Advances in the removal of precursors of disinfection by-products by ultraviolet-coupled advanced oxidation processes

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ABSTRACT

Disinfection is an indispensable water treatment process to kill pathogens in water and prevent water-borne diseases. However, the disinfection by-products generated in the process have become the main cause of threats to human health and the ecological environment. Many studies have shown that removing the precursors of disinfection by-products is currently one of the most effective methods to reduce the production of disinfection by-products. Ultraviolet-coupled advanced oxidation processes can generate strong oxidizing free radicals through ultraviolet light activation to efficiently remove disinfection by-product precursors. It makes up for the deficiencies of traditional oxidation technology, has important significance in reducing the generation potential of disinfection by-products, and improving water quality conditions, with broad development prospects. This paper reviews the mechanisms and advances of several UV-coupled advanced oxidation processes for the treatment of disinfection by-product precursors, UV/ozone (UV/O₃), UV/hydroperoxide (UV/H₂O₂), UV/persulfate (UV/PS), UV/chlorine (UV/Cl₂) included. The treatment effects, advantages, and disadvantages of various advanced oxidation processes are compared, moreover, the future research directions and problems to be solved for the removal of disinfection by-products and precursors are proposed to promote the achievement of practical engineering application of UV coupled advanced oxidation processes.

Keywords: Ultraviolet; Ultraviolet-coupled advanced oxidation processes; Disinfection by-products; Precursor

1. Introduction

Disinfection is the key to ensuring the safe use of municipal drinking water. Chlorination disinfection reduces the incidence of water-borne diseases, for instance, cholera, typhoid fever, and dysentery [1–3]. It has the advantages of low economic cost, simple operation, and long-lasting disinfection effect, which is currently the most commonly used disinfection method in water plants. However, when the disinfectant (e.g., chlorine or chloramine) reacts with organic matter or inorganic anions (e.g., Br⁻ and I⁻) in the water, the disinfection by-products (DBPs) such as halogenated organic matter with toxicity will be generated [4].

In 1974, Dutch water chemist Rook discovered that the content of chloroform in drinking water disinfected with chlorine was higher than that in raw water, which makes trihalomethanes (THMs) the first disinfection by-product to be found in drinking water. In 1976, the National Cancer Institute of the United States classified CHCl₃ as a carcinogen based on animal studies. Chloroform is usually one of the final products of chlorination and chloramine disinfection in drinking water, which is the most frequent DBPs among THMs, because of its high stability when it coexists with chlorine and chloramine [5]. By the turn of that decade, THMs were tightly regulated in the USA at 100 µg L⁻¹ because of its potential toxicity and the risk of cancer, especially bladder cancer [6]. A second disinfection
by-product, haloacetic acid (HAA), was then tested in drinking water at levels comparable to THMs [6]. Later, halogenated acetonitrile (HAN), as a very important nitrogen disinfection by-product (N-DBPs), was also detected in chlorinated natural water [7]. The maximum contaminant levels of THMs are 80, 100, and 100 µg L\(^{-1}\) and those of HAAs are 60, 25, and 60 µg L\(^{-1}\) in the U.S., European Union, and China, respectively. Thereinto, dimethylnitrosamine (NDMA) has a 10 ng L\(^{-1}\) notification level in China, respectively. The advanced free radicals, including hydroxyl radicals (\(\cdot\)OH) and sulfate radical (\(\cdot\)SO\(_4\)), can effectively deal with difficult-to-degrade organic pollutants have stable chemical structure, a hydrophobic organic pollutants in water. However, hydrophobic organic pollutants in water. It should be noted that when the dosage of alum/UV\(_{254}\) stoichiometric dose was 180 ± 25 mg alum cm\(^{-2}\), the process could always achieve the goal of removing DBP precursors to the maximum extent. However, the above-mentioned technologies usually cannot make organic matter mineralisation thoroughly [14,15]. Besides, they can only remove large molecular weight and hydrophobic organic pollutants in water. However, hydrophilic organic pollutants have stable chemical structure, a long half-life, and obvious bioaccumulation. Traditional physical adsorption and chemical oxidation methods are usually difficult to meet the treatment requirements and may generate more toxic DBPs like bromate. The advanced oxidation processes (AOPs) proposed by Glaze and Kang [16] in the 1980s can effectively deal with difficult-to-degrade organic pollutants in water, which has been widely applied in the field of water treatment. AOPs generate different free radicals, including hydroxyl radicals (\(\cdot\)OH) and active chlorine substances (RCS) (\(\cdot\)OCl\(^{-}\), \(\cdot\)Cl\(_2\), ClO\(^{-}\)) [17–19], and then uses the strongly oxidising properties of free radicals to remove most of the contaminants that cannot be removed by conventional treatment processes. Because of its mild reaction conditions, simple operation, as well as controllability, it is gradually being applied to water treatment.

The ultraviolet-coupled advanced oxidation processes (UV-AOPs) do not require an additional solution, have broad-spectrum sterilization, will not cause secondary pollution to the treated water [20]. When used in combination with other processes, it is often synergistic, and the rate of treatment is greater than the simple addition of the two processes used alone. The free radical can oxidise the precursor of disinfection by-product in water without selectivity, since the second-order reaction rate constant ranges from \(10^{-6}\) to \(10^{10}\) M\(^{-1}\) s\(^{-1}\) [21]. UV can be divided into four bands according to wavelength: long-wave ultraviolet UVA (315–400 nm), medium-wave ultraviolet UVB (280–315 nm), short-wave ultraviolet UVC (200–280 nm) and vacuum ultraviolet VUV (100–200 nm). The photochemical reaction must meet the following two conditions: one is that the energy of the radiated photon must be sufficient to change the chemical bond of the molecule, and the other is that the radiated photon can be absorbed by the molecule. According to the second law of photochemistry, the shorter the ultraviolet wavelength is, the higher the energy of the corresponding excited state is. However, because water molecules have a strong absorbing effect on VUV, the penetration thickness of vacuum ultraviolet in the water layer is very narrow, which also limits the large-scale application of UUV in the field of water treatment. Therefore, C-band ultraviolet (UV-C) with a wavelength between 200 and 280 nm plays a major role in promoting the generation of free radicals. Previous studies have found that persulfate can be activated by ultraviolet light with wavelengths between 193 and 351 nm, and sulfate radical production increases with wavelength reduction [22]. The highest absorption rates occur in the UVC range of 200 to 254 nm. In addition to stimulating the production of free radicals in water, UVC can make thymine in the DNA structure form T-T dimers when processing algae-containing waters, thereby losing the ability to replicate to achieve the purpose of algae killing and sterilization. To a certain extent, this avoids damage to algae cell walls caused by other oxidation methods such as pre-chlorination, thereby releasing the harm of algae toxins, and effectively reduces the generation of halogenated hydrocarbon disinfection by-product precursors in water. It should be noted that although the penetration ability of UVC is weaker than that of UVA and UBV, short-term radiation may burn the skin, and long-term or high-intensity radiation can also cause skin cancer. Moreover, ultraviolet radiation equipment is affected by many limiting factors and requires high daily management, which will increase some processing costs.

2. Disinfection by-products

2.1. Classification of DBPs

Currently, more than 700 types of DBPs have been identified and reported in the literature which account for only 30% of the total number of DBPs and the species most analyzed are THMs and HAAs [23]. The known DBPs can be roughly divided into three categories: carbon-containing...
Table 1
Different national approaches to the regulation of disinfection by-products in drinking water

<table>
<thead>
<tr>
<th>DBPs</th>
<th>Caner Group (EPA)</th>
<th>General toxicity</th>
<th>WHO</th>
<th>EU</th>
<th>US EPA</th>
<th>United Kingdom</th>
<th>Malaysia</th>
<th>China</th>
<th>Japan</th>
<th>Korea</th>
<th>Australia</th>
<th>New Zealand</th>
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<td>0.2</td>
<td>0.06</td>
<td>0.06</td>
<td>0.08</td>
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<tr>
<td></td>
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<tr>
<td></td>
<td>DBCM</td>
<td>C</td>
<td>0.1</td>
<td>0.08</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
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<td>B2</td>
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<td>THMs</td>
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<tr>
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<tr>
<td>Inorganic disinfection by-products</td>
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<tr>
<td></td>
<td>Chlorate</td>
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<td>0.25</td>
<td></td>
<td>0.7</td>
<td>0.6</td>
<td>0.8</td>
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<tr>
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<td>Bromate</td>
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<td>0.01</td>
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</table>

*Sum of ratio of concentration of each of its respective guideline values should not exceed 1;
Numerical unit is mg L⁻¹;
B2 = Probable human carcinogen based upon enough data from animal studies; C = Possible human carcinogen; D = Not classified as human carcinogenic.
disinfection by-products (C-DBPs), nitrogen-containing disinfection by-products (N-DBPs), and inorganic disinfection by-products. The classification and major precursors of disinfection by-products are recorded in Table 2.

C-DBPs mainly include THMs, haloacetic acids (HAAs), haloacetaldehydes (HALs), halo ketones (HKs), etc. THMs refers to the substitution of hydrogen atoms in methane (CH₄) by halogen atoms in water, and the main products are TCN, bromodichloromethane, bromochloromethane and tribromomethane. HAAs basically include 13 kinds of DBPs, including chloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromoacetic acid (MBAA), dibromoacetic acid (DBAA), tribromoacetic acid (TBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), iodoacetic acid (MIAA), diiodoacetic acid (DIAA), chloroiodoacetic acid (CIAA) and bromoiodoacetic acid (BDCAA). 

I-DBPs (I-HAM and I-THM) [29]

Table 2
Classification of disinfection by-products and their corresponding main precursors

<table>
<thead>
<tr>
<th>Classification</th>
<th>DBPs</th>
<th>Precursors</th>
</tr>
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<tbody>
<tr>
<td>C-DBPs</td>
<td>THMs, HAAs, HALs, HKs</td>
<td>Natural organic matter</td>
</tr>
<tr>
<td>N-DBPs</td>
<td>HANs, HAMS, HNMs, N-nitrosamine</td>
<td>Dissolved organic nitrogen</td>
</tr>
<tr>
<td>Inorganic disinfection by-products</td>
<td>Bromate, chlorate, chloride, iodate</td>
<td>Halide ions</td>
</tr>
</tbody>
</table>
(fulvic acid (FA) and HA) and no-humic substances (carbohydrates, lipids, and amino acids) [37]. Since no-humic substances are usually thoroughly mineralised before disinfection due to their biodegradability. Therefore, humic substances become the prime precursor of disinfection by-products. The principal precursors of THMs are HA and other small molecular organic compounds, such as aniline, phenolic compounds, algae, and their metabolites, proteins, amino acids, etc. By comparing the physicochemical properties, components, and disinfection by-products generation potential (DBPsFP) of algae organic matter (AOM) as well as natural organic matter in the eutrophic water, Wang et al. [38] found that the DBPsFP of AOM in the eutrophic lake was higher than that of NOM, especially the formation potential of N-DBPs. Lin et al. [39] used coagulation technology to remove precursors of halogenated disinfection by-products, then found that AOM harmed the instability of DOM. The coagulant polyaluminum chloride can effectively reduce the generation potential of THMs and HAA in the absence of AOM, but the DBPsFP increases in the presence of AOM. Compounds with active vacant carbon atoms containing two meta hydroxyl groups on the aromatic ring or ketone compounds with active vacant carbons containing two meta hydroxyl groups are the most effective precursors for THMs. Humic substances like NOM in water are also the main precursor of HAAs. The concentration of HAAs is mainly determined by the composition ratio of HA and fulvic acid. Furthermore, the yield of HAAs after chlorination of HA is higher than that of the corresponding fulvic acid. Besides, the reaction of amino acids and phenol with chlorine can also produce HAAs.

It is worth noting that the natural organic matter in water has two sides to the generation of disinfection by-products in the advanced oxidation process. Although DOM is a major disinfection by-product precursor, several studies have confirmed that DOM can effectively inhibit the formation of bromate, which is a typical inorganic disinfection by-product during advanced oxidation [40,41]. The inhibitory mechanism of DOM on bromate production can be mainly explained as the consumption of intermediate products: (1) NOM directly reacts with HOBr/OBr⁻, an important intermediate product in the process of bromate production, or generates reductive free radicals to reduce the intermediate product to Br⁻ [42]; (2) DOM as a kind of free radical scavenger will consume the hydroxyl radicals in the oxidation system, break the equilibrium relationship between hydroxyl radicals and Br⁻, and cut off the generation path of bromate. Experiments by Wang et al. found that when the concentration of bromide is 100 µmol L⁻¹, adding NOM (2 mg L⁻¹) to the UV/persulfate (UV/PS) reaction system can significantly inhibit the formation of bromate and prolong the lag phase [43], which was also investigated in Luo's study [44].

Dissolved organic nitrogen (DON) and hydrophobic acids are the most active parts for the formation of THMs, CHD (chloral hydrate), and HANs [45]. It is generally believed that DON is a precursor of HANs, which primarily consists of protein, nitrogen-containing heterocyclic nucleic acid, and amino acid structure in HA. Halogenated acetonitrile products are mainly DCAN. Research has further found that the hydrophilic organic acid (HIA) in

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Classification of several typical disinfection by-products</th>
</tr>
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<tbody>
<tr>
<td>THMs</td>
<td>Abbreviation</td>
</tr>
<tr>
<td>TCDD</td>
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NOM is the prime precursor of DCAN. The main precursors of NDMA are small molecular weight (MW < 1 kDa) and large molecular weight (MW > 10 kDa) compounds of NOM [46], such as dimethylamine (DMA), diethanolamine, triethanolamine, nucleic acid, protein, etc. It is proposed that dissolved organic nitrogen compounds (e.g., dimethylamine) are the main precursors of nitrosamines [47]. Previous studies have found that pH and chloro-nitrogen ratio are the key factors affecting the reaction of dimethylamine and chloramine to produce NDMA, and the production of NDMA reaches the maximum when pH = 7 and Cl/N = 7, respectively. Compared with DON, the contribution of particulate organic nitrogen (PON) in water to the potential generation of NDMA cannot be ignored. Hu et al. [48] found that PON accounted for 12.3%~41.7% of the total bioavailable organic nitrogen in wastewater, as well as 22.0%~38.4% of the total amount of NDMA precursors. Research by Alaba et al. [49] found that it is more economical to prevent the formation of NDMA by degrading or damaging the precursors compared with degrading the already formed N-nitrosamines. The aldehydes of compounds containing acetyl functional groups have a high potential to form HAL during the disinfection process. More importantly, its reaction with free chlorine in subsequent disinfection is the principal cause of HAL formation [50].

Dissolved organic carbon (DOC), UV$_{254}$, SUVA, and total fluorescence index (TF) can be used as indicators to monitor the generation potential of DBPs [51]. The best-performing indicator SUVA is usually positively correlated with the production of THMs and HAAs [52]. This approach is based on the fact that aromatic and humic compounds exhibit higher absorption properties at 254 nm than aliphatic and non-humic substances [53]. High SUVA value indicated that the main disinfection by-product precursor NOM in the aqueous matrix was mainly composed of hydrophobic organic compounds with high molar mass, whereas low SUVA value indicated that NOM was mainly composed of hydrophilic low molar mass compounds [54]. Hua et al. [55] explored the influence of the molecular weight, fluorescence composition, and SUVA (SUVA = UV$_{254}$/DOC × 100) value of the precursor on the formation of DBPs. Experiments have confirmed that the SUVA value is a useful indicator of the monitoring of DBPs. However, when the value of SUVA is low (<2 L/mg m), DBP generation should be monitored together with the above-related properties. In addition to studying the influence of the properties of the disinfection by-product precursors on the number of DBPs, it is necessary to further evaluate the impact of water quality conditions as well as seasonal changes [32] on the toxicity risk of DBP in the future.

3. Removal of precursors of DBPs by UV-AOPs

3.1. UV/ozone

As a strong oxidant, ozone can change the molecular structure of refractory organic matter in water. It has a high treatment efficiency for PPCPs in organic wastewater. Furthermore, the degradation efficiency can reach more
than 90% [56], which can be used for decreasing the oxidative disinfection of the precursor of DBPs or trace organic compounds (TorC) [57,58]. What's more, ozone can change the reaction characteristics of disinfection by-product precursors and chlorine in the subsequent disinfection process by depending on the reaction characteristics of different reactants, to reduce the amount of disinfection by-product generation. Pre-ozonation can change the subsequent UV light transmittance and DOM's reaction characteristics to free radicals, thus reduce the negative effects of DOM on UV advanced oxidation technology [59]. Hansen et al. [60] researched the ozonation of municipal swimming pool water. They found that ozone eliminated the reactivity of dissolved organic carbon to tap water and chlorine, thereby reducing the formation rate of total trihalomethane (TTHM). When Qi et al. [57] used ozone to oxidise the organics in wastewater, they found that the potential of trihalomethane generation decreased after the initial pre-ozonation. However, it increased to varying degrees as the degree of ozonation deepened, containing relatively high content of aromatic structures. That is, SUVA254 and aliphatic wastewater organic matter will significantly increase the DBPs generation. Ozonation can also effectively alleviate the generation potential of disinfection by-products brought by AOM. Lin et al. [61] found that when the ozone dosage was 1.5 mg L⁻¹, the target DBPs formed by AOM were the least. Finally, ozonation can reduce the potential toxicity of subsequent disinfection processes by changing the structure and properties of organic compounds in water, even if the precursor of DBPs in water cannot be completely mineralised. Nguyen et al. [62] found that when the ozone dosage was 3.1 mg L⁻¹, DOC in Saigon River water was converted into biodegradable organic carbon (BDOC). Meanwhile, trihalomethane formation potential was reduced by about 45%.

The combined process of ultraviolet and ozone (UV/O₃) has a strong oxidising ability, which can remove pesticides, food additives, and other trace pollutants in the water. It not only does not require an additional catalyst but also is easy to operate. Based on advanced ozone oxidation, the addition of ultraviolet radiation can increase the production efficiency of ‘OH and improve the oxidation capacity of the reaction system [63,64]. In addition to inducing the production of ‘OH from O₃, UV radiation can also stimulate the production of other ground-state substances and free radicals that would not be generated in a single O₃ oxidation process. In acidic medium, direct O₃ oxidation is the main mechanism, H₂O₂ generated by this process may accumulate in the solution, because of the slow photodegradation rate. When pH > 7, regardless of ultraviolet radiation, free radical reaction is the main control factor, H₂O₂ quickly reacts with the remaining O₃ causing complex O₃ decomposition chain reaction to accelerate the chain reaction. The oxidation rate can be increased to 10⁻²⁻¹⁰⁶ times by combining ultraviolet radiation with ozone oxidation. It can effectively degrade the precursors of DBPs, which are primarily NOM. Petronijević et al. [65] found that the removal efficiency of NOM followed the sequence of UV/O₃ > ozonation standalone > UV irradiation standalone through the study of NOM content in groundwater and the generation potential of disinfection by-products. Cheema et al. [66] proposed that when ultraviolet radiation and ozonation were used in swimming pool water together, ozonation eliminated the reactivity of organic matter in water to chlorine oxidation and weakened the system’s demand for chlorination during disinfection, thus the generation of DBP reduced. Srithep and Phattarapatattamong [67] found that DON, as the main precursor of halogenated acetonitrile in water, could only remove 28% of its content by conventional treatment processes (coagulation, precipitation, and filtration). However, when UV/O₃ process was used, the removal rate of HAN precursors could rise to 37% when the dosage of ozone was controlled to be 5 mg L⁻¹ and the irradiation dose of ultraviolet light was 220 mJ cm⁻². Agbaba et al. [68] found that the advanced oxidation process combined with UV/O₃/H₂O₂ could more easily modify the NOM in the aqueous matrix, that is, convert it from hydrophobic to hydrophilic, and at the same time reduce the formation potential of trihalomethane by 43% and haloacetic acid by 68%.

The disadvantage of the UV/O₃ process is that ozone is chemically unstable in aqueous solutions. When the dosage of ozone in water is 3 mg L⁻¹, the half-life is only about 30 min. Besides, the stability of ozone in water is affected by the pH value. When the pH value of the solution is high, the ozone decomposition rate is faster. Second, under the same conditions, the oxidation rate of ozone on different organic substances shows a significant difference from 10⁻² to 10⁴ orders of magnitude, which will lead to a phenomenon that one substance will be completely oxidised. In contrast, the other substance will be difficult to be treated when using the process to treat the precursors of DBPs. Moreover, the content of inorganic anions in water is an important factor affecting the generation potential of various DBPs. Previous studies have shown that nitrite is the main source of nitro groups in the formation of TCNM in solutions containing humus in ozone-chlorination reactions. When ozone is used to oxidize water containing nitrates, chlorination of fulmerum results in a tenfold increase in the production of TCNM. However, when the nitrite concentration was higher (3.0 mg L⁻¹), the increase of TCNMFP was not obvious. Finally, the amount of ozone should be controlled during the application of the UV/O₃ process [69], because excessive ozone will act as a free radical quenching agent in water and react with ‘OH to generate peroxide hydroxyl radical (HO•) with weak oxidation capacity, which reduces the oxidation capacity of the whole reaction system. Beyond that, the higher ozone dose can increase the total conversion percentage of bromine to brominated disinfection by-products (Br-DBPs) and thus increase the amount of Br-DBPs in water [65]. The photolysis rate of Br-DBPs is usually higher than that of chlorinated disinfection by-products, which will generate more toxic volatile disinfection by-products during repeated chlorination under ultraviolet irradiation [70].

### 3.2. UV/hydroperoxide

The mechanisms of UV and hydrogen peroxide combined process (UV/H₂O₂) to remove the precursors of DBPs can be summarised as follows: ① Direct oxidation of ultraviolet; ② Direct oxidation of H₂O₂; ③ Indirect oxidation of decomposition of H₂O₂ into ‘OH under ultraviolet irradiation. Compared with UV/O₃, the advantages of the UV/H₂O₂ process are reflected in the following two
the production of by-products produced during UV/H\textsubscript{2}O\textsubscript{2}ing, the results show that the DOC and UV\textsubscript{254} removal rate is method dissolving organic matter in wastewater process-

to form Br\textsuperscript{–} at a very rapid rate, which is much faster than that HOB\textsubscript{r} continues to be oxidised by 'OH to form BrO\textsuperscript{2–}. On the other hand, UV/H\textsubscript{2}O\textsubscript{2} has a high-efficiency oxidation capacity [71]. The oxidation rate of different organic substances is not much different, so it is difficult for one precursor to be degraded while another precursor is not degraded. As a strong oxidant, H\textsubscript{2}O\textsubscript{2} preferentially decomposes pollutants through the phenolic ring cracking reaction [72], which can completely mineralise more refractory organic matter in water and greatly weaken the toxicity of pollutants remaining in the water. Even if complete mineralisation cannot be obtained, the UV/H\textsubscript{2}O\textsubscript{2} process can also change the properties of precursors of DBPs in water and reduce the DBPsFP. Tak and Vellanki [73] proposed that when the UV irradiation intensity was 47 mJ cm\textsuperscript{–2} min\textsuperscript{–1} and the concen-
tration was 100 mg L\textsuperscript{–1}, the removal rates of DOC and UV\textsubscript{254} in surface water could reach 64% and 87%, respectively. Compared with O\textsubscript{3}/H\textsubscript{2}O\textsubscript{2} and O\textsubscript{3} when UV and H\textsubscript{2}O\textsubscript{2} are used in combination, the hydro-

phobicity score of the effluent decreases most obviously. Simultaneously, the formation potential of trihalomethane shows the most obvious attenuation. Qian et al. [74] studied the coagulants in combination with UV/H\textsubscript{2}O\textsubscript{2} oxidation method dissolving organic matter in wastewater processing, the results show that the DOC and UV\textsubscript{254} removal rate is higher, the removal rate of 75% and 92% respectively, the acid hydrophobic material acid, alginate and hydrophilic, and hydrophobic material removal of 92%, 87%, 70%, and 39% respectively. BOD\textsubscript{5}/COD value increased from 0.1 to 0.52.

NOM has been proven to be an important contributor to the production of by-products produced during UV/H\textsubscript{2}O\textsubscript{2} treatment [75]. UV/H\textsubscript{2}O\textsubscript{2} process can damage the aromatic and soluble organic nitrogen components of NOM, so it has a good effect on controlling the precursor of N-DBPs. Sindelar et al. [76] evaluated the removal effect of UV/H\textsubscript{2}O\textsubscript{2} process on the precursor of disinfectant by-products in high NOM matrix water, the Florida Everglades, and found that UV/H\textsubscript{2}O\textsubscript{2} process was one treatment option that had shown success at reducing high levels of NOM. When the UV irradiation dose was between 21.8–22.3 J cm\textsuperscript{–2} and the H\textsubscript{2}O\textsubscript{2} concentration was 100 mg L\textsuperscript{–1}, the removal rates of UV\textsubscript{254} and DOC were about 90% and 60%, respectively. After UV/H\textsubscript{2}O\textsubscript{2} peroxidation, the production of HAN, HNM, and HAM decreased by 52.1%–83.6%, 42.9%–87.3%, and 74.1%–100%, respectively. As the water toxicity was mainly contributed by HANs, the toxicity in solution was also reduced by 24.1%–82.7% [77]. Srithep and Phattarapatmatawanong [67] also proposed that UV/H\textsubscript{2}O\textsubscript{2}/O\textsubscript{3} and UV/H\textsubscript{2}O\textsubscript{2} processes could reduce the production of HAN by 54% and 42%, respectively. During increasing the ozone dosage from 1 to 5 mg L\textsuperscript{–1}, the removal rate of HAN precursors rose slightly. Dalmacia et al. [30] achieved the maximum reduction of trihalomethane formation potential and HAAFP through the O\textsubscript{3}/H\textsubscript{2}O\textsubscript{2}/UV process. On the other hand, controlling the lower dose of UV irradiation by using UV/H\textsubscript{2}O\textsubscript{2} process resulted in the most effective reduction of HANFP. Compared with raw water, the percentage of bromide incorporation of DBPs has almost no change. The effect of UV/H\textsubscript{2}O\textsubscript{2} on the control of NDMA precursors is better than that of the UV/H\textsubscript{OCl} process [78–80]. UV/H\textsubscript{2}O\textsubscript{2} treatment after O\textsubscript{3}/BAC/MF/RO process can reduce the yield of NDMA formed after chlorination from 30 to 10 ng L\textsuperscript{–1}, the weighted toxicity of NDMA and its precursors can be controlled to the maximum extent [81]. Also as a typical precursor of nitrogen-containing disinfection by-products, the chloram-

-phenicol (CAP), UV activated H\textsubscript{2}O\textsubscript{2} preoxidation can effect-
cively reduce the concentration of DOC in water, which is an effective process to control the generation of THMs, HAN, HNM and haloacetamide (HAcAms) in water where CAP and similar precursors commonly exist [82]. Furthermore, the UV/H\textsubscript{2}O\textsubscript{2} process performed well in removing the pre-
cursors of inorganic disinfection by-products, the number of halogenated disinfection by-products was also reduced in the meantime. Compared with the oxidation of UV alone and H\textsubscript{2}O\textsubscript{2} alone, ‘OH, O\textsuperscript{•} and other free radicals generated by UV/H\textsubscript{2}O\textsubscript{2} system could accelerate the conversion of IO\textsubscript{3–} to I\textsuperscript{–} in water, thereby reducing the generation of iodine disinfection by-products [83]. Similar conclusions were confirmed again by Zhang et al. [84]. After pre-oxidation with UV/H\textsubscript{2}O\textsubscript{2}, the production of I-THMs was reduced by 23% ± 3.5%. Moreover, the production of I-THMs after chlor-

ination was positively correlated with the amount of H\textsubscript{2}O\textsubscript{2}. UV/H\textsubscript{2}O\textsubscript{2} also has the function of removing odour sub-

stances in water. When Cai et al. [85] studied the formation of odour by-products in the chlorination process of major amino acids in East Taihu Lake, they found that the forma-
tion performance of odour by-products in the controlled chlorination process was better than that of UV/PS.

Generally speaking, the hydroxyl radical content in the aqueous solution will increase with the increase of the initial dosage of H\textsubscript{2}O\textsubscript{2}. However, it should be noted that H\textsubscript{2}O\textsubscript{2} itself acts as a hydroxyl radical quencher [86]. When it is added in excess, it will react with ‘OH in the water to generate hydrogen peroxide radicals (HO\textsuperscript{2•}) with rela-

tively weak oxidising power, which ultimately reduce the oxidation capacity of the reaction system [87,88].

### 3.3. UV/persulfate

Advanced persulfate oxidation uses SO\textsubscript{4}\textsuperscript{2–} as the main active substance. Although the UV/PS system cannot directly generate ‘OH, the generated SO\textsubscript{4}\textsuperscript{2–} will react with water and hydroxide to generate ‘OH. Acid-catalyzed PS reactions will occur under acidic conditions (Reaction 1-2), which is conducive to the generation of SO\textsubscript{4}\textsuperscript{2–} with higher redox potential. When the reaction is in alkaline condi-
tion, SO\textsubscript{4}\textsuperscript{2–} and ‘OH participate in the oxidation at the same time, but when the alkalinesence is stronger, there are two kinds of free radical degradation and mutual quenching reactions (Reaction 3-5).

\[
S_{2}O_{8}^{2–} + H^{+} \rightarrow H_{2}SO_{4}^{2–}\tag{1}
\]

\[
HS_{2}O_{5}^{–} + e^{-} \rightarrow SO_{4}^{2–} + SO_{3}^{2–} + H^{+}\tag{2}
\]
UV/PS system not only has strong oxidising and non-selective ‘OH, but also SO\textsuperscript{4}•–, which is more stable in water and can oxidise difficult-to-degrade micro-polluted organic matter. The UV/PS process has strong mineralisation ability and has prominent advantages in removing the precursors of DBPs. Due to the strong activation ability and stability of PS, low concentration of persulfate can be combined with ultraviolet radiation and transition metal ions to stimulate the generation of free radicals. Studies have confirmed that when the UV irradiation dose is 6,000 mJ cm\textsuperscript{-2} and the dosage of oxidant is 1.856 µmol L\textsuperscript{-1}, UV/PS/Fe\textsuperscript{2+}, UV/PMS/Fe\textsuperscript{2+} and UV/H\textsubscript{2}O\textsubscript{2}/Fe\textsuperscript{2+} oxidation processes can achieve TOC removal rates of 62.94%, 47.10% and 44.09%, respectively [89]. When Co\textsuperscript{2+} was used as a metal catalyst, the total organic carbon (TOC) removal rate of UV/PMS at 45 min was up to 99% [90]. et al. also further confirmed that metal ions (Fe\textsuperscript{2+}, Mn\textsuperscript{2+}, Zn\textsuperscript{2+}, Cu\textsuperscript{2+}) combined with UV/PS process can promote the production of sulfate radical and other free radical substances, in which UV/PS/Cu\textsuperscript{2+} process can increase the removal efficiency of quaternary ammonium compounds in water by up to 37.6%. In my opinion, the improved effect of UV/PS combined with metal activator on the removal of disinfectant by-products and their precursors needs to be studied in the future.

Under neutral conditions, SO\textsubscript{4}•– has a higher redox potential [91,92] and a half-life of 4 s than ‘OH, which prolongs the contact time between the free radical and the contaminant to be degraded, thus improving the removal effect of the technology on the precursor of DBPs in water. In contrast, ‘OH tends to oxidise precursors through non-selective dehydrogenation and addition reactions, whereas SO\textsubscript{4}•– is more likely to targeted electron transfer reactions and is more selective than ‘OH in degrading electron-donating groups (e.g., fluorophore groups and conjugated bonds in chromophore groups). The UV/PS advanced oxidation process has strong oxidation ability in a wide range of pH changes. Under acidic conditions, the UV/PS system is dominated by SO\textsubscript{4}•– oxidation degradation of organic matter. In this case, the process has selective removal of target pollutants. Under alkaline conditions, a large amount of SO\textsubscript{4}•– is converted to ‘OH, while the degradation of target pollutants by the reaction system is dominated by the oxidation of ‘OH. Also, there are sub-radical groups generated by ‘OH and SO\textsubscript{4}•– in the reaction system [93]. Examples are CO\textsubscript{3}•– (1.78 V), k\textsubscript{KCl/paracetamol} = (2.68 ± 0.71) × 10\textsuperscript{8} M\textsuperscript{-1} s\textsuperscript{-1} [94], BrCl\textsuperscript{•–} (1.85 V) and Br\textsuperscript{•–} or Br\textsuperscript{−} (2.04 or 1.09 V, k\textsubscript{BrCl/paracetamol} = (2.1 ± 0.1) × 10\textsuperscript{8} M\textsuperscript{-1} s\textsuperscript{-1}) [95]. Table 4 summarizes the formation mechanism and reaction rate constants of the above kinds of free radicals.

The formation of DBPs can be effectively controlled by chloramine disinfection after UV/persulfate pre-oxidation. Chu et al. [5] studied the effect that when using UV/PS as a pre-oxidation process on the formation of THMs, HANs, and HNMs. They found that after chlorination disinfection process, the THMs content slightly increased, while the N-DBPs (HANs and HNMs) content was slightly reduced. Increasing the pretreatment time, HANs and HNMs content increased after reducing first, most of the C-DBPs generation increase with the increase of persulfate dose, while the amount of N-DBPs began to decrease in the persulfate dosage of 10 µmol L\textsuperscript{-1}. The study also showed that the change of pH value and the presence of nitrous compounds during the pre-oxidation process had little effect on DBPs generation. What’s more, the UV/PS pre-oxidation process could significantly control the amount of HANs production. UV/PS pre-oxidation plays a vital part in reducing the generation of halogenated disinfection by-products. UV/PS pre-oxidation of water containing β-Cyclocitral decreased the yield of post-chlorinated TCM [50]. After UV/PS pretreatment of water containing 2,4-di-tert-butylphenol and other similar phenolic compounds, the production of TCM is reduced, and the toxicity is correspondingly decreased [96]. Compared with chlorination alone, chlorination disinfection followed by UV/PS pre-oxidation decreased the production of TCM, DCAN as well as CH produced by NOM respectively by 50%, 54%, and 23%. The production of TCM and DCAN continued to decrease with the prolonging of treatment time or the increase of persulfate dose [97]. Chu et al. [98] compared the inhibitory effects of UV/H\textsubscript{2}O\textsubscript{2} and UV/PS advanced oxidation processes on the yield of DBPs of water containing free amino acids under the same UV irradiation dose and oxidant concentration. The results showed that UV/PS pre-oxidation had a better control effect on HANs, although a small amount of chloroform was generated in the post-chlorination process.

In actual water treatment, the content of different substances in water will jointly affect the removal effect of UV/PS on the precursor of disinfectant by-products. For example, the high content of natural organic matter (such as HA, mass concentration > 10 mg L\textsuperscript{-1}) in the actual water sample has a certain inhibitory effect on the treatment of organic pollutants. The unsaturated functional groups contained in natural organic matter have a certain absorption capacity for UV. Its existence will not only reduce the efficiency of UV-activated persulfate to generate free radicals, but also can compete with the target pollutants ‘OH and SO\textsubscript{4}•–. Because SO\textsubscript{4}•– is more selective than ‘OH in reaction, natural organic compounds in water can capture ‘OH more effectively. The literature suggests that the reaction rate constants of NOM with ‘OH and SO\textsubscript{4}•– are (1.39–4.53) × 10\textsuperscript{8} M\textsuperscript{-1} s\textsuperscript{-1} and (8.16 ± 0.3) × 10\textsuperscript{7} M\textsuperscript{-1} s\textsuperscript{-1}, respectively [72]. Similarly, the reaction rate constants of DOM with ‘OH and SO\textsubscript{4}•– are 2.8 × 10\textsuperscript{8} M\textsuperscript{-1} s\textsuperscript{-1} and 7.8 × 10\textsuperscript{7} M\textsuperscript{-1} s\textsuperscript{-1} [99]. In addition, the influence of inorganic anions in water can not be ignored. The reaction rate of Br\textsuperscript{−} with SO\textsubscript{4}•– is faster than that of Cl\textsuperscript{−} with SO\textsubscript{4}•–, and similar reactions are more likely to occur to generate brominated organic compounds and Br-DBPs. When the bromide ion concentration is low, the oxidant concentration is much higher than the bromide ion concentration. Once the bromide ion changes to HOBr, it will be further oxidized to BrO\textsubscript{3} immediately. Therefore, the generation rate of BrO\textsubscript{3} will accelerate with the bromide ion concentration increasing. However, when bromide ion concentration is high, the HOBr generated by bromide ion oxidation will compete with bromide ion as oxidant, resulting in a decrease in the rate of bromate formation.
It has been reported that trichloronitromethane (TCNM) tends to form during chlorination following UV/PS pretreatment, especially in the presence of nitrite. Bu et al. found that when the UV irradiation dose was 225 mJ cm\(^{-2}\) and the dosage of persulfate was 1.0 mmol L\(^{-1}\), NO\(_2^-\) of 0.05 mmol L\(^{-1}\) could cause the concentration of TCNM to yield more than 2,000 µmol L\(^{-1}\) [100]. Bicarbonate can compete with the active radicals in UV/PS system and reduce the steady-state concentration of the free radicals that react with the target pollutants. When UV/PS removed sulfamethoxypyridazine (SMP) in water, the higher persulfate dose and lower pH value reduced the amount of CF, but the formation of DCAN increased. The increase of the HA content in water significantly promoted the production of TCM and DCAN [101].

Increasing the dosage of persulfate to reduce the influent of external factors on the removal of precursors of disinfection by-products by advanced oxidation technology may result in excessive sulfate content in water. The Turkish standard recommends a sulfate concentration of 30 mg L\(^{-1}\) as the threshold level for minimal disturbance to taste. When the amount of sulfate in water exceeds this value, it can cause damage to human health and cause symptoms such as diarrhea. Therefore, the dosage of persulfate should be strictly controlled. When the sulfate content in water is found to exceed the standard, nanofiltration technology can be considered to remove it [102].

### 3.4. UV/chlorine

Both OH and Cl\(^-\) are able to be produced during the operation of the UV/chlorine (UV/Cl\(_2\)) process [103]. The selectivity of Cl\(^-\) is stronger than that of HO\(^-\), and the activity of Cl\(^-\) is higher for compounds containing rich electronic structures such as aromatic rings. Free chlorine has a higher molar absorption coefficient and quantum yield for UV light. This oxidation process has higher utilisation efficiency for UV light and also reduces the treatment cost. Some references suggest that acidic conditions are more...
favorable to the formation of ‘OH and ·Cl. When the pH is less than 7.5, the free chlorine in the solution is mainly in the form of HOCl, while ClO− is the dominant in alkaline condition. ClO− shows a stronger free radical scavenging ability than HOCl. Wang et al. [104] pointed out that UV/Cl2 may exceed UV/H2O2 according to the formation of free radical at low pH (<6). Several typical free radicals generated in UV/chlorine oxidation system and their corresponding reaction rate constants are summarized in Table 5.

UV/Cl2 advanced oxidation process is a combination of two relatively mature oxidation processes, HO• and Cl•− in the system that play a significant part in the synergistic degradation of UV and chlorine [105], which can effectively remove part of the precursor of DBPs. It has the advantages of fast degradation speed, low cost, advanced equipment, simple operation and maintenance in the later stage. By observing the performance of UV/Cl2 on the removal of NOM, it was found that the removal rates of DOC, UV254, and FI could reach 15.1%–18.6%, 80%, and 76.4%–80.8%, respectively, which were higher than that of UV alone and chlorination alone [106]. The cytotoxicity and genotoxicity of the UV/chlorine advanced oxidation process were lower than that of the UV/H2O2 advanced oxidation process, which may due to the selective destruction of RCS to cytotoxic and genotoxic DBP precursors (e.g., nitrogen-containing and aromatic DBP). The yield of total organochlorine was positively correlated with the reduction of humus fluorescence in SUVA254 and EEM volumes, indicating the decrease of both aromatic and hydrophobicity [107].

When the UV/Cl2 advanced oxidation process is used to treat raw water with high actual ammonia nitrogen content, the nitrogen-containing disinfection by-product precursors in water can be effectively degraded by controlling the ratio of chlorine dosage to nitrogen content in water. Compared with the process of chlorination alone, the UV/chlorine process can reduce the amount of chlorine addition without affecting the removal effect of total nitrogen. With the increase of Cl2/N, the content of ammonia nitrogen and TN decreases gradually. When Cl2/N ≥ 1.6, the removal rate of ammonia nitrogen by the UV/chlorine process was close to 100%. When Cl2/N < 1.6, the degradation rate of TN by UV/chlorine process is about 30% higher than that of chlorination alone. It was found that the removal efficiency of PPCPs by the UV/chlorine process was 5%–7% higher than that by UV/H2O2 process in water with high ammonia concentration (3.14 mg N/L) and the generation rates of CH and HAN were also reduced [108]. However, recent studies have shown that high concentration of ammonia will increase the formation of TCNM in the chlorination process after UV/Cl2 process, which needs to be paid attention to in the subsequent studies [109].

What is noteworthy is that chlorine is susceptible to the effects of water quality components to produce DBPs with biological and genetic toxicity [110]. When using the UV/monochloramine process to degrade carbamazepine in water, it was found that more DBPs were produced in filtered water as the substrate than in deionised water and potable water plant influent. The corresponding reaction rate constant increased with the increase of NH2Cl dosage and was influenced by bicarbonate and NOM in water. Nitrogen-containing disinfection by-products were observed to decrease, but the formation potential of TCM increased [111]. Compared with chlorination alone, the UV/chlorine process promotes the formation of haloacetic acid as well as chloral hydrate when degrading NOM in water. The adsorbable organohalogen (AOX) generated by NOM in the UV/chlorine advanced oxidation process is 0.8 times higher than that generated by chlorination alone. At the same time, the cytotoxicity was 1.7 times as high as that generated by chlorination alone [106]. Liu et al. [112] found that in the process of UV/chloramine removal of NOM, the formation of DBPs was the highest in water containing HA, followed by FA and AOM. The addition of 1 mg L−1 bromide to the UV/chlorine process can significantly increase the formation of Br-DBPs and the total cytotoxicity and genotoxicity of DBPs [109]. Similar conclusions have been obtained by Gao et al. Due to reactive halogen species and free halogen conversion, bromide and iodide can significantly affect the degradation of HA and AOM and the formation of DBPs in the UV/Cl advanced oxidation process [113]. Dong et al. [114] and Gao et al. [113] also pointed out that when UV/Cl2 process was used to treat bromine-containing water and water containing AOM,

### Table 5

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Rate constant</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cl2 + H2O → HOCl + HCl</td>
<td>k = 3.84 × 10^{-5} M^{-2} L^{-1} s^{-1}</td>
<td>[132]</td>
</tr>
<tr>
<td>2</td>
<td>HOCl + hv → HO• + Cl•−</td>
<td>(1.3 ± 0.3) × 10^{5} M^{-1} s^{-1}</td>
<td>[133]</td>
</tr>
<tr>
<td>3</td>
<td>OCl− + hv → O•− + Cl•−</td>
<td>(9 ± 0.13) × 10^{9} M^{-1} s^{-1}</td>
<td>[133,134]</td>
</tr>
<tr>
<td>4</td>
<td>O•− + H2O → HO• + HO−</td>
<td>1.8 × 10^{8} M^{-1} s^{-1}</td>
<td>[135]</td>
</tr>
<tr>
<td>5</td>
<td>Cl•− + Cl2 → Cl2</td>
<td>6.5 × 10^{8} ~ 2.1 × 10^{9} M^{-1} s^{-1}</td>
<td>[136]</td>
</tr>
<tr>
<td>6</td>
<td>HO• + HOCl → H2O + ClO•</td>
<td>2.0 × 10^{9} M^{-1} s^{-1}</td>
<td>[19]</td>
</tr>
<tr>
<td>7</td>
<td>HO• + OCl− → HO− + ClO•</td>
<td>8.8 × 10^{8} M^{-1} s^{-1}</td>
<td>[19]</td>
</tr>
<tr>
<td>8</td>
<td>HO• + Cl2 → ClO2</td>
<td>4.3 × 10^{7} ~ 1.8 × 10^{8} M^{-1} s^{-1}</td>
<td>[19]</td>
</tr>
<tr>
<td>9</td>
<td>Cl•− + H2O → ClO•− + H•</td>
<td>3 × 10^{7} ~ 1.8 × 10^{8} M^{-1} s^{-1}</td>
<td>[137]</td>
</tr>
<tr>
<td>10</td>
<td>Cl2 + H2O → ClO•− + Cl−</td>
<td>24 M^{-1} s^{-1}</td>
<td>[136]</td>
</tr>
<tr>
<td>11</td>
<td>Cl2 + HO• → ClO•− + Cl−</td>
<td>7.3 × 10^{7} ~ 4.5 × 10^{8} M^{-1} s^{-1}</td>
<td>[132]</td>
</tr>
</tbody>
</table>
by-products of bromination disinfection increase with bromide ion concentration, so more attention should be paid.

4. Comparison of UV-AOPs on the removal of DBPs and their precursors

Through the above description of the mechanisms and advances of different UV-AOPs, the free radical generation mechanism of each process and the redox potential of the main free radicals in different systems are summarised in Table 6 and Fig. 2.

By comparing the treatment effects of the above UV-AOPs on DBPs and their precursors (Tables 6 and 7), it is found that compared with the traditional oxidation technology, the UV-AOPs has many advantages such as high oxidation efficiency, simple operation, mild reaction conditions, wide applicability and so on, which make up for the deficiencies of the traditional oxidation technology. UV-AOPs have great advantages in removing DBPs and their precursors, but they all have some disadvantages, which need to be further optimised in the later application process. According to the information provided in Tables 7 and 8, UV/H2O2 is an advanced oxidation process that is green, environment-friendly, and does not produce secondary pollution. The treatment process only requires H2O2 feeding equipment and UV lamp source, and there is no requirement for temperature and pressure. The process has a high removal rate of chloride-containing aromatic fatty acids, and in particular, it has a good effect on the control of odour by-products. The UV/O3 and UV/PS processes have strong oxidation ability, which can oxidise microbial metabolites with unsaturated double bonds and difficult-to-degrade organic pollutants in water. It can effectively avoid the degradation is not complete and in the subsequent process to generate more toxic DBPs. UV/O3 and UV/Cl2 are easily affected by water quality components and generate other kinds of DBPs with certain risks.

5. Conclusion and prospect

In this paper, the advances of UV-AOPs for removing precursors of DBPs in water was reviewed. The conventional treatment process is usually unable to completely mineralise the pollutants, and the treatment effect is not good, but also produces DBPs with a “tri-causing” effect. UV-AOPs degrade pollutants in water through direct photolysis and indirect oxidation of various free radicals, which makes up for the deficiency of traditional oxidation treatment and has obvious advantages in removing the precursors of DBPs.

Given the future research on UV-AOPs, it is urgent to solve the application of different influencing factors to UV-AOPs. For example, water quality changes will affect the ultraviolet transmittance, reducing the treatment efficiency, to provide a theoretical basis for UV-AOPs to remove pollutants in actual water.

5.1. Develop better techniques for removing DBPs and their precursors

The UV irradiation dosage used in the currently UV-AOPs usually has no significant effect on the removal of the DBPs produced in water, due to the low reaction rate constant (~10⁸ M⁻¹ s⁻¹) of the halogenated disinfection by-products with ‘OH [3]. The new UV-based reduction process (UV-ARP), which effectively breaks the C-X bond by introducing reactive-reducing species [115], is particularly suitable for treating halogenated disinfection by-products that have been generated. Also, biological filtration, membrane technology (RO, NF, MF), enhanced coagulation, as well as magnetic ion exchange technology are effective methods for removing the precursors of DBPs [116]. Eliminating pre-chlorination, optimising chlorine dosage through disinfection standards, and switching to chloramine for secondary disinfection can reduce the production of DBPs [1].

5.2. Analysis of degradation pathways and product toxicity

The conversion kinetics, mechanism, and toxicity of DBP deserve further study. The structural groups of the precursors of typical DBPs in real water are studied to explain the degradation laws based on UV-AOPs. In the process of oxidation, attention should be paid not only to the precursors of DBPs but also to the toxicity of intermediate products.

Table 6
Formation mechanism of free radicals in different UV-AOPs

<table>
<thead>
<tr>
<th>Process</th>
<th>Mechanism</th>
<th>Redox potential ( E^{\circ}<em>{\text{H}</em>{2} \text{O}} )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV/O3</td>
<td>( \text{O}_3 + \text{H}_2 \text{O} + \text{hv} \rightarrow \text{O}_2 + \text{H}_2 \text{O}_2 ) \n( \text{H}_2 \text{O}_2 + \text{hv} \rightarrow 2\text{OH} )</td>
<td>( 2.7 \text{ V} )</td>
<td>[63]</td>
</tr>
<tr>
<td>UV/H2O2</td>
<td>( \text{H}_2 \text{O}_2 + \text{hv} \rightarrow 2\text{OH} )</td>
<td>( 2.7 \text{ V} )</td>
<td>[138]</td>
</tr>
<tr>
<td>UV/PS</td>
<td>( \text{SO}_4^{2-} + \text{hv} \rightarrow 2\text{SO}_4^{2-} ) \n( \text{SO}_4^{2-} + \text{H}_2 \text{O} \rightarrow \text{HSO}_4^{-} + \text{OH} ) \n( \text{SO}_4^{2-} + \text{OH} \rightarrow \text{SO}_4^{2-} + \text{OH} )</td>
<td>( 2.5 \sim 3.1 \text{ V} )</td>
<td>[139,140]</td>
</tr>
<tr>
<td>UV/Cl2</td>
<td>( \text{HOCl} + \text{hv} \rightarrow \text{H}_2 \text{O} + \text{Cl}^{-} ) \n( \text{Cl}^{-} + \text{Cl}^{-} \rightarrow \text{Cl}_2^{\cdot} )</td>
<td>( 2.2 \sim 2.4 \text{ V} )</td>
<td>[108,141]</td>
</tr>
</tbody>
</table>

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Table 8
Comparison of effects of different UV-AOPs on DBPs

<table>
<thead>
<tr>
<th>Process Condition</th>
<th>Performance</th>
<th>Advantage</th>
<th>Disadvantage</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>UV/O3</strong></td>
<td>UV intensity: 0.58 mW cm⁻²; O₃ dosage: 1.0 mg L⁻¹; pH: 7; [NPYR]₀ = 1 µmol L⁻¹; reaction time: 120 s</td>
<td>N-nitrosopyrrolidine was completely degraded at 120 s</td>
<td>This method has a simple procedure, mild reaction condition</td>
<td>[143,144]</td>
</tr>
<tr>
<td><strong>UV/H₂O₂</strong></td>
<td>UV dose: &lt;200 mJ cm⁻²; H₂O₂ dosage: 10 mg L⁻¹; pH: 7.4; [DCL]₀ = 3 mg L⁻¹; [TCS]₀ = 2 mg L⁻¹</td>
<td>Removal rate of DCL and TCS reached 80%</td>
<td>High removal rate of chlorinated aromatic fatty acids and control the formation of odor by-products</td>
<td>[85,145]</td>
</tr>
<tr>
<td><strong>UV/PS</strong></td>
<td>UV intensity: 0.1 mW cm⁻²; PS dosage: 200 µmol L⁻¹; pH: 7; reaction time: 60 min</td>
<td>Dibutyl phthalate (DBP) removal rate was 90.6% after 30 min</td>
<td>Removal of halogenated organic compounds can be converted to halogen active compounds at neutral pH</td>
<td>[146]</td>
</tr>
<tr>
<td><strong>UV/Cl₂</strong></td>
<td>UV dose: 520 mJ cm⁻²; free chlorine dosage: 30 mg L⁻¹; pH: 7</td>
<td>Values of UV₂₅₄ decreased from 0.091 to 0.06 cm⁻¹</td>
<td>Free chlorine has a higher molar absorption coefficient and quantum yield to ultraviolet light, low operating cost</td>
<td>[106]</td>
</tr>
</tbody>
</table>
Toxicity tests should be carried out at different stages of treatment, and the toxicity of residual degradation products should be evaluated. Toxicity of degradation products to aquatic organisms (such as green algae, fish and daphnia) is mainly based on the structure–activity relationships (SARs), and can be tested using the ECOSAR program, which is freely available by the U.S. Environmental Protection Agency (US EPA) [117,118]. The cytotoxicity of various DBPs was evaluated by the ratio of the production potential of disinfection by-products (in dosages) to the LC50 value of the corresponding Chinese hamster ovary (CHO) cells [119].

5.3. Look for a more suitable oxidant

The results show that the removal effect of UV254 and DOC in water matrix with high NOM content by sodium percarbonate and sodium perborate in combination with UV is similar to that of UV/H2O2 [76]. To develop new low-cost, green and environmentally friendly oxidants with higher utilisation rate to ultraviolet light, to produce active substances such as free radicals with stronger oxidation capacity, and to establish the reaction rate constant of related free radicals (such as CO3•–, HPO4•–,·SO3–) with DBPs and precursors. Control the dosage of oxidants to achieve the best treatment effect while taking into account the economy.

5.4. Establish field-proven operating procedures

Field experiments are required to validate the practical application of the results in water supplies [113]. Future research should pay more attention to the establishment of field-proven operating procedures, from laboratory static tests to pilot tests, and to increase the engineering application value of the UV-AOPs. Systematic investigation and analysis of DBPs and their precursors in water are carried out, and a technical system for the generation and control of DBPs in actual drinking water is constructed to reduce the occurrence of undesirable by-products and side reactions in the real water matrix.

References


S. Szczuka, N. Huang, J.A. MacDonald, A. Nayak, Z. Zhang, W.A. Mitch, New insights into dimethylamine formation during UV/


