



## Effect of recycling filter backwash water on characteristic variability of dissolved organic matter in coagulation sedimentation process

Zhiwei Zhou, Yanling Yang\*, Xing Li, Zhaoyang Su, Yongwang Liu, Jiawei Ren, Yang Zhang

*Key Laboratory of Beijing for Water Quality Science and Water Environment Recovery Engineering, Beijing University of Technology, Beijing 100124, P.R. China  
Tel. +86 1067391726; email: yangyanling@bjut.edu.cn*

Received 21 March 2013; Accepted 12 August 2013

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### ABSTRACT

In this study, the physicochemical characteristics of the dissolved organic matter (DOM) in simulated raw water, corresponding filter backwash water (FBWW) and treated water at three recycling ratios of 2, 5, and 8%, including control without FBWW were evaluated using bulk properties, in addition to advanced characterization by molecular weight distribution (MWD), hydrophobicity, and fluorescence. The DOM characteristics of raw water and FBWW were primarily identified and compared, and it was found that DOM in FBWW was roughly hydrophilic as compared with raw water, and the FBWW was more refractory due to a substantial increment of low-MW (<3 KDa). Additionally, humic-like fluorophore (Peak A) and protein-like fluorophore (Peak T1), with maxima at the Ex/Em wavelengths of 245.0–265.0 nm/400.0–435.0 nm, 280.0–305.0 nm/305.0–345.0 nm, respectively, were the two main components in raw water and FBWW. Recycling trial results indicated that DOM removal efficiencies were improved with comparison to control. Specifically, all chemical fractions except hydrophobic neutral could enhance removal, but MWD was highly depended on the physical nature of raw water and FBWW. Fluorescence spectra of treated water indicated recycling FBWW could effectively improve humic-like substance (Peak A) removal, but the protein-like matter (Peak T1) was resistant to elimination or was enriched.

*Keywords:* Filter backwash water; Recycling; Dissolved organic matter; 3D-EEM

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### 1. Introduction

Most of the drinking water treatment plants use conventional methods in water treatment like oxidation, coagulation, flocculation, sedimentation, and sand filtration. Particulates, including colloidal and natural organic matter, metal salt precipitates, lime softening precipitates, iron and manganese precipitates and

microorganism are commonly removed in filtration processes. Filter backwashing is a necessary step in maintaining optimum filtered water quality and also prevents deterioration of the media. During such implementation, a great amount of waste water denoted as filter backwash water (FBWW) is produced. The proper reuse, recycling, and disposal of FBWW have always drawn great concern worldwide.

Commonly, FBWW are characterized by elevated concentrations of suspended solids, total organic

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\*Corresponding author.

carbon, and inorganics as well as the chemical precipitates derived from the inorganic coagulants [1,2]. Meanwhile, FBWW can be enriched with *Giardia*, *Cryptosporidium*, precursors of disinfection by-products and heavy metals [3,4]. Therefore, given the microbial and chemical risk posed to the users' health, it is not feasible to directly recycling FBWW blended with raw water without any pretreatment. The Filter Backwash Recycling Rule issued by U.S. Environmental Protection Agency is designed to reduce the likelihood that pathogenic organisms pass through the treatment process into finished drinking water [5].

However, it has been observed that directly recycling FBWW could enhance TOC, DOC, and  $UV_{254}$  removal in coagulation sedimentation process for low-turbidity water [1,6]. Gottfried et al. [1] observed that recycling 5 and 10% by volume of FBWW blended with the raw water characterized with a specific UV absorbance (SUVA) within 2–4 L/mg m could significantly enhance DOC removal, while a slight reduction in raw water TOC or  $UV_{254}$  was found with both 5 and 10% FBWW recycle as compared to control. Bourgeois et al. [6] pointed out that recycling 5% of combined backwash water resulted in the improved settled water quality as quantified by TOC,  $UV_{254}$  and color. However, the concentration of these indicative parameters is a collective measurement of organic matter in water, providing no information on the composition and distribution of constituents. Also, to our best knowledge, the characteristics of dissolved organic matter (DOM) in FBWW and in treated water were rarely investigated. Thus, it is essential to identify the physicochemical characteristics of DOM in raw water, FBWW, and treated water samples.

The purpose of this research was, therefore, to expound the DOM removal characteristic of recycling FBWW for a simulated low-turbidity source water. Specifically, the impact of recycling 2, 5, or 8% by volume of FBWW blended with raw water on bulk parameters, that is, DOC,  $UV_{254}$ , and SUVA removal was evaluated, as compared to control without FBWW. Advanced techniques, that is, XAD-4 and XAD-8 resin adsorption and ultrafiltration fractionation techniques, as well as three-dimensional excitation emission matrix (3D-EEM) fluorescence spectroscopy were employed for DOM fractionation.

## 2. Materials and methods

### 2.1. Materials and reagents

Kaolinite (solids content 31.87 g/L, analytical grade, Tianjin, China) prepared according to the

reference [7] was used as turbidity-causing matter. Humic acid (2.078 gDOC/L, Shanghai) is prepared as the representative organic matter. Aluminum sulfate hydrate ( $Al_2(SO_4)_3 \cdot 18H_2O$ , analytical grade, Tianjin, China) was used as coagulant. The optimal dosage of alum was determined by jar test, and it was 12 mg/L. DI water was used to prepare all reagents.

### 2.2. Simulated water and collection of FBWW

The raw water was simulated by adding filtered domestic sewage to local tap water (Beijing, China) at a volumetric ratio of 1:33. Meanwhile, 1.56 mg DOC/L humic acid and 8.27 mg/L kaolinite was introduced. The tap water had average turbidity,  $UV_{254}$ , and DOC concentrations of 0.538 NTU,  $0.012 \text{ cm}^{-1}$ , 2.237 mg/L, respectively. Before recycle trials, the raw water was stabilized at room temperature for 2 days. The main parameters of the simulated water were summarized in Table 1.

As depicted in Fig. 1, the experimental system includes a 2-stage mixer, 3-stage flocculating reactor, sedimentation unit, sand filter and FBWW on-line recycling system. In detail, the retention time and stirring speed of the mixer is 2 min, 450 rpm accordingly. The 3-stage flocculating reactor of each with retention time is 6, 6, and 3 min, respectively, and the stirring speed is 350, 250, 150 rpm in sequence. The upstream flow rate of sedimentation unit is 1.0–2.0 mm/s with retention time of 6–8 min. Settled water then went on to a 12 mm inner diameter filter column operating at 1.23 mm/s, containing 250 mesh ~180 mesh grade sand at a depth of 0.5–0.6 m. The filtration model is constant rate and varied head; generally, the head loss is increasing with the increase in filtration time and displays differences according to raw water quality. In this study, the filtration cycle is 2 days. The water backwash is performed when filtration cycle is reached, the intensity and duration of which is  $0.04 \text{ L}/(\text{s m}^2)$ , 5 min, respectively. Collected backwash water is denoted as FBWW, the main characteristic parameters are shown in Table 1.

During on-line recycle experiments, FBWW was continuously blended with raw water, and the volume was precisely controlled using metering pump and the volume ratio of recycling FBWW to total influent was investigated at 2, 5, and 8%, respectively. The mixing speed in the regulator was kept at 450 rpm. All recycling trials were carried out in continuous flow. The interim tank, as a constant head before the sand filter, was used in this study from which the settled water was withdrawn intermittently twice per day for DOM removal analysis.

Table 1  
Raw source waters and FBWWs characteristics

Analytes (units)	Raw water		FBWW	
	Rang	Average	Rang	Average
Temperature (°C)	11–17	14	12–17	15
pH	6.78–7.58	7.01	6.34–7.04	6.69
Turbidity (NTU)	5.51–14.3	9.91	–	–
UV <sub>254</sub> (cm <sup>-1</sup> )	0.034–0.046	0.040	0.037–0.053	0.042
DOC (mg/L)	2.016–3.026	2.462	2.128–3.987	2.758
SUVA (L/mg·m)	1.27–1.98	1.58	1.11–1.83	1.34
TSS (g/L)	–	–	0.626–0.68	0.657

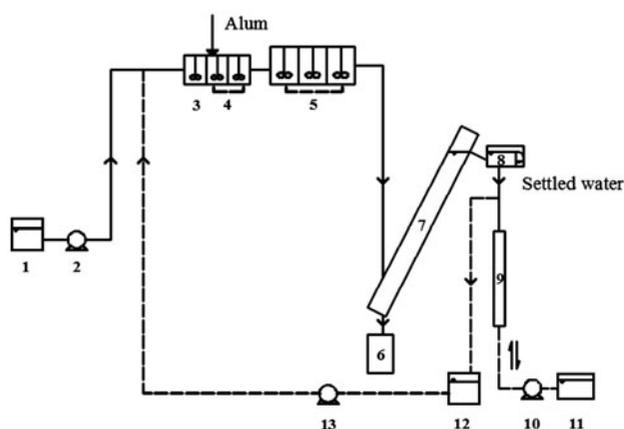


Fig. 1. Schematic diagram of on-line experimental set-up: 1—raw water, 2—feeding pump, 3—regulator tank, 4—two-stage mixer, 5—three-stage flocculation, 6—sludge storage tank, 7—sedimentation unit, 8—interim tank, 9—sand filter, 10—backwashing pump, 11—filtered water basin, 12—filter backwash water tank, 13—recycling pump.

### 2.3. DOM fractionation

Molecular weight distribution (MWD) of DOM was conducted using a dead-end batch ultrafiltration unit with a 300-ml capacity stirred cylindrical cell (MSC300, Mosu Corp., Shanghai, China). Meanwhile, the YM disc membranes (Amicon, nominal MWCOs are 3, 10, 30 kDa, Millipore Corp., USA) were used for DOM isolation and fractionation according to Wei et al. [8].

Resins were cleaned and conditioned as described by Leenheer [9]. The ratio of water sample volume to Supelite TM XAD-8 or Amblite XAD-4 resin volume (wet volume) was set at 35:1, and the initial water volume was 350 mL for avoiding fractions breakthrough. The flow rate of loading sample onto the resin was 15 bed-volumes h<sup>-1</sup>, which was permitted an adequate adsorption. DOM in water samples including the

influent, FBWW, and treated water were chemically fractionated into five parts following the procedure of Yan et al. [10]: hydrophobic bases (HoB), hydrophobic neutral fraction (HoN), hydrophobic acid (HoA), weakly hydrophobic acid (WHoA) and hydrophilic matter (HiM).

Fluorescence measurements were conducted using a spectrofluorometer (F-4500, Hitachi, Japan) equipped with a 150 W xenon lamp at ambient temperature of 24°C. A 1-cm quartz cuvette with four optical windows was used for the analyses. Emission scans were performed from 220 to 550 nm at 5 nm steps, with excitation wavelengths from 220 to 450 nm at 5 nm intervals. The detector was set to high sensitivity, and the scanning speed was maintained at 1,200 nm/min; the slit widths for excitation and emission were 5 and 3 nm, respectively. Under the same conditions, fluorescence spectra for DI water (Millipore Milli-Q, Billerica, MA, conductivity 18.2 Ω·m) were subtracted from all the spectra to eliminate water Raman scattering and to reduce other background noise.

### 2.4. Analytic method

A total carbon analyzer vario TOC<sup>®</sup> cube (Elementar, Germany) was used to analyze DOC. UV<sub>254</sub> was determined by using a UV/vis spectrophotometer (UV2600, China). Both DOC and UV<sub>254</sub> were measured after filtration through 0.45-μm acetate fiber membranes. SUVA calculated as one hundred times UV<sub>254</sub> divided by DOC concentration was used to estimate the chemical nature of DOM. Turbidity was monitored by 2100N Turbidimeter (Hach, USA). pH value was determined and calibrated daily using pH buffer solutions. Total suspended solid (TSS) content and solid content were measured using standard methods [11].

### 3. Results and discussion

#### 3.1. Characteristics of DOM in raw water and FBWW

Table 1 summarized the range of important parameters for source water and FBWW quality monitoring. Apparently, the raw water had a moderate level of DOC and  $UV_{254}$ , and low turbidity, which are the same characteristics as low turbidity and micro-polluted water. SUVA in raw water is 1.58 L/mg m, indicating the DOM is generally enriched in hydrophilic and low-MW components, and it is difficult to be coagulated [12]. A low solid content is typically found in FBWW, implying that the FBWW has not undergone any thickening. When compared to raw water qualities, the FBWW water qualities are basically consistent with level of  $UV_{254}$  and DOC concentration. However, the DOM characterization in raw water and FBWW may be different. The hydrophobicity, apparent MWD and fluorescence in the DOM of raw water and FBWW, is investigated as shown in Fig. 2.

In Fig. 2(a) it can be observed that HiM (47.2% as %DOC) and HoA (37.2% as % $UV_{254}$ ) dominated in raw water. Slightly differing from raw water, the largest fractions in FBWW were HiM (44.6% as %DOC) and HoN (34.1% as % $UV_{254}$ ). So, it is obviously that the DOM in FBWW was roughly hydrophilic as compared to raw water, and a large portion of hydrophobic fractions, for example, HoA, HoN also occurred. The reason for the highest percentage as % $UV_{254}$  of HoA fraction in raw water is that the humic acid stock solution was added and the aromatic, unsaturated organics in domestic sewage was introduced. In FBWW the HoN predominated as % $UV_{254}$ , which may be attributed to the lowest removal efficiency of this fraction and transformation of other hydrophobic fractions into HoN. Generally, the HoN fraction includes the compositions, such as hydrocarbon, pesticides, carbonyl compounds and synthetic detergents. The result here was similar to the findings of Chow [13], who pointed out that the recalcitrant fraction of NOM was indicated to be polysaccharides and their derivatives.

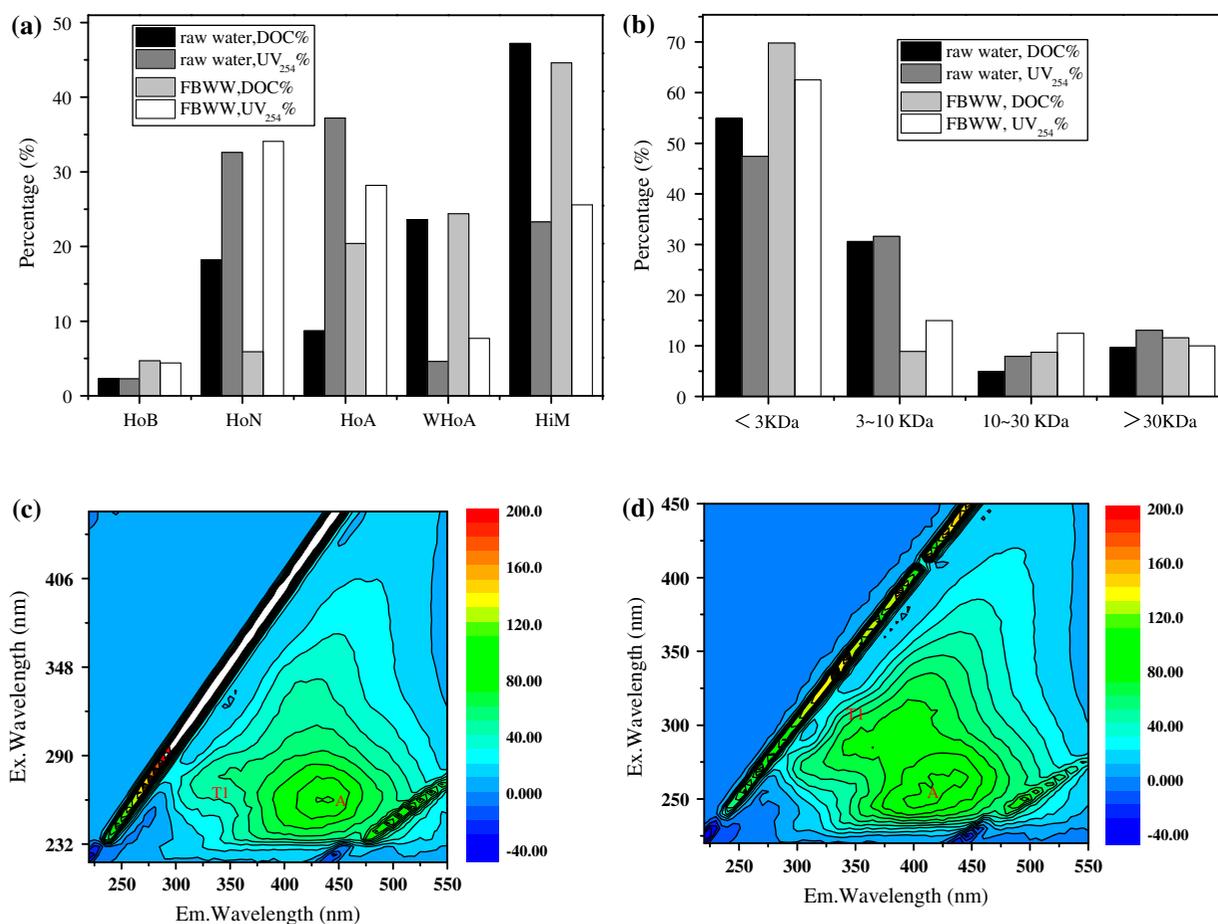


Fig. 2. Characteristics of DOM in raw water and FBWW (a) hydrophobicity, (b) apparent MWD, and DOM fluorescence EEM spectra (c) raw water and (d)FBWW.

As seen in Fig 2(b), <3 KDa fraction was the main constituent in both raw water and FBWW, and in the FBWW, there was 14.9% as DOC%, 15.1% as UV<sub>254</sub>%, respectively, higher than that in raw water (46.7% as %DOC and 34.2% as %UV<sub>254</sub>). Additionally, the proportion of 3–10 KDa and >30 KDa were lower than that in raw water. The phenomena can be explained that traditional coagulation–sedimentation–sand filter process could effectively remove DOM in medium MW (3–10 KDa) or higher MW(>30 KDa), but <3 KDa and 10–30 KDa were resistant to elimination.

There are commonly five key fluorescence peaks referred to as fluorophores A, C, T1, T2 and B in water samples [14–16]. In this study, the peaks (A and T1) distinctly identified are selected, because peaks B, C, and T2, have relatively lower fluorescence intensity. Peak A related to humic-like substance derived from the breakdown of plant material exhibit maximums at emission (Em) wavelength of 420–450 nm from excitation (Ex) at 230–260 nm [14]. Protein-like fluorophores including tryptophan-like (Peak T) and tyrosine-like (Peak B) materials are usually detected at enhanced levels in water impacted by domestic sewage. Peak T1 which is tryptophan-like (protein-like) exhibits a maximum at an Em wavelength of 340–350 nm from Ex at the 220–275 nm [14,15]. It could be seen in Figs. 2(c) and (d) that in the DOM of raw water and FBWW, fluorescent components were mainly humic-like fluorophore (Peak A) and protein-like fluorophore (Peak T1), with maxima at the Ex/Em wavelengths of 245.0–265.0 nm/400.0–435.0 nm, 280.0–305.0 nm/305.0–345.0 nm, respectively. Additionally, a broad Peak C, with relatively lower fluorescence intensity, was also observed. Compared to the fluorescence maxima of humic-like substance in raw water, the location of Peak A in the FBWW DOM had a blue shift. The location of Peak T1 in the FBWW DOM was 25 nm red-shifted along the Ex axis and 35 nm blue-shifted along the Em axis. As reported, a red shift is related to the presence of carbonyl-containing substituents, hydroxyl, alkoxy, amino groups, and carboxyl constituents, while a blue shift is associated with a decomposition of condensed aromatic moieties and the break-up of the large molecules into smaller fragments, such as a reduction in the degree of the p-electron system, a decrease in the number of aromatic rings, a reduction of conjugated bonds in a chain structure, a conversion of a linear ring system to a nonlinear system or an elimination of particular functional groups including carbonyl, hydroxyl and amine [17]. It was, therefore, concluded that traditional coagulation and sedimentation followed by sand filter process could decrease the number of aromatic rings and conjugated bonds of humic-like substance and lead to the increase of

hydroxyl, alkoxy, amino groups, and carboxyl constituents.

In general, the content and physicochemical characterization of DOM in FBWW in this study was analogous to source water, and the FBWW was inclined to more refractory due to the substantial increment of low MW fraction (<3 KDa). HoA, HoN as %UV<sub>254</sub> predominated in the DOM of raw water and FBWW, which were confirmed with Peak A fluorophore related to humic-like substances.

### 3.2. DOM removal characteristics

As observed in Fig. 3, DOM concentrations as quantified by DOC and UV<sub>254</sub> in settled water were positively impacted with 2, 5, and 8% FBWW compared with control, and the DOM removal rate of 2 or 5% was higher than 8%. Specifically, 2% was able to maximally reduce DOC from 2.735 mg/L in raw water to 1.830 mg/L with average 33.1% of DOC removal, which was 56.9% higher than control (21.1%). The highest UV<sub>254</sub> removal could be achieved at 5%, reaching up to 54.8%. From the variation curves of SUVA, it can be found that the DOM characteristic in treated water was significantly different. The lowest SUVA value, responding to the highest removal efficiency of UV<sub>254</sub>, was obtained at 5%. The enhanced removal of DOM in this study can be divided into three mechanisms, such as physical (i.e. increased collision sites of efficiency due to improved particle number concentration), physicochemical (i.e. increased collision sites and sweep flocculation due to insoluble aluminum hydroxides in FBWW), and physicochemical (charge neutralization or sweep flocculation of alum species freshly “preloaded”). Gottfried et al. [1] and Zhou et al. [18] reported that the increasing of seeding and nuclei of destabilized residual streams

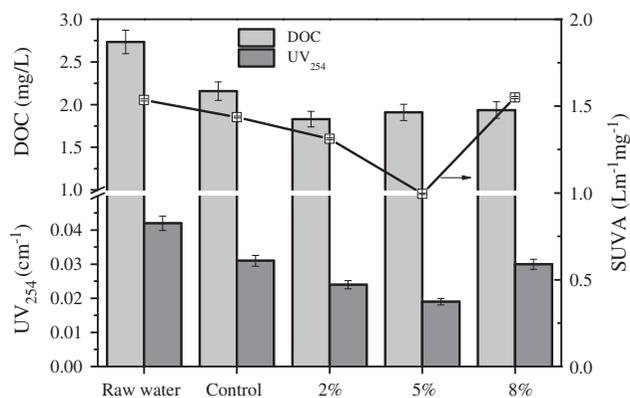


Fig. 3. FBWW recycling trials on DOM removal (error bars represent the  $\pm 5\%$  standard deviation).

particles was more significant for favoring coagulation. According to their statements, for the low-turbidity water, the improved removal of DOM could be obtained due to the increased number of particles introduced with the FBWW stream. The increase in the number of collision sites for DOM constituents in the raw water with the destabilized FBWW particles and impacts to flocs aggregation in the flocculation and settling stages could explain the improvements in DOM removal. Additionally, the breakage of recycling FBWW flocs may occur when exposed to higher shear force, so both aged and fresh precipitate particles coexist in the recycling process. There are more active groups on the fresh precipitate particles that are capable of binding the aged precipitates together [19]. Thus, the adsorption of newly formed soluble Al species on the surface of the aged flocs, giving improved adhesion.

Meanwhile, it should be noted that the trapped organics may release from flocs in FBWW into water, and the DOM concentrations and characterization may varied This aspect may play negative role in removing DOM, and consequently resulting in a comprised performance. Mass balance calculations using the analysis data from the raw water and FBWW sample in Table 1, suggesting that the highest recycling ratio of 8% FBWW would result in a slight improvement of blended water DOC of 0.221 mg/L, and that of  $UV_{254}$  was  $0.003\text{ cm}^{-1}$ . Thus, it would not lead to a significant change in DOC concentration,  $UV_{254}$  level or coagulant demand in the blended water matrix prior to coagulation. To study about the impact of DOM characteristics in recycling FBWW on the constituent of DOM in treated water, the hydrophobicity and MWD in control as reference was further investigated as shown in Fig. 4. Where  $\Delta\text{DOC}\%$  or  $\Delta UV_{254}\%$  means the percentage of a constant fraction in treated water after recycling at three observed recycling rates minus the percentage of the same fraction in control. The positive  $\Delta\text{DOC}\%$  or  $\Delta UV_{254}\%$  implies the fraction in treated water takes up a higher proportion, and the removal efficiency of this fraction declines when compared to control.

In control, HoA and HiM was dominant, which accounted for 38.1% as DOC% (or 35.5% as  $UV_{254}\%$ ) and 30.4% as DOC% (or 16.1% as  $UV_{254}\%$ ), respectively. And the largest physical fraction was mainly distributed in low-MW (<3 KDa), taking up 59.5% as %DOC (or 77.5% as  $UV_{254}\%$ ). For the samples at three observed recycling rates, the percentage of HoN in treated water subtracted that in control was always positive, excluding that calculated as DOC% at 8%. The positive value indicated that HoN could not be further eliminated. Except for HoN, the other four

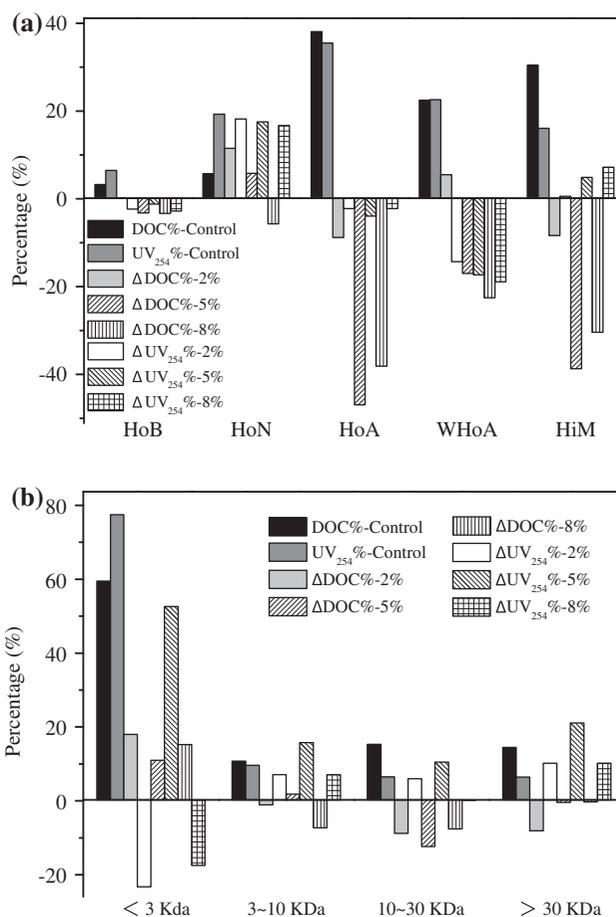


Fig. 4. The hydrophobicity (a) and MWD (b) in treated water compared with control.

fractions (HoB, HoA, WHoA and HiM) could be somewhat enhanced removal regarding  $\Delta\text{DOC}\%$ , implying recycling FBWW stream could improve the removal efficiencies of all chemical fractions except HoN. On the other hand, it was shown in the Fig 4(b) that three recycling ratios of FBWW played different roles in removing DOM with varied MW regions. Generally, the percentage of >3 KDa as  $\Delta\text{DOC}\%$  were negative, while the percentages of >3 KDa as  $\Delta UV_{254}\%$  were always positive regardless of the recycling ratio. In addition, the lower MW (<3 KDa) seemed to be enriched, for  $\Delta\text{DOC}\%$  of this fraction was consistently positive. There are two interpretations accounting for this result. Firstly, there was a great quantity of <3 KDa presenting in raw water and FBWW (shown in Fig. 2(b)), inevitably this fraction increased with the addition of recycling FBWW based on mass balance calculations, especially for the highest recycling rate at 8%. Secondly, from the analysis in Section 3.1, we know that the FBWW was inclined to more refractory and the traditional coagulation/ sedi-

mentation followed by sand filtration could not effectively remove low-MW fraction, thus the removal efficiency of <3 KDa was comprised. So, in the FBWW recycling process, MWD in treated water was highly depended on the physical nature of raw water and FBWW produced in the process train.

The fluorescence EEM spectra in the DOM of treated water samples were illustrated in Fig. 5. It can be seen that fluorescence EEM spectra in the DOM of treated water samples were similar to that of source water accordingly. The maxima of Peak A and T1 was at the Ex/Em 250.0–260.0 nm/400.0–435.0 nm and 275.0–285.0 nm/300.0–345.0 nm, respectively. Compared to the fluorescence maxima of humic-like substance, the location of Peak A in the DOM at 2, 5, and 8% had a 5–10 nm blue shift to shorter wavelength. The location of Peak T1 showed different shift trends specifically it shifted to shorter wavelengths at recycling rates below 5%, while shifted to longer wavelengths at 8%. Furthermore, the maximum fluorescence intensity of Peak A all decreased from 115.72 (in arbitrary unit, AU) in raw water to 105.63, 104.45, 90.95, and 104.94, corresponding to control, 2, 5, and 8%, respectively. The largest reduction rate of Peak A fluorescence intensity was targeted at 5%, reaching up to 21.4%. Conversely, the Peak T1 fluorescence intensity in treated DOM samples increased from 81.24 (in AU) in raw water to 87.16, 86.62, 82.35, and 110.39, corresponding to control, 2, 5, and 8%, respectively. The result indicated that the process of recycling FBWW could effectively improve humic-like substances (Peak A) removal, but the protein-like matters (Peak T1) were resistant to elimination. As known, compound T1 resulting from microbial activity may be low-MW and more soluble than compounds A and therefore more refractory to recycling process. The results in this study were well consistent with Gone et al. [15] and Baghoth et al. [16], who assumed that traditional coagulation could effectively improve humic-like substances removal, but large portion of protein-like matters that considered as an indicator of DOM residual were difficult to elimination.

The relationships of fluorescence-inferred removal for peak A between DOC,  $UV_{254}$  removal and SUVA in treated water are also investigated. It was found that the reduction rate of peak A fluorescence intensity showed linear relationship ( $Y_{[\text{reduction rate of A peak}]} = -25.52 C_{[\text{SUVA}]} + 50.163$ ,  $R^2 = 0.8058$ , number of samples,  $n = 10$ ) with SUVA in treated water, while the distributions of fluorescence-inferred removal for peak A between DOC removal ( $Y = 0.2717R_{[\text{DOC removal}]} + 9.9123$ ,  $R^2 = 0.0501$ ,  $n = 10$ ), and  $UV_{254}$  removal ( $Y = 0.3101R_{[\text{UV}_{254} \text{ removal}]} + 3.1287$ ,  $R^2 = 0.4616$ ,  $n = 10$ )

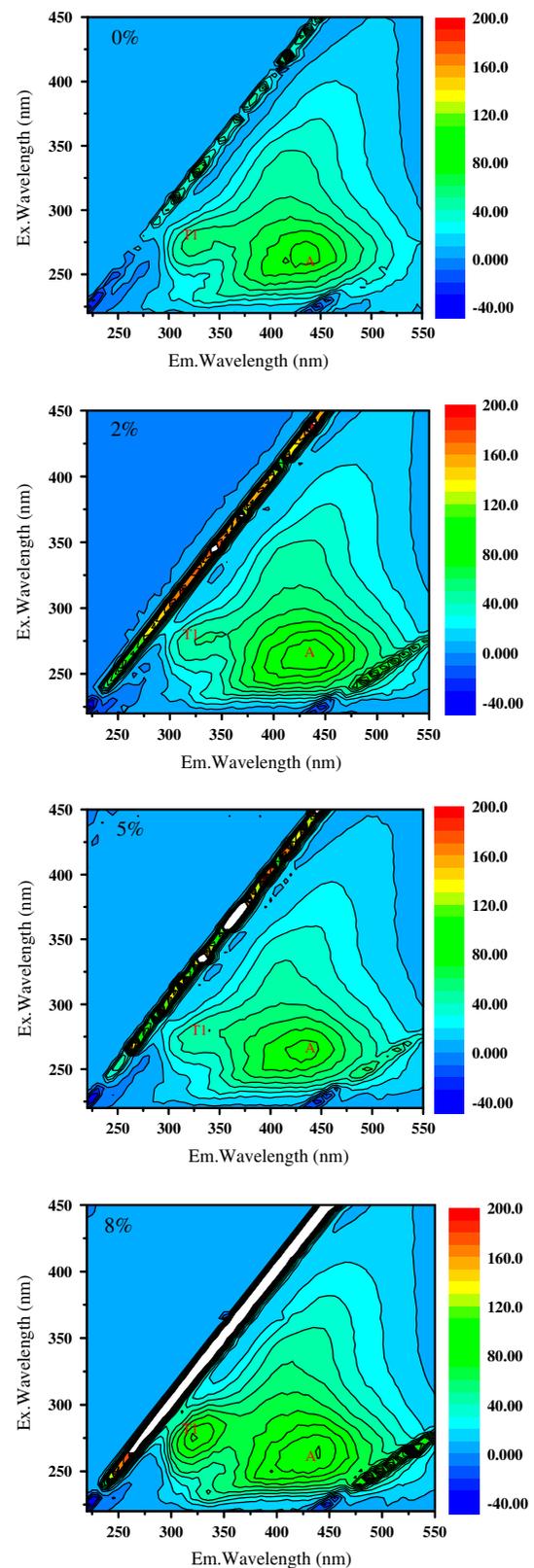


Fig. 5. Fluorescence EEM spectra in the DOM of treated water samples.

are scattered. The linear relationships of fluorescence-inferred removal for peak A between DOC,  $UV_{254}$  removal and SUVA in treated water were not good.

### 3.3. Remarks and conclusions

Strict regulations on the formation of DBPs have resulted in the increased need to understand not only the nature and reactivity of DOM. For example, variations in MWD could affect the efficiency of DOM removal through conventional or membrane treatment. Changes in SUVA will also influence the overall removal of DOM using coagulation and the reactivity toward formation of DBPs. Additionally, changes in hydrophobicity/hydrophilicity could affect the formation and speciation of DBPs [20]. Based on the results in this study, the DOM in FBWW was roughly hydrophilic compared with raw water, and a large portion of hydrophobic fractions, for example, HoA, HoN also occurred. From the perspective of slight changes in hydrophobicity/hydrophilicity, it is feasible to enhance the removal of DOM by recycling FBWW. However, the FBWW was inclined to more recalcitrant due to the substantial increment of low MW fraction (<3 KDa). This agreed with previous review that low-MW components are difficult to be removed in coagulation process [12]. Therefore, the DOM removal characteristics would become complex, and the different trends in the changes of MWD in treated water were well consistent with this hypothesis. Though the enhanced removal efficiencies of DOM in recycling trials were achieved, the concentration and physicochemical of DOM in FBWW indeed influenced.

Moreover, former studies [1,18] reported that the increasing of seeding and nuclei of destabilized residual streams particles was significant for favoring coagulation. So, the characteristics of recycling flocs in FBWW, that is, size, specific surface area and strength also played great roles in DOM removal. It is necessary to evaluate this hypothesis by characterizing the flocs before and after recycling in future studies to expound the influence of flocs characteristics on the removal efficiency of DOM. The effectiveness of reutilization of surface sites of the alum precipitates of particles in recycling FBWW also determined the removal of pollutant [7]. In order to fully exposure the residual chemical precipitants to the pollutants in raw water, it is useful to improve the mixing speed in the regulator tank to minimize the particles size and simultaneously increase the specific surface area of destabilized particles.

In addition, it is worth to noting that recycling FBWW could improve humic-like substances removal, but the protein-like matters were resistant to

elimination or were enriched in this study. The results were well consistent with worldwide researchers, using 3D-EEM fluorescence spectroscopy to identify the characteristics variability of DOM in different origins in coagulation phase [15,16]. As we know, traditional coagulation cannot efficiently remove low-MW and hydrophilic fractions. To improve the chemical safety and minimize the formation of DBPs in finished water, it is necessary to degrade or inactivate the constituents in FBWW that difficulty to be coagulated. Some suitable advanced pretreatment techniques, that is, advanced oxidation, adsorption, or membrane filtration should be carried out prior to recycling. At the same time, the destabilized flocs characteristics should be improved for subsequent solid/liquid separation in recycling process. The advanced techniques meeting the requirements mentioned above are ozone oxidation, ultrasonic irradiation, etc. among which ultrasonic irradiation may be one of the most effective pretreatments to minimize the particles' size, increase the adsorption sites on DOM and degrade the refractory fractions in FBWW.

The main conclusions of this work can be drawn as follows:

- The content and physicochemical characterization of DOM in FBWW was roughly analogous to source water, and the FBWW was inclined to more refractory due to the substantial increment of low MW fraction (<3 KDa). Humic-like fluorophore (Peak A) and protein-like fluorophore (Peak T1), with maxima at the Ex/Em wavelengths of 245.0–265.0 nm/400.0–435.0 nm, 280.0–305.0 nm/305.0–345.0 nm, respectively, were the two main components in raw water and FBWW.
- The removal efficiency of DOM as quantified by DOC and  $UV_{254}$  in settled water improved with FBWW, and the variability of SUVA implied DOM characterization was significantly different.
- At observed recycling rates, the removal efficiencies of all chemical fractions except HoN improved, but MWD was highly depended on the physical nature of raw water and FBWW.
- Recycling FBWW could effectively improve humic-like substances (Peak A) removal, but the protein-like matter (Peak T1) was resistant to elimination or was enriched. The linear relationships of fluorescence-inferred removal, for peak A between DOC,  $UV_{254}$  removal and SUVA in treated water were undesirable.
- Results of this study could be gained a better understanding of DOM removal and supported implications of potential benefits of backwash water recycle on treatment train performance.

## Acknowledgements

This research is funded by the National Natural Science Foundation (51278005) and Beijing Natural Science Foundation (8132007) of China. We would like to give our sincere thanks to the peer reviews for their suggestions and discussions.

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