Photochemical degradation characteristics of alga-sourced dissolved organic matter in Chaohu Lake, China

Guolian Li, Lu Li, Kang Song, Zhiwei Yuan, Shuguang Zhu, Jin Zhang and Fazhi Xie

ABSTRACT

Abundant algae-sourced dissolved organic matter (A-DOM) is produced during algal blooms in eutrophic lakes. Natural-light-driven photodegradation plays an important role in A-DOM function and its migration in aqueous systems. The photodegradation performance of A-DOM extracted from Chaohu Lake was tested and characterized under UV-A, UV-C irradiation, and dark condition, and the photochemical degradation characteristics and molecular weight changes of A-DOM during degradation were analyzed. A-DOM mainly includes four EEM-PARAFAC components, namely, C1 (protein-like tryptophan), C2 (protein-like tyrosine), C3 (long-wave humus), and C4 (short-wave humus). After irradiation for 168 h under UV-C, the protein-like components C1 and C2 had the highest fluorescence intensity reduction of 95.4% and 100%, respectively. The fluorescence intensities of fulvic-like components, namely C3 and C4, increased. The absorption coefficients ($A_{355}$) of A-DOM were decreased by 84.46%, 70.83%, and 52.98% with UV-A, UV-C irradiation, and dark condition, respectively. The degradation reaction of C1 and C2 fitted with the first-order kinetic equation with a half-life of 21.59–83.51 h. The SUVA$_{254}$ value decreased under UV irradiation and increased under dark condition, which is in accordance with the change of molecular weight results. The A-DOM photochemical reaction was driven by UV light irradiation, and the humification rate and molecular weight decreased.

Key words | alga-sourced dissolved organic matter, Chaohu Lake, fluorescence dissolved organic matter, photochemical degradation, UV irradiation

HIGHLIGHTS

- Alga-sourced dissolved organic matter (A-DOM) photodegradation was investigated.
- Color DOM was completely degraded under UV-A irradiation.
- UV could facilitate humus degradation.
- Dark-condition biodegradation could enhance the A-DOM humification.
- Chaohu Lake A-DOM has very strong photochemical degradation activity.

INTRODUCTION

As an important carbon source in aqueous systems, dissolved organic matter (DOM) is an important component of the global carbon cycle. Increase in DOM release in water systems could present challenges to drinking water treatment systems, pose an increment in disinfection by-product generation potential, and decrease drinking water biostability (Pivokonsky et al. 2016; Naceradska et al. 2019). It could also increase the risk of odors and toxins from the
drinking water treatment point of view (Ly et al. 2017). A substantial amount of DOM in natural water contains chromophores, such as the benzene ring, carboxyl, hydroxy, and carbonyl (Chin et al. 1994) and can absorb specific wavelengths of sunlight and produce a series of active radicals, such as hydrated electrons, singlet oxygen, and hydroxyl radicals (Page et al. 2011). These active radicals play important roles in the photochemical transformation of pollutants in natural water (Tai et al. 2012). Therefore, solar-irradiation-driven photodegradation is crucial to DOM properties and geochemical activity changes (Kieber et al. 1990; Miller & Zepp 1995). Dalzell et al. (2009) analyzed DOM photodegradation in estuary waters and found that photodegradation decreases the absorbance and molecular weights of different DOM sources, and the relative abundances of different compounds change. Cheng & Guo (2009) investigated the photodegradation of DOM in the seawater of Xiamen Bay and found that the humic-like fluorescence intensity of terrestrial source DOM was the highest. Chen et al. (2012) analyzed the photodegradation characteristics of Chlorella-sourced DOM and found that the half-life of its fluorescence components was only 1.6–5.0 days. A-DOM has strong photochemical degradation activity, and DOM can be produced during cyanobacterial growth and algal cell degradation in eutrophic waters and enriched A-DOM (Lee & Rhee 1997; Bittar et al. 2013a, 2015b).

Chaohu Lake has a traditional agriculture-based economy and over a hundred-year history of cultivation, located in east China (Tang et al. 2010). The Chaohu Lake eutrophication problem has existed for decades due to increasing environmental contamination. The wastewater inflow from source and non-source pollution has posed a heavy burden on the lake’s self-purification capacity (Fang et al. 2019). The inflow of nutrients has increased the algal bloom risk, and the release of A-DOM also can increase. Increased A-DOM in the Chaohu Lake can present considerable challenges to surrounding waterworks and water supply systems. Hence, A-DOM photodegradation performance and component change during the process should be investigated.

After a two-decade treatment, the Chaohu Lake eutrophication state was highly mitigated. The water quality including total nitrogen and total phosphorus was reduced 68.8% and 75.1% in 2018 as compared with the highest value in 1995. Water supply safety was maintained in east Chaohu Lake. The algal bloom still occurs every year, covering 44.5% and 58.0% of the Chaohu Lake in 2017 and 2018, respectively. The eutrophication state has been mitigated while the algal bloom state has been more serious in recent years. The internal and external pollution control has not been enough in the Chaohu Lake (Chen et al. 2020). In some areas of the Chaohu Lake, a high concentration of algae accumulated with a thickness over 10 cm. The high accumulation of algae could finally cause algae death and generate organic debris, with an ‘algal regrowth – algal bloom – death of algae – algae dormant’ growth cycle, and a large amount of algae dissolved organic matter could be generated and become a main source of lake DOM. A large portion of external polymer substrates such as polysaccharides and proteins, refractory organic matter such as humus and other small molecular acids could be generated during cyanobacteria growth and decline. The DOM in Chaohu Lake sediment was mainly based on biogenic sources, and the growth cycle of algae significantly affects the source and properties of DOM in Chaohu Lake (Zhang et al. 2009; Villacorte et al. 2015; Zhu et al. 2020).

In this study, the photodegradation of Chaohu Lake A-DOM was investigated. The A-DOM used was directly extracted from Chaohu Lake. Fluorescence excitation emission matrix combined with parallel factor analysis (PARAFAC) was used for the analysis of different components of A-DOM changes during degradation (Li et al. 2012). Kinetic study was used for the analysis of different components of A-DOM changes under different irradiation conditions. Furthermore, the degradation characteristics of A-DOM under simulated biological or photo-irradiation conditions were explored. This study can provide information about Chaohu Lake A-DOM changes under nature light irradiation.

MATERIALS AND METHODS

Study area

Chaohu Lake (30°58′–32°06′N, 116°24′–118°00′E) is one of the top five largest freshwater lakes in China with a water surface area of 780 km² and water storage capacity of 2.07 billion m³. It is located in the center of Anhui province, covering five cities and serving a high population of more than
9.65 million (Figure 1). Chaohu Lake is a typical large, shallow and subtropical lake, and the average water depth is 2.69 m. The average annual temperature and rainfall in this area are 15 to 16 °C and 1,100 mm. Chaohu Lake is subjected to a transitional subtropical to warm temperate monsoon climate (Tang et al. 2010; Huang et al. 2015).

**Figure 1** Study area – Chaohu Lake.

**Extraction of A-DOM**

Fresh microcystis liquid was first collected and washed by ultrapure water and then frozen for 24 h in a refrigerator (−20 °C) by a freezing and thawing method. Later, samples were thawed under room temperature and then frozen
again. This process was repeated three times for the disruption of cyanobacterial cells and acceleration of algal cell death. Algal suspension was then collected and centrifuged for 10 min at 10,000 rpm, the supernatant was then filtered using a 0.45 μm GF/F filter, and the filtrate was extracted A-DOM solution. To assure the validity of the samples in the test process, the A-DOM was used directly after extraction (Chen et al. 2016).

Photodegradation experiment

The extracted A-DOM was diluted to approximately 20 mg/L in a quartz bottle. Afterwards, the A-DOM was irradiated under two ultraviolet radiators (UV-C and UV-A, 20 W) and in the dark (the quartz bottle was wrapped in aluminum foil). Samples were collected at a fixed interval and filtered using a 0.45 μm filter for spectral analysis (Liu et al. 2019). The degradation experimental setup is shown in Figure 2.

Equilibrium osmotic membrane method

Molecular weight changes during A-DOM degradation were analyzed using the equilibrium osmotic membrane method. Different molecular weights (3,500, 7,000, and 10,000 Da) of penetration bags were used, and 400 mL of deionized water was added as external solution into beakers (500 mL). During the experiment, 10 mL of solution was collected from A-DOM samples under three degradation conditions at the beginning and end of experiments and stored in different penetration bags. Bags were kept tight by using built-in clips for the prevention of solution leakage. All the bags were placed in beakers for the completion of external solution immersion. The surface layer of the beakers was covered with polyethylene plastic bags, which prevented the evaporation of external solution. The experiment was carried out under low temperature (4 °C) and dark conditions to inhibit the degradation of A-DOM. The external solution was stirred irregularly to ensure effective effusion. In this experiment, the osmotic equilibrium time was set as seven days. After achieving equilibrium, the DOM infiltrated into the external solution was diluted. Residual DOC concentration in the internal solution was measured (Yin et al. 2019).

Fluorescence spectroscopy

A Hitachi F-7000 fluorescence spectrophotometer was utilized. The testing parameters were set as follows. PMT voltage = 700 V. The ranges of scanning wavelengths were set as excitation wavelength (Ex) = 200–450 nm and emission wavelength (Em) = 280–550 nm. The step lengths of excitation and emission slits were both 5 nm. The scanning speed was 2,400 nm/min. Response time was set to automatic, and the influences of Milli-Q blank water were eliminated. The expressions of three-dimensional fluorescence spectral characteristics were influenced by scattering peaks in 3D-EEMs. During scanning, a 290 nm edge filter was added at the side of the emission wave to eliminate second-order Rayleigh scattering (Li et al. 2018, 2020).
Ultraviolet spectrum and DOC analysis

A Shimadzu UV-1800 ultraviolet–visible spectrophotometer was utilized. The range of wavelength scanning was 200–400 nm, and the interval of scanning wavelength was 2 nm. The testing method was introduced by Korshin et al. (1997). The absorbance value of DOM at 355 nm was tested and recorded at \( A_{355} \). The specific ultraviolet absorbance (SUVA) value of the samples was calculated according to the ultraviolet absorption coefficient at 254 nm and dissolved organic carbon (DOC) content, which was determined using a total organic carbon analyzer (Elementar, Germany). The ultraviolet absorption coefficient was defined as follows:

\[
a_\lambda = 2.303 \cdot \frac{A_\lambda}{L}
\]

where \( a_\lambda \) is the ultraviolet absorption coefficient at the wavelength of \( \lambda \) nm (m\(^{-1}\)), \( A_\lambda \) is the absorbance at \( \lambda \) nm, \( L \) is the optical path of the cuvette (m), and \( A_{355} \) represents the contents of C-DOM (Color-DOM) in the solution.

RESULTS AND DISCUSSION

Three-dimensional fluorescence spectral analysis of A-DOM photodegradation

The four fluorescence components in the original algae solution were analyzed using the PARAFAC model (Table 1). The protein-like components were mainly composed of amino acids with fluorophores (e.g., tryptophan and tyrosine), peptides, and proteins. The fulvic-acid-like components, including fulvic acid and humic acid, might have come from the residual fragments of algal cells at freezing-thawing cycles. The analysis results of the A-DOM collected from Chaohu Lake were similar to those of the DOM collected from surface water in the growth region of planktonic algae in Taihu Lake (Hu et al. 2011).

The extracted A-DOM solution was degraded under three conditions. The spectral characteristics of A-DOM solution after degradation for 12, 24, 48, 96, 120, and 168 h are shown in Figure 3. In A-DOM, the initial fluorescence intensities of C1 and C2 were 3,823.6 and 2,800, respectively. The fluorescence intensities of the four components decreased after 168 h of UV-A irradiation. The degradation speed was high in the first 48 h. The fluorescence intensity of C1 decreased by 43.66% after 48 h and further decreased by 79.53% at the end of the experiment. Similarly, the fluorescence intensity of C2 decreased by 41.77% after 48 h and 86.40% at the end of the experiment. The fluorescence intensity of C3 decreased from 517.58 to 152.48. The degradation of C4 was slow, and its fluorescence intensity decreased from 268.95 to 161.37 possibly because C4 is a short-wave humus and has a high molecular weight and aromaticity. Therefore, C1 and C2 are sensitive to light in the UV-A region and easily degraded under UV-A irradiation. This result is in accordance with previous results (Bittar et al. 2015a, 2015b).

The results of A-DOM degradation under 254 nm UV-C light irradiation indicated that C2 was almost totally removed after 120 h of continuous degradation. Meanwhile, the fluorescence intensity of C1 decreased by 87.75% from 3,823.6 to 468.4. The fluorescence intensity of C3 increased from 512.2 to 713.6 in the first 72 h but decreased to 400.2 as irradiation continued. The main emission wavelength of UV-C concentrates at 254 nm and the excitation wavelengths of C1 and C2 were close to the wavelength range of UV-C, resulting in increased irradiation and quick degradation of C1 and C2. The fluorescence intensity of C4 increased in the first 96 h to 176.89% of the initial value. C3 has two peaks (Ex/Em = 275, 365/445 nm). The peak (Ex = 275 nm) at Ex/Em of 275/445 nm was in the wavelength section of UV-C, and the fluorescence intensity of C3 declined in the late stage. C4 tended to have a single peak (Ex/Em = 320/400 nm), and the peak Ex (320 nm)
Figure 3 | The fluorescence excitation emission matrix (FEEM) of A-DOM degradation under (a) UV-A, (b) UV-C and (c) black at irradiation time 12, 24, 48, 96, 120 and 168 h, respectively.
was in the UV-A region. Under photodegradation conditions, humus with a high molecular weight increases coplanarity structures, and interaction with other substance molecules in the solvent decreases. This will present a highlight of the fluorescence signal, and response increases accordingly (Fu et al. 2006). As a result, the fluorescence intensity of C4 increased in this study. According to the UV-C degradation contour map, the peak of the humus zone decreased, and the maximum point of the peak developed offsets, which could have been caused by the new substances produced. This result is in accordance with the degradation characteristics of DOM in Taihu Lake under ultraviolet irradiation reported by Zhang (2013). Long-wave humus might transform to short-wave humus during degradation (Lapiere & Del Giorgio 2014).

According to the biodegradation results under dark conditions, the fluorescence intensity of C1 decreased by 67.79%, from 3,823.6 to 1,231.4, and that of C2 decreased by 57.67%, from 2,800.5 to 1,185.3. Hence, the microbes seemed to use protein-like components with high utilization rates, which is in accordance with the results reported by Bai et al. (2015) for the degradation characteristics of DOM in Weishan Lake. The contributions of different components to total fluorescence intensity reduction during degradation under UV-A light irradiation were compared (Figure 4). The initial contribution rates of C1, C2, C3, and C4 were 51.63%, 37.82%, 6.91%, and 3.63%, respectively, and those at the end of the experiment were 54.15%, 25.13%, 10.09%, and 9.3%, respectively.

Under UV-C irradiation, the contribution of C1 and C2 to the total fluorescence intensity in the initial A-DOM was approximately 90%, whereas the contribution of C3 and C4 was approximately 10%. With the degradation of protein-like components, the contribution of C3 and C4 increased from 6.92% to 48.51% and from 3.63% to 30.38%, respectively. UV radiation significantly decreases the bioavailability of DOM (Obernosterer et al. 2001). This condition might be caused by the photodegradation of bioavailable organic matter or cross-linking reaction of organic matter that produces humus, which cannot be easily used by microorganisms (Kieber et al. 1997).

Under dark degradation, the contribution of C1 was approximately 15% higher than that of C2 in the beginning. The contribution of C1 was equal to that of C2 after 168 h. In general, the utilization of C1 by microorganisms is higher than that of C2. The fluorescence intensities of C3 and C4 increased continuously in the first 24 h, and these values were 133.27% and 107.71% of the initial value. This value decreased slightly afterward possibly because of the byproducts generated by the microbes (Kramer & Herndl 2004). Given the abundant degradation of protein-like components, the relative proportions of C3 and C4 increased from 6.92% and 3.63%
to 14.37% and 6.91% at the end of experiment. In this study, the degradation speed in dark conditions was slower than that from other literature, and this condition might be related to the low microorganism content or relatively high initial A-DOM concentration.

The degradation behaviors of DOM with different sources and compositions can be varied. The degradation characteristics of DOM from different sources were compared comprehensively (Table 2). Humus in soils has a high molecular weight, complicated structure, high content of phenolic groups, low proportion of carboxyl and color groups in total DOC content, and poor light sensitivity. Microorganism degradation occurs slowly with low bioavailability. DOM in natural water has higher light sensitivity than that in soil. The protein-like component in the water of Huangpu River is higher than 90%. Algal bloom occurs in Zhushan Bay, Taihu Lake in the whole year. Thus, the proportion of protein-like fluorescence peak reached 68.1%.

**FDOM (fluorescent dissolved organic matter) and DOC contents during degradation**

Protein-like components account for a large proportion in A-DOM, and the degradation of A-DOM under the three working conditions increased quickly in the first 48 h (Figure 5(a)). The final total degradation proportions of A-DOM under UV-A, UV-C, and dark conditions were 79.53%, 88.86%, and 59.01%, respectively. The highest degradation occurred in the UV-C irradiation condition. Under UV-A irradiation, the fluorescence intensities of the four components did not increase in the whole degradation period, indicating the complete degradation of the four components of A-DOM under UV-A irradiation. The total fluorescence intensity did not decrease after 120–168 h under UV-C irradiation. According to the three-dimensional fluorescence spectra, the two independent maximum peak points of humus had a gradual offset, and the fluorescence intensity declined, indicating that new substances causing fluorescence signals were produced. Under dark conditions, the total fluorescence intensity of A-DOM abruptly decreased in the first 48 h, but the reduction decelerated gradually. This condition reflects that the microorganisms utilized A-DOM during degradation. However, the degradation had a stagnation behavior from 48 to 96 h, and this condition might be caused by the strengthened fluorescence signal due to the by-products of humus. Under this circumstance, the utilization rate of microorganisms was close to the production rate of by-products. The degradation rates after 144–168 h increased again in a small range, and this condition might be attributed to the use of macromolecular substances by microorganisms.

Under different light conditions, the changes of DOC content in A-DOM samples are shown in Figure 5(b). The total degradation rates under UV-A, UV-C, and dark conditions were 51.7%, 62.8% and 44.8%, respectively. Owing to UV irradiation, the DOC content significantly decreased. This condition occurred possibly because DOM absorbs photons to produce excited-state energy, thereby

**Table 2 | The degradation character of DOM from various sources**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Light source</th>
<th>Time (h)</th>
<th>FDOM degradation rate (%)</th>
<th>DOC degradation rate (%)</th>
<th>pH</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Huangpu River</td>
<td>UV (11 W)</td>
<td>24</td>
<td>95</td>
<td>7–36</td>
<td>–</td>
<td>Ma et al. (2014)</td>
</tr>
<tr>
<td>Haicao district – Hainan</td>
<td>Spectronics EB-180C (8 W)</td>
<td>120</td>
<td>44.15</td>
<td>54.08</td>
<td>–</td>
<td>Wu et al. (2015)</td>
</tr>
<tr>
<td>Heko district – Hainan</td>
<td></td>
<td>120</td>
<td>54.03</td>
<td>28.86</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Aquaculture area – Hainan</td>
<td></td>
<td>120</td>
<td>43.64</td>
<td>66.89</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Zhushan Bay – Taihu</td>
<td>Mercury lamp (18w)</td>
<td>312</td>
<td>91.54</td>
<td>59.58</td>
<td>7.61–8.11</td>
<td>Zhang (2015)</td>
</tr>
<tr>
<td></td>
<td>Visible light (18 W)</td>
<td></td>
<td>60.8</td>
<td>26.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Black</td>
<td></td>
<td>72.75</td>
<td>49.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface soil in Dianchi</td>
<td>Mercury lamp (20 W)</td>
<td>84</td>
<td>27.08–44.32</td>
<td>7.41–9.35</td>
<td>5.97–6.48</td>
<td>Li (2017)</td>
</tr>
<tr>
<td></td>
<td>Mercury lamp (36 W)</td>
<td></td>
<td>41.36–62.44</td>
<td>10.43–16.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-DOM</td>
<td>UV-A (20 W)</td>
<td>168</td>
<td>79.52</td>
<td>51.72</td>
<td>7.29</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>UV-C (20 W)</td>
<td></td>
<td>88.86</td>
<td>62.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Black</td>
<td></td>
<td>59.01</td>
<td>44.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
decomposing macromolecular matter into micromolecular products (Glaeser et al. 2010; Liu et al. 2020). The UV irradiation process could produce reactive oxygen species (ROS), such as hydroxyl radicals (·OH), and other strong oxidizing agents. Those ROS lead to the photodegradation of A-DOM (Alvim et al. 2020). The best degradation performance was observed under UV-C irradiation, because A-DOM contains DOC components that can be degraded directly. Similar substances might be degraded or transformed initially under UV-C irradiation.

**UV spectral characteristics of A-DOM degradation solution**

The abundance of C-DOM is generally expressed by the absorption coefficient at a selected wavelength. In this study, the abundance of C-DOM was expressed by the absorption coefficient at 355 nm ($A_{355}$) (Li et al. 2014). Changes in $A_{355}$ under three degradation conditions are shown in Figure 5(c). Under UV-A, UV-C irradiation, and dark conditions, $A_{355}$ decreased by 84.46%, 70.83%, and 52.98%, respectively. The adsorption coefficient of the UV-A group decreased sharply in the first 72 h and then tended to be stable, indicating that most of the amount of C-DOM was consumed. The $A_{355}$ of the UV-C group fluctuated in the early period, and this condition might be related to the production of new C-DOM during photodegradation. Kieber et al. (1990) demonstrated that only solar light with wavelength higher than 320 nm can degrade DOM into carbonyl compounds with molecular weights lower than 200. The $A_{355}$ of the dark condition degradation group after 36 h increased slightly, and this increase might be related to the by-products of microorganisms.

$SUVA_{254}$ is an important spectra parameter used to represent the aromaticity degree of DOM components (Trulleyová & Rulík 2004). A high $SUVA_{254}$ value indicates

![Figure 5](http://iwaponline.com/ws/article-pdf/20/8/3083/814234/ws020083083.pdf)
a high amount of aromatic unsaturated bonds in DOM. Changes in SUVA_{254} are as shown in Figure 5(d). Given that aromatic substances, which are sensitive to photodegradation, are decomposed quickly, SUVA_{254} dropped quickly in the first 48 h and then tended to be stable under UV-A irradiation. This result agrees with the results of Bai et al. (2015). SUVA_{254} increased slightly in the first 24 h under UV-C irradiation, and this condition might have been caused by the production of substances rich in aromatic rings. As the proportion of humus rich in aromatic rings increased gradually because of the complete consumption of non-/weakly aromatic substances, the final value of SUVA_{254} under UV-C irradiation was higher than that under UV-A irradiation. Under the dark environment, SUVA_{254} generally increased continuously. This result indicated that DOM was transformed from a non-humification state to a humification state (Trulleyová & Rulík 2004). The aromaticity of A-DOM substances was enhanced by microorganisms. Nishijima & Speitel (2004) pointed out that the UV absorption coefficient at 254 nm might be inversely proportional to the content of bioavailable organic matter.

**Photodegradation dynamics analysis of A-DOM**

The \( A_{355} \) and intensity of different fluorescence components were fitted with irradiation time according to the first-order kinetic model. Degradation kinetics basically fitted to the first-order reaction equation, and the half-life of each component was calculated (Table 3). The half-life of \( A_{355} \) under UV-A irradiation was shorter than that under UV-C irradiation, and thus chromophores degraded quickly under UV-A irradiation. The half-life values of C1 and C2 in the fluorophore under UV-C irradiation were 36.9 and 21.6 h, reflecting the highest degradation speed. The degradation speeds of C3 and C4 under UV-A irradiation were relatively low. The fluorescence intensity under UV-C irradiation and the contribution rate of fluorescence intensity both increased continuously, and this condition might be related to the production of humus. Chen et al. (2015) reported that the half-life of natural photodegradation (\( a_{350} \)) of small spheres, protein-like component, short-wave excited humus, and long-wave excited humus are 38.4, 79.2, 64.8, and 105.6 h, respectively. The half-life of protein-like components under the UV-light photodegradation of A-DOM is shorter than that under the degradation of *Chlorella*, and the half-life of humic-like components is higher. Yu (2009) pointed out that the half-life of \( a_{350} \) in surface water in England from the Tyne estuary to the North Sea was similar (33.6–69.6 h), and the half-life of the protein-like component was 86.4 h, indicating that degradation conditions and source can affect the half-life of organic matter degradation significantly.

**A-DOM molecular weight during cyanobacteria degradation**

According to the membrane permeation experiment, the DOC contents of A-DOM in three dimensions of penetration bags were negatively correlated with molecular weight (Figure 6). The DOC proportions under different molecular weight ranges in the total concentration are listed in Table 4. The

### Table 3 | Photodegradation kinetic parameters of A-DOM

<table>
<thead>
<tr>
<th>Light source</th>
<th>Parameters</th>
<th>0</th>
<th>168</th>
<th>Degradation rate (%)</th>
<th>Degradation coefficient ( k ) (h(^{-1}))</th>
<th>Half-life ( t_{1/2} ) (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV-A ( A_{355} ) (m(^{-1}))</td>
<td>14.74</td>
<td>2.29</td>
<td>84.46</td>
<td>0.0103</td>
<td>67.3</td>
<td></td>
</tr>
<tr>
<td>( F_{\text{max}} ) (C1)</td>
<td>3,823.6</td>
<td>821.11</td>
<td>78.52</td>
<td>0.0083</td>
<td>83.5</td>
<td></td>
</tr>
<tr>
<td>( F_{\text{max}} ) (C2)</td>
<td>2,800.52</td>
<td>381.01</td>
<td>86.39</td>
<td>0.0121</td>
<td>57.3</td>
<td></td>
</tr>
<tr>
<td>( F_{\text{max}} ) (C3)</td>
<td>512.21</td>
<td>152.99</td>
<td>70.13</td>
<td>0.0073</td>
<td>93.7</td>
<td></td>
</tr>
<tr>
<td>( F_{\text{max}} ) (C4)</td>
<td>268.95</td>
<td>140.99</td>
<td>40.14</td>
<td>0.0027</td>
<td>256.7</td>
<td></td>
</tr>
<tr>
<td>UV-C ( A_{355} ) (m(^{-1}))</td>
<td>14.74</td>
<td>4.31</td>
<td>70.83</td>
<td>0.0087</td>
<td>79.7</td>
<td></td>
</tr>
<tr>
<td>( F_{\text{max}} ) (C1)</td>
<td>3,823.6</td>
<td>174.65</td>
<td>95.44</td>
<td>0.0188</td>
<td>36.9</td>
<td></td>
</tr>
<tr>
<td>( F_{\text{max}} ) (C2)</td>
<td>2,800.52</td>
<td>0</td>
<td>100</td>
<td>0.0321</td>
<td>21.6</td>
<td></td>
</tr>
<tr>
<td>( F_{\text{max}} ) (C3)</td>
<td>512.21</td>
<td>400.238</td>
<td>21.86</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>( F_{\text{max}} ) (C4)</td>
<td>268.95</td>
<td>250.724</td>
<td>6.78</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>
The molecular weight composition of DOM was closely related to its internal components. Micromolecular-weight DOM (<3,500 Da) mainly includes micromolecular protein-like substances, including amino acids, alcohols, and ketones. Medium-molecular-weight DOM (3,500–10,000 Da) mainly includes humic-like acid substances. Macromolecular-weight DOM (>10,000 Da) mainly includes humus and high-molecular protein substances with low ultraviolet absorption. These results agree with the conclusions of Yang et al. (2018) that the A-DOM in the Dian Lake is mainly composed of macromolecular-weight polysaccharide, micromolecular-weight protein, and free amino acids.

In this study, the proportions of micromolecular-weight DOM (<3,500 Da), medium-molecular-weight DOM (3,500–10,000 Da), and macromolecular-weight DOM (>10,000 Da) in the initial A-DOM samples were 29.06%, 38.42%, and 32.45%, respectively. The proportions of micromolecular-weight DOM (<3,500 Da) in the UV-A group were the highest (64.92%) under the three degradation conditions, while the proportions of medium-molecular-weight DOM (3,500–10,000 Da) and macromolecular-weight DOM (>10,000 Da) decreased to some extent compared with those in the initial A-DOM samples. The proportion of the molecular weight range of the UV-C group was negatively correlated with molecular weight. However, the proportion of micromolecular-weight DOM in the UV-C group was lower than that in the UV-A group. The molecular weight change characteristics of A-DOM were in accordance with the changes of SUVA254 value.

CONCLUSIONS

The fluorescence components in A-DOM in Chaohu Lake mainly include proteinoids (C1 and C2) and humic-like components (C3 and C4). The contribution rate of C1 and C2 to the total fluorescence intensity was 90%. After biodegradation under 20 W ultraviolet light (UV-A light and UV-C light) and dark conditions, the degradation rates of fluorescence intensity were 79.52%, 88.86%, and 69.01%, and those of DOC were 51.72%, 62.77%, and 44.8%. The adsorption coefficient of A-DOM degradation solution under UV light and the degradation kinetics of fluorescence components (C1 and C2) both fitted to the first-order kinetic model. The protein-like fluorophore under UV-C irradiation was degraded more thoroughly than the chromophore. The C-DOM was completely degraded under UV-A irradiation. The SUVA254 value indicated that UV can facilitate humus degradation, whereas dark condition biodegradation can enhance the A-DOM humification. The molecular weight distributions before and after degradation imply that A-DOM has strong photochemical degradation activity.

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<table>
<thead>
<tr>
<th>Molecular weight (Da)</th>
<th>&lt; 3,500</th>
<th>3,500–7,000</th>
<th>7,000–10,000</th>
<th>&gt; 10,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial A-DOM</td>
<td>29.06%</td>
<td>10.62%</td>
<td>27.8%</td>
<td>32.45%</td>
</tr>
<tr>
<td>UV-A: 168 h</td>
<td>64.92%</td>
<td>18.17%</td>
<td>7.94%</td>
<td>8.89%</td>
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<tr>
<td>UV-C: 168 h</td>
<td>45.18%</td>
<td>19.79%</td>
<td>21.81%</td>
<td>13.18%</td>
</tr>
<tr>
<td>Black: 168 h</td>
<td>23.26%</td>
<td>10.96%</td>
<td>23.34%</td>
<td>42.8%</td>
</tr>
</tbody>
</table>
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