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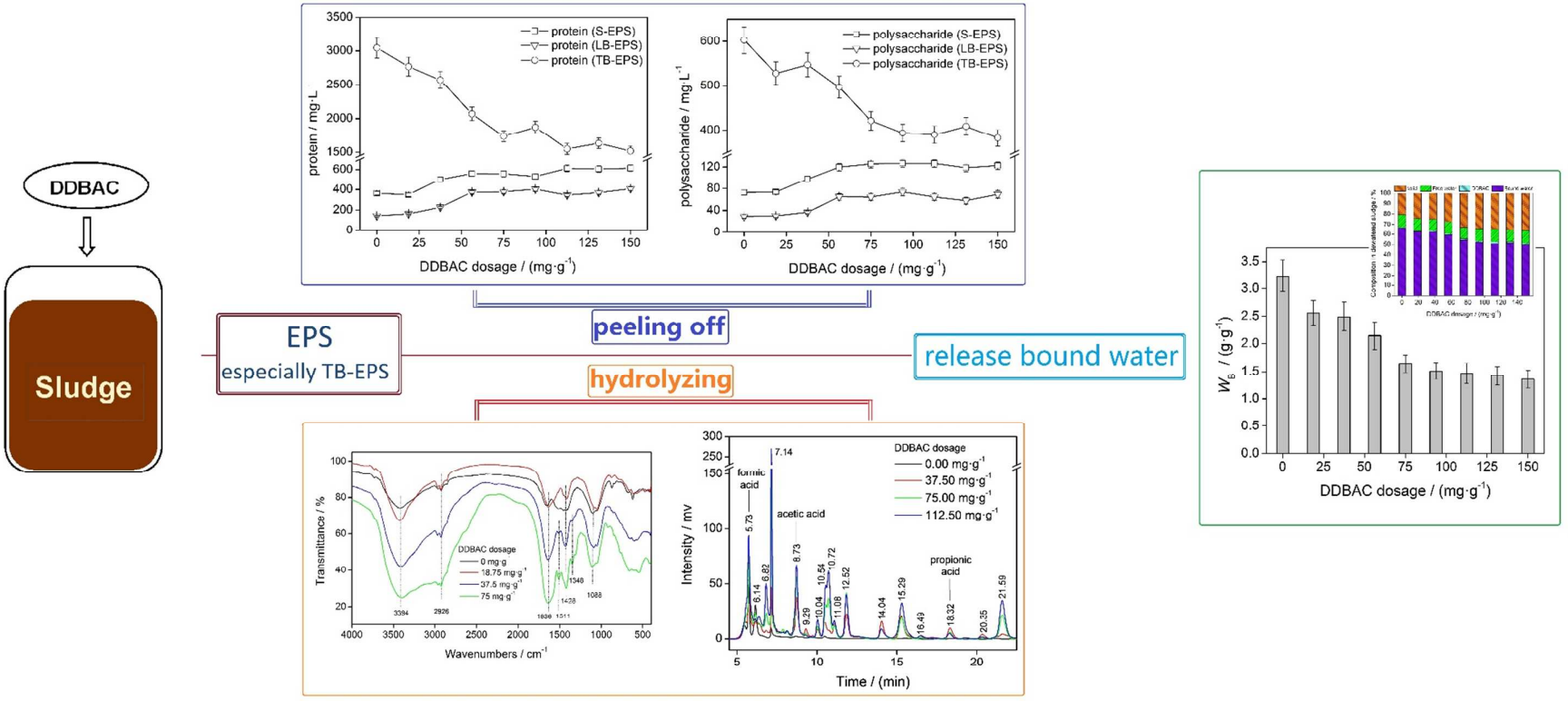
Graphical abstract

Surfactant DDBAC boosts EPS, especially TB-EPS, peeling off from sludge flocs and partly hydrolyzing into small molecular organics, and more bound water is released than without DDBAC adding.



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Effect of surfactant on bound water content and extracellular polymers substances distribution in sludge

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The effect of surfactant conditioning on bound water and extracellular polymers substances (EPS) in sludge was investigated in this study. Results showed that loosely bound EPS (LB-EPS) and slime layer EPS (S-EPS) contents were increased by adding dodecyl dimethyl benzyl ammonium chloride (DDBAC), while tightly bound EPS (TB-EPS) and bound water contents (W_B) were reduced. As a result, dewatering performance of sludge was enhanced. When DDBAC of 75 mg·g^{-1} was added, W_B in sludge decreased to 1.64 g·g^{-1}, and water content of dewatered sludge (W_C) dropped to 66.61%. EPS partially hydrolyzed into small molecular organics under DDBAC conditioning. What's more, the quantity and species of organic functional groups in S-EPS were increased obviously. TB-EPS content accounted for the majority of EPS in sludge and the protein and polysaccharide in TB-EPS had significant positive correlation with bound water, which was the main factor affecting W_B in sludge.

1 Introduction

In municipal sewage treatment plants, moisture content of sludge is typically over 95%. Sludge dewatering is the most significant process among sewage treatments in sludge reduction, harmless treatment, reutilization.[1, 2] However, urban sewage sludge is rich in organic substance, which leads to the formation of colloidal structure in sludge floc particles. These particles are very hydrophilic as they combined with water molecules in different ways effortlessly. Thus, they make it difficult to remove this part of water from sludge.[3] A more detailed classification of water distribution in sludge can be divided into four types of patterns, namely, free water, pore water, adsorbed water, and bound water.[4] However, this division currently has no quantitative measurements. Moisture is usually divided into free and bound types of water through usual quantitative method.[5] Free water is not restrained by sludge floc bondage. It can be separated from sludge through concentration or mechanical dewatering. Meanwhile, bound water has a strong bond with sludge flocs. It is specifically tightly restrained in sludge and it is difficult to be removed through mechanical force.[6]

The presence of bound water has a close relationship with extracellular polymers substances (EPS) in sludge. EPS is an insoluble organic matter attached to the surface of the sludge bacterial cell, which is the third largest composition besides bacterial cells and water.[7] EPS accounting for 50% to 90% of total organic matter in activated sludge can stabilize sludge floc structure by connecting microbial cells and other substances.[8] EPS binds water to the solid surfaces or capture water inside the cells or flocs because of its strong water binding capacity.[9-11] Thus, EPS is a key factor that affects the stability and dewatering of sludge.[12] Main components of EPS are proteins and polysaccharides, which account for 70% to 80% of total EPS.[13,14] According to the combination degree between organic matter and sludge flocs, EPS can be divided into slime layer EPS (S-EPS), loosely bound EPS (LB-EPS), and tightly bound EPS (TB-EPS).[15] Jin *et al*.[6] argued that polymeric component such as protein and carbohydrate have contributed significantly to improving the water binding ability of sludge flocs.

In studies of sludge dewatering, numerous researchers concluded that adding surfactants could improve sludge dewatering performance.[16-20] Chen *et al*.[16] reported that besides the enhancement of the ability of demolishing sludge structure, the dissolution of suspended solids and digestion of extracellular could be enhanced by the introducing of surfactant (lauryl betaine) compare to traditional sludge conditioner ($FeCl_3$, CaO). Furthermore, protein and carbohydrate concentration in sludge liquid was increased while dewatering and filtering performance was also enhanced. Yuan *et al*.[20] used electrolysis and surfactant joint conditioning sludge in their study. The results demonstrated that adding surfactant helped increase the concentration of S-EPS, reduce viscosity and Zeta potential of the sludge, and improve the sewage sludge dewatering performance. Current studies focus on the relationship between S-EPS content and sludge dewatering performance under surfactant conditioning. The effect of surfactant on LB-EPS and TB-EPS, and the relation between EPS layers (S-EPS, LB-EPS, and TB-EPS) and bound water under surfactant conditioning is still not known well.

The effect of surfactant (dodecyl dimethyl benzyl ammonium chloride, DDBAC) conditioning on EPS and bound water in sludge was investigated in this study. By studying the impact of surfactant on dewatered sludge water content, bound water content, the content of protein and polysaccharide in different EPS layers, and the relation between bound water content and EPS distribution was

analyzed. Fourier transform infrared spectroscopy (FTIR) and high-performance liquid chromatography (HPLC) were used to test sludge supernatant to demonstrate the changes of organic matter in quantity and variety. The aim is to provide a more comprehensive study on the sludge dewatering mechanism under surfactant conditioning.

2 Materials and methods

2.1 Materials

The sludge used in this study was collected from the sludge concentration tank in Xiaohongmen sewage treatment plant, Beijing. It was dewatered to 95% in terms of water content before employed as test sample. The properties of the sludge before conditioning in this study are shown in Table 1. All experiments were completed within 48 h and the sludge was kept in a freezer at 4 ˚C beforehand.

Table 1 Properties of sludge used in this study before conditioning

Parameters		Units	Value
TSS		$mg \cdot L^{-1}$	48952.55±244.78
VSS		$mg \cdot L^{-1}$	32843.52±1644.26
pH value		--	7.19±0.12
Water content		%	95.07±0.15
Bound water		$g \cdot g^{-1}$	3.24±0.26
S-EPS	Protein	$mg \cdot L^{-1}$	363.31±18.23
	Polysaccharide	$mg \cdot L^{-1}$	72.68±6.74
LB-EPS	Protein	$mg \cdot L^{-1}$	143.16±7.57
	Polysaccharide	$mg \cdot L^{-1}$	29.06±3.34
TB-EPS	Protein	$mg \cdot L^{-1}$	3045.02±150.46
	Polysaccharide	$mg \cdot L^{-1}$	602.54±33.52

Sludge conditioner is a cationic surfactant (dodecyl dimethyl benzyl ammonium chloride, DDBAC) with a chemical formula of $C_{21}H_{38}NCl$ and has a relative molecular mass of 340.00.

2.2 Experimental methods

2.2.1 Surfactant conditioning sludge. Different portions of DDBAC were added in 100 ml sludge in a 150 ml beaker. The mixture was stirred for 10 min under intensity of 100 $r \cdot min^{-1}$ and then was left static for 30 min. After conditioning, 50 ml sludge was placed into a Büchner funnel 150nm in diameter. Filtration dehydration under a vacuum pressure of -0.055 MPa was then conducted. The filtration dehydration was complete when the filtrate flow was absent for 30s.

2.2.2 Water content. Sludge dewaterability was evaluated in terms of the water content in dewatered sludge (W_C). The W_C was calculated as follows:

$$W_C = \frac{W_1 - W_2}{W_1 - W_{DDBAC}} \times 100\% \quad (1)$$

where W_1 is the weight of dewatered sludge and W_2 is the weight of dewatered sludge under 105 ºC drying to constant weight and W_{DDBAC} is the weight of DDBAC adsorbed on dewatered sludge.

2.2.3 Bound water content. Bound water content (W_B) was measured by differential scanning calorimetry (DSC) method.[21] With a certain amount of dewatered sludge in the DSC analyzer (NETZSCH, 404 F3 Pegasus, Germany), sludge samples were cooled down to -30 ºC at a rate of 5 $ºC \cdot min^{-1}$, then warmed up to room temperature at the same rate. Theoretically, samples would release heat and show a significant exothermic peak in the process of freezing and present a clear endothermic peak at heating stage. Because bound water does not freeze at -30 ºC, heat released during measuring reflected free water content in the sludge. W_B is the difference between total water content and free water content. The formula is as follows:

$$W_B = \frac{W_T - \Delta H/\Delta H_0}{W_{DS} - W_{DDBAC}} \quad (2)$$

where W_T is total water content of sample, ΔH is DSC endothermic of sample, W_{DS} is the weight of dry sludge in sample, and ΔH_0 is the standard fusion heat of ice, 334.7 $J \cdot g^{-1}$.

2.2.4 EPS extraction and determination. EPS were extracted via centrifugation and ultrasonication.[22] 30 ml sludge after conditioning was centrifuged for 15 min at 3000 $r \cdot min^{-1}$. Collected supernatant was considered as S-EPS. Precipitate was diluted into original volume (30 ml) with deionized water and centrifuged for 15 min at 7400 $r \cdot min^{-1}$. Then, the supernatant was filtered through a 0.45 μm membrane. Organics in solution were considered as LB-EPS. The sediment left was then diluted into original volume (30 ml) with deionized water again and treated by ultrasonic (20 kHz, 480 W, 10 min) before centrifugation (20 min and 15000 $r \cdot min^{-1}$) was applied. Supernatant was filtered through a 0.45 μm membrane, in which the residual organics in filtrate were regarded as TB-EPS.

Folin-phenol (Lowry) method was employed to determine extracellular protein content, and anthrone colorimetric method was used to measure polysaccharide content .[23, 24]

2.2.5 FTIR study. S-EPS were freeze-dried to observe the organic functional groups by freeze-drier (FDU-1100, Eyela, Japan). Residual solid was compressed via KBr and then determined by using a Fourier transform infrared spectrometer (FTIR) (IR-408, Shimadzu, Japan).

2.2.6 HPLC study.

① The content of DDBAC in sludge filtrate was determined by the high performance liquid chromatography (HPLC) (LC-20AD, Shimadzu, Japan), and the absorption amount of DDBAC in sludge were calculated as the DDBAC dosage minus the DDBAC content in sludge filtrate.

Chromatographic was employed under following conditions: mobile phase was 90% CH_3CN -0.10 $mol \cdot L^{-1}$ CH_3COONH_4 solution (V/V) filtered through a 0.45 μm membrane and then degassed by ultrasonic for 10 min. Flow rate was 0.5$ml \cdot min^{-1}$, column temperature was at 25 ± 1 ºC, measurement wavelength is 262 nm, injection volume is 20 μL, and high peak is quantified via the external standard method.

② Organic matter hydrolysis in sludge supernatant was analyzed by liquid chromatography. HPLC was applied to determine the content of small molecular organic acids (formic acid, acetic acid, and propionic acid). Liquid chromatogram could measure the organic compound hydrolysis.

Chromatographic was employed under following conditions: mobile phase was 7% CH_3OH-0.20 $mol \cdot L^{-1}$ KH_2PO_4 (pH = 4.0) buffer solution (V/V) filtered through a 0.45 μm membrane and then degassed by ultrasonic for 10 min. Flow rate was 0.5$ml \cdot min^{-1}$, column temperature was at 40 ± 1 ºC, measurement wavelength is 215 nm, injection volume is 20 μL, and high peak is quantified via the external standard method.

3 Results and discussion

3.1 Changes of W_C and composition in dewatered sludge after conditioning with surfactant DDBAC

As shown in Fig. 1, the dewatering performance of sludge under conditioning significantly improved with increasing surfactant (DDBAC) dosage. W_C decreased from 79.36% (DDBAC dosage was 0 mg·g^{-1}, mg·g^{-1} indicated DDBAC dosage of per gram dry sludge in sample, similarly hereinafter) to 62.95% (DDBAC dosage was 150 mg·g^{-1}), indicating a 16.41% decline. When DDBAC dosage increased from 56.25 mg·g^{-1} to 75 mg·g^{-1}, W_C decreased significantly from 72.05% to 66.61%, representing a 5.44% decline. And when DDBAC dosage was greater than 75.00 mg·g^{-1}, the downward trend of W_C slowed down. These results were in agreement with Chen *et al.*[16] and Yuan *et al.*[20], who observed similar results that sludge dewatering performance improved significantly under surfactants condition.

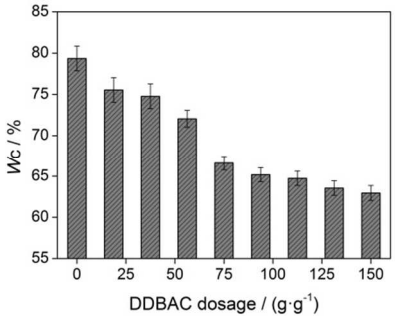

Fig. 1 W_C of dewatered sludge after DDBAC conditioning

The decreasing trend of W_C was due to the reduction of W_B. W_B was held firmly in the floc matrix, bound to the sludge or trapped between sludge particles and could not be removed by mechanical methods. It was considered to be the limit of mechanical dewatering. According to Colin and Gazbar [25], W_B could be used to directly measure the difficulty degree of mechanical dewatering. More bound water resulted in more difficult mechanical dewatering, whereas less bound water resulted in easier mechanical dewatering. The W_B under conditioning with surfactant DDBAC was presented in Fig. 2(a). Addition of DDBAC could significantly reduce W_B. When DDBAC dosage increased from 0 mg·g^{-1} to 75 mg·g^{-1}, W_B quickly decreased from 3.24 g·g^{-1} (g·g^{-1} indicated W_B of per gram dry sludge in sample, similarly hereinafter) to 1.64 g·g^{-1}, indicating a drop of 49.38%. When DDBAC dosage continuously increased, the decreasing trend of W_B slowed down. W_B and W_C were ramping down in a similar trend (Fig. 1 and Fig. 2(a)). These results indicated that the introducing of DDBAC was beneficial to releasing bound water from sludge, and then caused the decrease of W_C. Eventually, when DDBAC dosage was 150 mg·g^{-1}, W_B reduced to 1.36 g·g^{-1}, representing a 58.02% decline. These findings were in agreement with research reported by Wang *et al.*[26] who observed that surfactant released bound water from sludge effectively, due to its superior surface activity and strong adsorption/bridge capacities with sludge.

Approximately 42% of bound water in sludge could not be released. A reasonable explanation was that this part bound water combined with sludge flocs through a considerably strong chemically/physically bond, and was not easily influenced by DDBAC or released into the liquid phase.

Relative proportions of solid, bound and free water in dewatered sludge obviously changed after conditioning with DDBAC, as shown in Fig. 2(b). After conditioning with DDBAC, the proportion of bound water in sludge cake significantly decreases from 66.87% (unconditioned sludge cake) to 49.69% (DDBAC dosage was 150 mg·g^{-1}), and the proportion of solid increases from 20.64% to 36.58%. W_B was considered as a critical factor for the sludge dewatering performance. Surfactant DDBAC conditioning significantly did not only reduced W_B and W_C, but also increase total solid proportion in the dewatered sludge. The proportion of free water in the sludge cake slightly changed and remained between 11% and 13%, which indicated the presence of free water in the sludge cake. It's because mechanical strength in the dehydration process was not enough to remove the free water. The removal rate of free water by mechanical force depended on the mechanical dewatering device and had no correlation with sludge conditioning.

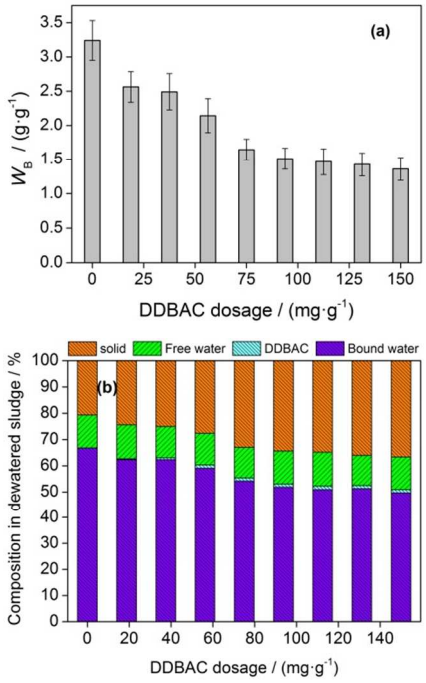

Fig. 2 W_B and composition distribution of dewatered sludge: (a) W_B; (b) composition in dewatered sludge

3.2. Effect of EPS on bound water under the surfactant DDBAC condition

3.2.1. Changes of EPS content and DDBAC adsorption amounts in sludge.

EPS was thought to be one of the most important factors affecting sludge dewaterability.[27-30] The EPS components protein and carbohydrate had a significant contribution to enhance the water binding ability of the sludge flocs.[6] Analyzing the change of each layer of EPS in sludge could help clarify the mechanism of bound water release under surfactant conditioning. The distribution and changes of protein and polysaccharide in sludge under surfactant DDBAC conditioning were shown in Fig. 3. Protein and polysaccharide in the original sludge were mainly distributed in the TB-EPS, accounting for 85.74% of total protein and 85.55% of total polysaccharide. In the LB-EPS, protein accounted for 4.03% and polysaccharide

4.12%. In the S-EPS, protein and polysaccharide accounted for 10.23% and 10.32%, respectively. In the original sludge, the distribution of protein and polysaccharide in every EPS layer was different. They were mainly distributed in the TB-EPS and were less distributed in both the LB-EPS and S-EPS. Wang[31] also have obtained similar results that more than 80% of the EPS was TB-EPS.

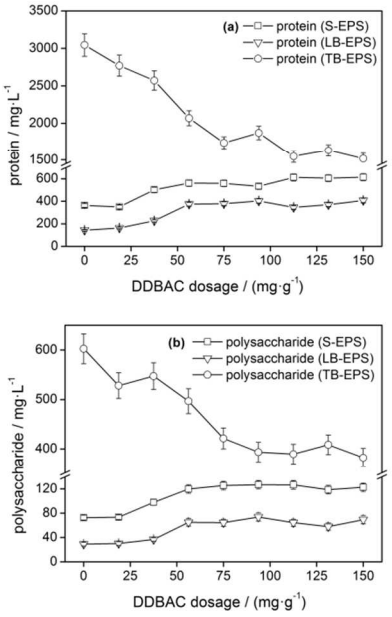

Fig. 3 Changes of EPS in sludge: (a) distributions and changes of protein in EPS layers; (b) distributions and changes of polysaccharide in EPS layers

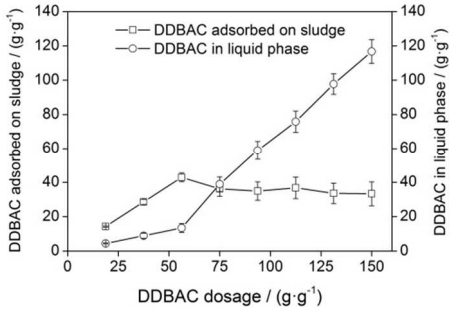

Fig. 4 Adsorption amounts of DDBAC in sludge

After conditioning with surfactant DDBAC, protein and polysaccharide contents in EPS layers obviously changed. These contents in TB-EPS were decreased by adding DDBAC. When the DDBAC dosage was 75 mg·g^{-1}, the contents of protein in TB-EPS drop to 1737 mg·L^{-1} when it was 3045 mg·L^{-1} beforehand, and polysaccharide from 602 mg·L^{-1}to 421 mg·L^{-1}, indicating a decrease of 42.96% and 30.07%, respectively. When the DDBAC dosage continued to increase, the decreasing rate of protein and polysaccharide contents in the TB-EPS slowed down. On the contrary, the introducing of DDBAC caused these contents to increase in LB-EPS and S-EPS. When the DDBAC dosage was 75 mg·g^{-1}, protein in LB-EPS increased from 143 mg·L^{-1} to 374 mg·L^{-1} and polysaccharide from 29 mg·L^{-1}to 65 mg·L^{-1}, indicating an increase of 161.54% and 124.14%, respectively. At the same time, the protein and polysaccharide contents in S-EPS increased from 363 mg·L^{-1} to 561 mg·L^{-1} and from 73 mg·L^{-1} to 120 mg·L^{-1}, indicating an increase of 54.55% and 64.38%, respectively. These results were in accordance with study of Chen *et al.*[16] and Yuan *et al.*[30], they observed that the EPS content of sludge supernatant (correspond to S-EPS) increased with the increasing surfactant. When the surfactant DDBAC dosage was more than 75 mg·g^{-1}, it had a less significant effect on protein and polysaccharide contents in the LB-EPS and S-EPS.

The surfactant DDBAC can help dispersing and dissolving. The binding effect of sludge flocs on the TB-EPS and LB-EPS will be weakened by adding surfactant. Therefore, parts of TB-EPS could turn into LB-EPS or S-EPS, and LB-EPS could turn into S-EPS. In the meanwhile, insoluble EPS (TB-EPS and LB-EPS), which had high hydrationability, can be turned into soluble EPS (S-EPS). Soluble EPS left the sludge flocs surface and easily entered the sludge liquid phase. Thus, bound water previously combined with EPS was released and turned to free water, and sludge dewatering performance could be improved. This process was in accordance with the decrease of TB-EPS content, increase of LB-EPS and S-EPS contents, and decline of W_B under DDBAC conditioning (Figs. 2 and 3). Similar conclusions were reached by S Kavitha [32] and Huang [43], whose researches indicated surfactant could not only dispersed sludge flocs efficiently, but also be beneficial to organic matters solubilization.

The adsorption amounts of DDBAC in sludge were illustrated by Fig. 4. The adsorption process between EPS and surfactant was influenced by both electrostatic effect and hydrophobic effect.[34] Under those two effects, EPS was desquamated from sludge flocs, and DDBAC got into the sludge liquid-phase with peeled LB-/TB-EPS. The adsorption amounts of DDBAC in sludge increased before decreasing. When DDBAC dosage was 56.25mg·g^{-1}, the maximum adsorption amounts of DDBAC could be obtained with 42.82 mg·g^{-1}, Then the adsorption amounts of DDBAC decreased to 36.13 mg·g^{-1} when DDBAC dosage increased to 75 mg·g^{-1}. With DDBAC dosage increasing continually, the DDBAC adsorption amounts plateaued, and the alterations of W_B and EPS became small indicating the conditioning effect of DDBAC on sludge weakened (Fig.2 and 3). Therefore, 75mg·g^{-1} was considered to be the optimal dosage of DDBAC.

3.2.2. Effect of EPS on W_B. The amount of EPS was positively correlated with bound water. The correlation between W_B and protein, as well as polysaccharide contents in EPS layers were presented in Fig. 5 and Table 2. Linear regression and Pearson correlation indicated that protein and polysaccharide contents in the S-EPS had significant negative correlation with W_B (R^2 = 0.7748, R = -0.880, P < 0.01; R^2 = 0.8193, R = -0.905, P < 0.01). Similarly, high negative correlation was observed between W_B and protein and polysaccharide contents in the LB-EPS (R^2 = 0.8310, R = -0.912, P < 0.01; R^2 = 0.7818, R = -0.884, P < 0.01). Compared with S-EPS and LB-EPS, the correlation which indicated positive (R = 0.976, P < 0.01 and R = 0.987, P < 0.01) between bound water and protein and polysaccharide contents in the TB-EPS was more significant (R^2 = 0.9745; R^2 = 0.9521). Similar results were also revealed by Jin *et al.*[6], W_B had a significant positive correlation with amount of protein and carbohydrate measured in the TB-EPS.

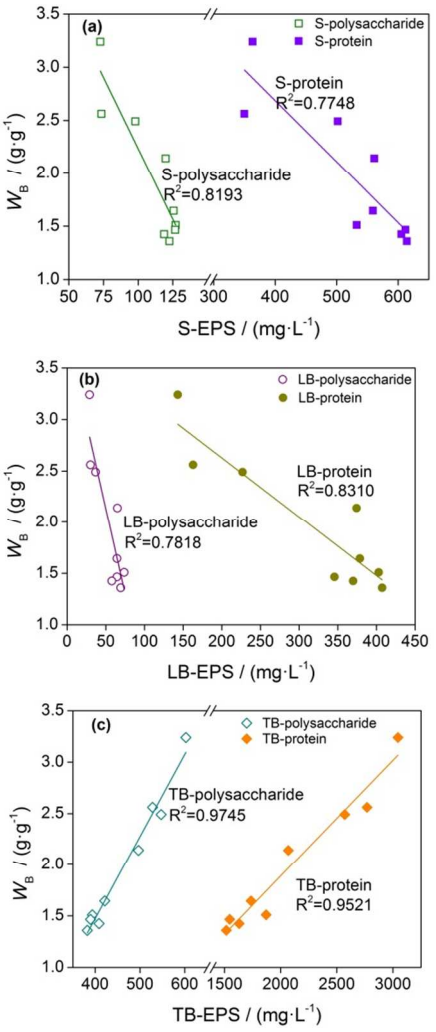

Fig. 5 Correlation between protein, polysaccharide contents in EPS layers and W_B: (a) Correlation between S-EPS and W_B; (b) Correlation between LB-EPS and W_B; (c) Correlation between TB-EPS and W_B.

Table 2 Pearson correlation coefficients between protein, polysaccharide contents in EPS layers and W_B

Composition	EPS layer	W_B	Composition	EPS layer	W_B
Protein	S-EPS	-0.880**	Polysaccharide	S-EPS	-0.905**
	LB-EPS	-0.912**		LB-EPS	-0.884**
	TB-EPS	0.976**		TB-EPS	0.987**

** P <0.01 (2-tailed)

Correlation analysis demonstrated that S-EPS, LB-EPS, and TB-EPS had strong correlations with bound water. The increment of protein and polysaccharide contents in the S-EPS and LB-EPS and their decrease in the TB-EPS could cause a drop of W_B. TB-EPS accounts for over 85% of total EPS in original sludge. The reduction of protein and polysaccharide contents in TB-EPS led to the increase of such contents in the LB-EPS and S-EPS under DDBAC conditioning (Fig. 3). Thus, it can be inferred that most of the bound water trapped in the TB-EPS and the TB-EPS content was the main factor that influenced W_B. These findings were similar to research reported by Dursun[35], who observed that EPS could result in fairly tenacious retention of water within the sludge. Song *et al.*[36] also draw the conclusion that high contents of EPS, especially insoluble EPS was responsible for the relatively higher W_B. Yuan *et al.*[30] who observed similar phenomenon that TB-EPS may be responsible for water retention of sludge and could highly influence sludge dewatering and drying.

3.3. Change of organic functional groups in S-EPS

The FTIR spectra of S-EPS extracted from sludge under conditioning with different DDBAC dosages were shown in Fig. 6. S-EPS in the original sludge exhibit several obvious absorption peaks at 3394 cm^{-1}, 2926 cm^{-1}, 1636 cm^{-1}, 1428 cm^{-1}, and 1108 cm^{-1}. Absorption maxima near 3340 cm^{-1} (H-bound OH in polysaccharides), 2950 cm^{-1} (aliphatic C-H stretching), 1600 cm^{-1} to 1660 cm^{-1} (C = O in amides, protein peptide bond), 1420 cm^{-1} (C = O in carboxyl groups), and 1090 cm^{-1} (C-O-C stretching of polysaccharides) had been reported in other studies.[37-39] In all the spectra we observed, the broad band at 3394 cm^{-1} confirmed the presence of abundant OH groups, which would indicate that S-EPS may contain polysaccharides.[39] Absorption band in the region of 2926 cm^{-1} corresponded to the stretching vibrations of aliphatic C-H bonds that show the existence of lipids. The presence of amides I was shown by strong absorbance at 1636 cm^{-1}, corresponded to protein in the S-EPS.[37] The weak absorption band at 1428 cm^{-1} indicated the existence of carboxyl because of the stretching vibration of C = O.[37] The strong absorption band at 1088 cm^{-1} was caused by the stretching of C-O-C, which demonstrated the existence of polysaccharide in S-EPS.[38]

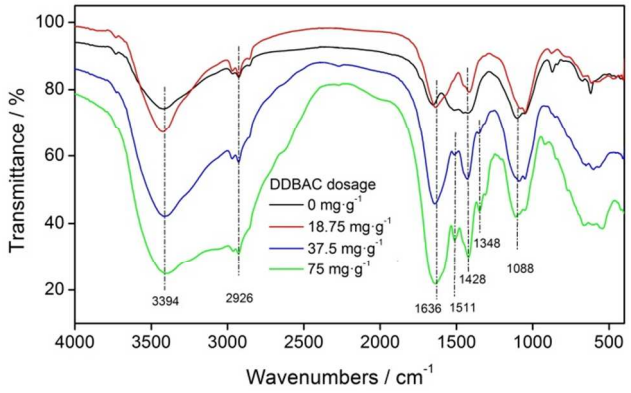

Fig. 6 FTIR spectra of S-EPS in sludge

Peak intensity at 3394 cm^{-1}, 1636 cm^{-1}, 1428 cm^{-1}, 1108 cm^{-1} enhanced significantly after DDBAC conditioning. The increase of amides and polysaccharides (at 3394 cm^{-1}, 1636 cm^{-1}, and 1108 cm^{-1}) indicated that a large amount of protein and polysaccharides turned from their insoluble state into dissolved one under DDBAC conditioning and could be found in sludge liquid phase. This observation was in accordance with the decrease of TB-EPS content and the increase of LB-EPS in earlier results. A significant enhancement in peak intensity at 1428 cm^{-1} indicated that the most possible reason of carboxyl increment was that the hydrolysis of TB-EPS and LB-EPS generated a certain amount of carboxylic acid, carboxylic acid salts, and other small molecular organics. When DDBAC dosage was more than 37.5 $mg \cdot g^{-1}$, two new adsorption bands were observed at 1511 cm^{-1} and 1348 cm^{-1}. According to the

previous studies, the absorption band at 1511 cm^{-1} was likely the consequence of the vibrations of amides II and/or of N-H bonds.[40, 41] It indicated that more new types of insoluble protein in TB-EPS and LB-EPS turned into dissolved one in S-EPS, and bound water get released in deep degree. A weak band was observed at 1348 cm^{-1}, which was related to C = O in carboxylic acid and H-bound OH in alcohols and phenols. And this finding indicated that EPS had been hydrolyzed in some degree.

3.4. Analysis of EPS hydrolysis under the conditioning of surfactant DDBAC

The liquid chromatogram of organics in the sludge supernatant was shown in Fig. 7(a), and the changes of short-chain fatty acids (formic acid, acetic acid, and propionic acid in this study) contents were reported in Fig. 7(b). The sequence of chromatography peak in reversed-phase high-performance liquid chromatography was relevant to molecular weight and polarity of the organics. Generally, the peak of organics that had small molecular weight and strong polarity appear earlier than those that have significant molecular weight, high polymerization degree, and strong polarity. Peak intensity was positively in accordance with the amount of organic content. In this study, retention time of formic acid, acetic acid, and propionic acid peak was 5.73 min, 8.73 min, and 18.32 min, respectively. According to previous studies, those organics that had retention times between 5 min and 22.5 min were small

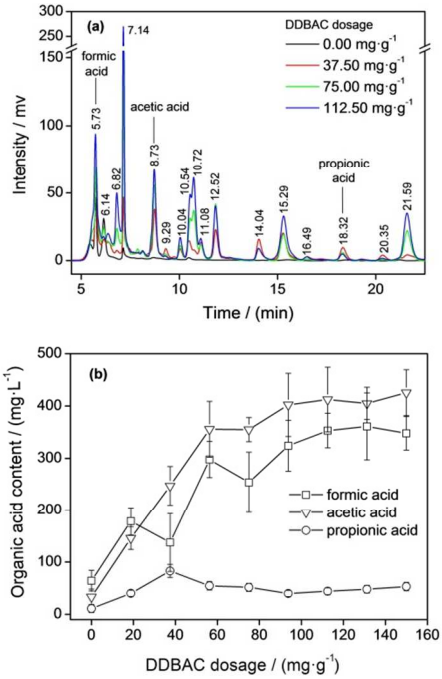

Fig. 7 EPS hydrolysis under the conditioning of DDBAC: (a) Liquid chromatogram of organics in sludge supernatant, (b) organic acid contents in sludge supernatant

molecular organics. In Fig. 7(a), the number and intensity of chromatographic peaks significantly increased after DDBAC conditioning, which demonstrated an increase in the species and contents of small molecular organics. Hydrolysis was demonstrated by short-chain fatty acids concentration in sludge supernatant. The three organic acids, particularly formic acid and acetic acid, significantly increased along with the increase of DDBAC dosages, which indicated that the DDBAC could improve the hydrolysis of organics in sludge (Fig. 7(b)). Luo *et al.*[42] observed that surfactants can be used for enhancing the hydrolysis of sludge hydrolysis, and make the short-chain fatty acids concentration increase. Furthermore, Huang *et al.*[33] pointed out the high surface activity of the surfactant may be the fundamental reason to the enhancement of organic matters solubilization and hydrolysis，which was beneficial to small molecular organics production. Chen *et al.*[43] raised another reason, he reported that surfactant caused protein structure change and benefited protein hydrolysis. Therefore, surfactant DDBAC was not only able to dissolve and desquamate the combined extracellular polymeric substance in sludge flocs, but also boost macromolecular organic compounds, such as protein and polysaccharide in EPS, hydrolyzing into small molecular organics, which had a beneficial effect on the release of bound water in sludge.

4 Conclusions

Surfactant DDBAC could effectively reduce W_B and improve the dewatering performance of sludge. When DDBAC dosage was 75 $mg \cdot g^{-1}$, W_B dropped from 3.24 $g \cdot g^{-1}$ to 1.64 $g \cdot g^{-1}$, a 49.38% decrease was observed. In the meantime, W_C decreased to 66.61%.

The binding effect of sludge flocs on TB-EPS and LB-EPS layers was weakened by adding DDBAC, which made the solubility of TB-/LB-EPS enhanced. Therefore, parts of TB-EPS turned into LB-EPS and S-EPS, and parts of LB-EPS turned into S-EPS.

The quantities of organic functional groups and small molecular organics increased obviously in sludge supernatant, which showed EPS was hydrolyzed by DDBAC as well.

The amount of TB-EPS was more than 85% in total EPS in sludge. Protein and polysaccharide contents in TB-EPS had significant positive correlation with W_B. TB-EPS were considered to be the main factor influencing W_B.

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Notes and references

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