Wastewater sludge dewaterability enhancement using hydroxyl aluminum conditioning: Role of aluminum speciation

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ABSTRACT

Chemical conditioning is one of the most important processes for improve the performance of sludge dewatering device. Aluminum salt coagulant has been widely used in wastewater and sludge treatment. It is generally accepted that pre-formed speciation of aluminum salt coagulants (ASC) has an important influence on coagulation/flocculation performance. In this study, the interaction mechanisms between sludge particles and aluminum salt coagulants with different speciation of hydroxy aluminum were investigated by characterizing the changes in morphological and EPS properties. It was found that middle polymer state aluminum (Al_b) and high polymer state aluminum (Al_c) performed better than monomer aluminum and oligomeric state aluminum (Al_a) in reduction of specific resistance to filtration (SRF) and compressibility of wastewater sludge due to their higher charge neutralization and formed more compact flocs. Sludge was significantly acidified after addition Al_a , while pH was much more stable under Al_b and Al_c conditioning due to their hydrolysis stability. The size of sludge flocs conditioned with Al_b and Al_c was small but flocs structure was denser and more compact, and floc strength is higher, while that formed from Al_a is relatively large, but floc structure was loose, floc strength is relatively lower. Scanning environmental microscope analysis revealed that sludge flocs conditioned by Al_b and Al_c (especially $PAC_{2.5}$ and Al_{13}) exhibited obvious botryoidal structure, this is because sludge flocs formed by Al_b and Al_c were more compact and floc strength is high, it was easy generated plentiful tiny channels for water release. In addition, polymeric aluminum salt coagulant (Al_b , Al_c) had better performance in compressing extracellular polymeric substances (EPS) structure and removing sticky protein-like substances from soluble EPS fraction, contributing to improvement of sludge filtration performance. Therefore, this study provides a novel solution for improving sludge dewatering property by controlling aluminum speciation.

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Introduction

Wastewater treatment processes produce large quantities of sludge commonly containing over 90% water. The management of wastewater sludge accounts for a major portion of the cost of the wastewater treatment process and represents great technical challenges. In order to reduce the costs of transportation and

handling, the most important part of sludge treatment prior to disposal is the reduction of the sludge volume by solid-water separation (Niu et al., 2013; Qi et al., 2011).

To improve the dewaterability of sludge, different pretreatment processes have been widely studied and developed including thermal, chemical, magnetic mechanical, acoustic, electric, electro-acoustic and their hybrid treatment processes (Li et al., 2016). It is well known that sludge is a heterogeneous colloidal system in which small sludge particles form a stable suspension in water and are very difficult separated from water phase. The microorganisms are embedded in a matrix of extracellular polymeric substances (EPS) can be regarded as key constituents in the dewatering process of sludge (Mikkelsen and Keiding, 2002). EPS (EPS and water held

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Table 1
Aqueous hydroxyl Al(III) species.

Degree of polymerization	Possible chemical formula	Ferron assay
Monomer	Al^{3+} , $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_4^-$	Al_a
Oligomer	$\text{Al}_2(\text{OH})_4^{2+}$, $\text{Al}_2(\text{OH})_5^+$, $\text{Al}_3(\text{OH})_5^{3+}$	Al_b
Low-mer	$\text{Al}_6(\text{OH})_{12}^{6+}$, $\text{Al}_6(\text{OH})_{15}^{3+}$, $\text{Al}_8(\text{OH})_{20}^{4+}$	
Mid-mer	$\text{Al}_{13}(\text{OH})_{32}^{7+}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ (Al_{13})	
High-mer	$\text{Al}_{15}(\text{OH})_{36}^{8+}$, $\text{Al}_{30}\text{O}_8(\text{OH})_{12}^{12+}$ (Al_{30})	Al_c
Sol, Gel	$(\text{Al}_{13})_n$, $\text{Al}(\text{OH})_3 \bullet$	
Precipitates	$[\text{Al}(\text{OH})_3]_n \bullet$	

within the EPS structure) accounts for 80% of the mass of waste activated sludge, and it has double layers including the loosely bound EPS (LB-EPS) which is diffused from the tightly bound EPS (TB-EPS) that surrounds the cells, and it was found sludge dewaterability was only associated with LB-EPS fraction (Li and Yang, 2007; Ramesh et al., 2006). Moreover, the water retained in the EPS-structure is bound mainly by the polysaccharides (PS) and proteins (PN) of the EPS in the activated sludge. In addition, Qi et al. suggested that sludge dewatering behavior was found be related to soluble EPS, especially protein-like substances in it (Qi et al., 2011). Also, Novak et al. suggested that the clogging or blinding of pores in the filter cake is primarily responsible for the deterioration in filtration.

Dewatering is a vital step to reduce the sludge volume to be disposed in the whole sludge treatment process. Now, chemical conditioning of sludge prior to mechanical dewatering is often necessary to enhance the operating efficiency of dewatering device. Addition of traditional chemical conditioners (inorganic salt coagulants and organic polymers) can agglomerate fine sludge colloids to form large flocs through charge neutralization and bridging, which can be more easily separated from the water (Niu et al., 2013; Zhang et al., 2014a). The most commonly inorganic flocculants in water and wastewater treatment are aluminum and iron salts. It is well known that aluminum speciation has important effects on its coagulation and flocculation ability. Polymeric aluminum salt coagulant (PACI) has many advantages over conventional coagulants including less sludge production, insensitive on change of temperature and pH and high charge neutralization property (Matsui et al., 2003).

PAC always contains a different speciation of hydroxy aluminum (Lu et al., 1999). The study on chemical speciation of aqueous aluminum hydroxyl clusters has achieved significant progress in recent years (Tang, 2006; Sposito, 1997). Their classification could be exemplified in Table 1. In which the oligomers are limited and denoted only as Al_2 and Al_3 clusters to show their special importance. The Al_a , Al_b , and Al_c are the categories of species defined by Ferron assay. Al_a is mainly composed by monomer aluminum and oligomeric state aluminum, Al_b is mainly composed by middle polymer state aluminums, Al_c was primarily related to high polymer state aluminums.

So far, few studies has investigated the interactions between aluminum salt with different speciation of hydroxy aluminum and activated sludge particles and evaluated their sludge conditioning performance. Thus, the major objectives of this study are to (1) explore the effects of aluminum salt with different speciation of hydroxy aluminum obtained from alkalinity adjustment on sludge dewatering performance in terms of CST and compressibility. (2)

Table 3
The speciation distribution of PACI samples.

	Al_a (%)	Al_b (%)	Al_c (%)	Al_T (g/L)
$\text{PAC}_0(\text{AlCl}_3)$	94.88	5.22	0	5.38
$\text{PAC}_{0.5}$	87.76	12.24	0	5.24
$\text{PAC}_{1.5}$	46.03	47.81	6.16	5.19
$\text{PAC}_{2.5}$	0	60.03	39.97	5.16
Al_{13}	4.3	91.3	4.4	9.22

investigate changes in morphological characteristics under chemical conditioning by using laser light scattering and SEM; and (3) understand the effects of chemical conditioning with aluminum salt coagulants with different speciation of hydroxy aluminum on distribution and composition of EPS to unravel the reaction mechanisms involved.

1. Materials and methods

1.1. Materials

1.1.1. Activated sludge

The surplus activate sludge was taken from Beijing North creek sewage treatment plant, China. The sewage treatment plant is mainly used membrane bioreactor (MBR) and handling capacity 0.2 million cubic meter per day. Sample was stored at 4 °C and analyzed within 7 days after sampling. Characteristics of the sludge are listed in Table 2.

1.1.2. Chemical agents

The aluminum salts coagulations was preparation by the method of (Xu et al., 2010). The reagents used in preparing the coagulants were of analytical grade and deionized water was used in all solutions. The procedures of preparing PAC and Al_{13} polymer can be described as follows: PAC with a basicity value (B, OH/Al molar ratio) was synthesized by adding pre-determined amount of Na_2CO_3 slowly into AlCl_3 solution under intense agitation. Al_{13} polymer was separated and purified from PAC by adding the pre-determined volume of ethanol and acetone slowly under gentle agitation. The detailed procedures can be found in other paper (Zhao et al., 2002). Five different aluminum salt coagulants was prepared and used in this test and their properties are summarized in Table 3. Total Al concentration (Al_T) was determined by ICP-OES (PerkinElmer, Optima 8300, UK). The speciation distribution of PACI was measured by the Ferron method, based on the reaction kinetic difference of the reactions between the aluminum and ferron reagent, the Ferron method enables one to partition soluble aluminum species in to such categories as monomeric, medium polymer, and larger polymer species and/or solid phase $\text{Al}(\text{OH})_3$, denoted simply as Al_a , Al_b , and Al_c respectively (Hu et al., 2006; Wang et al., 2004). Many investigations proved that the Al_b species could be regarded as the Al_{13} (Hu et al., 2006).

1.2. Methods

1.2.1. Sludge conditioning

Sludge samples were reacted with coagulants by using magnetic stirrer, the reacted procedure can be described as follows: a rapid

Table 2
Characteristics of activated sludge.

Indicator	Moisture content (%)	pH	VSS/TSS	CST (s)	$d_{0.5}$ (μm)	Zeta potential (mV)	SCOD (mg/L)
Value	98.3	6.9	0.72	320	62	−15.2	130

mix period for 2 min at 400 rpm followed by a slow mix period for 8 min at 40 rpm. The coagulation was added under agitation using graduated pipette.

1.2.2. Normalized CST and SRF determination

CST was measured with a CST instrument (model 319, Triton, UK) equipped with an 18-mm diameter funnel and Whatman No.17 chromatography-grade paper. The CST values were normalized by dividing them by the initial TSS concentration and then expressed in units of seconds of per liter per gram TSS (Merlo et al., 2007).

Since the determination of specific resistance to filtration (SRF) has the similar physical process to the high pressure dewatering, it was also used to evaluate the sludge dewaterability in this work. The SRF was conducted in a 250 mL Buchner funnel using a filter with 0.45 μ m filter paper. The Buchner funnel was filled with 100 mL of the sludge suspension, and a constant pressure of 0.6 MPa was applied by an air pump. The volume of filtrate under pressure was continuously recorded every 10 s before surface cracking was detected. The SRF of the sludge was calculated by:

$$r = \frac{2PA^2b}{\mu\omega} \quad (1)$$

where P (kg/m²) is the pressure applied, A (m²) is the filter area, u (kg s/m²) is the KV, w (kg/m³) denotes dry solid weight per unit volume sludge on the filtrate media, b is the time-to-filtration ratio, which is the slope of the curve that is obtained by plotting the ratio of the time of filtration to the volume of filtrate (t/V) versus the filtrate volume (V) (Niu et al., 2013).

1.2.3. Evaluation of sludge compressibility

The sludge cake compressibility measures the ability to compact the sludge when a normal pressure is applied (Qi et al., 2011). In practice sludge compressibility is often quantified as the slope of a log-log plot of the SRF versus the differential pressure applied. The coefficient of compressibility (s) is obtained by fitting data to Eq. (1) (Zhao and Bache, 2001)

$$\frac{SRF_1}{SRF_2} = \left(\frac{P_1}{P_2}\right)^s \quad (2)$$

In which P_1 and P_2 are two different filtration pressures (Pa), SRF_1 and SRF_2 are specific resistance to filtration at P_1 and P_2 , respectively.

1.2.4. Characterization of morphological properties of sludge

Floc size, fractal dimension (D_f), recovery factor (R_f) and strength factor (S_f) were studied to compare the properties of floc. A higher D_f normally corresponds to a more compact interior floc structure (Wang et al., 2009). An increased value of S_f indicates flocs that are better able to withstand shear and thus should be considered stronger than a floc with lower value. Likewise an increase in the recovery factor shows flocs that have better regrowth after high shear (Jarvis et al., 2005).

Floc breakage and regrowth experiments were carried out and repeated three times as follows: a regular coagulation process without sedimentation followed by a breakage phase at 400 rpm for 1 min and a regrowth phase at 40 rpm for 10 min. A small-angle light scattering instrument (Malvern Mastersizer 2000, Malvern, UK) was used to measure dynamic floc size and fractal dimension (D_f) as the coagulation process proceeded (Liu et al., 2013). The R_f and S_f may be calculated as follows (Jarvis et al., 2005):

$$S_f = \frac{d_a}{d_b} \times 100\% \quad (3)$$

$$R_f = \frac{d_c - d_a}{d_a - d_b} \times 100\% \quad (4)$$

Where d_a is the average floc size of the plateau before breakage, d_b is the floc size after the floc breakage period, and d_c is the floc size after regrowth to the new plateau.

The sludge samples were made by low temperature drying method treatment at 50 °C for 24 h. With samples dried, FE-SEM analysis BET analysis were used by HITACHI SU8020 FE-SEM and ASAP2020HD88, respectively.

1.2.5. EPS characterization

1.2.5.1. EPS extraction. The method of EPS extraction is from (Niu et al., 2013). but some conditions was modified. Take 50 ml sludge by 50 ml centrifugal tube and centrifugate at 3000 rpm for 10 min, the supernatant is soluble EPS. The sludge pellet in the tube was resuspended into 50 ml of 0.05% NaCl, sonicated at 20 kHz for 20min, shaken horizontally at 150 rpm for 10min in shaker, sonicated again for an additional 2 min. The liquor was centrifuged at 5000g for 10 min to separate solids and supernatant. The collected supernatant was regarded as the LB-EPS. The residual sludge pellet left in the centrifuge tube was resuspended in a 0.05% NaCl solution, sonicated for 3 min, then heated at 60 °C for 30 min, finally centrifuged at 5,000g for 10 min to collect TB-EPS.

1.2.5.2. EPS analysis. The concentrations of different EPS fractions were indicated by Total Organic Carbon (TOC) analyzer (Shimadzu, Japan). Fluorescence EEMs were measured on a Varian Eclipse fluorescence spectrophotometer (Hitachi F7000, Japan) in scan mode. EEM spectra were gathered with scanning emission Em spectra from 220 to 550 nm at 5 nm increments by varying the excitation Ex wavelength from 200 to 400 nm at 5 nm increments. The spectra were recorded at a scan rate of 12,000 nm/min, using excitation and emission slit bandwidths of 5 nm. The voltage of the photomultiplier tube PMT was set to 500 V for low level light detection.

Molecular weight (MW) was determined by a Waters liquid chromatography system that consisted of a Waters 2487 Dual λ Absorbance Detector, Waters 1525 pump system. A Shodex KW 802.5 gel chromatography column (Shoko, Japan) was used for organic materials separation. The mobile phase, namely Milli Q water buffered with 5 mM phosphate to pH 6.8, and 0.01 M NaCl, was filtered through a 0.22 μ m membrane, and then degassed for 30 min by means of ultra-sonication before use. A 600 μ L sample was injected at a flow rate of 0.8 mL min⁻¹. Polystyrene sulfonate standards (Sigma-Aldrich, USA) of MWs 1.8–32 kDa were used for apparent molecular weight (AMW) calibration (Chow et al., 2008; Wang et al., 2010).

1.2.6. Other indicators

pH was measured by pH meter (pHS-3C, Shanghai, China). Zeta potential measurements were performed on a Zetasizer (Zetasizer 2000; Malvern, UK). Other sludge parameters, including TSS, volatile suspended solids (VSS), chemical oxygen demand (COD), were analyzed following APHA-AWWA-WEF (1998).

Fig. 1. The effect of different aluminum salt coagulants on sludge dewatering performance.

2. Results and discussion

2.1. Effect of different speciation of hydroxyl aluminum on sludge dewatering

Fig. 1 presented the result of sludge treated with different aluminum salt coagulants. It can be seen that sludge CST_n was decreased with increasing Al dosages and reached the balance point at the dosage of 0.05 gAl/gTSS, and CST no obvious change when continuing increase coagulants dosage. It can be seen from Table 1 $AlCl_3$ and $PAC_{0.5}$ main component is Al_a , $PAC_{1.5}$ main component is Al_a and Al_b , $PAC_{2.5}$ main component is Al_b and Al_c , Al_{13} main component is Al_b . From Fig. 1 can also see that at 0.05 gAl/gTSS dosage the CST conditioned by $AlCl_3$, $PAC_{0.5}$, $PAC_{1.5}$, $PAC_{2.5}$, Al_{13} was 2.56, 2.13, 1.92, 1.74, 1.27 s*L/g respectively, sludge conditioned by high alkalinity PACI and Al_{13} has better performance on sludge

dewatering compared with low alkalinity PACI, this indicate that Al_b and Al_c compared with Al_a is more conducive to sludge dewatering.

There are two parallel processes for the polymerization and hydrolysis of hydroxyl aluminum in the polymeric aluminum salt coagulant. In the process of polymerization, the polymer is continuously increasing and the charge is enhanced, the increase of charge will hinder its further polymerization, and make the various compounds in solution state at stable condition (Tang, 2006). So polymer state aluminum (Al_b and Al_c) are more stable and more charged than Al_a . One of the remarkable characteristics of polymeric flocculant is its ability to neutralize the particles. Al_b and Al_c has stronger charge neutralization ability than Al_a , and they has stronger adsorption capacity and better electrical neutralization ability on negatively charged particles (Tang, 2006), so in the sludge conditioning, polymer state aluminum (Al_b and Al_c) formed more compact flocs and water trapped in EPS more easy released into sludge bulk solution.

2.2. The influence of different speciation of hydroxy aluminum on sludge flocculation

The application of fractal geometry is now a well-established means of describing the complicated structure of floc aggregates, the larger fractal dimension value represent the flocs more regular and the flocs structure more compact (Jarvis et al., 2005). Fig. 2 showed at the same dosage 0.05 gAl/gTSS, the sludge flocs size and fractal dimension conditioned by different aluminum salts coagulants. During slow agitation phase, the size of sludge particles conditioned by $PAC_{2.5}$ and Al_{13} ranged from 350 to 450 μm which were smaller than that conditioned by other coagulants, but the flocs fractal dimension value between 1.8 and 1.9 is higher than that of sludge flocs conditioned by $AlCl_3$, $PAC_{0.5}$ and $PAC_{1.5}$, whose fractal dimension value was ranged from 1.6 to 1.7. This result demonstrated that flocs formed by Al_b and Al_c were smaller but floc structure was more compact, so floc strength is relatively higher. Although Al_a formed flocs is larger, floc structure was looser, and floc strength is relatively lower. From Table 4 we can see that the S_f of sludge flocs conditioned by $AlCl_3$, $PAC_{0.5}$, $PAC_{1.5}$ were 54.41, 57.17 and 56.46 respectively, while the sludge flocs S_f conditioned by $PAC_{2.5}$ and Al_{13} were higher at 62.58, 64.73. In general, S_f is an

Fig. 2. Effects of different polymeric aluminum salt coagulants on sludge flocs.

Table 4

Floc parameters of different aluminum salt coagulants under the same shear condition.

Coagulants	R _f (%)	S _f (%)
PAC ₀	6.07	54.41
PAC _{0.5}	47.98	57.17
PAC _{1.5}	55.29	56.46
PAC _{2.5}	5.16	62.58
Al ₁₃	5.56	64.73

indication of interaction force between the primary particles, this demonstrates that formed sludge flocs after conditioned by Al_b and Al_c compared with Al_a more difficult to be broken and thus exhibited higher structural strength. In the sludge particles re-growth stage, the R_f conditioned by AlCl₃, PAC_{0.5}, PAC_{1.5} were 6.07, 47.98 and 55.29, while the R_f of sludge particles conditioned by PAC_{2.5} and Al₁₃ respectively is 5.16 and 5.56. These results demonstrated that Al_a was more able to promote the regrowth of the broken sludge in comparison to Al_b and Al_c. This observation was consistent with the study results of Yu et al. (Yu et al., 2010), who found that Al_a could produce the cohesive force which was weaker than charge force, this cohesive force was conducive to sludge particles reflocculation. However, Al_b and Al_c did not exhibited this property.

2.3. The influence of different speciation of hydroxy aluminum on sludge cake properties

2.3.1. Sludge compressibility

Activated sludge flocs always showed high compressibility which results in sludge cake particles being deformed under pressure following cake growth which cause cake void closure and a subsequent decline in sludge filterability (Smollen and Kafaar, 1997). Thus, increase of pressure is not be conducive to sludge dewatering due to this property (Sveegaard et al., 2012). It is crucial to evaluate the compressibility of sludge under chemical conditioning. In this test, we selected the same dosage of 0.05gAl/gTSS for different aluminum salt coagulants. As can be seen in Fig. 3, raw

sludge compressibility coefficient was 0.92, sludge compressibility coefficient was reduced after conditioned by all aluminum salt coagulants. This observation was in agreement with the report of Novak et al., who found that sludge conditioned by inorganic chemical coagulants are generally less compressible and easier to dewater under pressure filtration (Qi et al., 2011; Novak and Huang, 1988). The sludge compressibility coefficient obtained from AlCl₃ conditioning was 0.898, which was higher than that the conditioned by PAC_{2.5} and Al₁₃ of 0.849. This result was consistent with CST test. The lower compressibility coefficient was always related to better dewatering property of sludge. It was demonstrated that the sludge flocs conditioned by Al_b and Al_c were more compact and resistant to compress than that formed by Al_a treatment, which was in agreement with the changes of D_f.

2.3.2. Structural characteristics of sludge cake

Sludge dewatering difficulties can be associated with filter medium blinding and cake blinding, i.e. small scale solids trapped in the filter cake and/or filter media. Novak et al. (Novak and Huang, 1988) suggested that the clogging or blinding of pores in the filter cake is primarily responsible for the deterioration in filtration rather than the blinding of the filtering media. So filtration was always governed by cake-layer once formed, the structure of sludge cake had a crucial impact on sludge filtration performance (Qi et al., 2011). During filtration dewatering, the clogging of pores in the filter cake is primarily responsible for the deterioration in filtration rather than the blinding of the filtering media (Novak and Huang, 1988). Therefore, it is necessary to analyze the structure of sludge cake after filtration dewatering. After SRF measurement, the cake was dried under 50 °C and microscopic structure was observed by using field emission scanning electron microscopy (Japan Hitachi, SU-8020) and characterized by BET(N₂ adsorption-desorption experiment). From Fig. S1 (see in supporting information), it can be seen that sludge cake conditioned by PACI with higher basicity exhibited lower moisture content and more evident cracks after filtration. The SEM analysis of sludge cake after vacuum filtration was presented in Fig. 4. The surface of raw sludge cake is relatively smooth, whilst the sludge surface become rough after aluminum salt coagulants conditioning. Especially, the pore structure of

Fig. 3. The SRF(a) and compressibility coefficient(b) of sludge conditioned by aluminum salt coagulants.

Fig. 4. The microscopy picture of sludge cake conditioned by different aluminum salt coagulants.

sludge cakes conditioned by PAC_{1.5}, PAC_{2.5} and Al₁₃ were well-developed and exhibited obvious botryoidal structure in which abundant pores and channels distributed. From Fig. S2 and Table S2 it can be seen that the isotherms belong to type IV with a distinct hysteresis loop observed in the range of 0.5–1.0 p/p⁰, which is characteristic of mesoporous materials. According to the IUPAC recommendations (Kruk and Jaroniec 2001), the above hysteresis

loops can be categorized as type H₃ loops, which are reported for materials comprised of aggregates (loose assemblages) of plate-like particles forming slit-like pores. The pore sizes and surface areas of products are increased with the increase of PACI basicity. This observation confirmed that more plentiful pores and channels were located within sludge cake formed by Al_b and Al_c conditioning. This difference was very likely to be attributed to sludge floc strength, sludge flocs conditioned by polymer state aluminum (Al_b and Al_c) were more compact and can act as skeleton builders during pressure dewatering. As a result, the porous cake could function as a draining media for the withdrawal of water and was conducive to sludge pressure dewatering.

2.4. The influence of hydroxyl aluminum conditioning with different speciation on sludge EPS properties

Many previous studies have demonstrated that sludge EPS component play an important role in sludge dewatering process (Mikkelsen and Keiding, 2002; Jin et al., 2004; Yang and Li 2009; Poxon and Darby, 1997; Forster, 1971), so the variations in EPS distribution and composition were investigated.

2.4.1. EPS distribution

Fig. 5 showed that at the same dosage (0.05gAl/gTSS) obvious distinctions in EPS distribution were observed for different aluminum salt coagulants. As shown in Fig. 5, concentrations of all sludge EPS fractions were decreased under chemical conditioning with different aluminum salt coagulants, indicating that both LB-EPS and TB-EPS were compressed. Therefore, the sludge flocs became more compact upon the addition of aluminum salt

Fig. 5. The effect of different aluminum salt coagulants on sludge EPS distribution.

Fig. 6. Influence of different aluminum salt coagulants on EEM profile of different sludge EPS fractions (SEPS and LB-EPS samples were diluted by 10 times, and TB-EPS sample was diluted by 100 times.).

Table 5
EEM profile of different EPS fractions after different aluminum salt coagulants treatment ^a.

PACI	SEPS				LB-EPS				TB-EPS			
	Tryptophan protein	Aromatic protein	Humic acid	Fulvic acid	Tryptophan protein	Aromatic protein	Humic acid	Fulvic acid	Tryptophan protein	Aromatic protein	Humic acid	Fulvic acid
$\lambda_{\text{ex/em}}$	280/335	225/340	330/410	275/425	280/335	225/340	330/410	275/425	280/335	225/340	330/410	275/425
Raw sludge	513.2	156	33.05	65.15	39.27	17.6	15.09	21.65	572.4	285.7	15.09	88.84
PAC ₀	496.5	163.8	56.47	147.4	122.9	44.53	12.34	43.02	69.48	42.31	5.334	33
PAC _{0.5}	486.6	139.2	41.78	108.9	143.1	37.48	12.92	48.85	55.23	29.46	5.554	31.88
PAC _{1.5}	483.2	139.8	26.75	69.38	173.3	55.99	10.53	42.65	63.94	44.47	4.171	27.33
PAC _{2.5}	148.9	61.6	25.07	51.86	24.36	10.98	9.046	17.65	218.4	113.2	24.3	50.63
Al ₁₃	102.8	47.93	24.38	44.81	20.01	14.91	8.525	16.23	391.4	237.1	13.14	53.75

^a The dosages of aluminum salt coagulants were 0.05gAl/gTSS, SEPS and LB-EPS samples were diluted by 10 times, and TB-EPS sample was diluted by 100 times.

coagulants and floc strength was enhanced. This observation was in agreement with the report of Zhang et al., who found that EPS compression was the major mechanism of sludge conditioning with inorganic coagulants. From Fig. 5 can see that the concentration of extractable EPS (LB-EPS and TB-EPS) reduced when the sludge was treated with aluminum salt coagulants. SEPS concentrations conditioned by Al₁₃ and PAC_{2.5} were lower than other aluminum salt coagulants, decreased from 8.85 mgDOC/gTSS to 4.06 and 5.99 mgDOC/gTSS respectively. This observation demonstrated that Al_b and Al_c showed better performance in compressing EPS structure than Al_a. It was consistent with particle size analysis, the sludge flocs formed by Al_b and Al_c were more compact and less compressible. In addition, acidification was observed after addition of aluminum salt coagulants, it was more evident for aluminum salts with low basicity (see in Table S1). As mentioned above, this acidification might affect the subsequent sludge treatment and disposal. It was reported that acidic treatment significantly change the chemical structure of organic matters (e.g. protein-likes) and this might lead to the dissolution of sludge EPS and cations (e.g. Ca²⁺, Mg²⁺, Al³⁺ and Fe³⁺, etc.) (Zhang et al., 2015a). From Fig. 5 can see that the TB-EPS concentrations conditioned by Al₁₃ and PAC_{2.5} increased again comparing to other aluminum salt coagulants, this also indicated that Al_b and Al_c showed better performance in compressing EPS structure than Al_a, which made SEPS and LB-EPS transfer into TB-EPS, so TP-EPS conditioned by Al₁₃ and PAC_{2.5} increased when SEPS and LB-EPS concentration conditioned by Al₁₃ and PAC_{2.5} decrease, so their TB-EPS concentration was increased. Many studies have demonstrated that sludge filtration property was mainly dependent on properties of SEPS fraction, and the high content of protein in SEPS was always detrimental to sludge filterability (Zhang et al., 2014a, 2014b, 2015b). In addition, reduction of SEPS concentration contributed to improvement of sludge filterability, it was obvious that PAC with high alkalinity and Al₁₃ were more effective in removal of SEPS. In order to get insights into the changes in chemical composition, EPS samples were characterized by EEM and HPSEC later.

2.4.2. EPS composition

2.4.2.1. 3D-EEM analysis. Fluorescence excitation-emission matrix (EEM) spectroscopy is a highly sensitive and selective tool and had been extensively utilized to characterize natural organic matter (NOM), especially from microbial activity (Henderson et al., 2009). Fig. 6 showed EEM profile of different EPS fractions after PACI treatment. It was obvious that four fluorescent peaks were detected in SEPS and LB-EPS fractions of raw sludge: Peak A ($\lambda_{\text{ex/em}}$ = 280/335) - tryptophan-like protein, Peak B ($\lambda_{\text{ex/em}}$ = 230/330) - aromatic protein, Peaks C ($\lambda_{\text{ex/em}}$ = 275/455) - fulvic acid and Peak D ($\lambda_{\text{ex/em}}$ = 350/420) - humic acid; while only two peaks

(A and B) related to proteins were observed in TB-EPS. All three EPS fraction had similar chemical components, which was mainly composed by tryptophan-like and aromatic-like substances. No apparent change in EEM contours of SEPS were observed after conditioning by AlCl₃, PAC_{0.5} and PAC_{1.5}, while the two fluorescent intensities associated with protein-like substances were significantly weakened after conditioning by PAC_{2.5} and Al₁₃. As presented in Table 5, the intensities Peak A and Peak B in the SEPS fraction conditioned by PAC_{2.5} and Al₁₃ were decreased from 513.2 to 156 to 102.8 and 61.6 respectively. This result was in agreement with total EPS content determination. In our previous studies, it was found that sludge dewatering was strongly dependent on concentration of protein-like substances in SEPS (Zhang et al., 2015b), low proteins concentration in SEPS fraction was always related to better dewaterability. This result consisted with sludge dewaterability test. PAC_{2.5} and Al₁₃ treatment was more effective in sludge dewatering improvement due to their better protein-like substances removal efficiency.

2.4.2.2. HPSEC. EPS can be divided into three parts according to molecular weight distribution: macromolecular fraction (>4000Da)-mainly consisting of carbohydrates and proteins, mid molecular fraction (1000–4000Da)-consisting of humic substances and peptides, low molecular fraction (<1000Da) - consisting of building blocks and organic acids (Lyko et al., 2008). The variation

Fig. 7. Peak intensities in SEPS determined by SEC.

Fig. 8. Change in physicochemical properties of sludge floc under different speciation of hydroxy aluminum conditioning.

of molecular weight distribution of SEPS under chemical conditioning with different aluminum salt coagulants can be found in Fig. S2. There are mainly seven peaks in SEPS including 175Da, 1020Da, 1080Da, 1180Da, 1250Da, 14000Da and 140000Da. Fig. 7 depicted the change in each peak intensity of SEPS under chemical conditioning. All MW peaks in SEPS were significantly reduced, especially supramolecular biopolymers with MW of 140,000 and 14,000 Da was almost completely removed after aluminum salts addition. In addition, the PACI with high alkalinity (Al_b and Al_c) had better performance in removing mid- and low MW substances which were mainly associated with protein-like substance. In addition, it was interesting to note that there appear a new peak 1020Da with addition of coagulants, it was likely to be related to the production of Al-EPS complexes.

2.5. Model of change in physicochemical properties of sludge floc under different speciation of hydroxy aluminum conditioning

Sludge dewaterability was always related to the concentration of protein-like substances in SEPS, sludge compressibility and sludge cake structure. According to results of this study, the models of changes in sludge flocs conditioned with different aluminum salts was summarized in Fig. 8. As mentioned above, EPS compression was very likely to be the major mechanism in sludge conditioning with inorganic coagulants. Hydrolyzed products of aluminum salts could act as skeleton builders to support the cake structure and reduce the sludge compressibility.

Hydrolysis speciation had important effects on sludge conditioning efficiency of aluminum salt coagulants. Al_b and Al_c exhibited stronger charge neutralization ability than Al_a , hence they also showed better performance in EPS compression and protein-like substance removal. Sludge flocs conditioned by Al_b and Al_c was more compact and resistant to compress than that conditioned by Al_a . Sludge filtration dewatering process was mainly dependent on cake structural properties. More plentiful pores and channels were located within sludge cake formed by Al_b and Al_c conditioning, which were conducive to water drainage under pressure filtration.

In addition, it should be pointed out sludge after conditioned by PACI with low alkalinity was evidently acidified due to further

hydrolysis of Al^{3+} , it might affect the subsequent disposal of waste sludge, such as land use and incineration. However, sludge pH remained unchanged under chemical conditioning with PACI of high alkalinity because of their hydrolysis stability.

2.6. Environmental implication

Inorganic coagulants were always used in high-pressure dewatering process (such as filter press), since their hydrolysis products can support sludge floc structure and reduce sludge compressibility. High-pressure dewatering processes have been widely used in current China to alleviate the pressure of steadily increasing sludge production. Ferric chloride and lime were commonly used as chemical conditioners prior to high-pressure dewatering process, so a large amount of reagents was added in the system and sludge reduction efficiency of high-pressure dewatering was alleviated. In addition, sludge system always become strongly alkaline due to addition of lime. Therefore, the sludge conditioning efficiency of aluminum salt coagulants was evaluated by considering their chemical speciation. In this work, it found that PACI with high basicity was more effective in improving sludge dewaterability than mono-Al, and no pH adjustment was needed under sludge conditioning using Al_b/Al_c due to hydrolysis stability. High basicity PACI conditioning was a more efficient and simpler method for enhancing sludge dewaterability than $FeCl_3$.

3. Conclusion

In this study, the effects of chemical conditioning using different alkalinity PACI on dewatering performance were evaluated, the interaction mechanisms between sludge particles and aluminum salt coagulants with different speciation of hydroxy aluminum were unravelled by characterizing the changes in morphological and EPS properties.

- In sludge conditioning, polymer state aluminum (Al_b and Al_c) are more stable and more positively charged than Al_a , so they performed better in sludge dewaterability improvement. Sludge

flocs conditioned by Al_b and Al_c were less compressible than that formed by Al_a treatment.

- Al_b and Al_c formed flocs were smaller but floc structure was more compact, and floc strength is relatively higher. Although Al_a formed flocs is larger, floc structure was looser, and floc strength is relatively lower. Al_a could produce cohesive force in sludge flocculation, so the sludge flocs re-grew more easily after shearing. Sludge conditioned by polymer state aluminum (Al_b and Al_c) showed more compact structure and could act as skeleton builders to support the floc structure under pressure dewatering.
- Al_b and Al_c exhibited better performance in EPS compression and removal of protein-like substances, which was conducive to improvement of sludge filterability.
- Significant acidification was observed after being conditioned by low alkalinity PACI it might cause adverse effects for subsequent sludge disposal. However, since high alkalinity PACI showed better hydrolysis stability, sludge pH was almost affected.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2016.09.016>.

References

- Chow, C.W., Fabris, R., Van, L.J., Wang, D., Drikast, M., 2008. Assessing natural organic matter treatability using high performance size exclusion chromatography. *Environ. Sci. Technol.* 42 (17), 6683–6689.
- Forster, C.F., 1971. Activated sludge surfaces in relation to the sludge volume index. *Water Res.* 5 (10), 861–870.
- Henderson, R.K., Baker, A., Murphy, K.R., Hambly, A., Stuetz, R.M., Khan, S.J., 2009. Fluorescence as a potential monitoring tool for recycled water systems: a review. *Water Res.* 43 (4), 863–881.
- Hu, C., Liu, H., Qu, J., Wang, D., Rut, J., 2006. Coagulation behavior of aluminum salts in eutrophic water: significance of $Al(III)$ species and pH control. *Environ. Sci. Technol.* 40 (1), 325–331.
- Jarvis, P., Bruce Jefferson, A., Parsons, S.A., 2005. Breakage, regrowth, and fractal nature of natural organic matter flocs. *Environ. Sci. Technol.* 39 (7), 2307–2314.
- Jin, B., Wilén, B.-M., Lant, P., 2004. Impacts of morphological, physical and chemical properties of sludge flocs on dewaterability of activated sludge. *Chem. Eng. J.* 98 (1–2), 115–126.
- Kruk, M., Jaroniec, M., 2001. Gas adsorption characterization of ordered organic-inorganic nanocomposite materials. *Chem. Mater.* 13, 3169–3183.
- Li, X.Y., Yang, S.F., 2007. Influence of loosely bound extracellular polymeric substances (EPS) on the flocculation, sedimentation and dewaterability of activated sludge. *Water Res.* 41 (5), 1022–1030.
- Lu, G., Qu, J., Tang, H., 1999. The electrochemical production of highly effective polyaluminum chloride. *Water Res.* 33 (3), 807–813.
- Li, Y., Yuan, X., Wu, Z., Wang, H., Xiao, Z., Wu, Y., Chen, X., Zeng, G., 2016. Enhancing the sludge dewaterability by electrolysis/electrocoagulation combined with zero-valent iron activated persulfate process. *Chem. Eng. J.* 303, 636–645.
- Liu, Y.Y., Zhang, W.J., Yang, X.Y., Xiao, P., Wang, D.S., Song, Y., 2013. Advanced

- treatment of effluent from municipal WWTP with different metal salt coagulants: contaminants treatability and floc properties. *Sep. Purif. Technol.* 120, 123–128.
- Lyko, S., Wintgens, T., Al-Halbouni, D., Baumgarten, S., Tacke, D., Drensla, K., Janot, A., Dott, W., Pinnekamp, J., Melin, T., 2008. Long-term monitoring of a full-scale municipal membrane bioreactor: characterisation of foulants and operational performance. *J. Memb. Sci.* 317 (1), 78–87.
- Matsui, Y., Matsushita, T., Sakuma, S., Gojo, T., Mamiya, T., Hiroshi Suzuoki, A., Inoue, T., 2003. Virus inactivation in aluminum and polyaluminum coagulation. *Environ. Sci. Technol.* 37 (22), 5175–5180.
- Merlo, R.P., Trussell, R.S., Hermanowicz, S.W., Jenkins, D., 2007. A comparison of the physical, chemical, and biological properties of sludges from a complete-mix activated sludge reactor and a submerged membrane bioreactor. *Water Environ. Res.* 79 (3), 320–328.
- Mikkelsen, L.H., Keiding, K., 2002. Physico-chemical characteristics of full scale sewage sludges with implications to dewatering. *Water Res.* 36 (10), 2451–2462.
- Niu, M., Zhang, W., Wang, D., Chen, Y., Chen, R., 2013. Correlation of physico-chemical properties and sludge dewaterability under chemical conditioning using inorganic coagulants. *Bioresour. Technol.* 144, 337–343.
- Novak, J.T., Huang, J.C., 1988. The blinding of sludges during filtration. *J. Water Pollut. Control Fed.* 60 (2), 206–214.
- Poxon, T.L., Darby, J.L., 1997. Extracellular polyanions in digested sludge: measurement and relationship to sludge dewaterability. *Water Res.* 31 (4), 749–758.
- Qi, Y., Thapa, K.B., Hoadley, A.F.A., 2011. Application of filtration aids for improving sludge dewatering properties – a review. *Chem. Eng. J.* 171 (2), 373–384.
- Ramesh, A., Lee, D.J., Hong, S.G., 2006. Soluble microbial products (SMP) and soluble extracellular polymeric substances (EPS) from wastewater sludge. *Appl. Microbiol. Biotechnol.* 73 (1), 219–225.
- Sposito, G., 1997. The Environmental Chemistry of Aluminum. *Environmental Chemistry of Aluminum*.
- Smollen, M., Kafaar, A., 1997. Investigation into alternative sludge conditioning prior to dewatering. *Water Sci. Technol.* 36 (11), 115–119.
- Sveegaard, S.G., Keiding, K., Christensen, M.L., 2012. Compression and swelling of activated sludge cakes during dewatering. *Water Res.* 46 (16), 4999–5008.
- Tang, H.X., 2006. *Inorganic Polymer Flocculation Theory and Flocculant*. China Building Industry Press (in chinese).
- Wang, Y., Gao, B.Y., Xu, X.M., Xu, W.Y., Xu, G.Y., 2009. Characterization of floc size, strength and structure in various aluminum coagulants treatment. *J. Colloid Interface Sci.* 332 (2), 354–359.
- Wang, D., Xing, L., Xie, J., Chow, C.W.K., Xu, Z., Zhao, Y., Drikas, M., 2010. Application of advanced characterization techniques to assess DOM treatability of micro-polluted and non-polluted drinking source waters in China. *Chemosphere* 81 (1), 39–45.
- Wang, D., Sun, W., Xu, Y., Tang, H., Gregory, J., 2004. Speciation stability of inorganic polymer flocculant-PACI. *Colloid. Surf. A* 243 (1–3), 1–10.
- Xu, W., Gao, B., Yue, Q., Wang, Y., 2010. Effect of shear force and solution pH on flocs breakage and re-growth formed by nano- $Al(III)$ polymer. *Water Res.* 44 (6), 1893–1899.
- Yang, S.-f., Li, X.-y., 2009. Influences of extracellular polymeric substances (EPS) on the characteristics of activated sludge under non-steady-state conditions. *Process Biochem.* 44 (1), 91–96.
- Yu, W., Gregory, J., Campos, L.C., 2010. Breakage and re-growth of flocs formed by charge neutralization using alum and polyDADMAC. *Water Res.* 44 (13), 3959–3965.
- Zhang, W., Peng, Y., Yang, X., Zhan, C., Wang, D., 2015a. Insights into the respective role of acidification and oxidation for enhancing anaerobic digested sludge dewatering performance with Fenton process. *Bioresour. Technol.* 181, 247–253.
- Zhang, W., Xiao, P., Liu, Y., Xu, S., Xiao, F., Wang, D., Chow, C.W.K., 2014b. Understanding the impact of chemical conditioning with inorganic polymer flocculants on soluble extracellular polymeric substances in relation to the sludge dewaterability. *Sep. Purif. Technol.* 132 (132), 430–437.
- Zhang, W., Yang, P., Xiao, P., Xu, S., Liu, Y., Liu, F., Wang, D., 2015b. Dynamic variation in physicochemical properties of activated sludge floc from different WWTPs and its influence on sludge dewaterability and settleability. *Colloid. Surf. A* 467, 124–134.
- Zhang, W., Peng, S., Xiao, P., He, J., Yang, P., Xu, S., Wang, D., 2014a. Understanding the evolution of stratified extracellular polymeric substances in full-scale activated sludges in relation to dewaterability. *Appl. Spectrosc.* 41 (2), 260–264.
- Zhao, Y.Q., Bache, D.H., 2001. Conditioning of alum sludge with polymer and gypsum. *Colloid. Surf. A* 194 (1–3), 213–220.
- Zhao, H.Z., Luan, Z.K., Su, Y.B., Wang, S.G., 2002. Separation, purification and characterization of Al_{13} . *Chem. J. Chin. U* 23 (5), 751–755 (in chinese).