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Characteristics and recycling effect of solubilized organics derived from drinking water treatment sludge using ultrasound

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ABSTRACT

Ballast flocculation by recycling drinking water treatment sludge (DWTS) is an alternative to traditional coagulation and pretreatment of the membrane-based process. However, the enhancement of organics removal is limited due to the release of organics derived from sludge. This study mainly focused on the characteristics of solubilized organics derived from DWTS exposed to different ultrasound conditions (ultrasound dose of 2.53, 5.10, 7.73, 10.42, and 15.79 W h/L, frequency of 25/40 kHz). The effect of solubilized matter in the coagulation process of recycling pre-sonicated DWTS on organics removal was also assessed. The results indicated that protein-like substances (Peaks T_1 and T_2) and humic-like substance (Peak *A*) occurred in raw DWTS samples. The kinetic model of soluble chemical oxygen demand (SCOD) solubilization was pseudo-linear, and the rate of SCOD released at 40 kHz was higher than that at 25 kHz, which could be confirmed by the increase in fluorescence intensities of Peaks *A*, T_1, and T_2 in the supernatant of sonicated DWTS. Additionally, the release velocity of protein-like substances at 40 kHz was more rapid than that at 25 kHz. The results of recycling trials indicated that solubilized organics could deteriorate the settled water quality, independent of the ultrasound conditions used.

Keywords: Ultrasound; Drinking water treatment sludge; Recycling; Organic solubilization; Three-dimensional excitation emission matrix

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1. Introduction

Natural organic matters (NOM), autochthonous, or allochthonous widely exist in micro-polluted surface water. NOM affects significantly the performance of the unit processes, application of water treatment chemicals, and biological stability of water. Moreover, NOM has been noted to be the major contributor for the formation of disinfection by-products (DBPs). Thus, an effective water treatment should be done in order to maximize the removal of the NOM. The extent of organics reduction by coagulation largely depends on the type and dosage of coagulant, mixing intensity, and raw water quality. Enhanced coagulation proposed by the US Environmental Protection Agency is an effective approach to improve the organics removal, and to reduce the potential formation of chlorinated DBPs while maintaining a higher turbidity removal [1,2]. Ballast flocculation of recycling drinking water treatment sludge (DWTS), as one form of enhanced coagulation, is effective for improving

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the water quality in terms of turbidity and organics removal [3]. However, the enhancement of organics removal is limited due to the release of organics derived from sludge during recycling.

Ultrasound (US) can effectively disrupt activated sludge, which has been widely used as a pretreatment of anaerobic digestion [4,5]. It has been confirmed that sonication plays a critical role in the disruption for the formation and behavior of cavitation bubbles, and the transient bubbles are regarded as the major contributor. Low-frequency US, particularly at 20 kHz, is widely used for sludge disintegration, while high-frequency US regards the decontamination of water and wastewater through sonochemical reactions. According to the documents [6,7], US treatment at low-frequency and high-intensity facilitated sludge disintegration due to the elevated mechanical shear force produced by the implosion of the cavitation bubbles. Low density US caused the release of substances capable of solubilizing, such as nucleic acids, lipids, humic acids, and proteins [8]. Although the organic constitution and flocs characteristics of DWTS are significantly different from those of activated sludge, the organic solubilization of DWTS exposure to US will naturally occur. To identify the characterization of solubilized organics is significantly critical for the subsequent recycling process.

Three-dimensional excitation emission matrix (3D-EEM) fluorescence spectroscopy has been used to distinguish different types and origins of organic matters, and to capture specific fluorescence features which correspond to humic- and protein-like substances in a single matrix in terms of fluorescence intensities in water samples from different aquatic environments [9–14]. The most common fluorophores are divided into humic and fulvic acids, and correspond to specific spectral features, including *A* peaks ($\lambda_{ex}/\lambda_{em}$ 220–260/400–450 nm) and C peaks ($\lambda_{ex}/\lambda_{em}$ 300–350/400–460 nm), together with signatures that represent protein-like substances with peaks similar to those of the fluorescent amino acids tryptophan, represented by *T* peaks ($T_1 = \lambda_{ex}/\lambda_{em}$ 270–295/330–380 nm and $T_2 = \lambda_{ex}/\lambda_{em}$ 210–240/330–380 nm) and tyrosine, represented by *B* peaks ($\lambda_{ex}/\lambda_{em}$ 210–230/305–320 nm).

In reality, the characterization of solubilized organics derived from DWTS and the application of US on DWTS are yet to be derived. The overall purpose of this research was, therefore, to investigate the characteristics of solubilized organics derived from DWTS, exposed to different US conditions from quantitative and qualitative analysis, then to assess the organics removal in the coagulation process of recycling DWTS with/without solubilized matters to clarify the influence of solubilized organics on the recycling process.

2. Materials and methods

2.1. Raw water and DWTS

The raw water and DWTS taken simultaneously from a drinking water treatment plant, Beijing, China, were used in this study. The raw DWTS included water treatment residuals generated by aluminum and ferric salt coagulants. Only 0.15 mg/L Fe species were observed in the supernatant of the DWTS matrix. Meanwhile, the residual Al species in it were below the detection limit 0.015 mg/L. All tests started within 2 h after sampling to prevent sludge changes. The main physicochemical characteristics of the raw water and DWTS are summarized in Table 1.

2.2. Solubilization treatment

In each solubilization experiment, 15L of raw DWTS sample was sonicated by the US waves, emitting from a rectangular sonochemical reactor (250 mm (L) × 250 mm (W) × 300 mm (H)). US frequencies of 25 and 40 kHz, with energy density as low as 0.03 W/mL were evaluated. The actual ultrasonic power dissipated into the suspension was measured using calorimetry [15]. Each sample was sonicated for 5, 10, 15, 20, and 30 min. At each sampling time, about 150 mL sonicated sludge was withdrawn from 150 mm below the surface, and the corresponding US doses were 2.53, 5.10, 7.73, 10.42, and 15.79 W h/L, respectively. All US reactions were conducted under air atmosphere without controlling the rise of temperature considering the practical application.

2.3. Recycling trials for organics removal in the coagulation process

A series of jar tests were carried out to determine the optimum dosage of $FeCl_3$ and recycling ratio of raw DWTS. The coagulation–flocculation procedures were as follows: 350 rpm ($G = 449\ s^{-1}$), 0.5 min; 300 rpm ($G = 367\ s^{-1}$), 1 min, adding $FeCl_3$ or ($FeCl_3$+ raw DWTS); 120 rpm ($G = 106\ s^{-1}$), 1 min; 50 rpm ($G = 33\ s^{-1}$), 15 min; and settling, 20 min. After settling, the samples were collected 3 cm below the water surface for UV_{254} and DOC measurement. We determined that the optimum dosage of $FeCl_3$ calculated as Fe was 6.3 mg/L and the recycling ratio of the raw DWTS was 8%.

We also conducted another series of jar tests to clarify the impact of solubilized organics in the recycling process. The detailed operation procedures were described in Fig. 1. When recycling pre-sonicated DWTS without solubilized organics, the raw DWTS

Table 1
Main physicochemical characteristics of raw water and DWTS

Analytes (units)	Raw water average	Analytes (units)	Raw DWTS average
Turbidity (NTU)	1.38	Moisture content (%)	99.87
UV_{254} (cm^{-1})	0.027	TS ($g\,L^{-1}$)	1.33
DOC ($mg\,L^{-1}$)	1.855	VS ($g\,L^{-1}$)	0.40
SUVA (L/mg m)	1.456	TCOD ($mg\,L^{-1}$)	338.6
Zeta potential (mV)	−15.8	SCOD in supernatant ($mg\ L^{-1}$)	10.55

Notes: UV absorbance at 254 nm wavelength (UV_{254}); dissolved organic carbon (DOC); specific UV absorbance (SUVA); total solids (TS); volatile suspended solids (VS); total chemical oxygen demand (TCOD); and souble chemical oxygen demand (SCOD).

was firstly exposed to US apparatus under different US conditions, and then the sonicated sludge was collected at a given sonication time and put aside for static precipitation for about 120 min. The supernatant of each sonicated sludge was discharged; meanwhile, the condensate factor of the maintained thickened sludge was about 0.6–0.8. Secondly, we added the same volume of DI water as the supernatant into the condensate DWTS to maintain a constant total solid content as before. Finally, the treated DWTS was added into the beaker of the jar tester during the flocculation stage of 120 rpm.

2.4. Analytical methods

All analyses were evaluated using chemicals of analytical grade. TS, VSS, TCOD, and SCOD were determined by the standard methods [16]. A total carbon analyser vario TOC® cube (Elementar, Germany) was used to analyze DOC. UV_{254} was determined by using a UV/Vis spectrophotometer (UV2600, China). Both DOC and UV_{254} were measured after filtration through 0.45 μm acetate fiber membranes.

Fluorescence measurements were conducted using a spectrofluorometer (F-4500, Hitachi, Japan) equipped with a 150-W xenon lamp at an ambient temperature of 24°C. A 1-cm quartz cuvette with four optical windows was used for the analysis of solubilized organic matter. 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 1200 nm/min; the slit widths for excitation and emission were 5 nm and 3 nm, respectively. Under the same conditions, fluorescence spectra for deionized water (Milli-Q, conductivity 18.2 Ω m) were subtracted from

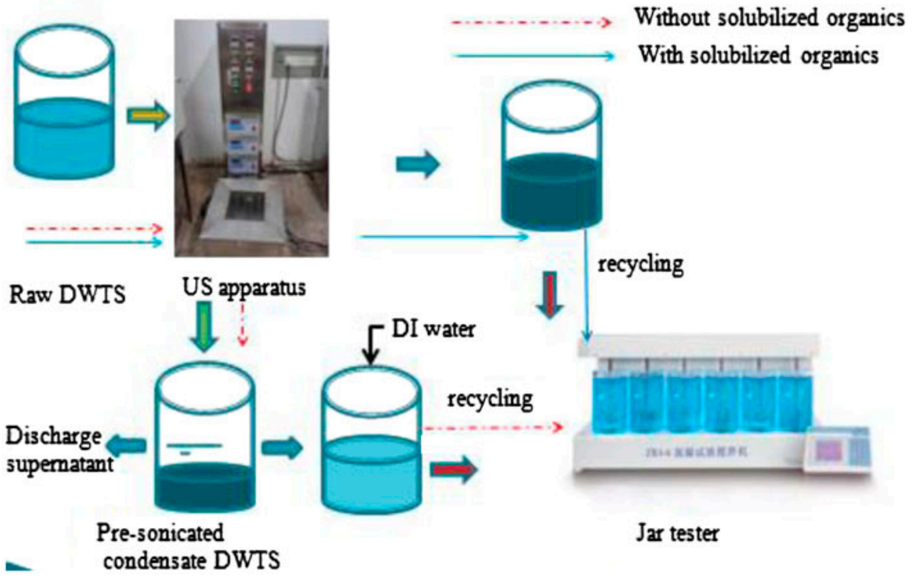

Fig. 1. The detail operation procedures for recycling trials with/without solubilized organics.

all the spectra to eliminate water Raman scattering and to reduce other background noise. During the course of fluorescence analysis, the Raman scattering peak intensity for Milli-Q water (excitation, E_x at 350 nm; emission, E_m at 400 nm) was recorded as a standard to verify the instrument stability. Mean intensity of the Raman peak was 32.10 units and the differences were less than 3%, confirming that there were no significant fluctuations in the performance of the spectrofluorometer in the experiments.

3. Results and discussion

3.1. Characteristics of raw water and DWTS

As indicated in Table 1, the turbidity and levels of organic carbon of the tested raw water were low, which showed the same characteristics as those of low-turbidity and micro-polluted water. The SUVA calculated as one hundred times UV_{254} divided by DOC concentration in raw water was 1.456 L/mg m, indicating the organics were generally enriched in hydrophilic and low-molecular-weight components and were difficult to eliminate by the traditional coagulation process [1]. The average TS, VS, and TCOD concentration, of raw DWTS were 1.33, 0.40, and 338.6 mg L^{-1}, respectively, and the SCOD in supernatant was 10.55 mg L^{-1} and its pH was 7.67. The low ratio of VS to TS in the raw DWTS, 30.08%, indicated that the raw DWTS mainly consisted of inorganic substances. Moreover, the SCOD to TCOD ratio was 3.12%, which indicated that a large quantity of the COD could be solubilized into the supernatant. The high moisture content was found in the raw DWTS, which implied that the raw DWTS had not been thickened.

As stated in previous literature [17], the organic removal efficiency in the recycling process largely depended on the concentration and characteristics of organics in raw water, and those in the recycled streams. Therefore, it is necessary to obtain more information on the organic characteristics. The fluorescence of the organics in raw water and in the supernatant of raw DWTS was investigated, as illustrated in Fig. 2. The fluorescence parameters, such as peak location, maximum fluorescence intensity, and peak intensity ratio extracted from excitation emission matrix (EEM) fluorescence spectra are summarized in Table 2, which could be employed for quantitative analysis.

Here, the peaks (A, T_1, and T_2) distinctly identified were selected because fluorescence intensity of peaks B and C was relatively lower. It can be seen in Fig. 2 that, as to the fluorescence spectra of dissolved organic matter in raw water, Peak T_1 was located at E_x/E_m wavelength of 285.0/315.0 nm, while Peak T_2 was detected at the E_x/E_m of 235.0/340.0 nm. These two peaks have been reported as protein-like peaks, in which the fluorescence is associated with the aromatic protein-like substances (Peak T_1) and tryptophan protein-like substances (Peak T_2). A third main peak observed at the E_x/E_m of 255.0/445.0 nm (Peak A) has been reported to be associated with humic acid-like substances. Similarly, for the fluorescence spectra of dissolved organic matter in supernatant of raw DWTS, Peak T_1, T_2, and A was located at E_x/E_m wavelengths of 280.0/335.0 nm, 235.0/345.0 nm, and 255.0/425.0 nm, respectively.

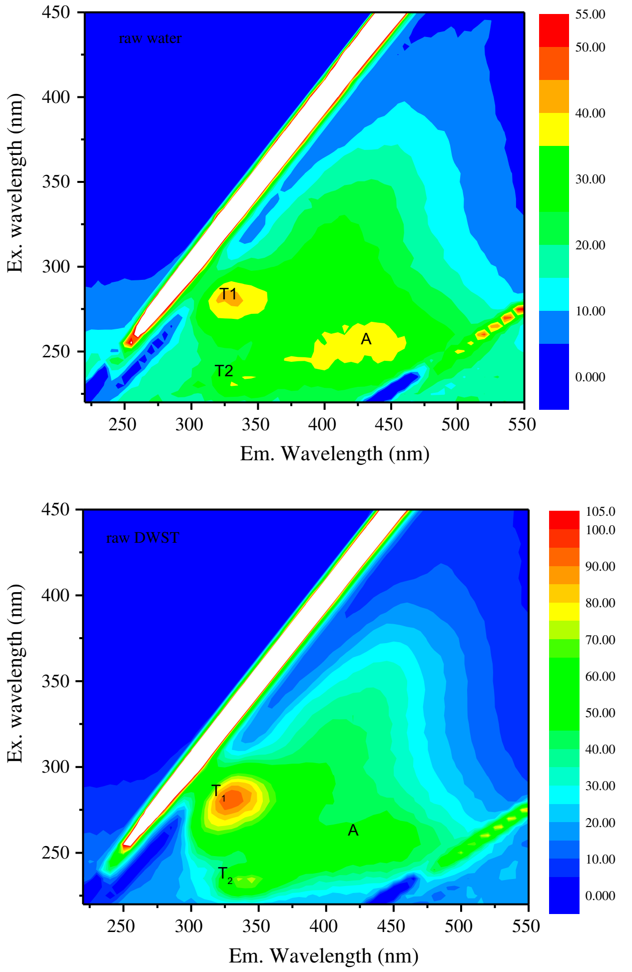

Fig. 2. Fluorescence EEM spectra of dissolved organic matter in (a) raw water; and (b) the supernatant of raw DWTS.

Additionally, as observed in Table 2, the fluorescence intensity of Peaks A, T_1, and T_2 of dissolved organic matter in the supernatant of raw DWTS was accordingly higher than that in the raw water, indicating that traditional coagulation–flocculation process could remove these three fluorescent substances from

Table 2
Fluorescence spectral identifications of dissolved organic matter samples in raw water and supernatant of sonicated DWTS

Samples		Peak A		Peak T_1		Peak T_2			
		E_x/E_m	Int.[a]	E_x/E_m	Int.[a]	E_x/E_m	Int.[a]	T_{I}/A	T_2/A
Raw water		255.0/445.0	38.46	285.0/315.0	42.47	235.0/340.0	35.45	1.10	0.92
Raw DWTS		255.0/425.0	57.16	280.0/335.0	93.31	235.0/345.0	70.55	1.63	1.23
25 kHz	2.53	255.0/440.0	61.15	280.0/330.0	80.98	230.0/340.0	74.54	1.32	1.22
	7.73	255.0/425.0	63.02	280.0/335.0	93.31	230.0/340.0	89.42	1.48	1.42
	15.79	255.0/440.0	57.12	280.0/325.0	86.97	230.0/335.0	86.96	1.52	1.52
40 kHz	2.53	255.0/445.0	62.69	280.0/325.0	98.25	230.0/335.0	105.36	1.57	1.68
	7.73	250.0/420.0	55.87	280.0/335.0	112.81	230.0/340.0	111.42	2.02	1.99
	15.79	255.0/435.0	60.87	280.0/330.0	123.76	230.0/340.0	154.02	2.03	2.53

[a] Intensity.

the raw water. As a result, they were enriched in the DWTS. Location of the peak was another parameter to indicate the characteristics of organics. Compared to the fluorescence maxima in raw water, the location of Peak A in the supernatant of raw DWTS was 20 nm blueshifted along the E_m axis. For Peak T_1, it was 5 nm blueshifted along the E_x axis and 20 nm redshifted along the E_m axis, while for Peak T_2, it was 5 nm redshifted along the E_m axis. As reported, a redshift is related to the presence of carbonyl containing substituents, hydroxyl, alkoxyl, amino groups, and carboxyl constituents, while a blueshift is associated with the decomposition of condensed aromatic moieties and the breakup of the large molecules into smaller fragments, such as a reduction in the degree of the π-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 [18]. It was, therefore, concluded that the traditional coagulation process could decrease the number of aromatic rings and conjugated bonds of humic-like substances, and partially lead to the increase of hydroxyl, alkoxyl, amino groups, and carboxyl constituents, which was consistent with the findings of Gone et al. [12] and Baghoth et al. [13], who recently revealed that traditional coagulation–sedimentation process was inclined to improve humic-like substances removal, but protein-like matters considered as an indicator of organics residual were resistant to elimination.

3.2. Characterization of solubilized organics after sonication

The effect of US dose on the extent of organic solubilization from DWTS quantified by the release of SCOD was investigated. As shown in Fig. 3(a), the release of SCOD increased continuously with US dose, and it exhibited similarity at the initial 7.73 W h/L for the two frequencies, after which it sequentially boosted and was more apparent at 40 kHz than that at 25 kHz. At US dose of 15.79 W h/L, the release of SCOD was respective 5.67 and 6.11 times of the initial SCOD value. Several studies [19,20] concerning the US pretreatment on activated sludge demonstrated that the release of the SCOD was attributed mainly to the following two aspects: (1) High power US at low frequency can generate intensive cavitation, which results in vigorous and effective sludge disruption leading to the release of intra-cellular materials; and (2) Insoluble particulate organics may become soluble under cavitation effect. Here, these two aspects also played significant roles in the release of SCOD from DWTS, though the organic constitution and flocs characteristics of DWTS were different from those of activated sludge.

Meanwhile, the kinetic model of SCOD solubilization, denoted as $d[\mathrm{SCOD}_{\mathrm{increase}}]/dt$, was analyzed using the linear regression method. The figure inserted in Fig. 3(a) indicated that the kinetic model of SCOD solubilization was pseudo-linear and the rate of SCOD released at 40 kHz was $1.2398\,\mathrm{mg\,L^{-1}\,min^{-1}}$, which was 0.3339 higher than that of 25 kHz. These results indicated that 40 kHz with US dose of 7.73 W h/L or more had greater potential than 25 kHz to solubilize the organics from the DWTS into the bulk liquid.

Studies have shown that it is at the moment of bubble implosion that non-linear energy transformation occurs within a very small volume that could trigger localized extreme temperatures and high pressure. Hence, transient bubbles should be regarded as the major contributor to sludge disruption. The time for

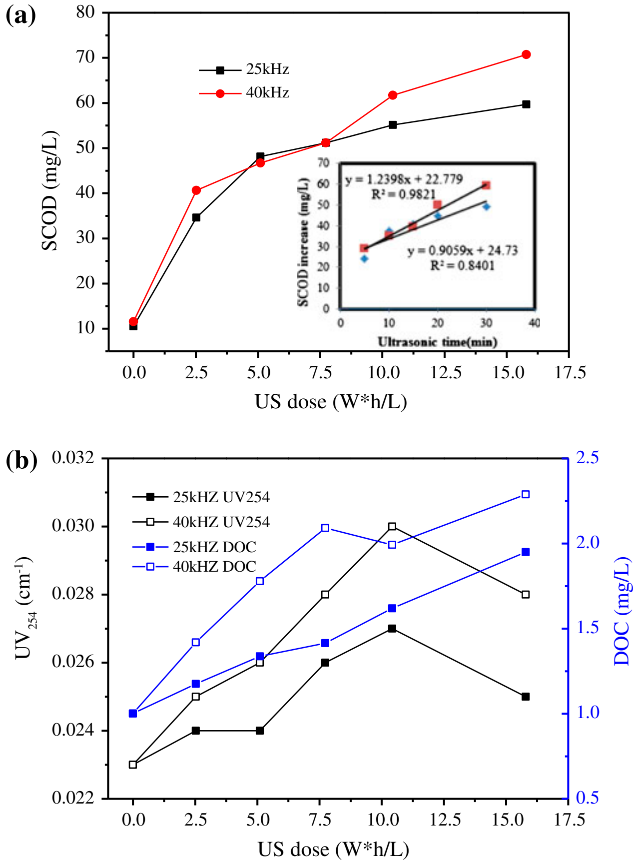

Fig. 3. Effect of US dose on (a) release of SCOD; and (b) UV_{254} levels and DOC concentration in the supernatant after sonication (sonication density was constant at 0.03 W/mL, the mean SCOD of raw DWTS was 10.55 mg/L, and the UV_{254} levels and DOC concentration in the supernatant of raw DWTS was 0.023 cm^{-1} and 1.001 mg/L, respectively).

transient bubble collapse can be calculated from the following Equations, according to the reference [21].

$$R_{\max} \approx 3.28\frac{1}{f} \tag{1}$$

$$\tau_c = 0.915R_{\max}\sqrt{\frac{\rho_L}{P_0}} \approx 3.00\frac{1}{f}\sqrt{\frac{\rho_L}{P_0}} \tag{2}$$

where τ_c is the collapse time, f is the US frequency, $R_{\max}$ is the resonant or maximum radius (cm), ρ_L is the density of liquid, and P_0 is the pressure of the system. For a given system, the τ_c is inversely proportional to the US frequency, f. Therefore, a high frequency of 40 kHz has a shorter collapse time than that at 25 kHz, leading to a higher extent of sludge disintegration and organic solubilization.

The organic concentration, i.e. UV_{254} levels and DOC concentration in the supernatant at 25/40 kHz after sonication was examined and it was found that the organic concentration at 40 kHz was higher than that at 25 kHz at all US doses observed, as evidenced in Fig. 3(b). It could be indicated from the results in Fig. 3(a) and 3(b) that the larger the extent of organic solubilization was, the higher the organic concentration in the supernatant could be.

It is also worth noting that, in this study, the highest sludge disintegration calculated by the Eq. (3) [22] was only 16.81 and 18.03%, respectively, at 25 and 40 kHz, indicating the solubilization may be restricted which might be ascribed to the low US energy density used here.

$$\text{Disintegration degree}\,(\%) = \frac{\text{SCOD}_{\text{after}} - \text{SCOD}_0}{\text{TCOD}_0 - \text{SCOD}_0} \times 100 \tag{3}$$

where $\text{SCOD}_{\text{after}}$ is the souble chemical oxygen demand of the sonicated sludge, SCOD_0 is the souble COD of the raw DWTS, and TCOD_0 is the total COD of the raw DWTS.

In order to clarify the composition and distribution of organic constituents in supernatant, we analyzed the characteristics of solubilized organics using 3D-EEM fluorescence spectroscopy. The fluorescence EEM spectra of dissolved organic matter in the supernatant were comparatively displayed in Fig. 4 after sonication at 25 and 40 kHz with US dose of 2.53, 7.73, and 15.79 W h/L. The fluorescence characteristics parameters are also summarized in Table 2.

As indicated, fluorescence EEM spectra of dissolved organic matter in the supernatant after sonication at 25 or 40 kHz with US dose of 2.53, 7.73, and 15.79 W h/L were similar to that of raw DWTS accordingly. The maxima of peak A, T_1, and T_2 was at the E_x/E_m 250.0–255.0/420.0–445.0 nm, 280.0/325.0–335.0 nm, and 230.0/335.0–340.0 nm, respectively. In addition, it could be observed in Table 2 that the fluorescence intensities of the three Peaks A, T_1, and T_2 were firstly increased and then decreased with the rise of US dose at 25 kHz while significantly increased with the rise of US dose at 40 kHz, which indicated that both humic-like and protein-like substances were released into the supernatant during sonication. The different trends of fluorescence intensity at 25 and 40 kHz might be ascribed to the extent of sludge disintegration and organic degradation together with US. Specifically, on one hand, as previous stated, 40 kHz had greater potential to disrupt the sludge flocs and led to a larger quantity of solubilized organics in the supernatant than 25 kHz. Consequently,

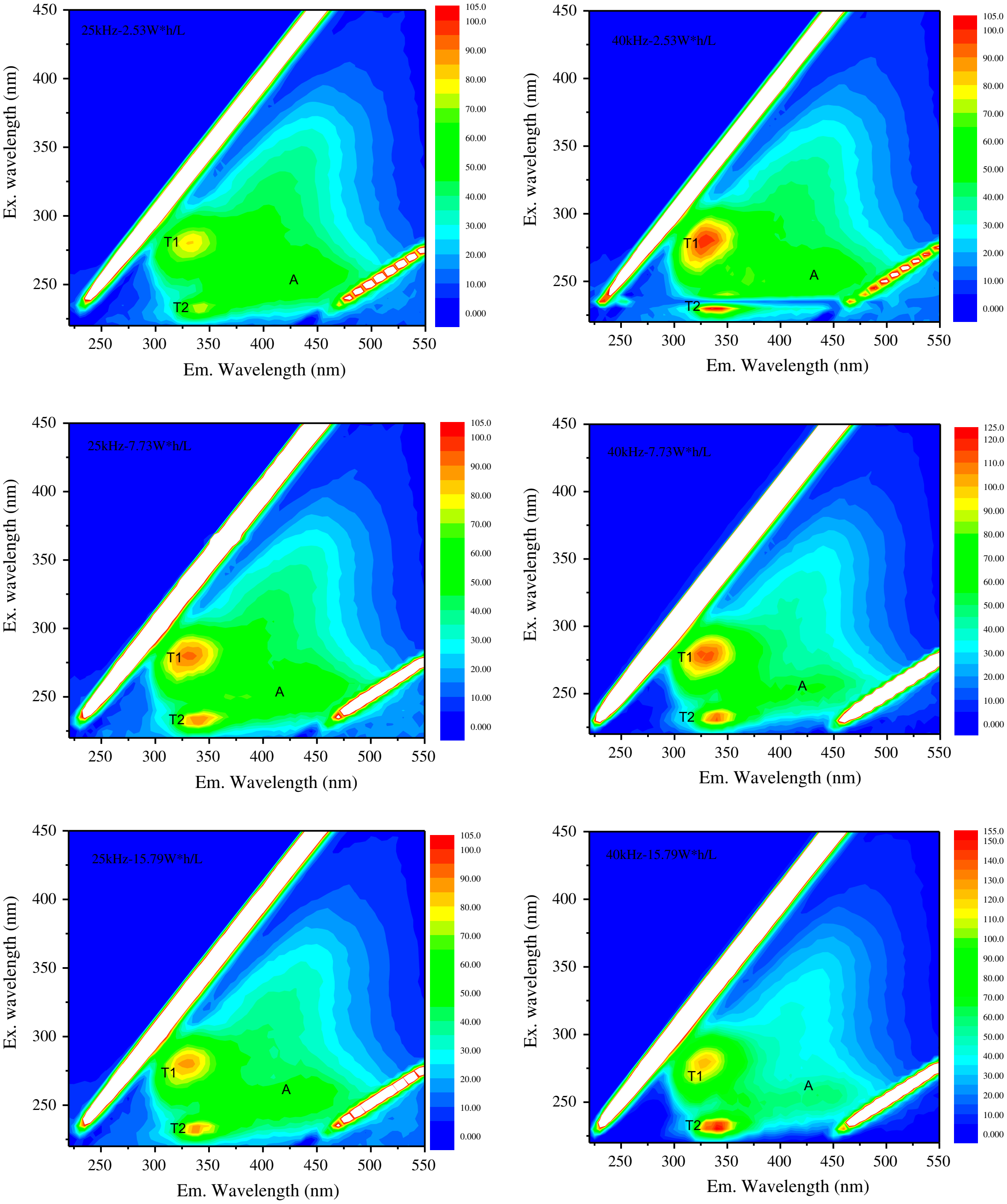

Fig. 4. Fluorescence EEM spectra of dissolved organic matter in the supernatant after sonication at 25 or 40 kHz with US dose of 2.53, 7.73, and 15.79 W h/L.

the concentration and fluorescence intensity of solubilized organics sonicated at 40 kHz was higher than that at 25 kHz. On the other hand, with reference to the theoretical fundamentals of US, some sonochemical processes can result in a decrease in the content of color organic compounds in water. Increasing the intensity of the ultrasonic field enhances the occurrence of sonochemical processes including the destruction of high-molecular organic compounds or the oxidation reactions with radicals [23]. Thus, US can fractionate the chromophoric organic matter into smaller chromophoric fractions and succeed in breaking chromophoric groups within the structure to decrease fluorescence intensity. The differences in peak intensity ratios of EEM fluorescence spectra also implied that US was responsible for the compositional variation of the fluorescent compounds in dissolved organic matter samples. The intensity ratio of Peaks T_1/A at 25 kHz with US dose of 2.53, 7.73, and 15.79 W h/L was, respectively, 1.32, 1.48, and 1.52, as compared to 1.63 of raw DWTS. Under such conditions, the intensity ratio of Peaks T_2/A showed the similarity with that of Peaks T_1/A. Contrastively, at 40 kHz with US dose of 2.53, 7.73, and 15.79 W h/L, the intensity ratio of Peaks T_1/A was 1.57, 2.02, and 2.03, respectively, which was slightly higher than that at 25 kHz. This result indicated that the release velocity of protein-like substances (Peak T_1 or T_2) at 40 kHz was more rapid than that at 25 kHz. Therefore, it was reasonable to deduce that 25 kHz was more beneficial to biological stability of treated water in the recycling process and restraint of bacterial regrowth in the distribution system.

3.3. Organics removal with/without solubilized organics in coagulation process

The residual UV_{254} level and DOC concentration in the coagulated water of control trial by adding 6.3 mg/L $FeCl_3$ calculated as Fe alone was 0.021 cm^{-1} and 1.558 mg/L respectively. As compared to control, the residual UV_{254} level and DOC concentration with addition of 8% raw DWTS was a little higher, reaching up to 0.0022 cm^{-1} and 1.593 mg/L accordingly. Through mass balance calculations using the data from the raw water, and UV_{254}, and DOC concentration in the supernatant of the DWTS sample, it could be deduced that recycling 8% of the DWTS results in at least 8.89 and 8.00% improvement of UV_{254} relative to raw water at 40 and 25 kHz, respectively, and DOC improvement was 9.87 and 8.41%, respectively, at 40 and 25 kHz. Thus, it would lead to an obvious change in DOC concentration, UV_{254} level, or coagulant demand in the blended water matrix, which ultimately compromised the organics removal.

Additionally, it was found in Fig. 5(a) that the residual UV_{254} in the settled water by recycling DWTS without solubilized organics was absolutely lower than that with solubilized organics, regardless of the US conditions used. Furthermore, on the condition of recycling DWTS without solubilized organics, 25 kHz displayed better capacity for UV_{254} removal than 40 kHz at the same US dose. Specifically, at sonication of 2.53 or 10.42 W h/L at 25 kHz, the lowest residual UV_{254}, 0.019 cm^{-1}, was achieved compared with 0.027 cm^{-1} of raw water. As to residual DOC, it showed a similar trend with residual UV_{254}, and the minimum residual DOC was 1.359 mg/L compared with 1.855 mg/L of raw water. This result further confirmed that the solubilized organics could impede the organics removal in the coagulation process, and only when excluded from the recycling system, could the organics removal be greatly improved.

In the recycling process, the breakup of recycling DWTS flocs may occur when exposed to shear force in the field of US, so the encapsulated iron hydroxide precipitation would appear on the surface of the recycled flocs, which would afford more adsorption sites for organics. Moreover, in the recycling process, aged and fresh precipitate particles formed by hydrolysate of $FeCl_3$ coexist. Liu et al. [24] assumed that there

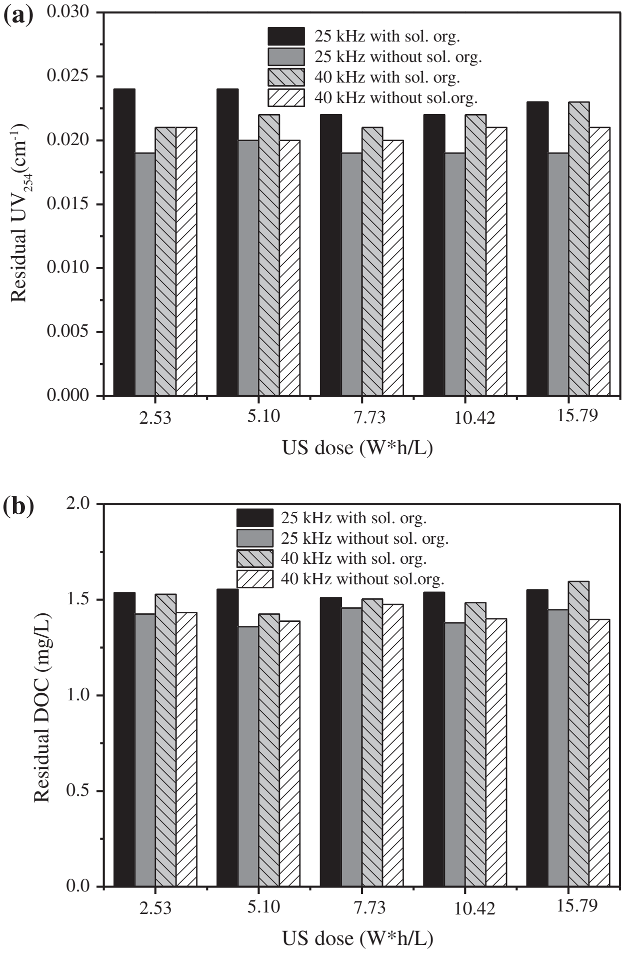

Fig. 5. Residual UV_{254} and DOC with/without solubilized organics in coagulation process (under all cases, the dosage of $FeCl_3$ was constantly 6.3 mg/L calculated as Fe and the recycling ratio of the DWTS was 8%. Average UV_{254} and DOC in raw water were 0.027 cm^{-1} and 1.855, mg/L respectively).

were more active groups on the fresh precipitate particles which were capable of binding the aged precipitates together. Thus, the adsorption of newly formed soluble Fe species on the surface of the aged flocs could give improved adhesion.

4. Conclusion

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

- Three main peaks including Peak T_1 and Peak T_2 related to protein-like substances and Peak A associated with humic-like substances could be identified from the 3D-EEM fluorescence spectra in raw water and raw DWTS samples.
- The kinetic model of SCOD solubilization was pseudo-linear and the rate of SCOD released at 40 kHz was higher than that at 25 kHz. As a result, the organic concentration in the supernatant at 40 kHz was higher than that at 25 kHz at all US doses observed.
- The fluorescence intensities of Peaks A, T_1, and T_2 were firstly increased and then decreased with the rise of US dose at 25 kHz, while significantly increased with the rise of US dose at 40 kHz. It was found from the ratio of Peak T_1/A or Peak T_2/A that the release velocity of protein-like substances (Peak T_1 or T_2) at 40 kHz was more rapid than that at 25 kHz.
- The settled water quality by recycling DWTS without solubilized organics was absolutely better than that with solubilized organics, regardless of the US conditions used. Furthermore, on the condition of recycling DWTS without solubilized organics, 25 kHz displayed better capacity for UV_{254} removal than 40 kHz.

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