



The removal characteristics of natural organic matter in the recycling of drinking water treatment sludge: Role of solubilized organics



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ABSTRACT

To clarify the role of solubilized organics derived from drinking water treatment sludge (DWTS) in the elimination of natural organic matter (NOM) in the DWTS recycling process, a probe sonoreactor at a frequency of 25 kHz was used to solubilize the organics at varied specific energies. The coagulation behavior related to NOM removal in recycling the sonicated DWTS with and without solubilized organics was evaluated, and the effect on organic fractionations in coagulated water was determined. The study results could provide useful implications in designing DWTS recycling processes that avoid the enrichment of organic matter. Our results indicate that DWTS was disrupted through a low release of soluble chemical oxygen demand (SCOD) and proteins, which could deteriorate the coagulated water quality under the specific energy of 37.87–1212.1 kW h/kg TS. The optimal coagulation behavior for NOM removal was achieved by recycling the sonicated DWTS without solubilized organics at 151.5 kW h/kg TS specific energy. Recycling the sonicated DWTS could increase the enrichment potential of weakly hydrophobic acid, hydrophilic matter, and <3 kDa fractions; the enrichment risks could be reduced by discharging the solubilized organics. Fluorescent characteristic analysis indicated that when recycling the sonicated DWTS without solubilized organics, the removal of humic-like substances was limited, whereas removal of protein-like substances was enhanced, lowering the enrichment potential of protein-like substances.

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1. Introduction

Drinking water treatment sludge (DWTS), the byproducts generated at water treatment plants that is primarily composed of amorphous Fe/Al hydroxides, is generally produced during flocculation–sedimentation or flotation processes because Fe/Al-based coagulants are usually used. DWTS and solids within filter backwash water (FBWW) are the major components of water treatment residual. Okuda et al. [1] have reported that global production of solid residuals “might be totally 10,000 tons per day,” of which European countries including Ireland, Germany, the Netherlands, United Kingdom, and Portugal make up 10.38%, and the United States and Chinese Taiwan account for 72.6% and 0.003%, respectively [2]. An increased generation of water treatment residues, coupled with environmental restrictions on disposal methods, has led to increased research into their reuse, which is an important avenue in realizing a reduction and reclamation of total waste residues. There is a general understanding of the role of magnetic seeding, micro-sand, diatomite, and recycled DWTS in

enhancing coagulation. Magnetic seeding and micro-sand assisted flocculation are now widely accepted technical alternatives to strengthen separation during the treatment of drinking water, reclaimed water, or landscape water [3–8]. However, the application of recycled DWTS from drinking water treatment is restricted due to potential negative effects of complex components within the recycled DWTS. A major issue influencing the water quality in the recycling process is the release of extracellular or intracellular organics that originate from the DWTS [9]; therefore, an effective organic solubilization is key in the DWTS recycling process.

Several approaches to sewage sludge solubilization have been investigated, including thermal, chemical, acoustic-mechanical disintegration, and a combination of chemical and acoustic-mechanical methods [10–15]. Ultrasound can cause a series of compression and rarefaction cycles, which generate cavitation bubbles. Millions of these bubbles implode yielding localized temperatures as high as 5000 °C, pressures of 100 MPa and free radicals, e.g., ·OH, ·HO₂, and ·O [16]. The synergetic effects of high mechanical shear force, radical reactions, and thermal breakdown can cause the organic solubilization, the destruction of microbiological cells, and the oxidation of toxic chemical compounds [16].

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In previous studies [9,17], we have proposed ultrasound as a pretreatment in the coagulation process of recycling DWTS. We observed that ultrasound could effectively solubilize extracellular and intracellular organics, which was confirmed by the release of soluble chemical oxygen demand (SCOD), proteins, and polysaccharides, and the increase in fluorescent intensity of humic-like and protein-like substances. Meanwhile, we found that the coagulated water quality worsened after the addition of sonicated DWTS containing solubilized organics, as compared to conditions without solubilized organics. We assumed that the solubilized organics adversely affected the coagulation efficacy of the DWTS recycling process. However, according to Liu et al. [18], the extracellular polymeric substances (EPS) of aerobic and anaerobic sludge, mainly composed of carbohydrates, proteins, and humic substances, had the same properties of bio-flocculant and could thus play a key role in sludge aggregation. The researchers pointed out that the loosely bound EPS always displayed a positive effect on the sludge aggregation as indicated by negative interaction energy. Furthermore, Yuan et al. [19] assumed polysaccharides in EPS excreted from *Bacillus megaterium* TF10 exhibited a high flocculation activity, whereas the proteins had no flocculation ability, conflicting with the findings of Takeda et al. [20], in which proteins in EPS extracted from *Nocardia amarae* did have flocculation ability. Additionally, Wen et al. [21] found that the addition of aluminum ions (Al^{3+}) could improve the flocculation and turbidity removal of activated sludge with an increasing single dosage, but deteriorate the sedimentation of activated sludge. To the best of our knowledge, the effects of extracellular or intracellular organics derived from DWTS on the flocculation behavior of DWTS have not been studied, and the effects on natural organic matter (NOM) removal in the DWTS recycling process remains unclear.

On the other hand, results of our previous investigation [9] have demonstrated that the residual dissolved organic carbon (DOC) and the residual UV at the wavelength of 245 nm (UV_{254}) in the coagulated water after recycling sonicated DWTS without solubilized organics, regardless of the ultrasound dose used, were lower than incidences with solubilized organics. However, these indicative parameters provided no insight into the composition and distribution of NOM. The common NOM properties are molecular weight (MW) distribution, hydrophobicity, and fluorescence [22]. Generally, lower-MW NOM tend to be more hydrophilic and biolabile, while higher-MW NOM tends to be more aromatic and hydrophobic, with a higher adherence to adsorption [23]. During the traditional coagulation step for drinking water treatment, the hydrophilic, low molecular weight (LMW), and protein-like compounds of NOM appear to be less efficiently removed than the hydrophobic, high molecular weight (HMW), and humic-like compounds; after the coagulation step, LMW, hydrophilic, and protein-like NOM are dominant in the residual organic matter [22–24]. In our previous study [25] of recycling FBWW to enhance coagulation of two low-turbidity source waters, we observed that high organic concentrations and increased low-MW fractions within the recycled FBWW did not enhance UV_{254} and DOC removal. Hydrophobic acid could be further eliminated when recycling particles produced mainly by sweep flocculation. Weakly hydrophobic acid and a hydrophilic fraction removal could be enhanced through recycling particles formed mainly by charge neutralization. Moreover, recycling FBWW could effectively improve the removal rate of humic-like substances, but protein-like substances were resistant to elimination.

Currently, little research exists on the NOM removal characteristics of the DWTS recycling process, and the effects on organic fractionations in coagulated water also need to be investigated further. In this study, to clarify the role of solubilized organics in the elimination of NOM in the DWTS recycling process, a probe sonoreactor

at a frequency of 25 kHz was used to solubilize the extracellular or intracellular organics. The coagulation behavior during the recycling process with and without solubilized organics was then evaluated, particularly NOM removal, measured as UV_{254} and DOC removal. The XAD-4 and -8 resin adsorption and ultrafiltration technique, as well as three-dimensional excitation emission matrix (3D-EEM) fluorescence spectroscopy, were employed to fractionate the NOM.

2. Materials and methods

2.1. Raw water and DWTS used in the experiments

The raw DWTS sample used in the experiments was collected from a water treatment plant (Beijing, China) that handles 1,500,000 m^3/day using a coagulation, flocculation, sedimentation, and sand filtration process. Poly-aluminum chloride and ferric chloride ($FeCl_3$) were used as the coagulant. The alum and ferric sludge settled in the sedimentation basin and was discharged to the thickener. The DWTS samples were transferred immediately to the laboratory and stored at 4 °C. Prior to each experiment, sludge samples were warmed to room temperature. All of the experiments were performed within a week of sampling. As indicated in the Table 1, the characteristics of the raw DWTS were as follows: total solids (TS); volatile suspended solids (VSS); total chemical oxygen demand (TCOD) concentrations of raw DWTS, which were $1.10 \pm 0.12 \text{ g L}^{-1}$, $0.26 \pm 0.03 \text{ g L}^{-1}$, and $423.29 \pm 15.91 \text{ mg L}^{-1}$, respectively; the SCOD; and the proteins in the supernatant of raw DWTS, which were $15.36 \pm 1.71 \text{ mg L}^{-1}$ and $4.75 \pm 0.84 \text{ mg L}^{-1}$, respectively. A low VSS to TS ratio in the raw DWTS, 23.64%, indicated a primarily inorganic makeup. The SCOD to TCOD ratio in the raw DWTS was 3.63%, indicating that a small proportion of the COD was associated with the soluble phase. The polysaccharide in the supernatant of raw and sonicated DWTS was not considered, as it was detected at very low levels.

Raw water was collected from the same water treatment plant as the raw DWTS samples. The main physicochemical characteristics of the raw water were as follows (seen in Table 1): pH 8.21 ± 0.12 ; turbidity $0.774 \pm 0.241 \text{ NTU}$; UV_{254} $0.039 \pm 0.009 \text{ cm}^{-1}$; and DOC $6.003 \pm 1.212 \text{ mg/L}$. The average specific UV absorbance, calculated as 100 times UV_{254} divided by DOC concentration, was 0.75 L/mg m, indicating the NOM was generally enriched in hydrophilic and LMW components and were difficult to eliminate through a traditional coagulation method [26].

Table 1
Main physicochemical characteristics of raw water and DWTS.

Analytes (Units)	Raw water Mean \pm SD	Analytes (Units)	Raw DWTS Mean \pm SD
Temperature (°C)	12 \pm 0.5	Temperature (°C)	13 \pm 0.5
pH	8.21 \pm 0.12	TS (g L^{-1})	1.10 \pm 0.12
Turbidity (NTU)	0.774 \pm 0.241	VSS (g L^{-1})	0.26 \pm 0.03
Ultraviolet absorbance at 254 nm (UV_{254}) (cm^{-1})	0.039 \pm 0.009	VSS/TS (%)	23.64
Dissolved organic carbon (DOC) (mg/L)	6.003 \pm 1.212	TCOD (mg L^{-1})	423.29 \pm 15.91
Specific UV absorbance (SUVA) (L/mg m)	0.75 \pm 0.15	SCOD in supernatant (mg L^{-1})	15.36 \pm 1.71
Zeta potential (mV)	-14.9 \pm 1.4	SCOD/TCOD (%)	3.63
		Proteins in supernatant (mg L^{-1})	4.75 \pm 0.84

Note: SD means standard deviation. Number of measurements (n): for temperature and pH, $n = 5$; for total solids (TS), volatile suspended solids (VSS), total chemical oxygen demand (TCOD), SCOD and proteins, $n = 10$.

2.2. Ultra-sonication experiments

A probe-type sonoreactor (XH-2008DE, Xianghu Ultrasonic Instrument Co., Beijing, China) operating at a fixed frequency of 25 kHz and a nominal power output up to 1500 W, was used to solubilize extracellular or intracellular organics derived from DWTS. 100 ml raw DWTS samples were placed in a double-wall, jacketed glass container and subjected to continuous ultrasound irradiation emitted through a 18 mm diameter tip at a power input ranging from 100 W to 400 W, under the ultra-sonication time of 20 min, corresponding to the specific energy of 303.0–1212.1 kW h/kg TS. The ultra-sonication time (2.5, 5, 7.5, 10, and 15 min, respectively) was also looked at with an energy density of 1 W/ml, corresponding to the specific energy of 37.87–303.1 kW h/kg TS. During each ultra-sonication experiment, the samples were mixed using a magnetic stirrer at 250 rpm. The raw DWTS volume remained constant at 100 ml, and neither temperature nor pH was regulated. The specific energy (E_s) was defined (Eq. (1)) as the product of the ultrasonic power (P) and time (t) divided by the product of the sample volume (V) and the initial concentration of total solids (TS_0):

$$E_s = \frac{P \cdot t}{V \cdot TS_0} \quad (1)$$

2.3. Coagulation procedures of the DWTS recycling process with and without solubilized organics

Coagulation experiments were performed in a six-paddle stirrer with impellers equipped with 50 mm (L) × 40 mm (W) rectangular blades (ZR4-6, Zhongrun Water Industry Technology Development Co., Ltd., China). A series of jar tests were carried out to determine the optimum dosage of coagulant ($FeCl_3$) and recycling ratio of raw DWTS. The coagulation-flocculation procedures were as follows: 350 rpm ($G = 449 \text{ s}^{-1}$), 0.5 min; 300 rpm ($G = 367 \text{ s}^{-1}$), 1 min, adding $FeCl_3$; 120 rpm ($G = 106 \text{ s}^{-1}$), 1 min, adding recycled DWTS (20–100 mL, corresponding to 2–10% recycling ratio); 50 rpm ($G = 33 \text{ s}^{-1}$), 15 min, settling, 20 min. The supernatant samples after settling were collected for measurements of turbidity, UV_{254} absorbance, and DOC.

Another series of jar tests was conducted to investigate the impact of solubilized organics. When recycling sonicated DWTS without solubilized organics, the raw DWTS was first exposed to a probe-type sonoreactor and the sonicated DWTS was collected at a predetermined condition and set aside for a 24 h static precipitation, after which the supernatant of each sonicated DWTS was discharged while maintaining a thickened DWTS settled factor (volumetric ratio of discharged supernatant to the “sludge-water” mixture) of 0.6875. Subsequently, the same volume of deionized (DI) water as discharged supernatant was added to the condensate DWTS to maintain a constant total solid content of 1.10 g L^{-1} . On the other hand, no supernatant was discharged or displaced when recycling the sonicated DWTS containing solubilized organics. The sonicated DWTS with or without solubilized organics was added to the beaker of the jar tester at the beginning of the second stage of the coagulation-flocculation procedure at 120 rpm.

2.4. NOM fractionation

MW distribution of the NOM in the coagulated water from the recycling process 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 molecular weight cut-offs of 3, 10, 30, and 100 kDa, Millipore Corp., USA) were used for organics isolation and fractionation according to Wei et al. [27].

Resins were cleaned and conditioned as described by Leenheer [28]. The ratio of water sample volume to Supelite™ XAD-8 or Amblite XAD-4 resin volume (wet volume) was set at 35:1 and the initial water volume was 350 ml to avoid fractions breakthrough. The flow rate of loading samples onto the resin was 15 bed-volumes h^{-1} , which permitted adequate adsorption. The XAD-8 resin favors the isolation of the hydrophobic, containing NOM of HMW matter with an aromatic character. XAD-4 resin adsorbs weakly hydrophobic acid (WHA) fractions, commonly defined as transphilic matter. The hydrophilic fraction does not adsorb onto either of the resins. The NOM in the coagulated water of the DWTS recycling process was chemically fractionated into five parts following the procedure described by Yan et al. [29]: hydrophobic bases (HoB), hydrophobic neutral fraction (HoN), hydrophobic acid (HoA), WHoA, and hydrophilic matter (HiM).

2.5. 3D-EEM fluorescence spectroscopy

The fluorescence characteristics of solubilized organics derived from DWTS (under optimal specific energy), and that of the NOM in the coagulated water of the DWTS recycling process, were measured using 3D-EEM fluorescence spectroscopy. A 1-cm quartz cuvette with four optical windows was used for the analysis using a spectrofluorometer (F-4500, Hitachi, Japan). 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 remained 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 DI water (Millipore Milli-Q, Billerica, MA, USA; conductivity $18.2 \text{ } \Omega \text{ m}$) were subtracted from all spectra to eliminate water Raman scattering and to reduce background noise. During the fluorescence analysis, the Raman scattering peak intensity for the DI water (excitation, ex at 350 nm; emission, em at 400 nm) was recorded as a standard to verify the instrument stability. Mean intensity of the Raman peak was 11.39 units and the differences were less than 5%, confirming the absence of significant fluctuations in the performance of the spectrofluorometer throughout the length of the experiment.

2.6. Other analytical methods

All analysis were performed using chemicals of analytical grade. pH was determined by a Thermo pH meter (Shanghai, China), which was calibrated daily using a pH buffer solution. Turbidity was monitored with a 2100N Turbidimeter (Hach, USA). TS, VS, TCOD, and SCOD were determined according to standard methods [30]. The proteins in the supernatant of the DWTS were determined spectrophotometrically with a UV/Visible spectrophotometer (UV2600, China) after centrifuging at 4000 rpm for 10 min. A total carbon analyzer vario TOC® cube (Elementar, Germany) was used to analyze DOC. UV_{254} was determined by a UV/Vis spectrophotometer (UV2600, China). Both DOC and UV_{254} were measured after filtration through $0.45\text{-}\mu\text{m}$ acetate fiber membranes. In all cases, analysis was carried out in triplicate and mean values were recorded as results.

3. Results and discussion

3.1. The release of extracellular or intracellular organics

Fig. 1 presents the effect of energy densities ranging from 1.0 to 4.0 W/ml with an ultra-sonication time of 20 min (specific energy of 303.0–1212.1 kW h/kg TS) on the release of organics, quantified by SCOD and proteins, in the supernatant of sonicated DWTS. An

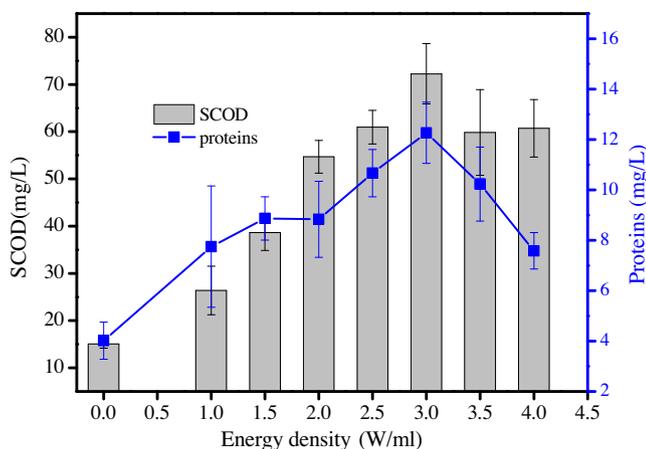


Fig. 1. Effect of energy density on the release of SCOD and proteins under ultra-sonication time of 20 min.

increase in SCOD or proteins indicates DWTS disintegration (including cell lysis) that releases extracellular or intracellular organics in the DWTS-to-water phase. The ultrasonic process did not alter the quantity of TS or TCOD. Therefore, in terms of specific supplied energy (E_s) input, the ultrasonic treatment did not induce evaporation or mineralization. As indicated in Fig. 1, both the released SCOD and proteins increased, plateaued with an increase in energy density, and then declined. At an energy density of 3.0 W/ml (specific energy input of 909.1 kW h/kg TS), the highest released SCOD and protein levels, 72.24 ± 6.39 and 12.27 ± 1.22 mg/L, respectively, were reached, a magnitude of 4.66 and 3.06 times that of the raw DWTS (15.05 ± 0.87 and 4.01 ± 0.74 mg/L, respectively). The organic concentration quantified by SCOD in the supernatant of sonicated activated sludge at specific energy input of 7.22 kW h/kg TS was determined by Feng et al. [31] as an approximately 12.33-fold increase from raw sludge. Wang et al. [32] found that supernatant protein and COD concentrations differed by nearly 10–20 times between sludge that was and sludge that was not pretreated by ultrasound. The low organic solubilization in this study could have resulted from (a) a relatively low concentration of SCOD and proteins in raw DWTS; and (b) the DWTS contained mainly non-degradable substances such as sand and metal hydroxides that are not easily disrupted, as compared to activated sludge, which is composed mainly of biological solids that are easily disrupted.

3.2. Coagulation behavior of recycled sonicated DWTS with and without solubilized organics

From the preliminary jar tests, the optimum amount of FeCl_3 , calculated as Fe, was determined to be 14.08 mg/L. At this level, turbidity, UV_{254} , and DOC removal reached 57.12%, 43.13%, and 28.53%, respectively. At the optimum FeCl_3 , the optimum recycling ratio of raw DWTS by volume was determined to be 6%, with a removal of turbidity, UV_{254} , and DOC at 20.92%, 44.84%, and 19.99%, respectively.

Fig. 2 illustrates the coagulation behavior of recycled sonicated DWTS with and without solubilized organics at energy densities ranging from 1.0 to 4.0 W/ml and an ultra-sonication time of 20 min (specific energy of 303.0–1212.1 kW h/kg TS). As shown in Fig. 2, the turbidity removal efficiency of recycled raw DWTS without solubilized organics increased to $(52.76 \pm 2.31)\%$ from the sample containing solubilized organics of $(20.92 \pm 3.04)\%$. In addition, the turbidity removal efficiency of sonicated DWTS improved as compared to raw DWTS containing solubilized

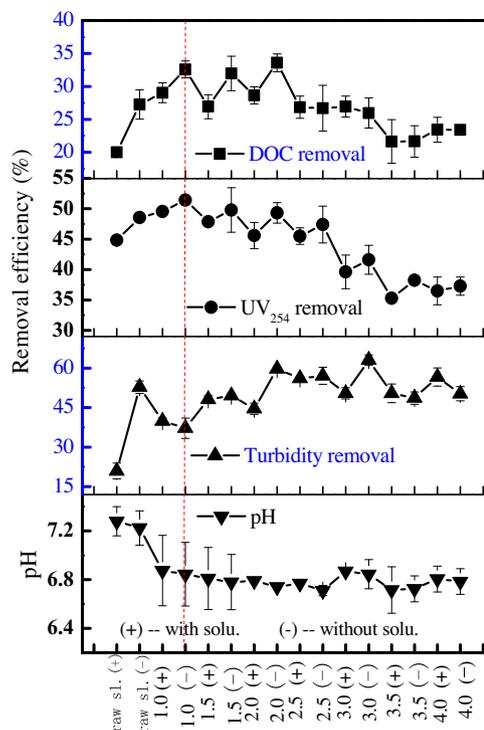


Fig. 2. Coagulation behavior of recycled sonicated DWTS with and without solubilized organics at varied energy density ranging from 1.0 to 4.0 W/ml with ultra-sonication time of 20 min (In all cases, the dosage of FeCl_3 was 14.08 mg Fe/L, DWTS recycling ratio of 6%. The average pH, turbidity, UV_{254} and DOC of raw water were 8.22 ± 0.15 , 0.870 ± 0.131 NTU, 0.043 ± 0.003 cm^{-1} and 5.202 ± 0.627 mg/L, respectively).

organics following exposure to varied energy densities. The turbidity removal efficiency of sonicated DWTS, regardless of solubilized organics, was lower than that of raw DWTS without released organics. Thus, ultrasound with varied energy densities was favorable to turbidity removal, which was similar to the effect of 24 h static precipitation. The highest turbidity removal of $(63.02 \pm 2.01)\%$ was achieved at 3.0 W/ml (specific energy of 909.1 kW h/kg TS) without solubilized organics. Results of our previous study [33] revealed that the coagulation behavior of recycled sonicated DWTS was largely dependent upon the organic solubilization and characteristic variability of sludge flocs, and that the organic solubilization could contribute to the deterioration of water quality. Linear regression analysis of the released concentrations of SCOD/proteins between the turbidity removal efficiency under the cases with solubilized organics/ Δ turbidity removal was conducted to quantify the turbidity removal with the released concentrations of solubilized organics, as seen in Fig. 1S (seen in Supplementary file). Here the Δ turbidity removal refers to the difference of the turbidity removal between the cases with solubilized organics and the cases without solubilized organics under a same energy density. The Δ turbidity removal means the extent of the deterioration or improvement of coagulated water. As seen from Fig. 1S, there was no significant linear relationship between SCOD/proteins and the turbidity removal efficiency with solubilized organics/ Δ turbidity removal. Thus, the turbidity removal of recycling process did not depend on the concentration of solubilized organics. The turbidity removal might be related to the distribution of the particles in the raw water, sonicated DWTS and resultant coagulated water.

Meanwhile, the UV_{254} removal efficiency of recycled raw DWTS without solubilized organics slightly increased to $(48.54 \pm 0.67)\%$ from the sample containing solubilized organics of $(44.84 \pm 0.56)\%$, indicating that the content of aromatic and

unsaturated double bond compounds in raw DWTS was relatively low. The UV_{254} is well correlated to the concentration of humic and fulvic acids, and these two hydrophobic fractions of humic substances rich in conjugated double bonds are the most targeted by coagulation [24]. Thus, the slight improvement in UV_{254} removal efficiency from recycled raw DWTS without solubilized organics suggested a minimal content of humic-like substances within the recycled DWTS, which could be confirmed through fluorescent characteristic analysis (see Section 3.4). Moreover, after exposure to energy densities below 2.5 W/ml (1.0, 1.5, 2.0, 2.5 W/ml), the UV_{254} removal efficiency of sonicated DWTS, regardless of solubilized organics, improved compared to that of raw DWTS containing solubilized organics, which showed the opposite tendency at energy densities above 2.5 W/ml (3.0, 3.5 and 4.0 W/ml). Thus, the lower energy density was more conducive to UV_{254} removal. Additionally, UV_{254} removal was always higher in conditions without solubilized organics than with solubilized organics. Therefore, the humic-like substance in the solubilized organics adversely affected UV_{254} removal despite its low levels. The highest UV_{254} removal of $(51.44 \pm 0.43)\%$ could be achieved at 1.0 W/ml without the solubilized organics. DOC removal was similar to UV_{254} removal and the highest DOC removal was $(32.58 \pm 1.29)\%$. Considering organic removal efficiency and energy consumption, the energy density of 1.0 W/ml was selected.

Through mass balance calculations of SCOD in the supernatant of the DWTS sample, it was deduced that recycling 6% of raw DWTS or sonicated DWTS treated at optimal ultrasound conditions resulted in a minimum of 0.922 mg/L and 2.077 mg/L improvement of SCOD, respectively, in the blended raw water matrix. Thus, an obvious change in the organic carbon concentration or coagulant demand in the blended raw water matrix would result, compromising the organics removal. However, the slightly improved organic removal achieved in this study could be obtained, mainly for the following reasons: first, in our previous study, we assumed floc sweeping and physical adsorption were the main coagulation mechanisms of the DWTS recycling process, which was the favored coagulation according to Gottfried et al. [34], Sun et al. [35], and Zhou et al. [8]. Second, the breakup of recycled DWTS flocs occurred after exposure to shear force in the ultrasound field, in which encapsulated Fe hydroxides were exposed to the surface, allowing for increased adsorption sites for organics. According to Guan et al. [36], the major positive effect of ultrasound on pollutant removal in the recycling process was the creation of a larger quantity of particles with larger specific surfaces. In our previous study [17], the Brunauer, Emmett, and Teller (BET) specific surface area of sonicated DWTS flocs increased as ultra-sonication was prolonged at lower energy densities of 1 W/ml from $80.28 \text{ m}^2/\text{g}$ of raw DWTS to $105.77 \text{ m}^2/\text{g}$ with an ultra-sonication time of 30 min. This hypothesis was also consistent with the conclusion of Kobayashi et al. [37] whereby the number of adsorption sites of flocs increased with an increase of adsorption capacity, resulting from the increased specific surface area of flocs induced by ultrasound.

In addition, the pH of coagulated water was always lower in scenarios without solubilized organics than in scenarios containing solubilized organics. Although the DWTS had a strong acid and alkalinity buffering capacity and the ultrasound had a slight effect on the sonicated DWTS [17], the dilution of recycled sludge through adding DI water lowered the pH of recycled sludge, leading to a decreased pH in coagulated water.

In order to further reduce the energy consumption while maintaining a high NOM removal efficiency, we investigated the effects of an ultra-sonication time of less than 20 min at an energy density of 1 W/ml on organic solubilization of raw DWTS and its impact on NOM removal in the recycling process.

The release of SCOD and proteins in the supernatant of sonicated DWTS is illustrated in Fig. 3. It is evident that the released concentrations of SCOD and proteins continuously increased as the ultra-sonication time was prolonged at an energy density of 1 W/ml, indicating that a lower specific energy input ($37.87\text{--}303.1 \text{ kW h/kg TS}$) was insufficient to disrupt the DWTS, as compared to the highest specific energy input of 909.1 kW h/kg TS (demonstrated in Fig. 1). Additionally, at established ultra-sonication times, turbidity, UV_{254} , and DOC removal efficiency was always higher in cases without solubilized organics than in cases containing solubilized organics (see Fig. 4). The highest UV_{254} and DOC removal rates, 52.30% and $(35.85 \pm 2.33)\%$, respectively, could be achieved at the ultra-sonication time of 10 min without solubilized organics, which showed the approximate organic removal with the UV_{254} and DOC removal of $(51.44 \pm 0.43)\%$ and $(32.58 \pm 1.29)\%$, respectively at the ultra-sonication time of 20 min. The result further indicated that the most desirable ultrasound level for NOM removal in the DWTS recycling process did not correspond to the highest organic solubilization of raw DWTS. The relatively shorter ultra-sonication duration (10 min) and lower energy density (1 W/ml) might be more favorable for NOM removal.

It can thus be concluded that DWTS was affected by the relatively low release of SCOD and proteins, which could deteriorate coagulated water quality at the specific energy input of $37.87\text{--}1212.1 \text{ kW h/kg TS}$. Moreover, the most desirable coagulation behavior regarding NOM removal could be achieved by recycling sonicated DWTS without solubilized organics with a specific energy of 151.5 kW h/kg TS (energy density of 1 W/ml, ultra-sonication time of 10 min). However, it is worth noting that the specific energy corresponding to the highest NOM removal in the recycling process was 151.5 kW h/kg TS , which differed from the specific energy corresponding to the highest organic solubilization of 909.1 kW h/kg TS (see Fig. 1). This discrepancy might be ascribed to the characteristics of solubilized organics and organic fractionations.

3.3. Effects on organic fractionations in coagulated water

NOM can be chemically fractionated into hydrophobicity and hydrophilicity. The hydrophobic portion is rich in aromatic carbon, having phenolic structures and conjugated double bonds, while hydrophilic NOM contains a higher proportion of aliphatic carbon and nitrogenous compounds, such as carbohydrates, proteins,

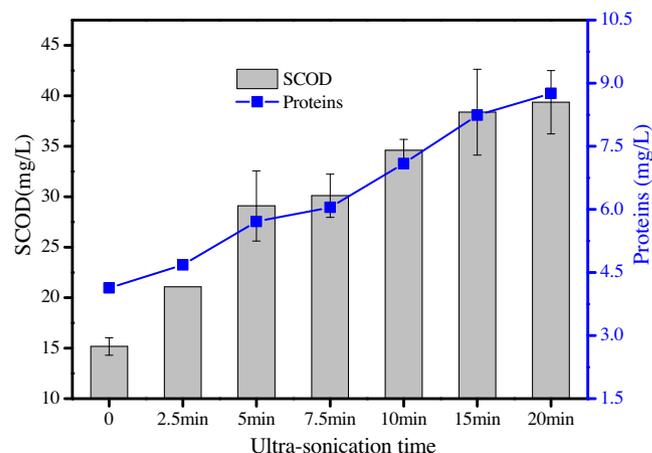


Fig. 3. Effect of ultra-sonication time on the release of SCOD and proteins under energy density of 1 W/ml.

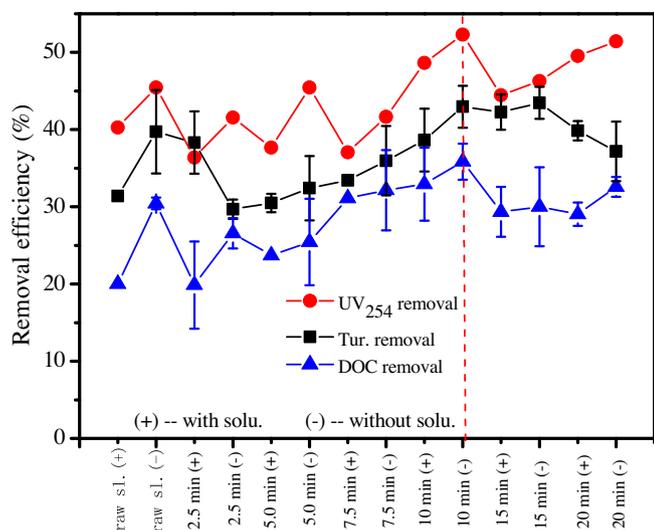


Fig. 4. Coagulation behavior of recycled sonicated DWTS with and without solubilized organics at varied ultra-sonication time with energy density of 1.0 W/ml (In all cases, the dosage of FeCl_3 was 14.08 mg Fe/L, DWTS recycling ratio of 6%. The average pH, turbidity, UV_{254} and DOC of raw water were 8.20 ± 0.15 , 0.678 ± 0.004 NTU, $0.0365 \pm 0.0007 \text{ cm}^{-1}$ and 6.204 ± 0.527 mg/L, respectively).

sugars, and amino acids [22]. The solubilized organics of activated sludge included intracellular polymers (mainly polysaccharide and proteins) and extracellular LMW lignocelluloses including hemicellulose, cellulose, and lignin [38]. Proteins are hydrophilic and resistant to removal through coagulation, while the lignocelluloses are hydrophobic and difficult to degrade by microorganisms. In addition, Yu and Graham [39] have speculated that protein-associated substances of the EPS extracted from an ultrafiltration membrane tank were HMW (10^4 – 10^5), while the humic-associated substances were LMW (10^2 – 10^4). To elucidate the NOM variability characteristics of the DWTS recycling process, the hydrophobicity and MW distribution of organics under different conditions were investigated, as follows: A—raw water; B—traditional coagulation, control test; C—traditional coagulation + 6% recycled raw DWTS containing solubilized organics; D—traditional coagulation + 6% recycled raw DWTS without solubilized organics; E—traditional coagulation + 6% recycled sonicated DWTS containing solubilized organics; and F—traditional coagulation + 6% recycled sonicated DWTS without solubilized organics (see Fig. 5).

As shown in Fig. 5(a), organics in the raw water (A) mainly consisted of HiM and HoA, accounting for 44.73% and 43.67% of DOC, respectively. Meanwhile, the most abundant portion distributed in low-MW (<3 kDa) accounted for 86.19% (see Fig. 5(b)). The result indicated that the raw water was mainly composed of hydrophilic and LMW compounds that were difficult to remove through traditional coagulation methods, as evident by the result under condition (B) the percentage of HiM increased while HoA decreased. This suggested the hydrophilic fractionation was recalcitrant and HoA could be eliminated, which was consistent with the findings of Xing et al. [40] and Wang et al. [41]. Moreover, the percentage of <3 kDa declined to 78.28%. When recycling raw DWTS containing solubilized organics (C), the HiM percentage was nearly the same as that in the raw water (A), indicating that the concentration of hydrophilic material in the recycled DWTS was relatively low (as indicated by low concentrations of proteins in raw DWTS shown in Fig. 3). As for MW distribution, the percentage of >100 kDa increased compared to traditional coagulation methods by adding FeCl_3 alone (B), which indicated the recycled DWTS contained some amount of organics distributed in >100 kDa. According to Yu and Graham [39], the >100 kDa fractionation may be related to

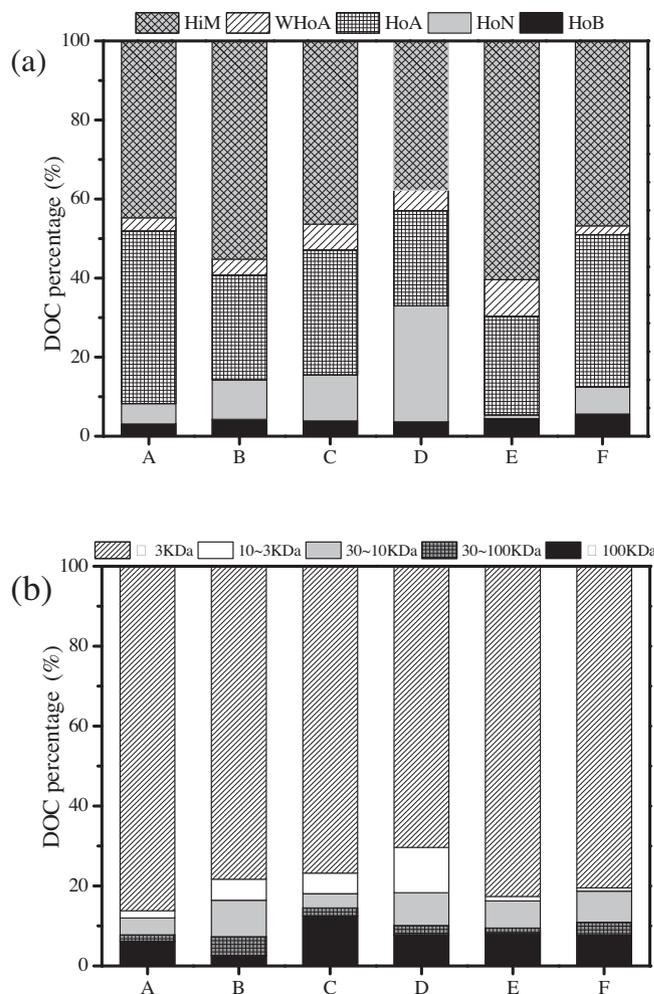


Fig. 5. Hydrophobicity (a); and MW distribution (b) of organics under different conditions. (A—raw water; B—traditional coagulation; C—traditional coagulation + 6% recycled raw DWTS; D—traditional coagulation + 6% recycled raw DWTS without solubilized organics; E—traditional coagulation + 6% recycled sonicated DWTS containing solubilized organics; F—traditional coagulation + 6% recycled sonicated DWTS without solubilized organics).

protein-associated substances. Compared to scenarios containing solubilized organics (C), when discharging the supernatant of raw DWTS after a 24 h static precipitation (D), the percentage of HiM and that of <3 kDa both declined.

After ultrasound treatment at specific energy of 151.5 kW h/kg TS, the hydrophilic proteins were solubilized, leading to an increase in the HiM in coagulated water in the scenario recycling sonicated DWTS containing solubilized organics (E). When recycling the sonicated DWTS without solubilized organics (F), the percentage of HiM greatly decreased as compared to the scenario with solubilized organics (E), suggesting that discharging the solubilized organics from recycled DWTS could reduce the enrichment risk of HiM. Meanwhile, the percentage of <3 kDa decreased when recycling sonicated DWTS without solubilized organics (F), which indicated that the risk of enrichment of <3 kDa could be reduced when discharging the solubilized organics in recycled DWTS subjected to ultrasound.

In order to study which organic fractionation has the greatest enrichment potential, the DOC percentage of a constant fraction in treated water minus the percentage of the same fraction in a control test, defined as $\Delta\text{DOC}\%$, was investigated. A larger positive $\Delta\text{DOC}\%$ implied a greater enrichment potential, and a larger negative $\Delta\text{DOC}\%$ implied a further removal (see Fig. 6).

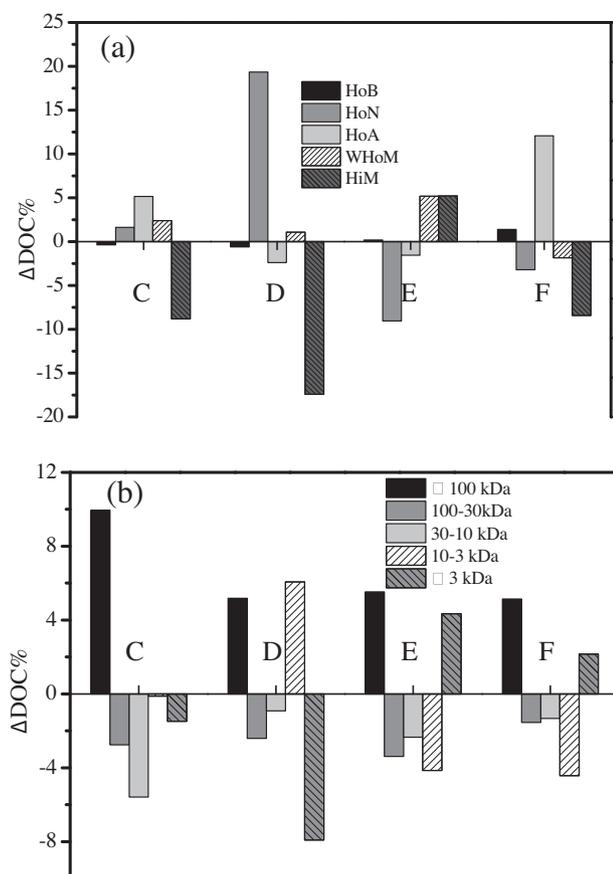


Fig. 6. Enrichment potential of organic fractionations in coagulated water. Hydrophobicity (a); and MW distribution (b). C–F was the same as in Fig. 5.

As seen in Fig. 6(a), the $\Delta\text{DOC}\%$ of HoN, HoA, and WHoA under the condition C was a positive value compared to the control test, indicating these fractions were enriched. Under the condition D, when discharging the supernatant containing solubilized organics, the $\Delta\text{DOC}\%$ of HiM, HoA, and WHoA became negative compared to C, suggesting the solubilized organics contained all such fractions. The enrichment of WHoA and HiM occurred under E compared to C, further confirming the solubilized organics contained WHoA and HiM fractions. With comparison to E, after discharging the solubilized organics (F) the enrichment potential of WHoA and HiM greatly decreased. All results indicated that recycled DWTS mainly contained WHoA and HiM compounds. The enrichment potential of WHoA and HiM increased after the recycled DWTS was exposed to ultrasound and the risk of enrichment could be reduced by discharging solubilized organics.

Additionally, as indicated in Fig. 6(b), the highest positive value of $\Delta\text{DOC}\%$ for >100 kDa fraction indicated that recycled DWTS contained large amounts of HMW compounds. Likewise, the negative value of $\Delta\text{DOC}\%$ for <100 kDa suggested that the DWTS recycling process could promote the removal of middle- and low-MW compounds. Comparing conditions C and D, it was found that the <3 kDa fraction could be further removed. After the raw DWTS was treated by ultrasound, the enrichment risk of <3 kDa greatly increased (comparing C and E), indicating that the solubilized organics contained a large portion of <3 kDa fraction. As compared to condition E, the enrichment potential of <3 kDa fraction could be reduced under condition F.

In general, the main organic fractionations in recycled DWTS were WHoA and HiM, with the MW distribution of >100 kDa and <3 kDa. Recycling sonicated DWTS containing solubilized organics

could increase the enrichment risks of WHoA, HiM, and <3 kDa fractions, but discharging the solubilized organics could reduce enrichment risks.

3.4. Fluorescent characteristic analysis

There are five commonly referred to key fluorescence peaks, fluorophores A, C, T1, T2, and B, found in water samples [42–44]. These have been classified according to Coble [42] as follows: peak A—humic-like ($\lambda_{\text{ex/em}} = 237\text{--}260/400\text{--}500$ nm); peak C—humic-like ($\lambda_{\text{ex/em}} = 300\text{--}370/400\text{--}500$ nm); peak B—tyrosine-like ($\lambda_{\text{ex/em}} = 225\text{--}237/309\text{--}321$ nm and $\lambda_{\text{ex/em}} = 275/310$ nm); peak T1—tryptophan-like ($\lambda_{\text{ex/em}} = 275/340$ nm); and peak T2—tryptophan-like ($\lambda_{\text{ex/em}} = 225\text{--}237/340\text{--}381$ nm). Peaks A and C are related to humic-like substances derived from the breakdown of plant material, while tryptophan-like (peaks T1 and T2) and tyrosine-like (peak B) materials are usually detected at increased levels in water impacted by domestic sewage. In this study, distinctly identified peaks A and T1 were selected because peaks B, C, and T2 had relatively lower fluorescence intensities.

The fluorescence spectra of dissolved organic matter (DOM) in the supernatant of raw DWTS and sonicated DWTS with a specific energy of 151.5 kW h/kg TS (energy density of 1 W/ml, ultra-sonication time of 10 min) are illustrated in Fig. 7(a) and (b). As seen in Fig. 7(a) and (b), the fluorescence spectra of DOM in the supernatant of raw DWTS and sonicated DWTS for peak A were located at ex/em wavelengths of 250.0/425.0 nm and 260.0/420.0 nm, respectively. For Peak T1, the fluorescence spectra were located at 275.0/335.0 and 280.0/345.0, respectively. Additionally, the fluorescence intensity of peaks A (40.71, in arbitrary unit, AU) and T1 (83.38) in the supernatant of sonicated DWTS was higher than that of raw DWTS (25.31 for peak A and 41.18 for peak T1), indicating that both humic-like and protein-like substances were released into the supernatant during sonication, which was consistent with the result illustrated in Fig. 3. Moreover, the increased ratio of fluorescence intensity for peaks A and T1 as compared to that of raw DWTS was 1.59 and 2.02, respectively.

The fluorescence EEM spectra in the DOM of coagulated water samples from the recycling process are illustrated in Fig. 7(d)–(g). It can be seen that fluorescence EEM spectra in the DOM of coagulated water samples were similar to that of raw water. The maxima of peak A and T1 were $\lambda_{\text{ex/em}}$ of 250.0–255.0 nm/420.0–435.0 nm and 275.0–280.0 nm/340.0–345.0 nm, respectively. Furthermore, the maximum fluorescence intensity of peak A decreased from 44.78 in raw water to 21.75, 20.43, 22.72, and 20.80, corresponding to the conditions of C, D, E, and F, respectively, as addressed in Fig. 5. Moreover, the reduction rate of peak A fluorescence intensity remained nearly the same regardless of whether the recycled DWTS contained solubilized organics, indicating that humic-like substance (peak A) removal through the discharge of solubilized organics was limited when the recycled DWTS contained small amounts of such substances. Analogously, the peak T1 fluorescence intensity in treated DOM samples also decreased from 43.18 in raw water to 26.19, 19.68, 38.12, and 22.58, corresponding to the conditions of C, D, E, and F, respectively. It is worth noting that the reduction rate of peak T1 fluorescence intensity was greater when recycling DWTS without solubilized organics, which indicated that increased removal of protein-like materials (peak T1) could be achieved when recycling DWTS without solubilized organics. Compound T1, resulting from microbial activity, may be LMW and more soluble than compound A, and therefore more refractory to the recycling process [25]. Traditional coagulation can effectively improve humic-like substance removal, but large portions of protein-like materials indicative of residual DOM are difficult to eliminate [24]. In this study, to

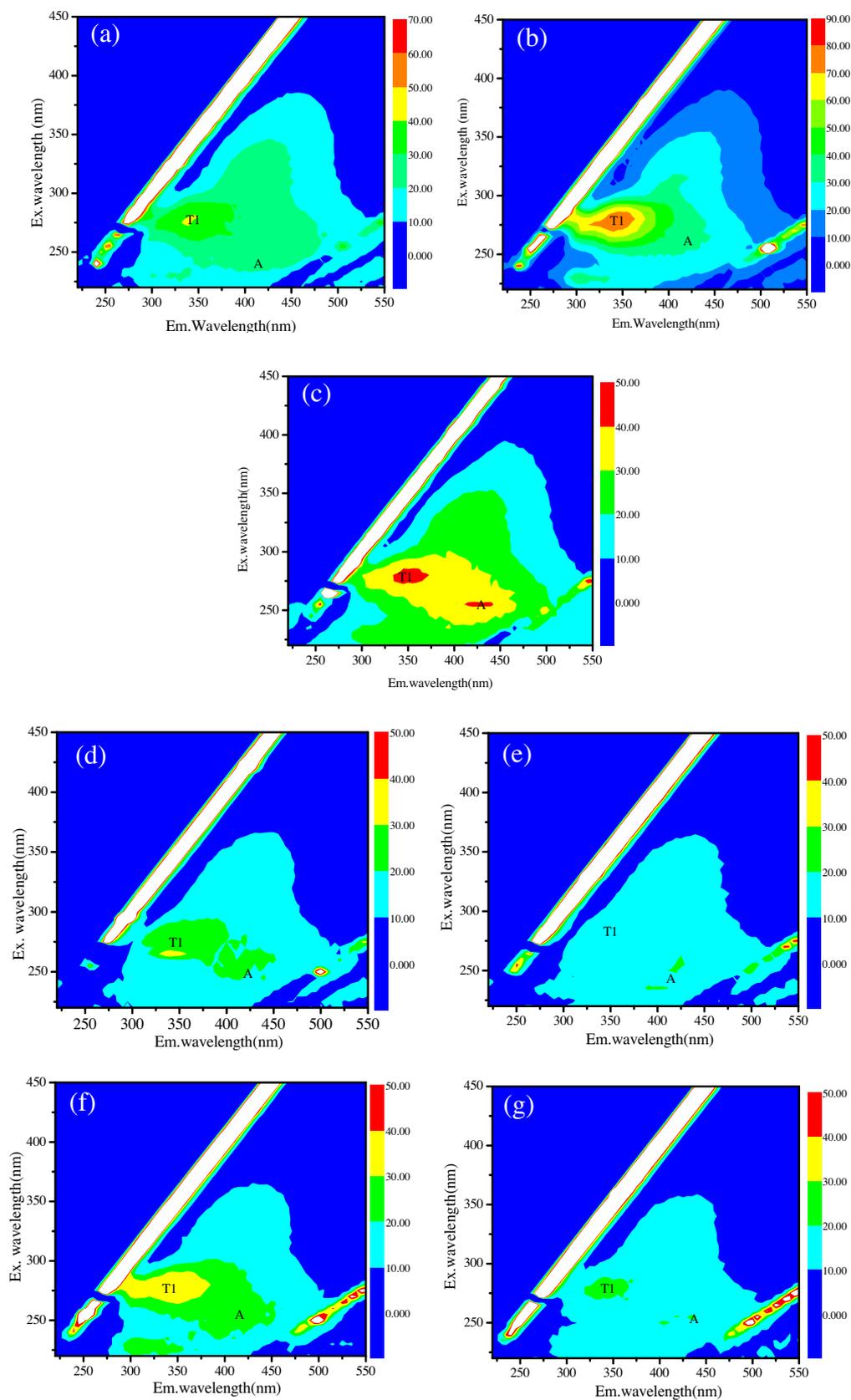


Fig. 7. Fluorescence spectra of dissolved organic matter (a) in the supernatant of raw DWTS; (b) in the supernatant of sonicated DWTS (1 W/ml, 10 min); (c) raw water; (d–g) corresponding coagulated water under the conditions as in Fig. 5 C–F.

some extent, discharging protein-associated substances within the solubilized organics of recycled DWTS could reduce the enrichment risk of protein-like materials (peak T1) in coagulated water. Study results could provide a useful strategy in using ultrasound as a pretreatment of DWTS followed by the discharge of solubilized organics to enhance protein-like substance removal, or to prevent the enrichment of protein-like substances within the DWTS recycling process.

3.5. Energy cost analysis

The operating cost of treatment is the primary selection criteria when determining economic viability of water treatment techniques. Taking lead from this concept, the ultrasound pretreatment cost had been calculated for the experimental UV₂₅₄ and DOC removal of coagulated water obtained with varied ultra-sonication time and energy densities based on electrical power consumption. The average price of 1 kWh was taken as 1 Yuan (RMB) based on the electricity prices in China. The ultrasonic treatment cost for 1 L of DWTS was calculated using Eq. (2). The cost of ultrasound pretreatment under varied parameters were summarized in Table 2:

$$\text{Cost of the treatment} = \text{ultrasonic energy density} \times \text{cost of 1 kWh} \quad (2)$$

The most cost effective ultrasonic parameters and their cost figures were put in bold and italic font to differentiate them from the other parameters. It should be noted here that the cost provided here only concerns the treatment cost and can constructively be used in combination with the analysis of the capital and maintenance cost to reach a rational decision with regards to the application of ultrasonic DWTS pretreatment in water treatment practices.

4. Remarks and conclusions

The physical application of recycled DWTS is restricted due to possible negative effects of complex components within the recycled DWTS. In order to avoid the organic enrichment of recycle design, in this study, we firstly used ultrasound to solubilize the organics derived from DWTS, and then elucidated their impacts on the NOM removal and enrichment characteristics of each organic fractionation in coagulated water. According to our previous study [17], ultrasound could disrupt the DWTS flocs and solubilize the organics into the supernatant of DWTS, resulting in the increasing of SCOD, polysaccharides and proteins. In this study, the released SCOD and proteins increased and then decreased with the increasing specific energy input. At the specific energy input of 909.1 kW h/kg TS, the maximum release of SCOD and proteins was achieved. Meanwhile, it can be found that too high energy density (3.5 and 4.0 W/ml) led to the decline of proteins which might be related to the proteins denature induced by the large amounts of produced ·OH and high rise in temperature from 13 °C to 40 °C.

On the one hand, from the perspective of NOM removal in the recycling process, we found that the UV₂₅₄ and DOC removal for the cases without solubilized organics was absolutely higher than those with the solubilized organics, and the highest NOM removal was achieved at 151.5 kW h/kg TS (energy density of 1.0 W/ml and ultra-sonication time of 10 min), which differed from the specific energy corresponding to the highest organic solubilization of 909.1 kW h/kg TS. This result demonstrated that solubilized organics played adverse effects on the NOM removal, and a low specific energy input was more economic effectiveness (seen in Table 2). From cost consumption and NOM removal effectiveness, the specific energy input of 151.5 kW h/kg TS was recommended when ultrasound was used as pretreatment of such DWTS. To some

Table 2
The cost of ultrasound pretreatment under varied parameters.

Electrical power (W)	Sonication time (s)	NOM removal of recycling pre-sonicated DWTS without solubilized organics		Cost electrical power of 1 L DWTS (RMB/L)	Cost electrical power of 100 mL DWTS (RMB/0.1 L)
		DOC removal (%)	UV ₂₅₄ removal (%)		
100	1200	32.579	51.437	0.0333	0.00333
150	1200	31.962	49.802	0.0500	0.00500
200	1200	33.578	49.323	0.0667	0.00667
250	1200	26.691	47.414	0.0833	0.00833
300	1200	25.964	41.614	0.100	0.0100
350	1200	21.650	38.233	0.117	0.0117
400	1200	23.385	37.292	0.133	0.0133
100	150	26.564	45.455	0.00417	0.000417
100	300	25.445	41.667	0.00833	0.000833
100	450	32.158	52.296	0.0125	0.00125
100	600	35.855	46.296	0.0167	0.00167
100	900	30.008	51.437	0.0250	0.00250

extent, it is attemptable to use ultrasound as a pretreatment in the DWTS recycling process at an actual drinking water treatment plant. Moreover, we theoretically inferred that enhanced organics removal was mainly ascribed to the increased adsorption capacity of recycled DWTS triggered by ultrasound. However, it remains necessary to determine the functional groups interacting with the surface of sonicated DWTS flocs, the nature of the interaction, and the structure of the sonicated DWTS flocs to fully understand NOM-adsorption of the DWTS interface.

Additionally, it was observed that the DWTS recycling process could increase the enrichment risk of WHoA, HiM, and <3 kDa fractions, as well as protein-like substances in coagulated water. Yet the enrichment risk could be greatly reduced through the discharge of solubilized organics from recycled sonicated DWTS. The results could aid facilities using the DWTS recycling process in avoiding the organic enrichment risk, thereby increasing the chemical safety of the finished water of the treatment train. However, as we know, all those enriched fractionations are difficult to remove by coagulation process, further advanced techniques, i.e., advanced oxidation process or dual/multiplied-frequency ultrasound to effectively degrade solubilized organics for recycle design are needed.

The main conclusions drawn from this work are as follows:

- (1) DWTS was disrupted by the relatively low release of SCOD and proteins, which could deteriorate the coagulated water quality under the specific energy input of 37.87–1212.1 kW h/kg TS.
- (2) The most desirable coagulation behavior in regards to NOM removal was achieved by recycling sonicated DWTS without solubilized organics, which could be achieved with a specific energy of 151.5 kW h/kg TS.
- (3) The main organic fractionations in recycled DWTS were WHoA and HiM, with the MW >100 kDa and <3 kDa. Recycling sonicated DWTS containing solubilized organics could increase the enrichment potential of WHoA, HiM, and <3 kDa fractions. By discharging the solubilized organics this enrichment risk could be reduced.
- (4) Fluorescent characteristic analysis confirmed that both humic-like (peak A) and protein-like (peak T1) substances were released into the supernatant of sonicated DWTS. By discharging the solubilized organics in the recycled sonicated DWTS, the humic-like substances could not

increasingly be removed, whereas the enhanced removal of protein-like substances could be achieved, lowering the enrichment potential of protein-like substances.

- (5) A useful strategy using ultrasound as a pretreatment of DWTS and then discharging the solubilized organics was recommended to avoid the organic enrichment risk of the DWTS recycling process.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ultsonch.2015.07.016>.

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