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## Interactions between copper(II) and DOM in the urban stormwater runoff: modeling and characterizations

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### ABSTRACT

Dissolved organic matter (DOM) can strongly interact with both organic and inorganic contaminants to influence their transportation, transformation, bioavailability, toxicity and even their ultimate fate. Within this work, DOM was extracted from urban stormwater runoff samples collected from a regular sampling site of a typical residential area in Beijing, China. Copper(II) ions were selected as model to investigate the interactions between DOM and typical heavy metals. Both ultraviolet (UV) absorbance and fluorescence titration methods were introduced to determine the complex capacities ( $C_L$ ) and conditional stability constants ( $\log K_M$ ) of bonding between DOM and copper (II) ions, which revealed that the values of  $C_L$  were 85.62 and 87.23  $\mu\text{mol mg}^{-1}$  and the  $\log K_M$  values were 5.37 and 5.48, respectively. The results suggested the successful complexation between DOM and copper(II) ions. Furthermore, morphology of the DOM binding to copper(II) ions was confirmed by both energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS), which can facilitate to clarify the corresponding mechanism. The Cu 2p<sub>3/2</sub> peak at 933.7 eV and the characteristic shake-up peaks of Cu–O were found in the XPS spectra, implying that copper(II) ions might coordinate with hydroxyl (aliphatic or phenolic) or carboxyl groups. With these profitable results, it can be concluded that DOM in urban stormwater runoff has a strong binding affinity with copper(II) ions, which may further lead to potentially significant influence on their migration and transformation.

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Stormwater runoff; dissolved organic matter; copper ions; titration; interaction mechanism

## 1. Introduction

Urban stormwater runoff was regarded as an increasing pollution source of surface water due to the increasing impervious surface and the substantial contaminants from urban areas [1–3]. Both heavy metals and organic pollutants are of particular concerns considering their undesirable impact to aquatic organisms and their persistence in the environment [4–6], in which the metal-DOM (dissolved organic matter) species were found to be most widespread [7,8]. Zhao et al. [1,9] found that the UV humic-like substances with functional groups such as carboxylic, phenolic, carbonyl, and hydroxyl were the primary components of DOM in urban stormwater runoff in Beijing, China. As a ubiquitous and reactive fraction, DOM plays a crucial role in controlling the solubility, mobility, bioavailability and toxicity of trace heavy metals in aquatic environments resulting from its strong interaction with metal ions [10]. Some attentions were paid on the interactions between heavy metal ions and DOM extracted from different sources such as lake sediment [11], landfill leachate [12,13] via series

analytical methods, including but not limited to anodic stripping voltammetry [14,15], ion-selective electrode potentiometry [16], equilibrium dialysis [17,18], ultrafiltration [19,20], and absorbance/fluorescence quenching titration [12,21,22]. Both UV–vis and EEM fluorescence spectroscopy are the simple, sensitive and nondestructive techniques, which can provide valuable information such as molecular structure and composition change of DOM [1,23,24]. The conditional stability constant and binding capacity are important parameters to estimate the biological availability of copper in aquatic systems in the presence of DOM [12,25], the assumption of 1:1 stoichiometry and nonlinear fitting model equation were adopted to calculate the above-stated two parameters [12].

Copper(II) ion was selected as the heavy metal model due to its common existence in stormwater runoff of various land uses [4,6,26]. The parameters such as  $\log K_M$  and  $C_L$  of complexes formed from the interactions between copper(II) ions and DOM were obtained via the modified Stern–Volmer equation [11] and fluorescence

titration method [12,13]. Nason and co-workers investigated the species of copper complexes in highway stormwater runoff, and they selected fulvic acid extracted from the Suwannee River as organic ligands to investigate the corresponding binding strength between copper(II) and DOM [7]. Up to now, few studies were conducted to clarify the interactions between the copper(II) ions and DOM extracted from the real stormwater runoff samples.

Within this work, DOM extracted from stormwater runoff was characterized by UV-visible (UV-vis) spectroscopy and excitation-emission matrix (EEM) fluorescence spectroscopy to expound its chemical and structure properties. Both scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDX) and X-ray photoelectron spectroscopy (XPS) were introduced to clarify the interactions between the copper(II) ions with the major functional groups of the DOM. [27,28]. XPS was used to provide valuable and important information on the electronic structure change of copper(II) ions before and after interactions with DOM, which can facilitate us to gain an insight on the interactions between metal ions and organic substances [29,30]. In all, the objectives of this study are: (a) to determine and discuss comparatively the complex capacity and the stability constant of copper (II)-DOM complexes; and (b) to investigate the interactions between copper(II) ions and DOM in urban stormwater runoff.

## 2. Material and methods

### 2.1. Reagents and instruments

All chemicals with analytical grade were commercially available from J&K Chemical Corporation (Beijing, China) and used directly without any further purification. The solutions including 4.0 and 0.1 mol L<sup>-1</sup> HNO<sub>3</sub>, 0.1 mol L<sup>-1</sup> NaOH, 1.0 mol L<sup>-1</sup> KClO<sub>4</sub>, 0.02 mol L<sup>-1</sup> CuSO<sub>4</sub>·5H<sub>2</sub>O, 1000.0 mg L<sup>-1</sup> NaCO<sub>3</sub>, 1000.0 mg L<sup>-1</sup> NaHCO<sub>3</sub>, 1000.0 mg L<sup>-1</sup> potassium biphthalate, 1000.0 µg mL<sup>-1</sup> copper standard solution, and 1 µg L<sup>-1</sup> quinine sulfate were prepared using ultra-pure water with a resistivity of 18.2 MΩ cm<sup>-1</sup> (Milli-Q). The concentrations of CuSO<sub>4</sub> titrant were standardized with the EDTA solution [31].

The copper(II) concentrations in the samples were determined by a Perkin-Elmer AA-PinAAcle™ 900 flame atomic absorption spectrometry (Fremont, USA). The concentrations of dissolved organic carbon (DOC) were

measured on a Jena multi N/C 3100 analyzer (Jena, Germany) [32–34]. UV-vis spectra of the samples were recorded on a Perkin-Elmer lambda 650S spectrophotometer (Fremont, USA) from 240 to 400 nm using 1 cm quartz cell [32,33]. Fluorescence spectra were obtained on a Hitachi F-7000 Fluorescence spectrophotometer (Tokyo, Japan) equipped with a Xenon flash lamp using 1 cm quartz cells. Fluorescence measurements were conducted by making emission scans from 200 to 550 nm with excitation wavelengths ranging from 200 to 550 nm. Standard quinine sulfate units (QSU) were chosen to quantize the relative fluorescent intensities of DOM in the samples, in which one QSU (1 QSU = 1 µg L<sup>-1</sup> = 1 ppb quinine sulfate in 0.05 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>) is equivalent to 58.6 intensity unit [35,36]. Rayleigh scatter effects and Raman scatters were eliminated by adding zero to the EEMs in the two triangle regions ( $E_m \leq E_x + 20$  nm and  $\geq 2E_x - 10$  nm) [37], and by subtracting the ultra-pure water blank spectra [33], respectively. The morphological and elemental distributions were observed on a Hitachi SU8020 scanning electron microscope (Tokyo, Japan) equipped with EDX. The XPS spectra were reported by using the Thermo ESCALAB 250Xi system with non-monochromatized Al Kα radiation as excitation source (Waltham, USA).

### 2.2. Sampling and pretreatment

Urban stormwater runoff sample was collected on 13 August 2015 at a fixed sampling station of the Dongluoyuan residential area (39°51'N, 116°24'E), a typical residential area close to the southern third ring road of Beijing, China. The underlying surface material of the sampling area is asphalt pavement. Meteorological data including rainfall amount, rain duration, surface temperature, relative humidity, pressure, antecedent dry period and watershed area are described in Table 1. The collected sample in this study was eligible for subsequent experiments, as the storm event completely satisfied the corresponding requirement drafted by US EPA [38].

The sample was collected immediately with well-pretreated glass bottle (1000 mL) after the start of runoff [1,9]. The obtained sample was transported to the laboratory and filtered with hydrophilic PVDF Millipore membrane filters (0.45 µm), and afterwards tested as soon as possible.

**Table 1.** The meteorological data of the rainfall event (13 August 2015).

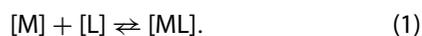
Rain amount (mm)	Rain duration (min)	Relative humidity (%)	Pressure (in mmHg)	Watershed area (m <sup>2</sup> )	Surface temperature (°C)	Antecedent dry period (d)
32.3	207	93	28.67	855	23	7

### 2.3. Copper(II)-DOM interaction experiments

The pH value of the sample was 6.8, and the DOC concentration was 22.0 mg L<sup>-1</sup>. Before titration, the DOC content of the sample was adjusted to ca. 5.0 mg L<sup>-1</sup>, and the ionic strength of the solution was adjusted with 0.1 mol L<sup>-1</sup> KClO<sub>4</sub> to minimize inner filter effect [39,40]. Fifteen samples (50 mL DOM solutions) were derived from the 1000 mL collected sample, and transferred into each 100 mL conical flasks, followed by the addition of 0.02 mol L<sup>-1</sup> CuSO<sub>4</sub> aqueous solution to prepare a series of solutions with the initial concentrations of copper(II) from 0 to 600 μmol L<sup>-1</sup> with the concentration interval of 40 μmol L<sup>-1</sup>. The background concentration of copper(II) in the sample was too low (approximately 0.775 μmol L<sup>-1</sup>) to influence the titration process. The pH of each targeted sample was adjusted to 6.00 ± 0.10 using either 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> or 0.1 mol L<sup>-1</sup> NaOH solutions, and the total amount of added acid or alkali solutions should not exceed 200 μL. Previous studies had demonstrated that the reaction between copper(II) and DOM can reach equilibrium within 15 min [12,41], so the samples were shook for 15 min at 150 rpm with the temperature of 25°C ± 1°C. After equilibrium, the supernatants were filtered through 0.45 μm hydrophilic PVDF Millipore membranes, and 50 mL DOM solution with the ionic strength of 0.1 mol L<sup>-1</sup> KClO<sub>4</sub> was chosen as the blank to conduct the UV-vis and EEM fluorescence measurement. All the samples were treated with flash freezing in a Freeze Dry System (FD-1, Songyuan Huaxing Corp., Beijing, China). The system was maintained at -41°C or lower before the samples were added, and afterwards the pressure of the system was kept at ≤ 20 Pa for about 72 h to ensure complete sublimation of water molecules.

### 2.4. Complexation modeling

The 1:1 stoichiometric model has been successfully applied to study the binding abilities between organic substances and copper(II) [12,13,15]. Therefore, the reaction between DOM in urban stormwater runoff (L) and copper(II) ions (M) can be quantitatively described as follows:



The corresponding conditional stability constant ( $K_M$ ) at a certain experimental condition can be expressed as follows:

$$K_M = \frac{[ML]}{[M][L]}. \quad (2)$$

The Ryan-Weber nonlinear equation as expressed as

Equation (3) was widely used to study DOM binding with metal ions in fluorescence quenching titration method [22]. The complexation parameters, such as conditional stability constant  $K_M$ , binding capacity  $C_L$  and  $F_{ML}$  (the limited fluorescence intensity after metal ion titration), could be obtained by the nonlinear regression analysis on a plot of  $F/F_0$  vs.  $C_M$  using the following equation:

$$\frac{F}{F_0} = 1 + \left( \frac{F_{ML}}{F_0} - 1 \right) \left( \frac{1}{2K_M C_L} \right) \left[ 1 + K_M C_L + K_M C_M - \sqrt{(1 + K_M C_L + K_M C_M)^2 - 4K_M^2 C_L C_M} \right], \quad (3)$$

where  $F_0$  and  $F$  are the fluorescence intensities at the beginning of the titration (without adding metals) and at the metal concentration of  $C_M$ , respectively.

Similarly, the nonlinear equation can be used in the absorbance titration calculation as listed as follows:

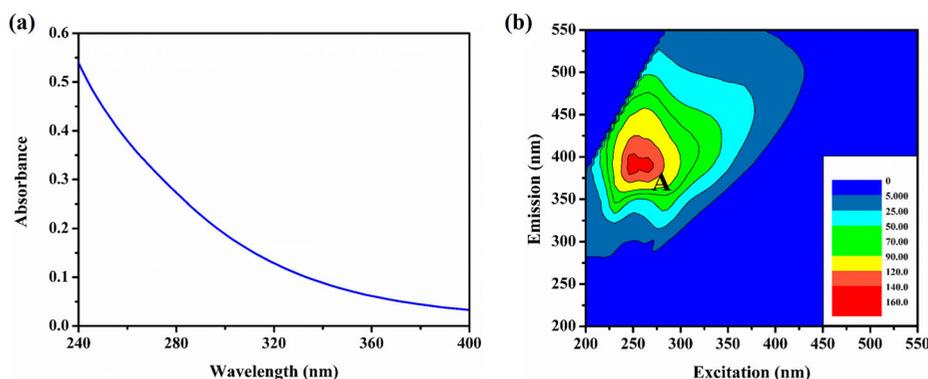
$$\frac{l}{l_0} = 1 + \left( \frac{l_{ML}}{l_0} - 1 \right) \left( \frac{1}{2K_M C_L} \right) \left[ 1 + K_M C_L + K_M C_M - \sqrt{(1 + K_M C_L + K_M C_M)^2 - 4K_M^2 C_L C_M} \right]. \quad (4)$$

where  $l_0$ ,  $l$ , and  $l_{ML}$  are the absorbance intensity without metal ion added, with metal ion added, and the lower limiting absorbance intensities after metal ion titration, respectively. Totally, both  $K_M$  and  $C_L$  can be calculated in Equations (3) and (4) using the Origin Pro<sup>TM</sup> 9.1 (The OriginLab Inc., Massachusetts, USA).

## 3. Results and discussion

### 3.1. UV-vis and EEM fluorescence spectra

The UV-vis spectrum for the DOM in urban stormwater runoff is depicted in Figure 1(a). The decrease in absorbance with wavelength followed a trend similar to that previously observed for wet precipitation and urban runoff samples [1,32,33], which could be attributed to the large number of organic compounds with different structures and chromophores [42]. It was reported that the UV-vis spectra of DOM before and after binding to copper(II) showed no obvious location changes [12]. In this study, the wavelength of 254 nm was selected to monitor the absorbance during the titration process of DOM with copper(II), considering that the absorbance at 254 nm is widely used to study the spectral properties of DOM [43]. As an important parameter for identifying the source and composition of DOM [44], fluorescence spectra were used to explore the position of fluorescence peaks. The major fluorescence regions have been designated by letters A, C, M, B and T [45] as listed in Table 2.



**Figure 1.** The UV-vis absorbance (a) and fluorescence (b) spectrum of DOM in urban stormwater runoff.

The fluorescence spectrum of the sample as shown in Figure 1(b) could be characterized by a unique main fluorophore centered at an excitation ( $E_x$ )/emission ( $E_m$ ) wavelength pair of 255/388 nm, which demonstrated that UV humic-like compounds were the major fluorescent components in the DOM of stormwater runoff samples [1,9]. The peak located at  $E_x/E_m = 255/388$  nm was chosen to monitor the changes of DOM during the copper(II) ions binding process in the afterwards titration processes.

### 3.2. Comparison of absorbance and fluorescence quenching titration

The variation trend of absorbance and fluorescence intensities of DOM coordinated with copper(II) ions with different concentrations is exhibited in Figure 2. The UV absorbance of the coordinated DOM increased promptly with the concentrations of added copper(II) ranging from 0 to  $0.0004 \text{ mol L}^{-1}$ , similar to previous studies [46]. When the concentrations of copper(II) ions were more than  $0.0004 \text{ mol L}^{-1}$ , the UV absorbance of copper(II)-added DOM increased slowly, and finally tended to be constant, as illustrated in Figure 2(a), implying that the complexation of copper(II) with DOM is in accordance with a certain stoichiometric relationship. When the complexation equilibrium was achieved, the UV absorbance tends to become a nearly constant value. While the fluorescence intensity did not decrease significantly for the concentrations of copper ions higher than  $0.0004 \text{ mol L}^{-1}$  as demonstrated in Figure 2(b),

which was a common phenomenon during fluorescence quenching titration of humic substances with metal ions [12,13,47].

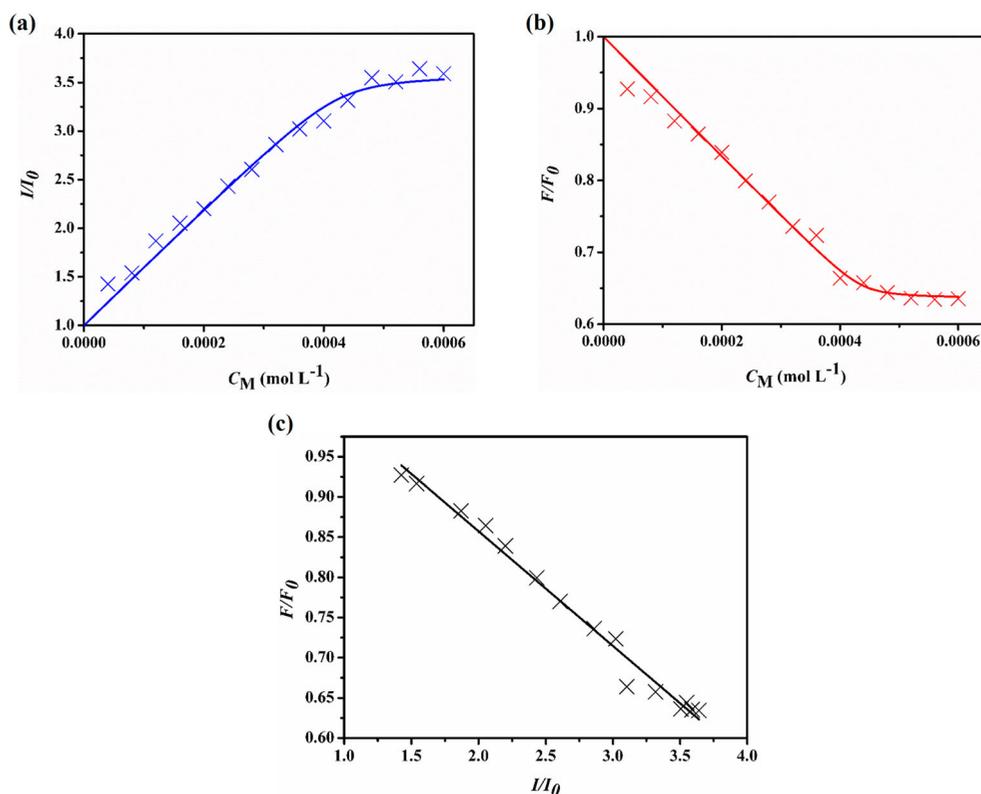
There were significant negative correlations between DOMs' UV absorbance and fluorescence intensity during the titration ( $R^2 = 0.98$ ) (Figure 2(c)). It is generally believed that the major binding sites in humic substances are attributed to some carboxyl or phenolic hydroxyl groups [48]. Previous studies had demonstrated that the above functional groups could enhance fluorescence by increasing the transition probability between the singlet and ground state [49,50]. Furthermore, these structures increased dislocation of electrons, thus resulting in the increase in UV absorbance [12]. The simultaneous changes in UV absorbance and fluorescence intensities observed in this study suggested that the formation of complexes between DOM and copper(II) ions had occurred during the titration process.

### 3.3. Conditional stability constants and complex capacities

The log  $K_M$  values in this study calculated from the absorbance and fluorescence quenching titration experiments were 5.37 and 5.48, respectively, which were higher than those of commercial humic acids (Sigma-Aldrich Co., USA, approximately 4.99–5.26) [10] and humic-like components in freshwater (approximately 4.54–5.29) [51]. Furthermore, the values of  $C_L$  in this study were much higher ( $85.62$  and  $87.23 \text{ } \mu\text{mol mg}^{-1}$ , respectively) than the DOM samples isolated from the Suwannee River fulvic acid (approximately  $0.01$ – $5.12 \text{ } \mu\text{mol mg}^{-1}$ ) [51] and lake surface waters (approximately  $6.91$ – $7.54 \text{ } \mu\text{mol mg}^{-1}$ ) [12], which were mainly attributed to the large content of oxygenated reactive functional groups such as carboxylic, phenolic, alcoholic and carbonyl groups [1,10,25,47]. Previous studies had demonstrated that asphalt pavement was more prone to produce the aromatic substances [52,53], which could

**Table 2.** Peaks, description, and excitation/emission maxima of DOM [45].

Peaks	Description	Excitation max (nm)	Emission max (nm)
A	UV humic-like, less aromatic	<260	380–460
C	Visible humic-like, more aromatic	320–360	420–460
M	Marine-humic-like	290–310	370–410
B	Tyrosine-like substances	260	280
T	Protein-like tryptophan	250–300	305–355



**Figure 2.** Experimental data and nonlinear model fitting curves for DOM titration with copper(II). (a) UV absorbance; (b) fluorescence intensity; and (c) the UV absorbance vs. fluorescence intensity during the titration.

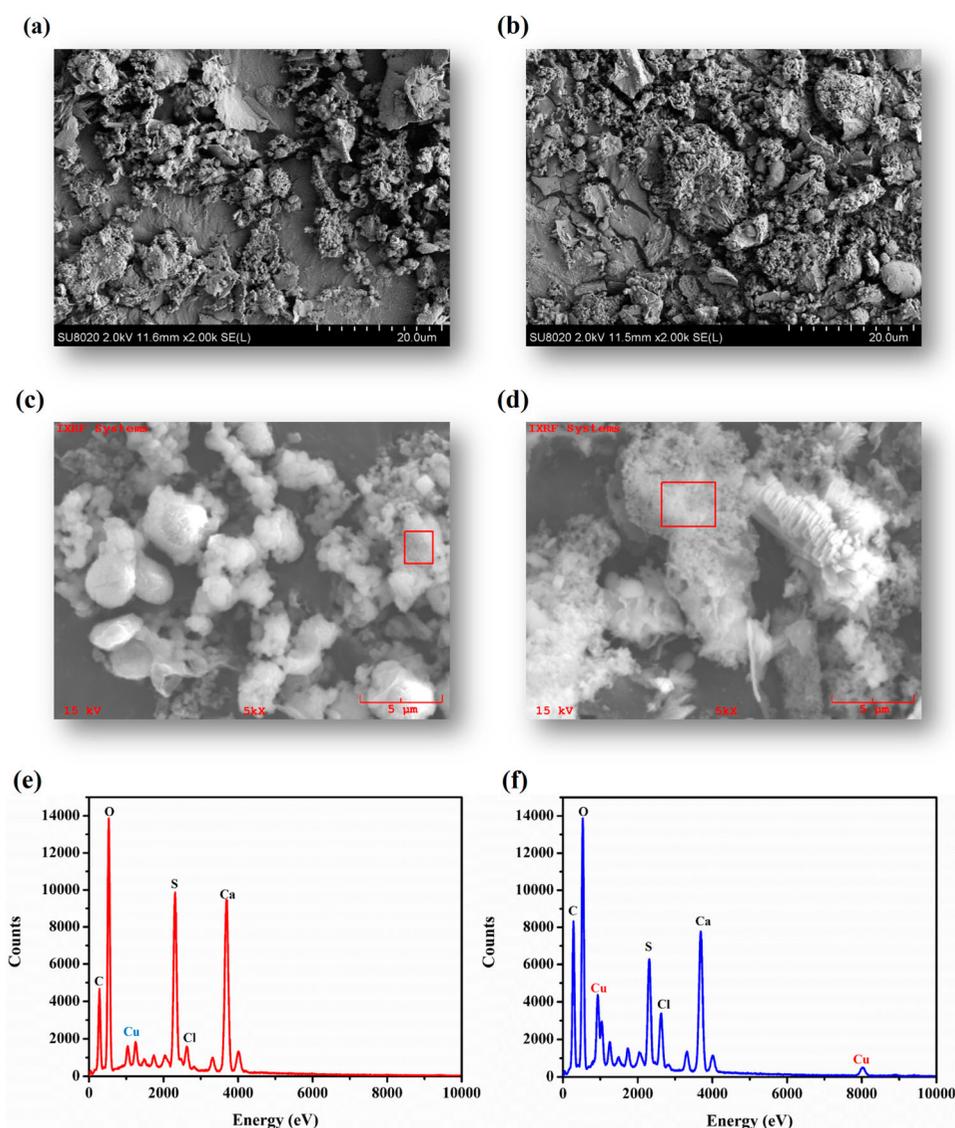
produce highly stable complexes with copper(II). Generally, in natural waters, the organic ligands with strong complexing ability are present in lower concentrations, while the ligands with weak complexing ability exist in higher concentrations [23,54]. Moreover, the ratio of copper to DOM is known to affect the strength of copper binding by DOM [55]. Generally, at low Cu/DOM ratios ( $\leq 10^{-3}$ ), copper tends to bound with the strongest ligands in the DOM, which may result from nitrogen and sulfur-containing functional groups [56,57]. However, the large values of Cu/DOM in this study (0.2–3) and high copper(II) ion concentrations (micromolar level) led to a quick saturation of the strong binding sites and that the majority of copper(II) ions become bound to the weak sites (carboxylic, phenolic, hydroxyl and carbonyl). Therefore, the  $\log K_M$  values calculated from both the titration methods could be considered as overall averaged constants. The relative standard deviations of  $\log K_M$  and  $C_L$  for the three parallel titration experiments were less than 2.8% and 4.6%, indicating that the corresponding results were reliable.

### 3.4. SEM-EDX and XPS analysis

In this study, the morphology characteristics and chemical compositions (especially the presence of copper(II)) of

original and copper(II)-added samples were investigated via SEM equipped with EDX. SEM micrographs for original and copper(II)-added samples are illustrated in Figure 3(a,b). No significant morphological changes were detected after the introduction of copper(II) ions. Three representative micro analytical regions of each sample were selected to explore the element (especially copper(II)) distribution, as illustrated in Figure 3(c,d). Meanwhile, the EDX semi-quantitative analysis corresponding to the original and copper(II)-added samples is shown in Figure 3(e,f), respectively, from which it could be seen that the copper contents increased from 0.16 atomic% in original DOM to 2.29 atomic% in copper(II)-added sample.

Unfortunately, the increase in Cu content in the copper(II)-added sample supported by EDX only implied the presence of foreign Cu, while could not clarify the binding status of copper(II)-DOM in the copper(II)-added sample. In order to further elucidate the coordination mechanism between copper(II) ions and DOM, XPS was introduced to characterize the difference of several elements' chemical state and electronic state in original sample and copper(II)-added sample, as depicted in Figure 4. The main peaks at binding energies of 284.8 and 531.9 eV could be assigned to the C 1s and O 1s (Figure 4(a)) [30]. Furthermore, a minor peak of Cu 2p



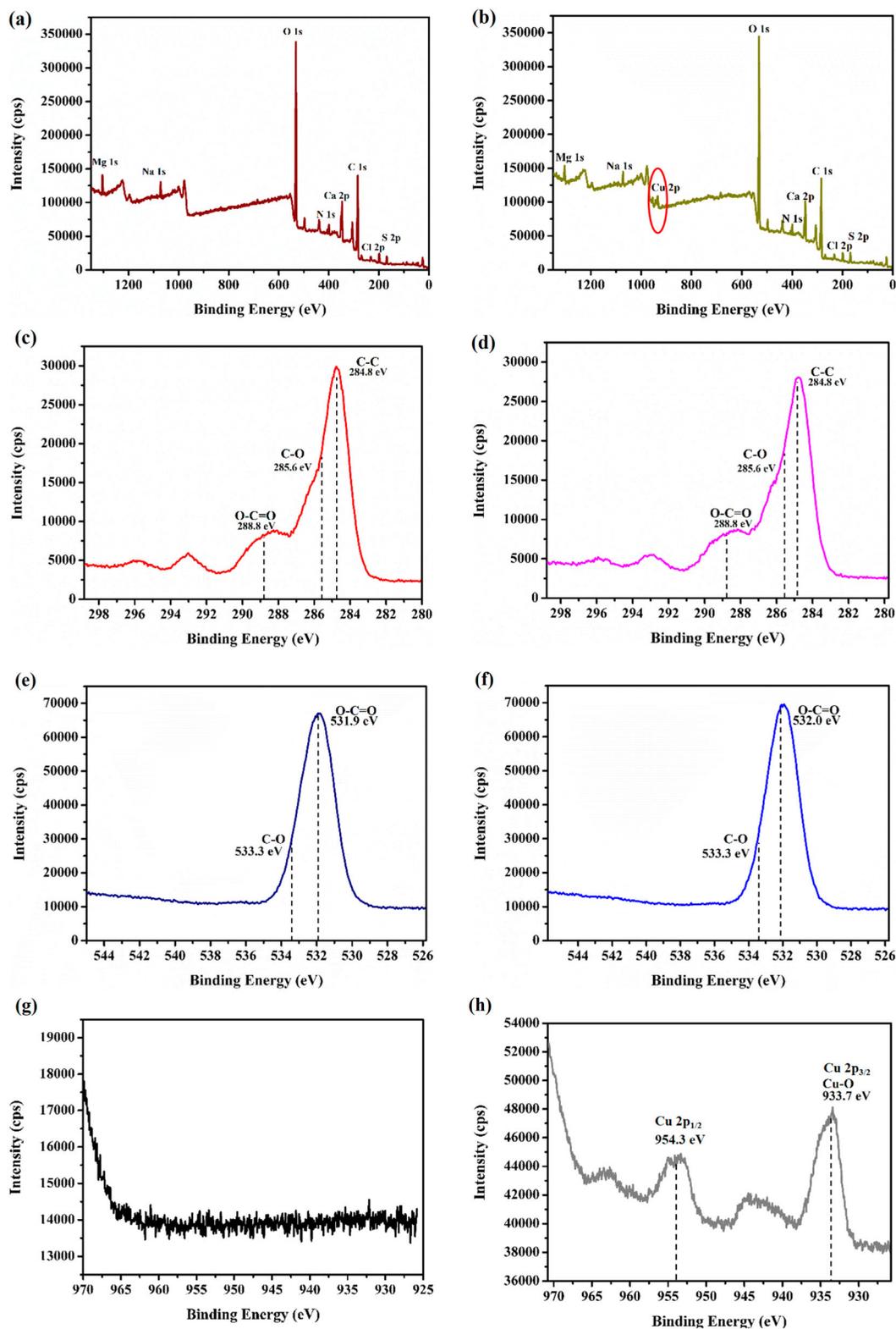
**Figure 3.** (a) SEM micrographs of original sample; (b) SEM micrographs of copper(II)-added sample; (c) EDX image of original sample; and (d) EDX image of copper(II)-added sample; (e) EDX spectrum of original sample; and (f) EDX spectrum of copper(II)-added sample.

was found in the wide scan XPS spectrum of copper(II)-added samples (Figure 4(b)), suggesting that copper ions are involved in the bonding with the DOM.

The high-resolution core-level spectra of C 1s, O 1s, and Cu 2p regions of before and after copper(II) ions bonding with DOM are shown in Figure 4(c)–(g). The C 1s peaks at 284.8, 285.6, and 288.8 eV (for original and copper(II)-added samples) in Figure 4(c,d) were assigned to C–C, C–O (ether or alcohol), and O–C=O bonds (carboxyl), respectively [30,58], which can be further confirmed by the findings from the analysis of conditional stability constants and binding capacities.

The O 1s spectra can be deconvoluted into two individual component peaks, which come from different functional groups (Figure 4(e,f)). The peaks with binding energies of 531.9, 533.3 eV for the original

sample and 532.0, 533.3 eV for the copper(II)-added sample can be assigned to the oxygen atom in the forms of O–C=O (carboxyl groups) and of C–O (ether or alcohol hydroxyl), respectively [29,30]. Furthermore, the shift of the oxygen signals from 531.9 eV in copper-unloaded sample to 532.0 eV in copper(II)-added one was probably assigned to the interactions between the copper(II) ions and oxygen atoms [59,60]. The Cu 2p core-level spectra of original sample and copper(II)-loaded sample were demonstrated in Figure 4(g,h). Two main peaks of Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> were observed at 933.7 eV and 954.3 eV in Figure 4(h), respectively, which further confirmed the binding of Cu with DOM. Previous studies had demonstrated that the binding energy of the Cu 2p<sub>3/2</sub> main photoelectron peak of Cu–O bond was equal to 933.7 eV [61–63]. In



**Figure 4.** (a) Representative XPS spectrum of survey of original sample; (b) the XPS spectrum of survey of copper(II)-added sample; (c) C 1s of original sample; (d) C 1s of copper(II)-added sample; (e) O 1s of original sample; (f) O 1s of copper(II)-added sample; (g) Cu 2p of original sample; and (h) Cu 2p of copper(II)-added sample.

addition, the pronounced shake-up peaks found in Figure 4(h) were characteristic peaks of Cu–O, implying that Cu–O bond was formed via complexation of copper

(II) ions with oxygen-containing functional groups, such as carbonyl, carboxyl, and aliphatic/phenol hydroxyl groups.

## 4. Conclusions

In this work, the UV absorbance and fluorescence quenching titration were used to quantitatively characterize the binding abilities of copper(II) ions to DOM in urban stormwater runoff, in which the higher  $\log K_M$  and  $C_L$  values were attributed to more aromatic substances and binding sites (i.e. oxygenated reactive functional groups) of DOM in real urban stormwater runoff. The presence of the copper in the copper(II)-added sample was confirmed by EDX due to the noticeable increase in copper content. And the presence of Cu–O bond proved by XPS suggested that copper(II) ions were more inclined to be bound with carbonyl, carboxyl, and aliphatic/phenol hydroxyl groups. Generally, DOM in urban stormwater runoff has a higher copper(II) ions binding affinity that may affect the status of ecosystem. Considering the dramatically temporal and spatial variability of stormwater, more efforts will be devoted to conduct the experiments similar to this study to confirm its repeatability and reproducibility. Moreover, further investigations should be carried out to study the relationship of DOM from different land uses with the other contaminants like heavy metals and some typical organic pollutants in urban stormwater runoff.

## Disclosure statement

No potential conflict of interest was reported by the authors.

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