

Effect of Chemical Conditioning of Sewage Sludge on Dewatering Performance and Structural Components

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Abstract: Chemical conditioning is a commonly used sewage sludge pretreatment method of dewatering in wastewater treatment plants. As a result of a large number of chemicals used, the cost of sewage treatment plants increased, and negative environmental impact might be happened. Therefore, it is necessary to illustrate the dewatering performance and structural components during chemical conditioning, in order to control the dosage of chemicals. In this paper, the excess sludge was treated by cationic polyacrylamide (CPAM). The physical and chemical properties of excess sludge were analyzed. The moisture content of sludge filter cake, the change of moisture distribution, the specific resistance of filtration, and capillary suction time (CST) of sludge were used as dewaterability parameters. The Zeta potential and particle size of sludge were measured, and the change of fractal dimension was analyzed. The changes of protein and polysaccharide content in extracellular polymeric substances (EPS) during conditioning were explored. Results showed that with the optimal CPAM dosage of 0.225 g/L, the moisture content of sludge cake reached 70.19 %, the specific resistance of sludge was 0.15×10^{12} m/kg, and CST was 6.45s. After conditioning, the Zeta negative electricity decreased, the particle size increased, the fractal dimension increased, and the contents of protein and polysaccharide in EPS increased. Tight EPS (TB-EPS) was released to loosen EPS (LB-EPS) and dissolved EPS (S-EPS), indicating that cationic polyacrylamide (CPAM) can effectively improve the dewatering performance of sludge.

1 INTRODUCTION

With the rapid development of urbanization and industrialization, the total amount of sewage discharge and the output of municipal sludge in China have increased significantly. The disposal and management of sewage sludge is urgent. High moisture content in excess sludge causes a huge volume, which is the mainbottleneck problem for effective disposal (Zhou et al., 2014). Dewatering was known as the most useful approach to improve the treatment and reuse of excess sludge. Conditioning is commonly used as pretreatment method to increase the sludge cake volume (Zhen et al., 2018). Among various conditioning methods, chemical coagulants such as ferric and aluminum salts and bioflocculant are the most commonly method to improve sludge dewatering performance in wastewater treatment plant, due to the easy operation (Guo et al., 2021). However, large number of chemical coagulants have great negative impact on

disposal equipment, and huge adding dosage also increases the operation cost of WWTP.

Compared with inorganic coagulants, organic polymer coagulants have the advantages of small consumption, safe treatment, simple operation, weak acidity or weak alkalinity in water and small corrosiveness in sludge conditioning. Cationic polyacrylamide (CPAM) is a typical and common organic polymer coagulant. CPAM conditioning greatly improved the dewatering performance of sludge (Wu et al., 2021). Guo et al (2020). found that CPAM was a chain polymer with a large number of positive charge groups, which is opposite to the charged property of surplus sludge and can play its electric neutralization role. Moreover, CPAM has high characteristic viscosity and strong adsorption and bridging effect on sludge particles.

EPS plays an important role in the water capacity of sludge, and a large amount of combined water in sludge is in EPS. (Guo et al., 2021). CPAM had a good promoting effect on proteins in EPS (Bi et al., 2015).

As an organic colloidal substance, CPAM was adsorbed on the outside of cells. The surface of activated sludge EPS was negatively charged, and CPAM combined with the negative functional groups on proteins to promote the secretion of proteins by cells.

Although a lot of research has been done on sludge dewatering and conditioning, it is difficult to further improve the sludge dewatering performance due to the lack of understanding of the structural component changes in sludge conditioning process. Therefore, it is necessary to illustrate the changes mechanisms of components and properties of sludge flocs, such as surface charge, particle size distribution fractal division.

Based on this, CAPM is used as conditioner to adjust the excess sludge to improve the sludge dewatering performance. The relationship between sludge structure and dewatering performance was studied by measuring the specific resistance of sludge, moisture content of sludge cake, capillary suction time and the change of sludge water transfer law and fractal dimension during conditioning. At the same time, in order to further explore the mechanism of CPAM on improving the dewatering performance

of excess sludge, Zeta potential and EPS component changes in excess sludge were measured and analyzed. The implementation of this study will contribute to the improvement of sludge dewatering and thus the management of wastewater treatment plants.

2 MATERIALS AND METHODS

2.1 Sources and Basic Properties of Experimental Sludge Samples

The sludge used in the experiment was taken from the surplus sludge of the second sedimentation tank of Xi'an No. 4 sewage treatment plant and stored in a refrigerator at 4°C after being retrieved. Table 1 shows the basic physical and chemical properties of the raw sludge in this experiment. At least three parallel samples were taken for each characteristic index, and it was found that there was no significant change in the characteristics of sludge sampled three times during the experiment.

Table 1: Basic physicochemical properties of raw sludge.

	moisture content %	organic matter %	Specific resistance of filtration $\times 10^{12}$ m/kg	CST s	Zeta potential of supernatant mV	Redox potential mV
L1	96.12	36.34	0.45	23.25	-18.93	-280.0
L2	96.07	36.30	0.49	23.21	-18.71	-280.3
L3	96.15	36.52	0.53	23.74	-19.14	-280.2

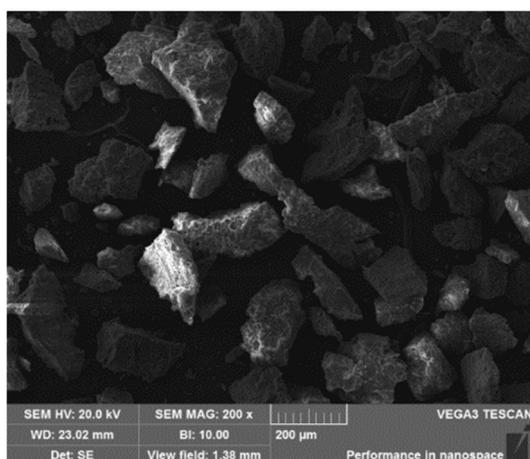
The scanning electron microscope was used to observe the raw sludge, as shown in Figure 1. The internal structure of the raw sludge is composed of granular and dense particles, and the surface is relatively smooth, complete and basically non-porous.

SEM can qualitatively describe the sludge floc structure. The effect of CPAM conditioning on the surface structure of sludge flocs was analyzed. Scanning electron microscopy (SEM) was used to observe the raw sludge and CPAM treated sludge. As shown in Figure 1, the internal structure of the raw sludge is composed of dense granular particles with smooth surface and complete block structure. After CPAM conditioning, the internal pore structure of sludge particles is more abundant, and it is easier for water to flow out, so the filtration performance is the best.

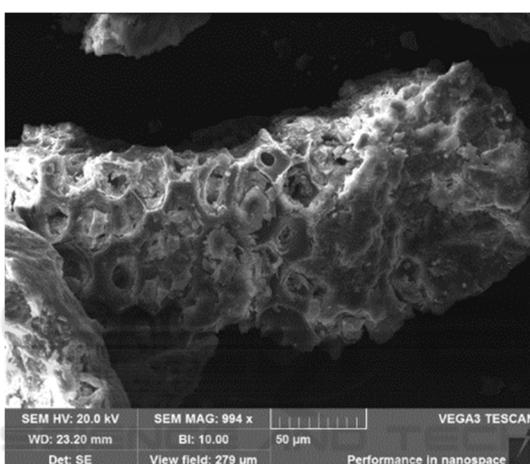
2.2 Main Instruments and Reagents

Six-axis mixer (JJ-4, Changzhou Zhiborui Instrument Manufacturing Co, LTD.); Uv-visible spectrophotometer (DR5000, Hach Company); Electronic Balance (CP213, Ohaus Instrument Co, LTD.); Specific resistance of filtration measuring device (TG-250, Shanghai Tongguang Science and Education Instrument Co, LTD.); Zeta potential Analyzer (ZS90, Malvern); Fluorescence spectrophotometer (F-7000, Hitachi); Laser particle size analyzer (BT-9300S, Dandong Baxter Instrument Co, LTD.).

Cationic polyacrylamide (CPAM), sodium hydroxide (NaOH), anthrone (C₁₄H₁₀O), concentrated sulfuric acid (H₂SO₄), Folin-phenol reagent, glucose and potassium dichromate (K₂Cr₂O₇) were analytically pure.



(a) Raw sludge 200 µm



(b) CPAM treated sludge 50µm

Figure 1: Caption to Scanning electron microscope (SEM) images of raw sludge.

2.3 Experimental Methods

Six 250 mL conical bottles were added to 100 mL of surplus sludge, and 0.0375, 0.075, 0.15, 0.225, 0.3, 0.375 g/L of 0.3% CPAM solution were added, respectively, stirring at 300 r/min for 5 min. After conditioning, the sludge dewatering index was determined; The composition and distribution of sludge EPS were analyzed. At least three groups of parallel samples were set up in each experiment.

2.4 Analysis Method of Experimental Indexes

In this experiment, 12 million CPAM was configured into 0.3% solution for determination, and the brinell funnel method was used to determine specific

resistance of filtration. The moisture content of sludge was determined by gravimetric method (Klomklao et al., 2017); The particle size distribution of sludge was determined by laser particle size analyzer (Zeng et al., 2019).

Modified Folin-Lowry method and anthrone-sulfuric acid method were used to determine the concentration changes of proteins and polysaccharides in EPS before and after sludge conditioning. Extraction of EPS from Sludge by NaOH method (Sun et al., 2017), and the residual cells and other substances in the extract were removed by 0.45µm filter membrane.

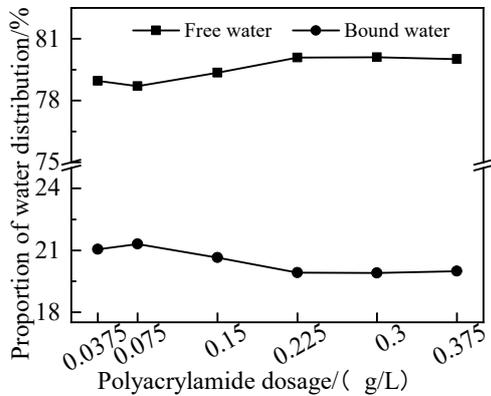
A fluorescence spectrophotometer (F-7000, Hitachi) was used to determine the three-dimensional fluorescence spectrum. The parameters were set as the excitation wavelength (Ex) was 240 ~ 550 nm, the emission wavelength (Em) was 260 ~ 600 nm, the step length was 4 nm, and the slit width was 3 nm.

3 RESULTS AND DISCUSSION

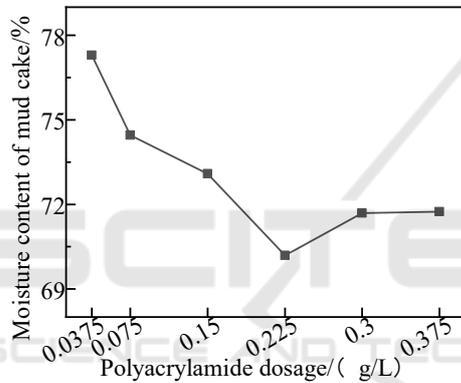
3.1 Effect of Cationic Polyacrylamide Conditioning on Sludge Dewatering Performance

The influence results of moisture content and moisture distribution of sludge cake under different dosage of CPAM are shown in Figure 2. As can be seen from Figure 2, with the increase of CPAM dosage, the moisture content of mud cake decreased first and then increased. When the dosage of CPAM was 0.225 g/L, the moisture content of mud cake reached the lowest value of 70.19%, and the reduction rate was 26.99%. With the increase of CPAM dosage, the proportion of free water in sludge firstly increased and then decreased, and reached the maximum value of 80.08% when CPAM dosage was 0.225 g/L. The change trend of bound water was just opposite to the change of free moisture content, which reached the minimum value of 19.92% when CPAM dosage was 0.225 g/L. The reason for this phenomenon may be that sludge particles become unstable under the action of electrical neutralization and aggregate into flocs, which gradually form larger flocs through the action of long chain bridge and net capture of flocculant, and then settle under the drive of gravity and external force (Wang et al., 2014). The low dosage of flocculant leads to the weak effect of electric neutralization, which is insufficient to make most of the suspended sludge particles accumulate and settle. Excessive flocculant will lead to electrostatic effect

and certain space between particles, which can restore the stability of sludge particles and fail to achieve the effect of flocculation and dehydration.



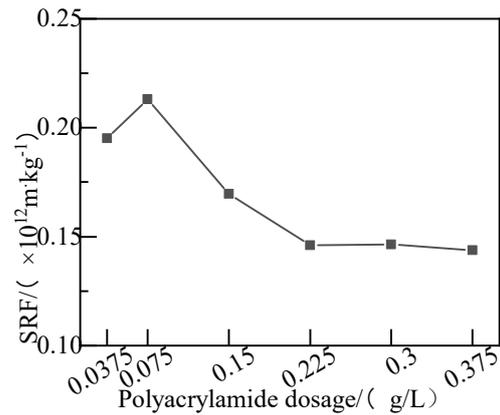
(a) Sludge moisture distribution



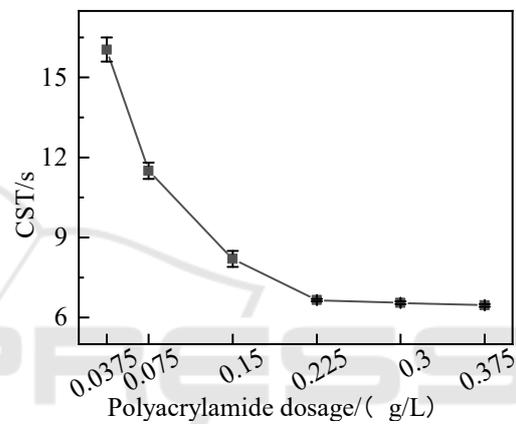
(b) Sludge moisture content

Figure 2: Caption to Effect of different CPAM dosage.

The changes of specific resistance and CST under different CPAM dosage were shown in Figure 3. With the increase of CPAM dosage, the specific resistance of sludge first increased, then gradually decreased to the minimum value and remained basically unchanged. When the CPAM dosage was 0.225 g/L, the specific resistance reached the minimum value of 0.15×10^{12} m/kg, and the reduction rate was 66.67%. With the increase of CPAM dosage, CST gradually decreased to the minimum value and remained basically unchanged. When the CPAM dosage was 0.225 g/L, CST reached the minimum value of 6.45 s, and the reduction rate was 72.26%. The sludge dewatering performance was significantly improved.



(a) Specific resistance of filtration



(b) Capillary suction time

Figure 3: Caption to Effect of different CPAM dosage.

3.2 Analysis of Sludge Zeta Potential, Particle Size and Fractal Dimension

The change of Zeta potential of sludge after CPAM conditioning was shown in Figure 4(a). With the increase of CPAM dosage, the Zeta potential increased first and then decreased, and reached the maximum value of -12.07 mV when CPAM dosage was 0.225 g/L. The Zeta potential determines the flocculation and sedimentation performance of colloidal particles, and the decrease Zeta potential negative electricity indicates that the dewatering performance of sludge has been improved (Hiroyuki, 2019).

It can be seen from Figure 4(b) that with the increase of CPAM dosage, the repulsion between sludge flocs decreases, and the particle size of sludge particles increases, which strengthens the adsorption bridging effect of sludge flocs (Dai et al., 2018). The fine sludge particles after conditioning firstly destabilise and aggregate through the effective

electroneutralization of CPAM, and then form large and dense sludge flocs under the action of net capture and sweep between long-chain polymer molecules with large specific surface area. The large and dense floc structure determines its excellent settlement performance.

The cumulative yield under the sieve under different CPAM dosages is shown in Table 2. The grain size-cumulative yield under the sieve is drawn in the log-log coordinate system, and its slope value B is obtained after fitting. The fractal dimension D of

sludge can be calculated according to the formula $D = 3 - b$, as shown in Table 3. Fractal dimension is a measure of fractal irregularity (Li et al., 2020). The higher the value of D, the more compact the flocs (Tang et al., 2020). As can be seen from Table 3, with the increase of CPAM dosage, the fractal dimension D also gradually increases, indicating that the sludge dewatering performance becomes better after CPAM conditioning.

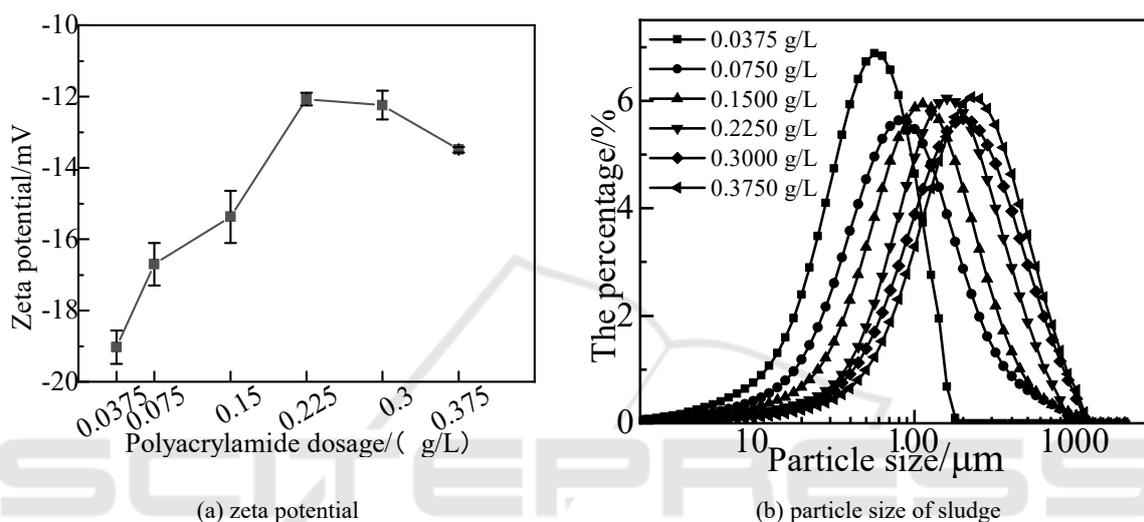


Figure 4: Caption to Effect of different CPAM dosage.

Table 2: Distribution of cumulative yield under screen at different CPAM dosages.

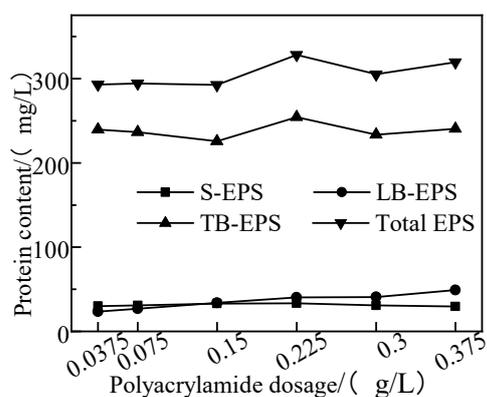
Particle size /μm	Cumulative yield under screen/%					
	CPAM dosing quantity g/L					
	0.0375	0.075	0.15	0.225	0.3	0.375
5	0	0.09	0.13	0.34	0.55	1.96
10	0.28	0.68	0.76	1.39	2.09	4.69
30	1.96	4.77	4.24	7.56	12.57	25.13
50	4.57	8.16	8.44	15.99	25.91	47.57
70	8.33	15.33	15.07	27.13	40.15	66.06
100	15.66	20.76	26.64	42.99	56.93	84.18
300	71.22	71.87	81.54	90.58	92.97	98.04
500	88.33	88.49	94.24	96.83	96.95	98.04
1000	100	99.96	99.87	99.66	99.45	98.04
2000	100	100	100	100	100	100

Table 3: Fractal dimension of sludge after CPAM conditioning.

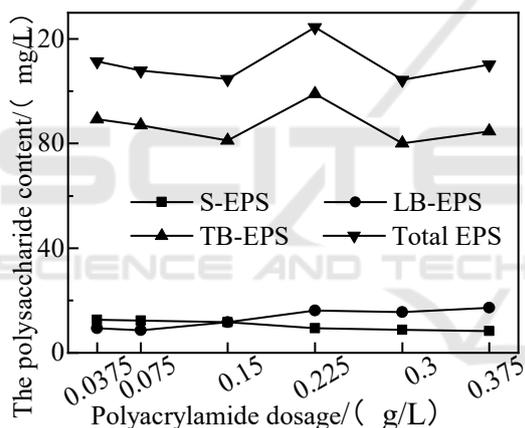
Fractal dimension	CPAM dosing quantity g/L					
	0.0375	0.075	0.15	0.225	0.3	0.375
b	1.14	1.13	1.11	0.94	0.84	0.63
D	1.86	1.87	1.89	2.06	2.16	2.37

3.3 Effect of Cationic Polyacrylamide Conditioning on the Structure Characterization of EPS

3.3.1 Effect of Conditioning Process on EPS Component and Content Change



(a) Distribution of protein when adding CPAM



(b) Distribution of polysaccharide when adding CPAM

Figure 5: Caption to effect of different CPAM dosage.

EPS is a highly hydrated biopolymer, which plays an important role in the stability of biological flocculation and the separation of solid and water (Salama et al., 2016). Proteins and polysaccharides account for about 70% ~ 80% of the total EPS (Zhang et al., 2021). The analysis of the changes in protein and polysaccharide contents of EPS layers in sludge helps to clarify the mechanism of sludge dewatering

performance. The changes of protein and polysaccharide contents in different sludge components under different CPAM dosages are shown in Figure 5.

Figure 5(a) shows the changes of protein content in different components of EPS. With the addition of CPAM, protein content concentration in total EPS increases. When the dosage of CPAM was increased from 0.0375 g/L to 0.15 g/L, the protein content in total EPS decreased gradually. When the dosage of CPAM was 0.15 g/L to 0.3 g/L, the protein content in total EPS increased first and then decreased, and reached the maximum value at 0.225 g/L. The change trend of protein content in TB-EPS was consistent with that in total EPS, and reached the maximum when CPAM dosage was 0.225 g/L. The protein content of S-EPS decreased slightly with the increase of CPAM dosage. The change trend of protein in LB-EPS was just opposite to that in S-EPS, which gradually increased with the increase of CPAM dosage. This indicates that the addition of CPAM transfers proteins in S-EPS layer to LB-EPS layer and TB-EPS layer, which changes the distribution pattern of proteins in sludge stratification, thus achieving the purpose of sludge particle flocculation and improving the dewatering performance of sludge (Tripathy et al., 2001).

It can be found from Figure 5(b) that when the dosage of CPAM increased from 0.0375 g/L to 0.15 g/L, the polysaccharide content in total EPS decreased slowly. When the dosage of CPAM was 0.15 g/L to 0.3 g/L, the polysaccharide content in total EPS increased first and then decreased, and the polysaccharide content reached the maximum at 0.225 g/L. The change trend of polysaccharides in LB-EPS was exactly opposite to that in S-EPS, and gradually increased with the increase of CPAM dosage. The change trend of polysaccharide content in TB-EPS was consistent with that in total EPS, and reached the maximum when the dosage of CPAM was 0.225 g/L. The results showed that after CPAM was added, the distribution pattern of polysaccharides in sludge stratification was changed by compressing the double layer and the principle of electrical neutralization. The polysaccharides in S-EPS were transferred to LB-EPS and TB-EPS, so that the sludge particles were flocculated (Zhang et al., 2017).

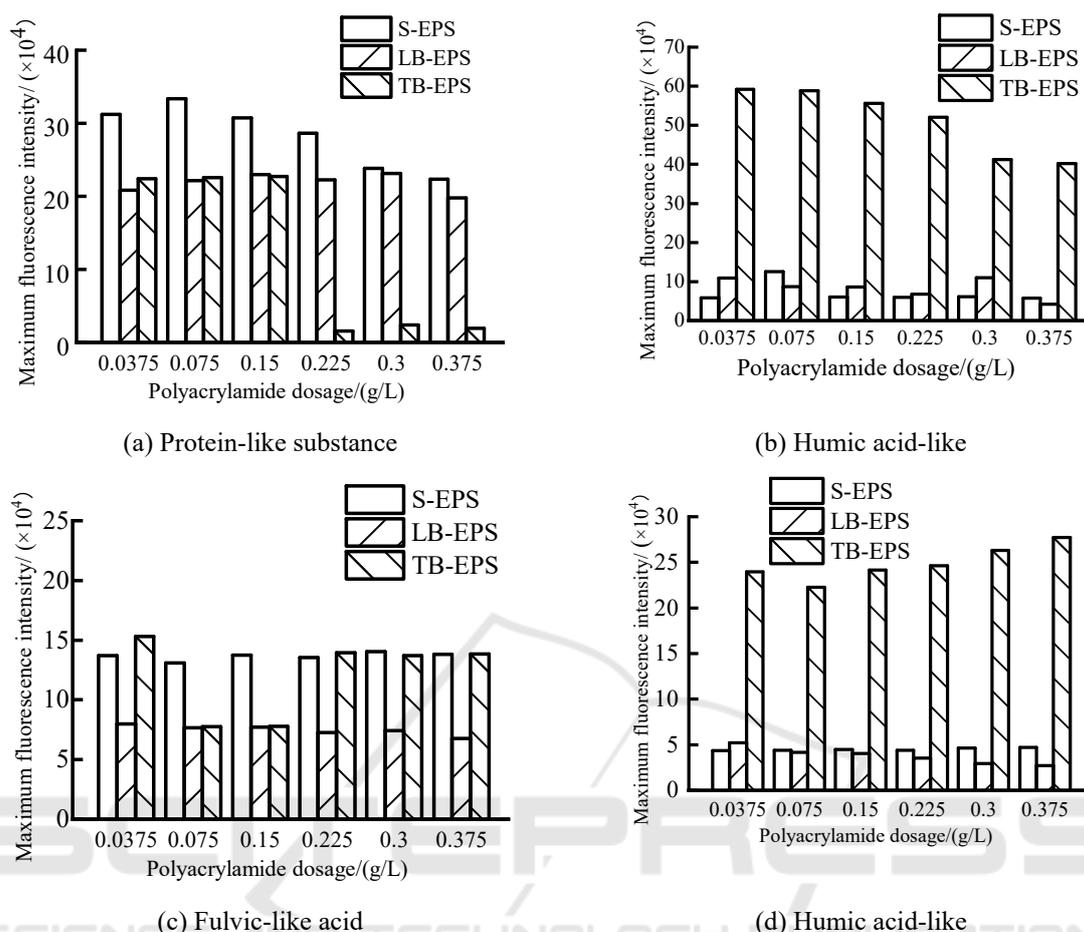


Figure 6: Effect of cationic polyacrylamide dosage on the distribution of maximum fluorescence intensity of different components: (a) Soluble microbial by-product-like; (b) Tyrosine protein; (c) Humic acid-like; (d) Humic acid-like.

3.3.2 Analysis of EPS Fluorescence Characteristics

Fluorescence spectroscopy is a sensitive method for the analysis of organic matter, which has been widely used in the analysis of organic matter in sludge EPS. To study the changes of fluorescent organic matter in sludge dewatering process treated by CPAM conditioning, three-dimensional fluorescence spectroscopy analysis of raw sludge and sludge after conditioning was carried out (Zhu et al., 2012).

Figure 6 is the distribution map of the maximum fluorescence intensity of EPS components under different CPAM dosage. From Figure 6(a), with the addition of CPAM, the protein-like substances in EPS gradually decreased, Zhang et al (2016) pointed out that the decrease of protein-like content is helpful for sludge dewatering. It can be seen from Figure 6(b) that with the addition of CPAM, the content of marine humic substances in LB-EPS and S-EPS changed

little, and the content in TB-EPS decreased gradually. It can be seen from Figure 6 (c) that the addition of CPAM had little effect on the fulvic-like acid content, and the fulvic-like acid content in EPS was basically unchanged. It can be seen from Figure 6(d) that the total amount of humic acids in sludge after CPAM conditioning increased, and the content of TB-EPS increased significantly. The content of LB-EPS decreased slightly, while the content of S-EPS remained basically unchanged. The increase in humic-like substance content indicates that organic substances in sludge form humic acid through polymerization, and charged substances are condensed into polymers, so that the charge on the surface of sludge is low, which is conducive to sludge dewatering. The increase in humic-like substance content in TB-EPS may be due to the release of substances wrapped by EPS in cell phase into EPS.

4 CONCLUSION

(1) The optimal dosage of CPAM was 0.225 g/L for the dewatering performance of excess sludge. Under these conditions, the moisture content of sludge filter cake was 70.19%, the specific resistance of sludge was $0.15 \times 10^{12} \text{m/kg}$, and the CST was 6.45s.

(2) After the conditioning of cationic polyacrylamide (CPAM), the sludge particle size increased, the fractal dimension increased, the sludge Zeta potential increased from -18.93 mV to -12.07mV, the electronegativity decreased.

(3) After CPAM conditioning of the surplus sludge, through the action of electrical neutralization and dehydration, colloidal particles are destabilized to form large flocs, which changes the distribution of proteins and polysaccharides in each layer of sludge, so that intracellular substances and TB-EPS are released into LB-EPS and S-EPS, so as to improve the performance of sludge dehydration.

(4) After conditioning, the protein-like concentration of S-EPS in surplus sludge EPS decreased, while the humic acid-like concentration of TB-EPS increased.

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