

# 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

Jinghui Zhang, Hong Yang, Wei Li, Yang Wen, Xingmin Fu and Jing Chang

## ABSTRACT

Anaerobic digestion with thermal hydrolysis pretreatment (THP), also called advanced anaerobic digestion (AAD), is a mainstream technology for sludge treatment. AAD changes sludge, it can degrade extracellular polymeric substances (EPS), release EPS from the sludge, and alter the particle size distribution. We synthesized PFS–PDMDAAC from the inorganic coagulant polyferric sulfate (PFS) and the organic coagulant polymer polydimethyldiallylammonium chloride (PDMDAAC) in various PFS:PDMDAAC weight ratios. We investigated the effects of PFS–PDMDAAC pretreatment on AAD sludge dewaterability, and developed an explanation for them. Capillary suction time (CST) was used as a measure of sludge dewaterability. Dissolved organic matter, the three-dimensional excitation emission matrix, particle size ( $d_{0.5}$ ), zeta potential, and sludge microstructure were observed in order to explain changes in sludge dewaterability that resulted from different compositions and dosages of coagulants. Treatment with PFS alone gave no significant improvement in sludge dewaterability. PDMDAAC used alone greatly improved sludge dewaterability. Synthesized PFS–PDMDAAC which had a relatively high proportion of PDMDAAC by weight performed similarly to PDMDAAC. PFS–PDMDAAC synthesized in the ratio (PDF:PDMDAAC) 1:5 by weight provided good dewaterability. The dosage can be reduced by 16.7% of the dosage for conditioning by PDMDAAC alone.

**Key words** | advanced anaerobic digestion sludge, dewaterability, polymerization

**Jinghui Zhang**  
**Hong Yang** (corresponding author)  
 Department of Civil Engineering,  
 Beijing University of Technology,  
 100 Pingleyuan, Beijing 100124,  
 China  
 E-mail: [yhong106@126.com](mailto:yhong106@126.com)

**Jinghui Zhang**  
**Wei Li**  
**Yang Wen**  
**Xingmin Fu**  
**Jing Chang**  
 Beijing Drainage Group Co. Ltd,  
 B 37 Chegongzhuang Street North Lane, Beijing  
 100044,  
 China

## LIST OF ABBREVIATIONS

3D-EEM	three-dimensional excitation emission matrix	PFS	polyferric sulfate
AAD	advanced anaerobic digestion	RS	raw sludge
AS	AAD sludge	SEM	scanning electron micrograph
CST	capillary suction time	THP	thermal hydrolysis pretreatment
DOC	dissolved organic carbon	TSS	total suspended solids
DOM	dissolved organic matter	VSS	volatile suspended solids
EPS	extracellular polymeric substances	Wr	weight ratios
FTIR	Fourier transform infrared spectroscopy	WWTP	wastewater treatment plant
PDMDAAC	polymer polydimethyldiallylammonium chloride	XRD	X-ray powder diffraction
PFAC	polymeric ferric aluminum chloride		

This is an Open Access article distributed under the terms of the Creative Commons Attribution Licence (CC BY-NC-ND 4.0), which permits copying and redistribution for non-commercial purposes with no derivatives, provided the original work is properly cited (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

doi: 10.2166/wst.2018.387

## INTRODUCTION

Wastewater treatment produces large quantities of sludge. Sewage sludge management is a large challenge for water

industries. By the end of June 2017, China treated 178 million m<sup>3</sup>/d wastewater. At a rate of 1.2 t dry sludge per 10,000 m<sup>3</sup> sewage, annual sludge generation in China in 2017 was 38.98 Mt (with 80% moisture content).

The Norwegian company Cambi developed a thermal hydrolysis process (THP) that heats the sludge to temperatures of 150 °C to 165 °C under high pressure before anaerobic digestion in order to increase the rate and extent of digestion. The combination of THP and anaerobic digestion is known as advanced anaerobic digestion (AAD), which is becoming the major form of sludge treatment in China. Sludge dewatering is critical to reducing downstream transport and processing costs. Plate and frame filter presses have been used in Beijing for deep dewatering of AAD sludge, producing >1,200 t DS/d. An effective AAD sludge dewatering reagent suitable for a large scale practical project is desperately needed. However, few such dewatering reagents have been identified or studied.

Many inorganic compounds and organic polymers have been widely used for their solid–water separation performance both in research and in practice. Inorganic coagulants do not aggregate floc as well as organic polymeric coagulants. High cost limits the usage of organic polymers although they also have the advantages of less dosage being needed and less pH dependence.

Inorganic compounds and organic polymers are conventionally added separately to sludge, requiring two reagent addition systems. To avoid this problem, research has been directed towards the synthesis of new composite inorganic–organic polymers which result in better sludge dewaterability than traditional inorganic coagulants, and cost less than organic polymers (Wang *et al.* 2016; Liao *et al.* 2017). Sun (Sun *et al.* 2012) synthesized polymeric ferric aluminum chloride (PFAC) and the organic coagulant polymer polydimethyldiallylammonium chloride (PDMDAAC), and found that the composite coagulants performed better than PFAC alone in reducing turbidity and removing dissolved organic matter (DOM). They identified bridge formation and charge neutralization as the main coagulation mechanisms. Wang synthesized chitosan-g-PDMDAAC, a highly effective activated sludge flocculant (Wang *et al.* 2016).

PFS is an inorganic reagent that is widely used to improve sludge dewaterability. Preliminary toxicity studies suggest that drinking water treated with PFS is safe for human consumption. PDMDAAC is a highly-charged cationic polymer flocculant that is non-toxic, extremely soluble and cost-effective to use. A literature search shows that the use of synthetic PFS–PDMDAAC to improve sludge dewaterability has not been investigated. This study is intended to gain insight into the dosage (by weight ratio, Wr) of PFS–PDMDAAC as a conditioner for AAD sludge and its effects on sludge dewaterability. Sludge dewaterability was measured by capillary suction time (CST). The conditioning mechanism was investigated by analyzing DOM, the three-dimensional excitation emission matrix (3D-EEM), particle size ( $d_{0.5}$ ), zeta potential, sludge microstructure, and any correlations between them.

## MATERIALS AND METHODS

### Materials

The AAD sludge was obtained from the Gaobeidian wastewater treatment plant (WWTP), Beijing, China. This WWTP treats approximately 1,000,000 m<sup>3</sup>/d with A/O processes. The serial process of thickening, pre-dewatering, thermal hydrolysis (160 °C, 30 min), anaerobic digestion (hydraulic retention time, HRT, 20 d, 40 °C) and plate frame press dewatering is used for sludge treatment. Table 1 lists the characteristics of the raw sludge (RS), thermal hydrolyzed sludge, and AAD sludge.

Tianjin Guangfu Fine Chemical Research Institute, China supplied the PFS. SNF China Flocculant Co., Ltd supplied the 40% w/w aqueous solution of PDMDAAC, which had 100% charge density. The PDMDAAC solution was added to the PFS solution while being continuously stirred at 60 °C, to prevent the formation of insoluble byproducts, until they were thoroughly mixed. The coagulant mixtures were prepared with different PFS:PDMDAAC weight ratios (Wr) of 20, 10, 5, 1, 0.2 and 0.1.

**Table 1** | Characteristics of sludge

Indicator	Moisture content (%)	VSS:TSS (%)	CST (s)	$d_{0.5}$ (μm)	Zeta potential (mV)	DOM (mg/L)
Raw sludge	98.1	57.2	171.3	55.8	–12.09	608
Thermal hydrolyzed sludge	–	50.2	465.2	21.86	–14.12	10 560
AAD sludge	95.5	47.3	366.8	18.56	–17.81	1,810

## Batch test

### Chemical re-flocculation

Sludge samples were prepared at room temperature of  $24 \pm 1$  °C. In each case, a 500 mL sludge sample was homogenized by stirring at 200 rpm for 5 min in a 1 L tank. The desired dosage amount of coagulant mixture was added to the sludge sample. The coagulants used were PFS only, PFS-PDMDAAC with  $Wr = 20, 10, 5, 1, 0.2,$  and  $0.1$  and PDMDAAC only. After coagulant addition the mixture was rapidly stirred for 2 min, followed by a 10 min slow stir at 100 rpm to flocculate the sludge.

### Analytical methods

The IR spectrum was obtained by Fourier transform infrared spectroscopy (FTIR, Nicolet Nexus 410, USA) to see if PFS and PDMDAAC formed a copolymer. The scanning wavenumber was in the range  $4,000\text{--}400\text{ cm}^{-1}$ .

The X-ray powder diffraction (XRD) patterns of the polymers were obtained by an X-ray powder diffractometer (Bruker AXS D8 Advance, Germany) with graphite-monochromatized Cu ( $\lambda = 1.54056\text{ \AA}$ ) and Co ( $\lambda = 1.79026\text{ \AA}$ ) radiation.

Sludge dewaterability was measured using CST apparatus (Model 319, Triton, UK) with an 18 mm diameter funnel and Whatman No. 17 chromatography-grade filtration paper.

3D-EEM fluorescence spectra were obtained by a Hitachi F-4500 fluorescence spectrophotometer with an excitation range 200–400 nm and an emission range 220–550 nm. The spectra were recorded at a scan rate of 12,000 nm/min, using excitation and emission slit band widths of 5 nm.

Zeta potential, an indicator of the electrostatic potential generated at the surface of the flocs was measured by a Malvern Zetasizer 3000 (Malvern Instruments Ltd, Malvern, UK).

Sludge floc size was determined by a Mastersizer 2000 particle size analyzer (Malvern Instruments Ltd, UK). The  $d_{0.5}$  value given is the median value.

DOM content is indexed by dissolved organic carbon (DOC), which was measured using a TOC analyzer (Shimadzu, Kyoto, Japan).

The powdered sample was pretreated by sputtering with gold before a scanning electron micrograph (SEM) was used to scan the polymer samples to determine the surface morphology. SEM magnification was  $10\,000\times$  in this study.

All samples were measured in duplicate.

## RESULTS AND DISCUSSION

### Effect of $Wr$ on sludge dewaterability

The thermal hydrolysis process affects dewaterability of waste activated sludge (Oosterhuis *et al.* 2014). As shown in Figure 1, dewaterability, as indexed by CST, did not improve when the AAD sludge was conditioned with PFS only, even at a high dosage. Conditioning with PDMDAAC only showed greatly improved sludge dewaterability at a low dosage.

The weight ratio,  $Wr$ , of PFS-PDMDAAC significantly affects AAD sludge dewaterability. When  $Wr = 10$  or  $5$ , CST decreases only slowly from 380 s to 260 s as the dosage increases. This is because AAD reduces particle size and increases the number of smaller particles in sludge (Neyens *et al.* 2004; Lee *et al.* 2012; Zhang *et al.* 2018). AAD sludge consists of a large number of negatively charged micro particles, and the adsorption bridges of PDMDAAC in the polymer chains importantly affect sludge structure (Yu & Somasundaran 1996). With coagulant dosage in the range 0.01 to 0.13 g/g DS, the positive charge and the bridge-forming effects of PFS and of high  $Wr$  PFS-PDMDAAC were insufficient to affect CST. However, a low dosage of PFS-PDMDAAC with a higher PDMDAAC content provided excellent sludge dewaterability. When the coagulants were PDMDAAC only and PFS-PDMDAAC with  $Wr = 0.1$  or  $0.2$ , the differences in CST were small at a dosage of 0.03 g/g DS, giving excellent sludge dewaterability. At a dosage of 0.03 g/g DS, the effective dosage of PDMDAAC in PFS-PDMDAAC with

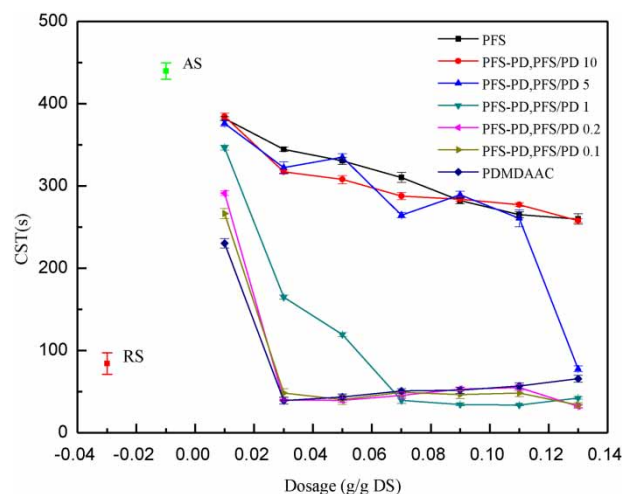


Figure 1 | Effect of PFS, PFS-PDMDAAC, and PDMDAAC dosages at different  $Wr$  on CST (RS: raw sludge; AS: AAD sludge).

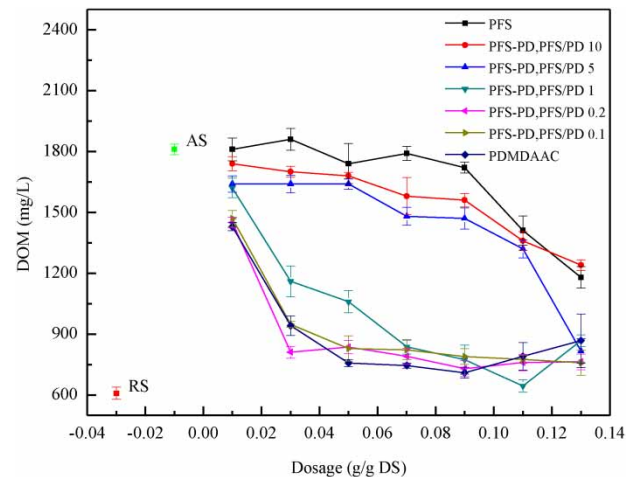
$Wr = 0.2$  is 0.025 g/g DS, and the actual dosage of PFS is 0.005 g/g DS. At a PFS-PDMAAC dosage of 0.05 g/g DS with  $Wr = 1$ , the effective dosage of PDMDAAC is also 0.025 g/g DS, and the effective dosage of PFS is 0.025 g/g DS, giving CST of 119.3 s. The actual dose of PDMDAAC at the above two points is identical. The actual dosage of PFS at the second point is higher than that of the first, but the CST value is much higher than the first, which means the dewaterability of the first point is much better than that of the second point, indicating the effect of PFS-PDMAAC is not a superposition of the separate effects of PFS and PDMDAAC. This is similar with the conclusion obtained by (Moussas & Zouboulis 2012), they find that the PFS-CP exhibit a better performance compared to PFS + CP, highlighting the composite coagulant with enhanced properties possibly due to the various interactions between the effective components. Electrostatic interaction between particles increases, molecular and particle structures are adjusted and reconfigured, and bridging between particle clusters is enhanced (Liu et al. 2003).

As coagulant dosage increased, CST first decreased rapidly to a minimum, and then slowly increased. As dosage increased after this minimum point flocs became positively charged and re-stabilized which resulted in decreased dewaterability (Huang et al. 2015). This trend is consistent with the typical behavior of polyelectrolytes in the flocculation process (Li et al. 2017). In terms of improved sludge dewaterability and lowering economic costs, the optimal synthesis of PFS and PDMDAAC is  $Wr = 0.2$  with sludge treatment at a dosage of 0.03 g/g DS, giving CST of 39.7 s.

### Effect of $Wr$ on DOM

Sludge comprises microbial, organic and inorganic matter. Extracellular polymeric substances (EPS), which are high water binding and constitute approximately 80% of activated sludge (Tian & Zheng 2006), cause the sludge dewatering efficiency to be increasing by degrading the EPS. THP can alter the structure of the sludge, degrade EPS and release EPS from sludge solids, transform some of the suspended organic solids into soluble compounds, release the EPS-bound water which leads to an increased concentration of proteins and polysaccharides in the supernatant and reduced their water retention properties (Wang et al. 2016). We investigated the changes in EPS by analyzing DOM in the filtrate (Cao et al. 2018).

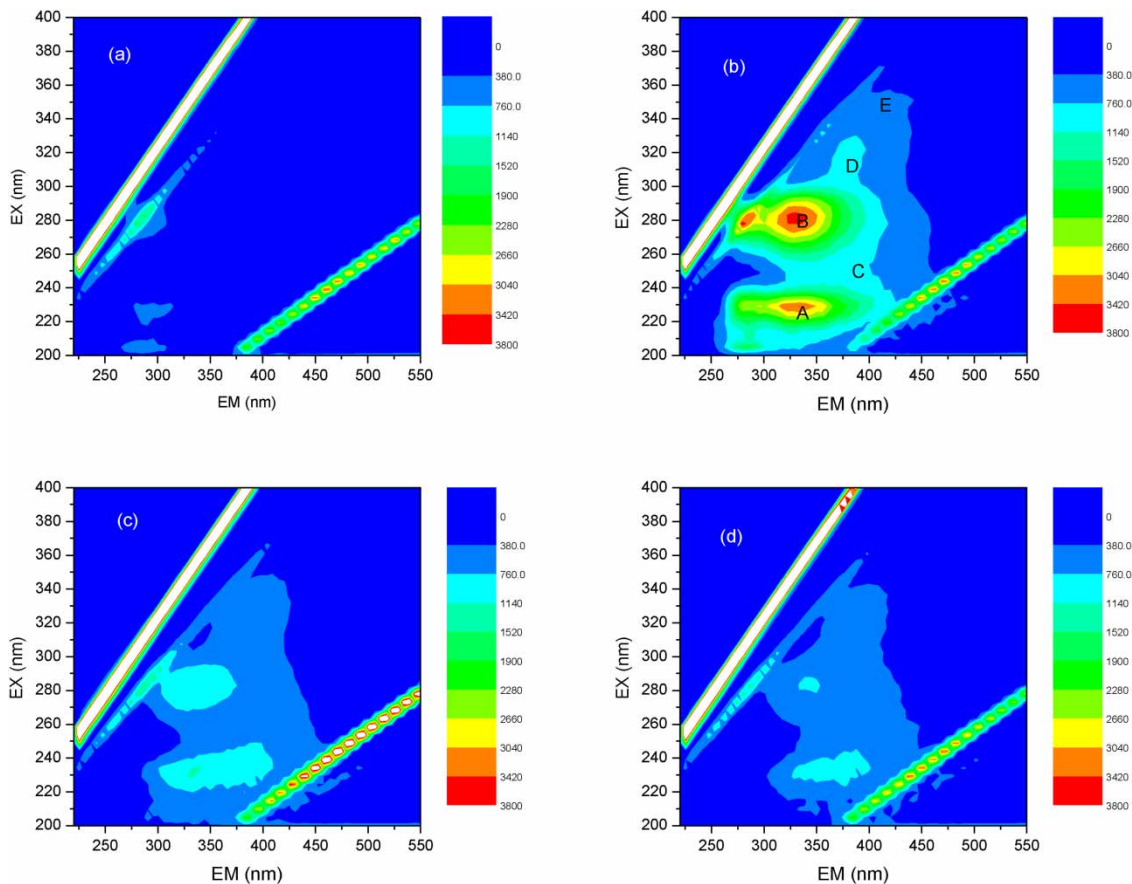
DOM content in the RS was 608 mg/L, and increased to 10,560 mg/L after dissolution and the release of a large amount of EPS during THP. AAD reduced sludge DOM



**Figure 2** | Effect of PFS, PFS-PDMAAC, and PDMDAAC dosage and  $Wr$  on DOM (RS: raw sludge; AS: AAD sludge).

content to 1,810 mg/L. Figure 2 shows that sludge DOM content decreased slowly when conditioned with PFS only and PFS-PDMAAC with  $Wr = 10$  or 5. Similar to the behavior of CST (Figure 1), when conditioned with PDMDAAC only and PFS-PDMAAC with  $Wr = 0.2$  or 0.1, DOM decreased rapidly as the coagulant dosage increased before reaching a value at which further dosage had little additional effect. These results show that PDMDAAC can increase colloid sludge flocculation when AAD sludge DOM content is much higher than that of RS.

3D-EEM is a highly sensitive and selective tool and had been extensively utilized to characterize DOM. At low concentrations, DOM is directly proportional to fluorescence intensity. The three-dimensional fluorescence spectrum was divided into five major regions: peak A ( $E_x/E_m = 225-240/340-350$ ), tryptophan-like protein; peak B ( $E_x/E_m = 260-290/300-350$ ), aromatic protein; peak C ( $E_x/E_m = 240-270/370-440$ ) and peak D ( $E_x/E_m = 310-360/370-450$ ), fulvic acid; and peak E ( $E_x/E_m = 350-440/430-510$ ), humic acid (Baker 2001). Figure 3(a) shows only one fluorescence peak, which indicates aromatic protein in the RS. The characteristics of the sludge changed after THP, which improves the breakage of floc structure by means of solubilisation and degradation of EPS and cellular lysis. Figure 3(b) shows that after THP all five peaks showed greater intensity as EPS in the sludge dissolved, especially peak B. Organic matter became degraded in the digestion process, which decreased the organic content of the sludge. The results agree with the previous analysis that EPS in sludge solids degraded into the supernatant, which led to an increase in protein concentration. As Figure 3(c) shows, the five peaks of AAD sludge decreased significantly



**Figure 3** | 3D-EEM of sludge: (a) raw sludge; (b) thermal hydrolyzed sludge; (c) AAD; (d) AAD +0.03 g/g DS, PFS-PDMAAC with  $W_r = 0.2$ ; the sample was diluted 1,000 $\times$ .

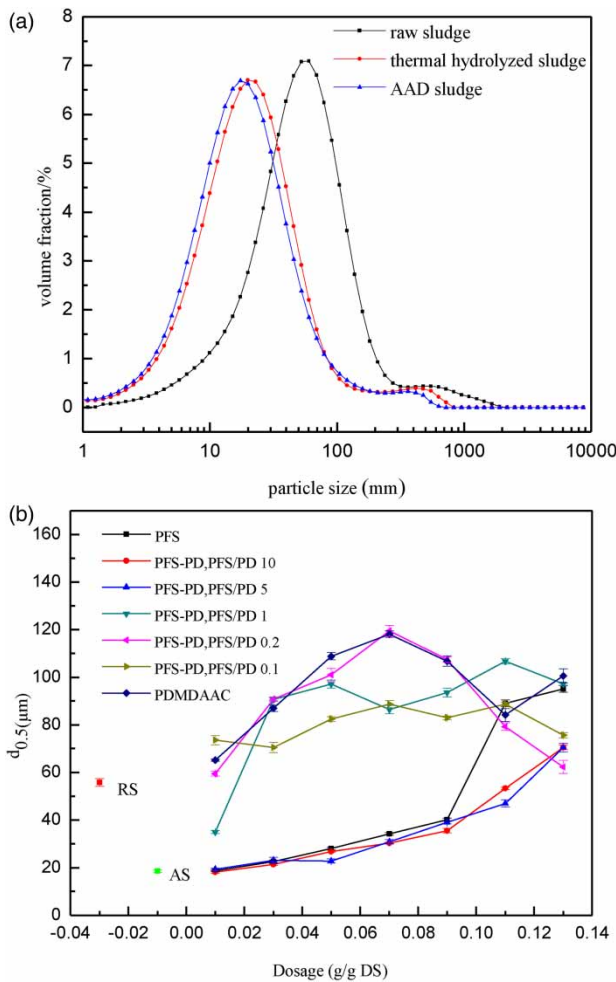
in intensity compared to the THP sludge. This suggests that in THP, large quantities of insoluble organic matter were converted into DOM. Although most soluble organic matter is degraded during digestion, any remaining undissolved organic matter and organic matter newly-produced by the digestion process can result in the dissolved organic content of the digested sludge being higher than that of the RS. This conclusion is borne out by Figure 3(d), which shows that at a dosage of 0.03 g/g DS PFS-PDMAAC with  $W_r = 0.2$  the fluorescence intensities of peaks A and B were further diminished.

### Effect of $W_r$ on floc

Rapid decompression during THP, due to steam release, causes rupture which results in changed EPS structure. After THP, the digested sludge is much finer in structure. Figure 4(a) shows that after thermal hydrolysis, the particle size distribution curve shift left, and further shift left after digestion. Which indicating that the particle size becomes smaller and the number of smaller particles in sludge increase. This is in agreement with the conclusion obtained

by Zhang (Zhang *et al.* 2018) that smaller particle size and larger surface area of sludge were induced by thermal hydrolysis and anaerobic digestion treatments. The  $d_{0.5}$  value is the median for particle size. Barber (Barber 2010) observed a change in average particle size from 70  $\mu\text{m}$  to 35  $\mu\text{m}$  following THP at 165  $^{\circ}\text{C}$  for 0.5 h. Neyens (Neyens *et al.* 2004) observed a change in average particle size from 107  $\mu\text{m}$  to 66  $\mu\text{m}$  following THP. Figure 4(b) shows that the average particle size ( $d_{0.5}$ ) of RS was 55.8  $\mu\text{m}$ , which was changed to 21.86  $\mu\text{m}$  after THP at 160  $^{\circ}\text{C}$  for 0.5 h. This value further decreased to 18.56  $\mu\text{m}$  as a result of microbial activity during anaerobic digestion, which breaks down sludge particles. Note that CST was inversely proportional to particle size; further study into the influence of particle size on dewaterability is required (Baber 2016).

For sludge conditioned with PFS only and with PFS-PDMAAC with  $W_r = 10$  or 5,  $d_{0.5}$  gradually increased from 20  $\mu\text{m}$  to 70  $\mu\text{m}$  as the coagulant dosage increased. Floc size increased significantly after the addition of PDMAAC only and PDF-PDMAAC with  $W_r = 1, 0.2,$  or 0.1, and  $d_{0.5}$  continued to increase until it reached a



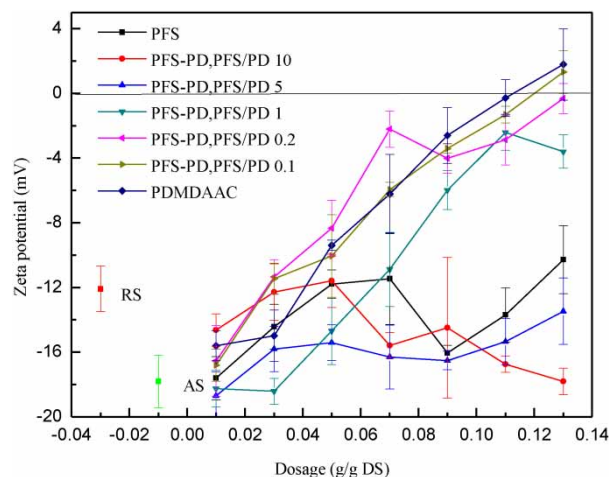
**Figure 4** | (a) Change of sludge particle size distribution during the AAD process; (b) effect of different dosages of PFS, PFS-PDMAAC for various  $Wr$  values, and PDMDAAC on  $d_{0.5}$  (RS: raw sludge; AS: AAD sludge).

maximum after which it gradually decreased. Additional dosages decreased  $d_{0.5}$  by causing the particles to be covered by the absorbed polymers, which resulted in increased electrostatic repulsion. Sludge floc size has a direct effect on sludge dewaterability. Moussas and Zouboulis found that PFS-PAM improved flocculation over PFS and that the main flocculation mechanism of PFS-PAM was bridge formation (Moussas & Zouboulis 2009). In this study, PFS-PDMAAC with a higher PDMDAAC concentration absorbed a large quantity of tiny particles from the sludge and agglomerated them to large and dense floccules. This decreased the quantity of tiny particles in the sludge and increased the formation of large voids. This, in turn, increased free water flow and decreased the quantity of capillary water. It has been shown elsewhere that larger

sludge particle size improves of dewaterability (Li *et al.* 2017).

Change in the zeta potential of sludge flocs is generally used as a measure of the destabilization ability of coagulation reagents. Colloids in sludge are usually negatively charged; as shown in Figure 5, the zeta potential of the test AAD sludge was  $-17.81$  mV. Cationic flocculants are suitable for charge neutralization and are suitable for flocculation (Gao *et al.* 2005). Figure 5 plots zeta potential versus coagulant dosage. There are significant differences between the curves. The curves for composite PFS-PDMAAC with higher concentrations of PDMDAAC (lower  $Wr$ ) show higher and more positive charges, which neutralize the negative charges of the colloids and polymer chains, and are thus more effective in destabilizing sludge particles. However, for PFS and PFS-PDMAAC with  $Wr = 10$  or 5, due to the fragmentation of the sludge by THP, the neutralization of coagulant does not effective, the change in zeta potential is very slight and zeta potential remains negative for all dosages. These results can be explained by the properties of PDMDAAC. PDMDAAC is an organic coagulant that has a high positive charge (Gao *et al.* 2005) and which can increase the neutralization ability of the coagulants.

When dosing AAD sludge with PDMDAAC only and PFS-PDMAAC with  $Wr = 0.2$  or  $0.1$ , zeta potential did not reach the isoelectric point at a dosage of  $0.03$  g/g DS. However, CST had been reduced to the minimum and subsequently CST changed little. This result indicates that when coagulation by PFS-PDMAAC was optimal, charge neutralization was crucial but it was not the sole parameter that influenced coagulation (Pefferkorn 2006; Shen *et al.* 2017). Adsorption and bridging were possibly the dominant



**Figure 5** | Effect of PFS, PFS-PDMAAC, and PDMDAAC dosage and  $Wr$  on zeta potential (RS: raw sludge; AS: AAD sludge).

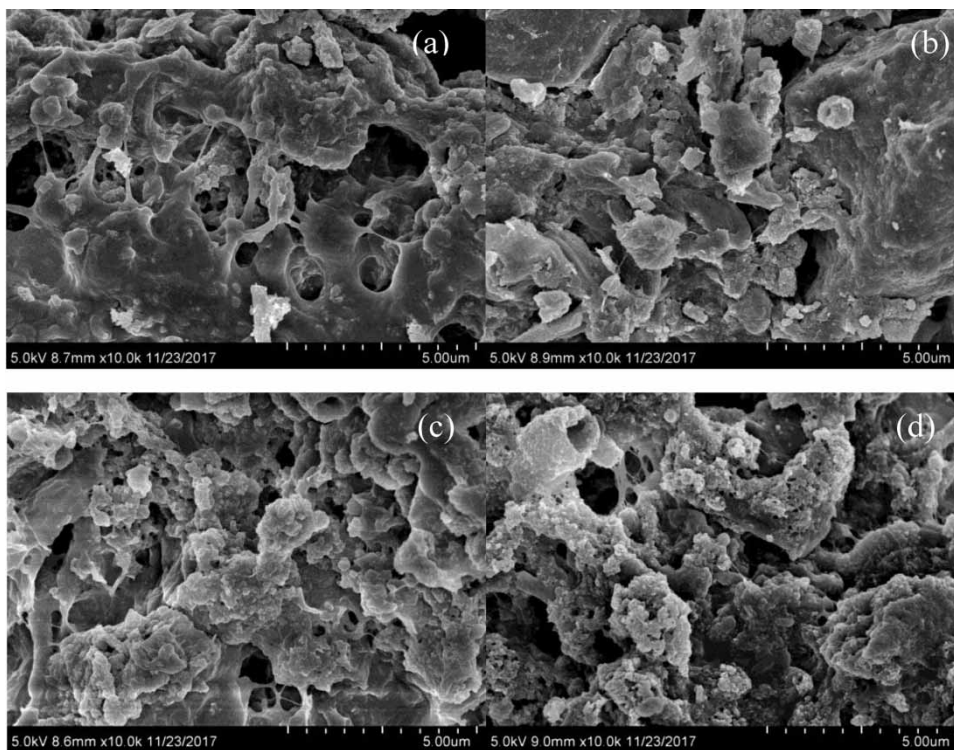
mechanisms. This view agrees with the conclusion of Zhao *et al.* (Zhao *et al.* 2011). Letterman showed that when the zeta potential of the inorganic polymer flocculant approaches zero, the flocculation effect is optimal (Letterman & Asolekar 1990). However, for organic polymer flocculants, especially cationic organic polymer flocculants, the zeta potential for optimal flocculation is often not zero. This is mainly because the action of inorganic polymer flocculants (such as PFS) mainly depends on the neutralizing effect of adsorption due to the positive charge of the hydrolytic polymer, while the hydrolyzed polymer has a smaller molecular weight, so the adsorptive bridging function is weak (Besra *et al.* 2004). Cationic organic polymer flocculants such as PDMDAAC act differently. Their larger molecular weight and flexible linear molecular chains enable them to fully exert the adsorptive bridging function, and the adsorptive neutralization effect is not the only mechanism in the flocculation process (Shen *et al.* 2017). Thus, PDMDAAC is particularly effective in improving the dewaterability of AAD sludge, which has a relatively small particle size.

Figure 6(a) shows that AAD sludge was sticky and had a relatively smooth surface, which indicates little water permeability and poor dewaterability. Figure 6(b) shows that flocs conditioned with 0.13 g/g DS PFS were more

fragmented because charge neutralization combined negatively charged colloidal particles. However, flocculation is limited and the flocs are not uniform, which indicates poor dewaterability. Figure 6(c) clearly shows that sludge flocs were aggregated after flocculation with 0.03 g/g DS PFS-PDMAAC with  $Wr = 0.2$ , as they also were after treatment with PDMDAAC only, as shown in Figure 6(d). Bridging tended to aggregate particles and flocs to form small, dense flocs. These agglomerated sludge particles were porous and the sludge had good dewaterability. In general, the morphologies of hydrolyzed digested sludge and conditioned sludge illustrate the results of dewatering experiments, and support the interpretation of the microstructure.

### Correlation between sludge dewaterability and physicochemical properties of flocs

We also analyzed the correlations between CST, DOM,  $d_{0.5}$  and zeta potential. Table 2 shows Pearson's coefficients of correlation for AAD sludge parameters. CST correlated well with  $d_{0.5}$  ( $r = -0.854$ ,  $p < 0.01$ ) and with zeta potential ( $r = -0.751$ ,  $p < 0.01$ ), which indicates that increasing floc size and reduced negative zeta potential will improve sludge dewaterability. In addition, there was a strong



**Figure 6** | Sludge floc morphology by SEM: (a) AAD sludge; (b) AAD sludge +0.13 g/g DS, PFS; (c) AAD sludge +0.03 g/g DS, PFS-PDMAAC with  $Wr = 0.2$ ; and (d) AAD sludge +0.03 g/g DS, PDMDAAC.

**Table 2** | Pearson coefficients of correlation,  $r$ , between CST, DOM,  $d_{0.5}$  and zeta potential.

	DOM	$d_{0.5}$	Zeta potential
CST	0.970**	-0.854**	-0.751**
DOM	1	-0.885**	-0.746**
$d_{0.5}$	-	1	0.610**
Zeta potential	-	-	1

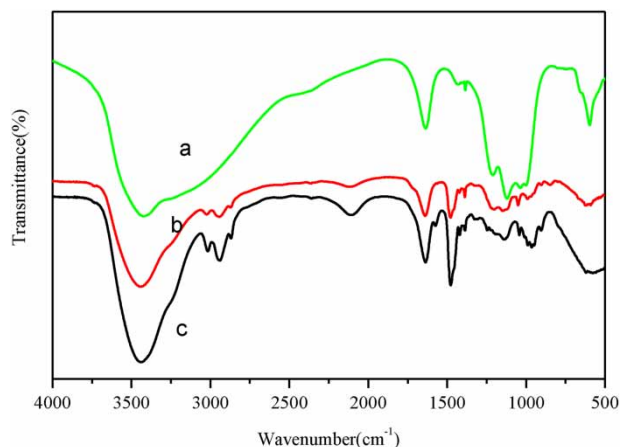
\*\* $p < 0.01$  (2-tailed).

positive correlation between CST and DOM ( $r = 0.97$ ,  $p < 0.01$ ). These results show that not only charge neutralization but also adsorption and bridging are responsible for the improved dewaterability of AAD sludge that is preconditioned with PFS-PDMDAAC.

### Structure and morphology of PFS-PDMDAAC coagulants

#### FTIR analysis

Figure 7 shows the FTIR spectra of the samples treated with PFS only, with PFS-PDMDAAC with  $Wr = 0.2$ , and with PDMDAAC only. The PFS-PDMDAAC spectrum is similar to the PFS spectrum. The absorption peak of Fe-O stretching vibrations is at  $598 \text{ cm}^{-1}$ . The absorption peak of Fe-O-Fe is at  $990 \text{ cm}^{-1}$ . The absorption peak of the  $\text{SO}_4^{2-}$  group is at  $1,129 \text{ cm}^{-1}$ . The absorption peaks at  $1,221 \text{ cm}^{-1}$  and  $1,431 \text{ cm}^{-1}$  show Fe-OH stretching vibrations and the  $\text{SO}_4^{2-}$  group respectively. The absorption peaks at  $1,637 \text{ cm}^{-1}$  and  $3,436 \text{ cm}^{-1}$  show O-H stretching vibrations. Comparison of Figure 7(a) and 7(b) shows that all the absorption peaks of PFS are also peaks for PFS-PDMDAAC. The absorption

**Figure 7** | FTIR spectra of (a) PFS, (b) PFS-PDMDAAC with  $Wr = 0.2$ , and (c) PDMDAAC.

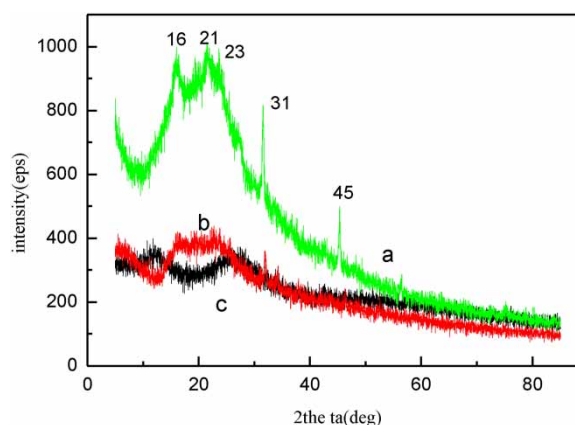
peak at  $1,473 \text{ cm}^{-1}$  in Figure 7(b) shows C-H bending vibrations. Overall, the FTIR analysis of PFS-PDMDAAC does not reveal the formation of a new chemical bond. However, Moussas found that the addition of PDMDAAC affects the concentration and the distribution of the chemical iron species, it is more than possible that some kind of interactions might occur between PFS and PDMDAAC (Moussas & Zouboulis 2012).

#### XRD analysis

Figure 8 illustrates the XRD interference patterns of PFS, PFS-PDMDAAC with  $Wr = 0.2$ , and PDMDAAC. The XRD pattern for PFS shows distinct crystalline peaks (Moussas & Zouboulis 2009). The peaks around  $2\theta = 25^\circ$  and  $45^\circ$  have a characteristic A-type X-ray diffraction pattern. The XRD pattern for PDMDAAC exhibits a broad shoulder and it has no characteristic peaks, indicating the amorphous nature of PDMDAAC. The XRD pattern for PFS-PDMDAAC has a dispersive broad peak and shows that the substance is amorphous with some trace of crystallinity. Less crystallinity suggests that the introduction of PDMDAAC to PFS destroyed the original ordered structure of PFS (Wang et al. 2013). This is in agreement with the conclusion provided by Li that the lack of characteristic peaks of XRD in the reagent suggests that there were no adsorbing chemical compounds. PDMDAAC dispersedly interweaved into PAM, forming a composite system with inorganic-organic complex interpenetration networks (Li et al. 2015).

#### Economic analysis

PFS-PDMDAAC with  $Wr = 0.2$  greatly improved sludge dewaterability at a dosage of  $0.03 \text{ g/g DS}$ . With the price of

**Figure 8** | XRD of (a) PFS, (b) PFS-PDMDAAC with  $Wr = 0.2$ , and (c) PDMDAAC.



commercial PDMDAAC at 12,000 yuan/t and the price of commercial PFS at 1,500 yuan/t, the use of PFS-PDMDAAC with  $W_r = 0.2$  instead of PDMDAAC can reduce PDMDAAC dosage by 16.7%, which represents a 14.6% cost saving.

## CONCLUSIONS

AAD sludge dewaterability did not significantly improve when PFS was used alone, even at a high dosage. Use of PDMDAAC alone greatly improved dewaterability at a low dosage because of the reduction in particle size and the increased proportion of smaller particles in AAD sludge due to the higher positive charge and an increase in bridging. PFS-PDMDAAC with  $W_r = 0.1$  or  $0.2$  performed similarly to PDMDAAC due to the high proportion of PDMDAAC in the polymers that were formed in the reaction between PFS and PDMDAAC. The use of PFS-PDMDAAC with  $W_r = 0.2$  will ensure good dewaterability, and uses about 16.7% less PDMDAAC, which reduces the reagent cost by about 14.6%. Nevertheless, more research is needed into the development of other suitable reagents for AAD sludge dewatering that produce good performance at a reasonable cost.

## REFERENCES

- Baker, A. 2001 Fluorescence excitation emission matrix characterization of some sewage-impacted rivers. *Environmental Science & Technology* **35**, 948–953.
- Barber, W. P. F. 2010 The influence on digestion and advanced digestion on the environmental impacts of incinerating sewage sludge—a case study from the UK. *Proceedings of the Water Environment Federation* **4**, 865–881.
- Barber, W. P. F. 2016 Thermal hydrolysis for sewage treatment: a critical review. *Water Research* **104**, 53–71.
- Besra, L., Sengupta, D. K., Roy, S. K. & Ay, P. 2004 Influence of polymer adsorption and conformation on flocculation and dewatering of kaolin suspension. *Separation and Purification Technology* **37**, 231–224.
- Cao, B. D., Zhang, W. J., Du, Y. J., Wang, R., Usher, S., Scales, P. & Wang, D. S. 2018 Compartmentalization of extracellular polymeric substances (EPS) solubilization and cake microstructure in relation to wastewater sludge dewatering behavior assisted by horizontal electric field: effect of operating conditions. *Water Research* **130**, 363–375.
- Gao, B. Y., Wang, Y. & Yue, Q. Y. 2005 The chemical species distribution of aluminum in composite flocculants prepared from polyaluminum chloride (PAC) and poly-dimethyldiallyl ammonium chloride (PDMDAAC). *Acta Hydrochimica et Hydrobiologica* **33**, 365–371.
- Huang, X., Gao, B. Y., Rong, H. Y., Yue, Q., Zhang, Y. & Teng, P. 2015 Effect of using polydimethyldiallylammonium chloride as coagulation aid on polytitanium salt coagulation performance, floc properties and sludge reuse. *Separation and Purification Technology* **143**, 64–71.
- Lee, K. E., Morad, N., Teng, T. T. & Beng, T. 2012 Development, characterization and the application of hybrid materials in coagulation/flocculation of wastewater: a review. *Chemical Engineering Journal* **203**, 370–386.
- Letterman, R. D. & Asolekar, S. R. 1990 Surface ionization of polynuclear species in Al(III)hydrolysis-1. Titration results. *Water Research* **24**, 931–939.
- Li, S. M., Lv, Y. K. & Liu, Z. M. 2015 Preparation of composite coagulant of PFM-PDMDAAC and its coagulation performance in treatment of landfill leachate. *Water Reuse and Desalination* **05** (2), 177–188.
- Li, X., Zheng, H. L., Gao, B. Y., Chun, Z. & Sun, Y. J. 2017 UV-initiated polymerization of acid- and alkali-resistant cationic flocculant P(AM-MAPTAC): synthesis, characterization, and application in sludge dewatering. *Separation and Purification Technology* **187**, 244–254.
- Liao, Y., Zheng, X. Y., Zhang, Z. Q., Xu, B., Sun, Y. J., Liu, Y. Z. & Zheng, H. L. 2017 Ultrasound-assisted polymerization of P(AM-DMDAAC): synthesis, characterization and sludge dewatering performance. *Journal of Environmental Chemical Engineering* **5**, 5439–5447.
- Liu, L. H., Gong, Z. Q. & Zheng, Y. J. 2003 Synthesis and structure characterization of diethylammonium chloride. *Journal of Central South University of Technology* **10**, 347–352.
- Mathijs, O., Davy, R., Alexander, H. & Paul, R. 2014 Thermal hydrolysis of waste activated sludge at Hengelo Wastewater Treatment Plant, The Netherlands. *Water Science & Technology* **70** (1), 1–7.
- Moussas, P. A. & Zouboulis, A. I. 2009 A new inorganic-organic composite coagulant, consisting of polyferric sulphate (PFS) and polyacrylamide (PAA). *Water Research* **43**, 3511–3524.
- Moussas, P. A. & Zouboulis, A. I. 2012 Synthesis, characterization and coagulation behavior of a composite coagulation reagent by the combination of polyferric sulfate (PFS) and cationic polyelectrolyte. *Separation and Purification Technology* **96**, 263–273.
- Neyens, E., Baeyens, J., Dewil, R. & Heyder, B. D. 2004 Advanced sludge treatment affects extracellular polymeric substances to improve activated sludge dewatering. *Journal of Hazardous Materials* **106**, 83–92.
- Pefferkorn, E. 2006 Clay and oxidized stabilization induced by mixedalum/macromolecular flocculation aids. *Advances in Colloid and Interface Science* **120**, 33–45.
- Shen, X., Gao, B., Huang, X., Bu, F., Yue, Q. Y., Li, R. H. & Jin, B. 2017 Effect of the dosage ratio and the viscosity of PAC/PDMDAAC on coagulation performance and membrane fouling in a hybrid coagulation-ultrafiltration process. *Chemosphere* **173**, 288–298.
- Sun, C. Z., Yue, Q. Y., Gao, B. Y., Cao, B. C., Mu, R. M. & Zhang, Z. B. 2012 Synthesis and floc properties of polymeric ferric aluminum chloride-polydimethyl diallylammonium chloride

- coagulant in coagulating humic acid-kaolin synthetic water. *Chemical Engineering Journal* **185–186**, 29–34.
- Tian, Y., Zheng, L. & Sun, D. Z. 2006 Functions and behaviors of activated sludge extracellular polymeric substances (EPS): a promising environmental interest. *Journal of Environmental Science* **18**, 420–427.
- Wang, D. F., Zhao, T. Q., Yan, L. Q., Mi, Z. M., Gu, Q. & Zhang, Y. M. 2016 Synthesis, characterization and evaluation of dewatering properties of chitosan-grafting DMAAC flocculants. *International Journal of Biological Macromolecules* **92**, 761–768.
- Wang, J.-P., Yuan, S.-J., Wang, Y. & Yu, H. Q. 2013 Synthesis, characterization and application of a novel starch based flocculant with high flocculation and dewatering properties. *Water Research* **47**, 2643–2648.
- Yu, X. & Somasundaran, P. 1996 Role of polymer conformation in inter particle-bridging dominated flocculation. *Journal of Colloid & Interface Science* **177**, 283–287.
- Zhang, J. S., Li, N., Dai, X. H., Tao, W. Q., Jenkinson, I. R. & Li, Z. 2018 Enhanced dewaterability of sludge during anaerobic digestion with thermal hydrolysis pretreatment: new insights through structure evolution. *Water Research* **131**, 177–185.
- Zhao, Y. X., Gao, B. Y., Rong, H. Y., Shon, H. K., Kim, J.-H., Yue, Q. Y. & Wang, Y. 2011 The impacts of coagulant aid-polydimethyldiallylammonium chloride on coagulation performances and floc characteristics in humic acid-kaolin synthetic water treatment with titanium tetrachloride. *Chemical Engineering Journal* **173**, 376–384.

First received 6 April 2018; accepted in revised form 16 August 2018. Available online 5 September 2018