Enhancement of waste activated sludge dewaterability using calcium peroxide pre-oxidation and chemical re-flocculation

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ABSTRACT

The effects of combined calcium peroxide (CaO₂) oxidation with chemical re-flocculation on dewatering performance and physicochemical properties of waste activated sludge was investigated in this study. The evolutions of extracellular polymeric substances (EPS) distribution, composition and morphological properties were analyzed to unravel the sludge conditioning mechanism. It was found that sludge filtration performance was enhanced by calcium peroxide oxidation with the optimal dosage of 20 mg/gTSS. However, this enhancement was not observed at lower dosages due to the absence of oxidation and the performance deteriorated at higher dosages because of the release of excess EPS, mainly as protein-like substances. The variation in soluble EPS (SEPS) component can be fitted well with pseudo-zero-order kinetic model under CaO₂ treatment. At the same time, extractable EPS content (SEPS and loosely bound EPS (LB-EPS)) were dramatically increased, indicating sludge flocs were effectively broken and their structure became looser after CaO₂ addition. The sludge floc structure was reconstructed and sludge dewaterability was significantly enhanced using chemical re-flocculation (polyaluminium chloride (PACl), ferric iron (FeCl₃) and polyacrylamide (PAM)). The inorganic coagulants performed better in improving sludge filtration dewatering performance and reducing cake moisture content than organic polymer, since they could act as skeleton builders and decrease the sludge compressibility.

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1. Introduction

Due to the improvement and popularization of municipal wastewater treatment, sludge production was dramatically increased in recent decades (Kim et al., 2002). It will pose a significant threat to the ecological system without effectively treatment and disposal (Wei et al., 2003). Wastewater treatment plant (WWTP) disposal of excess sludge with traditional treatment are quite expensive, which accounts for up to 60% of the total operation

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(Low et al., 2000). In addition, treatment and disposal of waste sludge is also faced with many technical problems and challenges. Waste activated sludge from secondary settling tank generally contains over 99 wt% water. Especially, sludge with high moisture content may result in the issues of great bulk, expensive cost and difficult for transportation. Therefore, the development of high performance dewatering processes has been one of the most important research areas in current China. In general, the moisture in sludge system can be classified into free water (accounted for about 70 wt%), interstitial water (about 20 wt%), adsorbed water (about 7 wt%) and bound water (about 3 wt%) (Vaxelaire and Cezac, 2004). Except for sludge properties, the dewatering performance was mainly dependent on selection of sludge devices and chemical conditioning methods (Beauchesne et al., 2007).

Extracellular polymeric substances (EPS) account for about 60–80% of total sludge mass (Liu and Fang, 2002) and significantly affect other sludge physicochemical properties, such as surface

charge, floc stability and rheological behavior (Mikkelsen and Keiding, 2002). Many previous studies have demonstrated that EPS was the most crucial deciding factor for sludge dewatering (Mikkelsen and Keiding, 2002; Niu et al., 2013; Chen et al., 2015). Houghton et al. (2001) reported that the dewaterability was determined by the contents of EPS and there existed an optimal EPS content for each sludge, at this time, the sludge exhibited the best dewatering property. Many researchers found that proteins and polysaccharides ratios had more significant effect on sludge dewatering property (Higgins and Novak, 1997a). Murthy and Novak (1999) suggested that high proteins/polysaccharide ratio was detrimental for sludge dewatering performance. Recent years, EPS was found to have double layers including the loosely bound EPS (LB-EPS) which is diffused from the tightly bound EPS (TB-EPS) that surrounds the cells (Li and Yang, 2007; Poxon and Darby, 1997; Ramesh et al., 2006). Moreover, some researchers reported that only the LB-EPS was related to the sludge dewaterability (Li and Yang, 2007; Ramesh et al., 2006; Raynaud et al., 2012). Yu et al. (2008) suggested that sludge floc was composed by five fractions: supernatant, slime, LB-EPS, TBEPS, and pellet, and the sludge dewatering performance was mainly influenced by soluble EPS characteristics.

Generally speaking, it is essential to precondition the sludge particles with chemicals properly before the dewatering in order to improve the operating performance of devices. For example, addition of inorganic or organic flocculants 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., 2014). EPS fraction in activated sludge was highly hydrated, and the traditional chemical flocculants was ineffective to destroy EPS structure and convert bound water into free water (Neyens et al., 2004). Therefore, the advanced sludge technologies (AST) were developed to improve sludge dewatering property and cake solid content by solubilizing EPS components. The established AST includes photo-Fenton/Fenton oxidation technology (Liu et al., 2013; Neyens and Baeyens, 2003; Tokumura et al., 2007), thermal hydrolysis, acid and alkali treatment (Zhu et al., 2013), heat treatment (Neyens et al., 2004), enzymatic treatment (Chen et al., 2015; Thomas et al., 1993) and integrated processes.

Calcium peroxide (CaO_2) is one of the most traditional and safest solid inorganic peroxy compounds which can be considered a “solid form” of H_2O_2 (Qian et al., 2013). CaO_2 dissolved in water may generate O_2 and H_2O_2 which is known to be a strong oxidant; calcium ions generated at the same time could act as coagulants (Higgins and Novak, 1997b). Besides its stable oxidation capability, CaO_2 also possesses the capacities of bleaching, disinfection, and deodorizing. Hence, CaO_2 has been widely used in agriculture, aquaculture, and medicine (Ma et al., 2007). CaO_2 can be used to promote organic pollutant degradation in contaminated soil due to its oxidation (Ndjou'ou and Cassidy, 2006). According to Zhang et al. (2015a), CaO_2 was very effective in sludge solubilization and removal of endocrine disrupting compounds (EDCs). In addition, CaO_2 can be also function as an alkali to improve the sludge hydrolysis due to formation of $\text{Ca}(\text{OH})_2$ (Wu et al., 2010; Zhu et al., 2013).

As mentioned above, the sludge dewatering is one of the critical steps toward sludge treatment, whilst it would finally make significant influence on sludge reduction and disposal. EPS fraction was highly hydrated, CaO_2 oxidation was able to solubilize sludge EPS and result in release of water binding to them. Then, the chemical flocculation could be used to agglomerate sludge tiny flocs and improve sludge filterability. However, few of previous studies have investigated the feasibility of combined CaO_2 treatment and chemical re-flocculation on dewatering performance.

Especially, the evolution of EPS and morphological properties under chemical conditioning was still not clear. Thus, the objectives of this study were to: (a) investigate the effect of combined CaO_2 pre-oxidation and chemical re-flocculation on sludge dewatering performance and optimize the process combination modes and dosage of sludge conditioners; (b) get insights into the kinetic variation in distribution and composition of EPS under CaO_2 hydrolysis reaction; (c) unravel the mechanism and clear the enhancement of activated sludge dewatering performance by analyzing the EPS and morphological properties under treatment by CaO_2 in combination with re-flocculation process.

2. Materials and methods

2.1. Waste sludge and reagents

Waste activated sludge was obtained from the Beixiaohe WWTP in Beijing city. This WWTP treats approximately 1,000,000 m^3 daily by combined membrane bioreactor (MBR) and ozonation process. The raw sludge characteristics were given in Table 1, which can be used as baseline background reading.

All the reagents were analytical reagents (AR) except for calcium peroxide (Chemically Pure, CP), polyaluminium chloride (PACl) and polyacrylamide (PAM). All of reagents were purchased from Sino-pharm Chemical Reagent Co., Ltd in China except for PACl and PAM. The concentration of self-made ferric iron (FeCl_3) and PACl solution were 100 g/L.

2.2. Batch test

2.2.1. CaO_2 hydrolysis test

An aliquot of 150 mL of sludge was placed into Erlenmeyer flasks with different dosages of CaO_2 . Then the flasks were put into a horizontal oscillator ($25 \pm 1^\circ\text{C}$) at the speed of 200 rpm/min for 1 h. The following procedures at the end of this test were the measurement of specific resistance to filtration (SRF) and EPS extraction and analysis.

With regard to the kinetic test, 800 mL of sludge was placed into 1 L beaker with mixing by using cantilever-type stirrer after CaO_2 addition of 100 mg/gTSS. Meanwhile, 50 mL of sludge samples were taken out and placed into centrifuge tubes at different time intervals within 120 min. The samples were promptly centrifuged and filtered by membrane of 0.45 μm so as to stop the reaction in tubes.

2.2.2. Chemical re-flocculation

Sludge samples of 100 mL were used in the experiments. The following mixing procedure was used: a rapid mix period for 30 s at 200 rpm/min followed by a slow-stir phase at 50 rpm/min for 10 min. The coagulants (PACl, FeCl_3 or PAM) were added with agitation using a graduated finnpipette. At the end of mixing, the conditioned sludge was allowed to settle in the beaker for 30 min. Finally, the floc morphology and characteristics of soluble EPS were determined as the measurements expanded upon in following sections.

2.2.3. Determination of sludge dewaterability

SRF represents the resistance of unit mass of sludge in unit filtration area under a certain pressure, it has the similar physical process to the pressure filtration dewatering. The SRF was conducted in a 100 mL Buchner funnel using a quantitative filter paper (see Fig. S1 of supporting information (SI)). The Buchner funnel was filled with 50 mL of sludge suspension, and a constant pressure of 60 kPa was applied by a vacuum pump. The volume of filtrate under pressure was continuously recorded every 2 s by METTLER TOLEDO

Table 1
Characteristics of sludge obtained from Beixiaohe WWTP.

Indicator	Moisture content (wt%)	pH	VSS/TSS	SRF (m/kg)	d _{0.5} (μm)	Zeta potential* (mV)	SCOD (mg/L)
Value	98.3	6.81	0.78	1.53×10^{13}	58.68	−14.3	132

*Samples for zeta potential were diluted by 10 times.

balance connected with computer and it stopped after 10 min. The SRF of the sludge was calculated by:

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

Where P (kg/m²) is the pressure applied, A (m²) is the filter area, μ (kg·s/m²) is the kinetic viscosity (KV), ω (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).

2.3. Analytical methods

2.3.1. Floc morphology

Sludge floc size and fractal dimension (D_F) were measured by Malvern Mastersizer 2000 (UK) with stirrer speed of 300 rpm/min. Each sample was determined three times with its measuring time of 10 s. Light scattering method has been widely used for the determination of aggregate mass fractal dimension (Wei et al., 2009). The technique involves measurement of light intensity I as a functions of the scatter vector Q .

For independently scattering aggregates, the relationship among I , Q and the fractal dimension D_F can be represented by Eq. (2):

$$I \propto Q^{D_F} \quad (2)$$

The relationship shown in Eq. (2) indicates the determination of D_F , which can be given by the slope of $\log I$ versus $\log Q$ by fitting a straight line.

2.3.2. Extraction and analysis of EPS

2.3.2.1. EPS extraction. A heat extraction method was modified to extract the LB-EPS and TB-EPS from the sludge (Niu et al., 2013). A sludge suspension was firstly dewatered by centrifugation in a 50 mL tube at 3000 g for 10 min. The supernatant was collected as SEPS. The sludge pellet in the tube was then resuspended into 15 mL of 0.05% NaCl, sonicated at 20 kHz for 2 min, shaken horizontally at 150 rpm/min for 10 min and sonicated again for an additional 2 min. The liquor was centrifuged at 8000 g 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 12,000 g for 20 min to collect TB-EPS.

2.3.2.2. Chemical composition analysis of EPS

2.3.2.2.1. Three-dimensional excitation emission matrix (3-DEEM). It was reported that 3-DEEM analytic technique has been widely used in characterization of natural organic matters in water body and has the advantages of high sensitivity and accuracy (Henderson et al., 2009). 3-DEEM was measured by a Hitachi F-4500 fluorescence spectrophotometer with an excitation range from 200 to 400 nm and an emission range from 220 to 550 nm. The spectra were recorded at a scan rate of 12,000 nm/min, using excitation and emission slit bandwidths of 5 nm. The EPS samples

were diluted by different times noted in figures.

2.3.2.2.2. High-performance size exclusion chromatography (HPSEC). 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 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 200 μ L sample was injected at a flow rate of 0.8 mL/min. Polystyrene sulfonate standards (Sigma-Aldrich, USA) of MWs 1.8–32 kDa were used for apparent molecular weight (AMW) (Chow et al., 2008; Wang et al., 2010).

2.3.2.3. Field emission scanning electron microscope (FE-SEM) and fourier transform infrared (FTIR) analysis. The sludge samples were made by freeze-drying treatment under vacuum at −60 °C for 72 h, which were analyzed by FTIR NICOLET 8700 spectrometer to identify various functional groups in the EPS samples. All the spectra were in a scanning range from 500 to 4000 cm^{−1}. With samples freeze-dried, FE-SEM analysis was used by HITACHI SU8020 FE-SEM.

2.3.3. Other indicators

Dissolved organic carbon (DOC) was determined by using Total Organic Carbon Analyzer (TOC-L, SHIMADZU Inc., Japan). Concentrations of metal ions were measured with inductively coupled plasma optical emission spectrometer (ICP-OES). Other sludge parameters, including total suspended solid (TSS), volatile suspended solids (VSS) were determined according to standard methods (APHA, 1998). pH was measured by a PHS-3C (Shanghai, China) pH meter.

Each treatment sample was analyzed in triplicate and the relative deviations of all analyses were always less than 5%.

3. Results and discussion

3.1. Effects of CaO₂ treatment on sludge dewaterability

Fig. 1 (a) showed that with the increase of CaO₂ addition, SRF initially decreased before passing through a minimum at a dosage of 20 mg/g TSS and then increased at higher dosages. Meanwhile, the evolution of cake moisture content had the same tendency. It reached the minimum of 86.31 wt% when the dosage of CaO₂ was 20 mg/gTSS and the SRF was 1.28×10^{13} m/kg. According to the value of SRF, sludge can be classified into poor dewaterability ($>1 \times 10^{13}$ m/kg), medium dewaterability, ($0.5\text{--}0.9 \times 10^{13}$ m/kg) and good dewaterability ($<0.4 \times 10^{13}$ m/kg) (Zhang et al., 2014). By comparison, although addition of CaO₂ can improve sludge dewatering performance, the minimum SRF value can not reach the sludge with good dewaterability. Thus, a link to the chemical re-flocculation work is required at this point.

Fig. 1. Effects of CaO₂ dosage on sludge: (a) dewatering performance; (b) floc morphological properties.

3.2. Effects of CaO₂ dosage on physicochemical properties of waste sludge

3.2.1. Effects of CaO₂ dosage on sludge floc morphological properties

As depicted in Fig. 1 (b), for average sludge floc size ($d_{0.5}$, μm), with the increase of CaO₂ addition, there was a sharp increase. It reached the maximum of 66.25 μm when the dosage of CaO₂ was 20 mg/gTSS. After CaO₂ dosage was further increased to above 30 mg/gTSS, the pattern approached to a flat. As a matter of fact, calcium peroxide had double effects on oxidation and flocculation. Due to the combinative effects of calcium ions coagulation and oxidative lysis of EPS in CaO₂ treatment, sludge flocs initially agglomerated into larger ones under charge neutralization (Higgins and Novak, 1997b). Since the solubilization of sludge flocs was gradually enhanced with CaO₂ oxidation at higher dosages, so that the average floc size then decreased.

Generally, the higher the D_F always means the more irregular surface of the sludge. A floc with a D_F close to 3 indicates a close interior packing, and an extremely loose packing feature appears at a D_F close to 1 (Hung et al., 1996). Eriksson and Alm found that higher charge-density coagulants interact strongly with negatively charged surfaces, and thus it would have a flat adsorption conformation. Therefore, the flocculated particles will come in close contact with each other, which gives a strong binding and reduces the possibility of movement of the particles relative each other (Eriksson and Alm, 1993). The change of D_F can be seen in Fig. 1 (b). Generally, it rose firstly and then fell with the increase of CaO₂ addition. When dosage of CaO₂ was 20 mg/gTSS, the sludge floc

average size and density reached the maximum due to the double effects of CaO₂, meanwhile the sludge SRF reached the minimum as previously mentioned. Therefore, the sludge filtration dewatering performance was enhanced by using calcium peroxide pre-oxidation at optimal dosage.

3.2.2. Effects of CaO₂ dosage on EPS distribution and composition

As depicted in Fig. 2 (a), with the increase of CaO₂ addition,

Fig. 2. Effect of CaO₂ dosage on EPS distribution and composition: (a) EPS concentration; (b) Calcium distribution in EPS; (c) Total calcium distribution.

sludge SEPS and LB-EPS components significantly increased from 1.10 to 0.65 mgDOC/gTSS to 2.57 and 1.62 mgDOC/gTSS respectively. However, TB-EPS components decreased from 47.42 to 40.32 mgDOC/gTSS but goes through a maximum of 54.72 mgDOC/gTSS. According to our previous study, the solubilization of organic matters by sludge floc lysis with oxidation of peroxides may lead to the gradual transformation from TB-EPS to LB-EPS then to SEPS. Furthermore, it was reported that the high molecular weight biopolymer in SEPS had a more crucial influence on sludge filtration properties (Lyko et al., 2008). Raynaud et al. (2012) suggested that a sludge with poor filterability is usually related to such flocs with a loose packing, less fine particle retention and a more compressible cake structure. Therefore, sludge filtration performance was deteriorated due to release of organic matters after CaO₂ treatment at high dosages. The chemical composition of organic matters released would be characterized by EEM and HPSEC later.

In addition, Fig. 2 (b) showed that calcium ions in SEPS and LB-EPS components reached the maximum of 64.836 and 35.074 mg/L, respectively, when the dosage of CaO₂ was 20 mg/gTSS. However, the concentration of calcium ions in TB-EPS components rose steadily with an increase of CaO₂ addition. With regard to Fig. 2 (c), after CaO₂ addition of 20 mg/gTSS, the concentration of calcium in sludge EPS reached the equilibrium while the rest of calcium in sludge pellet sharply increased. It suggested that the calcium ions generated by CaO₂ mainly existed in sludge solid including LB-EPS, TB-EPS and pellet rather than SEPS.

3.2.3. 3-DEEM analysis

3D-EEM method is widely used for characterization of natural organic matters in various water bodies with the advantages of high sensitivity and selectivity (Henderson et al., 2009). According to the report of Sheng and Yu (2006), fluorescence intensity of EEM could be used to measure EPS content as DOC content in samples was less than 10 mg/L. It was investigated that three dimensional fluorescence spectrum is divided into five major regions, which are soluble microbial byproducts (tryptophan-like protein), aromatic protein I, aromatic protein II, humic acid and fulvic acid respectively (Chen et al., 2003). Fig. 3 showed that two fluorescent peaks in the SEPS, LB-EPS and TB-EPS: Peak A ($\lambda_{\text{ex/em}} = 280/335$) — tryptophon-like proteins, Peak B ($\lambda_{\text{ex/em}} = 230/335$) — aromatic proteins. It can be seen from Fig. 3 and Table 2, intensities of tryptophon-like and aromatic proteins in SEPS and LB-EPS components were obviously enhanced, while they were weakened in TB-EPS from 1580 to 792.8 to 1463 and 697.9 respectively. This may suggest that with CaO₂ treatment, sludge flocs were effectively hydrolyzed and protein-like substances were released. The results were in agreement with the analysis of DOC variation previously that protein-like organic matters in TB-EPS component transformed to LB-EPS and SEPS. As a result, the increase in concentrations of protein-like substances caused deterioration of sludge filtration dewatering performance (Zhang et al., 2015b).

3.2.4. Molecular weight distribution analysis

In MW measurement, it should be noted that carbohydrates contain no conjugated double bond, so the detection of them was only possible if they were present as part of molecular complexes such as glycoproteins and glycolipids (Lyko et al., 2007). Lyko et al. (2007) suggested that three main molar mass fractions can be distinguished: high MW organic compounds (>5000 Da) mainly composed of proteins and polysaccharides, mid-MW compounds (1000–5000 Da) and organic matter of low MW (<1000 Da). Bhatia et al. (2013) found that the MW of protein-like substances in EPS samples extracted from activated sludge was in a wide range of 1–600 kDa. The impact of CaO₂ dosage and reaction time on MW distributions of SEPS fractions was presented in Fig. S2 of SI, and

five MW peaks were observed in the SEPS fraction: 900 Da, 1500 Da, 2200 Da, 3000 Da and 50,000 Da. As can be seen in Fig. 4 (a), with the increase of CaO₂ addition, intensity of each MW peak was enhanced except for the peak of 3000 Da. These results indicated that after CaO₂ treatment, sludge flocs were effectively dissolved and released organic matters, which led to the increase of substances with various molecular weights, especially the mid and low MW compounds, which were always associated with protein-like substances. In addition, Kiss et al. (2003) suggested the average molecular weight (AMW) of humic-like substances (HULIS) was in the range of 100–800 Da. Therefore, few humic compounds were released due to CaO₂ addition, which could be confirmed by EEM spectrum without the signals of humic substances. In addition, Fig. 4 (b) demonstrated that the same five MW peaks were found in SEPS fraction after CaO₂ addition with reaction time. This suggested that organic polymeric substances were effectively hydrolyzed to organic matters with lower MW.

3.2.5. FTIR analysis

As depicted in Fig. S3 of SI, varieties of characteristic peaks were found on IR spectrum of the control sample. Due to the complexity of EPS components and the presence of a large numbers of functional groups on the EPS, the exact characteristic absorption values are very difficult to determine in the IR spectrum. The broad absorption band between 3200 and 3400 cm⁻¹ in the spectrum was assigned to the stretching vibrations of the O–H groups of polymeric substances (Sheng et al., 2006; Tapia et al., 2009). The peaks from 2925 to 2935 and 2850–2860 cm⁻¹ demonstrated the existence of aliphatic chains of polysaccharides, proteins and humic substances (Sheng et al., 2006; Wang et al., 2014). Chai et al. (2007) reported that the absorption of wavelengths between 2930 and 1650 cm⁻¹ was related to humic acids (stretching vibrations of C=C). But, the IR identification of humic-like substances is very complicated because other organic groups also absorb in the same regions. The absorption band between 1635 and 1655 cm⁻¹ was associated with the stretching vibrations of C=O and C–N of amide I of the protein (Bhatti and Hamid, 2014; Sun et al., 2012; Tapia et al., 2009). The band from 1445 to 1455 was due to the deformation of the CH₃ and CH₂ groups of amide III. The spectral band observed from 1035 to 1070 cm⁻¹ (stretching vibration of O–H groups) was a characteristic absorption region of polysaccharides of EPS (Omoike and Chorover, 2004; Sun et al., 2012; Tapia et al., 2009). Hence, the IR data confirmed the existence of protein and polysaccharides in the sludge samples. However, after CaO₂ addition, the absorption intensities of peaks of 2852, 2926 and 1037 cm⁻¹ was decreased, especially with the combined treatment of CaO₂ and coagulants. This indicated that EPS components mainly composed by proteins and polysaccharides were oxidized and degraded after CaO₂ oxidation, which was consistent with previous results.

3.3. Kinetics of sludge solubilization by calcium peroxide conditioning

3.3.1. Kinetics of SEPS component

As depicted in Fig. 5 (a), SEPS component significantly increased and it reached the equilibrium of 2.47 mgDOC/gTSS from 1.74 mgDOC/gTSS when the reaction time was 60 min. In addition, Fig. 5 (b) displayed that the EEM fluorescence intensities of tryptophon-like and aromatic protein were strengthened from 29.25 to 20.56 to 87.47 and 78.33 respectively after the time of 1 h, which was similar to the change in SEPS. This may due to the sludge floc lysis and release of organic matters to SEPS component after CaO₂ addition.

Kinetic modelings (see supporting information) were used to get further insights into the kinetic variation in EPS characteristics

Fig. 3. Influence of CaO_2 dosage (mg/gTSS) 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 50 times).

Table 2
Influence of CaO₂ dosage on intensities of fluorescent peaks in different EPS fractions.

Ca ₂ O dosage (mg/gTSS)	SEPS		LB-EPS		TB-EPS	
	Tryptophan protein	Aromatic protein	Tryptophan protein	Aromatic protein	Tryptophan protein	Aromatic protein
λ (Ex/Em)	280/335	230/335	280/335	230/335	280/335	230/335
0	34.56	13.21	19.53	19.45	1580	792.8
10	36.98	29.96	34.98	21.58	1594	836.4
20	51.91	51.08	44.52	32.78	1629	723.2
30	61.66	47.85	54.45	41.62	1721	947.0
50	72.37	54.90	93.53	61.17	1344	626.6
70	82.94	57.89	114.0	71.10	1444	665.3
90	92.94	71.24	120.4	74.26	1463	697.9

*SEPS and LB-EPS samples were diluted by 10 times, and TB-EPS sample was diluted by 50 times.

under calcium peroxide oxidation. The fitting results were given in Fig. S4 of SI. According to correlation coefficient (R^2), it was clear that the variation in SEPS component could be fitted well with pseudo-zero order kinetic equation due to its R^2 of 0.926, and the reaction rate was 0.252 mg/(L·min), and sludge solubilization rate 0.0148 mg/(gTSS·min). Thus, it suggested that EPS solubilization rate under CaO₂ oxidation was not affected by sludge concentration. Sahinkaya et al. (2015) also found that the process of sludge

hydrolysis by Fenton oxidation could be divided into two steps which were fast and slow oxidation, meanwhile the rapid hydrolysis followed the zero order kinetic model.

3.3.2. Kinetics of calcium ion

The change in concentration of calcium ion with reaction time in SEPS can be found in Fig. 6. It showed that the concentration of Ca²⁺ carried on rising obviously within the reaction time of 1 h. Then it

Fig. 4. Effects of CaO₂ oxidation on peak intensities of MW distribution in SEPS: (a) dosage; (b) reaction time (Samples were diluted by 10 times).

Fig. 5. Variation in SEPS component after CaO_2 addition with reaction time: (a) SEPS content; (b) Fluorescent intensities in EEM contours (Samples for EEM were diluted by 10 times).

Fig. 6. Variation of Ca^{2+} in SEPS with reaction time.

reached the equilibrium of 89.018 mg/L from 58.179 mg/L. In addition, the procedure of CaO_2 solubilization was fitted well with zero order kinetic model (see in Fig. S5 of SI), which was consistent

with the kinetics of SEPS component. And its R^2 and reaction rate were respectively 0.974 and 0.481 mg/(L·min).

Reaction Equations (7) and (8) can be used to illustrate the process of CaO_2 solubilization (Khodaveisi et al., 2011):

The sludge hydrolysis with CaO_2 addition was due to the oxidation of hydrogen peroxide generated by CaO_2 dissolution rather than CaO_2 itself. Hence, solubilization of sludge flocs was the rate-limiting reaction of CaO_2 dissolution which was confirmed by the lower reaction rate of 0.252 mg/(L·min). The change in SEPS component followed the pseudo-zero order kinetics. However, with hydrogen ions consumption and pH rising, the CaO_2 dissolution and hydrogen peroxide generation were gradually suppressed. Therefore, the concentration of Ca^{2+} trended to be stable after 1 h reaction and the variation in SEPS reached the equilibrium at the same times. Sahinkaya et al. (2015) suggested that the reaction rate of sludge hydrolysis were up to 50.10 and 33.95 mg/(L·min) by using conventional Fenton and Fenton type process respectively. Northup and Cassidy (2008) reported that CaO_2 was able to maintain oxidation reactions over a long period of time since it was dissolved slowly in water. By contrast, the sludge conditioning by CaO_2 oxidation lasted a long time but it was safe due to its lower reaction rate.

3.4. Sludge conditioning with calcium peroxide pre-oxidation and chemical re-flocculation

3.4.1. Sludge dewatering performance

It revealed that sludge condition with inorganic coagulants might be divided into two steps. Initially, sludge particles rapidly aggregated into large flocs due to bridging and charge neutralization, hydrolysis products of inorganic coagulants could neutralize the surface charge of the particles and the suspension would be destabilized (Higgins and Novak, 1997b); And then the floc size decreased gradually owing to water stripping from aggregates caused by double electric layer compression as reaction time was going on. Finally, when the balance between the rate of aggregation and the rate of breakage for a given shear condition was reached, the size of flocs reached a steady plateau (Biggs et al., 2001). As depicted in Fig. 7, after CaO_2 addition with PACl, FeCl_3 and PAM conditioning, the sludge SRF decreased significantly from initial 3.46×10^{13} m/kg to 3.55×10^{12} , 4.36×10^{12} and 2.75×10^{11} m/kg, respectively, which were lower than control tests accordingly. It should be noted that the sludge cake moisture content with CaO_2 treatment decreased much more than control experiments, which dropped from 91.83% to 79.46, 79.27 and 81.32%, respectively. This observation revealed that combination with CaO_2 pre-oxidation and chemical flocculation was high-efficiency in sludge dewatering performance, especially cake moisture content reduction. This may due to the conversion from bound water to free water which was easy to remove in sludge flocs by using CaO_2 oxidation (Neyens et al., 2004). In addition, with regard to re-flocculation, inorganic coagulants of PACl and FeCl_3 were more effective in cake moisture content reduction than PAM, which resulted in the reduction to 80% below. It was reported that density of sludge flocs would be enhanced by PACl and FeCl_3 with their high charge density and the free water in sludge EPS could be efficiently removed under compression of double electric layer (Niu et al., 2013). In addition, the hydrolytic products of Al and Fe salts can act as skeleton builders to enhance the floc strength and reduce the sludge compressibility.

Fig. 7. Effects of chemical re-flocculation with different coagulants on sludge dewatering performance and floc size distribution: (a) (b) (c) PACl; (d) (e) (f) FeCl_3 ; (h) (i) (j) PAM.

3.4.2. Morphological properties of sludge flocs

3.4.2.1. Sludge floc size. After flocculation with PACl and FeCl_3 (see Fig. 7 (c) and (f)), original sludge floc size obviously increased from 58.68 μm to 231.65 and 81.37 μm respectively when the dosages were 15 g/gTSS. However, there was no noticeable change in floc size when sludge was conditioned with CaO_2 pre-oxidation. In addition, as depicted in Fig. 7 (j), both raw and pre-treated sludge had a significant increase in floc size from 58.68 μm to 570.98 and 497.82 μm after PAM addition. Firstly, it should be noted that coagulated sludge floc size was slightly reduced after oxidative pretreatment. It was very likely that organic matters with high MW in sludge EPS was converted into smaller organic compounds, and alleviated the electrostatic and hydrophobic interactions between hydrolyzed products of coagulants and EPS components (Lee and Liu, 2001). It was obvious that flocs formed by PACl coagulation were larger than that conditioned with FeCl_3 . It was likely that Al_b and Al_c accounted for 60–80% of total Al, while the hydrolytic products of Fe^{3+} existed in the form of iron hydroxides (Niu et al., 2013). Therefore, the binding sites of PACl are much abundant than that of iron hydroxides, hence the larger flocs were produced. It is interesting to note that the largest flocs with the poorest dewatering property were produced by using PAM flocculation after CaO_2 pre-oxidation. As depicted in Fig. S6 of SI, this could be

suggested that organic polymeric flocculants (eg. PAM) were able to generate larger and but loose flocs with good settling property through bridging and sweeping compared to metal salt coagulants (Wong et al., 2006).

3.4.2.2. FE-SEM analysis. The sludge floc morphology under FE-SEM can be seen in Fig. 8. The raw sludge floc had a relative smooth surface (see Fig. 8 (a)) while after CaO_2 oxidation, the structure of flocs demonstrated the characteristics including loose and complexity of pore distribution. And more CaO_2 was dosed, the higher degree of fragmentation on sludge floc surface can be seen (see Fig. 8 (b) and (c)). It is not difficult to demonstrate that sludge flocs were significantly solubilized with CaO_2 pre-treatment. In addition, sludge flocs were obviously aggregated after chemical re-flocculation with coagulants. In addition, it was interesting to note that pore structure of sludge flocs treated with CaO_2 oxidation were more plentiful and which might provide more channels for water release (see in Fig. 8 (b) and (c)). Furthermore, the flocs conditioned with inorganic coagulants (Al and Fe salts) had bigger fragmentations and more abundant porous structure than conditioned with PAM, indicating that more stronger flocs formed in inorganic coagulants flocculation seen in Fig. 8 (d), (e) and (f). This observation was in agreement with the change in floc size and D_f (Niu et al., 2013).

Fig. 8. Sludge floc morphology by FE-SEM (Magnified by 20,000 times): (a) raw sludge; (b) 20 mg/gTSS CaO_2 ; (c) 90 mg/gTSS CaO_2 ; (d) CaO_2 + 15 g/gTSS PACl; (e) CaO_2 + 15 g/gTSS FeCl_3 ; (f) CaO_2 + 15 g/gTSS PAM.

Fig. 9. Variation in SEPS concentration after chemical re-flocculation with different coagulants.

3.4.3. Change in EPS properties under combined conditioning

Fig. 9 presented that SEPS content was decreased under chemical flocculation, this observation was more noticeable after CaO_2 addition. The SEPS concentration was reduced from 2.95 mgDOC/gTSS to 1.64, 1.43 and 2.30 mgDOC/gTSS with PACl, Fe^{3+} and PAM addition respectively, revealing that FeCl_3 was more effective in removing organic matters in sludge. It was suggested that ferric ions exhibited higher affinity to protein-like substances (Yu et al., 2008). In addition, according to our previous report, protein like substances in SEPS fraction were found to be the main influencing factor of sludge filtration dewatering performance (Zhang et al., 2015c). It is obvious that FeCl_3 conditioning performed better in removal of SEPS due to strong binding strength between ferric ions and protein-like substances, which contributed to improvement of sludge filtration behavior. In addition, the change of characteristic absorption curve after coagulants addition can be attributed to formation of organic-metal complexes, which can also be reflected by FTIR spectra in Fig. S3 of SI.

4. Conclusion

This study attempted to use CaO_2 pre-oxidation and chemical re-flocculation to improve sludge dewatering performance.

- Waste activated sludge dewaterability was relatively enhanced by using optimal CaO_2 pre-oxidation and the optimum dosage was 20 mg/gTSS. However, sludge filtration performance was worse due to the absence of oxidation with lower dosage and the release of protein-like substances at higher dosage.
- Sludge floc was effectively broken and its structure became much looser after CaO_2 addition. Meanwhile, protein-like substances in TB-EPS component gradually converted into LB-EPS and SEPS.
- The variation in SEPS component can be fitted well with pseudo-zero-order kinetic model. sludge solubilization rate 0.0148 mg/(gTSS·min) under CaO_2 treatment.
- Sludge floc structure was reconstructed and sludge dewaterability was significantly enhanced after chemical re-flocculation by using coagulants (PACl, FeCl_3 and PAM). The sludge cake moisture content could be decreased to 80 wt% below under addition of inorganic coagulants of PACl and FeCl_3 due to their higher charge neutralization and skeleton builders of hydrolysis products.

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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.2016.07.018>.

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