10 min).

The first stage is that H_2O_2 formation from O_3 photolysis, and then H_2O_2 decomposes to •OH radical by UV irradiation. The second stage is that not only •OH radical joins into the cycle of radical reactions, but also NOM participates in the reaction cycle and produces O_2^- that is a strong catalysis for O_3 decomposition. Subsequently, •OH radical is mainly generated from O_3 decomposition by O_2^- catalysis [35]. Therefore, O_3–UV system had a higher concentration level of •OH radical than UV, O_3 alone, leading to rapidly decrease in DOC and UV_{254}.

Compared with UV irradiation and O_3 oxidation, the kinds and concentration levels of aldehydes and carboxylic acids were obviously reduced. Furthermore, the concentration levels of aldehydes and carboxylic acids decreased with increase in light intensity, except that formic and fumaric acids had a certain increase at 15W-UV irradiation (Figs. 7(a)–(f)). At high O_3 dosage, aldehydes concentration slowly increased, while fumaric and benzoic acids concentration gradually decreased (Figs. 8(a)–(f)). Due to the

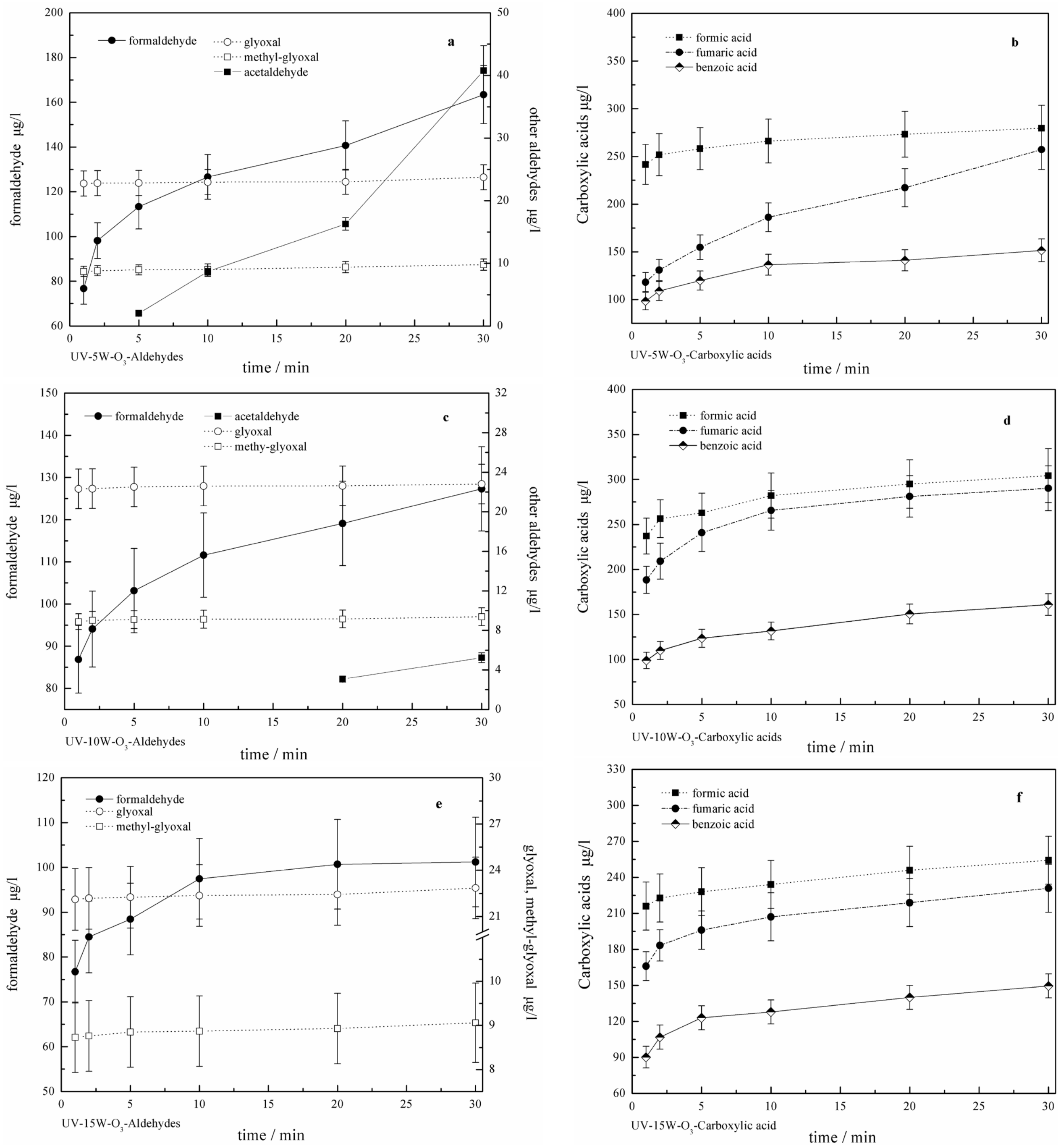

Fig. 7. Oxidation intermediates formation disinfected by O_3–UV at different contact time and light intensity (initial FA = 20 mg/L, $[O_3]_0$ = 1.0 mg/L, *t* = 1, 2, 5, 10, 20 and 30 min). (a) UV-5W-O_3-Aldehydes; (b) UV-5W-O_3-Carboxylic acids; (c) UV-10W-O_3-Aldehydes; (d) UV-10W-O_3-Carboxylic acids; (e) UV-15W-O_3-Aldehydes and (f) UV-15W-O_3-Carboxylic acids.

fact that the high concentration level of •OH radical made UV–O_3 system has higher oxidability and lower selectivity. •OH radical could mineralize some organics which could not be mineralized by O_3. Normally, the synergistic effect of O_3–UV system has two reasons: first, organics were activated by UV irradiation, which could be easily decomposed by O_3; second, O_3 decomposed into •OH radical by UV irradiation, thereby accelerating the removal rate of organics in water [6].

It was important to note that 3-hydroxybenzoic acid was detected and the concentration of it ranged from 6.2 to 23.55 μg/l, and then disappear soon (Figs. 8(a) and (b)). It was difficult to be detected. Because 3-hydroxybenzoic acid could be further oxidized by excess O_3 or •OH. Pillar et al. [36],

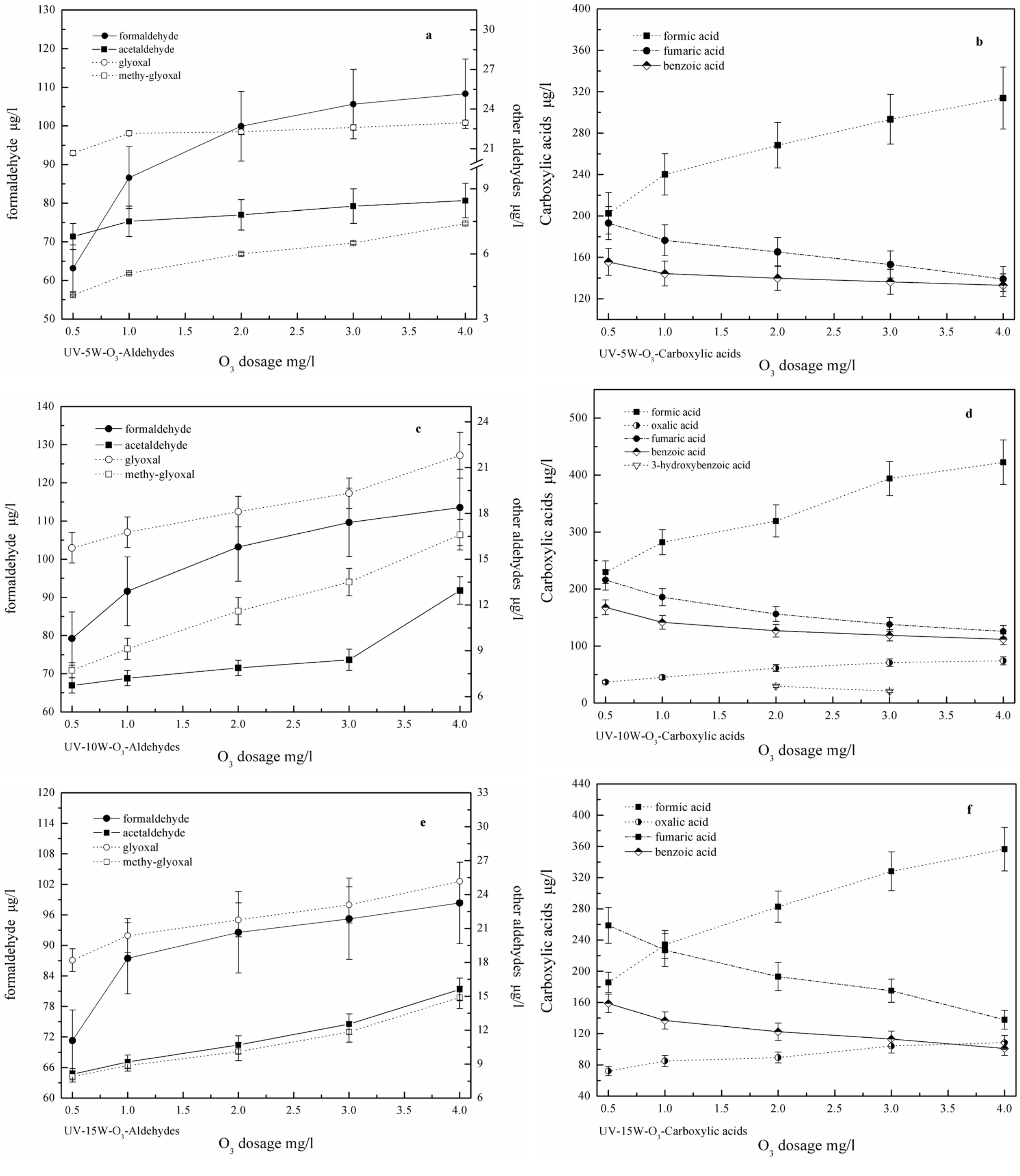

Fig. 8. Oxidation intermediates formation disinfected by O_3–UV at different O_3 dosage and light intensity (initial FA = 20 mg/L, $[O_3]_0$ = 0.5–4.0 mg/L, t = 10 min). (a) UV-5W-O_3-Aldehydes; (b) UV-5W-O_3-Carboxylic acids; (c) UV-10W-O_3-Aldehydes; (d) UV-10W-O_3-Carboxylic acids; (e) UV-15W-O_3-Aldehydes and (f) UV-15W-O_3-Carboxylic acids.

also reported that the reaction rate constants of hydroxybenzoic acids with O_3 and •OH were 5.2×10^5 M^{-1} S^{-1} and 1.1×10^{10} M^{-1} S^{-1}, respectively. It can be deduced that 3-hydroxybenzoic and benzoic acids were the main oxidation transformation products, and the formation of formic, oxalic and fumaric acids may be the further oxidation products of 3-hydroxybenzoic and benzoic acids.

In order to remove precursors and avoid chlorination–DBPs formation, AOPs were adopted. However, carbonyl compounds as an important kind of newly formed AOC, which are a significant part of organic DBPs in the DWTPs [29,37,38]. Ordinarily, compared with precursors, the short-chain aldehydes and carboxylic acids are easier biodegradable, and they have been proved to be related with bacterial regrowth and biofilm formation in water distribution systems. Therefore, it is necessary to understand the sources and the amount of carbonyl compounds with different disinfectant.

3.4. DBPs formation

FA was oxidized by UV, O_3 and O_3–UV system, resulting in the formation of more polar organic compounds, which is reflected through the increases in the hydrophilic non-acidic and hydrophilic acid fractions. Carbonyl compounds are considered to be primary by-products.

As shown in Figs. 9(a) and (b), direct chlorination disinfection and UV (60 min), O_3–UV ($[O_3]_0$ = 1.0 mg/L, t = 10 min) chlorination disinfection generated a number of chloroform, dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA), chlorination condition: pH of 7, 25°C ± 1°C in the dark for 24 h. Compared with UV alone, FA and oxidation intermediates could be mineralized in a short time, due to O_3 addition. Although UV–O_3 system reduced DBPs generation to a certain extent, they could not be ultimately eliminated. Therefore, not only NOM were the main DBPs precursors, the oxidation intermediates of NOM but also could be the DBPs precursors, and they gave a certain amount of DBPs. Our previous study also showed that FA was ubiquitous presence in the terrestrial environment, and it generated aromatic acids and low-molecular-weight carbonyl compounds during oxidation [20]. Consequently, aromatic acids and carbonyl compounds should be under control in DWTPs.

O_3 and OH radical oxidize NOM generate great amounts of methylketone-like structures which are regarded as major precursors of THMs. Besides, it was generally known that the aromatic content of NOM was oxidized to produce a series of aliphatic carbonyl compounds, such as aldehydes, carboxylic acids and ketones [39]. These carboxylic acids or compounds could readily be converted to β-ketoacids by decarboxylation in the presence of hypochlorous acid, and gave high yields of THMs when chlorinated in near neutral solutions. As far as the DCAA formation was concerned, a previous study demonstrated that during chlorination the phenolic hydroxyl group is likely to form TCAA, whereas carboxyl and alcoholic hydroxyl groups were prone to form DCAA [40].

4. Conclusions

This work determined the species and the yields of the intermediates during UV, O_3 and UV–O_3 oxidation of FA, as well as DBPs formation. The obtained conclusions were as follows:

- In UV system, DOC had a certain increase and UV_{254} had a slight decline. Due to UV irradiation, FA broke down into smaller molecules which were more hydrophilic. Meanwhile, unsaturated conjugated double bonds in the structure of FA were destroyed, which lead to UV_{254} a slight decrease. Formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, glyoxal, methylglyoxal, formic, fumaric and benzoic acids were predominant oxidation intermediates. The yields of aldehydes and carboxylic acids increased steadily with UV irradiation time and light intensity.
- In O_3 system, DOC and UV_{254} gradually decreased with time. In addition, the intermediates described above, protocatechuic and 3-hydroxybenzoic acids were also generated. They were initially formed, and then declined rapidly.
- In O_3–UV system, DOC and UV_{254} significantly decreased and remained stable after the reaction of 10 min, due to the synergistic effect of O_3–UV. It was indicated that O_3–UV system had a stronger potential of mineralization and

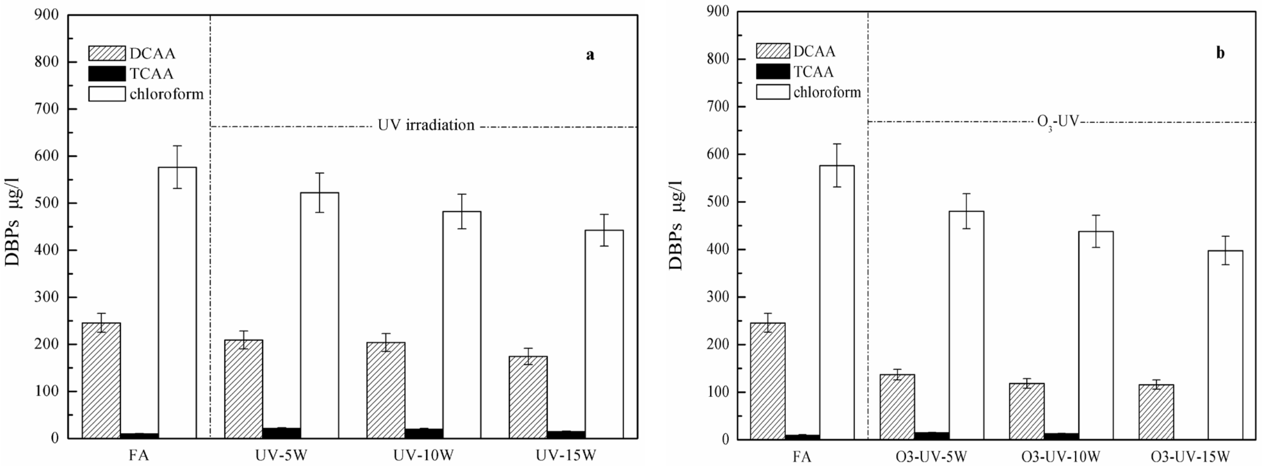

Fig. 9. DBPs formation from UV disinfectant and O_3–UV disinfectant.

lower selectivity. The kinds and concentration levels of the intermediates were obviously reduced with increase in light intensity. While at high O_3 dosage, the concentrations of fumaric and benzoic acids gradually decreased, which were relatively inert to O_3. Due to the fact that the high concentration level of •OH radical that could mineralize some organics which could not be mineralized by O_3.

- Although O_3–UV system reduced DBPs generation to a certain extent, they could not be ultimately eliminated. Thus, not only NOM were the main DBPs precursors, the oxidation intermediates of NOM but also could be the DBPs precursors, and they gave a certain amount of DBPs.

Although the full-scale applications of AOPs treatment in DWTPs are still very limited, mainly due to high cost, lack of experience, requirement of high degree of pre-treatment and operational difficulties, the most AOPs studies concerning drinking water purification and disinfection gained very promising results. Based on the above experimental results, AOPs can be used as a pre-treatment to enhance the biodegradability of NOM, and the resulting intermediates are easily degradable in a further biological treatment.

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References

[1] A. Matilainen, M. Sillanpää, Removal of natural organic matter from drinking water by advanced oxidation processes, Chemosphere, 80 (2010) 351–365.
[2] E.M. Thurman, Organic Geochemistry of Natural Waters, M. Nijhoff, Springer, Netherlands, 1985, pp. 165–174.
[3] S.W. Krasner, H.S. Weinberg, S.D. Richardson, S.J. Pastor, R. Chinn, M.J. Sclimenti, G.D. Onstad, J. Alfred, D. Thruston, The occurrence of a new generation of disinfection by-products, Environ. Sci. Technol., 40 (2006) 7175–7185.
[4] T. Bond, E.H. Goslan, B. Jefferson, F. Roddick, L. Fan, S.A. Parsons, Chemical and biological oxidation of NOM surrogates and effect on HAA formation, Water Res., 43 (2009) 2615–2622.
[5] G. Hua, D.A. Reckhow, Characterization of disinfection byproduct precursors based on hydrophobicity and molecular size, Environ. Sci. Technol., 41 (2007) 3309–3315.
[6] A. Chin, P.R. Bérubé, Removal of disinfection by-product precursors with ozone-UV advanced oxidation process, Water Res., 39 (2005) 2136–2144.
[7] A.A. Yavich, K. Lee, K. Chen, L. Pape, S.J. Masten, Evaluation of biodegradability of NOM after ozonation, Water Res., 38 (2004) 2839–2846.
[8] T. Ratpukdi, Removal of Natural Organic Matter (NOM) by Ozone and Ultraviolet Based Advanced Oxidation Processes: Development of NOM Fractionation Technique, Process Performances, and Bromate Formation, PhD Thesis, North Dakota State University of Agriculture and Applied Science, 2009, pp. 1–24.
[9] N.J.D. Graham, Removal of humic substances by oxidation/biofiltration processes – a review, Water Sci. Technol., 40 (1999) 141–148.
[10] T. Oppenländer, Photochemical purification of water and air, Chem. Int., 25 (2003) 31–31.
[11] Y. Qi, Ozonation of water and waste water: a practical guide to understanding ozone and its application, Int. J. Environ. Stud., 5 (2010) 795–796.
[12] Y. Choi, Y. Choi, The effects of UV disinfection on drinking water quality in distribution systems, Water Res., 44 (2010) 115–122.
[13] W. Buchanan, F. Roddick, N. Porter, M. Drikas, Fractionation of UV and VUV pretreated natural organic matter from drinking water, Environ. Sci. Technol., 39 (2005) 4647–4654.
[14] E.H. Goslan, F. Gurses, J. Banks, S.A. Parsons, An investigation into reservoir NOM reduction by UV photolysis and advanced oxidation processes, Chemosphere, 65 (2006) 1113–1119.
[15] J. Thomson, F.A. Roddick, M. Drikas, Vacuum ultraviolet irradiation for natural organic matter removal, J. Water Supply Res. Technol. AQUA, 53 (2004) 193–206.
[16] R. Lamsal, M.E. Walsh, G.A. Gagnon, Comparison of advanced oxidation processes for the removal of natural organic matter, Water Res., 45 (2011) 3263–3269.
[17] D.H. Metz, M. Meyer, A. Dotson, E. Beerendonk, D.D. Dionysiou, The effect of UV/H_2O_2 treatment on disinfection by-product formation potential under simulated distribution system conditions, Water Res., 45 (2011) 3969–3980.
[18] X. Yang, J. Peng, B. Chen, W. Guo, Y. Liang, W. Liu, L. Liu, Effects of ozone and ozone/peroxide pretreatments on disinfection byproduct formation during subsequent chlorination and chloramination, J. Hazard. Mater., 239–240 (2012) 348–354.
[19] J. Nawrocki, J. Swietlik, U. Raczyk-Stanisawiak, A. Dabrowska, S. Bilozor, W. Ilecki, Influence of ozonation conditions on aldehyde and carboxylic acid formation, Ozone Sci. Eng., 25 (2003) 53–63.
[20] X. Zhong, C.W. Cui, S.L. Yu, The determination and fate of disinfection by-products from ozonation-chlorination of fulvic acid, Enviromen. Sci. Pollut. Res., 24 (2017) 6472–6480.
[21] APHA, American Water Works Association, Water Environment Federation, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington, D.C., USA, 1999.
[22] X. Zhong, C.W. Cui, S.L. Yu, Determination of benzenoid acids in water by solid-phase extraction/ultra-high performance liquid chromatography, Chin. Water Wastewater, 32 (2016) 1–7.
[23] P. Schmittkopplin, N. Hertkorn, H. Schulten, A. Kettrup, Structural changes in a dissolved soil humic acid during photochemical degradation processes under O_2 and N_2 atmosphere, Environ. Sci. Technol., 32 (1998) 2531–2541.
[24] M. Schnitzer, S.U. Khan, Humic substances in the environment, Soil Sci. Soc. Am. J., 39 (1975) 186.
[25] N. Corin, P. Backlund, M. Kulovaara, Degradation products formed during UV-irradiation of humic waters, Chemosphere, 33 (1996) 245–255.
[26] P. Backlund, Degradation of aquatic humic material by ultraviolet light, Chemosphere, 25 (1992) 1869–1878.
[27] B. Allard, H. Borén, C. Pettersson, G. Zhang, Degradation of humic substances by UV irradiation, Environ. Int., 20 (1994) 97–101.
[28] D. Magallanes, J.L. RodriGuez, T. Poznyak, M.A. Valenzuela, L. Lartundo, I. Chairez, Efficient mineralization of benzoic and phthalic acids in water by catalytic ozonation using a nickel oxide catalyst, New J. Chem., 39 (2015) 7839–7848.
[29] T. Zhang, J. Lu, J. Ma, Z. Qiang, Comparative study of ozonation and synthetic goethite-catalyzed ozonation of individual NOM fractions isolated and fractionated from a filtered river water, Water Res., 42 (2008) 1563–1570.
[30] W. Huang, G. Fang, C. Wang, The determination and fate of disinfection by-products from ozonation of polluted raw water, Sci. Total Environ., 345 (2005) 261–272.
[31] S. Zehra, M. Gurol, Formaldehyde formation during ozonation of drinking water, Ozone Sci. Eng., 25 (2003) 41–51.
[32] U.V. Gunten, Ozonation of drinking water: part I. Oxidation kinetics and product formation, Water Res., 37 (2003) 1443–1467.
[33] R. Hu, L. Zhang, J. Hu, Study on the kinetics and transformation products of salicylic acid in water via ozonation, Chemosphere, 153 (2016) 394–404.
[34] M. Vincenti, F. Fasano, M.C. Valsania, P. Guarda, S.D. Richardson, Application of the novel 5-chloro-2,2,3,3,4,4,5,5-octafluoro-1-pentyl chloroformate derivatizing agent for

the direct determination of highly polar water disinfection byproducts, Anal. Bioanal. Chem., 397 (2010) 43–54.
[35] Z. Wang, Study on the Mechanism of General catalytic Ozonation of Oganic Compounds, Zhejiang University of Technology, Zhejiang, China, 2008, pp.30–35.
[36] E.A. Pillar, R.C. Camm, M.I. Guzman, Catechol Oxidation by ozone and hydroxyl radicals at the air–water interface, Environ. Sci. Technol., 48 (2014) 14352–14360.
[37] A. Papageorgiou, D. Voutsa, N. Papadakis, Occurrence and fate of ozonation by-products at a full-scale drinking water treatment plant, Sci. Total Environ., 481 (2014) 392–400.
[38] B. Jurado-Sánchez, E. Ballesteros, M. Gallego, Occurrence of carboxylic acids in different steps of two drinking-water treatment plants using different disinfectants, Water Res., 51 (2014) 186–197.
[39] H. Gallard, U. von Gunten, Chlorination of natural organic matter: kinetics of chlorination and of THM formation, Water Res., 36 (2002) 65–74.
[40] A. Li, X. Zhao, H. Liu, J. Qu, Characteristic transformation of humic acid during photoelectrocatalysis process and its subsequent disinfection byproduct formation potential, Water Res., 45 (2011) 6131–6140.