Freeze–thaw combined with activated carbon improves electrochemical dewaterability of sludge: Analysis of sludge floc structure and dewatering mechanism

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Abstract

Freeze–thaw (F/T) and electrochemistry are environment-friendly and efficient sludge treatment technologies. In this study, F/T and electrochemistry were combined in the pretreatment of sludge dewatering in the laboratory, and activated carbon (AC) was added to improve the electrochemical dewatering performance of sludge. During the experiment, the effect of F/T on the floc structure was analyzed by a laser particle analyzer and scanning electron microscope. F/T treatment not only improved the dewatering performance of sludge, but also promoted the aggregation of sludge flocs into larger particles. The median diameter (D50) increased from 45.27 μm to 128.94 μm. Then, the intracellular polymer of large-particle sludge was analyzed by three-dimensional excitation–emission matrix (3D-EEM). The tightly bound extracellular polymeric substances (TB-EPS) still contained a large amount of protein substances, which hindered the improvement of sludge dewatering performance. AC was added to the thawed sludge solution before electrochemical treatment (EP). The conductivity of AC enhanced the effect of EP, thereby cracking the sludge flocs. Thus, the light intensity of TB-EPS in the 3D-EEM fluorescence spectroscopy was decreased, and the D50 was also reduced to 105.3 μm. The final specific resistance of filtration and water content were reduced by 96.39% and 32.17%, respectively. Element analysis of the sludge cake after dehydration showed that the addition of AC significantly improved the combustion efficiency of the sludge cake. Moreover, preliminary economic analysis showed that the cost of this research was low, which indicated the potential application value of combined treatment.

1. Introduction

In recent years, the treatment of sludge has gradually been paid more attention, and sludge dewatering has been proven to be an effective means to save the operating cost of water plants and reduce the risk of environmental pollution. Therefore, dehydration has become an important step before the sludge is disposed and used (Guo et al. 2019; Neyens 2004). Among the many dehydration technologies, green environmental treatment methods are popular among researchers, such as freeze–thaw (F/T) and electrochemical pretreatment (EP).

F/T is an efficient sludge dehydration technology. The primary reason for dehydration is the formation of ice crystals during freezing (Halde 1980; Mowla et al. 2013; Tuan and Sillanpää 2010). In general, the freezing temperature is the primary factor affecting the efficiency of sludge F/T dehydration, whereas the thawing conditions have little effect on the sludge dehydration performance (Wu et al. 2020b). According to the research of Vesilind et al. (Vesilind and Martel 1990), slow freezing rate can result in good dewatering performance of the sludge during freezing, and slow freezing rate is determined by high freezing temperature. Hu et al. (Hu et al. 2011) also confirmed this finding in the study of sludge F/T dehydration. Sludge that has been slowly frozen at − 20°C has a better dehydration effect than that quickly frozen at − 80°C. F/T treatment can not only improve the dewatering performance of sludge, but also reduce the activity of harmful microorganism cells and kill microorganisms. According to Diak et al. (Diak and Örmeci 2018), in the study of ferrate pretreatment combined with F/T dehydration, ice crystals formed by freezing would puncture part of the microbial cells to reduce the microbial activity and the content of harmful cells in the sludge. Therefore, F/T is applied in cold areas to improve the sludge dewatering performance and avoid the difficulty of biological treatment and the freezing of equipment caused by low temperature (Martel 1993). Although F/T has many advantages in sludge treatment, the large particles of sludge formed by the extrusion of ice crystals during freezing will cause the material and water inside the floc to be more tightly combined (Sun et al. 2018). If such substances are released, then the sludge dewatering performance will be improved.

EP is an advanced oxidation technology that generates strong oxidizing free radicals when electrolyzing water. In recent years, it has gradually become a popular research direction in sludge dewatering (Fountoukidis 1990; Rajeshwar et al. 1994). During EP, electrophoresis, electromigration, and chemical reactions on the electrode will occur when an electric field is applied. These processes directly or indirectly affect the sludge flocs, prompting the extracellular polymeric substances (EPS) to release the contained substances and moisture, and improve the sludge dewatering performance (Mahmoud et al. 2010). For example, Yuan et al. (Yuan et al. 2010) studied the effects of voltage, time, and electrode spacing on the electrochemical dehydration of sludge. When the voltage is 21 V, the electrode distance is 5 cm; the electrolysis time is 12 min, and CST reduction efficiency is 18.8%±3.1%. According to the research of Zeng et al. (Zeng et al. 2019), EP can not only reduce the moisture content of the sludge, but also stabilize the sludge and reduce the number of microbial cells in the sludge. When the voltage is 15 V, the cell wall is destroyed, resulting in a reduction in particle size up to 50%. The concentration of *Escherichia coli* and indicator pathogens dropped by 5 log10, reaching the US Environmental Protection Agency's health standards. Compared with traditional methods, EP has a negligible impact on the environment and has a better sludge pretreatment effect; thus, it is considered as an environment-friendly sludge decomposition technology (Yuan et al. 2010). However, after a single EP, the dewatering performance of sludge still needs further improvement (Lv et al. 2019), and reducing the energy consumption of electric dewatering is also a problem that scholars are more concerned about (Anh and Sillanpää 2020). Activated carbon (AC) has excellent electrical conductivity, which can improve electrochemical performance and reduce energy consumption (Hadi et al. 2015; Sheng et al. 2010). In the electro-osmotic dewatering of sludge, Cao et al. (Cao et al. 2019) added AC to increase the electrophoretic mobility of the sludge solution, increase the current and conductivity, improve the efficiency of electro-osmosis, and reduce energy consumption. In addition, AC, as a carbon-based material, has a higher calorific value, and using it as an additive material can increase the calorific value of the final product (Wu et al. 2020a).

Therefore, in this study, a method of combining F/T and EP was proposed, and AC was added to improve electrochemical efficiency and sludge dewatering performance and reduce energy consumption. The operating parameters such as freezing temperature, electrochemical voltage time, and AC dosage were optimized on the basis of the changes in specific resistance of filtration (SRF) and water content (Wc) during treatment. The electrical properties and structural changes of floc in the sludge were tested after F/T and EP treatments. After the treatment, the three-layer EPS in the sludge flocs were extracted to analyze the changes in the internal organic matter of the flocs and explore the dehydration mechanism. After dehydration, the calorific value of the sludge cake was analyzed to determine the benefits of AC.

Finally, an economic analysis of the energy consumption in the research process was carried out to evaluate the potential of this research in practical applications.

2. Material And Methods

2.1 Waste activated sludge

The activated sludge sample used in this study was collected from a sludge thickening tank in a sewage plant in Hohhot, China. The wastewater treatment capacity of this water plant is 50,000 m^3/day. The retrieved samples were filtered through a 4 mm screen to remove large particles of impurities and then stored at 4°C for 2 days to ensure that no major change in the composition of the sludge samples occurred during the experiment. The primary characteristics of the sludge are shown in Table 1.

Table 1

Physicochemical properties of waste activated sludge.

Wc (%)	SRF ($\times 10^{13}$ m/kg)	Vss/Tss	Zeta potential (mV)	pH	Conductivity (mS/cm)
99.39	1.83	0.585	−8.91	7.627	16.85

2.2 Experimental procedures

2.2.1 F/T treatment

The F/T treatment was designed to simulate the effect of the cold environment on the sludge in winter, and the lowest temperature in Hohhot in winter could reach − 25°C. Two liters of sludge was collected and frozen at − 5°C, − 10°C, − 15°C, − 20°C, and − 25°C. Then, the sludge sample was placed in a plastic bottle and wrapped with a foam barrier to simulate an environment where the temperature gradually decreased under natural conditions. Preliminary experiments showed that the sludge was completely frozen within 18 h; therefore, 18 h was selected for all experiments. In addition, considering that long-term thawing would cause anaerobic reaction of the sludge to change the properties of the sludge (B. Ormeci and Vesilind 2001), the frozen sludge was thawed at room temperature for 12 h.

2.2.2 Dosing of AC

The AC used in this experiment was purchased from Fuchen Chemical Reagent Co., Ltd., with an average particle size of 75 μm. Before the experiment, AC was dried in an oven, sealed, and stored. One liter of thawed sludge was collected and poured into the reaction vessel. On the basis of the total suspended solid (Tss) content in the sludge, the corresponding amount of AC was added and magnetically stirred at 200 r/min for 20 min to evenly mix the AC and sludge solution without breaking the sludge flocs.

2.2.3 EP

After stirring for 20 min, the electrode plate was inserted into the sludge for EP, and stirring was continued to prevent the sludge from settling and affecting the EP effect. The anode of the EP device was a ruthenium-plated iridium titanium mesh to reduce anode corrosion, and the cathode was pure titanium mesh (China, Qinghe County Yunxuan Metal Material Co., Ltd.). The mesh shape could reduce the obstruction of the electrode plate to the stirring process and make the charge flow generated during EP uniform. The distance between the two plates was 4 cm; the size was 12 cm×6 cm, and the effective area in contact with liquid was 60 cm^2. The power supply required for the device was the adjustable DC power supply of Maisheng MS605D (0–5 A, 0–60 V).

2.2.3 Water removal

One hundred milliliters of treated sludge sample was collected and poured into a Buchner funnel for dehydration. A constant pressure of 0.04 MPa was applied to the sludge sample. Meanwhile, the filtration time and filtrate volume were recorded until no filtrate seeped out. The method, calculated as SRF and Wc, was provided by Liu et al. (Liu et al. 2016).

2.3 Analysis method

2.3.1 Analysis of sludge properties

A multimeter was used to measure the instantaneous current, and a conductivity meter (China, Liangyi DDS-307) was used to measure the conductivity change of the supernatant. According to the DLVO theory, a Zeta potential analyzer (Malvern, UK) was used to measure the Zeta potential of the filtrate. Each sludge sample was tested three times to maintain the accuracy of the experimental results, and the average value was calculated.

2.3.2 Changes in the sludge floc structure

A laser diffraction particle size analyzer (BT-9300S, China) was used to analyze the particle size distribution of the original sludge and treated sludge, and FE-SEM (S-4800, Hitachi) was used to observe the microscopic morphology of the dehydrated cake.

2.3.3 EPS analysis

A three-dimensional fluorescence spectrometer (F-7100, Hitachi, Japan) was used to detect the 3D-EEM spectrum of the EPS extraction, and the EPS was extracted according to the method provided by Li et al. (Li et al. 2019). The primary components of sludge EPS were protein and polysaccharides, and the changes of protein and polysaccharides had a great relationship with the dehydration performance. Therefore, in this study, the Folin-phenol method was used to determine the protein content in EPS, and the anthrone colorimetric method was used to determine the polysaccharide content in EPS, and the change mechanism of substances in EPS was analyzed.

2.3.4 Other methods

The multimeter was connected to the EP device to measure the current change in the electrochemical process. The treated sludge was sampled in a 100 mL graduated cylinder, and the sedimentation effect was observed after standing for 30 min. The mass percentages of [C], [H], [N], [O], and [S] were measured by an elemental analyzer (Vario EL cube, Elementer, Germany), and the calorific value of sludge was calculated by elemental analysis.

2.4 Economic analysis

Economic analysis is a necessary condition to determine whether a new technology could be applied. The cost of this study primarily included the energy consumption of the electrochemical device and the cost of adding AC. The electricity price adopted the general industrial and commercial use standard, which was $0.0854/kWh. Therefore, energy consumption was calculated according to formula (2) (Brillas 2009):

$$\text{Energy consumption（kWh/L）} = \sum_{t=0}^{n} E_{cell}\, {}^{It}/_{1000V_S} \qquad (1)$$

where E_{cell} is the applied voltage (V); I is the current (A); t is the time (h), and V_s is the sample volume (L).

The cost of buying AC is $16.9686/kg. Therefore, the total cost is calculated according to formula (3) (Olvera-Vargas et al. 2019):

where E_{cell} is the applied voltage (V); I is the current (A); t is the time (h), and V_s is the sample volume (L).

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$$\text{Total Cost \$/L sludge} = {}^{Power\ cost\ +\ Materials\ cos}/_{Volume\ of\ sample\ （L）} \qquad (2)$$

3. Results And Discussion

3.1 Effect of EP, AC, and F/T on sludge dewaterability

Figure 1(a) shows that without F/T treatment, 15 V is used to control the EP during EP and EP + AC; the AC dosage is 20% g/gTss, and SRF and Wc change with EP time. SRF and Wc decrease with the treatment time. EP + AC had a better treatment effect than EP alone in 20 min. SRF was reduced from 0.535×10^{13} m/kg to 0.271×10^{13} m/kg. Wc was reduced from 88.93–85.56%. As shown in Fig. 1(b), EP and AC are combined after F/T treatment in advance; the EP time and voltage are controlled to 15 V and 20 min; the AC dosage is 20% g/gTss, and the SRF and Wc change with freezing time. As shown in Fig. 1(b), remarkable dehydration performance is achieved after F/T + AC + EP treatment at − 15°C; SRF decreases from 0.107×10^{13} m/kg to 0.066×10^{13} m/kg, and Wc decreases from 77.85–67.42%. The reduction rate of sludge SRF is 96.39%, and the reduction rate of Wc is 32.17%, which is better than F/T and F/T + EP alone. As shown in Fig. 1(c), the dehydration performance of F/T + AC + EP combined treatment is significantly better than that of single treatment, and it has evident advantages compared with other studies (Gao et al. 2020; Hu et al. 2020; Yang et al. 2020; Zeng et al. 2020).

As shown in Fig. 1(a) and (b), the addition of AC can improve the treatment effect of sludge EP because AC has good conductivity (Mowla et al. 2013), which can further enhance the release of materials and moisture inside the floc during EP. After combining F/T and EP + AC, the sludge dewatering performance is further improved, but its dewatering mechanism needs to be studied. Therefore, this study will discuss the effect of F/T and F/T combined with EP + AC on the structure of sludge flocs and explore its dehydration mechanism.

3.2 Changes in sludge electrical properties and sludge morphology

3.2.1 Changes in current and conductivity

Sludge treatment is accompanied by changes in its properties. For example, EP will break the flocs, and the internal substances will be released, leading to changes in current and conductivity in the electrochemical process (Lv et al. 2019; Zeng et al. 2019). Figure 2(a) shows the current change with time during sludge treatment, showing a state of increasing first and then becoming stable. The current detected in the EP + AC process is the largest, and the current in the F/T + EP process is the smallest. The currents obtained by EP and F/T + AC + EP are found between EP + AC and F/T + EP. This change may be due to the increased EP cracking efficiency of sludge flocs, releasing more conductive substances and increasing the efficiency of charge conduction; thus, the current is the largest in the process of EP + AC treatment. For the sludge that has undergone F/T treatment first, the conductive substances in the sludge solution are tightly compressed, resulting in a smaller current in the F/T + EP process. In the F/T + EP + AC process, with the enhancement of AC, the current will only increase slightly, but based on the SRF and Wc, the dehydration effect is best at this time. Figure 2(b) shows that the change trend of conductivity is basically the same as the current change. Therefore, EP and F/T affect the structure of sludge flocs and increase the dewatering performance, accompanied by changes in the properties of the sludge.

3.2.2 Changes in Zeta potential

In addition to changes in current and conductivity during the treatment process, the release of negatively charged organic matter in each layer of EPS will also cause changes in the Zeta potential in the sludge solution (Hu et al. 2020). Figure 2(c) shows the change trend of Zeta potential with processing time and freezing temperature. The zeta potential of raw sludge is 8.85 mV, and the Zeta potential when the best dehydration performance is obtained after F/T + AC + EP treatment is − 15.8 mV. After treatment, the Zeta potential of the sludge increases, indicating that F/T and AC can enhance the electrophoretic mobility of the sludge during EP, and the increased electrophoretic mobility will weaken the polarity between the substances in the sludge, resulting in the reduction of hydrophilicity, thereby enhancing the dehydration performance, which is consistent with the study of Cao et al. in electro-osmotic dehydration of sludge

(Cao et al. 2019). Moreover, according to the DLVO theory, the negative increase of the Zeta potential in the sludge solution can enhance the electrostatic repulsion between the flocs and prevent the sludge from forming tighter flocs and difficult dewatering (Guo et al. 2017).

3.3 Analysis of the sludge floc structure

3.3.1 Changes in sludge particle size

We used a wet laser particle sizer to measure the sludge particle size distribution and the effect of particle size on sludge dewatering performance. Figure 3(a) shows the cumulative percentage of sludge particles with a particle size of 0–200 μm. The cumulative percentage curve of sludge particle size after F/T treatment moves to the right, indicating that the percentage of large particles in the treated sludge is greater than that in the original sludge. The percentage curve after F/T + EP + AC treatment shifts to the left, indicating that large-particle sludge is broken into relatively small particles. Zeng et al. (Zeng et al. 2020) used Pearson"s correlation analysis to determine the correlation between the median diameter D50 and the dewaterability of sludge. Therefore, we can indicate the relationship between the size change of the particle size and the dehydration performance by analyzing the change of the median diameter D50 during processing. As shown in Fig. 3(b), the D50 of the original sludge is 45.27 μm, and the D50 after F/T treatment is 128.94 μm. The D50 of the sludge treated by F/T + EP + AC is 105.3 μm, and the F/T + EP + AC treatment has the best dehydration performance. The larger or smaller the particle size, the better the dehydration performance. Feng et al. (Feng et al. 2009) found that CST and SRF decreased with the increase of sludge particles in the process of polyelectrolyte combined with ultrasonic treatment of sludge. This finding is due to the bridging effect of polyelectrolyte between the sludge flocs, thereby forming large sludge particles (LEE and LIU 2000). Zeng et al. (Zeng et al. 2020) found that CST and SRF decreased with the decrease of sludge particles during the electrochemical treatment of sludge, and the irreversible disintegration of sludge caused by electrochemistry was the primary reason for dehydration. In our research, the sludge after F/T treatment will form larger particles because of extrusion, and the larger sludge particles will be broken apart after EP treatment to form smaller sludge particles. Therefore, we hypothesize that the dewatering performance of sludge is not determined by the size of sludge particles, but the process of F/T and EP affects the structure of sludge flocs, which leads to changes in sludge particle size. In this process, internal moisture is released.

3.3.2 Changes in the sludge cake structure

The analysis of the sludge cake of the original sludge and the treated sludge can enhance the understanding of the structural changes of sludge. As shown in Fig. 4, the SEM image of the treated sludge cake was analyzed through two different magnifications. Figures 4 (a–c) is the morphology of 500 μm sludge cake after treatment with raw sludge, F/T, and F/T + EP + AC. The whole raw sludge is finely broken and dense, with uniform particle size distribution (Fig. 4a). As shown in Fig. 4(b), the sludge treated by F/T is frozen and squeezed to form large massive particles, and many cracks are generated for the water supply to escape. As shown in the sludge treated by F/T + EP + AC (Fig. 4c), the particles of the sludge are reduced because of electrochemical action, and the particles are more loose. Figures 4 (d–e) is the morphology of the sludge cake observed at 20 μm after treatment of raw sludge, F/T, and F/T + EP +

AC. The surface of the original sludge is smooth without pores and cracks, which makes the removal of water difficult (Fig. 4d). The sludge after F/T treatment (Fig. 4e) has large irregularly shaped massive particles, voids, and cracks that can be used for water removal, which is similar to the sludge morphology under medium and low magnifications (Fig. 4b). In sludge treated by F/T + EP + AC (Fig. 4f), the fine pores and cracks disappeared, forming a porous and loose pore structure. The porous structure observed during the treatment is the same, which is conducive to the release of water.

3.4 EPS analysis

During sludge dewatering, the properties and structure of the sludge changed, which causes the sludge EPS flocs and microbial cells to crack, thereby releasing internal substances and moisture and improving the sludge dewatering performance (Sheng et al. 2010). Studies have shown that sludge EPS is composed of microorganisms and their metabolites, and the primary components of which are protein, polysaccharides, and other organic substances (Wei et al. 2019). 3D-EEM fluorescence spectrum analysis was performed on the extracted three-layer EPS to explore the changes of organic matter in EPS, and the results are shown in Fig. 5. Figure 5 shows four peaks (A, B, C, and D) in the original sludge TB-EPS. According to previous studies (Li et al. 2016; Lv et al. 2019), different peaks correspond to different types of protein substances. The wavelength Ex/Em of peak A is 230/350, which is in the range of aromatic proteins. The wavelength Ex/Em of peak B is 280/350, which is in the range of tryptophan-like proteins. The wavelength Ex/Em of peak C is 235/315, which is in the range of tyrosine proteins. The wavelength Ex/Em of peak D is 275/300, which is a by-product of soluble microorganisms. Based on the fluorescence spectrum in Fig. 5, the light intensity in the TB-EPS in the raw sludge is the largest, and the fluorescence intensity in the other two layers of EPS is weak. After treatment with different methods, the fluorescence intensity of each layer of sludge EPS will change differently. The fluorescence intensity in TB-EPS is all reduced, and the fluorescence intensity in S-EPS gradually increases. By contrast, in LB-EPS, the change of fluorescence intensity is small, which is similar to the change of EPS fluorescence intensity in the study by Zhen et al. (Zhen et al. 2012), when persulfate oxidation improves sludge dewatering. Combining the fluorescence intensities at different peaks (Table 2), the fluorescence intensities of the four substances in TB-EPS have greater changes during EP and EP AC treatments, and more protein substances are released to S-EPS. When F/T + EP and F/T + EP + AC are processed, fewer substances are released from TB-EPS species. This phenomenon may indicate that the sludge flocs are compacted during F/T treatment, and the internal substances are more tightly bound and difficult to release. Based on the change in fluorescence intensity (Fig. 5), the internal substances of the flocs will transfer among different EPS layers during sludge treatment. From the research of Zhang et al. (Zhang et al. 2020), we learned that these substances were released. The transfer changes of proteins and polysaccharides are closely related to dehydration performance.

Table 2

Changes of fluorescence intensity in each layer of EPS under different treatment methods.

Treatment	EPS fractions	Aromatic proteins	Tryptophan protein-like substances	Protein-containing tyrosine	Soluble microbial by-product
		Peak A	Peak B	Peak C	Peak D
Raw	S-EPS	437.1	127	502.4	148
	LB-EPS	809.8	126.7	968	297.7
	TB-EPS	4321	4876	9843	2123
EP	S-EPS	1357	251.1	1618	416.3
	LB-EPS	799	292.3	938.4	303.6
	TB-EPS	2944	5136	8752	1778
EP + AC	S-EPS	3515	440.8	5432	966.3
	LB-EPS	437.1	127	502.4	148
	TB-EPS	1283	216.1	1576	332.1
F/T	S-EPS	1566	2999	5818	1242
	LB-EPS	3001	4377	6401	1787
	TB-EPS	2440	5393	8861	1904
F/T + EP	S-EPS	1804	3233	6701	1317
	LB-EPS	1501	2895	5957	1220
	TB-EPS	1483	3708	7356	1375
F/T + AC + EP	S-EPS	2815	3810	8240	1716
	LB-EPS	2353	3024	5650	1633
	TB-EPS	1842	3553	6822	1313

We compared the percentage changes of protein and polysaccharides in EPS of each layer of sludge treated with raw sludge and different methods (Fig. 6). The protein content in the original sludge TB-EPS accounts for more than 54%, and the polysaccharide content accounts for 45%. During EP and EP + AC treatment, the proportion of protein in TB-EPS has been significantly reduced to 33%, whereas the proportion of polysaccharides has not changed significantly. Murthy et al. (Murthy and Novak 1999) found that the binding effect of protein on bound water in TB-EPS is greater than that of polysaccharides; therefore, releasing more protein improves the dewatering performance of sludge. The reduced protein in TB-EPS is reflected in S-EPS, and its proportion has increased from 23–44%. In the treatment of F/T + EP and F/T + EP + AC, the proportion of protein and polysaccharide in TB-EPS has a small decrease, and the

SRF and Wc effects of the sludge are the best. The EP + AC treatment will increase the release of substances in the aggregates formed by F/T to improve the dewatering performance of sludge. However, in LB-EPS, the proportion of protein and polysaccharides does not change significantly, which may hinder the further improvement of the dehydration performance; this result is consistent with the research of Liu et al. (Liu et al. 2020).We compared the percentage changes of protein and polysaccharides in EPS of each layer of sludge treated with raw sludge and different methods (Fig. 6). The protein content in the original sludge TB-EPS accounts for more than 54%, and the polysaccharide content accounts for 45%. During EP and EP + AC treatment, the proportion of protein in TB-EPS has been significantly reduced to 33%, whereas the proportion of polysaccharides has not changed significantly. Murthy et al. (Murthy and Novak 1999) found that the binding effect of protein on bound water in TB-EPS is greater than that of polysaccharides; therefore, releasing more protein improves the dewatering performance of sludge. The reduced protein in TB-EPS is reflected in S-EPS, and its proportion has increased from 23–44%. In the treatment of F/T + EP and F/T + EP + AC, the proportion of protein and polysaccharide in TB-EPS has a small decrease, and the SRF and Wc effects of the sludge are the best. The EP + AC treatment will increase the release of substances in the aggregates formed by F/T to improve the dewatering performance of sludge. However, in LB-EPS, the proportion of protein and polysaccharides does not change significantly, which may hinder the further improvement of the dehydration performance; this result is consistent with the research of Liu et al. (Liu et al. 2020).

3.5 Analysis of calorific value of sludge cake

The calorific value is an important evaluation method for the sludge used for incineration treatment (Tan et al. 2015). The raw sludge and the sludge cake produced after treatment were collected, and the actual situation was simulated. Afterward, the sludge cake was placed in a ventilated place for 24 h for drying and then sampled. The moisture content was measured, and an element analyzer was used to determine the [C], [H], [N], [S], and [O] in the sludge cake The percentage of element content was calculated using the formula provided by Coskun et al. (Coskun et al. 2020) to determine the HHV and LHV of the sludge cake, such as formulas (1) and (2):

$$\mathrm{HHV}=78.33C+338.89(H-{}^{O}/_{8}) + 22.21S + 5.78N \qquad (3)$$

$$\mathrm{LHV} = HHV - (9H + H_2O) \cdot 5.8278 \qquad (4)$$

[C], [H], [N], [S], and [O] in the formula are the mass percentages of carbon, hydrogen, nitrogen, sulfur, and oxygen in the sludge, respectively, and H_2O represents the percentage of water in the sludge. HHV is the general term for the heat of combustion during fuel combustion and the heat of condensation generated by the moisture. LHV is the heat of combustion only generated by the fuel when the moisture is completely evaporated. A higher LHV represents a better fuel production effect. Table 3 shows the HHV and LHV of the raw sludge and treated sludge cake. The HHV and LHV of the original sludge are 1806.79 kcal/kg and 1045.04 kcal/kg, respectively, which are both smaller than the treated sludge (299.83 kcal/kg and 2285.40 kcal/kg), which increased by 66.04% and 118.79%, respectively. This result is due to the AC added during treatment, which is a carbon-based material with high calorific value (Wang et al. 2020).

Using AC as an auxiliary additive can improve not only the EP treatment effect and dewatering performance of the sludge, but also the final sludge. The combustion performance of the cake is conducive to the subsequent disposal and utilization of the dehydrated cake.

Table 3

Changes of element mass percentage and calorific value in sludge cake before and after treatment.

Samples	Element mass percentage(%)					H_2O(%)	Calorific value (kcal/kg)	
	C	H	N	S	O		HHV	LHV
RAW	20.11	3.48	3.39	0.37	23.03	91.33	1806.79	1045.04
F/T + AC + EP	28.91	6.13	5.0	0.45	32.60	67.42	2999.83	2285.40

3.6 Economic analysis

Table 4

Cost analysis of various dehydration methods

Treatment methods	Power cost ($/m^3 sludge)	Material cost($/m^3 sludge)	Chemical cost($/m^3 sludge)	Total cost ($/year)	References
EP	0.48	-	-	8,760,000	(Zeng et al. 2020)
F/T + AC + EP	0.0336	0.00464	-	697,883.18	This study
ECP-EF	7.83	-	17.28	458,257,500	(Olvera-Vargas et al. 2019)
Classical Fenton	-	-	0.0295	538,000	(Zhou et al. 2015)
PAM + $FeCl_3$ + mineral powders	-	-	1.04	18,980,000	(Zhai et al. 2012)

A new technology required preliminary economic analysis before its application. The cost of sludge pretreatment was calculated to be $0.03824/m^3, which included the power consumption during the pretreatment and the cost of AC. Olvera-Vargas et al. (Olvera-Vargas et al. 2019) spent $25.11/m^3 in the study of electrochemical peroxidation–electro-Fenton (ECP-EF) treatment of anaerobic sludge (excluding dry-sludge disposal and anode consumption). Zhai et al. (Zhai et al. 2012) mixed PAM, $FeCl_3$, and mineral powder as a conditioning agent, with a chemical cost of \$1.04/m^3. Zhou et al. (Zhou et al. 2015) found that the traditional Fenton method adjusted the sludge cost to \$0.0295/m^3. Assuming that the service population of the sewage treatment plant is 100,000, the total cost of the two methods is compared in Table 4. The Fenton method required reaction under acidic conditions. The experimental conditions were harsh and expensive. In this study, the reaction conditions were loose; no chemical agents were used; no pollution was generated, and costs were saved.

4. Conclusions

This research combines F/T, EP, and AC and explores the potential application of combined treatment in sludge dewatering, aiming to improve the dewatering performance of sludge and increase the utilization efficiency of dry sludge cake through green and energy-saving treatment technology. The analysis of the sludge floc structure during the research shows that the dewatering performance of the sludge is not always positively or negatively correlated with the size of the sludge, but the sludge is released when EP and F/T change the sludge floc structure. The internal moisture is removed, and the sludge particle size changes. Through EPS analysis, F/T will make the internal materials of EPS more closely combined, and EP has the opposite effect, cracking EPS and releasing internal materials. AC can further enhance the treatment effect of EP by enhancing the electrophoretic mobility during EP. Therefore, we use the squeezing effect of F/T and the cracking effect of EP, combined with AC to treat water-containing sludge and improve the dewatering performance of sludge. Under optimal conditions (– 15°C, 15 V, 25 min, and 20%g/gTss), the sludge was conditioned; the Wc of the sludge cake was reduced from 99.39–67.42%, and the SRF was reduced from 1.83×1013 m/kg to 0.066×1013 m/kg. The reduction rates were 32.17% and 96.39%, respectively, and good treatment effects were obtained. In addition, the calorific value of the sludge after the addition of AC has been improved, which promotes the utilization efficiency of the sludge cake, and the economic analysis also shows that this research consumes less energy and exhbits application value.

Declarations

Ethical Approval

Not applicable

Consent to Participate

Not applicable

Consent to Publish

Not applicable

Authors Contributions

Data analysis and the lead in writing the manuscript were performed by Kai Hui. Lei Song contributed to the study conception and design. Zhenzhou Yin contributed to writing. Hongwei Song contributed to theory, and helped shape manuscript structure. Material preparation was performed by Zehao Wang. Data collection was performed by Wenjian Gao. Lili Xuan commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Competing Interests

The authors declare that they have no competing interests.

Availability of data and materials

All data generated or analysed during this study are included in this published article.

References

Anh TP, Sillanpää M (2020) Sewage sludge electro-dewatering. In: Advanced Water Treatment. pp 163-225. doi:10.1016/b978-0-12-819227-6.00003-6

Ormeci, Vesilind PA (2001) Effect of dissolved organic material and cations on freeze-thaw conditioning of activated and alum sludges. Wat Res 35(18):4299–4306. doi:10.1016/S0043-1354(01)00174-9

Brillas E, Sirés, I., Oturan, M.A (2009) Electro-Fenton Process and Related Electrochemical Technologies Based on Fenton's Reaction Chemistry. Chemical Reviews 109:6570–6631

Cao B, Wang R, Zhang W, Wu H, Wang D (2019) Carbon-based materials reinforced waste activated sludge electro-dewatering for synchronous fuel treatment. Water Research 149:533-542. doi:10.1016/j.watres.2018.10.082

Coskun C, Oktay Z, Koksal T, Birecikli B (2020) Co-combustion of municipal dewatered sewage sludge and natural gas in an actual power plant. Energy 211. doi:10.1016/j.energy.2020.118615

Diak J, Örmeci B (2018) Stabilisation and dewatering of primary sludge using ferrate(VI) pre-treatment followed by freeze-thaw in simulated drainage beds. Journal of Environmental Management 216:406-420. doi:10.1016/j.jenvman.2017.10.065

Feng X, Deng J, Lei H, Bai T, Fan Q, Li Z (2009) Dewaterability of waste activated sludge with ultrasound conditioning. Bioresour Technol 100:1074-1081. doi:10.1016/j.biortech.2008.07.055

Fountoukidis GPaE (1990) Disinfection of water by electrochemical treatment. Water Res 24: 1491-1496

Gao S, Wang Y, Zhang D, Fan X, Guo Y, Li E, Zheng H (2020) Insight to peroxone-Fe(III) joint conditioning-horizontal electro-dewatering process on water reduction in activated sludge: Performance and mechanisms. J Hazard Mater 402:123441. doi:10.1016/j.jhazmat.2020.123441

Guo J, Jiang S, Pang Y (2019) Rice straw biochar modified by aluminum chloride enhances the dewatering of the sludge from municipal sewage treatment plant. Science of The Total Environment 654:338-344. doi:10.1016/j.scitotenv.2018.10.429

Guo X, Wang Y, Wang D (2017) Permanganate/bisulfite (PM/BS) conditioning–horizontal electro-dewatering (HED) of activated sludge: Effect of reactive Mn(III) species. Water Research 124:584-594. doi:10.1016/j.watres.2017.08.027

Hadi P, Xu M, Ning C, Sze Ki Lin C, McKay G (2015) A critical review on preparation, characterization and utilization of sludge-derived activated carbons for wastewater treatment. Chemical Engineering Journal 260:895-906. doi:10.1016/j.cej.2014.08.088

Halde R (1980) Concentration of impurities by progressive freezing. Water Res 14 (1980): 575–580

Hu K, Jiang JQ, Zhao QL, Lee DJ, Wang K, Qiu W (2011) Conditioning of wastewater sludge using freezing and thawing: role of curing. Water Res 45:5969-5976. doi:10.1016/j.watres.2011.08.064

Hu S et al. (2020) Integration of electrochemical and calcium hypochlorite oxidation for simultaneous sludge deep dewatering, stabilization and phosphorus fixation. Sci Total Environ 750:141408. doi:10.1016/j.scitotenv.2020.141408

LEE CH, LIU JC (2000) Enhanced sludge dewatering by dual polyelectrolytes conditioning. Water Res 34(18):4430-4436. doi:10.1016/S0043-1354(00)00209-8

Li H et al. (2019) Highly efficient enhancement of municipal sludge dewaterability using persulfate activation with nZVI/HA. Water Sci Technol 79:1309-1315. doi:10.2166/wst.2019.126

Li Y et al. (2016) Enhancing the sludge dewaterability by electrolysis/electrocoagulation combined with zero-valent iron activated persulfate process. Chemical Engineering Journal 303:636-645. doi:10.1016/j.cej.2016.06.041

Liu J et al. (2016) Enhanced dewaterability of waste activated sludge by Fe(II)-activated peroxymonosulfate oxidation. Bioresour Technol 206:134-140. doi:10.1016/j.biortech.2016.01.088

Liu Y et al. (2020) Synthesis of novel chitosan-based flocculants with amphiphilic structure and its application in sludge dewatering: Role of hydrophobic groups. Journal of Cleaner Production 249. doi:10.1016/j.jclepro.2019.119350

Lv H et al. (2019) The effects of aging for improving wastewater sludge electro-dewatering performances. Journal of Industrial and Engineering Chemistry 80:647-655. doi:10.1016/j.jiec.2019.08.049

Mahmoud A, Olivier J, Vaxelaire J, Hoadley AFA (2010) Electrical field: A historical review of its application and contributions in wastewater sludge dewatering. Water Research 44:2381-2407. doi:10.1016/j.watres.2010.01.033

Martel CJ (1993) Fundamentals of sludge dewatering in freezing beds. WatSciTech 28:29-35

Mowla D, Tran HN, Allen DG (2013) A review of the properties of biosludge and its relevance to enhanced dewatering processes. Biomass and Bioenergy 58:365-378. doi:10.1016/j.biombioe.2013.09.002

Murthy SN, Novak JT (1999) Factors Affecting Floe Properties During Aerobic Digestion: Implications for Dewaterin. Water Environ Fed 71:197– 202

Neyens E (2004) Advanced sludge treatment affects extracellular polymeric substances to improve activated sludge dewatering. Journal of Hazardous Materials 106:83-92. doi:10.1016/j.jhazmat.2003.11.014

Olvera-Vargas H, Zheng X, Garcia-Rodriguez O, Lefebvre O (2019) Sequential "electrochemical peroxidation – Electro-Fenton" process for anaerobic sludge treatment. Water Research 154:277-286. doi:10.1016/j.watres.2019.01.063

Rajeshwar K, Ibanez JG, Swain GM (1994) Electrochemistry and the environment. Journal of Applied Electrochemistry 24. doi:10.1007/bf00241305

Sheng GP, Yu HQ, Li XY (2010) Extracellular polymeric substances (EPS) of microbial aggregates in biological wastewater treatment systems: a review. Biotechnol Adv 28:882-894. doi:10.1016/j.biotechadv.2010.08.001

Sun F, Xiao K, Zhu W, Withanage N, Zhou Y (2018) Enhanced sludge solubilization and dewaterability by synergistic effects of nitrite and freezing. Water Res 130:208-214. doi:10.1016/j.watres.2017.11.066

Tan P, Zhang C, Xia J, Fang Q-Y, Chen G (2015) Estimation of higher heating value of coal based on proximate analysis using support vector regression. Fuel Processing Technology 138:298-304. doi:10.1016/j.fuproc.2015.06.013

Tuan P-A, Sillanpää M (2010) Effect of freeze/thaw conditions, polyelectrolyte addition, and sludge loading on sludge electro-dewatering process. Chemical Engineering Journal 164:85-91. doi:10.1016/j.cej.2010.08.028

Vesilind PA, Martel CJ (1990) Freezing of water and wastewater sludges. Journal of Environmental Engineering 166(5):854862

Wang J, Liu H, Deng H, Jin M, Xiao H, Yao H (2020) Deep dewatering of sewage sludge and simultaneous preparation of derived fuel via carbonaceous skeleton-aided thermal hydrolysis. Chemical Engineering Journal 402. doi:10.1016/j.cej.2020.126255

Wei L et al. (2019) Adsorption mechanism of ZnO and CuO nanoparticles on two typical sludge EPS: Effect of nanoparticle diameter and fractional EPS polarity on binding. Chemosphere 214:210-219. doi:10.1016/j.chemosphere.2018.09.093

Wu B, Dai X, Chai X (2020a) Critical review on dewatering of sewage sludge: Influential mechanism, conditioning technologies and implications to sludge re-utilizations. Water Res 180:115912. doi:10.1016/j.watres.2020.115912

Wu Y et al. (2020b) Experimental study on treating landfill sludge by preconditioning combined with vacuum preloading: Effects of freeze-thaw and FeCl3 preconditioning. Sci Total Environ 747:141092. doi:10.1016/j.scitotenv.2020.141092

Yang M, B H, Bai Y, Liu R, Hu C, Qu J (2020) Using activated peroxymonosulfate by electrochemically generated FeII for conditioning and dewatering of anaerobically digested sludge. Chemical Engineering Journal 391. doi:10.1016/j.cej.2019.123603

Yuan H, Zhu N, Song L (2010) Conditioning of sewage sludge with electrolysis: Effectiveness and optimizing study to improve dewaterability. Bioresource Technology 101:4285-4290. doi:10.1016/j.biortech.2009.12.147

Zeng Q, Hao T, Yuan Z, Chen G (2020) Dewaterability enhancement and sulfide mitigation of CEPT sludge by electrochemical pretreatment. Water Res 176:115727. doi:10.1016/j.watres.2020.115727

Zeng Q, Zan F, Hao T, Biswal BK, Lin S, van Loosdrecht MCM, Chen G (2019) Electrochemical pretreatment for stabilization of waste activated sludge: Simultaneously enhancing dewaterability, inactivating pathogens and mitigating hydrogen sulfide. Water Research 166. doi:10.1016/j.watres.2019.115035

Zhai L-F, Sun M, Song W, Wang G (2012) An integrated approach to optimize the conditioning chemicals for enhanced sludge conditioning in a pilot-scale sludge dewatering process. Bioresource Technology 121:161-168. doi:10.1016/j.biortech.2012.06.093

Zhang W, Dai X, Dong B, Dai L (2020) New insights into the effect of sludge proteins on the hydrophilic/hydrophobic properties that improve sludge dewaterability during anaerobic digestion. Water Res 173:115503. doi:10.1016/j.watres.2020.115503

Zhen G et al. (2012) Novel insights into enhanced dewaterability of waste activated sludge by Fe(II)-activated persulfate oxidation. Bioresour Technol 119:7-14. doi:10.1016/j.biortech.2012.05.115

Zhou X, Wang Q, Jiang G, Liu P, Yuan Z (2015) A novel conditioning process for enhancing dewaterability of waste activated sludge by combination of zero-valent iron and persulfate. Bioresour Technol 185:416-420. doi:10.1016/j.biortech.2015.02.088

Figures

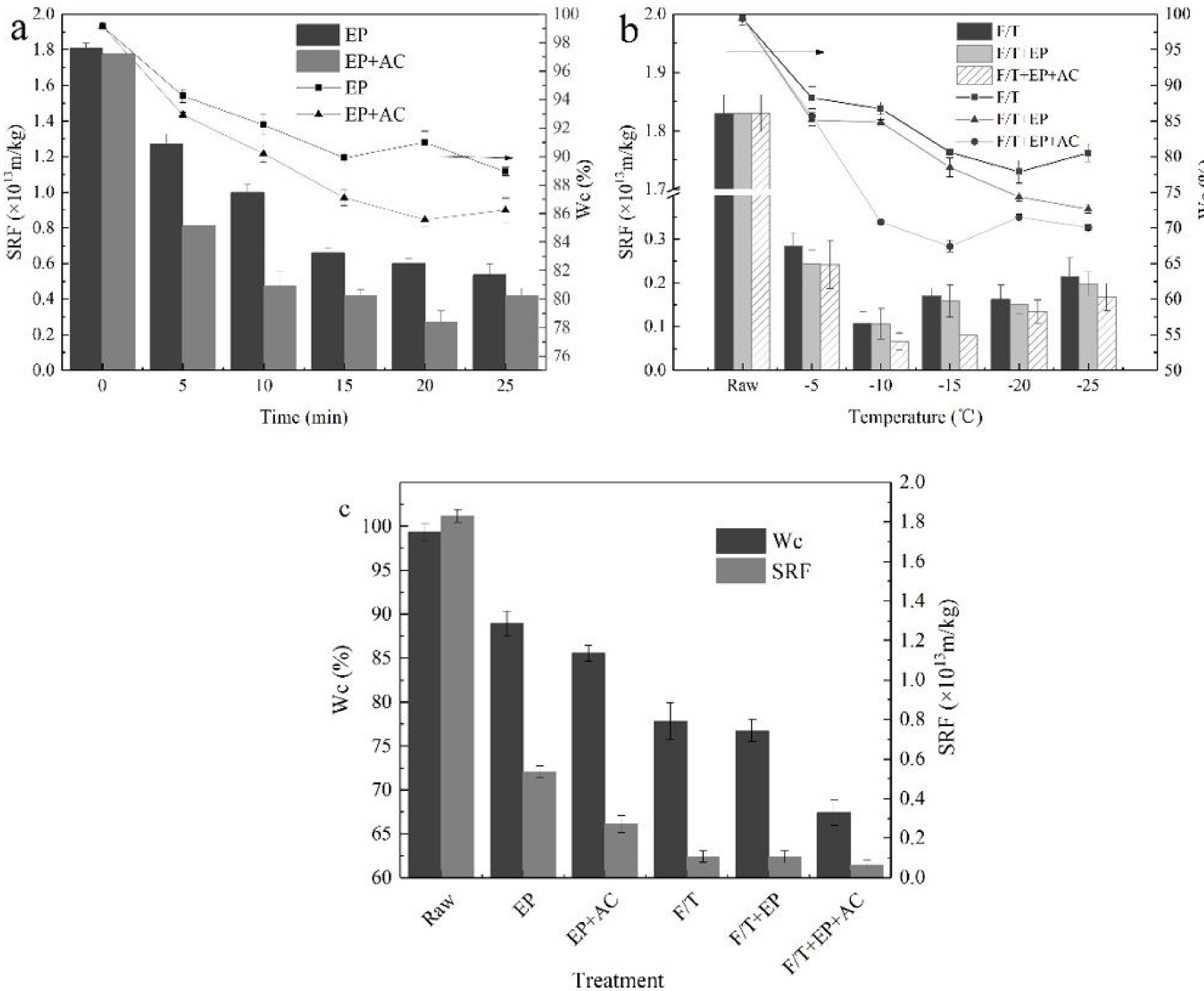

Figure 1

Effect of EP, AC, and F/T treatment and their combined treatment on the performance of sludge dewatering.

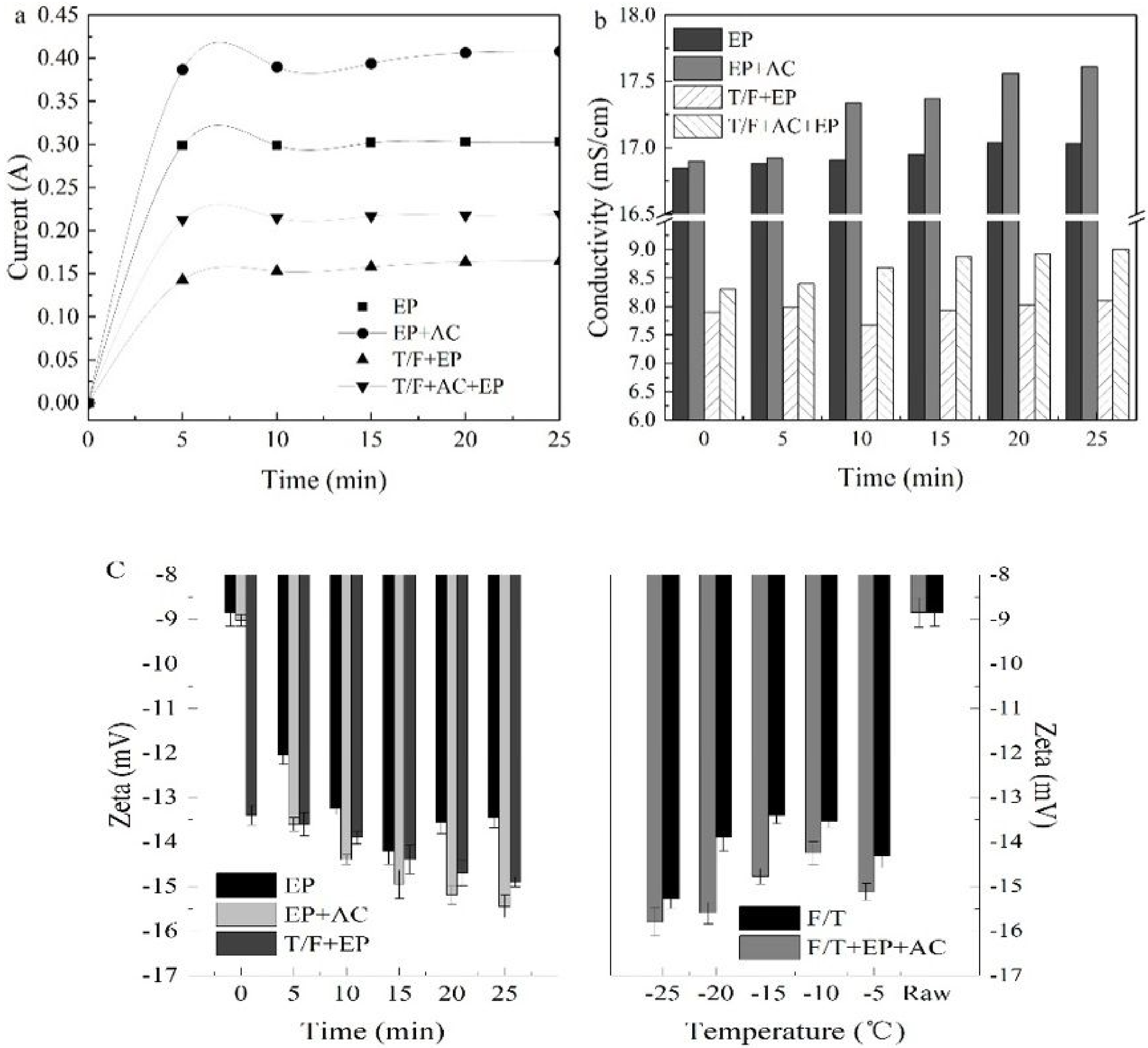

Figure 2

Changes in the electrical properties of sludge during EP, AC, and F/T treatment and their combined treatment: (a) current change, (b) conductivity change, and (c) Zeta potential change.

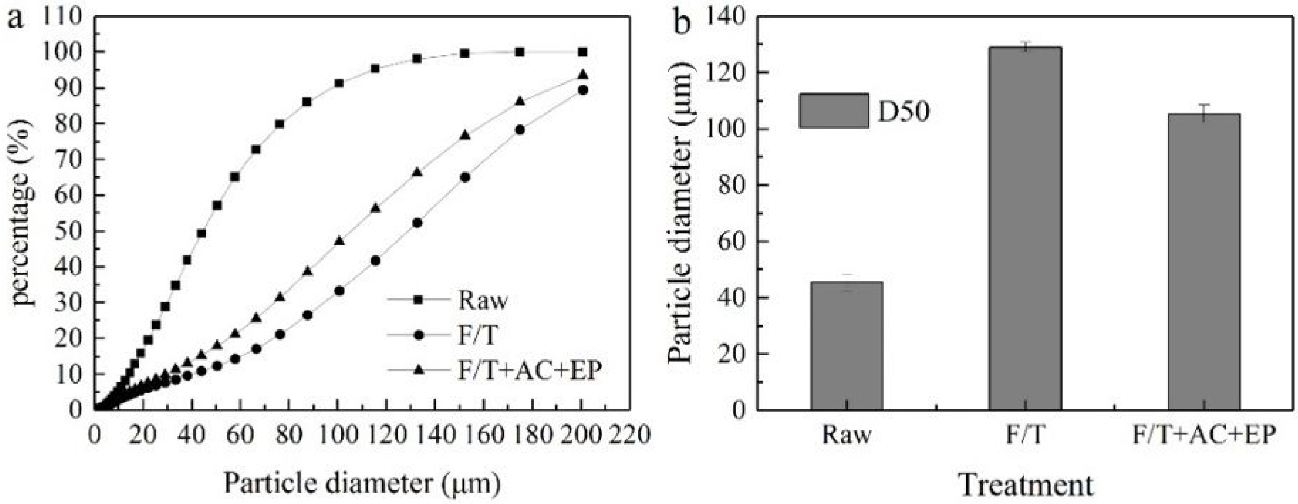

Figure 3

Changes in sludge particle size: (a) cumulative percentage and (b) change in median diameter D50.

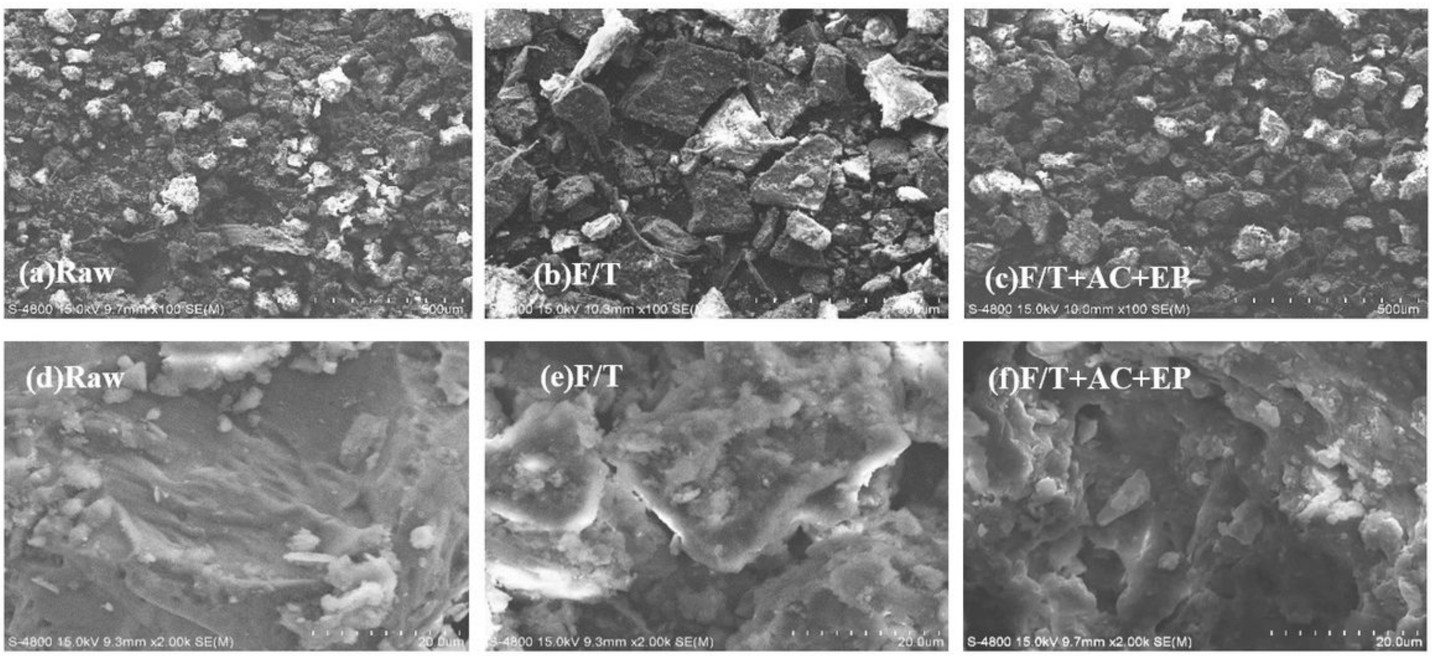

Figure 4

Structural change of sludge cake under different sizes: (a–c) is 500 μm; (d–f) is 20 μm.

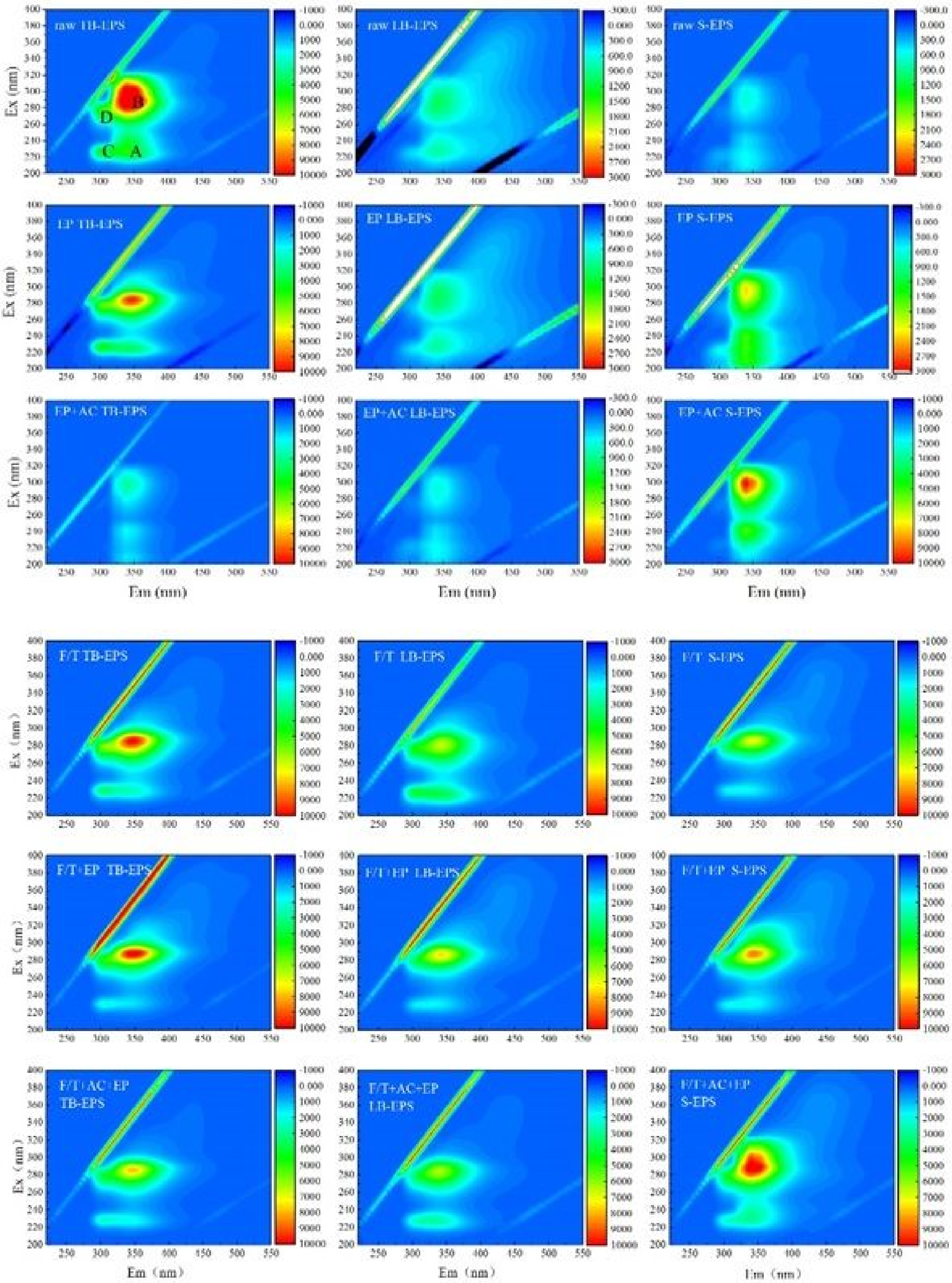

Figure 5

Three-layer EPS three-dimensional excitation–emission matrix.

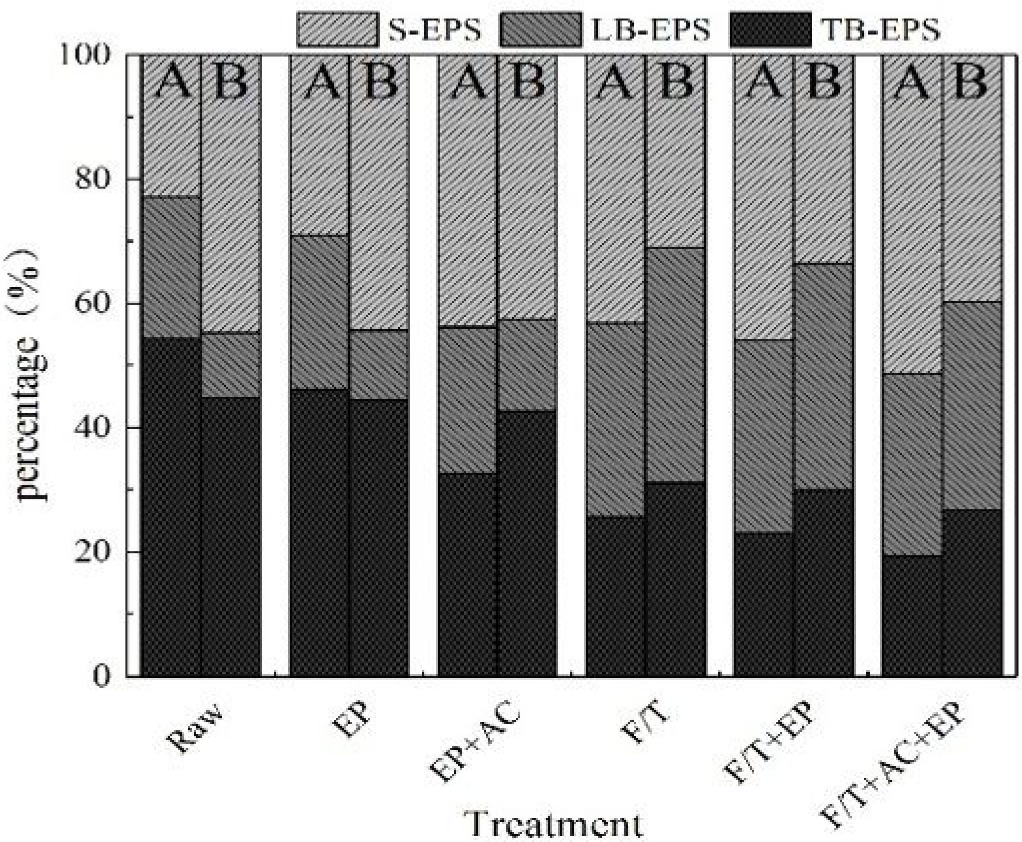

Figure 6

Percentage change of protein and polysaccharide content in each layer of EPS.

Supplementary Files

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- GraphicalAbstract.jpg