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Effect of a novel cationic surfactant on dewaterability of activated sludge

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ABSTRACT

The addition of the surfactant can greatly reduce the moisture content of the sludge. But little research has been done on the synthesis of surfactants and the mechanism of dehydration. Thus, a novel cationic surfactant ZWY-28 with higher surface activity and more surface charge was investigating for sludge dewatering in this research. Results showed that when the content of ZWY-28 was 1% (0.14 g/L), the specific resistance to the filtration of sludge had a minimum value of 2.04×10^{12} m/kg, the moisture content of the dehydrated sludge cake reached a minimum of 78.9%, the bound water reduced to 6.32 g/g, decreased by 39.2%. What's more, the ZWY-28 is extremely helpful in releasing Extracellular polymers substances from sludge, lead to the removal of bound water, which is the key point of affecting sludge dewatering. The study clearly illustrated that the surfactant ZWY-28 accelerated the dewatering process and could be used as a potential agent for sludge. Meanwhile, it provides ideas for the selection and structure design of surfactants in sludge dewatering.

Keywords: Cationic surfactant; Sludge dewatering; Extracellular polymers substances; Water binding; Sedimentation rate

1. Introduction

The wastewater treatment process not only brings a great deal of sludge but also costs a lot of manpower and resources [1–3]. At present, sludge dewatering is the most important treatment process of realizing the sludge reduction, harmless treatment, and reutilization [4,5]. Traditional filtration, centrifugation, and other mechanical methods are extensively used in sludge dewatering and sludge volume reduction due to relatively low energy consumption [6,7]. However, the abundant organisms in sludge may lead to extremely hydrophobic colloidal structure in sludge floc particles, which will make the dewatering special difficult [8]. There are four types of water in sludge: free water, pore water, adsorbed water, and bound water [9], which usually can be divided into free water and bound water by the quantitative method [10]. Free water will not be trapped by sludge floc and can be removed by concentration and mechanical separation. In opposite, bound water has a strong adhesive with sludge floc, and it is hard to remove by mechanical operation [11,12].

Extracellular polymers substances (EPS) is a sort of insoluble organics attaching in sludge bacterial surface, it is one of the three major components in sludge except for the bacteria and water [13]. EPS can form stable sludge floc structure by connecting with microorganisms and other substances [14], and bind water on sludge surface or inside of flocs [15–17], which is the main factor of influencing the sludge dewatering [18]. Proteins and polysaccharides are the main compositions of EPS, which account for 70%–80% in the total mass of EPS [19,20].

Pretreatment is the key step of sludge disposal, has a crucial impact on sludge dewatering, currently the main

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methods are as follows, the freezing-thawing, ultrasonic, chemical addition, and biological treatment [21,22]. Between those methods, chemical methods can conveniently and efficiently destroy polymer matrix, facilitate the release of EPS, and bound water in sludge [23–27]. The most of additives used in chemical addition methods are sulfate, polyelectrolyte, and surfactant [25]. Among them, surfactants can effectively decrease interface tension, thus can change microbial cell structure, then produce tremendous effects on EPS and bound water, ultimately improve the effect of sludge dewatering [26,27]. Present studies have shown that surfactants can be used as a dehydrating agent and extremely decrease moisture in sludge [28,29]. Chen et al. [28] have found that when the solution has a lower pH, the addition of cationic surfactant hexadecyltrimethylammonium bromide (CTAB) could release EPS from the sludge surface to the supernatant, so that makes the moisture content of sludge cake which after dehydration and filtration lower.

Currently, the commonly used surfactants are sodium dodecyl sulfate, CTAB, etc., studies on new synthesis surfactants are few. Fu et al. [30] studied on cationic Gemini surfactants, and just researched the effects of different lengths of carbon chain on sludge dewatering and sedimentation performance. García et al. [31] analyzed the influence of alkyl benzyl bonds in a series of alkyl trimethylammonium compounds on sludge. Actually, there is a wide range of surfactants and each one has its own special structure. If we learn more about the surfactant's effects on sludge dewatering, it cannot only increase the choice for sludge dewatering but also investigate the surfactant sludge dewatering mechanism more deeply. From previous research, the surfactants with oxyethylene groups are widely used in the pharmaceutical, cosmetic, coating, detergent, and leather industries [32,33]. Although there are some researches about surfactants with oxyethylene group have a completely opposite effect with the long-chain alkyl surfactants, no relevant studies focus on the surfactants with oxyethylene group which applied in sludge dewatering are reported.

In this research, novel cationic surfactant ZWY-28 ($[C_{18}H_{37}(CH_2CH_2O)_{20}OOCCH{=}CHCOOCH_2CH_2N(CH_3)_3]Cl$) with a lot of oxyethylene group CH_2CH_2O (EO) was adopted, and the urban sludge dewatering behavior of ZWY-28 was illustrated through studying on the surface of the sludge adsorption, surface tension, critical micellar concentration (CMC), surface charge, sludge specific resistance, EPS, combined water and heating value index. Moreover, on that basis, the mechanism of cationic surfactants on the urban sludge dewatering was further expounded.

2. Materials and methods

2.1. Materials

The municipal sewage sludge was taken from the sludge thickener of the sewage treatment plant in Taizhou City, China. After collected, the sludge was kept in polyethylene plastic buckets and preserved in a 4°C refrigerator. CTAB, 99% was purchased from Shanghai Macklin Biochemical Co. Ltd., (Shanghai, China). Cationic polyacrylamide (CPAM) was purchased from Aladdin Chemistry Co. Ltd., (Shanghai, China). The basic physicochemical properties of sludge were measured immediately after collection, shown in Table 1. In this experiment, the sludge was mixed with a six-jar-stir device, and a certain concentration of ZWY-28 was added to the sludge, to make its concentration in sludge was 0.5% (0.07 g/L), 1% (0.14 g/L), 1% (0.28 g/L), 4% (0.56 g/L), and 8% (1.12 g/L) respectively, then rapid mixing at the speed of 160 rpm for 30 s, after that turn the stirring speed to 50 rpm for 2 min, to make the surfactant thorough mixing with sludge. Each treatment carried with three parallel experiments.

2.1.1. Synthesis of surfactants ZWY-28

The synthesis route scheme of ZWY-28 is shown in Fig. S1 and the specific synthesis steps are as follows.

The procedure for the preparation of henicosaoxatriocta-cont-2-enoic acid (B). The solution of $C_{18}H37(CH_2CH_2O)_{20}OH$ (A, 58.70 g, 0.051 mol) and Maleic anhydride (4.90 g, 0.050 mol) were stirred in a melted state at 80oC for 1 h. Heptane (100 mL) was added to the reaction mixture and stirred for some minutes until form a homogeneous solution. The solution was left at room temperature for 3h, then at 15°C for 2 h, with mixing from time to time. The precipitate formed was collected and recrystallized from heptane (100 mL) in a similar way. White bright crystals of monododecyl maleate (50.01 g, 81.0%) were obtained.

Preparation of $[C_{18}H_{37}(CH_2CH_2O)_{20}OOCCH{=}CHCOOCH_2CH_2N(CH_3)_2]$ (C). The 2-dimethylaminoethanol (2.67 g, 0.03 mol) was added (drop by drop) into the solution of B (24.98 g, 0.02 mol), 4-dimethylaminopyridine (0.049 g, 20 mol%), triethylamine (6.06 g, 0.06 mol) and dichloromethane (100 mL). They were stirred at room temperature for 12h. Then, the solvent was removed off in a vacuum.

Preparation of $[C_{18}H_{37}(CH_2CH_2O)_{20}OOCCH{=}CHCOOCH_2CH_2N(CH_3)_3]Cl$ (D). The crude product of C (1 g) was dissolved in the solution of ethanol (5 mL). Then, the solution-processed in Schlenk-type glassware under CH_3Cl gas. The reaction mixture was kept at 30°C for 12 h, under magnetic stirring. Then, the solvent mixture was evaporated under reduced pressure, washed with heptane (10 mL × 3). The product was isolated as a yellow oil.

The synthetic ZWY-28 was characterized by ^1H NMR (^1H nuclear magnetic resonance spectroscopy) and ^{13}C NMR (^{13}C nuclear magnetic resonance spectroscopy) spectrum as shown in Fig. S2.

2.2. Characterization methods

2.2.1. Surface charge

The surface charge was measured by colloid titration [34]. Add 5 mL sample, 2 mL (3% w/w) poly (diallyl

Table 1
Basic physicochemical properties of the sludge

Parameters	Value
pH	7.24
Solid content, %	3.25
Organic matter content, %	46.6
SRF, m/kg	1.71×10^{13}
Zeta potential, mV	–20.8

dimethylammonium chloride) solution and 2 drops of 0.1% (w/v) toluidine blue in a 50 mL baker, then swing lightly to ensure uniform mixing. Afterward, add potassium salt of polyvinyl sulfate (0.0025 N) to inverse titration the mixture, until the color turns from blue to purple and keep 10 s. Then compare the sample's milliequivalent charge with pure water, conclude the surface charge of the sample.

2.2.2. Content of cationic surfactant

The disulfide blue method [35] was used to analyze the content of the cationic surfactant, the main principle of the measurement is that the cationic surfactant can form a soluble chloroform blue complex with the anionic dye disulfide blue, which can be measured through absorbance with a spectrophotometer.

2.2.3. Surface tension

The surface tension was determined by the Wilhelmy plate technique, using a Krüss K-12 tensiometer (Krüss GmbH, Germany) equipped with a sandblasted platinum plate at 25°C.

2.2.4. Zeta potential and particle size

The zeta potential and particle size of the surfactant treated sludge samples were determined using a nanoparticle analyzer (Zetasizer Nano-ZS, Malvern Instrument, England).

2.2.5. Sludge resistance

Take 50 mL sludge to determine the sludge resistance, according to the standard methods. A standard Buchner funnel test apparatus with a 7 cm Buchner funnel and Whatman No. 42 filter paper was used for the dewatering rate and the moisture content of dewatered sludge cake. The specific resistance to filtration (SRF, m/kg) was used to measure the sludge dewatering capacity. The activated sludge samples were filtered under a pressure of 0.6 MPa with a sample volume of 50 mL. Filtrates were collected and the volume was recorded as a function of time.

2.2.6. Water content

The sludge cake remaining from the filtration was collected to measure the water content of the dewatered sludge and the was dried at 105°C for 24 h and its dry weight was used to calculate the water content of the dewatered sludge as well as the dry solids base for bound water content. The water content of the dewatered sludge is calculated by the following formula:

$$\frac{\left(\omega_1 - \omega_2\right)}{\omega_1} \times 100\% \tag{1}$$

where ω_1 is the weight of the wet cake after filtration, ω_2 is the weight of the filtered sludge cake dried at 105°C for 3 h.

2.2.7. Bound water content

The combined water content was investigated by differential scanning calorimetry (DSC) [23]. The filtered and dehydrated sludge cake was placed in the DSC analyzer (NETZSCH, 404 F3 Pegasus, Germany), cooling to –30°C at a rate of 5°C/min, then heating to room temperature at the same rate. During the cooling phase, the sample releases heat and produces a significant exothermic peak. Correspondingly in the heating phase, the sample absorbs heat and forms a distinct endothermic peak. Since the combined water does not freeze into ice at minus 30°, the measured change in heat is free water. W_B is the difference between total water content and free water content. The formula is as follows:

$$W_B = \frac{\left(W_T - H / H_0\right)}{\left(W_s - W_r\right)} \tag{2}$$

where W_T is the total water content, H is the DSC enthalpy of the sample, W_s is the dry weight of sample sludge, W_r is the weight of the ZWY-28 adsorbed on the dewatering sludge, and H_0 is the standard fusion heat of ice, 334.7 J/g.

2.2.8. Sludge sedimentation index

The 1 L treated sludge was put into a 1 L measuring cylinder for sedimentation experiment. Observe and record the volume of the settled sludge every 5 min and settled for 30 min, to measure the effects of the pretreatment of ZWY-28 cationic surfactant and CTAB cationic surfactant on sludge sedimentation performance. The turbidity of the supernatant after 30 min of sedimentation was measured with a HACH 2100N turbidimeter, (Hach Company, America), and 30 mL of the supernatant was put into a turbidimeter sample cell, and the turbidity value was read in the signal average mode.

2.2.9. Extraction and determination of sludge EPS

The sludge was centrifuged at 15,000 × g, 4°C for 20 min, the supernatant was passed through a 0.45 μm filter, the EPS in the obtained filtrate was the total EPS in the sludge. Then used the anthrone-sulfuric acid method and Coomassie brilliant blue solution to determine polysaccharides and protein in the EPS [36].

2.2.10. Fourier-transform infrared spectroscopy study

Fourier-transform infrared spectroscopy (FTIR) were measured on a Nicolet 20XB FTIR spectrophotometer (USA) in the 500–4,000 cm^{-1} region. Samples were prepared by dispersing the sample in KBr and compressing the mixture to tables. All spectra were baseline corrected.

2.2.11. Scanning electron microscopy study

Before scanning electron microscopy (SEM) tests, the sludge samples were first chemically fixed, dehydrated using ethanol, dried with critical-point CO_2, and coated with gold. Gold-coated flocs were observed using SEM (Nano SEM 200).

3. Results and discussion

3.1. Infrared spectrum of surfactant

Fig. 1 is the FTIR spectra and the chemical structure of ZWY-28. From the IR spectra, we can obviously see the

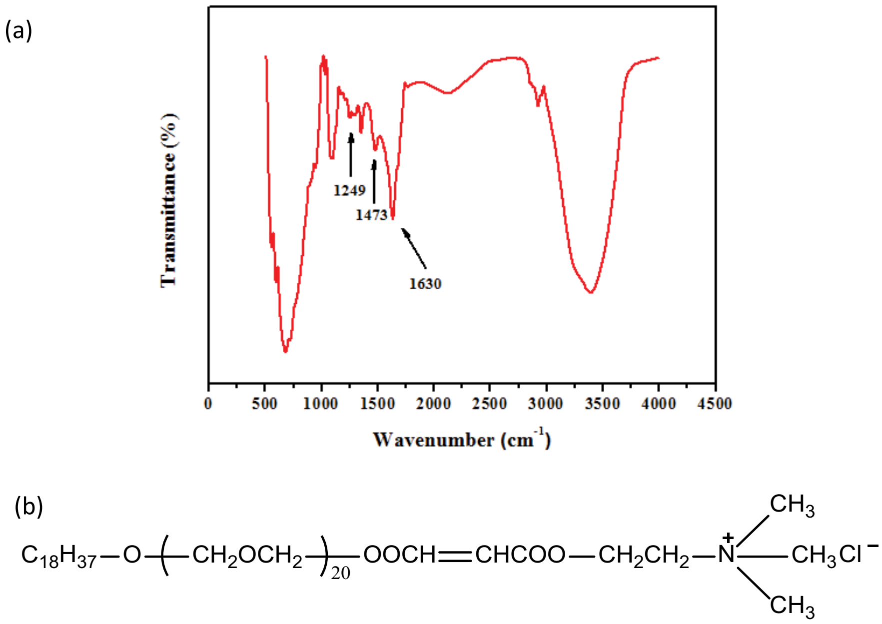

Fig. 1. (a) FTIR spectra of ZWY-28 and (b) chemical structure of ZWY-28.

characteristic absorption peaks of C–O–C at 1,249 cm^{-1}, C=C at 1,630 cm^{-1}, $–CH_2–N^+$ at 1,473 cm^{-1}. This result is consistent with the chemical structure of ZWY-28.

3.2. CMC value of the surfactant

The CMC value is a measure of surfactant activity and surface charge density. The surfactant with higher activity will be more favorable to combine with the sludge surface to promote the sludge disintegration and release EPS. Moreover, more surface charge is beneficial to neutralize the charge on the sludge surface and reduces the repellency force, thus increase the flocculation intensity effectively. Du Noüy ring can be used to test the CMC value of the surfactant at 25°C. The CMC is obtained by calculating the inflection point of the balanced surface tension curve. Fig. 2 shows the corresponding relationship between surface tension and the concentration of ZWY-28 at 25°C. It can be seen, the content of surfactant increase, surface tension decrease. When the concentration is more than 0.01 moL/L, as the concentration of surfactant increases, surface tension decreases slowly. It is a common phenomenon as surfactants containing a certain amount of free fatty alcohol at the liquid/air interface. The CMC of ZWY-28 at 25°C is $(6 \pm 0.5) \times 10^{-3}$mol/L by calculation. It is lower than reported dodecyl trimethyl ammonium bromide (15×10^{-3} mol/L) and ethanediyl-1,2-bis (propyl dimethylammonium bromide) $(4.5 \pm 0.5) \times 10^{-2}$ mol/L). The lower CMC of ZWY-28 indicates higher surface activity and more surface charge, which is propitious to sludge dewatering.

3.3. Surfactant effects on sludge dewatering performance and moisture content of dehydrated sludge cake

The effect of surfactant on sludge dewatering performance is shown in Fig. 3. When surfactant ZWY-28 mass

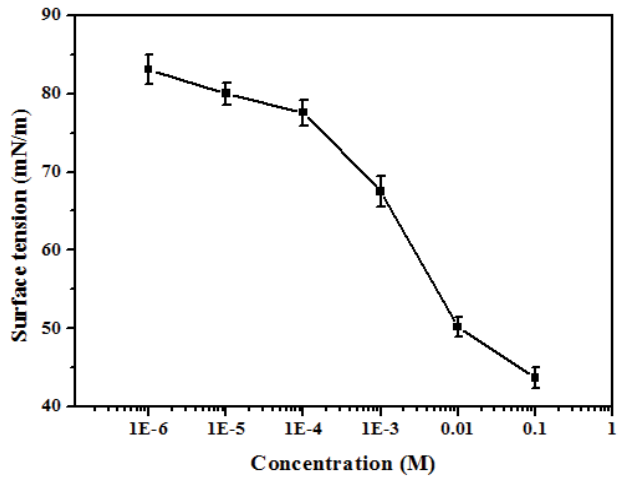

Fig. 2. Plots of surface tension vs. molar concentration for ZWY-28 in the water at 25°C.

fraction increases to 0.5%, the SRF of sludge can be reduced to 3.58×10^{12} m/kg from the original 1.34×10^{13} m/kg, the sludge SRF decreased by 73.3%. This result indicated that the dewatering capacity of sludge was significantly enhanced. With the addition of ZWY-28 increases, the sludge SRF continuously decreases. When the addition of ZWY-28 was 1%, the sludge SRF had a minimum value of 2.04×10^{12} m/kg. After that, the addition of surfactant increases will result in a sludge SRF worsening. It shows excessive surfactant may deteriorate the dewatering performance of sludge.

The addition of surfactant ZWY-28 can not only improve the sludge dewatering rate but also increase sludge dewatering extent. Fig. 4 shows that the effect of ZWY-28 on the moisture content of the filtered and dehydrated sludge cake. When ZWY-28 mass fraction was 0.5%, the moisture content

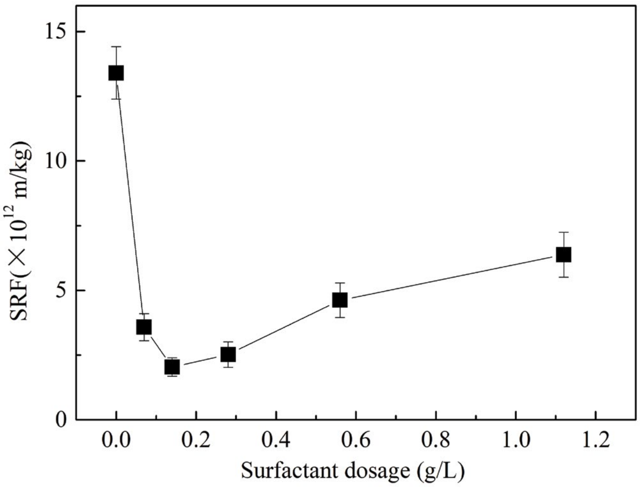

Fig. 3. Effect of adding ZWY-28 on specific resistance to filtration (SRF) of sludge.

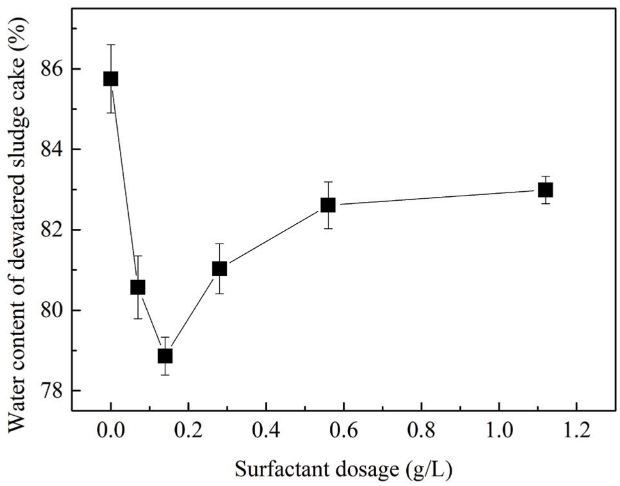

Fig. 4. Effect of adding ZWY-28 on the water content of dewatered sludge cake.

of the dehydrated sludge cake decreased from the original 85.7% to 80.6%. As the surfactant mass fraction increased to 1%, the moisture content of the dehydrated sludge cake reached a minimum of 78.9%. Then with the increase of surfactant concentration, the sludge cake moisture changing trend was slowly. This result can be explained by that the removal rate of free water by mechanical force relays on the mechanical dewatering device, and has no relationship with sludge condition. More bound water, the mechanical dewatering more difficult, and less bound water, easier of mechanical dewatering. When the bound water firmly fixed in the sludge matrix, combined with EPS, or trapped by sludge floc, can't be removed by the mechanical method is considered to be the limit of mechanical dewatering [37]. Surfactant is able to damage the EPS matrix and has a significant effect on the water-binding capacity of activated sludge, thus can remove more bound water [38,39]. In Fig. 5, it is clearly shown the bound water content of dewatered sludge cake is decreasing with the increase of the dosage of the synthetic cationic

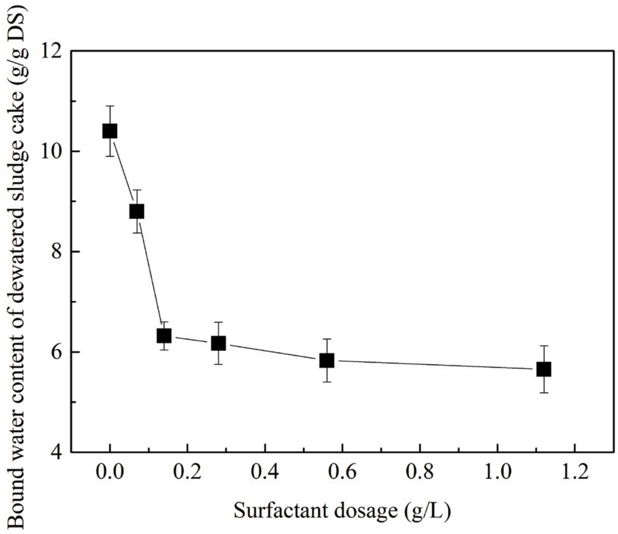

Fig. 5. Effect of adding ZWY-28 on the bound water content of dewatered sludge cake.

surfactants. After treated by surfactant ZWY-28 with mass fraction 0.5%, the bound water content of dehydrated sludge cake dropped from 10.4 g/g DS to 8.80 g/g DS. As the addition was 1%, the bound water reduced to 6.32 g/g, decreased by 39.2%. Although the continuous addition of ZWY-28 can further reduce bound water content in the dehydrated sludge cake, the reduction effect is not significant. Those results show that the cationic surfactant of ZWY-28 is helpful to lower the bound water content and facilitates further dewatering of sludge. Wang et al. [36] observed that surfactants have excellent surface activity, which can form strong adsorption/bridge force with sludge, making it effective to release bound water from sludge. The remaining bound water in the sludge cannot be released, mainly because the chemical/physical binding of the bound water is strong and is not effectively released through the surfactant ZWY-28 [37]. These results indicate that the cationic surfactant ZWY-28 has great use in reducing the moisture content of SRF and filter dehydrated sludge cake.

3.4. *Effects of surfactants on sludge settling properties*

The effect of ZWY-28 on sludge settling performance is shown in Fig. 6. From which we can see that without surfactants, after an hour, the sedimentation volume of the sludge decreased from 100% to 94.8%, which was only 5.2%. But once the surfactant of ZWY-28 is added, the sedimentation performance of the sludge will be greatly improved. And with the surfactant ZWY-28 mass fraction gradually increases from 0% to 1%, the sedimentation volume of sludge increases, when the mass fraction was 1%, the sedimentation volume of the sludge was 14.6%, more than 5.2% that without surfactant, the sedimentation performance of activated sludge was obviously promoted. As we can see, the addition of 2% mass fraction ZWY-28 and the addition of 1% mass fraction ZWY-28 made not much difference in the sedimentation volume of sludge. However, when the addition amount of ZWY-28 continued to increase

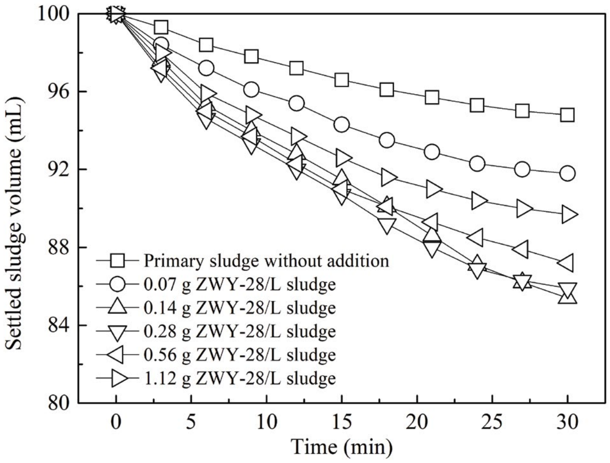

Fig. 6. Effect of adding ZWY-28 on sludge settling performance.

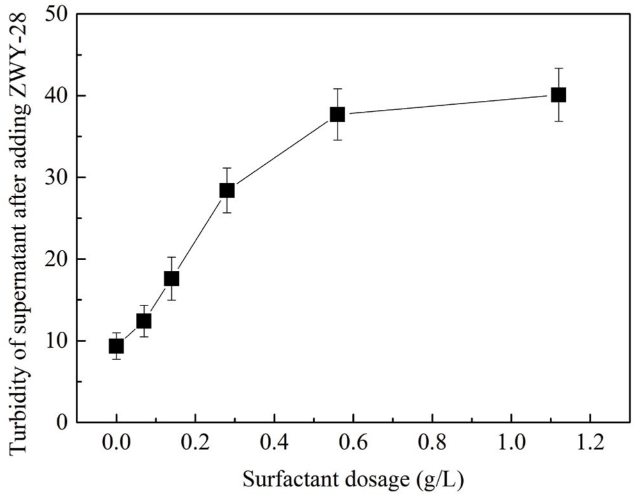

Fig. 7. Effect of adding ZWY-28 on the turbidity of supernatant.

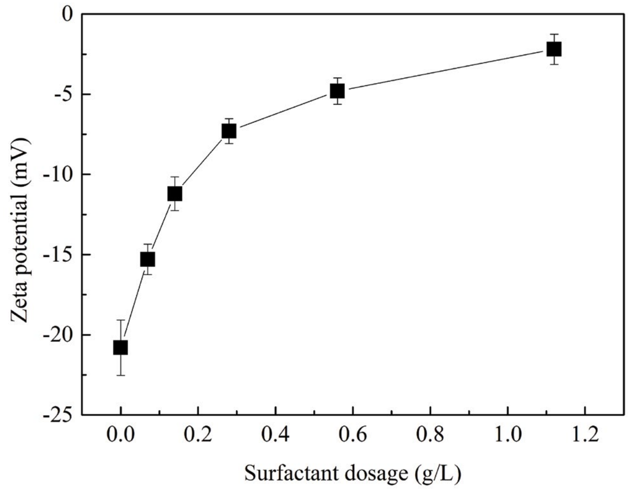

Fig. 8. Effect of adding ZWY-28 on zeta potential of sludge.

to 4% and 8%, the sedimentation rate in the early stage was still fast, but the final sedimentation effect deteriorated. ZWY-28 is a cationic surfactant that neutralizes the electronegativity of sludge and makes the sludge unstable. The sludge particles are more likely to aggregate to form sludge flocs, which improves the sedimentation performance of the sludge flocs. However, the excess surfactant causes the sludge particles to be positively charged, causing a repulsive force between the sludge particles to be re-stabilized. At the same time, the excessive surfactant makes the sludge particles decompose more seriously, destroying the stability of the sludge particles, and goes against sludge settling. The effect of surfactant on the turbidity of sludge supernatant also testified this conclusion (Fig. 7). As the concentration of surfactant ZWY-28 increases, the turbidity of the supernatant first rises rapidly, from 9.35 NTU without addition to 28.4 NTU with 2% addition, then slowly rises, and finally reaches 40.1 NTU of 8% addition. The result shows that when the added surfactant ZWY-28 mass fraction is less than 2%, there was linear dependence between the amount of surfactant added and supernatant turbidity, and the sludge settling performance is gradually strengthened.

3.5. Mechanism of surfactant improving sludge dewatering performance

The charge that exists on the surfactant surface has some effect on sludge sedimentation and condensation [26,40]. Fig. 8 shows that with the concentration of surfactant increases, the negative electricity on the surface of sludge decreases. The result indicates that the surfactant ZWY-28 can neutralize the negative charge on the surface of sludge. As we know, the charge on the surface of sludge may produce influences on sludge dispersion, thus has a significant effect on sludge dewatering [41]. Its main principle is that reduce the negative charge on the surface of sludge is able to lower the repulsive force, enhance the sludge condensation, and improve the sludge dewatering capacity [8]. Although the addition of a high concentration of surfactant can further reduce the negative charge of sludge, it deteriorates sludge dewatering performance. Therefore, except for the charge of the sludge, there are other reasons that affect the sludge dewatering performance.

Fig. 9 indicates that the change of sludge particle size with different concentration of cationic surfactant ZWY-28. Before the addition of surfactant ZWY-28, the average sludge particle size is 21 μm. After adding ZWY-28, the sludge sample's average particle size remarkable reaches 200 μm. With the concentration of the cationic surfactant ZWY-28 continues to increase, the particle size of the sludge sample gently rises. The change of sludge particle size is connected with the surface charge, as the concentration of the charge reduces, small sludge particles tend to aggregate into large particles, thus decrease the specific surface of sludge flocs (Table 1). There are some studies indicate that super colloid particles (1~100 μm) have the greatest influence on dehydration. The proportion of supercolloid particles higher, the sludge dewatering worsen [42]. The primary reason is that for sludge with small particle size, the resistance of the filter cake is very high, and some fine particles can easily block the pores so that the dewatering effect is greatly reduced. It can

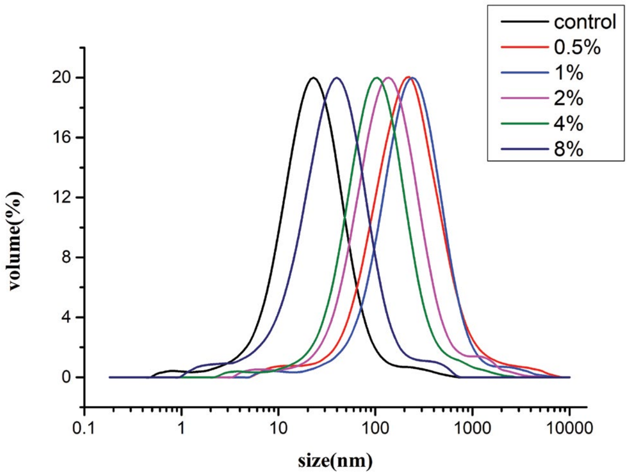

Fig. 9. Effect of adding ZWY-28 on the particle size of sludge floc.

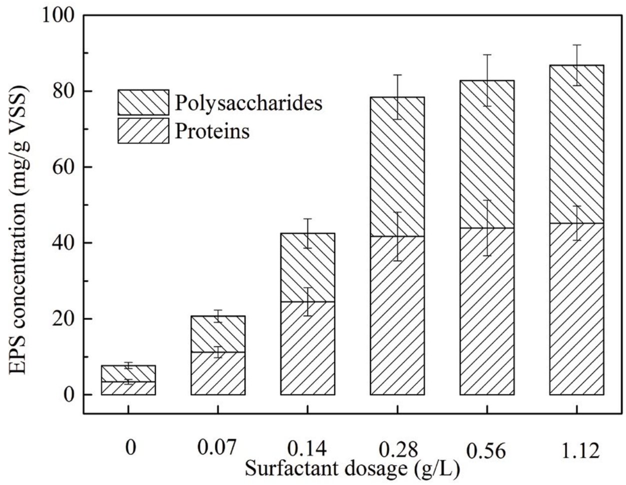

Fig. 11. Effect of adding ZWY-28 on EPS of sludge (polysaccharide and protein).

be observed from the SEM image (Fig. 10) that without surfactant, the internal structure of the activated sludge floc is small and dense, which is not favorable to activated sludge dewatering [43]. When ZWY-28 is used, due to the electrostatic interaction between ZWY-28 and the sludge floc, the reintegration structure of sludge flocs large and loose. From the particle size and SEM test results, the addition of surfactant ZWY-28 contributes to reducing the proportion of supercolloids in sludge floc, which helps to improve sludge dewatering performance.

In the activated sludge, EPS can account for more than 90% of the total mass, which is the key factor affecting the sludge dewatering properties [44]. The content protein and carbohydrate polysaccharide of EPS have significant contributions to improving the water-binding capacity of sludge floc [41,45–47]. Therefore, analysis of the content change of protein and polysaccharide in EPS is conducive to clarify the mechanism of the release of sludge bound water under the condition of surfactant ZWY-28. The effect of surfactant ZWY-28 on the release of protein and polysaccharides shown in Fig. 11. Compared with without surfactant, the addition of ZWY-28 leads to the obvious content changes of protein and polysaccharide in EPS of the supernatant, and the change is related to the dose. With the ZWY dosage increases from 0.5 wt.% to 8 wt.%, the release of protein in EPS increases from 9.5 to 41.6 mg/g VSS (VSS – volatile suspended solid), polysaccharide increases from 11.2 to 45.2 mg/g VSS. Those results are consistent with the studies of Chen et al. [29] and Yuan et al. [45], which also observed the content of EPS in sludge supernatant increased with the increase of surfactant. When the addition of ZWY-28 more than 2 wt.%, the release rate of EPS in sludge cut down. The polysaccharide in EPS is highly hydrated, which makes difficulties in sludge dewatering [16,44]. Moreover, in various components of EPS, protein has the greatest capacity to bind to water [11,26]. The release of EPS, especially protein is extremely important. The novel surfactant ZWY-28 has a positive charge which can easily adsorb on the negative charge sludge surface and the EPS surface. The long-chain alkyl groups have a barrier effect, making the sludge floc separate. At the same time, a large number of polar oxyethylene groups make surfactants readily interact with the proteins and carbohydrate polysaccharide in EPS, lead to the release of EPS [44]. Accordingly, with the addition of surfactant, sludge floc is separated, the binding effect of sludge floc on EPS is weakened, thus makes EPS turn to soluble EPS as illustrated in Fig. 12. The soluble EPS leaves

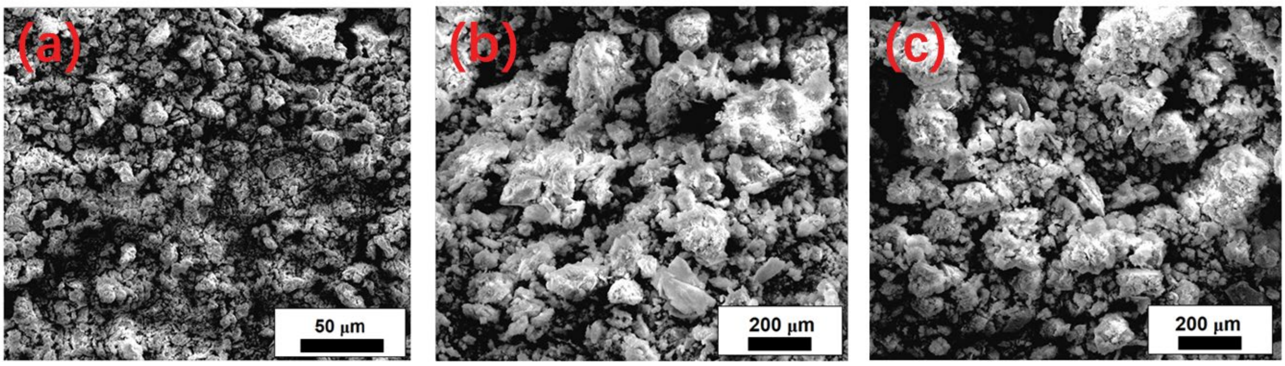

Fig. 10. SEM image of sludge particles after adding different content of ZWY-28, (a) 0%, (b) 1%, and (c) 2%.

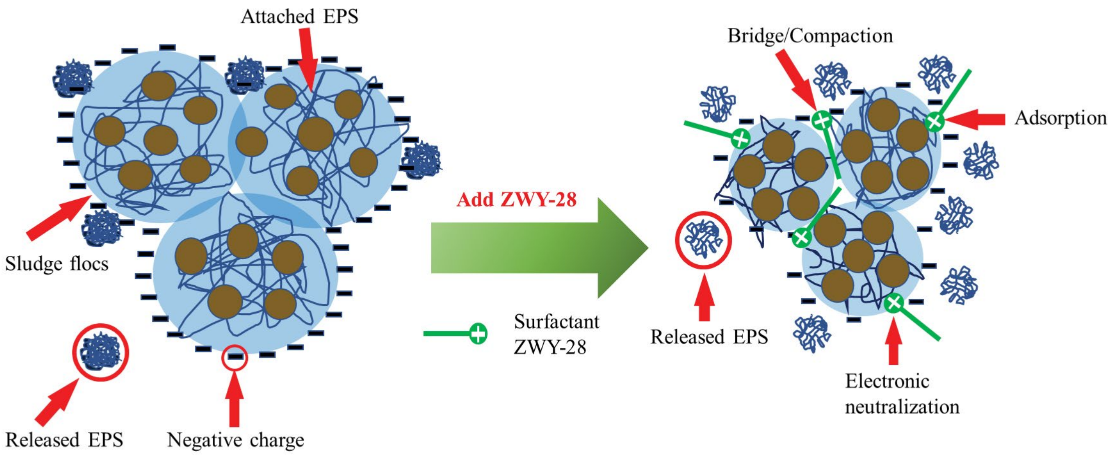

Fig. 12. Picture of the interaction mechanism between EPS and surfactant ZWY-28.

from the surface of sludge floc, eventually, enter into the sludge supernatant [37]. Therefore, the surfactant ZWY-28 is helpful to the dispersion and dissolution of the EPS in activated sludge. The release of EPS in sludge will result in the decrease of adhesion force of sludge floc, and the adhesion of EPS plays a crucial role in the sludge sedimentation and dewatering, which has been proved by other studies [12,41].

The method of EPS extraction and determination refers to Kawamura et al. [34]. The effect of surfactant ZWY-28 on the EPS of different layers of sludge is shown in Fig. 13. The EPS of the sample sludge is mainly concentrated in (TB – tightly bound) TB-EPS, accounting for 85.9% of the total EPS. Slime-EPS and (LB – loosely bound) LB-EPS only accounted for 9.1% and 5.0% of the total EPS, respectively. The results are similar to those of Wang et al. [48] (more than 80% of the EPS in the sample sludge is mainly concentrated in TB-EPS). After adding the surfactant ZWY-28 to the sample sludge, the polysaccharide and protein content in the EPS of different layers changed significantly, and the TB-EPS content began to decrease. When the surfactant was added at 1%, the polysaccharide and protein content in TB-EPS decreased sharply to 15.4 and 16.2 mg/L, respectively, which were 25.2% and 37.0% lower than the initial ones. In contrast, both the polysaccharide and protein content of slime-EPS and LB-EPS increased. The polysaccharide and protein content in slime-EPS increased rapidly to 8.3 and 11.1 mg/L, which were 3.2 times and 4.8 times their initial values, respectively. The results are consistent with the results of Wang et al. [48] and Hong et al. [37]. They both observed that the EPS (i.e., slime-EPS) content in the sludge supernatant increased with the increase of the surfactant dose. Although the content of polysaccharides and proteins in LB-EPS increased, the rate was not as good as slime-EPS. Surfactants have the characteristics of dispersing and dissolving, which can weaken the adsorption of sludge particles on TB-EPS and LB-EPS, make TB-EPS easily convert to slime-EPS and LB-EPS, and make LB-EPS easy to convert slime-EPS. Surfactants make the release of EPS in the inner layer of sludge particles into outer EPS, which makes it easier to remove EPS. At the same time, the release of sludge combined with water turns into free water and is easy to remove. When the surfactant dosage exceeds 1%, although the TB-EPS content is still decreasing, and the slime-EPS and B-EPS content are still increasing, the rate of change becomes slower. The effect of surfactant ZWY-28 on EPS of sludge began to weaken.

3.6. Effect of pH, temperature and other surfactants on sludge dehydration

Firstly, adjusting the original sludge's pH value to 3, 5, 7, 9, and 11 respectively by using dilute sulfuric acid and sodium hydroxide solution. Secondly, adding 1% ZWY-28 into the sludge. Thirdly, stirring the sludge as 160 rpm 30 s and 50 rpm 2 min, Finally, measuring the specific resistance of sludge. The influence of surfactant ZWY-28 on the dewatering performance of sludge with different initial pH value is elaborated in Fig. 14. When the initial pH value of the sludge is 5 and 7, the sludge dewatering performance will be optimal after adding ZWY-28, which is 1.89×10^{12} m/kg and 2.04×10^{12} m/kg respectively, the performance results are not significantly different under two pH scenarios. Both too high and too low initial sludge pH value will degrade the sludge dewatering performance. This is because excessive acid and alkali will make the sludge particles to be decomposed excessively, the surfactant will further decompose the sludge particles which will result in deterioration of sludge dewatering performance. In conclusion, adjusting the initial pH value of the sludge is not mandatory for the municipal sludge treatment by using surfactant ZWY-28.

Four sample sludges are heated to 15°C, 20°C, 25°C, and 30°C, respectively, and then 1% of ZWY-28 is added into the four samples. The next step is to mix each sample at the speed of 160 rpm for 30 s, after that turn the stirring speed to 50 rpm for 2 min. After that, measures each sample sludge's specific resistance. The effect of adding 1% surfactant ZWY-28 at different treatment temperatures on sludge dewatering performance is shown in Fig. 15. At different treatment temperatures, the addition of a 1% surfactant can reduce the specific resistance of sludge to $1.95 \sim 2.16 \times 10^{12}$ m/kg. There were no significant differences in the specific resistance of the sludge at 4 different

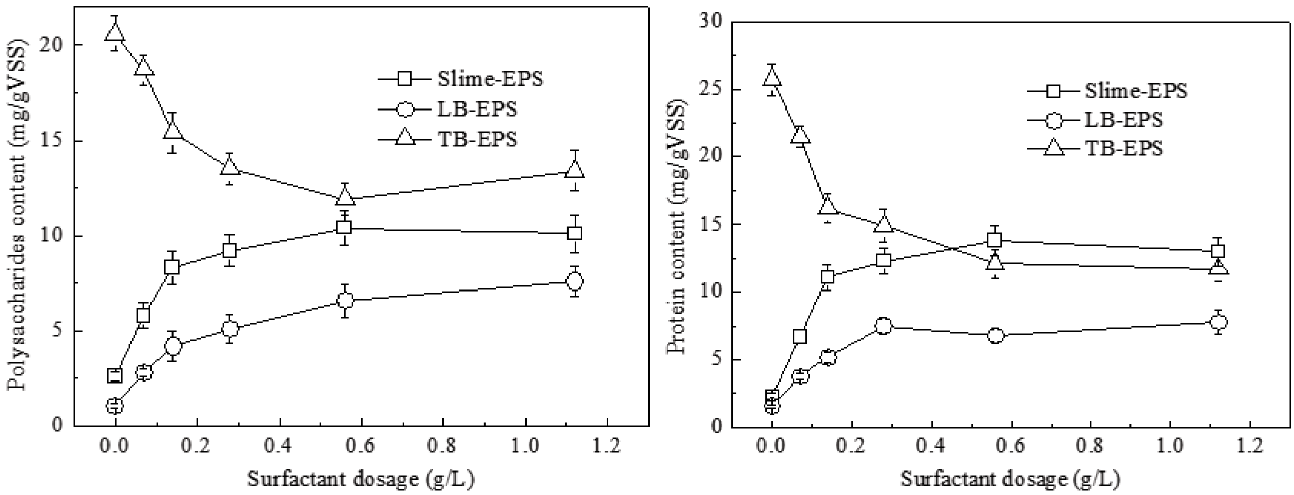

Fig. 13. Effect of surfactant ZWY-28 on the EPS of different layers of sludge.

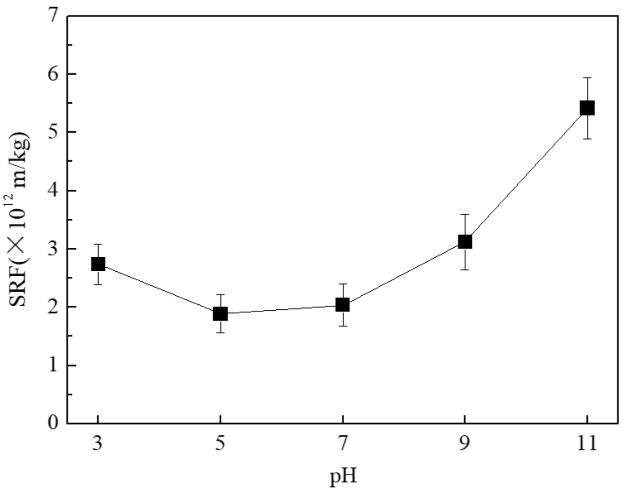

Fig. 14. Effect of surfactants on specific resistance of sludge with different initial pH.

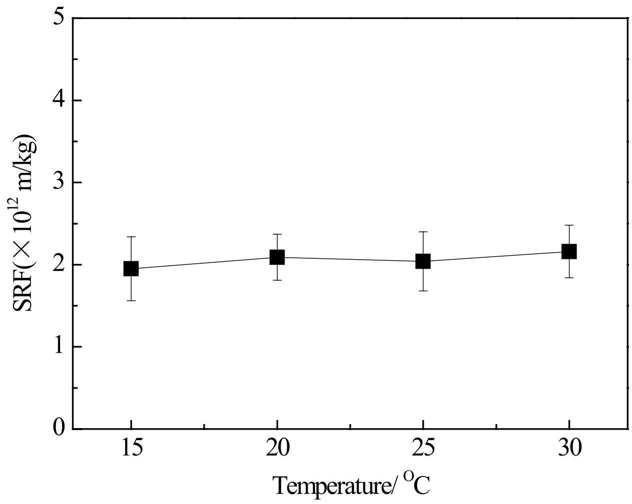

Fig. 15. Effects of surfactants on specific resistance of sample sludge at different temperatures.

treatment temperatures. Therefore, the temperature has little effect on the improvement of sludge dewatering performance by surfactants.

The original sludge was firstly added with 1% surfactant ZWY-28 and CPAM (flocculating agent) afterward to make the concentration in the sludge as 0, 5, 10, 20, 40 and 60 mg/L respectively. Then, the specific resistance of sludge was measured by stirring the sludge as 160 rpm for 30 s (quick-stir) and 50 rpm for 2 min (slow-stir) differently. At the same time, the control data was setup by adding with only CPAM (flocculating agent) to the original sludge for comparison purposes. The effect of surfactant ZWY-28 combined with cationic flocculant CPAM on the dewatering performance of sludge is shown in Fig. 16. CPAM is widely used in the dewatering treatment of municipal sludge. Adding CPAM only to sludge can accelerate the dewatering process of sludge. The specific resistance of sludge is reduced to 3.72×10^{12} m/kg when the dosage of CPAM reached to 40 mg/L, which is 72.2% lower when it is original. However, if the dosage of CPAM continuously goes up, the specific resistance of the sludge will increase which will make dewatering performance go down. The dehydration is accelerated by the function of CPAM. It is more obviously performed by combining surfactant ZWY-28 with CPAM. 1% surfactant can reduce the specific resistance of sludge to 2.04×10^{12} m/kg. Surfactant ZWY-28 combined with CPAM can further improve sludge dewatering performance. When the dosage of CPAM is 10 mg/L, the specific resistance of sludge will be decreased to the minimum which is 1.67×10^{12} m/kg, it is reduced by 87.5% compared with the original sludge. When the dosage of CPAM exceeds 10 mg/L, the sludge dewatering performance will be deteriorated. Therefore, instead of increasing the dosage of CPAM, adding CPAM, the surfactant ZWY-28 can positively impact the performance of sludge dewatering.

3.7. Different surfactants on dewatering performance

The effect of new type surfactant and common surfactant CTAB on dewatering performance is shown in Fig. 17. According to the figure, both surfactants can improve the dewatering performance. When the amount of surfactant added is 0.5%, the specific resistance of sludge treated with ZWY-28 can be reduced to 3.58 × 10^{12} m/kg, which is 73.3% lower than that of the original sludge, while the treatment with CTAB only decreases to 6.54 × 10^{12} m/kg. Due to the excellent characteristics of surfactants (what are the characteristics), Sustained increase in surfactant dose can further improve the sludge dewatering performance. When the surfactant is increased to 1%, the specific resistance of the sludge treated with ZWY-28 was reduced to the minimum, 2.04 × 10^{12} m/kg, which was 84.8% lower than the original sludge's specific resistance. However, the specific resistance of the sludge treated with CTAB was only reduced to 4.15 × 10^{12} m/kg. However, further increasing the amount of surfactant added to 2% will increase the specific resistance of sludge treated with ZWY-28 and reduce the dewatering performance. The specific resistance of the sludge treated with CTAB was reduced to a minimum of 1.93 × 10^{12} m/kg, which was 85.8% lower than that of the original sludge. Its effect is slightly better than that of the "ZWY-28" treatment (1%). The excessive surfactant will cause the sludge particles to be decomposed excessively, and the sludge dewatering performance will be deteriorated rapidly. Therefore, compared with the commonly used surfactant "CTAB", the new surfactant "ZWY-28" can have better dewatering performance with less use.

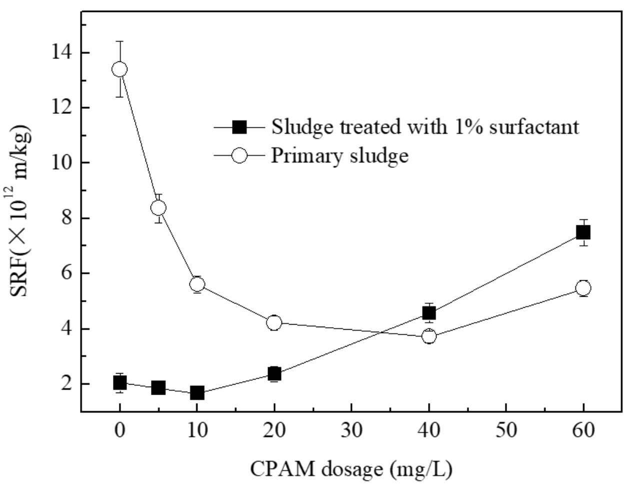

Fig. 16. Effect of CPAM dosage on specific resistance of sludge.

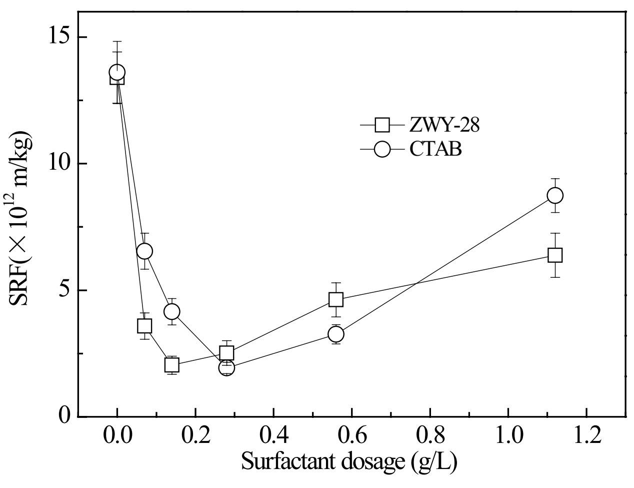

Fig. 17. Effect of different surfactants on dewatering performance.

4. Conclusions

In this study, a novel cationic surfactant ZWY-28 was used for studying the effect on the activated sludge dewatering. The results show that the surfactant ZWY-28 can adsorb on activated sludge, lower the negative charge of the sludge surface at the same time, which would be beneficial to reduce the proportion of super colloid in the sludge floc, thus improve the sludge dewatering performance. In the activated sludge, the content of EPS can account for a high proportion of the total mass of the sludge, which is an important factor affecting the sludge dewatering performance. The surfactant ZWY-28 can weak the binding action between the sludge floc and EPS, to release EPS in the sludge. Therefore, the addition of ZWY-28 can produce a significant effect on the water binding ability of activated sludge, which can remove more combined water and improve the dewatering performance of the sludge. What's more, the surfactant of ZWY-28 can promote the sedimentation rate, hence improve the dewatering effect. Based on the above, ZWY-28 is considered to be environmentally friendly and applicable to antibacterial agents, polymerizable emulsifiers, and pharmaceutical formulations. Further studies may focus on the potential risks of the residual surfactant in the filtered sludge cake.

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Data availability

The raw/processed data required to reproduce these findings can't be shared at this time as the data also forms part of an ongoing study.

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Supplementary information

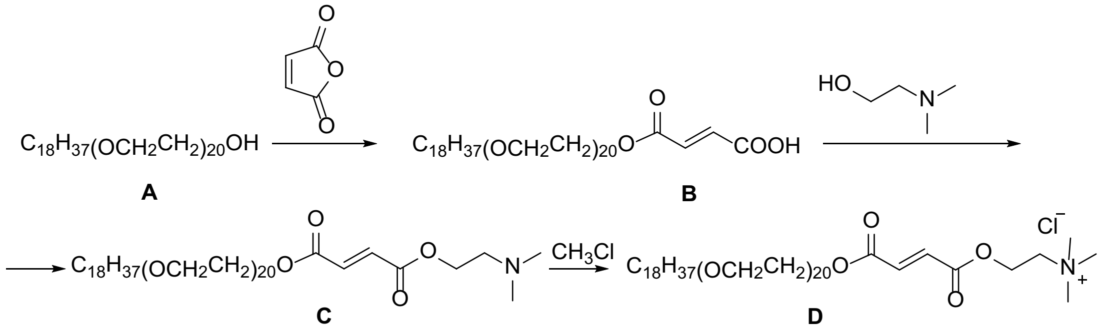

Fig. S1. Synthesis route scheme figure of ZWY-28.

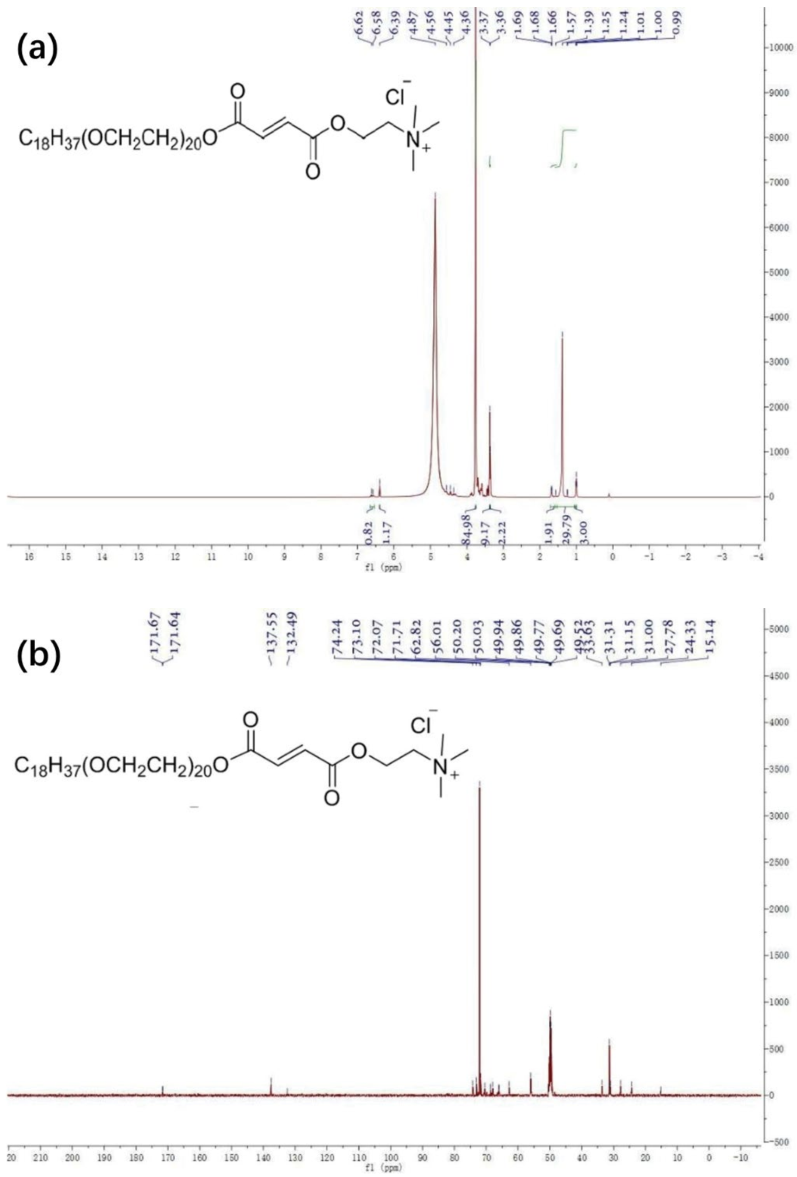

Fig. S2. (a) ^{1}H NMR (^{1}H nuclear magnetic resonance spectroscopy) and (b) ^{13}C NMR (^{13}C nuclear magnetic resonance spectroscopy) spectrum of ZWY-28; ^{1}H NMR (600 MHz, CD3OD) 6.62 (*s*, 1H), 6.39 (*s*, 1H), 3.76–3.75 (*m*, 84H), 3.37 (*s*, 9H), 3.36 (*s*, 2H), 1.68 (*t*, *J* = 12 Hz, 2H), 1.41–1.39 (*m*, 30H), 1.00 (*t*, *J* = 6 Hz, 3H); ^{13}C NMR (150 MHz, CDCl3) 171.7, 171.6, 137.5, 132.4, 74.2, 73.1, 72.0, 71.7, 70.4, 68.6, 67.9, 66.0, 65.8, 62.8, 56.0, 50.2, 50.0, 49.9, 49.8, 49.7, 49.6, 49.5, 33.6, 31.3, 31.1, 31.0, 27.7, 24.3, 15.1.