Photocatalytic degradation of DOM in urban stormwater runoff with TiO₂ nanoparticles under UV light irradiation: EEM-PARAFAC analysis and influence of co-existing inorganic ions

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A B S T R A C T

In situ photocatalytic degradation of dissolved organic matter (DOM) of stormwater runoff can efficiently improve the aquatic environment quality and relieve the wastewater treatment pressure. In this work, photocatalytic degradation of DOM in TiO₂ (AEROSIL® P-25) photocatalyst under illumination of ultraviolet (UV) light was carried out, considering the influence of various factors like TiO₂ dosage, solution pH along with the existence of co-existing ions (Cu²⁺ and HPO₄⁻). Generally, the variations of dissolved organic carbon (DOC), UV-based parameters and peak intensities of fluorescent constituents with UV exposure time fitted perfectly with the pseudo-first-order kinetics model. The total DOM removal efficiency was affected by diversiform factors like adsorption capacity of TiO₂, UV light utilization efficiency, reactive free radicals produced and the influence of co-existing ions. The results of fluorescence excitation-emission matrix (EEM) coupled with parallel factor analysis (PARAFAC) modeling demonstrated that all the photodegradation rates for three identified fluorescent constituents (protein-like constituent 1 and 3, humic-like constituent 2) were faster than UV-absorbing chromophores, suggesting the DOM molecules in urban stormwater runoff contained much more π→π* transition structures. In addition, HPO₄⁻ ions affected the photodegradation of DOM by capturing positive holes (h⁺) and hydroxyl radical (·OH), whereas Cu²⁺ ions were inclined to generate Cu-protein complexes that were more difficult to degrade than the other Cu-DOM complexes. This study supplied novel insights into the photocatalytic degradation mechanism of individual organic constituent in urban stormwater runoff and explored the influences of co-existing contaminants on their adsorption-photocatalysis processes.

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1. Introduction

With the acceleration of urbanization, the problem of urban stormwater runoff pollution has become a hot topic discussed by researchers and engineers (Goonetilleke et al., 2005; Hong et al., 2017; McElmurry et al., 2014). In stormwater systems, dissolved organic matter (DOM) is mainly composed of organic substances with multiple functional groups and molecular sizes (Chen et al., 2002; Santos et al., 2012; Zhao et al., 2015; Zhao et al., 2016).

DOM compositions and structures are influenced by their sources and biogeochemical processes. (McElmurry et al., 2014; Schulten and Gleixner, 1999). As a ubiquitous and reactive fraction, DOM can forcefully interact with the co-existing contaminants and nutrient substances, thus altering their migration, transformation, bioavailability, toxicity and fate (Kieber et al., 2005; Kieber et al., 2004). Furthermore, considering that current methods to protect aquatic environments are massively inoperative and even guided by the "end-of-pipe" operations, the inefficient DOM treatment by former stormwater facilities will significantly increase the difficulty of sewage treatment plants. Previous researches had proved that DOM could lead to the formation of disinfection by products (DBP) and membrane fouling (Zhang et al., 2008).

Among various treatment technologies, heterogeneous photocatalysis employing UV light and TiO₂ catalyst has proved its high-
efficiency in photodegrading a large number of ambiguous recal-
citrant organic substances into steadily biodegradable sub-
stances. Moreover, under the appropriate conditions, it is possible to
ultimately mineralize organic molecules to form pollution-free
CO₂ and H₂O (Cai et al., 2018; Li et al., 2018). The dominating re-
action mechanism of photocatalytic degradation is based on the
generation of clean and environmentally friendly free radicals with
strong oxidizing ability (Wang et al., 2017; Zou et al., 2015). As well,
the strong stability (including chemical-, thermal- and photo-
stability), the undemanding experimental conditions (ambient
temperature and pressure), the efficient recyclability and low
operating costs promote wide application of UV/TiO₂ technique in
wastewater treatment (Wang et al., 2016; Wang et al., 2014).

In former studies of photocatalytic DOM degradation, dissolved
organic carbon (DOC) concentrations and some parameters fitted
from UV-visible spectral data were mainly applied as indicators for
estimating the total removal efficiency (Raja and Bodzek, 2013;
Zanardi-Lamardo et al., 2004). However, these indexes are insuffi-
cient to fully clarify the behaviors of the extremely non-homoge-
nous DOM. As a credible and hypersensitized optical instrument,
fluorescence spectroscopy can be used to efficiently identify the
different types of organic compounds (Baker et al., 2004; Coble,
1996; Her et al., 2003). Furthermore, the photocatalytic DOM
decomposition performances have been explored applying
fluorescence-based instruments in a range of aquatic environments
(Kavurmaci and Bebektoy, 2014; Patel-Sorrentino et al., 2004;
Zanardi-Lamardo et al., 2004). However, the previous studies
assessed the photodegradation tendency of DOM simply via the
analysis of changes in intrinsic fluorescence intensity or peak po-
sition, neglecting the possible error caused by the spectral overlaps
from a complicated mixture of various fluorescent compounds.

As the most popular stoichiometry technique, parallel factor
analysis (PARAFAC) can deconvolute the complicated EEMs spectra
to independent fluorescent organic substances that represent
different types of fluorophores with similar physicochemical
properties and structures (Ishii and Boyer, 2012; Stedmon and Bro,
2008). The EEM-PARAFAC technique has been widely utilized to
monitor the activities of various DOM substances in water envi-
ronments (Hudson et al., 2010; Sereďyn&SakaRobeka et al., 2011;
Stedmon et al., 2011; Yang et al., 2015). The peak locations and
intensities of the separate PARAFAC constituent reflect the water
quality and treatment performance. Therefore, the photocatalytic
degradation behaviors of different constituents can be effectively
identified by utilizing EEM-PARAFAC technique, and the overlaps
between various fluorescent will be effectively avoided. It is
noteworthy that Phong and Hur (2015) explored the photo-
degradation behaviors of different fluorescent by EEM-PARAFAC,
in which the litter-derived DOM, Elliott soil humic acid and Pony
lake fulvic acid were selected as DOM references. But up to now,
few researchers applied EEM-PARAFAC technique to investigate the
adsorption-photocatalytic processes and mechanism of urban
stormwater runoff DOM in UV/TiO₂ system.

More importantly, dissolved inorganic ions are quite ubiquitous
in DOM-containing urban stormwater runoff (Brown and Peake,
2006; Gammons et al., 2005; Zhao et al., 2017). They may appreci-
ably affect the photocatalytic reactions for DOM disposal. There-
fore, it is important to explore the influences of different inorganic
species on photocatalytic DOM decomposition in UV/TiO₂ system,
which will be beneficial to clarify the photocatalytic degradation
mechanism of DOM in real stormwater runoff samples. This study
will aim (1) to demonstrate the practicability of the environmen-
tally friendly and cost effective UV/TiO₂ system for the elimination
of DOM in urban stormwater runoff, (2) to compare the variations
in DOC concentrations, UV parameters and fluorescence identified
by EEM-PARAFAC of urban stormwater runoff DOM in UV/TiO₂
system under different experimental conditions, including TiO₂
doses and pH values, and (3) to examine the effects of co-existing
inorganic ions (Cu²⁺ and H₃PO₄) that are common in stormwater
runoff on DOM degradation with TiO₂ as catalyst under UV light
illumination.

2. Materials and methods

2.1. Sampling and pretreatment

The runoff water samples were collected directly with 1000 mL
fully cleaning glass containers after the generation of surface runoff
on 2nd August of 2017 at a regular sampling point of Daxing
campus (39°51′ N, 116°24′ E) of Beijing University of Civil Engi-
neering and Architecture (BUCUE). The sampling site was covered
by asphalt pavement, and the pavement precipitates, uncleaned
waste and the other organic substances washed by rainfall could be
the potential DOM sources. Weather parameters like quantity of
precipitation, rainfall duration, ground temperature, air dampness,
dry period, atmospheric pressure and catchment area were shown in
Table 1. The stormwater runoff samples were qualified for the
corresponding analyses because the rainfall event matched well
with the standard of EPA US (Smullen et al., 2003).

All types of glassware were dipped in NaOH solution (0.1 M) for
30 min before sampling, then cleaned by distilled water, subse-
sequently another immersion in HNO₃ solutions (4.0 M) for 1 d,
finally treated with ultrapure water. After sampling, the samples
were filtered with 0.45 μm PTFE filter and measured immediately.
The background concentrations of co-existing contaminants of the
filtered DOM samples were shown in Table 5. Subsequent analysis
must ensure that the extracted DOM samples were restored to
room temperature.

2.2. Reagents and instruments

AEROXIDE® P-25, a type of commercial TiO₂ purchased from
InnoChem Corporation (Beijing, China), was selected as photo-
catalyst, whose specific surface area and the average particle
diameter was reported to be 50 ± 15 m² g⁻¹ and 21 nm, respectively
(Phong and Hur, 2015). The point zero of charge (PZC) of the AER-
OXIDE® P-25 was 6.25 (Singh et al., 2008). Other analytical grade
reagents were commercially available and used without any further
pretreatment. The solutions like 4.0 M HNO₃, 0.1 M HCl, 0.1 M
NaOH, 1000.0 mg L⁻¹ NaHCO₃, 1000.0 mg L⁻¹ Na₂CO₃, 1000.0 mg L⁻¹ potassium biphthalate, 0.01 M CuCl₂ and 0.01 M
NaH₂PO₄ solutions were prepared with ultrapure water.

DOC was calculated from the difference between total carbon
(TC) and total inorganic carbon (TIC) determined on a Jena multi
C 3100 analyzer (Zhao et al., 2015; Zhao et al., 2017). All the values
were reported as the mean values of three parallel measurements.

The UV-visible absorption spectra of the DOM were measured on a Perkin-Elmer lambda 650S spectrophotometer. DOM samples with ultra-absorptive UV light will be diluted with ultrapure water to make A₂₅₀ (the absorbance at 250 nm) less than 0.02 to eliminate inner filter effect (Green and Blough, 1994; Yang and Hur, 2014). Ultrapure water was selected as the blank control of the UV-visible absorption spectra.

EEM spectra were detected by a Hitachi F-7000 Fluorescence
spectrophotometer, with both emission wavelengths and excitation
wavelengths ranging from 200 to 550 nm (Muller et al., 2008; Pará
et al., 2011). Both Rayleigh and Raman scatterings were eliminated
by zeroing the measured EEMs data in the two triangle regions at
E₂₅₀ ≤ Ex + 20 nm and Em ≥ 2Ex − 10 nm (Stedmon and Bro, 2008),
and by deducting the ultrapure water blank spectra, respectively
(Santos et al., 2009). Relative precisions of UV-visible and EEMs
measurements were routinely controlled within 2% (Santos et al., 2012).

2.3. Photocatalytic experiments

The photocatalytic experiments for removal of the DOM substances were conducted at ambient conditions in 50 ml quartz bottles. The bottles were placed in the photochemical reaction system (PCX-50A, Beijing Perfectlight Co. Ltd.) equipped with nine identical LED lamps (λ = 385 nm, power density = 300 mW cm⁻²). Under the condition of the fixed DOM concentration (approximately 10 mg L⁻¹), the effects of different TiO₂ doses (10, 20, 30, 40 mg) on photocatalytic experiments were investigated. Before the UV irradiation, 0.1 M HCl or NaOH solutions were applied to regulate the pH of DOM aqueous solutions, stirring in the dark for 60 min to achieve the adsorption-desorption equilibrium between TiO₂ and DOM (Phong and Hui, 2015). In addition, the liquid-solid heterogeneous photocatalytic reaction system was also prepared by addition of inorganic ions (Cu²⁺ and H₂PO₄⁻) at optimal TiO₂ dose and pH value to examine their effects on the photocatalytic DOM degradation. During the 4 h photocatalytic degradation experiments, 20 ml aliquots were extracted using a 0.45 µm PTFE filter to determine the residual DOM concentration, in which the pH values were regulated to 7.0 prior to subsequent analysis (Valencia et al., 2013).

2.4. PARAFAC modeling

PARAFAC modeling utilizes the chemometrics principles to decompose the EEM spectral dataset into separate fluorescent constituents and to provide the relative contents of different fluorophores (Bro, 1997; Ohno et al., 2008; Stedmon and Bro, 2008). In this application, original EEM fluorescent data were composed of three-ways arrays of X with I x J x K, where I, J, K are the amount of samples, emission wavelengths, and excitation wavelengths, respectively. The EEM-PARAFAC model can be expressed as Eq (1):

$$X_{ijk} = \sum_{f=1}^{F} a_{if} b_{jf} c_{kf} + \epsilon_{ijk} \quad i = 1...I \quad j = 1...J \quad k = 1...K$$

where \( F \) defines the numerical order of fluorophores in this model, \( X_{ijk} \) is the fluorescent peak intensity of the \( th \) sample at the \( th \) dependent variable (emission wavelength) and \( th \) dependent variable (excitation wavelength), \( a_{if} \) is in proportion to the content of the \( th \) fluorophore in the \( th \) sample, \( b_{jf} \) is a rateable assessment of the fluorescence quantum efficiency of the \( th \) fluorophore. Similarly, \( c_{kf} \) is linearly related to the specific absorption coefficient at excitation wavelength \( k \). Finally, \( \epsilon_{ijk} \) is the residual matrix, which is used to minimize the sum of squared residuals by alternating least squares algorithm (Stedmon et al., 2003).

EEM-PARAFAC dataset (495 samples x 55 emissions x 55 excitations) was operated via the N-way toolbox in the MATLAB 7.1 computation program (Kowalczyk et al., 2009; Stedmon and Bro, 2008). The fluorescent intensity of individual organic constituent was described by \( F_{max} \), which can represent the relative contents of individual constituent. The data was divided into two independent parts and calculated independently. The PARAFAC models (2–8 types of constituents) were then obtained from the two datasets independently. Accuracy and reliability of the model were performed by contrasting the spectral shapes of the fluorescent constituents derived by the two separated datasets.

3. Results and discussion

3.1. Variations of DOC concentrations during photocatalytic degradation

DOC is the most comprehensive and frequently-used parameter that can quantify the amount of DOM in water systems, because organic substances in natural environment generally represent a significant fraction of the carbonateous organic constituents (Croué et al., 2003). The variation trends of DOC concentrations in adsorption and photocatalysis processes under UV light illumination were shown in Fig. 1. Without TiO₂ as photocatalyst, DOC concentrations of urban stormwater runoff exhibited minimal variations at pH being 7 upon UV light illumination after 4 h. However, when TiO₂ was used as the photocatalyst, the total removal characterized by DOC increased to 46–71% according to various TiO₂ loadings and solution pH values. Being compared to the optimal condition, the presence of Cu²⁺ or H₂PO₄⁻ ions can inhibit the processes of adsorption and photodegradation of DOM, the total removal of DOC reduced to 19–47%. Furthermore, an uncomplicated pseudo-first-order kinetics model has been applied to depict the photocatalytic degradation of DOM in the recent researches (Abargues et al., 2018; Zhang et al., 2017). In this research, most of the changed trends of the DOC concentrations conformed to the pseudo-first-order kinetics model (\( R² = 0.95–0.98 \)), while the experiment with the presence of Cu²⁺ did not fit the model well (\( R² \) was approximately 0.75). The results revealed that the co-existing Cu²⁺ species might exert negative impact to the DOM degradation via competitive effects with oxidizing free radicals or forming hardly degradable substances (Cai et al., 2003). In addition, even after the 4 h irradiation, the DOM in urban stormwater runoff was not fully mineralized in DOC concentrations, suggesting that a large amount of the DOM molecules might be resistant to UV light, or they may convert into the other organic substances that were more difficult to be photodegraded (Cho and Choi, 2002).

3.1.1. Influences of TiO₂ loading for adsorption-photodegradation reactions

Influences of TiO₂ loading (0.00, 0.25, 0.50, 0.75, 1.00 g L⁻¹) for this reaction system were investigated at pH = 7 without co-existing ions (as illustrated in Fig. 1(a) and (b)). As expected, the gradual increase of TiO₂ dosages (ranged from 0.25 to 1.00 g L⁻¹) enhanced their adsorption capacities toward DOC (rose from 4.49% to 12.32%), presumably due to the enhanced total adsorption sites of TiO₂ particles. With the increase of TiO₂ dosage up to 0.75 g L⁻¹, the removal efficiency and the apparent photodegradation rates calculated by DOC concentrations increased correspondingly. With respect to the maximum loading (1.00 g L⁻¹) applied in this work, the total removal efficiency and the rate constant were significantly decreased than that of TiO₂ dosage = 0.75 g L⁻¹. The reason for the decrease of photocatalytic efficiency under higher catalyst loading might be the excessive amount of TiO₂ particles can produce light
screening effect that reduced the adsorption and utilization efficiency of UV light, thus affecting the photocatalytic processes (Gaya and Abdullah, 2008; Meng et al., 2010). The turbidity measured in this research were 898, 1964, 2640 and 3176 NTU for the photocatalyst dosages increasing from 0.25 to 1.00 g L⁻¹. Previous studies have demonstrated that the optimal dosage of TiO₂ particles varied depending on the styles of photocatalytic reactor and the chemical compositions of organic substances (Pu et al., 2006; Phong and Hur, 2015); therefore, any selected dosage should be manipulated below the saturation level of the specific photocatalyst to guarantee effective photons absorption.

3.1.2. Influences of solution pH values for adsorption–photodegradation reactions

The influences of pH on the photocatalytic degradation of DOM in urban stormwater runoff were investigated at solution pH being 4, 7 and 10 under the optimal TiO₂ loading (0.75 g L⁻¹). As illustrated in Fig. 1(c) and (d), the adsorptive capacities of TiO₂ reinforced with the incrementation of solution pH values (up to pH = 10), which can be interpreted by the charge property of DOM and the PZC of TiO₂. When operating pH = 4 < PZC (6.25), the surface charge of TiO₂ became positively charged and gradually absorbed the DOM with negative charge via electrostatic interactions (Saffur Rahman et al., 2013; Yan et al., 2013). At pH = 10 > PZC (6.25), the TiO₂ surface was negatively charged and exerted the reverse force to DOM in urban stormwater runoff. Surprisingly, the maximum adsorption capacity of TiO₂ (pH = 4) did not achieve the optimal removal efficiency. The overall removal efficiency calculated by DOC concentrations at pH = 4, 7, 10 was 46.39, 70.69 and 53.33%, respectively. Moreover, the photodegradation rates of DOC were 0.00214, 0.00503 and 0.00285 min⁻¹, following the order pH being 7 > pH being 10 > pH being 4. The inconformity between the adsorption capacity of DOC and the total removal efficiency might be due to surface behaviors of TiO₂ particles, the aggregation of TiO₂ particles, and the decrease of free radicals with oxidizing ability in the DOM solutions. The former studies verified that the interaction between DOM molecules and TiO₂ particles could lead to the conversion of the photochemical characteristics of the TiO₂ surface (Phong and Hur, 2015; Yang et al., 2009). The decrease of pH led to the aggregation of TiO₂ particles, which reduces the photons utilization efficiency (Palmer et al., 2002). The interpretation is partly affirmed by the turbidity values measured at different pH
values, namely that the turbidity values were 2237, 2549, 2865 NTU at pH = 4, 7 and 10, respectively. Meanwhile, because of the complicated structures and large molecular weight of DOM molecules, photogenerated holes (h+) with powerful oxidation ability can directly degrade the DOM constituents adsorbed on the surface of TiO2 into smaller organic fragments. Therefore, the oxidation of the smaller molecules produced during the photocatalytic processes and other non-UV-adsorbing organic substances was the rate limiting step of this reaction system. More advantageous production of -OH through the hole oxidation of OH- in the solution at neutral and alkaline conditions (Franch et al., 2002; Nguyen et al., 2003), contributed to more efficient -OH attack toward DOM in urban stormwater runoff and subsequently higher photocatalytic degradation rates.

3.1.3. Influences of co-existing ions for adsorption–photodegradation reactions

The concentrations of Zn2+, Cu2+, N-containing and P-containing ions in urban stormwater runoff were much higher than the other co-existing inorganic ions (as shown in Table S1). However, previous studies had demonstrated that Zn2+ and NO3- had negligible influences on photocatalytic oxidation of organic substances over UV illuminated TiO2 (Abdullah et al., 1990; Butler and Davis, 1993; Chen and Liu, 2007). Therefore, Cu2+ and H2PO4- ions were selected as the model cation and anion to explore their influences on adsorption-photocatalytic degradation of urban stormwater runoff DOM under UV/TiO2 systems (Erickson et al., 2012; Lee and Bang, 2006; Walker et al., 1999). In this study, the 0.01 M CuCl2 and Na2HPO4 solutions were prepared to explore the influences of co-existing ions (Cu2+ and H2PO4-) on the photodegradation of DOM. As shown in Fig. 1(e) and (f), the adsorption of DOC slightly decreased with existence of Cu2+ and H2PO4- at pH = 7. The overall DOC removal and degradation rates decreased on the order of Cu2+ > H2PO4- > without ions. The results may be attributed to the presence of Cu2+ suppressed the mineralization of DOM in urban stormwater runoff, significantly in relation to the resistance of DOM-Cu complexes to oxidation (Ugguner and Bekbolet, 2010). Okomoto and co-workers proved that Cu2+ can only strengthen the photocatalytic performance at its concentration up to 0.0001 M, while further increases in its concentration weaken the overall reaction efficiency (Okamot et al., 1985). However, the free and adsorbed H2PO4- reacted with positive h+ and -OH to generate H2PO4- (as shown in Eqs (2) and (3)), which was less active than -OH and h+ (Hu et al., 2003). Therefore, the excess H2PO4- had an inhibition influence for the photocatalytic degradation of DOM in urban stormwater runoff.

\[ H_2PO_4^- + OH^- \rightarrow H_2PO_4^- + OH^- \]  
(2)

\[ H_2PO_4^- + h^+ \rightarrow H_2PO_4^- \]  
(3)

3.2. Changes in UV parameters during adsorption–photodegradation reactions

Before investigating the changes of UV-related parameters during the whole reactions, the differences in spectroscopic properties between stormwater runoff and typical water DOM were compared. The parameters for comparison were spectral slope coefficients (S), the specific ultraviolet absorbance at 254 or 280 nm (SUVA254 or SUVA280), the fluorescence index (FI), the humification index (HIX) and the biological index (BIX) (the calculation details of the corresponding parameters were shown in Electronic Supplementary Information). They can provide information about molecular weight (Singh et al., 2008), aromaticity (Weishaar et al., 2003), source (Mcknight et al., 2001), humification degree (Huguet et al., 2009) and biological activity (Huguet et al., 2010), respectively. As shown in Table 2, the 5 values of DOM in urban stormwater runoff were minimum (9.32–9.57 µm-1), suggesting that the average molecular weight of DOM in urban stormwater runoff was relatively larger. Oppositely, the SUVA254 values in this study were in the range of 3.10–3.16 L.mg C^-1 m^-1 (SUVA254 was applied in the rest of studies), which were much higher than those in the other water environments, indicating that DOM in urban stormwater runoff contained much more aromatic structures. Furthermore, the fluorescence properties of DOM in different water environments were similar except that the higher humification degree was found in some lake, fogwater and sediment pore water DOM samples. It was well known that HIX values greater than 10 typically indicated strong humification (Huguet et al., 2009). Therefore, the fluorescence results revealed that the DOM in stormwater runoff had weak humic character with both terrigenous and microbial contribution. The concentrations of a large number of contaminants in aquatic environment, such as lignin, tannic acid, fulvic/humic acid and large amounts of aromatic organic substances can be characterized by UV254 values (Altmann et al., 2016; Kulovaara et al., 1996). Thus, UV254 can be regarded as a reasonable parameter for detecting the photodegradation efficiency of DOM (Meng et al., 2013; Saadi et al., 2006). Without the influence of co-existing ions, the photodegradation rates calculated by UV254 values basically fitted the pseudo-first-order kinetics model ($N^0 = 0.81–0.98$), and the total removal efficiency was relatively higher than those of DOC based experiments, ranging from 75.24 to 93.40%. Moreover, there was a positive correlation between UV254 values and the DOC concentrations ($R^2 = 0.76–0.85$), suggesting that chromophoric DOM substances were the important and ubiquitous contributors to the DOC pool in stormwater runoff. It is noteworthy that the trends of the DOM adsorption degree with different TiO2 doses, pH values and the presence of co-existing ions were same for the UV340 and DOC values (as shown in Fig. 2(a)–(d)). However, the adsorptive removal calculated by UV254 values (21.83–42.15%) were much higher than characterized by DOC concentrations (7.26–14.97%) under the identical experimental conditions, which may be due to the terminal functional groups (such as hydroxyl and carboxyl) of aromatic compounds reinforced the adsorption affinity of the surface of TiO2 particles (Tachikawa et al., 2004). Comparing with DOC based experiments, the total removal with the presence of Cu2+ ions increased dramatically when using UV254 values to monitor photocatalytic reaction process (Fig. 2(f)). As the UV254 mainly represents the content of aromatic substances in aquatic environment, the results suggested that the Cu2+ ions in urban stormwater runoff may react with the other non-UV-absorbing and macromolecular substances that were difficult to photocatalytic degradation. Yuan and co-workers (Yuan et al., 2017) applied 2D-COS technique to demonstrate that protein-like substances in stormwater runoff preferentially chelated with Cu2+ ions, indicating that Cu-protein complexes may be the major resistant substances in this experimental system.

In addition, the photodegradation rates on the basis of UV254 (0.0025–0.0078 min$^{-1}$, the median was 0.0057 min$^{-1}$) were congruently higher than the DOC based experiments (0.0005–0.0048 min$^{-1}$, the median was 0.0029 min$^{-1}$), revealing that the chromatophores in DOM mainly contained macromolecular sized aromatic constituents, could be quickly decomposed into micro-molecular sized non- aromactic compounds (Sanly et al., 2007). To further confirm this hypothesis, S and the SUVA280 values were estimated through the entire adsorption–photocatalysis process under the optimal condition (TiO2 dose = 0.75 g L$^{-1}$, pH = 7). The variation trends of S and SUVA280 values with reaction time were
Table 2
Summary of spectroscopic characteristics of DOM in typical water environment systems.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$S$ (μm$^{-1}$)</th>
<th>SUVA (L mg C$^{-1}$ m$^{-1}$)</th>
<th>FL</th>
<th>HIX</th>
<th>BIX</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stormwater runoff</td>
<td>9.32–9.57</td>
<td>3.10–3.16</td>
<td>1.58–1.67</td>
<td>4.38–4.92</td>
<td>0.78–0.85</td>
<td>This study</td>
</tr>
<tr>
<td>Sea water</td>
<td>15.10–34.80</td>
<td>0.595–1.22</td>
<td>1.46–1.77</td>
<td>0.92–4.60</td>
<td>0.74–1.38</td>
<td>(Heims et al., 2013)</td>
</tr>
<tr>
<td>River water</td>
<td>13.10–14.60</td>
<td>0.36–2.68</td>
<td>1.68–1.95</td>
<td>0.75–0.79</td>
<td>0.75–0.83</td>
<td>(Xu et al., 2016)</td>
</tr>
<tr>
<td>Lake water</td>
<td>13.80–22.90</td>
<td>0.70–2.90</td>
<td>1.60–1.80</td>
<td>2.00–4.10</td>
<td>—</td>
<td>(Phang et al., 2014)</td>
</tr>
<tr>
<td>Fegwater</td>
<td>—</td>
<td>0.15–0.79</td>
<td>1.42–1.83</td>
<td>1.76–6.79</td>
<td>0.64–1.02</td>
<td>(Birdwell and Valsaraj, 2010)</td>
</tr>
<tr>
<td>Drinking water</td>
<td>—</td>
<td>1.50–3.00</td>
<td>1.41–6.31</td>
<td>0.85–0.93</td>
<td>0.54–0.79</td>
<td>(Lavonen et al., 2015)</td>
</tr>
<tr>
<td>Sediment pore water</td>
<td>—</td>
<td>0.20–1.50</td>
<td>1.10–1.80</td>
<td>0.7–7.5</td>
<td>0.7–10</td>
<td>(Chen et al., 2015)</td>
</tr>
</tbody>
</table>

3.3.3. PARAFAC constituents and their behaviors during adsorption-photocatalysis reactions

3.3.3.1. EEM fluorescent constituents identified by PARAFAC technique

Three independent fluorophores (C1, C2, and C3) were resolved by the PARAFAC modeling based on the original 495 EEM spectra from 55 independent experiments (Fig. 3(a)-(c)). Moreover, the excitation and emission loadings accurately confirmed the peak locations of the three constituents (as shown in Fig. 3(d)-(f)). Constituent 1 (C1) exhibited a fluorescent peak at Ex/Em wavelength pair of 230/350 nm. Similar constituents were previously assigned to a protein-like or a tryptophan-like (peak T) constituent, such as aromatic amino acids (Chen et al., 2003; Coble, 1996; Korshin et al., 2018; Stedmon and Markager, 2005; Wu et al., 2011). This constituent mainly originated from anthropogenic input and correlated to terrestrial fluorescent materials (Carstea et al., 2010; Yamashita et al., 2008). Constituent 2 (C2) can be described as two peaks (peak A and C) with excitation wavelength at 250 nm and 300 nm, along with an emission wavelength at 440 nm, indicating the existence of a humic-like fluorescence (Coble, 1996; Huang et al., 2015) or a FA (fulvic acid)-like constituent with aromatic terrestrial structures and macromolecular weight (Santín et al., 2009). In consideration of the disadvantages caused by the traditional peak picking method (peak shifting and overlapping), infallible distinctions between two types of humic substances at peaks A and C cannot be made, thus leading to UV humic-like compounds turned out to be the dominating fluorescent constituents in the DOM of urban stormwater runoff samples in the former studies (Zhao et al., 2015; Zhao et al., 2016; Zhao et al., 2017). This significant result confirmed the diversity of organic compositions in urban stormwater runoff and provided valuable references for subsequent studies. Constituent 3 (C3), another protein-like constituent, was characterized by peaks at 275/313 nm. It was defined as tyrosine-like fluorophore and attributed to traditional peak B (Yamashita and Jaffe, 2011; Yamashita and Tanoue, 2003). However, a red shift occurred in the maximum peak position as being compared to the peak B described by Coble (1996), suggesting that the aromaticity of tyrosine-like substances in urban stormwater runoff was stronger than those present in freshwater/marine environments (Banerjee et al., 2006), and it might integrate with the structural condensation and ploymeryzation of DOM.

3.3.2. Photocatalytic degradation of individual fluorescent constituent at different conditions

Just like DOC and UV$_{254}$ experiments, the whole of decomposed fluorescent constituents showed stronger adsorption capacity under higher TiO$_2$ doses, lower pH values and without the influence of co-existing ions conditions (as illustrated in Fig. 4(a)-(i)). It is noteworthy that the remarkable decreases with UV irradiation were uniformly detected for all the PARAFAC fluorophores, suggesting that every identified fluorophore was affected by the direct photochemical degradation reaction (Phong and Hur, 2015). The photocatalytic degradation rates of the identified constituents match well with the pseudo-first-order kinetics calculated by the $k_{obs}$ values with $R^2$ being 0.82–0.99. Considering that the degradation behaviors of the three identified constituents followed the first order exponential decay process, which was proven to be a successful expression for DOM photocatalysis degradation with irradiation time (Del Vecchio and Blough, 2002), thus the photocatalytic degradation changes of the C1, C2 and C3 constituents with their kinetic rates can be compared directly. Without the influences of co-existing ions on photocatalytic oxidation process, the total removal efficiencies of the three identified fluorophores ranged from 83.06 to 99.40% (as listed in Table 3).

When there was no TiO$_2$ in the reaction system, the total removal ratios in the $F_{obs}$ values of the C1, C2 and C3 also reached to 10.23, 21.54 and 13.52%, and the rates corresponded to 0.00043, 0.00096 and 0.00059 min$^{-1}$, respectively (as shown in Table 3), following the order of C2 > C3 > C1, which contrasted with the negligible self-photodegradation process characterized by DOC values. This phenomenon revealed that fluorophores were more sensitive to the UV illumination than the rest of non-fluorescent organic substances, indicating that fluorophores can be used as a powerful proof to monitor the subtle changes of organic substances in stormwater runoff. Furthermore, the above results were in line with the previous researches on photo-bleaching DOM samples collected from the other water environments (Hur et al., 2011; Moran and Sheldon, 2000; Mostofa et al., 2007), in which the protein-like fluorophores were more refractory to photocatalytic degradation than the A, M, C fluorophores. The more interesting findings in this study were that the total removal efficiencies characterized by the individual fluorophore peak of DOM in urban stormwater runoff were uniformly stronger than those of DOC, along with that the photodegradation rates were higher than DOC and UV$_{254}$ based experiments (Table 3). Comparing with the UV-absorbing chromophores, the faster photocatalytic degradation of fluorophores may be due to the fluorescence was caused by the π-$\pi$ transitions in organic molecules and its fast disappearance upon UV light illumination (Phong and Hur, 2015).
When TiO$_2$ was present in the reaction system, the total removal ratios of the C1, C2 and C3 constituent reached 95.37, 99.40, and 96.34% under the optimum condition (TiO$_2$ dose = 0.75 g L$^{-1}$, pH = 7, without co-existing ions), the degradation rates complied with the order of C2 > C3 > C1 (Table 3). The photocatalytic degradation behaviors of the identified fluorophores can be elucidated by counterparts (Chen et al., 2014; Schneider et al., 2014). The suppositional mechanism of this photocatalytic degradation process was shown in Fig. 5, briefly, e$^-$ and h$^+$ pairs are produced in conduction and valence band upon illumination, and photocatalytic processes for the degradation of DOM are initiated by the formation of reactive free radicals by photo-generated h$^+$ and e$^-$ on surface of TiO$_2$. In this study, h$^+$ may oxide water molecules or hydroxyl ions to generate -OH, which oxidized most of the DOM molecules existed in the solution. The adsorption degree of C2 constituent onto TiO$_2$ nanoparticles was lower than the others, resulting in a large proportion of C2 constituent can be photodegraded by -OH present in the solution and the maximum photodegradation rate.
among the three fluorophores. In other words, the higher adsorption degree of C1 and C3 constituents onto TiO₂ nanoparticles can also lead to the reduction in active sites and photons utilization in reaction system, thus inhibiting the photodegradation of C1 and C3 constituents (Fu et al., 2018; Liu et al., 2016; Zhao et al., 2018).

Meanwhile, the reactive h¹ may directly participate in oxidation processes and decompose macromolecular organic substances into smaller fragments. Furthermore, the photo-induced e⁻ reacted with dissolved oxygen to generate ·O₂⁻, which can also oxidize the DOM molecules. In addition, the UV light absorption by individual fluorescent constituents facilitated to the generation of reactive intermediates like singlet oxygen (¹O₂) and the triplet states of DOM (¹DOM*). ¹DOM* may react with target organic substances directly through electron and energy transfer; thus imposing the great influence on UV degradation of the identified fluorophores (Lester et al., 2013).

The adsorption and photocatalytic degradation processes of the three constituents were dramatically suppressed with the presence of Cu²⁺ and H₃PO₄ ions, suggesting that the fluorescent organic substances had the similar physicochemical properties as other non-absorbing compounds. Moreover, the inhibitory effects of H₃PO₄ on the three fluorescent constituents were identical, evidenced by that the total removal ratios of C1, C2 and C3 increased to 64.33, 72.84 and 71.04%, respectively (Table 3). These results can be contributed to h¹ and ·OH radicals were captured by H₃PO₄, the oxidation capacity of H₃PO₄ free radicals was much weaker than the other radicals (Hu et al., 2003). However, as shown in Fig. 4(g)-(i), the inhibitory effects of Cu²⁺ ions on the protein-like constituents (C1 and C3) were stronger than the humic-like or fulvic-like constituent (C2). Croué and co-workers (Croué et al., 2003) applied XAD-4 and XAD-8 resins to demonstrated that Cu²⁺ ions primarily reacted with the low-affinity functional groups of humic constituents. whereas the functional groups containing nitrogen element similar to those of peptides and amino acids were inclined to chelate with Cu²⁺ ions to generate relatively stable complexes in natural aquatic systems. Therefore, the results proved that Cu-protein complexes were more difficult to photodegrade, further affirming the assumption in UV254 values.

4. Conclusions

The fundamental behaviors of DOM in urban stormwater runoff with the changes of TiO₂ dosages during adsorption-photodegradation processes were identical for DOC, UV254 and EEM: the faster reduction corresponding to higher TiO₂ loadings. But the decreases of photodegrading ratios at excess TiO₂ loading were attributed to the reduced absorption efficiency of the TiO₂ particles resulting from the enhance turbidity. The prominent changes of DOM photocatalytic rates with different solution pH values were attributed to surface modification of the photocatalyst by different adsorptive degrees, the aggregation of TiO₂ particles, and the production of oxidizing free radicals. The changes in DOC, UV254 and individual constituent identified by PARAFAC matched well with the pseudo-first-order kinetics. The photodegradation rates calculated by DOC concentrations were lower than UV254 and fluorescence peak-based experiments, revealing the preferential removal of aromatic substances under UV illumination. This study
affirmed the practical applications of EEM-PARAFAC method to explore the different responses and the behaviors originated from different fluorescent constituents in urban stormwater runoff upon photocatalytic degradation. Comparing with protein-like constituents (C1 and C3), the humic or fulvic-like constituent (C2) was more effectively removed during adsorption-photodegradation processes mainly due to its direct oxidative degradation by OH·. More importantly, the presence of Cu²⁺ and
H₃PO₄ were detrimental for the photodegradation DOM in urban runoff. The H₃PO₄ ions inhibited the photocatalytic performance of the TiO₂ by capturing h⁺ and -OH. But Cu²⁺ ions were inclined to generate refractory Cu-DOM complexes with protein-like constituents to reduce photocatalytic efficiency. In general, this study showed that EEM-PARAFAC method can be used as a valuable tool for investigating the photocatalytic mechanisms of various organic constituents in urban stormwater runoff. Considering the low photon and quantum utilization efficiencies of TiO₂ particles, further researches should to develop new photocatalysts that can be utilized in photodegradation of DOM in aquatic environments under visible or UV–visible irradiation.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.08.062

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