Water Science & Technology

IWA PUBLISHING

Water Science & Technology Vol 87 No 7, 1600 doi: 10.2166/wst.2023.044

Combined conditioning of inorganic coagulant and polyamine to improve the dewaterability of municipal sludge, minimize dosage and reduce the influence of filtrate

Baolv Hua[a,b,c], Shichao Zhao[a,b] and Fengting Li[a,b,d,]*

[a] State Key Laboratory of Pollution Control and Resources Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China
[b] Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, People's Republic of China
[c] Jiangsu Runyang Yueda Century Photovoltaic Technology Co., Ltd, Yancheng, Jiangsu 224007, People's Republic of China
[d] Present address: College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China
*Corresponding author. E-mail: fengting@tongji.edu.cn; fengting@mail.tongji.edu.cn

ABSTRACT

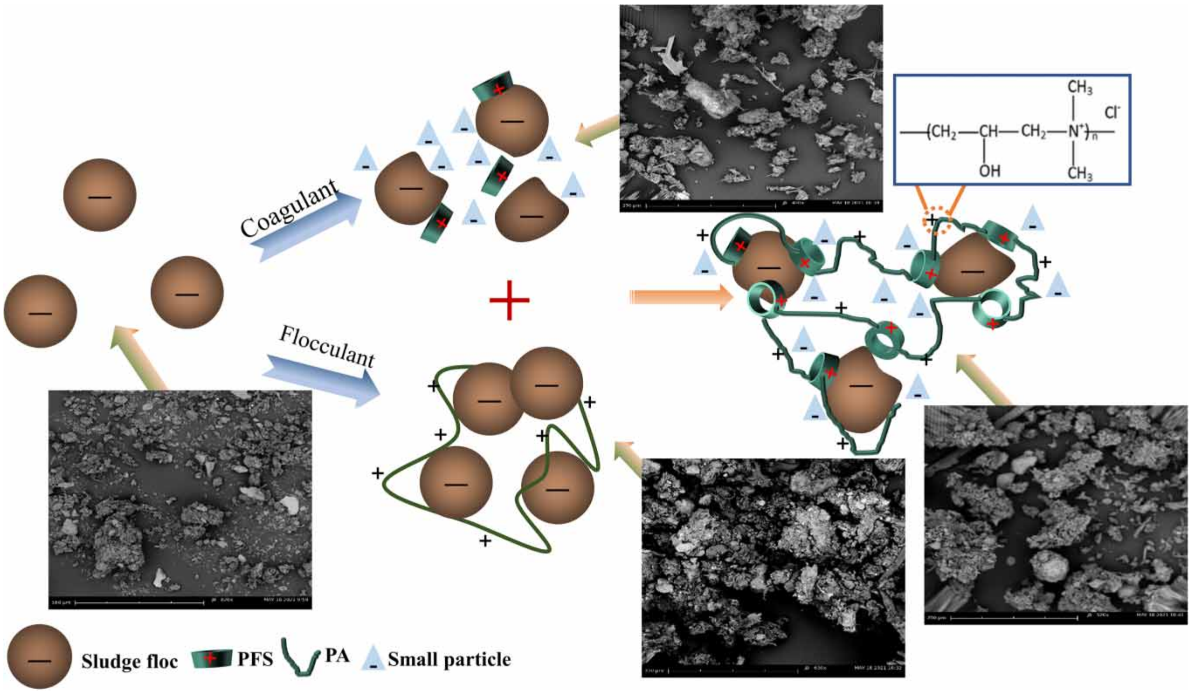
Efficient dewatering of sludge is necessary for its cost-effective transportation and final disposal. However, the common method of using polyferric sulfate (PFS) and polyacrylamide (PAM) requires a large amount of dosage and produces high iron ion content in the filtrate. This study examined a solution of applying polyamine (PA) coupled with inorganic coagulant PFS. The results demonstrated that using PFS + PA together could achieve the same or similar filtering rates as using PFS + PAM. The capillary suction time (CST) of PFS + PA (89.0 s) was equivalent to that of PFS (75.1 s) and better than that of PA (117.1 s) and raw sludge (RS, 403.8 s). Compared with PFS + PAM, the combination of PFS and PA efficiently removed Fe ions and chemical oxygen demand (COD) in sludge water content, with Fe ions in the sludge filtrate reduced by 97.8% and COD reduced by 78.9%, respectively. By analyzing the basic physicochemical properties of the sludge system, including the synergistic effect of coagulation and flocculation, sludge hydrolysis and flocculation, it indicated that PA + PFS could reduce bound water. These results demonstrated that combining PFS and PA to improve sludge dewatering performance is more beneficial than utilizing a coagulant or flocculant alone, even PFS + PAM.

Key words: coagulation–flocculation process, polyamine (PA), reject water, sludge dewatering optimization

HIGHLIGHTS

- Pretreatment of sludge with minimal chemicals.
- Reduction of metal content in the treated sludge filtrate.

GRAPHICAL ABSTRACT



1. INTRODUCTION

The management of sludge remains a major challenge in wastewater treatment, which has attracted the attention of society and scientists for a variety of reasons (Wang *et al.* 2019). Activated sludge treatment is a method of treating wastewater by using suspended microbial flocs, which is a kind of aerobic microbial treatment method. The excess sludge (ES), referring to the proliferation of microorganisms caused by the biochemical reaction in the ES aeration tank, which is usually discharged from the secondary sedimentation tank to maintain the stable operation of the activated sludge system, needs effective treatment and disposal. Dewatering is the key to reducing the volume of ES with a moisture content of 99% (Wang *et al.* 2017a). When the water content of sludge is high (higher than 99%), it belongs to Newtonian fluid, and its flow characteristics are close to water flow. With the increase of solid concentration, the flow of sludge shows the characteristics of semi-plastic or plastic fluid, the initial shear force must be overcome before the flow can begin. As a highly hydrophilic non-Newtonian fluid, when the water content is lower than 99%, sludge is difficult to dewater, so a variety of physicochemical and biological conditioning methods have been developed to achieve effective separation of the solid–liquid portion (Wu *et al.* 2019). High-performance dewatering processes need to be developed to reduce the amount of sludge used for disposal, and chemical conditioning pretreatment measures are often essential. The main types of water in sludge are free water, interstitial water and bound water. Although free water can be separated by mechanical dehydration, the removal of bound water requires energy-intensive thermal drying. In other words, the dewatering performance of sludge can be improved by converting bound water into free water (Tunçal 2021; Tunçal & Mujumdar 2022).

Deep dewatering has been widely used to reduce sludge volume and relieve pressure on disposal caused by a rapid increase in sludge production. Generally, some pretreatments were used to improve sludge sedimentation, accelerate sludge filtration and promote the release of bound water to achieve good performance (Guan *et al.* 2017; He *et al.* 2017). The main technique for sludge conditioning is chemical conditioning using inorganic coagulants (aluminum and iron salts) or organic flocculants (polyacrylamide, PAM), followed by physical dewatering. Chemical regulators can be combined with the extracellular polymer (EPS) components through electrostatic neutralization, and inorganic coagulants can be hydrolyzed into hydroxides to increase the strength of flocculation by acting as skeleton construction agents (Qi *et al.* 2011). EPS compression is the main mechanism of sludge dewatering under the regulation of inorganic coagulants because inorganic coagulants can remove viscous biopolymers, destroy microbial cells and induce the release of intracellular compounds (Niu *et al.* 2013; Zhang *et al.*

2016a). However, the flocculation effect of polyaluminum chloride was easily affected by water quality, such as pH, alkalinity, suspended solid (SS) concentration, and natural organic matter (NOM) (Yang *et al.* 2019). Sludge filtrate is a very important index, which refers to the liquid separated from sludge and water when sludge is dried and dehydrated. The treatment method of sludge filtrate is mainly to return to the front of the sewage treatment grid and mix it with the influent water for treatment, which will increase the treatment water volume, increase the treatment load, easily damage the biochemical system and increase energy consumption. Fe^{3+} coagulation had been reported to improve the sedimentation and dewaterability of sludge, while other methods, including ozonation and sulfate oxidation, reduce the filterability of sludge and bring additional difficulties to post-treatment and disposal (Wu *et al.* 2018, 2019).

In fact, the combined use of coagulants and flocculants is a highly efficient and simple method used in water and wastewater treatment facilities worldwide. Traditional coagulants can promote the release of bound water from sludge particles due to hydrolysis and charge neutralization (Teh *et al.* 2016; Yu *et al.* 2016). Gradually, the combined effect of inorganic chemicals and organic polymers in sludge conditioning has also been studied. It was proposed that the combined action of calcium peroxide (CaO_2) oxidation and PAM can improve dewaterability, but the inorganic chemicals used in this study mainly act as oxidants rather than coagulants (Chen *et al.* 2016). As one of the most commercialized flocculants, PAM has been used for sludge conditioning for a long time to improve its filterability in the mechanical dewatering process. However, it also has the limitation of deep sludge dewatering because PAM cannot effectively degrade EPS or intracellular material, and PAM can be partially hydrolyzed into toxic monomers such as acrylic acid and organic amine that lead to producing secondary pollution in the sludge treatment process (Zhang *et al.* 2007; Wang *et al.* 2017b; Hennecke *et al.* 2018). Moreover, PAM provides less cations per unit mass than polyamines (PA), which increases the dosage of chemicals used. And the use of organic flocculants can greatly reduce the chemical dosage required for the coagulation/flocculation process (Lee *et al.* 2014; Yousefi *et al.* 2020a). PA, also known as epichlorohydrin dimethylamine copolymer, is a strong cationic linear homopolymer with good water solubility and resistance to chlorine degradation. Previously, PA was mainly used in printing and dyeing enterprises as a chemical reagent for fixing, and it can fix and chelate dyes. It is precise because of these characteristics that it can also combine with some pollutants in sewage and sludge, thus extending the PA from the dye field to the sewage sludge treatment field. It can be compounded with inorganic coagulants to enhance its flocculation effect (Yousefi *et al.* 2020a). Therefore, it is of great significance to explore whether coagulants and flocculants can be used in combination to achieve better sludge filterability, chemical reduction and high-efficiency water reduction.

Therefore, the purpose of this study was to explore the performance of the combined coagulation–flocculation (PFS as a coagulant and PA as a flocculant) process for the dehydration of aged sludge. By adding PA to reduce the dosage of PFS, the filtrate can be improved. To achieve a comprehensive understanding, the water content of sludge cake using a single coagulant (PFS), a flocculant (PA) and a combination of coagulant and flocculant (PFS + PA) was explored first. Then, the basic physical and chemical properties of these conditioned sludge samples were measured to study the effect of different pretreatments, and their hydrodynamic properties were evaluated by rheological tests. Furthermore, the mechanisms of dewatering performance between different treatments were discussed.

2. MATERIALS AND METHODS

2.1. Raw sludge and chemicals

The original sludge was taken from a sewage treatment plant in Shanghai, China, and the sludge was aged anaerobic sludge. The initial solid concentration was 480.5 g/L and then slowly diluted to 37.2 g/L. The sludge sample was stored at 4 °C (<1 week) prior to use. The characteristics of sludge samples are shown in Table 1. PFS (content = 11%, industrial grade) and PA (solid content = 49.69% ± 0.31%, industrial grade) were purchased from Shanghai Wanshi Environmental Technology Co., Ltd (Shanghai, China). The EPS of the sludge was extracted with NaCl (Sinopharm Reagent, analytical pure). NaOH, Na_2CO_3, $CuSO_4$, bovine serum albumin, sodium tartrate, and Folin reagent (Sinopharm Reagent, analytically pure) were used to test the protein in EPS. Anthrone and H_2SO_4 (Sinopharm Reagent, analytical pure) were used to test polysaccharides in EPS.

2.2. Sludge conditioning and dewatering

In this study, coagulation was simply defined as the addition of an inorganic flocculant, such as PFS, to the sludge, while flocculation was defined as the addition of an organic flocculant, such as PA, to the sludge (Figure 1).

In this study, the conditioning agent was added to 100 ml of sludge during each conditioning test. The filterability of the sludge sample was evaluated by a capillary suction time (CST) instrument (Type 304M; Trion, Sanford, NC, UK). To explore

Table 1 | Characteristics of the sludge

pH	7.63 ± 0.04
TS (g/L)	37.15 ± 0.45
VSS (g/g TS)	0.26 ± 0.018
CST (s)	403.8 ± 0.5
Sludge viscosity (mPa·s)	5.33 ± 0.67
Floc size d_{50} (μm)	28.71
Zeta potential (mV)	−33.8 ± 0.29

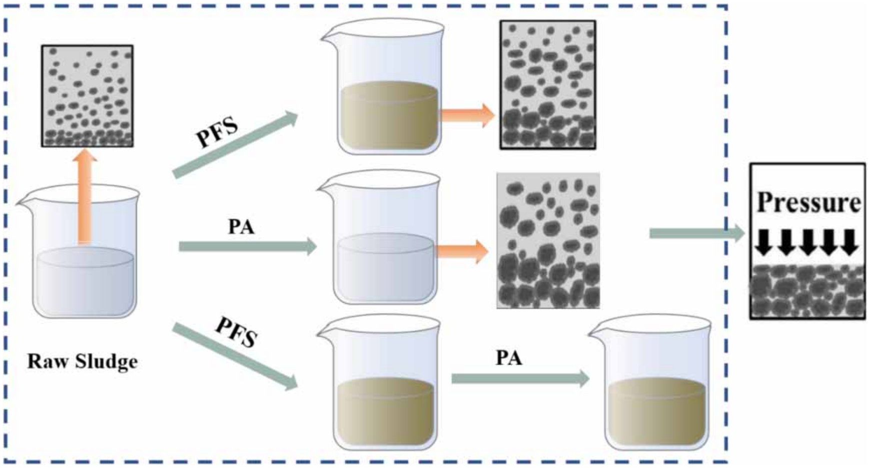


Figure 1 | Schematic illustration for pretreatment sludge.

the feasibility of a combined coagulation and flocculation process for sludge dewatering, PFS, PA and PFS + PA were selected for conditioning. As shown in Table 2, three different sludge conditioning modes were carried out: no conditioning; coagulant or flocculant used alone and coagulation–flocculation-coordinated treatment. As shown in Table 2, three different sludge conditioning modes were carried out: no conditioning; coagulant or flocculant used alone; and coagulation–flocculation-coordinated treatment.

The sludge was first quickly mixed with the coagulant, followed by the flocculant. Then, the dewatering performance and related physical and chemical properties of these sludge samples were analyzed. The dewatering performance was evaluated by the water content of the dewatered filter cake. In this study, sludge samples were dewatered for 3 min at 0.05 MPa by filtering through a Buchner funnel. All the above tests were conducted in triplicate.

Table 2 | Different sludge conditioning procedures

		Dosage (mg/g TS)			
Symbol	**Conditioners**	**PFS**	**PA**	**Conditioning procedures**	**CST (s)**
RS	None	0	0	300 rpm/3 min	403.8 ± 0.5
PFS	PFS	2.96	0	PFS solutions → 300 rpm/3 min	75.1 ± 0.2
PA	PA	0	2.69	PA solutions → 300 rpm/3 min	117.1 ± 0.7
PFS + PA	PFS + PA	2.96	2.69	PFS solutions → 300 rpm/3 min → PA solutions → 300 rpm/3 min	89 ± 0.4

2.3. Analytical methods

Total solids (TS) and volatile SS (VSS) were measured by the weight method at 105 and 600 °C, respectively. The total organic carbon (TOC) concentration was measured by a TOC-L CPH analyzer (Shimadzu, Japan). The EPS components of sludge, including soluble EPS (S-EPS), loosely bound EPS (L-EPS) and tightly bound EPS (T-EPS) were stratified using a method described by Niu *et al.* (2016b). The protein and polysaccharides in EPS were determined by the Lowry method and the anthrone method, respectively (Niu *et al.* 2016a; Wu *et al.* 2019).

The sludge moisture content tester (LXT-200s, Shenzhen Recht Co., China) was used to monitor the sludge moisture content. The CST was measured using a portable 304M instrument (Triton, UK) equipped with an 18 mm diameter funnel and a Whatman No. 17 chromatography-grade paper. The particle size was monitored using Mastersizer 3000 (Malvern Instruments Co., Malvern, UK). The sludge morphology was analyzed by using the JSM-7800F field emission scanning electron microscope (Hitachi, Japan). A Nicolet 5700 FTIR spectrometer (Nciolet 5700, Thermo Fisher, USA) was used to analyze the changes in functional groups in the sludge. The Nano ZS Zeta Potential Analyzer (Malvern Instruments Co., Malvern, UK) was used to analyze the charge of the sludge. These tests above were measured twice. A F-4700 fluorescence spectrophotometer (Thermo Fisher, USA) was used to measure the three-dimensional excitation-emission matrix (3-DEEM) spectroscopy (Wu *et al.* 2011). Based on the centrifugal method described by Jin *et al.* and an improved thermal analysis method using differential scanning calorimetry (DSC; DSC-60; Shimadzu, Japan) to measure bound water content (Jin *et al.* 2004; Wang *et al.* 2019). The heat uptake during the phase transition of free water (W_f) can be calculated with the following equation:

$$W_f = Q/\Delta H \tag{1}$$

where Q is the heat absorbed in the melting process and ΔH is the water heat of fusion. The amount of bound water can be acquired from the difference between the total water content and the free water content.

3. RESULTS AND DISCUSSION

3.1. Effects of conditioning on sludge dewatering performance

As can be seen from Figure 2, the water content, CST and Zeta potential of the raw sludge were different from those of the sludge samples after treatment with different treatment methods. The retention water content of sludge samples treated with PFS + PA was slightly lower than that of RS. The dewatering performance of sludge can be evaluated by sludge CST (Lo *et al.* 2001; Menon *et al.* 2020). In comparison, the CST of sludge samples treated with PFS + PA decreased from 403.8 s (RS) to 75.1 s (PFS), 117.1 s (PA) and 89 s (PFS + PA), respectively. Compared with unconditioned sludge, the pretreatment of sludge reduces the moisture content of the sludge cake. For example, the moisture content of the filtered cake decreased from 95.6% for RS to 88.7, 91.8 and 74.5% after conditioning with PFS, PA and PFS + PA, respectively. Zeta potential is one of the key factors affecting sludge dewatering (Liu *et al.* 2016). All pretreatment modes of sludge tested imparted a positive charge to the sludge. Compared with PA flocculant, PFS has a better neutralization effect. The Zeta potential values of these sludge samples are arranged: PFS + PA > PFS > PA > RS (see in Figure 2). Generally, the addition of coagulants will destroy the stability of colloidal flocculates by charge neutralization, and bridge-aggregation ability will be gained by flocculants.

3.2. Particle size

The decrease of sludge negative charge will result in the decrease of particle repulsive force and the enhancement of particle density (Yu *et al.* 2014). The use of coagulants and flocculants increases the particle size of sludge flocculate and the filtration rate of sludge (Wang *et al.* 2019). The positively charged PFS and PA neutralize the negative charge of the sludge flocs due to the electrostatic effect, which may destroy the stability of the flocs and accelerate the aggregation of the sludge flocs (Lau *et al.* 2017; Chi *et al.* 2018). Thus, the increase in particle size during the coagulation–flocculation process was caused by charge neutralization and bridge-aggregation. Moreover, adding PFS can reduce the thickness of the hydration shell formed by the colloid by compressing the electric double layer of the colloid (Ge *et al.* 2020). In addition, the positively charged Fe in PFS and the N in PA can adsorb many tiny negative colloids in the sediments to form large and dense flocs. Figure 3 illustrates changes in the size of the sludge flocs. As shown in Figure 3, when the flocculant (PA) was used alone, the maximum particle size was obtained, and when PFS was used alone, the sludge particle size was slightly increased compared to RS (Wu *et al.* 2006). These results reflected that in the sludge with the same or similar filtration performance, the use of flocculant PA had a

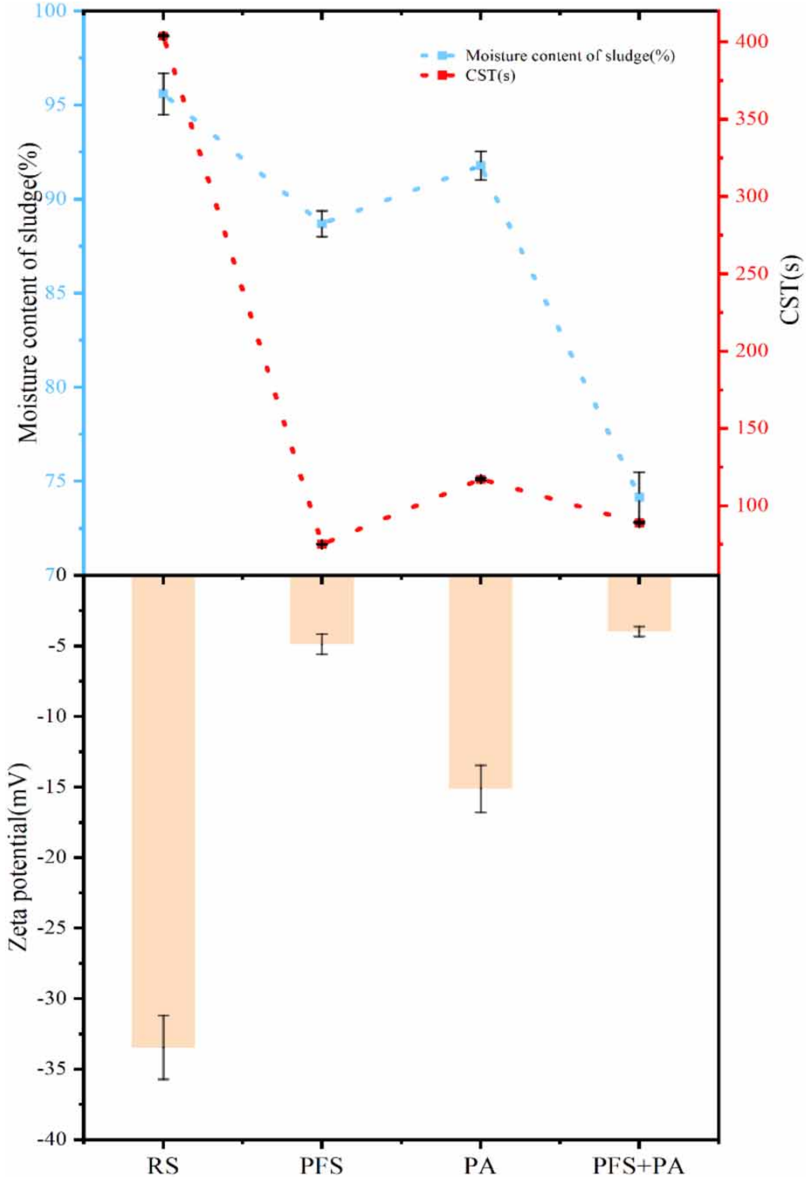
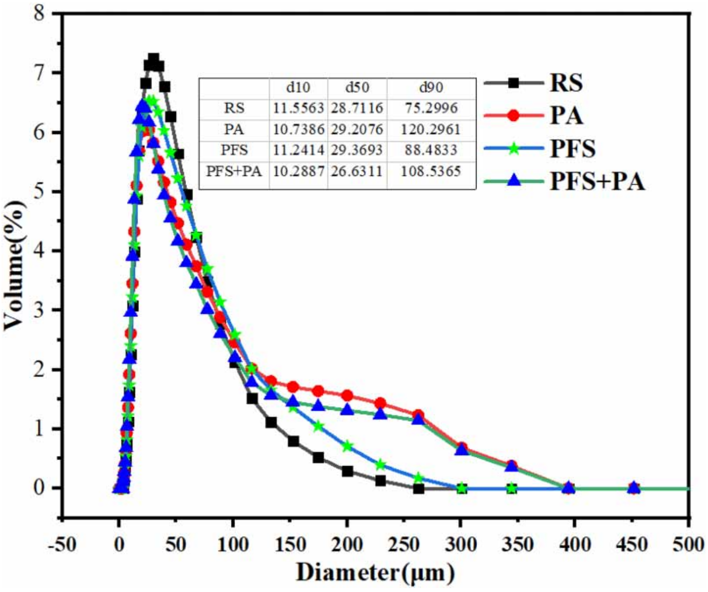


Figure 2 | Moisture content of filtered cake (%) after 3 min of filtration under a vacuum pressure of 0.05 MPa for sludge pretreated with or without PFS,PA and PFS + PA.

greater impact on the change in the particle size of sludge flocs than the use of coagulant PFS. In addition, the increase in the size of sludge flocs in the coagulation–flocculation process was smaller than that of sludge treated with flocculant alone, but larger than that when coagulant was used alone. According to the previous literature, the increase in particle size is helpful to the improvement of sludge dewatering performance (Zhen *et al.* 2012).

3.3. Composition of biopolymers in the sludge

EPS as the most important component of sludge can bind large amounts of water, especially bound water, which is believed to affect the sedimentation rate, flocculation and dewatering behavior (Peng *et al.* 2017). Many studies have demonstrated that the filtration performance of sediments depends mainly on EPS content, lower EPS content always improves the filtration performance of sediments and the release of EPS is beneficial for sludge dewatering (Chi *et al.* 2018). Therefore, the distribution and composition of EPS in sediments were studied (Figure 4). The changes in the main organic compounds in different parts of the EPS were measured. As shown in Figure 4(a) and 4(b), the content of PN and PS in the S-EPS of the



	d10	d50	d90
RS	11.5563	28.7116	75.2996
PA	10.7386	29.2076	120.2961
PFS	11.2414	29.3693	88.4833
PFS+PA	10.2887	26.6311	108.5365

Figure 3 | Effect of chemical conditioner dosages on the average particle size and particle size distributions.

sludge adjusted by coagulation alone or combined with flocculant decreased significantly (70.56, 70.31, 25.90 and 15.78%, respectively), whereas the biopolymer content of the sludge using PA alone is slightly different from that of RS. These results indicated that the dose of PA nearly caused changes of biopolymers in the sludge. Apart from this, the distributions of both PN and PS in L-EPS and T-EPS of the conditioned sludges and RS and the variations of PN and PS within L-EPS and T-EPS of these sludges were slightly different, and there was no obvious trend. Meanwhile, the variations in TOC contents in S-EPS, L-EPS and T-EPS before and after conditioning were similar to the changes in biopolymers detected in related EPS components (Figure 4(c)). The addition of PFS caused the reduction of TOC in S-EPS, while the addition of PA did not change significantly. In addition, there was no obvious trend of variation in TOC in L-EPS and T-EPS that conditioned sludges and RS.

These results implied that the part of EPS of sludge conditioned with coagulant PFS alone or in combination with flocculant PA was degraded and released into liquid, which destroyed the colloidal complex, reduced the viscosity of sediment solution, improved the filterability of the sediment and reduced the bound water in sediment cakes, which also indicated

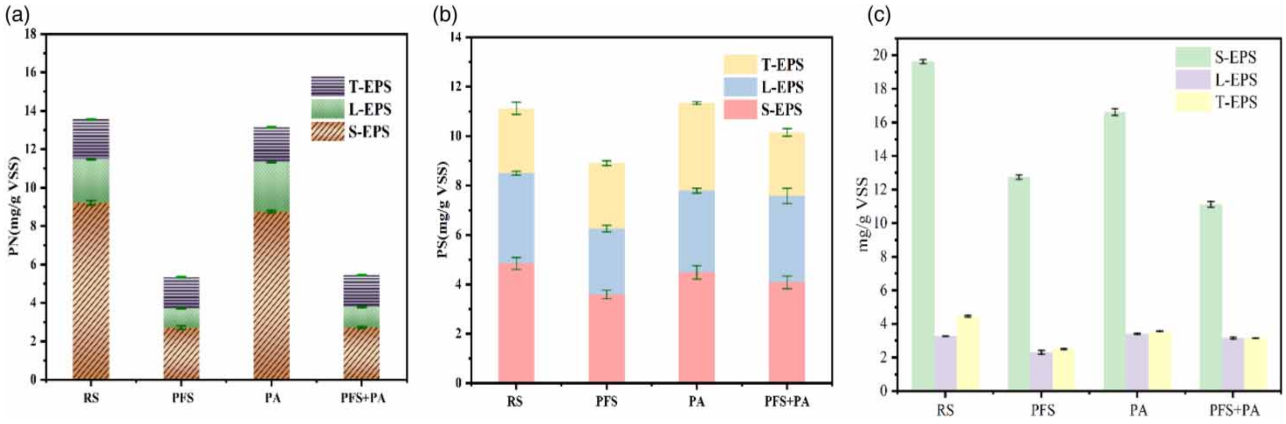


Figure 4 | (a) PN content of S-EPS, L-EPS and T-EPS for the sludge pretreated with or without PFS/PA/PFS + PA; (b) PS content of S-EPS, L-EPS and T-EPS for the sludge pretreated with or without PFS/PA/PFS + PA; (c) quantities of S-EPS, L-EPS and T-EPS in terms of TOC content for the sludge pretreated with or without PFS/PA/PFS + PA.

that the release of biopolymers in the sludge was mainly due to the use of the coagulant PFS instead of the flocculant PA used in this study (Chi *et al.* 2018; Wang *et al.* 2019). Moreover, since the amount of coagulant used in the coagulation–flocculation process was less than that used by coagulant alone, the use of coagulant alone appeared to have a better effect on the release of biopolymers. Moreover, since the amount of coagulant used in the coagulation–flocculation process was less than that used by coagulant alone, the use of coagulant alone appeared to have a better effect on the release of biopolymers. The coagulation–flocculation process enhanced sediment accumulation by reducing excess negative charge in the sludge, which was another important factor in improving dehydration.

Three-dimensional fluorescence spectroscopy was commonly used to detect NOM in water, which was highly sensitive and had a low detection limit (Zhang *et al.* 2021). There were more kinds of organic compounds with larger molecular weights in RS, and the fluorescence intensity of each molecular weight was larger. After PFS conditioning, the fluorescence intensity of small- and medium-molecule organic matter decreased, and the large-molecule organic matter disappeared. The possible reason was that the large molecular weight components of DOM may be removed by coagulation, and some proteins and polysaccharides with large molecular weight may be hydrolyzed into humic acid with small molecular weight (Zhang *et al.* 2020). The concentration of small molecular components of DOM also decreased, indicating that they were also removed by coagulation/flocculation (Li *et al.* 2021).

The main fluorescence intensity of the sludge filtrate under different treatment methods is shown in Figure 5. The results showed that the peaks of E_m/E_x at 390 nm/280–290 nm, 440–450 nm/250 nm were fulvic acid and E_m/E_x at 370–390 nm/290–310 nm were soluble by-product-like substances (see Figure 5(a)) (Jacquin *et al.* 2017). However, the peak of E_m/E_x in the filtrate conditioned by PFS was BOD_5 at 350–380 nm/210–230 nm, and the peak of E_m/E_x at 480–640 nm/210–270 nm was humic acid-like substances, which meant that PFS can hydrolyze large molecules into small molecules (see Figure 5(b)) (Cheng *et al.* 2019). As shown in Figure 5(c), the E_m/E_x peak of sludge filtrate conditioned by PA was mainly at 510–520 nm/210–230 nm, which was a fulvic acid-like substance, and the peak at 370 nm/290 nm was soluble by-product-like substance, which was similar to the component of RS, meant that PA cannot change the large molecular weight DOM of sludge into small molecular weight substances, resulting in poor dewaterability. Figure 5(d) shows the sludge filtrate after PFS + PA treatment. The peak of E_m/E_x at 330–380 nm/ 210–240 nm was BOD_5, the peak at 380 nm/280 nm was fulvic acid-like substances and humic acid substances, the peak at 490–550 nm/210–220 nm was fulvic acid-like substances, and peak at 420 nm/350 nm was related hydrophobic acids. It was noted in Figure 5(d) that the fluorescence intensity of the filtrate decreased, which meant that the components were more easily solidified after PFS + PA treatment. Therefore, after PFS + PA conditioning, the binding capacity of sludge particles with protein and humic acid was enhanced, and the flocs structure was more dense, leading to the reduction of sludge cake compressibility.

3.4. Effect of PFS and PA in sludge conditioning

The FTIR spectrum in Figure 6 illustrated that the spectrum of sludge changes when the sludge was conditioned by different types of dosages. The addition of PA did not have an important effect on the properties of the sludge, which mainly affected the area of 1,120–1,036 cm^{-1} (carbohydrates) (Zhu *et al.* 2012). The absorption peak at 877 cm^{-1} indicated the bending vibration of C–H. The addition of PFS destroyed the primary amide of fatty acids at 1,650 cm^{-1} and affected the carboxyl group at 1,400 cm^{-1}. The absorption peaks at 1,205 and 1,405 cm^{-1} showed the Fe–OH stretching vibration and the SO_4^{2-} group, respectively (Zhang *et al.* 2018). By comparing the spectra of sludge treated by PA PFS and PFS + PA, it can be found that PA had a major effect on 1,120–1,036 cm^{-1}, while PFS was used to destroy the amide bond and the carboxyl functional group of fatty acid at 1,650, 1,205 and 1,400 cm^{-1} in the sludge, PFS + PA was able to combine their advantages. Overall, FTIR analysis of PFS–PA did not reveal the formation of new chemical bonds.

In most cases, the EPS matrix is a complex network structure, and biopolymers combine with each other to form an organic compound (Zhang *et al.* 2016b). The polymer matrix constitutes activated sludge, which can retain a large amount of water, thereby affecting the dewatering of activated sludge (He *et al.* 2017). To verify the influence of the EPS matrix on the bound water, DSC thermograms and the change curve of total bound water content in different types of sludge are shown in Figure 7. In this study, the value of K was calculated to be 2.73×10^{-3} mg/mJ from the pure water thermogram (Figure 7(a)). It was found that the amount of pure water was proportional to the integral area of the DSC thermogram. The endothermic curve ranged from −5 to 8 °C and showed a similar reaction pattern to that described previously (Ealias *et al.* 2016; Chi *et al.* 2018). The DSC sediment sample thermograms were similar to that of pure water. Thereby, the bound water present in the sediment samples could be calculated by Equation (1).

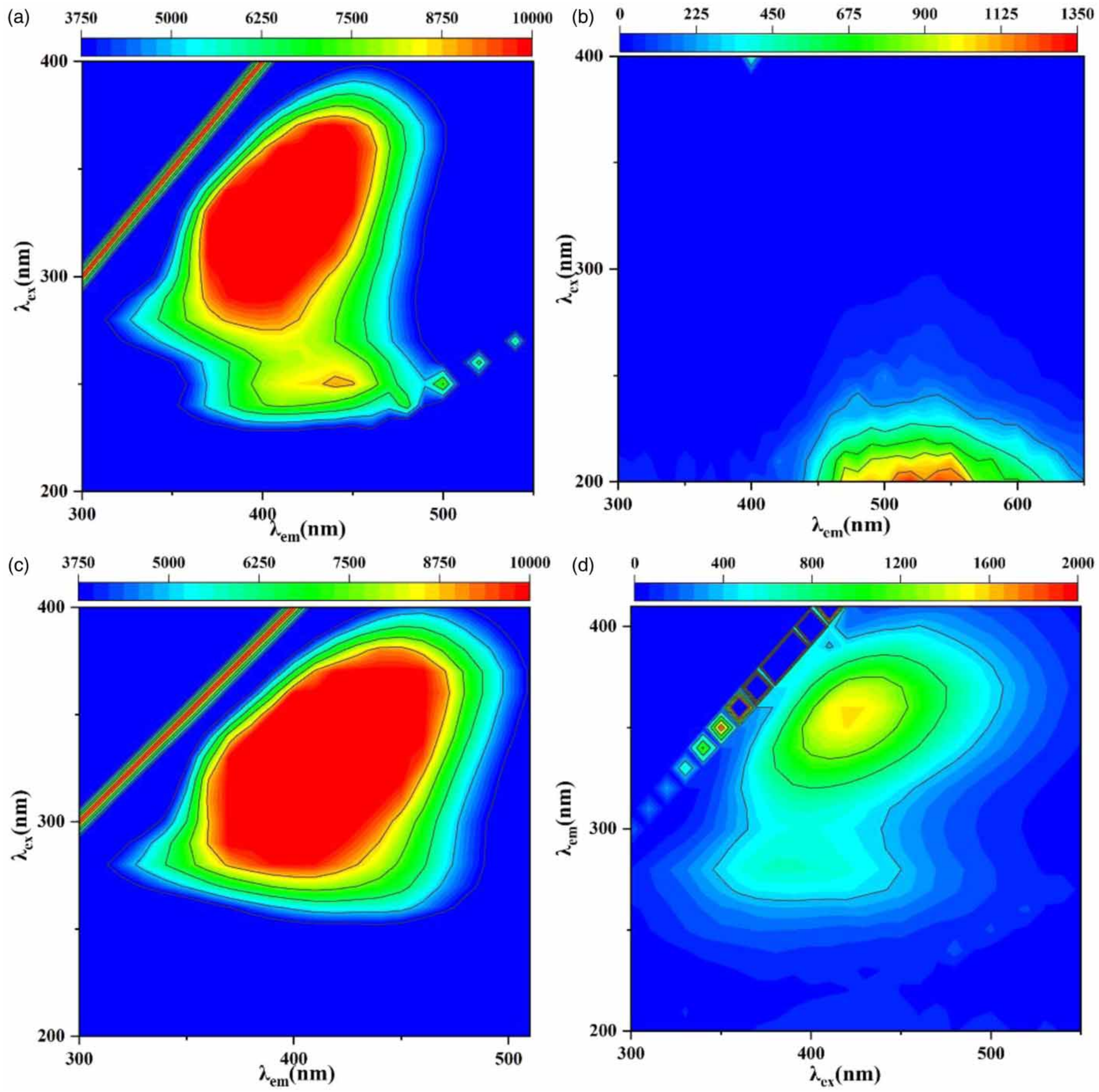


Figure 5 | Three-dimensional fluorescence images of filtrate in (a) RS, (b) conditioned by PFS, (c) conditioned by PA, and (d) conditioned by PFS + PA.

The bound water was reduced after the raw sludge was chemically conditioned (Figure 7(b)). After conditioning the sludge, the bound water of PFS and PFS + PA decreased from 0.79 g/g VSS in the raw sludge to 0.64 and 0.63 g/g VSS, respectively, and the bound water was reduced to 0.77 g/g VSS when PA was used. This significant decline indicated that the bound water stored in the colloid was converted to free water under the action of PFS, thus improving sludge dewatering. Therefore, some bound water was transformed into free water with PFS, resulting in more water removal and lower water content in the sludge cakes.

3.5. Rheological profile of the sludge samples

The dewatering performance of sludge largely depends on the solid–liquid separation in the sludge (Stickland 2015; Wang *et al.* 2019). The rheological properties of these sludge systems were studied to determine the influence of physicochemical

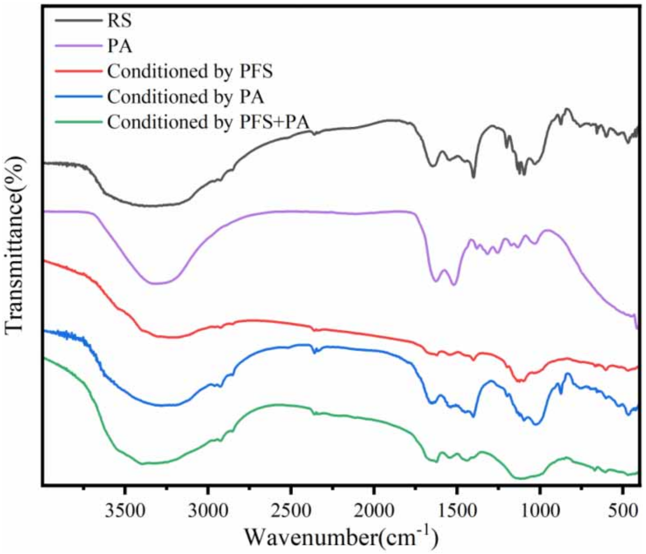


Figure 6 | FTIR spectra of RS, PA and conditioned sludge by PFS, PA and PFS + PA.

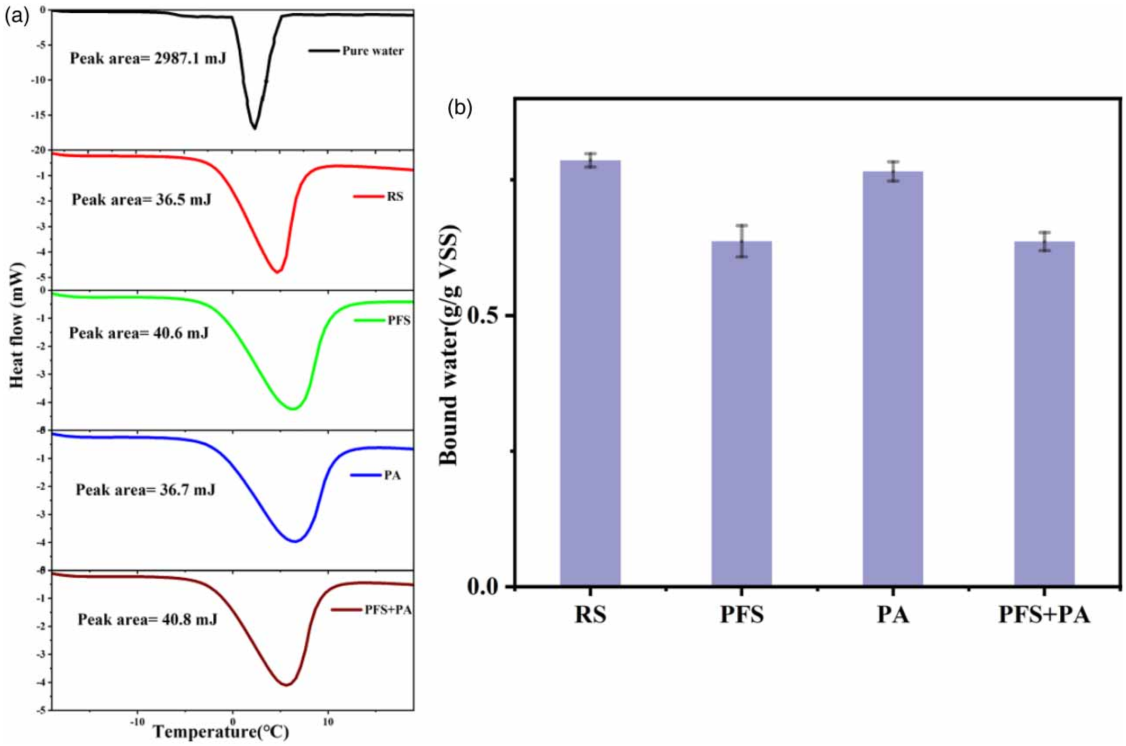


Figure 7 | (a) DSC thermograms of pure water and sediments and (b) bound water of RS and sediments conditioned with PFS, PA and PFS + PA.

properties and bound water changes in the sludge. Figure 8(a) illustrates the overall rheological behavior of sludge samples from low shear to high shear. All pretreated and unpretreated sludge samples showed non-Newtonian characteristics and shear-thinning behavior. Notably, sludge conditioned with PA alone or jointly conditioned with PFS initially showed greater network strength at low shear rates compared to RS, while greater shear dissipated the network and brought about a lower

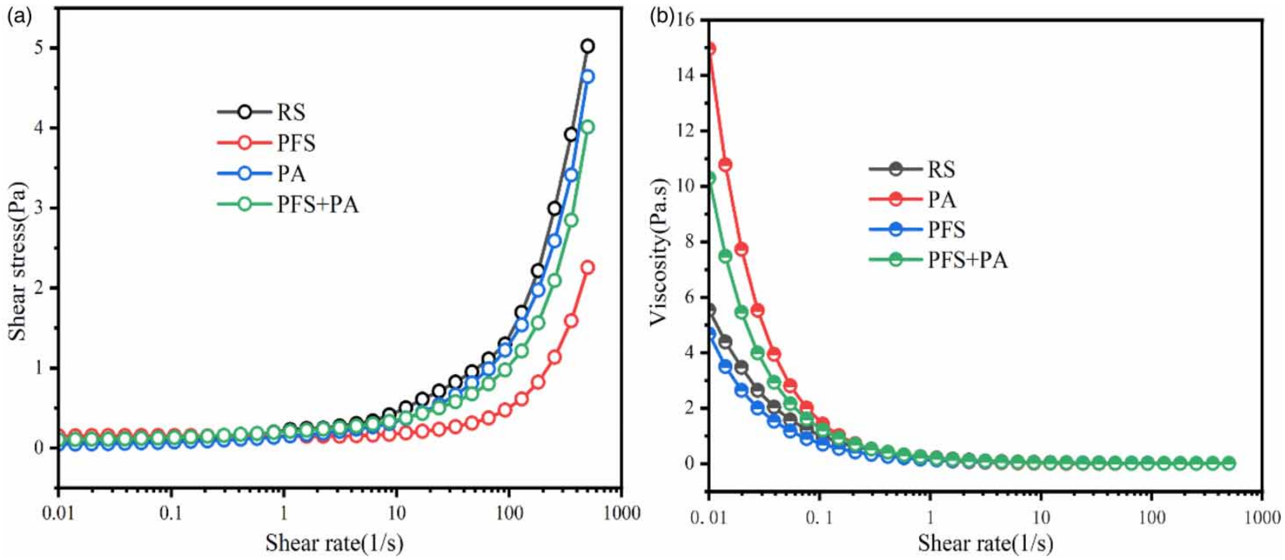


Figure 8 | Dynamic strain sweep curves of raw and conditioned sludge.

apparent viscosity. These results were consistent with previous studies in the literature regarding the rheological behavior of the PA-conditioned sludge system and slightly improved the effect of PAM (Yousefi *et al.* 2020b). Namely, sludge flocs and PA had better resistance to external stress and reduce erosion or fracture. However, as the reduction of bound water resulted in more water to flow, the greater shear force dissipated the network in the sludge and better flowability of the sludge was achieved. From low shear to high shear, the apparent viscosity of sludge was lower than RS when PFS is used alone (as is shown in Figure 8(b)). In the coagulation–flocculation process, sludge flocs first underwent the disintegration of microbial cells or sludge flocs caused by PFS. The dose of flocculant (PA) caused the formation of a large agglomeration from these small destabilized colloid particles. As a result, the flow curve of sludge in the coagulation–flocculation process was similar to the flow curve of PA-conditioned sludge. However, in the coagulation–flocculation process, the apparent viscosity of the sludge conditioned by PFS or PFS + PA was the lowest, indicating that the sludge obtained the best fluidity during the coagulation–flocculation process.

3.6. Influence of sludge filtrate

In sludge treatment, the filtrate is equally important, but it is found that the sludge filtrate is always ignored in the literature and enterprises are often unwilling to pay too much attention to the treatment of sludge filtrate. The excessive addition of reagents may lead to excessive metal or inorganic ions in the filtrate, which may increase the front-end treatment pressure of the plant, or the effect of diluting sludge with the filtrate becomes worse. The on-site process of sludge obtained in this experiment was PFS + PAM, which can help with dewatering, but it brought many problems. For example, the Fe ion content produced by a large amount of PFS in the filtrate reaches 10,638.6 mg/L, leading to the sewage treatment enterprises being unwilling to treat it. It increased the cost of sludge treatment. In addition, the high amount of PAM also resulted in high COD levels up to 760 mg/L. Therefore, it was urgent to find a method that adapted to the on-site facilities and reduced the cost of subsequent treatment of the filtrate.

When using PFS + PA instead of PFS + PAM to treat this sludge, not only the use of PFS and PA was less than that of PFS and PAM in the original process, but also the relevant indicators in the filtrate decreased. Compared with the original treatment method, the Fe ion concentration had dropped by 97.8% from 10,638.58 to 231.5 mg/L, SO_4^{2-} dropped by 73.5% from 13,300 to 3,520 mg/L and S^{2-} dropped by 99.6% from 2.37 to 0.01 mg/L (as is shown in Figure 9(a)–9(d)). PA is a strong cationic linear homopolymer with good water solubility, and it can be compounded with inorganic coagulants to enhance its flocculation effect, thus greatly reducing the use of inorganic coagulant PFS. It provides a more positive charges per unit mass than currently used cationic products. Due to this feature, its consumption was also much lower than CPAM, and the COD in the filtrate decreased from 760 to 166 mg/L (as is shown in Figure 8(b)).

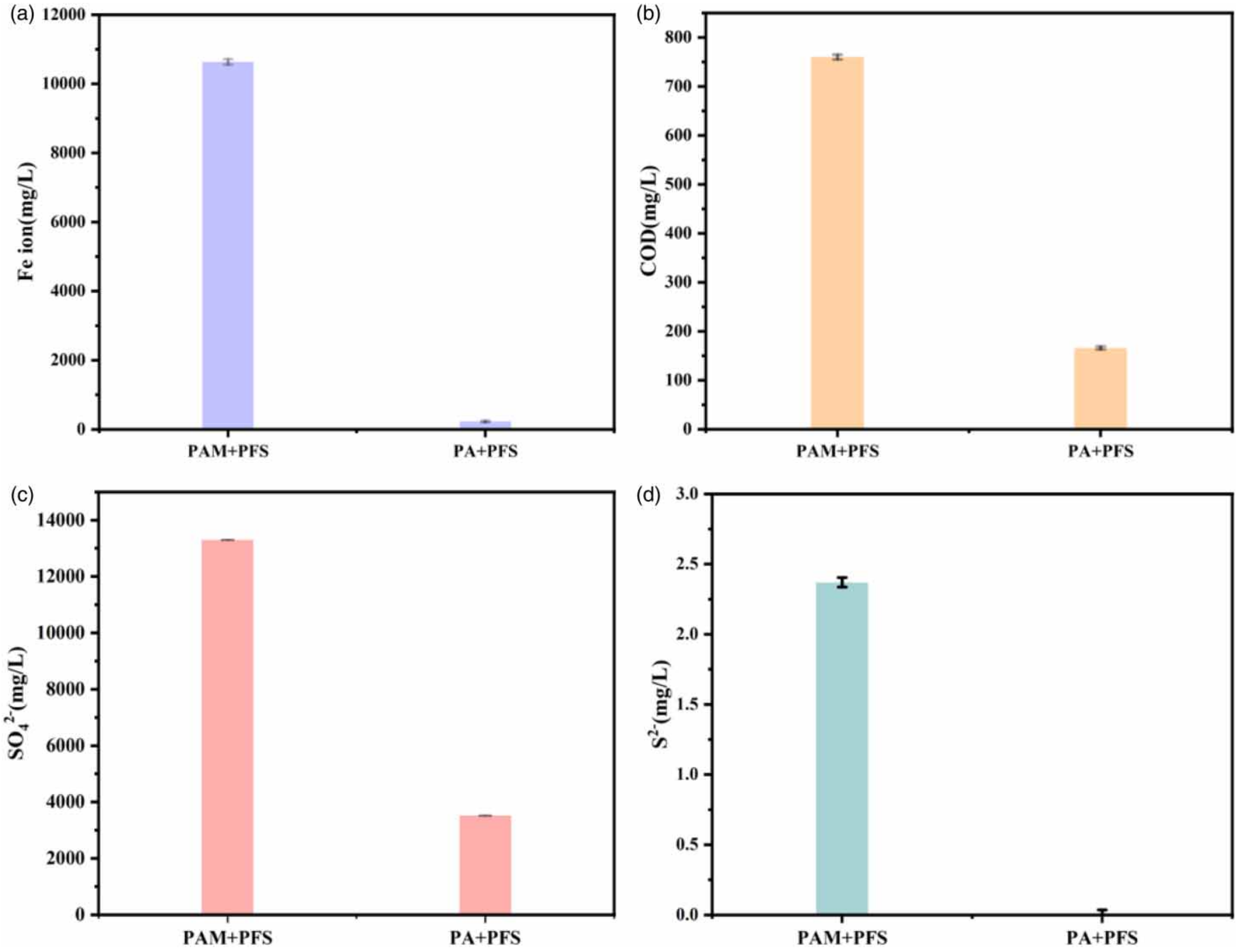


Figure 9 | The concentration changes of (a) Fe ion, (b) COD, (c) SO_4^{2-} and (d) S^{2-} in sludge filtrate of different conditions.

3.7. Implication of conditioner on the floc internal structure and dewaterability

The characteristics of conventional PAM conditioning sludge are large particles, loose structure, and high compressibility, and the water content dewatering is about 80% (Wu *et al.* 2019). It was stated that the obvious phenomenon of thixotropy meant that it was difficult to transport fluids and consumed more energy to dewater the sludge (Tang *et al.* 2017). The unit mass of PA can provide more positive charge than cationic PAM, which can be very helpful for sludge dewatering. The influence of PFS and PA on the above problems can be explained by the potential relationship between rheological behavior and the regulation of sludge particle size. PFS made conditioned sludge flocs more dispersed under shear force, weakened the bridging effect and eventually led to the decreasing particle size of conditioned sludge. Moreover, the smaller particle size of sludge conditioned by PFS meant less intra-floc water and rigid structure, decreasing the compressibility and energy-consuming.

The effect of PA on sludge dewatering was more significant than that of PFS, indicating that PFS disrupted the bridging and neutralization of PA and reduces the strength of flocs. The effect of PA + PFS on CST and particle size after sludge treatment was more significant than that of PA and PFS, respectively, indicating that PFS enhanced the function of PA and increased the floc strength. Figure 10 presents the possible mechanism of conditioning sludge flocs before and after. PFS slightly destroyed the flocculation of PA, but first neutralized the organic fragments as the core of condensation, which was conducive to linear PA bridging to form large aggregates.

It should be noted that the coagulation–flocculation method increased the overall size of the conditioned sludge (Figure 3), but the results provided by scanning electron microscope (SEM) (Figure 10) did not indicate that the larger flocs had a

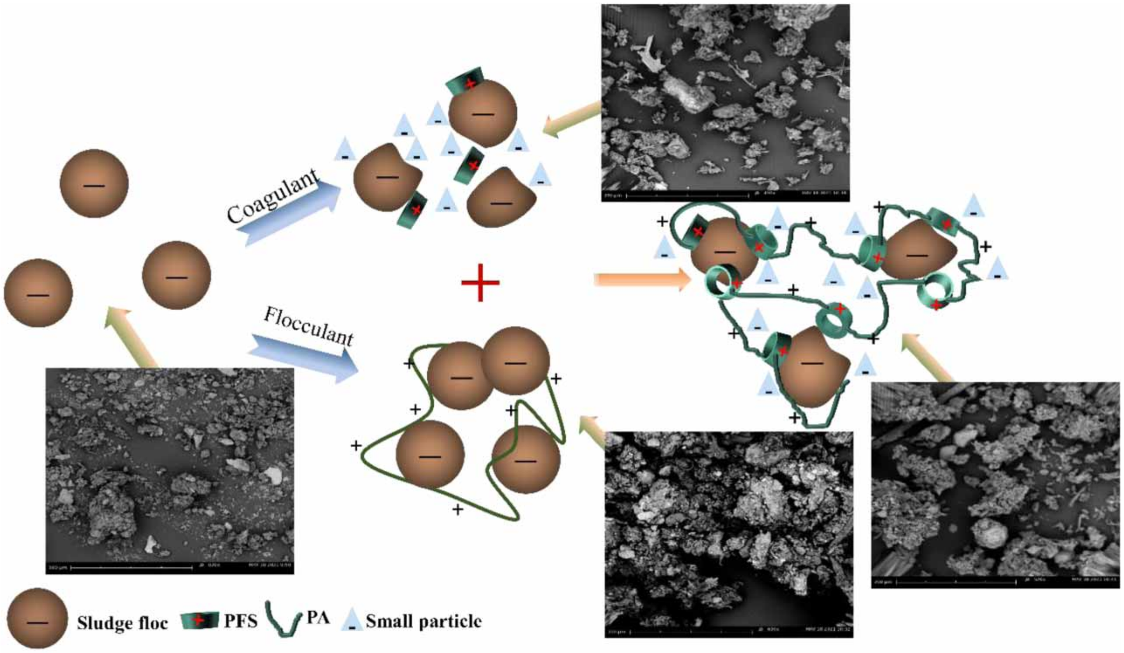


Figure 10 | Proposed mechanism for the coagulation– flocculation process.

stronger internal structure. Floc strength is related to the type of conditioner and the chemical structure itself (Wu *et al.* 2019). As conventional dewaterability measuring techniques, CST was found to have a good correlation with soluble biopolymers (To *et al.* 2016a). Although CST successfully measured the filtration rate, it failed to predict the maximum cake solid content that could be achieved during the overall dewatering process (To *et al.* 2016b). Because the laboratory conditions are different from the actual dewatering situation, the selection of the type and dosage of the conditioner depends on the dewaterability and filterability of the conditioned sludge, and the difference in the flocculation formation process and the flocculation strength among conditioned sludge samples need to be studied by more methods.

4. CONCLUSION

This study investigated the combined use of inorganic coagulant polyferric sulfate and cationic PA in sludge dewatering. The main findings of this study were that the sludge conditioned by coagulant and flocculant had better dewatering performance compared to the individual use of coagulant or flocculant because of the much lower dosage and higher efficiency in reducing water content. The mechanism is the synergy of coagulation and flocculation to most effectively reduce the bound water and the lowest apparent viscosity, and the PA provides more cations per unit mass than PAM, so the amount of PFS and PA used is less than that of traditional coagulants and flocculants. PFS + PA can neutralize the charge of sludge and can also remove macromolecular components in DOM through coagulation/flocculation or hydrolyze macromolecular components into small- and medium-molecular weight components, thereby reducing the concentration of small- and medium-molecular weight components. Moreover, on the premise of maintaining good sludge dewatering effect, the addition of PA reduces the amount of PFS, resulting in an extreme reduction of Fe ions and sulfate ions in sludge filtrate, which is conducive to the subsequent treatment of filtrate. The combined use of coagulant PFS and cationic PA is a feasible and potential method to improve the dewatering performance of sludge and the properties of filtrate.

ACKNOWLEDGEMENTS

The authors are grateful for financial support from the National Natural Science Foundation of China (No. 51978491). I am very grateful to my tutor Prof. Li Fengting for his support and help as always. And thanks to Prof. Wu Yi-nan for his continued help. Thanks to Mr Yuan Xiao for taking the trouble to assist. Thanks also to Ms Qian Yuhua for her perseverance.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

REFERENCES

Chen, Z., Zhang, W. J., Wang, D. S., Ma, T., Bai, R. Y. & Yu, D. Z. 2016 Enhancement of waste activated sludge dewaterability using calcium peroxide pre-oxidation and chemical re-flocculation. *Water Research* **103**, 170–181.

Cheng, H. W., Ai, J., Zhang, W. J., Fu, X. M., Du, Y. J. & Wang, D. S. 2019 Preparation of biological activated carbon (BAC) using aluminum salts conditioned sludge cake for the bio-refractory organic contaminants removal from anaerobically digested liquor. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **561**, 89–100.

Chi, Y. L., Guo, L. F., Xu, Y., Liu, J. W., Xu, W. & Zhao, H. Z. 2018 Rapid removal of bound water from dredged sediments using novel hybrid coagulants. *Separation and Purification Technology* **205**, 169–175.

Ealias, A. M., Jose, J. V. & Saravanakumar, M. P. 2016 Biosynthesised magnetic iron nanoparticles for sludge dewatering via Fenton process. *Environmental Science and Pollution Research* **23** (21), 21416–21430.

Ge, D. D., Xiao, J. M., Bian, C., Yuan, H. P. & Zhu, N. W. 2020 Exploring the efficacy and mechanism of tannic acid/Fe^{3+} conditioning for enhancing waste activated sludge dewaterability. *Separation and Purification Technology* **240**, 116643–52.

Guan, R. P., Yuan, X. Z., Wu, Z. B., Wang, H., Jiang, L. B., Li, Y. F. & Zeng, G. M. 2017 Functionality of surfactants in waste-activated sludge treatment: a review. *Science of the Total Environment* **609**, 1433–1442.

He, D. Q., Zhang, Y. J., He, C. S. & Yu, H. Q. 2017 Changing profiles of bound water content and distribution in the activated sludge treatment by NaCl addition and pH modification. *Chemosphere* **186**, 702–708.

Hennecke, D., Bauer, A., Herrchen, M., Wischerhoff, E. & Gores, F. 2018 Cationic polyacrylamide copolymers (PAMs): environmental half life determination in sludge-treated soil. *Environmental Sciences Europe* **30**, 1–13.

Jacquin, C., Lesage, G., Traber, J., Pronk, W. & Heran, M. 2017 Three-dimensional excitation and emission matrix fluorescence (3DEEM) for quick and pseudo-quantitative determination of protein- and humic-like substances in full-scale membrane bioreactor (MBR). *Water Research* **118**, 82–92.

Jin, B., Wilen, B. M. & Lant, P. 2004 Impacts of morphological, physical and chemical properties of sludge flocs on dewaterability of activated sludge. *Chemical Engineering Journal* **98** (1–2), 115–126.

Lau, S. W., Sen, T. K., Chua, H. B. & Ang, H. M. 2017 Conditioning of synthetic sludge and anaerobically digested sludge using chitosan, organic polyelectrolytes and inorganic metal cations to enhance sludge dewaterability. *Water Air and Soil Pollution* **228** (9), 1–13.

Lee, C. S., Robinson, J. & Chong, M. F. 2014 A review on application of flocculants in wastewater treatment. *Process Safety and Environmental Protection* **92** (6), 489–508.

Li, L. Q., Song, Z. Z., Zhang, W. J., Wu, H. J., Liu, W. W., Yu, J. X. & Wang, D. S. 2021 Performance and mechanisms of dredged sludge dewaterability enhancement with slag-based polymeric titanium aluminum coagulant. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **630**, 127514.

Liu, J., Wei, Y., Li, K., Tong, J., Wang, Y. & Jia, R. 2016 Microwave-acid pretreatment: a potential process for enhancing sludge dewaterability. *Water Research* **90**, 225–234.

Lo, I. M. C., Lai, K. C. K. & Chen, G. H. 2001 Salinity effect on mechanical dewatering of sludge with and without chemical conditioning. *Environmental Science & Technology* **35** (23), 4691–4696.

Menon, U., Suresh, N., George, G., Ealias, A. M. & Saravanakumar, M. P. 2020 A study on combined effect of Fenton and free nitrous acid treatment on sludge dewaterability with ultrasonic assistance: preliminary investigation on improved calorific value. *Chemical Engineering Journal* **382**, 123035.

Niu, M. Q., Zhang, W. J., Wang, D. S., Chen, Y. & Chen, R. L. 2013 Correlation of physicochemical properties and sludge dewaterability under chemical conditioning using inorganic coagulants. *Bioresource Technology* **144**, 337–343.

Niu, T. H., Zhou, Z., Ren, W. C., Jiang, L. M., Li, B. Y., Wei, H. J., Li, J. & Wang, L. C. 2016a Effects of potassium peroxymonosulfate on disintegration of waste sludge and properties of extracellular polymeric substances. *International Biodeterioration & Biodegradation* **106**, 170–177.

Niu, T. H., Zhou, Z., Shen, X. L., Qiao, W. M., Jiang, L. M., Pan, W. & Zhou, J. J. 2016b Effects of dissolved oxygen on performance and microbial community structure in a micro-aerobic hydrolysis sludge in situ reduction process. *Water Research* **90**, 369–377.

Peng, H. L., Zhong, S. X., Xiang, J. X., Lin, Q. T., Yao, C., Dong, J. H., Yin, G. C., Yao, K., Zeng, S. Y. & Zhong, J. 2017 Characterization and secondary sludge dewatering performance of a novel combined aluminum-ferrous-starch flocculant (CAFS). *Chemical Engineering Science* **173**, 335–345.

Qi, Y., Thapa, K. B. & Hoadley, A. F. A. 2011 Application of filtration aids for improving sludge dewatering properties – a review. *Chemical Engineering Journal* **171** (2), 373–384.

Stickland, A. D. 2015 Compressional rheology: a tool for understanding compressibility effects in sludge dewatering. *Water Research* **82**, 37–46.

Tang, B., Feng, X. F., Huang, S. S., Bin, L. Y., Fu, F. L. & Yang, K. H. 2017 Variation in rheological characteristics and microcosmic composition of the sewage sludge after microwave irradiation. *Journal of Cleaner Production* **148**, 537–544.

Teh, C. Y., Budiman, P. M., Shak, K. P. Y. & Wu, T. Y. 2016 Recent advancement of coagulation-flocculation and its application in wastewater treatment. *Industrial & Engineering Chemistry Research* **55** (16), 4363–4389.

To, V. H. P., Nguyen, T. V., Vigneswaran, S., Nghiem, L. D., Murthy, S., Bustamante, H. & Higgins, M. 2016a Modified centrifugal technique for determining polymer demand and achievable dry solids content in the dewatering of anaerobically digested sludge. *Desalination and Water Treatment* **57** (53), 25509–25519.

To, V. H. P., Nguyen, T. V., Vigneswaran, S. & Ngo, H. H. 2016b A review on sludge dewatering indices. *Water Science and Technology* **74** (1), 1–16.

Tunçal, T. 2021 Enhancing sludge conditioning and dewatering characteristics by active surfaces modified with fast recombining immobilized nanoparticles. *Drying Technology* **40** (10), 2128–2139.

Tunçal, T. & Mujumdar, A. S. 2022 Modern techniques for sludge dewaterability improvement. *Drying Technology* 1–13.

Wang, H. F., Ma, Y. J., Wang, H. J., Hu, H., Yang, H. Y. & Zeng, R. J. 2017a Applying rheological analysis to better understand the mechanism of acid conditioning on activated sludge dewatering. *Water Research* **122**, 398–406.

Wang, H. F., Wang, H. J., Hu, H. & Zeng, R. J. 2017b Applying rheological analysis to understand the mechanism of polyacrylamide (PAM) conditioning for sewage sludge dewatering. *RSC Advances* **7** (48), 30274–30282.

Wang, H. F., Hu, H., Wang, H. J. & Zeng, R. J. 2019 Combined use of inorganic coagulants and cationic polyacrylamide for enhancing dewaterability of sewage sludge. *Journal of Cleaner Production* **211**, 387–395.

Wu, J. L., Chen, F. T., Huang, X., Geng, W. Y. & Wen, X. H. 2006 Using inorganic coagulants to control membrane fouling in a submerged membrane bioreactor. *Desalination* **197** (1–3), 124–136.

Wu, J., Zhang, H., He, P. J. & Shao, L. M. 2011 Insight into the heavy metal binding potential of dissolved organic matter in MSW leachate using EEM quenching combined with PARAFAC analysis. *Water Research* **45** (4), 1711–1719.

Wu, B. R., Su, L. H., Dai, X. H. & Chai, X. L. 2018 Development of sludge-derived mesoporous material with loaded nano cao$_2$ and doped Fe for re-utilization of dewatered waste-activated sludge as dewatering aids. *Chemical Engineering Journal* **335**, 161–168.

Wu, W., Zhou, Z., Chen, L. Y., Chen, G., Zhang, Y., Jiang, L. Y., Qiu, Z., He, K. K. & Wu, Z. C. 2019 Conditioning for excess sludge and ozonized sludge by ferric salt and polyacrylamide: orthogonal optimization, rheological characteristics and floc properties. *Chemical Engineering Journal* **373**, 1081–1090.

Yang, P., Li, D. D., Zhang, W. J., Wang, N., Yang, Z. Y., Wang, D. S. & Ma, T. 2019 Flocculation-dewatering behavior of waste activated sludge particles under chemical conditioning with inorganic polymer flocculant: effects of typical sludge properties. *Chemosphere* **218**, 930–940.

Yousefi, S. A., Nasser, M. S., Hussein, I. A. & Benamor, A. 2020a Enhancement of flocculation and dewaterability of a highly stable activated sludge using a hybrid system of organic coagulants and polyelectrolytes. *Journal of Water Process Engineering* **35**, 101237.

Yousefi, S. A., Nasser, M. S., Hussein, I. A., Benamor, A. & El-Naas, M. H. 2020b Influence of polyelectrolyte structure and type on the degree of flocculation and rheological behavior of industrial MBR sludge. *Separation and Purification Technology* **233**, 116001.

Yu, J., Guo, M. H., Xu, X. H. & Guan, B. H. 2014 The role of temperature and CaCl$_2$ in activated sludge dewatering under hydrothermal treatment. *Water Research* **50**, 10–17.

Yu, W. B., Yang, J. K., Shi, Y. F., Song, J., Shi, Y., Xiao, J., Li, C., Xu, X. Y., He, S., Liang, S., Wu, X. & Hu, J. P. 2016 Roles of iron species and pH optimization on sewage sludge conditioning with Fenton's reagent and lime. *Water Research* **95**, 124–133.

Zhang, Z. Q., Lin, B., Xia, S. Q., Wang, X. J. & Yang, A. M. 2007 Production and application of a novel bioflocculant by multiple-microorganism consortia using brewery wastewater as carbon source. *Journal of Environmental Sciences* **19** (6), 667–673.

Zhang, J., Zhang, J., Tian, Y., Li, N., Kong, L. C., Sun, L., Yu, M. & Zuo, W. 2016a Changes of physicochemical properties of sewage sludge during ozonation treatment: correlation to sludge dewaterability. *Chemical Engineering Journal* **301**, 238–248.

Zhang, W. J., Cao, B. D., Wang, D. S., Ma, T., Xia, H. & Yu, D. H. 2016b Influence of wastewater sludge treatment using combined peroxyacetic acid oxidation and inorganic coagulants re-flocculation on characteristics of extracellular polymeric substances (EPS). *Water Research* **88**, 728–739.

Zhang, J. H., Yang, H., Li, W., Wen, Y., Fu, X. M. & Chang, J. 2018 Variations of sludge characteristics during the advanced anaerobic digestion process and the dewaterability of the treated sludge conditioning with PFS, PDMDAAC and synthesized PFS-PDMDAAC. *Water Science and Technology* **78** (5), 1189–1198.

Zhang, W. J., Cheng, H. W., Peng, S. N., Li, D. D., Gao, H. Y. & Wang, D. S. 2020 Performance and mechanisms of wastewater sludge conditioning with slag-based hydrotalcite-like minerals (Ca/Mg/Al-LDH). *Water Research* **169**, 115265.

Zhang, W. J., Tang, M. Y., Li, D. D., Yang, P., Xu, S. W. & Wang, D. S. 2021 Effects of alkalinity on interaction between EPS and hydroxy-aluminum with different speciation in wastewater sludge conditioning with aluminum based inorganic polymer flocculant. *Journal of Environmental Sciences* **100**, 257–268.

Zhen, G. Y., Lu, X. Q., Wang, B. Y., Zhao, Y. C., Chai, X. L., Niu, D. J., Zhao, A. H., Li, Y. Y., Song, Y. & Cao, X. Y. 2012 Synergetic pretreatment of waste activated sludge by Fe(II)-activated persulfate oxidation under mild temperature for enhanced dewaterability. *Bioresource Technology* **124**, 29–36.

Zhu, L., Qi, H. Y., Lv, M. L., Kong, Y., Yu, Y. W. & Xu, X. Y. 2012 Component analysis of extracellular polymeric substances (EPS) during aerobic sludge granulation using FTIR and 3D-EEM technologies. *Bioresource Technology* **124**, 455–459.

First received 7 July 2022; accepted in revised form 31 January 2023. Available online 13 February 2023