Non-catalytic and catalytic photodegradation of effluent dissolved organic matter under UVA-and UVC-irradiation tracked by advanced spectroscopic tools

Diep Dinh Phong a, b, Jin Hur a, *

a Department of Environment and Energy, Sejong University, Seoul, 143-747, South Korea
b Vietnam Academy of Science and Technology, Hanoi, Viet Nam

A R T I C L E   I N F O

Article history:
Received 1 June 2016
Received in revised form
12 August 2016
Accepted 31 August 2016
Available online 1 September 2016

Keywords:
EEM-PARAFAC
2D-COS
Photocatalytic degradation
Effluent
Dissolved organic matter

A B S T R A C T

Non-catalytic and catalytic photodegradation of effluent dissolved organic matter (EfDOM) was examined under two different light sources (UVA and UVC). The degradation behavior was tracked by dissolved organic carbon (DOC), UV absorbance, and different fluorescent components. Catalytic UV irradiation resulted in much higher degradation rates than those without photocatalysts (TiO2 and ZnO) regardless of the tracking variables. For non-catalytic degradation, the highest removal rates of UV absorbance were found at wavelengths close to the irradiation of either UVC or UVA, while the photocatalytic degradation rates were consistently higher at longer wavelengths. The pseudo first-order rates of UV absorbance individually calculated at several representative wavelengths were very consistent with the sequential orders interpreted from two-dimensional correlation spectroscopy (2D-COS). Excitation emission matrix — parallel factor analysis (EEM-PARAFAC) identified one tryptophan-like (C1) and two humic-like (C2 and C3) components from EfDOM samples. Among those, C1 exhibited the lowest adsorption extent and the highest degradation rates for both photocatalysts, suggesting that the photocatalysis is mainly governed by hydroxyl radicals in aqueous solution. All observed degradation behaviors were well explained by the irradiation wavelengths, the extent of adsorption onto catalysts, and the presumed structure of the tracked component. Our study demonstrated that EEM-PARAFAC and 2D-COS could provide further insights into both non-catalytic and catalytic degradation of EfDOM upon UV-irradiation.

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1. Introduction

Non-biodegradable organic compounds in wastewater are not completely removed in conventional treatment facilities primarily based on biological processes. Effluent dissolved organic matter (EfDOM) poses risks to receiving aquatic environments due to its persistent nature and the potential presence of toxic chemicals (Luo et al., 2014; Maeng et al., 2015). It is also linked with unwanted pollution issues because it may facilitate the transport of micro-pollutants and increase disinfection by-products in receiving water upon the chlorination of effluent (Shon et al., 2006). EfDOM is typically described as a heterogeneous mixture of soluble organic substances with complex structures and various functional groups (Michael-Kordatou et al., 2015).

Due to growing demands for sustainable use of water resources as well as for strict regulations on wastewater discharges, a great deal of effort has been made to maximize the removal of EfDOM by employing advanced treatment options including membrane processes, activated carbon adsorption, advanced oxidation processes (AOPs), and their combinations (Acero et al., 2010; Giannakis et al., 2015; Rizzo et al., 2015). UV-assisted photocatalytic processes have been recently highlighted as an effective method for eliminating recalcitrant organic matters in wastewater (Miranda-Garcia et al., 2011; Zhang et al., 2016) because they have the superior advantages of a high removal efficiency, recyclable and chemically stable catalyst, and no sludge production (Chong et al., 2010). As light sources, ultraviolet C (UVC, 100–280 nm) and ultraviolet A (UVA, 315–400 nm) lights are preferred and frequently used for removing organic compounds (Baransi et al., 2012; Joseph et al., 2016). Most related studies have focused on removing individual organic
compounds in wastewater, while very limited reports are available on the photodegradation of EfDOM (i.e., bulk effluent itself).

Fluorescence spectroscopy is a non-destructive, reliable, and highly sensitive optical technique for fast probing dissolved organic matter (DOM) in aquatic environments (Henderson et al., 2009). Excitation emission matrix fluorescence combined with parallel factor analysis (EEM-PARAFAC) has proved over the last decade its successful applications for tracking the behaviors of dissimilar DOM constitutes in many engineered systems (Ishii and Boyer, 2012; Yang et al., 2015). Recently, the technique was applied to trace the changes in individual fluorescent DOM components in UVA/TiO2 systems (Phong and Hur, 2015), successfully providing new insight into photocatalytic degradation of DOM. However, the information obtained from EEM-PARAFAC is limited to fluorescent compounds within bulk EfDOM, which heightens the necessity of combining it with other characterization tools.

Two dimensional correlation spectroscopy (2D-COS) has been employed as a powerful tool for examining subtle and/or hidden DOM spectral changes upon varying external factors (e.g., metal addition, irradiation, and chemical dose) (Hur et al., 2011; Hur and Lee, 2011). The combined information of the synchronous and asynchronous maps derived from 2D-COS provides a clear picture of the sequential and parallel spectral changes in response to external perturbations (Jung and Noda, 2006). 2D-COS has already proven successful in delineating spectral responses of DOM to UV irradiation at continuous wavelengths, providing essential information on the underlying mechanisms (Hur et al., 2011). Despite its proven usefulness, however, its application has been very limited for engineered systems in DOM studies.

In this work, we investigated the photodegradation of EfDOM using TiO2 and ZnO as catalysts, and UVA and UVC as light sources. The objectives of this study were (1) to track the degradation behaviors of bulk EfDOM and the individual fluorescent components under different experimental setups (UVC/UVA, TiO2/ZnO), and (2) to explore the applicability of 2D-COS and EEM-PARAFAC for a better understanding of non-catalytic and catalytic photodegradation of EfDOM. For this study, 2D-COS was utilized to maximize the information on the changes of UV-visible spectra upon the irradiation, which can describe detailed degradation behaviors of all light-absorbing moieties in EfDOM.

2. Materials and methods

2.1. Reagents

Two catalysts of TiO2 (AEROXIDE® P25) and ZnO (NanoAmor), which have comparable particle sizes (an average size of 21 nm and 20 nm, respectively), were used for this study without further purification. The BET surface areas were 50 ± 15 m2/g and 40 m2/g, and the points of zero charge (PZC) were reported 6.2 to 6.9, and 9.2 to 9.3, respectively (Dutta et al., 2004; Mohd Omar et al., 2014; Zhang et al., 2008). Each catalyst was mixed with Milli-Q water to prepare a slurry solution, which was added to concentrated EfDOM solutions for further experiments.

The original EfDOM sample was collected after a clarifier in a municipal wastewater treatment plant located in the city of Uijeongbu, Korea. The facility has a treatment capacity of 200,000 m3/day, and it adopts an advanced biological treatment process, namely, the MLE (Modified Ludzack Ettinger) process. Dissolved organic carbon (DOC) concentration of the collected sample was 3.6 ± 0.4 mg C/L. The original sample was concentrated in a freeze dryer and filtered through a pre-cleaned 0.45 μm pore size membrane filter (cellulose acetate, Advantec) prior to use. The initial DOC concentration of EfDOM for photodegradation experiments was ~15 mg C/L. The relatively high concentration of the sample was advantageous to obtain clear trends in the variations during subsequent photodegradation.

2.2. Non-catalytic and catalytic photodegradation experiments

The photodegradation systems for this study is well described in our previous work (Phong and Hur, 2015). Briefly, the experiments were conducted in a stirred cylindrical quartz reactor with a working volume of 1 L and an inner diameter of 95 mm. The reactor was placed in the middle of a closed cabinet equipped with twelve lamps inside as a light source. Two types of light sources, UVA and UVC, were used for the study, which corresponded to 8W-UVA lamps (Sankyo Denki, F8T5BL) and 8W-UVC lamps (Sankyo Denki, G8T5) with the wavelengths centered at 352 nm and 254 nm, respectively. The light intensities were measured at the center of the reactor with a UVA/B light meter (model 85,009, Sper Scientific) and a UVC light meter (model 850,010, Sper Scientific), which were 6540 mW/cm2 and 2390 mW/cm2, respectively.

The reactor temperature was maintained at 25 ± 3 °C by circulating cooling air with fans. Before irradiation, the pH of the EfDOM solutions was adjusted to 7.0 using 0.1 N HCl or NaOH solutions. They were stirred in the dark for 1 h to reach the adsorption-desorption equilibrium between EfDOM and the catalysts. The catalyst’s dose was fixed at 0.5 g/L for all experiments. An aliquot (20 mL) of the EfDOM solution was taken at appropriate time intervals. Excitation and emission slits were adjusted to 10 nm and 5 nm, respectively, and the scanning speed was set at 6540 mW/cm2 and 2390 mW/cm2, respectively.

2.3. Analytical methods

DOC concentrations were determined using a TOC analyzer (Shimadzu V-CPH). UV–visible spectra of the samples were recorded from 200 to 700 nm using a UV–visible spectrophotometer (UV–1800, Shimadzu) with a 1-cm quartz cuvette. Fluorescence EEMs were measured with a fluorescence spectrophotometer (F-7000, Hitachi) by scanning the emission spectra from 280 to 550 nm at 1 nm wavelength increments and stepping through the excitation wavelengths from 220 to 500 nm at 5 nm intervals. Excitation and emission slits were adjusted to 10 nm and 5 nm, respectively, and the scanning speed was set at 12,000 nm min−1. To limit second order Raleigh scattering, a 290 nm-cutoff filter was used for all the measurements. The samples with the UV absorbance at 254 nm (UV254) exceeding 0.05 cm−1 were diluted to avoid the inner-filter correction. The background fluorescence EEM from a blank solution (Milli-Q water) was also taken into account. Fluorescence intensity was normalized using quinine sulfate equivalent units (QSU), in which 1 QSU corresponds to the maximum fluorescence intensity for 1 μg L−1 of quinine in 0.1 N H2SO4 at Ex/Em of 350/450 nm (Chen et al., 2007). Relative precisions of <2% were routinely obtained based on replicated UV–visible and fluorescence measurements.

2.4. PARAFAC modeling

PARAFAC modeling was performed using MATLAB 7.1 (MathWorks, Natick, MA, USA) with the DOMFluor Toolbox (http://www.models.life.ku.dk). The detail of the modeling is well described elsewhere (Nguyen et al., 2013; Stedmon and Bro, 2008). Split-half analysis was used to validate the identified fluorescent components and their number. The modified Turker’s Congruence Coefficient (mTCC) was employed to compare the identified components with
a library containing 38 PARAFAC models (He and Hur, 2015; Parr et al., 2014). The mTCC values of >0.95 was considered as the exact match between the two components (Table S1). The maximum fluorescence intensities (\(F_{\text{max}}\)) of the individual components were used to represent their relative concentrations. The EEM data for the PARAFAC modeling were obtained based on 78 EEM data from 6 separate experiments.

2.5. 2D-COS

Measured UV-visible absorption data was transformed into a new spectral matrix suitable for 2D-COS maps by using the “2D Shige” program released by Kwansei-Gakuin University (Nakashima et al., 2008). 2D-COS generates a synchronous and an asynchronous map. The former is drawn based on auto-correlations between two different dynamic spectra, and the latter is derived from cross-correlations between the dynamic spectrum and its orthogonal spectrum. The two spectra can be mathematically written as follows (Noda et al., 2000):

\[
\Phi(v_1, v_2) = \frac{1}{T_{\text{max}} - T_{\text{min}}} \int_{T_{\text{min}}}^{T_{\text{max}}} y(v_1, t) \times y(v_2, t) \, dt \tag{1}
\]

\[
\Psi(v_1, v_2) = \frac{1}{T_{\text{max}} - T_{\text{min}}} \int_{T_{\text{min}}}^{T_{\text{max}}} \tilde{y}(v_1, t) \times \tilde{Z}(v_2, t) \, dt \tag{2}
\]

Where \(\Phi\) and \(\Psi\) represent the synchronous and the asynchronous spectra of 2D-COS, respectively. The parameters of \(v\) and \(t\) are a spectral variable (i.e., wavelengths) and an external perturbation (i.e., irradiation for this study), respectively. \(y\ (v, t)\) is the dynamic spectrum, and \(\tilde{y}\ (v, t)\) is the Hilbert-transformed orthogonal spectrum. The relationships between the two generated spectra and the interpretations concerning the signs and the event sequence with respect to the wavelength ranges are described in detail elsewhere (Hur and Lee, 2014; Jung and Noda, 2006; Noda et al., 2000). Briefly, the sign of the synchronous cross-peaks indicates the direction of the spectral changes, while the asynchronous map provides the information on the sequence of the events associated with the external perturbation. If the signs of synchronous and asynchronous cross-peaks are the same at given wavelength ranges, the spectral change at x axis precedes the change at y axis. If they are different, the reaction proceeds in the opposite direction (i.e., Noda’s rules (Noda et al., 2000).

3. Results and discussion

3.1. Changes in DOC during photodegradation

Table 1 summarizes the major results on DOC adsorption and the responses of DOC to UV irradiation. In the absence of the catalysts, the reduction of DOC under 4 h-UVA irradiation reached only 4.0% (Exp. #2). This result was consistent with many previous reports, in which no change or a slight removal of DOC was observed under the irradiation of UVA light (Liu et al., 2008; Phong and Hur, 2015) or solar simulated light (Valencia et al., 2013a). The UVC-irradiation resulted in a higher degree of the DOC removal (i.e., 9.6%) (Exp. #1), probably due to the higher photon energy of UVC versus UVA.

Under UVC and UVA lights, the total removal of DOC reached 83.0% and 45.1% in the presence of TiO2 and 45.2% and 36.0% with ZnO, respectively (Table 1), which were much higher values than those without the catalysts. Despite the fact that the adsorption of EFDOM on the catalysts was comparable between TiO2 (8.6–9.2%) and ZnO (9.5–9.9%), the total removals were much higher for TiO2 than for ZnO under the same light source (Table 1). This is unexpected because the band gap energy and thus the photocatalytic capacity is likely to be similar between ZnO and TiO2 (i.e., 3.3 eV vs. 3.2 eV). The difference may be explained by the photo-corrosion phenomenon frequently occurring in ZnO under UV light. This phenomenon has been regarded as a main reason for decreased photocatalytic activity of ZnO in aqueous solutions (Fu et al., 2008; Hariharan, 2006).

A pseudo-first order kinetic model has been widely used to describe the photodegradation of wastewater in previous literature (Choi et al., 2014; Pirilä et al., 2015). For this study, all observed trends in DOC with the irradiation followed the pseudo-first order kinetic model although the degree of the model fitting depended on the experimental setups. For example, the photolysis without the catalysts (Exp. #1 and #2) showed relatively low degrees of the model fitting (\(R^2 = 0.82–0.88\) (Table 1). A relatively low degree of the model fitting (\(R^2 = 0.90\)) for a photocatalysis system (Exp. #4) could be attributed to the substantial release of DOC from the

### Table 1

<table>
<thead>
<tr>
<th>No.</th>
<th>Experimental conditions</th>
<th>Change of DOC and UV254</th>
<th>Adsorption (%)</th>
<th>Photodegradation (%)</th>
<th>Photodesorption (%)</th>
<th>Total removal (%)</th>
<th>Photodegradation rate (min⁻¹)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>UVC</td>
<td>DOC</td>
<td>–</td>
<td>9.6</td>
<td>–</td>
<td>12.1</td>
<td>0.0004 ± 0.0000</td>
<td>0.88</td>
</tr>
<tr>
<td>2</td>
<td>UVA</td>
<td>DOC</td>
<td>UV254</td>
<td>70.2</td>
<td>–</td>
<td>70.3</td>
<td>0.0059 ± 0.0003</td>
<td>0.94</td>
</tr>
<tr>
<td>3</td>
<td>UVC</td>
<td>TiO2</td>
<td>DOC</td>
<td>8.6</td>
<td>74.3</td>
<td>–</td>
<td>83.0 ± 0.0004</td>
<td>0.96</td>
</tr>
<tr>
<td>4</td>
<td>UVC</td>
<td>TiO2</td>
<td>U254</td>
<td>8.5</td>
<td>84.3</td>
<td>–</td>
<td>92.8 ± 0.0009</td>
<td>0.98</td>
</tr>
<tr>
<td>5</td>
<td>UVC</td>
<td>ZnO</td>
<td>DOC</td>
<td>9.9</td>
<td>35.4</td>
<td>–</td>
<td>45.2 ± 0.0003</td>
<td>0.99</td>
</tr>
<tr>
<td>6</td>
<td>UVC</td>
<td>ZnO</td>
<td>UV254</td>
<td>14.9</td>
<td>68.4</td>
<td>–</td>
<td>83.3 ± 0.0003</td>
<td>0.97</td>
</tr>
</tbody>
</table>

* Adsorption percentage was calculated based on the following equation: Adsorption (%) = 100 – [C0 – Cads]/C0 where C0 is the DOC at t = 0, Cads is the DOC at t = 60 min (i.e., adsorption for 60 min-contact with photocatalyst).

* Photodesorption percentage was calculated based on the following equation: Desorption (%) = 100 – [(Cdes – Cads)/(C0 – Cads)] where Cdes is the highest DOC value after irradiation (Shahid et al., 2014).
catalyst’s surface (i.e., photo-desorption), which corresponded to 26.2% of the adsorbed DOC amount (Phong and Hur, 2015; Shahid et al., 2014). For all the catalytic photodegradation, the photo-desorption was the most pronounced at the first 15 min of irradiation as shown by the lag phase and/or the low reduction in DOC during the initial period (Fig. 1). Afterward, the DOC changes appear to be fully controlled by photolysis, displaying consistent decreasing trends.

It was previously reported that the photocatalytic behavior of organic compounds was affected by UV-irradiation wavelengths as well as the properties of the individual compounds (especially, UV absorption capability) (Ali et al., 2011; Bayarri et al., 2007). In this study, the comparison between the photolytic (Exp. #1 and #2) and the photocatalytic degradation experiments (Exp. #3-6) revealed the higher removal efficacy of UVC versus UVA irrespective of the catalysts. Again, this difference may be attributed to the facts that a shorter wavelength is associated with a greater photon energy and thus that the band gap excitation of the electrons with 254 nm can promote electrons to the conduction band with a high kinetic energy. In this case, the electrons can reach solid-liquid interface easily, suppressing electron–hole recombination in comparison to those of 365 nm (Bhatkhande et al., 2002; Venkatachalam et al., 2007).

3.2. Changes in UV absorbance during photodegradation

UV254 has been widely accepted as a surrogate for probing the degradation rates of DOM (Rajca and Bodzek, 2013; Uyguner and Bekbolet, 2005). In this study, the total reduction of UV254 were 70.3% and 7.6% for the catalyst-free photolysis with UVC and UVA, respectively (Table 1), and the removal was further enhanced by TiO2 up to 92.8% and 81.5%, and by ZnO up to 83.3% and 76.2% under UVC- and UVA-irradiation, respectively.

Similar to DOC, both photolytic and photocatalytic degradation rates of UV254 followed the pseudo first-order kinetics well ($R^2 = 0.91–0.98$). However, the kinetic rates were much higher than those of DOC (Table 1), and the lag phase due to photo-desorption was not observed for UV254 (Fig. 1). These differences suggest that the UV-absorbing moieties in EfDOM, which mostly consist of high molecular sized aromatic rings, could be rapidly broken down into smaller sized non-aromatic structures (Sanly et al., 2007). Our results agreed with a previous report

Fig. 1. Changes in normalized DOC, UV254, and PARAFAC components of (a) control experiment with irradiation of UVC and without catalyst; (b) control experiment with irradiation of UVA and without catalyst; (c) UVC and TiO2; (d) UVA and TiO2; (e) UVC and ZnO and; (f) UVA and ZnO under the irradiation systems with 0.5 g/L catalysts at pH 7.
demonstrating that aromatic and olefinic moieties in wastewater were more strongly degraded by photocatalysis than aliphatic structures (Liu et al., 2013).

3.3. Sequential order of UV–visible spectral changes upon UV irradiation

2D-COS was applied to identify the sequential order of the responses of UV–visible spectra (or UV-absorbing compounds) to UV irradiation with respect to the wavelengths (Fig. 2 and Table 2). For this study, no cross-peak appeared in all synchronous maps, and intense auto peaks were centered at a short wavelength range (246–255 nm) except for the UVA photolytic degradation (Exp. #2), in which a broad autopeak was placed in a middle wavelength range (~327 nm). The synchronous maps indicate the UV absorbance consistently decreased at the indicated wavelength ranges. The autopeak represents the overall susceptibility of the corresponding spectral region to an external perturbation (Jung and Noda, 2006) (i.e., irradiation for this study). The asynchronous map from the photolysis under UVC showed a negatively signed
crosspeak at 303/250 nm (Fig. 2a), indicating the degradation at the wavelength of 250 nm preceded the event at 303 nm (i.e., 250 nm → 303 nm). For the UVA-irradiation, however, different features were found in the asynchronous map with two cross-peaks appearing at 327/275 nm (positive sign) and 383/327 nm (negative sign) (Fig. 2b), suggesting that the degradation occurred in the wavelength order of 327 nm → 383 nm → 275 nm. The dissimilar trends in the wavelength sequences between UVC- and UVA-irradiation were in line with previous studies (Del Vecchio and Blough, 2004), in which direct photobleaching took place first at the same wavelengths as the irradiation, while the secondary absorption losses occurred outside the irradiation wavelengths.

For the photocatalytic degradation, all synchronous maps showed a similar pattern with a broad and positively signed peak centered at 254 nm (Fig. 2c–f). However, the features of the asynchronous maps were not the same. For the UVC-irradiation with TiO₂, one positive, and one negative signed peaks appeared at 332/280 nm and 282/254 nm of the asynchronous map, respectively (Fig. 2c). This result indicates that the degradation sequence occurred from longer wavelengths (300–330 nm) to shorter wavelengths (250–285 nm). The sequences were opposite to those of the previous catalyst-free UVC irradiation (i.e., 250 nm → 303 nm), suggesting that the degradation behaviors of UV-absorbing moieties in EfDOM with respect to the wavelengths might be completely different for the irradiation systems with and without the photocatalysts. The asynchronous map from the photocatalysis under UVA also revealed a similar trend of the degradation sequence occurring from longer to shorter wavelengths as evidenced by the positive broad peak at 320/250 nm and the negative peak at 275/257 nm (Fig. 2d). Meanwhile, the photocatalysis with ZnO showed a similar peak in the asynchronous irrespective of the light sources (Fig. 2e and f).

From the peak locations of all the asynchronous maps, four representative wavelengths of 250 nm, 275 nm, 325 nm, and 380 nm, were selected to confirm the degradation sequences of the UV-sensitive EfDOM moieties. The interpreted sequences from the 2D-COS were further compared with the orders of the kinetic rates directly calculated at the corresponding wavelengths (Table 2). The photodegradation rates at the representative wavelengths fit the pseudo-first-order kinetics with the R² values from 0.85 to 0.99 and from 0.87 to 1.00 for the photolytic and the photocatalytic degradation, respectively. The orders of the calculated rates were very consistent with the wavelength sequences interpreted from our 2D-COS results (Table 2). For example, the catalyst-free degradation rate with UVC (Exp. #1) was higher in the order of UV250 → UV325 → UV380, changing from 0.0055 min⁻¹ to 0.0028 min⁻¹, which was the same sequential order from the 2D-COS results. The UVA-irradiation (Exp. #2) resulted in different sequential order of UV325 → UV380 → UV275 → UV250, consistent with the calculated rates (Table 2). In contrast to those without catalysts, the degradation sequence of the photocatalysis was nearly the same for the two light sources with the wavelength order of 380 nm → 325 nm → 275 nm → 250 nm (i.e., from longer to shorter wavelengths). The results agreed with a previous report of (Sen Kavurmaci and Bekbolet, 2014), in which the photocatalysis of a humic acid under UVA irradiation with TiO₂ was faster at the wavelengths of 436 nm > 280 nm > 254 nm. The higher degradation rates at longer wavelengths appears to relate to the higher adsorption tendency of UV-absorbing components at longer wavelengths, which was already evidenced by our previous results that the extent of the adsorption on the photocatalysts were greater with longer wavelengths (Table 2) with the order of 380 nm > 325 nm > 275 nm > 250 nm (p < 0.05). Furthermore, the percent adsorption was highly correlated with the degradation rates (p < 0.01).

Our study demonstrates that 2D-COS can be a powerful tool to visualize the spectral changes of UV-absorbing moieties in EfDOM occurring at a wide range of wavelengths upon both photolytic and photocatalytic degradation, providing the sequential order of the wavelengths associated with the degradation kinetics. From the application points of view, comparing 2D-COS with other useful spectroscopic methods such as spectral slope (Roccaro et al., 2015) and differential absorbance spectroscopy (Yan et al., 2014) would be an interesting topic for the future study in tracking degradation behaviors of EfDOM upon irradiation.

Table 2
Comparison of the adsorption and photodegradation of UV absorbance at the representative wavelengths selected from the 2D-COS maps.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Wavelength</th>
<th>Adsorption (%)</th>
<th>2D-COS results (signs and sequences)</th>
<th>Photodegradation Rate (min⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp.#1: UVC, no catalyst</td>
<td>250 nm</td>
<td>–</td>
<td>(+) – (+) – (+) – (+) 250 → 275 → 325 → 380</td>
<td>0.0055 ± 0.0003</td>
<td>0.92</td>
</tr>
<tr>
<td>275 nm</td>
<td>–</td>
<td>(+) – (+) – (+) – (+)</td>
<td>0.0052 ± 0.0001</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>325 nm</td>
<td>–</td>
<td>(+) – (+) – (+) – (+)</td>
<td>0.0044 ± 0.0001</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>380 nm</td>
<td>–</td>
<td>(+) – (+) – (+) – (+)</td>
<td>0.0028 ± 0.0002</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>Exp.#2: UVA, no catalyst</td>
<td>250 nm</td>
<td>–</td>
<td>(+) (+) (+) (+) 325 → 380 → 275 → 250</td>
<td>0.0003 ± 0.0000</td>
<td>0.89</td>
</tr>
<tr>
<td>275 nm</td>
<td>–</td>
<td>(+) (+) (+) (+)</td>
<td>0.0005 ± 0.0000</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>325 nm</td>
<td>–</td>
<td>(+) (+) (+) (+)</td>
<td>0.0018 ± 0.0001</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>380 nm</td>
<td>–</td>
<td>(+) (+) (+) (+)</td>
<td>0.0015 ± 0.0001</td>
<td>0.86</td>
<td></td>
</tr>
<tr>
<td>Exp.#3: UVC, TiO₂</td>
<td>250 nm</td>
<td>8.1</td>
<td>(+) (+) (+) (+) 380 → 325 → 275 → 250</td>
<td>0.0105 ± 0.0010</td>
<td>0.95</td>
</tr>
<tr>
<td>275 nm</td>
<td>14.4</td>
<td>(+) (+) (+) (+)</td>
<td>0.0174 ± 0.0005</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>325 nm</td>
<td>19.1</td>
<td>(+) (+) (+) (+)</td>
<td>0.0196 ± 0.0009</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>380 nm</td>
<td>26.0</td>
<td>(+) (+) (+) (+)</td>
<td>0.0252 ± 0.0011</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>Exp.#4: UVA, TiO₂</td>
<td>250 nm</td>
<td>9.0</td>
<td>(+) (+) (+) (+) 380 → 325 → 275 → 250</td>
<td>0.0088 ± 0.0007</td>
<td>0.87</td>
</tr>
<tr>
<td>275 nm</td>
<td>14.3</td>
<td>(+) (+) (+) (+)</td>
<td>0.0100 ± 0.0005</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>325 nm</td>
<td>17.5</td>
<td>(+) (+) (+) (+)</td>
<td>0.0117 ± 0.0005</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>380 nm</td>
<td>23.4</td>
<td>(+) (+) (+) (+)</td>
<td>0.0144 ± 0.0004</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>Exp.#5: UVC, ZnO</td>
<td>250 nm</td>
<td>13.7</td>
<td>(+) (+) (+) (+) 380 → 325 → 275 → 250</td>
<td>0.0062 ± 0.0003</td>
<td>0.96</td>
</tr>
<tr>
<td>275 nm</td>
<td>17.5</td>
<td>(+) (+) (+) (+)</td>
<td>0.0086 ± 0.0004</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>325 nm</td>
<td>27.7</td>
<td>(+) (+) (+) (+)</td>
<td>0.0115 ± 0.0007</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>380 nm</td>
<td>45.5</td>
<td>(+) (+) (+) (+)</td>
<td>0.0160 ± 0.0011</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>Exp.#6: UVA, ZnO</td>
<td>250 nm</td>
<td>14.8</td>
<td>(+) (+) (+) (+) 380 → 325 → 275 → 250</td>
<td>0.0051 ± 0.0002</td>
<td>0.98</td>
</tr>
<tr>
<td>275 nm</td>
<td>17.7</td>
<td>(+) (+) (+) (+)</td>
<td>0.0070 ± 0.0002</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>325 nm</td>
<td>25.7</td>
<td>(+) (+) (+) (+)</td>
<td>0.0095 ± 0.0004</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>380 nm</td>
<td>40.9</td>
<td>(+) (+) (+) (+)</td>
<td>0.0134 ± 0.0006</td>
<td>0.98</td>
<td></td>
</tr>
</tbody>
</table>
3.4. PARAFAC components and their behaviors upon photodegradation

3.4.1. Fluorescence components identified by PARAFAC modeling

Three fluorescent components (C1, C2, and C3) were decomposed by PARAFAC modeling on the EEM dataset of all 78 samples from six degradation experiments (Fig. 3). The number of components was identified based on split-half validation. The mTCC values were all above 0.95 (Table S1), indicating a good agreement between our results and the reported components (Parr et al., 2014).

C1 displayed a peak at Ex/Em of 235 (280)/350 nm, indicating the presence of tryptophan-like (peak T) or a protein-like substances (Stedmon et al., 2007). C2 and C3 exhibited the maxima at 245 (330)/410 nm and 255 (370)/449 (Ex/Em), respectively. Both C2 and C3 are characterized by a mixture of the traditional EEM peaks A and C, but the maximum fluorescence of C3 was located at longer Ex and Em wavelengths (Coble, 2007). In this study, the three components, C1, C2, and C3, which were commonly found in wastewater treatment plants, were assigned to tryptophan-like component or protein/amino acid-like, microbial humic/fulvic acid-like, and terrestrial humic/humic acid-like components, respectively (Yang et al., 2015). Lee et al. (2015) reported that red-shifting of the EEM peak maxima into longer emission wavelengths is likely related to a larger molecular size of a humic acid. Therefore, C3 could be more associated with larger sized humic-like molecules than C2. C1 is a fluorescent component abundant in raw wastewater (Guo et al., 2010) and preferentially removed by microbial degradation processes (Cohen et al., 2014; Yang et al., 2014; Yu et al., 2015). The original EfDOM sample in this study showed the highest abundance of C1 (40.1–41.3%) followed by C2 (33.3–35.6%) and C3 (24.2–25.4%) (Table S2).

3.4.2. Adsorption and photodegradation of different fluorescent components

Adsorption of C2 and C3 was comparable to each other, and both components showed greater adsorption on the catalysts than C1 (Table 3). This can be explained by the close linkage of the humic-like components with larger sized and/or more hydrophobic DOM fractions (Hur and Kim, 2009; Ishii and Boyer, 2012), which typically have a higher adsorption affinity on the catalysts (Mwaanga et al., 2014; Valencia et al., 2013b). Irrespective of the components, the adsorption onto ZnO was higher than that on TiO2. Considering that the solution pH of 7 is close to and lower than the PZC of TiO2 and ZnO, respectively, the net surface charge of ZnO is likely to be positively charged, promoting the adsorption of negatively charged EfDOM through electrostatic attraction (Erhayem and Sohn, 2014; Yang et al., 2009).

Both photolytic and photocatalytic degradation rates of the identified fluorescent components fitted well the pseudo-first order kinetic model in the Fmax values ($R^2 = 0.93–1.00$). Without the photocatalysts, the total removals ranged from 78.8 to 91.5% under UVC, and from 23.9 to 55.4% under UVA, showing that UVC was more efficient in removing fluorescent EfDOM than UVA. The total removals upon the photocatalysis were also higher, ranging from 97.1 to 99.8% (Table 3). The degradation rates of the fluorescent components were consistently greater than those based on DOC and UV254 for both photolytic and photocatalytic conditions ($t$-test, $p < 0.05$). These results were supported by the previous reports demonstrating that fluorescent components were much more sensitive to UV light than other non-fluorescent structures (Phong and Hur, 2015; Sen Kavurmaci and Bekbolet, 2014). The faster degradation of fluorescent components versus UV-absorbing moieties can be attributed to the fluorescence arising from the π*- π transitions in organic molecules followed by its rapid extinction.

Fig. 3. PARAFAC model output showing (a) the three fluorescent components and (b) the corresponding excitation/emission loadings (b). Excitation/emission loadings consist of two independent halves of the dataset (red and blue dotted lines) and the complete dataset (black lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
under UV irradiation (Cho and Choi, 2002). The higher degradation rates of DOM fluorescence versus DOC also agreed with other prior studies on photobleaching of natural water (Mostofa et al., 2007) and photocatalytic oxidation of DOM (Phong and Hur, 2015; Valencia et al., 2013a). This finding implies the usefulness of EfDOM fluorescence as a surrogate for fast and sensitive probing the photodegradation behavior.

It was also found from the photolysis experiments that the removal was the highest for the fluorescent components with the excitation peak wavelengths close to the irradiation wavelength range, followed by those with longer to shorter peak excitation wavelengths (Del Vecchio and Blough, 2002; Ishii and Boyer, 2012). For example, C1, with peak excitation wavelengths of 235 nm and 280 nm, exhibited the highest degradation rate under UVC (UVC wavelength range: 200–280 nm). In contrast, the degradation order under UVA was C2 > C3 > C1 with the lowest rate shown for C1. The higher rate of C2 versus C3 may be ascribed to the main excitation wavelength of C2 (i.e., 410 nm) close to the UVA band (i.e., 315–400 nm). Our results were consistent with the prior photo-bleaching studies using aquatic DOM samples with solar/UVA light (Moran et al., 2000; Mostofa et al., 2007) or using humic substances under UVA-irradiation (Phong and Hur, 2015), in which protein-like fluorescence was more resistant to UVA than other fluorescent components.

For photocatalytic degradation, however, C1 had the highest degradation rates among the three fluorescent components irrespective of the light sources (Table 4). For example, the rates of C1, C2, and C3 under UVC irradiation were 0.0701 min⁻¹, 0.0363 min⁻¹, and 0.0362 min⁻¹, respectively. The orders of the higher rates were C1 > C2 > C3 for TiO₂ and C1 > C3 > C2 for ZnO although the UVC-irradiation consistently resulted in the higher rates than that of UVA for all the components (Table 4). Again, it is very interesting to note that the rate orders of the components were completely different from those of the photolysis without the catalysts. The different degradation behaviors of the fluorescent components may be explained by the catalyst-associated reaction pathway previously proposed (Liu et al., 2008; Nguyen et al., 2003). In other words, the component adsorbed on the catalyst's surface to a lesser extent (i.e., C1) is likely to be more preferably degraded by hydroxyl radicals in the solution, leading to the highest degradation rate. Meanwhile, such an oxidation path could be a limiting step for the other components with greater adsorption affinity (i.e., C2 and C3). Furthermore, reactive holes may also be involved in oxidizing the adsorbed DOM components with large size into smaller fragments, which could delay the overall degradation process (Bekbolet and Sen-Kavurmaci, 2015) have demonstrated that small molecular size fractions (<3 kDa) were formed from larger sized fractions through the photo-oxidation of a humic acid under TiO₂-assisted UVA irradiation.

Although the four-hour irradiation of this study is relatively long from the practical point of view, the findings of this study can provide fundamental and valuable information in choosing the proper types of catalysts and UV light to target the removal of particular optical components within bulk EfDOM, which is advantageous for optimizing subsequent treatment processes. For example, protein-like fluorescent components are susceptible to biodegradation while formation potential of trihalomethane is more strongly correlated with humic-like components than protein-like components (Yang et al., 2015).

### 4. Conclusions

Regardless of the EfDOM tracking variables, a greater extent of photodegradation was consistently found for TiO₂ versus ZnO catalysts and for UVC versus UVA-irradiation. In the non-catalytic photolysis, the degradation rates based on UV absorption were relatively higher at a shorter wavelength range (250–285 nm) under UVC, and at longer wavelengths (325–380 nm) under UVA irradiation. However, the photocatalytic degradation resulted in higher rates at the longer wavelengths irrespective of the light sources. The sequential orders of the absorption changes interpreted from the 2D-COS results were very consistent with the pseudo-first order kinetic rates individually calculated at several representative wavelengths. In the non-catalytic photolysis, the highest degradation rates were found for the fluorescent component with the excitation peak wavelength close to the irradiation wavelength range. For the photocatalysis, however, the protein-like component exhibited the highest degradation rate irrespective of the light sources. The rate sequences of the optical parameters were well explained by the irradiation wavelengths, the adsorption onto...
the catalysts, and the presumed component’s structure. Our study demonstrated that both EEM-PARAFAC and 2D-COS could serve as powerful tools in providing new insights into the photodegradation behavior of EfDOM.

Acknowledgments

This work was supported by a National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (No. 2014R1A2A209049496). Additional support was provided by R&D Center for Green Patrol Technologies through the R&D for Global Top Environmental Technologies funded by the Ministry of Environment (no. 201500184002).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2016.08.068.

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